The hyper-Raman effect: A new approach to vibrational mode classification and assignment of spectral lines

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The theory of vibrational hyper-Raman scattering (inelastic second harmonic light scattering) is developed within the framework of quantum electrodynamics. The dynamical system comprises the molecule and the radiation field, coupled by multipolar interactions. In the present work, the electric dipole approximation is employed and the results involve the hyperpolarizability tensor. In contrast to previous work, full index symmetry of this tensor is not assumed. The tensor is decomposed into irreducible weights forming the basis for a new vibrational mode classification scheme. A set of five experiments is specified which allows unambiguous assignment of an active mode to one of six classes. The scheme has been applied to several molecules and compared with some experimental results. Explicit expressions for scattering intensities for a wide variety of experimental configurations are given; results for depolarization ratios are also presented.

I. INTRODUCTION

With recent advances in laser technology a wide variety of new spectroscopic techniques involving the nonlinear interaction of radiation with matter has been developed. The new techniques provide information about atomic and molecular systems not normally available from conventional types of spectroscopy. For example, because of different selection rules, two-photon spectroscopy makes it possible to study transitions which are not one-photon allowed. An example involving nonlinear scattering is the hyper-Raman effect. It is a three-photon process involving the absorption of two photons from the incident laser light and the emission of one photon of frequency ω', approximately twice the incident frequency ω. The mismatch $(2\omega - \omega')$ corresponds to a vibrational or a rotational transition frequency of the molecule or a lattice vibrational frequency in the case of a crystal. The possibility of this type of nonlinear scattering was first considered by Decius and Rauch[1] in 1959, and the first experimental observations were made by Terhune, Maker, and Savage[2] in 1965. The intensity of scattered light depends quadratically upon the incident intensity, and with the rapid development of powerful lasers there has been an increasing interest in the study of hyper-Raman scattering.[3-6] Although hyper-Raman spectra have as yet only been recorded with pulsed lasers, the development of laser pulsing techniques and multichannel spectrometers has substantially reduced the time required to obtain a hyper-Raman spectrum, thus increasing the scope for experimental studies.

Theoretical studies of hyper-Raman scattering have been based mainly on the extension of Placzek's polarizability theory of the Raman effect where the electromagnetic field is treated classically.[7] This approach is based on the fact that when a molecule is subjected to the influence of an external field $\mathbf{E}$ the induced polarization can be expressed as

$$P_i = \alpha_{ij}E_j + \tfrac{1}{2}\beta_{ijk}E_jE_k + \cdots , \qquad (1.1)$$

where α_{ij} and β_{ijk} are the polarizability and hyperpolarizability tensors, respectively. The theory of the Raman effect is based on the linear response of the molecule to the external field as represented by the first term of Eq. (1.1). For strong fields the nonlinear terms can be important.[8] For example, theories of hyper-Rayleigh and hyper-Raman scattering involve the second term of Eq. (1.1) which is quadratic in the applied field E. The scattered intensities depend on the square of the induced polarization and hence on the square of the intensity of the incident light. For a beam of intensity 10^{15} W m^{-2} the ratio of the hyper-Raman to Raman scattered radiation is only of the order of 10^{-6}. Clearly, only the high intensities now available from pulsed lasers can render the observations of hyper-Raman scattering feasible. For example, typically 10^4 laser shots from a ruby laser of 2 MW power and 10^{-7} s duration have been required to record the hyper-Raman spectra of hydrocarbons.[3]

Hyper-Raman spectroscopy is a potential source of information about molecules not normally available from infrared (ir) or Raman studies. For example, vibrational modes which are ir- and Raman-inactive can frequently be hyper-Raman active. In their original derivation of selection rules and depolarization ratios for hyper-Raman scattering Cyvin, Rauch, and Decius[9] had assumed full index symmetry of the hyper-polarizability tensor β_{ijk} in Eq. (1.1) (see also Ref. 10). It was pointed out later by Christie and Lockwood[11] that β_{ijk} in general has only j, k symmetry, and they gave the appropriate selection rules.

In the present work the theory of hyper-Raman scattering is developed using quantum electrodynamics. In contrast to the semiclassical approach the molecules and the radiation field together constitute the dynamical system and the latter is conveniently described with second-quantized formalism. This method takes proper account of the changes in the field during the scattering process. In contrast to previous treatments we decompose the hyperpolarizability tensor into irreducible components in order to obtain a systematic classification of the hyper-Raman-active vibrational modes. This enables us to make some predictions concerning various polarization ratios. We present for the first time explicit expressions for scattering intensities for a wide variety of experimental configurations. Also, we show

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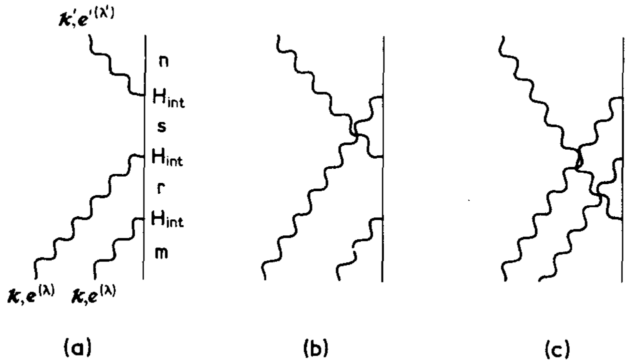

FIG. 1. Time-ordered diagrams for hyper-Raman scattering.

that by collecting the hyper-Raman spectra for five specified configurations it is possible to assign each active mode to one of six classes. Finally, the hyper-Raman selection rules are applied to a number of molecules.

II. THEORY

In the quantum electrodynamical approach the molecules and the radiation field together constitute the dynamical system. The Hamiltonian for the system is

$$H = H_{\mathrm{rad}} + \sum_{\xi} H_{\mathrm{mol}}(\xi) + \sum_{\xi} H_{\mathrm{int}}(\xi)\,, \tag{2.1}$$

where H_{rad} is the Hamiltonian for the radiation field, and $H_{\mathrm{mol}}(\xi)$ is the Hamiltonian for molecule ξ. In the electric dipole approximation the interaction Hamiltonian is given by

$$H_{\mathrm{int}}(\xi) = -\boldsymbol{\mu}(\xi)\cdot \mathbf{e}^{\perp}(\mathbf{R}_{\xi})\,, \tag{2.2}$$

where μ and $\mathbf{e}^{\perp}$ are the electric dipole moment and the transverse electric field operators, respectively. The transition rate Γ_{fi} for the process $|f\rangle \leftarrow |i\rangle$ is given by the Fermi rule

$$\Gamma_{fi} = \frac{2\pi}{\hbar}\,|\mathcal{M}_{fi}|^2 \rho_f\,, \tag{2.3}$$

where ρ_f is the density of final states and $\mathcal{M}_{fi}$ is the matrix element connecting the initial and final states, expressible as a perturbation series

$$\mathcal{M}_{fi} = \langle f|H_{\mathrm{int}}|i\rangle + \sum_{\mathrm{I}}{}' \frac{\langle f|H_{\mathrm{int}}|\mathrm{I}\rangle\langle \mathrm{I}|H_{\mathrm{int}}|i\rangle}{(E_i - E_{\mathrm{I}})} + \sum_{\mathrm{I},\mathrm{II}}{}' \frac{\langle f|H_{\mathrm{int}}|\mathrm{II}\rangle\langle \mathrm{II}|H_{\mathrm{int}}|\mathrm{I}\rangle\langle \mathrm{I}|H_{\mathrm{int}}|i\rangle}{(E_i - E_{\mathrm{I}})(E_i - E_{\mathrm{II}})}\,. \tag{2.4}$$

In Eq. (2.4) the primes imply that the initial and final states are excluded from the summation. For hyper-Raman scattering the leading term of Eq. (2.4) is of third order. Before writing down the explicit expression for this term we explain our notation. The state of molecule ξ with energy E_r is denoted by $|r^{\xi}\rangle$. The state of the radiation field with occupation number p for the incident mode of wave vector $\mathbf{k}$ and polarization λ (frequency $\omega = c|\mathbf{k}|$) and p' for the scattered photon mode of wave vector $\mathbf{k}'$ and polarization λ' (frequency $\omega' = c|\mathbf{k}'|$) is denoted by $|p,p'\rangle$. The product state is written as $|r^{\xi};p,p'\rangle$ with its bra vector $\langle p',p;r^{\xi}|$. Let us consider one particular molecule ξ which undergoes the transition $|n^{\xi}\rangle \leftarrow |m^{\xi}\rangle$ due to hyper-Raman scattering. The initial and final states of the system—molecules plus the radiation field—are $|m^{\xi};n,0\rangle$ and $|n^{\xi};(n-2),1\rangle$. The states of the other molecules and radiation modes remain unchanged and need not be shown explicitly. The corresponding matrix element $\tilde{M}^{\xi}_{fi}$ is easily obtained from the time-ordered diagrams shown in Fig. 1. The graphs represent the three topologically different time sequences of absorption and emission. In each case r and s denote the virtual states through which the molecule passes during the scattering process. The matrix element $\tilde{M}^{\xi}_{fi}$ is

$$\begin{aligned}\tilde{M}^{\xi}_{fi} = \sum_{r,s}\Bigg[&\frac{\langle 1,(n-2);n^{\xi}|H_{\mathrm{int}}(\xi)|s^{\xi};(n-2),0\rangle\langle 0,(n-2);s^{\xi}|H_{\mathrm{int}}(\xi)|r^{\xi};(n-1),0\rangle\langle 0,(n-1);r^{\xi}|H_{\mathrm{int}}(\xi)|m^{\xi};n,0\rangle}{(E_{ms}+2\hbar\omega)(E_{mr}+\hbar\omega)}\\ &+\frac{\langle 1,(n-2);n^{\xi}|H_{\mathrm{int}}(\xi)|s^{\xi};(n-1),1\rangle\langle 1,(n-1);s^{\xi}|H_{\mathrm{int}}(\xi)|r^{\xi};(n-1),0\rangle\langle 0,(n-1);r^{\xi}|H_{\mathrm{int}}(\xi)|m^{\xi};n,0\rangle}{(E_{ns}-\hbar\omega)(E_{mr}+\hbar\omega)}\\ &+\frac{\langle 1,(n-2);n^{\xi}|H_{\mathrm{int}}(\xi)|s^{\xi};(n-1),1\rangle\langle 1,(n-1);s^{\xi}|H_{\mathrm{int}}(\xi)|r^{\xi};n,1\rangle\langle 1,n;r^{\xi}|H_{\mathrm{int}}(\xi)|m^{\xi};n,0\rangle}{(E_{ns}-\hbar\omega)(E_{nr}-2\hbar\omega)}\Bigg]\,.\end{aligned} \tag{2.5}$$

In Eq. (2.5) we have used the energy conservation condition

$$E_n - E_m \equiv E_{nm} = \hbar(2\omega - \omega') \tag{2.6}$$

to express the energy denominators in terms of the incident frequency ω. The use of a mode expansion for the electric field operator allows one to write the matrix element $\tilde{M}^{\xi}_{fi}$ as a product of a position-independent term M^{ξ}_{fi} and a position-dependent phase factor

$$\tilde{M}^{\xi}_{fi} = M^{\xi}_{fi}\, e^{i(2\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_{\xi}}\,. \tag{2.7}$$

The phase factor arises from the exponentials of the field operators corresponding to the annihilation of two photons of wave vector $\mathbf{k}$ and the creation of one photon of wave vector $\mathbf{k}'$. Though M^{ξ}_{fi} is independent of $\mathbf{R}_{\xi}$, it is still ξ dependent in the sense that it is a function of the molecular orientation with respect to the incident beam.

