Molecular Structure and Properties from High Resolution Raman Spectra of Gases

W. J. Jones

Email alerting service	Receive free email alerts when new articles cite this article - sign up in the box at the top right-hand corner of the article or click **here**

Molecular structure and properties from high resolution Raman spectra of gases

By W. J. Jones†

Department of Physical Chemistry, Lensfield Road, Cambridge, CB2 1EP, U.K.

Despite the weakness of spontaneous Raman scattering, it can frequently provide structural information of comparable precision to the best infrared studies. In addition, because of the less restrictive selection rules which operate, more types of transitions are permitted so that rotational constants which may not be obtained from infrared spectra can be obtained via Raman studies. In addition to structural data, high-resolution Raman spectroscopy has recently been used to determine explicit values for the principal components of the polarizability tensor and it is beginning to provide information on how these components vary with the molecular vibration. The potential availability of such information is of considerable interest, since the polarizability provides an insight into the electronic structure of a molecule. It is perhaps surprising that there is at present no adequate treatment of the manner in which the molecular polarizability changes with vibration. Additional information on the components of the polarizability tensor can only serve to promote our understanding of the electronic structure of molecules.

Introduction

Studies of Raman spectra at high resolution are generally concerned with transitions among the rotational energy states of molecules. In spite of the development of high-power laser sources, the observation techniques have not changed markedly from those developed with such outstanding success for gases by Welsh and Stoicheff using high-power mercury arcs. Nor has the resolution attained improved dramatically since these earlier studies in which the resolution limit was set by the spectral width, *ca.* 0.25 cm^{-1}, of the mercury exciting line. Present-day lasers may have line widths of some three orders of magnitude less than this but the spectra obtained, in resolution terms, are frequently little better; modern instruments can generate spectra at a resolution of *ca.* 0.07 cm^{-1} for very strong scatterers, but at a resolution some three times poorer than this for the very weak vibration–rotation bands. Lasers have, however, brought significant advantages to this field of study; in particular the intensity of radiation scattered from a particular volume element may be much higher, so that smaller sample volumes are required, the collection efficiency is higher and the troublesome effects of stray light are less significant.

The experimental techniques employed are conceptually simple; radiation from a high-power visible laser is incident on a gas sample and the scattered radiation is imaged on to the slit of a diffraction-grating spectrograph. (Spectrometers in which spectral elements are recorded consecutively, rather than simultaneously, suffer in comparison with spectrographs in sensitivity so that the latter are almost invariably employed in high-resolution studies.) Modern instruments can produce good quality pure-rotation spectra from strong scatterers in a few

† Present address: Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth, SY23 1NE, U.K.

minutes and vibration–rotation bands in a few hours, but because of the wide variation in the intensities of Raman bands, exposure times of several days may still be necessary in order to record certain very weak bands.

All molecules can be classified according to the relative values of the three principal moments of inertia, I_A, I_B and I_C, which are related to the corresponding rotational constants A, B and C, by the expressions $A = h/8\pi^2 c\, I_A$, etc., with the convention $I_A \leqslant I_B \leqslant I_C$. The rotational term value expression (the energy expressed in cm^{-1} units) for a prolate symmetric top $(I_A < I_B = I_C)$ in the vibrational ground state is:

$$F(J, K) = BJ(J+1) + (A-B)K^2 - D_J J^2 (J+1)^2 - D_{JK} J(J+1) K^2 - D_K K^4. \tag{1}$$

J is the quantum number characterizing the total rotational angular momentum and K is its component along the top axis, with $K \leqslant J$. D_J, D_{JK} and D_K are centrifugal distortion constants introduced to allow for the non-rigidity of the rotating molecule. With $K = 0$ equation (1) can also be used to represent the rotational energy state of linear $(I_A = 0,\ I_B = I_C)$ and spherical top $(I_A = I_B = I_C)$ molecules; for oblate symmetric tops $(I_A = I_B < I_C)$ A must be replaced by C. Although J remains a good quantum number for an asymmetric top $(I_A \neq I_B \neq I_C)$ K does not, but being intermediate between prolate and oblate tops their energy states are represented in terms of these limiting cases and equation (1) is also of direct relevance to an understanding of asymmetric-top spectra.

