RAMAN SPECTRA OF INORGANIC COMPOUNDS

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Introduction

Description of Raman Effect.—In 1928 Raman announced [1] his discovery of the molecular light-scattering effect which is now known by his name. Since then it has established itself as one of the recognised methods for the detection of molecular species and the investigation of their structure. When a beam of light traverses a transparent medium free from dust particles and the like, the frequency being chosen so as not to lie in an absorption region, most of the light passes through unaffected ; but (as was known before Raman's work) some is scattered by the molecules. The total intensity of this scattering is very small relative to the incident intensity, and varies from material to material. For liquids and light in the visible region, the total scattered intensity may be of the order of 10^{-5} of the incident. Long before Raman's discovery, the inverse proportionality to the fourth power of the wavelength had been made the basis of the well-known explanation of the blue of the sky. In this so-called classical or Rayleigh scattering the wavelength or frequency of the light remains unchanged, so that with a monochromatic primary beam the spectrum of the scattered light consists merely of the same single line as does that of the incident light.

Raman found that the scattered spectrum also contains new lines, whose frequency displacements relative to the primary line are characteristic of the molecular species involved. Thus for any particular substance a similar pattern of lines (the Raman spectrum) is always found, no matter what the incident frequency. In practice, visible or ultraviolet light is used, and the frequency chosen to avoid regions of absorption. Raman spectra can be observed for all states of aggregation, solid, liquid, and gas. Most work has been done with liquids, for which in general the Raman effect is of the order of a thousand times less intense than the Rayleigh scattering, which is itself only feeble.

Simple Account of Molecular Light-scattering.—The frequency shifts of the Raman lines relative to the primary line (Raman frequencies) are found to be equal to frequencies of vibrational or rotational transitions of the scattering molecules. The vibrational shifts (order 10^2 or 10^3 cm.$^{-1}$) are large enough to be observed conveniently with prism spectrographs, and have been most widely studied. The pure rotational shifts give Raman lines lying so close to the relatively much stronger Rayleigh line that their observation is impracticable except for molecules of relatively low moment of inertia, and may require the high resolving power of a grating instrument.

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[1] Raman and Krishnan, *Nature*, 1928, **121**, 501 ; Raman, *Indian J. Phys.*, 1928, **2**, 387 ; Raman and Krishnan, *ibid.*, p. 399.

In what follows we shall, unless otherwise stated, be considering only vibrational Raman spectra.

A very simple account of molecular light-scattering can be given as follows. In Rayleigh scattering the incident light quantum (energy $h\nu^0$) collides with a molecule and is simply scattered without change of frequency. In the Raman effect, on the other hand, the collision induces the molecule to undergo a transition. If, for example, this is a vibrational transition from $n = 0$ to $n = 1$ corresponding to the frequency ν_v, the light quantum is scattered with correspondingly diminished energy $h(\nu^0 - \nu_v)$, i.e., shows a frequency shift $\Delta\nu = \nu_v$ towards the red. If, however, the molecule happens to be in the state $n = 1$ when the quantum collides with it, the transition $1 \to 0$ may be induced, in which case the quantum will be scattered with correspondingly enhanced energy, i.e., will show a shift of the same magnitude as before, but in the opposite sense. The two Raman lines are known respectively as the Stokes line and the anti-Stokes line for the frequency involved. At ordinary temperatures the ratio of the numbers of molecules with $n = 1$ and $n = 0$ will usually be small, so that anti-Stokes lines will be considerably weaker than the corresponding Stokes lines. In fact anti-Stokes lines are not normally observed, except for relatively low values of ν_v.

The name " Stokes line " is taken over from usage in connection with fluorescence ; but fluorescence is in principle quite different from the Raman effect. In fluorescence, the exciting light must be absorbed by the molecule involved, which is thereby raised to an excited electronic state having a " half-life " of the order of 10^{-8} sec. or longer. At the end of this time the excited molecule may fluoresce, i.e., may re-radiate a part of its excitation energy, thereby emitting light of frequency lower than that of the original light. In the Raman effect, on the contrary, the incident light is chosen so as to be incapable of being absorbed by the scattering molecule and there is therefore no question of re-radiation from an excited state. Rather must we say that the effect of the incident radiation is to perturb the molecule and so induce it to undergo a vibrational (or rotational) transition, the frequency of the light being correspondingly altered in the scattering act. Accordingly, it is found that fluorescence can be quenched by the addition of suitable agents which are able to rob the excited molecules of their energy by collisions before they can re-radiate. Such quenching is impossible for the Raman effect.

The fact that Raman shifts are equal to frequencies of transitions such as are observable in infrared absorption spectroscopy, has led to statements to the effect that the Raman effect brings infrared spectra into the more convenient region of the visible or ultraviolet. Such statements, however, are loose and misleading. The mechanisms of Raman scattering and infrared absorption are quite different, and consequently information can often be obtained from the one type of spectrum which cannot be obtained from the other.

Recent Advances in Technique.—It is not an object of this Review to give a detailed account of experimental arrangements. Some of the more

Doering and Zeiss's model [28, 2c] has been expressed in a different terminology. It is effectively based on the same picture, in that the leaving group is supposed to occupy a solvation site on one side of the plane of the carbonium ion. With a stable carbonium ion, the anion is replaced by a solvent molecule during the life of the ion, producing a symmetrical carbonium ion (and racemisation) ; an unstable carbonium ion is attacked by solvent before the anion has separated. The distinctive feature of the scheme is the hypothesis that only two sites (one on each side of the plane containing the carbonium valencies) are considered to be involved in the solvation of the carbonium ion. Furthermore, it is speculated that the two solvent molecules (or one solvent molecule and one leaving group) are held covalently (see formula 8). In all discussions of these phenomena it is possible to replace the concept of " life-time " of the carbonium ion by the equivalent one of rate constants for the replacement of the shielding ion by a solvent molecule and for the attack of solvent on the carbonium ion, as is done by Doering and Zeiss.

Steric Acceleration.—The formation of a planar carbonium ion from a molecule of tetrahedral configuration implies an opening-out of the remaining bonds from an initial (tetrahedral) angle of around 109° to one of 120°. Thus, any congestion existing between the groups attached to the central atom will be alleviated during ionisation. An effect of this kind is likely to be observed in the values of the equilibrium constants for the formation of triarylcarbonium ions with bulky *ortho*-substituents.[16, 18]

It is also to be expected that the solvolysis of organic halides having a congested structure would be faster than that of similarly constituted but non-congested structures, since, at the transition state of ionisation, the bonds will have opened out to somewhere between 109° and 120°. Such behaviour has been reported in solvolyses of a number of bulky tertiary alkyl compounds, e.g., tri-*tert.*-butyl halides,[38] but it must be borne in mind that alternative explanations of this steric acceleration are sometimes possible, e.g., hyperconjugation[39] or the formation of bridged carbonium ions.[40, 17]

Bridgehead Carbonium Ions.—Just as the steric compressions between groups attached to the central carbon atom in certain tertiary halides can be relieved during ionisation and lead to faster solvolysis, so structures which prevent the increase in bond angles which is the concomitant of ionisation should show diminished reactivity in unimolecular reactions. Such behaviour has been observed in bicyclic halides in which the halogen is attached to a bridgehead carbon atom. Thus, refluxing 1-*apo*camphanyl chloride (9) with aqueous-ethanolic potassium hydroxide or silver nitrate failed to remove the halogen.[41] The bromotriptycene (10) showed a similar lack of reactivity, despite the presence of three phenyl groups. In a favourable

[38] *E.g.*, Bartlett and M. S. Swain, *J. Amer. Chem. Soc.*, 1955, **77**, 2801 ; H. C. Brown, *J.*, 1956, 1248.

[39] Hughes, Ingold, and Shiner, *J.*, 1953, 3827.

[40] Ingold, ref. 20, p. 417 ; cf. H. C. Brown and Kornblum, *J. Amer. Chem. Soc.*, 1954, **76**, 4510.   [41] Bartlett and Knox, *ibid.*, 1939, **61**, 3184.

slight, the spectrum of a mixture is the simple superposition of the spectra of the components. Since, in general, only comparatively sharp lines are involved, these spectra remain distinct and recognisable despite fortuitous coincidences. We have here a useful method for qualitative analysis. Moreover, the intensity with which a Raman line appears is in general directly proportional to the volume concentration of the scattering species, and so intensity measurements can form the basis of quantitative analytical determinations. The method has the advantage that it does not consume any of the sample.

Applications of these kinds do not require any detailed knowledge of the mechanism of Raman scattering, though a deeper insight into chemical problems may often be obtained by taking into account the relation of Raman spectra to molecular structure (see p. 192).

