Raman Spectroscopy: Theory

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1 INTRODUCTION

As has been shown in previous articles, the most straightforward way of observing vibrational transitions of molecules is through absorption (or emission) of infrared (IR) radiation. The interaction of matter with electromagnetic radiation is subject to selection rules, hence not all vibrations may give rise to absorption (or emission) bands in the IR spectrum. The prerequisite of IR activity is the change in dipole moment of the molecule during a given *normal mode of vibration*. Because of this the stretching vibration of a homonuclear diatomic molecule (such as H_2, O_2, etc.) or the totally symmetric vibrations of larger molecules having a center of symmetry, as well as any other vibrations that do not generate a vibrating electric dipole, cannot absorb or emit electromagnetic radiation; these vibrations are said to be IR inactive. In order to detect such vibrations, it is necessary to consider the inelastic scattering of light – a phenomenon usually referred to as Raman scattering (described in Russian literature as combination scattering). This is governed by different selection rules compared to the absorption or spontaneous emission of light.

The possibility of light scattering with significant change of frequency was first predicted on theoretical grounds by Smekal[1] in 1923. The first observations of the phenomenon were made in liquids by Raman and Krishnan,[2] then in crystals by Landsberg and Mandelstam,[3] both in 1928. The first comprehensive treatise of the underlying theory was offered by Placzek[4] in 1934.

This article gives a short general description of the phenomenon and properties of radiation by electric dipoles, then the vibrational Raman effect is described covering the most important aspects in terms of both classical theory of electromagnetic radiation and quantum theory. More in-depth treatments are available elsewhere.[5,6]

1.1 The Raman effect – phenomenological description

When a transparent liquid, gas or crystal is illuminated with a beam of monochromatic light of wavenumber $\tilde{\nu}_0$, most of the incident light is transmitted without change, while a small portion of it is scattered within the whole solid angle. (Scattering refers to light deflected from the original direction of propagation of the incident light.) Spectral analysis of the scattered light shows that, in addition to scattering without change of wavenumber of the incident light (Rayleigh scattering), it contains also discrete components of altered wavenumber. In general, there are pairs of new lines appearing in the spectrum at wavenumbers positioned symmetrically with respect to the Rayleigh line, i.e. $\tilde{\nu}' = \tilde{\nu}_0 \pm \tilde{\nu}_M$, where the wavenumbers $\tilde{\nu}_M$ correspond to transitions between rotational or vibrational (rarely electronic) energy levels of molecular systems. The appearance of altered frequencies (wavenumbers) in scattered light is called the *Raman effect* or *Raman scattering*, after its discoverer.

Raman scattering is a very feeble effect; it is always accompanied with Rayleigh scattering with an intensity usually 3–5 orders of magnitude greater. Note, however, that Rayleigh scattering itself is only about 10^{-4}–10^{-3} of the intensity of the incident exciting radiation. The new components appearing in the spectrum of the scattered radiation at shifted wavenumbers are termed Raman lines or Raman bands, and collectively they are referred to as the Raman spectrum. The Raman bands at wavenumbers less than the exciting wavenumber (i.e. $\tilde{\nu}_0 - \tilde{\nu}_M$) are referred to as Stokes

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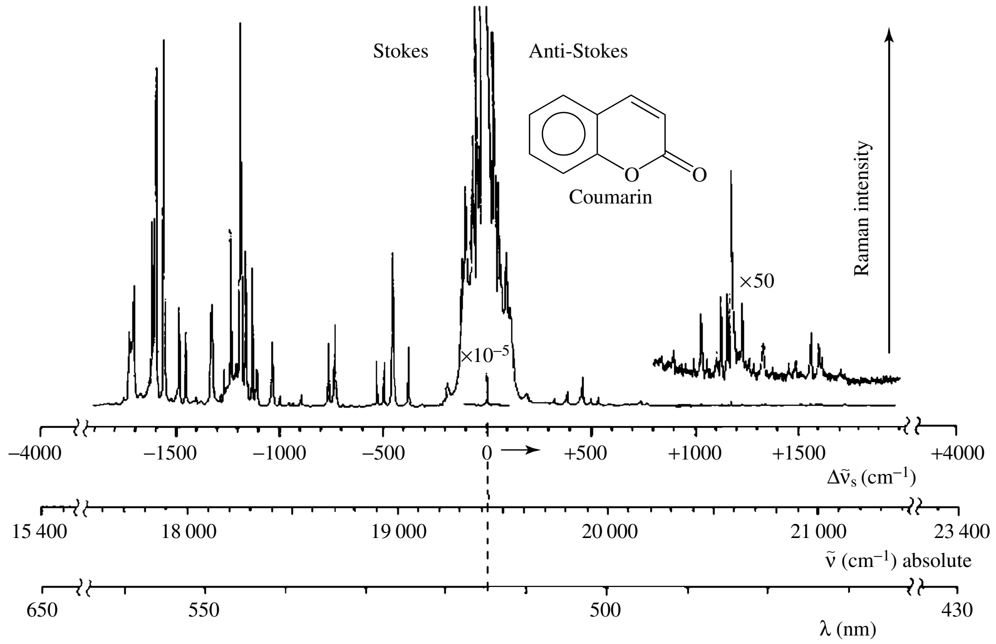

Figure 1. A typical Raman spectrum of a polycrystalline substance (coumarin) showing the Rayleigh line, and both the Stokes and anti-Stokes sides of the Raman spectrum on wavelength, absolute wavenumber, and relative wavenumber (or Raman shift) scales. (Reproduced from Schrader[7].)

lines, whereas those appearing at higher wavenumbers (i.e. $\tilde{\nu}_0 + \tilde{\nu}_M$) as anti-Stokes lines.

As an example, the Raman spectrum of an organic compound (coumarin) is shown in Figure 1, with the intense Rayleigh line positioned in the middle, at $\tilde{\nu}_0$, and the Stokes and anti-Stokes lines to the left and to the right of it, respectively.[7] Note the typical intensity relationships, with the anti-Stokes lines being considerably weaker and quickly diminishing in intensity with increasing $\tilde{\nu}_M$ as compared to their Stokes counterparts. The frequency shifts in the Stokes and anti-Stokes Raman spectra usually correspond to the frequencies of the normal modes of molecular vibrations; thus the shift values are more convenient for characterizing the band positions than the absolute wavenumbers themselves. In view of all this, in most applications of Raman spectroscopy only the more readily observable Stokes side of the Raman spectrum is considered, plotted in a relative wavenumber scale, as $\tilde{\nu}_0 - \tilde{\nu}' = \tilde{\nu}_M$, in the range of Raman shifts from 4000 to $0\,\mathrm{cm}^{-1}$ (with the upper and lower limits depending on the actual instrument). In terms of absorption spectroscopy, this corresponds to the IR and far-infrared (FIR) regions, i.e. to vibrational and rotational transitions of molecules, including the lattice vibrations of crystals.

It should be noted that, when applying lasers as sources of incident exciting radiation, Raman spectroscopy is not limited to the examination of transparent samples, although the theory of ordinary Raman scattering considers the case when the exciting light (typically visible or near-infrared (NIR) light) is not absorbed by the sample to be studied and its wavelength is several orders of magnitude greater than the scattering particles (typically molecules).

1.2 Interaction of light and matter: absorption/emission and scattering of light

According to the classical theory, the most efficient source of electromagnetic radiation is an oscillating electric dipole: the intensity of its radiation is several orders of magnitude greater than that of other sources of radiation, such as oscillating magnetic dipoles, electric quadrupoles, or higher-order multipoles. Thus in order to understand the origin of emission/absorption or scattering of light by molecules, we must consider the distribution of electric charges within the molecule and establish whether there is a permanent or induced electric dipole that could oscillate when modulated by the normal vibrations.

An electric dipole formed by a pair of point charges $-q$ and $+q$ separated by a distance r is characterized by its dipole moment vector $\boldsymbol{\mu}$, defined as

$$\boldsymbol{\mu} = q\mathbf{s} \tag{1}$$

where $\mathbf{s}$ is a vector pointing from $-q$ to $+q$. If such a dipole oscillates with a frequency ν (corresponding to circular frequency $\omega = 2\pi\nu$, or wavenumber $\tilde{\nu} = \nu/c$, where c is the speed of light), then it emits electromagnetic radiation of the same frequency.

In a polyatomic molecule, an electric dipole is formed if the center of positive charges and the center of negative charges do not coincide. Thus, depending on the symmetry of the molecule at the equilibrium configuration of atomic nuclei, the molecule may or may not have a permanent electric dipole moment. But irrespective of this, the dipole moment may *change* during certain normal vibrations as the nuclei are displaced from their equilibrium positions. This change is periodical in time, with the frequency of the given normal vibration ν_M, i.e.

$$\boldsymbol{\mu} = \boldsymbol{\mu}_0 \cos 2\pi\nu_\mathrm{M} t \qquad (2)$$

where $\boldsymbol{\mu}_0$ is the amplitude vector of the oscillating dipole. (Note that $\boldsymbol{\mu}_0$ is *not* the permanent dipole moment, and $\boldsymbol{\mu}$ is only the difference between the instantaneous and permanent dipole moment vectors, whereas the latter may or may not differ from zero; that is, it is only the dipole contributed by vibrations of the nuclei that matters.) This oscillating dipole of the molecule is capable of producing electromagnetic radiation of frequency ν_M; it is also capable of absorbing radiation of the same frequency, which will excite the given molecular vibration. Emission and absorption bands associated with molecular vibrations can be observed in the IR region of the spectrum.