Raman displacements correspond to the energy separations of the molecular states involved in the transitions and the spectra carry information in the form of line positions, line shapes and intensities. Naturally they are not independent but in general structural data comes from line positions whilst the intensities give polarizability information. The following two sections consider both these aspects of Raman scattering.

Rotational constants from high-resolution Raman spectra

Although the symmetry of a molecule may frequently be inferred from the pattern of vibrational bands observed in infrared and Raman spectra, detailed rotational analyses are required for the determination of molecular dimensions. From the moments of inertia obtained from such analyses it is frequently possible to evaluate some or all of the internuclear distances.

Raman spectra arise when the dipole induced by the incident radiation varies with the molecular motion; pure-rotation spectra arise through the anisotropy in the polarizability, and vibrational spectra when the polarizability changes with the vibrational frequency. Pure-rotation spectra thus arise for all molecules other than spherical tops, and certain modes of all molecules give rise to vibrational Raman spectra.

For all molecules, other than spherical and asymmetric tops, rotational spectra are governed by the changes

$$\Delta J = 0, 1, 2; \quad \Delta K = 0. \tag{2}$$

One then obtains $R(\Delta J = 1)$ and $S(\Delta J = 2)$ branches ($\Delta J = 0$ gives only the undisplaced Rayleigh line), with displacements (in cm^{-1} units)

$$\Delta\nu_R = |\nu_0 - \nu| = 2B_0(J+1) - 2D_{JK}(J+1)K^2 - 4D_J(J+1)^3, \tag{3a}$$

$$\Delta\nu_S = |\nu_0 - \nu| = (4B_0 - 6D_J)(J+\tfrac{3}{2}) - 4D_{JK}(J+\tfrac{3}{2})K^2 - 8D_J(J+\tfrac{3}{2})^3. \tag{3b}$$

For linear molecules R branch transitions are absent and one observes only S branch lines of separation *ca.* $4B$. The precision attainable in Raman spectroscopy is reflected in recent studies of the spectra of N_2 and O_2 (Butcher, *et al.* 1971; Bendtsen 1974; Butcher & Jones 1974). Individual lines could be measured with a typical error of 0.002 cm^{-1}, leading to B_0 and D_J values accurate to *ca.* 1 part per 10^5 and 10^3, respectively. Unfortunately, however, this accuracy is insufficient to detect any deviation from the Born–Oppenheimer approximation, as described by Watson (1973a) although such a deviation has been found for CO by using microwave and infrared data (Watson 1973a, b).

In spite of the rather lower accuracy, however, many species which do not possess permanent dipole moments may only be examined by Raman techniques, since vibration–rotation or electronic band structures of large molecules are frequently too complex to be analysed. Thus Weber & Schlupp (1972) were able to obtain well defined B_0 and D_J values from the pure-rotation spectra of such large symmetric top molecules as cyclohexane and hexafluorobenzene, some with line separations as little as *ca.* 0.07 cm^{-1}. In their analyses slightly different values of B_0 and D_J were obtained from separate analyses of R and S branch data, a discrepancy that pinpoints an inherent disadvantage in pure-rotation Raman spectroscopy for structure determinations. Since the resolution of the technique is limited, the measured 'line' position represents an average of all the transitions lying within the observed contour. For the species studied by Weber & Schlupp only about 10–20% of the molecules exist in the vibrational ground state, the remaining molecules lying in excited vibrational states which also contribute to the pure-rotation spectrum. Apart from this, each measured 'line' contains contributions from all the K levels populated, transitions from differing K levels lying at slightly different frequencies owing to the effect of D_J and D_{JK} in equations (3). Because of the differing intensities of R and S branch lines from a particular K level (Placzek & Teller 1933) this latter blending effect will be different for the two line series. Correction for these effects would scarcely have been possible for the species studied by Weber & Schlupp, although they have been allowed for in the analysis of boron trifluoride (Freedman & Jones 1975a), a more favourable molecule to analyse since there is only one low-lying vibrational state with a population of only *ca.* 20% of that of the ground state. The effects of line blending due to non-zero D_J and D_{JK} terms may be allowed for, as shown by the latter study, but until the available resolution is dramatically improved, constants derived from pure-rotation Raman spectra are likely to remain as average values for all the vibrational levels populated.

