

TWENTY-FIVE YEARS OF RESEARCH ON THE RAMAN EFFECT

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1. OVER-ALL PICTURE

INTENSIVE experimental work on the scattering of light carried on continuously at Calcutta since the year 1921 culminated in the discovery by Professor Raman in 1928 of the new radiation phenomenon, now known as the Raman Effect. The first announcement of the discovery with a description of its principal features was made in a lecture by Professor Raman under the title "A New Radiation" on March 16, 1928, and the text of that epoch-making paper is being reproduced in these *Proceedings*. This year marks its twenty-fifth anniversary and it appears appropriate to present a review of the large amount of scientific literature that has grown around this branch of knowledge.

A statistical analysis of the trends in this subject was made by Hibben¹ in 1938 with some interesting results. He observed that even by that time, there appeared nearly seventeen hundred publications on different aspects; India being the most prolific producer of research in this subject as an individual geographical unit. The subject was being investigated in the laboratories of practically every country in the world, but Germany, United States, France, Italy, Belgium and Japan had made notable contributions. Though the early interest was exhibited essentially by physicists, its gradual passage into the hands of chemists and physical chemists became quickly evident. The present position is that we have over 3,000 published papers on the subject, the United States and India together accounting for nearly half of them. Even now there is a wide and sustained interest and the indications are that workers desire to explore new fields of investigation to which this powerful tool may be applied, and it is likely that such an interest will continue for a long time in specific schools of research that have come to be established but perhaps not in the general laboratories.

In the field of spectroscopy, the study of Raman effect has furnished numerous data which are complementary in nature in several important

¹ *Proc. Ind. Acad. Sci.*, 1938, **8**, 294.

cases to those obtained from a study of the infra-red region and this aspect has in a large measure been the motive force which attracted experimental spectroscopists and resulted in a simultaneous development of the technique both in the infra-red and the visible regions. The rapidly accumulating results from these two fields gave a fresh impetus to the study of molecular constitution and the normal oscillations of postulated molecular structures with special reference to the inter-atomic forces that exist in such structures. Quite an appreciable number of simple molecules have been dealt with in an exhaustive manner by rigorous theoretical methods and fundamental results have been obtained in regard to their structures. Empirical methods of great ingenuity have also been devised from time to time for dealing with the more complicated structures and much progress made.

In the field of chemistry, an amazing variety of problems such as polymerisation, hydrogen bonding, free rotation, identification of isomers and the nature of valency have been viewed and tackled from such new angles with this new tool that a distinctive branch of chemical physics may be said to have been born in the past decade or two.

The study of isotopes, verification of polarization and intensity rules and an analysis of the rotational and vibrational branches in the Raman spectra of simpler molecules were some of the earliest directions in which the physicists interested themselves. The results of such studies are now fairly widely accepted and they constitute considerable portions of treatises dealing with modern molecular physics. An interesting consequence of the experimental work having gone ahead of the theory, as soon as Raman effect began to be applied to a study of molecular structure, is the pressing into service of more powerful mathematical methods for such purposes. The theory of groups has been one such and its application to problems of molecular physics has been greatly enriched in the years that followed the discovery of Raman effect.

A study of the solid and liquid states, covering purely physical as well as physico-chemical aspects, has also been stimulated. Contributions of a fundamental nature have been made and the subject of crystal physics in particular, may be said to have been given a new orientation altogether. In the following pages, these and other advances will be described by way of summarizing the achievements of the last two and a half decades that followed the discovery of the Raman effect.

2. INTRODUCTION

The equipment, originally used by Raman, consisting of the scattering substance, *viz.*, a glass bulb of distilled liquid or a block of ice or of optical

glass, a quartz mercury lamp with a condensing lens and a pocket spectro-scope is the simplest experimental set-up which one can think of in connection with a major effect of this kind in Physics. Such an assembly, which is generally available in almost any laboratory, may still be used very successfully for demonstrating the effect. For purposes of detailed studies with liquids, the glass bulb has been replaced by more complicated containers; the mercury lamp by a variety of more powerful sources and the pocket spectro-scope by high dispersion and large aperture spectrographs. In fact, some very spectacular developments in these directions have taken place in recent years that to-day we are able to photograph weak Raman lines with exposures of a few seconds only. Some of these will be briefly described in the following pages.

As actually observed, the effect is now well known to consist in the appearance of new lines (or in some cases bands) and generally also some unresolved continuous radiation in the spectrum of the scattered light, besides the lines originally present in the incident radiation. Each line in the incident spectrum, if of sufficient intensity, gives rise to its own set of lines or bands and associated continuous spectrum; the frequency shifts of each of these new lines as measured from the parent one being independent of the incident radiation and therefore characteristic of the material studied and to some extent the nature of its aggregation. The effect may be observed in a great variety of substances and in diverse physical states and conditions. The lines themselves generally show easily recognisable differences in their intensity and in their width, some being sharp and others diffuse or even broad.

The radiations (Raman lines) when observed in transversely scattered light are often strongly polarized. The degree of polarization varies much from one line to another; sharp lines which are completely polarized on the one hand and broad bands and unresolved continuum depolarized nearly completely (86%) on the other being extreme examples between which all other cases lie.

The continuous spectrum also shows great variations in intensity with different materials. It generally appears as wings extending unsymmetrically on either side of the parent line and showing limiting depolarization. In this case, it is most probably an unresolved and unquantised rotational effect. A continuous spectrum, having possibly a different origin, appears with very viscous liquids and sometimes may be so strong as to overpower all the other lines. A similar effect develops progressively in liquids which undergo chemical change on exposure to light.

In the case of free molecules scattering light, we encounter three different kinds of effect, an electronic effect, a rotational effect and a vibrational effect, the classification indicating the particular type of energy in the molecule which is added to or given up. The most common type of Raman scattering, encountered in matter of all states, is the vibrational effect and consists of lines or bands with moderate or large frequency shifts. In liquids generally, the rotation of molecules ceases to be quantised and owing to closeness of packing and large moments of inertia, unresolved wings in the neighbourhood of the parent line are frequently observed. Matters become even more complicated in the case of solids and these wings are replaced by broad bands, sometimes even sharp lines, indicating that we are there dealing with exchange of energy between the solid and the incident radiation involving specific quanta which we now know to correspond to oscillations of the crystal lattice. Lines which arise from a parent radiation on its lower frequency side as a result of the light quantum giving up some of its energy to the molecule ($h\nu + \text{molecule} \rightarrow \text{molecule}^* + h\nu^-$) are called Stokes Raman lines. Some of them, if strong enough, have their counterparts, called Anti-Stokes Raman lines, arising from the same parent radiation but appearing on its higher frequency side as a result of the light quantum getting more energy from the molecule which is already in an excited condition ($h\nu + \text{molecule}^* \rightarrow \text{molecule} + h\nu^+$).

The above features are so marked and so general that in the first few days or months of the discovery, they were all noticed and recorded. They are now regarded as the highlights of Raman effect which, every one who starts experimental work in the subject, seeks to reproduce and verify.