As an alternative to conventional chemical analysis, the Raman effect has been most useful for mixtures of hydrocarbons. Of the comparatively few applications in the inorganic field we may mention the quantitative analysis of mixtures of sodium nitrate and nitrite in aqueous solution.[9] Raman spectra have occasionally been used as a guide in preparative work; for instance, to determine the most favourable conditions for the preparation of chlorotrimethylsilane from silicon tetrachloride by the Grignard reaction.[10] Another example is the confirmation of the completion of the reaction $SeF_4 + SeO_2 = 2SeOF_2$ by the disappearance of the lines due to SeF_4 and the appearance of the $SeOF_2$ spectrum.[11]

Mixed Halide Formation, etc.—It is in cases where ordinary chemical methods are not applicable that the Raman effect has made its most significant contributions in detecting and estimating molecular species. We refer to systems involving labile chemical equilibria between species which either cannot be isolated at all, or at least not without disturbing the equilibria involved. Here the Raman method is especially useful, since (provided only that the compounds are not photochemically unstable) its application leaves the system completely unaffected.

As a first example we may take the investigations, mostly carried out by Delwaulle and Francois,[12] of mixed halide formation. The Raman spectrum of a mixture of carbon tetrachloride and carbon tetrabromide, or of a mixture of the corresponding halides of silicon, is found (as expected) to consist of a simple superposition of the two components: but mixtures of stannic chloride and stannic bromide give Raman spectra containing new lines [13] not attributable to either constituent. By comparison with the spectra of the isolable compounds $SiCl_3Br$, $SiCl_2Br_2$, $SiClBr_3$, and the carbon analogues, the new lines have been shown to be due to the formation of corresponding mixed halides in labile equilibrium with one another and with the stannic chloride and bromide from which they are instantaneously formed. These mixed halides cannot be isolated by such processes as distillation, etc.

[9] Stamm, *Ind. Eng. Chem. Anal.*, 1945, **17**, 318.
[10] Goubeau, Siebert, and Winterwerb, *Z. anorg. Chem.*, 1949, **259**, 240.
[11] Rolfe and Woodward, *Trans. Faraday Soc.*, 1955, **51**, 778.
[12] Delwaulle and Francois, *J. Chim. phys.*, 1949, **46**, 80.

Raman spectra also show that similar labile compounds are formed on mixing $SnCl_4$ and SnI_4,[13] $SnBr_4$ and SnI_4,[13] or $TiCl_4$ and $TiBr_4$.[14]   In this respect germanium appears to occupy an interesting intermediate position between silicon and tin.   Whereas no mixed halide formation is observed for silicon,[15] and the reaction is instantaneous for tin, Delwaulle, François, Delhaye-Buisset, and Delhaye [13] report that with a mixture of germanium tetra-chloride and tetrabromide there is a slow formation of mixed halides which can be followed by taking successive Raman spectra. '

The presence of the species PCl_2Br and $PClBr_2$ in mixtures of phosphorus trichloride and tribromide has likewise been shown [16] by the Raman method, and a similar result has been obtained [17] with a mixture of the trichloride and tribromide of arsenic.   When $PFCl_2$ and $PFBr_2$ are mixed, new Raman lines appear [17] owing to the formation of the compound PFClBr.   No mixed halide formation is found, however, for a mixture of arsenic trichloride and trifluoride : [17] it appears that the facility of exchange shown by chlorine and bromine is not shared by fluorine.   It is also interesting that the spec-trum of a mixture of $POCl_3$ and $POBr_3$ is simply the superposition of the spectra of these two compounds,[18] showing that exchange of the halogen atoms does not occur at ordinary temperatures.

In the same way it has recently been shown [19, 20] that analogous mixed halide formation occurs with the trichloride and tribromide of boron. Rough intensity determinations indicate [20] that the equilibrium constant at ordinary temperature for $BCl_3 + BBr_3 \rightleftharpoons BCl_2Br + BClBr_2$ is approxim-ately 8.

The simplest cases of mixed halide formation, however, are encountered with the mercuric compounds.   Equilibria of the kind $HgX_2 + HgY_2 \rightleftharpoons 2HgXY$, where X or Y is Cl, Br, I, or CN, have been investigated in alcoholic solution.[21]   Measurements of the intensities of the Raman lines have given the value $2 \cdot 0 \pm 0 \cdot 2$ for the equilibrium constant of $HgCl_2 + HgBr_2 \rightleftharpoons 2HgClBr$ at $15°$.   The corresponding value for $HgBr_2 + Hg(CN)_2 \rightleftharpoons 2HgBr(CN)$ is found to be about 10 times smaller.

Increase of molecular complexity due to association can also be detected by the Raman effect.   A very simple example is furnished by nitric oxide. As is to be expected for the diatomic molecule NO, only one Raman line is found for the gas.   If it is borne in mind, however, that NO is an " odd molecule ", it is interesting that the liquid shows extra lines,[22] indicating the presence of dimers $(NO)_2$.

[13] Delwaulle, François, Delhaye-Buisset, and Delhaye, J. Phys. Radium, 1954, **15**, 206.
[14] Delwaulle and François, Compt. rend., 1945, **220**, 173.
[15] Idem, ibid., 1944, **219**, 335.
[16] Delwaulle, ibid., 1947, **224**, 389 ; Theimer, Acta Phys. Austriaca, 1947, **1**, 188.
[17] Delwaulle and François, J. Chim. phys., 1949, **46**, 80.
[18] Idem, Compt. rend., 1945, **220**, 817.
[19] Long and Dollimore, J., 1954, 4457.
[20] Goubeau, Richter, and Becher, Z. anorg. Chem., 1955, **278**, 12.
[21] Delwaulle, Compt. rend., 1939, **208**, 999 ; Delwaulle and François, Bull. Soc. chim., 1940, **7**, 359.
[22] Vodar, Jardillier, and Mayence, Compt. rend., 1946, **222**, 1343 ; Smith, Keller, and Johnston, J. Chem. Phys., 1951, **19**, 189.

Ionic Equilibria in Solution.—Raman spectroscopy is just as applicable to charged species as to neutral molecules and has proved a very direct and elegant method for the study of ionic equilibria in solution. Soon after its discovery, the Raman effect was used [23] to show the incompleteness of the ionisation of nitric acid in aqueous solution. All metal nitrates in solution have the same Raman spectrum, which is evidently characteristic of the NO_3^- ion. Dilute solutions of nitric acid show the same spectrum; but as the concentration is increased, new lines due to the undissociated HNO_3 molecule appear, while at the same time the lines due to the nitrate ion diminish in intensity. This system has been the subject of a number of subsequent investigations, amongst which special mention may be made of the quantitative measurements by Redlich and Bigeleisen.[24] These workers determined the concentration of nitrate ions in nitric acid solutions by comparison of the intensity of the principal NO_3^- line with its intensity in sodium nitrate solutions, assumed completely ionised. They found that the maximum concentration of NO_3^- in nitric acid solutions occurs when the acid is about 7M. The value of the dissociation constant obtained by extrapolation to zero concentration shows reasonable agreement with deductions from other evidence. The same method has been applied to solutions of perchloric acid [25] and has shown, as expected, that this is a considerably stronger acid than nitric. The two stages of ionisation of sulphuric acid have been followed as a function of concentration by means of Raman spectra [26] and the method has also been applied to iodic acid [27] and phosphoric acid.[28] A feeble band which appears in the Raman spectrum of very concentrated solutions of hydrochloric acid in water has been attributed [29] to undissociated HCl molecules.

Interesting results have been obtained by Ingold, Millen, and Poole [30] on the behaviour of nitric acid in very acidic solvents like pure sulphuric acid. It had been observed by Chédin [31] that a Raman line at $\Delta\nu = 1400$ cm.$^{-1}$, very weakly present in the spectrum of anhydrous nitric acid, is enhanced in intensity by the addition of anhydrous sulphuric acid. At the same time another line at about 1050 cm.$^{-1}$ appears. As he had also found that two lines of practically these frequencies were the sole observable features of the Raman spectrum of solid dinitrogen pentoxide, Chédin concluded that the effect of the addition of anhydrous sulphuric acid to anhydrous nitric acid was to produce dinitrogen pentoxide by dehydration. Ingold, Millen, and Poole, however, showed that the Raman frequency 1400 cm.$^{-1}$ can be produced without 1050 cm.$^{-1}$ by the addition

[23] Rao, *Proc. Roy. Soc.*, 1930, *A*, **127**, 279.
[24] Redlich and Bigeleisen, *J. Amer. Chem. Soc.*, 1943, **65**, 1883.
[25] Redlich, Holt, and Bigeleisen, *ibid.*, 1944, **66**, 13.
[26] Woodward and Horner, *Proc. Roy. Soc.*, 1934, *A*, **144**, 129 ; Rao, *Indian J. Phys.*, 1940, **14**, 143.
[27] *Idem, ibid.*, 1942, **16**, 71.
[28] *Idem, ibid.*, 1943, **17**, 357.
[29] Karetnikov, *Zhur. Fiz. Khim.*, 1954, **28**, 1331.
[30] Ingold, Millen, and Poole, *J.*, 1950, 2576.
[31] Chedin, *Ann. Chim.*, 1937, **8**, 243.

