

# STRUCTURE AND BONDING 36

R. J. H. Clark, B. Stewart  
The Resonance Raman Effect. Review  
of the Theory and of Applications in Inorganic Chemistry

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Alkali Metal Suboxides

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## *Contents*

The Resonance Raman Effect. Review of the Theory and of Applications in Inorganic Chemistry R. J. H. Clark, B. Stewart	1
Structure and Bonding with Alkali Metal Suboxides A. Simon	81
The Electronic Structure of Cobalt(II) Complexes with Schiff Bases and Related Ligands C. Daul, C. W. Schläpfer, A. von Zelewsky	129

# The Resonance Raman Effect— Review of the Theory and of Applications in Inorganic Chemistry

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## Table of Contents

1	Introduction . . . . .	2
2	Résumé of the Theory of the Resonance Raman Effect . . . . .	4
2.1	The Dispersion Equation . . . . .	4
2.2	The Vibronic Nature of the Scattering Tensor . . . . .	6
2.3	Normal Raman Scattering . . . . .	8
2.4	Resonance Raman Scattering . . . . .	9
2.5	Totally Symmetric Modes and Franck-Condon Scattering . . . . .	13
2.6	The Vibronic View of Franck-Condon Scattering . . . . .	15
2.7	Excitation Profiles for Totally Symmetric Modes . . . . .	21
2.8	Combination-Band Progressions Involving Solely Totally Symmetric Modes . . . . .	24
2.9	Non-Totally Symmetric Modes and Herzberg-Teller Scattering . . . . .	27
2.9.1	Overtone and Combination Bands of Herzberg-Teller Active Modes . . . . .	29
2.9.2	Antisymmetric Tensor Contributions to Resonance Raman Scattering . . . . .	32
2.10	Combination-Band Progressions Involving One or Two Quanta of a Non-Totally Symmetric Modes . . . . .	36
2.11	Depolarisation Ratios and the Symmetry of the Scattering Tensor . . . . .	37
2.11.1	Totally Symmetric Modes . . . . .	40
2.11.2	Non-Totally Symmetric Modes . . . . .	42
2.12	Harmonic Wavenumbers and Anharmonicity Constants . . . . .	45
3	Techniques . . . . .	47
4	Review of Experimental Results on Inorganic Systems . . . . .	50
4.1	Diatomic Species . . . . .	50
4.1.1	Molecular Iodine . . . . .	50
4.1.2	Ionic Species . . . . .	52
4.2	Triatomic Species . . . . .	57
4.3	Tetrahedral Species . . . . .	57
4.4	Square Planar and Octahedral Species . . . . .	60
4.5	Metal-Metal Bonded Species . . . . .	62
4.6	Bridged Species . . . . .	66
4.7	Mixed-Valence Species . . . . .	68
4.8	Haem Proteins and Other Biological Systems . . . . .	71
4.9	Other Applications . . . . .	77
	References . . . . .	78

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## 1 Introduction

Raman spectroscopy provided most of the early experimental data on molecular vibrational frequencies, but with the advent of commercial infrared spectrometers in the 1940's, the technique stagnated with respect to infrared spectroscopy. This was despite the fact that Raman spectroscopy enjoyed, and still enjoys, certain natural advantages over infrared spectroscopy, *viz.*

- (i) The possibility of working with glass or silica cells, which are much easier to handle and which are less fragile and moisture-sensitive than the alkali-halide windows used in infrared spectroscopy;
- (ii) Water is an excellent solvent for Raman studies, but a difficult one for infrared work; this is because the Raman scattering from water is weak whereas the infrared absorption by it is strong;
- (iii) For solids, no mulling agents are necessary and so no complications arise from bands of the mulling agent;
- (iv) Totally symmetric modes of vibration may be identified by Raman spectroscopy by polarisation studies, even for freely rotating fluids; and
- (v) Raman shifts of low frequency can be measured as easily at (say)  $100\text{ cm}^{-1}$  as at  $1000\text{ cm}^{-1}$ , whereas the degree of sophistication of infrared equipment must increase rapidly for low frequency studies; this is principally because of the very low intensity of the infrared emission by any source in the low frequency region.

