

The Raman Effect and Molecular Structure.*

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1. INTRODUCTION.

THE great interest evinced by scientists in molecular spectroscopy in recent years is not surprising, because with that is connected the exact determination of many physical constants defining a molecule such as the frequencies of vibrations, the nuclear distance of the constituent atoms, the valence angle, the force of attraction between the atoms or groups of atoms and its variability with environment, the moment of inertia and the symmetry of the molecule as a whole. Many of the physical and chemical properties of substances depend upon one or other of these molecular constants and hence the importance of the spectroscopic study of substances cannot be overestimated. These constants are calculated from the vibration and rotation frequencies of the molecule, based on a suitable assumption for the form and structure of the molecule. The first progress in molecular spectra was made by observations in the ultra-violet and the infra-red and much valuable information was obtained regarding the structure of simple molecules. But the experimental technique for the determination of frequencies especially by infra-red observations is difficult and laborious and the presence of a large number of overtones and combinations makes the interpretation of the observed bands especially in the complicated molecules rather uncertain. This made the progress necessarily slow.

The discovery of the Raman effect by Sir C. V. Raman in 1928, marked a new era in Molecular Spectroscopy. It furnished a simple means of obtaining from a single photograph a fund of information regarding the vibration frequencies and allied properties of any molecule. It has the advantage over the infra-red in that these frequencies are rendered easily accessible in the visible and the ultra-violet part of the spectrum where the dispersion of the spectrograph and the sensitiveness of the photographic plate are both great. Unlike the infra-red,

the occurrence of the overtones and harmonics is rare and consequently, the identification of the frequencies is easy and their interpretation is more accurate. Thus it is no wonder that the number of investigations in this new field of research has far surpassed those which have been stimulated by any other scientific discovery in recent times.

2. INFRA-RED ABSORPTION.

The absorption or emission of radiation by a molecule depends upon the probability of transition of the molecule from one of its stationary states to another as contemplated by quantum theory. This transition may be either electronic in which case the absorption takes place in the *Ultra-violet* and the visible regions or it may be either rotational or vibrational in which cases the absorption takes place in the *Infra-red*. The wave-length corresponding to the absorption of the incident radiations in the infra-red gives the frequency of vibration or rotation (or their overtones and combinations) of the molecule. But only those vibrations of the molecule are active in absorption which are accompanied by changes in the *permanent electric moment* of the molecule. The vibrations of the atoms within the molecules, which are symmetrical with respect to the centre, therefore, cause no absorption in the infra-red. Thus the vibration frequency of molecules like H_2 or O_2 or the breathing frequency of a tetrahedral molecule is 'inactive' in the infra-red.

3. RAMAN SPECTRA.

The Raman spectrum owes its origin to the interaction between a light quantum and a molecule. When a transparent substance is irradiated with monochromatic light of frequency ν and the scattered light is examined by means of a spectrograph, several new frequencies are observed. The incident light quantum interacts with the molecule and raises it to a higher energy level. The molecule immediately drops either to the ground level itself giving rise to the classical, coherent '*Rayleigh Scattering*'

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or to one or other of the excited vibrational or rotational levels of the molecule giving rise to the 'incoherent' or 'modified' lines called 'Raman lines' or 'Raman rays'. If the molecule happens to be in an excited state during collision with the light quantum, transference of energy may take place from the molecule to the light quantum and the scattered light will consequently possess enhanced frequencies and give rise to 'anti-Stokes lines'. While the infra-red absorption involves only one process, the Raman effect is the result of a double transition involving three stationary levels. If the incident light contains more than one wave-length as is the case in practice, each of them would give rise to its own set of new lines having exactly identical frequency shifts. Thus the phenomenon is essentially different from *fluorescence* which appears in the same region of the spectrum irrespective of the wave-length of the exciting radiation. The difference in wave-numbers between the frequency of the exciting line and the new frequencies of the scattered light is of the order of the infra-red frequencies and often coincide with the latter.

The selection rules governing the appearance of a Raman line have been worked out exhaustively by Placzek¹ who has shown that the vibrations of the molecule which introduce changes in the *induced electric moment* (i.e., polarisability) of the molecule are active in the Raman effect. The symmetrical oscillations of the molecule which are usually missed in the infra-red consequently, come out most prominently and the anti-symmetrical vibrations are either weak or inactive in the Raman scattering. Thus the Raman spectra and the infra-red absorption are not identical but complementary in character. The frequency shift, the intensity which depends upon the change in the polarisability of the molecule during the vibration, the state of the polarisation of the line which depends upon the symmetry character of a particular vibration and its appearance or non-appearance in the infra-red are the four features that are necessary for the identification of the mode of vibration responsible for any particular Raman line.

