INFRA-RED ABSORPTION SPECTRA
AND MOLECULAR STRUCTURE OF
TRIATOMIC MOLECULES.

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Published work submitted by A. B. D. Cassie for the D.Sc. degree.

FOREWORD.

This is not a thesis, but is a summary of work carried out by the candidate during the period 1930-33. It was originally compiled as a report to the Department of Scientific and Industrial Research on work carried out during tenure of a Senior Research Award.

It is included with published work submitted for the D.Sc. degree to indicate to examiners that part of the work due to the candidate. Much of this work has been published conjointly with Mr. C. R. Bailey, Lecturer in Chemistry at University College, London, and the report will enable the examiners to distinguish the joint authors' separate contributions. Thus the candidate has been responsible for the entire experimental work and the mathematical investigations associated with interpretation of observed bands. Mr. Bailey has undertaken correlation of observed force constants and other molecular parameters with quantities of interest to chemists, such as heats of dissociation.

A thesis submitted to the University of London for the Ph.D. degree included work published in references (1) to (4) and part of reference (5). This thesis was submitted in June 1931, and the degree was granted in July of the same year.

PREFACE.

This report is written as a résumé of investigations of infra-red absorption spectra of triatomic molecules carried out during tenure of a Senior Research Award. It might have been written in thesis form giving details of experimental and other work, but much of this has already been published, and copies of the papers have been sent the Department; these papers run into some hundred pages of print, and a thesis would merely form unnecessary repetition occupying almost double this number of typewritten pages. A résumé which brings together the results, and gives the now well established methods of interpreting infra-red absorption spectra of triatomic molecules, seems therefore the more satisfactory form for the report.

Published work will be referred to as follows:

'Investigations in the Infra-Red Region of the Spectrum"

(1). Part I (Proc. Roy. Soc., 1930, A, 130, 133).

(2). Part II. (ibid, 1930, A, 130, 142).

(3). Part III. (ibid, 1931, A, 132, 236).

(4). Part IV. (ibid, 1931, A, 132, 252).

(5). Part V. (ibid, 1932, A, 135, 375).

(6). Part VI. (ibid, 1932, A, 137, 622).-

(7). Part VII. (ibid, 1932, A, 138, 531).

(8). Part VIII. (ibid, 1933, A, 140, 193).

(a). Part IX. (ibid, 1933, A, 142, 129).

(b). Part X (ibid, 1934, A, 145, 338).

(9). 'Infra-Red and Raman Bands of Carbon Dioxide, Carbonyl

Sulphide, and Carbon Disulphide'. (Z. Physik, 1932, 79, 35).

(10). 'Molecular Configuration of N_2O.' (Phys. Rev., 1932, 39, 534).

(11). 'Infra-Red Absorption Spectrum of Nitrogen Dioxide'. (Nature, 1933, 131, 239).

(12). 'The Asymmetrical Rotator and its Infra-Red Spectrum'. (Trans. Faraday Soc., 1930, XXVI, 197).

(13). 'A Method of Eliminating Magnetic Disturbance of High Sensitivity Galvanometers'. (J. Sci. Inst., 1930, VII).

(14). 'Structure of Triatomic Molecules'. A. B. D. Cassie (Nature, 1933, 131, 438).

(15). 'Investigations of the Infra-Red Absorption Spectra of Sulphur Dioxide, Carbon Disulphide, and Carbonyl Sulphide'. A thesis for the Ph.D. degree at London University, by A. B. D. Cassie, June 1931.

(16). 'Investigations in the Infra-Red Region of the Spectrum Part XI - The Absorption Spectrum and Molecular Configuration of Boron Trichloride, and the Effect of Strain on Plane Groups of the Type XY_3. (Proc. Roy. Soc., 1935, A, 148, 87).

This work has been published in collaboration with Mr. C. R. Bailey, Lecturer at University College, London, apart from references (13), (14), (15), and (16).

CONTENTS.

SECTION I. Experimental.

SECTION II. Observed spectra and their interpretation in terms of molecular structure.

SECTION III. Theoretical conclusions on the formation of triatomic molecules.

INTRODUCTORY.

Two equally important aspects of infra-red absorption spectra have always been recognised: they are the experimental determination of the positions of the bands and their resolution into branches or lines, and the interpretation of these observations in terms of the structure of the molecule. Recently a third, and no less important aspect has assumed considerable prominence; this is the possibility of predicting the structure of a molecule from the number of electrons available for binding, together with the available proper functions which the electrons may occupy. This report will deal with all three, and is divided into three sections: experimental, experimental results and their interpretation in terms of molecular structure, and finally, theoretical conclusions on the formation of triatomic molecules.

The greater part of the author's time during tenure of the Award has been spent in developing experimental methods and in applying them to determination of the spectra, but as this work has been fully described in papers (1), (4), (7), (13), and (15), it will occupy only a short section of the report. The interpretation of results in terms of molecular structure has also been dealt with in other communications; however as experimental results and theoretical deductions have accumulated some of these have been revised, and none of the communications give a connected account of the methods employed; this section is therefore the longest of the three.

The third section indicates how investigations of infra-red absorption spectra may in future be used to develop an 'Aufbau' principle for more complicated molecules.

SECTION I. EXPERIMENTAL.

(1). GENERAL. The general experimental method is described in reference (1) (see p.2), and details of the calibration of the spectrometer for use with either quartz, fluorite, rock-salt or sylvine prisms will be found in (15). These followed closely the work of Robertson and Fox (Proc. Roy. Soc., 1928, A. 120, 128). These references also give details of possible errors during working of the instrument, and of corrections for temperature variations affecting the readings of the wave length drum.

A point of general interest not given in (1) is the effect of a non-homogeneous magnetic field at the suspended system of the galvanometer on the elimination of mechanical disturbances.

The galvanometer used was a moving magnet instrument of Paschen-Downing design (cf. J. Sci. Inst., 1926, 3, 331). It has an approximately astatic system suspended by a very fine quartz fibre, and the point of attachment of the fibre is carefully adjusted to be vertically above the centre of gravity of the suspended system; if this condition is not fulfilled vibration of the support leads to oscillation of the suspended system.

There are clearly two methods of increasing the sensitivity of such instruments; the system can be rendered more nearly astatic, when, in a homogeneous field, the restoring couple diminishes; or the field intensity at the suspended system may be reduced by magnetic shielding and subsidiary magnets, when the restoring force again diminishes. The second method was used in the present investigations.

Mr. Downing has succeeded in making instruments so nearly astatic that in the earth's magnetic field they have a sensitivity of 10^{-10} to 10^{-11} amp. per mm. deflection at a scale distance of one metre, and he finds that they are remarkably free from mechanical disturbances that would render an instrument of the second type unworkable. In fact, mechanical disturbance of an almost astatic instrument in the homogeneous earth's magnetic field is of a different character from that of the shielded instrument. In the astatic instrument mechanical disturbance is a very rapid oscillation of the galvanometer zero: the motion is probably best described as a "dither", and is clearly due to the point of attachment of the quartz fibre to the astatic system not being vertically above the centre of gravity of this system; the disturbance disappears when this error is corrected. In the shielded instrument the zero oscillation is slower and is of larger amplitude. This larger and slower motion cannot be transmitted through the quartz fibre and must be associated with the controlling magnetic field. The unshielded instrument uses the earth's homogeneous field and this remains at rest despite oscillation of the galvanometer support: the shielded instrument, on the other hand, uses a field determined by the position of the shields and control magnets relative to the astatic system. This field is unlikely to be homogeneous at the suspended system, and any motion of it relative to the astatic system will vary the control and cause rotation of the galvanometer needle. Thus a shielded instrument must be much more carefully insulated from mechanical disturbances than the unshielded one. Magnetic communication of vibration to the needle could be overcome if the shields and control magnets were so arranged that the residual field was homogeneous at the astatic system: this has not been tried, and may be impracticable, but it may account for the efficiency of one system of shielding and support and the inefficiency of an apparently identical system.

(2). THE MONOCHROMATOR METHOD. At the commencement of the Award the programme for future work included investigation of the infra-red absorption spectra of chlorine monoxide and dioxide; these gases are known to undergo very rapid dissociation in the presence of visible and ultra-violet light, and the full spectral range of the Nernst filament could not be passed through these gases whilst under investigation. The alternative procedure was to use the spectrometer as a monochromator so that only a small spectral range of infra-red radiation passed through the gas.

This method has, however, another great advantage over the conventional method: the sensitive width of elements forming the thermopile is considerably greater than the collimator and telescope slit widths, and this gave rise to the possibility of contriving a system of mirrors that would pass the monochromated beam first through an empty tube, and second through a tube containing the gas under investigation. Preliminary experiments proved that this was so, and the system described in (4) (see p. 2) was developed.

Little need be added to the description given in (4). The method has been so successful that it has been used for most of the investigations carried out during tenure of the Award, and no material modification has been required. One considerable advantage of the method not mentioned in (4), is the use of two thermopiles in series and in opposition. The limit to which the sensitivity of the galvanometer may be increased is now determined by heating and cooling disturbances of the thermopile. The two thermopiles used in the monochromator system are contained in one housing, and heating and cooling affects the two to an almost equal degree; they are coupled in opposition, and the resultant galvanometer deflections are consequently very much reduced. This heating and cooling must not be identified with adiabatic compression and rarefaction of the atmosphere; the latter must be overcome by housing the thermopiles in airtight casings, and even a small leak in either of these gives very large galvanometer fluctuations. In practice, a manometer system is used to eliminate these leaks, and as a rough working rule, it may be stated that if a mercury manometer falls a mm. per minute with a pressure difference of one half an atmosphere, the leak is just too great.

(3). THE GRATING SPECTROMETER. The success of the monochromator method and the ease with which the empty and full tube readings may be interchanged, suggested that even a grating spectrometer might best be run as a monochromator. Preliminary experiments showed that despite the long radiation train and the many reflections at different mirrors, this system would succeed. The actual grating spectrometer was therefore designed primarily for use as a double monochromator.

The instrument is described in (7), and has worked without modification to give results described in subsequent papers. Nothing need therefore be added to the description of reference (7), which in addition to describing the instrument, discusses possible errors and resolving power.

SECTION II.

OBSERVED SPECTRA AND THEIR INTERPRETATION IN TERMS OF MOLECULAR STRUCTURE.

Introductory. A Triatomic molecule must fall into one of four possible structures, linear and unsymmetrical, linear and symmetrical, triangular and unsymmetrical, or triangular and symmetrical; without further evidence one might say that the last two classes should be replaced with scalene, isosceles, and equilateral triangles, but at present there is no evidence of a member of the third class, even ozone having an isosceles triangular structure. This means that the normal frequencies of the above four systems must be algebraically determined before progress in interpreting observed spectra can be made. This mathematical investigation immediately reveals that the triangular models split into two further classes: in general one of the three atoms may be regarded as the central atom, and the existence of two possible force systems at this atom gives rise to the two new classes. The central force system assumes linear elastic restoring forces acting between each pair of the three atoms; thus, if we call the central atom, at the vertex of the triangle, B, and the other two A. and C, then this system assumes linear restoring forces acting along

AC, AB, and BC. The valence force system, on the other hand, assumes the force along the base AC replaced by a restoring couple acting about an axis normal to the plane of the triangle and passing through B. There are thus six classes which shall be designated I, II, IIIA, IIIB, IVA, and IVB: I is the linear and symmetrical molecule,

II is the linear and unsymmetrical molecule,

III A is the isosceles triangle with central forces,

III B is the isosceles triangle with valence forces,

IV A is the scalene triangle with central forces,

IV B is the scalene triangle with valence forces.

The linear molecules must obey the valence force system as a linear restoring force between the extreme molecules offers no resistance to deformation inclined to the line joining the three atoms.

The immediate problem is to determine from observed spectra the class to which any given molecule belongs. Here selection rules provide most guidance. The older quantum mechanics using the correspondence principle showed that a vibrating electric doublet could only change its rotational quantum number, m, by ± 1 when the axis of rotation is normal to the doublet; this is verified by the new quantum mechanics. This rule is often quite sufficient to decide whether or not a triatomic molecule is linear; the two longitudinal normal modes of the linear molecule must have vibrating electric doublets normal to the axis of rotation, and the corresponding bands can have no Q branch. If the resultant electronic orbital angular momentum is not zero this rule may be violated, but the resulting Q branch will be of low intensity compared with that due to a triangular structure. Experimental results show that the frequencies of the longitudinal normal modes are always of higher frequency than that of the transverse; hence, if any but the longest wave length band shows an intense Q branch, the molecule must be triangular.

The spectrum of a symmetrical linear molecule must conform to further restrictions. The normal modes of this system are shown in fig. 1. The symmetrical mode, (a), has zero resultant vibrating electric doublet and therefore cannot absorb radiation in the infra-red. Further, this mode gives the greatest change in polarisation of the molecule and therefore gives the most intense Raman line. Hence if a band be missing in the infra-red and strong in the Raman spectrum, and at the same time fits this frequency, the molecule must be linear and symmetrical. A further criterion for the symmetrical linear molecule has been developed by Dennison

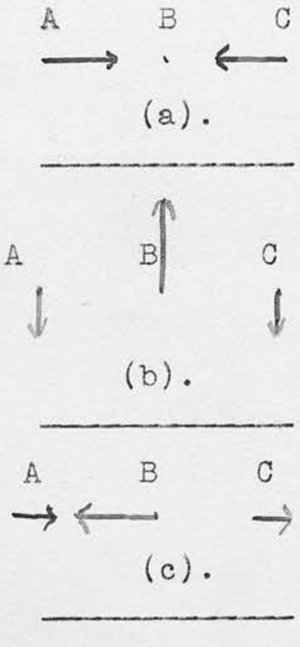

Fig. 1.

(Rev. Mod. Physics, 1931, 3, 291): if three atoms are collinear and symmetrical, then the sum of any two observed infra-red bands will not be the frequency of an active or observable overtone.

These rules together with the vanishing of the electrical doublet of the molecule give a safe guide as to whether or not the molecule is linear, and if so, whether or not it is symmetrical.

There are thus good guides as to whether or not a triatomic molecule is linear, but a choice between classes III A, III B, IV A, and IV B, requires a more detailed investigation of the problem, and this is given in the individual treatment of the six classes.

I. THE LINEAR SYMMETRICAL MOLECULE. This is the simplest form the triatomic molecule can assume, and here the frequency equation can be solved for each of the three normal frequencies; they are:-

for the normal mode, fig. 1a.

$$\nu_1 = \frac{1}{2\pi}\sqrt{K_1/m}$$

for the normal mode, fig. 1b.

$$\nu_2 = \frac{1}{2\pi}\sqrt{2K_\theta\,\frac{M+2m}{Mm}}$$

for the normal mode, fig. 1c.

$$\nu_3 = \frac{1}{2\pi}\sqrt{K_1\,\frac{M+2m}{Mm}}$$

where M is the mass of the central atom, m is that of A and

C; K_1 is the linear restoring force per unit displacement of AB or AC, and K_θ is the linear restoring force per unit arc displacement of the angle ABC. Thus from either ν_1 or ν_3, K_1 may be determined, and from ν_2, K_θ; ν_1 is, of course, the inactive frequency that appears in the Raman spectrum, and from ν_3, which appears in the infra-red, the Raman frequency may be calculated, and the check so provided is good evidence as to whether or not the assumption of a linear symmetrical form is correct.

There is, however, a complication peculiar to linear molecules which must next be discussed, and which for some time complicated the interpretation of spectra observed for CO_2, COS, and CS_2. This complication was first noted by Bailey in the spectrum of CO_2. He observed (Nature, 1929, 123, 205) that the CO_2 infra-red and Raman bands tended to appear in pairs; thus, certain of the bands predicted by the formulae given above were replaced by two bands approximately 107 cm^{-1}. apart. Fermi (Z. Physik, 1931, 71, 250) put forward the theory that this doubling of the bands might be due to resonance of the first harmonic of the transverse mode, (1b), with the fundamental of the inactive mode; for all three molecules the frequency of the transverse mode happens to be approximately one half that of the inactive mode, and therefore this explanation might apply to all of them.

First one must consider why this phenomenon does not appear with triangular molecules, for in SO_2, the longest wave length fundamental has approximately one half the frequency of a shorter wave length fundamental frequency. The presence of the phenomenon in linear molecules and its absence from triangular molecules is due to the symmetry of the potential of linear molecule: Thus if B (fig. 1) be displaced above the line ABC, the increase of potential of the system equals that of the system with B displaced an equal distance below ABC; hence the coupling potential of the transverse mode with any other mode must be proportional to the square of the normal co-ordinate of the transverse mode, for the linear but not for the triangular molecule. The matrix element of coupling must accordingly be proportional to the matrix element of the square of this normal co-ordinate, and this vanishes for all but transitions in which the corresponding vibrational quantum number changes by two; hence only systems with this symmetry of potential may have a first harmonic coupled with a fundamental.

Again the energy level of longitudinal quantum number 2 must be of approximately the same value as the level corresponding to one quantum of the longitudinal mode and two quanta of the transverse mode, and here too the matrix elements of coupling do not always vanish. This means that this energy level must split into new levels, and one might therefore expect that the first harmonic of the longitudinal mode would be replaced by two or more bands. Empirical results suggested that this was so, and that two levels appeared with approximately the same separation as the two levels replacing the longitudinal fundamental. The problem is investigated theoretically in reference 9 (see p. 3), where the separation of the higher levels is shown to be $\sqrt{2}$ times that of the lower levels, contradicting the observed constant separation. This difficulty has been to some extent cleared up by Dennison (Phys. Rev., 1932, 41, 304,) who has shown that although the coincidence of first harmonic and fundamental levels is close enough in CO_2 for resonance coupling to occur, yet these levels are not sufficiently close in CS_2, and this is also so for COS.

Hence the correct interpretation of the CS_2 bands is that originally given by Bailey and Cassie (Nature, 1930, 126, 350). This allocation is given in Table I which includes the long wave length band investigated by Dennison and Wright (Phys. Rev., 1931, 38, 2077).

TABLE I.

The infra-red spectrum of carbon disulphide and the origin of the bands.

Band	Origin	Band centre (u).	(cm^{-1}.)	Maxima.	P − R (cm^{-1}.)	(cal).	Difference, (cm^{-1}.)
	ν_2	25.2	397	406 397 389	16.4		
R	ν_1	15.3	656	-			
A	$\nu_3 - \nu_1$	11.391	878	855 872	13	867.5	-11
B	ν_3	6.566	1253	1530 1518	12		
C	$\nu_3 + \nu_1$	4.613	2167	2175.3 2162.0	13.3	2178	11
D	$\nu_3 + 2\nu_2$	4.292	2330			2318	-12

Band C has been investigated with the grating spectrometer, reference 8, and the values for the centre and maxima given in table I were obtained with this instrument.

The force constants for this molecule are determined from the formulae given on p. 16; they are K_1 equals $7.0 \cdot 10^5$ dynes/cm., and the restoring couple per unit angular displacement of ABC is $6 \cdot 10^{-12}$ dyne.cm. These values might suggest that the restoring couple constant is in error, but the tangential restoring force per unit arc displacement is in dynes/cm., and roughly equals the couple constant multiplied by the distance CS which is approximately $1.5 \cdot 10^{-8}$ cm.

This concludes the summary of observations made of the spectra of symmetrical linear triatomic molecules during the present investigations, and the significance of the values of the various force constants will be discussed in Section III.

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2. The linear unsymmetrical molecule. When the infra-red absorption spectra of CO_2 and CS_2 were known, it became of interest to investigate the spectrum of the intermediate substance COS. Interpretation of this spectrum is, however, possible only when the frequencies of the normal modes of the unsymmetrical linear molecule are determined in terms of the force constants and masses of the constituent atoms. The results of this theoretical investigation, together with the experimental observations are given in reference (5).

The equation relating the normal frequencies to the force constants and the masses of the atom cannot be completely factorised for the unsymmetrical linear molecule. The frequency of the transverse mode can be determined independently of the frequencies of the longitudinal modes in terms of the masses, the restoring couple constant, and the atomic separations, but the frequencies of the longitudinal modes appear as the roots of a quadratic equation involving the masses of the atoms and the two longitudinal force constants. The mathematical calculation is sketched in reference (5). The transverse frequency is given by -

$$p^2 = K_q \frac{\left[\frac{a^2}{m_1^2}\left(\frac{1}{m_2}+\frac{1}{m_3}\right)+\frac{b^2}{m_2^2}\left(\frac{1}{m_3}+\frac{1}{m_1}\right)+\frac{c^2}{m_3^2}\left(\frac{1}{m_1}+\frac{1}{m_2}\right)+\frac{2}{m_1m_2m_3}(bc+ca-ab)\right.}{\left(\frac{a}{m_1}-\frac{b}{m_2}\right)^2\left(\frac{b}{m_2}+\frac{c}{m_3}\right)^2}$$

where p is related to the frequency in wave numbers by $p = 2\pi c\nu$, c being the velocity of light; a and b, see fig.2. The frequencies of the longitudinal modes are the two roots of the equation

$$p^4 - p^2\left[K_1\left(\frac{1}{m_1}+\frac{1}{m_2}\right)+K_1'\left(\frac{1}{m_2}+\frac{1}{m_3}\right)+K_1K'\left(\frac{1}{m_1m_2}+\frac{1}{m_2m_3}+\frac{1}{m_3m_1}\right)\right]=0$$

The appropriate masses are shown in fig. 2.

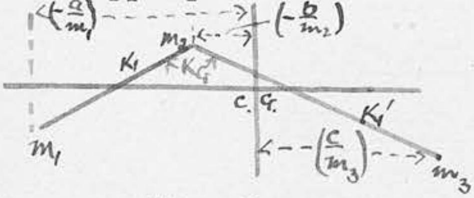

Fig. 2.

The second formula is most conveniently used by considering the sum and product of the roots in terms of the coefficient of p^2 and the constant term. These are

$$p_1^2 + p_2^2 = K_1\left(\frac{1}{m_1}+\frac{1}{m_2}\right) + K_1'\left(\frac{1}{m_2}+\frac{1}{m_3}\right)$$

and

$$p_1^2 p_2^2 = K_1K_1'\left(\frac{1}{m_1m_2}+\frac{1}{m_2m_3}+\frac{1}{m_3m_1}\right)$$

The spectrum observed for COS, using the prism spectrometer, and the allocation of the bands is given in Table II.

TABLE II.

The infra-red spectrum of carbonyl sulphide and the origin of the bands.

Band.	Origin.	Band Centre. (μ).	(cm^{-1}.)	Maxima	P - R (cm^{-1}.).	(cal.).	Difference. (cal. -ob.)	In. Intensity.
A	ν_2	18.96	527	522 541	19	-		3.5 (6)
B	ν_1	11.64	859	854 868	14	-		15 (4)
C	$2\nu_2$	9.516	1051	1047 1051 1061	14	1054	3	12 (8)
D	$2\nu_1$	5,842	1718	1709 1722	13	1718	0	1.8 (10)
E	$\nu_1 + 2\nu_2$	5.272	1898	1898		1913	15	2 8
F	ν_3	4.810	2079	2079		-		29 (16)
G	$\nu_3 + \nu_1$	3.443	2904	2904		2938	34	13 (10)
H	$\nu_3 + 2\nu_2$	3.231	3095	3095		3133	38	2.1 (11)
I	$\nu_3 + 2\nu_1$	2.672	3742	3742		3797	55	1.5 (14)
J	$2\nu_3$	2.449	4084	4084		4158	74	1.5 (15)

The intensities given in the last column are only estimates, and the slit widths used are given in brackets in cm^{-1}.

The outstanding feature of this spectrum is the large number of bands observed compared with the spectra of the symmetrical molecules. This is to some extent to be expected, as the inactive mode (fig. 1a, p.15) of the symmetrical molecule becomes active for the unsymmetrical form. Thus a third fundamental frequency becomes active. In addition many combination bands appear, and the large differences appearing in the second last column of Table II, indicate that the anharmonic constants are greater for this molecule than for the symmetrical neighbours CO_2 and CS_2.

The third maximum appearing in the 9.52 µ band might be taken as a Q branch, and the molecule might therefore be triangular; this supposition has been tried, but the data cannot be reconciled with the unsymmetrical triangular form. The third maximum is naturally explained on the present hypothesis, for ν_2 is a symmetrical vibration, and according to Dennison's selection rules (Rev. Mod. Physics, 1931, 3, 280), the first harmonic has the same direction of effective electric moment as the fundamental; this should have a Q branch, and therefore so also should have the harmonic. The Q branch has not been observed in the fundamental, but this is probably due to lack of resolution; the fundamental was investigated with the prism instrument, and in no case has a prism revealed the Q branch of the transverse fundamental, although re-investigation with grating spectrometers has always shown a narrow and intense Q branch (cf., Dennison and Wright, Phys. Rev., 1931, 38, 2077, for CS_2, and Martin and Barker, ibid, 1932, 41, 291, for CO_2).

When observed bands have been allocated the immediate problem becomes the evaluation of the force constants. This is unfortunately not free from ambiguity for the unsymmetrical molecule. The two longitudinal force constants are determined from the sum and product of the squares of the observed frequencies, according to the formulae given on p. 21. This gives two sets of possible values, K_1 equal to 6.2 or 13.5, and K_1' equal to 18.5 or 8.5 . 10^5 dynes/cm. respectively. Comparison with the force constants obtained for CO and CS immediately suggests that the ~~first~~ second set of values is the correct one. There may also be a tendency for the force constants to even out over the molecule, and although the assumption that K_1 equals K_1' does not give so good a fit with the observed frequencies as the values quoted above, yet a tendency towards equalisation cannot be definitely excluded.

The mean P - R branch separation obtained from table II, may be taken as 14 cm^{-1}.; this gives possible CO and CS distances as 1.1 and 1.96 Å respectively.

A second unsymmetrical linear molecule which has been investigated by Snow (Proc. Roy. Soc., , A, ,), and Barker (Phys. Rev., 1931, 38, 1827), is N_2O. Reference (10) gives an application of the frequency formulae to this molecule which Barker has shown to be NNO, and the resulting force constants are:

$K_1(N-N)$ equals $14 \cdot 10^5$ dynes/cm.
$K_1'(N-O)$ " $14 \cdot 10^5$ " "
and K_G " $6 \cdot 10^{-11}$ dyne.cm.

The above discussion of the linear molecule has neglected entirely the effect of the degeneracy arising from the vanishing of two of the three principal moments of inertia. This problem has been theoretically investigated by Dennison (Rev. Mod. Physics, 1931, <u>3</u>, 280, and Phys. Rev., 1932, <u>41</u>, 304). He has shown that new energy levels are introduced, but the resulting bands appear superimposed on the already known bands, and only become of significance when the longer wave length bands are investigated with a grating spectrometer. Unfortunately a suitable grating has not been available for the present series of investigations, and accordingly none of the observed bands show the effects of this degeneracy.

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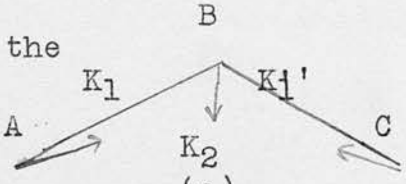
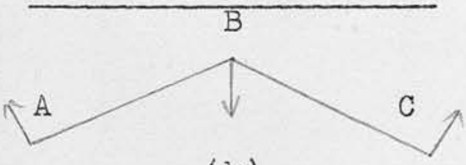
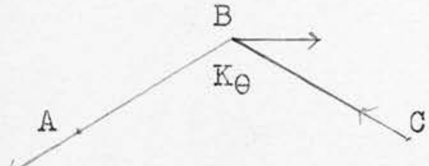
3. <u>The symmetrical triangular molecule.</u> The normal modes of this molecule are shown in fig. 3. They are, of course, the generalised equivalents of the normal modes of the linear symmetrical molecule. 3a, whose fundamental frequency is designated ν_1, corresponds to 1a; likewise 3b has the fundamental frequency ν_2, and corresponds to 1b, and 3c has the frequently ν_3, corresponding to 1c.



(a).



(b).



(c).

Fig. 3.

The bisector of the vertical angle of the triangle is the line of symmetry of this molecule, and shall be used as a reference line; (3a) and (3b) are thus referred to as symmetrical modes, and (3c) as an unsymmetrical mode.

The fundamental frequencies of these normal modes have been determined by Bjerrum (Verhand. Deutsche Physikal. Gesell., 1914, 16, 737) and Dennison (Phil. Mag., 1926, 1, 195). The fundamental frequencies cannot be determined explicitly in terms of the force constants and masses of the atoms, and resort must be had to methods similar to those used for the unsymmetrical linear molecule. If the molecule be truly symmetrical so that the force constant along AB equals that along BC, there are three unknowns to be determined from the frequencies; they are, the linear force constant along AB or BC, K_1, the linear force constant, K_2, along AC if the central force system be used (see p. 13 and 14), the restoring force, K_θ, per unit arc displacement of the angle ABC if the valence force system be used, and the semi-vertical angle of the triangle. If the frequency equation be factorised, it is found that the unsymmetrical frequency may be determined explicitly in terms of the force constant K_1, the masses, and the vertical angle, but the other two give a quadratic in the squares of the frequencies with the molecular parameters appearing in the coefficients; thus the normal procedure would follow exactly the lines adopted for the unsymmetrical linear molecule. In practice, however, another method is adopted. The frequency equation gives accurate enough values for the force constants, but only rough values for the vertical angle, and if the force constants were first determined with the accuracy required of them, the value obtained for the vertical angle would be much too inaccurate. The most efficient procedure is therefore to eliminate the force constants and so obtain an equation relating the semi-vertical angle to the frequencies. The various steps of the elimination involve much cumbersome algebra, and the final result is given in reference (6). The equations are written in the form

$$\begin{aligned}
&\left[\frac{4}{1+\frac{2m}{M}}\cdot\frac{m^2}{M^2}\cdot\frac{p_1^2p_2^2}{p_3^2}+\frac{2m}{M}\left(p_1^2+p_2^2+p_3^2\right)\right]\sin^4\alpha \\
&+\left[\frac{4}{1+\frac{2m}{M}}\cdot\frac{m}{M}\cdot\frac{p_1^2p_2^2}{p_3^2}+\left(1-\frac{2m}{M}\right)\left(p_1^2+p_2^2+p_3^2\right)-2\left(1+\frac{m}{M}\right)p_3^2\right]\sin^2\alpha \\
&+\left[\frac{1}{1+\frac{2m}{M}}\cdot\frac{p_1^2p_2^2}{p_3^2}-\left(p_1^2+p_2^2+p_3^2\right)+2\left(1+\frac{m}{M}\right)p_3^2\right]=0
\end{aligned}$$

for the central force system, and

$$\frac{p_1^2p_2^2}{p_3^2}\cdot\frac{x^3}{1+\frac{2m}{M}}-\left(p_1^2+p_2^2+p_3^2\right)x+2p_3^2\left(1+\frac{m}{M}\right)=0$$

where

$$x = 1+\frac{2m}{M}\sin^2\alpha$$

for the valence force system.

The force constants are then most readily obtained from the equations:

$$K_1 = \frac{m p_3^2}{1 + \frac{2m}{M} \sin^2 \alpha}$$

$$K_2 = \frac{m}{2}\left(p_1^2 + p_2^2\right) - \frac{1}{2}\left(1 + \frac{2m}{M} \cos^2 \alpha\right) K_1$$

$$K_\theta = 2 \frac{p_1^2 p_2^2}{p_3^2} \cdot \frac{m\left(1 + \frac{2m}{M} \sin^2 \alpha\right)}{1 + \frac{2m}{M}}$$

p_1, p_2, and p_3 are related to the frequencies in wave numbers by the relation p equals $2\pi c \nu$. The equations of p. 28 thus afford many possible solutions, for p_3 is not known a priori, and may be any of the three observed fundamental frequencies; and even when p_3 is known the central force system may give two values for α, and the valence force system gives three. Further, there is no a priori reason for giving preference to one force system over the other. The procedure adopted is to obtain all real values of α possible according to the equations of p. 28, and then from selection rules, the appropriate value is chosen. This necessarily entails much calculation, and the equations have been given in the form that appears to reduce this to a minimum; for example, large powers of ten completely disappear from the coefficients, and this eliminates one of the most frequent sources of arithmetical error.

When all possible values of the semi-vertical angle have been determined, selection rules predict which of the observed bands, fundamentals, harmonics and combination tones, should have Q branches; this is in general sufficient to determine the correct angle, but subsidiary evidence may be obtained from the relative intensities of the bands, from the resulting values of the force constants, and from the Raman effect.

The method of application of the selection rules is as follows. The orientation of the effective electric moment relative to the bisector of the vertical angle is first determined, and from the value of the semi-vertical angle and the masses of the atoms, the direction of the least moment of inertia relative to the bisector may be determined; hence the orientation of the effective electric moment relative to the least axis of inertia is determined. References (2) and (12) show that some form of Q branch is to be expected for the asymmetrical rotator when the effective electric moment vibrates parallel to the least axis of inertia, whilst if it is normal to this axis, the band will have the appearance of P and R branches only; this deduction was made according to the older quantum mechanics, and Dennison (Rev.Mod.Physics, 1931, 3, 280) has shown that the new mechanics gives qualitative agreement.

Reference (2) shows that the symmetrical fundamental frequencies have effective electric moments parallel to the bisector of the vertical angle, and Dennison (loc. cit.), with the aid of the new mechanics has obtained the direction of the effective moment for combination and over tones; if either of the symmetrical vibrational quantum numbers change by any integer, then the effective moment is parallel to the bisector; if the unsymmetrical vibrational quantum number changes by an odd integer, the effective moment is normal to the bisector, and if this quantum number changes by an even integer, the effective moment is parallel to the bisector. Thus the orientation of the effective moment relative to the bisector, and therefore relative to the least axis of inertia, is determined for all bands for every value of the semi-vertical angle possible according to the equations of p. 27.

The method of selecting the correct value of the semi-vertical angle outlined above depends entirely on the molecule being symmetrical with respect to force constants as well as masses. If the force constants for AB and BC were not equal, the normal modes would not have the symmetry shown in fig. 3, and the effective electric moments would not have the simple orientations normal and parallel to the least axis of inertia; this implies that the observed bands would have no definite branches, and in all probability could not be resolved into several maxima. This is borne out by results obtained for NOCl, which apparently has a triangular structure; if this be so, the structure is unsymmetrical, and correspondingly none of the bands show the two or three maxima observed for SO_2, and the other triangular molecules investigated. The appearance of the maxima in the bands of SO_2 is particularly interesting, for it implies that SO_2 is a symmetrical molecule, each SO having the same chemical linking. This observation also applies to ClO_2, and will be dealt with more fully in section III.

The method adopted for choosing the correct vertical angle is best illustrated by means of an example, and the example chosen is the observed spectrum of SO_2. Table III gives the experimentally observed spectrum, including the results published in references (2) and (8). Table IV gives the solutions possible according to the equations of p. 27.

TABLE III.

The infra-red spectrum of sulphur dioxide.

Band	Band Centre (μ)	Band Centre $(cm.^{-1})$	Maxima	P - R $(cm.^{-1})$	Pressure cm. Hg.	Maximal percent. absorption.
Raman	19.1	524	524	-		
A	16.5	606	606	-	63.5	37
B	8.680	1152	1169 1138	31	4.5	80
C	7.347	1361	1377 1361 1348	30	0.15	55
D	5.345	1871	1871	-	60	12
E	4.369	2290	2276 2303	27	64.5	47
F	4.014	2492	2510 2492 2485	25	64.5	89

TABLE IV.

Possible solutions for sulphur dioxide.

Possible unsymmetrical frequency.	Semi-vertical angle.	K_1 Dynes/cm. 10^{-5}	K_2 Dynes/cm. 10^{-5}	K_θ Dynes/cm. 10^{-5}
(a) Central force system.				
1152 cm^{-1}	32°	9.6	1.7	
1152	57°	7.25	5.2	
(b) Valence force system.				
1152	32°	9.6		4.6
1361	61°	9.8		3.3

The unsymmetrical frequency has an effective electric doublet normal or parallel to the bisector of the vertical angle according as the corresponding vibrational quantum number changes by an odd or an even integer. Hence to determine the orientation of the effective electric doublet relative to the least axis of inertia, the orientation of this axis to the bisector must be determined for the possible angles given on table IV. The least axis will be parallel to the bisector according as $\tan^2\alpha$ is less than $M/(M + 2m)$, and normal to the bisector according as $\tan^2\alpha$ is greater than $M/(M + 2m)$ (see reference 6). This criterion gives the allocation of the bands and the orientations of the doublets given in table V).

TABLE V.

Orientation of the effective electric doublets relative to the least axis of inertia for the various possible molecular models of sulphur dioxide.

Band	Allocation	Frequency (cm^{-1})	less than 35°	greater than 35°
			Central force system.	
C	ν_1	1361	Parallel	Perpendicular
-	ν_2	524	"	"
B	ν_3	1152	Perpendicular	Parallel
A	$\nu_3 - \nu_2$	606	"	"
D	$\nu_1 + \nu_2$	1871	Parallel	Perpendicular
E	$2\nu_2$	2305	"	"
F	$\nu_1 + \nu_3$	2499	Perpendicular	Parallel

In this table 1152 is the unsymmetrical frequency.

The valence force system gives no solution when the semi-vertical angle is greater than 35° with 1152 as the unsymmetrical frequency, and gives no solution with a vertical angle less than 70° if 1361 is the unsymmetrical frequency. The central force system gives no solution with 1361 as the unsymmetrical frequency. Hence there are left the possible solutions given in table V (continued).

TABLE V. (Continued).

Valence force system.

Band	Frequency	Unsymm. Mode s-v	1152 cm^{-1} Orientation less than 35°	Unsymm. Mode s-v	1361 cm^{-1} Orientation greater than 35°
C	1361	ν_1	Parallel	ν_3	Parallel
-	524	ν_2	"	ν_2	Perpendicular
B	1152	ν_3	Perpendicular	ν_1	"
A	606	$\nu_3 - \nu_2$	"	$\nu_1 - \nu_2$	"
D	1871	$\nu_1 + \nu_2$	Parallel	$\nu_2 + \nu_4$	Parallel
E	2305	ν_3	"	ν_1	Perpendicular
F	2499	$\nu_1 + \nu_3$	Perpendicular	$\nu_1 + \nu_3$	Parallel

Recalling that only bands with effective electric doublets parallel to the least axis of inertia can have Q branches, a comparison of tables III and V shows that the only solution consistent with the observed spectrum is that obtained assuming a valence force system with an angle greater than

70°, and consequently with 1361 cm^{-1}. as the unsymmetrical frequency. Sulphur dioxide must therefore form an isosceles triangle with a vertical angle of approximately 120°, with an SO force constant of $9.8 \cdot 10^5$ dynes/cm., and with a tangential restoring force per unit arc displacement of $3.3 \cdot 10^5$ dynes/cm.

The absorption spectrum observed for chlorine dioxide is surprisingly similar to that of sulphur dioxide. The method of interpretation follows exactly the lines of that for sulphur dioxide, and accordingly is omitted from the report. The experimental results will be found in reference (6), and the interpretation in (6) and (8). The allocation of the observed bands is given in table VI.

TABLE VI.

The infra-red spectrum of chlorine dioxide and the origin of the bands.

Band	Band Centre (u)	Band Centre (cm^{-1})	Origin	Maxima	P - R (cm^{-1})	(calc.)	Intensity at (cm^{-1}) slit.
B	10.57	946	ν_1	932 963	31	-	20 (5)
-	19.0	527	ν_2	-		-	-
C	9.017	1109	ν_3	1095 1106 1123	28	-	50 (7)
E	5.307	1884	$2\nu_1$	1870 1900	30	1892	2 (10)
F	4.916	2034	$\nu_1 + \nu_3$	-		2055	4 (15)

The solution giving the allocation of table VI is that using the valence force system; the vertical angle is approximately 130°, the ClO force constant $6.1 \cdot 10^5$ dynes/cm., and the tangential restoring force per unit arc displacement is $3.6 \cdot 10^5$ dynes/cm. The molecule is thus quite similar to sulphur dioxide apart from the difference in the ClO and SO force constants. This will be discussed in section III.

A third molecule which apparently belongs to class IIIB is ozone. An investigation of this molecule was in progress during the summer of 1932, when a letter by Gerhard and Sutherland appeared in "Nature" (1932, 130, 241) giving the result of an investigation of the Raman effect in ozone, and announcing a paper on the infra-red spectrum. Accordingly our work which had just finished a preliminary survey of the bands near 9.5 and 4.7 u, was suspended. Gerhard used much higher concentrations than had been used in our work, where only the ordinary Siemens' ozoniser was used. His work has since been published in full, and the 4.7 u band according to his investigation, has a powerful and broad Q branch, whereas our preliminary measurements revealed no such Q branch. We have since repeated our measurements with the grating spectrometer and find no trace of this branch in the ozone produced by the Siemens' ozoniser. The contours of the band near 9.5 u are consistent, and with the high concentration of ozone Gerhard has been able to trace the contours of bands at 7.4 μ and 11.38 μ; the latter he attributes to nitrogen pentoxide. Hence with the band near 14μ, reported by Hettner, Pohlman, and Schumacher (Naturwiss., 1933, <u>24</u>, 467), the three fundamentals of ozone are probably at 14, 9.5, and 7.4 μ. Following exactly the procedure adopted for SO_2 and ClO_2, O_3 is found to have a triangular structure with an angle less than 60° if the 4.7 μ band has a Q branch, and an angle of approximately 120° if this Q branch is absent; absence of any Raman lines eliminates the possibility of it being linear of an equilateral triangle. The conclusions deducted from the present available data are given in table VII, and details will be found in the note to be sent to the Phys. Rev.

TABLE VII.

Known bands of ozone and the orientation of the corresponding effective doublets, assuming the valence force system and a vertical angle of 120°.

Observed bands. (μ)	(cm^{-1})	Type of envelope	Mode	Orientation to least axis.
14	714	Doublet	2	Perpendicular
9.5	1053	Doublet	1	"
7.39	1355	Q branch	3	Parallel
4.7	2108	Doublet	2 1	Perpendicular

One must emphasise that this allocation has not been selected arbitrarily from a number of equally possible allocations; it is the only possible allocation that fits the observed types of envelopes. Nor have the valence force system and the angle 120° been arbitrarily chosen; they emerge from inserting the frequencies quoted in table VII in the formulae given on p. 28.

~~The force constants corresponding to the allocation of table VII are~~

Among molecules whose spectra have been observed during the present investigations, one appears to occupy class III A; this is chlorine monoxide, and the observed spectrum is given in table VIII.

TABLE VIII.

The infra-red absorption spectrum of chlorine monoxide.

Band.	Band Centre. (u)	(cm^{-1})	Maxima.	P - R (cm^{-1})	Intensity Slits (cm^{-1})
A	15.63	640	628 651	23	30 (5)
B	10.28	973	967 973 980	13	50 (5)
C	8.033	1245	1233 1260	27	20 (10)
D	7.625	1311	-		10 (10)

The possible semi-vertical angles and corresponding force constants obtained by taking bands A, B, and C as fundamental frequencies, are given in table IX.

TABLE IX.

Possible semi-vertical angles and force constants for chlorine monoxide.

Unsymm. mode.	CENTRAL FORCE SYSTEM			VALENCE FORCE SYSTEM		
3	s-va.	K(Cl-O)	K(Cl-Cl)	s-v a.	K(Cl-O)	K_θ
640	25°	4.4	15	35°	3.5	68
	17	5.8	11			
973	54	5.1	12	NO SOLUTION		
	36	7.8	4.5			
1245	NO SOLUTION			NO SOLUTION		

The orientations of the effective electric doublets for the observed bands using in turn each of the solutions given in table IX, are given in table X.

TABLE X.

Orientation of the effective electric doublets relative the least axis of inertia.

Band	CENTRAL FORCE SYSTEM.			VALENCE FORCE
(cm^{-1})	25°	17°	36° or 54°	35°
A (640)	parallel	normal	normal	parallel
B (973)	normal	parallel	parallel	normal
C (1245)	"	"	normal	"
D (1311)	"	"	"	"

Tables IX and X show the valence force system inapplicable on two counts; firstly, comparison with table VIII shows that the observed envelopes are not consistent with the orientation of the effective electric doublets obtained for the one possible solution with the valence force system; secondly, a tangential restoring force constant of 68 . 10^5 dynes/cm. is impossibly high. Hence the valence force system must be discarded for the chlorine monoxide molecule.

The central force system gives three values for the semi-vertical angle, 25°, 17°, and 36 to 54°; comparison of table X with the envelopes recorded in table VIII, shows that only the last value for the vertical angle is consistent with the experimental results. Hence the chlorine monoxide molecule must form an isosceles triangle with a vertical between 70 and 110°. Inspection of table IX shows that these two models are by no means the same, for the Cl-Cl force constant increases rapidly with increasing vertical angle whilst the ClO force constant diminishes. Fortunately the observed spectrum gives further evidence in the form of isotopic bands.

The relative number of the $Cl^{35}Cl^{35}O$ and the $Cl^{35}Cl^{37}O$ molecules is 3/2, and therefore bands due to the second molecule should be of intensity comparable to that due to the first; this is observed in the spectrum, and accounts for the large P - R branch separation of band C. The isotope effect is fully discussed in the paper on chlorine monoxide, which should appear very shortly, and only the results are briefly stated below.

Formulae have been deduced for the isotope separations of the various fundamentals; the deduction is given in the paper referred to (Part IX of the present series in the Proc. Roy. Soc.), and the actual formulae are;

$$\Delta n_{1,2} = -\frac{\Delta m}{2m} n_i + \frac{\Delta m K_1 \cos^2\alpha}{m M n_i} \cdot \frac{m n_i^2 - 2K_2}{2 m n_i^2 - \left[2K_2 + \left(1 + \frac{2m}{M}\cos^2\alpha\right)K_1\right]}$$

for the symmetrical modes, and

$$\Delta n_3 = -\Delta m K_1 / 2 m^2 n_3$$

for the unsymmetrical mode.

Isotope separations calculated for appropriate values of the semi-vertical angles and force constants are given in table XI; the Cl-O force constant has always been taken as $7 \cdot 10^5$ dynes per cm.; its possible variation between 5 and $7 \cdot 10^5$ dynes per cm. does not materially affect the isotope separations.

TABLE XII.

Isotope separations for chlorine monoxide.

s-v. angle.	38°			45°			55°			
K_2 d/c. 10^{-5}	2	7	14	2	7	14	2	7	14.	
$_2$(640)	13	6	3	14	6	3	22	6	2	(cm^{-1})
$_1$(1245)	13	13	5	13	13	16	14	14	16	(cm^{-1})

The unsymmetrical frequency is not sensitive to changes in the molecular parameters, the isotope separation remaining almost constant at 4 wave numbers. Table XII shows that band A is most sensitive to changes in the value of the Cl-Cl force constant. The actual separation appears to be small, and the most consistent values for the various parameters appear to be; K (Cl-Cl) 7 . 10^5 dynes/cm., K (Cl-O) 7 . 10^5 dynes/cm., and a vertical angle of approximately 100°.

This result is of considerable significance for present quantum mechanical theories of molecular structure. Quantum mechanics requires an approximately right angled triangular molecule for Cl_2O, whereas the polarisation theory requires a linear structure; the observed structure is distinctly in favour of the quantum mechanical model, and thus Cl_2O which forms the first crucial test of the quantum mechanical molecular structures, decides in favour of these. This aspect of the subject is more fully dealt with in section III.

This quantum mechanical structure ought also to hold for H_2O and H_2S, and known data for these molecules was therefore investigated by the method outlined above. Unfortunately the spectrum of H_2S appears at the moment to be incompletely investigated, but Plyler has given the fundamental frequencies of H_2O as 1597, 3745, and 5307 wave numbers, the band at 3745 having a Q branch and the others having P and R branches only. Following exactly the procedure adopted for Cl_2O, the only structure for H_2O which is consistent with the observed spectrum, consists of an isosceles triangle with a vertical angle of approximately 100°, and a central system of forces with the O-H force constant $7.5 \cdot 10^5$, and the H-H force constant $5 \cdot 10^5$ dynes/cm. Thus H_2O is in fact very similar to Cl_2O, the only outstanding point of difference being the larger force constant for the base of the triangle. This may be due to exchange of electrons between the Cl atoms; this may be expected on account of the much greater mean radius of the outer electronic shell of Cl compared with the single electron shell of the H atom.

IV. <u>The unsymmetrical triangle.</u> The one molecule belonging to this class which has so far been investigated is nitrosyl chloride. The reason for investigating this molecule is twofold: firstly, the S-O force constants of SO_2 have been assumed equal, as only in this case does theory predict bands which have definite P, Q, and R maxima, and this theory could be definitely tested by investigating an unsymmetrical triangular molecule which should only exhibit bands with single broad maxima; and secondly NOCl forms a molecule which should fit the scheme of molecular structures developed in section III.

The observed bands do not show any branch maxima, and thus confirm the hypothesis of equal force constants for the SO_2 molecule. The lack of branch maxima is however a great drawback in interpreting the results, particularly as there are now three force constants and the semi-vertical angle to be determined from the three observed fundamental frequencies; it is, of course, impossible to determine four unknowns from three equations, and investigation of the observed spectrum therefore resolves into a question of finding the best fit with experimental results consistent with data known for other molecules.

There is the further complication of two alternative force systems, and the possibility of the molecule fitting one or the other must first be investigated. Radakovic (Monat. fur Chemie, 1930, <u>56</u>, 447-460) has given an equation determining the normal frequencies in terms of the molecular constants for the central force system. The relations of the roots of this equation to its coefficients give the simplest way of investigating the problem. These relations are:-

$$p_1^2+p_2^2+p_3^2 = \frac{K_1}{\mu_1} + \frac{K_1'}{\mu_1'} + \frac{K_2}{\mu_2}$$

$$\Sigma\, p_1^2 p_2^2 = \frac{K_1K_1'}{\mu_1\mu_1'} + \frac{K_1'K_2}{\mu_1'\mu_2} + \frac{K_1K_2}{\mu_1\mu_2} - \frac{K_1K_2}{m_0^2}\cos^2\alpha_0 - \frac{K_1K_1'}{m_1^2}\cos^2\alpha - \frac{K_2K_1'}{m_2^2}\cos^2\alpha_2$$

$$p_1^2p_2^2p_3^2 = K_1K_1'K_2\left[\frac{1}{\mu_1\mu_1'\mu_2} - \frac{\cos^2\alpha_2}{m_2^2\mu_1} - \frac{\cos^2\alpha}{m_1^2\mu_2'} - \frac{\cos^2\alpha_0}{m_0^2\mu_1'} + \frac{2\cos\alpha_0\cos\alpha\cos\alpha_2}{m_0m_1m_2}\right]$$

The various constants are indicated in the figure (fig.4.), and the reduced masses are given by:

$$\frac{1}{\mu_1} = \frac{1}{m_0} + \frac{1}{m_1};$$

$$\frac{1}{\mu_1'} = \frac{1}{m_1} + \frac{1}{m_2}; \quad \frac{1}{\mu_2} = \frac{1}{m_2} + \frac{1}{m_0}$$

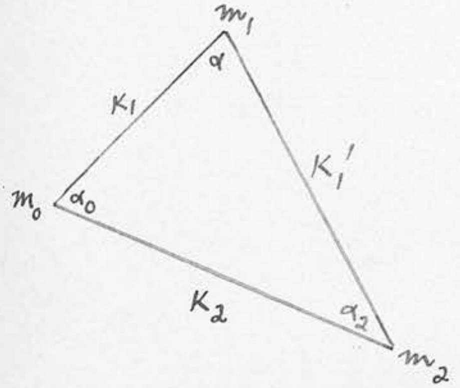


Fig. 4.

The valence system of force constants has been investigated by Lechner (Sitzungsberichte, Wein, 1932, 11a, 141 291), and the corresponding relations are:

$$p_1^2 + p_2^2 + p_3^2 = \frac{K_1}{\mu_1} + \frac{K_1'}{\mu_1'} + \frac{d}{\mu_4}$$

$$\sum p_1^2 p_2^2 = \frac{K_1 K_1'}{\mu_1 \mu_1'}\left[1 - \frac{\mu_1 \mu_1'}{m_1^2}\cos^2\theta\right] + \frac{K_1}{\mu_1}\frac{d}{\mu_4}\left[1 - \frac{\mu_1 \mu_4}{m_1^2}\left(\frac{s}{s_{23}}\right)^2 \sin^2\theta\right]$$

$$+ \frac{K_1'}{\mu_1'}\frac{d}{\mu_4}\left[1 - \frac{\mu_1' \mu_4}{m_1^2}\left(\frac{s}{s_{12}}\right)^2 \sin^2\theta\right]$$

$$p_1^2 p_2^2 p_3^2 = \frac{K_1}{\mu_1}\frac{K_1'}{\mu_1'}\frac{d}{\mu_H}\left[1 - \frac{\mu_1 \mu_1'}{m_2^2}\right],$$

where the reduced mass μ_4 is given by:

$$\frac{1}{\mu_4} = \frac{1}{\mu_1}\left(\frac{s}{s_{12}}\right)^2 + \frac{2}{m_2}\frac{s_2^2}{s_{12}s_{23}}\cos\theta + \frac{1}{\mu_2}\frac{s^2}{s_{23}^2}$$

d is equal to $K_\theta/4$, and θ is the complement of the vertical angle. The parameters, s, take into account the difference in length of the sides of the triangle, and have to be adjusted to suit the molecule under consideration.

The formulae of p. 44 look somewhat formidable, but the first immediately indicates that the sum of the squares of the frequencies is independent of the shape of the triangle and investigation of the second with appropriate values of the various constants reveals that the terms involving the angles are only one tenth the value of the other terms on the r.h.s. Hence we may neglect the angle in the second formula, and so obtain two equations to determine three force constants. Theoretically the three force constants cannot be determined from the two equations, but the ratio of K_1 to K_1' must lie between the limits 1 and 2. Assuming first the ratio 1, the two equations give a negative value for K_2. This means that the central force system cannot apply if the NO force constant be even approximately equal to the NCl constant. Assuming secondly the ratio 2, the equations give the very reasonable values of K_1 equal to 14, and K_1' equal to $7. 10^5$ dynes/cm. If, however, these values be substituted in the third equation with the value $1.3 . 10^5$ dynes/cm. for K_2, which is the value given by the first equations, agreement between the l. and r.h.s. cannot be obtained; the discrepancy is 30% even when assuming the most favourable values for the angles of the triangle.

The central force system does not therefore agree with the fundamental frequencies observed for NOCl.

