Vibrational contributions to the hyperpolarizabilities of homonuclear diatomic molecules

by D. P. SHELTON

Department of Physics, University of Manitoba, Winnipeg,
Manitoba, R3T 2N2, Canada

An expression for the off-resonance vibrational contribution to the hyper-polarizability of a homonuclear diatomic molecule is derived. This expression is written in terms of the Raman transition polarizability, and it explicitly gives the frequency dependence of all the independent tensor components of the hyperpolarizability of a randomly oriented, freely rotating molecule. The vibrational contributions to the hyperpolarizabilities of several molecules are evaluated and compared, both in the static limit, and also at optical frequencies. Several nonlinear optical processes are considered.

1. INTRODUCTION

Nonlinear optical phenomena have attracted much interest in recent years. The development of high power tunable lasers has made possible a wide range of nonlinear optical experiments and applications, ranging from coherent anti-Stokes Raman spectroscopy (CARS) to the generation and manipulation of ultra-short laser pulses [1–4]. The third-order nonlinear susceptibility $\chi^{(3)}$ which mediates these optical processes is the macroscopic expression of the microscopic molecular second hyperpolarizability tensor γ. Perturbation theory gives a single expression for γ, and the hyperpolarizabilities corresponding to each of the various nonlinear optical processes are just special cases of this general expression, differing only in their frequency arguments [5–7]. However, each process (e.g. dc Kerr effect, electric-field-induced second-harmonic generation (ESHG) and third-harmonic generation (THG)) has a characteristically different balance of contributions from the electronic, vibrational and rotational degrees of freedom of each molecule. It is important to disentangle the various contributions to γ, especially in the context of dynamic response to short pulses, because the different mechanisms are characterized by widely different time scales. Furthermore, such a decomposition will allow the results of experiments based on different nonlinear optical processes to be compared and combined. A basis for the comparison of the nonresonant electronic contributions to the hyperpolarizabilities of atoms and molecules has already been described [8]. Below we will derive an expression for the off-resonance vibrational contribution to γ.

2. POLARIZABILITY APPROXIMATION FOR γ^{v}

The starting point for the ensuing derivation will be an explicit quantum-mechanical expression obtained by Orr and Ward [5]. This expression is appropriate when damping may be ignored, and is suitable even in the static limit. For a nondipolar molecule their expression may be written as

$$
\gamma_{\alpha\beta\gamma\delta}(-\omega_\sigma; \omega_1, \omega_2, \omega_3) = \hbar^{-3} \sum_P \left\{ \sum_{\substack{m,n,p \\ (\neq g)}} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\delta|n\rangle\langle n|\mu_\gamma|p\rangle\langle p|\mu_\beta|g\rangle}{(\omega_{mg} - \omega_\sigma)(\omega_{ng} - \omega_1 - \omega_2)(\omega_{pg} - \omega_1)} \right.
$$
$$
\left. - \sum_{\substack{m,n \\ (\neq g)}} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\delta|g\rangle\langle g|\mu_\gamma|n\rangle\langle n|\mu_\beta|g\rangle}{(\omega_{mg} - \omega_\sigma)(\omega_{ng} - \omega_1)(\omega_{ng} + \omega_2)} \right\}, \qquad (1)
$$

where $\sum_P$ denotes summation of the 24 terms generated by permuting the frequencies with their associated spatial subscripts, $-\omega_\sigma + \omega_1 + \omega_2 + \omega_3 = 0$, $|g\rangle$ is the initial (ground) state of the system and μ_α is the α Cartesian component of the electric dipole moment operator. For the present purpose equation (1) is equivalent to the results obtained by other calculation schemes [6, 7], but its form is more convenient. Note that while the treatment of pure rotational transitions is analogous to the treatment of vibrational transitions, extra complications may arise if damping cannot be ignored. In this case the full 48 term expression for γ may be required [6, 7].