of either anhydrous selenic acid or anhydrous perchloric acid to nitric acid. In these cases the 1400 cm.$^{-1}$ frequency is accompanied by others which have been shown to be characteristic of the hydrogen selenate ion $HSeO_4^-$ and the perchlorate ion ClO_4^-, respectively.   In the mixture of nitric acid with sulphuric acid, therefore, the frequency 1050 cm.$^{-1}$ is to be attributed to the HSO_4^- ion and not to the same species as 1400 cm.$^{-1}$.   The latter is, in fact, the characteristic frequency of the nitronium ion NO_2^+, and Ingold, Millen, and Poole's results show that in these very acidic media nitric acid ionises thus : $HNO_3 + 2H_2SO_4 = NO_2^+ + 2HSO_4^- + H_3O^+$, and similarly for perchloric and selenic acids.   The appearance of a line at 1050 cm.$^{-1}$ along with 1400 cm.$^{-1}$ in the spectrum of solid dinitrogen pentoxide is due to the fortuitous circumstance that 1050 cm.$^{-1}$ is also the principal Raman frequency of the nitrate ion.   The spectrum shows, in fact, that in the solid state dinitrogen pentoxide is to be formulated [32] as the nitronium salt $(NO_2^+)(NO_3^-)$.   The Raman spectrum of dinitrogen pentoxide in solution in nitric acid likewise consists [33] entirely of the frequencies of NO_2^+ and NO_3^-, so that in this solvent the nitronium salt is simply ionised.   Millen has further shown [32] that the solid of composition $NClO_6$ obtained from the system $HNO_3 + HClO_4$ gives the nitronium ion frequency 1400 cm.$^{-1}$ together with the known frequencies characteristic of the perchlorate ion, and is therefore to be formulated as $(NO_2^+)(ClO_4^-)$.   Other solids which have similarly been shown to be nitronium salts include $(NO_2^+)(HS_2O_7^-)$ and $(NO_2^+)_2(S_2O_7^{2-})$, both derived from the system $N_2O_5 + SO_3 + H_2O$, and $(NO_2^+)(SO_3F^-)$ derived from the system $N_2O_5 + HSO_3F$.

Solutions of dinitrogen trioxide in sulphuric acid show [34] the frequency characteristic of HSO_4^- and also a new one at about 2300 cm.$^{-1}$, which must be due to the nitrosonium ion NO^+ since it appears (along with the frequencies of ClO_4^-) in the spectrum of nitrosonium perchlorate.[35]

Reverting to aqueous solutions, it has been concluded from measurements by various other methods that certain " strong " electrolytes, e.g., thallous hydroxide, are incompletely dissociated into ions ; and the question arises as to whether the undissociated part consists of covalently linked molecules or electrostatically bound ion-pairs.   Here the Raman method can give information ; in the former case a corresponding vibrational Raman spectrum will be expected, whereas in the latter case (as has been shown theoretically [36]) the effect will be relatively very weak and probably unobservable. In fact, for thallous hydroxide no Raman spectrum characteristic of the undissociated part could be observed,[36] so that this probably consists of ion-pairs $(Tl^+)(OH^-)$.

A very simple example of the use of Raman spectra for the detection of an ionic species is the verification by Woodward [37] that the mercurous ion in aqueous solution has the formula Hg_2^{2+}. If it were Hg^+, it could obviously

[32] Millen, *J.*, 1950, 2606.
[33] Ingold and Millen, *J.*, 1950, 2612.
[34] Millen, *J.*, 1950, 2600.
[35] Angus and Leckie, *Proc. Roy. Soc.*, 1935, *A*, **150**, 615.
[36] George, Rolfe, and Woodward, *Trans. Faraday Soc.*, 1953, **49**, 375.

give no vibrational Raman effect.   In fact one line is observed.   The same method applied to thallous [37] and argentous [38] ions shows that in neither case can an appreciable proportion be present in the double form.

A few examples must here suffice of the many applications of the Raman effect for the detection of complex ions.   In presence of excess of bromide ion in aqueous solution, Cd^{2+} gives a Raman pattern [39] which is clearly to be attributed to the complex ion $CdBr_4^{2-}$, since it is analogous to the pattern for the isoelectronic neutral molecule $SnBr_4$.   Similarly, in presence of excess of iodide ion the spectrum of CdI_4^{2-} is obtained.[40]   When both Br^- and I^- are simultaneously present, the spectrum obtained [41] depends upon their relative concentrations ;   the observations, which are analogous to those for mixtures of stannic chloride and bromide (p. 188), provide evidence for the presence of the mixed halide complex anions $CdBr_3I^{2-}$, $CdBr_2I_2^{2-}$, and $CdBrI_3^{2-}$.   Similar results are obtained for the halide complex ions $HgBr_4^{2-}$ and HgI_4^{2-} and the corresponding mixed halide species.[41]

Elementary Theory of Molecular Light-scattering

In the field of organic chemistry, where most of the molecules contain many atoms, much of the study of the relation between Raman spectra and molecular structure has necessarily been of an empirical character.   In-organic chemistry offers a variety of comparatively simple molecules and ions, for which valuable structural information can be obtained by the application of the theory of Raman scattering.

We may note in passing that vibrational frequencies, as determined from Raman spectra, may be used for the calculation of force constants.   In general, however, the number of observable frequencies is insufficient for the complete determination of the force field and, although additional in-formation can sometimes be obtained by the use of isotopic substitution, approximate assumptions are usually necessary.   This subject has been discussed in a Quarterly Review [42] by Linnett, who sums up thus :   '' For many polyatomic molecules we are by no means sure what sort of force field is best.''   We shall not pursue this question further here, nor shall we do more than mention that the Raman effect is helpful in giving vibra-tional frequency values for use in the calculation of entropies, etc., by the well-known statistical methods.   We wish rather to direct attention to the important fact that for molecules possessing some symmetry it is possible, without any knowledge of frequencies or force constants, to obtain from Raman spectra clear-cut decisions between different proposed models.   The method requires the determination only of the number of fundamentals permitted in the Raman effect and their states of polarisation.   It is even more powerful when used along with information from infrared absorption.

[37] Woodward, *Phil. Mag.*, 1934, **18,** 823.
[38] Waters and Woodward, *J.*, 1954, 3250.
[39] Delwaulle, François, and Wiemann, *Compt. rend.*, 1939, **208,** 1818.
[40] *Idem, ibid.*, p. 184.
[41] Rolfe, Sheppard, and Woodward, *Trans. Faraday Soc.*, 1954, **50,** 1275 ; Delwaulle, *Bull. Soc. chim.*, 1955, p. 1294.
[42] Linnett, *Quart. Rev.*, 1947, **1,** 73.

Undoubtedly the most useful theory of molecular light-scattering is that put forward by Placzek,[43] which starts with a classical description and then translates this into the language of wave-mechanics.   The chemist interested in the important rules of selection and polarisation can gain valuable insight (at least for fundamental frequencies) from a purely classical and largely non-mathematical treatment, such as is outlined in the following sections. (The occasional parentheses will serve to remind the reader that the phenomena being considered are essentially quantum-mechanical.)

Molecular Polarisability Ellipsoid.—A molecule may be regarded as an assemblage of positively charged nuclei embedded in a cloud of negative electricity.   In the equilibrium configuration the electrical centres of the positive and negative parts may be coincident (when the molecule will possess no permanent dipole moment) or not (when a permanent moment will be present).   In either case the application of an electric field will give rise to an *induced* electric dipole moment.   If the field oscillates with a frequency sufficiently large in comparison with nuclear vibration frequencies, only the electron cloud (of relatively very small inertia) will be able to " follow ", and the heavy nuclei will remain practically unaffected.

The relation between the applied field strength E and the induced dipole moment M can be written as $M = \alpha E$, where α is the *polarisability* of the molecule.   Both E and M are vectors.   In the simplest case of an isotropic molecule their directions are identical, *i.e.*, α is a scalar.   In general, however, the application of a field in a certain direction induces a moment in a different direction.   In general, therefore, α is a *tensor*.

The nature of α may be visualised as follows.   Let M_x, M_y, M_z be the components of the induced moment relative to a co-ordinate system fixed in space and in the molecule, and let the corresponding components of the applied field be E_x, E_y, E_z.   The fact that each component of E in general makes a contribution to each component of M can be expressed as follows :

$$M_x = \alpha_{xx}E_x + \alpha_{xy}E_y + \alpha_{xz}E_z$$
$$M_y = \alpha_{yx}E_x + \alpha_{yy}E_y + \alpha_{yz}E_z$$
$$M_z = \alpha_{zx}E_x + \alpha_{zy}E_y + \alpha_{zz}E_z$$

The tensor α is thus defined by the set of nine coefficients α_{xx}, α_{xy}, etc., which may be shown to reduce to six because $\alpha_{xy} = \alpha_{yx}$, $\alpha_{yz} = \alpha_{zy}$, and $\alpha_{zx} = \alpha_{xz}$.   Now, in order to represent α in a more " pictorial " way, we may make use of the six coefficients to form the equation of an ellipsoid, *viz.*,

$$\alpha_{xx}x^2 + \alpha_{yy}y^2 + \alpha_{zz}z^2 + 2\alpha_{xy}xy + 2\alpha_{yz}yz + 2\alpha_{zx}zx = 1$$

and henceforward we may identify this ellipsoid with the polarisability.