3. DEVELOPMENTS IN EXPERIMENTAL TECHNIQUE

During the early years, since it was necessary to study the Raman spectra of as many substances as possible, much attention was not paid to the development of powerful experimental technique. With comparatively less intense sources and moderately good spectrographs, satisfactory results were obtained. Liquids were the easiest to study. Certain special types of containers and arcs of special shapes (spirals and tubes) were developed in connection with the study of crystals and crystal powders but the real major advance was in connection with the study of the phenomenon in gases. The use of high pressure containers for gases and of the resonance λ 2537 of mercury from a cooled arc with a magnet to pull the discharge in the desired direction for illumination are noteworthy developments.

Very quickly, the need arose for more powerful methods by which to tackle substances available in very small quantities and also by which to

study with comparative ease, routine problems such as testing samples for the presence of specific constituents and so on. This resulted in a phenomenal development of both the source and the spectrograph. Arcs as well as lamps of the most varied designs have been employed and the trend was in the direction of using many high intensity (sometimes up to sixteen) mercury arcs arranged cylindrically round the container tube. In all such cases, since a large amount of energy is dissipated in the lamp, effective cooling is essential and now-a-days we have standardised sources of this type, specially intended for the study of Raman effect, manufactured by quite a few firms. With such sources and using reasonably powerful spectrographs, strong Raman lines in liquids can be readily seen with rested eyes and photographed with an exposure of a few seconds.

In many cases, investigators built their own spectrographs effecting an optimum compromise between the light gathering power and large dispersion, the two principal features required of such an instrument. The French school of physicists have pressed into service instruments with an aperture ratio as high as $F/0.7$ and some of the American workers used instruments which have a dispersion and resolving power sufficient to separate lines which are only 1 cm.^{-1} apart.

Special methods had also to be developed for obtaining the depolarization factors of Raman lines. Early investigations on this aspect have brought to light several interesting experimental points, which were hitherto overlooked. These relate to convergence errors, apparent polarization caused by the spectrograph and corrections that arise from the use of glass windows, photographic plates and the failure of reciprocity laws in photography, polarizers and so on. Some authors made the incident light perpendicular to the scattered beam, as nearly as feasible, by using narrow blackened grooves for collimating the light and others evaluated and applied corrections for convergence. If the horizontal and vertical components are photographed simultaneously, errors caused by variations in intensity and other related factors are eliminated. Errors introduced by the spectrograph have been eliminated in one investigation by using a nicol prism and a half-wave plate in front of its slit. For photographing the parallel component for illumination in a vertical plane, the axis of the Nicol is kept horizontal with that of the half-wave plate parallel thereto. In order to obtain the perpendicular component, the axis of the half-wave plate is rotated through 45° , thus rotating the electric vector of the light passing through it by 90° . Thus each component is photographed with the electric vector horizontally placed in both cases, thereby eliminating the losses due to reflection by the prisms of the spectrograph. Polaroids have also been

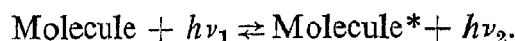
extensively used for this type of work. In one arrangement, the tube of liquid is wrapped with transparent polarizing material so that only light polarized with its electric vector parallel to the axis of the tube is allowed to illuminate the liquid. Four mercury arcs placed alongside the tube and round it furnished the illumination. Two exposures are made, one with all lamps lighted and the polaroid in place and the other with only some lamps lighted but the polaroid removed. This provides a rapid method of picking out the completely polarized lines as they will be greatly weakened in comparison with those that are depolarized. Polaroids have also come into fairly extensive use by investigators to suit their special requirements. Circularly polarized light has been employed by some authors for tackling special problems.

4. THEORY OF THE RAMAN EFFECT: GENERAL

A general theory of the Raman effect, based on quantum principles and the already known results of molecular physics, is now fairly well established. As has already been stated, the discovery of Raman effect, in its original form, consists in the appearance in the scattered light of new lines or bands and sometimes even continuous spectrum with changed frequencies, arising from one or other of the incident radiations when light falls on matter consisting of molecules. The state of aggregation of these molecules need not be confined to any particular type for the phenomenon to be exhibited, for the discoverer himself realised that solids—crystalline or amorphous; liquids and gases can all be made to scatter light and that the scattered light will contain new radiations characteristic of each case. It is, however, necessary that the interacting medium should consist of groups of atoms mutually linked by some sort of electronic forces as valencies in molecules and in other ways in solids but atoms alone in an isolated condition have not been known to exhibit the phenomenon. This is a feature which does not seem to have been clearly recognised and emphasised in the past by all the workers on Raman effect. There have been attempts to obtain and record an event which may ultimately be attributed to the exchange of energy between an atom and incident radiation in the way of Raman scattering but without success.² Raman effect thus may be regarded as elastic scattering of light by matter composed of groups of atoms joined together by molecular or other forces in any state of aggregation with attendant exchange of energy and a consequent frequency shift of the scattered light in relation to that of the incident light. It is a type of interaction between the nuclear-electronic

² The author of this article gave long exposures with Argon gas using mercury light in the ultra-violet for illumination, in the hope of recording some kind of Raman transitions in the visible region, but did not succeed.

system which we call the molecule in some cases and the lattice (crystalline, amorphous or quasi-crystalline) in others and incident radiation. All evidence is in favour of presuming that the grip for the radiation on the nuclear system is provided through the electron atmosphere when the incident radiation induces optical polarization in it. The differences between the wave number of the incident radiation and that of the scattered light are intimately connected with the energy states of the molecule or of the scattering system which may be a group of molecules if it is an extended solid. These energy differences, in the case of molecules, are mostly due to the different energy states (vibrational and rotational) and when studied, along with the results of infra-red absorption wherever necessary, furnish complete and most useful information about the molecules and their structures. In this picture, the scheme of exchange of energy is very simply depicted as



The exchange can take place in either direction. From left to right, the molecule is receiving energy and ν_2 the frequency of the Raman line will be less than ν_1 the frequency of the incident line. From right to left, the molecule is giving up surplus energy and ν_1 the frequency of the Raman line will be more than ν_2 the frequency of the incident line. In the former case, we get Stokes Raman lines and in the latter, we get anti-Stokes Raman lines.

In the fuller picture, the appearance or otherwise of a spectral line in Raman scattering resulting from a transition of the molecule from a vibrational state with the quantum number v_1 to that with the quantum number v_2 pertaining to the normal co-ordinate Q will depend upon the survival or the vanishing of the integral

$$\int a(Q) \psi_{v_1}^*(Q) \psi_{v_2}(Q) dQ,$$

where $a(Q)$ is the symmetric tensor relating to the polarizability of the molecule in the normal configuration Q . $a(Q)$ may be expanded as follows:

$$a(Q) = \alpha_0 + \left(\frac{\partial a}{\partial Q}\right)_0 Q + \frac{1}{2} \left(\frac{\partial^2 a}{\partial Q^2}\right)_0 Q^2 + \dots$$

and substituted in the integral. If the oscillations are simple harmonic, ψ_{v_1} and ψ_{v_2} are Hermite polynomials of degree v_1 and v_2 respectively and if we confine ourselves to $\Delta v = \pm 1$ and neglect higher powers, the portion of the integral involving α_0 vanishes on account of the orthogonality of the eigenfunctions, the intensity finally depending upon

$$\int \left(\frac{\partial a}{\partial Q}\right)_0 Q \psi_v(Q) \psi_{v+1}^*(Q) dQ.$$

If we substitute the actual values of the normalized eigenfunctions appropriate to a harmonic oscillator and simplify the above integral, we obtain the intensity as proportional to³

$$\frac{\alpha^2}{2} \left(\frac{\partial \alpha}{\partial Q} \right)_0^2 (v + 1).$$

Thus, a normal oscillation will give rise to a Raman line of finite intensity, only when there is a first order variation of the polarizability of the molecule with respect to the corresponding normal co-ordinate. In some cases, without going into the physical magnitude of such a variation, we may, by the application of certain tests, say whether the symmetry of the normal oscillation in question at all permits the existence of such a first order variation and if it does not, we conclude that the line is forbidden to appear as a fundamental in Raman scattering.