The valence force system proves much more likely to give a correct solution. The first and third equations for this system involve the angle only through u_4, and this may be calculated for various possible angles; its value for θ

equals 0, 60 and 90°, is 1/3.8, 1/3.1, and 1/(2.4 multiplied by $1.65 \cdot 10^{-23}$), respectively. Lack of P and R branch maxima indicates that the molecule is not linear, and θ is very probably near 60°. The value 1/(3 times $1.65 \cdot 10^{-23}$ grams) is therefore taken for u_4. This reduces the unknowns to three in number, and the first and last equations now permit an accurate evaluation of the force constants for the limiting cases of K_1 equal to K_1', and K_1 equal to $2K_1'$. The results are K_1 and K_1' equal to $10.2 \cdot 10^5$ dynes/cm., and K_θ equal to $4 \cdot 10^5$ dynes/cm. Insertion of these values in the second equation gives a negative value for $\sin^2\theta$, and this is therefore an unlikely model. The second limiting case gives K_1 equal to $2K_1'$ equal to $13 \cdot 10^5$ dynes/cm., and K_θ again equal to $4 \cdot 10^5$ dynes/cm.. Insertion of these values in the second equation gives θ equal to 34°.

The obvious conclusion from this analysis is that the most probable model consistent with the observed spectrum is that with a valence force system having the N-O force constant double that of the N-Cl force constant, and with the angle θ approximately 60° Very probably the N-O force constant may deviate considerably from double that of the N-Cl constant, and accordingly much significance need not be attached to the calculated value of 34° for θ; The point of significance is that this is the only force model that gives a real value for θ, and the comparative closeness of this value to the possible value of 60°, suggests that this is by far the most probable of the models investigated.

The resulting molecular constants for NOCl are summarised in Table XIII.

TABLE XIII.

Molecular constants of nitrosyl chloride.

Fundamental frequencies (cm^{-1}.).	Force constants. (10^{+5} dynes/cm.)			Vertical angle.
	K(N-O).	K(N-Cl).	K_{θ}	ONCl.
633, 923, and 1835	13.	6.5.	4.	120°:

SECTION III.

THEORETICAL CONCLUSIONS ON THE FORMATION OF TRIATOMIC MOLECULES.

Introductory. The most useful parameters deduced from the foregoing investigation of the infra-red absorption spectra of triatomic molecules are summarised in table XIV.

TABLE XIV.

Summary of molecular parameters deduced from infra-red absorption spectra.

Molecule.	Vertical	Force	Force constants (dy/cm.) Multiplied by: 10^5.					(dy.cm.). 10^{-12}
	angle.	system.	K_1	K_1'	$(K_1 + K_1')$	K_2	K_θ	K_G.
OCO	180°	Valence	14	14	28	-	-	6
SCS	180	"	7.5	7.5	15	-	-	6
ONO	180	"	7	7	14	-	-	6.5
SCO	180	"	8.5	13.5	22	-	-	6
NNO	180	"	14	14	28	-	-	6
HOH	100	Central	7	7	14	5	-	-
ClOCl	100	"	7	7	14	7	-	-
OSO	120	Valence	9.6	9.6	19.2	-	3.3	-
OClO	120	"	7	7	14	-	3.6	-
OOO	120	"	6.5	6.5	13	-	3	-
ONCl	120	"	13	6.5	19.5	-	4	-

The values of the various parameters in Table XIV are given in round numbers; more accurate values can be deduced from the observed frequencies, but as the calculations, particularly of the transverse force constants K_2, K_θ, and K_G(the restoring couple per unit angular displacement), provide only approximate values of the force constants and angles, the better procedure seems to be quotation of these in round numbers. The sum of the longitudinal force constants is given, as unsymmetrical molecules provide only somewhat arbitrary estimates of the individual longitudinal force constants, whilst they provide certain, though approximate, values for the sum of these constants.

The selection of K_G instead of K_θ for the linear molecules may seem arbitrary, but K_G is independent of the length of the side of the molecule and therefore gives the more accurate representation of the rigidity of these molecules; K_G may be obtained from K_θ by multiplying the latter by the length of the side squared, and this shows that the corresponding K_θ's for the linear molecules are of the order of $3 \cdot 10^5$ dynes/cm.

<u>Significance of force constants.</u> Force constants might appear to be parameters of little value in determining the formation of a molecule, but this is not so; for Mr. C.R. Bailey has shown that the force constants are apparently proportional to the energy required to break the corresponding chemical link. This might be expected in a qualitative way, for a force constant measures the curvature of the corresponding potential energy - nuclear separation curve, and the

greater this curvature the steeper is the curve likely to be, and correspondingly the greater will be the energy required to dissociate the linkage. A semi-qualitative explanation may be found in Morse's equation giving the potential energy of a diatomic molecule in terms of nuclear separation. This equation may be written:

$$U = D(1 - e^{-a(r - r_0)})^2 \qquad \text{-------- (1)}$$

where D is the energy required to dissociate the molecule, r is the nuclear separation, r_0 is the equilibrium nuclear separation, and a is a constant. The above equation is found to give values of U in agreement with experiment for large ranges of $(r - r_0)$, and for many diatomic molecules; it may therefore be taken to give a fair representation of the potential energy of separation of any two neighbouring atoms in a triatomic molecule, particularly if these atoms be linked by a chemical bond. d^2U/dr^2 is an approximate measure of the curvature of the curve given by equation (1), and when r equals r_0, this is given by:

$$d^2U/dr^2 = 2a^2D \qquad .\text{----------------(2)}$$

This suggests that the force constant for any link should be proportional to the energy required to dissociate the link for molecules, or rather linkages, with the same values of the constant a.

The above discussion suggests that an investigation of regularities among observed force constants will form to some extent an investigation of regularities in the energies of the various linkages of the molecules.

An 'aufbau' principle for triatomic molecules: Regularities among the various parameters recorded in table XIV suggest that the structure of a triatomic molecule may be determined by the number of valence electrons available for binding the three atoms together (cf reference 14, p.2). A stable structure is first obtained with four electrons. Examples are H_2O and Cl_2O, molecules which table XIV shows to have surprisingly similar structures: both have vertical angles near 90°, both satisfy only the central system of force constants, and both show a large resistance to deformation; further, the O-H and O-Cl force constants are approximately equal at $7 . 10^5$ dynes/cm., a value which appears to correspond to a single chemical bond.

Proceeding one step further, a fifth electron is added and a new structure, that characteristic of SO_2 is obtained. ClO_2 has five available valence electrons, has a vertical angle near 120°, satisfies only the valence system of force constants, and resists deformation to a much less degree than either H_2O or Cl_2O. These structural properties are all repeated in SO_2, where the sixth electron completely fills the structure, and raises the force constant acting along either side of the triangle from 7 to $9.6 . 10^5$ dynes/cm.

This structure is again repeated in NOCl, even though the force constants K_1 and K_1' are unequal, corresponding to the lack of symmetry of the atoms forming the molecule.

A typical example of a molecule with seven available binding electrons is NO_2. This molecule appears to be linear, and apart from the value $7 \cdot 10^5$ dynes/cm. observed for the N-O force constant, it is similar to the linear molecules CO_2, N_2O, CS_2, and COS, all of which have eight electrons available for binding.

Quantum mechanical basis of the 'aufbau' principle. The 'aufbau' principle sketched above appears to be in considerable agreement with the quantum mechanical theory of molecules.

Firstly, the similarity of a molecule with an odd number of electrons to that with an even number consisting of one more electron, suggests that the principle is governed by the Pauli principle. If this be so, a molecular proper function requires two electrons of opposite spin to fill it, and a further electron requires the next molecular proper function to accommodate it. The new proper function with but a single electron, does not exert its full bonding power, and the chemical force constants for the odd electron molecules should therefore be considerably less than those for the similar molecules with the new proper function completely filled; this is borne out by the molecules ClO_2 and SO_2, and by NO_2 and the other linear molecules, as table XIV shows.

There must thus exist for any three atoms forming a triatomic molecule, a series of molecular proper functions, just as there exists a series of proper functions for any atom; a triatomic molecule can, however, have various structures, and the series of molecular proper functions apparently correspond successively to the H_2O, SO_2, and linear structures.

This series of molecular proper functions is, in fact, suggested by quantum mechanics. The empirical observation that one molecule may usually be taken as the central atom, provides the key to the method of formation of the molecular proper functions. These proper functions will be primarily determined by the various proper functions possible for the central atom, and the maxima of the various proper functions possible for the central atom will determine the structure of the triatomic molecule.

Possible structures will therefore be given by the possible proper functions for the central atom. The atoms of the molecules investigated all belong to the second and third rows of the periodic table, and the electrons of these atoms are in s- or p- proper functions. Thus the atomic proper function for any given atom is made up of linear combinations of products of the single electron s- and p- proper functions, the combinations being such that the final proper function, including spin factors, is antisymmetrical with respect to interchange of any two electron co-ordinates. But s- and p- single electron space proper functions are chosen only because in the central field of the atom there are no matrix elements of coupling other than the diagonal elements; the interaction of the electrons does, of course, produce non-diagonal elements, and the final proper function is a linear combination such that these elements are zero or vanishingly small, consistent with the final function being antisymmetric in the electron co-ordinates. The feature of significance from the molecular point of view is that s- and p- proper functions are chosen for the isolated atom only because the matrix elements of the energy operator for the central field all vanish except the diagonal elements. One need not begin with the s- and p- single electron proper functions, but with any linear combinations of these single electron functions which are equally solutions of Schrodinger's equation assuming Coulomb's law. Thus in investigating the Stark effect, where the field is no longer wholly central, parabolic co-ordinates produce the necessary single electron functions, and these may be shown to be linear combinations of the s- and p- functions such that the linear field produces only diagonal matrix elements of coupling between the chosen single electron proper functions.

The molecular problem will be equally simplified if proper functions for the single electrons can be chosen such that the final molecular field produces no non-diagonal elements of coupling. Consider first the p- single electron functions. These have maxima along three directions at right angles, and for the central atom under its own central field, have no non-diagonal elements. If two atoms approach the central atom along two directions normal to one another, the maxima overlap maxima of the approaching atoms, and this produces large diagonal and small non-diagonal perturbation matrix elements. Hence the model of the triatomic molecule consisting of a triangle with a right angled vertex, is a likely model when there are four electrons available to fill what might be termed the two localised single electron proper functions. This is precisely the case of H_2O and Cl_2O, and these molecules apparently do conform to this structure.

If more than four electrons are available to fill the localised single electron functions, some other structure must be sought. A second set of linear combinations of the s- and p- proper functions has three maxima oriented at 120° in a plane, with a third maximum normal to this plane. Approach of two atoms to such a central atom can obviously use only two of these maxima, and resort must be had to non-localised bonds. These apparently maintain the 120° configuration when six electrons have to be accommodated, as is shown by the benzene ring (cf Pauling, J. Chem. Physics, 1933, 1, 362); the alternating double bonds of Kekule correspond to six electrons available for binding, and in SO_2 there must be resonance between the two structures consisting of a single bond for one S-O link and a double bond for the other, and that consisting of a double bond for the first and a single bond for the second, just as Pauling postulates resonance between the various possible Kekule structures; if this resonance were not present the SO_2 infra-red bands would exhibit no systematic P, Q, and R branch maxima.

The third set of linear combinations of s- and p- single electron proper functions which may be used, are those obtained from the investigation with parabolic co-ordinates, and these are obviously suited to the linear molecule rather than to any other model.

The three structures deduced from infra-red absorption spectra do therefore apparently fit the structures that are most plausible according to quantum mechanics. Objection might be raised to invoking s- proper functions for S as a central atom, for here the two electrons that are lacking must belong to p-single electron proper functions; the same objection will of course apply to their use with O and Cl. Thus the one structure that would remain a possibility is that of H_2O. Fortunately a closer study of the problem reveals that for atoms lacking two electrons from the closed shell, and occupying a central position in the molecole, s- single electron proper functions belonging to the next total quantum number, must be invoked when more than single bonds are formed by sharing of electrons available for binding the atoms together. Take, for example, SH_2, and SO_2: two S and two H electrons fill the localised single electron proper functions that make up the two bonds oriented at right angles; this means that the molecule is built up from a S atom with two vacant p- single electron functions, and these are just sufficient to give the two bonds at right angles to one another: SO_2 has, however, to accommodate six electrons, and S as the central atom provides only two of these six electrons; this means that only two p- single electron proper functions are available from the shell with total quantum number 3, and the third single electron proper function necessary to accommodate the six electrons in chemical bonds, must according to any scheme come from the shell of quantum number 4, and the single electron function of least energy is therefore an s- proper function. Similar arguments apply to O and Cl.

Observed force constants and the 'aufbau' principle. The scheme sketched above must yet be worked out in greater detail before many interesting features of the values of observed force constants can be elucidated. Firstly there is the rapid fall in exchange energy with nuclear separation, which may account for the force constants $7 \cdot 10^5$ dynes/cm.

observed for the C-S bond in CS_2 and COS being approximately one half that observed for the C-O bond in CO_2, for the N-N and N-O bonds in N_2O, and for the C-O bond in COS. A surprising feature of the couple constants in their constancy for all the linear molecules, including NO_2; this is particularly surprising for the molecules CS_2, and COS, which one might not expect to have the same rigidity as the other linear molecules even according to the 'aufbau' principle when the linear force constants vary so greatly from one group to the other. A simple calculation reveals, however, that the increase in distance from C-O to C-S is just compensated for, according to the classical polarisation theory, by the large polarisibility of the S atom compared with that of the O atom.

This observation may lead to an evaluation of the Coulomb and exchange forces acting within the molecule, and a knowledge of the latter forces should enable one to obtain a closer correlation of the molecular structure with the available valence electrons and their proper functions.

The force constant observed for NO_2 appears in comparison with those of the neighbouring structures SO_2 and N_2O to be too small; the constant for NO_2 is $7 \cdot 10^5$ dynes/cm., whilst those of SO_2 and N_2O are 9.6 and $14 \cdot 10^5$ dynes/cm. respectively. This low value of the force constant for the seven electron structure means that three of the four available electrons contribute nothing to the chemical bonds of the molecule; such a hypothesis may be correct if the electronic, as distinct from the potential energy due to nuclear separation, be high; or, in other words, some of the electrons occupy Herzberg's repulsive levels. Addition of the eighth electron must then bring the eight electrons into four single electron proper functions, and so bring out their full bonding power.

A similar difficulty appears for ozone. The infra-red absorption bands cannot on any allocation give force constants acting along the equal sides of the isosceles triangle greater than 7 . 10^5 dynes/cm.; this means that only two chemical bonds are distributed within the molecule, whereas SO_2 and NOCl have total chemical force constants of 19.5 . 10^5 dynes/cm., corresponding to almost three chemical bonds. This discrepancy may be due to a difference in the effective single electron proper functions of O and of S; the S proper functions will certainly have a greater mean radius, and may therefore give a greater resonance potential along the S-O bonds, compared with that given by the central O atom along the corresponding O-O bonds.

The above discussion ignores possible variation of the constant a of Morse's formula (1) (see p. 51). Variation of this constant from molecule to molecule will doubtless have to be taken into account, particularly when the atoms of the molecule belong to different rows of the periodic table. Thus, although the force constants may provide a measure of the energy required to dissociate any bond of a given molecule, it may not measure this energy from molecule to molecule, particularly if the atoms of the molecules have considerably different effective radii.

A feature of all molecules obeying the valence system of force constants is the constancy of the tangential restoring force constant, or alternatively, the constancy of the couple constants from molecule to molecule. This has already been remarked upon for the linear molecules, but it applies equally to the triangular molecules obeying the valence system. Thus even the unsymmetrical molecule NOCl has a tangential restoring force constant not very different from that of SO_2, ClO_2, and O_3; again, the values 3.6 and 3.3 . 10^5 dynes/cm. for the five and six electron molecules ClO_2 and SO_2 respectively, are remarkably close. Finally there is the surprising fact that the couple constant 6 . 10^{-12} dyne.cm. corresponds for a nuclear separation of 1.3Å, to a tangential restoring force constant of 3.5 . 10^5 dynes/cm. Hence an approximately common rigidity appears to characterise all the molecules obeying the valence force system. How much of this is due to compensation of the various polarisibilities of the constituent atoms by the various internuclear separations, and how much is due to the maintenance a given molecular structure by the corresponding molecular proper function, has yet to be determined.

Conclusion. The investigation of infra-red absorption spectra of triatomic molecules carried out during tenure of a Senior Award, has given much data on the various parameters of the molecules involved. Already regularities have been noted amongst the various structures obtained for these molecules, and also amongst the various force constants, which probably form very good measures of the energies of the various links. These regularities have been formulated in a scheme which predicts the structure of a given triatomic molecule in terms of the number of available binding electrons. This scheme appears to have its theoretical foundation in the proper functions possible for the molecule. These proper functions are at present developed from the single electron proper functions of the individual atoms, and complications due to lack of orthogonality of single electron proper functions belonging to neighbouring atoms, together with difficulties of evaluating the exchange integrals involved, prevent a detailed and quantitative explanation of the scheme and the observed values of the force constants. Future theoretical developments seem more likely to come from a semi-empirical examination of the energy levels of the constituent atoms and of the diatomic molecules which are iso-electronic with the chemically linked atoms of the triatomic molecule in question.

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INFRA-RED ABSORPTION SPECTRUM OF NITROGEN DIOXIDE

BY

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AND

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THE infra-red absorption spectrum of the equilibrium mixture of NO_2 and N_2O_4 was investigated in the region of comparatively short wave-lengths by Warburg and Leithäuser in 1907 and 1909, and again in 1910 and 1913 by von Bahr. Preliminary experiments on the spectrum of nitrosyl chloride indicated N_2O_4 as a troublesome impurity, and it was decided to repeat the earlier work and to extend the observations as far as 18μ.

At room temperature a complicated spectrum with bands at 15·6, 13·4, 7·92, 6·17, 5·75, 3·22, and 2·91μ is obtained. The absorption tube was then placed between the source of radiation and the spectrometer, and heated to 100° C.; the maximum of radiation emission characteristic of this temperature is beyond 20μ, and it was found with this arrangement that disturbances of the thermopile due to fluctuations of temperature in the absorption tube were avoided. The interesting observation was made that all the bands disappeared with the exception of those at 15·6 and 6·17μ, the two latter remaining with undiminished intensity, and having a doublet structure with a separation of 35 $cm.^{-1}$ and 32 $cm.^{-1}$ respectively. They may accordingly be ascribed to NO_2, and the simplicity of the spectrum renders it highly probable that the molecule is rectilinear and symmetrical. The N–O force constant is approximately 7×10^5 dynes per cm., the deformation force constant being some 6×10^{-12} dyne cm., and the calculated moment of inertia is 66×10^{-40} $gm.cm.^2$, with an interatomic separation of 1·1 A. If ν_3 is 6·17μ, and ν_2 is 15·6μ, then the position of the inactive fundamental ν_1 may be calculated as approximately 11·1μ.

Further confirmation of the suggested structure may be obtained in a very neat way. The determined force constant for NO_2 corresponds to a single bond between each oxygen and the central nitrogen atom.

If one more electron is available as in the case of the ion $[NO_2]^-$, the previously odd electron takes part in bond formation and we should have double bonds between the central and each external atom, with a corresponding elevation of the force constant to 14×10^5 dynes per cm., and, if the ion preserves the rectilinear structure, the Raman spectrum of the solution of an inorganic nitrite should provide a strong line with a separation giving the frequency of the inactive fundamental. Making the allowance for the difference in the force constants, we can calculate the approximate position of this line as 1328 $cm.^{-1}$, and experimental results show that aqueous solutions of inorganic nitrites have in fact an intense line at 1303 $cm.^{-1}$, the corresponding force constant being 14×10^5 dynes per cm.

Consideration of the manner in which given numbers of electrons available for bond formation may be allotted to definite electronic molecular properfunctions shows that in the case of $[NO_2]^-$, which has eight such electrons, it is probable that alternative states with near-lying energy levels are possible, and that reversion from the rectilinear structure characteristic of the ion in aqueous solution to an isosceles triangular form with a vertical angle of some 120° is rendered easy : the latter seems to be the structure of the ion in the crystalline nitrites.

Finally, where, by the establishment of a covalent link as in the case of the nitro- group, only six electrons are available for binding the atomic centres, the triangular form as above with the obtuse vertical angle (we may call this the SO_2 structure) is obligatory : and Dadieu and Kohlrausch from the results of Raman measurements find that the force constant for the NO link in $:NO_2$ is 9×10^5 dynes per cm. and the angle ONO is approximately 110°. As regards N_2O_4, the structure is probably best represented by Hendricks's suggestion of two plane nitro-groups at right angles to each other.

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STRUCTURE OF TRIATOMIC MOLECULES

BY
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RECENT investigations of infra-red and Raman spectra of triatomic molecules have shown that molecules with an odd number of electrons, such as ClO_2 and NO_2, are similar in structure to the molecules SO_2 and CO_2, each with one more electron. This observation suggests that the triangular molecules have structures depending on the number of valence electrons binding the three atoms together, and that a scheme might be formulated for obtaining the structures of these molecules from the total number of available valence electrons.

A stable structure is first obtained with four electrons. Examples are H_2O and Cl_2O, molecules which have surprisingly similar structures: both have vertical angles near 90°, both satisfy only the central system of force constants, and both show a large resistance to deformation measured by H–H and Cl–Cl force constants of at least 5×10^5 dynes/cm.; further, the O–H and O–Cl force constants are each 7×10^5 dynes/cm., corresponding to single chemical bonds. In fact, these molecules are excellent examples of the Slater-Pauling molecule formed from a central atom with two *p*-electrons available for chemical bonds.

Proceeding one step further, a fifth electron is added and a new structure, that characteristic of SO_2, is obtained. ClO_2 has five available valence electrons, has a vertical angle near 120°, satisfies only the valence system of force constants, and resists deformation to a much less degree than either H_2O or Cl_2O, its tangential restoring force constant being $3 \cdot 5 \times 10^5$ dynes/cm. These structural properties are all repeated in SO_2, where the sixth electron completely fills the SO_2 type of proper function; this is the one feature distinguishing SO_2 from ClO_2, for the S–O force constant is approximately $9 \cdot 6 \times 10^5$ dynes/cm. whereas the Cl–O constant is only 7×10^5 dynes/cm., indicating that the sixth electron of SO_2 brings out the full bonding power of this type of proper function.

Next we seek a molecule with seven electrons; the typical example is NO_2. The addition of a seventh electron again requires formation of a new type of proper function, and this is characterised by a linear structure and small resistance to deformation, measured by a restoring couple constant of $5 \cdot 5 \times 10^{-12}$ dynes × cm. Addition of an eighth electron fills this linear type proper function, and raises the force constant of the chemical bond from 7×10^5 to 14×10^5 dynes/cm. Addition of the eighth electron does not otherwise affect the structure, the similarity of the restoring couple constants being a remarkable feature of the linear molecules NO_2, N_2O, CO_2, COS and CS_2. The C–S force constant is less than 14×10^5 dynes/cm., and may be accounted for by the increased separation of the nuclei.

The above scheme seems also applicable to triatomic radicals, and has been used to explain apparently inconsistent structures observed for the NO_2 group[1]. It also predicts an SO_2 structure for NOCl, and preliminary observations of the infra-red absorption spectrum appear to confirm this.

[1] Bailey and Cassie, NATURE, **131**, 239, Feb. 18, 1933.

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Ultrarote und Ramanbanden des Kohlendioxyd-, Kohlenoxysulfid- und Schwefelkohlenstoff-Moleküls.

Von **A. B. D. Cassie** und **C. R. Bailey** in London.

Mit 2 Abbildungen. (Eingegangen am 15. Juli 1932.)

Fermis Annahme einer Resonanz zwischen dem ersten Oberton der transversalen Schwingung und dem Grundton der symmetrischen Schwingung des CO_2 und CS_2 wird dahin erweitert, daß auch Obertöne der symmetrischen Schwingung berücksichtigt werden. Die Rechnungen werden auf Versuchsergebnisse, die für CO_2, CS_2 und COS vorliegen, angewendet. Die theoretischen Rechnungen liefern nicht die experimentell beobachteten konstanten Frequenzdifferenzen zwischen den Banden eines Paares an der Stelle der symmetrischen Schwingung und denjenigen an der Stelle ihrer Obertöne.

Fermi[1]) hat vor kurzem eine Erklärung für das Auftreten von zwei Ramanlinien an Stelle einer einzigen Frequenzverschiebung, die der inaktiven Schwingung von CO_2 und CS_2 entspricht, gegeben. Seine Erklärung benutzt eine Resonanzerscheinung zwischen dem ersten Oberton der transversalen Schwingung und dem Grundton der inaktiven Schwingung. Die Theorie ist außerordentlich überzeugend und erklärt neben dem Auftreten von zwei intensiven Ramanverschiebungen auch dasjenige von zwei schwachen Ramanlinien, die in der Nähe der beiden Hauptverschiebungen liegen.

Die ultraroten Absorptionsspektren der Moleküle CO_2, COS und CS_2 zeigen alle dieselbe Erscheinung, nämlich das Auftreten von zwei Banden, während die gewöhnlichen Schwingungen des Moleküls nur eine bedingen würde. Ferner ist der Frequenzunterschied der beiden Banden eines Paares genau gleich dem Abstand der intensiven Ramanverschiebungen. So zeigte Rasetti[2]), daß die Ramanverschiebungen 1285 und 1388 cm^{-1} des CO_2 durch annähernd dasselbe Frequenzintervall getrennt sind, wie die ultraroten Banden bei 3617 und 3721 cm^{-1} [3]); und Bailey[4]) zeigte, daß der Frequenzabstand 107 cm^{-1} im Ultrarotspektrum des CO_2 wiederholt auftritt. Das Ramanspektrum des CS_2 hat seinerseits zwei Hauptlinien bei 655 und

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[1]) E. Fermi, ZS. f. Phys. **71**, 250, 1931.

[2]) F. Rasetti, Nature **123**, 205, 1929.

[3]) Vgl. Cl. Schaefer u. B. Philipps, ZS. f. Phys. **36**, 641, 1926.

[4]) C. R. Bailey, Nature **123**, 410, 1929.

795 cm^{-1}. Der Frequenzunterschied beträgt hier 140 cm^{-1}, und die Intensitäten der ultraroten Banden[1] erfordern die Zusammenfassung der Banden bei 2179 und 2230 cm^{-1} als ein Paar mit einem Frequenzabstand von 151 cm^{-1}; die Polarisation der Ramanlinien[2] erfordert anscheinend dieselbe Zuordnung der Banden.

COS ist ein unsymmetrisches gestrecktes Molekül, bei dem die Schwingungsarten, die im ultraroten Spektrum des CO_2 und CS_2 symmetrisch und optisch inaktiv sind, aktiv werden. Dementsprechend wurde für dieses Molekül Ultrarotabsorption im Gebiet der Ramanverschiebungsfrequenzen beobachtet[3]. Auch hier ersetzen zweifache Banden die für die gewöhnlichen Schwingungsformen geforderten einfachen Banden. Die optische Aktivität dieser Schwingung liefert einen weiteren vorzüglichen Beweis für die Fermische Theorie, da im ultraroten Spektrum im allgemeinen Obertöne der Grundfrequenzen beobachtet werden, während sie im Ramanspektrum der symmetrischen Schwingungen fehlen. So haben die COS-Banden bei 859 und 1051 cm^{-1}, die in der Gegend der Ramanverschiebungen liegen, eine Oberschwingung bei 1718 und 1898 cm^{-1}; das Frequenzintervall zwischen den beiden Banden eines Paares beträgt 192 cm^{-1} für den Grundton und 180 cm^{-1} für den ersten Oberton. Dies Intervall ist wahrscheinlich konstant und die angegebenen Werte deuten darauf hin, daß es beim Übergang von der Grundschwingung zum ersten Oberton eher ab- als zunimmt. Wenn daher die Fermische Theorie das Auftreten von Doppellinien in den Ramanspektren von CO_2 und CS_2 erklärt, so muß sie gleichzeitig das Auftreten von doppelten Dubletts in den ultraroten Absorptionsspektren von CO_2, COS und CS_2 erklären; und sie muß auch den fast konstanten Wert für den Frequenzunterschied der Banden der Grund- und ersten Oberschwingung erklären.

Die Theorie kann sicherlich den Ersatz der Grundfrequenz der optisch-inaktiven Schwingung oder der analogen Schwingung im COS durch doppelte Dubletts erklären; denn in allen drei Molekülen ist die Frequenz dieser Schwingung ungefähr doppelt so groß wie die der transversalen Schwingung. Das ist in Fig. 1 dargestellt, in der die Energieniveaus von Grund- und erstem Oberton der transversalen Schwingung sowie der Grundton der symmetrischen Schwingung graphisch aufgetragen sind. Nach der

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[1] C. R. Bailey u. A. B. D. Cassie, Proc. Roy. Soc. London (A) **132**, 240, 1931.

[2] N. Bhagavantam, Phys. Rev. **39**, 1020, 1932.

[3] C. R. Bailey u. A. B. D. Cassie, Proc. Roy. Soc. London (A) **135**, 375, 1932.

Fermischen Theorie läßt sich die Lage des Grundtones der symmetrischen Schwingung nur schätzen, da keine der beobachteten Banden oder Linien eines Paares mit dem ersten Schwingungsniveau zusammenfällt; jedoch besteht kaum ein Zweifel daran, daß für alle drei Moleküle die Beziehung $2\,\nu$ ungefähr gleich ν_1 wirklich erfüllt ist. Daher kann die Fermische Theorie das Auftreten von zwei Banden oder Linien an Stelle des ersten Schwingungsniveaus der symmetrischen Schwingung erklären.

Zum zweiten muß die Fermische Theorie den fast konstanten Wert des Frequenzabstandes der beiden Banden eines der Paare erklären können, die an Stelle des ersten und zweiten Schwingungsniveaus ν_1 und $2\,\nu_1$ liegen, und damit auch der an den Stellen $2\,\nu_1$ und $4\,\nu_2$ liegenden Energieniveaus, wenn die beiden Schwingungsarten gekoppelt sein sollen.

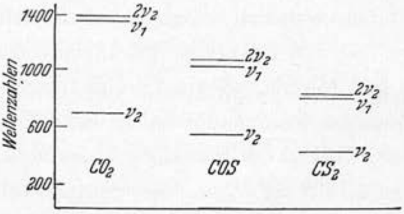

Fig. 1.

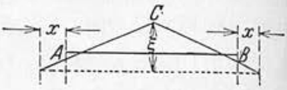

Fig. 2.

Die transversale Schwingung ist selbst entartet und Fermi eliminiert dies durch Einführung zweier Koordinaten ζ und η (Fig. 2), die die Verschiebungen des Zentralatoms gegen den Schwerpunkt der beiden äußeren Atome in zwei aufeinander senkrecht stehenden Richtungen bedeuten, und in der Ebene liegen, die das ungestörte Zentralatom enthält und auf der unverschobenen Verbindungslinie ACB senkrecht steht. Dann haben die folgenden Niveaus annähernd gleiche Energien und sind daher entartet: (1,00), (0,11), (0,20) und (0,02). Fermi konstruiert Matrixelemente des Koppelungspotentials $\beta x (\zeta^2 + \eta^2)$ für diese Eigenfunktionen. Durch die Lösung der Störungsgleichungen erhält er die Energiewerte nullter Ordnung und die Linearkombinationen der obigen Eigenfunktionen, die diesen neuen Energiewerten entsprechen. Die Linearkombinationen, für die die nichtdiagonalen Elemente der Energiematrix verschwinden, ergeben sich zu

$$(0{,}11),\ (0{,}02) - (0{,}20)$$

und

$$\frac{1}{P}\left\{\frac{A-B}{2} \pm \sqrt{2\,P^2 - \frac{(A-B)^2}{4}}\right\}(1{,}00) + (0{,}20) + (0{,}02),$$

wo

$$P = \frac{\beta h^{3/2}}{8\sqrt{2}\,\pi^3 \sqrt{\nu_1 m_1 \nu_2 m_2}}$$

und A und B die ungestörten Niveaus von (1,00) und (0,02) bedeuten. Die beiden ersten Linearkombinationen entsprechen dem ersten Oberton der transversalen Schwingung, und Übergänge zu diesen Niveaus werden im Ultrarot nur geringe Intensität haben. Die beiden anderen sind Kombinationen von (1,00) und Übergänge zu den entsprechenden Energieniveaus vom Grundniveau müßten mit einer Intensität auftreten, die dem der Übergänge zum (1,00)-Niveau vergleichbar ist, wenn zwischen ihm und dem ersten Oberton der transversalen Schwingung keine Resonanz bestünde. So erklärt die Fermische Theorie das Auftreten von doppelten Dubletts in den ultraroten Spektren beim CO und CS an Stelle von Banden, die $(n\,\nu_3 + \nu_1)$ entsprechen, wo ν_3 die aktive oder unsymmetrische longitudinale Schwingung bedeutet, und darüber hinaus beim COS auch diejenigen, die ν_1 ersetzen. Diese Serie umfaßt die Banden C und D bei 2179 und 2230 cm^{-1} des beobachteten ultraroten Absorptionsspektrums des CS_2[1], die Banden A bei 3617 und 3721 cm^{-1} und K bei 1061 und 961 cm^{-1} des CO_2[2] und die Banden B und C bei 859 und 1051 cm^{-1}, sowie G und H bei 2904 und 3095 cm^{-1} des COS[3].

Es bleiben zu erklären die doppelten Dubletts des CO_2 bei 4896 und 5009 cm^{-1}, die die Bande $\nu_3 + 2\,\nu_1$ ersetzen und bei 6139 und 6243 cm^{-1} an Stelle von $\nu_3 + 3\,\nu_1$; und das Spektrum des COS enthält Banden bei 1718 und 1898 cm^{-1}, die $2\,\nu_1$ ersetzen. Der Frequenzabstand der einzelnen Banden in diesen doppelten Dubletts ist angenähert gleich dem der Banden, die das Niveau ν_1 ersetzen; vorausgesetzt, daß die Zuordnung der Niveaus richtig ist, müßte die Fermische Hypothese diese Konstanz des Abstandes erklären.

Die Zustände annähernd gleicher Energie in der Nähe des ersten Obertones von ν_1 sind: (2,00), (1,11), (1,20), (1,02), (0,22), (1,13), (0,04) und (0,40). Das Niveau ist neunfach entartet und die Säkulardeterminante hat neun Reihen und Spalten. Jedoch liegen die Niveaus (1,11), (1,20) und (1,02) dem Niveau (2,00) näher als die übrigen Niveaus (0,22), (0,13), (0,31), (0,04) und (0,40), und wir werden nur die Entartung der vier ersten Eigenfunktionen betrachten.

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[1] Vgl. C. R. Bailey u. A. B. D. Cassie, Proc. Roy. Soc. London (A) **132**, 240, 1931.

[2] Vgl. Cl. Schaefer u. B. Philipps, ZS. f. Phys. **36**, 641, 1926.

[3] Vgl. C. R. Bailey u. A. B. D. Cassie, Proc. Roy. Soc. London (A) **135**, 375, 1932.

Fermi folgend setzen wir die üblichen Formeln für die nichtverschwindenden Matrixelemente der Koordinate eines Oszillators der Masse m an:

$$q_{n,\,n+1} = \sqrt{\frac{h}{8\,\pi^2\,\nu\,m}}\,(n+1)^{1/2}.$$

Daraus ergibt sich

$$x_{2,1} = \sqrt{\frac{h}{8\,\pi^2\,\nu_1\,m_1}}\,2^{1/2} \quad \text{mit } m_1 = 2\,m$$

und

$$(\xi^2)_{0,2} = \frac{h}{8\,\pi^2\,\nu_2\,m_2}\,2^{1/2} \quad \text{mit } m_2 = \frac{2\,m\,M}{m+M}.$$

Benutzen wir dasselbe Störungspotential wie Fermi, so lauten die nichtverschwindenden Matrixelemente dieser Störung zwischen den vier Eigenfunktionen:

$$U\,(2{,}00,\ 1{,}20) = U\,(2{,}00,\ 1{,}02) = \sqrt{2}\,P$$

und

$$U\,(2{,}00,\ 1{,}11) = U\,(1{,}11,\ 1{,}20) = \text{usw.} = 0.$$

Die Säkulardeterminante wird nun:

$$\begin{array}{c|cccc|} (2{,}00) & A & \sqrt{2}\,P & O & \sqrt{2}\,P \\ (1{,}20) & \sqrt{2}\,P & B & O & O \\ (1{,}11) & O & O & B & O \\ (1{,}02) & \sqrt{2}\,P & O & O & B \end{array}$$

Die Niveaus (2,00) usw. sind links angegeben, um die Funktionen anzudeuten, auf die die Elemente sich beziehen. Die säkulare Gleichung dieser Determinante hat die Eigenwerte B, B und

$$\frac{A+B}{2} \pm \sqrt{4\,P^2 + \left(\frac{A-B}{2}\right)^2},$$

wo die Eigenwerte B den Linearkombinationen (1,11) und (1,02) – (1,20) angehören. Diese entsprechen dem Niveau $(\nu_1 + 2\,\nu_2)$ und werden relativ zu den Linearkombinationen, die dem Niveau $2\,\nu_1$ angehören, geringe Intensität haben. Also auch hier führt die Fermische Hypothese zu doppelten Dubletts an Stelle von $2\,\nu_1$ und die neuen Energieniveaus lauten

$$\frac{A+B}{2} \pm \sqrt{4\,P^2 + \left(\frac{A-B}{2}\right)^2}$$

entsprechend den Linearkombinationen

$$\frac{1}{P}\left[\frac{A+B}{2} \pm \sqrt{4\,P^2 + \left(\frac{A-B}{2}\right)^2}\right] (2{,}00) + (1{,}20) + (1{,}02).$$

Da nun, wenn die Intensitäten der einzelnen Banden gleich werden, A gegen B geht, so ist der Abstand der das Niveau $2\,\nu_1$ ersetzenden Dubletts $2(2\,P)$, oder $\sqrt{2}$ mal gleich dem Abstand des Dubletts, das ν_1 ersetzt. Eine direkte Anwendung der Hypothese führt somit zu einem falschen Wert für den Abstand der Banden eines Paares. Der Fehler kann natürlich daran liegen, daß die übrigen Niveaus (0,22), (0,13), (0,31), (0,04) und (0,40) vernachlässigt wurden; wenn wir aber die exakte neunreihige Störungsdeterminante ansetzen, so sind die nichtverschwindenden nicht-diagonalen Elemente größtenteils größer als P. Denn sechs der nicht-diagonalen Elemente sind gleich P, vier sind gleich $\sqrt{2}\,P$, vier sind gleich $\sqrt{3}\,P$ und vier sind gleich $\sqrt{6}\,P$, die übrigen gleich Null. Daher ist es, selbst wenn wir diese Determinante auswerten könnten und so die Säkulargleichung genau berechnen könnten, unwahrscheinlich, daß die erhaltenen Energiewerte einen Abstand liefern würden, der gleich dem für die Banden an der Stelle von ν_1 gefunden wurde.

Diese Schlußweise vernachlässigt Änderungen in den Relativwerten von A und B infolge der gewöhnlichen Kratzerschen anharmonischen Korrektionen. Aber eine solche Erklärung der Abweichung zwischen beobachteten und berechneten Abständen scheint durch die Fermische Erklärung der schwächeren Komponenten der Ramanlinien ausgeschlossen zu sein. Diese anziehende Hypothese scheint daher in ihrer vorliegenden Form Ergebnisse zu liefern, die mit experimentellen Beobachtungen nicht übereinstimmen.

Die Konstanz des Abstandes der beiden Banden in der Grundschwingung und im Oberton schließt jede Erklärung durch die Annahme aus, daß es zwei verschiedene Werte für jede Kraftkonstante gibt, und legt nahe, daß die Erscheinung mit zwei verschiedenen Elektronenenergieniveaus in Verbindung zu bringen ist, die nur erscheinen, wenn das Molekül die optisch inaktive Schwingung ausführt. Die Intensität der Ramanlinien zeigt, daß diese Schwingungsform die Elektronenkonfiguration viel stärker stört als die anderen Schwingungen; daher ist das Auftreten der zweifachen Banden an der Stelle der symmetrischen Schwingung mit einer solchen Hypothese ganz verträglich. Man könnte meinen, daß eine Änderung des Elektronenenergieniveaus die Kraftkonstanten ändern und darum für Grundton und ersten Oberton verschiedene Aufspaltungen liefern müßte, aber die erforderliche Änderung der Elektronenkonfiguration ist nur klein und würde für keine Kraftkonstante eine merkliche Änderung ergeben. Die genaue Festlegung der beiden Niveaus muß solange hinausgeschoben werden, bis unsere Kenntnis von dem Elektronenaufbau dreiatomiger

Moleküle weniger unvollständig ist. Es ist jedoch zu bemerken, daß d Erscheinung bei dem vor kurzem untersuchten Spektrum des linea dreiatomigen Moleküls N_2O[1]) nicht auftritt; wahrscheinlich kommen zw solcher Niveaus nur in den linearen dreiatomigen Molekülen des Kohle stoffs vor.

Zusammenfassung. Die Fermische Hypothese von der Resona zwischen dem ersten Oberton der transversalen Schwingung und de Grundton der symmetrischen Schwingung der linearen Moleküle CO_2 u CS_2 wurde auf das Auftreten von doppelten Dubletts in den ultrarote Absorptionsspektren von CO_2, COS und CS_2 angewendet.

Die Hypothese erklärt das Auftreten von doppelten Dubletts an Stell der Grund- und Oberschwingungen der symmetrischen Schwingung. Abe der berechnete Abstand der Banden, die den ersten Oberton ersetze beträgt das $\sqrt{2}$fache des Abstandes für die Banden der Grundschwingun während die experimentellen Ergebnisse dahingehen, daß der Abstan angenähert konstant bleibt oder sogar kleiner wird, wenn man von de Grundschwingung zum ersten Oberton übergeht.

Die Konstanz dieses Abstandes und das Auftreten von doppelte Dubletts, die nur die symmetrische Schwingungsform ersetzen, legen nahe daß die Erscheinung mit zwei verschiedenen Elektronenniveaus des Molekü in Verbindung zu bringen ist.

Es ist den Verfassern ein Bedürfnis, Herrn Prof. F. G. Donnan für sein freundliches Interesse und seine stete Ermutigung zu danken, sowie dem Department of Scientific and Industrial Research für die Gewährung eines Senior Award an den einen von uns (A. B. D. Cassie) ihren Dank auszusprechen.

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[1]) Vgl. E. K. Plyler u. E. F. Backer, Phys. Rev. **38**, 1827, 1931; C. P. Snow, Proc. Roy. Soc. London (A) **128**, 294, 1930.

From the PROCEEDINGS OF THE ROYAL SOCIETY, A, Vol. 130, 1930.]

Investigations in the Infra-Red Region of the Spectrum.

Part I.—*Introductory and Experimental.*

Part II.—*The Absorption Spectrum of Sulphur Dioxide.*

BY C. R. BAILEY, A. B. D. CASSIE AND W. R. ANGUS.

[*Reprinted from the* PROCEEDINGS OF THE ROYAL SOCIETY, A, Vol. 130.]

Investigations in the Infra-Red Region of the Spectrum.
Part I.—*Introductory and Experimental.*

By C. R. BAILEY, A. B. D. CASSIE, and W. R. ANGUS, University College, London.

(Communicated by F. G. Donnan, F.R.S.—Received August 11, 1930.)

[PLATE 3.]

Robertson and Fox in their fundamental memoir* have published a comprehensive account of the precautions necessary for obtaining reliable results with a prism spectrometer in the infra-red between 1 and 17 μ. The authors feel, however, that some advantage to other workers may accrue if they in turn outline their own particular difficulties with the manner of their resolution. It may be stated at once that it is now possible to make scale readings to an accuracy of 1 mm. *during the day*, with a galvanometer sensitivity of 10^{-10} to 10^{-11} amp. per millimetre deflection at 1 metre distance. If it is realised that the work is carried out on the top floor of the Chemistry Department of this Institution, in a building which houses some dozen electrical generators and a large liquid air plant, with a stream of heavy bus traffic 10 yards from the building and a tube railway at 100 yards, it will be seen that the usual experimental difficulties have been completely overcome.

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* 'Proc. Roy. Soc.,' A, vol. 120, p. 128 (1928).

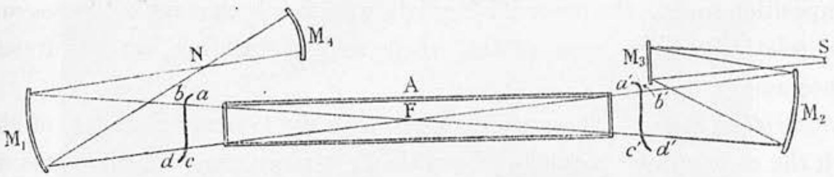
Preliminary experiments were made in a constant temperature room in the basement; the humidity was high and had a deleterious effect on the rocksalt portions of the apparatus, whilst the discomfort of night work in such a room was extreme. It was consequently decided to re-approach the problem from the beginning, but not before trials had shown that where the motion of the building as a whole is small, comparatively simple expedients serve to eliminate most of the mechanical disturbance. This was cut out by placing the galvanometer with its Paschen shields (total weight about 250 lb.) on a large block of wood supported by four pairs of inverted small porcelain crucibles placed at the corners. Eight of the thinnest available crucibles were selected; the two in a pair were placed one on top of the other and separated by a small piece of 5-ply wood and a few pieces of filter paper. If the galvanometer and shields are not too heavy, the replacement of the rubber shock absorber in the ordinary anti-vibration spider by a crucible and one or two layers of filter paper was found very efficient.

General Lay-out.

The room is supplied with electric power at a constant voltage of 250 from a battery of accumulators. The advantage of the assemblage chosen (discussed in detail below) is that all controls can be easily manipulated by one person without moving from his seat. The spectrometer was a Hilger D.42 constant deviation instrument, fitted with quartz, fluorite, rocksalt, and sylvine prisms. The light from a Nernst filament, N (see figure), contained in an asbestos housing, passes through the absorption tube, A, and is brought to a focus at the spectrometer slit, S, by means of a mirror, M_2. The thermopile is coupled to a sensitive Downing galvanometer carried on a modified Julius suspension. A mercury vapour lamp encased in an asbestos box is used in setting the Wadsworth mirror. The wave-length drum of the spectrometer is propelled by contact with a rubber-covered, low-geared wheel capable of rotation from a distance.

Source of Radiation.—Nernst filaments were procured from the Glasco Lampen Gesellschaft, M.B.H., Lausitzer Platz 4, Berlin, S.O.36; their life is considerably greater than the home product. An asbestos housing encloses the filament and is fitted with an aluminium shutter running in brass guides; this housing is so constructed that a constant air current flows past the filament which is operated at about 0·8 amp. and 90 volts from the constant voltage supply. Absolute constancy of filament current is maintained by the potentiometer device described by Robertson and Fox (*loc. cit.*). Fractures may occur in the filament and are repaired by cementing the break with a mixture of zirconium, cerium, thorium and yttrium oxides and a trace of borax, the whole made into a paste by the addition of a 12 per cent. solution of cane sugar.*

Focusing the Radiation on the Collimator Slit—Radiation from the condensing mirror, M_1, is focused at the centre, F, of the absorption tube,† and then diverges to M_2 which focuses it, after reflection at a plane mirror, M_3, on the collimator slit, S. A good image of the filament is obtained on S only if the errors introduced by M_1 are reversed by M_2.‡ A wave diverging from the Nernst filament, N, towards M_1 is after reflection distorted to some form *abcd*. When it has passed through F, its form will be *a′b′c′d′*, and this wave should be brought to a focus as nearly perfect as possible by M_2. If *abcd* were travelling from right to left instead of from left to right, M_1 would bring it to a correct focus at N. Hence the point to which the radiation converges should lie on that side of the direction of the oncoming wave which is turned away from the mirror; that is, the focus conjugate to F in the mirror M_2 should lie on the *a′* side of M_2. The focal length of M_2 should be such that the angular aperture of the spectrometer is just filled, and that of M_1 such that the image of the Nernst filament is just the length of the collimator slit. M_4 is a reflecting mirror which increases the effective solid angle subtended by M_1 at N.



Thermopile and Galvanometer.—After traversing the spectrometer, the radiation passes through the spectrometer slit on to a 20 junction bismuth-silver thermopile enclosed in an air-tight case,§ which may be evacuated; the Hilger thermopiles are constructed for maximum efficiency at atmospheric pressure in air, but it was found advantageous to maintain a slightly diminished pressure in the case. The galvanometer was of the Downing type‖ and was employed normally at a sensitivity of $10^{-10 \cdot 5}$ amp. per millimetre scale deflection at 1 metre; it was possible to obtain values of 10^{-11}, but the period became unduly long with the instrument employed; another of the same type has been procured with a lighter system to overcome this difficulty. Electro-

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* Griffiths, 'Phil. Mag.' [vi], vol. 50, p. 263 (1925).

† Snow and Taylor, 'Proc. Roy. Soc.,' A, vol. 124, p. 445 (1929).

‡ *Cf.* Czerny, 'Z. Physik,' vol. 61, p. 792 (1930).

§ Robertson and Fox, *loc. cit.*

‖ 'J. Sci. Inst.,' vol. 3, p. 331 (1926).

magnetic disturbances were suppressed by surrounding the galvanometer with a loosely wound copper and mu-metal shield ; over this were placed the two Paschen shields between which mu-metal was again loosely wound. The mass of the shields with base plates, etc., was determined and the centre of mass located. A modified Julius suspension was then constructed based very largely on the design of Johnsrud ;* it is illustrated in Plate 3. The tape-bound springs act as shock absorbers, and the adjustable cylindrical masses allow the centre of mass to be brought to the point of suspension of the magnet system. With all leads from thermopile to galvanometer enclosed in earthed composition tubing, the necessity for night work has been completely overcome. The relatively large mass of the whole makes shielding against draughts unnecessary.

Absorption Tubes.—These were 45 cm. long by 4·5 cm. diameter, of glass, with the ends ground parallel and polished ; the circular rocksalt plates were pressed against the ends with a trace of vaseline ; the tubes were then evacuated, and if leaks appeared shellac varnish was wiped over the join. The end caps and rings and the rocker are fully described by Robertson and Fox (*loc. cit*) ; the latter was operated from a distance and allowed of adjustments for parallelism and height, since the centres of the tubes must be at the same level as the centres of the Nernst filament and spectrometer slit for efficient working. The gas enters the absorption tube through a large glass spiral as described in the paper cited, thus allowing for the ready interchange of the evacuated control tube with that containing the gas ; the spiral is connected through phosphoric oxide tubes and a liquid air trap to a Hyvac pump and manometer.

The Spectrometer.—The spectrometer is a Hilger D.42 instrument ; it was encased in 5-ply wood painted dead black inside. The only parts which project are the wave-length drum, the collimator slit, and the thermopile eyepiece cover ; care was taken to ensure close fitting around these parts. The case was bored to take a thermometer and a tube for the evacuation of the brass, airtight thermopile case. The temperature of the case was maintained reasonably constant at 18° ; all results, however, are ultimately corrected for that temperature. A small quantity of desiccating agent was kept inside the case.

Quartz, fluorite, rocksalt and sylvine prisms, each of 45 mm. height and 70 mm. length of face, with prism angle 60°, were available. One drum was used for all four prisms and was calibrated by Robertson and Fox's method. We should like at this point to express our gratitude to Sir Robert Robertson

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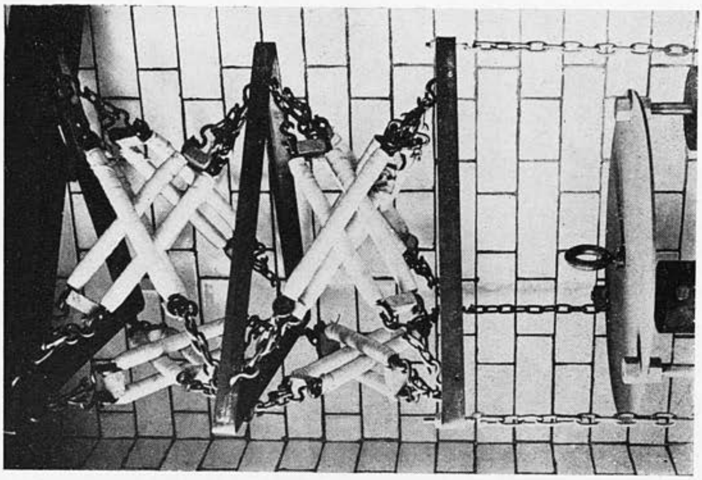
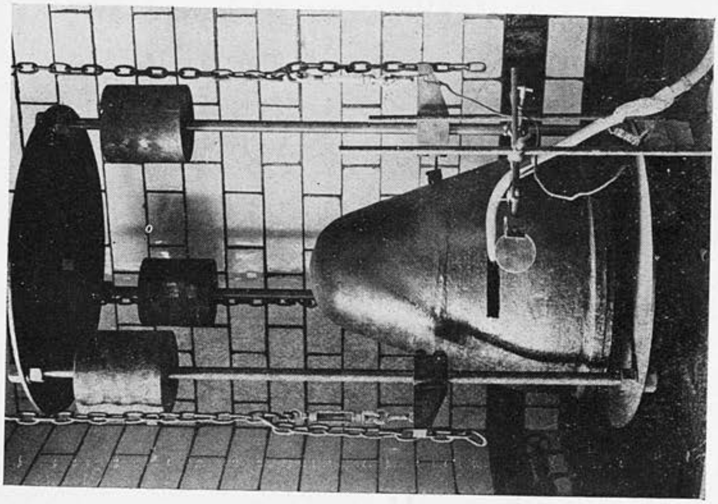
* ' J. Opt. Soc. Amer.,' vol. 10, p. 609 (1925).

Bailey, Cassie and Angus. *Proc. Roy. Soc., A, vol.* 130, *Pl.* 3.



Shock Absorbers.



Shielding system.

and his co-workers for their very ready help and guidance, and for the loan of an accurate steel tape measure and a telescope fitted with a high power eyepiece used in the calibration of the instrument.

Possibilities of Experimental Error.—Apart from the lengthy and laborious process of drum calibration, investigation into a number of other possible errors in the setting of the instrument is necessary before the potentialities of this type of spectrometer can be thoroughly exploited. The absence of any such data was found a great handicap at the beginning, and the valuable work of Robertson and Fox admits of supplement. It is proposed in what follows to discuss very briefly the sources of possible errors and to indicate their calculation.

The possible experimental errors are due to uncertainty in—

(i) drum reading ;
(ii) setting the prism at minimum deviation ;
(iii) value of the prism angle ;
(iv) temperature of the prism.

They are best calculated in terms of error in the rotation of the prism table.