The renaissance of Raman spectroscopy came about in the 1960's by way of several striking technical advances. The most dramatic of these was the discovery of the laser, which emits a coherent beam of light, and which has many advantages over the traditional sources, such as the mercury arc, whose commonly used excitation lines have wavelengths of 435.8 and 546.1 nm. These advantages include the following:

- (i) The power flux density of laser beams is much greater than that of traditional sources, e.g. Hg lamp  $\sim 1\text{ W cm}^{-2}$ , continuous wave (c.w.)  $\text{Ar}^+$  ion laser  $\sim 10^5\text{ W cm}^{-2}$ , pulsed glass lasers  $\sim 10^{12}\text{ W cm}^{-2}$ . As the intensity of the scattered radiation is directly related to that of the incident beam, it is clear that much more intense Raman spectra can be obtained by use of laser beams.
- (ii) With  $\text{Ar}^+$  and  $\text{Kr}^+$  ion lasers, there is the choice of about 20 different exciting lines with wavelength ranging from 333.6 to 799.3 nm. Thus the wavelength of the exciting line can be chosen so as either to avoid or alternatively to approach at will the maxima of absorption bands of the scattering molecules.
- (iii) Laser beams are very narrow (e.g. for the He/Ne laser,  $\Delta\nu_{1/2} = 0.05\text{ cm}^{-1}$ ) and can be made much narrower still by introduction of etalons. High resolution work, e.g. on the vibrational-rotational spectra of molecules in the gas phase, thus becomes more feasible with lasers than with conventional sources.
- (iv) The directional properties and linear polarisation of the laser beam make it invaluable for studies of single crystals in which the magnitudes of the individual components,  $\alpha_{\rho\sigma}$ , of the polarisability tensor governing the intensity of the Raman scatter-

ing, can be measured. The directional properties are also an advantage in the study of surfaces of opaque solids and of reaction products formed on the surfaces of electrodes.

The laser was not, however, the only technical advance in the field of Raman spectroscopy to take place in the 1960's. The introduction of extremely sensitive phototubes enabled Raman spectra to be recorded photoelectrically rather than photographically, with consequent enormous saving in recording times. Further, high quality double and triple monochromators of high efficiency have been developed so that it is now possible to scan to within about  $3\text{ cm}^{-1}$  of the exciting line and to obtain good quality Raman spectra. The consequence of these advances is that Raman spectroscopy has now reasserted itself so that it has become again the equal partner with infrared spectroscopy in the study of molecular vibrations.

Raman spectra known as resonance Raman spectra are obtained when a molecule in the vapour state at high pressure or in a condensed state is excited with a laser beam whose frequency corresponds or closely corresponds with that of the band maximum of an electric-dipole-allowed transition of the molecule. Such spectra are frequently characterised by an enormous enhancement to the intensity of the band arising from a totally symmetric fundamental of the molecule, together with the appearance of high intensity overtone progressions in this same fundamental. The technique provides detailed information about the chromophore, because it is only vibrational modes closely associated with atoms at the absorbing centre in the molecule which display the effect. The intensification of the Raman band is so great that compounds at concentrations of  $10^{-6}\text{ M}$  in water can now be detected. The technique has thus attracted considerable attention in biological circles, and much information on the chromophoric centres of molecules such as cytochrome c and haemoglobin has been obtained. The technique is also being used for the remote sensing of small amounts of atmospheric pollutants such as  $\text{NO}_2$  and  $\text{O}_3$ .

Many of the early studies of the resonance Raman effect, particularly of organic molecules possessing conjugated double bonds, were carried out by *Behringer* and *Brandmüller*, and comprehensive reviews of this area are available (1, 2). Comparable studies on inorganic complexes have only been carried out in the last ten years, the results till 1974 having been reviewed previously (3). However, within the last few years there has been an enormous increase in activity (theoretical as well as experimental) in this area, and accordingly it seems appropriate to review the subject as it now stands. Particularly important would appear to be the advances in our understanding of the different mechanisms of Raman scattering and of excitation profiles (plots of Raman band intensities versus excitation wavenumber), and the information these give pertinent to the assignment of the resonant electronic transitions.



## 2 Résumé of the Theory of the Resonance Raman Effect

### 2.1 The Dispersion Equation

The total intensity of radiation scattered into a solid angle of  $4\pi$  during a Raman process in which a molecular system, initially in a state  $|G\rangle$ , makes a transition to a final state  $|F\rangle$ , is given by

$$I_S^{\text{TOTAL}} = (2^7 \pi^5 / 9) I_L \nu_S^4 \sum_{\rho, \sigma} |(\alpha_{\rho\sigma})_{G \rightarrow F}|^2 \quad (1)$$

$I_L$  is the intensity of the incident radiation of wavenumber  $\nu_L$ .  $\nu_S$  is the wavenumber of the scattered radiation:  $\nu_S = \nu_L \pm \nu_{GF}$ , where the plus sign refers to anti-Stokes and the minus sign to Stokes scattering.  $\nu_{GF}$  is the wavenumber of the molecular transition  $|G\rangle \rightarrow |F\rangle$ .  $(\alpha_{\rho\sigma})_{G \rightarrow F}$  is the polarisability or scattering tensor for the process  $|G\rangle \rightarrow |F\rangle$  in which the polarisations of the incident and scattered radiation are represented by the indices  $\sigma$  and  $\rho$  respectively. ( $\sigma, \rho = x, y, z$ ).