Scattering of light by a molecule is associated with oscillations of an *induced* electric dipole. Electric dipoles may be induced in a molecule by external electric fields, either static or alternating. The external electric field will polarize the molecule: it will shift the negatively charged electrons and positively charged nuclei in opposite directions. If this induced dipole oscillates, it can produce electromagnetic radiation. In the case of a static external field, the induced dipole oscillates only with the frequencies of the normal vibrations of the molecule, just like permanent dipoles. However, in the case of an oscillating external field, such as a beam of visible light, the induced dipole follows the alternating electric field of the radiation and it is also modulated by the vibrations of the nuclei. As a result, it oscillates at the frequency of the electric field as well as at combination or beat frequencies of the external field frequency and the frequencies of normal vibrations, radiating at all these frequencies.

1.3 Radiation of an oscillating dipole

The amplitude E_0 of electric field intensity ($\boldsymbol{E}$) of the radiation produced by the oscillating dipole at a distance r is given by

$$E_0 = \frac{\pi\tilde{\nu}^2\mu_0 \sin\theta}{\varepsilon_0 r} \qquad (3)$$

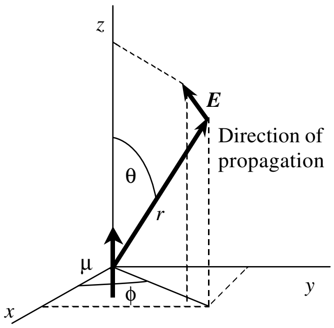

Figure 2. Coordinate system and relative orientation of vectors $\boldsymbol{\mu}$ (at the origin) and $\boldsymbol{E}$ (at a distance r from the origin).

where $\tilde{\nu}$ is the wavenumber of the radiation, μ_0 is the magnitude of the oscillating dipole, ε_0 is the permittivity of the medium, and θ is the angle the dipole makes with the direction of propagation considered (see Figure 2), whereas the electric field vector $\boldsymbol{E}$, being perpendicular to the direction of propagation, lies in the common plane of the dipole vector and the chosen direction of propagation.

The time-averaged value of the total energy density of radiation at a given position along the propagation direction (see Figure 3) is

$$\bar{\rho} = \frac{\pi^2\tilde{\nu}^4\mu_0^2 \sin^2\theta}{2\varepsilon_0 r^2} \qquad (4)$$

(Note that the $\tilde{\nu}^4$ factor should be replaced by $\tilde{\nu}^3$ in this and all related equations when using photon-counting detection.) The distribution of the energy density has axial symmetry with the rotation axis running along the dipole. It follows from equation (4) that the energy density of radiation is maximal in the equatorial plane around the dipole ($\theta = \pi/2$), and it decreases toward the poles and drops to zero at $\theta = 0$.

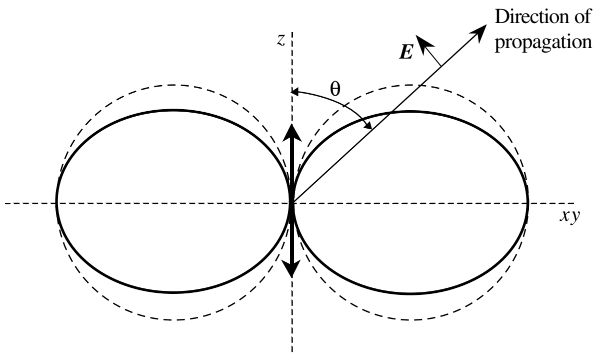

Figure 3. Angular distributions of the amplitude of $\boldsymbol{E}$ (broken line) and of the radiant intensity, I (solid line), of the oscillating electric dipole μ.

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The total power Φ radiated by the dipole in the whole solid angle is given by

$$\Phi = \frac{4\pi^3 c\tilde{\nu}^4 \mu_0^2}{3\varepsilon_0} \tag{5}$$

and the radiant intensity, I, of the dipole within the given element of solid angle $\mathrm{d}\Omega$ in a particular direction defined by the angle θ (see Figure 3) is

$$I(\theta) = \frac{\mathrm{d}\Phi}{\mathrm{d}\Omega} = \frac{\pi^2 c\tilde{\nu}^4 \mu_0^2 \sin^2\theta}{2\varepsilon_0} \tag{6}$$

1.4 The scattering cross-section

The above quantities can be used to characterize the intensity of scattered radiation and the scattering efficiency of the scattering particle as well. For the latter purpose it is customary to take the ratio of the total scattered power Φ to the irradiance J of the incident radiation to obtain the so-called scattering cross-section σ:

$$\sigma = \frac{\Phi}{J} \tag{7}$$

This has the dimension of area, as the total scattered power is proportional to the irradiance of incident radiation. This quantity refers to scattering in the whole solid angle around the scattering center. The fraction scattered into a given direction within a small element of solid angle $\mathrm{d}\Omega$ is called the absolute differential scattering cross-section or scattering coefficient:

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \frac{\mathrm{d}\Phi/\mathrm{d}\Omega}{J} \tag{8}$$

2 CLASSICAL TREATMENT OF RAYLEIGH AND VIBRATIONAL RAMAN SCATTERING

2.1 The induced dipole moment and the polarizability tensor

The classical theory of Rayleigh and Raman scattering is based on the concept that scattered light is generated by oscillating electric dipoles *induced* by the electric field of incident (exciting) radiation. The relation between the induced dipole moment vector $\boldsymbol{\mu}'$ and the electric field vector $\mathbf{E}$ can be written in the form of the following power series:

$$\boldsymbol{\mu}' = \boldsymbol{\alpha}\mathbf{E} + \tfrac{1}{2}\boldsymbol{\beta}\mathbf{E}\mathbf{E} + \tfrac{1}{6}\boldsymbol{\gamma}\mathbf{E}\mathbf{E}\mathbf{E} + \cdots \tag{9}$$

where $\boldsymbol{\alpha}$ is the polarizability, $\boldsymbol{\beta}$ the hyperpolarizability, and $\boldsymbol{\gamma}$ the second hyperpolarizability of the molecule. Polarizabilities $\boldsymbol{\alpha}$, $\boldsymbol{\beta}$, and $\boldsymbol{\gamma}$ are tensors of rank 2, 3, and 4, respectively. [Note that tensors are operators describing physical properties responsible for the connection between vectorial quantities. They are usually represented by matrices. Thus a tensor of rank two can be represented by a two-dimensional (eventually, a 3 × 3) matrix whose elements are specified by a symbol having two indices (e.g. α_{ij}); a tensor of rank 3 is represented by a three-dimensional array of matrix elements (e.g. β_{ijk}), and so forth.] The polarizabilities can be regarded as the measure of the flexibility of the electron cloud: the ease with which the electron cloud of the molecule can be deformed or displaced to produce an electric dipole under the influence of the external electric field. The nonlinear terms in equation (9) are usually so small compared to the linear term that they do not play a role in normal, linear Raman scattering. If we restrict the discussion to the linear term in equation (9), i.e.

$$\boldsymbol{\mu}' = \boldsymbol{\alpha}\boldsymbol{E} \tag{10}$$

then it can be written in the form of three linear equations,

$$\left.\begin{aligned} \mu'_x &= \alpha_{xx}E_x + \alpha_{xy}E_y + \alpha_{xz}E_z \\ \mu'_y &= \alpha_{yx}E_x + \alpha_{yy}E_y + \alpha_{yz}E_z \\ \mu'_z &= \alpha_{zx}E_x + \alpha_{zy}E_y + \alpha_{zz}E_z \end{aligned}\right\} \tag{11}$$

corresponding to the matrix multiplication

$$\begin{bmatrix} \mu'_x \\ \mu'_y \\ \mu'_z \end{bmatrix} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} \tag{12}$$

where the nine coefficients α_{ij} are the components of the polarizability tensor α. As this and similar tensors play key roles in Rayleigh and Raman scattering, some important properties of them will be discussed briefly.

The polarizability tensor can be described by a real, symmetric matrix, where all $\alpha_{ij} = \alpha_{ji}$; thus it has at most six independent components: three diagonal and three off-diagonal. This matrix is only necessarily symmetric in the case of nonresonant Raman scattering; for the case of resonance Raman scattering (RRS) see **Resonance Raman Spectroscopy**.

The polarizability tensor of any molecule can be represented graphically as an ellipsoid having, in general, three different half-axes. Although the shape of the polarizability ellipsoid of a molecule is independent of the choice of reference coordinate system, the actual values of tensor elements depend on the orientation of axes. With symmetric molecules it is good practice to choose the system axes in accordance with the symmetry elements of the molecule (to orient them along the axes of symmetry, or perpendicularly to the plane of planar molecules, etc. – as per the recommendations of the Joint Commission for Spectroscopy[8]). If so oriented, the axes of reference coincide with the principal axes of the polarizability ellipsoid,

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in which case the polarizability tensor takes on a simpler, diagonal form, when all off-diagonal elements vanish (i.e. $\alpha_{XY} = \alpha_{YZ} = \alpha_{ZX} = 0$), and the lengths of the half axes of the ellipsoid are: $\alpha_{XX}^{-1/2}$, $\alpha_{YY}^{-1/2}$, and $\alpha_{ZZ}^{-1/2}$.

It should be mentioned that, although the individual components of the polarizability tensor change on rotation of axes, certain combinations of them remain invariant. One such invariant is the so-called mean polarizability a, defined as

$$a = \tfrac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}), \tag{13}$$

The other is the anisotropy γ,

$$\gamma = \tfrac{1}{2}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6(\alpha_{xy}^2 + \alpha_{yz}^2 + \alpha_{zx}^2)] \tag{14}$$

These invariants of the polarizability tensor acquire special importance when, instead of space-fixed molecules, scattering from freely rotating or randomly reorienting molecules are considered. The power of the scattered radiation is then determined by the space averages of the squares of the polarizability components. It can be shown that all significant terms contained in these averaged squares can be expressed through the mean polarizability a and the anisotropy γ in the following way:

$$\overline{\alpha_{xx}^2} = \overline{\alpha_{yy}^2} = \overline{\alpha_{zz}^2} = \frac{45a^2 + 4\gamma^2}{45} \tag{15}$$

$$\overline{\alpha_{xy}^2} = \overline{\alpha_{yz}^2} = \overline{\alpha_{zx}^2} = \frac{\gamma^2}{15} \tag{16}$$

$$\overline{\alpha_{xx}\alpha_{yy}} = \overline{\alpha_{yy}\alpha_{zz}} = \overline{\alpha_{zz}\alpha_{xx}} = \frac{45a^2 - 2\gamma^2}{45} \tag{17}$$

The space averages of the remaining quadratic terms (the cross-products involving off-diagonal elements of the polarizability tensor) are all zero.[6]

2.2 Time dependence of the induced dipole in vibrating molecules

The time dependence of the induced dipole moment defined by equation (10) in a *vibrating molecule* is now considered, where the polarizability tensor may be modulated by the normal vibrations.