α , as has been mentioned above, is in fact a symmetric tensor and consists therefore of six components. The arguments outlined apply individually to each of these components and strictly speaking, a Raman transition between two vibrational levels v_1 and v_2 can have a finite intensity if the integral involving even one of these six quantities is different from zero.

Similarly, if a Raman line due to transition between two rotational levels is to have a finite intensity, we can see in a general way that $\left(\frac{\partial \alpha}{\partial Q} \right)_0$ should exist where Q is a normal co-ordinate corresponding to pure rotation. This term is obviously zero, if the molecule is optically spherically symmetrical, for rotations about all axes and such molecules cannot give rise to rotational Raman lines. In order that a molecule may give rise to rotational Raman lines, it should be optically anisotropic at least with reference to some one axis, the rotation about which will then cause a variation of the polarizability and the incident radiation can induce a Raman transition of the rotational type.

The above arguments are of a general nature and have to be carefully examined in greater detail, if we are to understand more fully the selection rules and the polarization phenomena. Further complications arise if a molecule is capable of going into more than one normal configuration in executing the dynamically permissible small oscillations about its equilibrium position. These aspects will be studied in the next section.

³ See S. Bhagavantam and T. Venkatarayudu, *Theory of Groups and Its Application to Physical Problems* (1951), for further details.

5. THEORY OF THE RAMAN EFFECT: VIBRATIONS OF POLYATOMIC MOLECULES

A molecule consisting of nuclei and electrons may be regarded as a system of particles, kept in equilibrium by certain forces. If we are dealing with nuclear oscillations, the presence of electrons, because of their relatively low mass, may be ignored to a first approximation, and the problem of studying its dynamics becomes simpler. A configuration in which this system of particles can remain permanently at rest is defined as an equilibrium configuration of the system. Suppose the system is initially displaced from such a stable equilibrium configuration but is still near it. The tendency is then to return to that position, which is one of lesser potential energy. Often, the particles in the system remain always in the neighbourhood of their respective equilibrium positions and never acquire large velocities or large amplitudes. Motions of this type are called vibrations about the equilibrium configuration with small amplitudes. If q_1, q_2, \dots, q_n are the co-ordinates necessary to specify a configuration, the kinetic energy of the system at any instant will be a homogeneous quadratic function of the time derivatives $\dot{q}_1, \dot{q}_2, \dots, \dot{q}_n$. Since T is always positive, it follows that it is a positive definite quadratic form in these time derivatives. If the equilibrium configuration is taken as the standard one and if the system is displaced from such a configuration to another described by q_1, q_2, \dots, q_n as above by a set of forces constituting a conservative force field, then work is done on the system and the potential energy acquired will be denoted by V , where V is a function of q_1, q_2, \dots, q_n . If we expand V in ascending powers of q_1, q_2, \dots, q_n , the term independent of the co-ordinates can be omitted as it does not enter the equations of motion which contain only the derivatives of V . There cannot be terms which are linear in the quantities q_1, q_2, \dots, q_n as $\frac{\partial V}{\partial q_r}$ should be equal to zero. Thus, only the second and higher degree terms in the potential energy function enter into the equations of motion.

If we choose q_1, q_2, \dots, q_n in such a way that they represent displacements or deviations from the equilibrium values of chosen parameters in respect of the molecular system, they are always necessarily small. In other words q_1, q_2, \dots, q_n may all be so chosen that they are individually zero in the standard or the equilibrium configuration. Since we are dealing with small oscillations about the equilibrium configuration, it follows that we need retain only the terms of the lowest order in the kinetic energy function T and replace the coefficients of the squares and products of q_1, q_2, \dots, q_n by the constant values which they assume when q_1, q_2, \dots, q_n are each put equal to zero. The kinetic energy is therefore a homogeneous quadratic

function of $\dot{q}_1, \dot{q}_2, \dots, \dot{q}_n$ with constant coefficients. Neglecting the higher terms in the potential energy expression also, V can be expressed as a homogeneous quadratic form in the co-ordinates q . The kinetic and potential energies of the system may thus be written generally as

$$T = \frac{1}{2} \sum a_{ij} \dot{q}_i \dot{q}_j; \quad i, j = 1, 2, \dots, n$$

$$V = \frac{1}{2} \sum b_{ij} q_i q_j; \quad i, j = 1, 2, \dots, n$$

n is the number of co-ordinates necessary and it will be so, if in this case the system has $\frac{n}{3}$ particles. These two expressions can be simultaneously reduced to canonical forms by a suitable choice of co-ordinates Q_1, Q_2, \dots, Q_n which are linear combinations of q 's giving

$$2T = \sum \dot{Q}_k^2; \quad 2V = \sum \lambda_k Q_k^2;$$

The Q 's are called the normal co-ordinates and each Q corresponds to a normal mode of oscillation. The λ 's in the latter expression can be shown to be the roots of the equation

$$\begin{vmatrix} b_{11} - \lambda a_{11} & b_{12} - \lambda a_{12} & \dots & b_{1n} - \lambda a_{1n} \\ \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots \\ b_{n1} - \lambda a_{n1} & b_{n2} - \lambda a_{n2} & \dots & b_{nn} - \lambda a_{nn} \end{vmatrix} = 0$$

The choice of q 's may be made in many ways. For instance if x_i, y_i, z_i are the Cartesian rectangular co-ordinates of the i th particle in the system chosen with reference to a set of co-ordinates whose origin is at the equilibrium position of the i th atom, then the set $x_1, y_1, z_1, \dots, x_{n/3}, y_{n/3}, z_{n/3}$ which will be n in number for $\frac{n}{3}$ particles may just as well be the q 's. In the equilibrium configuration, they will all be obviously zero. In the alternative, q 's may be suitable linear combinations of x, y, z 's and so on. The solution of the problem of normal oscillations in any one case is very much facilitated, if this determinantal equation can be factorized and it can be factorized in many cases.

Q 's thus obtained have special properties. When the kinetic and potential energies are put in terms of them, they assume the canonical form as already mentioned and we have

$$2T = \sum \dot{Q}_k^2; \quad 2V = \sum \lambda_k Q_k^2;$$

the Lagrangian equation of motion corresponding to any normal co-ordinate Q_r being written as

$$\frac{d}{dt} \left(\frac{\partial T}{\partial \dot{Q}_r} \right) - \frac{\partial T}{\partial Q_r} = - \frac{\partial V}{\partial Q_r}$$

which reduces to $\ddot{Q}_r = - \lambda_r Q_r$.

