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Coherent anti-Stokes Raman spectroscopy (CARS) Selection rules, depolarization ratios and rotational structure†

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By putting the non-linear susceptibility tensors in irreducible spherical form it is found that orientation averaging, selection rules, and the angular dependence of intensity on field polarizations all follow in a straightforward way. These spherical tensor techniques are used to treat coherent anti-Stokes Raman scattering (CARS) in detail and a comparison is made with conventional Raman scattering. The selection rules for both processes are shown to be the same. The paper concludes with a brief discussion of the rotational structure in CARS.

1. INTRODUCTION

In recent years coherent anti-Stokes Raman scattering (CARS) has been attracting much interest. It could prove to be an important spectroscopic technique, since in some situations it offers great experimental advantages over the usual spontaneous Raman spectroscopy [1–5]. In CARS, just as in spontaneous Raman scattering, it is necessary to know the selection rules, and to have expressions for depolarization ratios and the rotational intensity structure. In this paper we derive these by using spherical tensor techniques.

Spherical tensors offer many advantages for calculations in isotropic media such as molecular gases or liquids and have been widely used to treat Raman scattering, for example, see [6, 7]. In particular the angular dependence on polarization vectors is given quite generally in a direct and simple way and orientation averaging can be carried out without resorting to direction cosines, etc. We give here a detailed comparison of CARS and Raman scattering‡ in order to emphasize their similarities and also because the familiar process of Raman scattering provides a convenient vehicle for introducing spherical tensor techniques which may be less well known.

It is also possible to treat higher-order processes such as hyper Raman scattering in a similar way. The material presented in this paper in fact constitutes a special case of a more general treatment of *n*th-order non-linear processes by spherical tensor methods which will be presented in a further paper. The notation and the procedure we use here have been chosen to facilitate this

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† A preliminary account of this work was presented at the IXth Int. Quantum Electronics Conf., Amsterdam, 1976. See [18].

‡ With a few simple changes (see [8]) the analysis of this paper applies also to two-photon absorption.

extension to higher-order processes. The notation and conventions are established in § 2 and in § 3 the formulae are cast into spherical tensor form and the orientation average performed. Selection rules and depolarization ratios are discussed in § 4 and the paper concludes with a discussion of rotational structure in § 5.

2. Raman and CARS intensities

We use real monochromatic plane-wave electric fields written as

$$\mathbf{E}(\omega, \mathbf{r}, t) = \tfrac{1}{2}(\boldsymbol{\epsilon} E_\omega \exp[i(\mathbf{k}\,.\,\mathbf{r} - \omega t)] + \boldsymbol{\epsilon}^* E_{-\omega} \exp[-i(\mathbf{k}\,.\,\mathbf{r} - \omega t)]), \quad E_\omega{}^* = E_{-\omega}, \tag{1}$$

where in general the unit magnitude polarization vector $\boldsymbol{\epsilon}$ is a complex linear combination of the real Cartesian unit vectors $\boldsymbol{\epsilon}_i (i \in x, y, z)$.

We define the Raman polarizability α_R as

$$\alpha_\mathrm{R} = \sum_{ij} (\alpha_\mathrm{R})_{ij} (\epsilon_\mathrm{s}{}^*)_i (\epsilon_\mathrm{p})_j \tag{2 a}$$

$$= \frac{1}{\hbar} \sum_b \left(\frac{\langle f | \boldsymbol{\epsilon}_\mathrm{s}{}^* \,.\, \mathbf{Q} | b \rangle \langle b | \boldsymbol{\epsilon}_\mathrm{p} \,.\, \mathbf{Q} | a \rangle}{\Omega_{ba} - \omega_\mathrm{p}} + \frac{\langle f | \boldsymbol{\epsilon}_\mathrm{p} \,.\, \mathbf{Q} | b \rangle \langle b | \boldsymbol{\epsilon}_\mathrm{s}{}^* \,.\, \mathbf{Q} | a \rangle}{\Omega_{ba} + \omega_\mathrm{s}} \right), \tag{2 b}$$

where $\mathbf{Q}$ is the dipole moment operator, $|a\rangle$ and $|f\rangle$ are the initial and final states, b runs over all intermediate states, $\Omega_{ba} = (E_b - E_a)/\hbar$ is a molecular transition frequency, and the subscripts p, s refer to the laser (frequency ω_p) and Stokes (frequency ω_s) radiation. It is convenient to write α_R in terms of an operator $\hat{\alpha}_\mathrm{R}$ through $\alpha_\mathrm{R} = \langle f | \hat{\alpha}_\mathrm{R} | a \rangle$.

Then α_R is related to the macroscopic Raman susceptibility by [8]

$$\chi^{(3)}(-\omega_\mathrm{s}\,;\ \omega_\mathrm{p},\ -\omega_\mathrm{p},\ \omega_\mathrm{s}) = \frac{N/(6\hbar\epsilon_0)}{\Omega_{fa} + \omega_\mathrm{s} - \omega_\mathrm{p} + i\Gamma} \frac{\rho(a)}{g_a} \sum_{\deg f,a} \overline{|\langle f | \hat{\alpha}_\mathrm{R} | a \rangle|^2}, \tag{3}$$

where N is the number density of molecules, Γ is a damping constant, $\sum_{\deg f,a}$ is a sum over the degenerate states of energy $\hbar\Omega_f$ and $\hbar\Omega_a$ and $\rho(a)$ is the fraction of population in the g_a-fold degenerate initial level. The horizontal bar denotes an orientation average. (Note that SI units are used throughout this paper.)