A rotation of the co-ordinate system relative to the molecule will cause changes in the coefficients in the ellipsoid equation, and the new set will form the polarisability tensor referred to the new axes.   In particular, when the co-ordinate axes (X, Y, Z) are chosen to coincide with the three principal axes of the ellipsoid, the equation reduces to the form

[43] Placzek, " Handbuch der Radiologie ", 1934, **6/2,** 205.

$AX^2 + BY^2 + CZ^2 = 1$. Thus with this special choice of axes only the three " diagonal " coefficients $\alpha_{XX} = A$, $\alpha_{YY} = B$, and $\alpha_{ZZ} = C$ are different from zero. They are called the principal values of α.

Pure Rotational Raman Effect.—For a linear molecule one axis of the polarisability ellipsoid obviously lies along the line of the nuclei and the other two are equal. When the molecule rotates, it does so about an axis at right angles to the line of the nuclei and so the ellipsoid returns to an identical position after each half revolution. Thus each component of α (relative to space-fixed axes) varies with frequency $2\nu_r$, where ν_r is the rotational frequency of the molecule. Irradiation of the molecule with light of frequency ν^0 may be regarded as equivalent to the application of an oscillating electric field. The consequent induced dipole moment is given by αE, where now α varies with frequency $2\nu_r$, and E with frequency ν^0. Regarded classically, therefore, αE represents moments oscillating with the frequencies $\nu^0 \mp 2\nu_r$ and these will radiate the Stokes and anti-Stokes Raman lines respectively. (In terms of quantum theory this means that only rotational transitions with $\Delta J = \pm 2$ are Raman-active. This is the pure rotational selection rule for linear molecules. For non-linear molecules the result is less simple.)

Normal Vibrations and their Symmetry Properties.—The nuclei may be regarded as mass-points in a potential field due to the bonding. When they are slightly displaced from their equilibrium positions and then released, they perform vibrations which in general have complicated forms. It may be shown, however, that any such vibration is the superposition of a limited number of so-called *normal vibrations*, in general with different amplitudes and phases. Each normal mode is such that, in the absence of other normal modes, every nucleus performs simple harmonic oscillations in a straight line about its equilibrium position and that all these individual oscillations are in phase. Thus each normal vibration may be regarded as the simple harmonic oscillation of a so-called *normal co-ordinate*, so constructed as to express all the individual displacements of the nuclei involved. Each normal vibration has its own frequency. Two (or three) of these frequencies may be identical : the modes are then said to show 2-fold (or 3-fold) degeneracy.

The equilibrium nuclear configuration may have *symmetry elements*, such as a plane of symmetry, etc. To each such element there is a symmetry operation, such as reflection in the plane, etc., which produces a nuclear configuration indistinguishable from the original. The complete set of symmetry operations characterising any molecule is expressed shortly by the symbol of the *point group* to which the equilibrium configuration belongs.

The symmetry of the molecule determines the symmetry of the potential field and hence also the symmetry types of the normal vibrational modes. Thus, consider a molecule slightly distorted in the particular manner described by the normal co-ordinate q, and perform upon it any chosen symmetry operation characterising the undistorted molecule. The operation will transform q into the new distortion q_t, while leaving the potential energy unchanged. Since the potential energy for a distortion is proportional to the

square of the co-ordinate, it follows that q_t must have been formed from q in one or other of the three following ways.

First, $q_t = q$.   In this case the operation gives a distorted configuration identical with that from which we started.   The corresponding normal mode is said to be *symmetric* with respect to the symmetry operation in question. A mode which is symmetric with respect to every symmetry operation of the molecule is said to be *totally symmetric*.   An example is the mode of frequency ν_1 shown in Fig. 1.
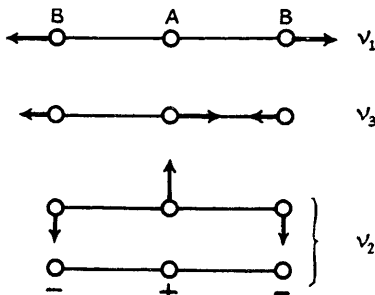

FIG. 1
Normal vibrations of linear symmetrical AB_2.
The plus and minus signs indicate displacements in opposite senses normal to the plane of the figure.

Secondly, $q_t = -q$.   Here we obtain a distorted configuration in which the displacement of every nucleus is equal in magnitude to, but opposite in sign from, what it was before.   The mode is then said to be *antisymmetric* with respect to the symmetry operation.   A mode which is antisymmetric with respect to any operation is called an antisymmetric mode, even though it may be symmetric with respect to others.   An example is the mode of frequency ν_3 in Fig. 1.   This is antisymmetric with respect to the plane of symmetry normal to the line of nuclei but is symmetric with respect to planes passing through this line.

Thirdly, q_t may be a linear combination of two (or three) normal co-ordinates, which are then degenerate.   Degeneracy only arises where the symmetry element is a rotational axis and the symmetry operation is a rotation through an appropriate angle about it. A very simple example of 2-fold degeneracy is that of the two bending modes shown in Fig. 1. Here the line of the nuclei in the equilibrium configuration is a rotational axis of infinite order, *i.e.*, rotation about it through any angle θ is a sym-

FIG. 2

metry operation.   In the end-on view shown in Fig. 2 the displacement of any chosen nucleus is represented by d_1 in the mode of normal co-ordinate q_1, and d_2 in that of q_2.   Rotation through θ is seen to transform d_1 into d_t, which is compounded of $d_1 \cos \theta$ and $d_2 \sin \theta$.   This is a simple instance of a
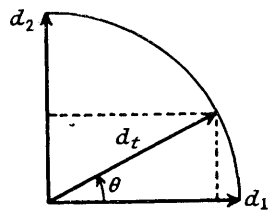
general behaviour shown by more complicated structures and for axes of finite orders.

The Derived Polarisability Tensor.—If the nuclei are displaced, the polarisability of the molecule will in general change. Considering in particular the distortion described by the normal vibrational co-ordinate q and confining ourselves to very small amplitudes, we may write to a first approximation

$$\alpha = \alpha_0 + (\partial\alpha/\partial q)_0 q$$

where the zero subscripts indicate values at the equilibrium configuration. This is a convenient way of expressing the fact that a relation of this kind holds for each of the six coefficients defining α. For the electric moment M induced by an applied field E we can now write

$$M = \alpha_0 E + (\partial\alpha/\partial q)_0 q E$$

Light incident upon the molecule may be regarded as an electric field oscillating with frequency ν^0. The first term on the right-hand side of the last equation represents a moment also oscillating with frequency ν^0. This gives rise to Rayleigh scattering. For a given amplitude of E (*i.e.*, a given incident intensity) it is clear that the intensity, etc., of the Rayleigh scattering are determined by the properties of the tensor α_0.

The second term contains the product of two time-dependent factors : q, which oscillates with the frequency ν_v of the nuclear vibration, and E which oscillates with the frequency ν^0 of the incident light. The term therefore represents electric moments oscillating with the frequencies $\nu^0 \mp \nu_v$, which give rise to Raman scattering (Stokes and anti-Stokes lines of the fundamental vibration frequency ν_v). For a given incident light intensity the Raman intensity will be determined by $(\partial\alpha/\partial q)_0$ and the amplitude of q. (This result is expressed in terms of classical theory, the amplitude of q being regarded as continuously variable. In quantum theory, where vibrational states are characterised by the integral quantum number n, the corresponding result is that the probability of the transition $n \rightarrow n + 1$ increases as n increases. It also follows that, for simple harmonic vibrations and in the approximation considered here, only transitions with $\Delta n = 1$ are permitted, overtones and combination tones being forbidden. This is quite well borne out in practice, and consequently Raman spectra are relatively simple as compared with infrared absorption spectra.)

At a given temperature the presence of q in the second term of the expression for M merely gives rise to a numerical factor. It follows therefore that the properties of the Raman radiation (intensity, state of polarisation, etc.) are determined by $(\partial\alpha/\partial q)_0$ in just the same manner as the corresponding properties of the Rayleigh radiation are determined by α_0 (see above). Like α_0, $(\partial\alpha/\partial q)_0$ is a tensor : each of its coefficients is the partial derivative of the corresponding coefficient of α. We shall speak of $(\partial\alpha/\partial q)_0$ as the *derived polarisability tensor* α'_0 for the normal vibration defined by q.

The derived tensor, however, is not so easy to picture as is α_0 itself. Its coefficients, being rates of change of the corresponding coefficients of α,

may be zero or negative. It cannot therefore in general be represented by an ellipsoid.

