ON THE EMISSION AND ABSORPTION BAND SPECTRA OF SELENIUM.

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Introduction.

The spectrum of a discharge through selenium vapour was measured by Messerschmitt[1] in 1907, who found that it consists of a large number of bands in the near ultra-violet and visible regions between λλ 3707 and 5881. In recent years, Rosen[2] obtained the bands of selenium vapour in absorption and was the first to propose a vibrational quantum analysis for them, which shows definitely that they are due to the diatomic molecule Se_2. All the bands observed in absorption were included in one electronic system for which the following equation was deduced:

$$\nu = 27307 + (247 \cdot 2\, v' - 2 \cdot 3\, v'^2) - (397 \cdot 5\, v'' - 1 \cdot 32\, v''^2). \qquad (1)$$

Nevin,[3] in a short note to *Nature,* confirmed in the main this analysis of Rosen but in addition found that the emission bands at longer wave-lengths which were not observed by the latter in absorption, could be arranged into two systems which arise in two different excited levels but have a common final state which is the same as the ground level of the molecule as found in absorption. According to him the spectrum therefore consists of three band-systems, the α-main system observed in emission and absorption, the β-diffuse blue emission bands and the γ-green-yellow emission bands. The following equations (in which $u = v + \frac{1}{2}$) are derived by Nevin for these three systems:

$$\alpha\text{-System}: \ \nu = 27371 + (254 \cdot 7\, u' - 2 \cdot 42\, u'^2) - (387 \cdot 8\, u'' - 0 \cdot 63\, u''^2) \qquad (2)$$

$$\beta\text{-System}: \ \nu = 21945 + (431 \cdot 1\, u' - 0 \cdot 83\, u'^2) - (373 \cdot 5\, u'' - 0 \cdot 66\, u''^2) \qquad (3)$$

$$\gamma\text{-System}: \ \nu = 18342 + (336 \cdot 3\, u' - 0 \cdot 19\, u'^2) - (386 \cdot 5\, u'' - 0 \cdot 59\, u''^2) \qquad (4)$$

Many of the bands of the α-system are also known in fluorescence. Isotopic effect has been observed by Olsson[4] for some of the bands of this system. This necessitated a revision of the v' numbering and accordingly Olsson corrected equation (2) to

$$\nu = 26010 + (287 \cdot 7\, u' - 2 \cdot 42\, u'^2) - (387 \cdot 8\, u'' - 0 \cdot 63\, u''^2). \qquad (5)$$

In a more recent paper Nevin[5] has confirmed the isotopic effect and has proposed the following slightly different equation to represent the bands of the α-system :

$$\nu = 26083 + (265 \cdot 1\, u' - 1 \cdot 878\, u'^2) - (381 \cdot 6\, u'' - 0 \cdot 144\, u''^2 + 0 \cdot 0088\, u''^3). \quad (6)$$

Moraczewska[6] added two more absorption band-systems in the ultra-violet so that till very recently the spectrum of Se_2 was analysed into five systems all of them having different excited states but a common final state.

Jevons[7] has summarised these results in his 'Report' from which the following term scheme is prepared, the position of B level being changed in view of the isotopic effect observed.

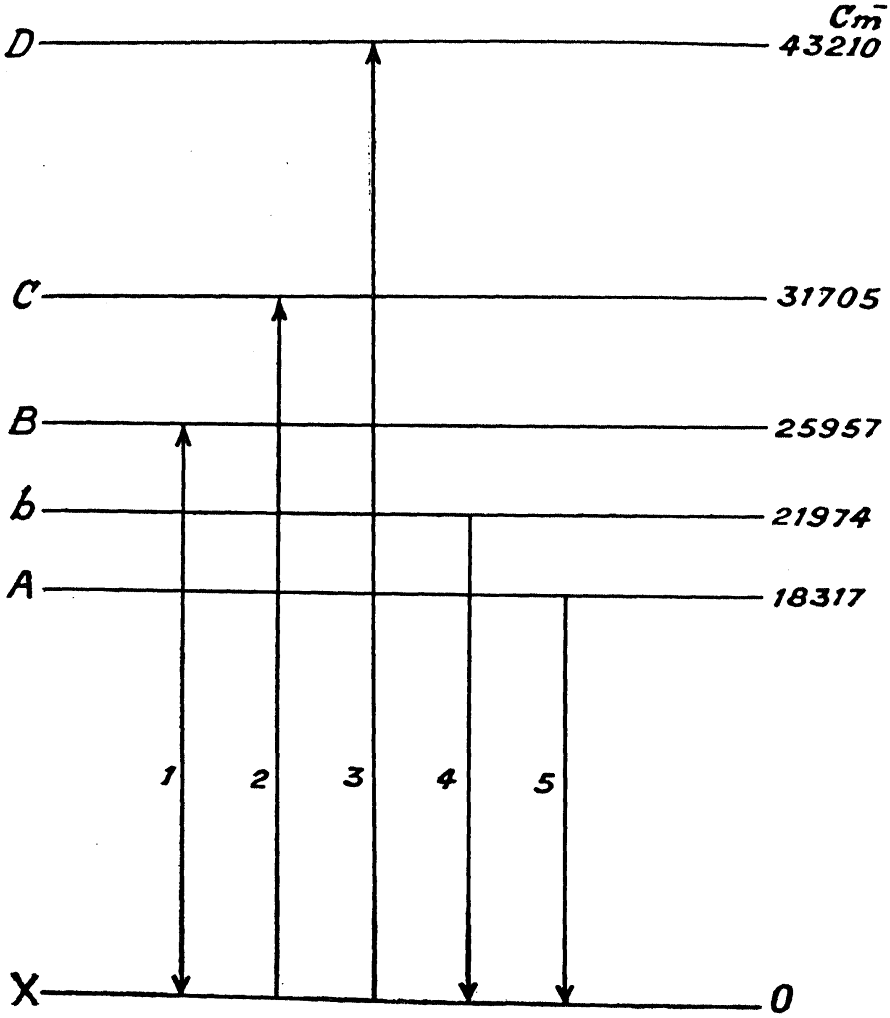

FIG. 1.

1. α-Main band-system in absorption, fluorescence and emission.
2 & 3. Weak absorption bands of Moraczewska.
4. β-diffuse blue emission bands of Nevin.
5. γ-green-yellow emission bands of Nevin.

In a series of papers, Rosen and Desirant[8] and Rosen and Monfort,[9] report a re-investigation of the emission spectrum of selenium vapour. In addition to α-system they find that the various bands observed by them can be classified into four more systems, three of which have their final state in common with the ground state of the molecule and the fourth has its initial state in common with the α-system but has a different final state so that according to them the term scheme of the molecule is given by the diagram of Fig. 2. The system of fluctuations, 6 of Fig. 2, is the same as the γ-green yellow system of Nevin but with a different analysis.