The important result follows that each normal co-ordinate corresponds to an independent mode of vibration of the system and this is called a normal mode. If the quantities $\lambda_1, \lambda_2, \dots, \lambda_n$ are positive, as is the case with a stable equilibrium configuration, they all represent the frequencies of various possible normal modes of oscillation about the equilibrium configuration. From the elementary laws of simple harmonic motion, we have

$$\lambda_r = 4\pi^2 \nu_r^2,$$

where ν_r is the frequency of Q_r . If the coefficient λ of any normal co-ordinate Q is distinct from other λ 's, the corresponding normal mode is said to be non-degenerate. On the other hand, if two or more Q 's have the same coefficient, the corresponding modes are said to be degenerate and the degree of degeneracy is equal to the number of Q 's which have the same frequency. In such a case, the choice of the particular Q 's is not unique.

In order to obtain the normal modes and frequencies in an actual case, we have to first set up the general quadratic forms of the potential and kinetic energies and find out suitable combinations of the variables so that the potential and kinetic energies expressed in terms of the altered variables may not contain cross terms. When the number of particles in a system is small, the above procedure may conveniently be followed. The method, however, becomes increasingly complicated with increasing number of particles in a dynamical system. One of the major developments in this branch, stimulated by the discovery of the Raman effect and its application to the study of normal vibrations of a large variety of molecular systems, has been the pressing into service of a new and powerful mathematic tool, namely, the Theory of Groups. Group theoretical methods, developed during the past decade or two, have greatly simplified the work and have yielded remarkable results. We shall now deal with them in some detail.

The symmetry properties of molecules permit the factorization of the determinantal equation relating to the normal oscillations and the methods of group theory have been very successfully applied for a study of these symmetry properties. Wigner,⁴ Placzek and Teller⁵ and Tisza⁶ had done

⁴ *Göttingen Nachrichten*, 1930, 133.

⁵ *Zeit. f. Phys.*, 1930, **81**, 209.

⁶ *Ibid.*, 1933, **82**, 48.

pioneering work in this field. Several other authors applied these methods in great detail. Molecules, if regarded as composed of nuclei alone, are systems of points and as such exhibit elements of symmetry. Rotational axes, reflection planes and their combinations are such elements of symmetry and these are called covering operations. They constitute, when enumerated fully, a point group which will be characteristic of the symmetry of the molecule. Each such element can be made to correspond to an analytical expression or a transformation matrix and the group of matrices arising from the group of covering operations is called a matrix representation thereof.

Let Q_1, Q_2, \dots, Q_p be a set of normal co-ordinates of a dynamical system. We consider a configuration in which all the normal co-ordinates, except one say Q_r with frequency ν_r , vanish. If we now perform a symmetry operation R of the point group appropriate to the molecule, we obtain a new configuration which we represent by the symbol RQ_r . Since a symmetry operation is such that the distance between any two points of the system remains unaltered, the configuration RQ_r has the same potential energy as Q_r , provided the potential energy remains invariant whenever the mutual distances between all points of the body remain unaltered. This is, of course, true if we make our original assumptions regarding the function V suitably. But RQ_r is not a normal co-ordinate of the original system as the individual particles are no longer in the neighbourhood of their respective equilibrium positions. In fact, the motion described in RQ_r is such that a particle leaves the neighbourhood of its equilibrium position and goes over into the neighbourhood of the equilibrium position of one of its equivalents. We can, however, derive from the configuration RQ_r , a geometrically identical configuration $\bar{R}Q_r$ in the following way. If by means of the operation R , the l th particle goes over to the k th particle, we shall suppose that the k th particle remains in its own neighbourhood but gets the motion of the l th particle. By applying this process to all particles, we keep them in their original neighbourhoods and this ensures the invariance of the kinetic energy. The new configuration thus obtained, namely, $\bar{R}Q_r$, has the same potential and kinetic energies as Q_r and therefore represents a normal co-ordinate having the same frequency ν_r as that of Q_r . It is either identical with Q_r or is distinct from Q_r but degenerate with Q_r . Adopting this procedure for all the symmetry operations of the point group appropriate to the system, we obtain the several normal co-ordinates $\bar{R}Q_r$ which have the same frequency ν_r . If Q_1, Q_2, \dots, Q_p is a complete set of linearly independent normal co-ordinates chosen from the whole lot $\bar{R}Q_r$, then the oscillation in question, with a frequency ν_r is said to be f -fold degenerate. Similarly, we

take another normal co-ordinate of frequency ν_s and as before obtain a set of linearly independent normal co-ordinates. Proceeding thus, we divide all the normal co-ordinates of the system into linearly independent sets, each set containing one or more normal co-ordinates but of the same frequency only.

In the language of group theory, the above process is to be described as one of separating the manifold of normal oscillations into irreducible sub-manifolds. Each irreducible sub-manifold may be associated with an irreducible representation of the group of symmetry operations. In the reducible representation Γ defined by all the normal co-ordinates, every symmetry operation R corresponds to an \bar{R} as defined above and every \bar{R} corresponds to an appropriate matrix made up of transformation matrices corresponding to the irreducible sub-manifolds f, s and so on arranged diagonally. This constitutes a representation defined by the normal co-ordinates. In this representation, the sum of all the diagonal elements in the matrix corresponding to a given R will be called the character of the operation R .

On the other hand, if we take any set of three mutually perpendicular axes X, Y, Z and through the equilibrium position of each particle in the given system, choose three axes parallel to the X, Y, Z system and if x_r, y_r, z_r are the co-ordinates of the r th particle in its displaced position with reference to the axes through its equilibrium position, we can describe any configuration Q_r in terms of x 's as well. In fact all the Q 's can be expressed as linear functions of x 's and the relation between the two sets of co-ordinates may be given by a transformation matrix in the form

$$\begin{pmatrix} Q_1 \\ Q_2 \\ \vdots \\ Q_n \end{pmatrix} = [T] \begin{pmatrix} x_1 \\ y_1 \\ \vdots \\ z_{n/3} \end{pmatrix}$$

where T is a matrix of n rows and n columns. While Q 's define a representation Γ of the point group, the x 's define an equivalent representation Γ' of the point group because every matrix in the representation Γ will only have to be transformed by T to give rise to the corresponding matrix in the representation Γ' . For this reason, the character of any operation R in the two representations Γ and Γ' is the same.⁷ It is easy to calculate the

⁷ For a proof of this statement and for a fuller amplification of these ideas, see S. Bhagavantam and T. Venkatarayudu, *Theory of Groups and Its Application to Physical Problems* (1951).

character of an operation R in the reducible representation defined by the co-ordinates x_1, y_1, \dots etc. If the symmetry operation R takes over the particle 1 into the position of particle k , we have in general a relation of the type

$$Rx_k = ax_l + by_l + cz_l$$

and the character arising from x_k is zero. Similarly the characters arising from y_k and from z_k are zero. If, on the other hand, the k th particle is invariant under the operation R , we have

$$Rx_k = x_k \cos \phi - y_k \sin \phi$$

$$Ry_k = x_k \sin \phi + y_k \cos \phi$$

$$Rz_k = \pm z_k,$$

the $+$ or $-$ sign in the last relation being used according as R is a pure rotation or a rotation-reflection through ϕ . In the above equations, the axis of rotation is taken as the Z axis itself and the X and Y axes lie in a plane perpendicular to it. This choice of axes may not coincide with that taken in the beginning but it will not affect the character arising from a given R . It, therefore, follows that $1 + 2 \cos \phi$ and $-1 + 2 \cos \phi$ are the characters for a pure rotation and a rotation-reflection respectively. We thus arrive at the result that an invariant point under the operation R gives rise to the character $\pm 1 + 2 \cos \phi$ whereas points which are not invariant do not contribute anything to the character. Hence in the reducible representation Γ' defined by the Cartesian co-ordinates, the character of any operation R is $U_R (\pm 1 + 2 \cos \phi)$, where U_R is the number of particles that remain in their original position when R is performed.