The separation of equation (1) into electronic, vibrational and rotational contributions is done by grouping terms according to whether they show resonances at electronic, vibrational or rotational transition frequencies. Since the matrix elements $\langle g|\mu_\alpha|m\rangle$ vanish by symmetry for transitions to states within the vibration–rotation manifold of the ground electronic state of a homonuclear diatomic molecule, the only terms which may show vibrational or rotational resonances come from a subset of the first group of terms in equation (1). The vibrational contribution to the hyperpolarizability is the sum of all terms which may exhibit vibrational resonances and is denoted γ^{v}. Thus, the vibrational contribution to γ is given by

$$
\gamma^{\mathrm{v}}_{\alpha\beta\gamma\delta}(-\omega_\sigma; \omega_1, \omega_2, \omega_3) = \hbar^{-3} \sum_P \sum_{n(\neq g)} \frac{1}{(\omega_{ng} - \omega_1 - \omega_2)}
$$
$$
\times \left\{ \sum_{m(\neq g)} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\delta|n\rangle}{(\omega_{mg} - \omega_\sigma)} \right\} \left\{ \sum_{p(\neq g)} \frac{\langle n|\mu_\gamma|p\rangle\langle p|\mu_\beta|g\rangle}{(\omega_{pg} - \omega_1)} \right\}, \qquad (2\,a)
$$

where states to be summed over are

$$
|g\rangle = |e, v, J, M\rangle, \qquad\qquad\qquad (2\,b)
$$

$$
|m\rangle, |p\rangle = |e'', v'', J'', M''\rangle, \qquad e'' \neq e \qquad\qquad (2\,c)
$$

$$
|n\rangle = |e, v', J', M'\rangle, \qquad v' \neq v \qquad\qquad (2\,d)
$$

and where e is the electronic quantum number, v is the vibrational quantum number and J, M are the rotational quantum numbers of a state. Note that the state specification is appropriate for a gas of noninteracting linear molecules. Since the molecular population is usually distributed over several initial states one must also average over the initial states $|g\rangle$ in equation (2) by means of a sum $\sum_g \rho(g)$, where $\rho(g)$ is the normalized population distribution function. Averaging over the M quantum number of $|g\rangle$ has the effect of an orientation average.

The vibrational contribution γ^v given by equation (2) is a measure of the induced dipole resulting from the displacement of the nuclear positions by the applied fields, and the separation of γ into electronic and vibrational contributions is analogous to the well known separation of the linear polarizability α into α^e and α^v [9]. Note that there is another contribution to γ (or α) which is vibrational in origin but which is not included in γ^v (or α^v). This contribution arises through the parametric dependence of γ^e on internuclear separation R. Thus, the observed γ^e is obtained by averaging $\gamma^e(R)$ over the vibrational coordinate of the ground vibrational state, which increases γ^e over its value at the equilibrium internuclear separation [18]. The γ^v given in equation (2) differs from this vibrational averaging contribution in that the dipole induced through γ^v arises from the nuclear motions driven (possibly resonantly) by the applied fields, rather than solely through electronic displacements with respect to the unperturbed nuclear positions.

The essential approximation that makes equation (2) tractable is that of replacing each of the last two factors of equation (2 a) by a Raman transition polarizability [10]. This approximation will be adequate when the electric field frequencies are all well below electronic resonance frequencies. In this case one may use the static limit of the Raman transition polarizability

$$\alpha_{\alpha\beta}^{gn} = \frac{2}{\hbar} \sum_{m(\neq g)} \frac{\langle g | \mu_\alpha | m \rangle \langle m | \mu_\beta | n \rangle}{\omega_{mg}} \tag{3}$$

to put equation (2 a) in the form

$$\gamma_{\alpha\beta\gamma\delta}^v(-\omega_\sigma; \omega_1, \omega_2, \omega_3) = \sum_P \sum_g \sum_{n(\neq g)} \frac{\rho(g)}{4\hbar} \frac{\alpha_{\alpha\delta}^{gn} \alpha_{\gamma\beta}^{ng}}{(\omega_{ng} - \omega_1 - \omega_2)}. \tag{4}$$

The restriction on states $|n\rangle$ given by equation (2 d) still applies. The averaging over initial states of a population of molecules has now been included, ensuring that the tensor γ^v is isotropic.

