Vibrational Infrared and Raman Spectroscopy in Inorganic Chemistry

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1 Introduction

A brief survey of recently published papers in inorganic chemistry indicates that, where i.r. and Raman spectra are reported, one of the principal interests lies in the use of these data as an aid to structural assignment. It is therefore important to consider from the outset how vibrational spectroscopy compares with other methods of structure determination for solids, liquids, and gases. It is also worth noting that one diffraction or microwave study may be of far greater fundamental significance than a collection of several papers using vibrational spectroscopy in a qualitative manner.

Table 1 summarizes several techniques of importance in structure determination.[1-16] Various less important methods have not been included, for example

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[1] See, for example, M. M. Woolfson, 'X-ray Crystallography', C.U.P., Cambridge, 1970.

[2] G. E. Bacon, 'Neutron Diffraction', O.U.P., Oxford, 1972; G. E. Bacon, *Adv. Struct. Res. Diffraction Methods*, 1966, **2**, 1.

[3] L. S. Bartell, in 'Physical Methods of Chemistry', Part III D, Volume 1, ed. A. Weissberger and B. W. Rossiter, Wiley, New York, 1972; also K. Kuchitsu in 'Molecular Structures and Vibrations', ed. S. J. Cyvin, Elsevier, Amsterdam, 1972; S. H. Bauer and A. L. Andreassen, *J. Phys. Chem.*, 1972, **76**, 3099; R. L. Hildebrandt and R. A. Bonham, *Ann. Rev. Phys. Chem.*, 1971, **22**, 279.

[4] A. J. Careless, M. C. Green, and H. W Kroto, *Chem. Phys. Letters*, 1972, **16**, 414.

[5] K. Kimura, K. Katada, and S. H. Bauer, *J. Amer. Chem. Soc.*, 1966, **88**, 416.

[6] C. Glidewell, A. G. Robiette, and G. M. Sheldrick, *Chem. Phys. Letters*, 1972, **16**, 526.

[7] J. Kraitchman, *Amer. J. Phys.*, 1953, **21**, 17; C. C. Costain, *J. Chem. Phys.*, 1958, **29**, 864.

[8] C. H. Townes and A. L. Schawlow, 'Microwave Spectroscopy', McGraw-Hill, New York, 1955; T. M. Sugden and C. N. Kenney, 'Microwave Spectroscopy of Gases', Van Nostrand, New York, 1965.

[9] See, for example, G. Herzberg, 'Infrared and Raman Spectra', Van Nostrand, New York, 1945.

[10] G. Herzberg, 'Electronic Spectra of Polyatomic Molecules', Van Nostrand, New York, 1966; D. M. Gruen, in 'Progress in Inorganic Chemistry', ed. S. Lippard, Wiley, New York, 1971, Vol. 14.

[11] J. A. Pople, W. G. Schneider, and H. J. Bernstein, 'High Resolution Nuclear Magnetic Resonance, Spectroscopy', McGraw-Hill, New York, 1959; J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy', Pergamon, Oxford, 1965.

[12] B. F. G. Johnson, J. Lewis, I. G. Williams, and J. M. Wilson, *J. Chem. Soc.* (*A*), 1967, 341.

[13] R. T. Grimley, D. W. Muenow, and J. L. La Rue, *J. Chem. Phys.*, 1972, **56**, 490.

[14] E. L. Muetterties, *Inorg. Chem.*, 1965, **4**, 769; S. E. Schwartz, *J. Chem. Educ.*, 1973, **50**, 609.

[15] P. Diehl and C. L. Khetrepal, in 'N.M.R. Basic Principles and Progress', ed. P. Diehl, E. Fluck, and R. Kosfeld, Springer-Verlag, Berlin, 1969; see also A. Pines, M. G. Gibby, and J. S. Waugh, *J. Chem. Phys.*, 1972, **56**, 1776.

[16] A. Weiss, *Angew. Chem. Internat. Edn.*, 1972, **11**, 607.

Table 1 *Comparison of some physical techniques for structural studies*

Technique	*Nature of the Effect*	*Information*	*Interaction time*[a]	*Sensitivity*[b]	*Comments*
X-Ray diffraction	Scattering, mainly by electrons, followed by interference ($\lambda = 0.1$—10 Å)	Electron density map of crystal	10^{-18} s but averaged over vibrational motion	crystal *ca.* 10^{-3} cm^3	Location of light atoms or distinction between atoms of similar scattering factor difficult in presence of heavy atoms[1]
Neutron diffraction	Scattering, mainly by nuclei, followed by interference ($\lambda = 1$ Å)	Vector internuclear distances	10^{-18} s but averaged over vibrational motion	crystal *ca.* 1 cm^3	Extensively used to locate hydrogen atoms. May give additional information due to spin $\frac{1}{2}$ on neutron leading to magnetic scattering[2]
Electron diffraction	Diffraction (atom or molecule) mainly by nuclei, but also by electrons ($\lambda = 0.1$—1 Å)	Scalar distances due to random orientation	10^{-18} s but averaged over vibrational motion	1 Torr	Thermal motions cause blurring of distances. Preferably only one (small) species present. Heavy atoms easy to detect[3–6]

[a] Classical time-scale. In the absence of a transition probability factor apparently violates the uncertainty principle.[14]
[b] 1 Torr = 3×10^{16} mol cm^{-3}, mean free path 0.1 nm.

Microwave	Absorption of radiation due to dipole change during rotation ($\lambda = 0.1$—30 cm; 300—1 GHz in frequency)	Mean value of r^{-2} terms; potential function.[7]	10^{-10} s	10^{-4} Torr	Mean value of r^{-2} does not occur at r_e even for harmonic motion. Dipole moment necessary. Only one component may be detected. Analysis difficult for large molecules of low symmetry[8]
Vibrational infrared	Absorption of radiation due to dipole change during vibration ($\lambda = 10^{-1}$—10^{-4} cm)	Qualitative for large molecules	10^{-13} s	1 Torr	Useful for characterization. Some structural information from number of bands, position and possibly isotope effects. All states of matter[9]
Vibrational Raman	Scattering of radiation with changed frequency due to polarizability change during a vibration (λ = visible usually)	Qualitative for large molecules	10^{-14} s	100 Torr[c] (ν^4 dependent)	Useful for characterization. Some structural information from number of bands, position, depolarization ratios, and possibly isotope effects. All states of matter

[c] Resonance Raman 1 Torr.

Table 1 (*continued*)

Electronic	Absorption of radiation due to dipole change during an electronic transition ($\lambda = 10^2$—10^3 Å)	Qualitative for large molecules	10^{-15} s	10^{-2} Torr[d]	Useful for characterization. Some structural information from number of bands and position. All states of matter[10]
Nuclear magnetic resonance	Interaction of radiation with a nuclear transition in a magnetic field ($\lambda = 10^2$—10^7 cm; 3 KHz to 300 MHz)	Number of magnetically equivalent nuclei in each environment[e]	10^{-1}—10^{-9} s	10 Torr (^{1}H)	Applicable to solutions and gases.[f] In conjunction with molecular weight measurements may be possible to choose one from several possible models[11]
Mass spectrometry	Detection of fragments by charge/mass	Mass number, plus fragmentation patterns	—	10^{-11} Torr	Useful for characterization of species in a vapour, complicated by reactions in spectrometer. Does not differentiate isomers directly. Important for detecting hydrogen in a molecule[12,13]

[d] Allowed transition (in absorption).

[e] For separate resonances to be observed $\tau_A \gg (\omega_A - \omega_B)^{-1} \ll \tau_B$ where $(\omega_A - \omega_B)/2\pi$ is the chemical shift difference (cycles per second) and τ_A and τ_B are mean life times on sites A and B. For multiplet structure $\tau_A \gg J^{-1}{}_{AB} \ll \tau_B$ where J_{AB} is the spin–spin coupling constant.

[f] Geometrical data are available from liquid-crystal studies,[15] also solids.[16]

Mössbauer,[17] photoelectron,[18] nuclear quadrupole resonance,[19] resonance fluorescence,[20] and e.s.r.[21] spectroscopy and molecular-beam electric deflection.[22] In addition, ancillary measurements such as molecular weight, dipole moment, conductance, and chemical analysis are important. For the solid state, where single crystals are obtainable, *X*-ray crystallography is the definitive technique. For solutions and melts n.m.r. spectroscopy may give unambiguous assignment of the molecular shape. In the gas phase, electron diffraction and microwave spectroscopy are of great value. Used in a qualitative manner the major value of i.r., Raman, and electronic spectroscopy is the ability to span all phases. Certainly, the less one is able to apply *X*-ray crystallography (owing to inability to grow single crystals for example), n.m.r. spectroscopy (owing to lack of magnetic nuclei or to exchange processes), electron diffraction (owing to the presence of several species in the vapour or large thermal amplitudes of vibration), and microwave spectroscopy (owing to lack of a dipole moment or the difficulty of analysis of data) so the more important becomes the qualitative approach. Another feature of interest is the level at which detection is possible in a routine study. In this respect mass spectrometry is unique. Double-resonance experiments using resonance fluorescence may result in detection levels below 10^{-8} Torr. In-cavity studies using laser techniques can lead to greatly improved detection levels in absorption experiments, while photoelectron spectroscopy, with detection levels of the order of 10^{-4} Torr, is becoming increasingly important for studying high-temperature species.[23]

In principle, it is possible to obtain quantitative information from the 'qualitative' techniques given in Table 1. Detailed information on molecular geometry may be obtained from rotational analysis of (i) a rotational spectrum (microwave), (ii) a vibrational band (i.r. and Raman), and (iii) a vibrational band of an electronic transition (electronic). The difficulty of the analysis is frequently iii > ii > i. There are also experimental problems.

The natural linewidth is given by[24]

$$\frac{\Delta E}{h} = \frac{1}{2\pi\tau} = \Delta\nu_{\frac{1}{2}}$$

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[17] V. I. Goldanski and R. H. Herber, 'Chemical Applications of Mössbauer Spectroscopy', Academic Press, New York, 1968.

[18] C. R. Brundle, *Appl. Spectroscopy*, 1971, **25**, 8; J. P. Maier and D. W. Turner, *J.C.S. Faraday II*, 1972, **68**, 711; D. G. Tinsley and R. A. Walton, *J.C.S. Dalton*, 1973, 1039.

[19] E. A. C. Lucken, 'Nuclear Quadrupole Coupling Constants', Academic Press, New York, 1969; W. van Bronswyk, *Structure and Bonding*, 1970, **7**, 87.

[20] R. F. Barrow, I. R. Beattie, W. G. Burton, and T. Gilson, *Trans. Faraday Soc.*, 1971, **67**, 583.

[21] A. Carrington and A. D. McLachlan, 'Introduction to Magnetic Resonance', Harper and Row, London, 1967.

[22] A. Büchler, J. L. Stauffer, W. Klemperer, and L. Wharton, *J. Chem. Phys.*, 1963, **39**, 2299; A. Büchler, J. L. Stauffer, and W. Klemperer, *ibid.*, 1964, **40**, 3471.

[23] T. P. Fehlner and D. W. Turner, *J. Amer. Chem. Soc.*, 1973, **95**, 7175; J. Berkowitz, J. L. Dehmer, and T. E. Walker, *J. Chem. Phys.*, 1973, **59**, 3645.

[24] See, for example, A. Carrington, 'Microwave Spectroscopy of Free Radicals', Academic Press, London, 1974.

where τ is the mean life in a given state, ΔE is the spread of energies in that state, and $\Delta\nu_{\frac{1}{2}}$ is the half-width of the spectral band. The lifetime for an isolated molecule in an excited state is given in terms of the Einstein A coefficient for spontaneous emission:

$$\tau = \frac{1}{A} = \frac{3hc^3}{64\pi^4\nu^3|\mu|^2}$$

(where μ is the appropriate electric transition moment). In the microwave or molecular rotation region ($\nu = 10^{10}$ Hz, $\lambda = 3$ cm) this gives a value *ca.* 10^{-8} Hz for $\Delta\nu_{\frac{1}{2}}$, which is negligible. Even in the near u.v. ($\lambda = 4000$ Å, 25 000 cm^{-1}) $\Delta\nu_{\frac{1}{2}}$ is still only of the order of 10^{-4} cm^{-1}.* However, Doppler broadening occurs due to the variable velocity component, v, of the random thermal motion of the molecules (relative to the detector). At room temperature for a molecular weight of 100 the average molecular velocity is *ca.* 2.5×10^4 cm s^{-1}. In the microwave region this leads to a value of *ca.* 10 kHz for $\Delta\nu_{\frac{1}{2}}$ ($\simeq \frac{v}{c} . \nu$) whereas at 4000 Å it is *ca.* 1 GHz (or, dividing by the velocity of light, 0.03 cm^{-1}) which is becoming serious for high-resolution studies. Formally the averaged effect on the linewidth for Doppler broadening is given by

$$\Delta\nu_{\frac{1}{2}} = 7.15 \times 10^{-7}\,(T/M)^{\frac{1}{2}}\nu$$

where T is the absolute temperature and M is the molecular weight.

The case of collision broadening is more complicated. It may be thought of as arising because a molecule emitting (or absorbing) a wave train undergoes a collision which destroys the phase coherence of the wave so that ΔE becomes correspondingly greater. Alternatively it may be considered as knocking a molecule from one quantum state to another, τ again becoming shorter and ΔE correspondingly larger. Using elementary collision theory one molecule in a gas of mol. wt. 150 at 700 K and 1 atm. pressure will suffer on average one collision every nanosecond. Using the approximate relationship $\Delta\nu_{\frac{1}{2}}\tau = 1$ this gives an uncertainty in the energy of 1 GHz or 0.03 cm^{-1}. A rough rule is that at room temperature pressure broadening is *ca.* 10 MHz Torr^{-1}. It must be remembered that broadening mechanisms will be different for i.r. and Raman bands and that *Q*-branches may be affected differently from rotational branches.

The klystron provides tunable radiation in the microwave region with the frequencies capable of being measured to the order of 1 part in 10^7, leading to precise determination of molecular geometry (*e.g.* 'bond lengths' to a precision of ± 0.001 Å, the limitation lying in the model used, not the data).

The increased availability of tunable, narrow-width lasers of relatively high power is potentially capable of transforming high-resolution spectroscopy from the u.v. through the visible to the i.r. and even into the microwave region. A variety of sophisticated experiments is possible and a few of these will be outlined to illustrate the power of such techniques. The most obvious application

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*In line with common practice, ν is used for both frequency (c/λ) and wavenumber ($1/\lambda$).

is an absorption experiment with the laser tuning used, instead of a conventional grating, to vary the wavelength. Thus commercial dye lasers are available, pumped with an argon laser and continuously variable through the visible region with linewidths of < 1 Å and powers of the order of hundreds of mW. The linewidth can be reduced by use of an etalon in the cavity. Similarly, pulsed tunable dye lasers, pumped by a nitrogen laser, with bandwidths of < 0.004 Å have been described.[25] However, much more exciting experiments are possible, making use of the very narrow linewidth, high power, and directional properties of lasers. In particular, Doppler broadening effects can be drastically reduced by the use of saturation phenomena, two-photon phenomena (whereby using two laser beams in opposite directions the component of the Doppler velocity cancels out) or molecular-beam techniques.

Saturation experiments, such as the Lamb dip phenomenon, can be used to reduce effective linewidths if they are Doppler broadened.[26] Consider the laser radiation, in a multipass system, interacting with molecules in the gas phase. This may be in an 'in-cavity' experiment or a 'saturating beam' may pass in one direction while the (weaker) analysis beam passes in the opposite direction. Either side of an absorption maximum the molecular absorption frequency will equal the (narrow, monochromatic) laser frequency for molecules with velocity components $\nu \pm \Delta\nu$ in *either* direction along the laser (photon) axis (where $\Delta\nu$ refers to the energy spread of the laser beam, not the Doppler-broadened absorption under study). By contrast, when the laser is tuned precisely to the centre of an absorption maximum, only waves $\nu_{\max} \pm \Delta\nu$ (*i.e.* one group of molecules, not two groups as before) are at the laser frequency. This means there is a sharp dip in the absorption curve at the band maximum if the first pass has already saturated the molecules of $\nu_{\max} \pm \Delta\nu$. As this is the centre of the Doppler-broadening band it corresponds to a Doppler velocity of $v = 0\ (\pm\ \Delta\nu)$ where the molecules are moving transversely to the light beam. Thus using saturation by the intracavity field, locking a maser on the 3.39 μm rotation–vibration line of methane [$P(7)$ of ν_3] gave a reproducibility[27] of better than 1 in 10^{11} (2.5 orders of magnitude better than the primary standard of length) and a linewidth of *ca.* 150 kHz—*i.e.* $\Delta\nu_{\frac{1}{2}}/\nu = 10^{-9}$. Similarly, using a magnetically tuned He/Ne maser, the Stark effect in methane (which has no permanent electric dipole) can be observed on one component at 2947.802 cm^{-1} of this $P(7)$ line.[28]

2 Vibrational Infrared and Raman Spectroscopy

Although vibrational spectroscopy is a relatively poor technique for structural studies it is important principally because it is a 'fast technique' in terms of stereochemical non-rigidity of molecules and because of its wide application.

