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Raman Spectra of the Simpler Hydrocarbons

By

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(Plate XVI.)

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ABSTRACT.

The paper describes the results of a study of the Raman scattering in gaseous methane and ethane and liquefied propane, butane and iso-butane, the two latter being reported on here for the first time. The data obtained are discussed in relation to infra-red absorption and molecular structure.

Frequencies 1304, 1520, 2918 and 3018 are chosen as representing the fundamental oscillations of the methane molecule. Of these, only the latter two appear in the Raman scattering : 2918 appearing with great strength and having no corresponding infra-red absorption is identified with the symmetric expansion of the tetrahedron as a whole and 3018 which is weak in scattering and giving rise to strong infra-red absorption is taken to represent an unsymmetrical mode of oscillation. A relatively weak infra-red absorption corresponding to a high frequency, *viz.*, 4217 which is taken by Dennison as one of the fundamentals is attributed to a combination of 1304 and 2918.

The appearance of a strong frequency 993 in gaseous ethane with no corresponding infra-red absorption suggests that it is due to a symmetric oscillation of the two methyl groups. The strong hydrogen frequencies at 2900 and 2955 are represented in infra-red absorption by one, presumably unresolved, band at 2950.

In propane a low frequency at 377 is recorded and is in accordance with what may be expected from a triangular configuration of the molecule. Unlike ethane, this molecule shows a strong Raman frequency at

1453 arising from a transverse oscillation of the hydrogen atoms. Butane and iso-butane also show an intense and rather broad band in precisely the same position. It is noted that acetylene and ethylene like methane and ethane do not also show this transverse oscillation and an explanation is suggested for its absence in these simple molecules. The spectrum of iso-butane presents a close analogy to the spectra obtained in chloroform, and bromoform, a result which is in conformity with the fact that all the three molecules possess very similar structures.

1. *Experimental Arrangements.*

Of the simpler members in the saturated hydrocarbon series, the Raman spectrum of methane in the gaseous state has been obtained by Dickinson, Dillon and Rasetti.[1] It has also been studied by McLennan, Wilhelm and Smith [2] in the liquid state. Daure [3] has obtained the Raman spectra of the two higher members, *viz.*, ethane and propane in the liquid state. There exist however no data regarding butane and isobutane. The present paper describes the results obtained in a systematic study of the Raman spectra of methane, ethane, propane, butane and isobutane. Methane and ethane have been studied in the gaseous state by the apparatus already described by the author in an earlier communication.[4] The other three gases are however liquefied and contained in strong glass tubes which are sealed off at low temperatures. At the room temperature the liquids are under the pressure of their respective vapours. The substances had to be purified by repeated distillation before the spectra obtained were free from fluorescent radiation. The containing tubes are painted black except for the illumination and the observation

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[1] Phys. Rev., **34**, 582 (1929).

[2] Trans. Roy. Soc. Canada, **23**, 279 (1929).

[3] Annal de Phys., **12**, 375 (1929).

[4] Ind. Jour. Phys., **6**, 319 (1931).

windows and a large glass condenser is used to focus the light of a mercury arc into the liquid. Such an arrangement avoids the parasitic light effectively with the result that the photographs are very free from undesirable continuous background. A glass Fuess spectrograph is used to photograph the scattered spectra. Plate XVI contains the pictures obtained with ethane, propane, butane and isobutane.

2. *Results.*

The frequencies may be divided into two distinct groups, one for which the mutual oscillations of the carbon atoms are principally responsible and the other for which the oscillations of the hydrogen atoms are responsible. In Tables I and II, the frequencies obtained are given.

TABLE I.

Carbon Oscillations.

Methane										
Ethane				993 (5)						
Propane		377 (2)		867 (10)			1055 (2*b*)		1155 (2)	
Butane	320 (0)	430 (6)	793 (4)	834 (10)	960 (3)	983 (3)	1060 (6)	1067 (0)	1146 (4)	1303 (3*b*)
Iso-butane	372 (4*b*)	436 (2*b*)		796 (10)	967 (5*b*)				1177 (5*b*)	1355 (4*b*)

TABLE II.

Hydrogen Oscillations.