The dependence of the molecular polarizability on the normal coordinates can be expressed in the form of the Taylor series

$$\alpha_{ij} = (\alpha_{ij})_0 + \sum_k \left(\frac{\partial \alpha_{ij}}{\partial Q_k}\right)_0 Q_k + \frac{1}{2}\sum_{k,l}\left(\frac{\partial^2 \alpha_{ij}}{\partial Q_k \partial Q_l}\right)_0 Q_k Q_l + \cdots \tag{18}$$

where α_{ij} is a component of the polarizability tensor, with $(\alpha_{ij})_0$ being its value at the equilibrium configuration; Q_k is the kth normal coordinate associated with vibration of wavenumber $\tilde{\nu}_k$; the subscripts 0 refer to derivatives taken at the equilibrium configuration. (For a definition of "normal coordinate" see **Calculation of Vibrational Frequencies by Molecular Mechanics**.) In order to further simplify the treatment, the double harmonic approximation is adopted that neglects both mechanical and electrical anharmonicity: on the one hand, instead of equation (18), linear dependence of polarizability on each vibrational coordinate (for small amplitude vibrations near the equilibrium) is assumed, i.e.

$$\boldsymbol{\alpha}_k = \boldsymbol{\alpha}_0 + \left(\frac{\partial \alpha}{\partial Q_k}\right)_0 Q_k \tag{19}$$

On the other hand, the normal vibrations are treated as being harmonic, i.e.

$$Q_k = Q_{k0} \cos 2\pi c \tilde{\nu}_k t \tag{20}$$

Let us consider now the time dependence of the induced electric dipole moment $\boldsymbol{\mu}'$, generated under the influence of the electric field of incident radiation of wavenumber $\tilde{\nu}_0$ (that is normally much higher than $\tilde{\nu}_k$) in a vibrating molecule. The variation of the electric field strength with time is given by

$$\boldsymbol{E} = \boldsymbol{E}_0 \cos 2\pi c \tilde{\nu}_0 t \tag{21}$$

Inserting equations (19)–(21) into equation (10) gives, for the kth vibration,

$$\boldsymbol{\mu}' = \boldsymbol{\alpha}_0 \boldsymbol{E}_0 \cos 2\pi c \tilde{\nu}_0 t + \left(\frac{\partial \alpha}{\partial Q_k}\right)_0 \times Q_{k0} \boldsymbol{E}_0 \cos 2\pi c \tilde{\nu}_0 t \times \cos 2\pi c \tilde{\nu}_k t \tag{22}$$

Trigonometric transformation yields

$$\boldsymbol{\mu}' = \boldsymbol{\alpha}_0 \boldsymbol{E}_0 \cos 2\pi c \tilde{\nu}_0 t + \frac{1}{2}\left(\frac{\partial \alpha}{\partial Q_k}\right)_0 Q_{k0} \boldsymbol{E}_0 \times [\cos 2\pi c(\tilde{\nu}_0 - \tilde{\nu}_k)t + \cos 2\pi c(\tilde{\nu}_0 + \tilde{\nu}_k)t] \tag{23}$$

The three cosine functions having three different arguments in this equation mean that the induced dipole oscillates with three distinct frequencies simultaneously, therefore it generates radiation at $\tilde{\nu}_0$ and also at wavenumbers shifted by $\pm\tilde{\nu}_k$. The first term describes Rayleigh scattering observable at $\tilde{\nu}_0$, whereas the second and third terms account for Stokes Raman and anti-Stokes Raman scattering at $\tilde{\nu}_0 - \tilde{\nu}_k$ and $\tilde{\nu}_0 + \tilde{\nu}_k$, respectively. These so-called beat frequencies are produced when the dipole oscillating at $\tilde{\nu}_0$ is modulated by the molecular vibration at wavenumber $\tilde{\nu}_k$.

It can be concluded that the classical theory successfully describes the frequency relationships of vibrational Raman

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scattering. It shows that the Raman shift is independent of the frequency (wavelength) of the incident radiation. Thus, whether one excites a molecule with the green or blue laser line of an Ar^+ ion laser or a NIR Nd : YAG (yttrium aluminum garnet) laser, one will obtain the same wavenumber pattern (but not necessarily the same relative intensities, see later), with Raman shifts characteristic of the scattering molecule.

2.3 Intensities, directional and polarization properties

According to equation (23), the oscillation amplitudes of the induced dipole moment are directly proportional to the amplitude of the electric field vector of the incident radiation $\boldsymbol{E}_0$. In addition, the intensity of Rayleigh scattering depends on $\boldsymbol{\alpha}_0$, the polarizability of the molecule at the equilibrium nuclear configuration, whereas that of Raman scattering (both Stokes and anti-Stokes) is governed by the so-called derived polarizability tensors, $\boldsymbol{\alpha}'_k$:

$$\boldsymbol{\alpha}'_k = \left(\frac{\partial \boldsymbol{\alpha}}{\partial Q_k}\right)_0 \tag{24}$$

These reflect the sensitivity of molecular polarizability to *changes* of nuclear configuration along the normal coordinate of vibration.

Considering the properties of the derived polarizability tensor (sometimes also referred to as the Raman tensor), there are similarities but also notable differences in comparison to those of $\boldsymbol{\alpha}_0$. The invariants of the derived polarizability tensor (its mean value a' and its anisotropy γ') are defined by analogy to those of α_0, in accordance with equations (13) and (14). Both $\boldsymbol{\alpha}_0$ and $\boldsymbol{\alpha}'$ are symmetric tensors (at least, as far as nonresonant Raman scattering is concerned), but although the components $(\alpha_{ij})_0$ of $\boldsymbol{\alpha}_0$ can only be positive and its diagonal terms always differ from zero (which ensures that the Rayleigh line is always present in the spectrum of the scattered light), the components $(\alpha'_{ij})_k$ of $\boldsymbol{\alpha}'_k$ can be positive, negative or zero. Consequently, the mean value of the derived polarizability tensor a' may also be zero for certain normal vibrations. This means that the derived polarizability tensor can no longer be represented as a real ellipsoid, because some of its axes may become zero or imaginary. Another important difference is that the *orientation* of principal axes of the derived polarizability ellipsoids pertaining to the various normal modes of vibration may differ from that of the equilibrium polarizability ellipsoid.

These differences in properties bring about differences in the directional and polarization properties of Rayleigh and Raman scattering. It is also clear from equation (23) that the derived polarizability tensor serves as the measure of Raman activity: those vibrations for which $\boldsymbol{\alpha}'_k = 0$ (meaning that *all* tensor components are zero) are inactive in Raman scattering, and those normal vibrations for which at least one component of $\boldsymbol{\alpha}'_k$ differs from zero, i.e.

$$(\boldsymbol{\alpha}'_{ij})_k = \left(\frac{\partial \alpha_{ij}}{\partial Q_k}\right)_0 \neq 0 \tag{25}$$

are Raman active.

The relative intensities and polarization properties of spectral lines in scattered radiation depend on different factors, such as the scattering geometry, the orientation of the molecule with respect to the incident light, and the state of polarization of the incident light. Determination of the state of polarization of the scattered radiation is of great importance because it can be correlated with the symmetry of the scattering species and the symmetry of the individual vibrational modes.

The scattering geometry is defined by the relative orientation of the directions of illumination and observation in a laboratory-fixed coordinate system according to Figure 4, where the scattering molecule is located at the origin O. By convention, the direction of illumination (by a monochromatic laser light) is set along the positive z axis (vertical), whereas the scattered light is observed along the direction Ow making an angle θ with the z axis (in the xz plane). The plane containing the direction of propagation of the incident light and the direction of observation is called the scattering plane (in this case the xz plane) that serves as a plane of reference when the state of polarization of the incident and scattered light is specified. For instance, the incident beam is said to be parallel polarized when its electric vector is parallel to the scattering plane (i.e. when $E_x \neq 0$ and $E_y = 0$), and it is said to be perpendicularly polarized when its electric vector is perpendicular to the scattering plane ($E_x = 0$ and $E_y \neq 0$).

We are interested in the radiant intensity I of the light scattered at an angle θ and in its polarization characteristics described by the so-called depolarization ratio ρ. The latter quantity can be defined in different ways. For the case of illumination with radiation polarized perpendicular to the

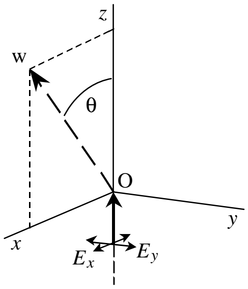

Figure 4. Orientation of axes for definition of illumination and observation geometry, where xz is the scattering plane.

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scattering plane, it is denoted $\rho_\perp$ and defined as

$$\rho_\perp(\theta) = \frac{{}^{\perp}I_{\parallel}(\theta)}{{}^{\perp}I_{\perp}(\theta)} \tag{26}$$

where the superscript preceding I refers to polarization of the incident radiation (perpendicular to the scattering plane for both ${}^{\perp}I_{\parallel}$ and ${}^{\perp}I_{\perp}$), and the subscript following I stands for the direction of polarization of the scattered light (parallel and perpendicular, respectively, to the scattering plane).