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[25] T. W. Hansch, *Appl. Optics*, 1972, **11**, 895.

[26] See, for example, W. Demtröder, 'Laser Spectroscopy Topics in Current Chemistry', No. 17, Springer-Verlag, Berlin, 1971; see also J. E. Bjorkholm and P. F. Liao, *I.E.E.E.J. Quantum Electronics*, in the press.

[27] K. Shimoda, Quantum Electronics Conference, Montreal, 1972.

[28] K. Uehara, K. Sakurai, and K. Shimoda, *J. Phys. Soc. Japan*, 1969, **26**, 1018.

It may be applied, for example, to open- and closed-shell compounds, to ions, to solids, liquids, solutions, and gases, to sorbed species and to species isolated in a matrix. Formally the amount of information present in a vibrational spectrum is considerable—it is the inability to interpret it that is at fault. For chemically interesting molecules the interpretation of the vibrational spectrum is essentially at a 'balls and springs' level. Intensity, half-width, band contour, and band position are frequently not understood in sufficient detail. Even for diatomic molecules the relationship between bond strength, force constant, and bond order is at best qualitative.

Nonetheless, the design of i.r. and Raman spectrometers to cover the frequency range 4000—50 cm^{-1} has now reached the stage that such investigations are almost routine. The only obvious advances yet to come appear to be the introduction of fully tunable lasers and an extension of interferometric techniques. It is evident that vibrational spectroscopy is likely to be even more extensively used in the future and it is reasonable to attempt to assess the value of this technique and its future application.

For a vibration to be observed in the i.r. spectrum the molecular dipole moment must change during the vibration under study. Put in a more formal way choosing real wavefunctions, integrals of the type

$$(\mu_x)_{ij} = (\partial\mu_x/\partial Q_k)_0 \int \psi_v{}^i . Q_k . \psi_v{}^j . d\tau$$

must be non-zero where $(\mu_x)_{ij}$ is the transition moment, $\mu'_x = (\partial\mu_x/\partial Q_k)_0$ is the magnitude of the x-component of the dipole moment derivative with respect to the appropriate normal co-ordinate Q_k, and i and j refer to two vibrational states; $d\tau$ is a volume element in configurational space and integration is over the whole of this space. (In general for an integral of the type $f_A f_B . d\tau$ to be non-zero the integrand must be invariant to all symmetry operations of the symmetry group to which the molecule belongs.) If i is the ground state, $\psi_v{}^i$ is totally symmetric. For the direct product $Q_k . \psi_v{}^j$ to contain the totally symmetric representation both Q_k and $\psi_v{}^j$ must belong to the same irreducible representation. Clearly, for this to be so, $\psi_v{}^j$ must have the same symmetry as the normal co-ordinate. Further, i and j must differ so that $\Delta v = 1$, for simple harmonic eigenfunctions.

Neglecting rotational quantization, the i.r. absorption intensity of a particular fundamental mode of vibration i is given by

$$I_i = \frac{1}{\nu_i} \frac{N\pi}{3c} |\mu_{ij}|^2$$

where N is the number of molecules per unit volume and ν_i is the (harmonic) frequency of the fundamental. Accurate values of absolute absorption intensity are difficult to obtain in the i.r. effect largely owing to the problem of finite slit width, leading to a beam which is not monochromatic. Two problems arise in the use of the above equation. One is that of sign due to the squared term. The other, more fundamental problem is that an 'accurate' force field is necessary to yield the form of the normal co-ordinate Q_i. The principal interest in such measurements and calculations, from the chemist's point of view, lies in discussions of the degree of covalency in a molecule.[29]

The criterion for Raman activity is more difficult to describe pictorially because it involves tensors. Whereas the i.r. effect is conventionally studied in transmission (although both emission and reflectance measurements can be made under appropriate conditions) the Raman effect is essentially a scattering phenomenon observed at a frequency different from that of the incident light. It is useful to look at the scattering phenomenon classically. The oscillating electric vector of the incident (monochromatic) light induces an oscillating dipole in the molecule under investigation. This dipole can then re-radiate with light of the same frequency as that of the exciting light (elastic or Rayleigh scattering). If the molecule belongs to one of the cubic groups ($x \equiv y \equiv z$) then as can be seen from Figure 1 the induced dipole is in the same direction as that of the inducing field. In considering this it is important to realize that during the time-scale of the observation the molecule may be considered to be fixed in space. If the excited state were long-lived (as occurs in resonance fluorescence processes for example) then classically the molecules (and hence the dipoles) would re-orientate during the time of the observation.

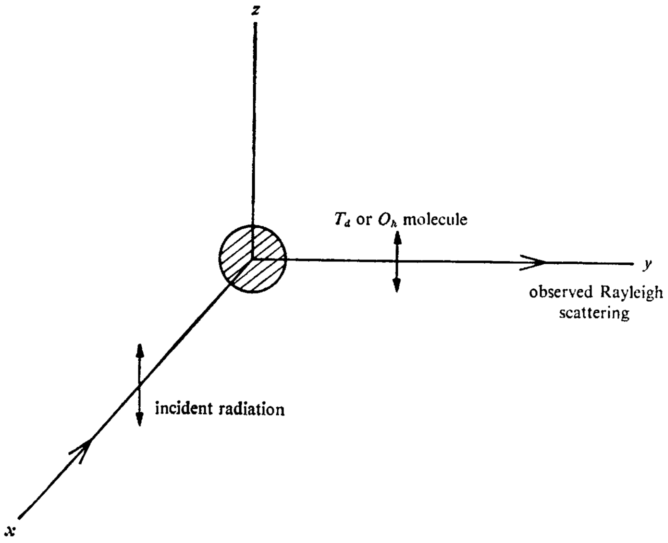

Figure 1 *Polarization of Rayleigh scattering for a molecule belonging to the cubic groups*

Consider a less symmetrical molecule $HgCl_2$ where $x \equiv y \not\equiv z$. If we carry out

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[29] D. Steele, *Quart. Rev.*, **1964**, **18**, 21.

the experiment illustrated in Figure 2 it is reasonable to suppose that the induced dipole lies along the z-direction. We may write

$$P_z = \alpha_{zz} E_z$$

where P_z refers to the induced dipole, E_z to the electric field of the incident light, and α_{zz} to the component of the polarizability in the z direction.

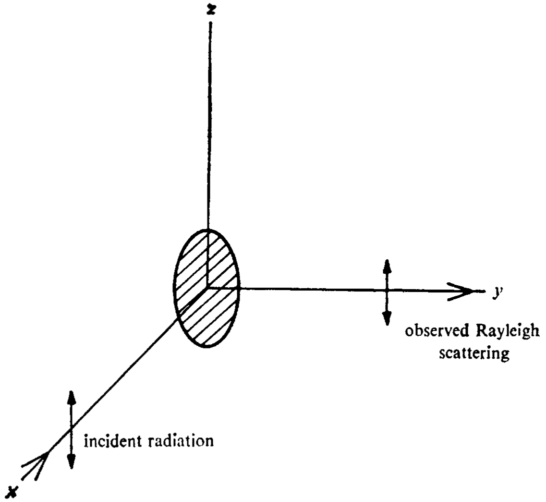


Figure 2 *Polarization of Rayleigh scattering for an oriented molecule of* $HgCl_2$

Suppose we now incline the $HgCl_2$ molecule relative to our fixed laboratory co-ordinate system. The molecular axes will be defined by x, y, z: the laboratory axes will be defined by X, Y, Z. The change in co-ordinate axes may be carried out by a similarity transformation (see also p. 128):

$$\alpha_{XYZ} = T\,\alpha_{xyz}\,T^{-1}$$

where T is a transformation matrix (note also that because the axis systems are orthogonal the inverse of T is also the transpose of T). The components of T are the direction cosines of the two axis systems. To simplify the algebra, consider rotation of the $HgCl_2$ molecule by an angle θ about laboratory Y. We then obtain the position shown in Figure 3. The first row of the transformation matrix is then formed by the direction cosines:

$$X \text{ on } x \qquad X \text{ on } y \qquad X \text{ on } z$$

which becomes

$$\cos\theta \qquad 0 \qquad \cos(90 - \theta)$$

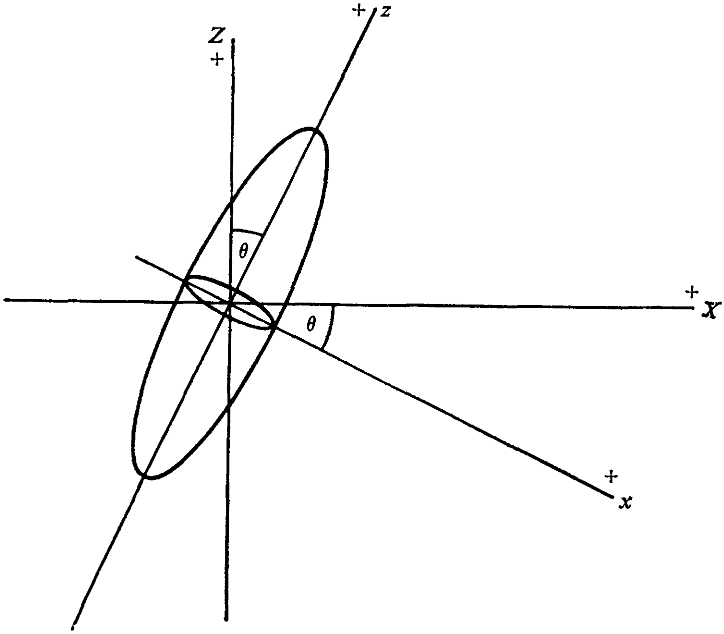


Figure 3

Continuing in this way, writing cos θ = cθ, cos (90 − θ) = sin θ = sθ and noting c(90 + θ) = −sθ, we obtain

$$T = \begin{pmatrix} c\theta & 0 & s\theta \\ 0 & 1 & 0 \\ -s\theta & 0 & c\theta \end{pmatrix}$$

Thus for this molecule, where $\alpha_{xx} = \alpha_{yy} = a \neq \alpha_{zz} = b$,

$$\begin{matrix} P_X \\ P_Y \\ P_Z \end{matrix} = \begin{pmatrix} c\theta & 0 & s\theta \\ 0 & 1 & 0 \\ -s\theta & 0 & c\theta \end{pmatrix} \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix} \begin{pmatrix} c\theta & 0 & -s\theta \\ 0 & 1 & 0 \\ s\theta & 0 & c\theta \end{pmatrix} \begin{matrix} E_X \\ E_Y \\ E_Z \end{matrix}$$

which on matrix multiplication yields

$$\begin{matrix} P_X \\ P_Y \\ P_Z \end{matrix} = \begin{pmatrix} ac^2\theta + bs^2\theta & 0 & (b - a)c\theta\, s\theta \\ 0 & a & 0 \\ (b - a)c\theta . s\theta & 0 & as^2\theta + bc^2\theta \end{pmatrix} \begin{matrix} E_X \\ E_Y \\ E_Z \end{matrix}$$

Note the appearance of the off-diagonal *XZ* terms. If θ = 0° or 90° the off-diagonal terms disappear and we are left with the matrices

$$\begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix} \text{ or } \begin{pmatrix} b & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix}$$

respectively. Thus in the discussion of Rayleigh and Raman scattering it is extremely important to distinguish laboratory fixed axes and molecular fixed axes.

Pictorially it is convenient to discuss the polarizability of a molecule in terms of a triaxial ellipsoid. Perhaps the easiest way of understanding this is to approach it *via* classical mechanics and the momental ellipsoid. Consider a rigid molecule composed of masses m_i and weightless connecting rods. The moment of inertia about any axis of rotation through the centre of mass is given by $I = \sum_i m_i r_i^2$, where r_i is the perpendicular distance of the mass m_i from the axis of rotation. By plotting $I^{-\frac{1}{2}}$ *along* the axis of rotation from the centre of mass for all possible rotation axes a closed surface is generated. Using the symmetry-dictated cartesian axes* as x, y, and z the surface corresponds to a triaxial ellipsoid of equation

$$kx^2 + ly^2 + mz^2 = 1$$

where k, l, m are constants.

In an exactly similar manner the polarizability—which may be regarded qualitatively as the ease with which the electrons can be made to redistribute in the molecule—can be represented by a triaxial ellipsoid:

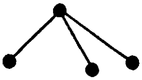
$$\alpha_{xx}x^2 + \alpha_{yy}y^2 + \alpha_{zz}z^2 = 1$$

To obtain this ellipsoid consider the polarizability α_E along the direction of the incident electric vector E. Thus

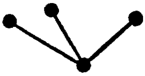
$$P_E = \alpha_E . E$$

If, as with the momental ellipsoid, $\alpha_E{}^{-\frac{1}{2}}$ is plotted for all directions of E the polarizability ellipsoid is obtained. If the cartesian axes are also the principal axes, no off-diagonal components arise. Note also that the *shortest* axis refers to the *greatest* magnitude of α_{ii}.

It is essential to realize that the polarizability ellipsoid of (1) (like the momental ellipsoid) *is in every respect identical* with that of (2).



(1)



(2)

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* For molecules of no symmetry the chosen axes are those along which $I^{-\frac{1}{2}}$ is a maximum and a minimum, together with a third axis mutually perpendicular to them.

This classically accounts for the different selection rules for pure rotation (rigid rotor) in the i.r. and Raman effects. In the i.r. effect a rotation about a line perpendicular to the (permanent) dipole axis results in the vector coming into an identical position once only per revolution. This gives the selection rule $\Delta J = 0, \pm 1$. For the Raman effect as we have seen the polarizability ellipsoid assumes an 'identical' position after half a revolution.* The frequency of change of aspect is thus twice that in the i.r. effect and the selection rule is $\Delta J = 0, \pm 2$.

If we now allow the molecule to vibrate, in essence the harmonic oscillations of the molecule are superimposed on the sine form of the incident electric vector. This combination of sine terms leads to the appearance of both sum and difference frequencies.

For small nuclear displacements, expanding in a Taylor series, the polarizability at any instant in time for the vibrating molecule is given by

$$\alpha_{xx}{}^{t} = \alpha_{xx}{}^{0} + \sum_{k} \left(\frac{\partial \alpha_{xx}}{\partial Q_k} \right)_0 Q_k + \ldots\ldots$$

together with similar terms for $\alpha_{xy}{}^{t}$, $\alpha_{xz}{}^{t}$, *etc.* Here $\alpha_{xx}{}^{0}$ refers to the undisplaced molecule and subscript 0 to displacements tending to zero.

We also have†

$$E_x = E_x{}^0 \cos(2\pi\nu t) \; etc.$$

and
$$Q_k = Q_k{}^0 \cos(2\pi\nu_k t) \; etc.$$

so that $P_x = (\alpha_{xx}{}^0 E_x{}^0 + \alpha_{xy}{}^0 E_y{}^0 + \alpha_{xz}{}^0 E_z{}^0) \cos 2\pi\nu t$

$$+ \sum \left[\left(\frac{\partial \alpha_{xx}}{\partial Q_k} \right)_0 E_x{}^0 + \left(\frac{\partial \alpha_{xy}}{\partial Q_k} \right)_0 E_y{}^0 + \left(\frac{\partial \alpha_{xz}}{\partial Q_k} \right)_0 E_z{}^0 \right]$$
$$\times Q_k \times \tfrac{1}{2} [\cos\{2\pi(\nu + \nu_k)t\} + \cos\{2\pi(\nu - \nu_k)t\}]$$

and similarly for P_y and P_z. (It is convenient to replace $\left(\frac{\partial \alpha_{xy}}{\partial Q_k} \right)$ by α'_{xy}). Note that although for Rayleigh scattering α_{ij} terms are zero ($i \neq j$), it does not follow that α'_{ij} terms will be zero. The first term refers to elastic (Rayleigh) scattering and the second term to inelastic (vibrational Raman) scattering, giving rise to light of frequency $(\nu + \nu_k)$ or $(\nu - \nu_k)$ where ν_k is a fundamental mode of vibration of the molecule. Because quantum mechanically the $(\nu + \nu_k)$ terms correspond to depopulation of an excited state the ratio of intensities for $(\nu + \nu_k)$ to $(\nu - \nu_k)$ follows a Boltzmann distribution. In conventional Raman spectroscopy it is the more intense $(\nu - \nu_k)$ terms which are recorded. The criterion for (vibrational) Raman activity is that there is a change in polarizability

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* For spherical tops there is no rotational Raman spectrum.