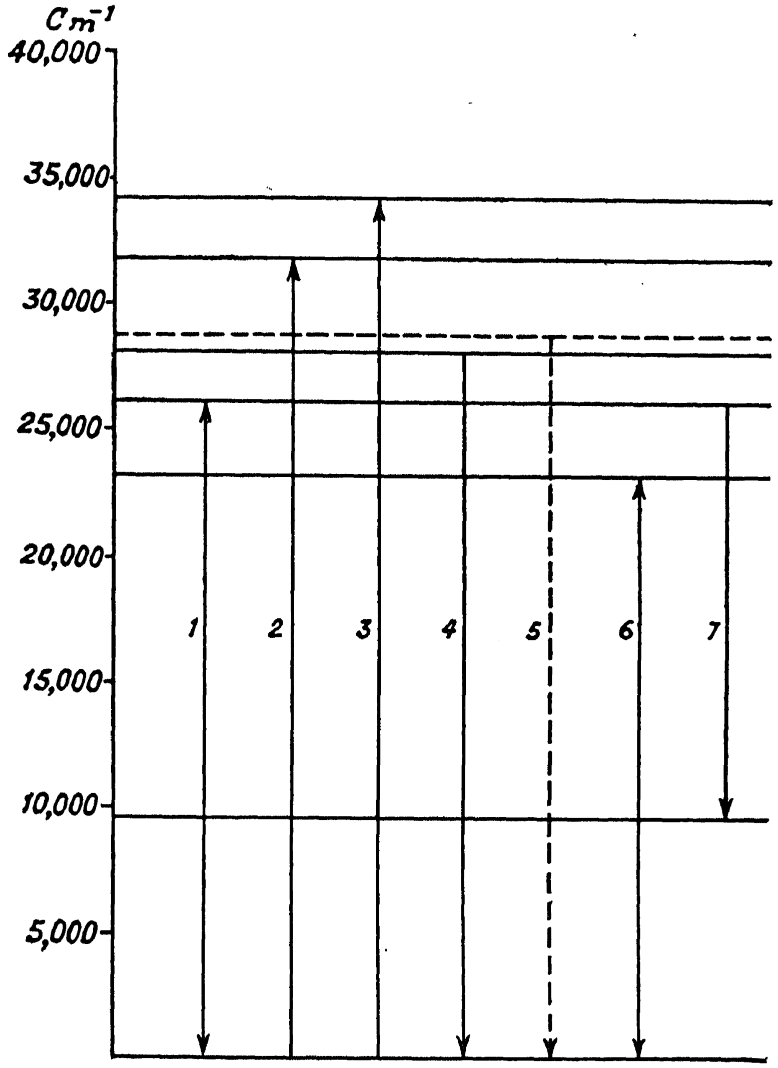

FIG. 2.

1. α-Main band-system.

2 & 3. Absorption bands of Moraczewska.

4 & 5. Bands of Rosen and Desirant.

6. System of fluctuations (same as system 5, Fig. 1 but with a different analysis).

7. Bands of Rosen and Monfort.

In analogy with the homologous molecules O_2 and S_2 the ground level of the molecule was assumed to be $^3\Sigma$ and the transition involved in the

α-main band-system to be $^3\Sigma - {}^3\Sigma$. Olsson,[4] however, has proposed a rotational analysis for some of the bands evidently belonging to this system, which shows that the transition involved is $^1\Sigma - {}^1\Sigma$. If the character of the levels B and X is $^1\Sigma$, considerable difficulty is encountered for correlating the molecular terms with the terms of separated atoms and consequently for deriving the energy of dissociation of Se_2 in its unexcited ground state. We shall discuss this later.

Another peculiarity of this system is that the spacings of the vibrational levels both in the initial and in final states are very irregular so that none of the equations (1), (2) and (5) represents the bands with the desired accuracy. Rosen and Desirant[8] have deduced the following equation which they develop from the five bands measured by Olsson[4] under high dispersion and with greater accuracy :

$$\nu = 25957 + (277 \cdot 8\, v' - 2 \cdot 25\, v'^2) - (391 \cdot 5\, v'' - 1 \cdot 06\, v''^2). \qquad (7)$$

This equation also fails to represent the bands satisfactorily. That the irregular spacing of the vibrational levels observed is not due to the inaccuracies in measurement is clear from the work of Nevin who has measured the whole system in absorption under high dispersion and derives equation (6). By an application of this equation he has been able to show that pronounced perturbations occur in certain levels of the excited state. The cubic term which is found necessary to represent the final vibrational function is quite indicative of the fact that the observed spacings of the vibrational levels of the final state are much more irregular than those of the initial state. In view of this state of our knowledge regarding the spectrum of Se_2, it was thought desirable to study it both in emission and absorption.

Emission Spectrum.

The spectrum was produced by an uncondensed discharge through selenium vapour in the presence of argon. For this purpose an H-type discharge tube having aluminium electrodes and the usual side bulbs containing P_2O_5 and selenium, was used. This discharge tube had a quartz window fitted on to it and was run on a ¼ kilowatt transformer. The side bulb containing selenium was fixed vertically to the middle of the horizontal part of the discharge tube. The bulb was heated until some of the selenium melted and flowed down to the horizontal part of the discharge tube. In order to get an intense spectrum, which was viewed end on, it was necessary to keep this selenium in the molten condition. The presence of argon facilitated the discharge but did not seem to play any other rôle. Commercial argon which contained slight impurities of nitrogen and oxygen, was completely purified before use, by allowing it to stand over heated calcium and magnesium turnings. The discharge obtained was of a brilliant blue colour. The spectrum was photographed on a three-prism glass spectrograph having a dispersion of 6 Å/mm. at 4000 Å.U. of about 14 Å/mm. at 5000 Å.U. and of about 26·5 Å/mm. at 5800 Å.U. A medium Hilger quartz-spectrograph was also used to investigate the spectrum in the ultra-violet. The dispersion of this instrument is rather low but since the glass spectrograph used could photograph the spectrum above 3800 Å.U. and since there are only a few bands below this region in the ultra-violet, for which more accurate data are available, no attempt was made to photograph them under higher dispersion. The last band registered on the plate however had a wave-length of λ 3451·6. Copper arc lines as well as lines of helium and mercury in some cases, were utilised as standards. The plates were measured on an Abbe comparator. The accepted values of wave-lengths of the bands represent the mean of three measurements. For bands which are well defined these values did not differ among themselves by more than 0·2 Å.U. The agreement has not been so good for a large number of diffuse bands, which, in general, showed a discrepancy of not more than 0·5 Å.U. among the three measurements. Table I contains the list of observed bands together with their visually estimated intensity and their classification as proposed in this paper. Fig. 3 is an enlarged spectrum of the bands and Fig. 4 shows the microphotograms of the bands. The spectrum did not show any bands in the near infra-red, the region investigated being up to 8500 Å.U.