(i) *Errors in Drum Reading.*—The error in the drum calibration itself is easily calculated and gives an error in rotation of the prism table less than 3 seconds of arc for any rotation of the drum.

(ii) *Errors in Setting the Prism at Minimum Deviation.*—Messrs. Hilger have shown in the tables of accompanying data supplied with the instrument that an error of 30 minutes in the minimum deviation setting corresponds to a maximum possible error of 7 seconds in the rotation of the prism table. The process depends finally on the setting of the prism by the aid of a jig in which the possible error is approximately 5 minutes ; hence the possible equivalent error in prism table rotation is 1·5 seconds.

(iii) *Value of the Prism Angle.*—A knowledge of the accuracy required for the prism angle is of great use, particularly for the rocksalt and sylvine prisms ; the faces of the latter may deteriorate and require repolishing. The refracting angle may be changed in the process ; if the change is not sufficient to give an equivalent error in prism table rotation greater than 1 second, the wave-length drum need not be recalibrated. The minimum deviation, δ, for any refractive index, n, and prism angle, A, is given by

$$n = \sin \tfrac{1}{2}(\mathrm{A} + \delta)/\sin \tfrac{1}{2}\mathrm{A}. \qquad (1)$$

Hence

$$\frac{\partial n}{\partial \mathrm{A}} = 0{\cdot}243\,\frac{\sin \frac{1}{2}\delta}{\sin^2 \frac{1}{2}\mathrm{A}},$$

where ∂n is the change in the fifth decimal place of refractive index per second of arc change in A; if $A = 60°$,

$$\frac{\partial n}{\partial A} = 0\cdot971 \sin \tfrac{1}{2}\delta. \tag{2}$$

The equivalent change in total deviation is obtained by multiplying (2) by $(\partial\delta/\partial n)$; from (1) we have

$$\left(\frac{\partial\delta}{\partial n}\right) = \frac{2 \sin \frac{1}{2}A}{\cos \frac{1}{2}(A + \delta)}. \tag{3}$$

Inserting appropriate values for rocksalt in (3), we obtain a change in total deviation per unit change in the fifth decimal place of refractive index of 3 seconds; this is approximately constant throughout the range of 1 to 16 μ, since $\frac{1}{2}(A + \delta)$ is large compared with the difference in the values of $\frac{1}{2}\delta$ at 1 μ and at 16 μ. Combining this with (2) we have

$$\left(\frac{\partial\delta}{\partial A}\right)_{1\mu} = 1\cdot0 \text{ second/second.}$$

$$\left(\frac{\partial\delta}{\partial A}\right)_{16\mu} = 0\cdot8 \text{ second/second.}$$

Hence the equivalent error in prism table rotation for an error of 1 second in A is 0·5 second at 1 μ and 0·4 second at 16 μ; the Wadsworth mirror is adjusted to give a correct setting at 1·014 μ, and the nett error at 16 μ is consequently 0·1 second. The permissible error in A is therefore 10 seconds of arc.

Similar calculations give the corresponding values for the other prism materials and they are tabulated below.

Table I.—Permissible Errors in Prism Angles at the Appropriate Wave-lengths.

Material.	$(\partial\delta/\partial n)$ in seconds.	$(\partial\delta/\partial A)$ in seconds/second.		Permissible error in A in seconds.
	(At 5th decimal place for n.)	At 1 μ.	At effective limit.	
Quartz, 60° 1′ 30″....	3·0	1·0	0·9 at 3·4 μ	20
Fluorite, 60° 0′ 0″....	2·9	0·78	0·61 at 8·5 μ	12
Rocksalt, 60° 0°0 ″	3·0	1·0	0·8 at 16 μ	10
Sylvine, 60° 0′ 37″	2·9	0·89	0·63 at 22 μ	8

(iv) *Variation of Refractive Index of Prism Material with Temperature.*—The variation is considerable with rocksalt, fluorite and sylvine. The temperature at which the Wadsworth mirror is set, and that at which the spectrometer drum is read, are both noted ; the spectrometer is calibrated to read correctly at 18° C., and if the Wadsworth mirror is not set at 18° there is an equivalent error in prism table rotation. The article by Coblentz on " Infra-red Transmission and Refraction Data " in the " Dictionary of Applied Physics " (vol. 4, p. 136) records the necessary temperature coefficients which give the change in refractive index ; when the latter is multiplied by $\frac{1}{2}(\partial\delta/\partial n)$ we obtain the equivalent correction in prism table rotation ; a similar calculation provides the temperature correction for the drum reading, and the algebraic difference of the two gives the nett correction for $\frac{1}{2}\delta$; the corresponding error in wave-length is given on multiplication by $2(\partial\lambda/\partial\delta)$. The temperature at which the Wadsworth mirror is set, and that at which the drum is read, should be accurate to 0·3°.

The greatest error, then, is in the uncertainty of prism table rotation with drum rotation. The maximum possible error in any wave-length reading may be taken as that due to an error of 4 seconds of arc in the semi-minimum deviation ; this error diminishes as the wave-length approaches 1·014 μ, where the Wadsworth mirror is set.

Resolving Power.

A knowledge of the difference in wave-numbers of any two consecutive maxima which can be distinguished by the instrument is useful inasmuch as it indicates what Bjerrum doublets in the infra-red might be separated into their constituent branches. A thermopile slit width of 0·01 inch subtends an angle of approximately 100 seconds of arc at the prism ; if the collimator slit is of the same width, maxima separated by the wave-numbers included in 100 seconds of arc of total minimum deviation should be resolved ; since the direction of incidence on the prism is constant for all wave-lengths, spectral lines must on emergence be separated approximately as the difference in their total minimum deviations. The problem is therefore to determine the wave-numbers included in 100 seconds of arc of total deviation at different wave-lengths. The range of wave-length included in 100 seconds of arc is calculated from the table of wave-length—semi-minimum deviation. The range of wave-numbers is then determined from the expression $d\nu = -d\lambda/\lambda^2$.

Table II appended gives the wave-numbers included in the slit width used for normal working of the spectrometer within the appropriate ranges for the available prism materials.

Table II.

	λ (μ).	Normal slit width (in 1/1000 in.).	Wave-number separation (cm.$^{-1}$).
(*a*) Quartz	1·0	3	70
	1·5	3	50
	1·75	3	20
	2·0	3	13
	2·7	5	9
	3·0	7	8
	3·4	7	7
(*b*) Fluorite	3·5	5	19
	4·0	5	14
	4·5	5	10
	5·0	7	8
	5·7	7	7
	6·4	10	6
	7·2	10	4
	8·1	10	3
(*c*) Rocksalt	8·0	10	12
	9·3	10	8
	10·4	10	5
	11·6	10	4
	12·8	10	3
	14·0	15	3
	15·1	15	2
d) Sylvine	15·5	15	4
	16·75	20	3·5
	17·9	20	3
	19·5	25	2·5
	21·5	25	2·5

The above wave-number separations are less, however, than those which in practice can actually be resolved, since curvature of the image of the collimator slit diminishes the resolving power. This defect might be considerably reduced if the spectroscope were designed so that the telescope mirror reversed the errors of the collimator mirror.* The P and R branches of the sulphur dioxide band at 4·003 μ, separated by Meyer, Bronk and Levin† with the aid of a grating instrument, show a difference between the envelope maxima of 24 cm.$^{-1}$; this degree of resolution was not attained with the fluorite prism in our possession; defects in the actual sample may be responsible for this failure, and generally with this prism and spectroscope, separable wave-numbers are 50 per cent. further apart than those given in the table.

Table II enables us to contrast the prism with the grating, and to show where the former may give the desired experimental data even more readily than the

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* See Czerny, *loc. cit.*

† 'J. Opt. Soc. Amer.,' vol. 15, p. 257 (1927).

later. Two factors have to be considered in infra-red measurements, viz., the resolving power of the instrument and the energy falling on the thermopile. The resolving power, $\lambda/d\lambda$, of the grating is greater than that of the prism at all wave-lengths ; at longer wave-length, however, a given frequency difference corresponds to a much larger wave-length difference than at shorter wave-lengths and the large resolving power is not essential ; in fact, $d\lambda \propto \lambda^2 d\nu$. The prism spectrometer at any given wave-length presents to the thermopile a greater amount of energy than a grating spectrometer. Hence, between 8 and 22 μ, where the available energy is very low, the prism spectrometer may give useful data more readily than a grating instrument.

Finally, Table III gives the moment of inertia corresponding to a definite Bjerrum separation ; it is useful since it indicates those molecules whose bands should be carefully examined.

Table III.

$\Delta\nu$ (cm.$^{-1}$)	70	50	20	13	9	8	7	6	5	4
J.g. cm.$^2 \times 10^{38}$........	0·1	0·2	1·1	2·6	5·5	7·0	9·0	12	18	28

In order to bring out the full resolving power of the instrument, it is essential to make observations at sufficiently frequent intervals ; four or six per slit width allow of this. 0·01 of a revolution of the wave-length drum moves the image of the spectrum line 0·0022 inch ; hence, when examining a band with a slit width of 0·01 inch, 90 to 120 readings have to be taken per revolution of the micrometer drum.

Investigations in the Infra-Red Region of the Spectrum. Part II.—The Absorption Spectrum of Sulphur Dioxide.

By C. R. Bailey, A. B. D. Cassie, and W. R. Angus, University College, London.

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It has been pointed out that if the precautions indicated in the previous paper are carefully observed, a high order of accuracy in infra-red measurements can be obtained with a prism spectrometer. Although the final word at present rests with the grating instrument on account of its higher resolving power, nevertheless a deal of useful work remains to be done with prisms. A band can be located (generally a necessary process for a prism spectrometer before the grating can be applied), the band centre and band type can often be determined, and the molecular constants can be approximately deduced.

It is proposed in these papers to examine the spectra of gases and vapours in which the molecule has three different moments of inertia. The rotational fine structure within a vibrational band due to an asymmetrical rotator is very complex and individual lines may lie so close and the constituent series so overlap that absorption may be practically continuous. The prism spectrometer enables the first step in the unravelling of the tangle to be accomplished, in that the envelope of the individual lines gives under favourable circumstances the branches of the Bjerrum doublets, and hence enables the moments of inertia to be determined and frequently provides a knowledge of what may be called the resultant electrical structure of the molecule.

Experimental.

Sulphur dioxide was taken from a commercial " syphon " and passed slowly through concentrated sulphuric acid into the phosphoric oxide and absorption tube system which had been previously evacuated. When the attached manometer showed a pressure of gas just greater than was required in the absorption tube, the tap connecting the sulphuric acid bubblers to the evacuated system was closed, the sulphur dioxide frozen in a liquid air trap, and the system again pumped out to remove any air that had passed with the gas into the absorption tube. This process was necessary in order to obtain the true pressure of sulphur dioxide in the tube. The liquid air trap was subsequently slowly warmed up until the desired pressure was shown by the manometer; the trap was then shut off and time allowed for pressure equilibrium to be attained throughout the system which included the glass spiral; the manometer was again read. The preliminary examination was carried out at a pressure of approximately 65 cm., when the positions and approximate absorptions of all the bands were determined, each band was then investigated individually at a pressure required to give a maximum percentage absorption of approximately 50 per cent. where the resolution of the bands is most readily effected.

The Observed Data.

The details of the bands revealed by this investigation are collected in Table I. The second and third columns give respectively the wave-lengths and wave-numbers of the band centres; the fourth and fifth columns give the maxima of the band envelope and their separations in wave-numbers; in the sixth and seventh are to be found the pressure of gas in centimetres of mercury with the maximal percentage absorption. The last three columns give the suggested origin of the band with the calculated value and the discrepancy between this and the observed. Coblentz* explored the spectrum as far as 15 μ with a rocksalt prism and his results are shown in fig. 1. When the individual bands are considered in detail below, it will be seen that there exist certain unexplained differences between the two sets.

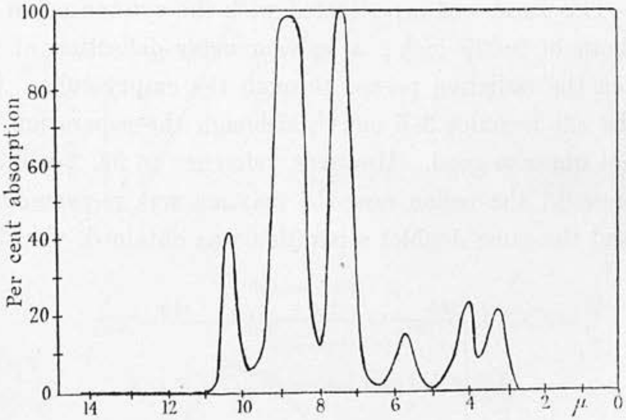

Fig. 1.—The Infra-Red Absorption of SO_2 according to Coblentz.

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* "Investigations of Infra-red Spectra," Part I, pp. 52 and 177.

Table I.

Band.	Band centre.		Maxima (cm.$^{-1}$).	P − R $\Delta\nu$ (cm.$^{-1}$).	Pressure cm. Hg.	Maximal per cent. absorption	Origin.	ν_c calculated (cm.$^{-1}$).
	λ (μ).	ν_0 (cm.$^{-1}$).						
A	16·494	606	$\left\{\begin{matrix}611\\602\end{matrix}\right\}$	9	63·5	37	ν_1	—
B	8·680	1152	$\left\{\begin{matrix}1169\\1138\end{matrix}\right\}$	31	4·6	80	ν_2	—
C	7·347	1361	$\left\{\begin{matrix}1377\\1361\\1348\end{matrix}\right\}$	30	0·15	55	ν_3	—
D	5·345	1871	1871	—	60	12	$\nu_3+\nu_2-\nu_1$	1907
E	4·338	2305	$\left\{\begin{matrix}2317\\2288\end{matrix}\right\}$	29	64·5	47	$2\nu_2$	2304
F	4·003	2499	2499	—	64·5	89	$\nu_2+\nu_3$	2513

The Individual Bands.

A. *Fundamental Band at* 16·494 (± 0·004) μ, $\nu = 606$ *cm.*$^{-1}$, *not observed by Coblentz.*—This band was investigated with the sylvine prism with actual slit widths both of 0·025 inch; a galvanometer deflection of 15 cm. was obtained when the radiation passed through the empty tube. Under these conditions the slit includes 3·5 cm.$^{-1}$, although the separation obtained in practice is not quite so good. However, reference to fig. 2 will show that a doublet is present; the region near the maxima was re-examined with slits 0·015 inch and the same doublet separation was obtained, viz., 9 cm.$^{-1}$, the

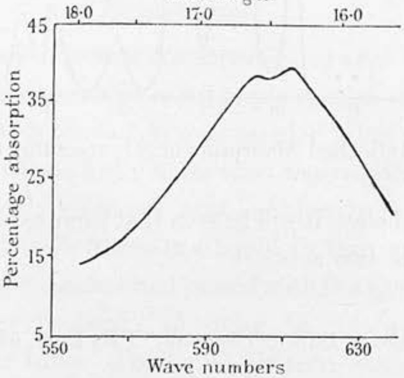

Fig. 2.—Fundamental Band at 16·5 μ.

band consisting of P and R branches. The doublet minimal percentage absorption observed with the narrower slit widths was only 3 per cent. lower than the maxima on either side, and it was not considered justifiable to assume the real existence of this separation until other possible sources of this small variation with wave-length had been investigated. The most likely cause would be a difference in the transmission of the two tubes at this point; accordingly both tubes were evacuated and the galvanometer throws again read. There was actually a very small difference in the transmissions, but this difference remained accurately constant throughout the range; the tube was then refilled and the doublet again appeared. There is then every justification for adopting the given value for the doublet separation.

B. *Fundamental Band at* 8·680 (± 0·004) μ, $\nu_2 = 1152$ *cm.*$^{-1}$; *Coblentz gives* 8·7 μ.—A rocksalt prism was used for this region, with slit widths 0·01 and 0·01 inch, including 10 cm.$^{-1}$. We have a well-defined doublet of P and R branches only, the separation being 31 cm.$^{-1}$. The observations in this as in the other bands were repeated at different pressures and with different samples of the gas, and the results were consistent. The mean maximum percentage absorption was determined at 0·9 and 4·6 cm. pressure and was found to be 23 and 80 per cent. respectively. The band is shown in fig. 3.

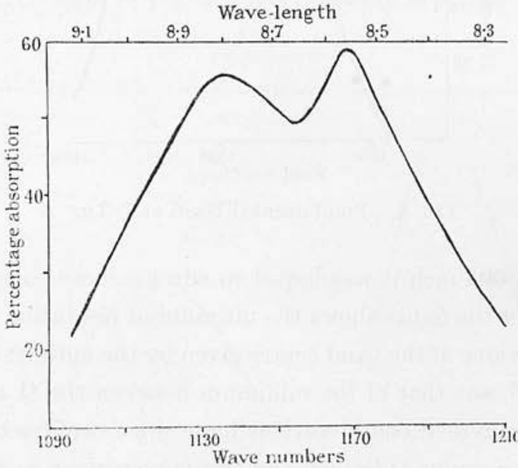

Fig. 3.—Fundamental Band at 8·68 μ.

C. *Fundamental Band at* 7·347 (± 0·002) μ, $\nu_3 = 1361$ *cm.*$^{-1}$ (*fig.* 4); *Coblentz gives* 7·4 μ.—This is the most intense band, and Table I enables the intensity relationships between the various bands to be approximately determined. Coblentz shows the two bands at 8·7 and 7·4 μ as having the same intensities; this is probably due to the fact that the maximum absorption in each case is 100 per cent., but there is no doubt that the latter band is much more powerful. It was examined with the fluorite prism, the slit widths being 0·007 inch in each case and including 4 cm.$^{-1}$: maxima 6 cm.$^{-1}$ apart should be separated. We have repeated observations on this band many times at different pressures, slit widths, and with different samples of gas; the same qualitative result was obtained in all cases. Reference to fig. 4 will show what appear to be P, Q and R branches, and by reducing the slit width as low as 0·004 inch it was hoped to effect a more complete separation of the Q and P, but the figure shows the ultimum of resolution under the given conditions. The value of the band centre given by the authors in a preliminary note to 'Nature,'* was that of the minimum between the Q and R branches, viz., 7·301 μ; theoretical considerations have since confirmed the suggestion that the band has a strong Q branch and this is now given as the band centre. The pressure 0·15 cm. of mercury given in the table must be taken as indicative of the order of magnitude since the presence of the glass spiral renders the determination of low pressures somewhat difficult; at any pressures comparable with those used for the other bands the galvanometer deflections were negligible.

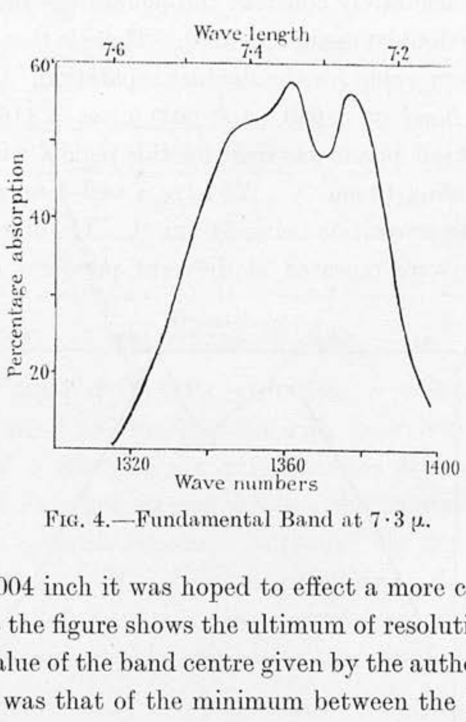

Fig. 4.—Fundamental Band at 7·3 μ.

D. *Combination Band at* 5·345 ($\pm$ 0·002) μ, $\nu = 1871$ *cm*$^{-1}$.—A very weak band explored with the fluorite prism and slit widths of 0·005 inch (includes 8 cm.$^{-1}$ and resolves 12 cm.$^{-1}$). Only one maximum was observed, chiefly

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* Vol. 126, p. 59 (1930).

because of the low absorption; to avoid the possibility of the presence of "false band" the tubes were tested for inequality of transmission as before, and the gas samples were varied. Coblentz reports a band at 5·68 μ, with a maximal percentage absorption of 15 to 20 per cent. in a cell length of 6·3 cm. at atmospheric pressure; it is difficult to say whether the two are identical, our band is certainly much weaker. The formulation $\nu_2 + \nu_3 - \nu_1$ fits the band centre better than any other; the discrepancy of 36 cm.$^{-1}$ may be attributed to the anharmony of the combination. The low intensity is in accord with the existence of a difference tone which is not unexpected, as one quantum of radiation of frequency 606 cm.$^{-1}$ is 10×10^{-14} ergs., whilst the kinetic energy of translation of the molecule at 17° C. is 4×10^{-14} ergs. There is, however, the possibility that this band is to be interpreted as the combination of the fundamental at 7·34 μ with a two-parameter band whose ground level is at 606 cm.$^{-1}$, of the type $\nu_2 + (2 - 1)\nu_1$; our experimental evidence does not allow us to say whether $(2-1)\nu_1$ exists.

E. *Combination Band at* 4·338 (± 0·003) μ, $\nu = 2305\,cm.^{-1}$ (*fig.* 5).—Coblentz shows a band at 3·97 μ; this has probably been resolved in the present work into the bands 4·34 and 4·00 μ (see below). The fluorite prism with slit widths 0·007 in each case was employed, the thermopile slit includes 12 cm.$^{-1}$ and maxima separated by 18 cm.$^{-1}$ resolved. Two indistinct maxima 29 cm.$^{-1}$ apart were distinguished and the band appears to consist of P and R branches; it is apparently the first harmonic of the second fundamental, ν_2; the calculated and observed values are exceptionally close.

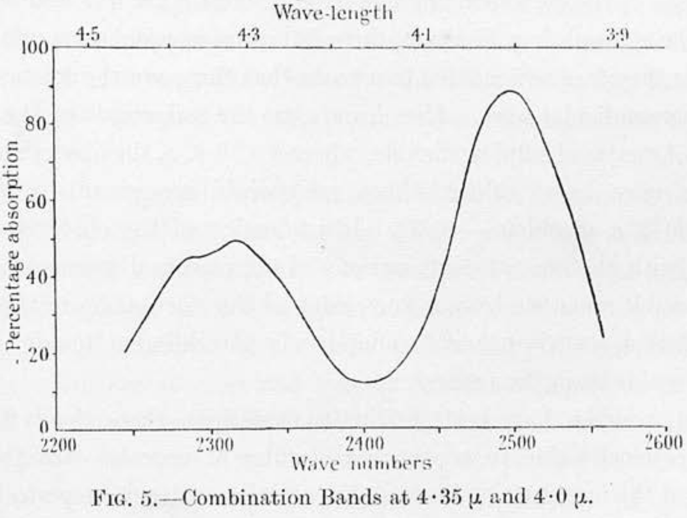

Fig. 5.—Combination Bands at 4·35 μ and 4·0 μ.

F. *Combination Band at* $4\cdot003$ ($\pm\ 0\cdot003$) μ, $\nu = 2499$ *cm.*$^{-1}$ (*fig.* 5).—This band was resolved by Meyer, Bronk, and Levin into P and R branches by means of a grating, the band centre, as far as one can judge from the very small figure provided, being at or near $4\cdot001\ \mu$ (2502 cm.$^{-1}$).[*] The separation of the maxima obtained by the above authors was 24 cm.$^{-1}$; we have failed to resolve this band, although this value appears to be just within the limits of possible resolution for the fluorite prism at the wave-length in question. The frequency calculated on the assumption that this band is represented by $\nu_2 + \nu_3$ is in good agreement with that observed.

The Sulphur Dioxide Molecule.

The existence of a permanent electric moment[†] indicates a triangular structure for this molecule; the infra-red data given above are in accordance with this assumption; we have three distinct fundamental frequencies resolvable into P and R or P, Q, and R branches. From the maximal separation in the Bjerrum doublets the classical values for possibly two of the moments of inertia of the molecule are easily calculated. If we accept the separations of 31 and 9 cm.$^{-1}$, the corresponding moments of inertia are $4\cdot7$ and 55×10^{-39} g. cm.^{2}; the molecule has, however, three finite and unequal moments of inertia and we are therefore not entitled to assume that these are the moments about any two perpendicular axes. If a, b and c are the reciprocals of the principal moments of inertia of sulphur dioxide, where $a < b < c$, the observed moments of inertia may have values whose reciprocals are given by $(a+b)/2$, $c-(a+b)/2$, c, a and $(c-a)/2$.[‡] Identification of the observed moments of inertia with the correct combinations of the principal moments of inertia is only possible when we have a knowledge of the orientation in the molecule of the different electric moments effective in the different bands; selection rules then guide us in the process.

Bjerrum[§] seems to have been the first to investigate theoretically the fundamental frequencies due to triatomic molecules of isosceles triangular form. He assumed the forces acting between the atomic centres to be perfectly elastic and calculated the fundamental frequencies in two cases: (1) where the restoring forces are central, and (2) where the restoring force between S and O is central, and a restoring couple acts about an axis passing through the S atom

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[*] 'J. Opt. Soc. Amer.,' vol. 15, p. 257 (1927).

[†] Zahn, 'Phys. Rev.,' vol. 27, p. 455 (1926).

[‡] See Bailey, Cassie and Angus, 'Trans. Faraday Soc.,' vol. 26, p. 197 (1930).

[§] 'Verhand. Deutsche Physikal. Gesell.,' vol. 16, p. 737 (1914).

and perpendicular to the molecular plane; the latter couple replaces the central restoring force acting between the oxygen atoms in case (1). Clearly Bjerrum's calculations are only a first approximation; the method has been amplified and extended.* It is nevertheless invaluable in assigning the different fundamental frequencies to different modes of vibration of the molecule, and is the general mathematical method employed in vibration problems. The determinant equation which gives the possible frequencies is a cubic; the relations between the roots of the equation and its coefficients give three equations in terms of the two elastic coefficients, the semi-angle, $\alpha/2$, of the isosceles triangle, the masses of the atoms, and the periods of the normal modes of vibration. The elastic coefficients can be eliminated to give an equation in the masses of the atoms, the periods of the normal modes, and α: it is a quadratic in $\cos^2 \alpha/2$. There are hence six possible values for $\cos^2 \alpha/2$ corresponding to the three permutations of the three periods; four of these are imaginary, and we have left two possible values of α. These are found to be approximately 40° and 140°, and we finally arrive at four solutions in all: two correspond to case (1) which with Bjerrum we shall refer to as a system of central forces, and two to case (2) which we shall call a system of valence forces. The relative amplitudes of vibration for the three atoms can also be calculated; the smaller value of α gives vibrations that are almost alike for the central restoring force and for the valence force systems; the larger value gives different modes in each case (figs. 6 and 7).

The nature of the optical absorption in the infra-red depends on the orientation of the vibrating electric doublet and on the magnitude of its vibration; the greater the amplitude of vibration of the electric doublet the greater is the percentage absorption. It is here taken as proportional to the vector sum of the amplitudes of vibration of the individual atoms.† If the central force system is chosen, the shortest and longest fundamental periods of vibration correspond to a vibrating electric doublet lying along the bisector of the vertical angle; and the other period to an electric doublet parallel to a line lying in the plane of the triangle and perpendicular to this bisector. The amplitude of the shortest period vibration is much greater than that of the largest; that is, the shortest wave-length infra-red absorption band should be considerably more intense than the longest. The larger angle model with central forces has these intensities reversed. The valence force system with the larger

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* Dennison, 'Astrophys. J.,' vol. 62, p. 84 (1925) and 'Phil. Mag.,' vol. 1, p. 195 (1926) Hund, 'Z. Physik,' vol. 31, p. 81 (1925) and vol. 43, p. 805 (1927).

† Dennison, 'Phil. Mag.,' *loc. cit.*

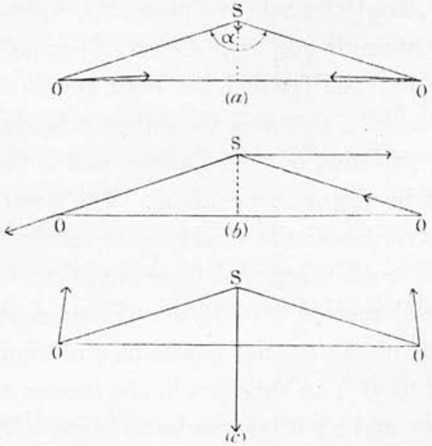


FIG. 6.—System of Central Forces $\alpha = 140°$.
(a) $\lambda = 7 \cdot 3\ \mu$; symmetrical.
(b) $\lambda = 8 \cdot 68\ \mu$; asymmetrical.
(c) $\lambda = 16 \cdot 5\ \mu$; symmetrical.

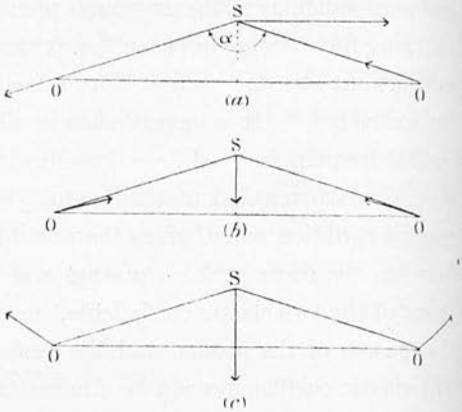
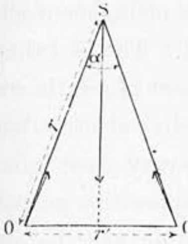


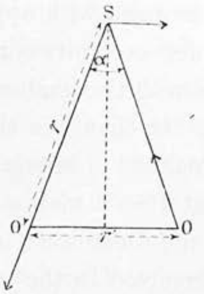
FIG. 7.—System of Valence Forces, $\alpha = 140°$.
(a) $\lambda = 7 \cdot 3\ \mu$; asymmetrical.
(b) $\lambda = 8 \cdot 68\ \mu$; symmetrical.
(c) $\lambda = 16 \cdot 5\ \mu$; symmetrical.

value for α interchanges the directions of the electric doublets effective in the two shorter periods, and the amplitude of the two longer periods are approximately equal.

The ratios of the experimentally observed intensities cannot be accurately determined as different pressures were required for observations in the different bands. The shortest wave-length band is by far the most intense; the middle band has approximately a maximal percentage absorption of 80 per cent. at 4·6 cm., while the longest has an absorption of only 37 per cent. at 63·5 cm. pressure. The great absorption of the shortest wave-length band compared with the others agrees only with the smaller value of α when the central force system is assumed. On the other hand, the large percentage absorption of the $8 \cdot 68\ \mu$ band compared with that of the $16 \cdot 5\ \mu$ band does not agree with the approximately equal absorptions predicted by the valence force system when the larger value of α is assumed. Thus we see that the intensity relationships of the fundamental bands leave one possible solution for α, namely, that α must be small.

Our model of the sulphur dioxide molecule is, therefore, qualitatively that shown in fig. 8. The shortest and longest wave-length bands have effective electric doublets whose changes during vibration lie along the bisector of the vertical angle; the middle wave-length band has an effective electric doublet whose changes lie wholly normal to this line, and in the plane of the triangle,





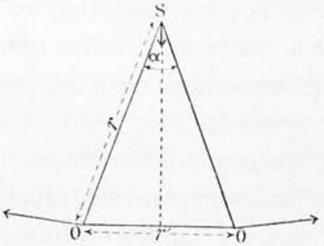


Fig. 8a.—Fundamental at $7 \cdot 3\ \mu$; symmetrical.

Fig. 8b.—Fundamental at $8 \cdot 68\ \mu$; asymmetrical.

Fig. 8c.—Fundamental at $16 \cdot 5\ \mu$; symmetrical.

$\alpha = 24°$. $r = 4 \cdot 8 \times 10^{-8}$ cm. $r' = 2 \times 10^{-8}$ cm.

The orientation of the change in electric moment is now known, and an interpretation of the branch separations is possible.

Band B at $8 \cdot 68\ \mu$ is a simple doublet. The electric moment effective in the absorption is normal to the bisector of the vertical angle; hence there should be no Q branch corresponding to spin about this axis, and the P and R branch separation gives the moment of inertia about this principal axis, *i.e.*, the least moment of inertia. The doublet separation is 31 cm.$^{-1}$, and the corresponding moment of inertia is $4 \cdot 7 \times 10^{-39}$ g. cm.^{2}.

Band A at $16 \cdot 5\ \mu$ is a simple doublet containing a P and R branch. The effective electric doublet is parallel to the bisector of the vertical angle or axis of least inertia. There should, therefore, be no separation corresponding here to the least moment of inertia, we must have a separation which corresponds either to the greatest moment of inertia or to the arithmetic mean of the greatest and intermediate principal moments of inertia according as the molecule spins about the axis of greatest or least inertia. Since the difference between the greatest and intermediate moments of inertia is small compared with the value of either, the difference between these effective moments of inertia is negligible. We therefore assume the separation of 9 cm.$^{-1}$ to correspond to the largest moment of inertia; its value is 55×10^{-39} g. cm.^{2}.

Band C at $7 \cdot 35\ \mu$ presents some difficulties. This band arises from an effective electric doublet parallel to the least axis of inertia. There should therefore be no P and R separation corresponding to the least moment of inertia; on our model the band should be similar to that at $16 \cdot 5\ \mu$. The observed band, however, has P and R branches separated by 29 to 30 cm.$^{-1}$, with a strong Q branch; the general form of the band, as shown by our resolution and by Coblentz's original diagram, makes it unlikely that we are dealing with two superimposed bands, although this possibility has always to be borne in mind, and study of the band with apparatus of higher resolving power has to be made before complete certainty is reached. The fact that the doublet separation does correspond with the smallest moment of inertia admits of interpretation if we assume that the change in the effective electric doublet is not wholly parallel to the least moment of inertia. The very great intensity of the band compared with that at 16·5 μ makes this supposition plausible; for Bjerrum's simple hypotheses and Dennison's assumption may be almost correct for the small amplitudes involved in the 16·5 μ vibration, and be no more than rough approximations for such large amplitudes as occur in the 7·35 μ band. The P and R branches are therefore assumed to be due to changes in rotation about the least axis of inertia. Since the Q branch has a greater intensity than either of the others, the effective electric doublet must have a larger component parallel to the least axis of inertia than perpendicular to it.

Band E at 4·34 μ is the first harmonic of the band at 8·68 μ and its characteristics tally with this assignment.

Band F at 4·00 μ has been resolved into P and R branches by Meyer, Bronk and Levin (*loc. cit.*). In assigning this band to a combination tone $\nu_2 + \nu_3$ of the fundamentals at 8·68 and 7·45 μ, we should have an effective electric doublet inclined to the axes of least and intermediate moments of inertia, but perpendicular to the axis of greatest. The separation of the P and R branches is given as 24 cm.$^{-1}$, which corresponds to a moment of inertia of $7 \cdot 7 \times 10^{-39}$ g. cm.^{2}. This value does not fit any of the theoretically possible combinations of the principal moments of inertia (55, 50 and $4 \cdot 7 \times 10^{-39}$ g. cm.^{2}). In the very small diagram provided, the authors show a curve with a very broad P branch compared with those we have observed ; the moment of inertia must depend on the amplitude of vibration of the atoms, and there is in fact no reason to assume that the moment of inertia given by the fundamental bands should in all cases be the same as that given by the harmonics or combination tones. It is even possible that the difference in values in the two cases might be used to deduce the ratio of the amplitudes of the atomic vibrations in a fundamental and combination tone.

A quantitative model based on the supposition that 55 and $4 \cdot 7 \times 10^{-39}$ g. cm.^{2} are the greatest and least principal moments of inertia offers the following characteristics :—

(i) $S - O = 4 \cdot 8 \times 10^{-8}$ cm.

(ii) $O - O = 2 \cdot 0 \times 10^{-8}$ cm.

(iii) $\widehat{OSO} = 24°$.

This model with the above interpretation of the fundamental vibrations is supported by the work of Hund (*loc. cit.*). He derived expressions for the frequencies of vibration of the water molecule, and his method is applicable to sulphur dioxide. We make the following assumptions: (i) sulphur loses four electrons, two to each atom of oxygen: (ii) the atom of sulphur has a constant polarisability; (iii) it attracts the oxygen atoms according to Coulomb's law, and repels them inversely as the fifth power of the distance $S-O$; (iv) the oxygen atoms repel each other according to Coulomb's laws. The constant polarisability and the charge effective in the $S-O$ inverse fifth power repulsion are eliminated by means of the equations determining the configuration of stable equilibrium. Thence, following Hund's calculation, the frequencies of the unsymmetrical and symmetrical vibrations are given by the expressions

$$\omega_2^2 = \left(\frac{1}{m} + \frac{2}{M}\sin^2\alpha\right)(A_{11} - A_{12}); \qquad (1)$$

and

$$\omega_{1,3} = p \pm \sqrt{(p^2 - q)}; \qquad (2)$$

where

$$p = \frac{\cos^2\alpha}{M}(A_{11} + A_{12}) + \frac{1}{2m}(2A_{00} + A_{11} + A_{12} + 4A_{01}\sin\alpha);$$

$$q = \cos^2\alpha\left(\frac{1}{m^2} + \frac{2}{mM}\right)[2A_{00}(A_{11} + A_{12}) - 4A_{01}^2];$$

and

$$A_{00} = \frac{3e^2}{s^3}, \quad A_{01} = -\frac{3e^2}{rs^2}, \quad A_{11} = \left(\frac{8}{r^3} + \frac{7}{s^3} - \frac{3}{r^2s}\right)e^2, \quad A_{12} = \left(\frac{9}{2r^2s} - \frac{3}{s^3}\right)e^2;$$

in which M = mass of sulphur atom; r = length of side of triangle; m = mass of oxygen atom; s = length of base of triangle; α = semi-vertical angle of triangle.

On insertion of the appropriate values as determined above, the ratios of the three frequencies appear as

$$13{\cdot}4 : 11{\cdot}4 : 6{\cdot}6,$$

where the middle value represents the unsymmetrical vibration, or that vibration whose effective electric doublet is normal to the axis of least inertia. The observed frequency ratios are as

$$13{\cdot}6 : 11{\cdot}4 : 6{\cdot}1,$$

the middle value corresponding to the vibration whose effective electric doublet was assumed normal to the axis of least inertia.

Comparison with the Original Observations of Coblentz.

Coblentz's original curve (fig. 1) shows a number of unresolved bands; we are unable to obtain bands corresponding to those at $3 \cdot 18$ and $10 \cdot 37$ μ, while in place of the band at $5 \cdot 68$ μ we have another at $5 \cdot 34$ μ. Coblentz prepared his gas by acting on sodium bisulphite with strong sulphuric acid, and purified it by subsequent fractional liquefaction and distillation without eliminating any of the observed bands. Most careful search has failed to reveal the missing bands; we have had constructed tubes of stainless steel, 1 metre in length, and are proposing to examine the absorption spectra of a number of gases under pressure; in this way we hope to add to the known bands of these gases and hence obtain further information regarding the molecular constants. Our search for the missing bands was made under pressures of 63 cm. of mercury with a column of gas 45 cm. long, and it seems likely that we should have observed them if they had been present inasmuch as Coblentz used a $6 \cdot 3$ cm. cell under $74 \cdot 4$ cm. pressure. Our gas was taken from the commercial "syphon," but the presence of any impurities would be more likely to add to the number of bands than to diminish them. It is of importance to point out that Coblentz noticed that the wave-number difference between his bands at $3 \cdot 18$ and $3 \cdot 97$ μ was 605 cm.$^{-1}$ (miscalculated, should be 626 cm.$^{-1}$) and between those at $5 \cdot 68$ and $8 \cdot 70$ μ was 612 cm.$^{-1}$. The closeness of these differences to the first fundamental at 606 cm.$^{-1}$ would indicate a positive existence for the missing bands; in that case $3 \cdot 18\ \mu = 3145$ cm.$^{-1}$ is $\nu_1+\nu_2+\nu_3$ (calculated from our results, 3109 cm.$^{-1}$); $5 \cdot 68\ \mu = 1762$ cm.$^{-1}$ is $\nu_1+\nu_2$ (calculated 1758); and $10 \cdot 37\ \mu = 965$ cm.$^{-1}$ might be $2\nu_2-\nu_1$ (calculated 944 cm.$^{-1}$), although the comparatively great intensity (40 per cent. maximum absorption) of this band is against this assumption.

The Raman Spectrum of Sulphur Dioxide.

The Raman spectrum of solutions of sulphur dioxide in water, carbon tetrachloride and other solvents has been determined by Harkins, Gans and Bowers;* they obtained prominent lines at 1150 and 1114 cm.$^{-1}$. Dickinson and West† repeated this work with liquid sulphur dioxide, and observed several lines corresponding to infra-red frequencies of 1146 (very strong) 1340 (medium and diffused), and 524 cm.$^{-1}$ (weak and diffused), but 1114 cm.$^{-1}$ was missing. We can identify all of these except the last as in Table II below.

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* 'Nature,' vol. 125, p. 464 (1930).

† 'Phys. Rev.,' vol. 35, p. 1126 (1930).

Table II.—The Raman and Infra-red Frequencies of Sulphur Dioxide.

Raman spectrum.	Infra-red spectrum.	Origin.	Calculated.
$cm.^{-1}$	$cm.^{-1}$		$cm.^{-1}$
1146	1152	ν_2	—
1340	1361	ν_3	—
524	—	$\nu_2 - \nu_1$	546

The Molecular Constants.

Until other combination- and over-tones have been obtained by an examination of the absorption of the gas under greater pressures, it is not possible to assign definite values to all the characteristics of the molecule ; these include the true vibration frequencies and the constants indicating the measure of anharmony in the various modes. We can, however, say at once from bands B and E that $a_2 + b_2$ is 1152 cm.$^{-1}$, and that $2a_2 + 4b_2$ is 2305 ; it follows then that a_2 is 1152 cm.$^{-1}$, and that b_2 is zero within the limits of experimental error, which is in keeping with the large moment of inertia. The difficulties encountered above in the analysis of band C place some doubt upon the value of the band centre, and further resolution must be awaited before a definite pronouncement can be made as to the values of a_3 and b_3. On the assumption then that band C contains a pronounced Q branch, the recognised constants of the sulphur dioxide molecule can be summarised as in Table III.

Table III.—The Molecular Constants of Sulphur Dioxide.

Moments of inertia in g. cm.^{2} × 10^{39}.	Lengths of side in cm. × 10^8.	Vibration frequencies in cm.$^{-1}$.
$J_1 = 55$	$S - O = 4{\cdot}8$	$a_1 + b_1 = 606$
$J_2 = 50$	$O - O = 2{\cdot}0$	$a_2 = 1152,\ b_2 = 0$
$J_3 = 4{\cdot}7$	whence angle OSO = 24°	$a_3 + b_3 = 1361$
$J_1 = J_2 + J_3$		

Summary.

1. The infra-red absorption spectrum of sulphur dioxide has been re-examined in the region 1 to 22 μ with a prism spectrometer fitted with quartz, fluorite, rocksalt, and sylvine prisms.

2. The spectrometer having been carefully calibrated and allowance made

for the change in dispersion of the prism materials with temperature, it is believed that the results are generally accurate to ± $0 \cdot 003\ \mu$.

3. The ascertained spectrum has been compared with the previous work of Coblentz.

4. The partial resolution effected in most of the bands has rendered possible the determination of a number of the molecular constants, in particular the size and shape of the molecule, the moments of inertia, and the fundamental vibrational frequencies.

5. The observed infra-red spectrum has been co-ordinated with the Raman spectrum of the liquid.

The authors wish to express their thanks to Prof. F. G. Donnan, C.B.E., F.R.S., for his interest and encouragement. During the period of the research, the authors have been aided by grants from various bodies and they hereby tender their grateful thanks to the following: C.R.B., to the Department of Scientific and Industrial Research for a grant which has enabled him to supplement the smaller grants in the following cases: A.B.D.C., Imperial Chemical Industries, Limited, and the Carnegie Trust for the Universities of Scotland; W.R.A., the Trustees of the Yuill Scholarship (Aberdeen University), and the Carnegie Trust.

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Investigations in the Infra-Red Region of the Spectrum.

Part III.—*The Absorption Spectrum of Carbon Disulphide.*

BY C. R. BAILEY AND A. B. D. CASSIE.

Part IV.—*The Monochromator Method in the Infra-Red.*

BY A. B. D. CASSIE AND C. R. BAILEY.

INVESTIGATIONS IN THE INFRA-RED REGION OF THE SPECTRUM. PART III.—THE ABSORPTION SPECTRUM OF CARBON DISULPHIDE.

BY

C. R. BAILEY

AND

A. B. D. CASSIE.

b

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Investigations in the Infra-Red Region of the Spectrum. Part III.—*The Absorption Spectrum of Carbon Disulphide.*

By C. R. Bailey and A. B. D. Cassie, University College, London.

(Communicated by F. G. Donnan, F.R.S.—Received March 13, 1931.)

The absorption spectrum of liquid carbon disulphide has been previously determined by Coblentz.*

The apparatus described in Part I of the present series† offers a higher degree of resolution and a greater range of the spectrum than were available to the former worker. It was accordingly decided to examine this substance in the vapour state, and this paper gives an account of the absorption spectrum between 1 and 22 μ.

Experimental.

It is unnecessary to add to the general description of the procedure and apparatus published in Part I. A monochromator method has been developed which is easy to use, and which eliminates from the absorption tube all radiation emitted by the Nernst filament except the small range of wave-lengths passing through the telescope slit. This was used in the confirmatory examination of one of the bands described below, but the general account is reserved for the following paper. It is pleasing to note that the order of accuracy of the experimental results for sulphur dioxide (Part II)‡ is high; the strong band located by us at 1152 cm.$^{-1}$ has been found in the Raman spectrum of the gas by Bhagavantam§ at 1154 cm.$^{-1}$.

The carbon disulphide supplied was specially prepared for refractive index work and no further purification was attempted. The vapour was passed into the absorption tube through a system similar to that used in the case of sulphur dioxide (Part II); a side tube with ground glass stopper replaced the sulphuric acid bubbler, and was connected to the main pumping system through a lead-in tap. The tube was then filled in the following manner: the liquid was poured into the side tube, and, with the lead-in tap closed, the main system and absorption tubes were evacuated. The tap was then opened

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* Part I, pp. 66 and 204.

† 'Proc. Roy. Soc.,' A, vol. 130, p. 133 (1930).

‡ 'Proc. Roy. Soc.,' A, vol. 130, p. 142 (1930).

§ 'Nature,' vol. 126, p. 995 (1930).

and the disulphide distilled into the liquid air trap. Air which had passed from the side tube into the absorption tube system was then pumped off, and the liquid air trap warmed up until the required pressure of vapour was obtained. The absorption tubes were 45 cm. long ; for preliminary work a gas pressure of 25 cm. was used throughout, while in the subsequent careful examination of the individual bands, the pressure was adjusted to give a maximum absorption of approximately 50 per cent.

Results.

The relative intensities of the bands may be approximately deduced from fig. 1, curve (*a*) ; the spectrum of the liquid as recorded by Coblentz is given in curve (*b*). The significant data have been summarised in Table I, and Table II gives Krishnamurti's values for the chief lines in the Raman spectrum.*

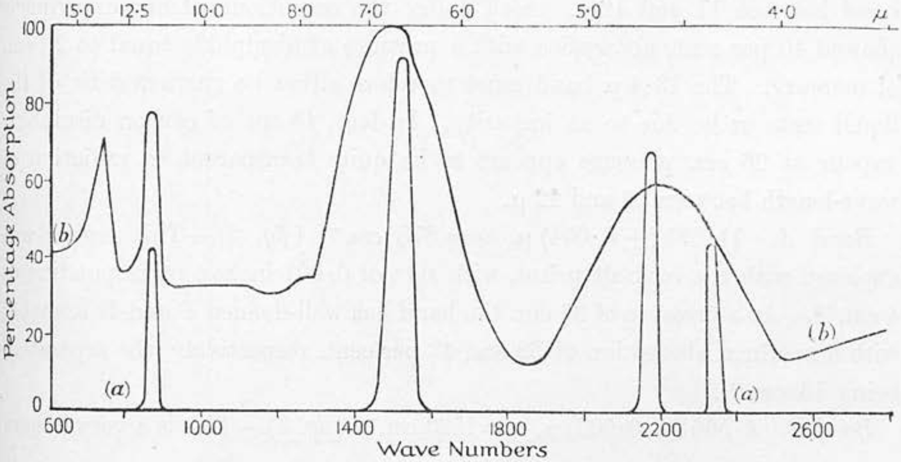

FIG. 1.

Table I.—The Infra-red Absorption Spectrum of Carbon Disulphide.

Band.	Approximate band centre.		λ in μ as given by Coblentz.	Maxima.		P − R $\Delta\nu$ (cm.$^{-1}$).
	λ (μ).	ν_0 (cm.$^{-1}$).		λ.	ν.	
A	11·391	878	11·65	11·301 11·470	885 872	13
B	6·566	1523	6·80	6·536 6·589	1530 1518	12
C	4·591	2179	4·60	4·583 4·603	2182 2173	10–12
D	4·292	2330	—	—	—	—

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* ' Ind. J. Physics.,' vol. 5, p. 109 (1930).

Table II.—The Raman Spectrum of CS_2 (according to Krishnamurti).

Line.	ν (cm.$^{-1}$).	λ (μ).	Intensity.
E	647·1	15·45	Faint, broad.
	655·5	15·26	Strong, sharp.
F	795·0	12·58	Weak.
	>795·0	—	Faint, too diffuse to measure.

The Individual Bands.

The Region 13–14 μ.—The sharp band shown by Coblentz between 13 and 14 μ could not be detected. Fig. 1 (*b*) shows it of intensity comparable with the band between 11 and 12 μ, which under the conditions of our experiment showed 40 per cent. absorption with a pressure of disulphide equal to 26 cm. of mercury. The 13·4 μ band must therefore either be characteristic of the liquid state or be due to an impurity. In fact, 45 cm. of carbon disulphide vapour at 26 cm. pressure appears to be quite transparent to radiation of wave-length between 12 and 22 μ.

Band A. 11·391 ($\pm$ 0·004) μ, $\nu = 878$ *cm.*$^{-1}$ (*fig.* 2).—This region was explored with the rocksalt prism, with slits of 0·001 inches, corresponding to 4 cm.$^{-1}$. At a pressure of 26 cm. the band has well-defined P and R branches with a maximal absorption of 39 and 43 per cent. respectively, the separation being 13 cm.$^{-1}$.

Band B. 6·566 ($\pm$ 0·003) μ, $\nu = 1523$ *cm.*$^{-1}$ (*fig.* 3).—This is a very intense

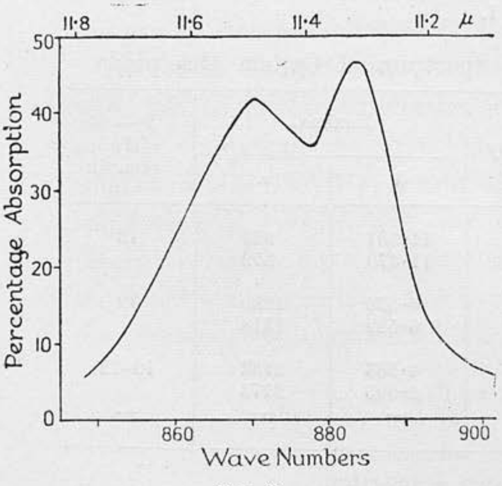

Fig. 2.

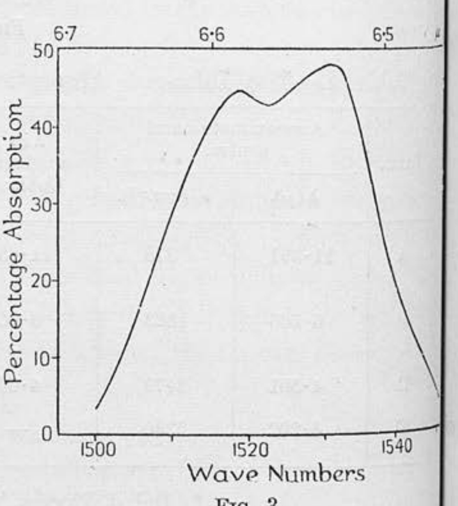

Fig. 3.

band, showing more than 90 per cent. absorption at 25 cm. pressure, and has proved somewhat difficult to investigate. The shape of the band could not at first be determined with any consistency; this might have been due to such a cause as the existence of a slight air leak into the absorption tube with a consequent increase in the intensity of absorption and a resulting deformation of the band shape. Repeated measurements with slit widths corresponding to 6 cm.$^{-1}$ indicated with a fair degree of certainty that this band consists of P and R branches separated by approximately 12 cm.$^{-1}$. Another cause of the fluctuations observed might have been the possible photo-dissociation of the vapour by the short wave radiation from the Nernst filament; it was as a consequence of this suggestion that the monochromator method described in the following paper was developed. The shape of the band was certainly more easily determined and the above measurements were confirmed.

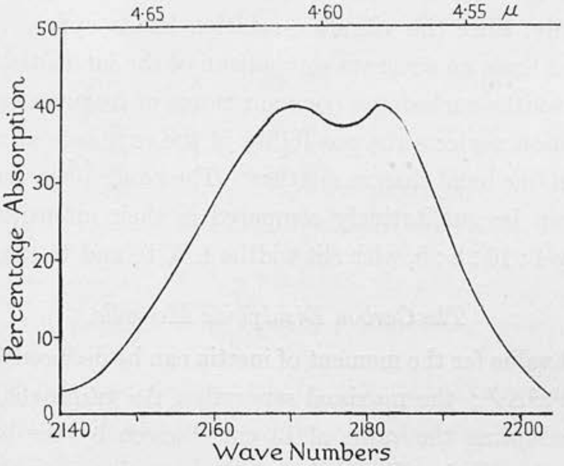

Fig. 4.

Band C. $4 \cdot 591 \ (\pm 0 \cdot 003) \ \mu$, $\nu = 2179$ *cm.*$^{-1}$ (*fig.* 4).—We have located two bands, C and D, in the place of the one shown by Coblentz near $4 \cdot 7 \ \mu$. C was investigated with the fluorite prism with slit widths of 0·005 and again 0·003 inches, corresponding to 10 and 6 cm.$^{-1}$ respectively. Resolution into P and R branches was just possible with the smaller slit width; the separation was of the order of 10 to 12 cm.$^{-1}$, but cannot be more accurately determined. The band gave an approximate maximal absorption of 90 per cent. at 25 cm. pressure.

Band D. $4 \cdot 292 \ (\pm 0 \cdot 003) \ \mu$, $\nu = 2330$ *cm.*$^{-1}$—We were unable to resolve this band even with slit width of 0·003 inches or 10 cm.$^{-1}$ It is considerably less intense than C; the maximal absorption at 25 cm. is some 45 per cent.