The total matrix element $\mathcal{M}_{fi}$ is simply a sum of the $\tilde{M}^{\xi}_{fi}$ over the $\mathcal{N}_m$ molecules with initial states of energy E_m. The scattered radiant intensity $I(\mathbf{k}')$, power per unit solid angle around $\hat{\mathbf{k}}'$ follows from the Fermi rule

$$I(\mathbf{k}') = \frac{Vk'^3}{4\pi^2\hbar}\left|\sum_{\xi} M^{\xi}_{fi}\, e^{i(2\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_{\xi}}\right|^2\,. \tag{2.8}$$

In the dilute gas approximation the molecules of the system are randomly positioned and oriented. Equation (2.8) then becomes

$$I(\mathbf{k}') = \frac{Vk'^3}{4\pi^2\hbar}\sum_{\xi}\langle |M^{\xi}_{fi}|^2\rangle \ . \tag{2.9}$$

The rotationally averaged factor $\langle\ \rangle$ on the right hand side of Eq. (2.9) is clearly ξ independent and we have

$$I(\mathbf{k}') = \frac{Vk'^3\mathfrak{N}}{4\pi^2\hbar}\langle |M_{fi}|^2\rangle \ , \tag{2.10}$$

where the superscript ξ in the matrix element has been deleted. The above result is valid provided $2\mathbf{k} \neq \mathbf{k}'$, which is true for hyper-Raman and incoherent hyper-Rayleigh scattering. It does not hold for second-harmonic generation where $2\mathbf{k} = \mathbf{k}'$.

To proceed further we employ the Born–Oppenheimer approximation to describe the molecular states; a state with electronic label n and vibrational label V is written as a product of electronic and vibrational wavefunctions $|\varphi_n\rangle|\chi_{nV}\rangle$; its energy is expressed as the sum of electronic and vibrational energies $E_n + \epsilon_{nV}$. In the hyper-Raman process the molecule remains in the electronic ground state in the initial and final states, but changes its vibrational state. Thus, the initial and final molecular states may be denoted by $|\varphi_0\rangle|\chi_{0M}\rangle$ and $|\varphi_0\rangle|\chi_{0N}\rangle$, respectively. From Eq. (2.5) we have

$$M_{fi} = -i\left[\frac{8\pi^3\hbar^3\omega^2\omega' n(n-1)}{V^3}\right]^{1/2}\bar{e}'_i e_j e_k \sum_{\substack{r,R\\ s,S}}\left[\frac{\langle\chi_{0N}|\mu_i^{0s}|\chi_{sS}\rangle\langle\chi_{sS}|\mu_j^{sr}|\chi_{rR}\rangle\langle\chi_{rR}|\mu_k^{r0}|\chi_{0M}\rangle}{(E_{0s}+\epsilon_{0M,sS}+2\hbar\omega)(E_{0r}+\epsilon_{0M,rR}+\hbar\omega)}\right.$$
$$\left.+\frac{\langle\chi_{0N}|\mu_j^{0s}|\chi_{sS}\rangle\langle\chi_{sS}|\mu_i^{sr}|\chi_{rR}\rangle\langle\chi_{rR}|\mu_k^{r0}|\chi_{0M}\rangle}{(E_{0s}+\epsilon_{0N,sS}-\hbar\omega)(E_{0r}+\epsilon_{0M,rR}+\hbar\omega)}+\frac{\langle\chi_{0N}|\mu_j^{0s}|\chi_{sS}\rangle\langle\chi_{sS}|\mu_k^{sr}|\chi_{rR}\rangle\langle\chi_{rR}|\mu_i^{r0}|\chi_{0M}\rangle}{(E_{0s}+\epsilon_{0N,sS}-\hbar\omega)(E_{0r}+\epsilon_{0N,rR}-2\hbar\omega)}\right] , \tag{2.11}$$

where $\mathbf{e}$ and $\mathbf{e}'$ are the polarization vectors of the incident and scattered photons; E_{rs} and $\epsilon_{rR,sS}$ stand for the electronic and vibrational energy differences

$$E_{rs} = E_r - E_s , \tag{2.12}$$

$$\epsilon_{rR,sS} = \epsilon_{rR} - \epsilon_{sS} \ . \tag{2.13}$$

In Eq. (2.11) and in the rest of this paper the repeated index summation convention is used. As in the theory of the Raman effect[12] we neglect the vibrational energy differences in the energy denominators (assuming that there are no near resonances), and effect closure over the intermediate vibrational levels to obtain

$$M_{fi} = -i[8\pi^3\hbar^3\omega^2\omega' n(n-1)/V^3]^{1/2}\,\bar{e}'_i e_j e_k \langle\chi_{0N}|\beta_{ijk}|\chi_{0M}\rangle , \tag{2.14}$$

where

$$\beta_{ijk} = \frac{1}{2}\sum_{r,s}\left[\frac{\mu_i^{0s}\mu_j^{sr}\mu_k^{r0}}{(E_{0s}+2\hbar\omega)(E_{0r}+\hbar\omega)}+\frac{\mu_j^{0s}\mu_i^{sr}\mu_k^{r0}}{(E_{0s}-\hbar\omega)(E_{0r}+\hbar\omega)}\right.$$
$$\left.+\frac{\mu_j^{0s}\mu_k^{sr}\mu_i^{r0}}{(E_{0s}-\hbar\omega)(E_{0r}-2\hbar\omega)}+\frac{\mu_i^{0s}\mu_k^{sr}\mu_j^{r0}}{(E_{0s}+2\hbar\omega)(E_{0r}+\hbar\omega)}+\frac{\mu_k^{0s}\mu_i^{sr}\mu_j^{r0}}{(E_{0s}-\hbar\omega)(E_{0r}+\hbar\omega)}+\frac{\mu_k^{0s}\mu_j^{sr}\mu_i^{r0}}{(E_{0s}-\hbar\omega)(E_{0r}-2\hbar\omega)}\right] . \tag{2.15}$$

The j, k symmetric form of β_{ijk} is adopted because the "polarization tensor" $\bar{e}'_i e_j e_k$ is itself j, k symmetric.

To calculate scattering intensities for a randomly oriented molecular system we need to perform a rotational average of $|M_{fi}|^2$. Using Latin indices for components with respect to a laboratory-fixed frame and Greek indices for the molecule-fixed frame we have

$$\beta_{ijk} = l_{i\lambda}l_{j\mu}l_{k\nu}\beta_{\lambda\mu\nu} , \tag{2.16}$$

where the l's are direction cosines connecting the two frames; $l_{i\lambda}$ is given by the (i,λ) element of the 3×3 Euler angle matrix. Assuming real wavefunctions we have

$$\langle|M_{fi}|^2\rangle = [8\pi^3\hbar^3\omega^2\omega' n(n-1)/V^3]\bar{e}'_i e_j e_k e'_l \bar{e}_m \bar{e}_n \langle\chi_{0N}|\beta_{\lambda\mu\nu}|\chi_{0M}\rangle\langle\chi_{0N}|\beta_{o\pi\rho}|\chi_{0M}\rangle I^{(6)}_{ijklmn;\lambda\mu\nu o\pi\rho} . \tag{2.17}$$

Here, $I^{(6)}$ refers to the isotropic tensor[13,14] resulting from the rotational average of the direction cosine product

$$I^{(6)}_{ijklmn;\lambda\mu\nu o\pi\rho} = \langle l_{i\lambda}l_{j\mu}l_{k\nu}l_{lo}l_{m\pi}l_{n\rho}\rangle . \tag{2.18}$$

Thus, we have for the scattered radiant intensity

$$I(\mathbf{k}') = \frac{\mathfrak{D}}{105}\{[30(\bar{\mathbf{e}}'\cdot\mathbf{e})(\mathbf{e}\cdot\mathbf{e}')(\bar{\mathbf{e}}\cdot\bar{\mathbf{e}}) - 12(\bar{\mathbf{e}}'\cdot\mathbf{e})(\mathbf{e}'\cdot\bar{\mathbf{e}}) - 12(\mathbf{e}\cdot\mathbf{e}')(\bar{\mathbf{e}}'\cdot\bar{\mathbf{e}}) - 10(\mathbf{e}\cdot\mathbf{e})(\bar{\mathbf{e}}\cdot\bar{\mathbf{e}}) + 8]\beta^{NM}_{\lambda\lambda\mu}\beta^{NM}_{\mu\nu\nu}$$
$$+[-12(\bar{\mathbf{e}}'\cdot\mathbf{e})(\mathbf{e}\cdot\mathbf{e}')(\bar{\mathbf{e}}\cdot\bar{\mathbf{e}}) + 16(\bar{\mathbf{e}}'\cdot\mathbf{e})(\mathbf{e}'\cdot\bar{\mathbf{e}}) + 2(\mathbf{e}\cdot\mathbf{e}')(\bar{\mathbf{e}}'\cdot\bar{\mathbf{e}}) + 4(\mathbf{e}\cdot\mathbf{e})(\bar{\mathbf{e}}\cdot\bar{\mathbf{e}}) - 6]\beta^{NM}_{\lambda\lambda\mu}\beta^{NM}_{\nu\nu\mu}$$
$$+[-10(\bar{\mathbf{e}}'\cdot\mathbf{e})(\mathbf{e}\cdot\mathbf{e}')(\bar{\mathbf{e}}\cdot\bar{\mathbf{e}}) + 4(\bar{\mathbf{e}}'\cdot\mathbf{e})(\mathbf{e}'\cdot\bar{\mathbf{e}}) + 4(\mathbf{e}\cdot\mathbf{e}')(\bar{\mathbf{e}}'\cdot\bar{\mathbf{e}}) + 8(\mathbf{e}\cdot\mathbf{e})(\bar{\mathbf{e}}\cdot\bar{\mathbf{e}}) - 5]\beta^{NM}_{\lambda\mu\mu}\beta^{NM}_{\lambda\nu\nu}$$
$$+[8(\bar{\mathbf{e}}'\cdot\mathbf{e})(\mathbf{e}\cdot\mathbf{e}')(\bar{\mathbf{e}}\cdot\bar{\mathbf{e}}) - 6(\bar{\mathbf{e}}'\cdot\mathbf{e})(\mathbf{e}'\cdot\bar{\mathbf{e}}) - 6(\mathbf{e}\cdot\mathbf{e}')(\bar{\mathbf{e}}'\cdot\bar{\mathbf{e}}) - 5(\mathbf{e}\cdot\mathbf{e})(\bar{\mathbf{e}}\cdot\bar{\mathbf{e}}) + 11]\beta^{NM}_{\lambda\mu\nu}\beta^{NM}_{\lambda\mu\nu}$$
$$+[-12(\bar{\mathbf{e}}'\cdot\mathbf{e})(\mathbf{e}\cdot\mathbf{e}')(\bar{\mathbf{e}}\cdot\bar{\mathbf{e}}) + 2(\bar{\mathbf{e}}'\cdot\mathbf{e})(\mathbf{e}'\cdot\bar{\mathbf{e}}) + 16(\mathbf{e}\cdot\mathbf{e}')(\bar{\mathbf{e}}'\cdot\bar{\mathbf{e}}) + 4(\mathbf{e}\cdot\mathbf{e})(\bar{\mathbf{e}}\cdot\bar{\mathbf{e}}) - 6]\beta^{NM}_{\lambda\mu\nu}\beta^{NM}_{\mu\lambda\nu}\} , \tag{2.19}$$

where

$$\beta^{NM}_{\lambda\mu\nu} = \langle \chi_{0N} | \beta_{\lambda\mu\nu} | \chi_{0M} \rangle \tag{2.20}$$

and

$$\mathfrak{D} = \frac{2\pi}{c} \mathfrak{N}_m k'^4 g^{(2)} \bar{I}_0^2 \; ; \tag{2.21}$$