Similarly, if the electric vector of incident light were polarized parallel to the scattering plane, the corresponding depolarization ratio $\rho_\parallel$ would be defined as

$$\rho_\parallel(\theta) = \frac{{}^{\parallel}I_{\perp}(\theta)}{{}^{\parallel}I_{\parallel}(\theta)} \tag{27}$$

In fact, the common governing principle in equations (26) and (27) is that the intensity of depolarized scattering (i.e. the scattering of altered polarization) is ratioed against the intensity of scattering with unaltered polarization, the states of polarization being considered with respect to that of the incident light. This allows for a simpler (but less rigorous) definition of the depolarization ratio as

$$\rho(\theta) = \frac{I_{\perp}(\theta)}{I_{\parallel}(\theta)} \tag{28}$$

where subscripts $\perp$ and $\parallel$ refer to the mutual orientation of the electric vectors of the incident radiation and the scattered light. Irrespective of the scattering geometry, this simpler notation is often used in applied spectroscopy, but the current discussion reverts to the notation introduced in equation (26).

In the practice of Raman spectroscopy two different scattering arrangements have become widely used: (a) 90° scattering ($\theta = \pi/2$), corresponding to illumination along the positive z axis (Figure 4) and observation along the positive x axis; and (b) 180° scattering or back-scattering ($\theta = \pi$), when illumination is along the positive z axis and observation is in the negative direction of the z axis. Note that although the convergence of the focused laser beam used for illumination is negligible, the scattered radiation is usually collected within a fairly large solid angle around the selected nominal direction of scattering, so as to increase the observed signal.

For samples consisting of freely rotating molecules (such as low-pressure gases) or an assembly of randomly orienting molecules (as in most liquids) and illumination with linearly polarized light, the radiant intensity for both Rayleigh and Raman scattering can be calculated using equation (6). This is achieved by substituting the appropriate frequencies and the corresponding components of the amplitude of the induced dipole moment from equation (23), then averaging over all orientations of the molecule. After performing this calculation (details given by Long[6]) for Raman scattering of perpendicularly polarized incident radiation at 90° scattering geometry (for an unspecified kth normal mode of vibration) we obtain

$${}^{\perp}I_{\perp}\left(\frac{\pi}{2}\right) \propto (\tilde{\nu}_0 \mp \tilde{\nu}_k)^4 \overline{(\alpha'_{yy})^2} Q_{k0}^2 J \tag{29}$$

$${}^{\perp}I_{\parallel}\left(\frac{\pi}{2}\right) \propto (\tilde{\nu}_0 \mp \tilde{\nu}_k)^4 \overline{(\alpha'_{zy})_k^2} Q_{k0}^2 J \tag{30}$$

where the minus sign refers to Stokes and the plus sign to anti-Stokes Raman scattering, and J is the irradiance of the incident (exciting) radiation. Although these expressions do not fully describe the real dependence of observed intensities on the wavenumber of the scattered radiation (e.g. the Stokes/anti-Stokes intensity ratios which can be correctly accounted for only by quantum mechanics), they are still useful and lead to the correct result when they are used to calculate the depolarization ratios.

For this purpose, the space averages of the squares of the derived polarizability components in equations (29) and (30) are replaced by the corresponding expressions given in terms of the invariants a' and γ' (by analogy with equations (15) and (16)) to yield

$${}^{\perp}I_{\perp}\left(\frac{\pi}{2}\right) \propto (\tilde{\nu}_0 \mp \nu_k)^4 \left\{\frac{45(a')_k^2 + 4(\gamma')_k^2}{45}\right\} Q_{k0}^2 J \tag{31}$$

$${}^{\perp}I_{\parallel}\left(\frac{\pi}{2}\right) \propto (\tilde{\nu}_0 \mp \nu_k)^4 \left\{\frac{(\gamma')_k^2}{15}\right\} Q_{k0}^2 J \tag{32}$$

The ratio of ${}^{\perp}I_{\parallel}$ to ${}^{\perp}I_{\perp}$ then gives the well known expression of depolarization ratio for the case of plane polarized incident radiation:

$$\rho_\perp\left(\frac{\pi}{2}\right) = \frac{{}^{\perp}I_{\parallel}(\pi/2)}{{}^{\perp}I_{\perp}(\pi/2)} = \frac{3(\gamma')_k^2}{45(a')_k^2 + 4(\gamma')_k^2} \tag{33}$$

If the sample is illuminated with natural (i.e. nonpolarized) light using the same scattering geometry as above, and the scattered light is analyzed with parallel and perpendicular settings of the polarizer to measure ${}^{n}I_{\parallel}$ and ${}^{n}I_{\perp}$, respectively, then the corresponding depolarization ratio can be calculated from a similar expression:

$$\rho_n\left(\frac{\pi}{2}\right) = \frac{{}^{n}I_{\parallel}(\pi/2)}{{}^{n}I_{\perp}(\pi/2)} = \frac{6(\gamma')_k^2}{45(a')_k^2 + 7(\gamma')_k^2} \tag{34}$$

Equations (33) and (34) show that the depolarization ratios of Raman bands depend on the mean values of the derived polarizability tensor and its anisotropy. As both a' or γ' can be zero in some cases, the intervals of the possible depolarization ratio values are

$$0 \le \rho_\perp\left(\frac{\pi}{2}\right) \le \frac{3}{4} \tag{35}$$

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and

$$0 \le \rho_n\left(\frac{\pi}{2}\right) \le \frac{6}{7} \tag{36}$$

Although we have considered only the case of 90° scattering above, the results can be extended for the case of 180° scattering. More precisely, depolarization results are, in principle, the same for 180° scattering when using polarized exciting radiation (i.e. for $\rho_\perp(\pi)$) as for 90° scattering with incident light perpendicularly polarized with respect to the scattering plane ($\rho_\perp(\pi/2)$):

$$0 \le \rho_\perp(\pi) \le \tfrac{3}{4} \tag{37}$$

Note that neither 90° scattering with parallel polarized incident light, nor 180° scattering with natural incident light can be used to determine the depolarization ratios, because they would give values of $\rho_\parallel(\pi/2) = 1$ and $\rho_n(\pi) = 1$ for all observed bands in randomly oriented samples.

The actual values of $\rho_\perp$ and ρ_n are determined by the symmetry properties of the derived polarizability tensor, that reflect the symmetry of the corresponding normal mode of vibration. Thus, the following cases can be distinguished:

1. For nontotally symmetric vibrations $a' = 0$ and $\gamma' \neq 0$, so that $\rho_\perp = 3/4$ ($\rho_n = 6/7$) and such Raman bands are said to be depolarized.
2. For totally symmetric vibrations both a' or γ' differ from zero, thus $\rho_\perp < 3/4$ ($\rho_n < 6/7$) and such bands are said to be partially polarized.
3. At an extreme, for totally symmetric vibrations of molecules belonging to cubic point groups $a' \neq 0$ and $\gamma' = 0$, when equation (33) yields $\rho_\perp = 0$ and the observed band is considered completely polarized.

As an example, the low-frequency part of the two differently polarized Raman spectra of liquid chloroform, $CHCl_3$, is shown in Figure 5. The strongest two bands at 669 and $368\,cm^{-1}$ are almost completely polarized, so they must belong to the totally symmetric a_1 species of the C_{3v} point group. Considering their wavenumbers, they can be assigned to the symmetric CCl_3 stretching (ν_sCCl_3) and symmetric CCl_3 deformation (δ_sCCl_3) vibrations, respectively, whereas the two depolarized bands (with $\rho = 0.75$) belong to the degenerate $\nu_{as}CCl_3$ ($761\,cm^{-1}$) and δCH ($263\,cm^{-1}$) vibrations.

Since the advent of lasers, polarized laser beams are almost exclusively used as the source of illumination for the measurement of Raman scattering, so the depolarization ratio $\rho_\perp$ is much more often used than ρ_n, the latter assuming illumination with natural light. However, there is a way of determining ρ_n experimentally with the use of plane polarized exciting light but no polarization analyzer in the path of the scattered radiation, as follows. Illumination is along the z axis (as shown in Figure 4) and the scattered intensity is detected in the direction of the x axis *without polarization*. In the first measurement the electric vector of the laser beam is polarized parallel to x (parallel to the scattering plane), in which case the measured intensity can be described as the sum of parallel and perpendicular scattered intensities, ${}^{\parallel}I_\parallel(\pi/2) + {}^{\parallel}I_\perp(\pi/2)$. For the second measurement the plane of polarization of the incident light is turned

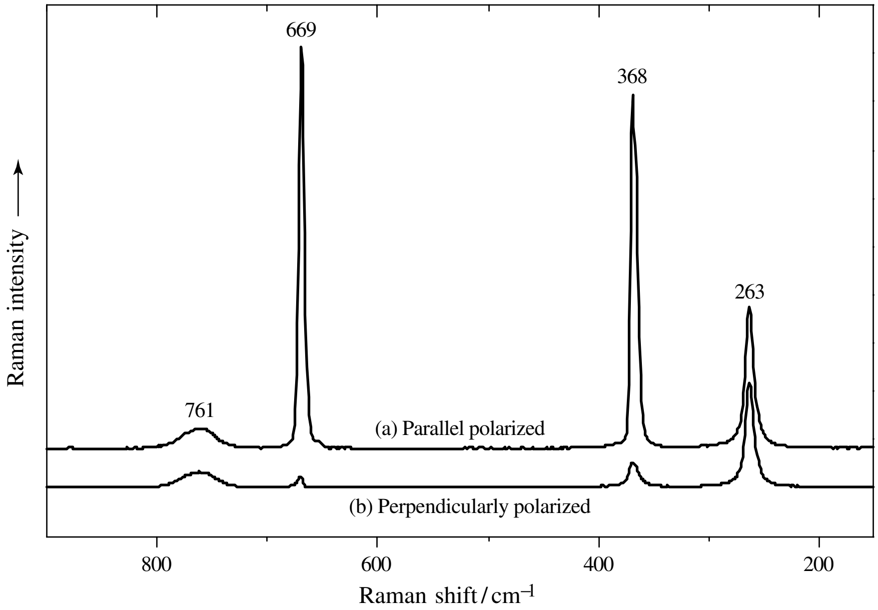

Figure 5. Part of the polarized Raman spectra of liquid chloroform, recorded with 180° scattering for determination of depolarization ratios. The scattered light is analyzed with the polarizer set (curve a) parallel and (b) perpendicular to the polarization direction of the incident radiation.