It has already been pointed out that the representations defined by the normal co-ordinates and the Cartesian co-ordinates are equivalent. The character of an operation R is therefore the same in the two representations. In the previous paragraph we obtained the character of an operation R in the representation defined by the Cartesian co-ordinates. The same expression, namely, $U_R (\pm 1 + 2 \cos \phi)$, should therefore be equal to the character of the operation R in the representation Γ defined by the normal co-ordinates Q_1, Q_2, \dots, Q_n . We have seen that the normal co-ordinates can be divided into sets of irreducible manifolds and each set corresponds to an irreducible representation Γ_i . If there are n_i such sets that belong to a particular irreducible representation Γ_i , it follows that n_i is the number of times the representation Γ_i is contained in the representation Γ . To obtain the number n_i we use the formula

$$n_i = \frac{1}{N} \sum h_\rho \chi_\rho' (R) \chi_i (R),$$

where N is the order of the point group G . $\chi_{\rho'}(\mathbf{R})$ is the compound character and stands for the expression $U_{\mathbf{R}}(\pm 1 + 2 \cos \phi)$ and $\chi_i(\mathbf{R})$ is the character of the operation \mathbf{R} in the i th irreducible representation of the group G .

The number derived in this manner includes the normal co-ordinates relating to translations and rotations of the point system as a whole. We can, however, exclude them by removing from $\chi_{\rho'}(\mathbf{R})$ the character arising from translations and rotations. Considering first translations, we note that the n vectors giving the displacements of the particles in a translation are equivalent to a single vector. The unit vectors X, Y, Z relating to the three translations transform under \mathbf{R} as

$$\begin{aligned} \mathbf{R}X &= X \cos \phi - Y \sin \phi \\ \mathbf{R}Y &= X \sin \phi + Y \cos \phi \\ \mathbf{R}Z &= \pm Z, \end{aligned}$$

the $+$ or $-$ sign in the last relation being used according as \mathbf{R} is a pure rotation or a rotation-reflection. Hence the character arising from the normal co-ordinates corresponding to translations is $\pm 1 + 2 \cos \phi$.

Next, let the displacements of the n particles be such that they represent a rotation of the system as a whole. This state may be expressed by means of the displacement l of a point with the co-ordinates x, y, z . The three components of l are

$$l_x = y\delta z - z\delta y; \quad l_y = z\delta x - x\delta z; \quad l_z = x\delta y - y\delta x;$$

if $\delta x, \delta y, \delta z$ are the components of the rotation vector. l transforms under a rotation through ϕ around the Z axis to l' where

$$\begin{aligned} l_x' &= l_x \cos \phi + l_y \sin \phi \\ l_y' &= -l_x \sin \phi + l_y \cos \phi \\ l_z' &= l_z. \end{aligned}$$

If the operation is a rotation-reflection through ϕ , the transformation will be

$$\begin{aligned} l_x' &= -l_x \cos \phi - l_y \sin \phi \\ l_y' &= l_x \sin \phi - l_y \cos \phi \\ l_z' &= l_z. \end{aligned}$$

Thus the character arising from a pure rotation is $1 + 2 \cos \phi$ and from a rotation-reflection is $1 - 2 \cos \phi$. Finally from the formula

$$n_i = \frac{1}{N} \sum h_{\rho} \chi_{\rho'}(\mathbf{R}) \chi_i(\mathbf{R}),$$

we obtain (1) the number of normal modes coming under Γ_i including translations and rotations, (2) the number of translations only, (3) the number of rotations only, (4) the number of normal modes excluding the translations and rotations if we use respectively for $\chi_p'(R)$ the four expressions

$$(1) \chi_p'(R) = U_R (\pm 1 + 2 \cos \phi)$$

$$(2) \chi_p'(R) = \pm 1 + 2 \cos \phi$$

$$(3) \chi_p'(R) = 1 \pm 2 \cos \phi$$

$$(4) \chi_p'(R) = (U_R - 2) (1 + 2 \cos \phi) \text{ or } U_R (-1 + 2 \cos \phi).$$

In the last case, the first alternative corresponds to a pure rotation and the second to a rotation-reflection.

These are most useful formulæ and have enabled the subject of vibrational Raman effect to be studied with great ease in many molecular systems. As has been shown by several authors, by the application of these methods, a considerable amount of useful information can be obtained, not only about how the determinantal equation relating to normal oscillations will factorize on account of the symmetry of the molecule but also about the selection rules and polarization characters of these oscillations as and when they are observed in either Raman effect or infra-red absorption.

6. RAMAN EFFECT AND CHEMICAL PROBLEMS

Apart from very extensive application to a study of molecular structure and chemical constitution, Raman effect has touched numerous other problems of chemistry and in fact to-day its pursuit has very much shifted from the hands of physicists to chemists and physical chemists. Hindered rotation, hydrogen bonding, study of chemical reactions, isotopic substitution, chemical analysis and identification of certain types of compounds are only a few of the recent developments.

In the study of molecular structure, the formulation of interatomic forces has been an important line of speculation and different types of forces have been tried from time to time. One of the principal assumptions has been that only central forces act between the atoms in a molecule, that is the force acting on a given atom in a molecule is the resultant of the attractions and repulsions by all the other atoms. These forces depend only on the distances between various atoms and lie along the lines connecting them. Consequently, the potential energy will be purely a quadratic function of the changes of the distances between the nuclei without any cross products. As an example, we may consider the pyramidal structures of the type XY_3 , represented by the tetratomic molecules like ammonia and the trichlorides

of P, As, Sb, Bi, etc. This structure possesses the symmetry elements appropriate to the point group C_{3v} and the Character Table and other necessary data for such molecules are given, as follows, in the usual notation.

Normal Modes of PCl_3 , etc.

C_{3v}	E	$2C_3$	3σ	ν_i	ν_i'	Raman	Infra-red
A_1 ..	1	1	1	3	2	P	A
A_2 ..	1	1	-1	1	0	f	f
E ..	2	-1	0	4	2	D	A
U_R ..	4	1	2				
$h\rho X_{\rho'}$..	12	0	6				
$h\rho \psi_{\rho'}$..	6	0	6				
$2 \cos \phi (\pm 1 + 2 \cos \phi)$..	6	0	2				
$\pm 1 + 2 \cos \phi$..	3	0	1				