In the usual experimental set up, the scattered radiation is collected in some small solid angle around an observation direction at  $90^\circ$  to that of the incident radiation. A schematic diagram of a typical laser Raman set-up involving  $90^\circ$  collection optics is shown in Fig. 1, together with the definition of the depolarisation ratio

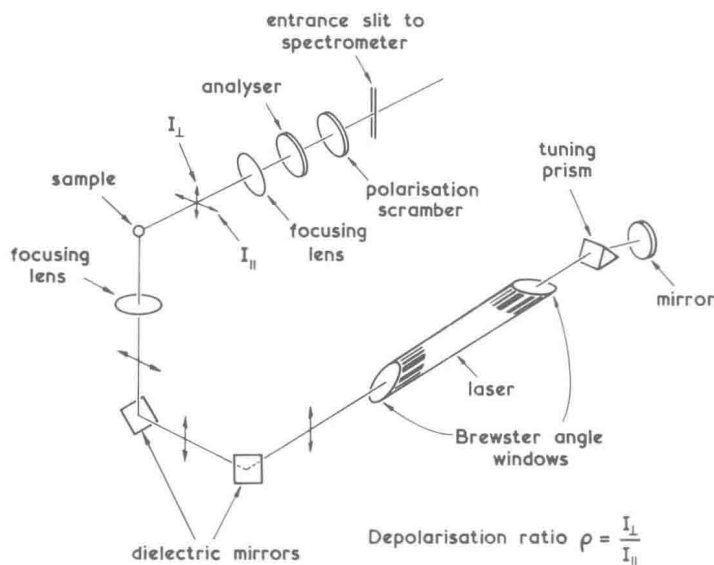


Fig. 1. Experimental set up ( $90^\circ$  collection optics) for the measurement of laser Raman scattering, illustrating the definition of the depolarisation ratio.  $I_{\parallel}$  and  $I_{\perp}$  are the intensities of light scattered, respectively, parallel and perpendicular to the polarisation of the incident exciting beam

$\rho_1 = I_{\perp}/I_{\parallel}$  for linearly polarised incident radiation. In this case, Eq. (1) must be multiplied by the factor  $(3/8 \pi) (1 + \rho_1)/(1 + 2 \rho_1)$ . (5a). If only the parallel component of scattered radiation is measured the factor is  $(3/8 \pi) (1 + 2 \rho_1)^{-1}$ . ( $I_{\perp} = \rho_1 I_{\parallel}$ ). For naturally polarised (unpolarised) or circularly polarised incident light the relevant factors are given in terms of the depolarisation ratio,  $\rho_n$ , for natural polarisation, where

$$\rho_n = 2 \rho_1 / (1 + \rho_1) .$$

Thus,

$$I(\pi/2) = (3/4 \pi) (2 + \rho_n)^{-1} I_S^{\text{TOTAL}}$$

and

$$I_{\parallel}(\pi/2) = (3/8 \pi) [(2 - \rho_n)/(2 + \rho_n)] I_S^{\text{TOTAL}}$$

The polarisability tensor is given by a second-order perturbation expression known as the *Kramers-Heisenberg* dispersion formula (4)

$$(\alpha_{\rho\sigma})_{G \rightarrow F} = \frac{1}{hc} \sum_E \left[ \frac{\langle F | \mu_{\rho} | E \rangle \langle E | \mu_{\sigma} | G \rangle}{\nu_{GE} - \nu_L + i \Gamma_E} + \frac{\langle F | \mu_{\sigma} | E \rangle \langle E | \mu_{\rho} | G \rangle}{\nu_{FE} + \nu_L + i \Gamma_E} \right] \quad (2)$$

where  $\mu_{\sigma}, \mu_{\rho}$  are the electric-dipole-moment operators e.g.  $\mu_{\rho} = - \sum_k e(r_k)_{\rho}$ , and  $(r_k)_{\rho}$  is the  $\rho$ -th component of the position vector of the  $k^{\text{th}}$  electron.  $\Gamma_E$  is the damping factor or natural half-width of the state  $|E\rangle$ . It must be noted that the sum over the intermediate states,  $|E\rangle$ , excludes the initial and final states  $|G\rangle$  and  $|F\rangle$ .