To make the connection between the susceptibility formalism and the more usual (for Raman scattering) expressions in terms of a cross section $d\sigma_\mathrm{R}/d\Omega$ we note that

$$6\chi^{(3)}(-\omega_\mathrm{s}\,;\ \omega_\mathrm{p},\ -\omega_\mathrm{p},\ \omega_\mathrm{s}) = \frac{16\pi^2\epsilon_0 c^4 N/\hbar\omega_\mathrm{p}\omega_\mathrm{s}{}^3}{\Omega_{fa} + \omega_\mathrm{s} - \omega_\mathrm{p} + i\Gamma} \frac{d\sigma_\mathrm{R}}{d\Omega}. \tag{4}$$

The differential cross section per molecule $d\sigma_\mathrm{R}/d\Omega$ is defined in terms of the ratio of the *number* of scattered to incident photons (rather than the ratio of *powers*) and has been integrated over all Stokes frequencies.

The spontaneous Raman power P_R scattered from a length l of medium into a solid angle $d\Omega$ is given by

$$P_\mathrm{R} = \frac{N l \omega_\mathrm{s}{}^4}{16\pi^2\epsilon_0{}^2 c^4} P_\mathrm{p}\, d\Omega \left\{ g_a{}^{-1} \rho(a) \sum_{\deg f,a} \overline{|\alpha_\mathrm{R}|^2} \right\}, \tag{5}$$

where P_p is the pump power. This establishes our notation for Raman scattering, and in deriving selection rules, depolarization ratios, etc. only the expression in braces need be considered.

We now write down expressions analogous to (2), (3) and (5) for CARS. The nature of the CARS process has been described in detail in the literature [1] and we need only summarize briefly here. It is a four-wave parametric process in which three waves (two of frequency ω_p, one of frequency ω_s) are mixed to generate a fourth wave of frequency ω_{as} (the anti-Stokes frequency) given by $\omega_{as} = 2\omega_p - \omega_s$. By analogy with the Raman polarizability we define a CARS polarizability :

$$\alpha_{\mathrm{CARS}} = \sum_{ij} (\alpha_{\mathrm{CARS}})_{ij} (\epsilon_p{}^*)_i (\epsilon_{as})_j \tag{6 a}$$

$$= \frac{1}{\hbar} \sum_b \left(\frac{\langle f | \boldsymbol{\epsilon}_p{}^* . \mathbf{Q} | b \rangle \langle b | \boldsymbol{\epsilon}_{as} . \mathbf{Q} | a \rangle}{\Omega_{ba} - \omega_{as}} + \frac{\langle f | \boldsymbol{\epsilon}_{as} . \mathbf{Q} | b \rangle \langle b | \boldsymbol{\epsilon}_p{}^* . \mathbf{Q} | a \rangle}{\Omega_{ba} + \omega_p} \right). \tag{6 b}$$

In terms of this polarizability, the CARS susceptibility $\chi_{\mathrm{CARS}} \equiv \chi^{(3)}(-\omega_{as} ; \omega_p, \omega_p, -\omega_s)$ can be written as

$$\chi_{\mathrm{CARS}} = \chi_{\mathrm{NR}} + \frac{N/(3\hbar\epsilon_0)}{\Omega_{fa} + \omega_s - \omega_p + i\Gamma} \frac{\rho(a)}{g_a} \sum_{\deg f, a} \overline{\langle f | \hat{\alpha}_{\mathrm{CARS}} | a \rangle^* \langle f | \hat{\alpha}_{\mathrm{R}} | a \rangle}. \tag{7}$$

χ_{NR} is a non-resonant term which produces a background in the CARS spectrum that is (usually) unwanted. For the most part we will assume the resonant part of the CARS susceptibility to dominate and so, unless otherwise stated, shall put $\chi_{\mathrm{NR}} = 0$. The intensity I_{as} (W m^{-2}) of the generated anti-Stokes radiation is found by the usual coupled wave approach [1] to be

$$I_{as} = \frac{\omega_{as}{}^2}{\eta_{as} \eta_p{}^2 \eta_s \epsilon_0{}^2 c^4} \left| \tfrac{3}{4} \chi_{\mathrm{CARS}} \right|^2 l^2 I_p{}^2 I_s \operatorname{sinc}^2 \left(\frac{\Delta k l}{2} \right), \tag{8}$$

where η_i is the refractive index at frequency ω_i, l is the interaction length and Δk is the wave vector mismatch, i.e. $\Delta k = 2k_p - k_s - k_{as}$. The dependence of I_{as} on the square of the CARS susceptibility is characteristic of parametric processes. A word of caution should be given here about the varying numerical factors ($\frac{9}{16}$ in our case) which different authors give in their versions of equation (8). These numerical factors have been discussed in detail by Orr and Ward [9], and Bogaard and Orr [10] have reconciled the differences arising from different conventions. Apart from a factor ϵ_0 which we incorporate in our definition of susceptibility (see [8]), our conventions are the same as those of Bogaard and Orr.