$g^{(2)}$ and $\bar{I}_0$ are the degree of second order coherence and the mean irradiance of the incident beam, respectively. The five β products appearing in Eq. (2.19) are the same as those previously used by other workers[15,16]; under the assumption of a full index symmetry in $\beta^{NM}_{\lambda\mu\nu}$ the first three β products of Eq. (2.19) become equal, as do the last two.

III. REDUCTION OF THE SCATTERING TENSOR INTO IRREDUCIBLE PARTS

Previous studies of selection rules for hyper-Raman scattering have been mainly based on the assumption of a full index symmetry of the tensor $\beta_{\lambda\mu\nu}$.[9,10] This assumption is valid only in the physically unrealistic limit when the incident frequencies are much smaller than electronic transition frequencies. In general, the β tensor is only symmetric in its last two indices, as is evident from Eq. (2.15), and this leads to a different set of selection rules. In particular, a number of modes which would appear to be inactive if full index symmetry were assumed can in fact be active in hyper-Raman scattering. This point has already been noted by Christie and Lockwood,[11] who have given a supplementary set of selection rules for such modes. In their analysis, however, they use an overcomplete set of β-tensor component combinations which are not well suited for intensity and polarization ratio calculations. A better starting point for such calculations and vibrational mode classification is the set of irreducible components of $\beta_{\lambda\mu\nu}$ discussed below.

In general, a third rank tensor has 27 independent components and can be decomposed into one term of weight 0, three of weight 1, two of weight 2, and one of weight 3. However, as $\beta_{\lambda\mu\nu}$ is μ, ν symmetric, it has only 18 independent components, and the reduction gives two terms of weight 1, one of weight 2, and one of weight 3. We note in passing that $\beta_{\lambda\mu\nu}$ with full index symmetry has ten independent components giving one term of weight 1 and one of weight 3. The full implications of this result are dealt with later. Using the results given in the Appendix the expressions for weights 1, 2, and 3 of $\beta_{\lambda\mu\nu}$ with μ, ν symmetry are

$$\begin{aligned}\sum_{n=A,B} {}^{1n}\beta_{\lambda\mu\nu} = \tfrac{1}{10}[\delta_{\lambda\mu}(3\beta_{\rho\rho\nu} - \beta_{\nu\rho\rho}) \\ + \delta_{\lambda\nu}(3\beta_{\rho\rho\mu} - \beta_{\mu\rho\rho}) - 2\delta_{\mu\nu}(\beta_{\rho\rho\lambda} - 2\beta_{\lambda\rho\rho})],\end{aligned} \tag{3.1}$$

$$\begin{aligned}{}^{2}\beta_{\lambda\mu\nu} = \tfrac{1}{6}\epsilon_{\lambda\mu\tau}(\epsilon_{\rho\sigma\tau}\beta_{\rho\sigma\nu} + \epsilon_{\rho\sigma\nu}\beta_{\rho\sigma\tau}) \\ + \tfrac{1}{6}\epsilon_{\lambda\nu\tau}(\epsilon_{\rho\sigma\tau}\beta_{\rho\sigma\mu} + \epsilon_{\rho\sigma\mu}\beta_{\rho\sigma\tau}),\end{aligned} \tag{3.2}$$

$$\begin{aligned}{}^{3}\beta_{\lambda\mu\nu} = \tfrac{1}{3}(\beta_{\lambda\mu\nu} + \beta_{\mu\nu\lambda} + \beta_{\nu\lambda\mu}) - \tfrac{1}{15}[\delta_{\lambda\mu}(2\beta_{\rho\rho\nu} + \beta_{\nu\rho\rho}) \\ + \delta_{\lambda\nu}(2\beta_{\rho\rho\mu} + \beta_{\mu\rho\rho}) + \delta_{\mu\nu}(2\beta_{\rho\rho\lambda} + \beta_{\lambda\rho\rho})].\end{aligned} \tag{3.3}$$

The decomposition of Eq. (3.1) into two independent weight-1 terms is not unique, but a convenient division is as follows:

$${}^{1A}\beta_{\lambda\mu\nu} = \tfrac{1}{10}(3\delta_{\lambda\mu}\beta_{\rho\rho\nu} + 3\delta_{\lambda\nu}\beta_{\rho\rho\mu} - 2\delta_{\mu\nu}\beta_{\rho\rho\lambda}), \tag{3.4}$$

$${}^{1B}\beta_{\lambda\mu\nu} = \tfrac{1}{10}(-\delta_{\lambda\mu}\beta_{\nu\rho\rho} - \delta_{\lambda\nu}\beta_{\mu\rho\rho} + 4\delta_{\mu\nu}\beta_{\lambda\rho\rho}). \tag{3.5}$$

These satisfy the following contraction relations:

$$\left.\begin{aligned}\delta_{\lambda\mu}{}^{1A}\beta_{\lambda\mu\nu} &= \delta_{\lambda\mu}\beta_{\lambda\mu\nu}, \\ \delta_{\lambda\nu}{}^{1A}\beta_{\lambda\mu\nu} &= \delta_{\lambda\nu}\beta_{\lambda\mu\nu}, \\ \delta_{\mu\nu}{}^{1A}\beta_{\lambda\mu\nu} &= 0, \\ \delta_{\lambda\mu}{}^{1B}\beta_{\lambda\mu\nu} &= 0, \\ \delta_{\lambda\nu}{}^{1B}\beta_{\lambda\mu\nu} &= 0, \\ \delta_{\mu\nu}{}^{1B}\beta_{\lambda\mu\nu} &= \delta_{\mu\nu}\beta_{\lambda\mu\nu}.\end{aligned}\right\} \tag{3.6}$$

This particular choice for ${}^{1A}\beta_{\lambda\mu\nu}$ and ${}^{1B}\beta_{\lambda\mu\nu}$ leads to rather simplified expressions for the scattering intensities, as we shall see later.

The tensor products that appear in Eq. (2.19) can now be expressed in terms of the irreducible weights (3.2)–(3.5) as follows:

$$\left.\begin{aligned}\beta^{NM}_{\lambda\lambda\mu}\beta^{NM}_{\mu\nu\nu} &= {}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1B}\beta^{NM}_{\mu\nu\nu}, \\ \beta^{NM}_{\lambda\lambda\mu}\beta^{NM}_{\nu\nu\mu} &= {}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1A}\beta^{NM}_{\nu\nu\mu}, \\ \beta^{NM}_{\lambda\mu\mu}\beta^{NM}_{\lambda\nu\nu} &= {}^{1B}\beta^{NM}_{\lambda\mu\mu}\,{}^{1B}\beta^{NM}_{\lambda\nu\nu}, \\ \beta^{NM}_{\lambda\mu\nu}\beta^{NM}_{\lambda\mu\nu} &= \tfrac{1}{5}(-2\,{}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1B}\beta^{NM}_{\mu\nu\nu} + 3\,{}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1A}\beta^{NM}_{\nu\nu\mu} \\ &\quad + 2\,{}^{1B}\beta^{NM}_{\lambda\mu\mu}\,{}^{1B}\beta^{NM}_{\lambda\nu\nu} + 5\,{}^{2}\beta^{NM}_{\lambda\mu\nu}\,{}^{2}\beta^{NM}_{\lambda\mu\nu} + 5\,{}^{3}\beta^{NM}_{\lambda\mu\nu}\,{}^{3}\beta^{NM}_{\lambda\mu\nu}), \\ \beta^{NM}_{\lambda\mu\nu}\beta^{NM}_{\mu\lambda\nu} &= \tfrac{1}{10}(6\,{}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1B}\beta^{NM}_{\mu\nu\nu} + {}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1A}\beta^{NM}_{\nu\nu\mu} \\ &\quad - {}^{1B}\beta^{NM}_{\lambda\mu\mu}\,{}^{1B}\beta^{NM}_{\lambda\nu\nu} - 5\,{}^{2}\beta^{NM}_{\lambda\mu\nu}\,{}^{2}\beta^{NM}_{\lambda\mu\nu} + 10\,{}^{3}\beta^{NM}_{\lambda\mu\nu}\,{}^{3}\beta^{NM}_{\lambda\mu\nu}).\end{aligned}\right\} \tag{3.7}$$

