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Hyper-Raman vibrational spectroscopy with circularly polarized light

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This paper presents a new method for the analysis of hyper-Raman vibrational spectra. It is shown that, by irradiating the sample with circularly polarized light, the measurement of two polarization ratios suffices for a complete analysis of vibrational symmetry. For this purpose a simple graphical method is introduced which can be applied for any convenient scattering geometry. Using this method, it is possible to test experimentally some of the assumptions in earlier hyper-Raman theories. These principles are illustrated by references to several specific molecular vibrations.

1. INTRODUCTION

The vibrational hyper-Raman effect is an inelastic three-photon scattering process in which molecules undergo the concerted absorption of two photons of frequency ω and the emission of a single photon of frequency $\omega' \approx 2\omega$. Energy is conserved in the process by vibrational transitions $N \leftarrow M$ in the irradiated molecules or, in the case of crystals, by coupling to lattice vibrations, such that

$$E_M + 2\hbar\omega = E_N + \hbar\omega'. \quad (1)$$

The selection rules are entirely different from those which apply to the Raman effect and to infrared absorption, although all infrared allowed vibrations are also hyper-Raman allowed.

Despite continuing theoretical interest in the hyper-Raman effect [1-5] relatively few experimental studies have been carried out since the original studies by Terhune *et al.* [6]. Some of the recent experiments have involved the study of lattice vibrations, taking advantage of the different selection rules to overcome problems associated with the use of infrared or Raman spectroscopy. The hyper-Raman effect is of particular value in the analysis of Raman-forbidden vibrations [7-10]. As an example, in the work of Vogt and Rossbroich [11] the optical dispersion of SrTiO₃ in the far infrared, where radiation is strongly absorbed by the crystal, has successfully been measured by hyper-Raman spectroscopy in the optical region and Raman-inactive lattice vibrations have been discovered. Recent hyper-Raman experiments on liquids have led to the observation of vibrations which are usually forbidden as fundamental frequencies; Schmid and Schrötter [12] have detected an infrared and Raman-forbidden a_{1u} mode in tetrachloroethylene, and an a_{1u} mode has also been reported in the hyper-Raman spectrum of cyclohexane by Hiraya *et al.* [13]

French *et al.* [14] have also reported the hyper-Raman spectra of liquid carbon tetrachloride and tin(IV) chloride.

In this paper we present a simple new method for the analysis of hyper-Raman spectra, basing our results on the earlier work of Andrews and Thirunamachandran [15]. More recent work by Andrews on two-beam three-photon absorption [16] has shown that it is possible to determine an excited state symmetry by carrying out just three independent polarization experiments, in contrast to the five required by an earlier analysis [17]. We show below that a similar simplification may be made to the analysis of hyper-Raman spectra.

In § 2 we first introduce the rate equations and selection rules for vibrational hyper-Raman scattering. We then derive specific expressions for the intensity of scattering using circularly polarized light and in § 3 we make use of these results to calculate the values of two polarization ratios at various angles of scattering. By a simple graphical method applied at any convenient angle, we then show how to derive comprehensive symmetry information from these two experimental measurements. Finally in the discussion in § 4 we show that some of the assumptions made in earlier hyper-Raman theories can be put to experimental test and we provide several examples for specific molecular vibrations.

2. RATE EQUATIONS AND SELECTION RULES

We begin with a description of the experimental configuration and a definition of the parameters which are involved in the rate equations. The incident light is characterized by a wave-vector \mathbf{k} and circular polarization vector ${}^{\circ}\mathbf{e}$, whilst the hyper-Raman scattered light has wave-vector \mathbf{k}' and in general an elliptical polarization state which may be analysed for polarization components of circular and linear character. We denote by ${}^{\circ}\mathbf{e}'$ the polarization vector for the scattered light corresponding to circular polarization of the *same helicity* as the incident light; ${}^{\parallel}\mathbf{e}'$ and ${}^{\perp}\mathbf{e}'$ are used to denote linear polarization vectors respectively lying in and perpendicular to the $(\mathbf{k}, \mathbf{k}')$ scattering plane, as shown in figure 1.

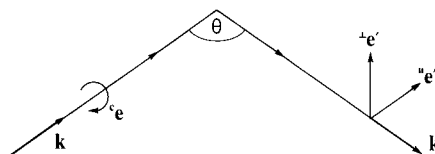


Figure 1. The scattering configuration.