Equation (2) (without damping factors) was originally developed by *Kramers* and *Heisenberg* by analogy with the classical theory of dispersion. The classical problem was the explanation of the lower velocity of light in materials compared to that in the vacuum and this was described in terms of the interference between scattered and unscattered waves. The quantum mechanical description is based on the model of the electric dipole moments induced in the system by the radiation field and the subsequent radiation by these dipoles. The dispersion formula was later verified by *Dirac* (6) using quantum electrodynamical arguments. Following *Heitler* (7), *Dirac* (8) introduced the damping terms in order to prevent the expression becoming infinite in the case of resonance scattering, for which the wavenumber of the incident radiation approaches and becomes equal to that of a molecular transition:  $\nu_L = \nu_{GE}$ . In these circumstances, the first term in square brackets of Eq. (2) may give rise to a large increase in scattered intensity, this increase being limited by the magnitudes of the appropriate matrix elements in the numerator and of the half-width,  $\Gamma_E$ , for the resonant state  $|E\rangle$ . The second term in the square brackets of Eq. (2) is non-resonant and produces a slowly varying background contribution, which is usually negligible compared to the resonant contribution when  $\nu_L$  is in the resonance region. However, both halves of the polarisability expression must be taken into account when  $\nu_L$  is far from resonance, as in the case in the normal Raman effect for which  $\nu_{GE} \gg \nu_L \gg \nu_{GF}$ .

This review is largely concerned with vibrational Raman scattering in which the states  $|G\rangle$  and  $|F\rangle$  differ only in the possession of one or more quanta of vibrational energy. In systems with electronically degenerate ground states it is impossible to avoid entirely the effects of simultaneous changes in the electronic and vibrational quantum numbers: This latter point is discussed briefly later on with respect to the Jahn-Teller effect as well as the electronic Raman effect.

## 2.2 The Vibronic Nature of the Scattering Tensor

To proceed further it is necessary to elaborate on the vibronic nature of the states and operators in the scattering tensor. The adiabatic Born-Oppenheimer (ABO) approximation will be employed in which the vibronic states are formed by products of pure vibrational states  $\Lambda_{i,u}(Q)$  with pure electronic states  $\Phi_i(Q, r)$ . The latter are referred to some fixed positions of the nuclei and are therefore parametrically dependent on the internuclear distances expressed as a set,  $Q_\xi$ , of normal coordinates.  $r$  is a set of electronic coordinates, and  $i, u$  are electronic and vibrational quantum numbers respectively. Thus

$$\Psi_{i,u}^{ABO}(Q_\xi, r) = \Phi_i(Q_\xi, r) \Lambda_{i,u}(Q_\xi) \quad (3)$$

and

$$\Lambda_{i,u}(Q_\xi) = \prod_{\xi} \phi_{i,u}^{\xi}(Q_\xi)$$

where  $\phi_{i,u}^{\xi}$  is usually a harmonic oscillator function for the  $\xi$ -th normal coordinate,  $Q_\xi$ , in the electronic state  $|i\rangle$ . In many instances it is necessary to consider only a single normal coordinate and therefore the index  $\xi$  will be dropped for these cases. A vibrational level will be conveniently written as  $|u_i\rangle$ .

The validity of the ABO approximation depends on the separability of the electronic and nuclear vibrational motions, which is contingent upon the smallness of the ratio of the electronic to the nuclear mass. The electronic part of the ABO product function [Eq. (3)] is accordingly defined for fixed nuclear positions and is known as a crude-adiabatic (CBO) electronic function. A CBO electronic function is an eigenfunction of a total electronic Hamiltonian which contains the electron-nuclear and nuclear-nuclear potential energies (for some fixed positions of the nuclei), but lacks the nuclear kinetic-energy terms. This approximation is a good one, provided the electronic states have large energy separations compared with a vibrational quantum, and it has the advantage that an adiabatic potential-energy curve for nuclear vibration is given by a plot of the total electronic energy for various fixed positions of the nuclei. When electronic states approach very closely in energy, strong vibronic coupling leads to narrowly avoided crossings of the adiabatic potential curves and in these regions the (neglected) nuclear momentum may cause non-adiabatic coupling between different ABO manifolds. In the diabatic BO (DBO) approximation, the basis states exact-

ly diagonalise the kinetic energy terms in the Hamiltonian and this gives a better description of the system near the avoided crossings but is a worse approximation everywhere else (30).