† Coincidence of molecular and laboratory axes has been assumed here for simplicity. This formally means $\alpha_{ij}{}^0 = 0$ for this case.

with normal co-ordinate ($\alpha'_{ii} \neq 0$). Alternatively, taking note of the dipole-dipole nature of Raman scatterings, terms of the form

$$P_{ij} = E\left(\frac{\partial\alpha}{\partial Q_k}\right)_0 \int \psi_v{}^i . Q_k . \psi_v{}^j . \mathrm{d}\tau$$

must be non-zero. The expression is closely similar to that used for the infrared effect. Again a selection rule of $\Delta v = \pm 1$ is operative for harmonic functions.

Where a molecule retains the same symmetry for the polarizability ellipsoid and the same directions of the axes for the polarizability ellipsoid in the undisplaced and the displaced (during a vibration) positions, the Raman scattering tensor, like the Rayleigh tensor, is diagonal. However, an important distinction arises when this is not so, giving rise to off-diagonal terms in the Raman scattering tensor such that, using molecular fixed axes, light polarized in the z-direction may give rise to scattered light polarized in the x-direction (an α'_{zx} term in the tensor). This may be considered for the π_g deformation of Hg_2Cl_2 where, if the xz-plane is the plane of the paper (Figure 4), clearly the x- and z-axes of the displaced polarizability ellipsoid differ in direction from those of the undisplaced ellipsoid. Only the y-axis remains unaltered in direction. This gives rise to an α'_{zx} term such that light introduced polarized along the z-direction will appear as scattered light polarized along the x-direction. Clearly this vibration is doubly degenerate ($x \equiv y$) so that by rotation of Figure 4 by 90° about the z-axis an α'_{zy} term is obtained.

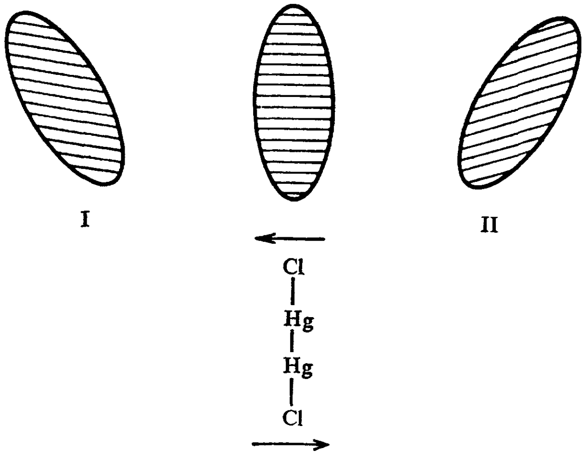


Figure 4 *Polarizability ellipsoids for the symmetric deformation of* Hg_2Cl_2 *at the undisplaced position and at either extreme of the vibration (Note that Raman activity occurs* via *an off-diagonal term because the directions of the ellipsoids* I *and* II *differ although they are otherwise identical)*

The Raman tensor for the π_g deformation of Hg_2Cl_2 is thus of the form

$$\begin{pmatrix} 0 & 0 & \alpha'_{xz} \\ 0 & 0 & 0 \\ \alpha'_{zx} & 0 & 0 \end{pmatrix}$$

where $\alpha'_{xz} = \alpha'_{zx}$ for normal Raman scattering.

Note that the *sum* of the diagonal terms (α'_{ii}) is zero in this case. This is always true for a non-totally symmetric vibration. In general, diagonal terms arise (*a*) for totally symmetric modes (where the full symmetry of the molecule is retained during a vibration); (*b*) for non-totally symmetric modes in the non-cubic groups where there is a polarizability change in the *xy*-plane perpendicular to an axis of higher than two-fold symmetry, when $x^2 - y^2$ (*i.e.* $\alpha'_{xx} = -\alpha'_{yy}$) terms may occur; and (*c*) in the cubic groups, where for non-totally symmetric modes $2z^2 - x^2 - y^2$ (*i.e.* $-\alpha'_{xx} = -\alpha'_{yy} = 2\alpha'_{zz}$) may occur.

A related important feature which arises from the tensor relationship in Raman scattering is the possibility of obtaining anisotropic information from homogeneous fluids. The random orientation of molecules in a fluid averages the oscillating dipoles (vectors) to zero. By contrast a tensor averaged over all orientations is not zero.

Consider Rayleigh scattering: the invariants of the tensor are

(i) a spherical portion, $\bar{\alpha} = 1/3\,(\alpha_{ii} + \alpha_{jj} + \alpha_{kk})$

(ii) an anisotropic portion,

$\gamma^2 = \frac{1}{2}[(\alpha_{ii} - \alpha_{jj})^2 + (\alpha_{jj} - \alpha_{kk})^2 + (\alpha_{ii} - \alpha_{kk})^2 + 6(\alpha^2{}_{ij} + \alpha^2{}_{ik} + \alpha^2{}_{jk})]$

The values of these two functions are invariant with respect to the orientation of the laboratory co-ordinate axes relative to those of the (molecular) polarizability ellipsoid. From the discussion of the momental ellipsoid and the polarizability ellipsoid it is also clear that were the natural axes to be used there would be no off-diagonal terms.

The measured intensity depends on squared terms, so that an oscillating dipole

$$\mu = \mu_0 \cos 2\pi\nu t$$

emits per solid angle in the *X*-direction

$$I = \frac{2\pi^3\nu^4}{c^3}\,(\mu_0{}^2{}_Y + \mu_0{}^2{}_Z)$$

Remembering that $P = \alpha E = \mu$, for the experimental arrangement shown in Figure 1 with plane-polarized radiation incident along the *X*-direction,

$$I_\perp = \frac{2\pi^3\nu^4}{c^3}\,\alpha_{ZX}{}^2\,E_0{}^2$$

$$I_\| = \frac{2\pi^3\nu^4}{c^3}\,\alpha_{ZZ}{}^2\,E_0{}^2$$

Again the off-diagonal term α_{ZX} arises because the laboratory frame of reference is not aligned with the principal molecular axes. To obtain a relationship between

α_{XYZ} terms and α_{xyz} terms we have to average over all orientations of the molecule to obtain:

$$\overline{(\alpha_{ZZ})^2} = \frac{1}{15}\gamma^2$$

$$\overline{(\alpha_{XX})^2} = \frac{45\bar{\alpha}^2 + 4\gamma^2}{45}$$

$$I_{\perp} = \frac{2\pi^3\nu^4}{c^3}\left(\frac{\gamma^2}{15}\right)NE_0{}^2$$

$$I_{\parallel} = \frac{2\pi^3\nu^4}{c^3}\left(\frac{45\bar{\alpha}^2 + 4\gamma^2}{45}\right)NE_0{}^2$$

where N is the number of molecules. Thus the depolarization ratio for Rayleigh scattering ρ_p is given by

$$\rho_p = \frac{I_{\perp}}{I_{\parallel}} = \frac{3\gamma^2}{45\bar{\alpha}^2 + 4\gamma^2}$$

where ρ_p refers to the use of incident polarized light and γ^2, where we choose principal axes, contains no α_{ij} terms. Clearly for a molecule in the cubic groups $\alpha_{xx} = \alpha_{yy} = \alpha_{zz}$, so that $\rho_p = 0$. The greatest value of ρ_p would be obtained for a molecule in which α_{xx} is finite but α_{yy} and α_{zz} tend to zero. In this case $\rho_p \rightarrow 1/3$.

For Raman scattering identical equations apply except that we must substitute α' for α and $(\gamma')^2$ for γ^2. For molecules belonging to the cubic groups, as for Rayleigh scattering, ρ_p for the totally symmetric vibration is zero ($\alpha'_{xx} = \alpha'_{yy} = \alpha'_{zz}$; $\alpha'_{xy} = \alpha'_{xz} = \alpha'_{yz} = 0$). For a vibration which is antisymmetric with respect to any symmetry element of the molecule as we have seen earlier $\alpha'_{xx} + \alpha'_{yy} + \alpha'_{zz} = 0$ so that $\bar{\alpha}'$ also is zero, but γ'^2 is finite and hence $\rho_p = \frac{3}{4}$. For totally symmetric bands (*i.e.* vibrations which maintain all the symmetry elements of the original molecule) the depolarization ratio for the experimental situation depicted in Figure 1 will lie between 0 and $\frac{3}{4}$.

The intensity of a Raman line at a displacement $\Delta\nu$ from ν_0 (the exciting frequency) is given by:

$$I_i = \frac{KN(\nu_0 - \Delta\nu)^4}{[1 - \exp(-h\Delta\nu/kT)]}\cdot|P_{ij}|^2$$

where K contains the constant terms. In this expression it is assumed that the scattering molecules are in a non-degenerate electronic ground state and that ν_0 is well removed from any region of absorption.

As with the i.r. effect, absolute intensities are difficult to measure in the Raman effect. It is customary to consider two factors, the geometrical optical effect based on spectrometer performance (including the refractive index of the sample) and the internal field effects intrinsic to the system under study. Where accurate intensity and depolarization measurements are made it is formally possible to calculate derived mean bond polarizabilities from the observed isotropic part of the Raman scattering [that proportional to $(\bar{\alpha}')^2$] using elementary Wolkenstein[30] theory.

The use which has been made of derived bond polarizabilities is limited. Their interest would be principally in calculating intensities of fundamental modes of vibration in the Raman effect. In considering Raman intensities pictorially from a sketch of the appropriate normal mode it is very easy to make errors by mentally adding vectors rather than tensor components.[31]

Before leaving this section it is useful to summarize some of the more important features:

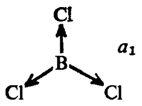
(i) Group theory enables the prediction of the i.r.- and Raman-active fundamental modes of vibration (and combination or overtone bands) for isolated molecules[32] or for crystals in the centrosymmetric space groups.[33]

(ii) Assuming approximate force fields to be available for the molecule under study, vibrational frequencies can be calculated from standard programmes requiring the input only of atomic masses, cartesian co-ordinates, and force constants. The extension to unit cells of crystals is straightforward.[34]

(iii) In the i.r. effect the criterion for activity is a change in dipole moment with normal co-ordinate. In the Raman effect the criterion is change of polarizability with normal co-ordinate and polarized bands (with ρ_p in the range 0—$\frac{3}{4}$) only occur for totally symmetric modes.*

Where a centre of symmetry is present i.r. bands are Raman inactive and Raman bands are i.r. inactive. Raman vibrations of centrosymmetric molecules (or crystals) retain the centre of symmetry.

We shall now briefly consider one molecule, boron trichloride. There is only one totally symmetric mode:



Clearly the polarizability ellipsoids are different at the extremes of the vibration; hence $\alpha' \neq 0$ and the vibration is Raman active. The directions of the axes of the polarizability ellipsoid and its symmetry remain unchanged and hence there are no off-diagonal terms. As $x \equiv y$ if z is chosen as the three-fold axis, the Raman tensor is

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* Note that pure rotational Raman bands are depolarized.

[30] M. Wolkenstein, *Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **30**, 791; M. Wolkenstein, *J. Phys. U.S.S.R.*, 1941, **5**, 185; M. Eleashevich and M. Wolkenstein, *J. Phys. U.S.S.R.*, 1945, **9**, 101, 326.

[31] S. F. A. Kettle, I. Paul, and P. J. Stamper, *Inorg. Chim. Acta*, 1973, **7**, 11.

[32] See, for example, F. A. Cotton, 'Chemical Applications of Group Theory', Interscience, New York, 1963.

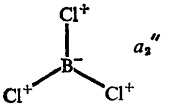
[33] R. Loudon, *Adv. Phys.*, 1964, **13**, 423 (errata, 1965, **14**, 621).

[34] I. R. Beattie, N. Cheetham, M. Gardner, and D. E. Rogers, *J. Chem. Soc.* (*A*), 1971, 2240.

$$\begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix}$$

There is no change of dipole during the vibration and the mode is i.r. inactive.

The only other non-degenerate mode of this molecule is the out-of-plane deformation. Clearly there is a dipole moment change in this vibration. The band is i.r. active with the transition moment transforming as z.



To examine the Raman activity, consider the undisplaced polarizability ellipsoid and the ellipsoids at either extreme (Figure 5).* (Note that in this vibration in the undisplaced position the dipole moment is zero. This is not true of the polarizability. The polarizability of an undisplaced molecule is always finite.)

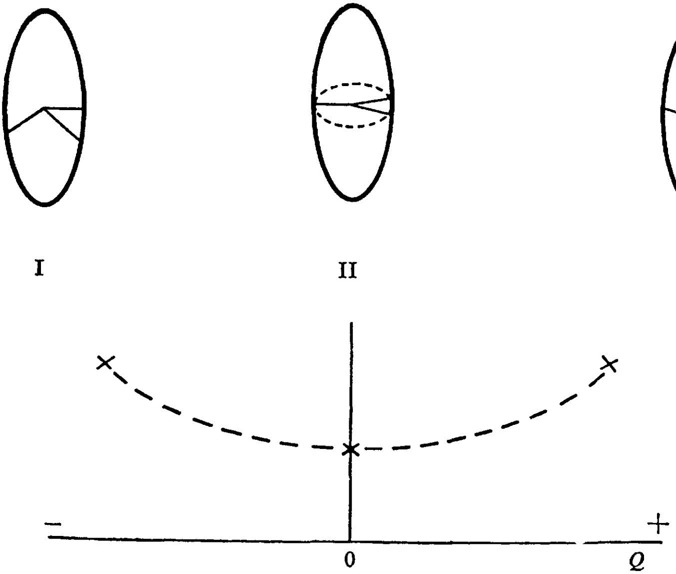


Figure 5

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* In the *Journal of Chemical Education* for 1967, vibrations ν_2 and ν_3 of carbon dioxide are depicted as producing no change of the polarizability ellipsoid from that of the undisturbed molecule. This error has recently been repeated in a monograph on Raman spectroscopy.

Ellipsoids I and III are identical but differ from the undisplaced ellipsoid II. Thus the polarizability change is of the form shown in Figure 5, so that $(\alpha')_0 \rightarrow 0$ and the band is Raman inactive. (In a non-centrosymmetric molecule, of which BCl_3 is an example, it is only vibrations of this type which are i.r. active and Raman inactive. All other i.r.-active vibrations are also Raman active.) This leaves four modes to find ($3n - 6$, less the two already given). These are the (degenerate) in-plane deformation and antisymmetric stretch, both of e' symmetry and most easily discussed using character tables.[35]

A. Solid State.—When radiation falls on an isotropic non-absorbing medium it is reflected and refracted, with changes in polarization characteristics. Ignoring fluorescence effects the refracted ray will be attenuated by elastic (Rayleigh) and inelastic (Brillouin and Raman) scattering.[36]

Crystals are not normally isotropic; they are birefringent, implying that the refractive index is not the same in all directions. The variation of refractive index with direction in the crystal may be represented by a triaxial ellipsoid called the indicatrix. For crystals of orthorhombic or higher symmetry the indicatrix axes coincide with the crystallographic axes. For the general triaxial ellipsoid there are two circular sections which pass through the origin. The directions perpendicular to these sections are termed the optic axes, leading to the term 'biaxial' for such crystals. In the case of uniaxial crystals the indicatrix is an ellipsoid of revolution and the optic axis is parallel to the principal symmetry axis.[37]

When radiation falls on a birefringent material in general two rays of different polarization characteristics are produced, both or one of which will not obey the normal laws of refraction. To avoid this splitting of the exciting (and observed) radiation it is essential in single-crystal studies to use the indicatrix axes, or axes of the appropriate elliptic section of the indicatrix. However, for uniaxial crystals, as one of the indicatrix axes is also an optic axis it is important to avoid propagation (or observation of Raman light) along the optic axis.[38] Because the elliptic section perpendicular to an optic axis is circular, if one is slightly off the axis in propagating the incident light, two rays may be produced which will interfere, resulting in loss of the polarization characteristics of the incident light. Such behaviour is less likely to occur for biaxial crystals as the optic axes are usually well removed from the indicatrix axes which are frequently also the crystallographic axes and hence also frequently the alignment axes.

If the crystal has intense absorption bands in the region under study the refractive index will undergo large changes in the region of these bands (Figure 6) leading to major changes in the reflectivity of the sample. Further, where the

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[35] For a general discussion of infrared and Raman spectroscopy see G. Herzberg, 'Infrared and Raman Spectra', Van Nostrand, New York, 1945; for the theory of the Raman effect see J. A. Koningstein, 'Introduction to the Theory of the Raman effect', Reidel, Dordrecht, 1972.

[36] M. Garbuny, 'Optical Physics', Academic Press, New York, 1965.

[37] N. H. Hartshorn and A. Stuart, 'Crystals and the Polarizing Microscope', Arnold, London, 1970; V. C. Varghese, *J. Opt. Soc. Amer.*, 1967, **57**, 1351.