There are two non-degenerate vibrations (ν_1 and ν_2) under the class A_1 , both active in Raman effect as well as infra-red absorption and two doubly degenerate vibrations (ν_3 and ν_4) under the class E, again both of which are active in Raman effect as well as infra-red absorption. The six degrees of freedom, excluding rotations and translations, are thus accounted for and if we designate the mass of the atom at the apex by M and that of each of the atoms at the base by m, we can obtain

$$\lambda_1 + \lambda_2 = \left(\frac{1}{m} + \frac{3}{M} \cos^2 \beta \right) K_1 + \frac{3K_2}{m} \quad (1)$$

$$\lambda_1 \lambda_2 = \frac{3}{m} \left(\frac{3m + M}{mM} \right) \cos^2 \beta K_1 K_2 \quad (2)$$

$$\lambda_3 + \lambda_4 = \left(\frac{1}{m} + \frac{3}{2M} \sin^2 \beta \right) K_1 + \frac{3K_2}{2m} \quad (3)$$

$$\lambda_3 \lambda_4 = \frac{3}{4m} \left(\frac{2 - \sin^2 \beta}{m} + \frac{3}{M} \sin^2 \beta \right) K_1 K_2 \quad (4)$$

The connection between λ and ν has already been explained. In the above expressions, K_1 and K_2 are force constants arising from the variation of distances between the apex and each of the base atoms and between the base atoms themselves respectively. β is the angle between one of the edges of

the pyramid and the axis of symmetry. These expressions were first obtained by Dennison and have since been derived by slightly varying methods by several authors.⁸ Validity of the assumption of central forces can be checked as, in many such molecules, all the four frequencies have been measured. The angle β may be obtained from the observed frequencies, for by dividing (4) by (2), we have

$$\cos^2 \beta = \frac{1}{4 \frac{\nu_3^2 \nu_4^2}{\nu_1^2 \nu_2^2} + \frac{3m - M}{3m + M}} \quad (5)$$

The following table, taken from Herzberg's book, is very instructive.

Fundamental Frequencies, Force Constants and Angles for the Pyramidal Molecules XY_3 , Assuming Central Forces

Molecule	Observed frequencies (cm. ⁻¹)				β observed	β calculated	Force constants from ν_3, ν_4, β observed, and equations (3) and (4)		Frequencies ν_1 and ν_2 from k_1, k_2, β observed, and equations (1) and (2)	
	ν_1	ν_2	ν_3	ν_4			k_1	k_2	ν_1	ν_2
NH ₃	3337	950	3414	1628	69°	73°	3.89	2.83	4473	859
ND ₃	2419	749	2555	1191	69°	72°	5.05	2.29	3133	679
PH ₃	2327	991	2421	1121	62°	63°	2.57	1.04	2991	784
PD ₃	1694	730	..	806	62°
PF ₃	890	531	840	486	62°	56°	3.58	2.93	1045	380
PCl ₃	510	257	480	190	64°	51°	1.94	0.63	459	184
PBr ₃	380	162	400	116	65°	55°	1.79	0.47	203	203
AsF ₃	707	341	644	274	60°	45°	3.23	0.88	723	240
AsCl ₃	410	193	370	159	59°	50°	1.73	0.51	404	154
SbCl ₃	360	165	320	134	57°	45°	1.49	0.38	357	130
BiCl ₃	288	130	242	96	57°	25°	0.94	0.20	270	90

The agreement between β observed and β calculated and ν_1 and ν_2 observed and ν_1 and ν_2 calculated is "fair in most cases although a few big

⁸ See G. Herzberg, *Infra-Red and Raman Spectra of Polyatomic Molecules* (1945). This form and the subsequent data have been taken from this book.

discrepancies occur". This is an illustration of the extent to which central forces generally agree with the facts of observation.

It is interesting to specialise the equations (1) to (4) by putting $\beta = \sin^{-1} 1/\sqrt{3}$; $m = M$ and $K_1 = K_2$ when they will become applicable to tetrahedral molecules like P_4 , studied by the author of the present article soon after the discovery of the Raman effect.⁹ The results are given below:

$$\lambda_1 = \frac{4K_1}{m}; \quad \lambda_2 = \lambda_3 = \frac{2K_1}{m}; \quad \lambda_4 = \frac{K_1}{m}.$$

They show that there should be three frequencies in the ratio of $2 : \sqrt{2} : 1$. Actually three frequencies at about 606, 465 and 363 cm.^{-1} have been observed with P_4 . There is a slight but significant departure between the expected ratio and the ratio of the observed frequencies, again indicating the inadequacy in detail but the adequacy in approximation of the picture furnished by the so-called central forces.

The next assumption widely employed in the literature is closer to the chemist's view of interatomic binding and is called the valence force system. In this system, a strong restoring force in the line of every valence bond is assumed whenever the distance between any two atoms bound by such a bond is changed. In addition, a restoring force opposing a change of the angle between two valence bonds connecting any one atom with two others is assumed. Non-linear symmetric triatomic molecules like H_2O are excellent examples of such studies. The expressions appropriate to the three normal frequencies, all of which are active in infra-red and Raman effect, are¹⁰

$$\lambda_1 + \lambda_2 = \frac{K_1}{m} \left(1 + \frac{2m}{M} \cos^2 \alpha \right) + \frac{2K_3}{m} \left(1 + \frac{2m}{M} \sin^2 \alpha \right)$$

$$\lambda_1 \lambda_2 = \frac{4K_1 K_3}{m} \left(\frac{1}{M} + \frac{1}{2m} \right)$$

$$\lambda_3 = \left(\frac{1}{m} + \frac{2 \sin^2 \alpha}{M} \right) K_1$$

K_1 is the force in respect of the stretching of the valency bond and K_3 is the resistance to the change of angle between the two valency bonds meeting at the central atom. M is the mass of the central atom, in this case O and m that of each of the outer ones, in this case H and α is the semi-angle between the valency bonds. Investigations of the above expressions by Penney and

⁹ *Ind. J. Phys.*, 1930, 5, 35.

¹⁰ See S. Bhagavantam and T. Venkatarayudu, *Theory of Groups and Its Application to Physical Problems* (1951).

Sutherland and a few others with reference to actual data have shown that in this type of molecules, the valence force field is much superior to the central field.

In the case of phosphorus, the present writer has obtained fuller expressions involving valence forces and in the notation of this article, the frequencies work out as

$$\lambda_1 = \frac{4K_1}{m}; \quad \lambda_2 = \lambda_3 = \frac{1}{m} \left[2K_1 + \frac{8K_2}{R^2} \right];$$
$$\lambda_4 = \frac{1}{m} \left[K_1 + \frac{6K_2}{R^2} \right].$$

R is the length of each valence bond and m is the mass of the phosphorus atom. Since two constants are involved in these three measurable frequencies, this set gives again a much better representation of facts.

It has often been found that neither the central force system nor the valence force system nor even a combination of both is able to account fully for the observed frequencies. More general force fields, in some cases approaching the most general one possible, have been tried and we shall not go into them now. One of the more interesting results, from the point of view of a chemist, is that the stretching and bending force constants for various bonds and bond angles are nearly invariant in different molecules. On the other hand, the fact that the stretching force constants for the $C \equiv C$, $C = C$ and $C - C$ links are approximately 15 , 10 and 5×10^5 dynes/cm. is noteworthy. The appearance of frequencies characteristic of specific groups or linkages has been of great help to the chemist in the analysis of the observed vibrational spectra particularly of organic molecules and complex structures.

Formation of molecular aggregates, either as regular polymers or by loose association such as hydrogen bonding and so on, has been extensively studied. Individual examples are many and all of them cannot be referred to here. The polymeric form of SO_3 at lower temperatures and its breaking up at higher temperatures is one of the earliest cases to be studied under this category. Water molecules and their associated forms in the liquid and solid states were the subject of investigation and discussion by a number of investigators. Cleveland¹¹ and co-workers have worked out a method, with the help of Raman spectra, of following the transition of the aldol-aldehyde mixture to the trimer of isobutyraldehyde. The breaking up of dimers and polymers by the addition of water in several acids, alcohols and so on has also been studied, mostly in a qualitative manner.