When α_{R} and α_{CARS} are non-resonant, i.e. all interacting frequencies are well away from any Ω_{ba}, it is usual to write $\alpha_{\mathrm{R}} = \alpha_{\mathrm{CARS}}$ and then (4) and (7) are combined to express χ_{CARS} in terms of $d\sigma_{\mathrm{R}}/d\Omega$. Clearly in the case of resonant Raman scattering or resonant CARS this equality need not apply. To preserve the generality of our treatment we avoid this assumption of equality here and using (7) and (8) we see that

$$I_{as} \propto \left| g_a{}^{-1} \rho(a) \sum_{\deg f, a} \overline{\alpha_{\mathrm{CARS}}{}^* \alpha_{\mathrm{R}}} \right|^2. \tag{9}$$

The close analogy between the expression in braces in (5) and the right-hand side of (9) can be seen. It is the latter expression from which the selection rules, etc. for CARS are to be derived.

3. Spherical tensor form and orientation averaging

As the reduction of $(\alpha_{\rm R})_{ij}$ to spherical tensor form is well known [11] we merely summarize here by stating that, by using the complex spherical coordinates (unit vectors $\mathbf{e}_q$, $q \equiv 0, \pm 1$) defined as

$$\left.\begin{aligned} \mathbf{e}_{\pm 1} &= \mp(\mathbf{e}_x \pm i\mathbf{e}_y)/\sqrt{2}, \\ \mathbf{e}_0 &= \mathbf{e}_z, \end{aligned}\right\} \tag{10}$$

then $(\alpha_{\rm R})_{ij}$ can be written in terms of $(\alpha_{\rm R})_{qq'}$.

The Raman spherical tensor is then given by

$$(\alpha_{\rm R})_Q{}^K = \sum_{qq'} \langle 1q1q' | KQ \rangle (\alpha_{\rm R})_{qq'}, \tag{11}$$

where the term in angular brackets is a Clebsch–Gordan coefficient. The rank K can take the values 0, 1 or 2, analagous to the S, P, D atomic terms arising from the coupling of two p electrons.

Similarly the polarization vectors $\boldsymbol{\epsilon}_{\rm p}$, $\boldsymbol{\epsilon}_{\rm s}$ may be coupled to form a spherical tensor

$$(\boldsymbol{\epsilon}_{\rm s}{}^*\boldsymbol{\epsilon}_{\rm p})_Q{}^K = \sum_{qq'} \langle 1q1q' | KQ \rangle (\epsilon_{\rm s}{}^*)_q (\epsilon_{\rm p})_{q'}. \tag{12}$$

Equations (2 *a*), (10)–(12) yield the result that

$$\alpha_{\rm R} = \sum_{KQ} (-1)^{K+Q} (\alpha_{\rm R})_Q{}^K (\boldsymbol{\epsilon}_{\rm s}{}^*\boldsymbol{\epsilon}_{\rm p})_{-Q}{}^K \equiv \sum_K (-1)^K (\boldsymbol{\alpha}_{\rm R})^K \cdot (\boldsymbol{\epsilon}_{\rm s}{}^*\boldsymbol{\epsilon}_{\rm p})^K. \tag{13}$$

It may then be shown (by the use of rotation matrices, or by group theoretical arguments) that

$$\overline{|\alpha_{\rm R}|^2} = \sum_{KQ} (2K+1)^{-1} |(\alpha_{\rm R})_Q{}^K|^2 \Theta_{\rm R}{}^K, \tag{14 a}$$

where

$$\Theta_{\rm R}{}^K = (\boldsymbol{\epsilon}_{\rm s}{}^*\boldsymbol{\epsilon}_{\rm p})^K \cdot (\boldsymbol{\epsilon}_{\rm p}{}^*\boldsymbol{\epsilon}_{\rm s})^K. \tag{14 b}$$

The angular factor $\Theta_{\rm R}{}^K$ has been evaluated for all combinations of linearly and circularly polarized light [8] and these results are summarized in table 1. For the special case of light linearly polarized along cartesian axes ρ, σ (14 *a*) becomes

$$\overline{|(\alpha_{\rm R})_{\rho\sigma}|^2} = \sum_{KQ} (2K+1)^{-1} |(\alpha_{\rm R})_Q{}^K|^2 C_{\rho\sigma}{}^K, \tag{14 c}$$

where $C_{\rho\sigma}{}^K$ can be written down from table 1. The equation (14 *c*) is exactly that given by Koningstein [7, 11]. Sharma and Levin [12] have obtained some of these factors for the special case of symmetric rotors but their procedure is very lengthy. Damen *et al.* [13] have experimentally confirmed these factors for linearly polarized light. Some care is needed in relating the results of table 1 to the particular geometry of their experiment.

Table 1. Angular factor $\Theta_R{}^K$ for Raman scattering (see also [8]).

Polarization vectors	$K=0$	$K=1$	$K=2$
Both linear†	$\frac{1}{3}\cos^2\beta_s$	$\frac{1}{2}\sin^2\beta_s$	$\frac{1}{6}(3+\cos^2\beta_s)$
Both circular‡			
Same sense	$\frac{1}{3}$	$\frac{1}{2}$	$\frac{1}{6}$
Opposite sense	0	0	1

† β_s is the angle between $\boldsymbol{\epsilon}_s$, $\boldsymbol{\epsilon}_p$.
‡ Propagation of both beams in same direction.