[38] S. P. S. Porto, J. A. Giordmaine, and T. C. Damen, *Phys. Rev.*, 1966, **147**, 608.

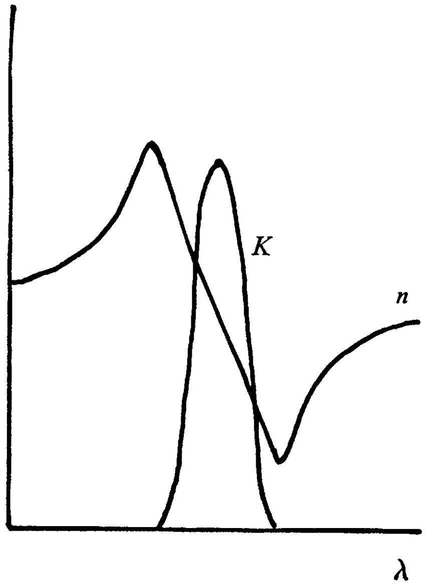

Figure 6 *Change of refractive index* (*n*) *in the region of an absorption band* (*absorption index K*)

indicatrix axes are not symmetry-determined not only will their magnitude change, but also their direction will change on passage through an absorption band. In the case of absorption measurements there is the additional difficulty of pleochroism (anistropy in the absorption index). For crystals of lower than orthorhombic symmetry the directions of the axes of the absorption index and the refractive index (indicatrix) need not coincide except in the case of the unique axis (*b*) for monoclinic crystals.

B. Raman Spectra of Single Crystals.—The problem here is to consider the interaction between the incident refracted light beam and elastic waves in the crystal. For centrosymmetric crystals the prediction of optically active modes can be made rigorously using group theory.[33] A factor-group analysis is an essential first step in solid-state spectroscopy, providing that the full *X*-ray structure is known.[39]

The procedure for a factor-group analysis is essentially the same process as carrying out a conventional point-group analysis on a molecule. The differences

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[39] See, for example, S. S. Mitra, and P. J. Geilisse, 'Progress in Infrared Spectroscopy', Plenum Press, New York, 1964, Vol. 2; see also R. S. Halford, *J. Chem. Phys.*, 1946, **14**, 8; S. Mitra, *Solid State Physics*, 1962, **13**, 1; C. H. Ting, *Spectrochim. Acta* (*A*), 1968, **24**, 1177; R. A. Cowley, *Proc. Phys. Soc.*, 1964, **84**, 281; J. E. Bertie and J. W. Bell, *J. Chem. Phys.*, 1971, **54**, 160; S. H. Chen and V. Dvorak, *J. Chem. Phys.*, 1968, **48**, 4060; W. Vedder and D. F. Hornig, *Adv. Spectroscopy*, 1961, **2**, 189; G. R. Wilkinson, W. C. Price, and E. M. Bradbury, *Spectrochim. Acta*, 1959, **14**, 284.

between molecules and crystals are: (i) the extended elements of crystals such as glide planes or screw axes become for molecules more restricted elements such as mirror planes or rotation axes; (ii) in the analysis a polyatomic grouping is regarded as invariant to a symmetry operation which causes only intramolecular rearrangements between molecules or ions which are related to one another solely by a primitive translation; (iii) a *primitive* unit cell (which is not necessarily that used by the crystallographer) is the one that is important for vibrational spectroscopy and may contain more than one complex ion or molecule leading to splitting of internal modes of vibration *via* correlation coupling; and (iv) the point group isomorphic with the corresponding factor group is useful in discussions of activity of modes. In considering crystals it is useful to examine both the factor group approach and the molecule or ion site symmetry, plus coupling with other units in the primitive cell. Thus in Volume I of International Tables for *X*-ray crystallography under Space Group number 62 we find $Pnma\text{-}D^{16}{}_{2h}$. The isomorphic point group is therefore D_{2h} and the complete notation given is $P2_1/n2_1/m2_1/a$. In addition the four-fold positions either have one mirror plane ($m \equiv C_s$) or a centre of symmetry ($\bar{1} = C_i$). The cell is of course primitive (P).

An example will indicate the elegance of single-crystal studies. For an orthorhombic crystal, if the plane-polarized laser beam is incident parallel to crystal z, with the electric vector in the x-direction and observation is made along y with the analyser set in the z-direction, then this is termed a $z(xz)y$ observation so that

$$\begin{pmatrix} 0 \\ 0 \\ P_z{}^{\nu} \end{pmatrix} = \begin{pmatrix} R_{xx} & R_{xy} & R_{xz} \\ R_{yx} & R_{yy} & R_{yz} \\ R_{zx} & R_{zy} & R_{zz} \end{pmatrix} \begin{pmatrix} \frac{1}{2}E_x{}^0 \cos 2\pi(\nu - \nu_i)t \\ 0 \\ 0 \end{pmatrix}$$

or $P_z{}^{\nu} = R_{xz}\frac{1}{2}E_x{}^0 \cos 2\pi(\nu - \nu_i)t = E^{\nu}$, where $P_x{}^{\nu}$ refers to the particular band under observation and R_{ij} ($= \alpha'_{ij}$) is the Raman tensor component of the crystal.

In this observation, ideally only the R_{zx} tensor component is active as the intensity observed depends only on $R_{zx}{}^2$. For the crystal of symmetry $Pnma\text{-}D^{16}{}_{2h}$ this implies that only b_{2g} modes will appear in the spectrum. By carrying out (xx), (xy), (xz), and (yz) observations on an orthorhombic crystal of this symmetry it is (ideally) possible to assign the observed bands unambiguously to symmetry classes[40] (Figure 7).

As chemists we are usually interested in molecules or ions in the crystal rather than in the whole primitive cell. We therefore may make an initial assumption that the molecule or ion carries over its derived polarizability tensor from the discrete species to the crystal unchanged. If the derived polarizability tensor of the molecule is α'_{ij} and that of the crystal R_{ij}, then transformation from molecular to crystal axes is required. It is, however, necessary to take care that the character

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[40] I. R. Beattie, M. J. Gall, and G. A. S. Ozin, *J. Chem. Soc.* (*A*), 1969, 1001.

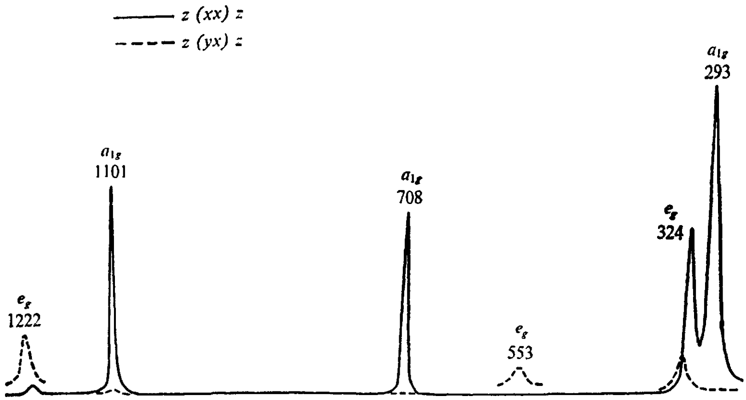

Figure 7 *Oriented single-crystal Raman spectra*[40] *of* $Na_2S_2O_6,2H_2O$

table 'axes' are lined up correctly with those used for crystal and molecular axes.[41]

For molecular axes

$$P_m^{\nu} = \alpha' E_m^{\nu}$$

For crystal axes

$$P_c^{\nu} = RE_c^{\nu}$$

Thus $P_c^{\nu} = TP_m^{\nu} = T\alpha' E_m^{\nu}$ where T is the appropriate transformation matrix. Similarly $E_c^{\nu} = TE_m^{\nu}$, so that

$$P_c^{\nu} = T\alpha' T^t E_c^{\nu}$$

$$\text{or } R = T\alpha' T^t$$

where T^t is the transpose of T. Because the matrices are orthogonal it is also the inverse of T.

In this way it is ideally possible from single-crystal measurements to obtain the relative magnitudes of the tensor components for *each* fundamental mode of vibration of the molecule or ion in the crystal. From these values it is possible to predict relative intensities of Raman bands in solution and their depolarization ratios—within the framework of the approximation used (see Table 2).

In the case of non-centrosymmetric crystals, predictions by group theory are not exact. Thus the case of zinc oxide which crystallizes in the system *P*6*mm*-C_{6v} with four atoms in the primitive cell has been carefully examined by Damen, Porto, and Tell.[42] There are $3 \times n(= 4) = 12$ phonon branches of which nine will be optical and three will be acoustic. (The quantum of energy

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[41] I. R. Beattie and G. A. Ozin, *J. Chem. Soc.* (*A*), 1969, 542.

[42] T. C. Damen, S. P. S. Porto, and B. Tell, *Phys. Rev.*, 1966, **142**, 570.

Table 2 *Relative intensities and depolarization ratios for* $Na_2S_2O_6,2H_2O$ *in the solid state and in aqueous solution*[40]

	Free ion mode	*Powder* I_{rel}		*Solution* I_{rel}		ρ_p	
		calc.	*obs.*	*calc.*	*obs.*	*calc.*	*obs.*
	ν_1	40	52	112	122	0.004	$0 < \rho < 0.02$
a_{1g}	ν_2	23	34	54	54	0.005	$0 < \rho < 0.02$
	ν_3	100	100	100	100	0.426	0.35 ± 0.03
	ν_4	17	18	26	16	0.75	0.74 ± 0.02
e_g	ν_5	16	22	14	13	0.75	0.73 ± 0.02
	ν_6	65	58	50	34	0.75	0.75 ± 0.02

in an elastic wave is termed a phonon by analogy with the term photon for an electromagnetic wave.) Application of group theory leads to the predictions for the optical modes

$$\Gamma_{\text{cryst}} = a_1 + e_1 + 2e_2 + 2b$$

of which the b branches are inactive and the e_2 branch is Raman active only. The only modifications which have to be made to the simple theory concern the a_1 and e_1 branches which are affected by the macroscopic electric field associated with the i.r.-active longitudinal optical (LO) mode. Thus the transverse optical modes (TO) and the longitudinal optical mode (LO) may appear at different frequencies. (In essence for LO modes the change in dipole occurs along the propagation direction for the phonon wave whereas in TO modes it occurs perpendicular to the propagation direction.) In i.r. absorption experiments it is the TO mode which interacts with the photons which, in wave terminology, are also transverse waves. For molecular crystals the change of dipole with vibrational co-ordinate may be small and hence the separation of LO and TO modes may be small.

In the case of zinc oxide we will deal with the non-degenerate case first: The character table for C_{6v} shows that for a_1 modes the Raman tensor components are $R_{xx} = R_{yy} = R_{zz}$; for the i.r. vector we have μ_z only. Consider an $x(zz)y$ observation. When a photon interacts with a phonon both energy and momentum must be conserved (Figure 8).

For conservation of energy

$$\nu_p = \nu_i - \nu_s$$

The momentum is given by $\hbar k$ where k is the wave vector defined by $k = 2\pi/\lambda$ (λ being the wavelength).[43] Thus for conservation of momentum

$$k_p = k_i - k_s$$

In Figure 8 the phonon propagates in the xy-plane (incident/observation plane)

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[43] C. Kittel, introduction to 'Solid State Physics', Wiley, New York, 1971; C. A. Wert and R. M. Thomson, 'Physics of Solids', McGraw-Hill, New York, 1964.

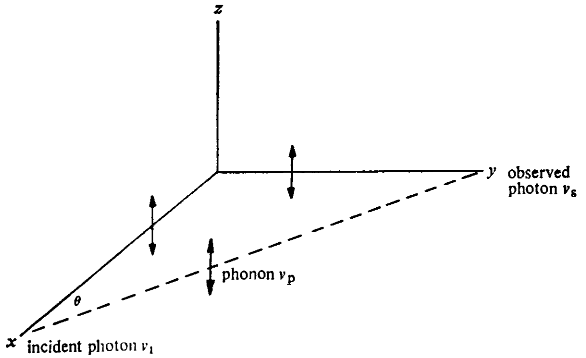

Figure 8 *Interactions of photon with phonon in a (zz) observation for zinc oxide*[42]

and the polarization is defined by the direction of the dipole moment change, noted above from character tables as μ_z. The double-headed arrows directing the polarization direction are thus all parallel to z. Because for the phonon ($\Delta\nu$ effectively) the polarization direction (z) is perpendicular to the propagation direction (xy-plane) the a_1 mode is a pure TO. (Note also that because $\Delta\nu \ll \nu$ *and* $(\nu - \Delta\nu)$, θ is *ca.* 45°.)

The case of the e_1 mode is much more complex because of the degeneracy. The character tables merely provide μ_x, μ_y; α_{xz}, α_{yz}, but do not tell us what pairs go together. We must either appeal to first principles or to a tabulation where this is made clear. It must be emphasized that although for a degenerate mode there is an infinite number of possible linear combinations which act as a representation of the mode concerned, by making an observation we select one 'half' of the combination and thereby define the other half. From Gilson and Hendra's book[44] we find,

$$e_1\text{:}\quad \mu_x \text{ with } \alpha_{xz}$$

$$\mu_y \text{ with } \alpha_{yz}$$

We thus obtain Figures 9a and 9b for $x(zx)z$ and $x(zy)z$ observations, bearing in mind that it is the i.r. vector that defines the polarization direction. It is clear that for the (zy) observation a pure TO mode is obtained (at 407 cm^{-1}). By contrast the (zx) observation shows the phonon polarization to be at *ca.* 45° to the propagation direction, giving both TO and LO observations with bands at 395 cm^{-1} (TO) and 581 cm^{-1} (LO).

Additional complications arise which will not be discussed here, due to interaction of the a_1 and e_1 phonons. Because dipolar interactions reinforce one another for LO modes, LO modes are perturbed relative to TO modes arising from the same factor group fundamental. Hence LO modes occur at the higher

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[44] T. R. Gilson and P. J. Hendra, 'Laser Raman Spectroscopy', Wiley, London, 1970.

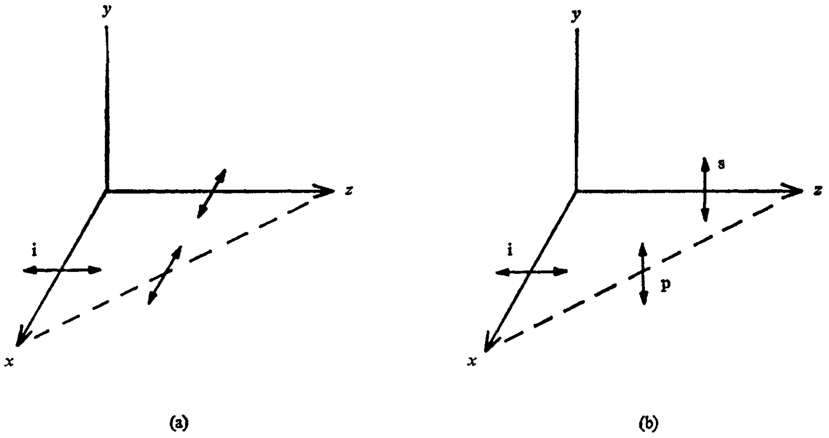

Figure 9 *Conservation of energy and momentum diagrams for zinc oxide:* (a) x(zx)z; (b) x(zy)z[42]

frequency, the difference in frequency giving a measure of the strength of the i.r. transition.

C. **Powders.**—The Raman spectra of powders generally yield less information than that obtained from single crystals of known structure. Further, because of scattering within the powder, depolarization ratios cannot normally be obtained. However, powders deriving from isotropic materials, if immersed in liquids of suitable refractive index, can yield useful depolarization ratios.

D. **Infrared Spectra of Single Crystals.**—In the i.r. effect the material under study, of necessity, has absorption bands in the wavelength region of interest. Thus there are major changes of reflectivity and refractive index as a function of wavelength. This contrasts sharply with Raman spectroscopy where the frequency of the exciting light is constant and the material under study has frequently no absorption bands in the region of interest if the laser line is carefully chosen.

For i.r. studies of crystals normally some form of preparation is necessary in terms of cutting, grinding, and polishing. This severely limits the value of single-crystal studies to the chemist who is dealing with reactive compounds. Further, the sample size necessary is usually appreciably greater than that for Raman studies, where in addition the crystal can be examined in a glass-walled vacuum ampoule.

In transmission spectroscopy of single crystals it is necessary to prepare thin sections in one or more crystallographically different directions. Similarly, for reflectance measurements it is necessary to prepare reasonably flat surfaces in one or more directions. Using commercially available instrumentation a sample area of not less than 0.25 cm^2 is desirable. (This size will be appreciably reduced if tunable i.r. lasers become available.)