When the ABO states are substituted into the polarisability expression (2) it is possible formally to complete the integrations over the electronic coordinates in the matrix elements. Thus, for example,

$$\langle G | \mu_\rho | E \rangle = \langle \Lambda_{g,u} | \rho_{ge}(Q) | \Lambda_{e,v} \rangle \quad (4)$$

where

$$\rho_{ge}(Q) = \int \Phi_g(Q, r) \mu_\rho \Phi_e(Q, r) dr$$

and  $\sigma_{ge}(Q)$  is defined similarly.

This is because the electric dipole operators,  $\mu_\rho$ , act only on the electronic coordinates, the contribution to the transition moment from the nuclear coordinates being negligible. The resulting matrix elements,  $\rho_{ge}(Q)$ , are still parametrically dependent on  $Q$  through the electronic states. This dependence is supposed to be a weak function of the internuclear coordinates and is therefore described by a rapidly converging Taylor series expanded about the equilibrium configuration,  $Q = 0$ , of the ground electronic state:

$$\rho(Q) = \rho(0) + \left( \frac{\partial \rho(Q)}{\partial Q} \right)_{Q=0} Q + \dots \quad (5)$$

If this expansion for the transition moments is used then the resonant part of the scattering tensor may be expressed, in terms to the first order in  $Q$ , as follows:

$$\begin{aligned} (\alpha_{\rho\sigma})_{u \rightarrow w} = & \sum_e \sum_v (E_{ev} - E_{gu} - E_L + i \Gamma_{ev})^{-1} \\ & \times [ \rho_{ge}^0 \sigma_{eg}^0 \langle w_g | v_e \rangle \langle v_e | u_g \rangle \\ & + \rho'_{ge} \sigma_{eg}^0 \langle w_g | Q | v_e \rangle \langle v_e | u_g \rangle \\ & + \rho_{ge}^0 \sigma'_{eg} \langle w_g | v_e \rangle \langle v_e | Q | u_g \rangle ] \end{aligned} \quad (6)$$

using the abbreviations  $\rho^0 = \rho(0)$ ,  $\rho' = (\partial \rho(Q)/\partial Q)_{Q=0}$ , etc.  $E_{ev}$  is the energy of the  $v$ -th vibrational level of the intermediate electronic state  $|e\rangle$ ,  $E_{gu}$  the energy of the  $u$ -th level of the ground state  $|g\rangle$  and  $E_L (= hc \nu_L)$  the energy of the incident light quantum. In the harmonic approximation,  $E_{ev} = E_{e0} + h\nu_e \nu$  for a fundamental of wavenumber  $\nu$ . The circular frequency  $\omega (= 2\pi\nu)$  is employed by many physicists, who therefore express vibrational energies as  $\hbar\omega$ .

The first term in the square brackets of Eq. (6) gives rise to the A term and the second and third terms to the B term of *Albrecht* (9, 10). The further analysis of this expression requires specification of the energy region of excitation.

### 2.3 Normal Raman Scattering

In the ideal limit of the normal (non-resonance) Raman effect the energy of the exciting radiation is far removed from any transition energy of the system. That is

$$E_{ev} - E_{gu} \gg E_L \gg \hbar\omega$$

The energy denominators in the resonant and non-resonant parts of the polarisability [Eq. (2)] are each large and insensitive to the vibrational quantum numbers,  $v_e$ , of the intermediate electronic state  $|e\rangle$ . Since the  $v_e$  represent a complete orthonormal set of states, the sums over them in Eq. (6) may be evaluated by using the closure theorem, provided that the  $v$ -dependence of the energy denominators is negligible. The closure theorem may be stated essentially as:  $\sum_{\text{all } v} |v\rangle\langle v| \equiv 1$ , and arises

from the matrix product rule  $\sum_j \mathbf{A}_{ij} \mathbf{B}_{jk} = (\mathbf{AB})_{ik}$ . This leads to the following simplifications in the vibrational matrix elements:

The matrix elements in the non-resonant part of the scattering tensor may be treated in the same manner. The final expression for Eq. (6), plus its non-resonant counterpart, is

$$\left. \begin{aligned} \sum_v \langle w_g | v_e \rangle \langle v_e | u_g \rangle &= \langle w_g | u_g \rangle = \delta_{u,w} \\ \sum_v \langle w_g | Q | v_e \rangle \langle v_e | u_g \rangle &= \sum_v \langle w_g | v_e \rangle \langle v_e | Q | u_g \rangle = \langle w_g | Q | u_g \rangle = \delta_{u,w \pm 1} \end{aligned} \right\} \quad (7a)$$

$$\delta_{u,w \pm 1} = \left( \frac{\hbar}{2\mu\omega} \right)^{1/2} [w^{1/2} \delta_{u,w-1} + (w+1)^{1/2} \delta_{u,w+1}] \quad (7b)$$