Using the above relationships Eq. (2.19) may now be written as

$$\begin{aligned}I(\mathbf{k}') = \frac{\mathfrak{D}}{525}\{&14[7(\bar{\mathbf{e}}'\cdot\mathbf{e})(\mathbf{e}\cdot\mathbf{e}')(\bar{\mathbf{e}}\cdot\bar{\mathbf{e}}) - 3(\bar{\mathbf{e}}'\cdot\mathbf{e})(\mathbf{e}'\cdot\bar{\mathbf{e}}) - 2(\mathbf{e}\cdot\mathbf{e})(\bar{\mathbf{e}}\cdot\bar{\mathbf{e}})]\,{}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1B}\beta^{NM}_{\mu\nu\nu} \\ &+ 7[-6(\bar{\mathbf{e}}'\cdot\mathbf{e})(\mathbf{e}\cdot\mathbf{e}')(\bar{\mathbf{e}}\cdot\bar{\mathbf{e}}) + 9(\bar{\mathbf{e}}'\cdot\mathbf{e})(\mathbf{e}'\cdot\bar{\mathbf{e}}) + (\mathbf{e}\cdot\mathbf{e})(\bar{\mathbf{e}}\cdot\bar{\mathbf{e}})]\,{}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1A}\beta^{NM}_{\nu\nu\mu} + 7[-4(\bar{\mathbf{e}}'\cdot\mathbf{e})(\mathbf{e}\cdot\mathbf{e}')(\bar{\mathbf{e}}\cdot\bar{\mathbf{e}}) + (\bar{\mathbf{e}}'\cdot\mathbf{e})(\mathbf{e}'\cdot\bar{\mathbf{e}}) \\ &+ 4(\mathbf{e}\cdot\mathbf{e})(\bar{\mathbf{e}}\cdot\bar{\mathbf{e}})]\,{}^{1B}\beta^{NM}_{\lambda\mu\mu}\,{}^{1B}\beta^{NM}_{\lambda\nu\nu} + 35[2(\bar{\mathbf{e}}'\cdot\mathbf{e})(\mathbf{e}\cdot\mathbf{e}')(\bar{\mathbf{e}}\cdot\bar{\mathbf{e}}) - (\bar{\mathbf{e}}'\cdot\mathbf{e})(\mathbf{e}'\cdot\bar{\mathbf{e}}) - 2(\mathbf{e}\cdot\mathbf{e}')(\bar{\mathbf{e}}'\cdot\bar{\mathbf{e}}) - (\mathbf{e}\cdot\mathbf{e})(\bar{\mathbf{e}}\cdot\bar{\mathbf{e}}) + 2]\,{}^{2}\beta^{NM}_{\lambda\mu\nu}\,{}^{2}\beta^{NM}_{\lambda\mu\nu} \\ &+ 5[-4(\bar{\mathbf{e}}'\cdot\mathbf{e})(\mathbf{e}\cdot\mathbf{e}')(\bar{\mathbf{e}}\cdot\bar{\mathbf{e}}) - 4(\bar{\mathbf{e}}'\cdot\mathbf{e})(\mathbf{e}'\cdot\bar{\mathbf{e}}) + 10(\mathbf{e}\cdot\mathbf{e}')(\bar{\mathbf{e}}'\cdot\bar{\mathbf{e}}) - (\mathbf{e}\cdot\mathbf{e})(\bar{\mathbf{e}}\cdot\bar{\mathbf{e}}) + 5]\,{}^{3}\beta^{NM}_{\lambda\mu\nu}\,{}^{3}\beta^{NM}_{\lambda\mu\nu}\}.\end{aligned} \tag{3.8}$$

This is a general result from which one can obtain a wide variety of data about the scattering system.

TABLE I. Irreducible components of the β tensor.

β_1	$\beta_{xxx}+\beta_{yyx}+\beta_{zzx}$	set A	weight-1
β_2	$\beta_{xxy}+\beta_{yyy}+\beta_{zzy}$		
β_3	$\beta_{xxz}+\beta_{yyz}+\beta_{zzz}$		
β_4	$\beta_{xxx}+\beta_{xyy}+\beta_{xzz}$	set B	
β_5	$\beta_{yxx}+\beta_{yyy}+\beta_{yzz}$		
β_6	$\beta_{zxx}+\beta_{zyy}+\beta_{zzz}$		
β_7	$\beta_{xyz}-\beta_{yzx}$		weight-2
β_8	$\sqrt{\frac{1}{3}}\,(\beta_{yzx}-2\,\beta_{zxy}+\beta_{xyz})$		
β_9	$\sqrt{\frac{1}{3}}\,(\beta_{yyz}-\beta_{zyy}+\beta_{zxx}-\beta_{xxz})$		
β_{10}	$\sqrt{\frac{1}{3}}\,(\beta_{yzz}-\beta_{zzy}+\beta_{xxy}-\beta_{yxx})$		
β_{11}	$\sqrt{\frac{1}{3}}\,(\beta_{zzx}-\beta_{xzz}+\beta_{xyy}-\beta_{yyx})$		
β_{12}	$\sqrt{\frac{2}{3}}\,(\beta_{xyz}+\beta_{yzx}+\beta_{zxy})$		weight-3
β_{13}	$\frac{1}{2}\,(\beta_{xxx}-2\,\beta_{yyx}-\beta_{xyy})$		
β_{14}	$\frac{1}{2}\,(\beta_{yyy}-2\,\beta_{xxy}-\beta_{yxx})$		
β_{15}	$\sqrt{\frac{1}{6}}(2\,\beta_{xxz}+\beta_{zxx}-2\,\beta_{yyz}-\beta_{zyy})$		
β_{16}	$\sqrt{\frac{1}{10}}\,(2\,\beta_{zzz}-2\,\beta_{xxz}-2\,\beta_{yyz}-\beta_{zxx}-\beta_{zyy})$		
β_{17}	$\sqrt{\frac{1}{60}}(8\,\beta_{zzx}+4\,\beta_{xzz}-3\,\beta_{xxx}-2\,\beta_{yyx}-\beta_{xyy})$		
β_{18}	$\sqrt{\frac{1}{60}}\,(8\,\beta_{zzy}+4\,\beta_{yzz}-3\,\beta_{yyy}-2\,\beta_{xxy}-\beta_{yxx})$		

IV. SELECTION RULES

The selection rules for hyper-Raman scattering can be derived by considering the integral associated with the transition $0N \leftarrow 0M$,

$$\langle \chi_{0N} \,|\, \beta_{\lambda\mu\nu} \,|\, \chi_{0M} \rangle \,. \tag{4.1}$$

We confine our attention to fundamental transitions, i.e., those with $N - M = \pm 1$. For such transitions the product of the vibrational wavefunctions transforms as the corresponding normal vibrational mode coordinate. If the integral (4.1) is not to vanish identically, then $\beta_{\lambda\mu\nu}$ must have at least one component belonging to the same irreducible representation as the normal mode. As we noted in Sec. III the β tensor can be reduced to two terms of weight 1, one of weight 2, and one of weight 3, with six, five, and seven irreducible components, respectively. Explicit expressions for these components are given in Table I. The selection rules are easily obtained by examining the symmetry properties of these components under the operations of the various molecular point groups. We list in Table II the irreducible representations spanned by these components for molecules of point group symmetry D_{5h}, D_{6h}, D_{4d}, D_{6d}, O_h, I_h, and $D_{\infty h}$. The corresponding representations for point groups of lower symmetry are easily obtained from correlation tables such as those given by Wilson, Decius, and Cross.[17] Using these results the vibrational modes of a molecule of given symmetry can be classified according to the weights of the β tensor that have the same representation. This scheme allows one to compare the hyper-Raman selection rules with ir and Raman selection rules. Further, it enables one to make predictions about intensity ratios, which are discussed in a later section. Before we discuss the details of the classification we make two important general remarks concerning the selection rules. First, all ir active modes are also hyper-Raman active since the weight-1 components of the β tensor transform like the electric dipole moment. Secondly, for centrosymmetric molecules since only *ungerade* modes are hyper-Raman allowed, such modes are Raman inactive. However, for noncentrosymmetric systems vibrational modes with the same symmetry as a weight-2 component of the β tensor can be Raman active. Although this is a necessary requirement, it is not sufficient because the weight-2 components of the Raman and hyper-Raman tensors, in general, transform differently under reflection. For example, we see from Table II that in D_{4d} only E_2 is *both* Raman and hyper-Raman active. However, in the pure rotation (chiral) groups C_n, D_n, T, O, and I any vibration belonging to the same representation as a weight-2 component of the β tensor is also Raman active. It is of interest to note that the assumption of full index symmetry for the β tensor leads to the erroneous conclusion that a mode cannot be both Raman and hyper-Raman active.

An examination of Table II shows that the hyper-Raman active modes may be classified into six types:

Class A: For modes belonging to this class the β tensor has contributions of weights 1, 2, and 3. These modes are also ir active. In view of the remarks made above no general rule can be made about Raman activity;

TABLE II. Infrared, Raman, and hyper-Raman activity: Irreducible representations of dipole μ, polarizability α, and hyperpolarizability β.

	Infrared	Raman		Hyper-Raman		
Group	μ (weight 1)	α (weight 0)	α (weight 2)	β (weight 1)	β (weight 2)	β (weight 3)
D_{5h}	$A_2''+E_1'$	A_1'	$A_1'+E_2'+E_1''$	$2\,A_2''+2E_1'$	$A_1''+E_1'+E_2''$	$A_2''+E_1'+E_2'+E_2''$
D_{6h}	$A_{2u}+E_{1u}$	A_{1g}	$A_{1g}+E_{1g}+E_{2g}$	$2A_{2u}+2E_{1u}$	$A_{1u}+E_{1u}+E_{2u}$	$A_{2u}+B_{1u}+B_{2u}+E_{1u}+E_{2u}$
D_{4d}	B_2+E_1	A_1	$A_1+E_2+E_3$	$2B_2+2E_1$	$B_1+E_1+E_2$	$B_2+E_1+E_2+E_3$
D_{6d}	B_2+E_1	A_1	$A_1+E_2+E_5$	$2B_2+2E_1$	$B_1+E_1+E_4$	$B_2+E_1+E_3+E_4$
O_h	T_{1u}	A_{1g}	E_g+T_{2g}	$2T_{1u}$	$T_{2u}+E_u$	$A_{2u}+T_{1u}+T_{2u}$
I_h	T_{1u}	A_g	H_g	$2T_{1u}$	H_u	$T_{2u}+G_u$
$D_{\infty h}$	$\Sigma_u^+ + \Pi_u$	Σ_g^+	$\Sigma_g^+ + \Pi_g + \Delta_g$	$2\Sigma_u^+ + 2\Pi_u$	$\Sigma_u^- + \Pi_u + \Delta_u$	$\Sigma_u^+ + \Pi_u + \Delta_u + \Phi_u$

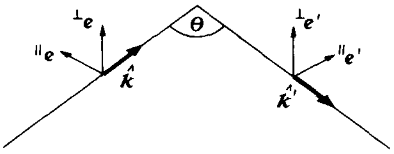

FIG. 2. The scattering geometry.

each case has to be analyzed using Table II, and, where necessary, the correlation tables. Examples of class A are the $\nu_3(E)$ antisymmetric stretching and $\nu_4(E)$ bending modes of ammonia which are Raman active and $\nu_7(B_{1u})$ molecular bending mode of ethylene which is Raman inactive.

Class B: For these modes the β tensor has contributions of weights 2 and 3. They are clearly ir inactive. Examples are the E'' modes (such as the ν_{13} methylene rocking mode) of cyclopropane and the Raman inactive $\nu_4(A_u)$ torsional mode of ethylene.

Class C: These modes have both weights-1 and -3 contributions. Consequently, they are always ir active and Raman inactive. An example of this type is the $\nu_3(A_{2u})$ out-of-plane bending mode in xenon tetrafluoride of D_{4h} symmetry.

Class D: For the class D modes the contributions are of weight 3 alone. Hence, these modes are both ir and Raman inactive. An example of this type is the $\nu_6(B_{1u})$ hydrogen stretch in benzene.

Class E: The β tensor for these modes has weight-2 contributions only. Hence, these modes are ir inactive, but can be Raman active. For example, the Raman-active $\nu_2(E)$ deformation modes of methane belong to this class, as does the Raman-inactive $\nu_4(A_1'')$ methylene twisting mode of cyclopropane.

Class F: The final class contains those modes which have only weight-1 contributions. These modes are ir active but Raman inactive. It is evident from Table II that molecules belonging to the common molecular point groups cannot have modes of this type; such modes are found only in molecules of icosahedral symmetry.