Methane							2918 (10)			3018 (2b)	3066 (1)
Ethane							2900 (9)	2955 (10)			
Propane	1453 (4)		2728 (3)	2767 (1)	2874 (10)	2908 (3)	2920 (5)	2948 (3)	2968 (3)		
Butane	1453 (10b)	2665 (1)	2706 (1)	2736 (2)	2864 (4)	2879 (8)	2910 (3)	2938 (6)	2964 (3)		
Iso-butane	1453 (10b)	2621 (1)	2720 (4)	2777 (2)	2870 (10)	2892 (2)	2910 (3)	2936 (3)	2962 (8)		

The figures in the brackets represent approximately the relative intensities of the lines. Fig. 1 is a diagrammatic representation of all the frequencies in these compounds.

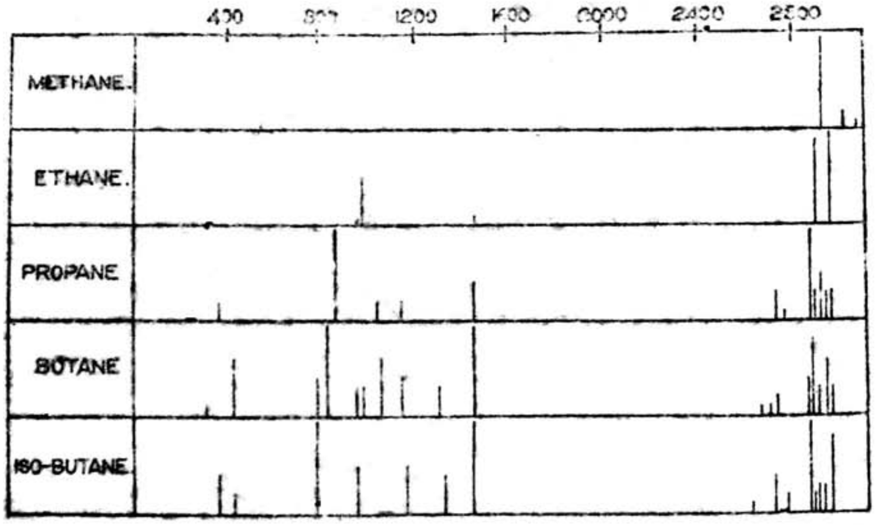
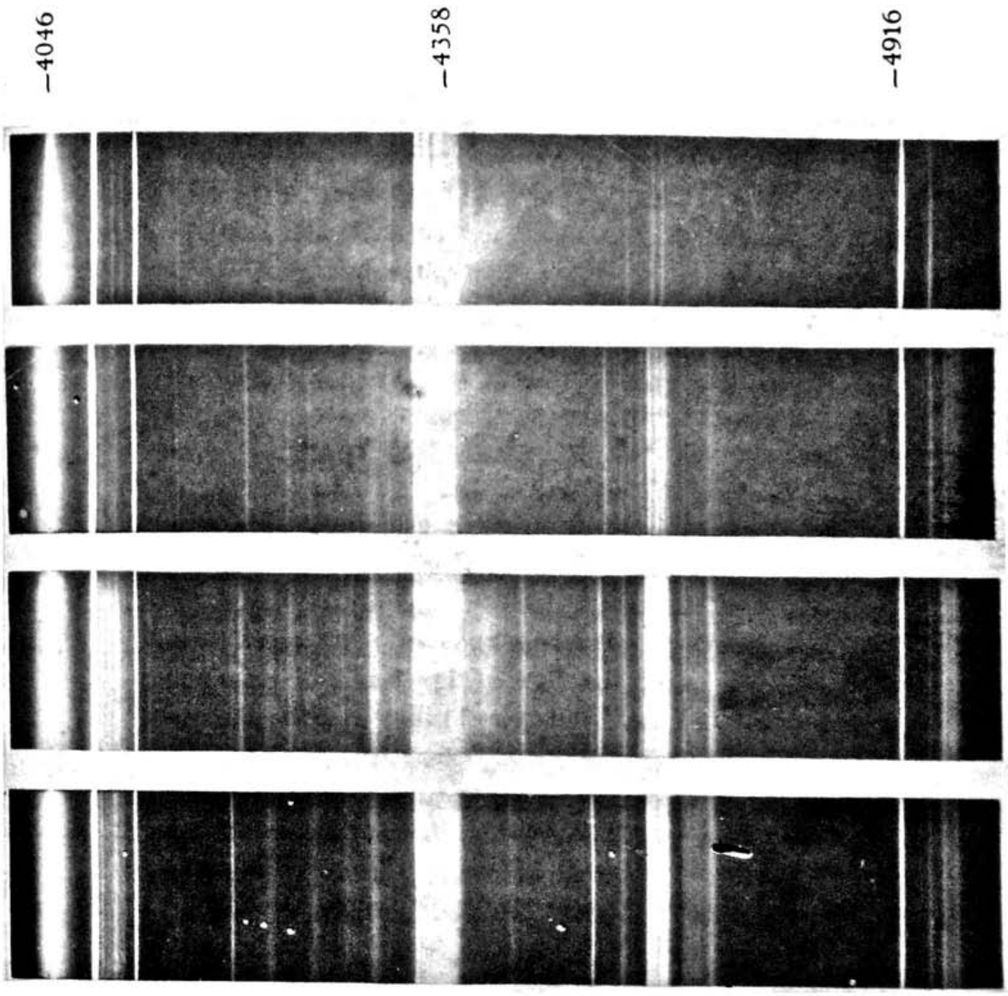