¹¹ *Jour. Amer. Chem. Soc.*, 1943, 65, 1714.

The C = O frequency has played a great part in enabling the Raman spectroscopists to study the phenomenon of hydrogen bonding. In carboxylic acids, there is a considerable shift of this frequency towards the lower side indicating the formation of dimers through this link. This frequency in a substance like acetone is considerably reduced when studied in the presence of water molecules, presumably as a result of hydrogen bonding between the donor group C = O and the acceptor group O - H. The C = O bond is pictured as delivering the necessary charge to maintain the hydrogen bond O...H resulting in a redistribution of the electron binding around the double bond and a consequent weakening of this bond. The corresponding C = O frequency is lowered appreciably. Such a phenomenon does not take place in neutral solvents like CCl₄.

Chemists have recognized for many years, the existence of stereo-isomers arising out of some kind of restricted rotation around a carbon-carbon double bond but always believed that free rotation existed about a carbon-carbon single bond. This means that compounds like CH₃-CH₃ and CH₂Cl-CH₂Cl can only occur in one form. In the past few years, considerable evidence based on Raman spectroscopy and thermal and electric measurements has been accumulated to indicate that the principle of free rotation is not correct and that in general there are distinct potential minima in one complete rotation about a single bond. Contribution of Raman effect studies to this branch of chemistry has been considerable and the most noteworthy results have been obtained by Langseth and Bernstein, Glockler and Sage and Mizushima and co-workers.¹² By studying the Raman spectra of some 1, 2-dihaloethanes in the liquid and solid states, they have shown that for many of them, there is only one potential minimum in one complete rotation about a carbon-carbon single bond as axis and the molecules generally assume what may be called the transform. Further, by comparing the Raman effect data with infra-red measurements, it has been shown that most of the lines observed only in the liquid state should be taken as arising from the vibrations of a second configuration becoming stable in the liquid besides the transform. The energy difference between these isomers is small but definite.

Similarly in ethane, recent investigations have established the existence of hindered rotation about the carbon-carbon bond, the potential restricting the internal rotation being about 2750 calories. This corresponds to a torsional frequency of one methyl group against the other of 275 cm.⁻¹ for

¹² An excellent summary is given by Mizushima in his Peter C. Reilly Lectures in Chemistry at the University of Notre Dame.

C_2H_6 and 200 cm.^{-1} for C_2D_6 . Using the Raman and infra-red data, calculations have been made¹³ of the entropy of methyl mercaptan (CH_3SH) and the results are shown to lead to the formulation of a potential of 1,460 calories per mole hindering the free rotation of the methyl group relative to the SH bond.

Structures of several interesting compounds like cyclohexane, cyclopropane, sulphur and so on have been fully discussed and in many cases established beyond all doubt.

Deuterium substitution has furnished a whole branch of organic chemistry for the study of isotope effects in relation to Raman scattering. A detailed study of the results obtained with H_2 , HD and D_2 in the gaseous state and of the results obtained with H_2O , HDO and D_2O in the liquid state has been of great utility in the realm of simpler molecules. Similarly, a study of benzene and deuterated benzenes has been of help in solving the problem of the structure of benzene in a most satisfactory manner. Many other fully deuterated or partly deuterated organic compounds have been studied with much success. Isotopes of carbon and chlorine are amongst the other elements which have played a part in the Raman spectra investigations.

Amongst the studies directed towards analysis and identification, particular mention should be made of the detection of specific hydrocarbons in samples of petroleum. Several authors have developed rapid and easy methods for such purposes. The octane number of aviation fuel and its relation to anti-knock properties has attracted the attention of Raman spectroscopists and the statement, first given by Bonino, namely, "The square root of the sum of the squares of the intensities of all Raman lines between 600 and $1,000\text{ cm.}^{-1}$ increases with the octane number of the fuel" is of considerable interest and shows the potentialities of this tool of research.

7. RAMAN EFFECT AND SOLID STATE

There are certain outstanding features regarding the Raman spectra of solids. They are (a) there is a general correspondence between the vibrational lines observed in the Raman spectrum of a solid and in that of the corresponding liquid, (b) in no case has quantised rotation been detected in solids but many of them show low frequency lines which may be explained as arising from oscillations of the lattice about the equilibrium configuration, (c) such lines are often replaced by continuous and unresolved wings in the Raman spectra of the corresponding melts, (d) the Raman lines

¹³ G. Glockler, *Rev. Mod. Phys.*, 1943, 15, 111.

observed in most solids, with probably the exception of the amorphous ones, are quite sharp and small in number, and (e) in ionic substances like NaCl, the effect is recorded only with great difficulty and that too in the second order.

The author of the present article has shown that much useful information may be gathered by studying the Bravais cell of the smallest size in a crystal as if it were a point group and treating it like a molecule with the appropriate symmetry. It is assumed that what is true of one Bravais cell is true of all cells both statically and dynamically. If the non-equivalent points in the Bravais cell can be divided into groups such that the forces between one group and the other are comparatively feeble, whereas the forces that exist between the members of any one group are quite strong, then it can be shown that the oscillation spectrum will consist of lines divided in a clear-cut manner into low frequency ones and high frequency ones. The low frequency ones are called external oscillations and they involve the movement of whole groups as such against each other. The high frequency ones are called internal oscillations and they involve the movement of individual points within a group against each other. Such studies have been extremely useful in throwing light on interatomic forces in different types of crystals and in quite a few cases, have helped the elucidation and extension of the existing knowledge.

A number of Indian and French workers studied the behaviour of Raman lines observed in different directions with incident polarized light and crystals oriented differently. The intensities of many of the Raman lines change considerably with changing orientations of the crystal axes with reference to the directions of incidence and observation. Such investigations are intimately connected with the interior structure of crystals and yield valuable information. For instance, Aynard¹⁴ studied the orientation of water molecules in gypsum. The Indian workers¹⁵ have studied calcite, sodium nitrate, gypsum, naphthalene and a few other substances by this method in great detail.

Diamond has been very extensively studied, in fact more fully than perhaps any other solid. It shows a sharp and intense line with a frequency shift of 1333.8 cm.^{-1} at -180° C. , 1332.1 cm.^{-1} at the room temperature and 1316.4 cm.^{-1} at 860° C. This line stands out most prominently in relation to the other feebler lines that have been recorded. Owing to the importance of this case, amongst others, R. S. Krishnan by using specially

¹⁴ *Compter Rendus*, 1940, 211, 647.

¹⁵ See papers by J. M. K. Nedungadi and by S. Bhagavantam in *Proc. Ind. Acad. Sci.*, 1939-42.

developed technique, has recorded its second order Raman spectrum and some very faint lines show up in his work. The frequency shifts observed by him are specific in number and are all explained as overtones or combinations of the eight fundamental frequencies, attributed to the diamond structure, a result which comes out of the ideas developed by Professor Raman in respect of crystal dynamics. The numerical values of these fundamental frequencies have been calculated by K. G. Ramanathan as 1332, 1250, 1232, 1149, 1088, 1008, 752 and 620 by making certain assumptions regarding the interatomic forces. The highest frequency 1332 is triply degenerate and is the only mode which is active in Raman effect. All other frequencies, which are also degenerate to different degrees, are inactive as fundamentals in Raman effect but may appear as overtones or combinations with varying intensities. In a series of papers in the *Proceedings of the Indian Academy of Sciences*, workers from the Bangalore school have tried to reconcile the experimental observations in all their details with the calculations of K. G. Ramanathan based on new ideas put forward by Professor Raman.