The convergence angle ϑ defines the direction in which hyper-Raman scattering is observed, relative to the incident laser beam, such that

$$\cos \theta = -\mathbf{k} \cdot \mathbf{k}'. \quad (2)$$

Finally, we define the mean irradiance of the incident light as \bar{I}_0 and the degree of second order coherence [18] as $g^{(2)}$.

A general expression for the intensity of hyper-Raman scattering under arbitrary polarization conditions has been obtained previously [15]. The

result is expressed in terms of irreducible components of the hyper-Raman scattering tensor $\beta_{\lambda\mu\nu}^{\text{NM}}$ which can be determined from the equations given by Coope *et al.* [19] and Jerphagnon [20] and are as follows

$$\beta_{\lambda\mu\nu}^{(1A)} = \frac{1}{10}(3\delta_{\lambda\mu}\beta_{\rho\rho\nu}^{\text{NM}} + 3\delta_{\lambda\nu}\beta_{\rho\rho\mu}^{\text{NM}} - 2\delta_{\mu\nu}\beta_{\rho\rho\lambda}^{\text{NM}}), \quad (3)$$

$$\beta_{\lambda\mu\nu}^{(1B)} = \frac{1}{10}(-\delta_{\lambda\mu}\beta_{\nu\rho\rho}^{\text{NM}} - \delta_{\lambda\nu}\beta_{\mu\rho\rho}^{\text{NM}} + 4\delta_{\mu\nu}\beta_{\lambda\rho\rho}^{\text{NM}}), \quad (4)$$

$$\beta_{\lambda\mu\nu}^{(2)} = \frac{1}{6}\epsilon_{\lambda\mu\tau}(\epsilon_{\rho\sigma\tau}\beta_{\rho\sigma\nu}^{\text{NM}} + \epsilon_{\rho\sigma\nu}\beta_{\rho\sigma\tau}^{\text{NM}}) + \frac{1}{6}\epsilon_{\lambda\nu\tau}(\epsilon_{\rho\sigma\tau}\beta_{\rho\sigma\mu}^{\text{NM}} + \epsilon_{\rho\sigma\mu}\beta_{\rho\sigma\tau}^{\text{NM}}), \quad (5)$$

$$\beta_{\lambda\mu\nu}^{(3)} = \beta_{\lambda\mu\nu}^{\text{NM}} - \beta_{\lambda\mu\nu}^{(1A)} - \beta_{\lambda\mu\nu}^{(1B)} - \beta_{\lambda\mu\nu}^{(2)}. \quad (6)$$

The tensors $\beta_{\lambda\mu\nu}^{(1A)}$ and $\beta_{\lambda\mu\nu}^{(1B)}$ have the transformation properties of polar vectors; $\beta_{\lambda\mu\nu}^{(2)}$ transforms as a symmetric traceless second-rank axial tensor and $\beta_{\lambda\mu\nu}^{(3)}$ as a fully index-symmetric and traceless third-rank polar tensor. The explicit result for the radiant intensity of hyper-Raman scattering from a circularly polarized beam is as follows

$$\begin{aligned} I = \frac{\mathcal{D}}{525} \{ & -42({}^c\mathbf{e} \cdot \bar{\mathbf{e}}')({}^c\bar{\mathbf{e}} \cdot \mathbf{e}')\beta_{\lambda\lambda\mu}^{(1A)}\beta_{\mu\nu\nu}^{(1B)} + 63({}^c\mathbf{e} \cdot \bar{\mathbf{e}}')({}^c\bar{\mathbf{e}} \cdot \mathbf{e}') \\ & \times \beta_{\lambda\lambda\mu}^{(1A)}\beta_{\nu\nu\mu}^{(1A)} + 7({}^c\mathbf{e} \cdot \bar{\mathbf{e}}')({}^c\bar{\mathbf{e}} \cdot \mathbf{e}')\beta_{\lambda\mu\mu}^{(1B)}\beta_{\lambda\nu\nu}^{(1B)} \\ & + 35[-({}^c\mathbf{e} \cdot \bar{\mathbf{e}}')({}^c\bar{\mathbf{e}} \cdot \mathbf{e}') - 2({}^c\mathbf{e} \cdot \mathbf{e}')({}^c\bar{\mathbf{e}} \cdot \bar{\mathbf{e}}') + 2]\beta_{\lambda\mu\nu}^{(2)}\beta_{\lambda\mu\nu}^{(2)} \\ & \left. + 5[-4({}^c\mathbf{e} \cdot \bar{\mathbf{e}}')({}^c\bar{\mathbf{e}} \cdot \mathbf{e}') + 10({}^c\mathbf{e} \cdot \mathbf{e}')({}^c\bar{\mathbf{e}} \cdot \bar{\mathbf{e}}') + 5]\beta_{\lambda\mu\nu}^{(3)}\beta_{\lambda\mu\nu}^{(3)} \right\} \quad (7) \end{aligned}$$