Region near 3 μ.—Coblentz shows a broad band of low intensity extending from 2·5 to 4 μ. It could not be detected in the mass of vapour used, but the maximum near 3·2 μ suggests that this is very likely the first harmonic of the intense band at 6·566 μ.

Relative Intensities of the Bands.

An exact quantitative comparison of the relative intensities is not easy. At 25 cm. pressure, the mean maximum absorption of 45 cm. of the vapour for bands A, B, C and D was 40, 95, 90 and 45 per cent. respectively. These values do not give a quantitative representation of the relative intensities for the following reasons: firstly, a percentage absorption of 95 is inaccurately determined because of the very small galvanometer deflections obtained with the full cell in position; secondly, as the gas pressure tends to zero, band B persists with a much greater intensity than the values given above would indicate; thirdly, since the vibration-rotation bands appear as the envelope of the rotational lines, an accurate comparison of the intensities would demand the use of slit widths enclosing a constant range of frequencies; finally, even the last precaution neglects the possibility of the existence of a more complex line structure in one band than in another. The bands observed in the present investigation can be qualitatively compared in their intensities for the ratio A : B : C : D by 4 : 10 : 8 : 5, with slit widths 4, 6, 10 and 14 cm.^{-1} respectively.

The Carbon Disulphide Molecule.

The classical value for the moment of inertia can be deduced from the expression $I_0 = kT/c^2\pi^2\Delta\nu^2$; the maximal separation $\Delta\nu$ varies slightly from band to band, but adopting the value of 13 cm.^{-1} given by the band at 11·39 μ which has the most distinct P and R branch separation, we obtain $I_0 = 264 \times 10^{-40}$ g. cm.^{2}. Recent refinements in technique have substantiated the fact that the temperature coefficient of the dielectric constant is zero.* There is no permanent electric moment, and carbon disulphide must be taken as a rectilinear molecule. The internuclear distance is then determined directly from I_0 as $1 \cdot 60 \times 10^{-8}$ cm. Wierl† has recently obtained the same value $1 \cdot 60 \times 10^{-8}$ cm. for this separation by the method of electron diffraction. Rankine‡ pointed out that following on the sharing of electrons in an attempt to reach the inactive gas configuration, the atoms in the rectilinear molecules

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* Zahn and Miles, 'Phys. Rev.,' vol. 32, p. 497 (1928); Zahn, *ibid.*, vol. 35, p. 848 (1930); Schwingel and Williams, *ibid.*, p. 885.

† 'Physik. Z.,' vol. 31, p. 1028 (1930).

‡ 'Phil. Mag.,' vol. 44, p. 292 (1922).

CO_2 and CS_2 can be represented by the juxtaposition of the corresponding inactive gas atoms. The radii of the neon and argon outer shells are 0·65 and 1·03 Å. respectively; CS_2 has an argon-neon-argon structure and the distance S–S on this scheme should be $2 \times 1{\cdot}03 + 2 \times 0{\cdot}65 = 3{\cdot}36$ Å. The correspondence is much closer than in the case of CO_2 and N_2O; it is interesting to contrast the values for the atomic separations in the rectilinear triatomic molecules and the corresponding diatomic substances as determined by different methods; they are given in Table III.

Table III.

Molecule.	Internuclear separation, r, in Å., as determined by—			
	Inactive gas structure.	Electron diffraction.	Vibration spectrum.	X-ray analysis.
OCO	2·60	2·26 (W)	1·95 (B)	2·10 (K)
CO	1·30	—	1·15 (S)	—
NON	2·60	2·38 (W)	2·04 (S)	2·30 (K)
NO	1·30	—	1·15 (S)	—
SCS	3·36	3·20 (W)	3·20	—
CS	1·68	—	(1·46)	—

W = Wierl (*loc. cit.*).
B = Barker, 'Astrophys. J.,' vol. 55, p. 391 (1922).
S = Snow, 'Proc. Roy. Soc.,' A, vol. 128, p. 294 (1930).
K = Keeson and de Smedt, 'Proc. K. Akad. Wet. Amsterdam, 'vo l.217, p. 839 (1924).

The value of the internuclear separation in the case of CS has been calculated from the binding forces in CS_2 and CS; the assumption is made that these are very similar (see below) and that they vary inversely as the square of the atomic distances.

The Raman Spectrum.

Before attempting to assign the observed bands to the fundamenta frequencies of the molecule and their combinations, it is necessary to consider the Raman spectrum in more detail. The following observers all agree in characterising this spectrum by the presence of two lines, one strong at 655 cm.$^{-1}$, and the other weak at 800 cm.$^{-1}$ approximately: Petrikaln and Hochberg (1); Gavesan and Venkateswaran (2); Schaefer, Matossi and Aderhold (3); Bhagavantam (4); Krishnamurti (5).* Krishnamurti's results

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* (1) 'Z. Physik. Chem.,' B, vol. 3, p. 217 (1929); (2) 'Nature,' vol. 124, p. 57 (1929); (3) 'Physik. Z.,' vol. 30, p. 581 (1929); (4) 'Nature,' vol. 126, p. 995 (1930); (5) *loc. cit.*

indicate a complete analogy between the spectra of CO_2 and CS_2 in that in each case we have one weak and one strong line, each with an external weak companion. The origin of the doublet structure of these spectra has provoked considerable speculation; they have been shown to be associated with the excitation of the symmetrical mode of vibration of the rectilinear molecule which is optically inactive, but capable of combining with the other modes of vibration to give bands in the infra-red, where the doublet structure was first observed. The explanations offered may be very briefly summarised: (i) Barker* suggested that one of the doublets corresponded to the vibrational transition $(0 \rightarrow 1)$, and the other to $(1 \rightarrow 2)$ for the same fundamental; he was not inclined to lay much stress on this supposition as it would have demanded the presence of the overtone $(0 \rightarrow 2)$, and this was certainly absent in the CO_2 spectrum when the strong band at $2 \cdot 7\ \mu$ was regarded as a fundamental; furthermore the approximately equal intensities of the components of that doublet implied an equal number of molecules in the first and zero states of vibration at ordinary temperatures; (ii) Dennison,† and Schaefer and Philipps,‡ on the assumption of a triangular model behaving approximately as a symmetrical top, ascribed the double doublets in the infra-red to the splitting of the fundamental frequency giving a rotational-vibrational band with a small effective moment of inertia; only two doublets are observed, however, in the place of the series one would expect, and Dennison§ later pointed out that half-quantum numbers would anyhow demand the presence of four at least; amplified discussions of these and similar points are given by Colby‖ and by Snow.¶

From the fact that the doublet structure is entirely lacking in nitrous oxide,** we have probably to associate its appearance with some peculiarity of the carbon compound. The Q branch (normally missing in the infra-red spectrum of rectilinear, triatomic even molecules) appears most strongly and as a single line in the Raman spectrum, and there is no reason to assume that such is not the case in the present instance; consequently one is forced to attribute the doublet structure to the excitation of two types of vibration associated with slightly different amounts of energy and corresponding to two types of binding.

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* 'Astrophys. J.,' vol. 55, p. 391 (1922).

† 'Phil. Mag.,' vol. 1, p. 195 (1926).

‡ 'Z. Physik,' vol. 36, p. 641 (1926).

§ 'Z. Physik,' vol. 38, p. 137 (1926).

‖ 'Bull. Nat. Res. Council,' No. 57, p. 65 (1926).

¶ 'Phil. Mag.,' vol. 8, p. 369 (1929); and 'Proc. Roy. Soc.,' A, vol. 128, p. 310 (1930).

** Dickinson, Dillon and Rasetti, 'Phys. Rev.,' vol. 34, p. 582 (1929).

Further evidence in support of this hypothesis is adduced below from a consideration of the binding forces in the molecule.

The most reasonable method of allocating the observed bands to the various modes of vibration is as follows: ν_3 is the most powerful infra-red band at 6·566 μ or 1523 cm.$^{-1}$; ν_2 is then the inactive frequency of two types, ν_2' and ν_2'', at 655 and 795 cm.$^{-1}$; there seems to be no justification for taking the mean value of these two frequencies (as has been done by some workers) as the band centre, since we should expect a null line here as generally in the Raman spectrum; ν_1 cannot be located directly as it lies outside the region covered by our spectrometer, and there is little evidence available from other sources. The absorption spectrum of the vapour in the ultra-violet has been observed by Wilson* and by Jenkins,† constant frequency differences of some 270 cm.$^{-1}$ were found to exist, and it is possible that ν_1 is of this order. An examination of our results shows that B and A can be represented as $\nu_1 + \nu_2'$, with $\nu_1 = 223$ cm.$^{-1}$; the frequency difference cited above by Jenkins varies in a more or less continuous fashion from 283 to 255 cm.$^{-1}$ in what seems to be a fairly rapidly diminishing series, and we may take it that we have here ν_1 in an electronically excited condition with a marked constant of anharmonicity.

The observed results can now be formulated as in Table IV; the measured intensities are in agreement with this assignment: the one discrepancy is that there is no band corresponding to $\nu_1 + \nu_2''$, *i.e.*, $795 + 223 = 1018$ cm.$^{-1}$. We should expect that this band would be weak, however, and hope to find traces of it when we eventually re-examine the gas in much longer columns.

Table IV.—The Fundamental Frequencies of CS_2 and their Combinations.

Band.	Formulation.	Calculated.	Found.
(G)	ν_1	223	—
E	ν_2'	—	655
F	ν_2''	—	795
A	$\nu_1 + \nu_2'$	878	878
(A′)	$\nu_1 + \nu_2''$	1018	—
B	ν_3	—	1523
C	$\nu_3 + \nu_2'$	2178	2179
D	$\nu_3 + \nu_2''$	2328	2330

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* 'Astrophys. J.,' vol. 69, p. 34 (1929).

† 'Astrophys. J.,' vol. 70, p. 191 (1929).

The alternative formulation suggested by us in our letter to ' Nature,'* in which the difference of approximately 150 cm.$^{-1}$ between the two Raman lines was proposed as a fundamental, was arrived at before the publication of Krishnamurti's work; the observed intensities are consistent throughout in Table IV, whereas band A on our original formulation had to be represented as a difference tone. Final confirmation depends upon two observations which we hope to attempt—first, to construct a wire grating which will enable us to explore the region in the neighbourhood of 200 cm.$^{-1}$, and secondly, as above-mentioned, to examine the spectrum of larger masses of gas in a search for other combination tones. It is surprising that with ν_1 approximately equal to kT, neither difference tones nor two-parameter bands of the type $(1 \rightarrow 2)$ are observed.

The fundamental modes of vibration of the symmetrical rectilinear molecule SCS may be summarised as below :—

$\mathrm{S}\ \overset{\uparrow}{\mathrm{C}}\ \mathrm{S}$	ν_1	$a_1 + b_1 = 223$ cm.$^{-1}$
$\overset{\rightarrow}{\mathrm{S}}\ \mathrm{C}\ \overset{\leftarrow}{\mathrm{S}}$	$\left\{\begin{matrix}\nu_2' \\ \nu_2''\end{matrix}\right\}$ (optically inactive)	$\left\{\begin{matrix}a_2' + b_2' = 655 \text{ cm.}^{-1} \\ a_2'' + b_2'' = 795 \text{ cm.}^{-1}\end{matrix}\right.$
$\overset{\rightarrow}{\mathrm{S}}\ \overset{\leftarrow}{\mathrm{C}}\ \overset{\rightarrow}{\mathrm{S}}$	ν_3	$a_3 + b_3 = 1523$ cm.$^{-1}$

We have not sufficient data to enable us to determine the values of the anharmonic constants, b_1, but the closeness of the calculated values for bands C and D to those observed makes it appear that they are very small.

The Rotational Fine Structure.

The moment of inertia I_0 is 264×10^{-40} g. cm.^{2}; the rotational line separation within a vibrational-rotational band is then given by $\delta\nu = h/4\pi^2 I_0 . c$, and is of the order of $0 \cdot 2$ cm.$^{-1}$; the molecule, however, is symmetrical and rectilinear, and the fine structure should exhibit alternating intensities corresponding to the symmetrical and antisymmetrical proper functions. One set should have an almost vanishing probability, and the apparent effective separation should be $0 \cdot 40$ cm.$^{-1}$; even with this advantage there is little hope of attaining the required degree of resolution with a grating. In this connection, it is interesting to note that it is possible to obtain confirmation of the rectilinear structure of carbon dioxide from Barker's results (*loc. cit.*) where the double

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* Vol. 126, p. 350 (1930).

doublet at 2·7 μ is reproduced from the original drawing on squared paper. The short wave component shows, of course, incomplete resolution, but nevertheless between 2·673 and 2·691 μ in the R branch, there are approximately 12 maxima with an average separation of 2·4 cm.$^{-1}$, and between 2·692 and 2·714 μ in the P branch again 12 with average separation 2·2 cm.$^{-1}$. The best value for I_0 from the maximal separation in the fundamental Bjerrum doublet at 4·25 μ is 50×10^{-40} g. cm.^{2}; the rotational separation corresponding to this is 1·1 cm.$^{-1}$, which is half that observed. It would certainly seem worth Professor Barker's while to re-examine this band.

The Force Constants.

Expressions relating the fundamental modes of vibration with the angle between the bonds and certain force constants have been devised for the triatomic molecule XY_2 by Bjerrum,[*] Dennison,[†] and recently by Yates[‡] and Radakovic.[§] The assumptions made by Bjerrum and by Dennison as to the nature of the forces and their direction in the molecule (central fields about each atom) are inapplicable when the triangle degenerates into a straight line; Dennison obtains the cubic

$$\frac{m\lambda}{K_1} - 1 - \frac{2m}{M}\sin^2\alpha\Big)\Big[\Big(\frac{m\lambda}{K_1}\Big)^2 - 2\Big(\beta + \tfrac{1}{2} + \frac{m}{M}\cos^2\alpha\Big)\frac{m\lambda}{K_1} + \frac{2\beta}{\mu}\cos^2\alpha\Big] = 0 \qquad (1)$$

for the symmetrical triangular molecule in which K_1 and K_2 are the force constants in the general potential function of the molecule, $\beta = K_2/K_1$, $\nu_i = (1/2\pi)\sqrt{\lambda_i}$, α is the semi-angle between the bonds, m the mass of the external atoms and M of the central atom, μ the reduced mass $M/(2M + m)$.[‖]

Bjerrum's calculations lead to the same frequency functions; it will readily be seen that for $\alpha = \pi/2$, the frequency corresponding to the motion of the central atom perpendicular to the line of the molecule becomes infinite.

Yates, on the other hand, assumes that the force tending to restore a particle after displacement is the sum of two types, the first acting along the line XY

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[*] 'Verh. Deuts. Physik. Ges.,' vol. 16, p. 737 (1914).

[†] 'Phil. Mag.,' vol. 1, p. 195 (1926).

[‡] 'Phys. Rev.,' vol. 36, p. 555 (1930).

[§] 'Monatsh,' vol. 56, p. 447 (1930).

[‖] For a discussion of the derivation of this expression and of the constants with their significance see Dennison (*loc. cit.*) and Snow, 'Proc. Roy. Soc.,' A, vol. 125, p. 471 (1929).

and obeying Hooke's law, the second an angular restoring force acting about X and proportional to the arc displacement of the Y's. His expression is :—

$$\left.\begin{aligned} \alpha^2 + \mathrm{K}_1\,[1/m + 2\,(\cos^2\theta)/\mathrm{M}] = 0 \\ \alpha^4 + [(\mathrm{K}_1 + 2\mathrm{K}_2)/m + 2\,(\mathrm{K}_1\sin^2\theta + 2\mathrm{K}_2\cos^2\theta)/\mathrm{M}]\,\alpha^2 \\ + 2\mathrm{K}_1\mathrm{K}_2\,(2/\mathrm{M} + 1/m)/m = 0 \end{aligned}\right\} \quad (2)$$

where $\alpha_i^2 = -p_i^2$, and $\nu_i = \frac{1}{2\pi}\cdot p_i$; θ is in this case the angle between the bonds. The expression can be transformed into one very similar to Dennison's by replacing α^2 by $-\lambda$ and multiplying throughout by m/K_1.

We will now apply (2) to the case where $\theta = \pi$, *i.e.*, the rectilinear molecule. We have

$$\left.\begin{aligned} \alpha^2 + \mathrm{K}_1\,(1/m + 2/\mathrm{M}) = 0 \\ \alpha^4 + [\mathrm{K}_1/m + 2\mathrm{K}_2\,(1/m + 2/\mathrm{M})]\,\alpha^2 + (k_1/m)\,2\mathrm{K}_2\,(1/m + 2/\mathrm{M}) = 0. \end{aligned}\right\} \quad (3)$$

The expression factorises and we have, substituting $-p_i^2$ for α_i^2 :—

$$p_1^2 = 2\mathrm{K}_2\,(1/m + 2/\mathrm{M}), \text{ and } \nu_1 = \frac{1}{2\pi}\sqrt{2\mathrm{K}_2\left(\frac{\mathrm{M}+2m}{\mathrm{M}m}\right)}, \textit{ i.e.}, \mathrm{S}\overset{\uparrow}{\mathrm{C}}\mathrm{S};$$

$$p_2^2 = \mathrm{K}_1/m \qquad, \text{ and } \nu_2 = \frac{1}{2\pi}\sqrt{\mathrm{K}_1/m} \qquad, \textit{ i.e.}, \overset{\rightarrow}{\mathrm{S}}\mathrm{C}\overset{\leftarrow}{\mathrm{S}};$$

$$p_3^2 = \mathrm{K}_1\,(1/m + 2/\mathrm{M}), \text{ and } \nu_3 = \frac{1}{2\pi}\sqrt{\mathrm{K}_1\left(\frac{\mathrm{M}+2m}{\mathrm{M}m}\right)}\ , \textit{ i.e.}, \overset{\rightarrow}{\mathrm{S}}\overset{\leftarrow}{\mathrm{C}}\overset{\rightarrow}{\mathrm{S}}.$$

We have calculated the K values for a number of triatomic molecules and compared them with the corresponding diatomic molecule where

$$\nu = \frac{1}{2\pi}\sqrt{\mathrm{K}\left(\frac{1}{m} + \frac{1}{\mathrm{M}}\right)}.$$

The results are embodied in Table V; with ν in frequency units and the mass of the hydrogen atom as $1\cdot65 \times 10^{-24}$ gm., K is in dynes per centimetre. We have tested the supposition of the two types of vibration in the molecules CO_2 and CS_2 by determining K_1 for each line in the Raman doublet with interesting consequences.

Table V.

Diatomics.

Molecule.	$CS^{(1)}$.	$S_2{}^{(2)}$.	C—C(3) diamond.	$SO^{(4)}$.	$O_2{}^{(5)}$.	$NO^{(6)}$.	$CO^{(7)}$.	$N_2{}^{(5)}$.
ν ($cm.^{-1}$)	1276	800	1333	1117	1552	1892	2155	2320
$\kappa \times 10^{-5}$ dynes/cm.	8·4	6·0	6·3	7·8	11·3	15·7	18·8	22·2

Triatomics (*a*) Rectilinear Molecules.

Molecule.	$\vec{X}\ \overset{\leftarrow}{Y}\ \vec{X}$.	K_1.	$\vec{X}\ \overset{\leftarrow}{Y}\ X$.	K_1.	$X\ \overset{\uparrow}{Y}\ X$,	K_2.
CS_2	1526	6·9	795 655	12·1 8·0	223	0·07
$CO_2{}^{(8)}$	2353	14·2	1388 1285	18·1 15·5	680	0·60
$N_2O^{(9)}$	2244	14·4	1317	14·2	450	0·30

Triatomics (*b*) Triangular Molecules.

Molecule.	ν.	K_1.
$SO_2{}^{(10)}$	1340	14·3
$NO_2{}^{(11)}$	1634	7·6

ν throughout is in $cm.^{-1}$, and K in dynes per cm. $\times 10^{-5}$. The force constant for the triangular molecules has been calculated from Dennison's formula.

(1) Jevons, 'Proc. Roy. Soc.,' A, vol. 117, p. 351 (1928).
(2) Henri and Teres, 'C. R.,' vol. 179, p. 1156 (1927).
(3) Robertson and Fox, 'Nature,' vol. 125, p. 704 (1930).
(4) Henri and Wolff, 'J. Physique,' vol. 10, p. 81 (1929).
(5) McLennan and McLeod, 'Nature,' vol. 123, p. 160 (1929).
(6) Snow and Rideal, 'Proc. Roy. Soc.,' A, vol. 126, p. 365 (1930).
(7) Snow and Rideal, 'Proc. Roy. Soc.,' A, vol. 125, p. 462 (1929).
(8) Dickinson, Dillon and Rasetti, 'Phys. Rev.,' vol. 34, p. 582 (1929).
(9) Snow, 'Proc. Roy. Soc.,' A, vol. 128, p. 294 (1930).
(10) Bailey, Cassie and Angus, *ibid.*, vol. 130, p. 142 (1930).
(11) Warburg and Leithaüser, 'Annalen,' vol. 28, p. 313 (1909).

It will be seen that the force constants group themselves according to the type of binding, the values for single, double and triple bonds being respectively 7, 14 and 21 × 10^5 dynes per centimetre. The full power of the triple bond is well seen in the case of the nitrogen molecule which has long been represented by G. N. Lewis* as $:\mathrm{N}:::\mathrm{N}:$. The case of carbon monoxide is of extreme interest: it is isosteric with nitrogen and their external physical properties are almost identical. The two molecules are built up differently, however: the nitrogen atoms each provide three electrons which are shared between them; the electronic formula of carbon monoxide is best represented by $:\mathrm{C}\overset{\circ}{:}\,\overset{\cdot}{:}\mathrm{0}:$ where the distinguished electron is transferred from the oxygen, the carbon being in effect still divalent and the molecule giving on dissociation two ^{3}P atoms of carbon and oxygen†; the transference of the electron is confirmed by the corresponding considerable decrease in the expected electric moment.‡ The force constant for this type of binding seems to be intermediate between the double and triple bond; a somewhat similar effect is found for the oxygen molecule, the ground state of which is $^3\Sigma$: since the normal state of the oxygen atom is also a triplet (^{3}P) with two uncoupled electron spins, the deduction is made that only one electron for each atom is paired and there is a one-valency binding:§ the force constant is certainly ower than that expected for the normal divalent bond.

The peculiar nature of the bond in carbon monoxide is reflected in the parachor; the force constants for the bindings $\mathrm{C}::\mathrm{O}$, $\mathrm{C}\overset{\circ}{\cdot}::\mathrm{O}$, and $\mathrm{C}:::\mathrm{0}$ are experimentally determined as 14·2 : 18·8 : 22; the calculated parachors for $\mathrm{C}::\mathrm{O}$ and $\mathrm{C}:::\mathrm{O}$ are 48 and 71·4, while that observed for carbon monoxide is 61·6,‖ the ratio being 14·2 : 18·4 : 21·2.

The oxides of nitrogen offer interesting contrasts: nitric oxide has a very slightly firmer binding than nitrous oxide; the former is $\cdot\ddot{\mathrm{N}}::\underset{\cdot\cdot}{\ddot{\mathrm{O}}}$, while the symmetrical nature of the latter is once again shown by the identity of values for K_1, the binding being divalent in each case, and the structure probably given by $\cdot\underset{\cdot\cdot}{\mathrm{N}}::\underset{\cdot\cdot}{\mathrm{O}}::\underset{\cdot\cdot}{\mathrm{N}}\cdot$. Nitrogen dioxide has one single and one double bond as already deduced by Mecke¶ from thermochemical considerations.

Similar observations have been made for characteristic groups in organic substances by Dadieu and Kohlrausch,** and by Andrews.†† Yates‡‡

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* 'Valence,' p. 127 (1923).

† Johnson, 'Trans. Faraday Soc.,' vol. 25, p. 649 (1929).

‡ Sidgwick and others, 'J. Chem. Soc.,' p. 1882 (1930).

§ Garner and Lennard-Jones, 'Trans. Faraday Soc.,' vol. 25 (1928).

‖ Sugden, 'The Parachor and Valency,' p. 170 (1930).

¶ 'Z. Physik. Chem.,' B, vol. 7, p. 114 (1930).

** 'Monatsh.,' vol. 55, p. 201 (1930).

†† 'Phys. Rev.,' vol. 36, p. 544 (1930).

‡‡ *Loc. cit.*

attempted to apply his derived equations to a number of substances, but the use of incorrect values for the fundamental frequencies vitiates the deductions.

The results and implications for carbon dioxide and disulphide will now be briefly considered. The two types of optically inactive vibrations are confirmed by the values for the force constants: ν_3 corresponds to a vibration in which there is a divalent linking between carbon and oxygen, to take the first substance, and the carbon is essentially tetravalent, whereas the two frequencies associated with ν_2 give us two force constants, the one being of exactly the same type as in carbon monoxide, and the other that for a double bond. The heats of dissociation for similar bonds in allied substances can be taken as approximately proportional to the binding forces; the heat of formation of CO_2 from gaseous and atomic carbon and oxygen is given by $(C) + 2(O) =$ 364 k. cal., and we can take half this value as representing a $C = O$ bond in CO_2, *i.e.*, 182 k. cal.: the heat of formation of carbon monoxide under similar conditions is 237 k. cal., and we calculate for $C = O$, $237 \times 14{\cdot}2/18{\cdot}8 = 179$ k. cal., in very close agreement.

Carbon disulphide differs from the dioxide in that it certainly seems to possess single linkings, the carbon atom being apparently divalent. The force constants for ν_2 are again of two types, one of which corresponds to carbon monosulphide with its monovalent linking, the other, as in CO_2, to a value intermediate between that and the next higher or divalent bond. The weakness of the binding is confirmed by the smallness of K_2, which is $0{\cdot}07 \times 10^5$ dynes per centimetre. Further contributory evidence is obtained from the examination made by Lindh of the K_1 absorption limits in the X-ray spectrum of sulphur-containing compounds; the work has been summarised by Siegbahn.* The mean values in X.U. for organic substances show constitutive influences due to the various possible sulphur valencies: the averages of a number of remarkably concordant results give the following characteristic wave-lengths in X.U.:—S_{II}, 5006·8; S_{IV}, 5001·9; S_{VI}, 4993·9. Hydrogen sulphide gives value of 5007·1 agreeing with the accepted formula H—S—H, but the interesting discovery is that carbon disulphide shows the anomalously long wave-length of 5011·4 X.U.: hence the single linkage can be taken as established.

Additional support is offered by thermochemical data: accepting once more the near proportionality of the heats of dissociation of the bonds and the force constants for closely allied substances, we can determine the heat

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* "The Spectroscopy of X-rays," p. 146 (1925).

of formation of carbon monosulphide in the gaseous state; the significant data for the gaseous molecules SO and S_2 can be derived from the predissociation spectra (for references see Table V), while the heat of formation of CS_2 from gaseous monatomic carbon and sulphur is 264 k. cals. The calculations and results are indicated in Table VI.

Table VI.

Molecule.	$K \times 10^{-5}$ dynes/cm.	Heat of linkage in k. cals.	Heat of linkage calculated for CS.
CS	$8 \cdot 36$	—	—
SO	$7 \cdot 8$	148	$148 \times 8 \cdot 4/7 \cdot 8 = 160$
S_2	$6 \cdot 0$	113	$113 \times 8 \cdot 4/6 \cdot 0 = 159$
CS_2	$6 \cdot 9$	$\frac{1}{2}CS_2 = 132$	$132 \times 8 \cdot 4/6 \cdot 9 = 161$

The agreement is remarkable; there is no direct determination of the heat of formation of gaseous CS: the application of the constant of anharmonicity to the evaluation of that quantity involves in effect a long extrapolation to a convergence limit in the band spectrum with the consequent uncertainty in the result. If we apply the method to Jevons' results (*loc. cit.*) we obtain 193 k. cal., a value of the right order and sufficient to justify the primary assumption made in developing the above table.

Finally in this connection we will mention the work of Donle and Volkert* on the dipole moment and ultra-violet absorption of ketones and thioketones; they have shown that the CS group in these substances has quite a different structure from that of the CO group, that in fact the former is analogous to carbon disulphide, but the latter is more like gaseous CO.

Carbon disulphide may have to be written $:\ddot{\underset{..}{S}}:C:\ddot{\underset{..}{S}}:$, though there are difficulties in accepting this; the dioxide is normal, $\ddot{\underset{..}{O}}::C::\ddot{\underset{..}{O}}$. The doublet structure in the inactive fundamental in each case is probably to be associated with some ready power of re-arrangement in the detailed electronic structure of the molecule, and due primarily to the variable valency of the carbon atom. Further study of this point may provide information upon the actual method of dissociation of the dioxide, and also upon the combustion of the monoxide.

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* 'Z. Physik. Chem.,' B, vol. 8, p. 60 (1930).

Summary.

(1) The infra-red absorption spectrum of carbon disulphide vapour has been examined between the limits of 1 and 22 μ. Four bands have been located and resolution into P and R branches has been achieved in three cases.

(2) The infra-red has been co-ordinated with the Raman spectrum, and the fundamental frequencies of the molecule have been deduced.

(3) The molecule has been shown to be rectilinear and the moment of inertia has been evaluated.

(4) The force constants characteristic of the linkages in this and similar molecules have been calculated, and deductions as to the nature of the binding have been made.

(5) A suggestion is offered for the explanation of the characteristic doublet in the Raman spectrum of carbon disulphide and dioxide.

Much of the apparatus used in the present series of investigations was purchased through grants made to the Chemistry Department of University College, London, by Imperial Chemical Industries, Ltd., to whom the authors extend their grateful acknowledgments.

Investigations in the Infra-Red Region of the Spectrum. Part IV.—*The Monochromator Method in the Infra-Red.*

By A. B. D. Cassie and C. R. Bailey, University College, London.

(Communicated by F. G. Donnan, F.R.S.—Received March 13, 1931.)

Absorption spectra in the infra-red are usually obtained by passing radiation from a Nernst filament through an absorption tube, and converging it to form an image of the filament at the collimator slit of the spectrometer. The radiation traverses the resolving train, and an image of the collimator slit is focused on the thermopile slit; a direct record of the energy curve of the Nernst filament is then made by means of a thermopile connected to a high sensitivity galvanometer, or an equivalent device. A shutter is inserted between the filament and collimator slit, and the percentage absorption at any wave-length is most conveniently determined by noting the galvanometer deflection on opening the shutter when (*a*) an empty, and (*b*) a full absorption tube lies in the path of the radiation. This necessitates the use of a device such as a rocker to exchange the full for the empty tube at each spectrometer setting.

The most important factor in the design of this rocker is that the empty and full tubes should occupy accurately the same position when either is in the path of the beam. If this condition is not satisfied, the image of the filament on the collimator slit may be displaced, and different longitudinal sections of the image will be presented at each interchange; the intensity of radiation traversing any longitudinal section of this image varies rapidly from the centre to the edge, and the displacement will give a difference in galvanometer deflections for the empty and full tubes even when no absorption occurs. In certain work which we propose to carry out later we shall require long absorption tubes of stainless steel, and a rocker of inconveniently heavy construction would be necessary. There is a further disadvantage of the rocker method in its use with gases; leads from a pumping system must either be flexible or be disconnected after each change in pressure. High purity of absorbing gas is desirable and rubber joins are to be avoided, hence glass to glass position seals must be made after each adjustment of pressure, or a large glass spiral of sufficient flexibility must be permanently incorporated in the system. The first method is almost impracticable; the second gives erroneous results in the determination of the very small gas pressures necessary when the fundamental bands of certain substances are under examination; it is of considerable importance to know this gas pressure accurately, and in some cases these bands are so intense that pressures of less than 1 mm. are required to give a maximal absorption of 50 per cent. under the conditions of the experiment.

There is an alternative method by which the radiation may be caused to traverse the full or empty tube at will. Instead of interchanging the position of the tubes we can swing the beam so that it passes through first one and then the other. The latter arrangement is possible if we interpose two plane mirrors rotating about vertical axes, one between the filament and the tubes, and the second between the tubes and collimator slit, when, by a suitable addition of concave mirrors to the system, the light train is in effect duplicated. Great care would have to be taken in the setting of the plane mirrors, as any slight error in this, particularly with the first mirror, would entail the above-mentioned displacement of the filament image on the slit. This difficulty can be avoided in the following way: the thermopile or telescope slit is usually narrow compared with the width of the thermopile junctions; if we use the spectrometer as a monochromator and contrive a similar system of mirrors to give an image of the telescope slit of unit or less magnitude on the thermopile junctions, a small error in the setting of the mirrors will give no error in the galvanometer reading. This conclusion was tested and found to be true.

There is, however, an additional and cogent reason for the use of a monochromated beam as opposed to the full source. At the normal working temperature of the filament (some 2600° abs.), the energy distribution is approximately that of a black body, and although the isothermal maximum is in the neighbourhood of $1 \cdot 5\ \mu$, there is a considerable proportion of energy emitted in the visible and short wave regions. Some of the substances we propose to investigate are known to undergo photochemical decomposition with great ease, in particular, carbonyl sulphide and the oxides of chlorine; for these substances the original method is impracticable, if not dangerous.

Experimental Details.

The final state of the apparatus is shown in plan in fig. 1. The light path in air is made as short as possible by introducing a plane mirror M_1 which gives a virtual image of the filament N and its backing mirror M somewhere within the spectrometer case. This arrangement also makes the component mirrors readily accessible, while the mercury arc H required for setting the Wadsworth mirror can be very conveniently housed behind M_2. The glass condensing lens C is left in position and focuses an image of the arc on S_1, the collimator slit. The only adjustment required for the use of the arc is to remove M_2 from a mounting which holds it in a fixed position ; this avoids

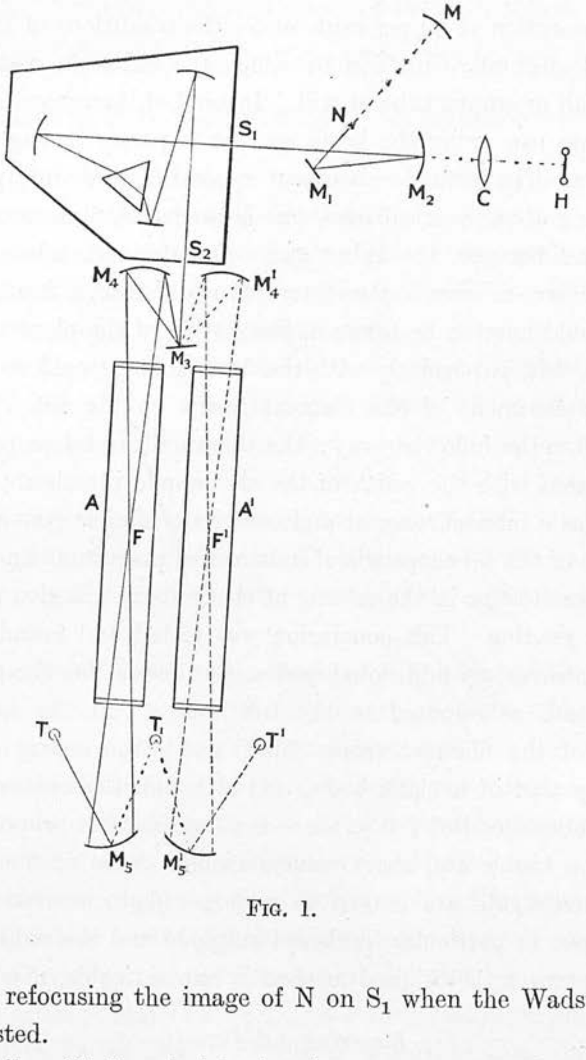

Fig. 1.

any trouble in refocusing the image of N on S_1 when the Wadsworth mirror has been adjusted.

The thermopile with its air-tight housing was removed from the position immediately behind the telescope slit. Approximately 6 inches from this slit is a small plane mirror mounted on a vertical axis with a device for turning it through a fixed angle. This is shown in detail in fig. 2. On the accuracy with which M_3 can be turned through this angle, does the accuracy of the final position of the image of the telescope slit S_2 on the thermopile junctions depend. The vertical axle K carrying M_3 was therefore passed through a ball bearing

B_1 mounted on the frustum of a lead cone described by Robertson and Fox,* and then through an ordinary bearing B_2. The lower end of the axle is conical in shape, the point of the cone resting on a flat piece of steel S, sunk into the lead block. Fixed to the axle is an arm A which comes into electrical contact with either of two stops R, according as the radiation is to occupy the position of the empty or of the full tube. This arrangement was found to give very accurate settings of the image of the telescope slit on the thermopile.

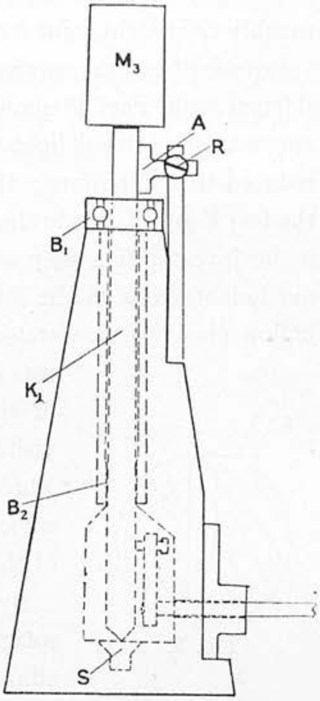

FIG. 2.

The radiation passes from M_3 (fig. 1) to either of the mirrors M_4 and M_4' and is directed accordingly through the empty or full tube. After emerging from the tubes A and A′, the beam falls on either of the mirrors M_5 or M_5' and is thus focused on either of the thermopiles T and T′. One thermopile would actually suffice, and, in fact, would receive an image of S_2 which satisfied Czerny's condition for minimum distortion of the image after two successive reflections at concave mirrors. The thermopiles available, however, had an angular aperture less than $M_5T_1M_5'$, whilst the use of two thermopiles gives easy adjustments. Distortion of the image is not of consequence since even the distorted image lies wholly within the surface area of the hot junctions. The thermopiles are enclosed in air-tight cases and surrounded by jackets of heat-insulating material. They are connected to the galvanometer in series and in opposition to each other; this was found to give less zero drift than when they were connected in the same sense.

Difficulties and Possible Sources of Error.

The first difficulty encountered was that of stray radiation. When M_3 was changed from one position to the other a very large galvanometer deflection was observed, even when the shutter between N and the spectrometer was closed; the effect was shown to be due to stray radiation which was focused

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* 'Proc. Roy. Soc.,' A, vol. 120, p. 132 (1928).

first on one thermopile and then on the other. To eliminate this the mirrors M_4, M_3 and M_4' were enclosed in one opaque housing, and M_5, M_5', T and T' in another. The tubes were painted black and fitted with ends which gave a roughly light-tight joint between them and the housings.

In order that the maximum of resolution indicated by the theoretical considerations in Part I* should be obtained, it is necessary that even the small amount of scattered light remaining after these precautions should be again reduced to a minimum; the further step was taken of inserting two stops at the foci F and F' inside the absorption tubes. To prevent attack by the gases under investigation they were made of glass, and we are glad to acknowledge our indebtedness to Mr. Nelson of this Department for their construction. A hollow glass vessel, watch-shaped, with aperture A (fig. 3), and inlet tube E, was formed of diameter equal to the internal diameter of the tube; through E was poured enamel opaque to visible and short wave infra-red radiation, and the whole dried in an oven; E was then drawn off and smoothed so as not to project beyond the circumference of the stop.

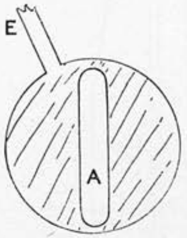

FIG. 3.

By this procedure the galvanometer deflection on rotation of M_3 was greatly diminished but not completely eliminated. The residual disturbance was shown eventually to be due to the fact that the surroundings of the spectrometer and of the thermopiles were at different temperatures on account of the heating lamps used to preserve the rocksalt surfaces. As the radiation path changes from the empty to the full tube we must expect a change in the galvanometer zero with the thermopiles coupled in opposite senses, since the mirror systems focus precisely S_1 (the proper radiation of which corresponds to the temperature of the spectrometer) on the thermopiles. If the latter were coupled in the same sense the zero change would disappear; it can be made very small even under the actual conditions of experiment.

A possible source of error which had to be taken into consideration, and which, if it had existed, would have rendered the method impracticable, was the chance that M_4 compared with M_4' and M_5 with M_5' might exhibit unequal specific reflecting powers. So far, however, we have been unable to detect any selective reflectivity of the mirrors which are silvered surfaces on glass, nor, as far as we know, does there exist any selective difference between the thermopile sensitivities.

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* 'Proc. Roy. Soc.,' A, vol. 130, p. 139 (1930).

Since the foregoing account was written, we have applied the method to the examination of carbonyl sulphide with every success; the substance has a rich and complicated spectrum which shows promise of many difficult but interesting points in its unravelling.

The authors owe their thanks to Professor F. G. Donnan, C.B.E., F.R.S., for his continued interest and encouragement, and to the Department of Scientific and Industrial Research for a senior award to A.B.D.C.

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Investigations in the Infra-Red Region of the Spectrum. Part V.— The Absorption Spectrum of Carbonyl Sulphide.

By C. R. BAILEY and A. B. D. CASSIE.

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Investigations in the Infra-Red Region of the Spectrum. Part V.— The Absorption Spectrum of Carbonyl Sulphide.

By C. R. BAILEY and A. B. D. CASSIE, University College, London.

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The symmetrical linear structure of both carbon dioxide and carbon disulphide is now well established. Recent developments in theory make it highly probable that a complete explanation of the Raman and infra-red spectra of these substances, with the concomitant selection rules, will shortly be available. It is in the meantime of consequence to examine the absorption spectrum of carbonyl sulphide, since the chemical and external physical properties of this molecule are intermediate to those of the other two, though the lack of symmetry in its structure predicts more complex intramolecular relationships. No previous determination of this spectrum appears to have been made.

Experimental.

Carbonyl sulphide was prepared by dropping sulphuric acid (5 parts of acid to 4 of water by volume) on to potassium thiocyanate in a flask maintained at 21° C. by means of a water bath. The chief impurities generated in the reaction are carbon disulphide, carbon dioxide, and carbon monoxide*; the

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* Mellor, "Comprehensive Treatise," vol. 5, p. 972.

gaseous product was led firstly through a trap immersed in a freezing mixture of salt and ice, secondly through a bubbler containing a 33 per cent. solution of potassium hydroxide, thirdly through a tube of active charcoal, fourthly through calcium chloride, and finally, through a trap immersed in a saturated solution of carbon dioxide snow in acetone, to the fume cupboard vent; glass to glass seals were used throughout. The traps and tubes removed in succession the major portion of the carbon disulphide, the carbon dioxide, the remaining carbon disulphide, and the water vapour; carbonyl sulphide boils at −50° C. and was condensed in the last trap at a temperature of −78°, any carbon monoxide passing on unabsorbed. When sufficient of the required substance had been collected, the trap was disconnected from the generating apparatus and connected to the absorption tube system, where the gas was transferred to an evacuated aspirator and stored over phosphoric oxide. The aspirator was totally enclosed to obviate possible decomposition of the carbonyl sulphide by light.

The Observed Data.

The region investigated lay between 1 and 20 μ; the monochromator method described in Part IV* was used throughout. A preliminary investigation of the region 1–17 μ was made with the rock-salt prism, using absorption tubes 45 cm. long at a pressure of 60 cm. of mercury; the sylvine prism was used for the longer wave-length. The regions of absorption thus located were subsequently examined with the appropriate prisms, and a pressure of carbonyl sulphide which gave a maximum absorption of some 50 per cent.

The complete spectrum is summarised in Table I; the ratios of the intensities of the bands at the slit widths employed are approximately indicated in the last

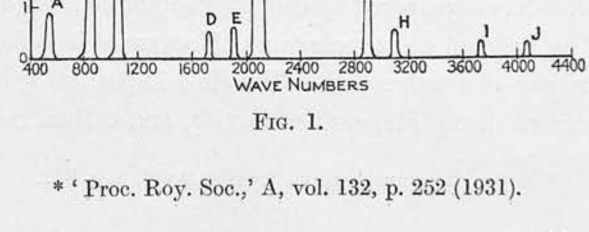

FIG. 1.

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* 'Proc. Roy. Soc.,' A, vol. 132, p. 252 (1931).

column : the remarks of Part III* with regard to the maximum percentage absorption shown by a band apply equally to the data in the present case.

Table I.

Band centre.		Maxima (cm.$^{-1}$).	P − R $\Delta\nu$ (cm.$^{-1}$)	Pressure cm. Hg.	Maximal per cent. absorption.	Intensity.	Slit width (cm.$^{-1}$).	Prism.
$\lambda(\mu)$.	ν_0 (cm.$^{-1}$).							
18·96	527	522 541	19	60	50	3·5	6	Sylvine
11·64	859	854 868	14	7	75	15	4	Rock-salt
9·516	1051	1047 1051 1061	14	7	55	12	8	Rock-salt
5·842	1718	1709 1722	13	70	56	1·8	10	Fluorite
5·272	1898	1898	—	70	68	2	8	Fluorite
4·810	2079	2079	—	1	70	29	16	Fluorite
3·443	2904	2904	—	4·5	43	13	10	Quartz
3·231	3095	3095	—	70	76	2·1	11	Quartz
2·672	3742	3742	—	70	50	1·5	14	Quartz
2·449	4084	4084	—	70	50	1·5	15	Quartz

The Individual Bands.

Bands A and B.—At 18·96 and 11·64 μ ; figs. 2 and 3. These were easily investigated and appeared consistently in observations made with samples of

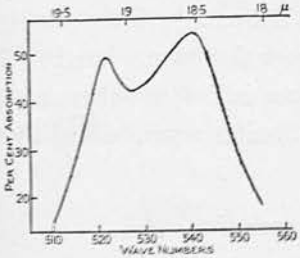

Fig. 2.

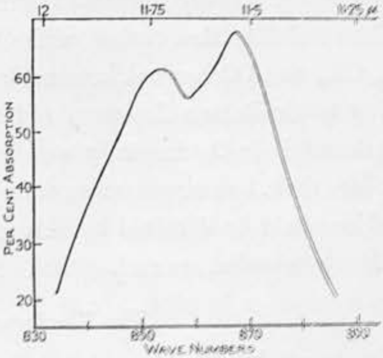

Fig. 3.

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* ‘Proc. Roy. Soc.,’ A, vol. 132, p. 240 (1931).

gas obtained from a preliminary and from an entirely reconstructed generating apparatus.

Band C.—At 9·516 μ; fig. 4. This band called for considerable care in its examination; at first only one maximum was evident, but narrower slit width revealed a contour similar to that of the sulphur dioxide band at 7·347 μ, with three maxima. The possibility of error due to selective reflectivity of the mirrors, or similar source of inequality in galvanometer deflections with the radiation traversing the empty and the full tube, was eliminated by means of a blank experiment with both tubes evacuated. The central maximum has been taken as the band centre.

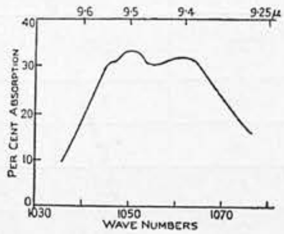

Fig. 4.

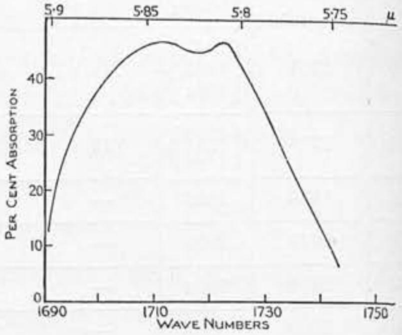

Fig. 5.

Band D.—At 5·842 μ; fig. 5. The curve shows the shape of the band under examination with a slit width of 10 cm.$^{-1}$.

Bands E, F, G, H, I, and J.—The contours of these bands are not reproduced as no resolution was obtained; the last four show a rather broad maximum making determination of the band centre somewhat uncertain. It is hoped to reinvestigate all six with a grating spectrometer now under construction. Band F at 4·810 μ is easily the most intense in the observed spectrum.

The possibility that certain of the bands might be due to impurities such as SO_2, CS_2, and CO has not been neglected; the 527 cm.$^{-1}$ band, for example, is close to the Raman displacement for SO_2 at 534 cm.$^{-1}$; if the observed band had its origin in the impurity we should expect the intense band at 7·347 μ, and less than 1 mm. pressure of the substance in 1 atmosphere of carbonyl sulphide could be detected by this means. Similar arguments show that all the bands recorded are real.

The Fundamental Frequencies.

The many bands observed in the spectrum of carbonyl sulphide with a comparatively small absorbing column of the gas distinguish it from its companions carbon dioxide and disulphide. The latter substances are symmetrical linear molecules, and have therefore an inactive frequency which, in the infra-red, is only observed in combination with other fundamentals. Because of its lack of symmetry carbonyl sulphide must have three active fundamental vibrations, and the immediate problem in elucidating the origin of the observed bands is to determine these ; we propose to examine this question in some detail since in many cases observers have accepted the existence of a numerical relationship as sufficient to identify a combination- or over-tone.

The longest wave-length band at 527 cm.$^{-1}$ cannot be accounted for as a difference tone of any shorter wave-length band ; hence it is either a fundamental or related to some fundamental of even longer wave-length. A comparison with the corresponding values for CO_2 and CS_2 makes it highly probable that this is ν_1 (Table II). Unfortunately, in the case of CS_2, this transverse or deformation frequency (whatever its actual value) must lie outside the range of the prism spectrometer ; we proposed 223 cm.$^{-1}$ as a possible value because of the appearance of a constant difference of this order in the ultra-violet emission spectrum of this substance. Placzek* in discussing our results suggests that a more probable value for this frequency lies in the neighbourhood of 400 cm.$^{-1}$, and we are inclined to accept this, particularly in view of the theoretical considerations presented in a recent paper of Fermi's† and discussed below. Furthermore, the emission spectrum of COS in the ultra-violet has been examined by Fowler and Vaidya‡ ; it is characterised by a group of bands with a constant frequency difference of some 370 cm.$^{-1}$. It seems possible that in both these cases we are dealing with a transverse frequency of the excited molecule.

There is no difficulty in allocating ν_3, which, on account of its intensity and position, must be the very intense band F at 2079 cm.$^{-1}$.

The assignment of the frequency ν_2 in this type of molecule has always been uncertain ; this is the inactive frequency of the symmetrical linear triatomic molecule, which should appear only in the Raman spectrum. The Raman effect for CO_2 and CS_2 shows, however, not one but two displacements ; this anomaly has been theoretically investigated by Fermi (*loc. cit.*). He has noted that the first harmonic of the transverse vibration almost coincides in frequency with the fundamental inactive vibration, and coupling of the two therefore promotes resonance phenomena ; hence in place of a single energy

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* 'Z. Physik,' vol. 70, p. 84 (1931).

† 'Z. Physik,' vol. 71, p. 250 (1931).

‡ 'Proc. Roy. Soc.,' A, vol. 132, p. 315 (1931).

level corresponding to the fundamental inactive frequency there emerge from the mathematical analysis several energy levels, and the intensities of the different transitions depend upon the corresponding proper functions.

A further complication arises with the triatomic linear molecule from the degeneracy of the transverse vibration*; this mode is independent of the plane in which it occurs, and Fermi eliminates the degeneracy by use of two rectangular co-ordinates normal to the nuclear axis and specifying the position of the carbon atom relatively to the centre of gravity of the system. Correspondingly two quantum numbers are required to characterise the vibration; we therefore choose as in Fermi's paper, three quantum numbers $(\overline{a, a'}, b)$ to specify a combination of the transverse and inactive frequencies; a and a' refer to the transverse mode, and b to the inactive mode, and the proper functions of the unperturbed system with approximately equal proper values are $(\overline{0, 0}, 1)$, $(\overline{2, 0}, 0)$, $(\overline{0, 2}, 0)$ and $(\overline{1, 1}, 0)$.

The Raman spectra of CO_2 and CS_2 are discussed by Fermi, and he shows that in place of the one expected Raman line corresponding to the inactive frequency of vibration there should appear two displacements whose separation is determined by the extent of coupling between the inactive and transverse modes, and by the closeness of the level $(\overline{0, 0}, 1)$ to $(\overline{2, 0}, 0)$, $(\overline{0, 2}, 0)$ or $(\overline{1, 1}, 0)$; an inspection of fig. 6 shows these conditions for CO_2 (the degeneracy due to ν_1 has been suppressed to avoid complicating the diagram). The relative intensity of the lines tends to unity as the energy level of the first harmonic of the transverse mode, and that of the fundamental inactive mode become equal.

We have now to ask what can be inferred of the SCO spectrum from Fermi's analysis. We are dealing with an asymmetrical and presumably linear molecule (see below); we should expect all three fundamental frequencies to be active in the infra-red as a consequence of the lack of symmetry, and with the linear structure there would be degeneracy of the transverse vibration. The spectrum of carbonyl sulphide reveals important similarities to that of the dioxide and disulphide; in place of one band corresponding to the fundamental mode, equivalent to the symmetrical mode of the symmetrical molecules, two bands of comparable intensity appear and their frequencies lie near to the frequency of the first harmonic of the transverse vibration. Thus SCO apparently shows the splitting of the energy level of mode ν_2 into sub-levels revealed by the Raman spectrum and combination tones of its symmetrical neighbours; accordingly this is to be associated with the resonance of $2\nu_1$ with ν_2 (see fig. 7).

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* Dennison, 'Rev. mod. Phys.,' vol. 3, p. 280 (1931).