Because of the vector–vector–vector relationship for i.r. spectroscopy compared with the vector–tensor–vector relationship for Raman spectroscopy, transference from molecular axes to crystal axes in the i.r. case merely requires the projection of the molecular axes on to the corresponding crystal axes to effect the required transformation (*i.e.* x on X, y on Y, and z on Z). The same problems arise in terms of orientation of the crystal with regard to the electric vector of the incident and collected radiation, except that for i.r. spectra of triclinic and monoclinic* crystals the indicatrix and absorption index axes (which need not coincide) may change in direction with frequency.

For a non-absorbing medium the variation of the reflectivity (R) with angle of incidence is shown in Figure 10. At the Brewster angle the reflected ray is plane polarized in the plane of incidence. Normally, i.r. reflectance and transmission measurements are carried out on single crystals at approximately normal incidence. The reflectivity is then given by

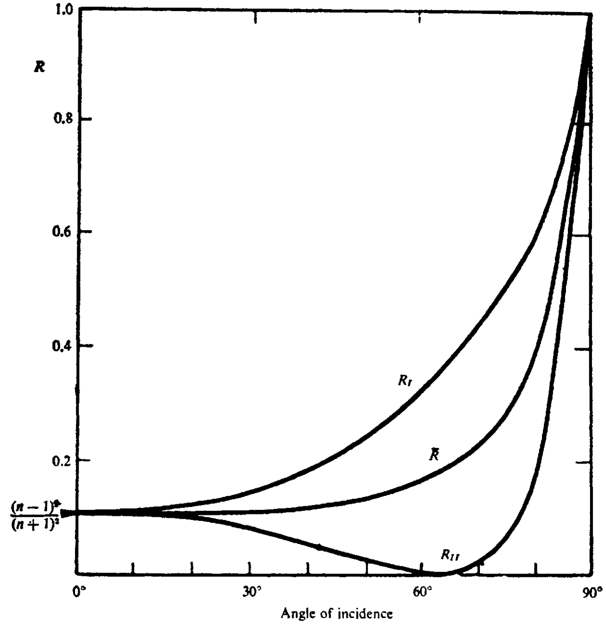

Figure 10 *Reflectivity as a function of angle of incidence for $n = 2$* (Reproduced by permission from M. Garbuny, 'Optical Physics', Academic Press, New York, 1965)

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$$

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* Except for the unique *b*-axis.

where k is the real absorption index and n is the real refractive index. On the low-frequency side of an absorption band the refractive index increases rapidly with the frequency leading to a high reflectivity (Figure 6). Thus errors occur in band intensity, position, and contour when carrying out measurements based solely on the amount of light transmitted. In certain cases erroneous bands have been found in transmission.[45]

In i.r. reflectance spectroscopy both n and k can in principle be obtained from measurements of R as a function of wavelength at a fixed angle of incidence.[46] The most widely used approach is a Kramers–Kroenig analysis based on phase and amplitude changes after reflection. The complex reflectivity

$$r^* = re^{i\theta} = (n^* - 1)/(n^* + 1)$$

with $n^* = n + ik$; θ is the phase (angle) change on reflection. Equating real and imaginary parts one obtains

$$n = \frac{(1 - r^2)}{(1 - 2r\cos\theta + r^2)}$$

and

$$k = \frac{2r\sin\theta}{(1 - 2r\cos\theta + r^2)}$$

Thus to find n and k it is necessary to determine θ. If ω ($= 2\pi\nu$) is the angular frequency and the chosen point on the frequency scale is ω_i, then an exact expression is known:

$$\theta(\omega_i) = \frac{\omega_i}{\pi}\int_0^\infty \frac{\ln R(\omega) - \ln R(\omega_i)}{\omega_i^2 - \omega^2}\,d\omega$$

where ω takes all values from 0 to ∞. Thus if the fractional reflectance $R(\omega)$ is known for all frequencies from zero to infinity the calculation is correct. Unfortunately only a section of the spectrum is measured and it is customary to generate the 'wings' by computational techniques.[47] In addition, the Kramers–Kroenig analysis is not sensitive to minor changes of reflectance in the restrahlen region and is very sensitive to the reflectance minima.[48] Certainly where the extinction coefficient is < 0.1, dispersion analysis is to be preferred. It is interesting to note that using a Kramers–Kroenig analysis in 1964 Hunt, Perry, and Ferguson[49] reported ν_3 of $KMgF_3$ at 140 cm^{-1} (lattice mode) whereas in 1967 Perry and Young,[48] using more reliable spectroscopic data at longer wavelengths, found 165 cm^{-1}, which compares favourably with the value of 168 cm^{-1} found

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[45] W. G. Spitzer, R. C. Miller, D. A. Kleinman, and L. E. Howarth, *Phys. Rev.*, 1962, **126**, 1710.

[46] See, for example, J. R. Sweet and W. B. White, *Appl. Spectroscopy*, 1969, **23**, 230; D. E. McCarthy, *ibid.*, 1969, **22**, 460; see also A. E. Tshmel and V. I. Vettegren, *Spectrochim. Acta*, 1973, **29A**, 1681.

[47] G. Andermann, A. Caron and D. Dows, *J. Opt. Soc. Amer.*, 1965, **55**, 1210; see also J. D. Neufeld and G. Andermann, *ibid.*, 1972, **62**, 1156.

[48] C. H. Perry and E. F. Young, *J. Appl. Phys.*, 1967, **38**, 4616.

[49] G. R. Hunt, C. H. Perry, and J. Ferguson, *Phys. Rev.*, 1964, **134**, A689.

using classical dispersion analysis. Transmittance data[50] on $KMgF_3$ in Nujol mulls or polythene discs yielded: ν_1 478, ν_2 300, ν_3 156 cm^{-1}. The reflectance data yielded[45] for the transverse modes: ν_1 458, ν_2 299, ν_3 168 cm^{-1}.

In a classical dispersion analysis each oscillator j is defined by its strength (ρ_j), width (γ_j), and frequency (ν_j).

Then
$$n^2 - k^2 = \epsilon_0 + \sum_j 4\pi\rho_j\nu_j^2 \frac{(\nu_j^2 - \nu^2)}{(\nu_j^2 - \nu^2) + \gamma_j^2\nu^2\nu_j^2}$$

and
$$nk = \sum_j 2\pi\rho_j\nu_j^2 \frac{\nu\nu_j\gamma_j}{(\nu_j^2 - \nu^2)^2 + \gamma_j^2\nu^2\nu_j^2}$$

The summation extends over all the lattice oscillators and ϵ_0 is the high-frequency dielectric constant (essentially the polarizability of the electrons with the nuclei fixed). The fractional reflectivity at normal incidence, R, can be calculated if the dispersion parameters are found.[51]

In Figure 11 the reflectivity, refractive index, and absorption index of quartz

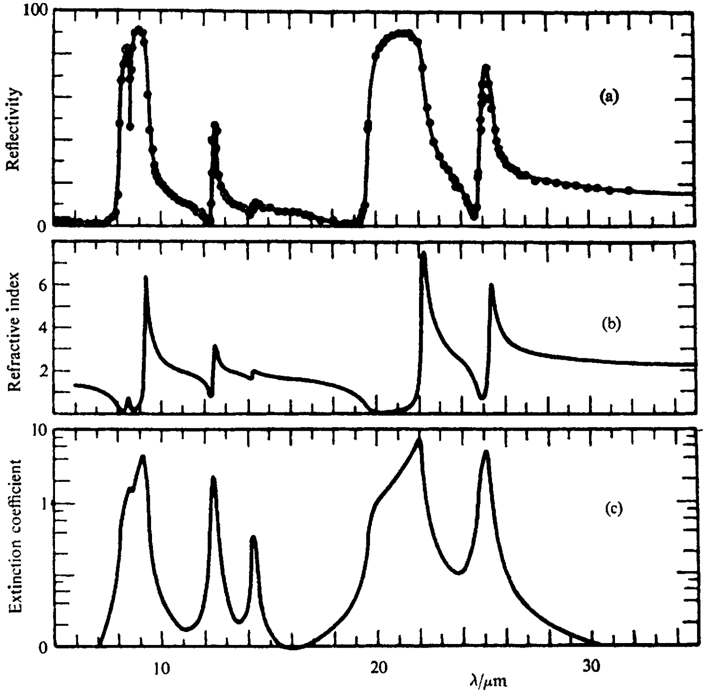

Figure 11 *Reflectivity, refractive index, and extinction coefficient of quartz for the ordinary ray:* (a) *theoretical curve adjusted to give best fit with experimental observations (points);* (b) *and* (c) *calculated values of n and K, respectively, from* (a)
(Reproduced by permission from M. Garbuny, 'Optical Physics', Academic Press, New York, 1965)

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[50] I. Nakagawa, A. Tsuchida, and T. Shimanouchi, *J. Chem. Phys.*, 1967, **47**, 983.

[51] W. G. Spitzer and D. A. Kleinman, *Phys. Rev.*, 1961, **121**, 1324.

for the ordinary ray (polarized perpendicular to the optic axis) are shown as functions of wavelength. This may be compared with the transmission spectrum of a single crystal for the ordinary ray of quartz, using a piece thinned to 0.0262 mm (or roughly one thousandth of an inch), shown in Figure 12.

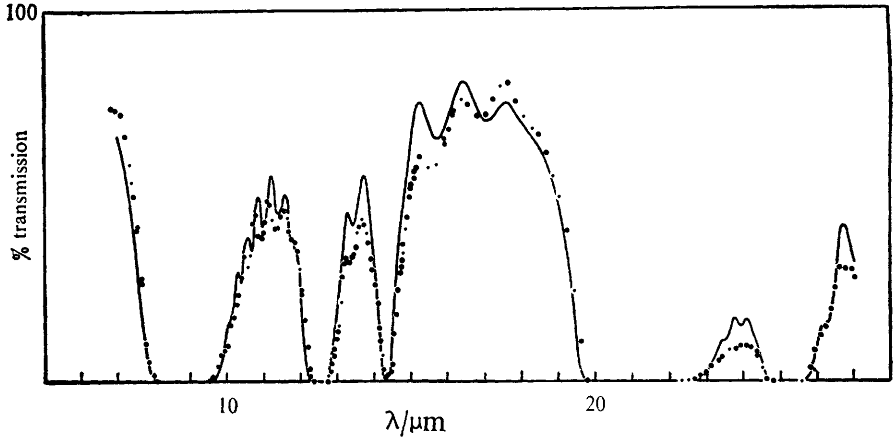

Figure 12 *The transmission of a quartz plate* 0.00262 cm *thick for the ordinary ray. The theoretical curve is adjusted to give the best fit to the experimental points*
(Reproduced by permission from *Phys. Rev.*, 1961, **121**, 1324)

E. Powders.—Nujol (and other) mulls are used routinely in the study of the i.r. spectra of solids. However, the problem of the transmission of light through an idealized assembly of isotropic spheres of the same diameter, separated by distances large compared with the wavelength of the light used and having absorption bands in the region of the wavelength under study is by no means clear. Bearing in mind the anisotropy of the crystalline material frequently studied, the random shape and size of the particles and the fact that they are frequently comparable in size to the wavelength of light indicate some of the difficulties in powder i.r. spectroscopy. (Attenuated total reflectance studies on powders are also worth considering.[52])

The theory of diffraction developed by Mie for an isotropic sphere[53] reduces to Rayleigh scattering (proportional to ν^4) where the radius of the sphere is much less than the wavelength of the incident radiation.[54] Where the radius of the sphere is much greater than the wavelength of the incident radiation the Mie formula leads to the Huygens–Kerchoff theory and for the radius tending to infinity it leads to geometrical optics. Conventional mulling leads to particles in the 1—50 μm range so that the Mie theory is important.

There is little point in attempting to develop the theory of the Nujol mull here,

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[52] M. H. Brooker, *J. Chem. Phys.*, 1970, **53**, 4100.
[53] See, for example, M. Born and E. Wolf, 'Principles of Optics', Pergamon, London, 1959.
[54] A. H. Pfund, *J. Opt. Soc. Amer.*, 1934, **24**, 143.

except to emphasize that band contours, band maxima, and band intensities can all be affected by the nature of the experiment carried out (particle size, mulling agent, *etc.*). A paper on the Christiansen filter effect is well worth reading,[55] but a few examples will indicate the difficulties.

Figure 13 shows the effect of refractive index of the medium on the absorption bands obtained: the curves are calculated.[56] This reference also contains an extensive discussion of the transmission of light through powders in substrates. As an experimental example, in Figure 14 the spectrum of Co[Hg(CNS)$_4$] in the C$\equiv$N stretching region is shown in (*a*) a potassium iodide disc and (*b*) a potassium chloride disc.[57] A difference of more than 50 cm^{-1} in the band maxima is apparent. It is, however, important to note the band distortion[58] in case (*b*).

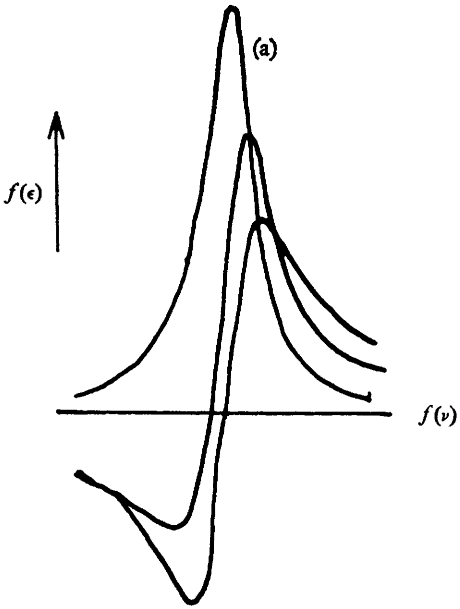

Figure 13 *A function of the frequency plotted against a function of the extinction coefficient for several values of the refractive index difference between compound and substrate:* [*$f(\nu)$ contains the refractive index difference and band width*; *$f(\epsilon)$ contains the radius of the particle. The original paper*[56] *should be consulted for details*]. *Curve* (a), *which is a normal absorption curve, occurs for a refractive index difference of zero*

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[55] R. B. Barnes and L. G. Bonner, *Phys. Rev.*, 1936, **49**, 732; see also R. L. Henry, *J. Opt. Soc. Amer.*, 1948, **38**, 775; J. M. Hunt, M. P. Wisherd, and L. C. Bonham, *Analyt. Chem.*, 1950, **22**, 1478.

[56] H. Primas and H. Gunthard, *Helv. Chim. Acta*, 1954, **37**, 360; see also G. Duyckaerts, *Spectrochim. Acta*, 1955, **7**, 25; R. N. Jones, *J. Amer. Chem. Soc.*, 1952, **74**, 2681.

[57] G. Duyckaerts, *Analyst*, 1959, **84**, 201.

[58] J. W. Otvos, H. Stone, and W. R. Harp, *Spectrochim. Acta*, 1957, **9**, 148; see also N. T. McDevitt and W. L. Baun, *Spectrochim. Acta*, 1964, **20**, 799.

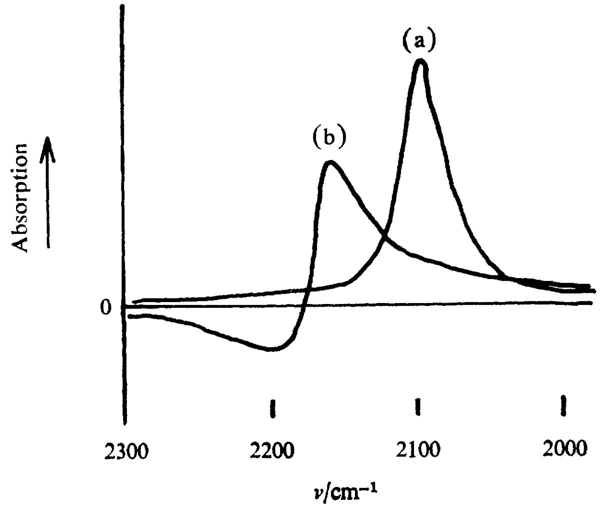

Figure 14 *Absorption band in the* C≡N *stretching region for* Co[Hg(CNS)$_4$] *dispersed in* (a) *potassium iodide* (b) *potassium chloride*[57]

Figure 15 shows the effect of particle size on the i.r. spectrum of quartz for the 12.5 μm band.[59] An article by Sherwood on bandshapes in solids for both i.r. and Raman spectra is of interest here.[60]

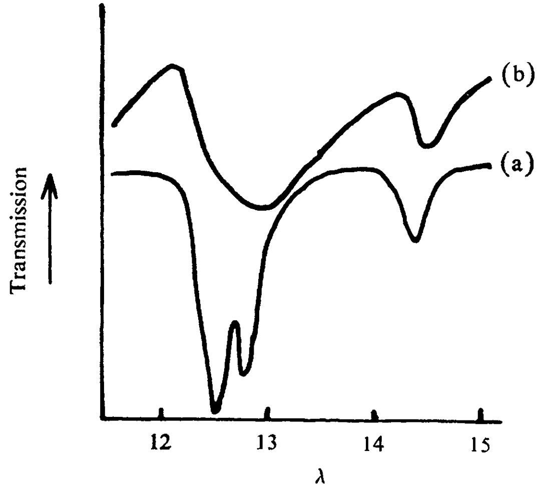

Figure 15 *Effect of particle size on the i.r. spectrum of quartz*: (a) < 2 μm (b) 14—16 μm[59]

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[59] W. M. Tuddenham and R. J. P. Lyon, *Analyt. Chem.*, 1960, **32**, 1630.