4. MOLECULAR STRUCTURE.

The most important direct information that is furnished by the study of the Raman

effect in a substance is the magnitude, the state of polarisation and the relative intensities of the frequencies of the different modes of vibrations executed by the atoms in a molecule. The co-relation of these natural frequencies with molecular structure can be effected only on the basis of some suitable model assumed for the molecule. Much progress has been made in this direction by the work of Dennison² and Bhagavantam³ and recently by Wilson,⁴ Rosenthal,⁵ Nagendra Nath,⁶ Manneback⁷ and others. The dynamical theory of vibrations of polyatomic molecules based upon the directed bond forces between particles has yielded fruitful results.

The rules governing the polarisation characteristics of vibrations have been dealt with in detail by Placzek¹ and a useful summary of the number of vibrations allowed in the Raman effect and in the infra-red absorption and their state of polarisation for a whole series of polyatomics has been published by Wilson.⁸

For a molecule containing N atoms, there are $3N$ degrees of freedom. Excluding three of these which produce only rotation as a whole and three which produce only translatory motion of the molecule, there are $3N - 6$ normal vibrations for a molecule. For a linear molecule there are only two degrees of freedom of rotation and hence the number of normal vibrations is $3N - 5$. The evaluation of the normal vibrations is very much simplified if the molecule possesses some form of symmetry.

The simplest case of an oscillator is obviously the diatomic in which the two atoms are bound together with a force F . This type of molecule possesses only a single fundamental frequency given by the expression $\nu = 2\pi \sqrt{F/\mu}$, where μ is the reduced mass given by $1/\mu = 1/m_1 + 1/m_2$, m_1 and m_2 being the masses of the constituent atoms.

Tri-atomic molecules.—With the molecules of the type AX_2 there are three possibilities, (1) in which the molecule is linear and symmetrical, (2) in which the molecule is linear but unsymmetrical, and (3) in which the molecule is non-linear or bent. To the first type belongs CO_2 and CS_2 . These molecules possess a centre of symmetry and give rise to a single Raman line, corresponding to the symmetrical oscillations of the extreme atoms towards or

away from the central carbon atom. This frequency is highly polarised and does not appear in the infra-red. But in both these cases another line appears in the Raman effect which is shown by Fermi⁹ as due to *accidental degeneracy* caused by the overtone of the lower frequency coinciding with the fundamental. Recently, the author¹⁰ has shown that the di-halides of Hg, Zn and Cd also belong to this type and this conclusion has been supported by the isoelectronic properties of these molecules as shown recently by Penny and Sutherland.¹¹ The second and the third group of molecules give rise to three lines in the Raman effect which enable the force constants and the valence angles to be calculated. A case of special interest is the N_3^- ion in the azides. Recent investigations by the author† have yielded four lines for sodium azide out of which one is due to accidental degeneracy and the other three are the normal frequencies. These results seem to show that the ion is either linear and unsymmetrical or bent.

Tetra-atomic molecules.—Molecules of the type AX_3 possess six normal frequencies out of which by reason of symmetry some may be multiply coincident or *degenerate*. These degenerate frequencies are shown by Placzek¹ to be completely depolarised. Cases of special interest in this type are (1) the plane triangular and (2) the pyramidal molecules. Both these types possess four normal vibrations two of which are single and parallel and two are perpendicular and doubly degenerate. Only CO_3 , NO_3 and guanidonium¹² ions are known to belong to the plane, equilateral type and one of the vibrations parallel to the symmetry axis is forbidden in the Raman effect. All the tri-halides, the chlorates, bromates and iodates and ammonia are pyramidal in structure. An experimental fact of some significance in this connection is the splitting of the parallel vibrations if the height of the pyramid is small. Placzek¹³ was the first to observe this in ammonia and he explained it as due to *positional degeneracy* in these modes of oscillations. Similar splitting in iodates,¹⁴ bromates,† and chlorates† have been observed. In iodates the symmetrical oscillation shows further splitting which has been tentatively ex-

plained as due to further accidental degeneracy. An interesting case of a tetra-atomic molecule where all the atoms are identical is the phosphorus molecule. The number of Raman lines and their states of polarisation¹⁵ indicate a perfectly tetrahedral structure for P_4 .