$\delta_{u,w} = 1$  if  $u = w$  and  $= 0$  otherwise, as a result of the orthonormality of the vibrational states.  $\delta_{u,w \pm 1}$  is defined in Eq. (7b) and results from the selection rule on the matrix elements of  $Q$  in the harmonic oscillator approximation (11).

$$\begin{aligned} (\alpha_{\rho\sigma})_{u \rightarrow w} &= \sum_e \left[ \frac{\rho_{ge}^0 \sigma_{eg}^0}{E_e - E_g - E_L} + \frac{\sigma_{ge}^0 \rho_{eg}^0}{E_e - E_g + E_L} \right] \delta_{u,w} \\ &+ \sum_e \left[ \frac{\rho'_{ge} \sigma_{eg}^0 + \rho_{ge}^0 \sigma'_{eg}}{E_e - E_g - E_L} + \frac{\sigma'_{ge} \rho_{eg}^0 + \sigma_{ge}^0 \rho'_{eg}}{E_e - E_g + E_L} \right] \delta_{u,w \pm 1} \end{aligned} \quad (8)$$

The half band-widths have been omitted on the grounds that  $E_e - E_g \pm E_L \gg \Gamma_e$  for the case of normal Raman scattering. More concisely, Eq. (8) may be written

$$(\alpha_{\rho\sigma})_{u \rightarrow w} = \alpha_{\rho\sigma}^0 \delta_{u,w} + \alpha'_{\rho\sigma} \delta_{u,w \pm 1}$$

since

$$\rho' \sigma^0 + \rho^0 \sigma' = (\rho\sigma)'.$$

This represents Placzek's results to the first order (5b). The first term gives rise only to Rayleigh scattering ( $u = w$ ) and depends on the electronic polarisability of

the scattering species at equilibrium in its ground state. The second term gives a Raman fundamental ( $u = w \pm 1$  for anti-Stokes and Stokes scattering, respectively) and depends on the first derivative of the polarisability with respect to the normal coordinate involved. To account for overtones which, however, are generally very weak or absent in the normal Raman effect, higher derivatives of the polarisability must be considered. In general,

$$\alpha_{\rho\sigma} = \sum_{n=0}^{\infty} \frac{1}{n!} \frac{\partial^n(\alpha_{\rho\sigma})}{\partial Q^n}$$

where the even derivatives contribute to Rayleigh scattering and to even harmonics (even multiples of the fundamental). Odd derivatives contribute to the fundamental scattering and the odd harmonics.

In summary, normal Raman scattering occurs via an intermediate state described by comparable contributions from a large number of excited electronic states,  $e$ , of the system. As a result the intermediate state has no well-defined electronic symmetry and the scattering tensor is symmetric in the indices  $\rho$  and  $\sigma$ . The symmetry of the tensor arises also if the contribution from the two halves of Eq. (2) are equal, which is true to a good approximation when  $\nu_L \ll \nu_{GE} \cong \nu_{FE}$ . This depends on the fact that, in the sum over  $E$ , the higher energy states predominate despite their unfavourable denominators. The states near and above the dissociation limit are important, presumably because of their high density and oscillator strengths, and there is a good empirical proportionality between the polarisability and the first ionisation potential (12). The insensitivity of the scattering to the vibrational structure of the intermediate states accounts for the zero contribution from the vibrational overlap integrals (Franck-Condon factors). This latter point, together with the fact that the second and higher derivatives of  $\alpha$  are usually negligibly small, explains the general weakness or absence of overtones in normal Raman scattering.

## 2.4 Resonance Raman Scattering

As resonance is achieved by allowing the incident light energy,  $E_L$ , to approach some molecular transition energy,  $E_{ev} - E_{gu}$ , the denominator  $(E_{ev} - E_{gu} - E_L + i\Gamma_{ev}) = \Delta E + i\Gamma_{ev}$  becomes small and the scattering tensor correspondingly large. When  $\Delta E$  is of the order of a vibrational energy-level difference,  $\hbar\omega$ , then obviously the approximation of neglecting the dependence of the denominators on the excited-state vibrational quantum numbers becomes inadequate. In this case, closure cannot be applied as it was in Eq. (7a) to reduce the polarisability to being a property of the ground state only. However, simplifications also take place in that, as  $E_L$  approaches some particular transition energy, the appropriate excited state will dominate the sum over states in the scattering tensor. It is therefore generally sufficient to consider only one, or at most two, electronic manifolds in accounting for resonance Raman scattering.