V. A SCHEME FOR THE DETERMINATION OF MOLECULAR INVARIANTS

The expression for the scattered intensity (3.8) contains five independent molecular invariants, namely, the different types of β products. These can be expressed in terms of the 18 irreducible components given in Table I; we have

$$ {}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1B}\beta^{NM}_{\mu\nu\nu} = \beta_1^{NM}\beta_4^{NM} + \beta_2^{NM}\beta_5^{NM} + \beta_3^{NM}\beta_6^{NM} \,, \tag{5.1} $$

$$ {}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1A}\beta^{NM}_{\nu\nu\mu} = (\beta_1^{NM})^2 + (\beta_2^{NM})^2 + (\beta_3^{NM})^2 \,, \tag{5.2} $$

$$ {}^{1B}\beta^{NM}_{\lambda\mu\mu}\,{}^{1B}\beta^{NM}_{\lambda\nu\nu} = (\beta_4^{NM})^2 + (\beta_5^{NM})^2 + (\beta_6^{NM})^2 \,, \tag{5.3} $$

$$ {}^{2}\beta^{NM}_{\lambda\mu\nu}\,{}^{2}\beta^{NM}_{\lambda\mu\nu} = (\beta_7^{NM})^2 + (\beta_8^{NM})^2 + (\beta_9^{NM})^2 + (\beta_{10}^{NM})^2 + (\beta_{11}^{NM})^2 \,, \tag{5.4} $$

$$ {}^{3}\beta^{NM}_{\lambda\mu\nu}\,{}^{3}\beta^{NM}_{\lambda\mu\nu} = (\beta_{12}^{NM})^2 + (\beta_{13}^{NM})^2 + (\beta_{14}^{NM})^2 + (\beta_{15}^{NM})^2 + (\beta_{16}^{NM})^2 + (\beta_{17}^{NM})^2 + (\beta_{18}^{NM})^2 \,. \tag{5.5} $$

Using Eq. (3.8) one can determine the values of the five molecular invariants (5.1)–(5.5) from a set of five different experimental observations. Although McClain[16] has proposed a similar method for determining the five β products which appear in Eq. (2.19), the above quantities are more useful as they can be immediately related to the vibrational mode classification discussed earlier. The various experimental configurations are conveniently described in terms of the propagation and polarization vectors of the incident and scattered photons. As shown in Fig. 2, $^{\perp}\mathbf{e}$ and $^{\perp}\mathbf{e}'$ are equivalent unit vectors normal to the $\hat{\mathbf{k}}\hat{\mathbf{k}}'$ plane. The in-plane vector $^{\parallel}\mathbf{e}$ is chosen such that $^{\parallel}\mathbf{e}$, $^{\perp}\mathbf{e}$, and $\hat{\mathbf{k}}$ form a right-handed set; the primed vector $^{\parallel}\mathbf{e}'$ is defined in a similar manner. For circular polarizations we use the optical convention, namely,

$$ \left.\begin{aligned} {}^{L}\mathbf{e} &= \frac{1}{\sqrt{2}}\,({}^{\parallel}\mathbf{e} + i\,{}^{\perp}\mathbf{e}) \,, \\ {}^{R}\mathbf{e} &= \frac{1}{\sqrt{2}}\,({}^{\parallel}\mathbf{e} - i\,{}^{\perp}\mathbf{e}) \,. \end{aligned}\right\} \tag{5.6} $$

Finally, the convergence angle θ is defined by

$$ \cos\theta = -\hat{\mathbf{k}}\cdot\hat{\mathbf{k}}' \,. \tag{5.7} $$

We use the shorthand notation $I_\theta(\lambda\rightarrow\mu)$ to denote the experimental configuration with incident and scattered photons having polarizations $^{\lambda}\mathbf{e}$ and $^{\mu}\mathbf{e}'$, respectively, θ being the convergence angle.

A convenient set of five intensity measurements is as follows:

$$ I_1 = I_{\pi/2}(\perp\rightarrow\perp) \,, \tag{5.8} $$

$$ I_2 = I_{\pi/2}(\perp\rightarrow\parallel) \,, \tag{5.9} $$

$$ I_3 = I_{\pi/2}(R\rightarrow\parallel) \,, \tag{5.10} $$

$$ I_4 = I_{\pi}(R\rightarrow R) \,, \tag{5.11} $$

$$ I_5 = I_{\pi}(R\rightarrow L) \,. \tag{5.12} $$

This particular set includes the two pairs of measurements which are required for the calculation of the reversal ratio and depolarization ratio. The details are given in the next section. The expressions for I_1 to I_5 follow directly from Eq. (3.8):

$$ I_1 = \frac{\mathfrak{D}}{525}\left(28\,{}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1B}\beta^{NM}_{\mu\nu\nu} + 28\,{}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1A}\beta^{NM}_{\nu\nu\mu} + 7\,{}^{1B}\beta^{NM}_{\lambda\mu\mu}\,{}^{1B}\beta^{NM}_{\lambda\nu\nu} + 30\,{}^{3}\beta^{NM}_{\lambda\mu\nu}\,{}^{3}\beta^{NM}_{\lambda\mu\nu}\right) , \tag{5.13} $$

$$ I_2 = \frac{\mathfrak{D}}{525}\left(-28\,{}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1B}\beta^{NM}_{\mu\nu\nu} + 7\,{}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1A}\beta^{NM}_{\nu\nu\mu} + 28\,{}^{1B}\beta^{NM}_{\lambda\mu\mu}\,{}^{1B}\beta^{NM}_{\lambda\nu\nu} + 35\,{}^{2}\beta^{NM}_{\lambda\mu\nu}\,{}^{2}\beta^{NM}_{\lambda\mu\nu} + 20\,{}^{3}\beta^{NM}_{\lambda\mu\nu}\,{}^{3}\beta^{NM}_{\lambda\mu\nu}\right) , \tag{5.14} $$

$$ I_3 = \frac{\mathfrak{D}}{105}\left(14\,{}^{2}\beta^{NM}_{\lambda\mu\nu}\,{}^{2}\beta^{NM}_{\lambda\mu\nu} + 5\,{}^{3}\beta^{NM}_{\lambda\mu\nu}\,{}^{3}\beta^{NM}_{\lambda\mu\nu}\right) , \tag{5.15} $$

$$ I_4 = \frac{\mathfrak{D}}{525}\left(-42\,{}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1B}\beta^{NM}_{\mu\nu\nu} + 63\,{}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1A}\beta^{NM}_{\nu\nu\mu} + 7\,{}^{1B}\beta^{NM}_{\lambda\mu\mu}\,{}^{1B}\beta^{NM}_{\lambda\nu\nu} + 35\,{}^{2}\beta^{NM}_{\lambda\mu\nu}\,{}^{2}\beta^{NM}_{\lambda\mu\nu} + 5\,{}^{3}\beta^{NM}_{\lambda\mu\nu}\,{}^{3}\beta^{NM}_{\lambda\mu\nu}\right) , \tag{5.16} $$

$$ I_5 = \frac{\mathfrak{D}}{7}\,{}^{3}\beta^{NM}_{\lambda\mu\nu}\,{}^{3}\beta^{NM}_{\lambda\mu\nu} \,. \tag{5.17} $$

These form a regular system of equations which can be solved to give

$$ {}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1B}\beta^{NM}_{\mu\nu\nu} = \tfrac{3}{2}\mathfrak{D}^{-1}(7I_1 - I_2 + 2I_3 - 3I_4 - 3I_5)\,, \tag{5.18} $$

$$ {}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1A}\beta^{NM}_{\nu\nu\mu} = \tfrac{3}{2}\mathfrak{D}^{-1}(4I_1 - 2I_2 - I_3 + 4I_4 - I_5)\,, \tag{5.19} $$

$$ {}^{1B}\beta^{NM}_{\lambda\mu\mu}\,{}^{1B}\beta^{NM}_{\lambda\nu\nu} = 3\mathfrak{D}^{-1}(3I_1 + 6I_2 - 2I_3 - 2I_4 - 2I_5)\,, \tag{5.20} $$

$$ {}^{2}\beta^{NM}_{\lambda\mu\nu}\,{}^{2}\beta^{NM}_{\lambda\mu\nu} = \tfrac{5}{2}\mathfrak{D}^{-1}(3I_3 - I_5)\,, \tag{5.21} $$

$$ {}^{3}\beta^{NM}_{\lambda\mu\nu}\,{}^{3}\beta^{NM}_{\lambda\mu\nu} = 7\mathfrak{D}^{-1}I_5\,. \tag{5.22} $$

Thus, the assignment of a spectral line to a mode of a particular class can be achieved by digital processing of the spectra obtained from the five experiments. For this purpose a knowledge of the relative intensities is sufficient. The linear combinations (5.18)–(5.22) can be used to generate five new spectra corresponding to the five β products. The appearance or nonappearance of a line at a particular frequency in the computed spectra then enables one to assign the corresponding vibrational mode to any one of the six classes discussed previously.

VI. REVERSAL RATIOS AND DEPOLARIZATION RATIOS

The reversal ratio, which is generally dependent on θ, may be defined as for Raman scattering by

$$ R(\theta) = \frac{I_\theta(R \to L)}{I_\theta(R \to R)}\,. \tag{6.1} $$

From Eq. (3.8) we get

$$ \begin{aligned} R(\theta) = {}&[7(1 + 2\cos\theta + \cos^2\theta)(-6\,{}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1B}\beta^{NM}_{\mu\nu\nu} + 9\,{}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1A}\beta^{NM}_{\nu\nu\mu} + {}^{1B}\beta^{NM}_{\lambda\mu\mu}\,{}^{1B}\beta^{NM}_{\lambda\nu\nu}) + 35(5 + 2\cos\theta - 3\cos^2\theta)\,{}^{2}\beta^{NM}_{\lambda\mu\nu}\,{}^{2}\beta^{NM}_{\lambda\mu\nu} \\ &+ 10(13 - 14\cos\theta + 3\cos^2\theta)\,{}^{3}\beta^{NM}_{\lambda\mu\nu}\,{}^{3}\beta^{NM}_{\lambda\mu\nu}]\,[7(1 - 2\cos\theta + \cos^2\theta)(-6\,{}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1B}\beta^{NM}_{\mu\nu\nu} + 9\,{}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1A}\beta^{NM}_{\nu\nu\mu} \\ &+ {}^{1B}\beta^{NM}_{\lambda\mu\mu}\,{}^{1B}\beta^{NM}_{\lambda\nu\nu}) + 35(5 - 2\cos\theta - 3\cos^2\theta)\,{}^{2}\beta^{NM}_{\lambda\mu\nu}\,{}^{2}\beta^{NM}_{\lambda\mu\nu} + 10(13 + 14\cos\theta + 3\cos^2\theta)\,{}^{3}\beta^{NM}_{\lambda\mu\nu}\,{}^{3}\beta^{NM}_{\lambda\mu\nu}]^{-1}\,. \end{aligned} \tag{6.2} $$

For forward scattering the result is simply I_5/I_4, whereas for right-angled scattering it is unity, as for Raman scattering. Also,

$$ R(\pi - \theta) = R^{-1}(\theta)\,. \tag{6.3} $$

For forward scattering we note that vibrational modes belonging to classes D and E take the values of 15 and 0, respectively, for the reversal ratio. For other classes the corresponding values are dependent on the scattering molecule.