Penta-atomic molecules.—Molecules of the AX_4 type possess nine normal vibrations. Most of them, e.g., the tetra-halides, sulphates, selenates, phosphates and chromates† are tetra-hedral and yield four Raman lines. Of these lines, one is symmetrical and single, one is doubly degenerate and two are triply degenerate. The crystal-line KIO_4 † however, yields a more complicated spectrum due probably to the fact that the ionic group IO_4 is distorted in the crystal lattice. A similar influence on the vibration frequencies by crystal forces has been clearly brought out recently by the work of Ananthakrishnan.¹⁶

In the case of complicated molecules, as is generally met with in organic chemistry, this mode of classification is almost impossible unless the molecule possesses a high degree of symmetry. But systematic researches of a large number of compounds of similar constitution and possessing the same groups by several investigators notably Kohlrausch¹⁷ and his school have led to the identification of certain frequencies with certain definite groups and their presence or absence has been made use of in settling important problems regarding molecular structure. Thus the frequency due to the C—H group falls in the neighbourhood of $3,000\text{ cm.}^{-1}$ and of OH at about $3,500\text{ cm.}^{-1}$ and it is easy to see that these frequencies cannot undergo any appreciable variation due to a change in the rest of the molecule; for the mass of the hydrogen atom is very low compared with the mass of the other atoms and therefore, the reduced mass of the oscillating group is determined almost entirely by the mass of the hydrogen atom. But it has been observed that the CH frequency in the aromatic compounds is greater than in the aliphatics. Recently, the author¹⁸ has observed that in the formate ion this frequency falls as low as $2,830\text{ cm.}^{-1}$. Similarly, the OH frequency shifts from $3,650\text{ cm.}^{-1}$ in KOH to about $3,400\text{ cm.}^{-1}$ in the alcohols and very much further down in the case of inorganic acids.† These

† Unpublished work of the author.

changes in the C—H or the O—H frequencies should only be due to the variation in the valence force between the hydrogen and the carbon or the oxygen and show the influence of the surrounding electric field on the properties of molecules.

This explanation of the constancy of the CH and the OH frequencies does not hold good for other groups where the vibrating particles are of comparable mass (e.g., C = O). In these cases the frequency of vibration is constant within certain limits; because when the forces holding the atoms together in the neighbouring groups are very dissimilar, the influence on the vibration of any one group due to its coupling with other groups is unimportant with the result that it vibrates without being appreciably influenced by the neighbouring atoms. This also accounts for the constancy of the double or the triple bond frequencies.

If however, there are more groups than one in a compound in which all the forces are of the same order, resonance will take place among the valence vibrations, which generally leads to the splitting of the lines. This is apparently the explanation for the multiplicity of the lines in many organic molecules.

A factor of great importance for the assignment of the Raman lines is their state of polarisation. Instances of this are furnished by the recent study of the polarisation of the Raman lines of many organic and inorganic substances in this laboratory.¹⁹

5. ELECTROLYTIC DISSOCIATION.

From what has been said about the molecular structure, it will be evident that some difference could be expected in the spectra of complete molecules and their products of dissociation. In fact, one of the fruitful applications of Raman spectra is for the determination of the degree and the manner of dissociation of solutions of electrolytes due to varying concentrations. The classical theory of electrolytic dissociation due to Arrhenius was based on the postulate that on solution in water electrolytes dissociate completely into positively and negatively charged ions. On the assumption that these ions are independent of one another Ostwald²⁰ deduced his well-known 'dilution law,' for the variation of conductivity of electrolytes with concentration. The