Equations (3) show that for a symmetric-top molecule the rotational constants A and D_K may not be obtained from the analysis of pure-rotation spectra, but in this area again Raman spectroscopy can provide information which could not be obtained by microwave or infrared methods. To obtain A (and D_K) it is necessary to examine a band in which the K rotational quantum number changes. Such changes in K generally arise for transitions from the ground state to degenerate vibrational states, but in such states each doubly-degenerate K level is split into two components as a result of Coriolis interaction between vibration and rotation (Herzberg 1956). The magnitude of this splitting, $2A\zeta K$, depends on the Coriolis constant ζ which, for a molecule like CH_3I, lies in the range -1 to $+1$ and is different for each degenerate vibration. For molecules of symmetry C_{3v} or D_{3d} the selection rules are $\Delta J = 0, \pm 1, \pm 2$; $\Delta K = \pm 1, \pm 2$. The most pronounced resolvable features are series of Q branches ($\Delta J = 0$) of separation $2[A(1-\zeta)-B]$ and $4[A(1+\frac{1}{2}\zeta)-B]$ corresponding to $\Delta K = \pm 1$ and ± 2, respectively (in the infrared one series only is observed of separation $2[A(1-\zeta)-B]$). Analyses of

Raman bands of this type (Lepard *et al.* 1966; Edwards & Brodersen 1975; Freedman & Jones 1975*b*) allow A, D_K and ζ to be obtained with high accuracy.

In the D_{2d} molecule, allene, the doubly-degenerate E vibrations give rise to transitions $\Delta K = \pm 1$ in infrared spectra as well as in the Raman effect: in the former case a particular ΔK transition terminates on one component of the Coriolis split levels, whereas the corresponding Raman transition terminates on the other component. In this case, therefore, it is possible to determine A by a combined infrared–Raman analysis, but not by either technique alone.

Another unusual feature in the Raman spectra of molecules like allene is that it is possible to obtain A without recourse to such a combined infrared–Raman analysis. The reason for this is that B_1 and B_2 vibrational modes, made Raman-active by derived polarizability components ($\alpha_{xx}-\alpha_{yy}$) and α_{xy} respectively, have selection rules $\Delta J = 0$, ± 1, ± 2; $\Delta K = \pm 2$. Since these vibrational states are singly degenerate there is no Coriolis interaction, and Q branch sequences of separation $\sim 4(A-B)$ are observed (Butcher & Jones 1973; Hegelund & Andersen 1975). The markedly different selection rules of the B_2 modes of allene in infrared ($\Delta J = 0$, ± 1; $\Delta K = 0$) and Raman spectra emphasize the differences in the mechanisms involved, and to understand how this provides additional information on the molecule it is necessary to consider the scattering process a little more fully.

POLARIZABILITY TENSOR COMPONENTS FROM GAS-PHASE RAMAN SPECTRA

The intensity of Raman scattering as defined by the Raman scattering cross section, $d\sigma/d\Omega$, is given, for plane-polarized incident radiation, by the expression (Placzek 1934):

$$\left(\frac{d\sigma}{d\Omega}\right)_{\perp} = C(\nu_0 - \Delta\nu)^4 \{45[\alpha^i]^2_{n'n''} + 4[\beta^2]_{n'n''}\}, \tag{4a}$$

$$\left(\frac{d\sigma}{d\Omega}\right)_{\parallel} = C(\nu_0 - \Delta\nu)^4 \{3[\beta^2]_{n'n''}\}, \tag{4b}$$

where n' and n'' represent the quantum numbers of the two states involved in the vibrational transition $n' \leftarrow n''$ of displacement $\Delta\nu$. The trace and anisotropy in the polarizability in the space-fixed axis system (X, Y, Z) are defined by

$$[\alpha^i]_{n'n''} = \tfrac{1}{3}\langle n'|\alpha_{XX} + \alpha_{YY} + \alpha_{ZZ}|n''\rangle, \tag{5a}$$

$$[\beta^2]_{n'n''} = \tfrac{3}{2} \sum_L |\langle n'|\alpha_L|n''\rangle|^2, \tag{5b}$$

where the α_L are linear combinations of the polarizability components given by:

$$\alpha_A = (\tfrac{1}{6})^{\frac{1}{2}}(\alpha_{XX} + \alpha_{YY} - 2\alpha_{ZZ}); \quad \alpha_B = (\tfrac{1}{2})^{\frac{1}{2}}(\alpha_{XX} - \alpha_{YY}),$$
$$\alpha_C = (\tfrac{1}{2})^{\frac{1}{2}}(\alpha_{XY} + \alpha_{YX}); \quad \alpha_D = (\tfrac{1}{2})^{\frac{1}{2}}(\alpha_{YZ} + \alpha_{ZY}); \quad \alpha_E = (\tfrac{1}{2})^{\frac{1}{2}}(\alpha_{ZX} + \alpha_{XZ}). \tag{6}$$