The depolarization ratio $\rho_\perp$ for plane polarized incident light is angle dependent and is defined as

$$ \rho_\perp = \frac{I(\perp \to \parallel)}{I(\perp \to \perp)}\,, \tag{6.4} $$

which is given by I_2/I_1. For class D vibrational modes the value of $\rho_\perp$ is 2/3, whereas for class E modes the ratio is infinite. The latter behavior is unknown in Raman scattering except under resonance conditions. The class D and class E results are of special interest since they correspond to modes which are active in hyper-Raman scattering but not in ir absorption; the other class of ir inactive modes, namely, class B, should exhibit reversal and depolarization ratios intermediate between the class D and class E values. It has previously been thought that all ir-inactive, hyper-Raman-active modes have the same reversal and depolarization ratios.[9] However, the present work shows that this is not the case and that three different types of behavior may be expected.

Before proceeding further we make an important remark concerning hyper-Raman scattering of unpolarized light. It is well known that for Rayleigh and Raman scattering of unpolarized light the intensity of the scattered light can be written as

$$ \begin{aligned} I(u \to \mu) &= \tfrac{1}{2}[I(\parallel \to \mu) + I(\perp \to \mu)] \\ &= \tfrac{1}{2}[I(L \to \mu) + I(R \to \mu)]\,, \end{aligned} \tag{6.5} $$

where u refers to unpolarized light. As pointed out elsewhere[18] the above relationships do not hold for nonlinear scattering of unpolarized light. The analogous relation for hyper-Raman scattering is

$$ I(u \to \mu) = \tfrac{1}{4}[I(\parallel, \parallel \to \mu) + 2I(\parallel, \perp \to \mu) + I(\perp, \perp \to \mu)]\,, \tag{6.6} $$

where $I(\lambda, \lambda' \to \mu)$ refers to the absorption of one photon of polarization λ and one of λ', and the emission of a photon of polarization μ. In obtaining Eq. (6.6) the mean irradiance of the incident light has been taken to be the same for all the terms. The equation may be viewed as resulting from independent summations over the polarizations of each of the incident photons. The middle term of Eq. (6.6) is not directly measurable. It can be shown that an equivalent expression for $I(u \to \mu)$ in terms of directly measurable quantities is

$$ \begin{aligned} I(u \to \mu) = \tfrac{1}{8}[&2I(\parallel, \parallel \to \mu) + 2I(\perp, \perp \to \mu) \\ &+ I(L, L \to \mu) + I(R, R \to \mu)]\,. \end{aligned} \tag{6.7} $$

The general expression for the scattered intensity in terms of the β tensors is

$$ \begin{aligned} I = \frac{\mathfrak{D}}{4200}\{&-14[3 + 5(\hat{\mathbf{k}}\cdot\mathbf{e}')(\hat{\mathbf{k}}\cdot\bar{\mathbf{e}}')]\,{}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1B}\beta^{NM}_{\mu\nu\nu} + 7[19 - 15(\hat{\mathbf{k}}\cdot\mathbf{e}')(\hat{\mathbf{k}}\cdot\bar{\mathbf{e}}')]\,{}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1A}\beta^{NM}_{\nu\nu\mu} \\ &+ 7[11 + 5(\hat{\mathbf{k}}\cdot\mathbf{e}')(\hat{\mathbf{k}}\cdot\bar{\mathbf{e}}')]\,{}^{1B}\beta^{NM}_{\lambda\mu\mu}\,{}^{1B}\beta^{NM}_{\lambda\nu\nu} + 35[3 + 5(\hat{\mathbf{k}}\cdot\mathbf{e}')(\hat{\mathbf{k}}\cdot\bar{\mathbf{e}}')]\,{}^{2}\beta^{NM}_{\lambda\mu\nu}\,{}^{2}\beta^{NM}_{\lambda\mu\nu} + 10[18 - 5(\hat{\mathbf{k}}\cdot\mathbf{e}')(\hat{\mathbf{k}}\cdot\bar{\mathbf{e}}')]\,{}^{3}\beta^{NM}_{\lambda\mu\nu}\,{}^{3}\beta^{NM}_{\lambda\mu\nu}\}\,. \end{aligned} \tag{6.8} $$

As for Raman scattering the depolarization ratio ρ_u may be defined as

$$ \rho_u(\theta) = \frac{I_\theta(u \to \parallel)}{I_\theta(u \to \perp)}\,. \tag{6.9} $$

For hyper-Raman scattering the explicit result in terms of the β tensor is

$$\begin{aligned}\rho_u(\pi/2) = (&-112\,{}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1B}\beta^{NM}_{\mu\nu\nu} + 28\,{}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1A}\beta^{NM}_{\nu\nu\mu} + 112\,{}^{1B}\beta^{NM}_{\lambda\mu\mu}\,{}^{1B}\beta^{NM}_{\lambda\nu\nu} + 280\,{}^{2}\beta^{NM}_{\lambda\mu\nu}\,{}^{2}\beta^{NM}_{\lambda\mu\nu} + 130\,{}^{3}\beta^{NM}_{\lambda\mu\nu}\,{}^{3}\beta^{NM}_{\lambda\mu\nu})\\ &\times(-42\,{}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1B}\beta^{NM}_{\mu\nu\nu} + 133\,{}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1A}\beta^{NM}_{\nu\nu\mu} + 77\,{}^{1B}\beta^{NM}_{\lambda\mu\mu}\,{}^{1B}\beta^{NM}_{\lambda\nu\nu} + 105\,{}^{2}\beta^{NM}_{\lambda\mu\nu}\,{}^{2}\beta^{NM}_{\lambda\mu\nu} + 180\,{}^{3}\beta^{NM}_{\lambda\mu\nu}\,{}^{3}\beta^{NM}_{\lambda\mu\nu})^{-1}\,,\end{aligned} \tag{6.10}$$

and the θ dependence is given by

$$\rho_u(\theta) = \rho_u\left(\frac{\pi}{2}\right) + \left[1 - \rho_u\left(\frac{\pi}{2}\right)\right]\cos^2\theta\,, \tag{6.11}$$

which is the same as for Rayleigh and Raman scattering. We note that $\rho_u(\pi/2)$ takes the value of 13/18 for class D modes and 8/3 for class E modes; again, intermediate values should be found for modes belonging to class B. Finally, we remark that in the special case where the hyperpolarizability tensor has full index symmetry the weight-2 β product vanishes, and the weight-1 products become equal. From Eq. (6.10) it then follows that $\rho_u(\pi/2)$ lies in the range $1/6 \leqslant \rho_u(\pi/2) \leqslant 13/18$, the lower limit being taken by pure weight-1 modes, and the upper limit by pure weight-3 modes. Use of Eq. (6.5) in deriving ρ_u results leads to the erroneous values of 1/5 for the lower limit and 4/5 for the upper limit.

VII. COMPLETE SET OF INTENSITY RESULTS FOR $\theta = 0, \pi/2$, AND π

In Tables III–V we present the intensity results for forward, backward, and right-angled scattering, respectively, in terms of I_1 to I_5, given by Eqs. (5.13)–(5.17), and I_6 to I_{11} by

$$I_6 = \frac{\mathfrak{D}}{2100}(-42\,{}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1B}\beta^{NM}_{\mu\nu\nu} + 63\,{}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1A}\beta^{NM}_{\nu\nu\mu} + 7\,{}^{1B}\beta^{NM}_{\lambda\mu\mu}\,{}^{1B}\beta^{NM}_{\lambda\nu\nu} + 175\,{}^{2}\beta^{NM}_{\lambda\mu\nu}\,{}^{2}\beta^{NM}_{\lambda\mu\nu} + 130\,{}^{3}\beta^{NM}_{\lambda\mu\nu}\,{}^{3}\beta^{NM}_{\lambda\mu\nu})\,, \tag{7.1}$$

$$I_7 = \frac{\mathfrak{D}}{1050}(-42\,{}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1B}\beta^{NM}_{\mu\nu\nu} + 63\,{}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1A}\beta^{NM}_{\nu\nu\mu} + 7\,{}^{1B}\beta^{NM}_{\lambda\mu\mu}\,{}^{1B}\beta^{NM}_{\lambda\nu\nu} + 35\,{}^{2}\beta^{NM}_{\lambda\mu\nu}\,{}^{2}\beta^{NM}_{\lambda\mu\nu} + 80\,{}^{3}\beta^{NM}_{\lambda\mu\nu}\,{}^{3}\beta^{NM}_{\lambda\mu\nu})\,, \tag{7.2}$$

$$I_8 = \frac{\mathfrak{D}}{210}(7\,{}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1A}\beta^{NM}_{\nu\nu\mu} + 7\,{}^{1B}\beta^{NM}_{\lambda\mu\mu}\,{}^{1B}\beta^{NM}_{\lambda\nu\nu} + 7\,{}^{2}\beta^{NM}_{\lambda\mu\nu}\,{}^{2}\beta^{NM}_{\lambda\mu\nu} + 10\,{}^{3}\beta^{NM}_{\lambda\mu\nu}\,{}^{3}\beta^{NM}_{\lambda\mu\nu})\,, \tag{7.3}$$

$$I_9 = \frac{\mathfrak{D}}{4200}(-42\,{}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1B}\beta^{NM}_{\mu\nu\nu} + 133\,{}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1A}\beta^{NM}_{\nu\nu\mu} + 77\,{}^{1B}\beta^{NM}_{\lambda\mu\mu}\,{}^{1B}\beta^{NM}_{\lambda\nu\nu} + 105\,{}^{2}\beta^{NM}_{\lambda\mu\nu}\,{}^{2}\beta^{NM}_{\lambda\mu\nu} + 180\,{}^{3}\beta^{NM}_{\lambda\mu\nu}\,{}^{3}\beta^{NM}_{\lambda\mu\nu})\,, \tag{7.4}$$

$$I_{10} = \frac{\mathfrak{D}}{2100}(-56\,{}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1B}\beta^{NM}_{\mu\nu\nu} + 14\,{}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1A}\beta^{NM}_{\nu\nu\mu} + 56\,{}^{1B}\beta^{NM}_{\lambda\mu\mu}\,{}^{1B}\beta^{NM}_{\lambda\nu\nu} + 140\,{}^{2}\beta^{NM}_{\lambda\mu\nu}\,{}^{2}\beta^{NM}_{\lambda\mu\nu} + 65\,{}^{3}\beta^{NM}_{\lambda\mu\nu}\,{}^{3}\beta^{NM}_{\lambda\mu\nu})\,, \tag{7.5}$$

$$I_{11} = \frac{\mathfrak{D}}{8400}(-154\,{}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1B}\beta^{NM}_{\mu\nu\nu} + 161\,{}^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1A}\beta^{NM}_{\nu\nu\mu} + 189\,{}^{1B}\beta^{NM}_{\lambda\mu\mu}\,{}^{1B}\beta^{NM}_{\lambda\nu\nu} + 385\,{}^{2}\beta^{NM}_{\lambda\mu\nu}\,{}^{2}\beta^{NM}_{\lambda\mu\nu} + 310\,{}^{3}\beta^{NM}_{\lambda\mu\nu}\,{}^{3}\beta^{NM}_{\lambda\mu\nu})\,. \tag{7.6}$$