results of experiment showed a quantitative agreement with the demands of this conception in the case of weak electrolytes; but there was almost a complete breakdown of the law even for dilute solutions of strong electrolytes. Obviously the failure of the theory was due only to the fact that in the strong electrolytes in which the ions are relatively large in number, the distance between the ions cannot be very great and therefore, bring the interionic attraction into play. To explain satisfactorily, this anomalous behaviour of strong electrolytes Debye and Hückel²¹ and later Onsager²² postulated a new theory of electrolytes based upon the assumption of an 'ionic atmosphere' as a point charge surrounding the ion in solution. The theory successfully explained many anomalies on the dependence of concentration in the measurements of osmotic and activity coefficients and solubility influences for completely dissociated strong electrolytes. The empirical law enunciated by Kohlrausch²³ that the percentage deviation of equivalent conductivity of moderately dilute solutions of strong electrolytes from their limiting value at infinite dilutions is proportional to the square root of the concentration, was also readily explained by the Debye-Hückel theory. An extension of the theory by Debye and Falkenhagen²⁴ led to the remarkable prediction of the dependence of the conductivity of electrolytic solutions upon the frequency, which was subsequently confirmed by Sack.²⁵ In the case of concentrated solutions of strong electrolytes, however, systematic deviations were observed from the theoretical laws of Debye and his co-workers. Recent advances in arriving at a rigid theory for concentrated solutions lie in the direction of attributing a finite diameter for the ionic atmosphere instead of treating it as a point charge. Further modifications are introduced by assuming association of ions in solution²⁶ and incomplete dissociation²⁷ in concentrated solutions of strong electrolytes. Before a more rigorous and satisfactory theory could be attempted it is important to determine exactly the degree of association of the ion and the degree of dissociation of the molecules at varying concentrations of electrolytes in solution.

X-ray studies of crystals afford some evidence in this direction. It has been

found that most salts belong to 'ionic' or 'heteropolar' type in which atoms or atom groups are present in the crystal as ions. The ions are separated by spaces in which electron density is small and the electrostatic forces of attraction which keep the crystals in tact affect equally all neighbouring ions and in all directions. If the crystal contains polyatomic groups, SO_4 , NO_3 , etc., the complex preserves the same characteristic in all salts and behaves as a single ion. This ionic character of the building units in a crystal and the absence of any molecular complex are responsible for the fact that most salts are ionised in the solid state as well as solutions and yield sharp Raman lines.

The Raman lines owe their origin to the vibrations of atoms within the molecule or the polyatomic ion. The fact that a large number of inorganic salts of metals have yielded only lines characteristic of the acid radical both in the state of crystals and solutions, shows that the lines are due to ionic groups in both cases and lends support to the ionic conception of these salts as revealed by X-rays.

When a salt dissolves in water, the regular arrangement of ions in the crystal disappears and ions remain either as separate entities, alone or as loosely bound complexes, or form a mixture of undissociated molecules and dissociated ions. In the latter case, the vibration characteristics of the separate units are different and each of them give rise to its own lines. If the product of the concentration and the time of exposure is kept constant, the intensity of each line would be proportional to the number of scattering particles responsible for it and the relative intensities of the lines due to the complete molecule and the ionisation products would give to a first approximation the degree of dissociation at different concentrations of the electrolyte.

The method of the Raman spectra, which is the only reliable method available at present for concentrated solutions, has been successfully applied at first for nitric acid by Ramakrishna Rao²⁸ and later for sulphuric acid,²⁹ iodic acid and selenic acid.³⁰ Phosphoric and selenious acids³¹ are comparatively weak; but they have also revealed that the dissociation is progressive and step-wise in character.

The case of sulphuric acid and selenic acid is particularly interesting; for it affords a method of comparing the behaviour of electrolytes belonging to the same homologous series. Unlike these two acids, telluric acid is a weak electrolyte and has given rise to three Raman lines† which further indicate that $\text{Te}(\text{OH})_6$ is octohedral in structure.

All the metallic salts of these acids, on the other hand, give only lines characteristic of the acid radical and are, therefore, completely dissociated even in concentrated solutions. This difference between the acids and the salts is obviously due to the fact that while the hydrogen atom in the acids is capable of forming both electrovalent and covalent linkages, the electropositive metals form only electrovalent compounds.

6. HOMOPOLAR AND HETEROPOLAR COMPOUNDS.

The above discussion leads us to the consideration of homopolar and heteropolar compounds. X-rays have revealed to us that two common types of atomic arrangements that exist in the solids are (1) the heteropolar or ionic compounds like NaCl in which the forces holding the atoms together are electrostatic and (2) the homopolar or molecular compounds like diamond or most of the organic substances in which the units of the crystals are molecules possessing covalent bonds. It was shown by Krishnamurti³² that the covalent type of binding gives rise to Raman lines and the electrovalent type does not give any Raman spectra. This empirical relation between the Raman effect and the nature of binding has been substantiated theoretically by Placzek³³ on the basis that no resultant change in polarisability is induced in the electrovalent molecules. Even after a comparatively long exposure under satisfactory conditions of experiment with rocksalt Fermi and Rasetti³⁴ succeeded in obtaining the Raman spectrum of only the second order, the first order not appearing because of the equal and opposite changes of polarisability of the ions in the crystal lattice. From the point of view of covalent chemistry it is interesting to know which of the salts of metals form covalent compounds and which of them form electrovalent compounds. X-rays have shown that halides of alkalis and the