The bands extend from λ 3800 to λ 5875 and are all degraded towards the longer waves. Except for one solitary band which happens to be the (0, 0) band of the β-system reported by Nevin no band degraded towards the shorter waves has been observed. Starting from the short-wave side bands are quite sharp up to about λ 4000. From λ 4000 to λ 4900 the bands are diffuse and are in addition masked by an overlapping continuum. From λ 4900 to λ 5400 the bands are still diffuse but they occur in definite groups and the overlapping continuum is much weaker. Above λ 5400 the bands are particularly sharp and appear also in definite groups. The reproduced microphotometer plates exhibit these peculiarities clearly. From λ 4800 upwards the appearance of the bands in distinct groups conveys, especially from the photometer records, a peculiar fluctuation of intensity. Such an intensity fluctuation, however, need not be emphasised and is by no means uncommon in band systems where bands belonging to different transition and having different intensities happen, by chance, to lie near together as if in a sequence. To a certain extent the main band-system of sulphur exhibits a similar behaviour of intensity fluctuation.

Analysis.

At the outset we should like to draw attention to the very irregular spacing of the vibrational levels, which appears to be a distinctive feature of this spectrum. There seems to be little doubt about the correctness of the already existing analysis of the α-system. In Tables II and III, data for the vibrational differences in both the states have been collected according to Nevin's[5] measurements. Figs. 5 and 6 represent the relation between ω (v) and v in the initial and final states according to Nevin's values.

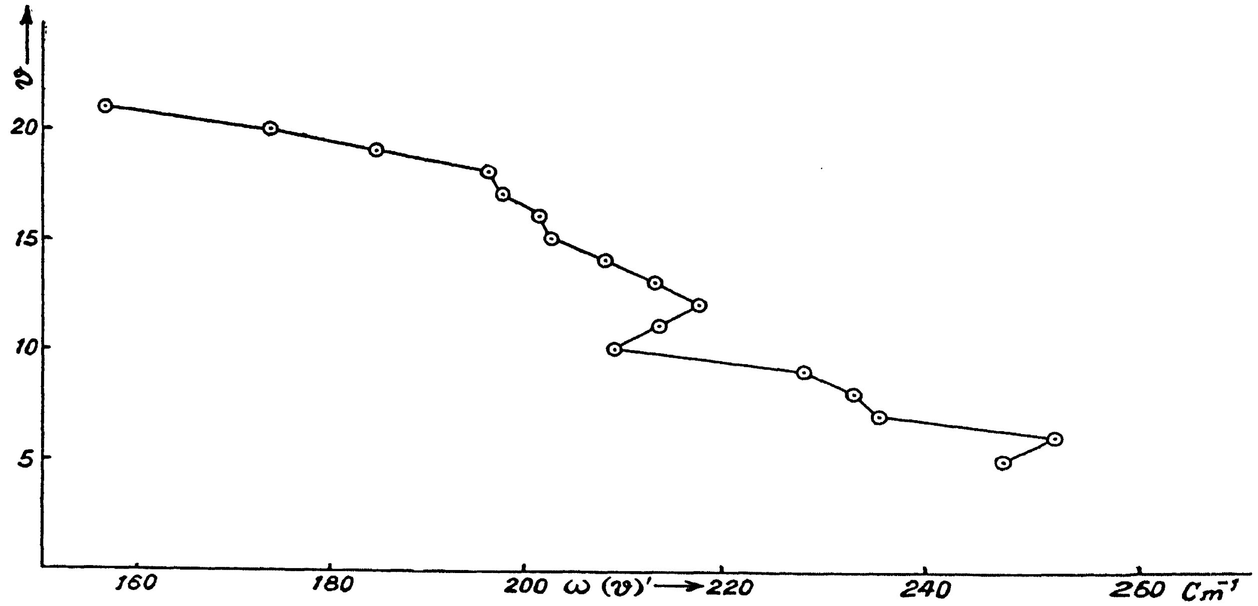

FIG. 5.

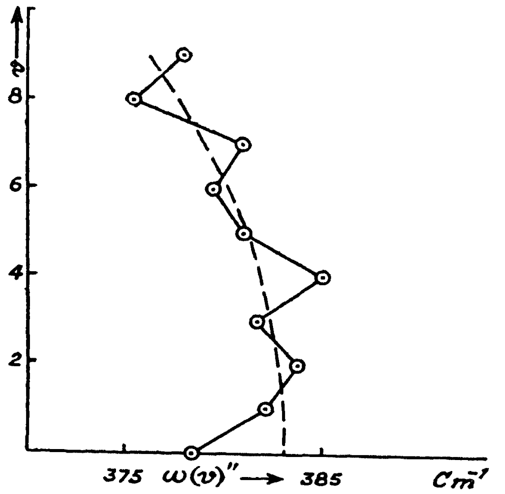

FIG. 6.

It will be seen that the mean vibrational differences both in the initial and final states are irregular in the extreme and even for the same vibrational difference which is obtained as the mean of many observations, the individual values differ very widely among themselves. It is clear that perturbations of an extensive nature occur. Nevin has drawn attention to this fact and shows that very pronounced perturbations occur in the levels $v' = 7$ to $v' = 11$. Bands having v' values in this range comprise practically 75% of the total number of bands observed in absorption. How far the irregularities and discrepancies observed in the final state are entirely due to these perturbations in the excited state is uncertain but it is possible that perturbations may be present even in the lower state itself brought about by the intersections of at least two potential curves namely of the $^1\Sigma$ and $^3\Sigma$ states both of which arise out of Se ^{3}P + Se ^{3}P. For an analysis of the emission spectrum where we get a large number of bands, a recognition of the existence of perturbations is to our mind important. It is possible to pick out a few bands which show a greater regularity of spacing and many such analyses have been tried by us, but in all cases they comprise only a small number of the total bands and show no interrelation among themselves.

We believe therefore that a correct interpretation of the bands does not lie this way and the very complicated nature of bands mars the simplicity of vibrational structure common to band-systems of a less extensive nature. Evidently, unless data of rotational analysis are obtained and the origins of the bands determined, expressions for the vibrational functions will be very approximate.