For CARS, $(\alpha_{\rm CARS})_Q{}^K$ is defined in an exactly analogous way to $(\alpha_R)_Q{}^K$, and this yields

$$\overline{\alpha_{\rm CARS}{}^*\alpha_R} = \sum_{KQ}(2K+1)^{-1}(\alpha_{\rm CARS})_Q{}^{K*}(\alpha_R)_Q{}^K\Theta_{\rm CARS}{}^K, \qquad (15\,a)$$

where

$$\Theta_{\rm CARS}{}^K = (-1)^K(\boldsymbol{\epsilon}_{\rm AS}{}^*\boldsymbol{\epsilon}_p)^K\,.\,(\boldsymbol{\epsilon}_p\boldsymbol{\epsilon}_s{}^*)^K. \qquad (15\,b)$$

This angular factor can be evaluated in a similar fashion to $\Theta_R{}^K$. In table 2 $\Theta_{\rm CARS}{}^K$ has been evaluated for two cases : (i) where all the waves are linearly polarized with polarization vectors lying in the same plane and (ii) where all the waves are circularly polarized in the same sense and propagating collinearly. Since the usual experimental arrangement for CARS involves approximately collinear beams (to ensure a significant interaction length) these two cases are the ones of most interest. It is readily seen that for linearly polarized light with $\beta_{as}=\beta_s$, then $(-1)^K\Theta_R{}^K=\Theta_{\rm CARS}{}^K$.

Table 2. Angular factor $\Theta_{\rm CARS}{}^K$ for CARS.

Polarization vectors	$K=0$	$K=1$	$K=2$
All linear†	$\frac{1}{3}\cos\beta_s\cos\beta_{as}$	$-\frac{1}{2}\sin\beta_s\sin\beta_{as}$	$\frac{1}{6}[4\cos\beta_s\cos\beta_{as}$ $+3\sin\beta_s\sin\beta_{as}]$
All circular‡			
Same sense	$\frac{1}{3}$	$\frac{1}{2}$	$\frac{1}{6}$

† β_s is angle between $\boldsymbol{\epsilon}_s$, $\boldsymbol{\epsilon}_p$; β_{as} is angle between $\boldsymbol{\epsilon}_{as}$, $\boldsymbol{\epsilon}_p$; $\boldsymbol{\epsilon}_s$, $\boldsymbol{\epsilon}_{as}$, $\boldsymbol{\epsilon}_p$ are coplanar. In [18], for $K=2$, cos β_{as} should be cos β_s.

‡ Propagation of all beams in same direction. For other senses of polarization the factor vanishes.

Equation (15 *b*) also applies to $\chi_{\rm NR}$, which may be expressed as

$$\chi_{\rm NR} = \sum_K (2K+1)^{-1}\chi_{\rm NR}(K)\Theta_{\rm CARS}{}^K.$$

However, the ' physical ' selection rules on K (discussed in the next section) do not apply to $\chi_{\rm NR}(K)$, and $\chi_{\rm NR}$ therefore consists of an indeterminate sum over the

${\Theta_{\mathrm{CARS}}}^K$ of different K†. It is in fact quite easy to show that any third-order susceptibility $\chi^{(3)}$ can be expressed as a sum over angular factors as in (15 *b*), with (in general) four different polarization vectors.

3. SELECTION RULES AND DEPOLARIZATION RATIOS

We make a distinction here between two classes of selection rules. The ' physical ' selection rules give the conditions under which $(\alpha_{\mathrm{R}})_Q{}^K$ or $(\alpha_{\mathrm{CARS}})_Q{}^K$ are non-vanishing whereas the ' geometrical ' selection rules give the conditions under which ${\Theta_{\mathrm{R}}}^K$ or ${\Theta_{\mathrm{CARS}}}^K$ are non-vanishing.

Now $(\alpha_{\mathrm{R}})_Q{}^K$ in equation (13) can be rewritten as $\langle f|(\hat{\alpha}_{\mathrm{R}})_Q{}^K|a\rangle$, where $(\hat{\boldsymbol{\alpha}}_{\mathrm{R}})^K$ is an irreducible spherical tensor operator. Similarly we can rewrite $(\alpha_{\mathrm{CARS}})_Q{}^K$ in (15 *a*) as $\langle f|(\hat{\alpha}_{\mathrm{CARS}})_Q{}^K|a\rangle$. These Raman and CARS spherical tensor operators of rank K belong to the irreducible representation (IR) ${D_g}^K$ of the full rotation–reflection group. Let ${D_g}^K$ decompose into a sum, denoted by $\{{D_g}^K\}$, over IR's of the molecular point group G and let $|a\rangle$ and $|f\rangle$ belong to the IR's $\Gamma(f)$, $\Gamma(a)$ of G. The identity IR of G is Γ_{E}. Then the ' physical ' selection rules for Raman and CARS are the same, viz. that

$$\Gamma_{\mathrm{E}} \in \Gamma(f)^* \times \{{D_g}^K\} \times \Gamma(a) \tag{16}$$

must be satisfied. If it is, then this means that for some Q in (14 *a*) and (15 *a*) the matrix elements are allowed. As all Q values are summed over it is sufficient therefore that (16) be satisfied—there is no need for a selection rule on the components labelled by Q. This is to be expected, for (14 *a*) and (15 *a*) describe orientation averaged media and so all operator components labelled Q are involved. For example, in electric dipole radiation it might be possible to assign (x, y) and z to separate IR's. However, in a gas, components of electric field exist along all axes x, y, z and so it is only necessary to know the aggregate of IR's to which (x, y, z) belong, i.e. $\{{D_g}^K\}$. (In fact the sum over Q must occur for an orientation averaged expression—it forms a scalar product of the two polarizabilities and this is needed to provide the required invariance under all proper rotations.)