[60] P. M. A. Sherwood, *Spectrochim. Acta*, 1971, **27A**, 1019.

F. Fluids.—Most of the features of the spectroscopy of liquids and solutions are covered by a study of gases, except that for liquids and solutions rotations are not quantized.[61] Early Raman spectroscopy was carried out on colourless (non-absorbing to mercury arc excitation), pure (to obtain the maximum concentration) liquids. By contrast there is a considerable literature on the gas-phase i.r. spectra of molecules. This difference in the literature reflects the experimental difficulty in studying the (weak) Raman effect for dilute gases (and solutions).

In the gas phase at low pressure the possibility of high-resolution studies in the determination of molecular structure, *e.g.* from the vibration–rotation band contours, becomes attractive for relatively simple molecules. This becomes particularly important for molecules which do not have a dipole moment and hence are not suitable for microwave studies, although it should be pointed out that the small dipole moment of $HC{\equiv}CD$ is sufficient for a microwave spectrum to be obtained. It is also interesting to note that even for tetrahedral molecules the ground vibronic state possesses a small dipole moment produced by centrifugal distortion effects. For methane $\mu = 5.38 \pm 0.10 \times 10^{-6}$ D, allowing the observation of the pure rotational spectrum in the i.r. effect.[62]

Finally we note that observation of torsional frequencies, for example, may allow the calculation of energy barriers for internal rotation.

3 Applications

This section is intended to direct interest to areas where vibrational spectroscopy can be of value. For reasons of space it cannot be exhaustive. Solids are discussed first, followed by melts, solutions, and gases, with a final section on Raman spectroscopy under resonance or near-resonance conditions. Very readable accounts of the use of lasers in light-scattering studies in general have been given by Porto[63] and by Smith.[64]

Vibrational spectroscopy is, in principle, applicable to all systems except dilute monatomic gases and can be of unique value as a purely analytical technique.[65] All the constituents in a mixture will ideally, if present in sufficient concentration, yield their own characteristic vibrational spectrum (as modified by the environment).

Where single crystals suitable for *X*-ray studies are available the contribution of vibrational spectroscopy to structural chemistry may be small. However, anomalous vibrational spectra in terms of band position, intensity, or number of bands may direct attention to compounds useful for detailed *X*-ray diffraction

[61] See, however, G. Birnbaum, *Mol. Phys.*, 1973, **25**, 241.

[62] A. Rosenberg, I. Ozier, and A. K. Kudian, *J. Chem. Phys.*, 1972, **57**, 568.

[63] S. P. S. Porto, *Spex Speaker*, 1968, **13** (2), 1; 1969, **14** (2), 1; see also T. C. Damen, R. C. C. Leite, and S. P. S. Porto, *Phys. Rev. Letters*, 1965, **14**, 9.

[64] R. A. Smith, *Endeavour*, 1970, **29**, 71.

[65] This includes the group frequency approach: L. J. Bellamy, 'The Infrared Spectra of Complex Molecules', Methuen, London, 1964.

techniques.[66] The Raman[67] and i.r.[68] spectra of oriented single crystals represent one of the most sophisticated uses of vibrational spectroscopy. However, from the point of view of the chemist the value of such studies is open to question. They are clearly of interest in studying intermolecular forces,[69] while a knowledge of lattice dynamics is frequently necessary in interpreting other phenomena in solids.

X-Ray diffraction studies on single crystals may yield ambiguous results for a variety of reasons, including the swamping of light atoms by heavy atoms, leading to inaccurate light-atom positions.

Close similarity of scattering factors (*e.g.*, *C* and *N*) and disorder can similarly lead to difficulties in interpretation. In such cases vibrational spectroscopy of oriented single crystals[70] or even powders[71] may be valuable in assigning structures. Order–disorder transitions,[72] defects in crystals,[73] and the dynamics of polynuclear ions doped into crystals[74] may be conveniently studied by this technique.

Isotopic substitution may define a particular point group, an example being provided by the recent studies of Nakamoto and co-workers[75] on octahedrally co-ordinated metal atoms. Isotopic substitution at this atom can demonstrate the presence or absence of a centre of symmetry. This technique, as with other spectroscopic methods, is particularly valuable for materials not suitable for rigorous *X*-ray diffraction studies.

Vibrational spectroscopy has assumed some significance in the study of surfaces[76] and non-crystalline materials[77] including biological systems.[78] The application of matrix isolation vibrational spectroscopy to elucidate the nature of high-temperature and 'short-lived' species has received much attention

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[66] J. Chatt, C. Eaborn, S. D. Ibekwe, and P. N. Kapoor, *J. Chem. Soc. (A)*, 1970, 1343.

[67] I. R. Beattie and T. R. Gilson, *Proc. Roy. Soc.*, 1968, **A307**, 407; J. F. Scott and S. P. S. Porto, *Phys. Rev.*, 1967, **161**, 903; J. F. Scott, L. E. Cheesman, and S. P. S. Porto, *Phys. Rev.*, 1967, **162**, 834.

[68] G. R. Wilkinson, W. C. Price, and E. M. Bradbury, 'Molecular Spectroscopy Conference Proceedings', ed. E. Thornton and H. W. Thompson, London, Pergamon, 1959; T. S. Robinson and W. C. Price, 'Molecular Spectroscopy', ed. G. Sell, Institute of Petroleum, London, 1954; T. S. Robinson and W. C. Price, *Proc. Phys. Soc.*, 1953, **B66**, 969.

[69] G. R. Wilkinson, 'Molecular Spectroscopy', ed. P. Hepple, Institute of Petroleum, London, 1968; J. R. Ferraro, 'Spectroscopy in Inorganic Chhmistry', 1971, Vol. 2, p. 57, Academic Press, New York.

[70] I. R. Beattie, K. M. S. Livingston, D. J. Reynolds, and G. A. Ozin, *J. Chem. Soc. (A)*, 1970, 1210.

[71] I. R. Beattie and D. J. Reynolds, *Chem. Comm.*, 1968, 1531.

[72] C. H. Wang and R. B. Wright, *J. Chem. Phys.*, 1973, **58**, 1411, 2934.

[73] See also R. C. Newman, 'Infrared Studies of Crystal Defects', Taylor and Francis, London, 1973.

[74] G. R. Field and W. F. Sherman, *J. Chem. Phys.*, 1967, **47**, 2378.

[75] K. Nakamoto, *Angew. Chem. Internat. Edn.*, 1972, **11**, 666.

[76] R. Eischens, *Accounts Chem. Res.*, 1971, **5**, 74; M. Fleischmann, P. J. Hendra, and A. J. McQuillan, *J.C.S. Chem. Comm.*, 1973, 80.

[77] D. J. Derouault, P. J. Hendra, M. E. A. Cudby, and H. A. Willis, *J.C.S. Chem. Comm.*, 1972, 1187.

[78] S. C. Erfurth, J. K. Kiser, and W. L. Peticolas, *Proc. Nat. Acad. Sci. U.S.A.*, 1972, **69**, 938.

recently.[79] An excellent example of this technique was provided by Claassen and Huston[80] who, using combined i.r. and Raman data, were able to demonstrate the D_{3h} molecular symmetry of the unstable species XeO_3F_2. The advantages of narrow linewidths, leading to well-resolved spectra and the possibility of accurate isotopic shift measurements,[81] are offset by the loss of rotational fine structure, and, more seriously, constraints imposed by the matrix, including site effects. Errors can arise due to the extremely low concentrations of material isolated in the substrate, normally < 1 mole percent, and ideally < 0.1 mole percent. Thus spurious bands are frequently observed due to ubiquitous impurities such as water and nitrogen;[82] despite the use of double oven techniques polymer formation may still predominate in the matrix;[83] impurities may react with highly reactive species produced in the matrix, leading to erroneous interpretation of experimental data;[84] and in the case of high-temperature species the compound under investigation may react with the Knudsen cell.[85] In the absence of adequate isotopic studies it is frequently difficult to be sure of the formula of the fragment present in the matrix, let alone whether or not it carries a charge. Nonetheless, matrix isolation is an important area of study and one which is receiving extensive attention.[86]

In the Raman effect, if the sample is strongly absorbing, leading to heating by the incident laser radiation, rapid rotation of the sample can be of value. In the i.r. effect, intensely absorbing samples can also be difficult to examine. In such cases attentuated total reflectance techniques are of interest for both crystalline and powdered materials.[87]

Passing on to melts and solutions, there is an important paper by Wilmshurst on the nature and existence of complex ions and ion pairs in strongly associated systems.[88] Thus in a melt of composition Li_2ZnCl_4 the observation of a band at *ca.* 318 cm^{-1} in the i.r. spectrum is not interpreted as due to ν_3 of $ZnCl_4^{2-}$ but to 'lattice-like vibrations of the system'. However the Raman spectrum of aqueous solutions thought to contain $ZnCl_4^{2-}$ species shows[89] ν_3 at 306 cm^{-1}. Examples of apparently clear-cut structural studies on melts occur for 'gallium

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[79] L. Andrews, *Ann. Rev. Phys. Chem.*, 1971, **22**, 109; J. S. Anderson and J. S. Ogden, *J. Chem. Phys.*, 1969, **51**, 4189; J. W. Hastie, R. H. Hauge, and J. L. Margrave, *J. Amer. Chem. Soc.*, 1969, **91**, 2536.

[80] H. H. Claassen and J. L. Huston, *J. Chem. Phys.*, 1971, **55**, 1505.

[81] S. D. Gabelnick, *J. Phys. Chem.*, 1972, **76**, 2483.

[82] H. Huber, M. Moskovits, and G. A. S. Ozin, *Nature Phys. Sci.*, 1972, **236**, 127; H. Dubost and L. Abouaf-Marguin, *Chem. Phys. Letters*, 1972, **17**, 269.

[83] N. Acquista and S. Abramowitz, *J. Chem. Phys.*, 1972, **56**, 5221; I. R. Beattie, S. B. Brumbach, D. Everett, R. Moss, and D. Nelson, *Faraday Symposium*, London, 1973.

[84] J. M. Kelly, H. Herman and E. Koerner von Gustorf, *J.C.S. Chem. Comm.*, 1973, 105; C. P. Marino and D. White, *J. Phys. Chem.*, 1973, **77**, 2929.

[85] R. D. Wesley and C. W. De Kock, *J. Phys. Chem.*, 1973, **77**, 466; see, however, J. W. Hastie, R. H. Hauge, and J. L. Margrave, in the press.

[86] J. W. Nibler and D. A. Coe, *J. Chem. Phys.*, 1971, **55**, 5133.

[87] K. Tsuji and H. Yamada, *Bull. Chem. Soc. Japan*, 1968, **41**, 1975; I. Simon, *J. Opt. Soc. Amer.*, 1951, **41**, 336; J. Fahrenfort and W. M. Visser, *Spectrochim. Acta*, 1962, **18**, 1103; W. N. Hansen, *Spectrochim. Acta*, 1965, **21**, 209.

[88] J. K. Wilmshurst, *J. Chem. Phys.*, 1963, **39**, 1779; see also J. P. Devlin, D. W. James, and R. Frech, *J. Chem. Phys.*, 1970, **53**, 4394.

[89] S. D. Ross, 'Inorganic Infrared and Raman Spectra', McGraw-Hill, New York, 1972.

dichloride' formulated as Ga[$GaCl_4$] [90] and for Re_2O_7,[91] which is apparently molecular as in the gas. In solution, depolarization and intensity measurements have been used to study the formation of complex ions in systems where the number of species formed is relatively restricted.[92] However, the elegant results of Evans and Dean[93] on $SnF_{6-n}X_n^{2-}$ (X = halogen) in solution using ^{19}F n.m.r. spectroscopy indicates the value of selecting the correct technique for the system under study. Intensity measurements on Group IV tetrahalides,[94] oxy-anions,[95] and complex oxy-acids[96] have been used to discuss the nature of the bonding in these species.

To some extent studies on liquids and gases merge in the sense that most of the earlier Raman work was on liquids, while the same compounds were frequently studied in the i.r. as gases, illustrating the relative sensitivity of the two techniques. A structural determination in terms of the distinction between two possible point groups may occasionally be made using vibrational spectroscopy, although assignment on the basis of non-observation of bands is open to question and has frequently led to results which have subsequently been shown to be erroneous. The series of compounds $(Me_3Sn)_3X$, where X = N, P, As, or Sb, were shown to be pyramidal by a combination of selection rules and band positions.[97] Rather less familiar uses of vibrational spectroscopy include a study of the kinetics of fast reactions using line-broadening in the Raman effect,[98] studies of intermolecular interaction from the observation of linewidths and bandshapes;[99] the use of Raman experiments in interpreting nuclear spin relaxation experiments in simple molecules such as nitrogen;[100] and the correlation of π-electron density with the vibrational frequencies of linear molecules.[101]

In the gas phase, high-resolution studies of vibration–rotation and pure rotation spectra are of importance for determining molecular parameters,[102] including internal rotation.[103] Where larger molecules are under study so that fine-structure analysis becomes extremely difficult both experimentally and theoretically, a study of band contours may be of value in assigning a structure or in developing a force field.[104] By use of forward scattering techniques,[105]

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[90] L. A. Woodward, G. Garton, and H. L. Roberts, *J. Chem. Soc.*, 1956, 3723.

[91] I. R. Beattie and G. A. S. Ozin, *J. Chem. Soc. (A)*, 1969, 2615.

[92] G. W. Chantry and R. A. Plane, *J. Chem. Phys.*, 1960, **33**, 736.

[93] D. Evans and P. A. W. Dean, *J. Chem. Soc. (A)*, 1968, 1154.

[94] L. A. Woodward and D. A. Long, *Trans. Faraday Soc.*, 1949, **45**, 1131.

[95] G. W. Chantry and R. A. Plane, *J. Chem. Phys.*, 1961, **34**, 1268.

[96] G. W. Chantry and R. A. Plane, *J. Chem. Phys.*, 1961, **35**, 1027.

[97] R. E. Hester and K. Jones, *Chem. Comm.*, 1966, 317; see also G. Engelhardt and P. Reich, *Z. Naturforsch.*, 1967, **22b**, 352.

[98] M. M. Kreevoy and C. A. Mead, *J. Amer. Chem. Soc.*, 1962, **84**, 4596.

[99] R. P. Young and R. N. Jones, *Chem. Rev.*, 1971, **71**, 219; A. K. Atakhodzhaev, *Optics and Spectroscopy*, 1964, **16**, 553.

[100] R. G. Gordon, *J. Chem. Phys.*, 1965, **42**, 3658.

[101] R. M. Gavin and S. A. Rice, *J. Chem. Phys.*, 1971, **55**, 2675.

[102] J. Overend, *Ann. Rev. Phys. Chem.*, 1970, **21**, 265.

[103] H. L. Strauss, *Ann. Rev. Phys. Chem.*, 1968, **19**, 419.

[104] F. N. Masri and W. H. Fletcher, *J. Chem. Phys.*, 1970, **52**. 5759; W. F. Edgell and R. E. Moynihan, *J. Chem. Phys.*, 1966, **45**, 1205.

Doppler broadening may be eliminated (analogous to the two-photon technique discussed on p. 113). Further, using pulsed techniques, 'picosecond spectroscopy' may be carried out.[106] Pulse techniques have also been used to reduce fluorescence* background.[107]

Gas-phase Raman spectra may be obtained routinely[108] to 1000 °C (much of the intensity coming from hot bands) in sharp contrast to studies using i.r. spectroscopy where the upper temperature limit for isothermal cells is of the order of 300 °C (owing mainly to problems of radiation from the windows and lack of availability of suitable window materials and gaskets). For non-isothermal cells much higher temperatures may be used[109] but there is a danger of formation of smokes, which can cause errors in interpretation. In the area of high-temperature chemistry, flames can be examined by Raman spectroscopy using lasers to obtain spatial resolution.[110] Raman spectroscopy has the disadvantage of being relatively insensitive, but the advantage of detecting homonuclear diatomics such as oxygen and nitrogen which are constituents of many flames. In this connection it is interesting that vibrationally excited nitrogen has been studied using Raman spectroscopy.[111]

Break down of selection rules in gases can occur *via* collisions or by the application of an electric field. Thus vibrational transitions in mixtures of carbon dioxide and hydrogen (under pressure) were observed in the i.r. effect at 6505 cm^{-1} and assigned as 2349(CO_2) + 4160(H_2) cm^{-1}.[112] Compressed nitrogen alone shows an i.r.-active band at 2331 cm^{-1}.[113] At fields in the region 5—30 kV and high pressures, the fundamental vibration-rotation spectrum of hydrogen can be studied in the region of 4160 cm^{-1}.[114] Finally we note that i.r. emission from gases has been studied using a radiofrequency discharge as the excitation source.[115]

4 The Use of Polarized Light

Excitation of Raman (or Rayleigh) scattering with circularly polarized light is important for chiral or non-chiral molecules. We consider initially species that are not optically active.