FIG. 1.



(a) Ethane gas.
(b) Propane liquid.
(c) Butane liquid.
(d) Iso-butane liquid.

Raman Spectra.

3. *Carbon Oscillations.*

As may be expected, gaseous ethane shows just one frequency in this region while there are none in methane. Its value agrees well with that obtained by Daure in the liquid state. In propane there are three carbon atoms presumably situated at the corners of a triangle and the whole structure may be treated as consisting of a central group of atomic weight 14 and two outer groups, each of an atomic weight 15. Such a configuration may be expected to give three frequencies and a calculation made by Dadieu and Kohlrausch [5] leads to the following values:

$$\nu_1=1080,\ \nu_2=980,\ \nu_3=400\ \text{cm}^{-1}.$$

The constants assumed are

$$f=4{\cdot}2\times10^5,\ f'=1{\cdot}4\times10^5,\ 2\alpha=110^\circ,$$

where f represents the force between the central and each of the outer groups and f' between the two outer groups themselves, while 2α is the angle between the carbon bonds. As may be seen from Table I, the observed frequencies are however appreciably different from the above and hence a revised calculation is made with the following values for the constants:

$$f=3{\cdot}08\times10^5,\ f'=1.37\times10^5,\ 2\alpha=112^\circ.$$

The resulting frequencies are

$$\nu_1=927,\ \nu_2=867,\ \nu_3=377$$

which may be compared with the set of observed values

$$\nu_1=1055,\ \nu_2=867,\ \nu_3=377.$$

It is interesting to note that both the calculations lead to a value for 2α which is very nearly equal to the tetrahedral angle, a result which is in general conformity with the

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[5] Wien. Ber., **139, 165** (1930).

structure of the long chain aliphatic compounds. The existence of an additional frequency of 1155 which is tentatively classed amongst the carbon oscillations cannot however be explained from the above simple considerations.

In butane and iso-butane molecules there are four carbon atoms and the spectrum is accordingly more complicated. It is interesting to note that the spectrum of iso-butane bears a close resemblance to the spectra obtained with chloroform and bromoform as may be expected from a consideration of their structures. The Raman frequencies of these three compounds are collected below.

$CH(CH_3)_3$:—	372	436	796	967	1335
$CH\,Cl_3$:—	261	366	667	761	1213
$CH\,Br_3$:—	154	228	539	655	1144

The frequencies gradually increase as we go up to iso-butane in conformity with the diminishing mass of the vibrating groups. Remarkable similarities already noticed by the author between the polarisation characters of the corresponding lines in chloroform and bromoform suggest that a study of the state of polarisation of these lines in iso-butane will be of special interest. The above classification includes all the carbon oscillations of iso-butane except the one at 1177 which is similar to the one at 1155 in propane.

4. *Hydrogen Oscillations.*

Gaseous methane shows only three frequencies in this region and the values given in Table II, are in good agreement with those obtained by Dickinson, Dillon and Rasetti. Ethane shows two frequencies, the values obtained being only slightly higher than those recorded by Daure in the liquid state. In addition to the above, Daure records a frequency of 1460 whose existence is not confirmed by the author's photographs. In the cases of propane, butane and iso-butane there are a large number of frequencies in this region. In addition to such a complex structure in the 3 μ region, the spectra of all these three substances show a prominent band in precisely the same position the centre of which corresponds to a frequency shift of 1453. In propane the band has a slightly smaller width than in butane or iso-butane. It will be noted that this frequency is also classed amongst the hydrogen oscillations and is presumably due to some kind of a transverse oscillation of the hydrogen atoms. The broad nature of this band is however very interesting and it is not unlikely that under higher dispersion, it might be resolved into a number of discrete lines like the corresponding oscillations of the hydrogen nuclei in the region of 3000 cm $^{-1}$. On this view its greater breadth in butane and iso-butane may be taken as analogous to the wider range of hydrogen oscillations in these molecules in the 3000 region. It is of interest to note, however, that its position is remarkably constant in all the three molecules; propane, butane and iso-butane.