alkaline-earth metals form ionic lattices and the halides of mercury, the metalloids and the non-metals form molecular lattices. The Raman spectra have confirmed the above conclusions and have shown further that the halides of zinc and cadmium are also covalent while those of magnesium and aluminium are electrovalent. Aqueous solutions of zinc chloride²⁵ show a gradual diminution of intensity of the Raman line as the dilution is increased and indicate that there is a progressive change from the covalent form to the electrovalent form. As explained before, the dissociation of acids also shows that the change from the covalent to the electrovalent form is only gradual.

7. CHANGE OF STATE AND RAMAN EFFECT.

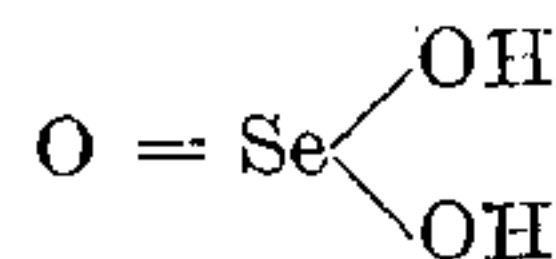
Closely connected with the nature of chemical bonds is the remarkable change that accompanies the Raman lines due to a change in the state of aggregation of a substance. It has been observed that generally covalent molecules like sulphur and phosphorus or ions like NO_3 do not undergo any appreciable change in frequency when they pass from the solid to the liquid and from the liquid to the gaseous state. On the contrary, molecules like HCl and HBr which are polar and which change to the electrovalent form in solution are accompanied by large changes in frequency, the shift of the line being smaller in the solid than in the liquid and in the liquid than in the vapour. Striking changes have been observed in the Raman lines of the selenic and selenious acids due to a change from the solid to the molten condition. The act of solution in water of zinc chloride and cadmium iodide has a similar effect on the magnitude of the frequency shift. If the process of solution is taken as akin to vapourisation, the measured changes in frequency can be easily understood as due to change of state.

Another change that has been observed especially in iodic, selenic and selenious acids when they are melted or dissolved in water is the remarkable broadening of the Raman lines. In the case of crystals of these acids the lines are sharp. As has been shown by the author, the ionisation of molecules of these acids start even in the solid state. The only difference between the solid and the liquid or the solution is,

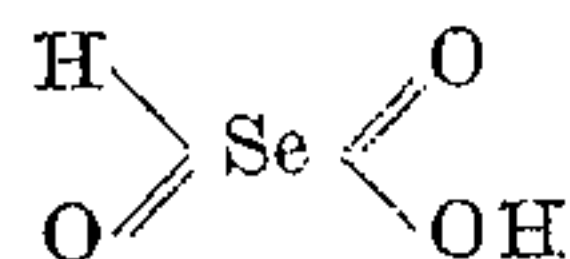
therefore, that while in the solid the molecules or the ions are rigid bodies arranged in a regular manner and incapable of forming complexes, in the liquids and solutions the lattices break up to some extent and the ions and molecules are free to form loosely bound complexes. Besides, of course, there is also the field due to the solvent in the case of solutions. It is not unreasonable to attribute the broadening of the lines in solutions of high concentrations at least partly, to the formation of associated or polymerised molecules or complex ions as postulated by Bjerrum. As the dilution progresses the complex breaks up giving rise to relatively sharper lines. These conclusions are supported by the fact that in water, formic acid and acetic acid which are known to be associated, the Raman lines are excessively broad. Thus while dissociation is accompanied by appreciable frequency shifts of characteristic lines, association of molecules or ions gives rise only to a broadening.

8. SOME CONSTITUTIONAL PROBLEMS.

Examples of the application of Raman spectra for solving questions concerning constitution of organic molecules are too well known to be repeated here. Some problems of interest which have been recently solved by the author are the constitutions of formic and selenious acids. In the former case³⁶ it has been able to show that the aldehyde group is present in the molecule and in the formate ion. Selenious acid³⁷ has been shown to exist in two forms, the symmetrical



and the unsymmetrical



in dynamical equilibrium with each other. The symmetrical form is predominant in aqueous solutions and the unsymmetrical form in solids and the alcoholic solutions. Other instances arising out of the recent investigations are the constitution of the 'chamber acid' by Angus and Leckie,³⁸ of phosphorus acid by Ananthakrishnan,³⁹ and of a large number of heavy compounds by American workers.