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parallel to the y axis when the total intensity measured is ${}^{\perp}I_{\parallel}(\pi/2) + {}^{\perp}I_{\perp}(\pi/2)$. This can be done conveniently by inserting a half-wave plate into the path of the laser beam, which will turn the plane of polarization by 90°. Then the ratio of these two measured intensity values is taken which gives:

$$\frac{{}^{\parallel}I_{\parallel}(\pi/2) + {}^{\parallel}I_{\perp}(\pi/2)}{{}^{\perp}I_{\parallel}(\pi/2) + {}^{\perp}I_{\perp}(\pi/2)} = \frac{6(\gamma')_k^2}{45(a')_k^2 + 7(\gamma')_k^2} = \rho_n\left(\frac{\pi}{2}\right) \tag{38}$$

i.e. ρ_n can be measured and equation (36) can be used also in the case of plane polarized exciting radiation.

Returning to the interpretation of the measured depolarization ratios, we have seen that in samples consisting of randomly orienting molecules it is possible to distinguish between Raman active vibrations belonging to totally symmetric and nontotally symmetric species only. A practical difficulty is that for some polarized bands the depolarization ratio $\rho_{\perp}$, although smaller than 0.75, may occasionally approach this value very closely, hence the intensity measurements should be of fairly high quality to make the distinction. This may involve calibration of the depolarization measurement or the use of an internal standard.

2.4 Polarization measurements in single crystals

It should be mentioned that the derived polarizability tensors show different patterns of entries for vibrations belonging to different symmetry species; so, if these patterns can be determined, all Raman active symmetry species can be distinguished from each other. Such a possibility is provided by Raman polarization measurements performed on single crystals, where the molecules have fixed orientations within the sample. In this case the relative magnitudes of all six independent components of the derived polarizability tensor can be determined for each Raman line by direct measurement at suitable orientation of the crystal and appropriate polarization settings. In single crystal measurements it is more convenient to use a system of reference axes tied to the crystal axes rather than laboratory-fixed coordinates. In this case the nomenclature recommended by Damen *et al.*[9] is used to describe the different arrangements. This involves four symbols, *a(bc)d* in general, where *a* stands for the propagation direction of the incident radiation, *b* for the orientation of the electric vector of the incident radiation, *c* for the orientation of the electric vector of scattered light (e.g. the setting of the polarization analyzer), and *d* for the direction of propagation of the scattered light. It follows from the definition that the most essential part of the notation is the two symbols enclosed in the round brackets, because they define the component of the scattering tensor being measured. Further details of single crystal Raman studies are provided by Gilson and Hendra,[10] Turrell,[11] and Wilkinson.[12]

3 PARTIAL QUANTUM MECHANICAL TREATMENT OF RAYLEIGH AND RAMAN SCATTERING

3.1 Refinement of the classical description

According to the basic principles of quantum mechanics, the energy associated with electronic, vibrational and rotational degrees of freedom of a molecule can assume values only from a discrete set, namely the quantized energy levels corresponding to the possible stationary states of the molecule. As well as their energies, these states are characterized by a specific set of quantum numbers describing the level of excitation of each quantized motional degree of freedom, and by a corresponding wavefunction, Ψ.

Using the terminology of quantum mechanics, radiation is absorbed or emitted by a molecular system as the result of an upward or downward transition between two energy levels. The radiation absorbed or emitted is also quantized, with the energy enclosed in discrete photons that can alternatively be viewed as electromagnetic waves. The loss or gain of energy by the molecule, ΔE, is equivalent to the energy of electromagnetic radiation emitted or absorbed (Figure 6). This energy is directly proportional to the frequency or wavenumber of radiation,

$$\Delta E = h\nu = hc\tilde{\nu} \tag{39}$$

where h is the Planck constant ($h = 6.62608 \times 10^{-34}\,\mathrm{J\,s}$), c is the speed of light (in vacuum $c = c_0 = 2.99792458 \times 10^{8}\,\mathrm{m\,s^{-1}}$), ν is the frequency, and $\tilde{\nu}$ is the wavenumber of the radiation.

In IR absorption or emission, there is a direct transition between two vibrational energy levels, most often between the vibrational ground state ($v = 0$) and the first excited state ($v = 1$). These transitions are simple one-photon processes – one photon is absorbed or emitted during the transition. In contrast to this, both Rayleigh and Raman scattering involve two almost simultaneous transitions proceeding via virtual states in which one photon of the incident radiation is annihilated and another photon, either of the same energy (Rayleigh scattering) or of lower energy (Stokes Raman) or higher energy (anti-Stokes Raman), is created. (The term "virtual state" refers to a transition state which does not correspond to an eigenstate of the molecule; so it is only an imaginary state, a practical convenience by which the energy exchange between the radiation field and

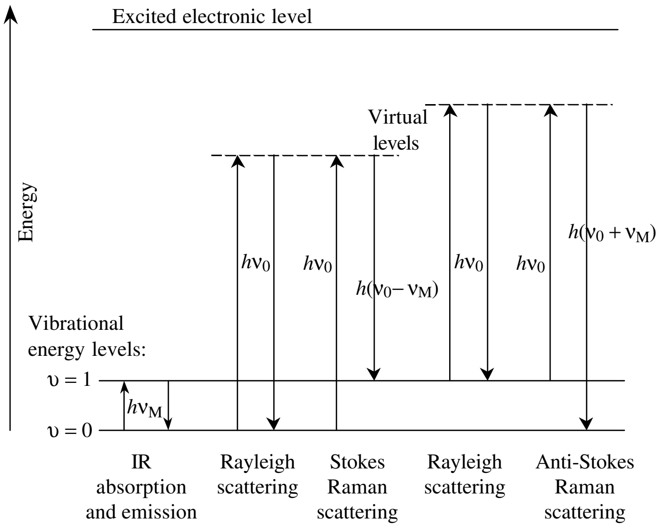

Figure 6. Diagram of transitions between vibrational energy levels corresponding to the processes of IR absorption/emission, and Rayleigh and Raman scattering.

the molecule during the scattering process can be split up into two one-photon transitions.)

To refine the classical description of Raman scattering we proceed by using the results of a partial quantum mechanical treatment in which the molecule is treated quantum mechanically and the radiation classically. Then, for the description of the interaction of light with matter, electromagnetic radiation is considered as a source of perturbation of the molecular system. This partial quantum mechanical treatment yields correct results for most spectroscopic processes including absorption, emission and also Rayleigh and Raman scattering.

It is anticipated that any direct transition between two energy levels is accompanied by emission or absorption of radiation if the dipole moment of the transition (which is called the transition moment) is nonzero:

$$\mu_{fi} = \langle \Psi_f | \hat{\mu} | \Psi_i \rangle \neq 0 \tag{40}$$

where Ψ_i and Ψ_f are the wavefunctions of the initial and final states, respectively, and $\hat{\mu}$ is the dipole moment operator. In equation (40) the so-called Dirac bracket notation is used to abbreviate the expression

$$\langle \Psi_f | \hat{\mu} | \Psi_i \rangle \equiv \int \Psi_f^* \hat{\mu} \Psi_i \, \mathrm{d}\tau \tag{41}$$

where the integral is over all the coordinate space. For absorption or emission $\hat{\mu}$ corresponds to the permanent electric dipole operator, whereas for light scattering $\hat{\mu}$ is the induced dipole moment operator.

The quantum mechanical equivalent to the amplitude of the induced dipole of equation (10) is the transition moment amplitude concerning a transition from an initial state i to a final state f induced by radiation of wavenumber $\tilde{\nu}_0$:

$$[\mu_0]_{fi} = \langle \psi_f | \boldsymbol{\alpha} | \psi_i \rangle \cdot \boldsymbol{E}_0 \tag{42}$$

where ψ_f and ψ_i are vibrational wavefunctions (but occasionally can be considered to be vibrational–rotational or pure rotational wavefunctions as well), and $\boldsymbol{\alpha}$ is the polarizability tensor. As the frequency dependence of Raman scattering was obtained correctly from the classical theory, we are now particularly interested in determining the intensity of scattered radiation for a given vibrational transition. In this case we can avoid consideration of the time dependence and examine only the transition moment amplitudes; then ψ_f and ψ_i are considered as time-independent vibrational wavefunctions.

The Raman selection rules (i.e. the Raman activity of transitions) and the intensity of scattered radiation will be determined by the properties of the transition polarizability tensor (sometimes referred to as Raman tensor or scattering tensor) $[\alpha]_{fi}$, whose components $[\alpha_{xx}]_{fi}$, $[\alpha_{xy}]_{fi}$, etc., are the matrix elements of the polarizability tensor for the transition $f \leftarrow i$. Thus it is necessary to examine the dependence of the transition polarizabilities on the vibrational normal coordinates in a manner similar to classical mechanics.