It is useful to discuss the factors determining the relative importance of the zeroth-order (Franck-Condon, FC) and first-order (Herzberg-Teller, HT) terms in the nuclear-coordinate expansion of the polarisability. In an early treatment of the resonance Raman effect by *Albrecht* 1961 (9), it was assumed that the closure procedure was still a good approximation even in regions of excitation close to absorption bands. If this were true then, as we have seen, the FC terms would be responsible only for Rayleigh scattering. The enhancement of Raman scattering must then be attributed to the first-order terms. These were explicitly developed by Albrecht from a (first-order) Herzberg-Teller perturbation description (13, 14) of vibronic coupling:

$$\mathbf{Q}'_{ge} = \sum_{s \neq e} \mathbf{Q}^0_{gs} \langle s | \partial \mathcal{H} / \partial Q | e \rangle_0 (E_e - E_s)^{-1} \quad (9)$$

where

$$\langle s | \partial \mathcal{H} / \partial Q | e \rangle_0 \text{ is written for } \int \Phi_s(Q, r) \left( \frac{\partial \mathcal{H}}{\partial Q} \right)_{Q=0} \Phi_e(Q, r) dr$$

and  $\mathcal{H}$  is the Hamiltonian for the total electronic energy of the molecule. In this approach, the derivative of the transition moment arises because the variation in the Hamiltonian with respect to the normal coordinate,  $Q$ , can mix the state  $|e\rangle$  with other states  $|s\rangle$  of the appropriate symmetry. Thus, by Eq. (9), a portion of the transition moment,  $\mathbf{Q}^0_{gs}$ , is acquired for the process  $|g\rangle \rightarrow |e\rangle$ . This mechanism is particularly useful when the transition to the state of interest is forbidden in zero order, i.e.  $\mathbf{Q}^0_{ge} = 0$  as, for example, in the Laporte-forbidden d-d or f-f transitions. However, since large scattering intensities are favoured by a strong intrinsic transition moment,  $\sigma^0_{eg}$ , in the relevant part of Eq. (6):

$$(\alpha_{\rho\sigma})_{u \rightarrow w} = \sum_v (E_{ev} - E_{gu} - E_L + i \Gamma_{ev})^{-1} \mathbf{Q}'_{ge} \sigma^0_{eg} \langle w_g | Q | v_e \rangle \langle v_e | u_g \rangle$$

[with  $\mathbf{Q}'_{ge}$  given by Eq. (9)], this approach led to the statement (9) that the modes enhanced in resonance are those most responsible for “forbidden” intensity in an *allowed* electronic band. This is true in the case of an allowed transition with FC terms which are accidentally very small or zero so that the HT terms then dominate the scattering mechanism. This implies that totally symmetric modes are only enhanced if they are active in vibronic coupling between two allowed electronic bands *of the same symmetry*. However, the situation just outlined is not generally encountered. More usually, allowed transitions have non-zero and often large FC integrals, and resonance scattering is dominated by these because the closure sum rule is not even approximately valid close to, or within an absorption band. Furthermore, a more general treatment must include vibronic coupling within a single electronic excited state via totally symmetric modes. Actually, these last two points are intimately related, since the one-state vibronic coupling (via a totally symmetric mode in a non-degenerate state) can be shown to give rise to the Franck-Condon effect; that is, ex-

tended overtone progressions in the frequency of the responsible totally symmetric mode. Progressions in the excited state frequency appear in an absorption spectrum at low temperature (Fig. 2). The ground-state frequency appears in relaxed fluorescence (Fig. 2) and in the resonance Raman effect (Fig. 3). In a converse approach, *Tang* and *Albrecht* (15) have shown that, when the nuclear-coordinate dependence of the energy denominators is explicitly taken into account in the A term, the FC contribution becomes equivalent to a one-state “B term”. The relation between the vibronic view and the overlap view of FC scattering is discussed in more detail in Section 2.6.

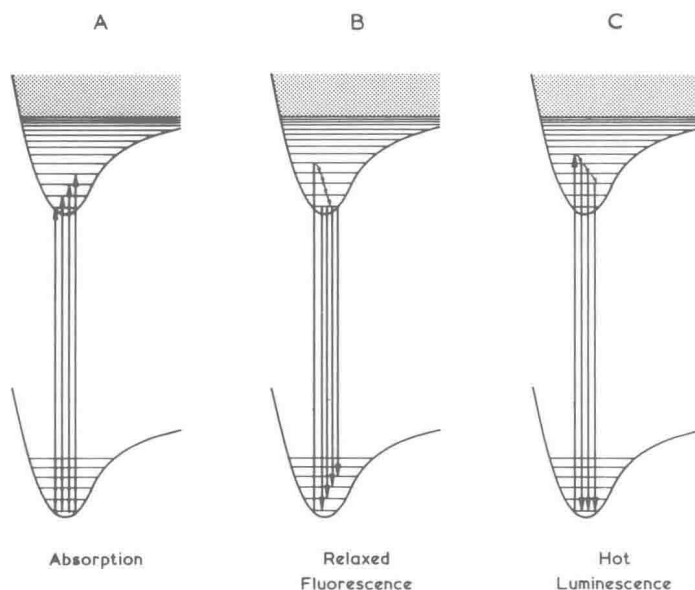


Fig. 2. The origin of vibrational progressions in absorption and emission processes.