The microphotographs Fig. 4, first suggested the possibility that the bands forming successive groups might belong to successive sequences. If we take the very distinct groups starting from λ 5458, it is indeed possible to arrange the three groups F, G and H into three successive sequences, as has been done by Nevin. These bands form part of the β-yellow green system of Nevin or the so-called system of fluctuations of Rosen and Monfort. Bands above λ 5400 when arranged according to this scheme yield vibrational differences for the final state, which are very close to the vibrational differences of the ground state. But since an extension of this analysis to the similar groups of bands at shorter wave-lengths was not satisfactory an attempt was made to arrange them in a slightly different way with a view to see if the analysis gave for the initial vibrational differences, values corresponding to those of the main band-system. If instead of taking successive bands, we arrange alternate bands (the best example is group G) as forming a sequence, it is found that the initial vibrational differences roughly correspond with those of the main band-system, while the final vibrational differences were of an order of magnitude which could be expected for high v'' values of the final vibrational term of the main band-system indicating that these bands belong to the α main band-system and do not form a new system. Extending this method to the group of bands on the shorter waves it was possible to arrange them in the same scheme. In most of these groups, however, it was found that the regularity of the alternate bands forming sequences was in many cases disturbed, till at last when we come to the group at λ 4800, the bands are completely confused. Between $\lambda\lambda$ 4800 and 4000 the bands possess no apparent regularity and present more or less a very chaotic distribution resembling that of the bands of a multi-atomic molecule. The procedure for the analysis proposed here has therefore been the following. The bands of the α-system were first placed in their proper positions in the table, the v' v'' numbering being the same as that given by Nevin and other workers. The groups F, G and H were then analysed and their v' numbering fixed as indicated by the rough correspondence of the initial differences of these bands with those of the main system. The gulf between the two sets of bands in the table was then bridged by arranging the successive groups of bands between $\lambda\lambda$ 5400 and 4900. The bands between $\lambda\lambda$ 4900 and 4000 being diffuse and more complicated offer the greatest difficulty and uncertainty for the analysis. A few bands could not be fitted into the scheme. These are given in Table IV. They are mostly diffuse and are probably only structure lines.

The analysis is displayed in Table V. The vibrational differences in the two states of this system as deduced from the analysis proposed here are given in Tables VI and VII. On account of the very irregular nature of the spacing we do not propose to derive the usual vibrational equation. The relation between ω (v) and v for the two states is shown in Figs. 7 and 8. Successive points are joined by continuous lines while the dotted curves probably represent the true relation between ω (v) and v in the absence of perturbations. As is well known this relation is in most cases not linear. The general form of the curve is such that for low values of v it has a negative curvature (concave to both axes) which after a point of inflexion changes into a positive curvature (convex to both axes). The curve for the initial state Fig. 7, appears to conform to such a general form. Except for slight deviations, it starts with a negative curvature. The point of inflexion is, however, at a surprisingly low value of v, *viz.*, 5, after which it shows a positive curvature, the smoothness being destroyed by what are apparently pronounced perturbations between $v = 10$ and 14. The curve for the final state (Fig. 8) is much more complicated. It is possible to draw two curves one with a negative curvature (dotted curve 1) for values of v up to 12 and

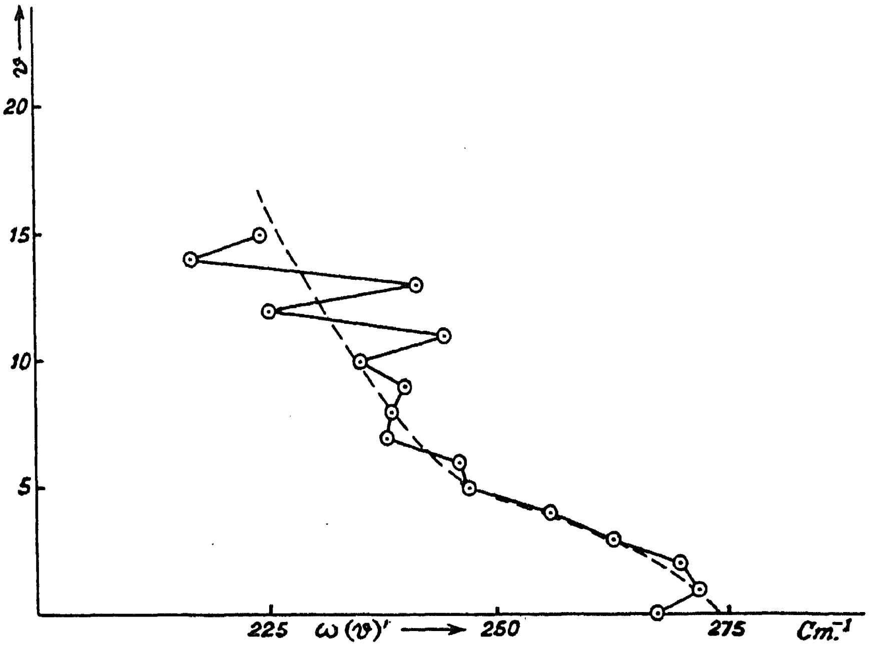

Fig. 7.