Degree of Depolarisation.—Because of its greater simplicity we will first discuss Rayleigh scattering. Consider irradiation by natural light along the y-axis (see Fig. 3) and scattering at right angles along the x-axis. The co-ordinate system x, y, z is fixed in space, and the orientation of the scattering molecule will for the present be supposed to be fixed also. The incident light may be regarded as consisting of two oscillating electric vectors E_x and E_z of equal amplitude, each of which will in general induce component moments M_x, M_y, M_z directed along the three axes. Since an oscillating dipole does not radiate in its own axial direction, only M_y and M_z will contribute to the scattering along the x-axis, producing respectively the plane-polarised components of intensities i and I (see Fig. 3). It is easily seen that for an isotropic molecule (polarisability ellipsoid a sphere) $i = 0$,
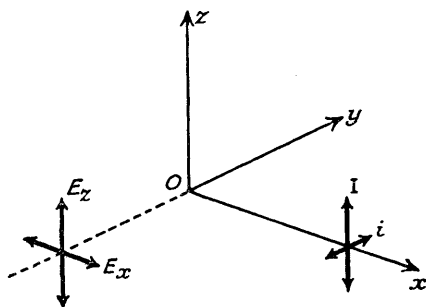

Fig. 3

and the scattering is completely polarised. For non-isotropic molecules ($i \neq 0$) the ratio i/I is called the *degree of depolarisation* and is designated by the symbol ρ.

Coming now to Raman scattering, we have seen that its properties depend upon α'_0 in just the same way as those of Rayleigh scattering depend upon α_0. Thus ρ for a Raman line is determined by the nature of the appropriate derived polarisability tensor and by the orientation of the scattering molecule.

Raman Effect in Crystals.—In fluids the scattering molecules will have random orientations in space. Only by the use of a sufficiently large single crystal is it possible to maintain a definite orientation relative to the directions of irradiation and observation. Hence, it appears that the study of crystals should offer the most favourable opportunities for obtaining information about molecular structure. It must be borne in mind, however, that molecules in a crystal are necessarily subject to strong interactions ; and these may give rise to considerable complications as compared with other states. Thus the Raman spectrum of a compound in the crystalline state will contain lattice frequencies which have no counterpart in the spectrum of the free molecule. Moreover, there are two factors which may cause a single frequency of the free molecule to give rise to more than one in the

N

crystal. First, if the vibrational mode concerned is degenerate for the free molecule, the degeneracy may be removed by the crystal field. Secondly, in the usual cases where the unit cell contains more than one molecule, a single molecular mode may give rise to more than one frequency on account of intermolecular coupling.

It would be too much to suggest that the Raman effect can at present compete with X-ray diffraction as a method for the elucidation of crystal structure. Nevertheless, in favourable cases Raman spectra can provide interesting auxiliary information, for example as to the arrangement of hydrogen nuclei. The method presents considerable experimental difficulties, as it requires the measurement of degrees of depolarisation for a single crystal placed successively in suitable different orientations relative to the directions of irradiation and scattering. Examples of the successful use of this method are the determination of the orientation of water molecules in hydrated crystals [44] and of ammonium ions in ammonium halides.[45] For a short account of the theory reference may be made to an article by Mathieu : [46] a full treatment is given in the book [47] by the same author.

Degrees of Depolarisation for Fluids.—In fluids it may be assumed that all orientations of the scattering molecules are equally probable, so that experimental determinations of ρ give an average value. The theoretical expression for this is most conveniently expressed in terms of the two *invariants* of the tensor involved. These are quantities whose values are unaffected by any change of orientation relative to the co-ordinate system.

Considering, first, the polarisability ellipsoid α_0, which is concerned with Rayleigh scattering, the *mean-value invariant* a is defined by $a = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$. Since it is an invariant, its value may be seen in particular to be $\frac{1}{3}(A + B + C)$, where A, B, C are the principal values. Hence, roughly speaking, we may say that a is a measure of the overall " size " of the polarisability ellipsoid. The other invariant, the *anisotropy γ*, is defined by

$$\gamma^2 = \tfrac{1}{2}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6(\alpha_{xy}^2 + \alpha_{yz}^2 + \alpha_{zx}^2)].$$

Considering again the special case when the co-ordinate axes coincide with the principal axes of the ellipsoid, we see that

$$\gamma^2 = \tfrac{1}{2}[(A - B)^2 + (B - C)^2 + (C - D)^2]$$

Hence, roughly speaking, we may say that γ is a measure of the departure of the shape of the ellipsoid from spherical.

The result of averaging over all orientations of the scattering molecule may be written

$$\rho = 6\gamma^2/(45a^2 + 7\gamma^2)$$

In accordance with the conclusion reached earlier, if the ellipsoid is a sphere

[44] Couture, " Contrib. Etude Structure mol., Vol. commem. Victor Henri ", 1947–48, p. 105 ; Couture-Mathieu and Mathieu, *Acta Cryst.*, 1952, **5**, 571.

[45] *Idem, J. Chim. phys.*, 1952, **49**, 226.

[46] Mathieu, *Ind. chim. belg.*, 1953, **18**, 219.

[47] *Idem*, " Spectres de Vibration et Symmetries des Molecules et des Cristaux ", Hermann, Paris, 1945.

($i.e.$, $\gamma^2 = 0$) then $\rho = 0$ and the Rayleigh scattering is completely polarised. In no circumstances can a^2 be zero, and so for all molecules ρ must always be less than $6/7$. Moreover, in no case can the intensity vanish altogether : Rayleigh scattering is never forbidden.

Coming now to Raman scattering, we are concerned with the derived tensor α'_0 in place of α_0. Although the derived tensor cannot be represented by an ellipsoid, it nevertheless possesses a mean-value invariant a' and an anisotropy invariant γ' which are exactly analogous to those of α_0. Hence for the degree of depolarisation of a Raman line we may write

$$\rho = 6(\gamma')^2/[45(a')^2 + 7(\gamma')^2]$$

However, owing to the differences in character between α'_0 and α_0, important differences arise for Raman scattering as compared with Rayleigh scattering. Thus, any of the coefficients of α'_0 may be zero or negative, with the result that either a' or γ' or both may vanish. If both vanish simultaneously, the intensities i and I are both zero, $i.e.$, the Raman line is *forbidden*. If γ' alone vanishes, then $\rho = 0$ and the line is *completely polarised*. If a' alone vanishes, then ρ has the maximum value of $6/7$ and the line is said to be *depolarised*. In all other cases ρ is between 0 and $6/7$ and the line is said to be *polarised*.

Rules of Selection and Polarisation.—From the above discussion it is clear that these rules for the Raman effect are determined by the properties of the α'_0 tensor. These are in turn determined by the symmetry properties of the vibrational modes and of the polarisability ellipsoid, both of which depend ultimately on the symmetry of the equilibrium nuclear configuration of the molecule. This is the basis of the method whereby it is possible to decide between alternative proposed structures having different symmetries. The conclusions so reached do not involve any knowledge of frequency values or force constants.

The total number of vibrational fundamentals of a molecule containing N nuclei is $3N - 6$ if the molecule is non-linear, or $3N - 5$ if linear. The numbers of fundamentals belonging to the various symmetry classes (totally symmetric, antisymmetric, or degenerate) are determined by the symmetry of the equilibrium nuclear configuration. We now wish to see how the symmetry class of a vibration determines the behaviour of its fundamental in the Raman effect.

For this purpose we must first refer back to the definitions of the invariants given above. Remembering that each coefficient of α'_0 is related to the corresponding coefficient of α_0 by equations of the kind $\alpha'_{xx} = (\partial\alpha_{xx}/\partial q)_0$, we note that $a' = (\partial a/\partial q)_0$ but that $\gamma' \neq (\partial\gamma/\partial q)_0$.

Now deformation of a molecule in the manner described by q may affect the polarisability ellipsoid in two different ways. First, it may cause an alteration in the " size " as expressed by $a = \frac{1}{3}(A + B + C)$; and secondly, it may cause the orientation of the ellipsoid to change. A change of orientation will produce changes in the coefficients such that, although the " size " as measured by a will remain unaffected and so $(\partial a/\partial q)_0 = a'$ will be zero, nevertheless the anisotropy γ' of the derived tensor (which as noted above

is not equal to the derivative of the anisotropy γ of the tensor α) will in general have a value different from zero.

Consider in particular a vibration that is antisymmetric with respect to some symmetry operation characteristic of the molecule in its equilibrium configuration. When the molecule is slightly deformed in the manner described by the normal co-ordinate q, its mean-value invariant is clearly $a_0 + (\partial a/\partial q)_0 q$, which we will write $a_0 + a'q$. The result of performing the symmetry operation upon the deformed molecule is to cause q to become $-q$. But the operation obviously gives an ellipsoid of exactly the same " size " as before (although in general with its axes differently oriented). Its mean-value invariant is thus unaffected, despite the fact that q has been changed to $-q$. Therefore we have : $a_0 + a'q = a_0 - a'q$, whence $a' = 0$. But since the orientation of the ellipsoid is in general affected by q, the other invariant γ' will not necessarily vanish. Hence the Raman line will not in general be forbidden ; but since $a' = 0$, it must have $\rho = 6/7$. We have thus proved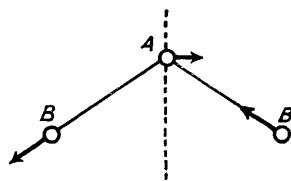 the polarisation rule that all permitted Raman lines of antisymmetric modes are depolarised. A simple example is the normal vibration of the non-linear AB_2 molecule (e.g., SO_2) illustrated in Fig. 4, where the arrows represent the nuclear displacements for the co-ordinate q. This mode is seen to be antisymmetric with respect to the plane of symmetry normal to the figure plane and indicated by the dotted line. Reflection of the distorted molecule in this plane reverses the displacement of each nucleus, and it is clear that the effect on the ellipsoid is to leave its

FIG. 4

Antisymmetric mode of non-linear symmetrical AB_2.