where \mathcal{D} is a scattering constant defined by

$$\mathcal{D} = \frac{2\pi}{c} \mathcal{N}_m k'^4 g^{(2)} \bar{I}_0^2 \quad (8)$$

and \mathcal{N}_m is the number of molecules with initial state $|m\rangle$ in the interaction volume at the focus of the laser. It is worth noting that the result (7) is expressed in terms of five independent molecular parameters, $\beta_{\lambda\lambda\mu}^{(1A)}\beta_{\mu\nu\nu}^{(1B)}$, $\beta_{\lambda\lambda\mu}^{(1A)}\beta_{\nu\nu\mu}^{(1A)}$, $\beta_{\lambda\mu\mu}^{(1B)}\beta_{\lambda\nu\nu}^{(1B)}$, $\beta_{\lambda\mu\nu}^{(2)}\beta_{\lambda\mu\nu}^{(2)}$ and $\beta_{\lambda\mu\nu}^{(3)}\beta_{\lambda\mu\nu}^{(3)}$. In [7] it was the evaluation of these five parameters by the performance of five separate polarization experiments which formed the basis for an analysis of the symmetry of hyper-Raman active vibrations.

Equation (7) can be evaluated for each of the various polarization components of the scattered light; the results may be expressed as $I({}^c\mathbf{e} \rightarrow {}^c\mathbf{e}')$, $I({}^c\mathbf{e} \rightarrow \parallel \mathbf{e}')$ and $I({}^c\mathbf{e} \rightarrow \perp \mathbf{e}')$, which for compactness we shall henceforth write as $I(c \rightarrow c)$, $I(c \rightarrow \parallel)$ and $I(c \rightarrow \perp)$ respectively. It may readily be shown that these results are expressible in terms of only three molecular parameters instead of the five in equation (7); these are $\beta_{\lambda\lambda\mu}^{(1C)}\beta_{\nu\nu\mu}^{(1C)}$, $\beta_{\lambda\mu\nu}^{(2)}\beta_{\lambda\mu\nu}^{(2)}$ and $\beta_{\lambda\mu\nu}^{(3)}\beta_{\lambda\mu\nu}^{(3)}$, where

$$\beta_{\lambda\mu\nu}^{(1C)} = 3\beta_{\lambda\mu\nu}^{(1A)} - \beta_{\nu\mu\lambda}^{(1B)} \quad (9)$$

defines a new third-rank tensor which again transforms as a polar vector. The intensity results are as follows

$$\begin{aligned} I(c \rightarrow c) = \frac{\mathcal{D}}{2100} \{ & 7(1 - \cos \theta)^2 \beta_{\lambda\lambda\mu}^{(1C)}\beta_{\nu\nu\mu}^{(1C)} + 35(5 + 3 \cos \theta)(1 - \cos \theta) \\ & \times \beta_{\lambda\mu\nu}^{(2)}\beta_{\lambda\mu\nu}^{(2)} + 10(13 + 14 \cos \theta + 3 \cos^2 \theta)\beta_{\lambda\mu\nu}^{(3)}\beta_{\lambda\mu\nu}^{(3)} \} \quad (10) \end{aligned}$$

$$I(c \rightarrow \parallel) = \frac{\mathcal{D}}{1050} \{7 \cos^2 \theta \beta_{\lambda\lambda\mu}^{(1C)} \beta_{\nu\nu\mu}^{(1C)} + 35(4 - 3 \cos^2 \theta) \beta_{\lambda\mu\nu}^{(2)} \beta_{\lambda\mu\nu}^{(2)} + 10(5 + 3 \cos^2 \theta) \beta_{\lambda\mu\nu}^{(3)} \beta_{\lambda\mu\nu}^{(3)}\} \quad (11)$$

$$I(c \rightarrow \perp) = \frac{\mathcal{D}}{1050} \{7 \beta_{\lambda\lambda\mu}^{(1C)} \beta_{\nu\nu\mu}^{(1C)} + 35 \beta_{\lambda\mu\nu}^{(2)} \beta_{\lambda\mu\nu}^{(2)} + 80 \beta_{\lambda\mu\nu}^{(3)} \beta_{\lambda\mu\nu}^{(3)}\}. \quad (12)$$