Degeneracy of $|a\rangle$, $|f\rangle$ does not affect (16) as only the IR's $\Gamma(f)$, $\Gamma(a)$ are needed. For simplicity we shall ignore degeneracy (except in § 5 on rotational structure) as it does not affect our main line of argument.

The selection rule (16) is rigorous within the electric dipole approximation. However, more detailed physical considerations will often allow one to ' factorize ' (16). For example, if it is a good approximation to write both the initial and final states in the form of a product of a vibrational (v) and electronic (e) part, then (16) becomes

$$\Gamma_{\mathrm{E}} \in \Gamma(e_f)^* \times \{{D_g}^K\} \times \Gamma(e_a) \tag{17 a}$$

for pure electronic scattering. For vibrational scattering $(e_f = e_a)$

$$\Gamma_{\mathrm{E}} \in \Gamma(v_f)^* \times \{{D_g}^K\} \times \Gamma(v_a), \tag{17 b}$$

provided e_a is non-degenerate. In the latter case only $K = 0,2$ should be used. If level e_a is degenerate, or if electronic scattering is considered (i.e. $e_f \neq e_a$), then

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† An exception to this is that in the factorization approximation (discussed in § 3) and with a non-degenerate initial electronic state, the $K = 1$ term vanishes.

$K=1$ may be allowed by (17 *a*). From table 1 it can be seen that if only the $K=1$ term is present, then with a linearly polarized pump the Stokes radiation is linearly polarized perpendicular to the pump.

In the case of resonant Raman scattering it is well known that the approximate selection rules (17 *a*, *b*) break down and the rigorous rule (16) must be used. The same is true of resonant CARS and important consequences of this are discussed in the next paragraph. First, however, we give an example from electronic Raman scattering in alkali atoms which illustrate very clearly the effect that an intermediate resonance can have in the selection rules. We assume the scattering to take place between ${}^2S_{1/2}$ initial and final states, and the intermediate states (see (2 *b*)) can therefore only be ${}^2P_{1/2,3/2}$ doublets. The selection rule (16) leads simply to the requirement that the three numbers ($J_a=\frac{1}{2}$, K, $J_f=\frac{1}{2}$) should satisfy the vector model triangle rule, so that $K=0$, 1 only are allowed. However, the absence of spin–orbit interaction in a ${}^2S_{1/2}$ state tempts one to write the wave functions for this state as a product of an orbital function and a spin function even though this may not be a good description of the intermediate state. In fact it is not immediately obvious that the mode of description of the intermediate state is of any relevance since it does not appear explicitly in the selection rules (16) or (17). The operator $(\hat{\alpha}_R)^K$ does not operate on the spin part of the wave function and the selection rule (17) then leads to the triangle rule on ($L_a=0$, K, $L_f=0$), i.e. $K=0$ only is allowed. In fact a study of (2) in the case of alkali atoms [8] shows that the $K=1$ term vanishes when ω_p is well removed from the ${}^2S_{1/2}\rightarrow{}^2P_{1/2,3/2}$ transitions (off-resonance case), hence the approximate selection rule, $K=0$ only, is well satisfied. However, when ω_p is close to resonance with the ${}^2S_{1/2}\rightarrow{}^2P_{1/2,3/2}$ transition the $K=1$ term becomes large and can actually dominate the $K=0$ term. This has been verified experimentally in the case of stimulated electronic Raman scattering in caesium [14] and leads to a flipping over of $\boldsymbol{\epsilon}_s$ from $\boldsymbol{\epsilon}_s \| \boldsymbol{\epsilon}_p$ to $\boldsymbol{\epsilon}_s \perp \boldsymbol{\epsilon}_p$. Put in a more general way, the operator $(\hat{\alpha}_R)^K$ is to a good approximation spin-independent if non-resonant, whence the orbital selection rule is satisfactory. When a resonance occurs, the operator becomes strongly spin-dependent inasmuch as the intermediate state multiplet structure is important, and so the selection rules must involve the multiplet description of initial and final states. This shows that the description of $|a\rangle$ and $|f\rangle$ used in (16) or (17) must be of a form compatible with the description of the intermediate states, and in the resonance situation considered above the intermediate state is not well described as a product function.

Now it has been proposed [4] to increase sensitivity in CARS by resonantly enhancing α_R or α_{CARS} so that I_{as} is increased and the effects of background diminished. It is quite possible then that the selection rules for CARS will *effectively* be different from Raman scattering. Because of the resonance it may be necessary to use (16) for α_R (or α_{CARS}), whereas (17) is adequate for α_{CARS} (or α_R). This combination of (16) and (17) can change the selection rules. Consider again the case of alkali atoms. Resonant Raman scattering allows $K=0$, 1 in α_R, by (16). If for the CARS process α_{CARS} is non-resonant, (17) allows $K=0$ only. Hence to a very good approximation $\alpha_{CARS}{}^*\alpha_R$ is non-zero for $K=0$ only, and the selection rules for the two processes are different. If however α_{CARS} were resonant but not α_R, then for both processes $K=0$ only would be allowed by (17) and the (approximate) rules therefore are the same. Thus, while (16) is always exact, showing the selection rules for Raman and CARS to be identical, physical information about resonance may effectively alter the application of approximations such as (17) to the extent that the rules may appear different for the two processes. Additionally there obviously is no reason for α_{R} and α_{CARS} to have the same magnitude when resonances occur.