" size " unaffected ($a' = 0$) but to change its orientation ($\gamma' \neq 0$). In the course of the vibration the ellipsoid merely oscillates. The corresponding Raman fundamental is permitted as a line with $\rho = 6/7$. A molecule may have further special symmetry properties which will cause an anti-symmetric vibration to be forbidden in the Raman effect. This will be so when in the course of the vibration the ellipsoid, in addition to remaining unaltered in " size ", also remains unaltered in orientation. This arises, for example, in the asymmetric vibration (ν_3) of the linear AB_2 molecule (e.g., $HgCl_2$) shown in Fig. 1. The line of the nuclei is here a rotational axis of the ellipsoid and in the course of the vibration the axes obviously remain unchanged in direction, whence $\gamma' = 0$. Since, as for all antisymmetric modes, $a' = 0$ also, the Raman line must be forbidden. This last example is a special case of a more general selection rule which states that all vibrations which are antisymmetric with respect to a centre of symmetry are forbidden in the Raman effect. The proof follows exactly as above. It may be shown that for a molecule possessing a centre of symmetry no vibration can be permitted in both Raman and infrared absorption spectra. In certain cases, however, a vibration may be forbidden in both.

Coming now to degenerate vibrations, consider for example the 2-fold degeneracy of the modes whose normal co-ordinates are q_1 and q_2. The

symmetry operation concerned must be rotation through an appropriate angle θ about an axis. We perform the operation on the molecule distorted by q_1 and the result (cf. Fig. 2) is to change this into $q_1 \cos \theta + q_2 \sin \theta$. Writing $(\partial a/\partial q_1)_0 = a'_1$ and $(\partial a/\partial q_2)_0 = a'_2$, we have for the mean-value invariant of the ellipsoid $a_0 + a'_1 q_1 \cos \theta + a'_2 q_2 \sin \theta$. If we had rotated the distorted molecule through $-\theta$, which is necessarily also a symmetry operation of the undistorted molecule, we should have arrived at the value $a_0 + a'_1 q_1 \cos \theta - a'_2 q_2 \sin \theta$. But the symmetry operations obviously leave the " size " of the ellipsoid unchanged, whence $a'_2 = 0$. By a similar argument it follows that $a'_1 = 0$ also. The Raman line for the degenerate modes is therefore depolarised. The same conclusion can be reached for 3-fold degenerate modes. The *general rule of polarisation* therefore runs : all Raman lines of antisymmetric and degenerate modes are depolarised. Only modes which are totally symmetric can have ρ less than $6/7$.

Under special symmetry conditions a Raman line may be completely polarised ($\rho = 0$). For this we must have both $\gamma' = 0$ and $a' \neq 0$, which can only occur for a vibration in the course of which the polarisability ellipsoid remains spherical throughout and merely oscillates in size. Examples are the totally symmetric " breathing " modes of regular tetrahedral molecules like P_4 or $SnCl_4$ and of regular octahedral molecules like SF_6.

In infrared absorption the derivative $(\partial\mu/\partial q)_0$, where μ is the electric dipole moment, plays a part analogous to that of $(\partial\alpha/\partial q)_0$ for the Raman effect. Consequently, the selection rules are quite different, and for the investigation of molecular structure the two kinds of spectra are complementary.

Molecular Structure : Some Results

The number of inorganic species whose Raman spectra have been investigated is very large. A complete bibliography [48] is available up to 1943, and many examples are discussed in the valuable books of Kohlrausch [49] and Herzberg,[50] published respectively in 1943 and 1945. Data are sometimes incomplete and conclusions doubtful. It will not be possible here to attempt anything like a complete survey : space will permit only of the mention of a few of the clearer examples in order to give an idea of the kind of results that can be obtained. References will be mostly to work since about 1945.

Rotational Raman Spectra.—For a molecule to show a pure rotational spectrum in absorption it must possess a permanent electric dipole moment ; in the Raman effect this condition is not necessary, and early in the history of the effect Rasetti [51] photographed the pure rotational Raman spectra of some non-polar diatomic molecules including N_2 and O_2. Corresponding results

[48] Hibben, " The Raman Effect and its Chemical Applications ", Reinhold Publishing Corporation, New York, 1939 ; together with Glockler, *Rev. Mod. Phys.*, 1943, **15,** 111.

[49] Kohlrausch, " Ramanspektren ", Becker and Erler, Leipzig, 1943.

[50] Herzberg, " Infra-red and Raman Spectra of Polyatomic Molecules ", Van Nostrand Co., New York, 1945.

[51] Rasetti, *Z. Physik*, 1930, **61,** 598.

were also obtained for CO_2 by Houston and Lewis.[52]   The spectra are in agreement with the selection rule $\Delta J = \pm 2$ (see above), which leads to $|\Delta\nu| = 4B(J + \frac{3}{2})$ where B is the usual rotational constant.   For N_2, successive rotational lines alternate in intensity, those for even J being the stronger.   From this it follows that the nitrogen nuclei conform to Bose statistics.   For O_2, lines of odd J do not appear at all, showing that the oxygen nuclei have zero spin.   More recently Andrychuk [53] has obtained the pure rotational spectrum of F_2.   Here lines corresponding to odd J are the stronger, which provides proof that the fluorine nuclei obey Fermi statistics.

Interest in pure rotational Raman spectra has been revived by the recent elegant work of Stoicheff and others in Canada.   Stoicheff [54] has described an apparatus with which pure rotational spectra of gases at ordinary pressure can be photographed in the second order of a 21-foot grating, the resolving power being as high as 10^5.   With this apparatus accurate rotational constants can be measured, and results have been published for N_2[55] and the linear C_2N_2.[56]

Until recently, comparatively little has been done upon the less intense rotational structure of vibrational Raman bands.   The problems of such high-resolution work have been discussed in a recent paper by Welsh, Stansbury, Romanko, and Feldman.[57]   Accurate rotational constants have been determined [58] from the structure of the ν_3 band of NH_3.   The ν_3 band [59] and the ν_2 band [60] of CH_4 have also been analysed.

Vibrational Raman Spectra.—As pointed out on p. 199 it is possible to decide between molecular models of different symmetries by determining the number of permitted fundamentals and the number of these which are polarised.   In practice a permitted fundamental may be so weak as to escape observation.   On the other hand, though overtones are usually extremely feeble and unobservable, one may possibly appear and be mistaken for a fundamental.   Also a fundamental may give rise to a doublet if there is a fortuitous near-coincidence with an overtone or combination tone of the same symmetry class (so-called Fermi resonance [61]).   If ρ is only slightly less than $6/7$ it may be difficult to decide whether a line is polarised or not.   Despite occasional difficulties of these kinds, the method has provided much valuable information.

Diatomic species.   In the Raman effect, unlike infrared absorption, the presence of a dipole moment is not necessary for the appearance of the single

[52] Houston and Lewis, *Proc. Nat. Acad. Sci.*, 1931, **17**, 229.

[53] Andrychuk, *Canad. J. Phys.*, 1951, **29**, 151.

[54] Stoicheff, *ibid.*, 1954, **32**, 330.

[55] *Idem, ibid.*, p. 630.

[56] Möller and Stoicheff, *ibid.*, p. 635.

[57] Welsh, Stansbury, Romanko, and Feldman, *J. Opt. Soc. Amer.*, 1955, **45**, 338.

[58] Cumming and Welsh, *J. Chem. Phys.*, 1953, **21**, 1119.

[59] Stoicheff, Cumming, St. John, and Welsh, *ibid.*, 1952, **20**, 498.

[60] Feldman, Romanko, and Welsh, *Canad. J. Phys.*, 1955, **33**, 138.

[61] Fermi, *Z. Physik*, 1931, **71**, 250.

vibrational fundamental. Homonuclear diatomic molecules (type A_2) investigated recently by this method are F_2[53] and Cl_2.[62] Molecules of type AB include ClF [63] and BrCl.[64] Notable amongst charged species of this type is the nitrosonium ion NO^+.[34, 35, 65]

Triatomic species. For types A_3 and AB_2, if linear and symmetrical (point group $D_{\infty h}$), the selection rules permit only ν_1 as a single polarised line (cf. Fig. 1). For less symmetrical shapes all three fundamentals are permitted. Familiar examples of linear symmetrical molecules are CO_2 and CS_2 ; yet for neither does the Raman spectrum consist of the expected single polarised line. For CO_2 a doublet is found [66] owing to Fermi resonance between ν_1 and the fortuitously nearly equal $2\nu_2$. For liquid CS_2 a similar doublet occurs [67] for the same reason, and the forbidden ν_2 has also been detected [68] as a very feeble line. The selection rule for the free molecule evidently loses its strict validity because of molecular interactions in the liquid.