In applying equations (10) to (12) we may apply the rule that, for a given hyper-Raman vibrational transition, each tensor $\beta_{\lambda\mu\nu}^{(1C)}$, $\beta_{\lambda\mu\nu}^{(2)}$ and $\beta_{\lambda\mu\nu}^{(3)}$ can only have non-zero elements if its representation under the symmetry operation of the molecular point group spans the irreducible representation of the molecular vibration. We thus find that hyper-Raman active vibrations fall into one of six distinct symmetry classes, according to which of the tensor components are non-zero. These six classes have been discussed in detail in [7] and in table 1 the classification is shown for the common molecular point groups.

Thus, for example, the a''_1 methylene twisting mode of cyclopropane is assigned to class *E* and is associated with a transition tensor which has weight-2 contributions alone, whereas the e'' methylene rocking mode is assigned to class *B* and is associated with finite contributions from both weights 2 and 3. As will be seen below, these properties are reflected in the results of polarization ratio measurements.

3. POLARIZATION RATIOS

In general, it is more convenient to measure intensity ratios than absolute intensities and for this purpose we introduce the parameters p_{\parallel} and p_{\perp} which are defined as follows

$$p_{\parallel} = \frac{I(c \rightarrow \parallel)}{I(c \rightarrow c)}, \quad (13)$$

$$p_{\perp} = \frac{I(c \rightarrow \perp)}{I(c \rightarrow c)}. \quad (14)$$

Both ratios specify the extent of ellipticity in the hyper-Raman scattered light and it is readily shown that they satisfy the relation

$$0 \leq (p_{\parallel} + p_{\perp})^{-1} \leq 1. \quad (15)$$

Here, $(p_{\parallel} + p_{\perp})^{-1}$ represents the fraction of the scattering which has circular polarization of the same helicity as the incident light: thus the lower limit $(p_{\parallel} + p_{\perp})^{-1} = 0$ corresponds to complete reversal of circular polarization whilst the upper limit $(p_{\parallel} + p_{\perp})^{-1} = 1$ corresponds to complete retention of circular polarization. The case of $(p_{\parallel} + p_{\perp})^{-1} = 0.5$ represents hyper-Raman scattering of light with plane polarization.

From equations (10) to (12) it is evident that both p_{\parallel} and p_{\perp} are dependent on the scattering angle. Nonetheless, these equations are not linearly independent for the usual scattering geometries where $\vartheta = 0^\circ$, 90° or 180° . For this reason, complete information about the various irreducible tensors involved in any particular hyper-Raman transition cannot be obtained in any of these experimental configurations. For any other value of ϑ , measurement of p_{\parallel} and p_{\perp} together provide an unambiguous method for determination of the symmetry class to which each transition belongs.

Table 1. Classification of hyper-Raman active vibrations for the common molecular point groups.