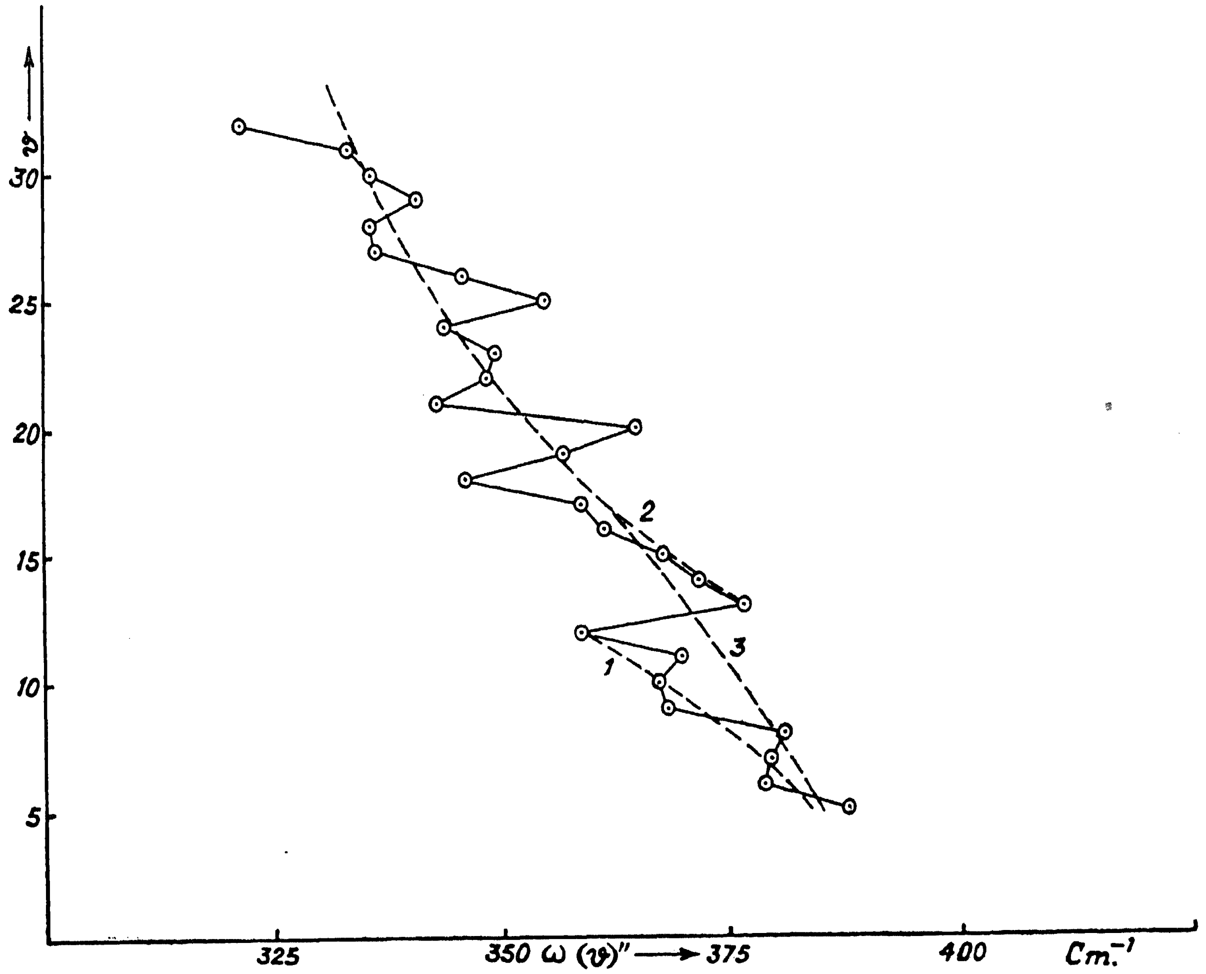

Fig. 8.

another with a positive curvature (dotted curve 2) from $v = 13$ onwards. In each case there are numerous perturbations, those for the curve with positive curvature being more pronounced between $v = 18$ and 20 and between $v = 25$ and 28. The break between the two curves occurs at the point of inflexion of the dotted curve 3 which probably indicates the general relation between $\omega (v)$ and v for this state.

The analysis proposed here differs in one essential respect from all the others proposed till now. All the bands except those found in absorption by Moraczewska (systems 2 and 3 in Fig. 2) and by Rosen and Monfort in emission (system 7 in Fig. 2) are comprised in one system. The γ-bands of Nevin (system 5 of Fig. 1) or the so-called fluctuation bands of Rosen and Monfort (system 6, Fig. 2) are parts of this system which is analogous to the extensive main band-system of sulphur. The present plates do not record any band degraded towards the short waves except one at λ 4552·3. This is probably the (0, 0) band of the β-diffuse blue emission band-system of Nevin (system 4, Fig. 1). If these bands are due to Se_2 the conditions of excitation appear to be different and since no detailed data regarding the bands are available further work is necessary. The new band-system recorded by Rosen and Monfort (system 7, Fig. 2) has according to them its initial state in common with the main band-system and has a frequency of 325 cm.$^{-1}$ for its lower state. It seemed, at first, possible to include these bands in the analysis proposed here, for the frequency of 325 cm.$^{-1}$ might be regarded as the frequency of vibration of the ground state for high v'' values. But it was found that such an extension was not possible. This therefore constitutes a new system which arises out of a transition from level B at 25957 cm.$^{-1}$ to a level at 9251 cm.$^{-1}$ above the ground level X.

Rosen and Desirant[8] describe another band-system obtained by high frequency discharge through selenium vapour. This they analyse into two systems, 4 and 5 of Fig. 2. The bands lie in the ultra-violet between λλ 2970 and 3417. They appear at low temperatures before the α-system develops but when the temperature is raised the α-bands become incomparably more intensified. They attribute these bands to the excitation of the Se_2 group in a polyatomic molecule of selenium and show that some of the bands agree in their wave-lengths approximately with the first set of absorption bands (system 2, Fig. 1) of Moraczewska. We shall show later that it appears probable that these bands are due to SeO_2.

Absorption Spectrum.

The absorption spectrum of selenium vapour has been studied by Rosen,[2] Moraczewska[6] and Nevin.[5] Rosen obtained the bands of the α-main band-system followed by a continuum. The bands however do not go to form a definite convergence limit, the spacing between the last two observed bands being still about 175 cm.$^{-1}$ Nevin has measured these bands under higher dispersion. Moraczewska found, in addition to this system, two more sets of bands (systems 2 and 3 of Fig. 1) on the shorter wave-length side of α-system. These were obtained at comparatively low temperatures (about 250° C.) and are not found to be followed by continua. Since the vapour of selenium is known to consist mainly of diatomic molecules only at temperatures higher than 900° C., the presence of these bands at low temperatures must mean either that they are not due to the diatomic molecule Se_2 or that the coefficient of absorption of Se_2 vapour is so great that even a very small percentage of diatomic molecules which will be present at this low temperature, is able to exhibit measurable absorption. This possibility is by no means remote because in our experiments the α-bands already appear at a temperature of about 400° C. which means that the coefficient of absorption is already very high in the region of 3300 Å.U. It is known that the coefficient of absorption increases very rapidly with the decreasing wave-length and therefore provided there be any absorption in the further ultra-violet, it will have a very high coefficient. The experiments in absorption were undertaken with the following objects :

(1) To trace the bands of α-system up to their convergence limit ;

(2) To search for similar convergence limits for the two band-systems of Moraczewska ; and

(3) To correlate the convergence limits to dissociation processes and derive the energy of dissociation of the ground level of the molecule.

Absorption cells of different lengths have been used. Two of these were of fused quartz with plane ends and of length 5 and 20 cm. These were kept in electric stoves which were sufficiently long to ensure a uniform temperature throughout the whole length of the absorption cell in each case. The substance was introduced into the cell through the T-piece which was also fused on to the cell. The T-piece was then attached to the vacuum part of the apparatus. Temperatures up to 500° C. were employed. The third absorption cell was a porcelain tube of length 80 cm., which was placed in an electric furnace whose temperature could be regulated up to 1000° C. To the two ends of the porcelain tube protruding out of the furnace, were fixed copper jackets to which quartz windows were cemented. Each of these jackets had a T-piece attached to it so that the absorption tube could be exhausted. The substance was contained in a porcelain boat which was introduced into the absorption tube before one of its ends was fitted with the copper jacket. For each fresh introduction of the substance, evidently the copper jacket had to be taken out and after introducing the substance it had to be again cemented on to the absorption tube. These jackets were surrounded by copper spirals through which cold water was kept circulating so that the clogging of the quartz windows was prevented. In all cases, a hydrogen tube giving rise to the continuous spectrum was employed as the source of continuous spectrum. Photographs were taken at different temperatures using a medium Hilger quartz-spectrograph as the resolving instrument.