Circularly polarized light is conveniently visualized as two plane-polarized waves at right angles to one another differing in phase by $\pi/2$ but otherwise identical. The y-component may lead the x-component (by $\pi/2$) or lag behind (by $\pi/2$).

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* Fluorescence lifetimes are usually $> 10^{-9}$ s.

[105] B. P. Stoicheff, *J. Mol. Spectroscopy*, 1970, **33**, 183.

[106] R. R. Alfano and S. L. Shapiro, *Phys. Rev. Letters*, 1971, **26**, 1247.

[107] P. P. Yaney, *J. Opt. Soc. Amer.*, 1972, **62**, 1297.

[108] I. R. Beattie and J. Horder, *J. Chem. Soc.* (*A*), 1969, 2655; I. R. Beattie, 'Molecular Spectroscopy', Institute of Petroleum, London, 1971.

[109] W. Klemperer and L. Lindeman, *J. Chem. Phys.*, 1956, **25**, 397; W. Klemperer, *ibid.*, p. 1066.

[110] C. J. Vear, P. J. Hendra, and J. J. Macfarlane, *J.C.S. Chem. Comm.*, 1972, 381.

[111] L. Y. Nelson, A. W. Saunders, A. B. Harvey, and G. Neeley, *J. Chem. Phys.*, 1971, **55**, 5127.

[112] J. A. A. Ketelaar, *Rec. Trav. chim.*, 1956, **75**, 857.

[113] M. F. Crawford, H. L. Welsh, and J. L. Locke, *Phys. Rev.*, 1949, **75**, 1607.

[114] M. F. Crawford and R. E. Macdonald, *Canad. J. Phys.*, 1958, **36**, 1022.

[115] H. M. Mould, W. C. Price, and G. R. Wilkinson, *Spectrochim. Acta*, 1960, **16**, 479.

These are represented as ± or left/right.

Consider a forward scattering experiment. For the totally symmetric mode of a molecule such as SF_6 or CCl_4 the induced dipole will be parallel to and in-phase with the incident field. Thus the observed Raman scattering will be either circularly polarized left or circularly polarized right, identically with the incident light. Now consider an *oriented* molecule AX_4 as shown in Figure 16. This α_{xy} term for the vibration shown turns y polarized light into x polarized and *vice versa.* Thus the vibration converts left circularly polarized light into right circularly polarized light and *vice versa.*

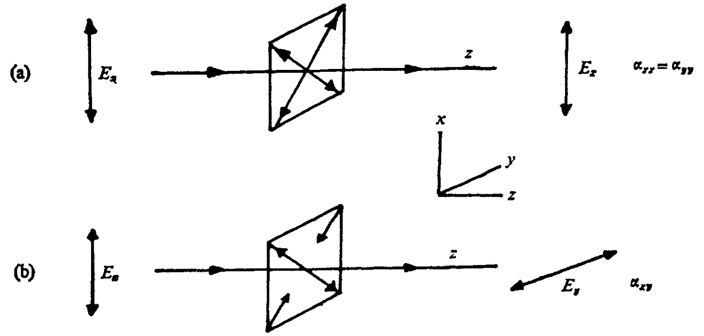

Figure 16 *Raman scattering of circularly polarized light for an oriented square-planar* AX_4 *species* (a) a_{1g} *mode* (b) b_{1g} *mode*

For randomly oriented molecules in a liquid it is (as discussed on p. 121) necessary to average over all orientations. This was originally discussed by Placzek,[116] who defined a 'reversal coefficient',

$$P = \frac{I_+}{I_-} = \frac{2\rho}{1 - \rho}$$

where ρ is the depolarization ratio. Figure 17 shows[117] a rather spectacular demonstration of this technique applied to antimony pentachloride,* where conventional depolarization measurements are hindered by the proximity of a strong depolarized band close to the weak polarized band.

The study of optically active materials in the i.r. and the Raman effect has also recently undergone a major change. The rotation of the plane of polarization of linearly polarized light by optically active materials is well known. In the region of an absorption band the dispersion (change with frequency) of the rotation becomes anomalous (optical rotatory dispersion) in a way similar to that shown in Figure 6 for the refractive index. Because of anomalous optical

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* I am indebted to Dr. A. J. McCaffery for permission to include this spectrum.

[116] G. Placzek, 'The Rayleigh and Raman Scattering', U.C.R.L. Translation 526(L), California, 1962; see also W. M. McClain, *J. Chem. Phys.*, 1971, **55**, 2789.

[117] R. Clark, S. R. Jeyes, A. J. McCaffery, and R. A. Shatwell, to be published.

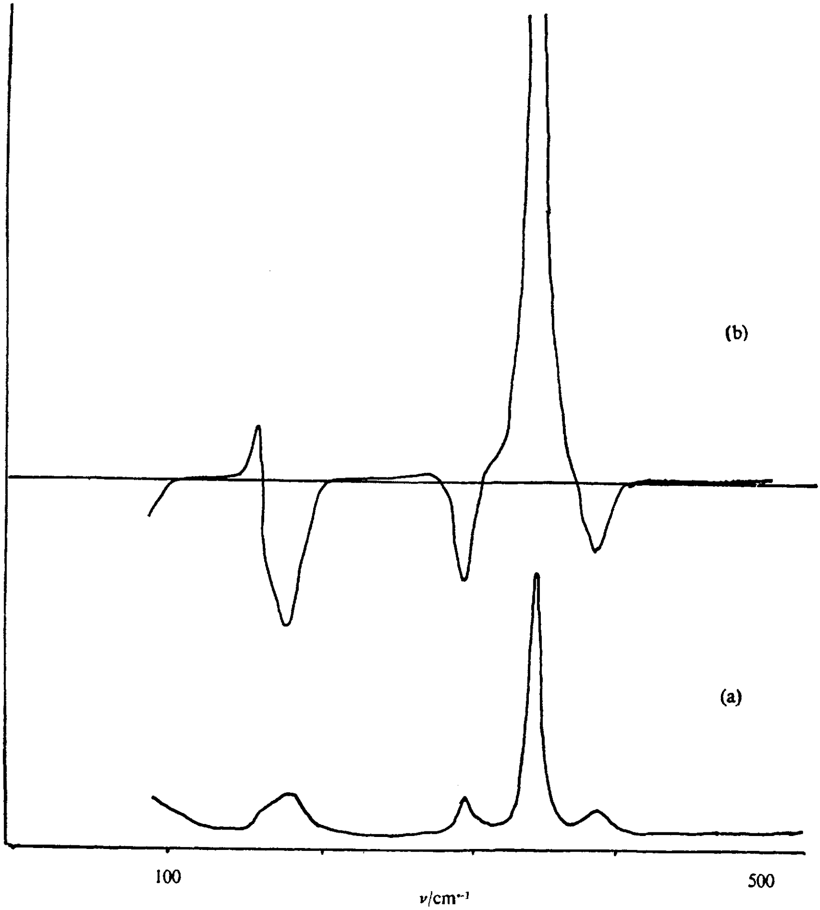

Figure 17 (a) *Circular polarization Raman spectrum of antimony pentachloride without polarization analysis* ($I^+ + I^-$)*;* (b) *circular polarization Raman spectrum of antimony pentachloride with polarization analysis* ($I^+ - I^-$)

rotation, coupled with the change in refractive index, there is also a differential absorption of left and right circularly polarized components (circular dichroism). These effects are known collectively under the term 'Cotton effect'. Optical rotation in the i.r. spectrum has been known and studied for a long time. It is only recently (1972) that vibrational Cotton effects have been detected.[118]

It has been known for some time that the intensity of Rayleigh and Raman scattered light from optically active molecules should show a slight difference for

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[118] R. J. Dudley, S. F. Mason. and R. D. Peacock. *J.C.S. Chem. Comm.*, 1972, 1084.

right and left circularly polarized light.[119] The principal Raman scattering from chiral molecules derives from the α'^2 term. However, there are minor contributions from the optical activity tensors G' and A. Whereas α'^2 terms may be considered to arise through dipole–dipole contributions and hence are symmetric, the $\alpha'G'$ and $\alpha'A$ terms are products of a *vector* dipole and a (symmetrical) axial vector for G' (the magnetic dipole) or a (symmetrical) field gradient tensor for A. The $\alpha'G'$ and $\alpha'A$ scatterings are *ca.* 10^3 times weaker than the α'^2 scatterings but they are different for left and right circularly polarized light in chiral molecules. The difference may be detected using modulation of the incident circular polarization and amplifying only the modulated component of the scattered light. It appears that Raman c.i.d. (circular intensity differential) spectroscopy may become an important technique for probing asymmetric centres.[120]

5 Resonance Processes

The discussion so far has relied heavily upon the Placzek theory of Rayleigh and Raman scattering.[116] However, when the frequency of the exciting radiation lies close to an electronic absorption band for the molecule under investigation the simple Placzek theory is not applicable and the approach of Albrecht and other workers must be adopted.[121] This approach has the great merit of showing the relationship between scattering processes and electronic transitions—respectively second-order and first-order interactions between light and matter.

Classically the picture of an oscillating dipole induced in the molecule by the incident electromagnetic radiation, with the sinusoidal movement of the nuclei superimposed to lead to Raman scattering, is attractive. Placzek showed that provided the ground electronic state of the molecule was $^1\Sigma$, that the Born–Oppenheimer approximation was applicable, and that the exciting frequency was much lower than any electronic absorption frequency of the molecule, then a quantum mechanical analogue of the classical picture could be applied. This introduced the Boltzman distribution leading to an explanation of the low intensity of anti-Stokes relative to Stokes lines. However, it still leaves open the origin of the intensity of the Raman effect.

A better quantum mechanical picture for the normal Raman effect is that, although the exciting radiation is much lower in frequency than the frequency of any electronic transition for the molecule, nonetheless on application of a perturbation the admixture of electronic excited states into the ground state will

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[119] P. W. Atkins and L. D. Barron, *Mol. Phys.*, 1969, **16**, 453; L. D. Barron and A. D. Buckingham, *Mol. Phys,*, 1971, **20**, 1111.

[120] L. D. Barron, M. P. Bogaard, and A. D. Buckingham, *J. Amer. Chem. Soc.*, 1973, **95**, 603; L. D. Barron and A. D. Buckingham, *J.C.S. Chem. Comm.*, 1973, 152.

[121] A. C. Albrecht, *J. Chem. Phys.*, 1961, **34**, 1476; A. C. Albrecht, and M. C. Hutley, *J. Chem. Phys.*, 1971, **55**, 4438; A. H. Kalantar, E. S. Franosa, and K. K. Innes, *Chem. Phys. Letters*, 1972, **17**, 335; J. Behringer and J. Z. Brandmüller, *Z. Elektrochem.*, 1956, **60**, 643; D. G. Rea, *J. Mol. Spectroscopy*, 1960, **4**, 499; O. S. Mortensen, *Mol. Phys.*, 1971, **22**, 179; W. L. Peticolas, L. Nafie, P. Stein, and B. Fanconi, *J. Chem. Phys.*, 1970, **52**, 1576; J. Behringer, 'Raman Spectroscopy', Plenum Press, New York, 1967; L. A. Nafie, P. Stein, and W. L. Peticolas, *Chem. Phys. Letters*, 1971, **12** 131.

occur. Further, those normal modes which are vibronically active in an electronic transition lying close to the frequency of the exciting light should exhibit major enhancement of their Raman intensity.[122] In this way those vibrations which contribute (*via* vibronic mixing) to the 'forbidden' intensity in an electronic transition close to the frequency of the exciting line will be enhanced.

Following on from the discussion it is apparent that if the exciting frequency (ν_0) lies close to an absorption band of the material under study, then those vibrations which mix the (excited) electronic level close to ν_0 with the nearest level corresponding to a strongly allowed transition will become greatly enhanced. This is the resonance Raman effect and Raman bands greater in intensity by several orders of magnitude may be obtained for appropriate fundamentals. By this method low concentrations of material may be examined using Raman spectroscopy; the interpretation of such data may be complicated because of the selective nature of the enhancement. Under resonance conditions (as with the electronic[123] Raman effect) the scattering tensor need not be symmetrical. Modes which are predicted to be inactive in the normal Raman effect may become active under resonance conditions. For example, the a_{2g} vibration of molecules belonging to point group D_{4h} is inactive in the normal Raman effect. However, the scattering tensor under resonance conditions is given by

$$\begin{pmatrix} 0 & \alpha_{xy} & 0 \\ -\alpha_{xy} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

The ρ_p values are also anomalous and for partially asymmetric tensors lie in the range $\frac{3}{4} < \rho_p < \infty$. For a completely asymmetric tensor such as the one above ρ_p becomes infinity. Although Placzek predicted this behaviour forty years ago, it has apparently been experimentally recognized for the first time only very recently. In an elegant paper on resonance Raman spectra of haemoglobin and cytochrome *c*, it was found that several prominent bands exhibited the inverse polarization.[124] In particular this led to rigorous assignment of the a_{2g} vibrations of the tetragonal haem chromophores.

An indication of the value of resonance Raman spectroscopy is found in a study of the I_2^+ ion in fluorosulphuric acid at 10^{-3} molar. The absorption maximum in the electronic spectrum is at 6400 Å and using 6328 Å (He/Ne laser) excitation an excellent resonance Raman spectrum is obtained showing the fundamental and a series of overtones.[125] This result may be compared with an experiment on iodine dissolved in carbon tetrachloride at 10^{-3} molar using i.r. excitation to avoid absorption.[126] A pulsed gallium arsenide laser as source led to *stimulated* emission (see p. 149) as shown by the nearly equal intensities of the Stokes and anti-Stokes lines (*ca.* 1% of the incident power) and the angular

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[122] A. H. Kalantar, E S Franzosa, and K. K. Innes, *Chem. Phys. Letters*, 1972, **17**, 335.

[123] J. A. Koningstein, 'Introduction to the Theory of the Raman Effect', Reidel, Dordrecht, 1972.

[124] T. G. Spiro and T. C. Strekas, *Proc. Nat. Acad. Sci. U.S.A.*, 1972, **69**, 2622.

[125] R. J. Gillespie and M. J Morton, *J. Mol. Spectroscopy*, 1969, **30**, 178.

[126] G. W. Chantry, H. A. Gebbie, and C. Hilsum, *Nature*, 1964, **203**, 1052.

correlation of the emitted light with the incident beam. Another example of the use of resonance Raman spectroscopy is the recent detection of the *p*-phenylenediamine radical in methanol at a concentration of the order of 10^{-4} molar.[127]

However, even under resonance conditions Raman spectroscopy is insensitive compared with many other physical techniques (Table 1). When carrying out experiments to observe Raman spectra, fluorescence phenomena may be observed. The relationship between resonance fluorescence, resonance Raman, and Raman spectroscopy is interesting. The wavelength of the incident light is normally of the order of 5000 Å leading to an oscillating dipole of period *ca.* 10^{-15} s, that of the molecular vibration being *ca.* 10^{-13} s. *Classically* these time-scales are much faster than the frequency of rotation of the molecule (*ca.* 10^{-11} s), accounting for the observation of anisotropic information from an apparently isotropic medium. The Raman effect is tensorial because two sets of axes are fixed in space: the laboratory frame of reference and the molecular axes for each randomly oriented molecule which is fixed in space for the lifetime of the observation.* Since this is a classical view the analogy must not be applied too literally.

The other extreme, that of resonance fluorescence, is well defined. The molecule may be regarded as capturing a photon, $h\nu$, thereby being raised from a particular rotational/vibrational level of the ground electronic state to a particular rotational/vibrational level of an excited electronic state[128] The selection rules are rigorous: Δv may take any value; ΔJ is dependent on the symmetries of the ground and excited states but for a $\sum - \sum$ transition is ± 1. The mean lifetime of the excited state is *ca.* 10^{-7} s so that, in a classical sense, the molecular axes now relax with time and there is only a vector relationship deriving from the laboratory axis, leading to a depolarization ratio of unity for the example cited.