$\langle n'|\alpha_L|n''\rangle (\equiv [\alpha_L]_{n'n''})$ is a matrix element for the transition $n' \leftarrow n''$. Herranz & Stoicheff (1963) were able to relate these matrix elements to an analogous set, l, defined in terms of the molecule-fixed axes, x, y and z, and to simplify the evaluation of the isotropic and anisotropic terms $[\alpha^i]_{n'n''}$ and $[\beta^2]_{n'n''}$. The α_l terms (with $l \equiv a, b, c, d, e$) are defined by equations (6) with X, Y, Z replaced by x, y, z, respectively.

Since this discussion is concerned with near-prolate top molecules, the z axis is identified with the A inertial axis and y with the C axis (in the near-oblate limit this choice would be reversed). In vibration–rotation spectra these polarizability tensor components are replaced by their derivatives with respect to the normal coordinate concerned. Each of these α_l terms, other than α^i which gives $\Delta J = \Delta K_p = 0$ only, leads to selection rules $\Delta J + 0, \pm 1, \pm 2$. The selection rules in K_p, however, depend on which of these terms is non-zero: α_a gives $\Delta K_p = 0$ only; α_b and α_c give $\Delta K_p = \pm 2$; α_d and α_e give $\Delta K_p = \pm 1$.

In the pure-rotation spectra of linear and symmetric top molecules only α^i and α_a are different from zero so that the anisotropy is determined by one component only of equations (6). In these instances, measurements of the depolarization ratios provide values for the ratio $|\alpha_a/\alpha^i|$. Knowing the Rayleigh scattering cross section, it is possible to evaluate the three components of the molecular polarizability directly. No further information on these components is provided by the analysis of the rotation spectrum.

For asymmetric-top molecules, however, the three components of the polarizability tensor are different and measurements of the depolarization ratio do not allow of the direct evaluation of α_{xx}, α_{yy} and α_{zz}. In the case of ethylene, both α_a and α_b are different from zero and since these anisotropies lead to different selection rules in K_p it is possible, by using the measured depolarization ratio (Bridge & Buckingham 1966), to obtain the components α_{ii}. The effects of the molecular asymmetry mix levels K with those of $K \pm 2$, and hence $\Delta K_p = 2$ transitions arise as a result not only of the non-zero α_b term but also of this mixing; and the latter term also, by virtue of this mixing, gives rise to transitions with $\Delta K_p = 0$. Because of this mixing it is possible, by means of a full band simulation with the asymmetric rotor energy levels, to evaluate the magnitude and sign of the ratio R_{ba}, defined by

$$R_{ba} = \alpha_b/\alpha_a. \tag{7}$$

By comparing such simulated spectra with the pure-rotation spectrum observed (Hills & Jones 1975 a) it was possible to show that, for ethylene, $R_{ba} = 0.22 \pm 0.03$, and hence to derive the value $\alpha_{zz} = 5.40 \times 10^{-30}$ m^3, $\alpha_{xx} = 3.86 \times 10^{-30}$ m^3, $\alpha_{yy} = 3.40 \times 10^{-30}$ m^3.

In other molecules of lower symmetry more than two of the terms of equation (6) may be non-zero. For example, in molecules of C_{2h} symmetry, such as butadiene, the selection rules on K_p are $\Delta K_p = 0, 1, 2$, the change $\Delta K_p = 1$ arising from the term α_e of equations (6) The observed spectrum (Hills & Jones 1975 b) consisted of extremely strong series of R and S branch lines corresponding to changes $\Delta K_p = 0$, $\Delta J = 1, 2$, accompanied by weak transitions with $\Delta K_p = 0$, $\Delta J = 0$. Because of the large disparity in the intensities of the branches it was not possible to measure the ratio R_{ba}. No transitions of the sort $\Delta K_p = 1$ were found, probably because α_e is small in comparison with α_b. Few other studies of this sort on the relative intensities of individual rotational lines in pure-rotation spectra have been carried out, although such work for asymmetric-top molecules can clearly provide additional information from which individual components of the polarizability tensor may be evaluated.