A. A progression in the excited-state frequency occurs in absorption. B. A progression in the ground-state frequency occurs in relaxed fluorescence where non-radiative relaxation processes occur faster than the emission process in the excited state. C. Excited state vibrational intervals may occur in hot luminescence where the speed of non-radiative relaxation is similar to, or slower than, that of the emission process

Since the H-T terms are developed from the first-order terms active in the non-resonance Raman effect, they are usually the most important source of preresonance enhancement whereas the FC terms are active in proportion to the extent to which closure fails for the vibrational levels of the intermediate state. Some physical insight into these different scattering mechanisms is furnished by the following interpretation of the energy denominators of the scattering tensor.



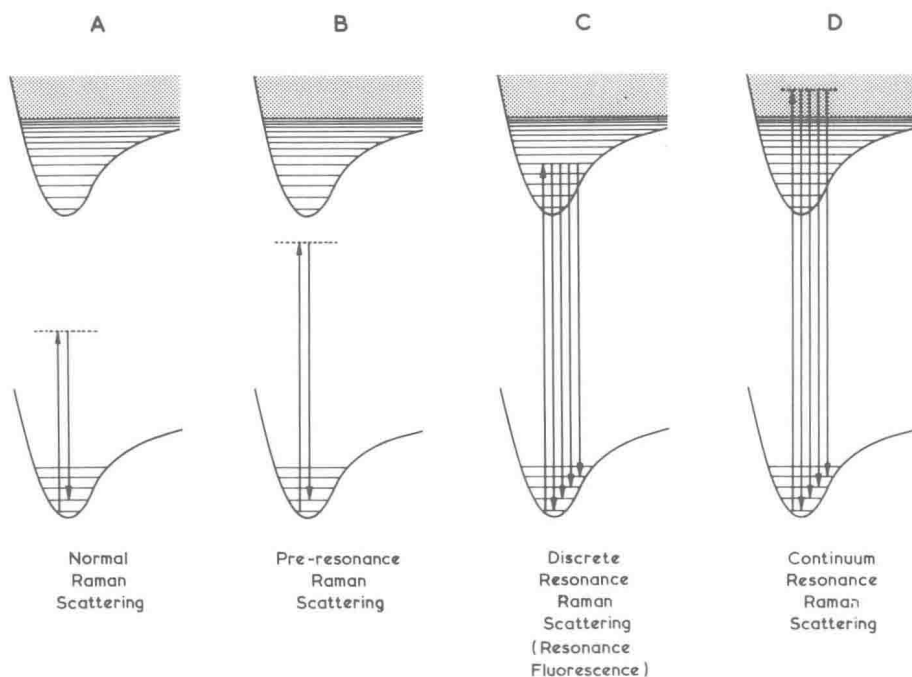


Fig. 3. Types of Raman scattering, depending on the proximity of the exciting light energy to the molecular transition energies.

A. Normal Raman scattering with excitation far from any real molecular transitions. B. Pre-resonance Raman scattering in which the excitation energy approaches that of a molecular transition. Enhancement to the scattering by fundamentals is observed. C. Excitation energy in the region of discrete rotational-vibrational levels of a single electronic intermediate state. This situation has been termed discrete resonance-Raman scattering (23) irrespective of whether or not the resonance is exact with a particular discrete level (resonance fluorescence limit). Overtone scattering may occur for totally symmetric modes with displaced potential curves in the excited state. D. The incident light energy is in the range of dissociative continuum levels. Overtone scattering occurs as in C

In the Raman effect, scattering occurs when the molecular system, interacting with the incident radiation, makes a transition from an initial stationary state to an intermediate state from which, by a second interaction, a transition occurs to the final stationary state. The intermediate state is not in general a stationary state of the molecular system. This virtual intermediate state is not the solution of a time-independent Schrödinger equation and therefore does not correspond to a well-defined value of the energy. The intermediate state is expanded in terms of the excited molecular eigenstates. In this expansion each eigenstate may be thought of as weighted in inverse proportion to the extent by which it fails to conserve energy in the inter-