5. *Relation to infra-red absorption and molecular structure.*

By virtue of its simplicity, a study of the methane molecule is of great importance in correlating the molecular structure with the characteristic frequencies of different models. The fundamental frequencies of this molecule have been chosen by Dennison [6] as 1304, 1520, 3019 and 4217. The first and the third appear with great intensity in infra-red absorption and are attributed to an unsymmetrical motion of the central carbon atom. 1520 and 4217 have been identified by Dennison with two symmetrical modes of oscillation. The lower frequency corresponds to the one in which the hydrogen atoms move on a sphere of constant radius while the higher frequency represents a radial expansion of the

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[6] Astrophys. Jour., **62**, 84 (1925).
See also J. P. Cooley, Astrophys. Jour., **62**, 73 (1925).

tetrahedron as a whole. That the evidence from the Raman spectrum is clearly against such a choice of fundamentals is seen from the following considerations.

The strong infra-red absorption at 3019 which is an active oscillation arising from an unsymmetrical motion of the nuclei is represented very accurately by a weak Raman line at 3018. On the other hand the most intense Raman frequency is given by 2918 and has evidently to be identified with the inactive oscillation arising from a symmetrical radial motion of the hydrogen nuclei. The value however does not agree with the high frequency at 4217 which has been taken by Dennison to represent this mode of oscillation and the complete absence of any line corresponding to this high frequency in the Raman spectrum of methane is clearly against the view that it is an inactive fundamental frequency.* A more probable origin of this high frequency is evidently from the combination of the fundamentals 2918 and 1304. If such a view is adopted, the case of methane is quite analogous to all the tetrachlorides which have presumably similar structures. In these compounds the most intense line which may be identified with the symmetric expansion of the tetrahedron comes just before the weaker line representing an unsymmetrical oscillation.

The fact that Dickinson, Dillon and Rasetti obtained rotational Raman lines on either side of the weaker 3018 line and not accompanying the more intense 2918 line is strongly in favour of the view that the latter represents a symmetric mode of oscillation whereas the former involves an asymmetry. In analogy with the tetrachlorides, it may also be expected that 3018 line would show an appreciable depolarisation whereas 2918 would be comparatively strongly polarised. Experiments are in progress to test this point.

In the case of ethane, the strong line at 993 is not

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* Reasoning based on the analogy of methane led the author (Ind. Jour. Phys. 5, 73 (1930), to erroneously identify the highest frequency with a symmetric expansion of the tetrahedron in the case of tetrachlorides.

represented in the infra-red absorption and hence may be identified with an oscillation in which the methyl groups move symmetrically against each other. The situation is closely analogous to that of a diatomic molecule and as such a study of its intensity and state of polarisation is of great interest. A point which needs special mention here is the absence of any line corresponding to the strong infra-red absorption in this gas at 6·85 μ. In this connection it may be noted that the strong absorptions in acetylene at 7·5 μ and in ethylene at 6·98 μ have no counterparts in the Raman scattering by these gases. The reason for this is clear from an analysis made by Mecke[7] of the oscillations of these molecules. He identifies them with such modes in which all the nuclei move in directions transverse to the chemical bonds. Such displacements will evidently give rise to oscillations which are intensely active in infra-red absorption but will not cause any Raman scattering as they involve no variation of the first order in either the refraction or the anisotropy of the molecules. Incidentally it may be remarked that in the series ethane, ethylene and acetylene, while the frequency of the transverse oscillation of the hydrogens diminishes, the frequency of the longitudinal oscillations increases from about 2950 in ethane to 3372 in acetylene.[8]

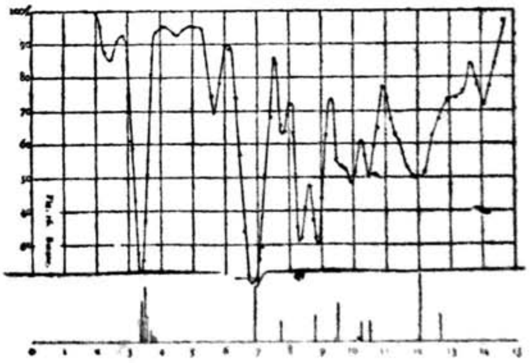

Fig. 2.