The value of the geometrical selection rules is that they provide information on the appropriate choice of geometry and polarization for a Raman or CARS depolarization measurement, which in turn provides information on state symmetries. The results for Raman scattering are usually summarized in the form of depolarization ratios. The connection between the spherical tensor polarizability $(\alpha_{\mathrm{R}})^K$ and the usual isotropy (α^2) and anisotropy (γ^2) terms is

$$\alpha^2 = \tfrac{1}{3}\left|(\alpha_{\mathrm{R}})_0{}^0\right|^2, \tag{18 a}$$

$$\gamma_{\mathrm{a}}{}^2 = \tfrac{3}{2}\sum_Q \left|(\alpha_{\mathrm{R}})_Q{}^1\right|^2, \tag{18 b}$$

$$\gamma_{\mathrm{s}}{}^2 = \tfrac{3}{2}\sum_Q \left|(\alpha_{\mathrm{R}})_Q{}^2\right|^2, \tag{18 c}$$

where $\gamma_{\mathrm{a}}{}^2$ and $\gamma_{\mathrm{s}}{}^2$ are the antisymmetric and symmetric parts respectively of γ^2. Thus from (14 *a*) we see that the angular dependence of Raman scattering is given by

$$\overline{|\alpha_{\mathrm{R}}|^2} = 3\alpha^2\Theta_{\mathrm{R}}{}^0 + \tfrac{2}{9}\gamma_{\mathrm{a}}{}^2\Theta_{\mathrm{R}}{}^1 + \tfrac{2}{15}\gamma_{\mathrm{s}}{}^2\Theta_{\mathrm{R}}{}^2. \tag{19}$$

Use of (19) and table 1 give the depolarization ratios immediately. For example, considering a linearly polarized pump, then the ratio of intensities of Stokes radiation polarized $\perp$ and $\|$ to the pump is given by

$$\rho_l = \frac{I_{\mathrm{R}}(\perp)}{I_{\mathrm{R}}(\|)} = \frac{5\gamma_{\mathrm{a}}{}^2 + 3\gamma_{\mathrm{s}}{}^2}{45\alpha^2 + 4\gamma_{\mathrm{s}}{}^2}. \tag{20}$$

When $\gamma_{\mathrm{a}}{}^2 = 0$ (the usual case for non-resonant ro-vibrational scattering) then (20) reduces to the usual textbook value. If $\gamma_{\mathrm{a}}{}^2$ only is non-zero (i.e. $K = 1$ only is allowed), then ρ_l is infinite.

For CARS one can, by analogy with (18) define $\bar{\alpha}^2$, $\bar{\gamma}_{\mathrm{a}}{}^2$ and $\bar{\gamma}_{\mathrm{s}}{}^2$ where the correspondence $\left|(\alpha_{\mathrm{R}})_Q{}^K\right|^2 \rightarrow (\alpha_{\mathrm{CARS}})_Q{}^{K*}(\alpha_{\mathrm{R}})_Q{}^K$ is made. Then the angular dependence of the CARS intensity is determined by the expression

$$\left|3\bar{\alpha}^2\Theta_{\mathrm{CARS}}{}^0 + \tfrac{2}{9}\bar{\gamma}_{\mathrm{a}}{}^2\Theta_{\mathrm{CARS}}{}^1 + \tfrac{2}{15}\bar{\gamma}_{\mathrm{s}}{}^2\Theta_{\mathrm{CARS}}{}^2\right|^2. \tag{21}$$

If for linearly polarized light we write $I_{\mathrm{as}} = I_{\mathrm{as}}(\beta_{\mathrm{s}}, \beta_{\mathrm{as}})$, where β_{s} is the angle between the polarization vectors $\boldsymbol{\epsilon}_{\mathrm{s}}$ and $\boldsymbol{\epsilon}_{\mathrm{p}}$ and β_{as} the corresponding angle between $\boldsymbol{\epsilon}_{\mathrm{as}}$ and $\boldsymbol{\epsilon}_{\mathrm{p}}$, with all three vectors in the same plane, then from (21) and table 2, we have

$$\frac{I_{\mathrm{as}}(\perp, \perp)}{I_{\mathrm{as}}(\|, \|)} = \left|\frac{-5\bar{\gamma}_{\mathrm{a}}{}^2 + 3\bar{\gamma}_{\mathrm{s}}{}^2}{45\bar{\alpha}^2 + 4\bar{\gamma}_{\mathrm{s}}{}^2}\right|^2. \tag{22}$$