Class	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>	<i>F</i>
Weights	1, 2, 3	2, 3	1, 3	3	2	1
Non-axial groups						
C_1	<i>a</i>	—	—	—	—	—
C_i	a_u	—	—	—	—	—
C_s	a', a''	—	—	—	—	—
Axial groups						
C_2	a, b	—	—	—	—	—
C_3	a, e	—	—	—	—	—
C_4	a, e	<i>b</i>	—	—	—	—
C_5	a, e_1	e_2	—	—	—	—
C_6	a, e_1	e_2	—	<i>b</i>	—	—
S_4	b, e	<i>a</i>	—	—	—	—
S_6	a_u, e_u	—	—	—	—	—
S_8	b, e_1	e_2	—	e_3	—	—
C_{2h}	a_u, b_u	—	—	—	—	—
C_{3h}	a'', e'	e''	—	a'	—	—
C_{4h}	a_u, e_u	b_u	—	—	—	—
C_{5h}	a', e'_1	e''_2	—	e'_2	—	—
C_{6h}	a_u, e_{1u}	e_{2u}	—	b_u	—	—
C_{2v}	a_1, b_1, b_2	a_2	—	—	—	—
C_{3v}	<i>e</i>	a_2	a_1	—	—	—
C_{4v}	<i>e</i>	b_1, b_2	a_1	—	a_2	—
C_{5v}	e_1	e_2	a_1	—	a_2	—
C_{6v}	e_1	e_2	a_1	b_1, b_2	a_2	—
Dihedral groups						
D_2	b_1, b_2, b_3	<i>a</i>	—	—	—	—
D_3	<i>e</i>	a_1	a_2	—	—	—
D_4	<i>e</i>	b_1, b_2	a_2	—	a_1	—
D_5	e_1	e_2	a_2	—	a_1	—
D_6	e_1	e_2	a_2	b_1, b_2	a_1	—
D_{2h}	b_{1u}, b_{2u}, b_{3u}	a_u	—	—	—	—
D_{3h}	e'	e''	a''_2	a'_1, a'_2	a''_1	—
D_{4h}	e_u	b_{1u}, b_{2u}	a_{2u}	—	a_{1u}	—
D_{5h}	e'_1	e''_2	a''_2	e'_2	a''_1	—
D_{6h}	e_{1u}	e_{2u}	a_{2u}	b_{1u}, b_{2u}	a_{1u}	—
D_{2d}	<i>e</i>	a_1, a_2	b_2	—	b_1	—
D_{3d}	e_u	a_{1u}	a_{2u}	—	—	—
D_{4d}	e_1	e_2	b_2	e_3	b_1	—
D_{5d}	e_{1u}	e_{2u}	a_{2u}	—	a_{1u}	—
D_{6d}	e_1	e_4	b_2	e_3	b_1	—
Linear groups						
$C_{\infty v}$	Π	Σ^+	Δ	Φ	Σ^-	—
$D_{\infty h}$	Π_u	Σ_u^+	Δ_u	Φ_u	Σ_u^-	—
Cubic groups						
T	<i>t</i>	—	—	<i>a</i>	<i>e</i>	—
T_h	t_u	—	—	a_u	e_u	—
T_d	—	t_1	t_2	a_1	<i>e</i>	—
O	—	t_2	t_1	a_2	<i>e</i>	—
O_h	—	t_{2u}	t_{1u}	a_{2u}	e_u	—
Icosahedral groups						
I	—	—	—	t_2, g	<i>h</i>	t_1
I_h	—	—	—	t_{2u}, g_u	h_u	t_{1u}

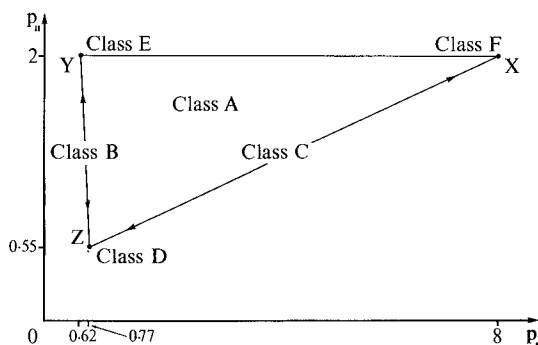


Figure 2. Symmetry assignment of a hyper-Raman active vibration using a convergence angle of 60° .

The simplest approach is to make use of a graphical method, which for convenience we shall illustrate for $\vartheta = 60^\circ$. Figure 2 shows the results of plotting p_{\parallel} against p_{\perp} and in this case the point $(p_{\perp}, p_{\parallel})$ has to lie within the confines of the triangle XYZ having vertices $(8, 2)$, $(0.62, 2)$ and $(0.77, 0.55)$. The interpretation is now as follows.

- (a) If $(p_{\perp}, p_{\parallel})$ lies at vertex X , Y or Z , then $\beta_{\lambda\mu\nu}^{NM}$ only contains contributions of weight 1, 2 or 3 respectively and hence the active vibration belongs to class F , E or D respectively:
- (b) If $(p_{\perp}, p_{\parallel})$ lies on the line XZ , then $\beta_{\lambda\mu\nu}^{NM}$ contains contributions of weights 1 and 3 and the vibration belongs to class C ; if $(p_{\perp}, p_{\parallel})$ lies on YZ then the tensor has contributions of weights 2 and 3 and the vibration belongs to class B :
- (c) Finally, if $(p_{\perp}, p_{\parallel})$ lies anywhere else within XYZ , then $\beta_{\lambda\mu\nu}^{NM}$ contains all three weights and the vibration may be assigned to class A .

The same principles (a), (b) and (c) can be applied if a different scattering angle is used for the experiment, but the positions of X , Y and Z must then be redefined; table 2 provides the coordinates for these vertices in various cases.