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[7] Z. f. Phys. 64, 173 (1930).

[8] Ind. Jour. Phys., 6, 319 (1931).

Unlike the case of these simple molecules where there are prominent and significant differences between infra-red absorption and Raman scattering, the spectra obtained with more complex molecules show a greater similarity for these two methods of study. Data for infra-red absorption are not available for propane. In Fig. 2, the curve obtained by Coblentz for butane vapour is reproduced along with the Raman lines drawn on the same scale. The heights represent approximately their relative intensities. In most cases the agreement between the infra-red and the Raman frequencies is very good. In the region of 3 μ, there are however a large number of Raman frequencies which are not represented in the infra-red absorption.

The author desires to express his grateful thanks to Prof. Sir C. V. Raman for his kind guidance.

Note added.—A subsequent picture with ethane gas, obtained by giving a long exposure, revealed an additional faint line corresponding to a shift of 975 cm.$^{-1}$ and a weak band at 1460 cm.$^{-1}$ This band agrees well in position with that recorded by Daure in liquid ethane but is fainter than even the pair of lines corresponding to 2900 and 2955 excited by the mercury radiation λ4077 A.U. Contrary to this, it may clearly be seen from the photographs published by Daure (Trans. Farad. Soc., *25*, 825, 1929) that it is of a very appreciable strength. In view of the fact that the ethane gas used by the author is from a cylinder labelled only 90% pure, it appears probable that the line arises from some impurity.

REVIEW

Chemischer Handatlas—By W. Walter Meissner, pp. *xi* +77 with 60 plates. Published by Verlag Georg Westermann, Braunschweig, Berlin. Price RM. 38.

In Prof. Meissner's work, the most important physical properties of all the known elements and of their simplest derivatives are depicted in an instructive way in the form of coloured plates. This method of presenting facts is unique and tends to familiarise the reader not only with the properties of the elements but also with their group similarities and variations in properties between members of the different groups. The descriptions of the plates are given in five different languages, so that no reader will find himself handicapped by insufficient knowledge of German. At the same time, full advantage of the explanatory text given opposite to every plate can only be taken by those who are familiar with this language.

The 60 many-coloured plates illustrate a large variety of properties and other facts concerning the elements which are of the greatest importance to the chemist, the physicist and the geologist. Among the physical properties depicted in the plates are density, specific and atomic heats, atomic volumes, atomic diameters, ionic radii, ionisation potentials, electrical conductivity, magnetic susceptibility, hardness, co-efficient of cubical and linear expansion, melting point and heat of fusion, boiling point, heat of combustion and crystal structure of the elements. Other facts regarding isotopes, packing effect, electronic shells of neutral atoms and ions, multiplet structure in the spectra, valencies in the hydrogen, halogen and oxygen derivatives and dipole moments of some simple compounds, are shown in the plates. The order followed is that of increasing atomic number, the periodic table being adhered to, the rare earth elements from lanthanum finding a separate place below the main table.

Plates have also been included illustrating the properties of important classes of compounds such as hydrides, oxides, chlorides, nitrates, nitrides, sulphates, sulphides, carbonates, etc. One plate is given for co-ordination numbers and complex compounds formed by the elements, and another illustrating the group separation of the elements in analytical chemistry. A few plates of interest to the geologist such as cosmic occurrence of the elements, their geo-chemical distribution and occurrence of ore deposits in various parts of the globe are also to be found. Exact data are given wherever possible, so that as a book of reference and for illustrating class lectures Prof. Meissner's book is exceedingly useful.

The book includes more than 400 references to books and to original papers of authors mentioned in the text, as well as complete author and subject indexes. Though usually neither chemistry nor physics is studied in the order given in the text, the new method of presentation links up the two subjects intimately and gives the reader an up-to-date knowledge of the developments in the fields of atomic physics and chemistry.

The preparation of so many plates accurately and in so many colours no doubt involves a good deal of painstaking effort and both the author and the publishers deserve to be congratulated in producing a book useful alike to the student, the teacher and the research worker.

P. K.