9. ROTATIONAL RAMAN EFFECT AND LATTICE OSCILLATIONS.

Hitherto we were concerned with only the vibration frequencies of molecules. But Raman lines also arise from transitions in the rotational energy levels. In the case of liquid and gaseous hydrogen and deuterium⁴⁰ and other gases whose moment of inertia is small, these rotational lines appear as discrete lines well separated from each other and from the Rayleigh line and their frequency shifts and intensities give valuable information regarding the moment of inertia and allied properties of the molecule. But if the moment of inertia is large as in benzene, the rotational Raman lines fall close together and very near to the Rayleigh line and appear as a *wing* accompanying the latter. Theoretically, the intensity of the wing should start from a minimum near the Rayleigh line and after reaching a maximum, should fall off rather abruptly. Experimentally several investigators⁴¹ have observed that the intensity starts from a maximum at the unmodified line itself and falls off only gradually. This difference between the theory and the experiment has led to various speculations regarding the origin of the wing in the liquids.

Recently Gross and Vuks⁴² found that this wing in the liquids breaks up into discrete bands when examined in the solid state. They have assigned these lines to vibrations characteristic of the crystal lattice and have put forward the hypothesis that the wing in the liquids is partly due to the rotation of individual molecules and partly due to lattice oscillations of crystal groups that persist in the liquid state. This observation if fully substantiated, is of enormous interest and lends strong support to the quasi-crystalline structure of fluid state.

Bhagavantam⁴³ is, however, of opinion that these low frequencies observed by Gross and Vuks are only due to the hindered rotation of solid molecules by virtue of their anisotropy.

Sirkar⁴⁴ has also observed low frequencies in a large number of organic crystals and in a few simple substances like H_2S , CS_2 and CCl_4 ; but he has suggested that these frequencies owe their origin to inter-molecular oscillations of polymerised groups of molecules in the solid state. His chief

objection for attributing these lines to lattice oscillations is that though these frequencies shift to a higher value due to a lowering of temperature as is to be expected, the coefficients of expansion of the crystals calculated from the observed changes of frequency with temperature are not of the proper magnitude. For the purpose of the calculations he has employed the generalised formula of Lindemann⁴⁵ which is strictly true only for monatomic cubic lattices. In a recent paper, Sirkar and Gupta⁴⁶ deduce this general expression from Braunbeck's formula⁴⁷ for the frequency of oscillation of any lattice composed of two kinds of atoms and argue that it is applicable to any crystal system. It may be pointed out that Braunbeck's formula is valid only for the *ionic* lattices like NaCl in which there is only a single mode of vibration which is supposed to take place between the layer composed of sodium atoms and the other layer composed of the chlorine atoms. But the formula ceases to be strictly valid for molecular lattices where one set of lattice units vibrates against a similar set of like molecules. In these cases there may occur more than one mode of vibration depending upon the complexity of the lattice, as is substantiated by the observed facts. Another objection raised by Sirkar and his co-worker is that some of these lines are more intense than the symmetric oscillations of the molecule itself and that this fact cannot be explained by Placzek's theory of polarisability of Raman lines. It is known that diamond yields a very intense line which has been shown by Nagendra Nath⁴⁸ to be due to a degenerate, yet symmetrical oscillation of the diamond lattice. Therefore, the intensity and the polarisation of the lines due to the lattice vibrations depend upon the symmetry and degeneracy of the oscillation; and it does not *a priori* follow that they should be less intense than any of the vibrations of the molecule. On the other hand, it is highly improbable that substances like carbon tetrachloride or carbon disulphide should form stable polymerised groups in the solid state.

The author⁴⁹ has recently obtained lines of low frequency in relatively simple molecules like sulphur and phosphorus and a fair agreement has been observed between the experimentally observed frequencies

and those calculated from the melting points, assuming the approximate validity of the Lindemann formula for molecular lattices of these substances. Phosphorus as well as carbon tetrachloride is isotropic and the occurrence of the depolarised low frequency in this case excludes the possibility suggested by Bhagavantam that it may be due to hindered rotation of solid molecules. There is also no chemical evidence that polymerised groups like P_4-P_4 or S_8-S_8 exist in these cases. Therefore, it may be safely concluded that the crystal lattice is responsible for these lines. Further evidence for this view has been furnished by the recent work of Vuks⁵⁰ with mixed crystals and various crystalline modifications of the same substance.

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