If we consider the most usual situation of $\bar{\gamma}_{\mathrm{a}}{}^2 = 0$, it is seen that the depolarization ratio defined in (22) takes the value zero for a completely polarized line and $\frac{9}{16}$ for a depolarized line ($\bar{\alpha}^2 = 0$). The latter is to be compared with the value of $\frac{3}{4}$ obtained for a depolarized line in Raman scattering. The ratios defined in (20) and (22) are rather similar and suffer from the disadvantage that it is difficult to determine whether a line is depolarized or partially polarized. However, using the freedom of the extra geometries that CARS can offer (three polarization vectors at our disposal rather than two in the case of Raman scattering) other depolarization ratios can be defined. For the remaining ' 90° ' geometries, we see from table 2 that $I_{\mathrm{as}}(\parallel, \perp)$ and $I_{\mathrm{as}}(\perp, \parallel)$ vanish. This follows from the isotropy of the medium introduced by orientation averaging. For example, if one chooses the particular polarization vectors $\boldsymbol{\epsilon}_{\mathrm{p}} = \boldsymbol{\epsilon}_{\mathrm{s}} = \mathbf{e}_z$ and $\boldsymbol{\epsilon}_{\mathrm{as}} = \mathbf{e}_x$ then $\alpha_{\mathrm{CARS}}{}^*\alpha_{\mathrm{R}} = (\alpha_{\mathrm{CARS}})_{xz}{}^*(\alpha_{\mathrm{R}})_{zz}$ and hence $\chi_{\mathrm{CARS}} = (\chi_{\mathrm{CARS}})_{xzzz}$. But this component of a fourth-rank tensor vanishes in an isotropic medium, as is well known (see, for example, [15]).

The use of circularly polarized radiation can offer some advantages in Raman scattering depolarization studies [16] and it is therefore of interest to consider if this is also true for CARS. It can be seen from table 2 that, when using circularly polarized light, I_{as} is non-zero only when the polarizations all have the same sense, i.e. $\boldsymbol{\epsilon}_{\mathrm{p}} = \boldsymbol{\epsilon}_{\mathrm{s}} = \boldsymbol{\epsilon}_{\mathrm{as}} = \mathbf{e}_{\pm 1}$. This requirement can also be deduced using an argument based on conservation of angular momentum. For if $\boldsymbol{\epsilon}_{\mathrm{p}} = \mathbf{e}_{q_p}$ $(q_{\mathrm{p}} = \pm 1)$, and so on for $\boldsymbol{\epsilon}_{\mathrm{s}}$, $\boldsymbol{\epsilon}_{\mathrm{as}}$, then the net change of angular momentum of the molecule as a result of the CARS process is $(2q_{\mathrm{p}} - q_{\mathrm{s}} - q_{\mathrm{as}})\hbar$. As the molecule ends up in the same state as its initial state (CARS is a parametric process) this change of angular momentum must be zero. Then as $2q_{\mathrm{p}} = \pm 2$, one must have $q_{\mathrm{s}} = q_{\mathrm{as}} = q_{\mathrm{p}}$. Clearly no ratio where all vectors are circularly polarized (and for collinear propagation) can be defined.

Returning to arrangements using linearly polarized light, and taking $\beta_s = \tan^{-1}(\frac{4}{3})$ and $\beta_{\mathrm{a}s} = \pm \pi/4$, we can define a ratio

$$\frac{I_{\mathrm{as}}\left(\tan^{-1}(\frac{4}{3}), -\dfrac{\pi}{4}\right)}{I_{\mathrm{as}}\left(\tan^{-1}(\frac{4}{3}), \dfrac{\pi}{4}\right)} = \left| \frac{45\bar{\alpha}^2 + (20/3)\bar{\gamma}_{\mathrm{a}}{}^2}{45\bar{\alpha}^2 - (20/3)\bar{\gamma}_{\mathrm{a}}{}^2 + 8\bar{\gamma}_{\mathrm{s}}{}^2} \right|^2. \tag{23}$$

Now if $\bar{\gamma}_{\mathrm{a}}{}^2 = 0$, then we see that in (23) the roles of $\bar{\alpha}^2$ and $\bar{\gamma}_{\mathrm{s}}{}^2$ are interchanged compared to (20) and (22) and measurement of this ratio could perhaps provide a better discrimination when nearly depolarized lines are being investigated. It should be emphasized however that the usefulness of CARS depolarization measurements through (22) and (23) will ultimately depend on the magnitude of the background χ_{NR} since the term corresponding to the background contribution must be added to numerator and denominator in (22) and (23). Other ratios may of course be defined and the use of table 2 makes their evaluation straightforward.

4. ROTATIONAL STRUCTURE

For a free molecule, any of its states may be written as $|\tau JM\rangle$ where J is the total angular momentum, M its projection on the space-fixed z-axis and τ labels any additional quantum numbers. Then from the Wigner–Eckart theorem

$$\sum_{M_f} \sum_{Q} |\langle \tau_f J_f M_f | (\hat{\alpha}_{\mathrm{R}})_Q{}^K | \tau_a J_a M_a \rangle|^2 = (2J_a + 1)^{-1} |\langle \tau_f J_f \| (\hat{\boldsymbol{\alpha}}_{\mathrm{R}})^K \| \tau_a J_a \rangle|^2, \tag{24}$$

where the $\sum_{\deg f}$ in (3) has become the $\sum_{M_f}$ in (24). Since from the right-hand side (24) can be seen to be independent of M_a, it follows that if the summation operation $g_a^{-1}\sum_{\deg a} = (2J_a+1)^{-1}\sum_{M_a}$ is carried out it simply multiplies each side by unity. It is of interest to note that the orientation average for an atom or rotating molecule is usually carried out by this last sum and the fact that this summation leaves (24) unchanged confirms that an orientation average has indeed been carried out.