No absorption bands were observed below 300° C. with any of the absorption cells. The absorption bands mentioned by Moraczewska[6] for the production of which low temperature is said to be favourable are absent in all our experiments under varying conditions of tube length, quantity of substance in the tube and temperature. The α-band-system invariably makes its appearance at 400° C. in all the experiments. The intensity of absorption increases with increase in temperature but in no case were we able to extend the stystem to its convergence point. Brown[10] by using a long absorption cell and low temperatures has pushed the absorption bands of iodine almost to the point where $\Delta\ \omega = 0$. We have tried at 400° C. the absorption cell of 80 cm. and with a trace of selenium but have not been able to photograph any band below λ 3239. Fig. 9 is a typical microphotometer curve of the absorption bands and the attendant continuum. It will be seen that though the bands do not go to the convergence point still the breadth of the continuum covers only a range of 23 Å.U. from λ 3223 to λ 3046, or from 3·8 to 4·1 e.v. The maximum of continuous absorption which is not so sharply distinguished is at λ 3168. Probably longer absorption cells are necessary to bring about the required development of the bands. In some of the experiments especially with the porcelain tube, we observed some absorption bands in the region of the first set of Moraczewska's bands ($\lambda\lambda$ 2758–3150) but we soon discovered that this was due to a small leak in the apparatus. This leads us to think that probably the Moraczewska bands are due to an oxide of selenium. The absence of a continuum following the bands, though the region where we expect it (roughly λ 2700) is investigated, further indicates that the bands may not be due to Se_2. Indeed, there is a fairly good coincidence between many of these bands of Moraczewska and those observed directly in the absorption spectrum of SeO_2.[11] This is shown in the following table in which also the wave-lengths of some of the bands of systems 4 and 5 (Fig. 2) of Rosen and Desirant which agree with those of Moraczewska's bands, are included.

TABLE VIII.

Moraczewska bands λ	Rosen and Desirant λ	SeO_2[11] λ
3150	3151	3158·1
3128	3129	
3107	3105	3107·5
3087	3082	3092·0
3064	3066	3070·4
3041	3043	3044·4
3018	3020	3008·9
2998	2999	3007·8
2979	2980	2986·5
2960		2963·6
2941		2950·9
2923		2928·6
2906		2906·6
2888		2884·5
2870		2872·7
2850		2851·4
2832		2831·4
2816		2819·8
2799		2800·6
2787		2788·3
2774		2772·7
2758		2750·3

It is clear that if Moraczewska's bands are due to SeO_2 Rosen and Desirant bands are also due to it. The second set of Moraczewska's bands also are not observed by us in absorption. They lie already in the limiting region of quartz and probably extend to still shorter wave-lengths. We have, however, no remarks to offer on this system.

Discussion.

The absorption and emission spectra of Se_2 therefore consist of two systems as shown in Fig. 10 both of which have a common initial level.

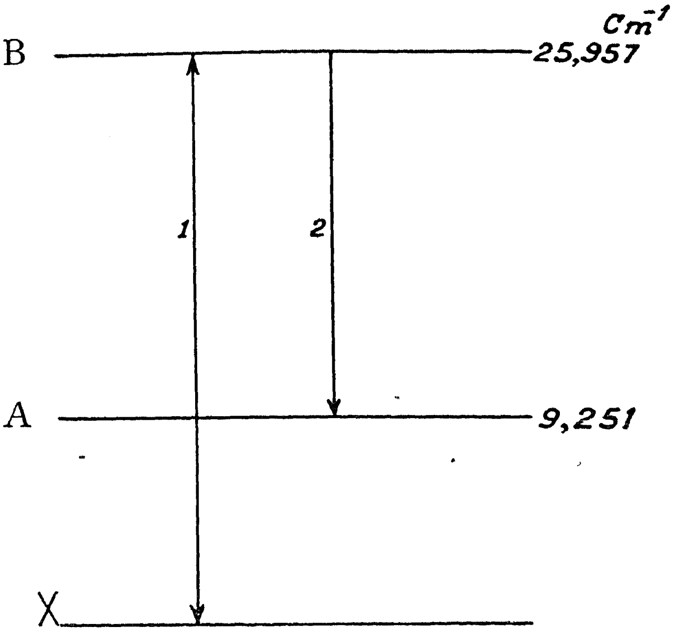

Fig. 10.

1. Absorption and emission main band system.
2. Bands of Rosen and Monfort[9] in emission.

For a correlation of these molecular terms to the terms of the separated atoms it is necessary to know the energies of dissociation of the molecule in the three states. One of the methods of determining this quantity is the extrapolation of the vibrational levels. While this method often leads to too high values, it has been recently shown[12] that under certain conditions this method can be used for such a correlation. One of these conditions is that the vibrational levels of the two states in question should be known with equal accuracy, so that the relative error in the evaluation of ω and ωx is small. For Se_2 this method is particularly unsuited because of the pronounced irregularities in the spacings of the vibrational levels in the ground state which render uncertain the evaluation of the anharmonic constant. The absorption spectrum on the other hand gives us, from the convergence limit, a very accurate measure of the energy of dissociation of the molecule in the excited state. In Se_2 the convergence limit, as is pointed out already, is not so clearly defined as in the more favourable example of I_2; but the witdh of the continuum following the bands, covers only a small spectral range between λ 3223 to λ 3046 (*i.e.*, from 3·8 to 4·1 e.v.), the maximum in the continuum being at λ 3168, which gives 31557 cm.$^{-1}$ = 3·9 e.v. If we deduct from this the energy of excitation of the level B, which is 3·2 e.v. corresponding to 25957 cm.$^{-1}$, we obtain for the energy of dissociation for the level B, the value 0·7 ± 0·2 e.v. In order to deduce the energy of dissociation of the ground state from the value of the convergence limit, we must know the character of the two terms B and X. Originally it was assumed that both these terms were of the ${}^3\Sigma$ type, in analogy with the homologous molecules of O_2 and S_2 for which the character of the terms has been definitely established. But the partial rotational analysis of some of the bands evidently belonging to the α-system, proposed by Olsson[4] indicates that the two levels in question are of ${}^1\Sigma$ type, the level B being ${}^1\Sigma_u{}^+$ and X being ${}^1\Sigma_g{}^+$.