Fermi examines the Raman transition $(\overline{0,\ 0},\ 1)$—$(\overline{0,\ 0},\ 0)$ and the linear combination of the proper function $(\overline{0,\ 0},\ 1)$ with the other proper functions of

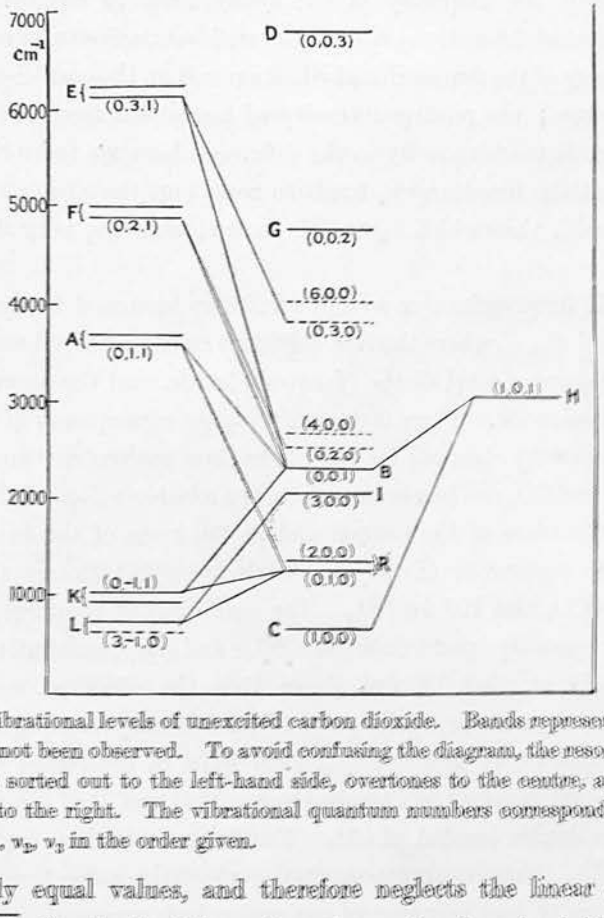

FIG. 6.—The vibrational levels of unexcited carbon dioxide. Bands represented by broken lines have not been observed. To avoid confusing the diagram, the resonance doublets have been sorted out to the left-hand side, overtones to the centre, and other combinations to the right. The vibrational quantum numbers correspond to the fundamentals ν_1, ν_2, ν_3 in the order given.

approximately equal values, and therefore neglects the linear combination $(\overline{0,\ 2},\ 0)$—$(\overline{2,\ 0},\ 0)$. In the infra-red spectrum of carbonyl sulphide, the transition $(\overline{0,\ 0},\ 0)$—$(\overline{0,\ 0},\ 1)$ would be more intense than the transitions $(\overline{0,\ 0},\ 0)$—$(\overline{2,\ 0},\ 0)$ and $(\overline{0,\ 2},\ 0)$, neglecting resonance, and the most intense bands when this quasi-resonance is considered will be those corresponding to transitions from the ground level to levels whose proper functions are linear combinations of $(\overline{0,\ 0},\ 1)$ with $(\overline{2,\ 0},\ 0)$, $(\overline{0,\ 2},\ 0)$, and $(\overline{1,\ 1},\ 0)$. The analysis discloses two proper values whose proper functions are linear combinations of $(\overline{0,\ 0},\ 1)$ and $(\overline{2,\ 0},\ 0)$ and $(\overline{0,\ 2},\ 0)$; the transitions from the ground level to these two levels will therefore show an intensity comparable with that expected for the transition to $(\overline{0,\ 0},\ 1)$ had this perturbation not occurred, and the relative intensity of the two new transitions tends to unity as $2\nu_1 \to \nu_3$.

These conclusions may be summarised as follows: if the frequency of the transverse mode of vibration, ν_1, of a linear triatomic molecule be approximately one-half the frequency of the symmetrical or equivalent mode ν_2, the energy level of the mode ν_2 splits into two levels, whose separation depends upon the energy of the two modes of vibration and on the coefficient of coupling between the two; the relative intensity of transitions from the ground level to the new levels tends to unity as the difference between twice the transverse frequency and the frequency ν_2 tends to zero, and the absolute intensity is comparable with that which ν_2 would possess, were $2\nu_1$ very different from ν_2.

In Table II frequencies due to this effect are indicated by symbols of the type $\nu'_{(2,\,1)}$ and $\nu''_{(2,\,1)}$, where the first subscript refers to the vibration quantum number of the upper level of the transverse mode, and the second to that of the symmetrical mode. There is one unfortunate consequence of this analysis, ν_2 cannot be directly observed for any of the three molecules; an approximate value for CS_2 and CO_2 can be obtained from the relation $\nu_3/\nu_2 = \sqrt{\{(2m+\mathrm{M})/\mathrm{M}\}}$, where M is the mass of the central and m the mass of the external atoms. The frequency separation of the two levels is approximately 145 cm.^{-1} for CS_2, 190 for SCO, and 105 for CO_2. The coefficient of coupling is at present an uncertain quantity, particularly for SCO, and the quantitative deductions are accordingly omitted. Fermi shows that the observed and calculated intensities and separations for CO_2 and CS_2 are in very good agreement.

These principles may presumably be extended to the region of absorption near $\nu_2 + \nu_3$ and invoked to explain the bands C and D of CS_2, G and H of SCO, and the double band A of CO_2. Furthermore we find that when, as in the case of CO_2, other bands representative of combination tones are isolated by examination of long columns of gas under high pressures, a similar interpretation appears to hold good. The data in Table II for CS_2 have been taken from Part III of the present series of investigations, and for CO_2 from the work of Schaefer and Philipps.* The interpretation of the levels $\nu'_{(4,\,2)}$, $\nu''_{(4,\,2)}$, $\nu'_{(6,\,3)}$ and $\nu''_{(6,\,3)}$ is somewhat uncertain, as the degeneracy of a transverse vibration of quantum number 4 is five-fold and of 6, seven-fold; the corresponding mathematical analysis is lacking. In dealing with CS_2, the present authors made the assumption that the doublet structure in the Raman effect was due to the existence of two frequencies characteristic of two types of binding to be associated with modifications in the detailed electronic structure of the molecule. If this were so, we should expect a two-fold and three-fold

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* 'Z. Physik,' vol. 36, p. 641 (1926).

increase in the separation between the members of the double doublets as we proceeded to the combinations formed from the second and third overtones of the inactive frequency, but inspection of the results for CO_2 shows that within the experimental error this difference is constant. This justifies an association of the bands D and E of SCO as in fig. 7 and Table II, for it must be pointed out that E is capable of interpretation as $2\nu_1 + \nu_2$, an assignment which scores on account of its simplicity. To explain the constant frequency separation we must resort to the Fermi hypothesis, or to a splitting of a vibrational frequency by association with rotational levels arising from a very small effective moment of inertia. The former seems to offer a more comprehensive explanation of the observed facts.

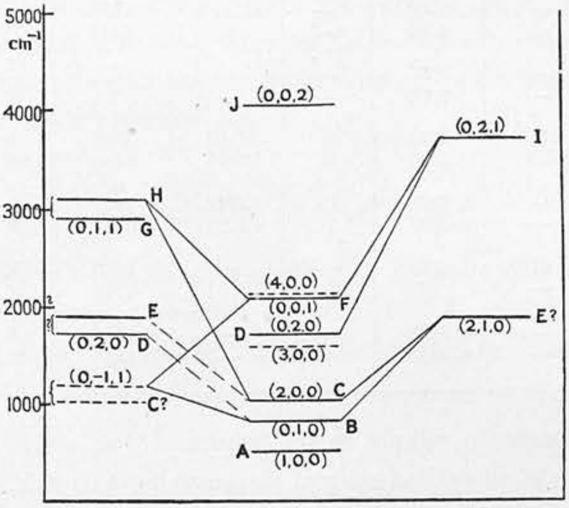

FIG. 7.—Vibrational levels of carbonyl sulphide.

An interesting feature of the frequencies $\nu'_{(4,\,2)}$ and $\nu''_{(4,\,2)}$ brought out by Table II is their absence in CS_2 and CO_2; this is in complete agreement with the above discussion, since they are inactive modes in those molecules, and therefore absent from the infra-red spectrum; as overtones they should also be absent from the Raman spectrum.*

Band J of SCO is probably complex, containing both $2\nu_3$ and $\nu_3 + \nu''_{(4,\,2)}$. It is important to note that the allocations $2\nu_3$, $3\nu_1$, $3\nu_3$, and $\nu_1 + \nu_3$ to the bands G, I, D and H of CO_2 are not in accordance with theory; Dennison (*loc. cit.*) has deduced that "if three atoms are collinear and symmetrical, then the sum of the frequencies of any two observed bands (overtones, combination

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* van Vleck, 'Proc. Nat. Acad. Sci.,' vol. 15, p. 754 (1929).

Table II.

Tone.	SCS.			SCO.			OCO.		
	Band.	Observed.	Calculated.	Band.	Observed.	Calculated.	Band.	Observed.	Cal
ν_1	—	—	c. 400	A	527	—	C	677	[illegible]
ν_2	—	—	610	—	—	c. 930	—	—	[illegible]
ν_3	B	1523	—	F	2079	—	B	2350	—
$\nu'_{(2,1)}$	R	655	—	B	859	—	R	1285	—
$\nu''_{(2,1)}$	R	795	—	C	1051	—	R	1388	—
$\nu'_{(4,2)}$	—	—	c. 1300	D	1718	c. 1718	—	—	[illegible]
$\nu''_{(4,2)}$	—	—	c. 1440	E	1898	c. 2008	—	—	[illegible]
$2\nu_3$	—	—	3046	J	4084	4158	G	4781	[illegible]
$3\nu_1$	—	—	1200	—	—	4158	I	2049	[illegible]
$3\nu_3$	—	—	4569	—	—	6237	D	6842	[illegible]
$\nu_1 + \nu_2$	—	—	1055	—	—	1386	—	—	[illegible]
$\nu_1 + \nu_3$	—	—	1900	—	—	2606	H	3052	[illegible]
$\nu_3 + \nu'_{(2,1)}$	C	2179	2178	G	2904	2938	A	3617	[illegible]
$\nu_3 + \nu''_{(2,1)}$	D	2230	2318	H	3095	3130	A	3721	[illegible]
$\nu_3 + \nu'_{(4,2)}$	—	—	c. 2823	I	3742	3977	F	4896	[illegible]
$\nu_3 + \nu''_{(4,2)}$	—	—	c. 2963	? J	4084	3987	F	5009	[illegible]
$\nu_3 - \nu'_{(2,1)}$	A	878	868	—	—	1220	K	1061	[illegible]
$\nu_3 - \nu''_{(2,1)}$	—	—	728	? C	1051	1028	K	961	[illegible]
$\nu_3 + \nu'_{(6,3)}$	—	—	c. 3488	—	—	c. 4656	E	6139	[illegible]
$\nu_3 + \nu''_{(6,3)}$	—	—	c. 3628	—	—	c. 4846	E	6243	[illegible]

bands, or fundamentals) will not be the frequency of an active or observable overtone," but the allocations referred to contradict this rule, and only the low intensity of the bands may be offered in partial explanation. This difficulty does not affect the assignment of the fundamental frequencies, particularly those of SCO which form the main subject of this paper.

The above considerations imply a rectilinear structure for the molecule; a preliminary note* describing this work was written before the appearance of Fermi's paper, and the possible interpretation of the spectrum mentioned therein, namely that there were two triangular modifications of carbonyl sulphide with fundamental frequencies of 527, 1051, and 2079 cm.$^{-1}$ in the one case, and 859, 1718 and 2079 cm.$^{-1}$ in the other, will not be further discussed.

The following comments on the structure of band C are necessary: the partial resolution obtained credits this band with a Q branch. Now a linear molecule shows Q branches only if it has a component of electronic angular

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* 'Nature,' vol. 128, p. 637 (1931).

momentum about the nuclear axis, and even then the Q branches are of low intensity, while, since the observed bands arise from the same electronic level, every band should show a Q branch. One cannot be certain about the detailed electronic structure of carbonyl sulphide since (see below) it appears to have a single linkage between the carbon and sulphur atoms and a double linkage between the carbon and oxygen, but the absence of the other Q branches seems decisive, and the molecule probably has a $^1\Sigma$ structure. The band in question is presumably complex; the linear combination of the proper functions $(\overline{2, 0}, 0)$ and $(\overline{0, 2}, 0)$ occurs with a measurable intensity and has a proper value corresponding to $2\nu_1$, so that the harmonic $2\nu_1$ should actually appear in the spectrum; the centre of band C is approximately 1051 cm.$^{-1}$ so that the band may not only contain $\nu''_{(2, 1)}$ as in Table II, but also $2\nu_1$ and $\nu_3 - \nu''_{(2, 1)}$.

All observed and calculated values in Table II are in wave-numbers; the calculated values are only approximate, since no account has been taken of the constants of anharmonicity.

The Molecule of Carbonyl Sulphide.

Vegard,* from X-ray measurements, has deduced that the molecule is rectilinear, with atomic separations $C - O = 1 \cdot 10$ Å., and $C - S = 1 \cdot 96$ Å.; the centre of mass of such a system will lie between the carbon and sulphur atoms at a distance of $0 \cdot 75$ Å. from the carbon atom, and the calculated moment of inertia, Σmr^2, is 178×10^{-40} g. cm.^{2}. If we apply the expression $I_0 = kT/c^2\pi^2\Delta\nu^2$ to bands B and D, where $\Delta\nu = 14$ cm.$^{-1}$, we have $I_0 = 230 \times 10^{-40}$ g. cm.^{2}, and from band A ($\Delta\nu = 19$ cm.$^{-1}$), $I_0 = 115 \times 10^{-40}$ g. cm.^{2} In the case of CO_2, the Bjerrum doublet separation for the transverse fundamental ν_1, and its combinations is unequivocally of a different order from that of the fundamental ν_3, and we have no certain knowledge of the moment of inertia effective in the transverse vibration-rotation band. If we argue by analogy for SCO, we should select the value given by ν_3, *i.e.*, 230×10^{-40} g. cm.^{2}.

Rankine,† from viscosity measurements in carbonyl sulphide, favoured the rectilinear structure, and on the supposition of the approach to the inactive gas type in the constituent atoms, carbon and oxygen being neon-like of radius $0 \cdot 65$ Å. and sulphur argon-like of radius $1 \cdot 03$ Å., obtained the value

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* 'Z. Krist.,' vol. 77, p. 411 (1931).

† 'Phil. Mag.,' vol. 44, p. 292 (1922).

2·98 Å. for the extreme interatomic separation, very close to Vegard's result of 3·06 Å. The internuclear separations in the three gases are accordingly :—

Molecule.	Distance CO in Å.	Distance CS in Å.
OCO	0·97	—
SCS	—	1·60
SCO	1·10	1·96

The electric moment has been determined by Zahn and Miles,* who found it to be 0·650 c.g.s.e.s. units ; at the same time they obtained the value $0 \cdot 326 \times 10^{-18}$ for CS_2, which is too high, the electric moment having since been shown to be zero. The value for SCO may, however, be taken to indicate the existence of a permanent electric moment, which is to be expected on account of the lack of symmetry in the structure.

Finally, if we apply considerations of the type employed by Debye† in discussing the stability of rectilinear and triangular forms for certain molecules, it can be shown that when the central atom in a triatomic molecule is of low polarisability and the external atoms are both of high polarisability, a rectilinear configuration is a stable one ; the conditions are those of the present case.

The Anharmonic Coefficients.

If we accept the rectilinear model, it becomes of interest to determine the force constants implied by the observed frequencies, and in order to do this we require the absolute values of the latter. The most convenient formula for calculating the anharmonic constants of the vibrational modes of a polyatomic molecule is that of Born and Brody,‡ which may be written as follows

$$\begin{aligned}\nu = {} & (n'_1 - n''_1)\, a_1 + (n'_2 - n''_2)\, a_2 + (n'_3 - n''_3)\, a_3 \\ & + (n'^2_1 - n''^2_1)\, b_1 + (n'^2_2 - n''^2_2)\, b_2 + (n'^2_3 - n''^2_3)\, b_3 \\ & + (n'_1 n'_2 - n''_1 n''_2)\, c_1 + (n'_1 n'_3 - n''_1 n''_3)\, c_2 + (n'_2 n'_3 - n''_2 n''_3)\, c_3, \qquad (1)\end{aligned}$$

where ν is the frequency of any observed band centre, a_i is the true frequency of the fundamental vibration when the system vibrates under forces obeying Hooke's law ; n'_k is the quantum number specifying the upper vibrational level, n''_k specifying the lower, and the anharmonic constants are given by the

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* 'Phys. Rev.,' vol. 32, p. 497 (1928).

† "Polar Molecules" (1929).

‡ 'Z. Physik,' vol. 6, p. 140 (1921).

b and c values. At room temperature we may take it that the upper vibrational levels are not excited, and n'_k will be zero.

Difficulties at once arise from the existence of sub-levels due to the resonance phenomenon which make the assumption of any value for ν_2 somewhat uncertain. But we have seen that in the case of CO_2 and CS_2 the calculated value lies very close to the observed band $\nu'_{(2, 1)}$, and the agreement obtained amongst the anharmonic coefficients when the latter value is employed justifies us in its use. Accordingly, with whole quantum numbers, we have the following probable determination: from bands A and C, $a_1 = 527$, $b_1 = 0$; from bands B and D, $a_2 = 859$, $b_2 = 0$; from bands F and J, $a_3 = 2042$, $b_3 = -37$; from B, F, G, $c_3 = -34$; from C and H, $c_3 = -35$; and from D, F, I, $c_3 = -28$ (all in cm.$^{-1}$). The agreement of the three independently derived values for c_3 is remarkable, the deviation from the mean of 32 cm.$^{-1}$ being well within the limits of experimental error.

The Force Constants.

Radakovic* has investigated the fundamental modes of vibration of three particles of unequal mass situated at the vertices of a scalene triangle, and acted on by central forces obeying Hooke's law, each with a different elastic coefficient. The method of central forces, however, is inapplicable to the straight line molecule, as the frequency of the transverse mode becomes infinite; we have therefore worked out the normal frequencies of the unsymmetrical linear molecule on the lines used by Yates† for the isosceles triangle, except that the restoring couple, about an axis through the central atom and perpendicular to the plane of the vibration, is assumed proportional to the angular displacement in place of Yate's couple proportional to the arc of the angular displacement.

The system is shown in fig. 8. The centre of gravity of the system is chosen as origin, and the undisplaced positions of m_1, m_2 and m_3 are $(-a/m_1, 0)$,

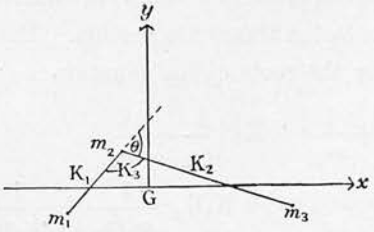

FIG. 8.

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* 'Monats. Chem.,' vol. 36, p. 447 (1930).

† 'Phys. Rev.,' vol. 36, p. 555 (1930).

$(-b/m_2, 0)$, and $(c/m_3, 0)$ respectively; the displaced positions of the masses are then

$$\left(-\frac{a-x_1}{m_1},\ \frac{y_1}{m_1}\right),\qquad \left(-\frac{b-x_2}{m_2},\ \frac{y_2}{m_2}\right),$$

and

$$\left(\frac{c+x_3}{m_3},\ \frac{y_3}{m_3}\right),$$

The co-ordinates x_1, y_1 and x_2 are chosen as the representative co-ordinates, and the remaining three co-ordinates are determined from the equations specifying zero motion of the centre of gravity, and zero resultant angular momentum of the system; that is from the equations:

$$x_1+x_2+x_3=0, \tag{2.1}$$

$$y_1+y_2+y_3=0, \tag{2.2}$$

and

$$-\frac{a}{m_1}\,y_1-\frac{b}{m_2}\,y_2+\frac{c}{m_3}\,y_3=0, \tag{2.3}$$

the equations of motion are then deduced in the usual manner, and are

$$\left(\frac{1}{m_1}+\frac{1}{m_3}\right)\ddot{x}_1+\frac{1}{m_3}\,\ddot{x}_2+\left(\frac{\mathrm{K}_1}{m_1{}^2}+\frac{\mathrm{K}_2}{m_3{}^2}\right)x_1+\left(\frac{\mathrm{K}_2}{m_2m_3}+\frac{\mathrm{K}_2}{m_3{}^2}-\frac{\mathrm{K}_1}{m_1m_2}\right)x_2=0 \tag{3.1}$$

$$\frac{1}{m_3}\,\ddot{x}_1+\left(\frac{1}{m_2}+\frac{1}{m_3}\right)\ddot{x}_2+\left[\mathrm{K}_2\left(\frac{1}{m_2m_3}+\frac{1}{m_3{}^2}\right)-\frac{\mathrm{K}_1}{m_1m_2}\right]x_1 \\ +\left[\frac{\mathrm{K}_1}{m_2{}^2}+\mathrm{K}_2\left(\frac{1}{m_2}+\frac{1}{m_3}\right)^2\right]x_2=0 \tag{3.2}$$

and

$$\ddot{y}_1+\mathrm{K}_3\,\frac{\left[\frac{a^2}{m_1{}^2}\left(\frac{1}{m_2}+\frac{1}{m_3}\right)+\frac{b^2}{m_2{}^2}\left(\frac{1}{m_3}+\frac{1}{m_1}\right)+\frac{c^2}{m_3{}^2}\left(\frac{1}{m_1}+\frac{1}{m_2}\right)+\frac{2}{m_1m_2m_3}(bc+ca-ab)\right]}{\left(\frac{a}{m_1}-\frac{b}{m_2}\right)^2\left(\frac{b}{m_2}+\frac{c}{m_3}\right)^2}\,y_1=0.$$

Equation (3.3) describes the transverse vibration; it is independent of x_1 and x_2, as is to be expected, since to a first approximation the linear restoring forces do not contribute to the transverse motion. The longitudinal vibration frequencies are given by the roots of the equation

$$p^4-p^2\left[\mathrm{K}_1\left(\frac{1}{m_1}+\frac{1}{m_2}\right)+\mathrm{K}_2\left(\frac{1}{m_2}+\frac{1}{m_3}\right)\right. \\ \left.+\,\mathrm{K}_1\mathrm{K}_2\left(\frac{1}{m_1m_2}+\frac{1}{m_2m_3}+\frac{1}{m_3m_1}\right)\right]=0, \tag{4}$$

where $p=2\pi c\nu$, whilst ν is the observed frequency in cm.$^{-1}$ and c the velocity of light.

The frequency of the transverse vibration is given by

$$=\mathrm{K}_3\,\frac{\left[\frac{a^2}{m_1{}^2}\left(\frac{1}{m_2}+\frac{1}{m_3}\right)+\frac{b^2}{m_2{}^2}\left(\frac{1}{m_3}+\frac{1}{m_1}\right)+\frac{c^2}{m_3{}^2}\left(\frac{1}{m_1}+\frac{1}{m_2}\right)+\frac{2}{m_1m_2m_3}(bc+ca-ab)\right]}{\left(\frac{a}{m_1}-\frac{b}{m_2}\right)^2\left(\frac{b}{m_2}+\frac{c}{m_3}\right)^2}. \quad (5)$$

The relations between the roots of equation (4) and the coefficients of p^2 are more useful for the determination of the force constants implied by the found frequencies than is equation (4) itself. The relations are

$$p_1{}^2+p_2{}^2=\mathrm{K}_1(1/m_1+1/m_2)+\mathrm{K}_2(1/m_2+1/m_3) \quad (6.1)$$

and

$$p_1{}^2p_2{}^2=\mathrm{K}_1\mathrm{K}_2(1/m_1m_2+1/m_2m_3+1/m_3m_1). \quad (6.2)$$

On substituting the absolute frequencies obtained above for the two longitudinal vibrations (859 and 2042 cm.$^{-1}$) in equations (6), we have the two following pairs of values for the binding forces K_1 and K_2, corresponding to the linkings CO and CS respectively :—

$$\mathrm{K}_1=6\cdot 2,\ \mathrm{K}_2=18\cdot 5\times 10^5 \text{ dynes per cm.},$$

and

$$\mathrm{K}_1=13\cdot 7,\ \mathrm{K}_2=8\cdot 5\times 10^5 \text{ dynes per cm.}$$

Of these the second solution is obviously the more reasonable.

It is instructive to compare the force constants for the three molecules, CS_2, CO_2, SCO, set out in Table III.

Table III.

Molecule.	Bond CO.		Bond CS.		Transverse vibration.	
	Frequency (cm.$^{-1}$).	K × 10^{-5} dynes/cm.	Frequency (cm.$^{-1}$).	K × 10^{-5} dynes/cm.	Frequency (cm.$^{-1}$).	K × 10^{27} dyne/cm.^{2}.
S_2	—	—	1526 655	6·9 8·0	c. 400	10
O_2	2353 1285	14·2 15·5	—	—	677	6
SCO	2042 859	13·7	2042 859	8·5	527	8

The relations between the above values are remarkable, particularly when we remember that the observed frequencies for SCO are compounded as a result of the asymmetry, and do not directly correspond to the CO and CS vibrations of the other molecules. The types of linking in CO_2 and CS_2 are the same as in SCO, and spectroscopically at least the molecule of carbonyl sulphide behaves as if its structural formula was O = C — S, the force constants of 7 and 14 × 10^5 dynes per centimetre corresponding to single and double linkages respectively. Shaw and Phipps* have recently shown that the ground state of S_2 is $^3\Sigma$, corresponding to a single valency linking between the atoms. This is confirmed by the value of $6 \cdot 0 \times 10^5$ dynes per centimetre for the force constant effective in the fundamental vibration of the S_2 molecule (800 cm.$^{-1}$). G. N. Lewis† pointed out some time ago that "the ability to form multiple bonds is almost, if not entirely, confined to elements of the first period of eight, and especially to carbon, nitrogen, and oxygen." Kipping‡ also remarks that "fresh evidence is continually being obtained that an ethylenic binding between carbon and silicon is either impossible or can only be produced under exceptional conditions." Further comments and additional evidence are offered by Lowry and Vernon.§

The values given for K_3 appear incomparable with those of K_1 and K_2; K_3, however, is the restoring couple per unit angular displacement, whilst K_1 and K_2 are the restoring forces per linear unit displacement. The restoring couple per unit angular displacement might be replaced by the tangential restoring force per unit arc displacement, and K_3 then becomes comparable though some ten times less than K_1 and K_2. The first definition is preferred primarily for the ease of determination for the asymmetric molecule; the restoring couples for the molecule CO_2, SCO and CS_2 are then roughly 6, 8 and 10×10^{-22} dyne cm.^{2}.

SCO accordingly occupies a position intermediate between CO_2 and CS_2, a result which could not have been determined immediately by inspection of the data from the second definition. A curious feature is the apparent increase in the value of the restoring couple as we pass from CO_2 with its strong bindings to CS_2 with its single linkages. At first sight, the comparatively large polarisability of the sulphur atom suggests itself as an explanation, but a simple calculation indicates that this is not the complete picture. In SCO sulphur has four times the polarisability of oxygen, but this is largely compensated by the fact that the distance CS is approximately twice the distance CO, so that the dipole moment induced in the sulphur atom by any electric charge on the carbon atom is just equal to that induced in the oxygen atom.

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* 'Phys. Rev.,' vol. 38, p. 174 (1931).

† "Valence," p. 94 (1923).

‡ 'J. Chem. Soc.,' p. 104 (1927).

§ 'Trans. Faraday Soc.,' vol. 25, p. 290 (1929).

From this point of view SCO is more nearly symmetrical and more like to CO_2 than is superficially apparent.

The Heat of Formation.

Finally, thermochemical data show very convincingly that the types of binding in CO_2 and CS_2 are those which exist in the intermediate compound. Taking advantage of the modern values for the heats of dissociation of oxygen and sulphur, we have the following calculations :—

(1) The heat of formation of carbon dioxide from gaseous atomic carbon and oxygen—

$$
\begin{array}{rl}
[C]_D + (O_2) = & (CO_2) + 94\cdot5 \text{ k. cal.} \\
(C) = & [C]_D + 141\cdot3 \text{ k. cal.} \\
2(O) = & (O_2) + 128\cdot0 \text{ k. cal.} \\
\hline
(C) + 2(O) = & (CO_2) + 363\cdot8 \text{ k. cal.}
\end{array}
$$

(2) The heat of formation of carbon disulphide from gaseous atomic carbon and sulphur—

$$
\begin{array}{rll}
(CS_2) + 3(O_2) = & (CO_2) + 2(SO_2) & + 252\cdot8 \text{ k. cal.} \\
(CO_2) = & [C]_D + (O_2) & - 94\cdot5 \text{ k. cal.} \\
[C]_D = & (C) & - 141\cdot3 \text{ k. cal.} \\
2(SO_2) = & 2[S]_{Rh} + 2(O_2) & - 138\cdot8 \text{ k. cal.} \\
2[S]_{Rh} = & (S_2) & - 28\cdot5 \text{ k. cal.} \\
(S_2) = & 2(S) & - 113\cdot0 \text{ k. cal.} \\
\hline
(CS_2) = & (C) + 2(S) & - 263\cdot3 \text{ k. cal.}
\end{array}
$$

(3) The heat of formation of carbonyl sulphide from gaseous atomic carbon, oxygen, and sulphur—

$$
\begin{array}{rll}
(SCO) + \frac{3}{2}(O_2) = & (CO_2) + (SO_2) & + 130\cdot3 \text{ k. cal.} \\
(CO_2) = & [C]_D + (O_2) & - 94\cdot5 \text{ k. cal.} \\
[C]_D = & (C) & - 141\cdot3 \text{ k. cal.} \\
(SO_2) = & [S]_{Rh} + (O_2) & - 69\cdot4 \text{ k. cal.} \\
[S]_{Rh} = & \frac{1}{2}(S_2) & - 14\cdot3 \text{ k. cal.} \\
\frac{1}{2}(S_2) = & (S) & - 56\cdot5 \text{ k. cal.} \\
\frac{1}{2}(O_2) = & (O) & - 64\cdot0 \text{ k. cal.} \\
\hline
(SCO) = & (C) + (S) + (O) & - 310 \quad \text{ k. cal.}
\end{array}
$$

If carbonyl sulphide is intermediate in its structure to CO_2 and CS_2 we should expect its heat of formation to be $(363\cdot8 + 263\cdot3)/2 = 313$ k. cal. The third series of calculations shows that agreement is complete.

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Investigations in the Infra-Red Region of the Spectrum. Part VI.—*The Absorption Spectra of the Dioxides of Chlorine and Sulphur.*

By C. R. BAILEY and A. B. D. CASSIE.

INVESTIGATIONS IN THE INFRA-RED REGION OF THE SPECTRUM. PART VI.—THE ABSORPTION SPECTRA OF THE DIOXIDES OF CHLORINE AND SULPHUR.

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Investigations in the Infra-Red Region of the Spectrum. Part VI.—*The Absorption Spectra of the Dioxides of Chlorine and Sulphur.*

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The infra-red spectrum of chlorine dioxide has not been previously determined, although its photochemical properties and its electronic band spectrum have been the subject of recent extensive enquiry.* From the latter attempts have been made to interpret the band spectrum, and to assign values to the characteristic frequencies of the fundamental modes of vibration in the ground electronic state. It will be seen from the following that the values so deduced are incorrect, and it is probable that in no case of a polyatomic molecule is a complete determination of its fundamental frequencies possible without resort to its infra-red spectrum.

Experimental.

The method of preparation described by Goodeve and Stein (*loc. cit.*) was followed. The gas passed under water-pump vacuum to a trap immersed in a carbon dioxide-acetone freezing mixture; it was then distilled through phosphoric oxide tubes and condensed in a second trap cooled by liquid air. This trap could be removed from the generating system by means of a glass seal and a spherical glass joint; the ground joint was of universal pattern and the trap containing the dioxide could therefore be readily transported and connected to the absorption tube system. The latter was of as small capacity as possible, and no manometer was included, pressure in the absorption tube being regulated by immersing the dioxide trap in a freezing mixture of known temperature. The greatest pressure used during the investigation was the vapour pressure of the gas at 0° C., or approximately 630 mm. The length of the absorbing column of gas was in all cases 45 cm.; the lubrication of taps

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* Mayer, 'Z. phys. Chem.,' vol. 113, p. 220 (1924); Booth and Bowen, 'J. Chem. Soc.,' vol. 127, pp. 342, 510 (1925); Goodeve and Stein, 'Trans. Faraday Soc.,' vol. 25, p. 738 (1929); Nagai and Goodeve, *ibid.*, vol. 27, p. 508 (1931); Wallace and Goodeve, *ibid.*, p. 648; Finkelnburg and Schumacher, 'Z. phys. Chem.,' Bodenstein Festb., p. 704 (1931); Urey, 'Ind. Eng. Chem.,' vol. 23, p. 1241 (1931); Urey and Johnston, 'Phys. Rev.,' vol. 38, p. 2131 (1931).

and of joints between the rocksalt end plates and the absorption tubes was effected by chlorinated vaseline.

The monochromator method described in Part IV* of the present series of investigations was used throughout without essential modification, and a pressure sufficient to give some 50 per cent. absorption was aimed at for detailed examination of any band. The tubes were painted a dead black, and no evidence of rapid decomposition was observed, the selective absorption of near infra-red radiation producing no appreciable decomposition of chlorine dioxide.

The Observed Data.

The results are summarised in Table I. The relative intensities are approximate estimates for the slit width employed. The last two columns give the suggested origin together with the calculated frequency ν_e.

Table I.

Band.	Band centre.		Maxima.	P–R separation.	Relative intensity.	Slit width.	Origin.	ν_e calculated.
	$\lambda(\mu)$.	ν_0.						
		cm.$^{-1}$	cm.$^{-1}$	cm.$^{-1}$		cm.$^{-1}$		cm.$^{-1}$
B	10·57	946	932	31	20	5	ν_3	—
C	9·017	1109	1095 1106 1123	28	50	7	ν_1	—
E	5·307	1884	1870 1884 ? 1900	30	2	10	$2\nu_3$	1892
F	4·916	2034	—	—	4	15	$v_1 + v_3$	2055

There is much evidence (Goodeve and Stein, Urey and Johnston (*loc. cit.*)) from the electronic band spectrum that the third fundamental vibrational frequency associated with the ground state is approximately 527 cm.$^{-1}$. A search was made for this band without success; the failure to detect the band was, as the result of other experiences in the neighbourhood of 19–22 μ, attributed to the existence of scattered radiation of shorter wave-length which could not be excluded from the themopiles. Conversion of the apparatus into a double manochromator confirmed this suspicion, since beyond 18 μ no galvanometer deflection was observed when the radiation traversed the

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* 'Proc. Roy. Soc.,' A, vol. 132, p. 252 (1931).

empty tube. With the apparatus as at present constructed 19 μ appears to be the approximate long wave limit for experimentation, even with the sylvine prism; all residual radiation appears to be absorbed by the rocksalt plates of the absorption tubes and thermopiles. The stops inserted in the absorption tubes during the measurements on CS_2 and COS* were not used during the present work; their position was found to be difficult to adjust, and they were omitted since stray radiation causing galvanometer deflections on changing over from the empty to the full tube had been otherwise eliminated. Clearly they eliminate much of the shorter wave-length radiation emitted by the Nernst filament and scattered within the spectrometer, for with them in position we were able to detect the COS band at 18·96 μ; even this procedure is not entirely satisfactory, however, since this band should show a Q branch which was not observed. We have consequently suspended investigation in the region 18 to 20 μ until some more satisfactory method had been developed.

The preliminary double monochromator was built up from monochromators of two types: the first employed the chromatic foci method first used in the long wave region by Rubens and Wood; the second was the prism spectrometer monochromator previously described. Fig. 1 indicates the arrangement of the first type; it was of an experimental nature and could almost certainly be improved upon, the only lenses available being of rocksalt, and of somewhat small focal aperture. N is the Nernst filament, M_1 a stainless steel mirror, L the lenses, S the spectrometer slit, and A is a stop just larger than the visible image of the filament which appears inside the focus S for radiation of wave-length 19 μ. M_1 was inserted to provide as large a solid angle of radiation falling on S as possible. The ratio of the distances LS : LA is equal to the ratio of $(\mu - 1)$ for 0·5 μ to $(\mu - 1)$ for 19 μ; this is surprisingly large, LS/LA being approximately 1·5. The stop A, which is placed nearer to S than the visible focus, cuts out most of the shorter wave-length radiation. Lenses

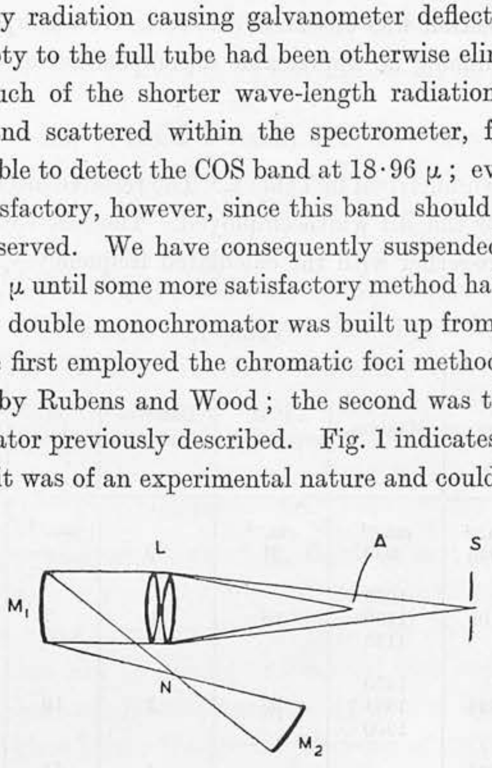

FIG. 1.

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* Part IV, *loc. cit.*

and plates of sylvine or potassium bromide would be required for the region beyond 18 μ, but the method might be used with advantage for shorter wave-lengths where scattered radiation of still shorter wave-length must falsify results to some degree.

The Individual Bands.

Band B (the bands are lettered to correspond with those previously determined for sulphur dioxide in Part II)*—10·57 μ, $\nu_3 = 946$ cm.$^{-1}$ (fig. 2). This fundamental was investigated with the rocksalt prism and a slit width containing 5 cm.$^{-1}$; resolution into P and R branches was achieved with a separation of 30–31 cm.$^{-1}$. No difficulty was experienced in the repeated detection of the band or in the determination of the shape of the contour of the envelope; these remarks apply equally well to the fundamental band C, and it follows that absorption of radiation through these fundamental modes of vibration produces zero or negligible decomposition of the molecule. The intensities and positions of the two bands confirm their choice as fundamentals; the corresponding frequencies selected by Urey and Johnston (*loc. cit.*) from the ultra-violet spectrum were 727 and 858 cm.$^{-1}$, and, for a molecule of this weight and probable force constants, obviously too low.

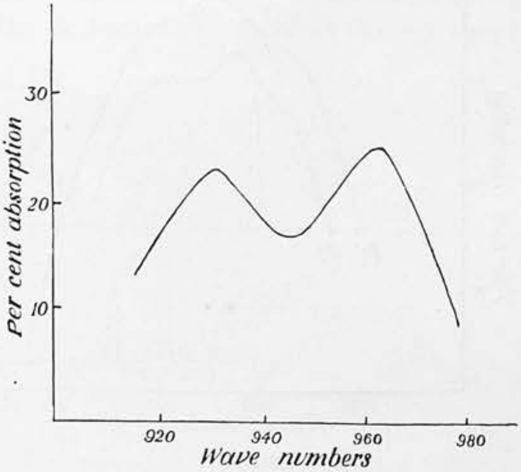

FIG. 2.

Band C.—9·017 μ, $\nu_1 = 1109$ cm.$^{-1}$, fig. 3. The rocksalt prism was used with a slit width enclosing 6–7 cm.$^{-1}$. It is by far the most intense band observed, and the shape of its envelope has always indicated the presence of a

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* 'Proc. Roy. Soc.,' A, vol. 130, p. 144 (1930).

Q branch, although no complete separation of the three branches was possible; the P-R separation is again 30 cm.$^{-1}$.

Band E.—5·307 μ, $2\nu_3 = 1884$ cm.$^{-1}$. With the fluorite prism, the slit width employed included some 10 cm.$^{-1}$. It is the first harmonic of band B; as will be seen from the discussion below, the presence or absence of a Q branch is of great importance in fixing the structure of the chlorine dioxide molecule, and many attempts were made to obtain definite evidence on this point. The resolution required is just within the theoretical limit of the instrument, and the shape of the contours observed when this condition holds must be accepted with caution. On the whole, the experimental evidence favours the existence of a Q branch, and we shall assume this to be the case. At a pressure of approximately 630 mm., 45 cm. of ClO_2 absorbed approximately 50 per cent. of the incident radiation.

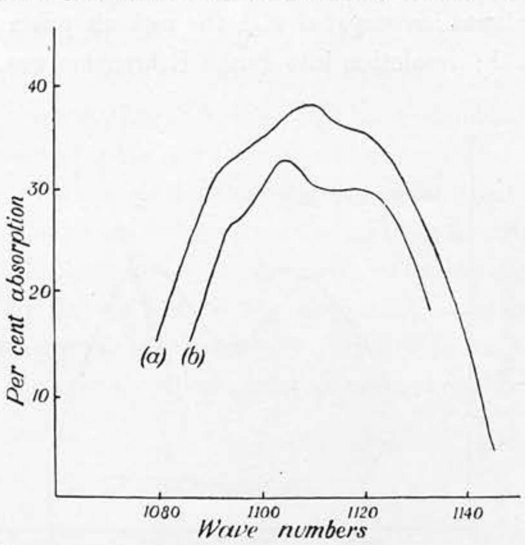

FIG. 3.

Band F.—4·916 μ, $\nu_1 + \nu_3 = 2034$ cm.$^{-1}$. No resolution was obtained with the fluorite prism, but it is hoped to reinvestigate the contour with a grating instrument. It is a summation tone, and once again the shape is of importance for the structure of the molecule. At 630 mm. the maximal absorption was approximately 90 per cent., the slits containing 10 cm.$^{-1}$.

The Molecules of ClO_2 and SO_2: Qualitative Discussion.

The outstanding feature of the spectra of the two substances is their very close similarity. This is clearly indicated in fig. 4, which shows the positions and approximate intensities of the bands in the two spectra, together with the resolution so far achieved. The SO_2 and ClO_2 bands at 525 and 527 cm.$^{-1}$ have not been completely observed in the infra-red and no estimate of their relative intensities can be given. Part II of the present series reports a band at 606 cm.$^{-1}$ for SO_2 and this was adopted by us as a fundamental frequency; it seems probable that this is to be interpreted as $\nu_3 - \nu_2$; the envelope reproduced on p. 144 of that communication indicates that the absorption falls to some low value at about 18 μ; this is precisely the long wave limit of the apparatus, and consequently too great stress is not to be laid upon either the shape of the envelope or the maximal separation observed. The work of Strong* in the far infra-red shows that considerable absorption exists beyond this point, and the most reasonable value for the long wave fundamental from measurements of the Raman spectrum by Dickinson and West,† and others, and from the ultra-violet by Henri,‡ seems to be 525 cm.$^{-1}$. The corresponding value for ClO_2 of 527 cm.$^{-1}$ is taken from Goodeve and Stein, and from Urey and Johnston (*loc. cit.*).

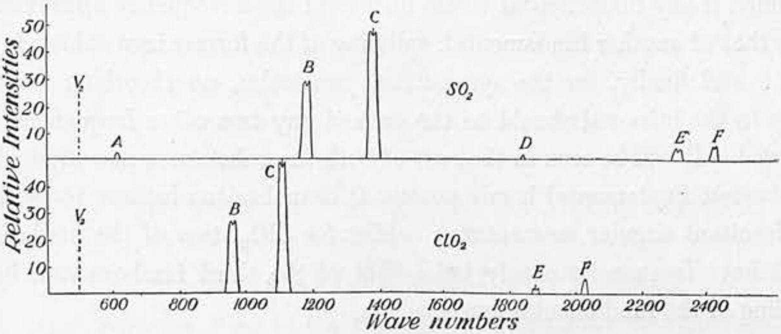

FIG. 4.

As we propose to utilise the great similarity between these two spectra to amplify and correct our earlier results for SO_2, we will emphasise this feature by referring once more to fig. 4; the relative intensities of the observed bands for the two substances show that for both of them, a column of gas 45 cm. long and at the same pressure absorbs the same percentage of the incident radiation for any given mode. The agreement is carried through into the contours of the bands.

These contours are determined by the orientation of the electric doublet,

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* 'Phys. Rev.,' vol. 37, p. 1484 (1931).

† 'Phys. Rev.,' vol. 35, p. 1126 (1930).

‡ See Placzek, 'Ber. sächs. Ges. (Akad.) Wiss. Leipzig, vol. 84, p. 98 (1931).

effective in the vibration concerned, relative to the different axes of the various moments of inertia of the molecule. For SO_2 the observed envelopes have been shown to be consistent with a triangular structure, and we are justified in assuming a similar construction for the ClO_2 molecule. The assumption of the triangular form is also supported by other evidence : for SO_2 by the high value of the permanent dipole moment, by the Kerr effect as shown by Stuart,* and by the presence of lines corresponding to all three fundamentals in the Raman spectrum ; for both molecules by the absence from their infra-red spectra of the peculiarities characteristic of the rectilinear triatomic molecules CO_2, CS_2 and SCO. For such substances we expect the following features: if the resultant electronic angular momentum be zero, only the longest wave-length fundamental should have a Q branch, and this should be of low intensity. Secondly, if any fundamental vibrational level has a frequency approximately twice that of another fundamental, splitting of the former into sublevels takes place ; and finally, for the symmetrical molecules, no absorbing frequency active in the infra-red should be the sum of any two other frequencies there observed. It will be seen in the case of both the substances now studied that the shortest fundamental bands possess Q branches too intense to be due to any resultant angular momentum ; whilst for ClO_2, two of the fundamental bands have frequencies nearly twice that of the third fundamental, but no doubling of the fundamental levels occurs.

Constants of the Triatomic Molecule.

Taking the triangular structure of the two substances as qualitatively established, we will now determine the various molecular constants, and of these we will first consider the vertical angles. The normal modes of vibration of the atoms in a molecule of type XY_2 have been evaluated by a number of workers.† Assuming the triangle to be isosceles, and the force constants for the two equal sides to be equal, we have two distinct vibrating systems to be discussed, namely, one in which a central restoring force acts between the base particles, and another where this restoring force is replaced by a restoring couple acting about an axis normal to the plane of the triangle and passing through the vertex. In both systems central restoring forces act between the mass at the vertex of the triangle and either mass at the base. We propose to apply Bjerrum's calculations to the observed spectra, and to show how the

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* 'Z. Physik,' vol. 55, p. 358, and vol. 59, p. 13 (1929).

† See III, 'Proc. Roy. Soc.,' A, vol. 132, p. 245 (1931).

lengthy computations demanded by the normal method of application may be considerably shortened.

Bjerrum takes as the three representative co-ordinates the projections of the extensions of either side on the original direction of side ; these appear to be the simplest and, using them, Radakovic has deduced for a system of central forces expressions for the normal frequencies and modes in the general case of three unequal masses at the vertices of a scalene triangle. Sidgwick* repeats the original suggestion of Langmuir that sulphur dioxide has the structure $O = S - O$; this would necessitate unequal force constants and presumably unequal sides to the triangle. This is believed to be the case with NO_2, but the heats of linking of the two oxygen atoms differ very greatly, much more so than for SO_2. The experimental results for the latter substance are satisfied by the simpler assumption, and we shall restrict ourselves to this.

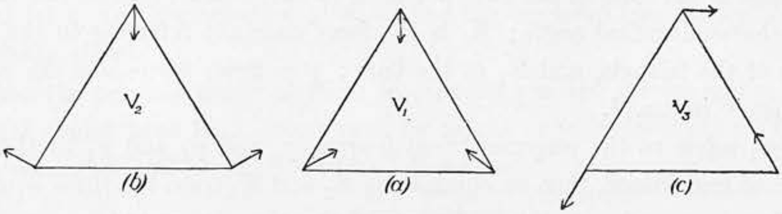

Fig. 5.

There are, corresponding to the three degrees of vibrational freedom, three normal modes, two of which are symmetrical about the bisector of the vertical angle, and a third unsymmetrical about this line, fig. 5. We shall refer to these as the symmetrical and unsymmetrical modes respectively, and, in conformity with Dennison's classification,† characterise them as ν_1, ν_2, ν_3.

The frequency equation from which the semi-vertical angle and the force constants are deduced is a cubic in the squares of the normal frequencies ; relations between the roots of the equation and its coefficients give three equations that determine the three above unknowns. These equations as usually written are cumbersome, and the arithmetical calculations involved are readily susceptible to error. Furthermore, there is normally no indication from the experimentally observed frequencies as to which is the unsymmetrical, and the general method for its determination is to try each of the three frequencies in turn, and to note which of the three gives real solutions for the required quantities. When the complete Raman spectrum is available, it is possible to

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* 'Ann. Rep. Chem. Soc.,' p. 400 (1931).

† 'Rev. Mod. Phys.,' vol. 3, p. 289 (1931).

apply the selection rules deduced by Placzek (*loc. cit.*); if, of the two short wave fundamentals, one is symmetrical and the other unsymmetrical, the more intense scattered line is to be attributed to the former. We shall revert to this point below. The simplest method of determining possible unsymmetrical frequencies is to eliminate the force constants, and so obtain an equation for the semi-vertical angle; the correct unsymmetrical frequency is that which gives a real value for this angle.

The frequency equation for the central force system may be written

$$\left[p^2 - \mathrm{K}_1\left\{\frac{1}{m} + \frac{2}{\mathrm{M}}(\sin^2\alpha)\right\}\right]\left[p^4 - \left\{\frac{2\mathrm{K}_2}{m} + \frac{\mathrm{K}_1}{m} + \frac{2\mathrm{K}_1}{\mathrm{M}}\cos^2\alpha\right\}p^2 + \frac{2\mathrm{K}_1\mathrm{K}_2}{m^2}\left(1 + \frac{2m}{\mathrm{M}}\right)\cos^2\alpha\right] = 0, \quad (1)$$

where m is the mass of the base particles, M the mass of that at the vertex; α is the semivertical angle; K_1 is the force constant referring to the equal sides of the triangle, and K_2 to the base; $p = 2\pi\nu c$, where ν is the normal frequency in cm.$^{-1}$.

If p_3 refers to the unsymmetrical frequency, and p_1 and p_2 to the symmetrical frequencies, then on eliminating K_1 and K_2 from the three equations relating p_1, p_2 and p_3 to the coefficients of equation (1), we obtain

$$\left[\frac{4}{\left(1+\frac{2m}{\mathrm{M}}\right)}\cdot\frac{m^2}{\mathrm{M}^2}\cdot\frac{p_1{}^2p_2{}^2}{p_3{}^2} + \frac{2m}{\mathrm{M}}(p_1{}^2 + p_2{}^2 + p_3{}^2)\right]\sin^4\alpha$$
$$+\left[\frac{4}{\left(1+\frac{2m}{\mathrm{M}}\right)}\cdot\frac{m}{\mathrm{M}}\cdot\frac{p_1{}^2p_2{}^2}{p_3{}^2} + \left(1-\frac{2m}{\mathrm{M}}\right)(p_1{}^2+p_2{}^2+p_3{}^2) - 2\left(1+\frac{m}{\mathrm{M}}\right)p_3{}^2\right]\sin^2\alpha$$
$$+\left[\frac{1}{\left(1+\frac{2m}{\mathrm{M}}\right)}\cdot\frac{p_1{}^2p_2{}^2}{p_3{}^2} - (p_1{}^2 + p_2{}^2 + p_3{}^2) + 2\left(1+\frac{m}{\mathrm{M}}\right)p_3{}^2\right] = 0, \quad (2)$$

which is an equation determining α. It is convenient to handle, since large multiples of 10 are eliminated, and the observed frequencies are readily interchanged.

For the valence force system we have as frequency equation

$$\left[p^2 - \mathrm{K}_1\left\{\frac{1}{m} + \frac{2}{\mathrm{M}}\sin^2\alpha\right\}\right]\left[\frac{m}{2}p^4 - \left[\left\{\left(1 + \frac{2m}{\mathrm{M}}\sin^2\alpha\right)\cos^2\alpha\right\}\mathrm{K}' + \left(\tfrac{1}{2} + \frac{m}{\mathrm{M}}\cos^2\alpha\right)\mathrm{K}_1\right]p^2 + \mathrm{K}_1\mathrm{K}'\left(\frac{1}{m} + \frac{2}{\mathrm{M}}\right)\cos^2\alpha\right] = 0, \quad (3)$$

where m, M, K_1 and α are as in equation (1), and

$$K' = \frac{K_\theta}{4\cos^2\alpha}.$$

K_θ is the tangential restoring force per unit arc displacement of the vertical angle, that is, the potential energy due to a displacement $d\theta$ of this angle is $\frac{1}{2}K_\theta l^2 (d\theta)^2$, where l is the length of either equal side. Performing the operations on equation (3) that we applied to equation (1), we have

$$\frac{p_1^2 p_2^2}{p_3^2}\cdot\frac{x^3}{1+\frac{2m}{M}} - (p_1^2+p_2^2+p_3^2)\,x + 2p_3^2\left(1+\frac{m}{M}\right) = 0, \tag{4}$$

where $x = 1 + \frac{2m}{M}\sin^2\alpha$. (4) is a cubic of reduced form to be numerically solved for x, and permutation of p_3 among the observed frequencies is comparatively simple.

When the possible unsymmetrical frequencies and the corresponding semi-vertical angles have been determined by means of formulæ (2) and (4), the force constants can be calculated as follows :—

$$K_1 = \frac{m p_3^2}{\left(1+\frac{2m}{M}\sin^2\alpha\right)}, \tag{5}$$

$$K_2 = \frac{m}{2}(p_1^2+p_2^2) - \frac{\left(1+\frac{2m}{M}\cos^2\alpha\right)}{2}\,K_1, \tag{6}$$

$$K_\theta = 2\,\frac{p_1^2 p_2^2}{p_3^2}\cdot\frac{m\left(1+\frac{2m}{M}\sin^2\alpha\right)}{\left(1+\frac{2m}{M}\right)}. \tag{7}$$

It should be noticed that equation (5) determines K_1 for both the central and valence force systems.

The Molecules of ClO_2 and SO_2: Quantitative Discussion.

On applying the above considerations to the observed spectra for SO_2 and ClO_2, we obtain the molecular characteristics displayed in Tables II (*a*) and (*b*); these give the possible unsymmetrical frequencies with their corresponding semi-vertical angles, and the force constants for the two systems.

Table II.

(*a*) Central Force System for SO_2 and ClO_2.

Molecule.	Possible unsymmetrical frequency ν_2.	Semi-vertical angle.	K_1.	K_2.
	$cm.^{-1}$	°	dynes/cm. $\times 10^{-5}$	dynes/cm. $\times 10^{-5}$
SO_2	1152	32	9·6	1·7
SO_2	1152	57	7·25	5·2
ClO_2	946	33	6·7	1·8
ClO_2	946	48	5·7	3·0

(*b*) Valence Force System for SO_2 and ClO_2.