In the study of vibration–rotation spectra the intensity of Raman scattering given by equation (4), depends not on the values of the components α_{ij} of the polarizability, but on their derivatives with respect to the relevant vibrational coordinate. Depending on the symmetry of the molecule studied, and on the particular vibrational mode considered, any one, or more, of the six components of the derived polarizability tensor may be different from zero, and, further, they may be either positive or negative with respect to the normal coordinate

concerned. Because of this, many different band types are to be expected in high-resolution Raman spectra and, for molecules of low symmetry, many of these will, as in infrared spectra of asymmetric tops, be hybrid bands.

Up to the present time, because of the difficulties of recording high quality vibration–rotation Raman bands at adequate resolution, only a few such studies have been carried out. Deroche *et al.* (1976) recorded and simulated the ν_3 and ν_5 bands of CH_2D_2. These bands are of symmetry A_1 and A_2 and arise because of the non-zero values of $[\alpha^i]$, $[\alpha_a]$ and $[\alpha_b]$, and of $[\alpha_d]$, respectively. The ν_5 band, which depends on only one of the polarizability components,
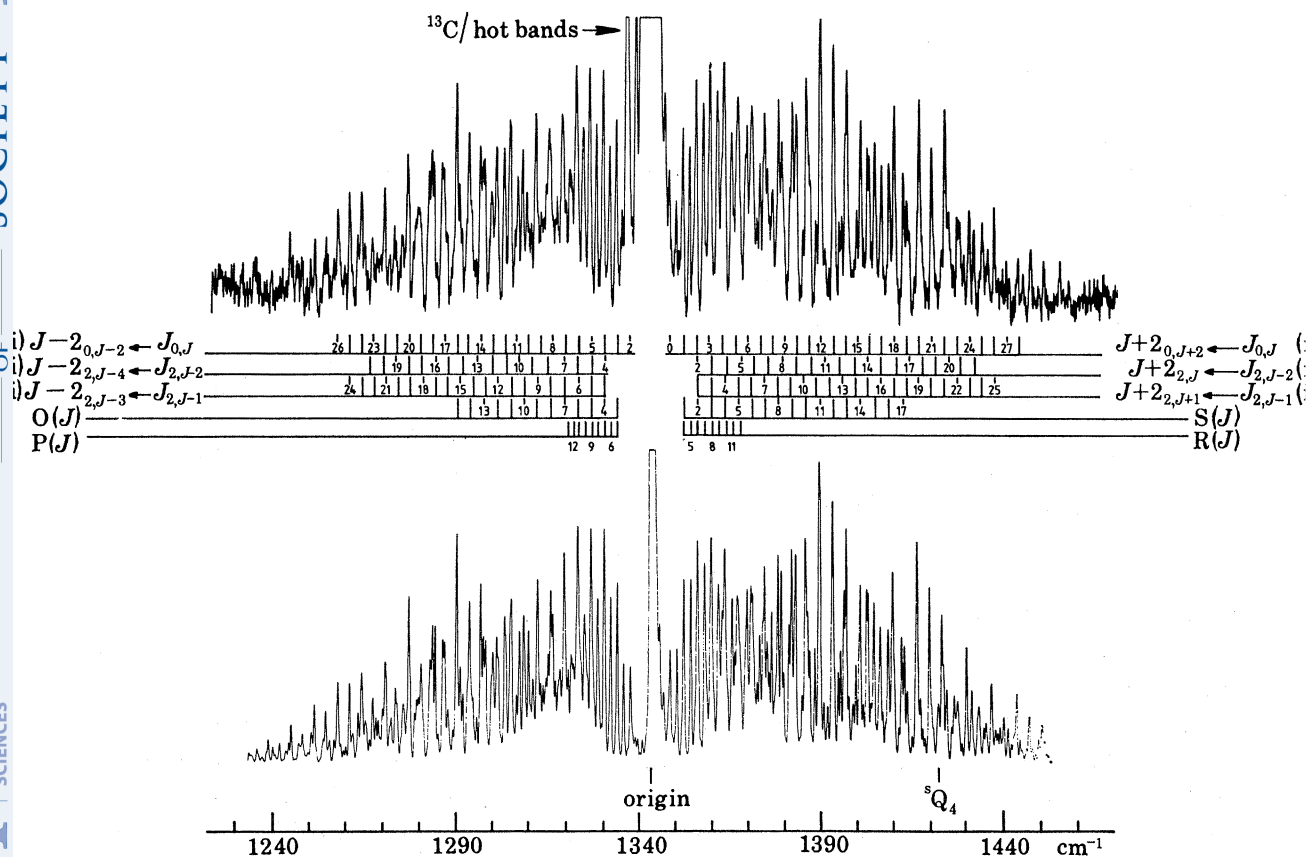