The intensities I_6 to I_{11} can, in fact, be expressed in terms of I_1 to I_5:

$$I_6 = \tfrac{1}{4}(2I_3 + I_4 + I_5)\,, \tag{7.7}$$

$$I_7 = \tfrac{1}{4}(I_4 + I_5)\,, \tag{7.8}$$

$$I_8 = \tfrac{1}{2}(I_1 + I_2)\,, \tag{7.9}$$

$$I_9 = \tfrac{1}{8}(2I_1 + 2I_2 + I_4 + I_5)\,, \tag{7.10}$$

$$I_{10} = \tfrac{1}{4}(2I_2 + I_3)\,, \tag{7.11}$$

$$I_{11} = \tfrac{1}{16}(2I_1 + 6I_2 + 2I_3 + I_4 + I_5)\,. \tag{7.12}$$

Except I_1, I_3, and I_5 all other expressions contain contributions from weights 1, 2, and 3. Consequently, the appearance of a mode in the spectra for the above scattering configurations does not provide a firm basis for classifying the mode. Since weight-3 contributions are present in all the intensity expressions, modes of classes A to D should always appear in the hyper-Raman spectra. Since A and C correspond to two of the three types of ir active modes, it is evidently not possible to exclude all such modes from the hyper-Raman spectra, as suggested by Maker.[19] However, the ir active modes of class F are inactive in I_3 and I_5. Further, class E modes remain inactive in I_1 and I_5.

In passing we note that the corresponding tables for Raman scattering are similar in form to Tables III–V except that entries corresponding to I_2, I_3, and I_{10} become equal, as do I_7, I_8, and I_9, and the pair I_6 and I_{11}.

VIII. SOME EXAMPLES

The hyper-Raman spectra of several molecules such as methane, ethane, and ethylene,[3] carbon tetrachloride, chloroform, and water,[4] and tetrachloroethylene[6] have been observed experimentally. We now discuss applications of our theory to some of these and other molecules.

Ethylene, of D_{2h} symmetry, has 12 vibrational modes of symmetry species $A_g(3)$, $B_{1g}(2)$, $B_{2g}(1)$, $A_u(1)$, $B_{1u}(1)$, $B_{2u}(2)$, and $B_{3u}(2)$. Of these only the six with *ungerade* character are hyper-Raman active; the B_u modes are

TABLE III. Intensities of hyper-Raman forward scattering ($\theta = \pi$).

$I(\lambda \to \mu)$	$\parallel$	$\perp$	L	R
$\parallel \to$	I_1	I_2	I_8	I_8
$\perp \to$	I_2	I_1	I_8	I_8
$L \to$	I_7	I_7	I_4	I_5
$R \to$	I_7	I_7	I_5	I_4
$u \to$	I_9	I_9	I_9	I_9

TABLE IV. Intensities of hyper-Raman backward scattering ($\theta = 0$).

$I(\lambda \to \mu)$	$\parallel$	$\perp$	L	R
$\parallel \to$	I_1	I_2	I_8	I_8
$\perp \to$	I_2	I_1	I_8	I_8
$L \to$	I_7	I_7	I_5	I_4
$R \to$	I_7	I_7	I_4	I_5
$u \to$	I_9	I_9	I_9	I_9

also ir active. The representations spanned by the components of the β tensor are obtained from Table II and correlation tables. They are

Weight 1: $2B_{1u} + 2B_{2u} + 2B_{3u}$,

Weight 2: $2A_u + B_{1u} + B_{2u} + B_{3u}$,

Weight 3: $A_u + 2B_{1u} + 2B_{2u} + 2B_{3u}$.

Thus, the B_u vibrational modes belong to class A (containing weights 1, 2, and 3) and the A_u modes belong to class B (with weights 2 and 3 only). The $\nu_4(A_u)$ torsional mode of ethylene, which is both ir and Raman inactive, provides an example of the usefulness of hyper-Raman spectra in the study of molecular vibrations. Using the data-processing technique discussed in Sec. V only the β products of weights 2 and 3 should be found to be nonzero for such a mode; these are given by

$$^{2}\beta^{NM}_{\lambda\mu\nu}\,{}^{2}\beta^{NM}_{\lambda\mu\nu} = (\beta^{NM}_{7})^2 + (\beta^{NM}_{8})^2\,, \tag{8.1}$$

$$^{3}\beta^{NM}_{\lambda\mu\nu}\,{}^{3}\beta^{NM}_{\lambda\mu\nu} = (\beta^{NM}_{12})^2\,, \tag{8.2}$$

and the intensity expressions follow from the results given earlier.

An example of class A modes is the molecular bending mode ν_7 of B_{1u} symmetry. In this case all five β products are expected to contribute to the scattering intensities; in terms of the irreducible components they are given by

$$^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1B}\beta^{NM}_{\mu\nu\nu} = \beta^{NM}_{3}\,\beta^{NM}_{6}\,, \tag{8.3}$$

$$^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1A}\beta^{NM}_{\nu\nu\mu} = (\beta^{NM}_{3})^2\,, \tag{8.4}$$

$$^{1B}\beta^{NM}_{\lambda\mu\mu}\,{}^{1B}\beta^{NM}_{\lambda\nu\nu} = (\beta^{NM}_{6})^2\,, \tag{8.5}$$

$$^{2}\beta^{NM}_{\lambda\mu\nu}\,{}^{2}\beta^{NM}_{\lambda\mu\nu} = (\beta^{NM}_{9})^2\,, \tag{8.6}$$

$$^{3}\beta^{NM}_{\lambda\mu\nu}\,{}^{3}\beta^{NM}_{\lambda\mu\nu} = (\beta^{NM}_{15})^2 + (\beta^{NM}_{16})^2\,. \tag{8.7}$$

The corresponding results for the B_{2u} and B_{3u} modes are easily written down.

In an experimental study of the hyper-Raman spectrum of ethylene Verdieck *et al.*[3] observed a strong line at 980 cm^{-1} under conditions where the polarization of the scattered photon was not specified; they assigned this line to the bending mode $\nu_7\,(B_{1u})$. On the basis of the selection rules due to Maker[19] this line was expected to disappear in the spectrum corresponding to the configuration $I_3 = I_{\pi/2}(R \to \parallel)$. However, the line still persisted weakly in this spectrum. Verdieck *et al.* suggested that the persistence of this line was due to the finite angle of collection of the spectrum. From our analysis, however, we note that the B_{1u} mode belongs to class A, with the β tensor containing weights 1, 2, and 3, and a perusal of the I_3 intensity expression (5.15) shows that this mode is expected to be active in this configuration.

A second example with an interesting feature is cyclopropane of D_{3h} symmetry. The components of the β tensor associated with the $\nu_4\,(A_1'')$ methylene twisting mode are entirely of weight-2 character; this mode, which is ir and Raman inactive, belongs to class E. We remark that earlier theories which have assumed full index symmetry for the β tensor failed to predict the hyper-Raman activity of such modes. For the A_1'' mode all the intensity expressions except I_1 and I_5 are expected to be nonzero and the symmetry assignment can be made unambiguously. The only nonzero β product is

$$^{2}\beta^{NM}_{\lambda\mu\nu}\,{}^{2}\beta^{NM}_{\lambda\mu\nu} = (\beta^{NM}_{7})^2\,. \tag{8.8}$$

As noted earlier the depolarization ratio $\rho_\perp$ for this type of mode is infinite, whereas the reversal ratio for forward scattering is zero.

The molecule XeF$_4$, with square planar symmetry (D_{4h}), has a $\nu_5\,(B_{2u})$ out-of-plane bending mode belonging to class B. Since this is the only vibrational mode of XeF$_4$ in this class, it may easily be characterized in a manner similar to that used for the A_u mode of ethylene. The nonzero β products are

$$^{2}\beta^{NM}_{\lambda\mu\nu}\,{}^{2}\beta^{NM}_{\lambda\mu\nu} = (\beta^{NM}_{9})^2\,, \tag{8.9}$$

$$^{3}\beta^{NM}_{\lambda\mu\nu}\,{}^{3}\beta^{NM}_{\lambda\mu\nu} = (\beta^{NM}_{15})^2\,. \tag{8.10}$$

The $\nu_3\,(A_{2u})$ out-of-plane bending vibration is an example of a class C mode (with weights 1 and 3); its nonzero β products are

$$^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1B}\beta^{NM}_{\mu\nu\nu} = \beta^{NM}_{3}\beta^{NM}_{6}\,, \tag{8.11}$$

$$^{1A}\beta^{NM}_{\lambda\lambda\mu}\,{}^{1A}\beta^{NM}_{\nu\nu\mu} = (\beta^{NM}_{3})^2\,, \tag{8.12}$$

$$^{1B}\beta^{NM}_{\lambda\mu\mu}\,{}^{1B}\beta^{NM}_{\lambda\nu\nu} = (\beta^{NM}_{6})^2\,, \tag{8.13}$$

$$^{3}\beta^{NM}_{\lambda\mu\nu}\,{}^{3}\beta^{NM}_{\lambda\mu\nu} = (\beta^{NM}_{16})^2\,. \tag{8.14}$$

Benzene (D_{6h}) has B_{1u} and B_{2u} modes belonging to class D (weight 3 only). For these modes the reversal ratio for forward scattering is 15, and the angle-independent depolarization ratio $\rho_\perp$ is 2/3. The only nonzero β products are

$$^{3}\beta^{NM}_{\lambda\mu\nu}\,{}^{3}\beta^{NM}_{\lambda\mu\nu} = (\beta^{NM}_{14})^2 \quad (B_{1u})\,, \tag{8.15}$$

$$^{3}\beta^{NM}_{\lambda\mu\nu}\,{}^{3}\beta^{NM}_{\lambda\mu\nu} = (\beta^{NM}_{13})^2 \quad (B_{2u})\,. \tag{8.16}$$

Finally, the $\nu_2(E)$ mode of methane belonging to class E (weight 2 only) can be assigned unambiguously as for the A_1'' mode of cyclopropane. However, in this case

TABLE V. Intensities of hyper-Raman scattering at right angles ($\theta = \pi/2,\ 3\pi/2$).

$I(\lambda \to \mu)$	$\parallel$	$\perp$	L	R
$\parallel \to$	I_2	I_2	I_2	I_2
$\perp \to$	I_2	I_1	I_8	I_8
$L \to$	I_3	I_7	I_6	I_6
$R \to$	I_3	I_7	I_6	I_6
$u \to$	I_{10}	I_9	I_{11}	I_{11}

the mode is also Raman active. In an experimental study of the hyper-Raman spectrum of methane[3] no strong absorption was observed around the infrared value of 1526 cm^{-1}. Our symmetry analysis indicates that this line should only be absent in the spectra for the I_1 and I_5 configurations.