Now the possible molecular Σ terms that arise from Se ${}^3P$ + Se ${}^3P$ are ${}^1\Sigma_g^+$, ${}^1\Sigma_g^+$, ${}^1\Sigma_u^-$, ${}^3\Sigma_u^+$, ${}^3\Sigma_u^+$, and ${}^3\Sigma_g^-$. If we restrict ourselves to terms of same multiplicity, these cannot combine with one another and therefore whether both the levels are singlets or triplets, they cannot both arise from unexcited atoms. Therefore, as in O_2 and S_2, the excited term B must involve an excited atom. It may be that both atoms are excited, if the analogy with O_2 and S_2 does not hold. On the assumption that the molecular terms are singlets and that the excited term involves only one excited atom of Se, it is clear that such an excitation must lead the Seatom to an excited triplet level so that in combination with Se ${}^3P$ it can yield a singlet molecular term. Such a level nearest to the ${}^3P$ ground level of Se, is the $4p^3\,5s$, ${}^3S$ which is 51001 cm.$^{-1}$ above Se $4p^4\,{}^3P$.[13] This leads to a negative value for the energy of dissociation of Se_2 in the ground state and has therefore to be rejected. We must then assume that the excited term is built up of two Se atoms each of which is excited to $4\,p^4\,{}^1D$ which is 9576 cm.$^{-1}$ above $4\,p^4\,{}^3P$. Deducting twice 9576 cm.$^{-1}$ from 31557 cm.$^{-1}$ we get 12405 cm.$^{-1}$ = 1·5 e.v. as D″ (Se_2). On this basis, the level A will also be ${}^1\Sigma_g^+$, produced by two unexcited Se atoms.

Rosen and Desirant, by a similar reasoning but by using extrapolated values for D′ (B), obtained D″ (X) = 1·9 e.v. To our mind the value deduced by the absorption experiments is more reliable especially in this case. In any case D″ (X) for Se_2 is unusually too low. From the energies of dissociation of O_2 (5·05 e.v.) and S_2 (3·8 ± 0·2 e.v.) and from considerations of various results in absorption spectra[14] we expect the energy of dissociation of Se_2 to be between 2·5 and 3·0 e.v. We have shown that such a value is impossible if the singlet character of the levels is established. If the ground level is ${}^1\Sigma$ Se_2 vapour must be diamagnetic. Recent work* on the measurement of magnetic susceptibility of selenium vapour at high temperatures seems to indicate that this is by no means true and that diatomic selenium is paramagnetic. Detailed investigation is in progress but preliminary results establish this fact beyond doubt. Therefore the ground term of Se_2 is very probably ${}^3\Sigma$ and its analogy with O_2 and S_2 seems to be complete. The level X then is ${}^3\Sigma_g^-$ and arises from Se 4 p^4 3 P + Se 4 p^4 3 P. The excited term B is ${}^3\Sigma_u^-$ and involves an excited Se atom in Se 4 p^4 ^{1}D so that the energy of dissociation D'' X (Se_2) is 31557 − 9576 = 21981 cm.$^{-1}$ = 2·7 ± 0·2 e.v. Now the level A lies at 9251 cm.$^{-1}$ = 1·14 e.v. above the ground level. It appears that the bands which involve this level require special methods of excitation because they have not been observed either by us or by other workers but have been obtained by Rosen and Monfort under high frequency discharge. Quite tentatively we suggest that the level A is a singlet level and forms the analogue of the level A ${}^1\Sigma_u^+$ in O_2, and that it arises likewise out of unexcited atoms.

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* Private communication from a forthcoming paper by Dr. Lessheim and Mr. Khanna, Lahore.

TABLE I.

Int.	λ-in air	ν-in vac.	v'	v''	Int.	λ-in air	ν-in vac.	v'	v''
3	3815·5	26201	10	6	2	4827·4	20709	7	19
2	3828·1	26115	8	5	0	4836·5	20670	0	14
5	3849·9	25967	9	6	1	4857·2	20582	8	20
2	3872·0	25819	10	7	0	4876·6	20500	15	25
4	3885·9	25727	8	6	0	4883·9	20470	2	16
6	3907·2	25587	9	7	0	4885·3	20464	6	19
*d*3	3921·3	25495	7	6	*db*2	4902·0	20394	3	17
7	3943·5	25351	8	7	*db*0	4910·5	20359	13	24
1	3959·8	25247	6	6	0	4912·1	20352	7	20
8	3980·7	25114	7	7	0	4918·6	20352	4	18
*d*5	4002·9	24975	8	8	0	4925·2	20298	0	15
2	4014·8	24901	11	10	0	4939·7	20239	11	23
2	4019·8	24870	6	7	0	4943·8	20222	5	19
*d*2	4032·9	24789	12	11	0	4948·6	20202	1	16
4	4041·7	24735	7	8	0	4965·7	20133	12	24
3	4049·0	24691	10	10	0	4971·1	20111	6	20
2	4064·4	24597	8	9	1	4993·3	20022	13	25
2	4082·9	24486	6	8	0	4998·5	20000	10	23
2	4088·3	24453	9	10	0	5003·8	19979	4	19
2	4093·6	24422	12	12	0	5017·6	19924	0	16
4	4103·9	24360	7	9	2	5023·6	19901	14	26
4	4148·9	24096	6	9	1	5028·0	19883	11	24
4	4168·6	23982	4	8	*d*2	5032·3	19866	8	22

TABLE I—(*Contd.*).

Int.	λ-in air	ν-in vac.	v'	v''	Int.	λ-in air	ν-in vac.	v'	v''
5	4216·9	23707	9	12	*b*1	5037·0	19848	5	20
7	4255·1	23495	5	10	*b*1	5042·0	19828	1	17
4	4258·0	23479	8	12	0	5052·1	19788	12	25
2	4290·2	23302	12	15	+0	5059·5	19758	9	23
7	4303·0	23233	7	12	1	5112·5	19554	0	17
3	4306·5	23214	4	10	*d*2	5114·4	19547	11	25
1	4389·0	22778	1	9	*d*2	5124·2	19510	8	23
2	4393·5	22755	8	14	3	5131·0	19484	5	21
1	4396·5	22739	5	12	4	5134·3	19471	1	18
1	4405·7	22692	2	10	4	5141·0	19446	15	28
2	4420·2	22617	6	13	5	5144·2	19434	12	26
1	4424·3	22596	3	11	*d*1	5150·7	19109	9	24
2	4438·2	22525	0	9	*d*0	5155·8	19390	6	22
1	4441·8	22507	7	14	+2	5162·4	19365	3	20
1	4445·6	22488	4	12	*d*2	5173·5	19324	16	29
2	4460·9	22411	1	10	*d*1	5180·2	19299	10	25
2	4467·1	22380	5	13	*d*1	5184·3	19284	7	23
1	4478·5	22323	2	11	*d*1	5194·6	19245	4	21
*d*2	4512·4	22155	0	10	*d*1	5205·3	19206	0	18
*d*2	4517·5	22130	4	13	*d*0	5010·1	19188	11	26
*d*3	4534·9	22045	1	11	*d*0	5215·0	19170	8	24
0	4556·2	21942	2	12	*d*2	5225·9	19130	1	19
0	4575·5	21849	3	13	*d*2	5234·0	19101	15	29

TABLE I—(*Contd.*).