FIGURE 1. A comparison of the observed (top) and simulated spectra of the ν_3 band of ethylene. The observed band was excited by 488 nm argon laser radiation with a gas pressure of 760 Torr; the simulation was obtained with a spectral slit width of 0.25 cm^{-1} and $R_{ba} = -0.32$.

could be analysed directly and a measurement of the intensity of this band would yield $|[\alpha_d]|$. The ν_3 band, on the other hand, which depends on three of these components, could be simulated only by determining the ratios $[\alpha_b]/[\alpha_a]$, yielding a value of -1.0 for this parameter.

A recent analysis of this sort was carried out for ethylene (Foster *et al.* 1977) as part of the high-resolution study of its Raman band structures. The totally symmetric A_g CH_2 deformation vibration, ν_3, at 1343 cm^{-1}, is made Raman active by tensor components $[\alpha^i]$, $[\alpha_a]$ and $[\alpha_b]$ and the simulated spectrum, compared with that observed in figure 1, was obtained for a value of $R_{ba} = -0.32$. This value of R_{ba} is significantly different from that obtained from the pure rotational spectrum, the difference providing an interesting insight into the behaviour of the

polarizability as the molecule vibrates. An even greater difference from the pure rotational spectrum was found with the ν_1 band; with $R_{ba} = 1.6$ this band is found to be dominated by Q branch transitions rather than the S and R branch transitions found in the case of ν_3.

The Raman active modes of V_h ($\equiv D_{2h}$) molecules (e.g. ethylene) of symmetry B_{1g}, B_{2g} and B_{3g}, are made Raman active by components α_d, α_e and α_c, with selection rules $\Delta K_p = \pm 1$, ± 1, and ± 2, respectively. Ethylene itself has no fundamental vibrations of symmetry B_{3g}, but modes of symmetry B_{1g} and B_{2g} have been recorded and analysed. These bands, however, although interesting in their own right, arise from one component only of the derived polarizability tensor so that the high resolution analysis provides no additional information on these components.

Murphy (1977) has carried out a fully study of the very weak ν_2 band of water vapour and has even managed to record the very much weaker overtone $2\nu_2$. The ratio R_{ba} was, of course, determined in this study and by measuring the depolarization ratio and the scattering cross section of the band he was able to make significant progress in the determination of the derived polarizability components. Since the total scattered intensity is given by equation (4), the signs of $[\alpha^i]$ and $[\beta]$ could not be determined from the data. Depending on the choice of sign made for these parameters, four sets of components were obtained which were compatible with his experimental results. Murphy used the bond polarizability theory in an attempt to choose between these sets, and although the theory was shown to be inadequate it did allow him to select two as being consistent with other knowledge of the molecular polarizability tensor. He suggests that the remaining ambiguity may be resolved by considering his results in combination with corresponding results for D_2O, when they become available.

No full asymmetric rotor analyses of vibration–rotation Raman bands from molecules of lower symmetry have, as yet, been carried out. Here again, however, the analysis of a Raman vibrational band can provide information on the derived polarizability tensor components. Consider a molecule of C_{2h} symmetry, such as butadiene or *trans*-dideuteroethylene. The Raman active modes have symmetry A_g and B_g (see table 1).