IX. DISCUSSION

Recent advances in the technology of lasers and multichannel spectrometers have led to a greatly enhanced interest in hyper-Raman spectroscopy. The high intensities available from modern pulsed lasers are particularly advantageous in view of the quadratic dependence of the scattered intensity on the irradiance. Although hyper-Raman intensities are small, they may be substantially enhanced by the use of an auxiliary tunable laser to stimulate scattering at the hyper-Raman Stokes frequency. It is also possible to obtain intensity enhancement by several orders of magnitude by approaching resonance conditions.[7]

The selection rules of hyper-Raman spectra are governed by the symmetry properties of the hyperpolarizability tensor β_{ijk}. In some of the previous work a full index symmetry of this tensor was assumed and this led to the incorrect conclusion that certain modes are hyper-Raman inactive. In our work we have decomposed the β tensor into irreducible tensors of weights 1, 2, and 3, which we have used as a basis for a new classification of hyper-Raman-active modes. It has also been shown that by collecting the hyper-Raman spectra for five specified configurations it is possible to assign each active mode to one of the six classes. It is important to note that, in contrast to the Raman behavior, the selection rules for hyper-Raman scattering are the same for nonresonant and near-resonant conditions; thus, the mode classification scheme still holds.

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APPENDIX: REDUCTION OF A THIRD RANK TENSOR INTO IRREDUCIBLE PARTS

A Cartesian tensor of rank n, in general, has 3^n independent components which form the basis for a reducible representation of the rotation group; this representation can be decomposed into a set of irreducible representations. To quote a well-known example a tensor of rank 2 may be expressed as a sum of three terms

$$T_{\lambda\mu} = T_{\lambda\mu}^{(0)} + T_{\lambda\mu}^{(1)} + T_{\lambda\mu}^{(2)}, \tag{A1}$$

where

$$\left.\begin{aligned} T_{\lambda\mu}^{(0)} &= \tfrac{1}{3}\delta_{\lambda\mu}T_{\nu\nu}, \\ T_{\lambda\mu}^{(1)} &= \tfrac{1}{2}(T_{\lambda\mu} - T_{\mu\lambda}), \\ T_{\lambda\mu}^{(2)} &= \tfrac{1}{2}(T_{\lambda\mu} + T_{\mu\lambda}) - \tfrac{1}{3}\delta_{\lambda\mu}T_{\nu\nu}. \end{aligned}\right\} \tag{A2}$$

The components of each of the three terms $T_{\lambda\mu}^{(0)}$, $T_{\lambda\mu}^{(1)}$, and $T_{\lambda\mu}^{(2)}$ transform among themselves under the operations of the rotation group and form the bases for the representations of a scalar, a vector, and a symmetric traceless second rank tensor. Because of the connection with angular momentum theory, they are said to have weights $j = 0, 1, 2$, each having $(2j+1)$ components, thus accounting for the nine independent components of a second rank tensor.

A similar reduction of a tensor of rank 3 gives (see also Ref. 20)

$$T_{\lambda\mu\nu} = T_{\lambda\mu\nu}^{(0)} + \sum_{n=A,B,C} T_{\lambda\mu\nu}^{(1n)} + \sum_{n=A,B} T_{\lambda\mu\nu}^{(2n)} + T_{\lambda\mu\nu}^{(3)}. \tag{A3}$$

The number of terms of each weight in Eq. (A3) follows from the results of coupling three inequivalent P states. The irreducible tensors $T_{\lambda\mu\nu}^{(0)}$ and $T_{\lambda\mu\nu}^{(3)}$ are determined uniquely since they occur only once in the decomposition. However, for weights 1 and 2 only the sums are determined uniquely; the decomposition into independent tensors is therefore arbitrary and some additional constraint is usually required.

The weight-0 term is clearly a constant times the isotropic tensor $\epsilon_{\lambda\mu\nu}$. Hence, we write $T_{\lambda\mu\nu}$ as

$$T_{\lambda\mu\nu} = A\epsilon_{\lambda\mu\nu} + R_{\lambda\mu\nu} \equiv T_{\lambda\mu\nu}^{(0)} + R_{\lambda\mu\nu}, \tag{A4}$$

where $R_{\lambda\mu\nu}$ has no totally antisymmetric component. In other words contraction of $R_{\lambda\mu\nu}$ with $\epsilon_{\lambda\mu\nu}$ gives zero. It follows from Eq. (A4) that

$$\epsilon_{\lambda\mu\nu}T_{\lambda\mu\nu} = 6A \tag{A5}$$

and the weight-0 term is therefore

$$T_{\lambda\mu\nu}^{(0)} = \tfrac{1}{6}\epsilon_{\lambda\mu\nu}\epsilon_{\rho\sigma\tau}T_{\rho\sigma\tau}. \tag{A6}$$

Since the weight-1 terms transform like vectors, they can be expressed as the linear combination

$$\sum_{n=\alpha,\beta,\gamma} T_{\lambda\mu\nu}^{(1n)} = \delta_{\lambda\mu}B_\nu + \delta_{\lambda\nu}C_\mu + \delta_{\mu\nu}D_\lambda, \tag{A7}$$

where B_ν, C_μ, and D_λ contain the pair traces of $T_{\lambda\mu\nu}$ with the Kronecker deltas. Thus, $R_{\lambda\mu\nu}$ is a sum of Eq. (A7) and another term $R'_{\lambda\mu\nu}$ which is traceless with respect to every pair of indices. So we can write

$$\begin{aligned} T_{\lambda\mu\nu} = {} & \tfrac{1}{6}\epsilon_{\lambda\mu\nu}\epsilon_{\rho\sigma\tau}T_{\rho\sigma\tau} + \delta_{\lambda\mu}B_\nu \\ & + \delta_{\lambda\nu}C_\mu + \delta_{\mu\nu}D_\lambda + R'_{\lambda\mu\nu}, \end{aligned} \tag{A8}$$

and B_ν, C_μ, and D_λ are easily obtained from Eq. (A8) by contracting both sides with $\delta_{\lambda\mu}$, $\delta_{\lambda\nu}$, and $\delta_{\mu\nu}$. For the sum of the weight-1 terms we then have

$$\begin{aligned} \tfrac{1}{10}[& \delta_{\lambda\mu}(4T_{\rho\rho\nu} - T_{\rho\nu\rho} - T_{\nu\rho\rho}) \\ & + \delta_{\lambda\nu}(-T_{\rho\rho\mu} + 4T_{\rho\mu\rho} - T_{\mu\rho\rho}) \\ & + \delta_{\mu\nu}(-T_{\rho\rho\lambda} - T_{\rho\lambda\rho} + 4T_{\lambda\rho\rho})]. \end{aligned} \tag{A9}$$

The three sets of terms in Eq. (A9) can be regarded as the three linearly independent weight-1 terms.

The remaining term $R'_{\lambda\mu\nu}$ of Eq. (A8) is a sum of the weight-2 and weight-3 terms. The weight-2 tensors transform like traceless, symmetric second-rank tensors, and their sum can be written as

$$\sum_{n=\alpha,\beta} T_{\lambda\mu\nu}^{(2n)} = \epsilon_{\lambda\mu\tau}E_{\nu\tau} + \epsilon_{\mu\nu\tau}F_{\lambda\tau}. \tag{A10}$$

It may be pointed out that a third term of the form $\epsilon_{\lambda\nu\tau} G_{\mu\tau}$ is not required in Eq. (A10) since it can be expressed as

$$\epsilon_{\lambda\nu\tau}G_{\mu\tau} = \epsilon_{\lambda\mu\tau}G_{\nu\tau} + \epsilon_{\mu\nu\tau}G_{\lambda\tau} \,. \tag{A11}$$

The terms on the right-hand side of Eq. (A11) are of the same form as in Eq. (A10) and are therefore not required to define the sum of the weight-2 terms. The relation (A11) follows by contracting the tensor identity

$$\epsilon_{\lambda\nu\tau}\delta_{\mu\sigma} = \epsilon_{\lambda\mu\tau}\delta_{\nu\sigma} + \epsilon_{\mu\nu\tau}\delta_{\lambda\sigma} - \epsilon_{\lambda\mu\nu}\delta_{\tau\sigma} \tag{A12}$$

with the traceless $G_{\sigma\tau}$. The tensors $E_{\nu\tau}$ and $F_{\lambda\tau}$ in Eq. (A10) are readily obtained by contracting Eq. (A3) with the antisymmetric tensors $\epsilon_{\lambda\mu\tau}$ and $\epsilon_{\mu\nu\tau}$, and using the fact that $T^{(3)}_{\lambda\mu\nu}$ is symmetric in all pairs of indices. Thus, we have

$$\begin{aligned}\sum_{n=\alpha,\beta} T^{(2n)}_{\lambda\mu\nu} = {} & \tfrac{1}{6}\epsilon_{\lambda\mu\tau}(2\epsilon_{\rho\sigma\tau}T_{\rho\sigma\nu} + 2\epsilon_{\rho\sigma\nu}T_{\rho\sigma\tau} + \epsilon_{\rho\sigma\tau}T_{\nu\rho\sigma} + \epsilon_{\rho\sigma\nu}T_{\tau\rho\sigma} \\ & - 2\delta_{\nu\tau}\epsilon_{\pi\rho\sigma}T_{\pi\rho\sigma}) + \tfrac{1}{6}\epsilon_{\mu\nu\tau}(2\epsilon_{\rho\sigma\tau}T_{\lambda\rho\sigma} + 2\epsilon_{\rho\sigma\lambda}T_{\tau\rho\sigma} \\ & + \epsilon_{\rho\sigma\tau}T_{\rho\sigma\lambda} + \epsilon_{\rho\sigma\lambda}T_{\rho\sigma\tau} - 2\delta_{\lambda\tau}\epsilon_{\pi\rho\sigma}T_{\pi\rho\sigma}) \,. \end{aligned} \tag{A13}$$

The two sets of terms may be regarded as the two independent $T^{(2)}_{\lambda\mu\nu}$ tensors.

Finally, using the theorem that the weight-n part of a tensor of rank n is symmetric in all its indices and traceless with respect to every pair of indices the $T^{(3)}_{\lambda\mu\nu}$ result immediately follows:

$$\begin{aligned} T^{(3)}_{\lambda\mu\nu} = {} & \tfrac{1}{6}(T_{\lambda\mu\nu} + T_{\lambda\nu\mu} + T_{\mu\lambda\nu} + T_{\mu\nu\lambda} + T_{\nu\lambda\mu} + T_{\nu\mu\lambda}) - \tfrac{1}{15}[\delta_{\lambda\mu}(T_{\rho\rho\nu} \\ & + T_{\rho\nu\rho} + T_{\nu\rho\rho}) + \delta_{\lambda\nu}(T_{\rho\rho\mu} + T_{\rho\mu\rho} + T_{\mu\rho\rho}) \\ & + \delta_{\mu\nu}(T_{\rho\rho\lambda} + T_{\rho\lambda\rho} + T_{\lambda\rho\rho})] \,. \end{aligned} \tag{A14}$$

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