By neglecting electrical and mechanical anharmonicity again and exploiting the properties of the harmonic oscillator wavefunctions, it is obtained that only those matrix elements differ from zero for which *one* vibrational quantum number changes by unity (i.e. $v^f{}_k = v^i{}_k \pm 1$); all other vibrational quantum numbers remain unchanged (i.e. $v^f{}_k = v^i{}_k$, for all $j \neq k$). Then for a typical matrix element of the transition polarizability associated with Stokes Raman scattering (for $v^f{}_k = v^i{}_k + 1$) at Raman shift $\tilde{\nu}_k$ we obtain (in molecule fixed axes x, y, and z),

$$\begin{aligned} [\alpha_{xy}]_{v^f v^i} &= (v_k^i + 1)^{\frac{1}{2}} b_{v_k} \left(\frac{\partial \alpha_{xy}}{\partial Q_k} \right)_0 \\ &= (v_k^i + 1)^{\frac{1}{2}} b_{v_k} (\alpha'_{xy})_k \end{aligned} \tag{43}$$

Similarly, for anti-Stokes scattering (when $v^f{}_k = v^i{}_k - 1$),

$$[\alpha_{xy}]_{v^f v^i} = (v_k^i)^{\frac{1}{2}} b_{v_k} \left(\frac{\partial \alpha_{xy}}{\partial Q_k} \right)_0 = (v_k^i)^{\frac{1}{2}} b_{v_k} (\alpha'_{xy})_k \tag{44}$$

where $b_{v_k}^2 = h/(8\pi^2 c \tilde{\nu}_k)$ is the quantum mechanical analog of the amplitude Q_k of the classical oscillator. It is clear from the last two equations that for such transitions to be Raman active it is also required that at least one component of the derived polarizability tensor be nonzero, just as in classical theory.

A very significant difference between the classical and quantum mechanical treatments is that in the latter there is a dependence on the quantum number v_k, which has important consequences concerning the intensities of Raman scattering. When we consider scattering from an assembly of N molecules, the initial distribution of molecules among the vibrational states at temperature T must be taken into account (utilizing the Boltzmann distribution law) to establish the fraction of molecules capable of a given transition. Thus, introducing the appropriate changes into equations (31) and (32) obtained from classical theory, we obtain for scattered intensity of Stokes lines (at 90° scattering):

$$ {}^{\perp}I_{\perp}\left(\frac{\pi}{2}\right) = \frac{hNg_k}{8\varepsilon_0^2 c\tilde{\nu}_k}\frac{(\tilde{\nu}_0-\tilde{\nu}_k)^4[45(a')_k^2+4(\gamma')_k^2]}{[1-\exp(-hc\tilde{\nu}_k/kT)]\times 45}J \qquad (45) $$

$$ {}^{\perp}I_{\parallel}\left(\frac{\pi}{2}\right) = \frac{hNg_k}{8\varepsilon_0^2 c\tilde{\nu}_k}\frac{(\tilde{\nu}_0-\tilde{\nu}_k)^4(\gamma')_k^2}{[1-\exp(-hc\tilde{\nu}_k/kT)]\times 15}J \qquad (46) $$

where g_k is the degeneracy of the kth vibration (all other symbols have been defined earlier). The corresponding equations for anti-Stokes lines can be obtained by substituting $(\tilde{\nu}_0+\tilde{\nu}_k)^4$ for $(\tilde{\nu}_0-\tilde{\nu}_k)^4$, and $[\exp(hc\tilde{\nu}_k/kT)-1]$ for $[1-\exp(-hc\tilde{\nu}_k/kT)]$. Note also that according to these equations the intensity of Raman scattering depends on the number of molecules (or scattering centers N) in the scattering volume and on the intensity of the exciting radiation J. By dividing equations (45) and (46) by J we arrive at the corresponding expressions for the absolute differential cross-section that characterizes the scattering efficiency of the sample.

Obviously, according to these relationships, the wavenumber dependence of relative intensities of Raman lines differ very strongly from those obtained from classical theory. However, as has been anticipated, quantum theory leads to the same depolarization ratios as classical theory, i.e. equation (33) is still valid, which can be verified by taking the ratio of the right-hand side of equation (46) to that of equation (45).

The most pronounced difference between the classical and quantum mechanical treatments of Raman scattering is found in the relative intensities of the corresponding Stokes and anti-Stokes Raman lines:

$$ \frac{I_{\text{Stokes}}}{I_{\text{anti-Stokes}}} = \frac{I_{\tilde{\nu}_0-\tilde{\nu}_k}}{I_{\tilde{\nu}_0+\tilde{\nu}_k}} = \frac{(\tilde{\nu}_0-\tilde{\nu}_k)^4}{(\tilde{\nu}_0+\tilde{\nu}_k)^4}\exp\left(\frac{hc\tilde{\nu}_k}{kT}\right) \qquad (47) $$

In addition to correctly accounting for the observed intensity relationships, this equation allows determination of the sample temperature (by contact-free measurement) provided that the measured Raman intensities are corrected for instrument response. Note that equations (45)–(47) are only correct when measuring the scattered power; in the case of photon counting (employed in many instruments) the fourth-power dependency reduces to a third-power one.

3.2 Raman scattering from absorbing samples: resonance Raman scattering

The previous discussion was based on polarizability theory assuming that the scattering sample is transparent to the exciting laser light. This corresponds to the requirement that the frequency of the incident radiation (ν_0) should be much higher than the frequencies of vibrational and rotational transitions (ν_{M}), but also much lower than those of any electronic transitions. For a given compound this condition determines the wavenumber range extending from NIR to some visible wavenumbers that can be safely used to excite Raman scattering. However, as the intensity of Raman scattering is proportional to the fourth power of the absolute wavenumber of scattered light, a significant improvement in Raman scattering efficiency can be expected when higher exciting wavenumbers are used. Thus on theoretical grounds, excitation with the green or blue lines of an Ar ion laser is to be preferred to the NIR radiation of a Nd:YAG laser, as they are expected to generate 16–20 times greater Raman intensities.

However, when the frequency of the incident light approaches that of an electronic transition or falls inside an electronic absorption band of the sample, resonances occur that may considerably enhance the intensities of certain Raman lines. This effect is called resonance Raman scattering (RRS) and is due to the coupling of electronic and vibrational transitions. This process can be described theoretically by time-dependent perturbation theory, showing that if a resonant frequency is approached, the induced dipole becomes abnormally large. Resonance enhancement of scattering is accompanied, of course, by absorption of both the incident and the scattered radiation, whereas excitation of fluorescence is not excluded either. Because of these competing processes, observation of resonance Raman spectra may need some expertise. The topic of resonance Raman scattering is described in **Resonance Raman Spectroscopy**.

4 VIBRATIONAL SELECTION RULES – CONTRASTING IR AND RAMAN SPECTROSCOPY

The foregoing discussion has shown that molecular vibrations are responsible for the appearance of absorption or emission bands in the IR spectrum and for scattering of light at shifted frequencies. We have also touched on the question of activity of normal modes in a general sense, without analyzing the conditions of activity for each normal mode separately. Recall that classical theory has led to the following criteria:

1. A given normal vibration of a molecule may appear in the IR spectrum if at least one component of the electric dipole moment of the molecule changes during this vibration, i.e. when the value of a dipole moment derivative, taken at the equilibrium, differs from zero:

$$\left(\frac{\partial \mu_i}{\partial Q_k}\right)_0 \neq 0 \tag{48}$$

2. A given normal vibration of a molecule may appear in the Raman spectrum if at least one component of the polarizability tensor changes during this vibration, i.e. when the value of a derived polarizability tensor component differs from zero:

$$\left(\frac{\partial \alpha_{ij}}{\partial Q_k}\right)_0 \neq 0. \tag{49}$$

According to quantum theory, oscillation of a permanent or induced dipole does not produce any radiation. For radiation to be emitted or absorbed, a transition should occur between different vibrational energy levels of the molecule (Figure 6) which may be concomitant with loss or gain of energy in the form of electromagnetic radiation. The classical analog of excitation of a molecule to a higher vibrational energy level is vibration with increased amplitude. With this, we can accept the conditions of IR and Raman activity in general as formulated above and examine whether they are fulfilled in the case of particular molecular vibrations having different symmetry properties.

4.1 Diatomic molecules

First we examine the fundamental transitions of diatomic molecules which have only one mode of vibration, the stretching of bond length. It is necessary to distinguish between X_2 type homonuclear and XY type heteronuclear diatomic molecules – since the former have a center of symmetry, and consequently no dipole moment, whereas the latter are polar molecules with an asymmetric electron distribution which creates a permanent dipole. The factors determining IR and Raman activity of the vibrations in these molecules are compared in Table 1.

During small-amplitude vibrations of a homonuclear diatomic molecule, the symmetry of the electron distribution is retained and no dipole is generated. Consequently, $(\partial\mu/\partial Q)_0 = 0$, so this vibration cannot be observed in the IR (it is IR inactive). To judge its Raman activity, it is necessary to examine the dependence of polarizability on internuclear distance. At equilibrium, the molecule must have a nonzero polarizability, with one axis of the polarizability ellipsoid oriented along the bond direction. The polarizability along this direction differs from that along any perpendicular directions (which are indistinguishable), but the mean polarizability will still be positive. Although it is not easy to predict the actual change of polarizability with internuclear distance in different directions, for qualitative predictions one may use the analogy between polarizability and the volume occupied by the electron cloud – as the bond is stretched, the volume of the electron cloud increases which will certainly affect its polarizability as well. Quantum chemical calculations confirm that for all homonuclear molecules $(\partial\alpha/\partial Q)_0 > 0$; thus, the vibrations of X_2 type molecules are Raman active.

In heteronuclear diatomic molecules (XY type) the dipole moment goes through a maximum if the internuclear distance changes from zero to infinity, but the position of the maximum differs from the equilibrium distance. According to this, the dipole moment derivative may be positive or negative, but generally different from zero, which means that the vibration is IR active. Regarding the change of polarizability, the same arguments hold as for homonuclear molecules above (see also Table 1), so this vibration will be Raman active as well.

4.2 Molecules with a center of symmetry and the principle of mutual exclusion

In polyatomic molecules, as the number of constituting atoms and the complexity of normal vibrations increases, it becomes ever more complicated to follow the change of dipole moment and polarizability with normal coordinates. The situation is still simple enough in the case of triatomic molecules where two typical examples are worth examining – linear and bent XY_2 molecules.