SO_2	1152	32	9·6	4·6
SO_2	1361	61	9·8	3·3
ClO_2	946	29	6·7	4·5
ClO_2	1109	70	6·1	3·6

The problem now is to determine which of these solutions is consistent with other observed data, and in effect to decide between the acute and obtuse angled triangles. At this point we can stress another similarity between the two molecules ; the electronic band spectra have been explored in the ultra-violet region, for SO_2 recently by Watson and Parker,* and for ClO_2 as already cited. The two spectra are very much alike ; in particular, in both cases the plot of the frequency difference between successive band heads against integers gives a straight line up to a definite integer, when the curve breaks to a second straight line inclined to the first. This phenomenon is of very rare occurrence, and Urey has attributed this discontinuity to the swinging of the isosceles triangle with a large vertical angle through a linear model to a second isosceles triangle with an acute vertical angle, the former corresponding to the ground electronic state. However, as we have seen, this hypothesis depends upon the assumption of incorrect values for the fundamental frequencies, and we have consequently no definite evidence from the ultra-violet upon the size of the vertical angle ; the remaining data from the infra-red provide (i) the relative intensities of the observed bands, and (ii) the contours of the envelopes, which indicate the presence or absence of a Q branch. We shall consider the latter feature in some detail.

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* 'Phys. Rev.,' vol. 37, p. 1484 (1931).

In Part II, the presence or absence of Q branches was shown to depend upon the orientation of the electric doublet effective in a given vibration relative to the axes of the three moments of inertia, and quantum mechanical investigations (Dennison, *loc. cit.*) give this orientation for the fundamental and combination tones. The results may be summarised thus: if the frequency of any observed infra-red band be given by $(n_1\nu_1 + n_2\nu_2 + n_3\nu_3)$, where ν_1 and ν_2 are the frequencies of the symmetrical modes, fig. 5, *a* and *b*, and ν_3 is the frequency of the unsymmetrical mode, fig. 5, *c*, then the electric doublet effective in the vibration is parallel to the bisector of the vertical angle when n_3 is even, and normal to this line when n_3 is odd; n_1 and n_2 may assume any value, and when n_3 is zero the effective doublet is always parallel to this bisector. Knowing the orientation relative to the bisector, we also know it with regard to the axis of least inertia, since this is either parallel or perpendicular to the former. Which of these cases holds depends finally upon the vertical angle and upon the masses of the atoms composing the molecule. The three moments of inertia are $A < B < C$, and since we are dealing with a plane molecule, $A + B = C$. Furthermore, the moment of inertia about the bisector of the vertical angle 2α is $2ml^2 \sin^2 \alpha$, and that about an axis perpendicular to this line, passing through the centre of mass, and lying in the plane of the triangle is $(2mM/(M + 2m))l^2 \cos^2 \alpha$. Hence the axis of least inertia will be parallel or perpendicular to the bisector of the vertical angle according as $(M/(M + 2m)) \cos^2 \alpha >$ or $< m \sin^2 \alpha$, *i.e.*, as $\tan^2 \alpha <$ or $> M/(M + 2m)$. For SO_2 and ClO_2 the critical value is found to be 35°. Hence if α is less than this value, the axis of least inertia is parallel to the bisector of the vertical angle, and perpendicular to it if α is greater than 35°.

This inequality, together with the selection rules derived from quantum mechanics and quoted above, gives the orientation of the electric doublet effective in the various bands relative to the axes of inertia for the various possible models. These are summarised in Table III; where the direction of vibration of the doublet is shown as either parallel or perpendicular to the least axis of inertia, since for the planar molecule there can be no vibrating doublet along the axis of greatest inertia, Table III specifies the orientation completely.

In the discussion in Part II referred to above, we also deduced qualitatively that if the effective electric doublet be perpendicular to the axis of least inertia, the observed band should consist only of P and R branches, whilst if the doublet be parallel to this axis, the band should show a Q branch in addition; this

Table III.—The Orientation of the Effective Electric Doublet relative to the Least Axis of Inertia for the various possible Molecular Models of SO_2 and ClO_2.

(*a*) The unsymmetrical frequency ν_3 is taken as 1152 and 946 cm.$^{-1}$ respectively.

Band.	Mode.*	Frequency.		Force system.			
		SO_2.	ClO_2.	Central.		Valence.	
				$\alpha < 35°$	$\alpha > 35°$	$\alpha < 35°$	$\alpha > 35°$
		cm.$^{-1}$	cm.$^{-1}$				
C	ν_1	1361	1109	Parallel	Perpendicular	Parallel	No solution
—	ν_2	524	527	,,	,,	,,	,,
B	ν_3	1152	946	Perpendicular	Parallel	Perpendicular	,,
A	$\nu_3 - \nu_2$	606	—	,,	,,	,,	,,
D	$\nu_1 + \nu_2$	1871	—	Parallel	Perpendicular	Parallel	,,
E	$2\nu_3$	2305	1184	,,	,,	,,	,,
F	$\nu_1 + \nu_3$	2499	2034	Perpendicular	Parallel	Perpendicular	,,

(*b*) The unsymmetrical frequency ν_3 is taken as 1361 and 1109 cm.$^{-1}$ respectively.

B	ν_1	1152	946	No solution	No solution	No solution	Perpendicular
—	ν_2	524	527	,,	,,	,,	,,
C	ν_3	1361	1109	,,	,,	,,	Parallel
A	$\nu_1 - \nu_2$	606	—	,,	,,	,,	Perpendicular
D	$\nu_2 + \nu_3$	1871	—	,,	,,	,,	Parallel
E	$2\nu_1$	2305	1884	,,	,,	,,	Perpendicular
F	$\nu_1 + \nu_3$	2499	2034	,,	,,	,,	Parallel

* See fig. 5, p. 629.

criterion has been quantitatively investigated by Dennison with the aid of the quantum mechanics, and he arrives at the same conclusion.

In applying these principles to the observed spectrum, it must be remembered that the accuracy of the deduction depends upon the degree of resolution obtainable, and that further examination by a grating spectrometer is necessary before finality is reached. Meyer, Bronk and Levin* explored band F in this way, and found no evidence of a Q branch of any intensity, while our own results for band B in both SO_2 and ClO_2 show P and R branches only. Table III renders this consistent with a vertical angle of less than 70° on both the force systems; the envelopes of band C are identical for the two substances,

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* 'J. Opt. Soc. Amer.,' vol. 15, p. 257 (1927).

and although complete resolution has not been attained, nevertheless the available evidence points to the existence of a powerful Q branch, thus denying the possibility of a central force system with vertical angle greater than 70° if C is a symmetrical frequency. On the other hand, the valence force system with the larger angle permits the presence of this Q branch when band C is taken as the unsymmetrical frequency. Now band E for ClO_2 occurs at some 400 $cm.^{-1}$ on the longer wave side for the corresponding band for SO_2 and the resolution obtained for the former is slightly better; the envelope shows traces of a Q branch in this band for ClO_2 which may be concealed in the broad P branch of the SO_2 band. If this is so, the only possible solution demands a central force system with an angle α of $< 35°$.

While the present work has been in preparation, Dadieu and Kohlrausch* have published a paper on the Raman effect and molecular structure of simple triatomic molecules. They adopt the obtuse angled triangle for SO_2, with 1361 $cm.^{-1}$ as the unsymmetrical frequency, and suggest that the Q branch observed by us in this band is due to the presence of water vapour. Whenever we have obtained the water vapour band in this region, we have always obtained easy resolution of the band into the two widely separated maxima; furthermore, the corresponding ClO_2 band has exactly the same shape but occurs some 260 $cm.^{-1}$ on the long wave side at 1109 $cm.^{-1}$. However, reference to Table III will show that the structure put forward by Dadieu and Kohlrausch requires the presence of a Q branch, and the suggestion of the presence of an impurity is thus inconsistent with their own deductions.

Dennison has demonstrated that the fine structure of the vibration-rotation bands in the infra-red is intimately bound up with the numerical ratio of the least to the intermediate moment of inertia, and some estimate of the shape of the envelope for a given band can be made from the extremely useful chart in his paper; this shows the variation in the fine structure as the above ratio changes from unity to zero. When the vertical angle is 35°, the two smaller moments are equal and our molecules are symmetrical tops; in that case the bands B and C would show the same envelope, contrary to observation. If A/B is $0 \cdot 65$ ($\alpha = 30°$), the chart indicates that band C should possess a considerable Q branch, while band B should have none. These points are emphasised to illustrate the considerable change to be expected in the spectrum for comparatively small changes in the vertical angle.

The degree of resolution obtained in the case of ClO_2 is, with the exception

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* 'Phys. Z.,' vol. 33, p. 165 (1932).

noted, not so satisfactory as in the previous work on SO_2. The slightly coarser outline of the bands is perhaps to be attributed to the isotope effect, and although it is not sufficient to produce any actual separation of maxima for the dioxide, it may well produce a broadening of the bands, and so render the observed maxima less distinct. In the case of the monoxide the effect may be expected to be considerable for certain bands.

Molecular Dimensions.

When Part II of the present series was written, in default of other evidence, band A at 606 cm.$^{-1}$ was chosen as a fundamental frequency; the existence of a frequency difference of this value had been previously recognised by Coblentz,* and peculiarly enough in two cases where we had failed to isolate the bands. The temptation to adopt this as a fundamental frequency was too great, and the assumption that the separation of 9 cm.$^{-1}$ observed corresponded to the greatest moment of inertia led to abnormally large values for the interatomic distances. Probably no great reliance is to be placed on the observed separation since the readings were taken at the extreme limit of usefulness of the spectrometer. The maximal P and R branch separations recorded for the other bands prove to be the same for both molecules. We accordingly have to associate these more accurately observed separations with the moments of inertia concerned; for this we must have recourse once more to the considerations propounded by Dennison in the paper cited.

We have seen that if the semi-vertical angle is 35°, the molecules become symmetrical tops with electric doublets vibrating in the plane normal to the symmetry axis or axis of greatest inertia, and observed bands have only P and R branches, while the separation of the two maxima corresponds to the greatest moment of inertia. Reference to Dennison's paper and to those of Kramers and Ittmann† shows that a top whose motions are governed by quantum mechanics behaves differently from a top moving according to classical mechanics; in particular, as the top changes from a symmetrical to an asymmetrical rotator, there is no abrupt change in its motions such as was demanded by the older system,‡ where the top may spin about its axis of greatest or of least inertia, and where its motions depend upon the axis of spin. According to the new system, the transitions for an asymmetrical top

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* "Investigations of Infra-red Spectra," Part I, p. 52.

† 'Z. Physik,' vol. 60, p. 663 (1930); *et ante.*

‡ Bailey, Cassie and Angus, 'Trans. Faraday Soc.,' vol. 26, p. 197 (1930).

change continuously from the limit where the smaller moments of inertia are equal to that where the least moment of inertia vanishes. At the first limit observed bands have only P and R branches whose separation gives the greatest moment of inertia, and at the second limit the band due to vibrations of the doublet parallel to the least axis of inertia has P and R branches with a Q branch vanishing because of the Boltzmann factor, whilst that due to vibrations parallel to the intermediate axis of inertia consists of lines which tend to become infinitely far apart, the separation corresponding to the vanishing least moment of inertia. Hence near the first limit the P and R branches approximate to those of a diatomic molecule whose moment of inertia equals the greatest moment for the triangular molecule. Near the second limit, the band due to vibrations parallel to the intermediate axis will have separations corresponding to those of a diatomic molecule with a moment of inertia equal to the least moment for the triatomic.

The models deduced for ClO_2 and SO_2 approximate to the first limit, and the P and R branch separation should give a moment of inertia rather less than the greatest. The frequency difference of 30 $cm.^{-1}$ corresponds to a moment of inertia of $4 \cdot 7 \times 10^{-39}$ g. $cm.^2$; if this were the greatest moment and the vertical angle 60°, the length of each side of the triangle would be 1·2Å. Wierl[*] using the electron diffraction method, found that the sulphur and oxygen nuclei in SO_2 were separated by 1·37 Å., and this value is consistent with the qualitative infra-red estimate of slightly greater than 1·2 Å. It is interesting to compare these measurements with the interatomic separation in sulphur monoxide, SO; Henri and Wolff obtained the rotational fine structure of this substance in the ultra-violet,[†] and found 1·34 Å. for this distance.

The same dimensions may be expected to hold good for the chlorine compound. The spectroscopic similarity leads one to enquire whether the phenomenon persists in other physical properties; we find the melting points, boiling points, surface tensions, and molecular volumes, of the ascertainable physical data, much the same in both cases. The cause of the similarity is probably to be found in the electronic structure of the two substances. The "odd" electron in the chlorine compound confers paramagnetic properties upon the dioxide, and is presumably responsible for its chemical instability; it appears, however, to be incorporated in the structure in such a way that,

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[*] 'Phys. Z.,' vol. 31, p. 1028 (1930).

[†] 'J. Phys. Radium,' vol. 10, p. 81 (1929).

although necessarily unpaired, it takes no part in structure formation, and the two substances are almost isosteres.

The recent work of Slater,* Pauling,† and Hund‡ exemplifies the quantum and wave mechanical significance of directed valence. Hund has extended and modified the conception; directed valences, equivalent to the valence stroke as written by chemists, are characterised by localisation of the electronic proper-functions concerned; he shows that localisation is obtained if there exist proper-functions of single electrons from each atom for binding purposes, and also sufficient electrons to fill the resulting proper-functions of the molecule. The most important case of non-localised bonds then arises when the electrons present are too few to satisfy each possible directed bond with two electrons. Hund's paper should be consulted for examples, but the general procedure in molecule formation is as follows: if localised bonds are possible, σ bonds take energetic preference over π bonds, while a double bond in all cases is a $\sigma\pi$ bond; the subsequent formation of triple bonds and the various spatial arrangements need not be discussed here, but it may be pointed out that when, for example, in a q^4 atom space considerations such as occur in the cyclo-paraffins prevent the formation of localised bonds, these are replaced by non-localised bonds with a smaller stability betrayed in a larger heat of combustion. In other cases where we have an electron deficiency we may have localised σ bonds with superimposed non-localised π bonds. In the case of sulphur dioxide, where for each atom, two electrons are lacking from a complete outer shell, the "holes" may be treated as electrons,§ the energy expression being the same as for the presence of two electrons outside a closed shell. The simplest picture of the formation of the molecule from the individual atoms would then suppose the formation of a σ bond between the sulphur and each oxygen atom, thus involving four "electrons" of probably the (2, 1, 0) type; the remaining electrons on the oxygen atoms (one each, of (2, 1, 1) or (2, 1, −1) type) may be deemed to occupy a proper-function giving a non-localised π bond. Proper-functions for two double bonds, which would consist each of a localised σ and a localised π bond, cannot be obtained from the two "electrons" of the sulphur, and would apparently necessitate a rectilinear structure in any case. The first structure suggested meets with confirmation from the value

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* 'Phys. Rev.,' vol. 37, p. 481, and vol. 38, p. 1109 (1931).

† 'J. Amer. Chem. Soc.,' vol. 53, p. 1367, and p. 3237 (1931).

‡ 'Z. Physik,' vol. 73, p. 1, and p. 565 (1931).

§ Heisenberg, 'Ann. Physik,' vol. 10, p. 888 (1931).

of the force constant K_1, which is approximately 9×10^5 dynes/cm., intermediate between the values for a single and a double bond.

Turning to the chlorine compound, we have five holes of a *p* type to allocate; it is important to note that in the allotment of electrons to the molecular proper-functions we must consider the molecule as a whole, and fill up the proper-functions with the available electrons; this procedure renders it likely that we have σ type single bonds between the chlorine atom and each oxygen, while the odd electron incompletely fills a non-localised proper-function, and thus accounts for the instability of the substance. The force constant is approximately 6×10^5 dynes/cm., and confirms the choice of the single bond plus an incompletely filled non-localised proper-function.

Reverting finally to the preference of the acute over the obtuse angled structure, we would emphasise that the choice of the former rests upon the assumptions that Dennison's selection rules are correct and that complete resolution has been obtained in the critical bands; the equilateral triangle also seems the most plausible structure for a triatomic molecule with a non-localised proper-function, and gives the correct interatomic separation, whereas the obtuse angled form gives a distance of some 2·3 Å. between the sulphur and oxygen atoms. Against this interpretation we have to set the fact that band B is the most intense in the Raman spectrum, and Placzek's selection rules indicate this as the symmetrical frequency of the two short wave fundamentals, while the change of electric moment, and consequently the intensity in the infra-red, is usually greatest for the unsymmetrical frequency, which should then be band C. It is possible that the introduction of the non-localised proper-function may contravert Placzek's rules, and we have in addition little knowledge of the actual amplitudes of vibration in the various fundamentals. Because of the difficulty of reconciling the diverse evidence, it may be best to leave the question open and to summarise the two possible structures as in Table IV. We have recently completed an examination of the infra-red absorption spectrum of chlorine monoxide, and propose to leave any discussion of the thermochemistry of the dioxide until we can collate the results for the two substances.

Summary.

(1) The infra-red absorption spectrum of chlorine dioxide has been examined and compared with that of sulphur dioxide.

(2) The two substances are spectroscopically and physically alike, and have similar structures.

Table IV.—The Molecular Characteristics of SO_2 and ClO_2 for the Acute and Obtuse Angled Forms.

(*a*) The Acute Angled Structure.

(Central forces provide the possible solution in each case.)

SO_2.		ClO_2.	
Fundamental frequencies.	Force constants.	Fundamental frequencies.	Force constants.
cm^{-1}. $\nu_1 = 1361$ $\nu_2 = 524$ $\nu_3 = 1152$	$\times 10^{-5}$ dynes/cm. K_1 9·6 (S – O) K_2 1·7 (O – O)	cm.$^{-1}$ $\nu_1 = 1109$ $\nu_2 = 527$ $\nu_3 = 946$	$\times 10^{-5}$ dynes/cm. K_1 6·7 (Cl – O) K_2 1·8 (O – O)
$\widehat{OSO} = 60°$; S–O and O–O = 1·37 Å.		$\widehat{OClO} = 60°$; Cl–O and O–O = 1·4 Å.	

(*b*) The Obtuse Angled Structure.

(Valence forces provide the possible solution in each case.)

cm.$^{-1}$ $\nu_1 = 1152$ $\nu_2 = 524$ $\nu_3 = 1361$	$\times 10^{-5}$ dynes/cm. K_1 9·6 (S – O) K_θ 3·3 (O – O)	cm.$^{-1}$ $\nu_1 = 946$ $\nu_2 = 527$ $\nu_3 = 1109$	$\times 10^{-5}$ dynes/cm. K_1 6·7 (Cl – O) K_θ 3·6 (O – O)
$\widehat{OSO} = 122°$; S–O = 2·3 Å., O–O = 3·9 Å.		$\widehat{OClO} = 140°$; Cl–O = 2·4 Å., O–O = 4·2 Å.	

(3) The available evidence permits of two possible structures with vertical angles of approximately 60° and 120° respectively, the weight of probability being slightly in favour of the acute angled form.

(4) The electronic structure has been discussed, and values for the molecular characteristics have been derived.

The authors gladly acknowledge the kindly interest and encouragement they have received from Professor F. G. Donnan, F.R.S., and the help and advice in the preparation of chlorine dioxide from Miss J. I. Wallace and Mr. C. F. Goodeve. The work in Parts V and VI was carried out while A.B.D.C. was in possession of a senior award from the Department of Scientific and Industrial Research, for which the authors tender their grateful acknowledgments.

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Investigations in the Infra-Red Region of the Spectrum. Part VII.—*An Infra-Red Grating Spectrometer as a Double Monochromator.*

BY A. B. D. CASSIE AND C. R. BAILEY.

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Investigations in the Infra-red Region of the Spectrum. Part VII.—*An Infra-red Grating Spectrometer as a Double Monochromator.*

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Part IV of the present series* describes a monochromator method for use in the infra-red region of the spectrum. The monochromator consisted of a single prism spectrometer with the absorption tubes placed between the telescope slit and the thermopiles, instead of the more usual disposition with the tubes between the Nernst filament and the collimator slit. The advantages of the method over the ordinary lay out are :—(i) double absorption tubes can be used and left permanently in position ; (ii) the introduction of stops can considerably reduce the quantity of scattered radiation of shorter wave-length reaching the thermopiles ; and (iii) only a small range of infra-red radiation traverses the gas under examination. The apparent disadvantage of the method is an increase in the number of reflections suffered by the infra-red beam, and a resultant loss in intensity ; in practice, however, it is found that this loss is small, and at shorter wave-lengths the same slit width was used as in the older method. As a consequence we decided to design a grating spectrometer for use as a double monochromator, and the present paper describes the instrument, with the method of use.

The Spectrometer.

The final arrangement is shown in fig. 1. The essential departure from the grating spectrometer constructed by Sleator† lies in the use of two mirrors in the spectrometer proper, instead of one. As was pointed out by Czerny,‡ in the simpler case, the error introduced in the image of the collimator slit on collimation of the beam will be approximately doubled when the reflected parallel beam is converged by the collimating mirror to form an image near the collimator slit ; if, however, two mirrors are used with the collimator slit on one side of the grating, and the telescope slit on the other, then the error introduced on collimation of the beam is approximately reduced to zero when

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* 'Proc. Roy. Soc.,' A, vol. 132, p. 252 (1931).

† 'Astrophys. J.,' vol. 48, p. 125 (1918).

‡ 'Z. Physik,' vol. 61, p. 792 (1930).

the reflected parallel beam is converged on the telescope slit by the second mirror. Czerny showed experimentally that this was so, and that considerably improved images are obtained by using separate collimator and telescope mirrors. In fig. 1, M_4 and M_5 are the collimator and telescope mirrors respectively, and S_2 and S_3 their accompanying slits. The image of S_2 at S_3 obtained with the two-mirror system proved to be very good over even long

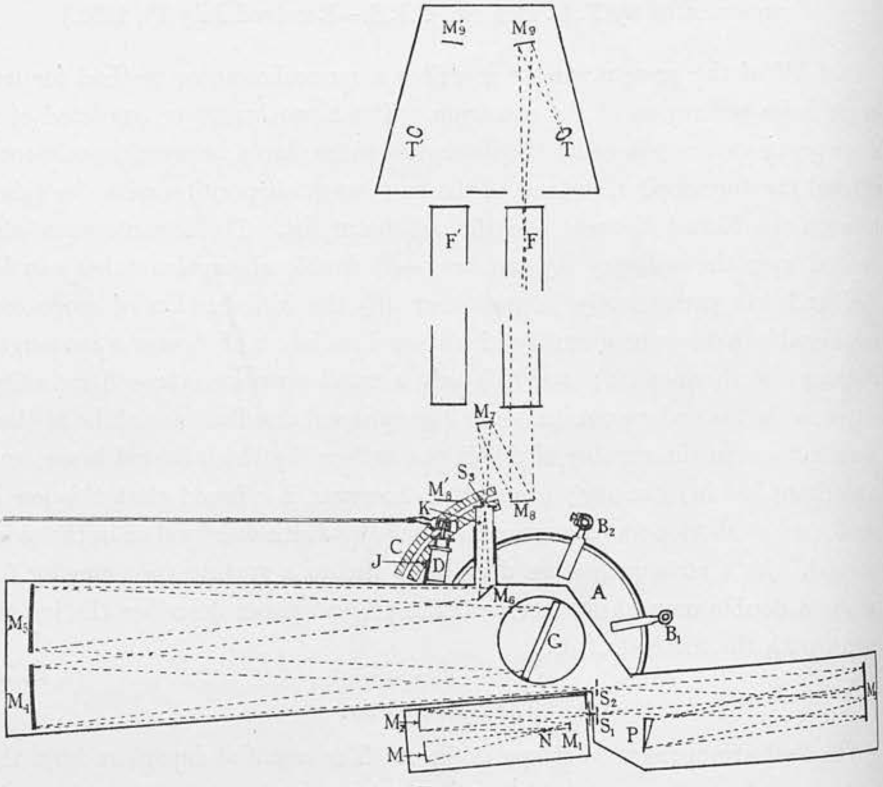

FIG. 1.

slit lengths, and the Hilger symmetrical slits were opened to their full aperture, 0·8 inch, instead of the usual 0·4-inch aperture.

The fore prism spectrometer has a focal length one half that of the grating spectrometer (16 inches and 32 inches respectively), so that the side of the prism need only be one-half the length of the rulings on the grating. We are indebted to Professor E. O. Salant, of New York University, for suggesting the focal lengths and mirror apertures used. The latter are of stainless steel, and of aperture 4 inches diameter; they were made by Zeiss.

The general design is straightforward; radiation from a Nernst filament, N, is reflected in the mirror M_1 and converged on to the collimator slit of the fore prism spectrometer by M_2. M serves as a backing mirror that increases the solid angle of radiation passing from the filament to the first slit of the spectrometer. It is the image of N in M_1, instead of N itself, which is converged on the first slit; this device increases the available distance between N and M_2, and facilitates orientation of the backing mirror to give a cone of radiation coincident with that falling on M_2 and converging on S_1 from N.

The radiation diverges from S_1 to M_3, and is there collimated and reflected towards an 18° rocksalt prism, P. The back surface of this prism is platinum sputtered, and this mirror reflects the radiation through the prism to M_3, which now converges it to S_2, the collimator slit of the grating spectrometer. The prism was obtained from Messrs. Steeg & Reuter, of Bad Homburg, Germany; it is mounted on a theodolite circle readable to 30 seconds of arc. From S_2 the radiation diverges to M_4, which collimates it and reflects it towards the grating, G. The only grating available was an echelette of 3600 lines per inch reflecting in the direction of the first order spectrum between 3·5 and 4 μ; it was ruled by R. W. Wood on a chromium-plated copper blank, the rulings being approximately 3 inches in length and extending over 4 inches. It is mounted on another theodolite circle readable to 1 second of arc; it is a standard circle of Messrs. E. R. Watts & Son, London, and we are much indebted to this firm for redesigning the mountings to suit this spectrometer. From the grating the parallel beam passes towards M_5, and is converged towards M_6, which reflects it to the telescope tubing which slides in a second tube firmly fixed to the spectrometer casing. This helps the focussing of the image of S_2 on S_3.

Absorption Tubes and their Mirrors.

From S_3 the radiation diverges to the mirror M_7, which is the mirror M_3 of the monochromator described in Part IV (*loc. cit.*). One important modification of the apparatus described in that paper was found necessary; the grating spectrometer has slits 0·8 inch long, as compared with slits of 0·4 inch used in the prism spectrometer; hence radiation diverging from the image F filled much more than the $1\frac{3}{4}$-inch aperture of the end plates of the absorption tube; this difficulty was overcome by bringing the image, F, to a point near this end plate, and using a larger aperture mirror, M_9, to converge the radiation on to the thermopile. The rapid divergence of the extreme rays is shown in fig. 2. O is an object illuminated by a cone of radiation whose solid angle is defined by the extreme rays intersecting a mirror, R, at A and B; these converge towards I as shown, one extreme ray crossing the axis at C, and the other passing directly to one end of I; the solid angle of radiation diverging from I is therefore defined by the lines drawn from C to either extremity of I, and the angle may be considerable. The position of I is accordingly adjusted so that the absorption tubes occupy a position KLMN relative to I.

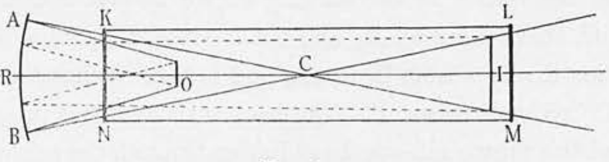

FIG. 2.

Spectrometer Casing and Mounting.

The fore prism spectrometer and grating spectrometer are mounted on a steel base $\frac{1}{4}$ inch thick, which is screwed to brick piers at either end and has four rigid supports near the centre. The brick piers are in turn screwed to a firm table on which the circles stand. The various mirrors and S_2 are in mounts screwed to the steel base; these mounts are provided with adjustments for rotation of the mirrors about vertical and horizontal axes, and S_2 may be rotated through a small angle about a horizontal axis passing through the centre of S_2. The prism and grating tables have the usual adjustments. The axle supporting the grating spectrometer table passes through the centre of a rubber ring, making the joint air-tight, and avoiding the imposition of any strains on the circle due to uneven expansion of the spectrometer case, the bearing for the spectrometer table is screwed to the steel base plate; this again gives a roughly air-tight joint, and affords the necessary bearing for the axle of the theodolite circle; no great accuracy is required of this circle provided it has a reasonably good fine adjustment.

A pressed steel casing encloses the spectrometer, and carries the first slit S_1; the casing is screwed to the base plate, and angle brackets give it rigidity where the telescopic tube, T, is welded to it. A lid is fitted and gives an approximately air-tight joint. Nozzles are fitted to either end of the casing so that a stream of air freed from carbon dioxide and water vapour can be passed through the instrument.

Method of Use.

The grating table is fitted with a micrometer screw and drum, D, similar to those supplied with the Hilger direct reading spectroscopes. The drum is uniformly graduated throughout the length of the spiral groove in which the index, J, moves. The end of this drum is fitted with a disc in which two slots are cut; two pins from a disc, rotated by worm motion from a distance, engage in the slots and so rotate the drum. It is read from a distance by means of a telescope. The disc with its two pins cannot remain fixed when the table is rotated through more than one degree, and this is allowed for by mounting the disc and its worm motion on a slide rest cut in a circle concentric with the axis of the table. The slide rest can be clamped in any position, with the pins passing through the slots in the end of D. Thus, when investigating a band the turntable is rotated to approximately the calculated position of the band and the pins are engaged in the slots of the drum; the band is then located by rotating D from a distance (actually at the galvanometer scale), and then finally carefully investigated by a rotation of D through the successive graduations on its surface. The band is plotted with readings of D as abscissæ, and the angles of required points are obtained by setting D at the corresponding graduations. The drum must, of course, be rotated in one direction when investigating the band, and in the same direction when determining the angles corresponding to given graduations on the drum, otherwise errors due to backlash of the micrometer screw may become considerable. This method of operating the spectrometer enables all the observations to be made by one person from one position in the room.

Setting-up the Spectrometer.

The mounts for the mirrors and slits were designed so that the centres of these parts were at one height above the base plate. The remaining adjustments were made with monochromatic light obtained by focussing a mercury arc on S_1; with M_3 approximately adjusted, the various mercury lines were observed near S_2, and M_3 could then be accurately adjusted for parallel light, and the slit S_2 rendered parallel to the image of S_1. M_4 was correctly focussed by reflecting light back towards it from the grating table by means of a plane mirror at the grating surface; M_5 was then set approximately at the correct position, and the final focussing of the image of S_2 on S_3 was made by the telescopic adjustment. An alternative to the use of monochromatic radiation is to focus the image of the Nernst filament on S_1, and to replace P and G with plane mirrors; this gives more intense illumination and was used in the preliminary work. The mirrors M_5 and M_6 were actually adjusted by first viewing (from S_3) M_5 in M_6, and then G in both M_5 and M_6. A similar method was adopted for setting up mirrors M_7 to M_9, as the visible light traversing this system is rather weak. The mirrors were removed from the prism and grating tables, and the grating was rotated until the most intense red spectrum fell on S_3; looking along the axis of the absorption tube the observer can see M_7 in M_8, and S_3 in the image of M_7 in M_8; finally M_9 was similarly adjusted and the thermopile placed at the image of S_3 formed by M_9.

Procedure.

When the various components of the spectrometer have been correctly adjusted, there remains to be determined the correct setting of the prism and grating to obtain radiation of given wave-length traversing S_3. The calibration of the prism need only be approximate, for so long as the wave-lengths 2 and 4 μ can be distinctly separated, the final setting of P can be made by means of the fine adjustment. Thus, if the grating be set so that wave-lengths of 4 μ in the first order spectrum traverse S_3, then on rotating P, from the position where visible wave-lengths traverse S_2 towards longer wave-lengths, the observed galvanometer deflections pass through one maximum, corresponding to the wave-lengths near 2 μ in the second order, and then a second maximum appears due to the wave-lengths near 4 μ in the first order; the second maximum gives the correct setting of P. A maximum may appear of wave-length between 2 μ and the visible corresponding to a third order spectrum, but a circle readable to 30 seconds of arc is sufficiently accurate to avoid any confusion of the maxima, and the final setting of the prism can be made by means of the fine adjustment while observing the galvanometer deflection at each setting.

The grating can be set approximately by means of the different orders of visible spectra, but final settings and any observations of a band require calculation by means of the usual dispersion formula. Thus for a spectrum of the nth order we have

$$a(\sin\theta + \sin\phi) = n\lambda, \tag{1}$$

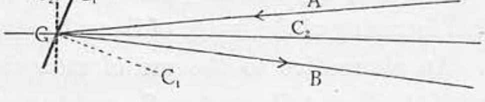

FIG. 3.

where a is the grating constant, θ is the angle of incidence, and ϕ is the angle of reflection. The grating as actually used is shown in fig. 3; AGC_1 is the angle θ, and BGC_1 the angle ϕ. The position of the grating when the zero order appears in S_3 is GG_2, and the normal occupies a position GC_2. If ψ be the angle turned through by the grating from the zero order to the wave-length λ in the nth order, then ψ is equal to C_2GC_1; hence θ is $(\psi + \alpha)$, and ϕ is $(\psi - \alpha)$, where 2α is the angle between the incident and diffracted rays. Formula (1) therefore assumes the simple form

$$n\lambda = 2a \sin \psi \cos \alpha. \tag{2}$$

The grating accordingly is set by observing the zero order in S_3, and rotating the turntable through an angle ψ determined from (2). Conversely, the wave-length corresponding to any setting of the turntable is determined from (2) on insertion of ψ.

Errors.

Errors in working the spectrometer arise from errors in ψ and α. Differentiating (2) for the first order spectrum, we have

$$\Delta\lambda = 2a (\cos \psi \cos \alpha \Delta\psi - \sin \psi \sin \alpha \Delta\alpha). \tag{3}$$

Since both ψ and α are small, error in ψ is the larger factor in the error, $\Delta\lambda$, occurring in λ. Determination of ψ involves reading two angles, that of the zero order spectrum and that of the table setting. The first point is the accuracy with which these readings can be made, and this involves the accuracy of the grating circle; this can be read to 1 second of arc, but the turntable as originally supplied had two micrometer eyepieces, one at each end of a diameter, and one of these had to be removed as it projected into the Nernst filament housing. The accuracy of the circle was tested with the two eyepieces in position, and readings on the two coincided to within 3 seconds of arc and we shall assume this to be the accuracy of the circle, and the error in setting the grating table. The greatest error arises in determining the position of the zero order spectrum; the position of S_3 renders impossible observations by an eyepiece, but a method which is quite as accurate is the following: the slit is covered with thin paper, and D is rotated until the edge of the image of S_2 is just visible; the corresponding setting of the circle is noted, and D is again rotated until the other edge of the image is visible, and the circle again read. The mean of these two readings then gives the position of the zero order. The method is as accurate as that involving an eyepiece, but observations to within much less than 7 seconds of arc appear impossible. Hence the total possible error in ψ is 10 seconds of arc; inserting this value in (3), and taking ψ as 17° and α as 5°, we obtain an error in λ equal to $0{\cdot}0007\ \mu$.

The permissible error in α must be determined: inserting $\Delta\lambda = 0 \cdot 0001\ \mu$ in (3), we find $\Delta\alpha$ approximately 1 minute, and α must be known accurately to within this value; this is easily attained by rotating G so that the zero order falls firstly on S_2, and secondly on S_3.

Wave-lengths determined with this instrument should therefore be accurate to $0 \cdot 001\ \mu$. Whilst the spectrometer was in use, a possible source of error was recognised; the reading of the zero order spectrum does not, unfortunately, remain constant over intervals of time of the order of 1 day, probably because of uneven expansion of the casing due to the heating lamps used to maintain the rocksalt parts at a slightly higher temperature than the surroundings; this involves rotation of the telescope tube carrying S_3. The error can be eliminated by observing the position of the zero order spectrum before and after determining the contour of a band. Reproducible results were obtained by this method.

Resolving Power.

This is also determined from formula (3). Inserting 1 minute of arc for the value of $\Delta\psi$, we obtain $\Delta\lambda$ equal to $0 \cdot 004\ \mu$; but since the direction of incidence is constant, the diffracted wave-lengths must spread at the rate 2ψ, *i.e.*, two diffracted wave-lengths separated by an angle of 1 minute must differ in wave-length by $0 \cdot 002\ \mu$. Again, a slit width of $0 \cdot 01$ second subtends an angle of approximately $0 \cdot 6$ minute at the grating; hence slit widths of $0 \cdot 01$ second, or 10 divisions, contain a wave-length range of 12 A., or $0 \cdot 8$ wave-numbers, near $4\ \mu$. Between $3 \cdot 5$ and $4\ \mu$, galvanometer deflections of $1 \cdot 5$ cm. were obtained with this slit width, and if the variations in percentage absorption are marked, this deflection is large enough to obtain reliable observations.

The bands actually observed all lay beyond $4\ \mu$, and the least slit widths used were 20 divisions, or 24 A for the $4 \cdot 003\ \mu$ band of SO_2. Other bands near $4 \cdot 35$ and $4 \cdot 6\ \mu$ required 40 divisions or approximately 50 A.

Elimination of Water Vapour and CO_2.

The spectrometer was ultimately to be used over regions where carbon dioxide and water vapour have considerable absorptive powers, and the instrument was therefore designed to be roughly air-tight. The method adopted to eliminate these impurities consisted in displacing the air in the case by dry purified air, and maintaining a slight excess pressure inside by means of a stream of gas from evaporating liquid air in a Dewar vessel. As the longer wave-length band of SO_2 overlaps the $4 \cdot 25\ \mu$ band of CO_2, the further precaution was taken of covering the slits S_1 and S_3 with rocksalt windows, and placing sticks of caustic soda in the case. When the contents of the small Dewar vessel were allowed to evaporate overnight, it was found that the CO_2 absorption was reduced approximately to that observed with the prism spectrometer; this residual absorption was presumably due to absorption in the path outside the casing; we hope eventually to enclose the total path length. When the spectrometer as treated was left over the week-end without liquid air evaporating into it, no appreciable increase in the absorption due to CO_2 was observed.

Before the impure air was removed from the case, it was not possible to obtain measurable deflections in the neighbourhood of the maximum of the CO_2 band at $4 \cdot 25\ \mu$; after purification readings were obtained throughout this region, and the setting of the spectrometer was checked against Barker's values for the band in question.*

Our acknowledgments are due to Professor F. G. Donnan, C.B.E., F.R.S., for his continued interest and encouragement; to Imperial Chemical Industries, Ltd., from whose grant to these laboratories certain portions of the apparatus were purchased; to Mr. G. W. Alliss, of this Department, who designed and made many of the parts; and to the Department of Scientific and Industrial Research for a Senior Award to A. B. D. C.

Summary.

(1) The construction of an infra-red grating spectrometer for use as a double monochromator is described.

(2) The method of working such a spectrometer is fully explained.

(3) The experimental errors and the resolving power are calculated.

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* 'Astrophys. J.,' vol. 55, p. 391 (1922).

Harrison and Sons, Ltd., Printers, St. Martin's Lane, London, W.C.2.

[*From the* PROCEEDINGS OF THE ROYAL SOCIETY, A, Vol. 140, 1933.]

Investigations in the Infra-red Region of the Spectrum. Part VIII—*The Application of the Grating Spectrometer to Certain Bands in the Spectra of Triatomic Molecules* (*Sulphur Dioxide, and Carbon Disulphide.*

BY C. R. BAILEY AND A. B. D. CASSIE.

thus band F at 4·01 μ includes a well-defined Q branch, and band E at 4·37 μ solely P and R branches. The two observations are consistent, and the only possible solution, giving a vertical angle of 120°, is obtained when a valence force system is applied to the fundamental frequencies allotted as in Table I, which incorporates the present results and those previously obtained with the prism instrument.

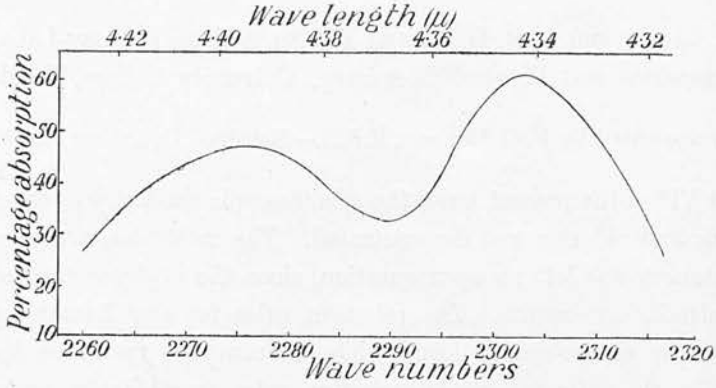

Fig. 1.

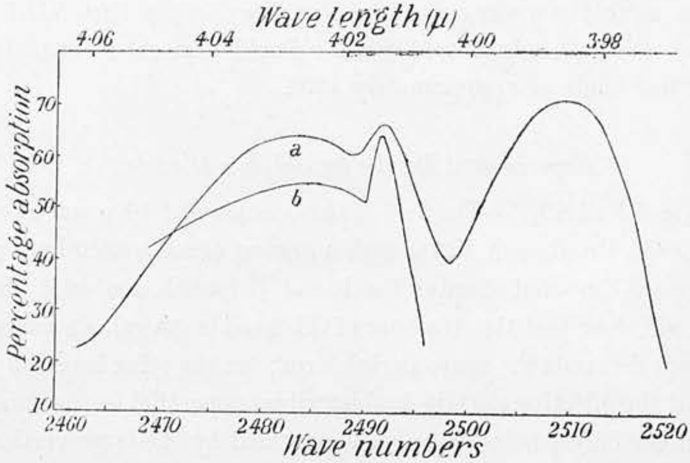

Fig. 2.

In Part II the centre of band F was given as 2499 cm.$^{-1}$, being the minimum between the supposed P and R branches; the present value of 2492 cm.$^{-1}$, or 4·014 μ, is probably correct to within 0·001 μ. For band E, the difference between the original determination of 2305 cm.$^{-1}$, and that given above, is too large to be accounted for by ordinary experimental error; a disturbing fact is that an almost equal lack of agreement appears in the 4·6 μ band for

CS_2. It is possible that this may be caused by the fluorite prism, which contains a number of flaws, and the refractive index of the prism may not be that of another fluorite. This is to a certain extent confirmed by our observation in Part I* that the resolving power of the given prism is only one-half that calculated.

Table II summarizes the most probable data for the two molecules, SO_2 and ClO_2.

Table I.

Band.	Origin.	Band centre.		Maxima.	P − R separation (cm.$^{-1}$).	ν_c (calc.).	Difference $\nu_c - \nu_0$.
		λ (μ).	ν_0 (cm.$^{-1}$).				
B	ν_1	8·680	1152	$\left\{\begin{matrix}1169\\1138\end{matrix}\right\}$	31	—	—
—	ν_2	19·1	524	—	—	—	—
C	ν_3	7·347	1361	$\left\{\begin{matrix}1377\\1361\\1348\end{matrix}\right\}$	30	—	—
A	$\nu_1 - \nu_2$	16·494	606	$\left\{\begin{matrix}611\\602\end{matrix}\right\}$	9(?)	628	22
D	$\nu_2 + \nu_3$	5·345	1871	1871	—	1885	14
E	$2\nu_1$	4·369	2290	$\left\{\begin{matrix}2276\\2303\end{matrix}\right\}$	27	2304	14
F	$\nu_1 + v_3$	4·014	2492	$\left\{\begin{matrix}2510\\2492\\2485\end{matrix}\right\}$	25	2513	21

Table II.

SO_2.		ClO_2.	
cm.$^{-1}$.	× 10^5 dynes per cm.	cm.$^{-1}$.	× 10^5 dynes per cm.
$a_1 = 1159, b_1 = -7$ $a_2 + b_2 = 524$ $a_3 + b_3 = 1361$ $c_2 = -21, c_3 = -14$	$K_1 = 9{\cdot}6$ (S − O) $K_\theta = 3{\cdot}3$ (O − O)	$a_1 = 950, b_1 = -4$ $a_2 + b_2 = 527$ $a_3 + b_3 = 1109$ $c_2 = -21$	$K_1 = 6{\cdot}7$ (Cl − O) $K_\theta = 3{\cdot}6$ (O − O)
$\widehat{OSO} = 122°$		$\widehat{OClO} = 140°$	

The observed combination and over-tones are not sufficient to determine the anharmonic constants completely. An estimate of the heat of dissociation corresponding to the symmetrical vibration ν, fig. 3, can be made from the experimental value for b_1, and is found to be of the order of 134 k. cal.; it is

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* 'Proc. Roy. Soc.,' A., vol. 130, p. 140 (1930).

interesting to see that this may reasonably correspond to dissociation according to the scheme $(SO_2) \rightarrow (S) + (O_2)$, since we have

$$\begin{aligned}
(SO_2) &= [S]_{rh} + (O_2) &&- 69 \text{ k. cal.}\\
[S]_{rh} &= \tfrac{1}{2}(S_2) &&- 14 \text{ k. cal.}\\
\tfrac{1}{2}(S_2) &= (S) &&- 51 \text{ k. cal.}\\
\hline
(SO_2) &= (S) + (O_2) &&- 134 \text{ k. cal.}
\end{aligned}$$

FIG. 3.

The close proportionality we have already observed to exist between the heats of dissociation and the force constants corresponding to the bonds in simple allied molecules is maintained. For CO_2 and SO_2, the ratio of the heats of linking of the central atom to the external oxygen atom is $182/126 = 1 \cdot 44$, and for the force constants is $14 \cdot 2/9 \cdot 6 = 1 \cdot 45$. One would expect a similar relationship to hold for the monoxides, particularly as the ratio of the heats of dissociation of the carbon-oxygen bonds in CO and CO_2 $(237/182 = 1 \cdot 31)$ is again the ratio of the force constants for these bonds in the two substances $(18 \cdot 8/14 \cdot 2 = 1 \cdot 32)$. One* of us has pointed out that the value of the heat of dissociation of SO as determined by Henri from the band spectrum of this substance, namely, 148 k. cal.,† is greater than the heat of dissociation of the oxygen molecule, and is probably incorrect. At the same time it was shown that a relationship of an approximately linear nature existed between these heats of dissociation and the position of the element in the periodic series, and that whether SO was regarded as the oxide of sulphur or the sulphide of oxygen by interpolation on the curves, the value should lie in the neighbourhood of 100 k. cal. The calculated value from the heat of the SO link in SO_2 and from the force constants for the mon- and di-oxides is $126 \times 7 \cdot 8/9 \cdot 6 = 102$ k. cal., and hence Henri's result represents dissociation into normal sulphur and excited oxygen atoms. We have accordingly

$$\begin{aligned}
SO &= S\,(^3P) + O\,(^1D) &&- 148 \text{ k. cal.}\\
O\,(^1D) &= O\,(^3P) &&+ 45 \text{ k. cal.}\\
\hline
SO &= S\,(^3P) + O\,(^3P) &&- 103 \text{ k. cal.}
\end{aligned}$$

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* 'Nature,' vol. 130, p. 239 (1932).

† 'J. Phys. Rad.,' vol. 10, p. 81 (1929).

The three methods of arriving at the heat of dissociation of sulphur monoxide into normal atoms give concordant results.

The Structure of the SO_2 *Molecule.*

A rigorous application of the octet rule to sulphur dioxide would indicate that the two oxygen atoms were differently bound to the central sulphur atom by four and two electron links respectively. Although this assumption gives the correct interatomic angle, it seems to us from first principles untenable; the values of the force constants indicate equivalence of binding, and furthermore, if the molecule were unsymmetrical, the contours of the various bands would follow no definite scheme such as the inter-consistent appearance of P, Q, and R branches. Hund's suggestion* of the presence of localized bonds accompanied by superimposed non-localized bonds, the former obtained from two p electrons providing directed valencies at 120°, seems more reasonable.

The interatomic dimensions can only be determined approximately from the data available; by analogy with carbon dioxide we are justified in assuming that the addition of another oxygen atom to the central atom will involve no considerable alteration in atomic distances. The rotational fine structure of the ultra-violet bands of sulphur monoxide as obtained by Henri (*loc. cit.*) gives the S–O distance as $1 \cdot 34$ A.; the corresponding distance in the dioxide was found by Wierl,† using the electron diffraction method, to be $1 \cdot 37$ A. The average value for the P–R separation in the doublets is 27 cm.^{-1}, this should by substitution in the formula $I = kT/c^2\pi^2\Delta\nu^2$ give an approximation to the largest moment of inertia, which is thus evaluated as $5 \cdot 1 \times 10^{-39}$ g. cm.^2. The three moments $A < B < C$ are given by $A = (2ml^2 \cos^2 \alpha)M/(M + 2m)$, $B = 2ml^2 \sin^2 \alpha$, and $C = A + B$, where α is the semi-vertical angle, l the S-O distance, M the mass of the central atom, and m of the external atoms. We can solve $C = A + B$ for l, and the value so obtained is $1 \cdot 2 \times 10^{-8}$ cm., in reasonable agreement with Wierl's determination. The interatomic separations in the case of ClO_2 will probably be of the same order but somewhat larger. If it be assumed that the P–R separation observed corresponds to the smallest moment of inertia, then the interatomic distances become apparently too large, and are as given in Part VI, the S–O value rising to $2 \cdot 3$ A.

Benzene offers another case where six electrons are available for every two chemical bonds, the angle between them being again 120°. The most intense

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* 'Z. Physik,' vol. 73, p. 1 and p. 565 (1931).

† 'Phys. Z.,' vol. 31, p. 1028 (1930).

Raman displacement is 992 cm.$^{-1}$, and according to Placzek's rules must be identified with the symmetrical expansion and contraction of the ring. When this is done, the force constant between the CH groups appears as approximately 7×10^{-5} dynes/cm., representing single links between these groups. The stability of the benzene ring is thus similar to that of the sulphur dioxide molecule.

Experimental Results for Carbon Disulphide.

Band C at 4·6 μ.—Reasonable galvanometer deflections were obtained in this region, and the band was therefore reinvestigated. Its contour as determined with slit widths of 50 A., or 3·5 cm.$^{-1}$, is shown in fig. 4; it has P and R branches, with a separation of slightly more than 13 cm.$^{-1}$, whereas the values for the bands at 11·4 and 6·57 μ in Part III* were 13 and 12 cm.$^{-1}$ respectively. Dennison and Wright† obtained the corresponding value for the band at 25·2 μ of 16·4 cm.$^{-1}$; our values are reproducible and easily determined, and, since both the grating and the prism give the same result, may be taken as definite. The discrepancy is too great either to arise from incomplete separation of the branches, or an increase in the effective moment of inertia owing to the vibrations of the constituent massive particles. The probable explanation is a coupling between oscillation and rotation such as Teller and Tisza‡ invoked to explain similar inconsistencies in the line separa-

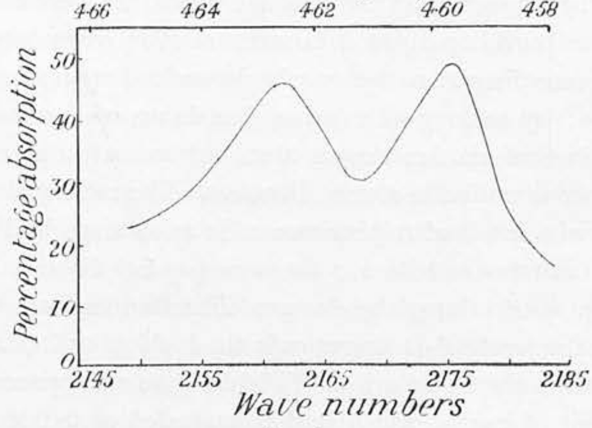

FIG. 4.

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* 'Proc. Roy. Soc.,' A, vol. 132, p. 236 (1931).

† 'Phys. Rev.,' vol. 38, p. 2077 (1931).

‡ 'Z. Physik,' vol. 73, p. 791 (1932).

tions observed in certain bands of the methyl halides. Inconstancy in P and R branch separations is even more marked in the infra-red spectrum of CO_2 and probably arises from the same cause.

The infra-red spectrum of CS_2 is given in Table III.

Table III.

Band.	Origin.	Band centre.		Maxima.	P − R separation (cm.$^{-1}$).	ν_c (calc.).	Difference $\nu_c - \nu_0$. (cm.$^{-1}$).
		$\lambda(\mu)$.	ν_0 (cm.$^{-1}$).				
—	ν_2	25·2	396·8	405·8 396·8 389·4	16·4	—	—
Raman	ν_1	15·3	655·5	—	—	—	—
A	$\nu_3 - \nu_1$	11·391	878	885 872	13	867·5	−11
B	ν_3	6·566	1523	1530 1518	12	—	—
C	$\nu_3 + \nu_1$	4·613	2167	2175·3 2162·0	13·3	2178	11
D	$\nu_3 + 2\nu_2$	4·292	2330	—	—	2318	−12

ν_1 is the optically inactive frequency appearing in the Raman spectrum at 655·5 cm.$^{-1}$, in conjunction with $2\nu_2$ at 795·0. The allocation of frequencies in Table III is in accordance with Dennison's recent paper on the "Vibrational Levels of Linear Symmetrical Triatomic Molecules."* In Part V we applied the resonance theory of Fermi† to the elucidation of the CS_2 and COS spectra; it seems probable, especially in view of the failure of Fermi's theory to explain the constancy of the separations in the double doublets,‡ that Dennison's allocation is correct, a similar interpretation being possible for the COS spectrum as in Table IV.

Table IV.—The Infra-red and Raman Spectrum of COS.

Mode.	Frequency (cm.$^{-1}$).		Mode.	Frequency (cm.$^{-1}$).	
	Observed.	Calculated.		Observed.	Calculated.
ν_2	527	—	ν_3	2079	—
ν_1	859	—	$\nu_3 + \nu_1$	2904	2938
$2\nu_2$	1051	1054	$\nu_3 + 2\nu_2$	3095	3133
$2\nu_1$	1718	1718	$\nu_3 + 2\nu_1$	3742	3797
$\nu_1 + 2\nu_2$	1898	1913	$2\nu_3$	4084	4158.

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* 'Phys. Rev.,' vol. 41, p. 304 (1932).

† 'Z. Physik,' vol. 71, p. 250 (1931).

‡ Cassie and Bailey, 'Z. Physik,' vol. 79, p. 35 (1932).

The band at 1051 cm.$^{-1}$ has a Q branch ; this is in accordance with Dennison's selection rules, since ν_2 is a symmetrical vibration, and the changes in electric moment have components along the axis of rotation. We have shown that failure to eliminate scattered radiation of shorter wave-length in the region of 18 μ results in poor resolution and a considerable diminution in the observed intensity of the band.* Before this was realized, any interpretation of the strong band at 1051 cm.$^{-1}$ as the first harmonic of the weaker band at 527 cm.$^{-1}$ was ruled out. The contour of the latter band as given in Part V indicates the incomplete resolution achieved, and in analogy to the similar long wave bands of CS_2 and CO_2, this band may be expected to contain a Q branch.