A further reduction of (24) can be made by refining the state descriptions. For example, given a symmetric rotor with states $|\gamma JKM\rangle$ it may be shown that (24) is

$$(2J_a+1)^{-1}\mathscr{L}^K(f,a)S_{\mathrm{R}}^K(f,a) \tag{25}$$

where the rotational structure factor $\mathscr{L}^K(f,a)$ is (assuming totally symmetric vibronic states)

$$\mathscr{L}^K(f,a) = (2J_a+1)(2J_f+1)\begin{pmatrix} J_f & K & J_a \\ -K_a & 0 & K_a \end{pmatrix}^2 \tag{26}$$

and the Raman line strength $S_{\mathrm{R}}^K(f,a)$ is

$$S_{\mathrm{R}}^K(f,a) = |\langle\gamma_f|(\hat{\alpha}_{\mathrm{R}})_0^K|\gamma_a\rangle|^2. \tag{27}$$

The matrix element in (27) is evaluated in the molecule-fixed frame. Note that the quantum number K_a is not to be confused with the tensor rank, K.

By analogy with (27), we write for CARS,

$$S_{\mathrm{CARS}}^K(f,a) = \langle\gamma_f|(\hat{\alpha}_{\mathrm{CARS}})_0^K|\gamma_a\rangle^*\langle\gamma_f|(\hat{\alpha}_{\mathrm{R}})_0^K|\gamma_a\rangle. \tag{28}$$

Then from (5), (14 a), (24) and (25) it can be seen that the Raman scattered intensity is proportional to

$$(2J_a+1)^{-1}\rho(\gamma_aJ_aK_a)\sum_K (2K+1)^{-1}\mathscr{L}^K(f,a)S_{\mathrm{R}}^K(f,a)\Theta_{\mathrm{R}}^K \tag{29}$$

and from (9), (15 a), (24) and (25) (with $S_{\mathrm{CARS}}^K(f,a)$ replacing $S_{\mathrm{R}}^K(f,a)$), the anti-Stokes intensity is found to be proportional to

$$|(2J_a+1)^{-1}\rho(\gamma_aJ_aK_a)\sum_K (2K+1)^{-1}\mathscr{L}^K(f,a)S_{\mathrm{CARS}}^K(f,a)\Theta_{\mathrm{CARS}}^K|^2. \tag{30}$$

From (26) we see that (J_a, K, J_f) must form a triangle and this selection rule is supplemented by the vibronic selection rules on (27), (28). The remarks made above concerning (16), (17) apply here of course—the factorization implicit in the labels γJKM may not be possible. (The triangle rule is a consequence of an equation (17 c) for rotational motion, viz. $\Gamma_{\mathrm{E}} = D_g^0 \in D_{(g,u)}^{J_f}\times D_g^K \times D_{(g,u)}^{J_a}$ where (g, u) is needed if the molecule possesses a centre of symmetry.)

We have assumed totally symmetric vibronic states (apart from g, u labelling), but this is not necessary. Then the main differences are that the $3j$ symbol is replaced by

$$\begin{pmatrix} J_f & K & J_a \\ -K_f & K_f-K_a & K_a \end{pmatrix}^2$$

and that in (27) and (28) the $Q' = K_f - K_a$ components of the tensor operators appear (rather than $Q' = 0$). Thus despite the fact that (24) was summed over

Q, (27) and (28) depend on the $Q' = K_f - K_a$ components of the Kth-rank tensors. This follows from the factorization of the states and the evaluation of the reduced matrix elements : Q' is not the Q in (24). Then (17) is supplemented by the rules on K_a, K_f implicit in the $3j$ symbol in (26) and any rules imposed by γ_a, γ_f. However, in some cases (not treated here) of non-totally symmetric vibronic states the factorization (25) cannot be made so simply.

For atoms $\mathscr{L}_{\mathrm{Atom}}{}^K(f, a) = 1$, the matrix elements in (27), (28) become reduced matrix elements like $\langle \gamma_f J_f \| (\hat{\boldsymbol{\alpha}}_{\mathrm{R}})^K \| \gamma_a J_a \rangle$ and the triangle rule is of course the embodiment of the rigorous rule (16).

The results of (29) and (30) show the power of the spherical tensor technique, for one sees that the intensity structure is the same for both Raman and CARS and indeed for the Kth-rank part of any non-linear process which can be written in the form (7).

By comparing (24)–(29) with other treatments (e.g. [17]) there should be no difficulty in writing down expressions analogous to (25) for other cases, such as diatomic molecules with electronic angular momentum. These factors and the absolute calculation of the line strength (including intermediate state rotational structure) will be discussed fully in a later paper dealing with nth-order non-linear processes.

5. DISCUSSION

We have used spherical tensor techniques to treat the coherent anti-Stokes Raman scattering process and have derived the orientation averaged susceptibility, the selection rules, and the angular dependence on polarization vectors. A brief discussion of rotational structure in CARS has also been given. For comparison the well-known case of Raman scattering was also treated, with the advantage that many results from Raman work can be used in CARS. The selection rules for CARS were discussed in detail, as they have been a source of confusion in the past. One can summarize these by saying that the rigorous rules are the same, but that in making the usual *approximations* to these rules (such as separation of vibrational and electronic states) care has to be taken if resonances occur. In the presence of resonances the same approximations cannot always be made for both processes, with the result that effectively the rules may differ.

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For CARS, Stimulated Raman Scattering and Two Photon Absorption/Emission, $g_a^{-1}\rho(a)$ should be replaced by $g_a^{-1}\rho(a) - g_f^{-1}\rho(f)$. This correction is particularly important in rotational CARS, and this can limit some applications.