Carbon dioxide is a good example of a linear molecule which has no permanent dipole moment due to the symmetrical arrangement of electric charges. This molecule has three normal vibrations shown schematically in Table 2: a symmetrical stretching (Q_1), an asymmetrical stretching (Q_2), and a degenerate pair of bending vibrations (Q_3). The center of symmetry is preserved in the molecule during the symmetrical stretching vibration (Q_1), thus during this vibration the molecule behaves as a homonuclear diatomic molecule – the vibration is IR inactive but Raman active.

However, when the molecule is distorted along the asymmetric normal coordinates Q_2 or Q_3, the symmetry of the distribution of charges is destroyed and dipoles are generated. In case of the asymmetric stretching vibration (Q_2) the dipole oscillates along the bond direction, whereas during the bending vibration (Q_3) it oscillates in a perpendicular direction. These two asymmetric vibrations are therefore IR active. The molecule at the equilibrium

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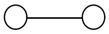
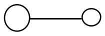
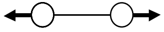
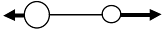
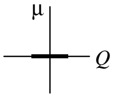
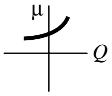
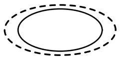
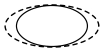
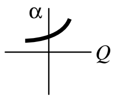
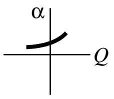
Table 1. Factors determining the IR and Raman activity of vibrations of homonuclear and heteronuclear diatomic molecules.

Parameter	Type of molecule	
	X_2 	X–Y 
Normal mode of vibration	X—X stretching 	X—Y stretching 
Dipole moment	0	⟶
Variation of dipole moment with normal coordinate		
Dipole moment derivative (at equilibrium)	$\left[\frac{\partial\mu}{\partial Q}\right]_0 = 0$	$\left[\frac{\partial\mu}{\partial Q}\right]_0 \neq 0$
Infrared activity	No	Yes
Shape of polarizability ellipsoid		
Variation of polarizability with normal coordinate (schematic)		
Polarizability derivative	$\left[\frac{\partial\alpha}{\partial Q}\right]_0 \neq 0$	$\left[\frac{\partial\alpha}{\partial Q}\right]_0 \neq 0$
Raman activity	Yes	Yes

position has nonzero polarizability which may change little during the asymmetric vibrations, as these distortions do not really alter the volume of the molecule. But even if there is some change, these asymmetric vibrations are, in fact, antisymmetric, which means that the distortion of polarizability ellipsoid during the first half period of vibration would be the mirror image of that during the second half period. The variation of polarizability is thus symmetric about the equilibrium position (see the corresponding graphs in Table 2) and the orientation of axes of the ellipsoid do not change either. So, its gradient (the polarizability derivative) at the equilibrium is zero and, consequently, these vibrations are inactive in Raman scattering.

Thus we have arrived at a notable result that in this molecule there is no overlap in the fundamental vibrational frequencies between IR and Raman spectra. In other words, there is mutual exclusion in IR absorption and Raman scattering, which is a property of molecules possessing a center of symmetry. As an example of a larger polyatomic molecule having center of symmetry, the IR and Raman spectra of liquid benzene are compared in Figure 7. The two strongest Raman lines at 3062 and 993 cm^{-1} correspond to totally symmetric vibrations belonging to a_{1g} species of the D_{6h} point group, which can be proved by depolarization measurements.

The occurrence of mutual exclusion demonstrates the complementary nature of IR and Raman spectroscopy best of all. In many other cases, when there is partial or even full overlap between the frequencies allowed in IR and Raman spectra, there may still be very great differences in relative band intensities. Transitions giving rise only to hardly detectable weak features in either the IR or the Raman spectrum may be strong or at least much easier to identify in the other.

In a bent triatomic molecule of XY_2 type, the two X–Y bonds are also equivalent by symmetry, but there is *no* center of symmetry here – the molecule belongs to the C_{2v} point group and all the three normal vibrations of it prove to be both IR and Raman active. This result can be obtained by the method employed above, i.e. by evaluating the dipole moment derivatives and the polarizability derivatives for each normal mode of vibration. However, as this method requires the knowledge of each normal mode as well as the contribution of the displacement of each atom to changes of dipole moment and polarizability, this becomes an insoluble task with larger molecules.

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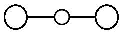
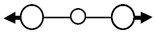
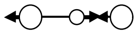
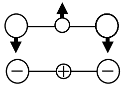
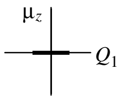
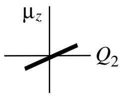
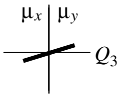
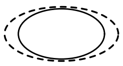
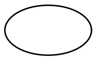
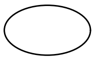
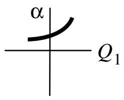
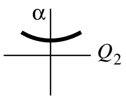
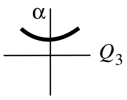
Table 2. Factors determining the IR and Raman activity of vibrations for a linear YXY molecule.

Parameter	Y−X−Y 		
Normal mode of vibration	Symmetric stretch, Q_1 	Asymmetric stretch, Q_2 	Bending, Q_3 
Dipole moment	0	↔	↕
Variation of dipole moment with normal coordinate			
Dipole moment derivative (at equilibrium)	$\left[\frac{\partial\mu}{\partial Q_1}\right]_0 = 0$	$\left[\frac{\partial\mu_z}{\partial Q_2}\right]_0 \neq 0$	$\left[\frac{\partial\mu_x}{\partial Q_3}\right]_0 \neq 0$
Infrared activity	No	Yes	Yes
Shape of polarizability ellipsoid			
Variation of polarizability with normal coordinate			
Polarizability derivative	$\left[\frac{\partial\alpha}{\partial Q_1}\right]_0 \neq 0$	$\left[\frac{\partial\alpha}{\partial Q_2}\right]_0 = 0$	$\left[\frac{\partial\alpha}{\partial Q_3}\right]_0 = 0$
Raman activity	Yes	No	No

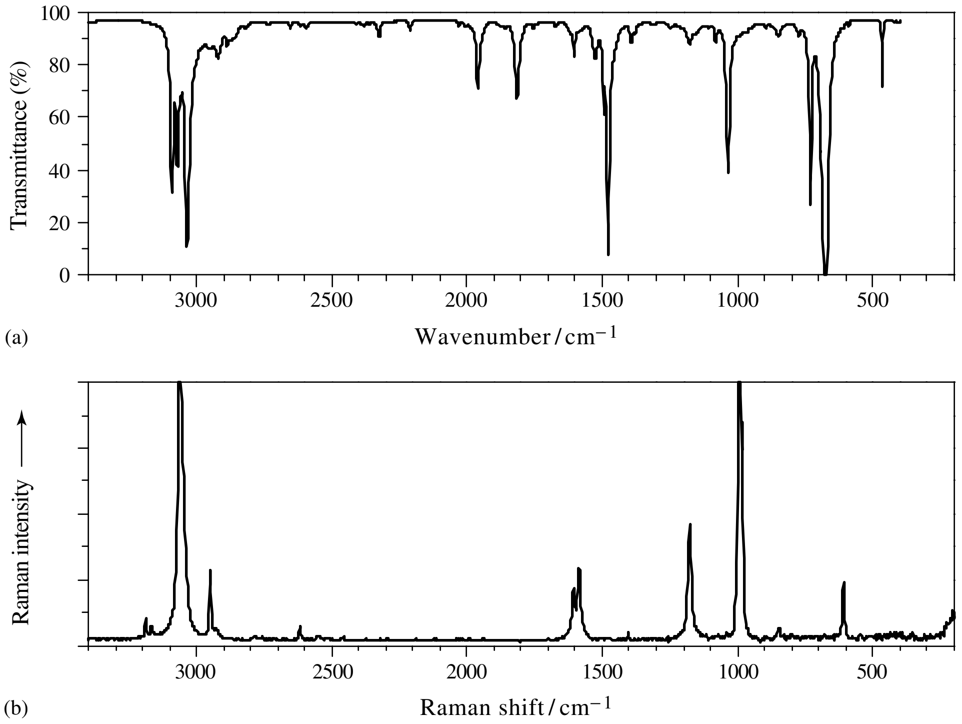


Figure 7. (a) Infrared and (b) Raman spectra of liquid benzene (illustrating the noncoincidence of fundamental transitions active in the two spectra).

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4.3 Polyatomic molecules

To simplify the procedure, and thereby make larger molecules more tractable, it is necessary to revert to the most general form of the selection rules derived from the quantum mechanical treatment, as follows:

1. A transition from vibrational state v^i to v^f (denoted $v^f \leftarrow v^i$) is *IR active* if at least one of the three vector components (matrix elements) of the type $[\mu_x]^k{}_{fi}$ differs from zero;
2. A transition $v^f \leftarrow v^i$ is *Raman active* if at least one of the six tensor components of the type $[\alpha_{xy}]^k_{fi}$ differs from zero.

For the fundamental transition of the kth vibration of a molecule this requires evaluation of integrals of the type

$$[\mu_x]^k{}_{fi} = \langle\psi_1(Q_k)|\mu_x|\psi_0(Q_k)\rangle \qquad (50)$$

and

$$[\alpha_{xy}]^k{}_{fi} = \langle\psi_1(Q_k)|\alpha_{xy}|\psi_0(Q_k)\rangle \qquad (51)$$

respectively, to see whether they differ from zero. This is fulfilled if the triple products under the integrals belong to a representation whose structure contains the totally symmetric species.