This account of complications occurring for such simple molecules may perhaps give the impression that all conclusions from Raman spectra about molecular symmetry are necessarily dubious. Such, however, is by no means the case. An interesting example is N_2O. This is known from *X*-ray evidence to be linear, and as it is isoelectronic with CO_2 a symmetrical structure might be expected. The Raman spectrum, however, shows [69] two widely separated polarised lines, both too strong to be explained as other than fundamentals. This at once excludes the symmetrical structure. The two Raman lines coincide in frequency with infrared absorptions, showing again that the molecule cannot have a centre of symmetry. Its structure must be N–N–O. For this all three fundamentals are permitted in the Raman effect. The third is evidently too weak to have been observed so far. Examples of linear symmetrical molecules of type AB_2 recently investigated are the halides of zinc in non-ionising solvents.[70]

If a molecule AB_2 is symmetrical but bent, all three fundamentals are permitted (two polarised). This is found, for example, with SO_2,[71] SCl_2,[72] and the ion NO_2^-.[73] On the other hand, the spectra show that the ions N_3^-,[74] NO_2^+,[30] and BO_2^-[75] are linear and symmetrical.

Species of type ABC may be either linear ($C_{\infty v}$: 3 lines, 2 polarised) or bent (C_s : 3 lines, all polarised). Linear examples whose Raman spectra

[62] Stammreich, Sala, and Forneris, *Anais Acad. Brazil Cienc.*, 1953, **25**, 375.
[63] Jones, Parkinson, and Burke, *J. Chem. Phys.*, 1950, **18**, 235.
[64] Stammreich and Forneris, *ibid.*, 1953, **21**, 944.
[65] Gerding, *J. Phys. Radium*, 1954, **15**, 406.
[66] Langseth and Nielsen, *Z. phys. Chem.*, 1932, B, **19**, 427.
[67] Giulotto and Caldirola, *ibid.*, 1941, B, **49**, 34.
[68] Wood and Collins, *Phys. Rev.*, 1932, **42**, 386.
[69] Cabannes and Rousset, *J. Phys. Radium*, 1940, **1**, 210.
[70] Delwaulle, *Compt. rend.*, 1955, **240**, 2132 ; *Bull. Soc. chim.*, 1955, 1294.
[71] Wagner, *Z. phys. Chem.*, 1943, A, **193**, 55.
[72] Stammreich, Forneris, and Sone, *J. Chem. Phys.*, 1955, **23**, 972.
[73] Langseth and Walles, *Z. phys. Chem.*, 1934, B, **27**, 209.
[74] Langseth, Nielsen, and Sorensen, *ibid.*, p. 100.
[75] Nielsen and Ward, *J. Chem. Phys.*, 1937, **5**, 201.

have been studied include ClCN [76, 77] and BrCN,[76, 78] as well as mixed halides like ClHgBr to which reference has already been made.[21] A number of molecules (ONCl, etc.) are known from other evidence to be non-linear ; but, if we except isotopically substituted species like DOH, etc., none appears as yet to have been investigated by the Raman method.

Tetra-atomic species. The only molecule of type A_4 to have been investigated is P_4. For both the tetrahedral model (T_d) and the plane square (D_{4h}) three fundamentals are permitted, one being polarised. Nevertheless a distinction is in principle possible, because for the first model the polarised line should have $\rho = 0$, whereas for the second it should have $\rho \neq 0$. In fact three lines are observed,[79] of which two are depolarised and the other has $\rho = 0$ within the limits of experimental accuracy. The Raman evidence thus favours the tetrahedral model, in accordance with the conclusion reached by other methods.

For species of type AB_3 a discrimination is possible between the symmetrical planar (D_{3h}) and pyramidal (C_{3v}) structures. For the former, 3 lines are permitted (one polarised), whereas for the latter 4 are permitted (2 polarised). A planar example is BF_3. It is true that only two of the three permitted fundamentals have so far been observed ; [80] but convincing evidence as to structure is afforded by the observation that one of the fundamentals shows no isotopic splitting due to [10]B and [11]B. In the corresponding vibrational mode, therefore, the boron atom must remain at rest. This is only possible for the " breathing " mode of the symmetrical planar structure. Other planar species are CO_3^{2-} [81] and NO_3^-.[81] Spectra characteristic of the pyramidal model are given by the Group V halides, *e.g.*, the recently investigated NF_3,[82] and the ions ClO_3^-, BrO_3^-, and IO_3^-.[83]

The interesting molecule ClF_3 has been found [84] to give at least five Raman lines, a result which rules out the above types of structure. Microwave evidence has recently shown this molecule to be T-shaped (C_{2v}), for which six Raman fundamentals are permitted.

C_2N_2 furnishes an example [85] of a linear symmetrical molecule of type A_2B_2 ($D_{\infty h}$). Here three fundamentals are permitted in the Raman effect, two being polarised. The spectrum of H_2O_2 shows [86] a larger number of lines, indicating a less symmetrical shape. The results for this molecule, as also for H_2S_2 [87] and S_2Cl_2,[88] have been interpreted in terms of a zigzag ABBA

[76] West and Farnsworth, *J. Chem. Phys.*, 1933, **1**, 402.
[77] Wagner, *Z. phys. Chem.*, 1941, *B*, **48**, 309.   [78] *Idem, ibid.*, 1943, *A*, **193**, 55.
[79] Venkateswaran, *Proc. Indian Acad. Sci.*, 1935, *A*, **2**, 260 ; 1936, *A*, **4**, 345.
[80] Yost, DeVault, Anderson, and Lassettre, *J. Chem. Phys.*, 1938, **6**, 424.
[81] Kujumzelis, *Z. Physik*, 1938, **109**, 586 ; Bacchus and Kastler, *Compt. rend.*, 1945, **220**, 398.   [82] Pace and Pierce, *J. Chem. Phys.*, 1955, **23**, 1248.
[83] Shen, Yao, and Wu, *Phys. Rev.*, 1937, **51**, 235.
[84] Jones, Parkinson, and Murray, *J. Chem. Phys.*, 1949, **17**, 501.
[85] Langseth and Möller, *Acta Chem. Scand.*, 1950, **4**, 725.
[86] Simon and Kriegsmann, *Naturwiss.*, 1955, **42**, 12.
[87] Feher and Baudler, *Z. Elektrochem.*, 1941, **47**, 844.
[88] Gerding and Westrik, *Rec. Trav. chim.*, 1941, **60**, 701 : for interpretation see also Bernstein and Powling, *J. Chem. Phys.*, 1950, **18**, 1018 ; Luft and Todhunter, *ibid.*, 1953, **21**, 2225.

model twisted so that the two B–A bonds are not in the same plane (C_2 : 6 lines, 4 polarised), rather than the planar *cis*-form (C_{2v} : 6 lines, 3 polarised) : but the Raman data appear to be inadequate to establish the former definitely.

The type ABC_2 may be planar Y-shaped (C_{2v} : 6 lines, 3 polarised, *e.g.*, $COCl_2$ [89] and FNO_2 [90]) or pyramidal (C_s : 6 lines, 4 polarised). The difference in the number of polarised lines has been used [91] to prove the pyramidal shape of $SOCl_2$. Other molecules of this kind that have been investigated recently include SOF_2 [92] and $SeOF_2$.[11] The solid of composition $POCl_3,SbCl_5$ is found [93] to show none of the Raman lines of either $POCl_3$ or $SbCl_5$: and it is therefore supposed to have the ionic form $(POCl_2{}^+)$ $(SbCl_6{}^-)$, involving a positive ion which is isoelectronic with $SOCl_2$.

Penta-atomic species. Most molecules and ions of type AB_4 have been found to show the characteristic pattern (4 lines, 1 completely polarised) of the regular tetrahedral shape (T_d). Examples are all the tetrahalides of Group IV elements and the corresponding complex halide ions of elements of Groups II and III. Recently studied ions include $ZnBr_4{}^{2-}$ and $ZnI_4{}^{2-}$,[94] $BF_4{}^-$,[95] $AlH_4{}^-$,[96] $AlCl_4{}^-$,[97] $GaBr_4{}^-$,[98] $InBr_4{}^-$,[99] and $TlBr_4{}^-$.[100] A complex ion of plane square shape whose Raman spectrum has been obtained is $AuCl_4{}^-$. The result [101] is in harmony with expectation (D_{4h} : 3 lines, 1 polarised).

In view of the prevalence of such highly symmetrical shapes for species of types AB_4, it is interesting that SeF_4 shows [102] a larger number of lines, indicating lower symmetry. This molecule has a valency shell of 10 electrons (compared with 8 for symmetry T_d) and it is evident that the " lone pair " plays a stereochemical rôle. The observed Raman spectrum indicates that the type here is either $AB_2B'_2$ (C_{2v}) or ABB'_3 (C_{3v}). Similar results have very recently been obtained for SF_4.[103] The spectrum of fused $TeCl_4$ has also been investigated [104] and interpreted in terms of ionisation to give pyramidal $TeCl_3{}^+$; but this interpretation leaves some weaker lines unexplained.