Int.	λ-in air	ν-in vac.	*v′*	*v″*	Int.	λ-in air	ν-in vac.	*v′*	*v″*
*d*4	4586·3	21798	10	18	*d*1	5239·1	19082	12	27
4	4591·8	21772	7	16	*d*2	5245·1	19060	9	25
3	4610·0	21686	1	12	*d*2	5250·7	19040	6	23
0	4616·0	21658	8	17	*d*2	5262·0	18999	3	21
2	4630·2	21591	2	13	*d*3	5266·7	18982	16	30
0	4639·6	21548	9	18	*d*1	5271·3	18965	13	28
2	4641·8	21537	6	16	*d*0	5280·9	18931	7	24
1	4653·4	21484	3	14	*d*1	5292·7	18889	14	29
1	4657·9	21417	0	12	*d*1	5303·7	18850	11	27
0	4673·5	21391	4	15	*d*0	5309·3	18830	8	25
1	4689·3	21319	1	13	*db*2	5318·2	18798	5	23
0	4713·3	21211	2	14	*d*0	5321·7	18786	1	20
1	4719·3	21184	6	17	*d*2	5329·9	18757	15	30
1	4747·2	21059	7	18	*d*1	5332·3	18748	12	28
0	4750·1	21046	0	13	*d*0	5338·5	18727	2	21
0	4754·0	21029	4	16	*d*2	5342·7	18712	9	26
0	4771·1	20594	14	23	*d*2	5350·5	18685	6	24
0	4776·0	20932	1	14	0	5358·7	18656	3	22
3	4794·3	20852	12	22	2	5381·2	18578	7	25
0	4803·5	20812	6	18	+4	5388·3	18554	4	23
*d*4	4819·6	20743	3	16	1	5393·4	18536	14	30
4	5400·9	18510	11	28	+5	5622·3	17781	8	28
2	5414·3	18464	8	26	4	5638·0	17732	12	31

TABLE I—(*Contd.*).

Int.	λ-in air	ν-in vac.	v'	v''	Int.	λ-in air	ν-in vac.	v'	v''
3	5420·2	18444	5	24	+ *d*3	5653·1	17685	9	29
*d*2	5426·5	18423	12	29	+ *d*3	5667·9	17638	6	27
*d*1	5445·2	18360	9	27	*d*2	5674·1	17619	13	32
3	5452·4	18335	6	25	+ *d*2	5683·9	17589	10	30
+2	5458·2	18316	3	23	+ 2	5698·0	17545	7	28
1	5464·5	18295	13	30	3	5714·1	17496	11	31
+5	5471·4	18272	10	28	4	5719·3	17480	4	26
+2	5485·1	18226	7	26	4	5730·8	17445	8	29
3	5488·7	18214	4	24	+ 3	5745·7	17400	12	32
3	5496·7	18188	14	31	+ 3	5761·5	17352	9	30
+5	5502·4	18169	11	29	+ 5	5779·6	17297	13	33
4	5518·5	18116	8	27	+ 3	5792·8	17258	10	31
+*d*1	5533·1	18068	12	30	+ 0	5808·9	17210	7	29
+*d*1	5547·6	18021	9	28	+ 0	5825·4	17161	11	32
+*db*2	5559·6	17982	6	26	1	5833·3	17138	4	27
+ *d*4	5576·0	17929	10	29	+ 1	5839·1	17121	8	30
+ 4	5591·3	17880	7	27	3	5858·0	17063	5	28
+ 4	5606·8	17831	11	30	+ 2	5873·0	17022	9	31

d = diffuse bands, *db* = diffuse and broad bands.

+, these bands form according to Nevin, the green yellow system which is the same as system of fluctuation No. 6, Fig. 2.

TABLE II.

able showing the vibrational differences for the initial state according to Nevin's measurements and analysis.)

v'' / v'	0	1	2	3	4	5	6	7	8	9	Mean
5—6					246·0	248·0	248·0				247·6
6—7		263·0			252·0	248·0	251·0	249·0	250·0		252·2
7—8	239·9	234·0			238·0	234·0	232·0	237·0	237·0	232·0	235·5
8—9	227·6	231·0	228·0	233·0	230·0	236·0	234·0	234·0	233·0	240·0	232·7
9–10	235·5	222·2	227·4	223·0	229·0	235·0	235·0	235·0	227·0	209·0	227·8
10–11	204·5	209·9		212·0							208·0
11–12	218·9			206·0							213·4
12–13	212·6		214·5	225·5							217·5
13–14	212·8	216·6	213·5	211·0							213·2
14–15	207·8										207·8
15–16	203·3										202·3
16–17	201·3										201·3
17–18	197·1										197·1
18–19	195·7										195·7
19–20	184·6										184·6
20–21	173·8										173·8
21–22	156·6										156·6

TABLE III.

(Table showing the vibrational differences for the final state according to Nevin's measurements and analysis.)

v'' / v'	0–1	1–2	2–3	3–4	4–5	5–6	6–7	7–8	8–9	9–10
5					385·0	381·0				
6		380·0			383·0	383·0	381·0	380·0		
7	371·0				387·0	378·0	383·0	379·0	371·0	
8	376·9	382·0	385·0	383·0	391·0	380·0	378·0	379·0	376·0	
9	373·5	385·0	380·0	386·0	385·0	382·0	378·0	380·0	369·0	
10	386·8	379·8	384·4	380·0	379·0	382·0	378·0	388·0	387·0	378·0
11	387·4									
12			391·0							
13	380·6	381·9	380·0	377·5						
14	376·8	385·0	382·5							
Mean	378·1	382·4	383·8	381·6	385·0	381·0	379·6	381·2	375·6	378·0

TABLE IV.

Unclassified bands.

Int.	λ-in air	ν-in vac.	Int.	λ-in air	ν-in vac.
*d*2	4415·8	22640	*d*1	4726·5	21151
*d*1	4482·3	22304	*d*1	4765·1	20980
*d*1	4486·2	22284	2	4782·5	20904
*d*2	4530·9	22065	*d*1	4783·6	20899
1	4583·2	21813	*d*1	4786·5	20886
*d*2	4604·9	21710	1	4792·7	20859
*d*1	4647·2	21512	*d*1	4812·2	20775
*d*2	4683·9	21344	*d*1	4842·6	20644
			*d*1	4866·7	20542

d = diffuse.