Such experiments have been extended to many other crystals as well and the fact that they furnish a spectroscopic method of directly obtaining information about the normal frequencies of a crystal lattice has in a way given a fresh impetus to the whole subject of crystal dynamics. Born was the first to develop a theory of crystal oscillations. He showed that the normal oscillations of an infinitely extending chain of atoms with harmonic binding between adjacent ones, fall into two distinct classes, which have been named the acoustical and the optical, the distinction arising from the fact that the sign of the displacement is the same for the neighbouring atoms in the acoustic case whereas it is different in the optical one. The frequencies are spread continuously over wide ranges, the actual distribution depending upon the masses and the forces. Born extended these arguments to infinitely extending three-dimensional crystal lattices and showed that similar results may be obtained for such cases as well. In contradiction to this result, Raman concludes that "in the normal modes of vibration of the structure of a crystal, equivalent atoms in adjacent cells have the same amplitude of vibration, while their phases are either the same or else opposite in successive cells of the lattice along each of its three axes". This gives $2 \times 2 \times 2$ or 8 distinct situations regarding the relative phases of the vibrations in a unit cell and in those surrounding it. If there are p atoms in the unit cell, there will be $3p$ variables and $24p$ solutions representing normal modes. Three of these are simple translations. $24p - 3$ solutions remain out of which $3p - 3$ will be such that in them, what is true of the phase in the chosen unit cell

will be true of the phase in all the other unit cells, whereas the remaining $21p$ are such that in them, the phases of vibration are opposite in adjacent cells along one, two or all three of the axes of the lattice. Symmetry of the crystal may result in some of these normal modes having identical frequencies owing to degeneracy.

The fact that the frequency shifts exhibited by crystals are in general sharply defined lines and are relatively few in number is explained by associating them with one or more of the $3p - 3$ primary oscillations. The remaining $21p$ modes are inactive in Raman effect but may appear as overtones and combinations in the second order as feeble lines, which is actually the case with many crystals.

Apart from stimulating the above new ideas regarding solid state, the discovery itself has proved a powerful experimental tool for collecting data regarding the spectra of many crystalline substances under varying physical conditions of temperature, orientation, polymorphic modification and so on.

8. RAMAN EFFECT AS A BRANCH OF SPECTROSCOPY

It was realised, almost immediately after the discovery, that practically all the data that were till then obtained by studying the near and far infra-red absorption spectra of molecules could be collected, in many cases with greater facility, by studying the Raman spectra. This becomes possible because the frequency shifts arise, as has already been explained, by transfer of rotational and vibrational energies between radiation and molecules and in that form they may be studied in the visible region of the spectrum. In quite a few cases, it was later realised that the selection rules operate in such a way, where the molecule possesses a centre of symmetry for instance, that the Raman frequencies and the infra-red frequencies are mutually exclusive so that studies in Raman effect serve as complementary to studies in infra-red. All this has meant the opening up of a new branch altogether of molecular spectroscopy and several laboratories have been devoting themselves to the collection of data regarding complicated organic molecules.

Besides this, a few aspects of interest to the physical spectroscopist have also lent themselves for study. For instance, the phenomenon of alternating intensities in the rotational Raman spectra, has been of great help in supplementing the conclusions reached regarding nuclear statistics, specific heats and molecular constants in simple molecules like hydrogen, deuterium, nitrogen, oxygen and so on. It may be shown¹⁶ that the ratio of the statis-

¹⁶ See Bhagavantam and Venkatarayudu, *Theory of Groups and Its Application to Physical Problems* (1951).

tical weights of the symmetric and anti-symmetric rotational levels is $\frac{I+1}{I}$ or $\frac{I}{I+1}$, depending on whether the nuclei follow Bose-Einstein or Fermi-Dirac statistics. I is the nuclear spin moment in Bohr units. Some of the important results obtained are that hydrogen nuclei obey Fermi-Dirac statistics with nuclear spins $\frac{1}{2}$; deuterium, nitrogen and oxygen nuclei obey Bose-Einstein statistics with nuclear spins one, one and zero respectively.

All diatomic molecules and all linear symmetrical polyatomic molecules exhibit a rotational Raman spectrum because of their optical anisotropy and the selection rule in such cases is $\Delta J = 0, \pm 2$.

Amongst the polyatomic molecules of the symmetrical type, CO_2 and C_2H_2 have been studied. In the case of CO_2 , all lines with odd J are missing just as in O_2 and in the case of C_2H_2 , all lines with even J are weak as in H_2 . These results are to be expected.

The absence of a rotational Raman spectrum for CH_4 has been used to conclude that CH_4 has tetrahedral symmetry with a point group T_d .

A line corresponding to a frequency shift of 121 cm.^{-1} has been recorded by Rasetti in the Raman spectrum of nitric oxide gas and this has been assigned to an electronic transition ${}^2P_{\frac{1}{2}} \rightarrow {}^2P_{3/2}$. Besides this, some electronic transitions have been reported in the Raman spectra of a few solutions of rare earth salts but they remain unconfirmed.

Amongst the other spectroscopically interesting phenomena observed and studied, mention may be made of (a) the Fermi resonance effect which consists in the splitting of a line, if its frequency is close to an overtone or combination of the appropriate type as in carbon dioxide, carbon tetrachloride and so on, (b) the Tunnel effect resulting in two lines in the place of one as in the case of ammonia where owing to two possible equilibrium positions of the nitrogen atom in relation to the plane of the three hydrogens, there can be two potential minima in the energy curve relating to the fundamental vibration, (c) appearance of overtone lines or second order Raman scattering in some cases, (d) splitting of degenerate frequencies when symmetrical groups of atoms go into building up of crystals with lower symmetry as with SO_4 group in gypsum and in anhydrite and (e) the verification of Teller-Redlich product rules in the spectra of isotopic molecules.

Thus, Raman spectroscopy to-day is a specialised branch and every spectroscopic laboratory makes provision for its study as an important tool of research,

9. CONCLUSION

In the foregoing pages, a very brief summary is given of the main trends in Raman effect studies since their inception by Professor Raman in 1928 to date. No attempt has been made to either give exhaustive references or treat any particular aspect in a complete manner because such an attempt would have immediately resulted in each section growing into a large volume by itself. There have appeared several monographs and a few good books dealing with the subject and this article is not intended to replace any of them in part or in whole. On the other hand, the author has tried to indicate in appropriate places the extent of the influence which the workers in Raman effect have been able to exert on different branches of modern physics and chemistry and also draw attention to the lines along which new work has been stimulated by this discovery. Solution of many chemical problems is an example of the former and the application of group theoretical methods to molecular oscillations is an example of the latter. There is still very sustained interest and twenty-five years of research on the subject has created for it a prominent place in the field of modern physics and of modern chemistry as an investigational tool of great power.