Correction to Part V.†

The values of the restoring couple per unit angular displacement are incorrectly given for the molecules CO_2, COS, and CS_2 on pp. 389 and 390. The three molecules are surprisingly similar, since in spite of the great polarizability of oxygen compared with sulphur, the restoring couple is the same in all three cases, and amounts to 6×10^{-12} dyne cm. The significance of this will be discussed in a future paper.

Our best thanks are due as always to Professor F. G. Donnan, F.R.S. One of us (A.B.D.C.) is indebted to the Department of Scientific and Industrial Research for a Senior Award.

Summary.

(1) The sulphur dioxide bands at 4·01 and 4·37 μ have been examined with a grating spectrometer, and the presence of a previously unrecognized Q branch in the former makes it certain that the molecule is triangular, with a vertical angle of 120°. Apparent contradictions between the selection rules for the Raman and infra-red spectra are thus removed.

(2) The carbon disulphide band at 4·61 μ, when explored with the grating instrument, confirms the previously determined separation for the P and R branches.

(3) The molecular structure of the above substances is discussed.

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* 'Proc. Roy. Soc.,' A, vol. 137, p. 623 (1932).

† 'Proc. Roy. Soc.,' A, vol. 135, p. 375 (1932).

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Investigations in the Infra-Red Region of the Spectrum.

Part IX.—*The Absorption Spectrum of Chlorine Monoxide* (Cl_2O).

BY C. R. BAILEY AND A. B. D. CASSIE.

[*Reprinted from the* PROCEEDINGS OF THE ROYAL SOCIETY, A, Vol. 142.]

Investigations in the Infra-Red Region of the Spectrum. Part IX.—*The Absorption Spectrum of Chlorine Monoxide* (Cl_2O).

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Recent applications of quantum mechanics to polyatomic molecules have given new theoretical rules governing molecular structure, and seem likely to provide much information regarding the nature of the forces acting between the constituent atoms. In many cases we find that the bonds between neighbouring atoms may be classified according to the resultant component of angular momentum of the bonding electrons in the direction of the line joining the atoms. Thus bonds may be of the σ-, π-, δ- and similar types, together with the non-localized bond obtained when the electrons available for bond formation are present in excess of the number usually required. Theory has almost outrun experiment in that data, especially of a spectroscopic nature, are at present confined to the simpler triatomic molecules in which no great constitutional difficulties are to be expected, and apart from the somewhat indefinite and doubtful hypotheses of semipolar and one-electron bonds, there is no experimental result which contradicts classical theory yet finds a natural explanation in quantum mechanics.

The structure of Cl_2O provides such a crucial test. The molecule consists of two atoms of chlorine each of large polarizability compared with the central oxygen atom to which they are joined; if the stability of a molecule be determined by the polarizability of the constituent atoms, the substance should have a linear structure, apart from any *ad hoc* evidence adduced from other sources as to the angle between two oxygen bonds. According to the quantum mechanics, however, the stable structure of a molecule is determined not by the polarizability alone, but rather by a combination of the polarizability of the atoms, and by the interactions of the valency electrons, the second factor playing by far the larger part in determining the structure. We shall see that the triangular molecule with a vertical angle not far removed from 90° is demanded by the quantum theory and supported by the experimental evidence. The gas absorbs continuously in the ultra-violet, and evidence as to the fundamental frequencies and force constants must consequently be sought in the infra-red.

Experimental.

The apparatus was similar to that used in the investigation of chlorine dioxide.* The gas required careful drying since the presence of traces of water vapour leads to rapid attack of the rocksalt end-plates, and the samples used were obtained by repeated distillation over phosphoric oxide. We are indebted to Mr. and Mrs. Goodeve of this Department for their kind advice in the preparation of this substance.

Observations.

The region investigated lay between 1 and 18 μ, and four bands were observed. Their characteristics are recorded in Table I.

Table I.—The Infra-red Absorption Spectrum of Cl_2O.

Band.	Band centre.		Maxima.		$\Delta\nu$ for P − R (cm.$^{-1}$).	Intensity.	Prism.
	λ (μ).	ν_0 (cm.$^{-1}$).	λ.	ν.			
A	15·63	640	15·91 15·35	628 651	23	30 (5)	Sylvine
B	10·28	973	10·33 10·28 10·20	967 973 980	13	50 (5)	Rocksalt
C	8·033	1245	8·111 7·937	1233 1260	27	20 (10)	Rocksalt
D	7·625	1311	7·625	1311	—	10 (10)	Rocksalt

The estimates of intensity at the slit-width used (the figure in brackets gives the extent of spectrum included in wave numbers) are rough approximations, the maximum pressure used for the preliminary exploration being that of Cl_2O at 0° C., some 70 cm. of mercury.

Individual Bands.

Band A at 15·63 μ.—This is shown in fig. 1, in company with the 14·87 μ band of CO_2. The two bands always appeared together and with much the same relative intensities; curve (*a*) was obtained with a smaller slit-width and lower pressure; and the doublet separation is the same as that given by

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* Part VI, 'Proc. Roy. Soc.,' A, vol. 137, p. 622 (1932).

Schaefer and Philipps* for the long-wave CO_2 fundamental, the band centres also coinciding. When the origin of the more intense component was suspected, fresh samples of the monoxide were prepared, but it was found impossible to remove the impurity. It is probable that CO_2 dissolves in liquid Cl_2O, and the maintenance of the relative intensities indicates that we may be dealing with a constant boiling point mixture; we have since learnt that solid sodium hypochlorite or normal calcium hypochlorite may be obtained, and distillation of a sample over either of these substances might offer a means of purification, but this has not been tried. No appreciable absorption was observed in the neighbourhood of the $4 \cdot 25\ \mu$ CO_2 band but Burmeister's original examination† shows that this band has only approximately one-tenth of the intensity of the band at $14 \cdot 87\ \mu$. On freezing the mixture, CO_2 seemed to be given off, since a white frost appeared on the central stem of the trap, but even by warming the upper part while keeping the monoxide frozen effected no appreciable separation on pumping off. The frequent attempts to remove the impurity were made not so much because of doubt as to the origin of the band, but because consideration of the isotope effect shows that it is possible that there may be a second Cl_2O band obscured by the CO_2.

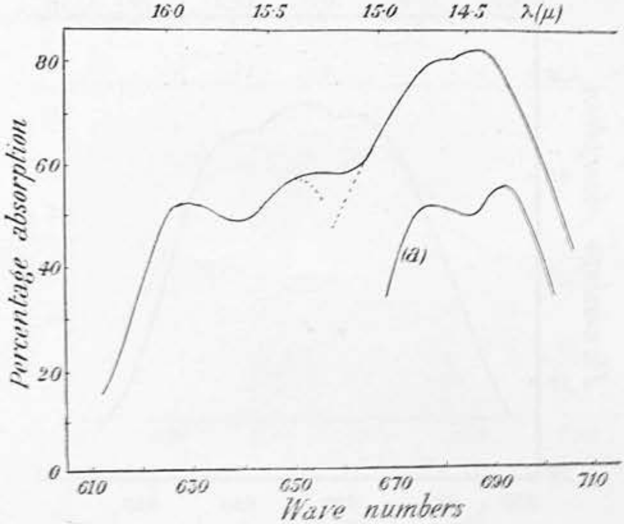

Fig. 1.

Band B at $10 \cdot 28\ \mu$ ($973\ cm.^{-1}$); fig. 2.—Trouble was experienced in the examination of this band since it appeared to gain in intensity with time;

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* 'Z. Physik,' vol. 36, p. 641 (1926).

† 'Verh. deuts. phys. Ges.,' vol. 15, p. 589 (1913).

the peculiarity was due to the presence of traces of water vapour which caused the monoxide to attack the rocksalt plates. Repeated distillation over phosphoric oxide at length produced a sample without effect on these, and with the band intensity completely under control. The solid obtained in the reaction may be sodium hypochlorite, the attacked plates absorbing at exactly the same wave-length as the gas. The band appears to have a Q branch, and is considerably narrower than the others.

Band C at 8·033 μ (1245 *cm.*$^{-1}$); fig. 3.—No difficulty was experienced in reproducing the observations for this band, and the peculiar contour with the flat portion between the two somewhat indistinct maxima is characteristic and definite. It will be seen that consideration of the isotope effect is required for the interpretation of the envelope.

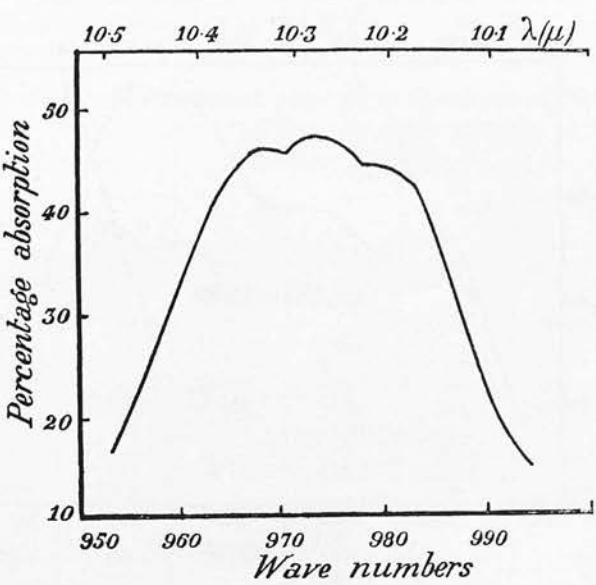

FIG. 2.

Band D at 7·625 μ (1311 *cm.*$^{-1}$).—No resolution was achieved, and the single maximum obtained is indicated at the short wave end of fig. 3.

The Band Assignments.

From the intensity of the bands, and from the isotope effect, it seems reasonable to assume that in Dennison's classification,* ν_1 and ν_3 are to be allotted to the two strong bands at 8·03 and 10·28 μ. One of these must be the

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* 'Rev. Mod. Phys.,' vol. 3, p. 289 (1931).

asymmetrical vibration ν_3, and since band B at $10\cdot28\ \mu$ is much the more intense in the infra-red, it is probable that it represents this fundamental mode, and that ν_1 is band C at $8\cdot03\ \mu$. The long-wave fundamental, ν_2, is more difficult to place; on account of the rigidity of the molecule as defined below, it is very likely that this symmetrical mode is responsible for band A at $15\cdot63\ \mu$, and consistent solutions for the force constants are obtained on this supposition. In spite of the comparative heaviness of the atoms, the type of structure for this molecule (as in H_2O and H_2S) demands a rather high frequency for this mode. The possibility that the observed band is the first harmonic of another at some 340 cm.$^{-1}$ has not been neglected, but does not lead to concordant solutions. Band D at 1311 cm.$^{-1}$ is probably $2\nu_2$; the calculated value is 1280 cm.$^{-1}$, and although it is uncommon to find the observed value of a band greater than the calculated value, the effect may be due to interaction between the electron shells of the chlorine atoms. It is to be noticed that unlike SO_2 and ClO_2, the monoxide has the asymmetric vibration, ν_3, at a lower frequency than the symmetric ν_1. The effect depends upon the masses of the atoms, and upon the ratio of the force constants in the molecule, and a full discussion is given by Kohlrausch* when various vertical angles are considered.

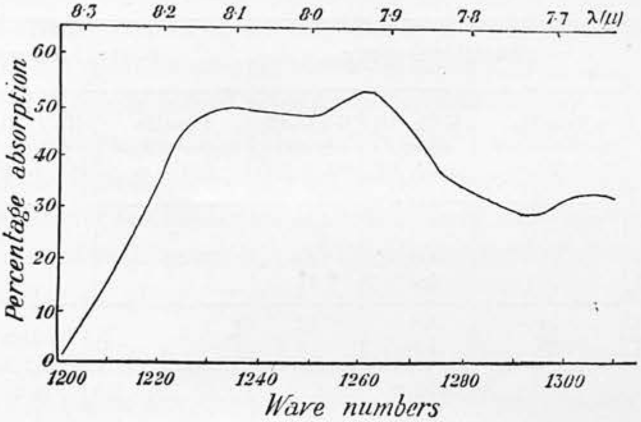

Fig. 3.

The Chlorine Monoxide Molecule.

When the fundamental frequencies have been selected, and inserted in formulæ (1) and (3) of Part VI (*loc. cit.*) various possible semi-vertical angles emerge; and for each possible value one of the fundamental frequencies corre-

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* "Der Smekal-Raman Effekt," p. 173 (1931).

sponds to a mode whose effective electric doublet lies perpendicular to the bisector of the vertical angle, the other two having effective doublets parallel to this line. Again, the least axis of inertia must be parallel or perpendicular to this bisector, and the choice between the two directions is determined by the known vertical angle. Hence the orientation of the various effective electric doublets relative to the least axis of inertia is known for all possible angles; and the selection rules tell us that for fundamental bands Q branches should appear only when the effective electric doublet is parallel to the least axis of inertia. The presence or absence of Q branches is thus final in deciding which of the possible vertical angles is correct.

Table II.—Possible Semi-vertical Angles, Transverse Frequencies, and Force Constants for Cl_2O.

Transverse frequency, ν_3 (cm.$^{-1}$).	Central force system.			Valence force system.		
	Possible semi-vertical angle, α.	K(Cl—O) dynes/cm. × 10^5.	K(Cl—Cl) dynes/cm. × 10^5.	Possible semi-vertical angle, α.	K(Cl—O) dynes/cm. × 10^5.	K dynes/cm. × 10^5
640	° 25 17	4·7 5·8	15 11	° 35	3·5	68
973	54 36	5·1 7·8	12 4·5	No solution		
1245	No solution			No solution		

The solutions obtained when the three fundamental frequencies are in turn considered as the asymmetric frequency, ν_3, are given in Table II. The force constants K (Cl—O) and K (Cl—Cl) are the ordinary linear coefficients; K_δ is the tangential restoring force per unit arc displacement of the vertical angle and appears only in the valence force system. The only possible solution with the latter system is provided by the unlikely assumption that the long-wave fundamental, A, represents the asymmetric vibration, and the value of K_δ obtained on this supposition is so large as to exclude this possibility, apart from other considerations. The solution in the same system with band B at 973 cm.$^{-1}$ as ν_3 gives $\sin \alpha$ as 1·06; with the approximations of the theory, this value might represent a rectilinear molecule, but in this case the asymmetric frequency becomes the asymmetric linear vibration, and the Cl—O force constant drops to $3 \cdot 5 \times 10^5$ dynes/cm., and by analogy with other triatomic molecules is excluded. Furthermore, simple calculation supplies the approximate positions of the other bands, and no agreement with observed results is found. It is unfortunate that no Raman spectrum is available for either Cl_2O or the hypochlorites, since the most powerful line in this spectrum has a displacement corresponding to the most symmetrical vibration, ν_1. The highest fundamental frequency in a rectilinear molecule is invariably the asymmetric mode, and if the binding corresponds to a single valence stroke as is probable in this case, the force constant is some 6×10^5 dynes/cm. Band B is too intense to be any but a fundamental tone, and it cannot be the symmetrical vibration in a symmetrical triatomic molecule as it must then be inactive in the infra-red. The possibility of the rectilinear structure is thus excluded on several counts.

In the possible triangular forms we have to determine the orientation of the least axis of inertia with respect to the bisector of the vertical angle. This axis is parallel or perpendicular to the bisector as $\tan^2 \alpha <$ or $> 1/(1 + 2m/\mathrm{M})$; and for Cl_2O this gives a critical value for the vertical angle, 2α, of 46°. The transverse fundamental mode has an effective electric doublet normal to the bisector, and the symmetric modes have doublets parallel to this line; the effective doublets for the harmonics of the transverse mode are alternatively parallel and normal to the bisector, while the doublets for the harmonics of the symmetric modes are always parallel to this line. Knowing the possible solutions of the frequency equations, we can orientate the effective electric doublets with regard to the least axis of inertia; the results are summarized in Table III.

Table III.—Orientation of the effective electric doublets with respect to the least axis of inertia for possible solutions of the frequency equation.

Band, cm.$^{-1}$.	Central force system.			Valence force system.
	Vertical angle 2α.			Vertical angle 2α.
	50°.	34°.	72° or 108°.	70°.
640	Parallel	Perpendicular	Perpendicular	Parallel
973	Perpendicular	Parallel	Parallel	Perpendicular
1245	,,	,,	Perpendicular	,,
1311	,,	,,	,,	,,

The band at 973 cm.$^{-1}$ is the only fundamental whose contour definitely suggests the presence of a Q branch due to asymmetry of the moments of inertia, and Table III indicates that the only solutions consistent with the observed contours are those with 973 cm.$^{-1}$ as the asymmetric frequency, giving on the central force system vertical angles of either 72 or 108°. The oxygen angle in the ethers has been determined by collision area methods, and from considerations of the dipole moments, and the bonds are found to be almost invariably at an angle of 110° to each other.* The approximations introduced enable us to say that in the case of chlorine monoxide, the vertical angle is slightly greater than 90°.

The Isotope Effect.

Further supporting evidence is provided by the isotope effect. The principal isotopes of chlorine have atomic weights of 35 and 37, in the frequency ratio of three to one. The probability of the chlorine atom in the dioxide having mass 35 is $\frac{3}{4}$ and for mass 37 is $\frac{1}{4}$, and the ratio of the intensity of the bands $Cl^{35}O_2$ to those of $Cl^{37}O_2$ is 3 : 1. Since the bands overlap to a large extent, the latter are almost unobservable with the resolution attained, but conditions are much more favourable with the monoxide. The relative intensity of the bands due to $(Cl^{35})_2\,O$ and $(Cl^{35}Cl^{37})\,O$ gives a ratio of less than 3 : 1 ; the probability of the first molecule is 9/16, of the second 6/16, and of $(Cl^{37})_2O$ is 1/16 : bands due to the last molecule may be neglected as too weak to detect under the experimental conditions, but the $(Cl^{35}Cl^{37})_2O$ band has an intensity 2/3 of that of the $(Cl^{35})_2O$ band, and should therefore be observable.

The isotope separation can be estimated from the frequency formula, and the central force system is adopted as giving the possible solution. The frequency of the asymmetric mode is given by

$$n_3{}^2 = K_1\,[1/m + (2\sin^2\alpha)/M], \tag{1}$$

where n is $2\pi c\nu$, M and m the masses of the oxygen and chlorine atoms, α the semi-vertical angle, and K_1 the Cl—O force constant. Differentiating with respect to m gives

$$\Delta n_3 = -\,\Delta m K_1/2m^2 n_3. \tag{2}$$

Formula (2) gives the isotope separation of bands due to $(Cl^{35})_2O$ and $(Cl^{37})_2O$, and we shall assume that the separation of bands due to $(Cl^{35})_2O$ and $(Cl^{35}Cl^{37})_2O$ is one-half this value.

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* Freudenberg, "Stereochemie," p. 262 (1932).

The symmetrical frequencies are given by

$$n_{1,2}^2 = \frac{1}{2m}\Big[2K_2 + \Big(1 + \frac{2m}{M}\cos^2\alpha\Big)K_1$$
$$\pm\sqrt{4K_2 + \Big[4 - 8\Big(1 + \frac{m}{M}\Big)\cos^2\alpha\Big]K_1K_2 + \Big(1 + \frac{2m}{M}\cos^2\alpha\Big)^2 K_1{}^2}\,\Big], \tag{3}$$

where K_2 is the Cl—Cl force constant. Differentiating with respect to m we have

$$\Delta n_i = -\frac{\Delta m}{2m}n_i + \frac{\Delta m K_1\cos^2\alpha}{mMn_i}\cdot\frac{mn_i{}^2 - 2K_2}{2mn_i{}^2 - \Big[2K_2 + \Big(1 + \frac{2m}{M}\cos^2\alpha\Big)K_1\Big]}. \tag{4}$$

The required separation is again assumed to be one-half that given by (4).

On insertion of the experimental value $\nu_3 = 973$ cm.$^{-1}$ in (2), we obtain an isotope separation of 4 cm.$^{-1}$ for the transverse mode. This separation depends only on the O—Cl force constant, K_1, which we have taken as 7×10^5 dynes/cm.; the actual value as seen from Table II may be slightly less, but it can never be sufficiently small to influence appreciably the calculated separation, which is likely to lead only to a blurring of the contour of the band, as shown in fig. 2.

The isotope separations of the symmetrical modes, ν_1 and ν_2, depend not only on K_1, but also on K_2 and the semi-vertical angle, α. The solutions of the frequency equations give a rather large range of possible values of K_2 and α, and we have accordingly calculated isotope separations for these modes from formula (4) for representative values of the variables; they are reproduced in Table IV. The separation for the ν_1 mode is seen to be comparatively insensitive to changes in K_2 and α, but the variation for the long wave ν_2 is considerable.

Table IV.—Calculated Isotope Separations.

Semi-vertical angle, α	38°.			45°.			55°.		
K_2 (dynes/cm. $\times 10^{-5}$)	2	7	14	2	7	14	2	7	14
$\Delta\nu_2$ cm.$^{-1}$ ($\nu_2 = 640$ cm.$^{-1}$)	13	6	3	14	6	3	22	6	2
$\Delta\nu_1$ cm.$^{-1}$ ($\nu_1 = 1245$ cm.$^{-1}$)	13	13	15	13	13	16	14	14	16

It will be gathered from the above that the band at 1245 cm.$^{-1}$ must consist of two superposed bands which have their centres some 13 cm.$^{-1}$ apart, and of relative intensities 3 : 2. Fig. 3 indicates that the observed band is in fact composite, as is shown by the rapid change in slope near 1220 cm.$^{-1}$, and by the flat portion between the extreme maxima. The latter accordingly represent the R branch of the shorter wave component and the P branch of the longer wave band, and an envelope resembling that observed can be constructed from two bands of the given relative intensities, with P and R branches separated as in band B by some 13 cm.$^{-1}$, and with band centres differing by 13 cm.$^{-1}$.

The general shape of the contour of the fundamental at 640 cm.$^{-1}$ may be reasonably due to an isotope separation of some 6 cm.$^{-1}$, but the interference of the CO_2 band prevents definite measurement.

The Force Constants.

Table II indicates the rapid increase of the force constant for the external atoms in a symmetrical triatomic molecule governed by central forces as the vertical angle is opened out. Owing to the uncertainty in the value of the vertical angle, we can only say that since it is not far removed from 90°, the force constant K_2 will lie in the neighbourhood of 7×10^5 dynes/cm. This is of the order corresponding to a single chemical bond, and at first sight seems large when we realize that the two atoms in question are probably not in chemical combination. It is twice that observed for SO_2 and ClO_2 ($3 \cdot 5 \times 10^5$ dynes/cm.), in which the valence force system provides the only possible solutions; the rigidities are not in the same ratio, since the valence system constant, K_θ, refers to the tangential restoring force per unit arc displacement, while the central force constant, K_2, refers to the restoring force per unit central displacement of the length of the triangle base.

We have to consider what is meant by the success of the valence force system in the one case, and its failure in the other. A possible solution with the valence force frequency equation implies a potential field such that the direction of least rate of increase of potential for motion of either atom at the base of the triangle is normal to the side of the triangle; and this in turn implies that the force constant acting along the side of the triangle is considerably greater than the force constant effective for displacements normal to this line. On the other hand, failure of the valence force system signifies that the force constant effective for displacements normal to the side of the triangle is comparable with, or even greater than that for displacements in the direction of the side. In fact a system that gives a solution with a large vertical angle with central forces clearly increases the length of either side rather than displaces the vertical angle from its equilibrium position. Thus we say that the vertical angle rigidity of Cl_2O is of a greater order than that of either SO_2 or ClO_2.

Similar Molecules.

The electronic structures of water vapour and hydrogen sulphide would suggest that these molecules are spectroscopically like chlorine monoxide. Considerable uncertainty still exists as to the fundamental frequencies of the first two compounds, but Plyler concludes that in the case of water vapour, they are given by $\nu_2 = 1597$, $\nu_3 = 3745$, and $\nu_1 = 5307$ cm.$^{-1}$. On insertion of these values in the frequency equations, we find in confirmation of our conclusions that a possible solution is provided only by the central force system; the vertical angle is some 110°, the O—H force constant is $7 \cdot 5 \times 10^5$ dynes/cm., and the H—H force constant, K_2, is 5×10^5 dynes/cm. The value for the vertical angle is only approximate, as the fundamental frequencies are not greatly sensitive to changes in its value. The rules developed in Part VI (*loc. cit.*) indicate from the presence of a Q branch in the 3745 cm.$^{-1}$ band that the vertical angle is greater than 85°, and since this is the asymmetrical frequency for the possible solution, the least axis of inertia must be perpendicular to the bisector of the vertical angle, and the larger value for this angle is confirmed. The deductions are in agreement with the absence of a Q branch in both the other fundamentals. For hydrogen sulphide the vertical angle must be greater than 88°, and the force constants are of the same order.

Electronic Structure.

Both H_2O and Cl_2O have a central oxygen atom which requires two ($2p$) electrons to complete its shell, while both hydrogen and chlorine require one electron. If we regard the electrons required to complete a shell as equivalent to electrons outside a closed one, we can say that oxygen has two ($2p$) electrons, hydrogen one ($1s$) electron, and chlorine one ($3p$) electron. The difference between the quantum orbits in the last two cases is not of vital importance in determining the configuration of the molecule; for Slater, Pauling, and Hund have all shown that a central atom with two ($2p$) electrons available for binding always tends to form bonds which lie at right angles to each other. Departure from this configuration will be due chiefly to other chemical bonds within the molecule, and these are lacking in the two cases considered, which form a close approximation to the ideal case of two p-electron bonds originating in one atom, and resulting in the attachment of external atoms by σ-bonds.

This discussion ignores the difference between the ($3p$) chlorine electron and the ($1s$) hydrogen electron. If the chlorine electron be placed in a ($3p_0$) proper function with respect to the O—Cl direction, the bonding power of this electron will be little different from that of a ($3s$) electron; the resulting effect will be to give a larger separation for O—Cl than for O—H, and the chlorine atom will have a larger polarizability, the last factor might be expected to constitute the greatest difference between the two molecules, and one would have anticipated its effect on the configuration of the molecule to be greater than the analyses of the infra-red bands suggests. The reasonable conclusion is that the polarizabilities of the constituent atoms are of much less importance than are the values of the exchange integrals. The main distinction between the two molecules lies in the values of the Cl—Cl and H—H force constants; both are large, but that for Cl—Cl is greater than that for H—H, and the difference may be due to exchange of electrons between the two chlorine atoms. If the angle ClOCl is approximately 90°, as is required by the infra-red data, and also theoretically by the orthogonality of the linear combinations of the *p* proper functions of oxygen, then there must be overlapping of the electron clouds of the two chlorine atoms. We might thus expect exchange integrals to be finite for two electrons one on each chlorine atom, with a resulting attraction. The chlorine shells are only virtually closed, certainly not in the same way as those of the inert gases. Cl_2O should thus be a rigid molecule on two counts, and the large force constant K_2 is consistent with the structure proposed. With the smaller hydrogen nucleus the rigidity is presumably due entirely to the fixed orientation of the oxygen bonds.

Other Molecular Data.

The rotational fine structure within the vibrational bands of an asymmetric rotator is extremely complex. The maximal separation within a Bjerrum doublet for such a molecule will accordingly give only approximate values for the moment concerned, and only an approximate estimate of the molecular dimensions can be made. The asymmetric vibration gives a rough indication of the greatest moment of inertia, and for Cl_2O the P and R branches in this band are separated by some 13 $cm.^{-1}$. The moment of inertia corresponding to this is 274×10^{-40} g. $cm.^2$, and the calculated value for the O—Cl distance is then 1·8 A. There is a general tendency for the interatomic distance to increase as one proceeds along a period towards Group VII (r_e for N_2, O_2, and F_2 is 1·1, 1·2 and 1·5 A.; and for CO, NO, and O_2 is 1·15, 1·15, and 1·20 A.; for SO it is 1·49 and for Cl_2, 1·98 A.), and taking into account the large force constants of the molecule, we shall perhaps be not far out in suggesting some 1·6 A. for the Cl—O distance, and accordingly some 2·5 A. for the Cl—Cl separation.

The breaking of each O—Cl link in Cl_2O requires the same energy, approximately 45 k.cals.,* and the phenomenon appears to be characteristic of the $p\sigma$ molecular bonds from a $(2p)^2$ atom, since we have the value of 111 k.cals. for each link in the H_2O molecule, and may be taken as another tribute to the fixed direction in space of these bonds. With ClO_2, where the available electrons are one in excess of those required for normal bond formation, we have an electronic rearrangement consequent upon dissociation of the first oxygen atom which involves some 66 k.cals., the second requiring again 46 k.cals. Similarly for SO_2 (where the rearrangement is greater with two excess electrons) the first oxygen needs some 149 k.cals. and the second, 103 k.cals. The two latter molecules are governed by valence forces, the vertical angle is slightly greater than 120°, and the comparative looseness of the structure is a result of the electronic arrangement indicated. It seems to be doubtful whether the first type of molecule can dissociate completely to give $O + Cl_2$, or $O + H_2$† as a first stage reaction, but it was shown in Part VIII‡ that SO_2 may reasonably give $S + O_2$ when the molecule collapses.

The force constant between the external atoms exists mainly by virtue of the rigidity of the structure, and although it is large, it does not contribute in any marked degree to the heat of dissociation of the molecule. Hence we are not dealing with a true chemical bond, and if the resonance effect referred to earlier exists between the chlorine shells, the bond is more of the type of the polarization bonds of metals.

The authors are glad to acknowledge their indebtedness to Professor Donnan, C.B.E., F.R.S., for his constant interest and help ; and to the Department of Scientific and Industrial Research for a Senior Award to A. B. D. C.

Summary.

(1) The infra-red absorption spectrum of chlorine monoxide, Cl_2O has been examined between 1 and 18 μ and four bands have been isolated.

(2) Fundamental frequencies have been assigned, and the molecular dimensions approximately evaluated.

(3) The isotope effect has been considered, and is shown to account for the envelopes of certain of the bands.

(4) Cl_2O and H_2O belong to the group of molecules whose vibrations are governed by central forces, and are characterized by a vertical angle of slightly greater than 90°, and a strong resistance to angular deformation.

(5) The electronic structure of the substance is discussed.

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* Finkelnburg, Schumacher and Stieger, 'Z. phys. Chem.,' B, vol. 15, p. 127 (1932).

† Finkelnburg, Schumacher and Stieger, *loc. cit.*

‡ 'Proc. Roy. Soc.,' A, vol. 140, p. 605 (1933).

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Investigations in the Infra-red Region of the Spectrum. Part X.—The Asymmetrical Molecule Nitrosyl Chloride, NOCl.

BY C. R. BAILEY AND A. B. D. CASSIE.

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Investigations in the Infra-red Region of the Spectrum. Part X.—The Asymmetrical Molecule Nitrosyl Chloride, NOCl.

By C. R. BAILEY and A. B. D. CASSIE, the Sir William Ramsay Laboratories of Inorganic and Physical Chemistry, University College, London.

(Communicated by F. G. Donnan, F.R.S.—Received January 20, 1934.)

The infra-red absorption spectrum of nitrosyl chloride was investigated with two objects in view. Firstly, if the substance is a covalent compound with normal valency linkings, the molecule will probably be asymmetrical and triangular. If this is so, the absorption bands will show no pronounced branch maxima such as are predicted and observed for symmetrical molecules, and the presence or absence of these maxima in the same conditions of resolution and concentration provides a test of the theory according to which the spectra of such gases as SO_2, ClO_2, and Cl_2O have been interpreted. The two former molecules are required by the theory to be symmetrical, although such symmetry is not to be expected from the ordinary rules of valence. The experimental fact that the characteristic P, Q, and R branch maxima are absent in NOCl thus provides a verification of the theory.

Secondly, six electrons are effectively available for binding in the molecule, and accordingly* the structure should be triangular with a vertical angle ONCl approximately 120°, and governed by a valence force system. The molecule should, therefore, show whether or not the structure of triatomics is determined primarily by the number of available binding electrons.

Experimental.

The absorption spectrum of NOCl prepared by heating dry sodium chloride with nitrosylsulphonic acid shows that such specimens are contaminated with

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[*] Cassie, 'Nature,' vol. 131, p. 438 (1933).

N_2O_4. The older method of direct union of nitric oxide and chlorine due to Gay Lussac as modified by Taylor and Denslow* was adopted. Chlorine was obtained from a commercial cylinder and carefully dried, while nitric oxide was produced by mixing and warming saturated solutions of sodium nitrite and ferrous sulphate acidified with sulphuric acid. Snow, Rawlins, and Rideal† have shown that the infra-red spectrum of the gas prepared in this way is free from bands due to NO_2. It was passed successively through water, sodium hydroxide, concentrated sulphuric acid, and finally dried by phosphoric oxide.

The complete system from the NO generator to the final NOCl receiver was of glass. Oxygen was removed by passing nitrogen through the apparatus for some time before the sodium nitrite solution was dropped into the acidified ferrous sulphate. Chlorine was liquefied in a trap, and the NOCl formed there distilled across P_2O_5 to a second trap where it was frozen, and any excess NO pumped off. The possible impurities are now chlorine and $NOCl_2$. The former has no infra-red spectrum, while a sample of NOCl on passing through a glass spiral heated to 150° gave all the bands previously obtained with unaltered relative intensities.

Observations.

The absorption spectrum is given in Table I. No distinct maxima were found in any of the bands, and the usual P − R branch separation of the symmetrical molecules is replaced by an estimate of the band width.

Table I.

Band.	Band centre.		Band width. (cm.$^{-1}$).	Intensity.	Slit width (cm.$^{-1}$).
	λ (μ).	ν (cm.$^{-1}$).			
A	15·8	633	25	6	5
B	10·83	923	15	10	5
C	8·33	1200	20	3	12
D	5·46	1832	20	7	8
E	4·64	2155	25	4	10

Band A at 15·8 μ.—This region was particularly carefully investigated for P, Q, and R maxima as the longest wave-length band is usually most readily

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* 'J. Phys. Chem.,' vol. 31, p. 374 (1927).

† 'Proc. Roy. Soc.,' A, vol. 124, p. 453 (1929).

resolved. A peculiar contour was obtained with a very broad maximum near 655 cm.$^{-1}$, and a smaller indistinct rise at 627 cm.$^{-1}$. None of the bands showed any of the characteristics of normal resolution such as was obtained in COS, a molecule which has only a slightly smaller molecular weight, or in the even heavier molecule, Cl_2O.

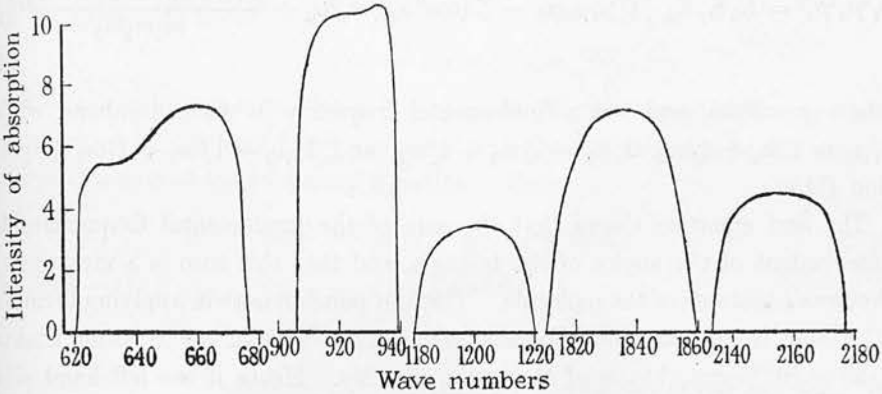

FIG. 1.—Infra-red absorption spectrum of NOCl.

Band B at 10·83 μ.—Two indistinct maxima were found some 10 cm.$^{-1}$ apart. The band is somewhat narrower than the others.

Bands C, D, E, at 8·33, 5·46, *and* 4·64 μ.—Broad maxima with undulating contours were obtained in each case.

Discussion.

Lack of pronounced branch maxima is a great handicap in fixing the structure and force system of the molecule, since these features have previously been used in deciding between the acute and obtuse angled structures, and in differentiating between the two possible force systems. Furthermore, the determination of a third force constant reduces the possibility of giving a precise interpretation of the spectrum in terms of the molecular parameters. However, by the use of reasonable assumptions and slight approximations we have reached what seem to us satisfactory conclusions.

The Central Force System.

The normal frequencies for the asymmetric molecule in this system have been evaluated by Radakovic,* and for the present purpose the relations of

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* 'Mhft. Chem.,' vol. 36, p. 555 (1930).

the roots to the coefficients of the frequency equations prove most useful. We have

$$p_1^2 + p_2^2 + p_3^2 = \mathrm{K}_1/\mu_1 + \mathrm{K}_2/\mu_2 + \mathrm{K}_3/\mu_3\,; \tag{1}$$

$$\Sigma\, p_1^2 p_2^2 = \Sigma\, \mathrm{K}_1\mathrm{K}_2/\mu_1\mu_2 - \Sigma\, \mathrm{K}_1\mathrm{K}_3\,(\cos^2\alpha_1)/m_1^2\,; \tag{2}$$

$$p_1^2 p_2^2 p_3^2 = \mathrm{K}_1\mathrm{K}_2\mathrm{K}_3 \left\{ 1/\mu_1\mu_2\mu_3 - \Sigma\,(\cos^2\alpha_3)/m_3^2\mu_1 + \frac{2\,(\cos\alpha_1\cos\alpha_2\cos\alpha_3)}{m_1 m_2 m_3} \right\}, \tag{3}$$

where $p = 2\pi c\nu$, and ν is a fundamental frequency in wave numbers, while $1/\mu_1 = 1/m_1 + 1/m_2$, $1/\mu_2 = 1/m_2 + 1/m_3$, and $1/\mu_3 = 1/m_3 + 1/m_1$ (equation (1)).

The first equation shows that the sum of the fundamental frequencies is independent of the angles of the triangle, and that this sum is a measure of the force constants of the molecule. The first point to note in applying formula (1) is that if the unit mass be taken as 10 times that of the H atom, that is $1\cdot65 \times 10^{-23}$ gm., $1/\mu$ is of the order of unity. Hence if the left-hand side of (1) be multiplied by this factor, the equation immediately indicates possible values for the force constants in dynes/cm. On assuming the most intense bands A, B, and D of Table I to give the fundamental frequencies, the left-hand side of (1) becomes $27\cdot2 \times 10^5$ dynes/cm., and possible values of the force constants might be $\mathrm{K}_1 = 9\cdot8$, $\mathrm{K}_2 = 9\cdot8$, and $\mathrm{K}_3 = 4 \times 10^5$ dynes/cm., or $\mathrm{K}_1 = 13$, $\mathrm{K}_2 = 6\cdot5$, and $\mathrm{K}_3 = 5 \times 10^5$ dynes/cm. The first solution would indicate a molecule like SO_2 with symmetrical bonds, and the second a double bond between N and O, and a single bond between N and Cl. Both structures may be considered in dealing with equations (2) and (3), and in taking $\mathrm{K}_1 = \mathrm{K}_2$, or $\mathrm{K}_1 = 2\mathrm{K}_2$ we effectively reduce the unknown force constants from three to two. Insertion of possible arithmetical values in (2) indicates that the terms involving the angles have but approximately one-tenth of the value of the other terms and as a first approximation may be neglected. From (1) and (2), if $\mathrm{K}_1 = \gamma\mathrm{K}_2$, then

$$(\gamma^2/\mu_2^2 + \gamma/\mu_1\mu_2 + 1/\mu_1^2)\,\mathrm{K}_1^2 - \Sigma\, p_1^2\,(1/\mu_1 + \gamma/\mu_2)\,\mathrm{K}_1 + \Sigma\, p_1^2 p_2^2 = 0. \tag{4}$$

I (*a*). $\gamma = 1$ gives $\mathrm{K}_1 = 2\cdot8 \times 10^5$ or $12\cdot3 \times 10^5$ dynes/cm. The first solution may obviously be discarded, while the second gives a negative value for K_3.

I (*b*). $\gamma = \frac{1}{2}$ gives $\mathrm{K}_1 = 4\cdot1$ or 14×10^5 dynes/cm. The first solution is impossible, while the second gives K_3 as $1\cdot3 \times 10^5$ dynes/cm., a not unlikely value. Insertion of the corresponding values in equation (3), even with the most favourable values of the angles, shows a discrepancy of 30% between the left- and right-hand sides of the equation. This fact in itself does not absolutely discredit the central force system, for the actual force constants may lie between the limits $\gamma = 1$ and $\gamma = \frac{1}{2}$, but we shall find that consistent agreement between all data is provided by the valence force system, and the latter is consequently to be preferred.

Valence Force System.

The normal frequencies for this system in the same conditions have been determined by Lechner,* and again we shall use the relations of the roots to the coefficients of the frequency equation. They are:

$$\Sigma p_1^2 = \mathrm{K}_1/\mu_1 + \mathrm{K}_2/\mu_2 + d/\mu_4\,; \tag{5}$$

$$\begin{aligned}\Sigma p_1^2 p_2^2 = (\mathrm{K}_1\mathrm{K}_2/\mu_1\mu_2)\,[1 - (\mu_1\mu_2/m_2)\cos^2\theta] \\ + (\mathrm{K}_1\, d/\mu_1\mu_4)\,[1 - (\mu_1\mu_4/m_2^2)\,(s/s_{23})^2\sin^2\theta)] \\ + (\mathrm{K}_2\, d/\mu_2\mu_4)\,[1 - (\mu_1\mu_4/m_2^2)\,(s/s_{12})^2\sin^2\theta]\,;\end{aligned} \tag{6}$$

and

$$p_1^2 p_2^2 p_3^2 = (\mathrm{K}_1\mathrm{K}_2\, d/\mu_1\mu_2\mu_4)\,[1 - \mu_1\mu_2/m_2^2]. \tag{7}$$

θ is the complement of α (equation (2)); s, s_{12}, and s_{23} are such that the potential energy of a displacement $\Delta\theta$ is given by

$$\mathrm{V} = \tfrac{1}{2}d_{12}\,(s_{12}\Delta\theta)^2 = \tfrac{1}{2}d\,(s\Delta\theta)^2 = \tfrac{1}{2}d_{23}\,(s_2\Delta\theta)^2, \tag{8}$$

where d_{12}, d, and d_{23} are tangential restoring force constants, and together with s_{12}, s, and s_{23} take into account the unequal sides of the triangle. d may be taken as equal to K /4, where K_θ is the tangential restoring force for the symmetrical triangle. Finally

$$1/\mu_4 = (1/\mu_1)\,(s/s_{12})^2 + (2s^2/m_2 s_{12} s_{23})\cos\theta + (1/\mu_2)\,(s/s_{23})^2.$$

Here again we investigate the limiting cases $\mathrm{K}_1 = \mathrm{K}_2$, and $\mathrm{K}_1 = 2\mathrm{K}_2$. Equations (5) and (7) are clearly the equations to take in solving for the unknown force constants, since θ only appears in these through μ_4. The value of $1/\mu_4$ is $3\cdot8/10m_{\mathrm{H}}$ when $\theta = 0$, $3\cdot1/10m_{\mathrm{H}}$ when $\theta = 60°$, and $2\cdot4/10m_{\mathrm{H}}$ when $\theta = 90°$, and so does not vary greatly with θ. Lack of branch maxima shows that the molecule is not linear like COS, and the most probable configuration has $\theta = 60°$, and the corresponding value of $1/\mu_4$ will be used. The effective radii of the neutral atoms are taken as N= $= 0\cdot61$, O= $= 0\cdot60$, N— $= 0\cdot71$, and Cl— $= 0\cdot97 \times 10^{-8}$ cm. s_{12}, s_{23}, and s will then be taken as 1·2, 1·7, and 1·4 A. Equation (5) now gives a measure of the force con-

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* 'SitzBer. Akad. Wiss., Wien,' vol. 141, p. 291 (1932).

stants equivalent to that given by (3) for the central force system. Eliminating K_2 and d/μ_4 from (5), (7), and the relation $K_1 = \gamma K_2$, we have

$$\gamma(1/\mu_1 + \gamma/\mu_2) K_1^3 - (\gamma\Sigma p_1^2) K_1^2 + (p_1^2 p_2^2 p_3^2)/(1/\mu_1\mu_2 - 1/m_2^2) = 0, \quad (9)$$

from which K_1 may be determined. Equation (9) does not contain the uncertain quantity $1/\mu_4$.

II (*a*). $\gamma = 1$. The possible solution is $K_1 = K_2 = 10 \cdot 2$, $K_\theta = 4 \times 10^5$ dynes per centimetre.

II (*b*). $\gamma = \frac{1}{2}$. $K_1 = 13$, $K_2 = 6 \cdot 5$, and $K_\theta = 4 \times 10^5$ dynes/cm. A choice of either of these two possible solutions may be made on investigation of equation (6). This involves only one quantity, θ, which is now unknown, and the solutions (*a*) and (*b*) are tested by solving (6) for θ. In this respect we may mention that we have tested other relations of K_1 to K_2, such as $\gamma = 1/3$, but the resulting agreement is poor. A negative value for $\sin^2 \theta$ is obtained from case II (*a*) while case II (*b*) gives θ as approximately 35°. Hence the valence force system with a vertical angle of some 140° most satisfactorily represents the characteristics of the molecule.

Band Assignments.

An unambiguous allocation seems impossible for the asymmetric molecule, even if the Raman spectrum were known. We have consequently assigned the vibration ν_3, which in the symmetrical triangle corresponds to the asymmetric mode and is generally the most intense in the infra-red, to band B at 923 cm.$^{-1}$, since this has the greatest intensity and least width. On this assumption the remainder of the bands are allotted as in Table II.

Table II.—Allocation of bands observed in the spectrum of NOCl.

Band.	Centre (cm.$^{-1}$).	Mode.	Calculated for (cm.$^{-1}$).	Difference.
A	633	ν_2	—	—
B	923	ν_3	—	—
C	1200	$2\nu_2$	1266	−66
D	1832	ν_1	—	—
E	2155	$2\nu_2 + \nu_3$	2189	−34

Alternative possibilities are: in the case of band C, $\nu_1 - \nu_2$ is calculated as 1199 cm.$^{-1}$, but in spite of the nearness of this value to that observed it seems preferable to adopt the interpretation given in Table II, since difference tones are likely to be weak; band E is capable of at least two other interpretations, and indeed may be due to a superposition of the three modes. The latter band has a comparatively high intensity, which might be further associated with the energy of activation of the NOCl molecule, which Taylor and Denslow (*loc. cit.*) have shown to correspond to $4 \cdot 77\ \mu$, and some form of resonance may anomalously increase the intensity of this combination tone.

The Molecular Structure.

The structure and force constants obtained are of considerable interest. In spite of the asymmetry of the molecule, the six valence electrons available for binding place the molecule in the SO_2 class* having a triangular structure with a vertical angle of some 120°, satisfying the valence force system, and with a tangential restoring force constant of approximately $3 \cdot 5 \times 10^5$ dynes/cm. Furthermore, the force constant total is the same for both SO_2 and NOCl, being $19 \cdot 5 \times 10^5$ dynes/cm. and the six binding electrons appear to make the same contribution in both.

The heat of the reaction $2(NO) + (Cl_2) = 2NOCl$ has been found by Dixon† to be $18 \cdot 6$ k. cals. Accordingly $(N) + (O) + (Cl) = 188$ k. cals., and allotting this value to the links in proportion to the force constants, we obtain 125 k. cals. for the $N = O$ bond, and 63 k. cals. for $N - Cl$. This is in agreement with the structure of the nitrous oxide molecule which we have shown to be $N = N = O$, with force constants $K_1 = K_2 = 14 \times 10^5$ dynes per centimetre, and a heat of formation of 256 k. cals. Again the force constant‡ for nitric oxide, NO, is $15 \cdot 7 \times 10^5$ dynes/cm., the heat of formation is 150 k. cals., and we have for the $N = O$ bond in NOCl, $150 \times 13/15 \cdot 7 = 124$ k. cals. in excellent agreement. The value of the $N - Cl$ link in nitrogen trichloride seems to be some 45 k. cals., the smaller heat being presumably associated with the instability of this substance.

Raman and other Spectra.

Dadieu and Kohlrausch§ were unable to obtain a Raman spectrum from liquid NOCl, and assumed that the liquid was too dark. It is probable that

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* Cassis, *loc. cit.*

† 'Z. phys. Chem.,' Bodenstein Festband, p. 679 (1931).

‡ Bailey and Cassie, 'Phys. Rev.,' vol. 39, p. 534 (1932).

§ 'Phys. Z.,' vol. 33, p. 165 (1932).

the asymmetry of the molecule results in comparatively weak displacements. The absorption spectrum in the visible and ultra-violet has been examined in part by Magnanini,* Kistiakowsky† and Leermakers and Ramsperger,‡ but apart from the recognition of a banded structure with partial resolution, no quantitative results are available. The photochemical reaction was interpreted by Kistiakowsky as involving $NOCl' + NOCl$ in spite of the fact that a large reduction in pressure, and the seven-fold addition of nitrogen had no effect on the quantum efficiency, γ retaining the value of 2 independent of λ. The reason given for the assumption was that the heat of dissociation of NOCl into $NO + Cl_2$ corresponded to 613 $\mu\mu$, whereas light of longer wave-length was effective; the calculated wave-length is incorrect as a consequence of the belief that the heat of formation of one mol. of NOCl from $NO + Cl_2$ was 18 k. cals., the latter value, however, corresponding to two mols. The complete quantum yield is thus more likely to be explained by primary dissociation, and the suggestions made by Allmand§ are probably correct.

The most reasonable values for the molecular constants of nitrosyl chloride may be summarized as in Table III.

Table III.—The Molecular Constants of NOCl.

Frequencies (cm.$^{-1}$).	Force constants (dynes/cm. × 10^{-5}).	Dimensions.
$\nu_1 = 1832$ $\nu_2 = 633$ $\nu_3 = 923$	$K_1 = 13$ (N = O) $K_2 = 6\cdot5$ (N − Cl) $K_\theta = 4$	$\widehat{ONCl} = ca.\ 140°$ $N - Cl = 1\cdot7$ A. $N = O = 1\cdot2$ A.

Taking ν_2 as $a_2 + b_2$, where b_2 from band C $(2a_2 + 4b_2)$ is -33 cm.$^{-1}$, we can calculate approximately the heat of dissociation corresponding to this vibration from the formula $D = a^2/4b$. The value is some 33 k. cals. which may reasonably correspond to the reaction $NOCl = NO + Cl - 38$ k. cals.

The authors once again thank Professor F. G. Donnan, C.B.E., F.R.S.; and the Department of Scientific and Industrial Research for a Senior Award to A. B. D. C.

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* 'Z. phys. Chem.,' vol. 4, p. 427 (1889).

† 'J. Amer. Chem. Soc.,' vol. 52, p. 102 (1930).

‡ *Ibid.*, vol. 54, p. 1837 (1932).

§ 'Chem. Soc. Discussion,' p. 34 (1931).

Summary.

The infra-red absorption spectrum of nitrosyl chloride, NOCl, has been examined from 1 to 18 μ. Five bands were isolated between 4 and 16 μ, but as a consequence of the expected asymmetry of the molecule, no resolution was obtained. The molecule falls into the sulphur dioxide class, having a vertical angle of some 140°, and obeying a valence force system. The force constants have been determined and associated with the heats of linking.

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INVESTIGATIONS IN THE INFRA-RED REGION OF THE SPECTRUM

XI—THE ABSORPTION SPECTRUM AND MOLECULAR STRUCTURE OF BORON TRICHLORIDE, AND THE EFFECT OF STRAIN ON PLANE GROUPS OF THE TYPE XY_3

By

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Investigations in the Infra-Red Region of the Spectrum

XI—The Absorption Spectrum and Molecular Structure of Boron Trichloride, and the Effect of Strain on Plane Groups of the Type XY_3

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(*Communicated by F. G. Donnan, F.R.S.—Received June* 22, 1934)

Investigations of force constants of molecules become less accurate as the number of atoms in the molecule increases. This is due to several obvious difficulties such as obtaining exact formulæ for the normal frequencies of a system with many vibrational degrees of freedom, and assigning correctly observed fundamental frequencies. There is, however, a less obvious source of error in dealing with molecules whose equilibrium configuration is one of strain. The force constant of any link measures the curvature of the nuclear separation-potential energy curve for the link in question at its equilibrium separation. This equilibrium separation corresponds to the minimum in this curve for diatomic and non-closed triatomic molecules. But if the link be under strain the equilibrium separation does not correspond to this minimum, and the curvature measured by the force constant may be very different from that for the same link joining the same atoms in a diatomic molecule. Hence force constants deduced from observed vibrational frequencies of a molecule whose bonds are under strain cannot be compared with those of similar bonds of diatomic molecules unless they are corrected for deviation from the minimum of the potential energy curve.

Boron trifluoride and trichloride are molecules likely to yield information regarding the effect of strain on observed force constants; they are stable gases at room temperature, and the chloride is readily prepared and purified. Further, quantum mechanics predicts that they should have a plane configuration, and allocation of fundamental frequencies should be possible with some degree of certainty.

The fluoride was first chosen for investigation as its moments of inertia seemed likely to be small enough for resolution of P, Q, and R branches with the prism spectrometer, and this would assist in correct allocation of the fundamental frequencies. A preliminary run with the trifluoride prepared from KBF_4, B_2O_3, and H_2SO_4 showed that the sample was very impure, and was insufficiently dry to prevent attack of the rock-salt plates. The run did, however, serve to locate several bands, and showed that P and R branches can be separated. It is hoped to reinvestigate this spectrum with a sample sufficiently pure and dry to overcome the difficulties encountered in the preliminary investigation.

The trifluoride can be prepared from the trichloride leaving the trichloride as the most probable impurity, and accordingly the trichloride was first investigated.

EXPERIMENTAL

Boron trichloride was obtained from British Drug Houses, Ltd., and was purified by distillation, the middle fraction being dried over phosphorus pentoxide and retained for the infra-red absorption measurements. Different samples gave all the bands of the same relative intensity, and none of the bands showed any peculiarities associated with impurities.

The observed spectrum is summarized in Table I, and the contours of the bands are indicated in fig. 1.