Table 2. Coordinates of triangle XYZ for various angles.

ϑ	X	Y	Z
0°	(∞, ∞)	(∞, ∞)	$(0.53, 0.53)$
30°	$(111, 84)$	$(1.96, 3.44)$	$(0.58, 0.53)$
45°	$(23.3, 11.7)$	$(0.96, 2.61)$	$(0.65, 0.53)$
60°	$(8, 2)$	$(0.62, 2)$	$(0.77, 0.55)$
90°	$(2, 0)$	$(0.40, 1.60)$	$(1.23, 0.77)$
120°	$(0.89, 0.22)$	$(0.38, 1.24)$	$(2.37, 1.70)$
135°	$(0.69, 0.34)$	$(0.41, 1.02)$	$(3.48, 2.83)$
150°	$(0.57, 0.43)$	$(0.45, 0.78)$	$(5.12, 4.64)$
180°	$(0.5, 0.5)$	$(0.5, 0.5)$	$(8, 8)$

4. DISCUSSION

Following the work of Bersohn *et al.* [21], and later Christie and Lockwood [22], it has been fully established that the hyper-Raman scattering tensor $\beta_{\lambda\mu\nu}^{\text{NM}}$ does not generally possess full (λ, μ, ν) index symmetry, but only symmetry in its last two indices (μ, ν) . Despite the fact that the tensor can very usefully be treated in terms of a simple extension of the Placzek polarizability theory, as demonstrated by Long and Stanton [23], this treatment does not in itself impose the condition of complete index symmetry. The assumption of full index symmetry was nevertheless an important feature in early work on the theory of hyper-Raman scattering [1] and is still widely adopted in experimental studies. We therefore wish to point out several features which clearly differentiate the results expected on the basis of complete (λ, μ, ν) or partial (μ, ν) index symmetry.

The principle effect of imposing (λ, μ, ν) symmetry on the scattering tensor is to rule out the possibility of any weight-2 contributions to the hyper-Raman transition, since the right hand side of equation (5) then vanishes. In this case the distinction between vibrations belonging to classes *A* and *C* disappears, as does the distinction between classes *B* and *D*. More important still is the fact that this assumption incorrectly leads to the conclusion that class *E* vibrations are hyper-Raman forbidden.

If we consider these implications in terms of figure 2, the result would be that the point $(p_{\perp}, p_{\parallel})$ would necessarily lie on the line *XZ*. It is therefore clear that any polarization measurements which correspond to points $(p_{\perp}, p_{\parallel})$ off this line, but within the triangle *XYZ*, demonstrate unequivocally that the scattering tensor does not possess full index symmetry.

We can illustrate these points by considering the hyper-Raman activity of vibrations in a few simple molecules. Consider first the case of benzene. The a_{2u} and the three e_{1u} vibrations are all infrared and hyper-Raman allowed, but whereas the a_{2u} vibration belongs to class *C*, the e_{1u} vibrations belong to class *A*. Thus whereas the point representing the polarization measurement $(p_{\perp}, p_{\parallel})$ should lie on the line *XZ* in the former case, it should lie away from this line in the latter case. Similarly the infrared forbidden b_{1u} , b_{2u} and e_{2u} vibrations may be distinguished by the fact that for all the b_u vibrations $(p_{\perp}, p_{\parallel})$ will lie at vertex *Z* (that is $p_{\perp} = 0.77$ and $p_{\parallel} = 0.55$ for $\vartheta = 60^\circ$) whereas for the e_{2u} vibrations the result will lie elsewhere along *YZ*. In each case the discrimination would not be possible on the basis of a theory involving a fully index-symmetric tensor.

The *e* mode of methane provides an example of a vibration which belongs to class *E*; far from being inactive, we can predict that this vibration should give a line in the hyper-Raman spectrum and that measurement of its polarization ratios at $\vartheta = 60^\circ$ should result in the values $p_{\perp} = 0.62$ and $p_{\parallel} = 2.00$. The infrared and Raman-forbidden a''_1 mode of cyclopropane provides a further example of this class which should exhibit the same polarization behaviour.

In conclusion, we have demonstrated that the index symmetry properties associated with hyper-Raman scattering are experimentally testable and have important physical consequences. We have also shown how, by using circularly polarized light, the measurement of just two polarization ratios at any convenient scattering angle provides all the information required for a complete symmetry analysis of each band in a vibrational hyper-Raman spectrum.

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