Fortunately, there is a fairly simple practical solution to this task that makes use of the symmetry properties of the transition dipole moment and the transition polarizability matrix elements. According to this, the above integrals differ from zero only if at least one component of the dipole moment (e.g. μ_x) or one component of the transition polarizability tensor (e.g. α_{xy}) have the same symmetry species as the normal coordinate Q_k. This follows from the fact that the vibrational wavefunction ψ_0 of the ground state ($v_k = 0$) is always totally symmetric, whereas that of the excited state ψ_1 ($v_k = 1$) has the same symmetry as the normal coordinate Q_k.[6]

The application of these general selection rules requires knowledge of the equilibrium symmetry (the point group) of the molecule and the distribution of normal modes among the symmetry species (the irreducible representations). Once the symmetry species of the vibration under consideration is known, all we have to do is to check whether any of the dipole moment or polarizability tensor components belong to that very symmetry species. At this step it is convenient to use the character tables containing this information, which are readily available in several monographs (as well as article **Infrared Spectroscopy: Theory** in this *Handbook*) for all point groups.[7,13]

This procedure is now illustrated on the planar four-atomic molecule formaldehyde, H_2CO. Based on its symmetry at equilibrium, the molecule belongs to the C_{2v} point group, and it has $3N - 6 = 6$ vibrational degrees of freedom. Let us put the molecule into a Cartesian coordinate system in accordance with the recommended practice:[8] the twofold rotation axis of symmetry C_2 running along the direction of the C=O bond and bisecting the H–C–H angle coincides with the z axis; the molecule lies in the yz plane (corresponding to the σ_{yz} plane of symmetry) so that the x axis (and the σ_{xz} plane of symmetry) is perpendicular to the plane of the molecule. Now we determine the distribution of vibrational degrees of freedom among the symmetry species (the structure of the irreducible representation) using the information available in the character table of the C_{2v} point group (Table 3), and apply the well established methods of group theory.[13,14] The following result is obtained:

$$\Gamma_{\mathrm{H_2CO}} = 3a_1 + b_1 + 2b_2 \qquad (52)$$

This information is added to the last column of Table 3: three normal vibrations are assigned to a_1, one to b_1, and two to b_2 species, numbered consecutively from Q_1 to Q_6. For this small, symmetric molecule it is still easy enough to predict the approximate shape of normal coordinates or normal modes of vibration (but note that it is *not* necessary to know them in order to determine their IR and Raman activity). For H_2CO they are depicted in Figure 8 and can be described roughly as follows:

- Q_1 (a_1) – practically pure (>99%) symmetric CH_2 stretching mode;
- Q_2 (a_1) – predominantly C=O stretching (~80%) combined with CH_2 bending (~20%);
- Q_3 (a_1) – predominantly CH_2 bending (~80%) combined with C=O stretching (~20%);

Table 3. Character table of point group C_{2v}, with extension for the fundamental vibrations of formaldehyde, H_2CO.

C_{2v} symmetry species	Symmetry operations						Activity		H_2CO normal modes, Q_k
	E	$C_{2v}(z)$	σ_{xz}	σ_{yz}	T	R	IR $[\mu]^k$	Raman $[\alpha]^k$	
a_1	1	1	1	1	z	–	μ_z	α_{xx}, α_{yy}, α_{zz}	Q_1, Q_2, Q_3
a_2	1	1	−1	−1	–	R_z	–	α_{xy}	–
b_1	1	−1	1	−1	x	R_y	μ_x	α_{xz}	Q_4
b_2	1	−1	−1	1	y	R_x	μ_y	α_{yz}	Q_5, Q_6

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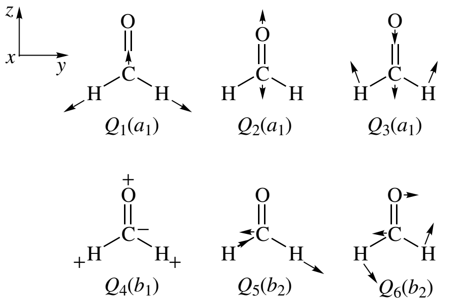

Figure 8. Approximate forms of normal vibrations of formaldehyde, H_2CO, with indication of their symmetry species (in parentheses).

- Q_4 (b_1) – out-of-plane bending mode (100%);
- Q_5 (b_2) – almost pure (>99%) asymmetric CH_2 stretching;
- Q_6 (b_2) – almost pure (>99%) CH_2 rocking vibration.

The description is based on calculated total energy distributions among the cited symmetry coordinates.

The assignment of vibrations to specific symmetry species and inspection of the corresponding rows of the character table immediately leads to information about their IR or Raman activity: we just have to look for components of the dipole moment and for components of the polarizability tensor. Thus finding μ_z (or z) in the symmetry species of Q_1, Q_2, and Q_3 means that these vibrations have nonzero transition moments (namely, in the z direction), so they are IR active. Finding α_{xx}, α_{yy}, and α_{zz} in the same row means that these vibrations change all three diagonal elements of the polarizability tensor as well, so they are also Raman active. Mode Q_4 will have transition moment along the x axis (μ_x) and will have a nonzero value for α_{xz}. Normal modes Q_5 and Q_6 will change the dipole moment along the y axis and have nonzero values for α_{yz}. Consequently, all six normal modes of this molecule are both IR and Raman active.

When we try to locate the fundamental transitions ($v_k = 1 \leftarrow v_k = 0$) in the measured spectra and assign them to specific symmetry species, we would like to use, in addition to information about coincidence or noncoincidence of frequencies observed in IR and Raman spectra, the polarization characteristics indicated in the character table as well. For IR absorption or emission bands this would require the use of oriented samples such as oriented single crystals or molecules aligned in anisotropic media.[11,15]

For samples consisting of freely rotating or randomly oriented molecules, only some part of this information can be utilized when interpreting the measured Raman depolarization ratios, as discussed in connection with the classical description. This amounts to distinguishing between totally symmetric and nontotally symmetric transitions only. In the example of formaldehyde, the Raman bands belonging to Q_1, Q_2, and Q_3 must be polarized ($\rho_\perp < 0.75$), whereas Q_4, Q_5, and Q_6 are depolarized ($\rho_\perp = 0.75$). In addition, the three bands belonging to the totally symmetric species a_1 are expected to be noticeably stronger than the others, because the diagonal elements of transition polarizability tensors are usually significantly greater than the off-diagonal elements.

4.4 Overtones and combinations

It is stated above that in the double harmonic approximation of molecular vibrations only fundamental transitions with $\Delta v_k = \pm 1$ are allowed in the IR and Raman spectra. In real molecules, however, mechanical anharmonicity can lead to the appearance of overtones and combinations as well. Furthermore, if electrical anharmonicity is also taken into account, then the third (and possibly further) terms in equation (18) describing the dependence of polarizability on normal coordinates must be considered. This introduces additional induced dipoles with wavenumbers $\tilde{\nu}_0 \pm 2\tilde{\nu}_k$ and $\tilde{\nu}_0 \pm (\tilde{\nu}_k \pm \tilde{\nu}_l)$, etc., corresponding to overtones and combinations of the fundamental vibrational frequencies. The intensities of these transitions would depend on second- (and possibly higher)-order derived polarizability tensors of the type

$$\left(\frac{\partial^2\alpha}{\partial Q_k^2}\right)_0, \quad \left(\frac{\partial^2\alpha}{\partial Q_k \partial Q_l}\right)_0, \quad \text{etc.} \tag{53}$$

Similar considerations are valid for activities of overtones and combinations in IR spectra where the intensities depend on the values of second order transition moments of the type

$$\left(\frac{\partial^2\mu}{\partial Q_k^2}\right)_0, \quad \left(\frac{\partial^2\mu}{\partial Q_k \partial Q_l}\right)_0, \quad \text{etc.} \tag{54}$$

The activity of overtones and combinations can be evaluated on the basis of the selection rules formulated in the most general way in equations (49) and (50), which are independent of assumptions about mechanical or electrical anharmonicity. The procedure is thus similar to that followed with fundamental transitions (if the transition starts from the ground state) – one has to determine the symmetry species of the final vibrational state and check the activity of that species. If the symmetry species of the fundamentals are already known, those of the overtones or combinations of nondegenerate vibrations are obtained using the appropriate character tables and calculating the direct products of the characters of the fundamentals involved. (The symmetry species of overtones of degenerate vibrations are discussed and tabulated in the monograph by Herzberg;[16] see also **Resonance Raman Spectroscopy**.

We can illustrate this with the character table of point group C_{2v} (Table 3). It is easy to see that a binary combination of any symmetry species with itself yields the totally

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symmetric species; for example, $b_2 \times b_2 = a_1$ for $2\tilde{\nu}_5$ or $\tilde{\nu}_5 + \tilde{\nu}_6$ of formaldehyde. In this point group, the first overtone of any normal vibration will be totally symmetric. In contrast, the combination $\tilde{\nu}_4 + \tilde{\nu}_6$ ($b_1 \times b_2 = a_2$) belongs to the a_2 species, thus it may appear in the Raman but not in the IR spectrum.

A noteworthy case is that of the linear triatomic molecules examined in Table 2. We have seen that due to the rule of mutual exclusion, asymmetric vibrations with wavenumbers $\tilde{\nu}_2$ and $\tilde{\nu}_3$ (normal modes Q_2 and Q_3) are inactive in the Raman spectrum. However, the wavefunctions of their overtones, $2\tilde{\nu}_2$ and $2\tilde{\nu}_3$ become symmetric with respect to the center of symmetry, thus the overtones turn out to be Raman active. This can also be explained within the frames of the classical picture in that the first derivative of polarizability for these vibrations (taken at equilibrium) is zero, whereas the second derivative is not.

Finally, it needs mentioning that overtones and combinations are relatively rarely observed in nonresonant Raman scattering because, even if allowed by the selection rules, these bands are invariably much weaker than the fundamentals. The reason for this can be traced back to the extent of mechanical and electrical anharmonicity responsible for the activity of these transitions. As most normal vibrations are only slightly anharmonic, the amplitudes of the anharmonic (higher-order) terms in the generalized Fourier series expression of the time dependence of normal coordinates are very small compared to that of the harmonic term.[17]

ABBREVIATIONS AND ACRONYMS

RRS	Resonance Raman Scattering
YAG	Yttrium Aluminum Garnet

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