TABLE I—THE INFRA-RED ABSORPTION SPECTRUM OF BORON TRICHLORIDE

Band	Band centre		Intensity (arbitrary units)	Slit width cm^{-1}	Prism
	μ	cm^{-1}			
A	14·00	714	4	5	Rock-salt
B	11·81	845	3	5	,,
C	10·44	958	100	5	,,
D	10·04	996	95	5	,,
E	8·290	1206	2	9	,,
F	7·208	1387	6	4	Fluorite
G	6·998	1429	6	4	,,
H	5·230	1912	2·5	8	,,
I	5·011	1995	2	8	,,

The bands do not call for individual comment apart from the relative intensity of C and D. These bands are much more intense than any of the others observed, and the rough scale of intensity used in Table I does not bring out their relative intensity: at one pressure of BCl_3, C gave a maximum absorption of 80% whilst D gave 40%, so that C is actually twice as intense as D. Fig. 1 is constructed to indicate the relative intensities of the bands except for C and D. The scale of percentage absorption is the same for all the bands in fig. 1, the variation of intensity being obtained by raising or lowering the position of each band without altering this scale. One scale of percentage absorption is used for all

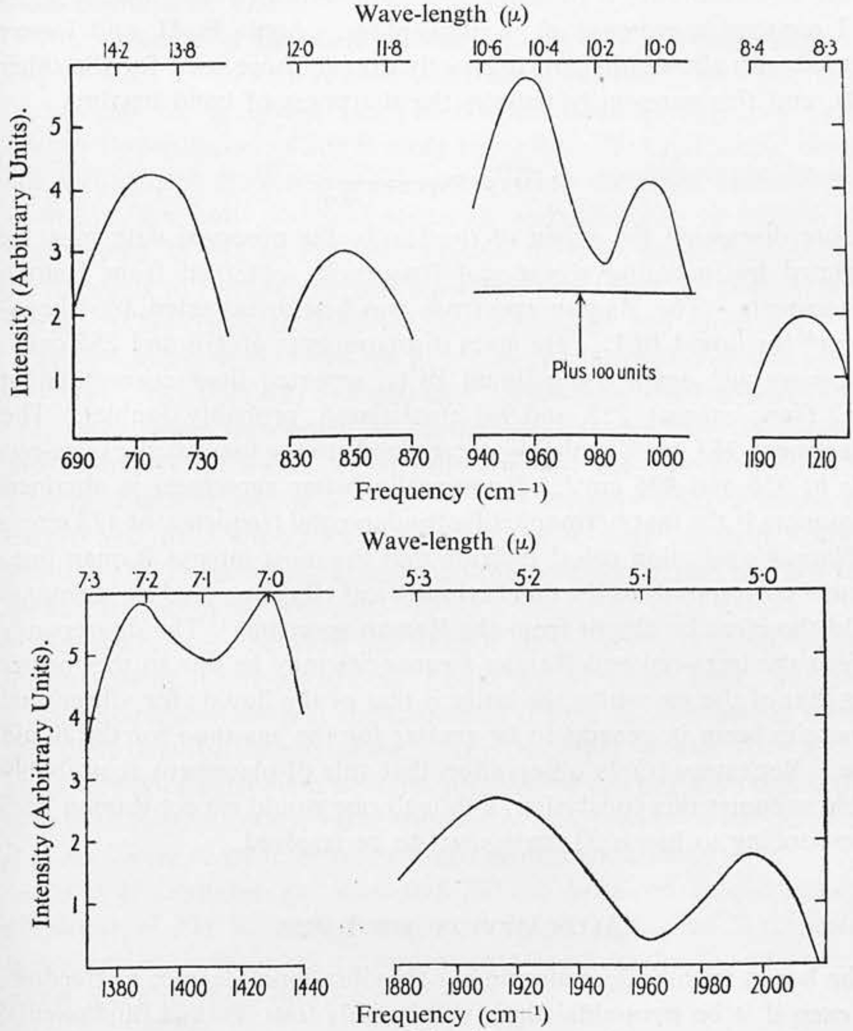

FIG. 1

the bands so that the figure may give an undistorted representation of the relative widths of the bands. Thus bands C and D are narrow compared with the others, whilst H and I are broad. This may represent a true variation in band width, but much of it will be due to the contours having been observed at different pressures and with different slit widths. C and D were observed with a pressure of a millimetre or less, whereas E, H and I required a pressure of an atmosphere. Again E, H, and I were observed with slit widths approximately double those used for the other bands, and this necessarily reduces the sharpness of band maxima.

RAMAN SPECTRUM

Before discussing the origin of the bands, the observed data must be completed by including vibrational frequencies obtained from Raman displacements. The Raman spectrum was first investigated by Bhagavantam[*] for liquid BCl_3. He gives displacements of 470 and 255 cm^{-1}. Venkateswaran[†] again using liquid BCl_3, reported lines corresponding to 472 (very intense), 255, and 947 cm^{-1} (weak, probably double). The displacement 947 cm^{-1} probably corresponds to the two intense infra-red bands at 958 and 996 cm^{-1}. Numerically better agreement is obtained by assuming it the first harmonic of a fundamental frequency at 472 cm^{-1}, but Placzek's selection rules[‡] indicate that the most intense Raman line, 472 cm^{-1} corresponds to the most symmetrical vibration, and its harmonic should therefore be absent from the Raman spectrum. The discrepancy between the infra-red and Raman frequencies may be due to the former being that of the gas whilst the latter is that of the liquid; for vibrational frequencies seem in general to be greater for the gas than for the liquid phase. Venkateswaran's observation that this displacement is probably double supports this conclusion, although one would expect Raman lines corresponding to bands 38 cm^{-1} apart to be resolved.

ALLOCATION OF THE BANDS

The boron trichloride molecule has six vibrational degrees of freedom, but even if it be pyramidal there will be only four distinct fundamental frequencies. A choice between the pyramidal and planar configurations could be made if infra-red observations were available up to 25 μ; this would include the region of 470 cm^{-1} where the most intense Raman line

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[*] 'Ind. J. Phys.,' vol. 5, p. 73 (1930).

[†] *Ibid.*, vol. 6, p. 284 (1931).

[‡] 'Liepziger Vorträge,' p. 78 (1931).

appears, and if the molecule be planar this frequency will be inactive in the infra-red, whereas if the molecule be pyramidal, it will be active. This region could not be included in the present observations, but the intensity of the Raman line suggests that it is due to simultaneous vibration of the three Cl atoms in phase, towards or away from a stationary boron atom in the same plane.

The molecule is therefore assumed to have a planar configuration, and we shall try to ascribe observed frequencies to the four fundamental frequencies ν_1, ν_2, ν_3 and ν_4. The normal mode of frequency ν_1 corresponds to oscillation of the B atom relative to the Cl_3 triangle along the line through the median point and normal to the plane of the molecule. ν_2 and ν_3 are both double frequencies corresponding to motion of the four atoms in the equilibrium plane. ν_4 is a single frequency, and corresponds to the symmetrical inactive mode where the B atom remains at rest. This choice of ν_1 to ν_4 follows Nielsen* and Menzies.†

The positions of the infra-red bands can be satisfactorily accounted for if we take 996, 958, 430 and 250 cm^{-1} as fundamental frequencies. The first three select themselves as fundamental frequencies on account of their intensity, provided we identify the 430 cm^{-1} frequency with the Raman displacement of 472 cm^{-1}. The 250 cm^{-1} displacement might correspond to a difference tone, but the relative intensities and the positions of the bands agree best with the assumption that this is a fundamental frequency.

The discrepancy between the Raman displacement, 472 cm^{-1}, and the corresponding inactive infra-red frequency is rather large, particularly when one remembers that the frequency for the liquid phase is generally less than that for the gas phase. Any frequency greater than 430 cm^{-1} gives very poor agreement with the infra-red bands, and although 430 cm^{-1} is only an estimate of the value required by observed infra-red frequencies, it is not likely to be in error by much more than 5 cm^{-1}.

Table II contains an allocation of the infra-red frequencies. The allocation of 996, 958, 250 and 430 cm^{-1} to ν_1, ν_2, ν_3 and ν_4 respectively, is not arbitrary, but is in agreement with the investigation of force constants given in the following paragraphs.

EVALUATION OF FORCE CONSTANTS

Formulæ relating fundamental frequencies to force constants have been given by Nielsen (*loc. cit.*) and Menzies (*loc. cit.*). Their results

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* 'Phys. Rev.,' vol. 32, p. 773 (1928).

† 'Proc. Roy. Soc.,' A, vol. 134, p. 265 (1931).

are not in agreement, and we shall use the expressions given by Menzies. The difference between the two sets of formulæ probably arises in approximations involved in transforming the potential function,

$$V = F(r) + f(a) + F'(r)(q_4 + q_5 + q_6) + \tfrac{1}{2}F''(r)(q_4^2 + q_5^2 + q_6^2) + f'(a)(q_1 + q_2 + q_3) + \tfrac{1}{2}f''(a)(q_1^2 + q_2^2 + q_3^2),$$

where r is the BCl separation, a the ClCl separation, q_1, q_2 and q_3 are the displacements of the sides of the triangle, and q_4, q_5 and q_6 are the displacements of BCl from their equilibrium separations. $F'(r)$ and $F''(r)$ are the first and second derivatives of the potential function $F(r)$ and $f'(a)$ and $f''(a)$ those of the potential function $f(a)$. The six independent co-ordinates used to specify the six vibrational degrees of freedom are q_1, q_2, q_3, x, y, and z, where x, y, and z are the rectangular co-ordinates of B relative to the centre of gravity of the Cl atoms. z is normal to the plane of the triangle, and x is parallel to one undisplaced side. The co-ordinates q_1 to q_6 in the expression for V must be replaced by q_1, q_2, q_3, x, y and z, and only approximate expressions can be obtained for the transformation. Menzies' results check with the approximation that the deviation of any angle ClBCl from 120° is due to the displacements x, y, z; this takes into account motion of the Cl atoms, for x, y and z are displacements of B relative to the centre of gravity of the Cl atoms, but a further approximation would include terms in q_1 to q_3 depending on the individual displacements of the sides of the triangle. This further approximation seems unnecessary, particularly for BCl_3, where the displacement of the light nucleus B will always be much greater than that of any Cl nucleus.

TABLE II—ALLOCATION OF OBSERVED INFRA-RED FREQUENCIES

Band	Centre cm^{-1}	Mode	Centre calculated cm^{-1}	(Cal. − obs.) cm^{-1}
A	714	$\nu_2 - \nu_3$	708	−6
B	845	$2\nu_4$	860	15
C	958	ν_2	—	—
D	996	ν_1	—	—
E	1206	$\nu_2 + \nu_3$	1208	2
F	1387	$\nu_2 + \nu_4$	1388	1
G	1429	$\nu_1 + \nu_4$	1426	−3
H	1912	$2\nu_2$	1916	4
I	1995	$2\nu_1$	1992	−3

Menzies' expressions for the frequencies are:

$$\nu_1 = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \sqrt{\beta\mu}, \tag{1}$$

$$\nu_2, \nu_3 = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

$$\sqrt{\tfrac{1}{4}[\mu(1+\beta)+(1+3\alpha) \pm \sqrt{[\tfrac{1}{4}\mu(1+\beta)+\tfrac{1}{4}(1+3\alpha)]^2-\tfrac{1}{4}\mu[(1+3\alpha)(1+\beta)-(1-\beta)^2]}} \tag{2}$$

$$\nu_4 = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \sqrt{(1+3\alpha)}, \tag{3}$$

where m is the mass of Cl, M that of B, μ is $\frac{M + 3m}{M}$, k is $F''(r)$, α is $\frac{f''(a)}{F''(r)}$, and β is $\frac{F'(r)/r}{F''(r)}$.

One notes that ν_1 is assumed to arise only from the strain of the molecule. This is unlikely to be the complete picture, for the molecule will resist displacement of B normal to the equilibrium plane even though strain be absent. In fact the molecule most likely possesses rigidity with respect to deformation of the plane configuration, just as linear triatomic molecules resist deformation of their straight line configuration.

The procedure adopted in the present discussion is to obtain the three unknown parameters k, α and β from the three known fundamental frequencies ν_2, ν_3 and ν_4. The value of β thus obtained depends only on the strain of the molecule, for all three normal modes involve only motion in the plane of the triangle. Deviation of the value of β obtained from ν_1 from this value, gives a measure of the rigidity of the plane configuration.

The most convenient method of discovering the correct allocation of the fundamental frequencies is to eliminate two of the unknown parameters k, α and β from the three equations contained in (2) and (3). Actually if α and β be eliminated, one obtains the expression:

$$[(\nu_2^2 + \nu_3^2)^2 - (\nu_2^2 - \nu_3^2)^2 + \mu\gamma(\gamma - \nu_4^2)]\,A^2 - 4\mu\gamma A + 4\mu = 0, \tag{4}$$

where A is $4\pi^2 \frac{m}{k}$, and γ is $\frac{\mu}{2}(\nu_2^2 + \nu_3^2 - \tfrac{1}{2}\nu_4^2)$.

The frequency 430 cm^{-1}, corresponds to the most intense Raman line, and must therefore be ν_4. There remain the frequencies 250, 958, and 996 cm^{-1} as possible values of ν_2 and ν_3. If the two higher frequencies be chosen as ν_2 and ν_3, imaginary values are obtained for A. Hence ν_2 and ν_3 must be either 996 or 958 and 250 cm^{-1}. According to Menzies' expressions ν_3 must have the lower frequency; hence ν_3 is 250 cm^{-1}. Two solutions are obtained with either 996 or 958 cm^{-1} as ν_2. These are given in Table III.

TABLE III—POSSIBLE VALUES OF POTENTIAL COEFFICIENTS FOR BORON TRICHLORIDE

F″ dynes/cm	f'' dynes/cm	F′ dynes	
$2 \cdot 6 \times 10^5$	$0 \cdot 36 \times 10^5$	$1 \cdot 3 \times 10^{-3}$	ν_2 equal to 996 cm^{-1}
$0 \cdot 74 \times 10^5$	$0 \cdot 97 \times 10^5$	$4 \cdot 4 \times 10^{-3}$	
$2 \cdot 6 \times 10^5$	$0 \cdot 36 \times 10^5$	$1 \cdot 0 \times 10^{-3}$	ν_2 equal to 958 cm^{-1}
$0 \cdot 74 \times 10^5$	$0 \cdot 97 \times 10^5$	$4 \cdot 1 \times 10^{-3}$	

Replacement of 996 by 958 cm^{-1} affects F″ and f'' negligibly, but the value of F'/r is appreciably altered. Table III gives F′ for r equal to 1·75 A, corresponding to Wierl's value* of 3·03 A for the Cl-Cl separation in BCl_3.

The value of F'/r obtained from ν_1 is $1 \cdot 65 \times 10^5$ dynes/cm, and is inappreciably changed by substitution of 958 for 996 cm^{-1} as this frequency; the corresponding value of F′ is approximately $2 \cdot 9 \times 10^{-3}$ dynes. Thus, the first solutions of Table III where F′ is near 1×10^{-3} dynes, corresponds to a molecule whose plane configuration would be maintained even though there was no strain due to repulsion of the Cl nuclei. The second solutions where F′ lies near 4×10^{-3} dynes corresponds to a molecule whose plane configuration can only be maintained by this repulsion; for the strain value of F′ is actually greater than that calculated from the deformation frequency.

EFFECT OF STRAIN ON FORCE CONSTANTS

The force constants given in Table III cannot be compared with those of similar links of unstrained molecules; for as has been indicated in the introductory paragraph, they do not measure the curvature of the potential nuclear separation curve at its minimum value, but at some point arbitrarily determined by the size of the atoms repelling one another. The actual stress in BCl_3 appears from the values of F′ given in Table III. The mass of the Cl atom is $5 \cdot 8 \times 10^{-23}$ gm, so that the acceleration due

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* 'Ann. Physik,' vol. 8, p. 521 (1931).

to a force of 10^{-3} dynes is of the order of 10^{20} cm/sec. The magnitude of this stress is probably better appreciated when one recalls that two particles of unit electronic charge 1·5 A apart repel one another with a force of approximately 10^{-3} dynes. Deviation from the minimum of the potential curve must therefore be appreciable, and the values of F″ given in Table III are unlikely to be even approximate values of the force constants.

APPLICATION OF MORSE'S FORMULA TO STRAINED BONDS

The true value of the force constant for the BCl bond can be obtained if the potential nuclear separation curve can be specified from observed values of F″ and F′. The most useful analytical expression describing this curve is due to Morse, and provided unknown parameters in the formula can be obtained from observed data, the curve can be specified and the true force constant evaluated. Morse's formula is:

$$\mathrm{F} = \mathrm{D}\, e^{-2a\,(r - r_0)} - 2\mathrm{D}\, e^{-a\,(r - r_0)},$$

where D is the energy of dissociation of the bond in question, r_0 the separation of the nuclei at the position of minimum potential, and a is a constant given for a diatomic molecule by:

$$a = 0{\cdot}245\,\sqrt{\mathrm{M}_0 w_0 x} \qquad \text{in A}^{-1},$$

M_0 being $\dfrac{\mathrm{M}_1 \times \mathrm{M}_2}{(\mathrm{M}_1 + \mathrm{M}_2)}$, where M_1 and M_2 are the masses of the atoms in terms of the mass of the H atom, and w_0x in cm^{-1} measures the deviation of the lower vibrational frequencies from their harmonic values.[*]

This formula has two unknown parameters, D and a; $(r - r_0)$ is also unknown, being the extent of the strain of the BCl bond. Analysis of the vibrational spectrum gives F′ and F″ for this value of $(r - r_0)$, so that some third relation must be obtained to evaluate F″ for r equal to r_0. This may be obtained by estimating D, or alternatively, the anharmonic constant a.

The heat of formation of $\mathrm{BCl_3}$ is given by Berthelot[†] as 90 k.cal., or 3·9 volts. This energy represents the net result of $\mathrm{Cl_2}$ molecules uniting with amorphous boron to give $\mathrm{BCl_3}$. Hence the energy associated with the three BCl bonds also contains the heat of atomization of $\mathrm{Cl_2}$ and the heat of sublimation of boron. Sidgwick[‡] gives for the first 1·25 volts.

[*] Condon and Morse, "Quantum Mechanics," McGraw-Hill, 1929, p. 163.

[†] 'Ann. Chim. Phys.,' vol. 52, p. 84 (1878).

[‡] "Covalent Bond in Chemistry," Cornell University Press, 1933, p. 100.

There appears to be no experimental determination of the heat of sublimation of boron, and one can only form a rough estimate from that of carbon. Sidgwick* gives the heat of sublimation of carbon as approximately 6·5 volts. The diameters of C and of B in the solid state are approximately equal,† and both have exceptionally high temperatures of sublimation, although the qualitative evidence available‡ indicates that boron sublimes more readily than carbon. Hence the two heats of sublimation are probably of the same order with that of carbon as the higher, and we shall take that of boron as 6 volts.

One-third of the heat of formation of BCl_3 and of the heat of sublimation of B, and one-half of the heat of atomization of Cl_2 will be associated with each BCl bond. This gives approximately 4 volts for D. There is, however, another factor to be taken into account, namely, the energy required to break down the *s-p* quantization of the normal boron atom to provide the trigonal quantization required for formation of the molecule. Thus, the normal boron atom has the electron configuration $2s^2\,2p\,{}^2P^0$, and that required for formation of BCl_3 must have two electrons in $2p$ orbitals, and must have in all three electrons with uncoupled spins. Pauling§ estimates the energy required for this change in electronic configuration as 9·3 volts. One-third of this will be associated with each BCl bond. This gives the rather large value of 7 volts for D. The last factor is the largest and probably the most doubtful; for the heat of sublimation may include some similar factor, when D would lie between 4 and 7 volts. Finally the repulsion of the Cl atoms must represent a loss in energy. The amount of this loss can be estimated from the values of F′ given in Table III, and appears to be roughly one-tenth of D, and may therefore be neglected.

The parameter a may also be estimated, and in fact there appears to be fewer doubtful factors involved in a than in D. a does not seem to vary over a large range; the observation that D is proportional to the force constant for unstrained bonds implies that a does not vary from bond to bond. Thus, taking Morse's formula, the true force constant is given by F″ for r equal to r_0; this is readily verified to be $2a^2D$, and if the force constant is proportional to D, a must remain constant. A reasonable value for w_0x for a diatomic molecule of the type BCl will lie between 5 and 10 cm^{-1}, or a will lie between 1·5 and 2·3 A^{-1}.

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* *Ibid.*, p. 109.

† *Cf. ibid.*, p. 84.

‡ *Cf.* Mellor's "Treatise on Inorganic Chemistry," vol. 5, p. 11.

§ 'J. Amer. Chem. Soc.,' vol. 53, p. 1375 (1931).

If a be taken as $2A^{-1}$, the calculated values of F′ and F″ given in Table III, are sufficient to evaluate D and F''_0, the value of F″ at r equal to r_0. The significant results are summarized in Table IV.

TABLE IV—VALUES OF D AND K, THE TRUE FORCE CONSTANT, FOR THE BCl BOND. ($a = 2A^{-1}$)

F″ dynes/cm	F′ dynes	F''_0 or K dynes/cm	D volts
$2\cdot6 \times 10^5$	$1\cdot24 \times 10^{-3}$	$12\cdot5 \times 10^5$	10
$2\cdot6 \times 10^5$	$1\cdot02 \times 10^{-3}$	10×10^5	7·8
$0\cdot74 \times 10^5$	$4\cdot2 \times 10^{-3}$	35×10^5	25·5

The data of Table IV immediately suggest that the solution with F″ equal to $0\cdot74 \times 10^5$ dynes/cm is impossible. The other solutions indicate that the allocation of 958 cm^{-1} to ν_2 gives the most reasonable values of D and K. The value of D may be decreased by taking a value of a greater than $2A^{-1}$. Thus, if a be taken as $3A^{-1}$, corresponding to approximately 20 cm^{-1} for w_0x, then D becomes 4·5 electron volts, and the true force constant 13×10^5 dynes/cm.

The values of F′ and of F″ obtained from vibrational frequencies do not correspond to values of these quantities at one value of r, but to mean values for the range of r corresponding to the amplitude of vibration. Since both F′ and F″ vary rapidly with r near the minimum of the potential nuclear separation curve, the effect of the amplitude of vibration on the values of K and D given in Table IV must be determined. The magnitude of the amplitude of vibration has been estimated from the intensities of X-rays scattered by the atoms in individual molecules. Gajewski* estimates the amplitude for molecules containing Cl as 0·2 A. The energy of vibration is presumably that of an unexcited molecule, and must therefore be $\frac{1}{2}h\nu$; this means that the amplitude in the first vibrational state will be greater than 0·2 A. If the amplitude of vibration of the Cl atoms be taken as 0·3 A, K becomes $8\cdot8 \times 10^5$ dynes/cm, and D 6·9 volts. 0·3 A seems rather large for the amplitude of vibration, but smaller values give K and D intermediate between these values and those quoted in Table IV.

There remains one interesting point in connection with the strain of the molecule, namely, the actual extent of the strain as measured by $(r - r_0)$. This is readily calculated from Morse's formula. If we take the second solution of Table IV, insertion of corresponding values of F′ or of F″, gives $(r - r_0)$ as 0·12 A. Wierl's value of the Cl-Cl separa-

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* ' Phys. Z.,' vol. 33, p. 123 (1932).

tion of 3·03 A gives r equal to 1·75 A. Hence the unstrained value of the BCl link is approximately 1·63 A. Sidgwick gives the radius of univalent Cl as 0·97 A, so that the radius of trivalent B in an unstrained molecule is 0·66 A. Pauling* gives 0·89 and 0·80 A for the radii of mono- and di-valent boron respectively, and this indicates that the trivalent atom should have a radius of approximately 0·7 A, in good agreement with the value just calculated.

The above calculation of the true force constant for a strained molecule can only be approximate, chiefly because D or a can be only roughly estimated; but it does show that force constants as ordinarily determined for such molecules may be in error, not by a few per cent., but by several hundred per cent. The other uncertainty in the calculation is how far Morse's curve can be used to represent the potential energy of bonds of molecules in general. The values of D and of K obtained for the BCl bond of BCl_3 are certainly reasonable though approximate, and it seems probable that if D or a could be accurately calculated, Morse's formula would be of considerable value in specifying this bond. Data at present available indicate that K is approximately 9×10^5 dynes/cm, and D is 7 volts; for these are the most likely values when amplitude of vibration is allowed for. Each BCl bond is a single link, and from known force constants for molecules formed from atoms in the boron row of the periodic table, this force constant is expected to be at least 7×10^5 dynes/cm; 9×10^5 dynes/cm is therefore quite a reasonable value. Again, although 7 volts is considerably greater than the heat of dissociation normally associated with a single link, the estimate given earlier suggests that the energy appropriate to D in Morse's formula, is in fact near this figure.

RIGIDITY OF THE MOLECULE

The rigidity of the molecule can be evaluated from observed fundamental frequencies. Suppose it is measured by a tangential restoring force constant K_θ, so that the potential energy associated with a deviation of one BCl bond from the plane configuration is given by:

$$V = \tfrac{1}{2}K_\theta \ (r^2\theta^2),$$

where θ is the angle between the displaced link and its equilibrium position. ν_1 is then given by

$$4\pi^2\nu_1^2 = \frac{1}{m}\,(K_\theta)\,\mu\,, \tag{5}$$

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* 'Proc. Nat. Acad. Sci.,' vol. 18, p. 293 (1932).

and Menzies' expression is:

$$4\pi^2\nu_1^2 = \frac{1}{m}\left(\frac{F'(r)}{r}\right)\mu. \tag{6}$$

Hence F'/r calculated from Menzies' relation gives K_θ, or the tangential restoring force constant. The value of K_θ calculated in this way must be corrected for the strain of the molecule. The frequencies of normal modes confined to the plane of the molecule give F'/r as $0{\cdot}6 \times 10^5$ dynes/cm, and this is due to strain alone. ν_1 gives F'/r as $1{\cdot}64 \times 10^5$ dynes/cm. Hence the true rigidity of each bond is given by a tangential restoring force constant of approximately 1×10^5 dynes/cm; or the rigidity associated with the central B atom in BCl_3 is 3×10^5 dynes/cm.

ELECTRONIC CONFIGURATION OF BORON TRICHLORIDE

Boron trichloride provides an excellent example of Pauling's trigonal quantization.* The B atom has five electrons, $(1s)^2$, $(2s)^2$, and $2p$. The $1s$ electrons may be assumed to remain in their closed shell, but as the atom is trivalent, the *s-p* quantization of the $2s$ and $2p$ electrons must be disturbed so that one of the two $2s$ electrons passes to a $2p$ orbit. The atom has now three electrons in separate orbits, one an *s* orbit and the other *p* orbits. An orthogonal linear combination of the corresponding proper functions has three maxima along three directions making 120° with one another in one plane. The chlorine orbits occupied by one electron will form bonds along these directions, giving the three orbitals necessary to accommodate the six valence electrons.

If this picture of the electron configuration be correct, the plane configuration should of itself possess rigidity. This agrees with the first solutions of Table III, but not with the second solutions. The extent of this rigidity according to the first solution is given by a tangential restoring force constant 3×10^5 dynes/cm for all three bonds. This is surprisingly close to the values $3{\cdot}3$ and $3{\cdot}6 \times 10^5$ dynes/cm observed for the same constant in SO_2 and ClO_2 respectively.† The fundamental feature of the electron configuration of these molecules seems also to be trigonal quantization of the central atom,‡ and this will account for the similarity of the three tangential restoring force constants. In fact, the observed rigidities of different molecules suggest that this may be determined to a first approximation by the particular quantization of the central atom. Thus, molecules belonging to one of the three types of central quantiza-

* 'J. Amer. Chem. Soc.,' vol. 53, p. 1381 (1931).

† *Cf.* Bailey and Cassie, 'Proc. Roy. Soc.,' A, vol. 140, p. 607 (1933).

‡ *Cf.* Cassie, 'Trans. Faraday Soc.,' vol. 30, p. 91 (1934).

tion so far investigated from this point of view, appear to have similar rigidities, whilst molecules belonging to different types have very different rigidities. Molecules whose central atom has *s-p* quantization, such as H_2O, appear very rigid with respect to deformation, those with trigonal central quantization are characterized by tangential restoring force constants near 3×10^5 dynes/cm, and those with linear central quantization are characterized by tangential constants of approximately 1×10^5 dynes/cm.

NITRATE AND CARBONATE IONS

X-ray, infra-red, and Raman investigations of the nitrate and carbonate ions are in general agreement with the plane configuration. Pauling* suggests that they are slightly pyramidal and merely simulate the plane configuration by vibration of the N or C nuclei through the oxygen plane. Menzies (*loc. cit.*) has shown that observed fundamental frequencies are consistent with the analytical expressions for the normal frequencies. He did not, however, distinguish rigidity from strain in relation to the frequency ν_1, nor did he attempt to evaluate the true force constants for the NO and CO bonds. The question of rigidity of the ions is clearly important if one is to decide whether the ions are planar because of their central quantization, or merely simulate the plane configuration due to strain tending to bring all four atoms into one plane. Evaluation of the true force constant, on the other hand, will indicate the type of link in the CO and NO bonds. Thus interesting information regarding the nitrate and carbonate ions should be obtained from an investigation of their fundamental frequencies along the lines followed for BCl_3.

The optical properties of crystals whose infra-red spectra have been examined automatically allocate observed frequencies to the four distinct normal frequencies;† in Menzies' notation, the CO''_3 frequencies are 880, 1430, 706 and 1087 cm^{-1} for ν_1, ν_2, ν_3 and ν_4 respectively. Insertion of these values in formula (4) gives the two possible solutions:

F″ dynes/cm	f'' dynes/cm	F′ dynes
$5 \cdot 3 \times 10^5$	$1 \cdot 9 \times 10^5$	$3 \cdot 0 \times 10^{-3}$
$2 \cdot 25 \times 10^5$	$2 \cdot 95 \times 10^5$	$6 \cdot 9 \times 10^{-3}$

F′ is obtained by taking the O-O separation as 2·25 A‡ or r as 1·30 A.

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* 'J. Amer. Chem. Soc.,' vol. 53, p. 1382 (1931).

† *Cf.* Schafer, Matossi and Anderhold, 'Phys. Z.,' vol, 30, p. 581 (1929).

‡ *Cf.* Pauling, 'J. Amer. Chem. Soc.,' vol. 53, p. 1382 (1931).

One notes that the stress in this ion is very much greater than in the BCl_3 molecule, and the curvature for the CO bond, even in the strained position, is much larger than for BCl_3. This means that a Morse curve fitted to the above data will give a large true force constant, and a large value for D. Actual calculation using various values of the true force constant, instead of estimating a or D, confirms these general conclusions. If the true force constant be taken as 21×10^5 dynes/cm, the first solution gives D as 20 volts, and the second gives D as 110 volts. Smaller values of K merely increase D, and as even 20 volts is too high, K is likely to be greater. The value of 110 volts given by the second solution excludes it from being a possible interpretation of the observed normal frequencies.

The large values of K and D might be due to neglecting the amplitude of the vibrations, but simple calculations reveal that an amplitude of 0·3 A increases D to 25 volts if K is to remain at 21×10^5 dynes/cm; smaller values of the amplitude give values of D intermediate between 25 and 20 volts. These results might seem to contradict similar results obtained for BCl_3, where averaging F'' and F' over a range of values decreased both D and K; but this is due to the ratio of F''/F' for BCl_3 being $2 \cdot 6 \times 10^8$ cm^{-1}, whilst this ratio is $1 \cdot 76 \times 10^8$ cm^{-1} for CO''_3.

The true force constant is unlikely to be as great as 21×10^5 dynes/cm, for this normally corresponds to a triple bond between C and O, so that D cannot be reduced below 20 volts to give a consistent interpretation of the observed spectrum. The difficulty is probably due to the bonds in CO''_3 not being at all localized along the CO directions. The BCl_3 molecule is in this respect quite unlike the CO''_3 ion. Trigonal quantization of the B atom gave just the condition for three bonds that could unite in the three BCl directions with monovalent Cl. The CO''_3 ion, on the other hand, has two possible electronic structures*: one corresponds to trigonal quantization of C^+ with three monovalent O^- ions, the other to the purely ionic structure of C^{4+} with three O^{--} ions. A linear combination of the proper functions for these two configurations gives the true structure, and localization of bonds associated with the trigonal quantization must be destroyed. Morse's curve, although it may satisfactorily represent a localized bond, is unlikely to represent the potential energy associated with two atoms in a group whose valence bonds are far from independent, as in CO''_3. Hence from this point of view, the impossible values obtained for D and K from Morse's formula are not at all inconsistent with the results obtained for BCl_3; they merely

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* *Cf.* Slater, 'Phys. Rev.,' vol. 38, p. 325 (1932).

indicate that trigonal quantization of the central atom in CO''_3 is an incomplete picture of the ion.

The conclusion that trigonal quantization is not maintained, is supported by the rigidity of the plane structure. The possible solution consistent with observed frequencies of normal modes in the equilibrium plane gives F'/r as $2 \cdot 3 \times 10^5$ dynes/cm. The transverse frequency, ν_1, is 880 cm^{-1}, and this substituted in equation (6) gives F'/r as $1 \cdot 5 \times 10^5$ dynes/cm. The true rigidity of the ion, as distinct from its strain rigidity, is therefore negative to the extent of K_θ equal to $0 \cdot 8 \times 10^5$ dynes/cm. This means that the CO''_3 would be pyramidal in the absence of the repulsion of the oxygen ions.

The nitrate ion gives results very similar to those of the carbonate ion. The normal frequencies are 835, 1389, 727, and 1070 cm^{-1} for ν_1, ν_2, ν_3 and ν_4. The modes in the equilibrium plane give the two possible solutions:

F'' dynes/cm	f'' dynes/cm	F' dynes
$5 \cdot 2 \times 10^5$	$1 \cdot 9 \times 10^5$	$3 \cdot 75 \times 10^{-3}$
$2 \cdot 8 \times 10^5$	$1 \cdot 5 \times 10^5$	$7 \cdot 3 \times 10^{-3}$

r is taken as $1 \cdot 30$ A.*

The true force constant and heat of dissociation of the NO bond calculated from Morse's expression have values close to those of the carbonate ion. Thus, the first solution appears to be the correct one, although even it gives too large values for K and D.

The deformation frequency, ν_1, gives F'/r as $1 \cdot 5 \times 10^5$ dynes/cm. If the strain value, $2 \cdot 9 \times 10^5$ dynes/cm be deducted from this value, the rigidity as measured by K_θ again appears negative, and of magnitude $1 \cdot 4 \times 10^5$ dynes/cm. The nitrate ion has therefore a greater tendency to become pyramidal than the carbonate ion. This is consistent with N having one more electron than C, and therefore requiring more energy to break down the *s-p* quantization.

An ion that might more closely follow central trigonal quantization is $(BO_3)^{3-}$. Unfortunately infra-red and Raman data are lacking for this ion, but Zachariasen's crystal structure data† suggest that it does follow this type of central quantization more closely than either CO''_3 or NO'_3. Zachariasen gives $1 \cdot 23$ A for the CO and NO separations, and $1 \cdot 35$ A for the BO separation. This means that the $(BO_3)^{3-}$ ion is

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* *Cf.* Pauling, ' J. Amer. Chem. Soc.,' vol. 53, p. 1382 (1931).

† ' J. Amer. Chem. Soc.,' vol. 53, p. 2124 (1931).

much less strained than the other two, and the true rigidity of this ion must be more nearly positive to maintain the plane configuration.

Zachariasen's value of the CO and NO separations is even smaller than that given by Pauling and used in the present paper. If the smaller value of 1·23 A is used, the values of K, D and the negative rigidity are still further increased, giving further support to conclusions regarding the difference in quantization for BCl_3 and for the two ions.

The author owes his thanks to Mr. C. R. Bailey for much helpful discussion throughout the course of the work, and to Professor F. G. Donnan, C.B.E., F.R.S., for his continued interest and encouragement.

SUMMARY

The infra-red absorption spectrum of boron trichloride has been examined between 1 and 18 μ. Nine bands have been located, but no branch maxima were observed.

The observed bands have been correlated with Raman displacements and fundamental frequencies assigned.

First and second derivatives of the potential with respect to nuclear separation of the BCl bonds have been evaluated for the equilibrium separation.

Morse's potential nuclear separation expression has been used to deduce the true force constant for the BCl bond.

The true rigidity of the plane configuration is distinguished from the strain rigidity; both are evaluated, and show that the plane configuration is not due to repulsion of the Cl atoms alone.

The electron configuration is discussed.

The carbonate and nitrate ions have been similarly investigated with respect to the true force constant and true rigidity. The true force constant shows that bonds of these ions are not localized as in boron trichloride; the true rigidity is negative, showing that only repulsion of the oxygen ions maintains the plane configuration.

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Molecular Configuration of N_2O

We should like to congratulate Professor Barker and Dr. Plyler on the beautiful experimental work described in "The Infrared Spectrum and the Molecular Configuration of N_2O" (Phys. Rev. **38**, 1827 (1931)). At the same time we feel we must comment upon the deductions made as to the molecular structure of nitrous oxide, which they suggest is $N\equiv N=0$. The force constants representing the bindings between the two nitrogen atoms and between the central nitrogen and the oxygen atom are stated to be $K_1=24\times 10^5$, and $K_2=22\times 10^5$ dynes per cm respectively. If these have been correctly evaluated, the formula of the substance should be $N\equiv N\equiv 0$, since such values correspond to triple linkings (see, for example, Bailey and Cassie, Proc. Roy. Soc. **A132**, 247 (1931)).

In a paper now in the course of publication in the Proceedings of the Royal Society, and dealing with the absorption spectrum of carbonyl sulphide, we have calculated the fundamental nodes of vibration for the asymmetrical rectilinear molecule: the relation between the masses, the force constants, and the frequencies will be found to be given by

$$p_1^2 + p_2^2 = K_1(1/m_1+1/m_2)+K_2(1/m_2+1/m_3),$$
$$\textit{and } p_1^2 p_2^2 = (1/m_1m_2 + 1/m_2m_3 + 1/m_3m_1)K_1K_2,$$

where $p=2\pi\nu c$. On substituting the frequencies corresponding to the two longitudinal vibrations, 1285 and 2224 cm^{-1}, it will be seen that $K_1+K_2=26.8\times 10^5$ dynes per cm and $K_1K_2=197\times 10^{10}$. The consistent solution is $K_1=K_2\simeq 14\times 10^5$ dynes per cm. These values correspond to double bonds in each case, the formula being $N=N=0$, or $:\ddot{N}::N::\ddot{O}:$, constructed from N^-N^+0.

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THE ASYMMETRICAL ROTATOR AND ITS INFRA-RED SPECTRUM

BY

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THE ASYMMETRICAL ROTATOR AND ITS INFRA-RED SPECTRUM.

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The purpose of the following paper is to indicate as briefly as possible the nature of the infra-red spectra to be anticipated from polyatomic molecules with three different moments of inertia. From the point of view of the new mechanics the problem has by no means reached completion; the most recent papers on this subject are those of Kramers and Ittmann,[4] Wang,[6] Witmer,[2] Schrödinger,[1] and Born and Oppenheimer,[3] but the results obtained are not yet in a form applicable to any observed spectra. The older quantum mechanics led to results of a more definite nature. Epstein,[8] Reiche,[9] Kramers,[11] Born and Hückel,[10] Born and Heisenberg,[12] and Witmer[13] have contributed to the solution of the problem. The investigation of most value to the spectroscopist, however, appears in a paper of Lütgemeier's [14] which seems to have escaped the attention it deserves. The quantisation here effected successfully predicts the separations to be observed in the fine structure of the vibrational-rotational bands, both of the symmetrical and asymmetrical rotators. It is proposed in this paper to deduce the general formulæ characterising the rotational spectrum and in the next to apply them as far as possible to the observed results for water vapour.

General Considerations.

Lütgemeier's analysis of the possible motions of the rotator is exhaustive and, as far as the experimental complexity of the spectrum allows, easy of application. The problem consists essentially in the establishment of approximation formulæ for the solution of the phase integrals determining the quantum conditions for the stationary states, in this case defined by the two rotational quantum numbers, j and i. The water vapour molecule, in particular, has three moments of inertia, A, B, and C, where $A > B > C$ and $A = B + C$, while we designate the reciprocals of these moments by a, b, and c.

There are three possible motions for such a body, corresponding to spin about each principal axis of inertia while this axis precesses about the invariable line. In practice, spin about C or A is a stable motion while spin about B is not. Lütgemeier shows that if we define δ by

$$\sin \delta = \sqrt{(b - a)/(c - a)} = q,$$

and g by

$$g = \delta \Big/ \frac{\pi}{2},$$

then the three possible motions correspond to :—

Case (I) . . .	$i/j > g$ (spin about C)
Case (II) . . .	$i/j < g$ („ „ A)
Case (III) . . .	$i/j = g$ („ „ B)

Since III is an unstable motion, Lütgemeier quantises only Cases I and II, and the geometrical significance of the ratio, i/j, in determining these cases is clearly and fully set out in the original paper.

Lütgemeier contents himself with an evaluation of the rotational energy for the above conditions; Kramers and Ittmann have recently succeeded in showing that in this, as in other cases, the wave mechanics demands half-quantum numbers where the older method gives integral values. Considerable uncertainty exists as to the selection principles demanded by the motions concerned; this investigation has been undertaken with the view of throwing some light on the complicated spectrum obtained for water vapour by Sleator in 1918 [18] and by Sleator and Phelps [20] in 1925. Unfortunately their results are presented in the form of energy curves and tables of lines, where no definite values exist for the observed intensities. It is accordingly not possible to say whether certain lines are missing at the centre of each band, the whole question being complicated by the existence in nearly all the bands of a powerful Q branch of considerable width, whose fine structure is also within the limits of resolution of the apparatus. We shall therefore satisfy ourselves with a deduction of the frequency separations to be expected from a differentiation of Lütgemeier's energy expressions with regard to j and i, leaving out of the question the general formula for any set of lines.

In the original paper, a table is given for values of q for water deduced from the angle HOH. Eucken [19] derives three moments of inertia, 3·2, 2·25, and $0{\cdot}98 \times 10^{-40}$ g.cm.^{2} for this molecule, and from these data Debye [21] evaluates this angle as 64°. The corresponding value of q is 0·35, and g is then of the order of $\frac{1}{4}$. The assumption of some such definite value is necessary in order that we may approximate the separations which we shall now proceed to deduce.

The Frequency Separations.

Case I.—$0 < a < b < c$; (For water vapour, $q \simeq 0{\cdot}35$, $g = \frac{1}{4}$). Case I holds while $j < ig^{-1}$, say $j < 4i$.

$$W_1 = \frac{h^2}{8\pi^2}\left\{\begin{aligned} & j^2\left[\frac{a+b}{2} + \frac{17}{32}(b-a)\left(q^2 + \frac{q^4}{2} + \ldots\right)\right] \\ & \quad + i^2\left[c - \frac{a+b}{2} + \frac{21}{16}(b-a)\left(q^2 + \frac{q^4}{2} + \ldots\right)\right] \\ & \quad - \left(\frac{5}{4}ji + \frac{3i^3}{4j} - \frac{5i^4}{32j^2} + \ldots\right)(b-a)\left(q^2 + \frac{q^4}{2} + \ldots\right) \end{aligned}\right\}$$

For convenience we shall write $q^2 + \frac{q^4}{2} + \ldots = X$ and differentiating first with respect to j we have :—

$$\left(\frac{\partial W_1}{\partial j}\right)_i = \frac{h^2}{8\pi^2}\left[\begin{aligned} & 2j\left[\frac{a+b}{2} + \frac{17}{32}(b-a)(X)\right] \\ & \qquad - (b-a)(X)j\left[\frac{5i}{4j} - \frac{3i^3}{4j^3} + \frac{5j^4}{16j^4}\right] \end{aligned}\right].$$

Taking, for the value of q cited, $X \simeq 0{\cdot}12$, we have

$$\frac{\partial W_1}{\partial j} = \frac{h^2}{8\pi^2} \cdot 2j\left\{\frac{a+b}{2} + 0{\cdot}12(b-a)\frac{17}{32} - \frac{\cdot 12}{2}(b-a)\left[\frac{5i}{4j}\right]\right\}.$$

Thus to a first approximation we have a line separation of

$$\frac{h}{4\pi^2}\left(\frac{a+b}{2}\right) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

to a second approximation, two line separations of

$$\frac{h}{4\pi^2}\left\{\frac{a+b}{2} + \frac{0{\cdot}12}{2}(b-a)\right\} \quad . \quad . \quad . \quad (1a)$$

and

$$\frac{h}{4\pi^2}\left\{\frac{5}{8}(0{\cdot}12)(b-a)\right\} . \quad . \quad . \quad . \quad . \quad (1b)$$

Now differentiating with regard to i we have

$$\left(\frac{\partial W}{\partial i}\right)_j = \frac{h^2}{8\pi^2}\left\{\begin{aligned} & 2i\left[c - \frac{a+b}{2} + \frac{21}{16}(b-a)(X)\right] \\ & \qquad - \left[\frac{5}{4}j + \frac{9i^2}{4j} - \frac{5i^3}{32j^2} + \ldots\right](b-a)(X) \end{aligned}\right\}.$$

$$= \frac{h^2}{8\pi^2}\left\{\begin{aligned} & 2i\left[c - \frac{a+b}{2} + \frac{21}{16}(b-a)(X)\right] \\ & \qquad - j\left[\frac{5}{4} + \frac{9}{4}\left(\frac{i}{j}\right)^2 - \frac{5}{32}\left(\frac{i}{j}\right)^3 + \ldots\right](b-a)(X) \end{aligned}\right\};$$

and to a first approximation we have a line separation of

$$\frac{h}{4\pi^2}\left\{c - \frac{a+b}{2}\right\} \quad . \quad . \quad . \quad . \quad . \quad (2);$$

or to a second approximation two line separations of

$$\frac{h}{4\pi^2}\left\{c - \frac{a+b}{2} - \frac{21}{16}(b-a)(\cdot 12)\right\} \quad . \quad . \quad . \quad (2a)$$

and

$$\frac{h}{4\pi^2}\left\{\frac{5}{8}(b-a)(\cdot 12)\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2b)$$

We have also the case of stable rotation round the c axis, when $j = i$ and the frequency difference is

$$\frac{h}{4\pi^2}c \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

For Case II, we have similarly

$$0 < a < b < c; \quad q \doteqdot \cdot 35; \quad g = \tfrac{1}{4}; \quad i < gj, \text{ say } 4i < j.$$

Lütgemeier's expression for the rotational energy is now :—

$$W_{11} = \frac{h^2}{8\pi^2}\left\{j^2 a + (c - a)\left[2jiq - \frac{i^2}{2}(1 + q^2) - \frac{i^3}{j} \cdot \frac{1 - 2q^2 + q^4}{8q} - \ldots\right]\right\}$$

$$\text{and } \left(\frac{W_{11}}{j}\right)_i = \frac{h^2}{8\pi^2}\left\{2ja + 2(c - a)(iq) + \frac{i^3}{j^2} \cdot \frac{1 - 2q^2 + q^4}{8q} + \ldots\right\}$$

$$= \frac{h^2}{8\pi^2}2j\left\{a + \frac{i}{j}(c - a)q + \left(\frac{i}{j}\right)^3 \cdot \frac{1 - 2q^2 + q^4}{16q} + \ldots\right\}$$

or to first approximation we have line separation of

$$\frac{h}{4\pi^2} \cdot a \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and to a second approximation we have

$$\frac{h}{4\pi^2} \cdot a \quad . \quad . \quad . \quad . \quad . \quad . \quad (4a)$$

and

$$\frac{h}{4\pi^2}(c - a)q \quad . \quad . \quad . \quad . \quad . \quad . \quad (4b)$$

While :—

$$\left(\frac{W_{11}}{i}\right)_j = \frac{h^2}{4\pi^2}\left\{(c - a)\left[jq - \frac{i}{2}(1 + q^2) - \frac{3i^2}{2j}\,\frac{1 - 2q^2 + q^4}{8q} - \ldots\right]\right\}$$

$$= \frac{h^2}{4\pi^2}j\left\{(c - a)\left[q - \frac{1}{2}\left(\frac{i}{j}\right)(1 + q^2) - \frac{3}{2}\left(\frac{i}{j}\right)^2\frac{1 - 2q^2 + q^4}{8q} - \ldots\right]\right\}.$$

A first approximation gives a frequency difference of

$$-\frac{h}{4\pi^2} \cdot \frac{i}{2}(c - a),$$

i.e. a constant separation of

$$\frac{h}{4\pi^2} \cdot \frac{c - a}{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and a second approximation gives a difference of

$$\frac{h}{4\pi^2}j(c - a)q,$$

i.e. a separation of

$$\frac{h}{4\pi^2}(c - a)q \quad . \quad . \quad . \quad . \quad . \quad . \quad (5a)$$

Finally, stable rotation round the a axis, when $j = i$, gives a frequency separation of

$$\frac{h}{4\pi^2} \cdot a \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

We have the following separations:—

TABLE I.

First Approximation.	*Second Approximation.*
(1) $\frac{h}{4\pi^2}\left[\frac{a+b}{2}\right]$	(1*a*) $\frac{h}{4\pi^2}\left\{\frac{a+b}{2}+\frac{\cdot 12}{2}(b-a)\right\}$ (1*b*) $\frac{h}{4\pi^2}\left\{\frac{5}{8}(\cdot 12)(b-a)\right\}$
(2) $\frac{h}{4\pi^2}\left\{c-\frac{a+b}{2}\right\}$	(2*a*) $\frac{h}{4\pi^2}\left\{c-\frac{a+b}{2}+\frac{21}{16}(\cdot 12)(b-a)\right\}$ (2*b*) $\frac{h}{4\pi^2}\left\{\frac{5}{8}(\cdot 12)(b-a)\right\}$
(3) $\frac{h}{4\pi^2}\cdot c$	
(4) $\frac{h}{4\pi^2}\cdot a$	(4*a*) $\frac{h}{4\pi^2}\cdot a$ (4*b*) $\frac{h}{4\pi^2}(c-a)q$
(5) $\frac{h}{4\pi^2}\left\{\frac{c-a}{2}\right\}$	(5*a*) $\frac{h}{4\pi^2}(c-a)q$
(6) $\frac{h}{4\pi^2}\cdot a$	

A consideration of the above results shows that generally to a first approximation, a number of well-defined frequency separations are obtained, while if the evaluation is effected with a higher degree of accuracy, additional lines are obtained with small separations providing a broadening of the main lines and furnishing a continuous background. As a consequence of the existence of two sets of conditions about a limiting case, we have to expect that in molecules where the three moments of inertia are not widely different, the conditions in the spectrum are extremely complicated owing to the fact that after a certain value of g the frequency separation changes from the value characteristic of W_1 to that of W_{11}. This deduction is also arrived at by Witmer[13] and by Kramers and Ittmann[4]; practical confirmation is offered in a striking and beautiful way by observations of Duncan[23] on the electronic bands of carbon dioxide at 34,512 and 34,673 cm^{-1}. Duncan remarks on the peculiar fact that in the P branch a constant frequency separation of 1·1 cm^{-1} holds through a series of 25 lines, after which we get a sudden change to another frequency difference of 2·5 cm^{-1}. On the assumption that this is the predicted phenomenon, we have

$$g = 1/25,\text{ and }\delta = \pi/50 = \cdot 0628 = \sin\delta = \sqrt{\frac{b-a}{c-a}}.$$

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A METHOD OF ELIMINATING MAGNETIC DISTURBANCE OF HIGH SENSITIVITY GALVANOMETERS

BY

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A METHOD OF ELIMINATING MAGNETIC DISTURBANCE OF HIGH SENSITIVITY GALVANOMETERS.

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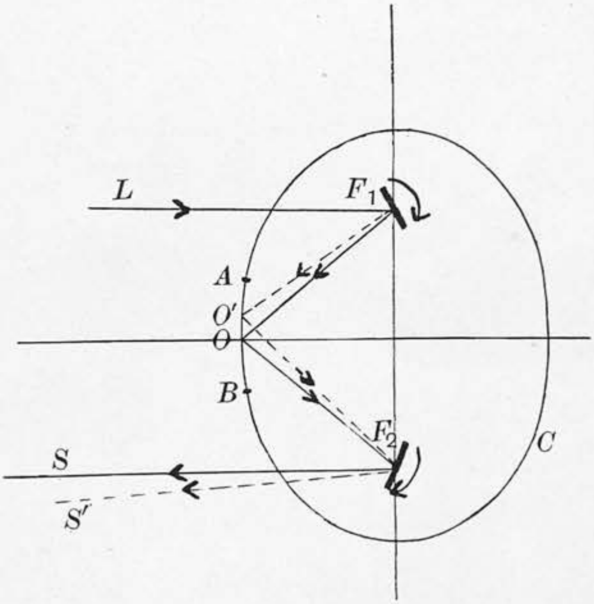
[*MS. received, 20th November*, 1929.]

ABSTRACT. Light reflected from two mirrors oscillating with equal amplitudes and frequency may, by the method described, be projected on a scale to give an image at rest, and this may be employed to eliminate changes in zero of certain galvanometers.

MOVING-MAGNET galvanometers are now obtainable which are so nearly astatic that their sensitivity in the earth's field is of the order of 10^{-11} amp per mm. at a scale distance of 1 metre. Disturbance of this field, such as occurs in a busy laboratory or in a large city, causes annoying fluctuations of the zero. This may be avoided in the following manner:

Two systems can be obtained with the same sensitivity and the same period of oscillation, and when mounted near one another move together when the earth's field is disturbed. The galvanometer mirrors are mounted at the foci, F_1 and F_2 of an ellipse $AOBC$ (see fig.). A beam of light LF_1 falls on F_1 and is reflected to a cylindrical mirror, AOB, whose curved surface fits the ellipse as shown. This mirror reflects the light to F_2. The beam F_2S is projected on a galvanometer scale. A disturbance which rotates the two needles in the direction shown by the curved arrows will displace F_1O to some position F_1O', and since the surface AOB is aplanatic with respect to F_1 and F_2 the narrow beam of light reflected from F_1 will again pass through F_2. Further, the angle OF_1O' equals the angle OF_2O', to a first approximation. If, then, F_2 had remained at rest, the final path of the beam would be F_2S' such that angle SF_2S' equals angle OF_1O' and equals twice the angle turned through by F_1. Since F_2 turned through an angle equal to that turned through by F_1 the final direction of the beam is again F_2S. The external disturbance thus causes no shift of the image on the galvanometer scale. In practice an elliptical mirror is not essential, and a spherical mirror of radius equal to the radius of curvature of the ellipse at O may be used.



Two astatic systems not being available, the optical system was tested by means of two moving-coil galvanometers. A spherical mirror of 9 inches radius of curvature was obtained and the two galvanometer mirrors placed at the foci of an appropriate ellipse. Small currents, adjusted to give deflections equal in magnitude and direction, were passed through the galvanometers. No deflection of S was observed for deflections of F_1 and F_2 up to 50 mm. on a scale at 1 metre scale distance, and such deflections are far in excess of any zero fluctuation observed with astatic galvanometers.