Type A_2B_3 is represented by carbon suboxide, C_3O_2, recent work upon

[89] Nielsen, Burke, Woltz, and Jones, *J. Chem. Phys.*, 1952, **20**, 596.
[90] Dodd, Rolfe, and Woodward, *Trans. Faraday Soc.*, 1956, **52**, 145.
[91] McDowell, *ibid.*, 1953, **49**, 371 ; Allen and McDowell, *J. Chem. Phys.*, 1955, **23**, 209.
[92] Bender and Wood, *ibid.*, p. 1316.
[93] Maschka, Gutmann, and Sponer, *Monatsh.*, 1955, **86**, 52.
[94] Delwaulle, *Compt. rend.*, 1955, **240**, 2132.
[95] Edwards, Morrison, Ross, and Schultz, *J. Amer. Chem. Soc.*, 1955, **77**, 266.
[96] Lippincott, *J. Chem. Phys.*, 1949, **17**, 1351.
[97] Gerding and Houtgraaf, *Rec. Trav. chim.*, 1953, **72**, 21.
[98] Woodward and Nord, *J.*, 1955, 2655.
[99] Woodward and Bill, *J.*, 1955, 1699.
[100] Delwaulle, *Compt. rend.*, 1954, **238**, 2522.
[101] Goulden, Maccoll, and Millen, *J.*, 1950, 1635.
[102] Rolfe, Woodward, and Long, *Trans. Faraday Soc.*, 1953, **49**, 1388.
[103] Dodd, Woodward, and Roberts, *ibid.*, in the press.
[104] Gerding and Houtgraaf, *Rec. Trav. chim.*, 1954, **73**, 737.

which [105] has been interpreted on the basis of a linear structure ($D_{\infty h}$: 3 fundamentals, 2 polarised). Other 5-atomic types are ABC_3, which may either have a 3-fold axis (C_{3v}: 6 lines, 3 polarised; e.g., SiIBr$_3$ [13] and VOCl$_3$ [106]) or be planar (C_s: 9 lines, 3 polarised, e.g., nitric acid O_2NOH [107]); and AB_2C_2 (C_{2v}: 9 lines, 4 polarised), examples being SiCl$_2$I$_2$,[108] SO$_2$Cl$_2$,[109] and SO$_2$F$_2$.[110]

Hexa-atomic species. Some AB_5 molecules are found to have Raman spectra according with the trigonal bipyramidal shape (D_{3h}: 6 lines, 2 polarised). Examples are liquid PCl$_5$ and SbCl$_5$.[111] Solid PCl$_5$, on the other hand, gives more lines,[112] interpretable in terms of the ionic structure $(PCl_4^+)(PCl_6^-)$. Recent investigations of the interesting molecules BrF$_5$ [113] and IF$_5$ [114] show with considerable certainty that the shape in both cases involves a tetragonal pyramid (C_{4v}). The number of lines and the number polarised are in agreement with the requirements (9 lines, 3 polarised) for this model.

An example of type A_2B_4 is hydrazine. From a recent consideration [115] of the selection and polarisation rules for the four N–H stretching modes, and from the observation that the intensities are temperature-dependent, it has been concluded that the solid contains only *trans*-molecules, but that in the liquid other rotational isomers are also present.

Hepta-atomic species. Group VI hexafluorides (type AB_6) give the expected spectrum [116] for the regular octahedral model (O_h: 3 lines, 1 polarised). It so happens that a plane hexagonal model (D_{6h}) would give the same result. A distinction (hardly necessary in view of other evidence) is possible, because for O_h (unlike D_{6h}) the polarised line must have $\rho = 0$ and also because the infrared selection rules differ. In view of the extra electron of the rhenium atom as compared with molybdenum, it is interesting that the recently observed Raman spectrum of ReF$_6$ [117] is (like that of MoF$_6$) in accordance with the regular octahedral structure. As expected, the same symmetry is found for the ions SnCl$_6^{2-}$ [118] and SbCl$_6^-$.[119] It has also been reported for SeCl$_6^{2-}$ [120]—a remarkable result in view of the

[105] Long, Murfin, and Williams, *Proc. Roy. Soc.*, 1954, A, **223,** 251; but compare Rix, *J. Chem. Phys.*, 1954, **22,** 429.
[106] Eichoff and Weigel, *Z. anorg. Chem.*, 1954, **275,** 267.
[107] Cohn, Ingold, and Poole, *J.*, 1952, 4272; Fréjacques, *Compt. rend.*, 1952, **234,** 1769.
[108] Delwaulle, Buisset, and Delhaye, *J. Amer. Chem. Soc.*, 1952, **74,** 5768.
[109] Cabannes and Rousset, *Ann. Physique*, 1933, **19,** 229.
[110] Bender and Wood, *J. Chem. Phys.*, 1955, **23,** 1316.
[111] Siebert, *Z. anorg. Chem.*, 1951, **265,** 303.
[112] Gerding and Houtgraaf, *Rec. Trav. chim.*, 1955, **74,** 5.
[113] Stephenson and Jones, *J. Chem. Phys.*, 1952, **20,** 1830.
[114] Lord, Lynch, Schumb, and Slowinski, *J. Amer. Chem. Soc.*, 1950, **72,** 522.
[115] Wagner and Bulgozdy, *J. Chem. Phys.*, 1951, **19,** 1210.
[116] Yost, Steffens, and Gross, *ibid.*, 1934, **2,** 311; Burke, Smith, and Nielsen, *ibid.*, 1952, **20,** 447.
[117] Gaunt, *Trans. Faraday Soc.*, 1954, **50,** 209.
[118] Mathieu and Cornevin, *J. Chim. phys.*, 1939, **36,** 271.
[119] Redlich, Kurz, and Rosenfeld, *Z. phys. Chem.*, 1932, B, **19,** 231.
[120] Redlich, Kurz, and Stricks, *Sitzungsber. Akad. Wiss. Wien, Abt.* 2b, 1937, **146,** 447.

structural difference between SeF_4 and the Group IV tetrahalides (see above).

An example of type A_2B_5 is dinitrogen pentoxide. Raman spectra show that in the solid [32] and in nitric acid solution [33] this exists as the ions NO_2^+ and NO_3^-. The spectrum of the undissociated N_2O_5 molecule has not been elucidated.

Octa-atomic species. A unique position is occupied by S_8 (sulphur as solid and in solution) whose Raman spectrum can be interpreted [121] in terms of the puckered octagon model (D_{4d} : 7 lines, 2 polarised).

One compound of type AB_7 has been studied, namely, iodine heptafluoride.[114] Seven Raman lines are observed, of which two are polarised. Consideration of the selection rules for various models leads to the conclusion that the shape is most probably a pentagonal bipyramid (D_{5h} : 7 lines, 2 polarised, as observed).

The type A_2B_6 can be briefly exemplified by the contrasted molecules C_2Cl_6 and B_2H_6. For the former an ethane-like structure may be assumed : the rules of selection and polarisation are then for the staggered form (D_{3d}), 6 lines permitted, 3 polarised ; and for either the eclipsed form (D_{3h}) or for free rotation about the C–C bond (D'_{3h}), 9 lines, 3 polarised. Experiment [122] shows 3 polarised and 3 depolarised lines. Thus, unless we make the unlikely assumption that three depolarised lines have escaped observation, the spectrum establishes that the molecule has the staggered configuration. On the interesting question of the structure of B_2H_6 the Raman effect has given valuable evidence. As was first shown by Bell and Longuet-Higgins,[123] the observations exclude an ethane-like model and favour a bridge structure $H_2BH_2BH_2$ (D_{2h} : 9 lines, 4 polarised). Molecules such as Ga_2Cl_6 [124] are probably similarly bridged.

Species with more than 8 atoms. With increasing number of nuclei the spectra tend to become less simple ; but useful information on structure can still be obtained, especially where there is high symmetry. Thus for the nona-atomic species $Ni(CO)_4$ the presence of just two completely polarised lines [125] at once establishes the regular tetrahedral configuration (T_d : 8 lines, 2 with $\rho = 0$). By way of contrast, the spectrum [126] of the $Pt(CN)_4^{2-}$ ion supports a plane square configuration (D_{4h} : 7 lines, 2 with $0 < \rho < 6/7$).

Conclusion. Not all the observed Raman spectra, even of species belonging to the types referred to above, are as yet completely understood. Nevertheless, it is hoped that the examples quoted will have served to show that, for the investigation of molecular symmetry, Raman spectroscopy is a widely applicable method capable of furnishing valuable independent evidence to supplement that obtained in other ways.

[121] Bernstein and Powling, *J. Chem. Phys.*, 1950, **18**, 1018.

[122] Hamilton and Cleveland, *ibid.*, 1944, **12**, 249.

[123] Bell and Longuet-Higgins, *Proc. Roy. Soc.*, 1945, *A*, **183**, 357 ; see also Lord and Nielsen, *J. Chem. Phys.*, 1951, **19**, 1.

[124] Gerding, Haring, and Renes, *Rec. Trav. chim.*, 1953, **72**, 78.

[125] Crawford and Horwitz, *J. Chem. Phys.*, 1948, **16**, 147.

[126] Mathieu and Cornevin, *J. Chim. phys.*, 1939, **36**, 271, 308.