This is an area which is important to chemists because of the possibility of examining species at very low concentrations. It is also an extremely interesting region of study, theoretically and practically, for understanding vibronic effects in molecular spectra and the basis of the Raman effect.† A fascinating observation is that the LO and TO modes of ZnSe, both of which arise from the same mechanical motion in the crystal, show completely different behaviour under resonance conditions. Thus the Raman excitation mechanism for these LO and

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*Rotational Raman bands are depolarized.

† In planning experiments in this area it must be appreciated that there is a (Fourier transform) relationship between the (Gaussian or Lorentzian) half-width in time and the corresponding half-width in frequency. Thus for a one picosecond pulse the half-width will be of the order of 10 cm^{-1}. The further one moves from the long-lived resonance fluorescence process the shorter the necessary time-scale becomes and hence the greater the uncertainty in the frequency of the exciting radiation (see also P. F. Williams, D. L. Rousseau, and S. H. Dwortsky, *Phys. Rev. Letters*, 1974, **32**, 196).

[127] E. Mayer, R. B. Girling, and R. E. Hester, *J.C.S. Chem. Comm.*, 1973, 192.

[128] See, for example, R. F. Barrow, I. R. Beattie, W. G. Burton, and T. R. Gilson, *Trans. Faraday Soc.*, 1971, **67**, 583; W. Holzer, W. F. Murphy, and H. J. Bernstein, *J. Chem. Phys.*, 1970, **52**, 399; W. J. Tango and R. N. Zare, *J. Chem. Phys.*, 1970, **53**, 3094; M. Kroll and D. Swanson, *Chem. Phys. Letters*, 1971, **9**, 115; I. R. Beattie and R. O. Perry, *J. Chem. Soc.* (*A*), 1970, 2071.

TO photons is different although the vibration leading to their occurrence is the same.[129]

6 Phenomena at Very High Fields

In discussing Rayleigh scattering we made use of the formula

$$P = \alpha E$$

which assumes a linear relationship between the induced electric dipole moment P and the electric field strength E. The Raman effect was then introduced as a dependence of α (and hence of P) on the normal co-ordinate Q. At very high fields, found for example in a pulsed laser beam, this approach is inadequate. Some idea of the fields involved is given by considering a 10^{11} W pulse focused to a 0.1 mm spotsize: fields of the order of 10^9 V cm^{-1} and 10^7 G (with radiation pressures of the order of 10^6 atm).

A more general statement of the relationship between induced polarization and electric field is:

$$P = \alpha E + \tfrac{1}{2}\beta E^2 + \tfrac{1}{6}\gamma E^3 \ldots\ldots$$

plus time and spatial dependent derivative terms.[130] The introduction of factors such as $\frac{1}{2}$ and $\frac{1}{6}$ varies with author; here the practice of Buckingham and Orr[131] has been followed. It should be noted that second harmonic generation arises from E^2 terms, which contain a $\cos^2$ function, leading to frequency components at $2\nu_0$. Similarly third harmonic generation arises from the E^3 term.

The above equation may be used to discuss a whole variety of non-linear phenomena including the Kerr effect (electric birefringence) and the intensity dependence of the refractive index. Prior to the invention of the laser the only non-linear optical effect involving high-frequency components in the field was the Raman effect. The Raman effect is a two-photon process—the simultaneous annihilation of one photon with the production of a new photon together with a molecular transition. The intensity of the scattered light for the spontaneous Raman process is directly proportional to that of the incident light.

The phenomena to be discussed below all involve high laser powers. An essential feature of such radiation fields is the occurrence of stimulated effects. The power radiated due to a transition from a state E_i to a state E_j is given by

$$p(\nu_{ij}) = h\nu_{ij}[n_i A_{ij} + (n_i - n_j)B_{ij}\, u(\nu_{ij})]$$

where A_{ij} is the Einstein coefficient for spontaneous emission, B_{ij} is the Einstein coefficient for stimulated emission, and n_i and n_j are the number of atoms in

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[129] R. C. C. Leite, T. C. Damen, and J. P. Scott, in 'Light Scattering in Solids', ed. G. B. Wright, Springer-Verlag, New York, 1969; see also T. C. Damen and Jagdeep Shah, *Phys. Rev. Letters*, 1971, **27**, 1506.

[130] R. W. Terhune and P. D. Maker, 'Non-Linear Optics', Chapter 4 of 'Lasers', ed. A. K. Levine, Arnold, London, 1968; P. D. Maker and R. W. Terhune, *Phys. Rev.* (*A*), 1965, **137**, 801; G. C. Baldwin, 'An Introduction to Non-Linear Optics', Plenum, New York, 1969.

[131] A. D. Buckingham and B. J. Orr, *Quart. Rev.*, 1967, **21**, 195.

states *i* and *j*, respectively. Note the occurrence of $u(\nu_{ij})$, the energy density, as a multiplier in the term for stimulated emission. This equation, given in 1917, is also fundamental to laser action. Note that a photon produced by stimulated emission is identical in phase and direction to the incident photon. Clearly such a process as that described by the second term of the equation above can lead to amplification of an electromagnetic wave.

A. The Hyper-Raman Effect.[132]—The term β is often called the first hyperpolarizability. Its components transform as the products (*ijk*) of the cartesian vectors *x*, *y*, *z*. For centrosymmetric materials and those in the point groups D_6, D_4, and *O*, β is zero.[133] In the same way that the Raman effect is conveniently thought of as arising from $\partial\alpha/\partial Q$ terms, the hyper-Raman effect may be considered as arising from $\partial\beta/\partial Q$ terms, the hyper-Raman tensor in β'_{ijk} is a third-rank tensor. Scattering occurs at $2\nu_0 \pm \nu_R$ (where ν_R is a molecular transition frequency). The selection rules for the hyper-Raman effect are different from those of the Raman effect; all i.r.-active bands are hyper-Raman-active and polarized; it is in principle also possible to observe modes forbidden in the i.r. and Raman effect. The intensity is typically *ca.* 10^{-6} that of the Raman effect. However, under resonance conditions, this may be greatly enhanced by many orders of magnitude giving scattering comparable to that of the normal Raman effect. Little use has been made of this technique.

B. The Stimulated Raman Effect.—As with the above section on non-linear phenomena, the discussion of the stimulated Raman effect will be extremely elementary. The Raman effect can be considered as a wave-mixing experiment: ν_0 incident, ν_S scattered, and a phonon wave representing a vibrational mode. The conventional Stokes Raman process is illustrated in Figure 18a. Note that the dotted line represents a so-called virtual state. A convenient way of considering this is to remember that there is a probability distribution associated with all energy levels in this molecule. A virtual state can be thought of as a region of low probability associated with several energy levels. As the virtual state approaches an eigenvalue of the system, so the more 'real' the state becomes.

Conventionally, we think of a molecular vibration as causing a change in polarizability and hence producing scattered light at a frequency shifted by $\pm\Delta\nu = \nu_R$ from the exciting line. The molecular (thermal) vibrations are random and hence the resultant scattered radiation is of low coherence. By contrast, at very high flux densities the electromagnetic radiation incident on the sample may be considered to cause the molecular oscillators to vibrate in a synchronous fashion. They may be termed to be 'phased coherently'. The non-linear driving force is second order in the field strength. The scattered photons will also create a high flux density, leading to stimulated phenomena.

The situation is complicated by self-focusing of the radiation at high fluxes

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[132] R. W. Terhune, P. D. Maker, and C. M. Savage, *Phys. Rev. Letters*, 1965, **14**, 681; S. J. Cyvin, J. E. Rauch, and J. C. Decius, *J. Chem. Phys.*, 1965, **43**, 4083.

[133] S. C. Abrahams, *J. Appl. Cryst.*, 1972, **5**, 143.

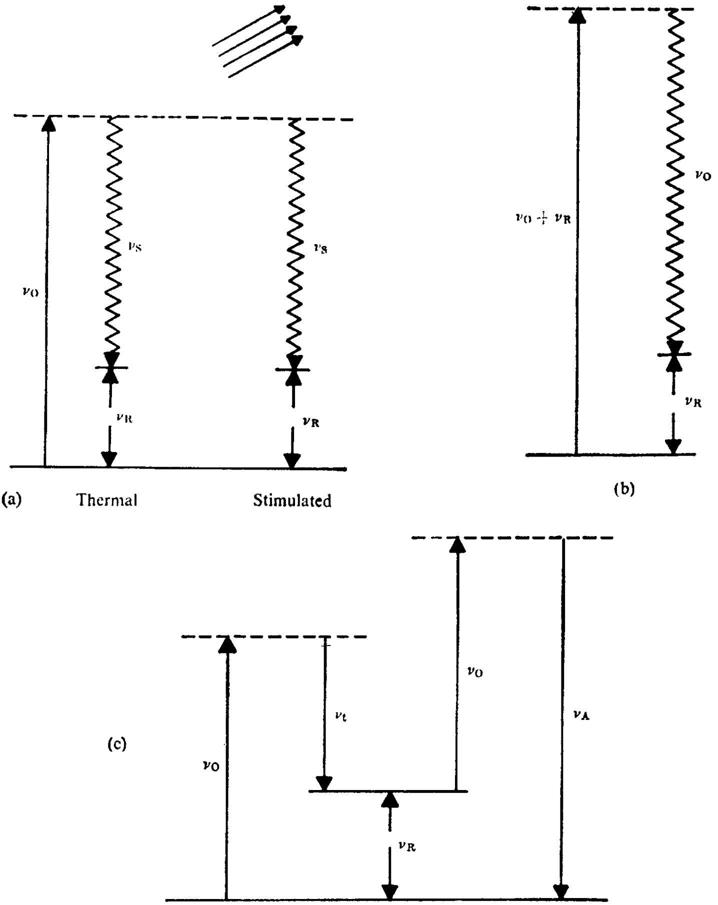

Figure 18 (a) *Stokes Raman scattering, thermal and stimulated;* (b) *inverse* (*Stokes*) *Raman scattering;* (c) *four-wave mixing experiment*

due to the intensity dependence of the refractive index, the refractive index being greater towards the centre of the beam, so that the beam gets narrower and narrower until diffraction spread equals the focusing effect. Further, although the incident laser beam at frequency ν_0 generates a Stokes-shifted beam ν_S and, in addition, an anti-Stokes shifted beam ν_A, these interact to produce Raman lines of higher order.[134] In the case of benzene, for example, the observed effect is a series of Stokes and anti-Stokes lines spaced at the 'breathing frequency' of

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[134] W. J. Woodbury and W. K. Ng, *Proc. Inst. Radio Engrs.*, 1962, **50**, 2367; B. P. Stoicheff, *Phys. Letters*, 1963, **7**, 186; see also A. J. Glass, *I.E.E.E. J. Quantum Electronics*, 1967, **3**, 516.

the carbon ring (992 cm^{-1}). These are not overtones as the frequency shifts are in the ratio 1:2:3 ... with no anharmonicity difference. Further, the lines have intensities comparable with that of the source. The anti-Stokes radiation may form a series of cones ($\nu_0 + \nu_R$, $\nu_0 + 2\nu_R$ .....) progressively out from the central beam which contains the unshifted frequency (ν_0) and the Stokes frequencies ($\nu_0 - \nu_R$, $\nu_0 - 2\nu_R$ .....). The appearance of these rings is associated with the conservation of wave vector.

The disadvantage of the stimulated Raman effect for chemists is that usually only one Raman-active frequency of the system is (selectively) excited. Further, stimulated Brillouin scattering may occur before the possible onset of stimulated Raman scattering. Experimentally the difference between stimulated Raman and stimulated Brillouin scattering is that the Raman process produces light while the Brillouin process produces sound as well (the frequency shifts for Brillouin scattering being much smaller than for the Raman effect).

C. The Inverse Raman Effect.—An alternative description of stimulated Raman scattering is that, in the presence of a photon ν_S, it is possible for a photon ν_0 to be annihilated with the creation of a further identical photon ν_S (together with a transition between molecular energy levels, ν_R). The two photons ν_S can clearly go on to create further ν_S photons leading (in a high ν_0 flux) to amplification at ν_S.

However, irradiation of the system with light at frequency $\nu_A = \nu_0 + \nu_R$ leads to absorption at that frequency. This is the basis of the inverse Raman effect.[135] Light of frequency ν_A is absorbed because it can be converted into molecular vibration quanta plus photons at the laser frequency ν_0 (Figure 18b). Experimentally this is achieved by the simultaneous irradiation of a sample with two intense, collinear beams of light, one of frequency ν_0 and one a continuum. Under these conditions *absorptions* are seen in the continuum at frequencies $\nu_A = \nu_0 + \nu_R$. A number of papers have been published on the use of pulsed lasers to enable inverse Raman spectroscopy to be carried out on the picosecond time-scale.[136] One clear advantage of this technique is the elimination of fluorescence effects.

D. Four-wave Mixing Experiments.—To complete this review it is worth mentioning a technique which is not a conventional study of a vibrational spectrum. The results of such experiments, however, yield vibrational data.

Consider the simultaneous irradiation of a sample with two intense laser beams, one at ν_0 and one at ν_t, where ν_t refers to a tunable laser. Under these conditions four-wave mixing can occur, leading to generation of radiation at $\nu = 2\nu_0 - \nu_t$. When $\nu_0 - \nu_t = \nu_R$ (a molecular transition frequency) the output at $2\nu_0 - \nu_t = \nu_A$ (see Figure 18c) can become large owing to resonant enhance-

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[135] W. J. Jones and B. P. Stoicheff, *Phys. Rev. Letters*, 1964, **13**, 657.

[136] R. R. Alfano and S. L. Shapiro, *Chem. Phys. Letters*, 1971, **8**, 631; R. A. McLaren and B. P. Stoicheff, *Appl. Phys. Letters*, 1970, **16**, 140.

ment.[137,138] The processes illustrated in Figure 18c are synchronous and phased coherently. As radiation is emitted at $2\nu_0 - \nu_t = \nu_0 + \nu_R = \nu_A$ (the anti-Stokes frequency) the phenomenon has been termed Coherent Anti-Stokes Raman Scattering. (This is not the same as stimulated anti-Stokes scattering which requires inversion between initial and final states of the molecule.) A gain of many orders of magnitude over conventional Raman spectroscopy may be obtainable. The beam is highly collimated and fluorescence effects are almost eliminated, a feature of great importance in biological materials for example. A spectacular demonstration of this effect is the observation of the Raman spectrum of benzene to which fluoroscein had been added.[139]

It is interesting to compare this new technique with conventional Raman spectroscopy. Two laser beams are focused and crossed in the cell. The crossing angle is usually *ca.* 1 °, is not critical, and is determined by wave-vector matching. Because the output beam (ν_A) is highly collimated (ideally diffraction limited) spatial filtering should be easily carried out. For benzene, using laser peak powers of the order of 1 kW, the four-wave mixing experiment shows an improvement over conventional Raman spectroscopy of the order of five orders of magnitude. Further, the Raman radiation is spread uniformly over 1 steradian. That for the four-wave mixing experiment is collimated to the order of 10^{-4} steradian. Thus the discrimination against fluorescence is of the order of nine orders of magnitude. Finally the CW equivalent power of the lasers need only be of the order of a few milliwatts and a monochromator may be unnecessary. It has been suggested that for peak powers of the order of 1 MW detection levels of *ca.* 10^{-6} Torr are feasible in gases.

The observed intensity is proportional to the square of (*a*) the number density of molecules, (*b*) the (normal) Raman scattering cross-section, and (*c*) the reciprocal of the (normal) Raman half-width. However, under some conditions the intensity may be directly proportional to (*a*), (*b*), and (*c*), although the signal may be masked by nearby strong Raman modes or electronic effects. A point of some importance for gases is that, although the signal increases as the pressure squared, it also increases as the square of the coherence length. Thus if the length of the laser path through the gas is greater than the coherence length the signal will be constant with pressure. For solids and liquids the coherence length is only of the order of 1 mm. For gases it is tens of centimetres.

It appears likely that this technique (Coherent Anti-Stokes Raman Spectroscopy or CARS) will profoundly affect some branches of Raman spectroscopy. Further, two incident light sources illuminate the sample, the one resultant ray being used for CARS observation. Clearly (as with the hyper-Raman effect) more types of polarization measurement are possible than with the conventional Raman effect. In this way it may be possible to differentiate not only totally symmetric modes, but also possibly non-totally symmetric modes of different symmetries. It should also be noted that all Raman modes are CARS active,

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[137] J. Lukasik and J. Ducuing, *Phys. Rev. Letters*, 1972, **28**, 1155.

[138] P. R. Régnier, F. Moya, and J. P. E. Taran, *Appl. Phys. Letters*, 1973, **23**, 240.

[139] R. F. Begley, A. B. Harvey, R. L. Byer, and B. S. Hudson, *J. Chem. Phys.*, 1974, **61**, 2466.

and in addition some Raman-inactive modes occur in the CARS or four-wave mixing experiment.[140]

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