TABLE 1. RAMAN VIBRATION–ROTATION BAND TYPES FOR C_{2h} SYMMETRY

(Hills *et al.* 1977)

	A_g modes				B_g modes	
contributing elements	$[\alpha^i]$,	$[\alpha_a]$,	$[\alpha_b]$,	$[\alpha_e]$	$[\alpha_c]$,	$[\alpha_d]$
ΔK_p	0,	0,	± 2,	± 1	± 2,	± 1
ΔJ	0,		$0 \pm 1 \pm 2$		$0 \pm 1 \pm 2$	
polarizability information available	$R_{ba} =$	$[\alpha_b]/[\alpha_a]$				
		$\|[\alpha_e]/[\alpha_a]\|$			$\|[\alpha_c]/[\alpha_d]\|$	

Asymmetry mixes levels with K differing by 2, thereby generating an interference term which enables the sign of R_{ba} to be found by simulating the spectrum. Because of the symmetry of the rotational Hamiltonian, sets of levels with K differing by unity cannot be mixed by asymmetry, so the B_g band type is a simple hybrid and only $\|[\alpha_c]/[\alpha_d]\|$ can be found by integrating the individual contributions. The same applies to $\|[\alpha_e]/[\alpha_a]\|$ in an A_g type band. Hills *et al.* (1977) have given model band contours for vibration–rotation Raman bands of ethylene and *trans*-dideuteroethylene to show how polarizability information can be extracted from such spectra. No spectra have been recorded with which these simulations may be compared but there is no doubt that the technique is a powerful one for providing additional information on the molecular polarizability.

[45]

I am deeply indebted to present and past members of my research group for their contributions in this area of spectroscopy and, additionally, to Mr R. B. Foster for his comments on the preparation of this paper.

References (Jones)

Bendtsen, J. 1974 *J. Raman Spectrosc.* **3**, 133.
Bridge, N. J. & Buckingham, A. D. 1966 *Proc. R. Soc. Lond.* A **295**, 334.
Butcher, R. J. & Jones, W. J. 1973 *J. Raman Spectrosc.* **1**, 393.
Butcher, R. J. & Jones, W. J. 1974 *J. chem. Soc. Faraday Trans.* II **70**, 560.
Butcher, R. J., Willetts, D. V. & Jones, W. J. 1971 *Proc. R. Soc. Lond.* A **324**, 231.
Deroche, J. C., Graner, G., Bendtsen, J. & Brodersen, S. 1976 *J. molec. Spectrosc.* **62**, 1976.
Edwards, T. H. & Brodersen, S. 1975 *J. molec. Spectrosc.* **54**, 121.
Foster, R. B., Hills, G. W. & Jones, W. J. 1977 *Molec. Phys.* **33**, 1589.
Freedman, P. A. & Jones, W. J. 1975a *J. molec. Spectrosc.* **54**, 182.
Freedman, P. A. & Jones, W. J. 1975b *J. chem. Soc. Faraday Trans.* II **71**, 650.
Hegelund, F. & Andersen, H. B. 1975 *J. Raman Spectrosc.* **3**, 73.
Herranz, J. & Stoicheff, B. P. 1963 *J. molec. Spectrosc.* **10**, 448.
Herzberg, G. 1956 *Infrared and Raman spectra of polyatomic molecules.* New York: Van Nostrand.
Hills, G. W. & Jones, W. J. 1975a *J. chem. Soc. Faraday Trans.* II **71**, 812.
Hills, G. W. & Jones, W. J. 1975b *J. chem. Soc. Faraday Trans.* II **71**, 827.
Hills, G. W., Foster, R. B. & Jones, W. J. 1977 *Molec. Phys.* **33**, 1571.
Lepard, D. W., Shaw, D. E. & Welsh, H. L. 1966 *Can. J. Phys.* **44**, 2353.
Murphy, W. F. 1977 *Molec. Phys.* **33**, 1701.
Placzek, G. 1934 In *Handb. Radiologie* (ed. E. Marx) **6** (2), p. 205. Leipzig.
Placzek, G. & Teller, E. 1933 *Z. Phys.* **81**, 209.
Watson, J. K. G. 1973a *J. molec. Spectrosc.* **45**, 99.
Watson, J. K. G. 1973b *J. molec. Spectrosc.* **48**, 479.
Weber, A. & Schlupp, J. 1972 *J. opt. Soc. Am.* **62**, 428.