Equation (4) becomes exact in the static limit. For nonzero field frequencies the approximation employed to obtain equation (4) amounts to ignoring the small dispersion of the nonresonant Raman polarizability [11, 12]. A measure of the accuracy of the approximation is obtained by considering the dispersion of the molecular polarizability between $\omega = 0$ and optical frequencies, which is about 2 per cent for the molecules to be considered (H_2, D_2, N_2, O_2) [4]. Therefore, at optical frequencies equation (4) may be expected to underestimate γ^v by about 4 per cent when the static transition polarizability is used. A better approximation might be to use the transition polarizabilities evaluated at some suitable average field frequency rather than at zero frequency.

3. Spherical tensor form and orientation averaging

The evaluation of γ^v is facilitated by re-expressing equation (4) in terms of irreducible spherical tensors, because both isotropic averaging and the sum over free rotor states are simpler in terms of spherical rather than Cartesian tensors. The method is that of Yuratich and Hanna [10, 13]. Thus, the isotropic average of the tensor product appearing in equation (4) may be written as

$$\overline{\alpha^*\alpha} = \sum_{KQ} (2K + 1)^{-1} \alpha_Q^{(K)*} \alpha_Q^{(K)} \theta^K. \tag{5}$$

The horizontal bar denotes an orientation average, $\alpha_0^{(K)}$ is the Q-th component of the K-th rank irreducible spherical tensor [14], and θ^K is a scalar function of the electric field polarizations alone [10, 13]. The angular factor θ^K is defined as the scalar product of two Kth tank tensors

$$\theta^K = (\mathbf{e}_0\,\mathbf{e}_3)^{(K)} \cdot (\mathbf{e}_2\,\mathbf{e}_1)^{(K)}, \tag{6}$$

where $(\mathbf{e}_0\,\mathbf{e}_3)^{(K)}$ is the Kth rank irreducible tensor product of vectors $\mathbf{e}_0$ and $\mathbf{e}_3$. The unit vectors $\mathbf{e}_0$, $\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{e}_3$ define the polarization states of the scattered and incident electric fields.

After putting equation (4) into spherical tensor form and using the state descriptions of equation (2b, d), one must then perform the sums over permutations P and over quantum numbers v', J', M', K and the averages over v, J, M, Q. Applying the Wigner–Eckart theorem gives

$$\sum_{M'} \sum_{Q} |\langle ev'J'M'|\alpha_Q^{(K)}|evJM\rangle|^2 = (2J+1)^{-1}|\langle ev'J'\|\alpha^{(K)}\|evJ\rangle|^2, \tag{7}$$

where $\langle\,\cdot\,\|\,\cdot\,\|\,\cdot\,\rangle$ denotes the reduced matrix element. The right hand side has no M dependence, so that averaging equation (7) over the M quantum number leaves it invariant. Thus, the result of sums over M, M', Q may be simply expressed in terms of the reduced matrix element. The value of the reduced matrix element is [10]

$$|\langle ev'J'\|\alpha^{(K)}\|evJ\rangle|^2 = (2J+1)(2J'+1)\begin{pmatrix} J' & K & J \\ 0 & 0 & 0 \end{pmatrix}^2 |\alpha_0^{(K)}|^2. \tag{8}$$

For a linear molecule the $Q = 0$ spherical tensor components are [14]

$$\alpha_0^{(0)} = -(1/3)^{1/2}(\alpha_\| + 2\alpha_\perp), \tag{9 a}$$

$$\alpha_0^{(1)} = 0, \tag{9 b}$$

$$\alpha_0^{(2)} = (2/3)^{1/2}(\alpha_\| - a_\perp), \tag{9 c}$$

where $\alpha_\|$ and $\alpha_\perp$ are the polarizabilities parallel and perpendicular to the molecular axis.

Combining equations (5), (7), (8) and substituting into equation (4) gives

$$\gamma_{\alpha\beta\gamma\delta}^v(-\omega_\sigma; \omega_1, \omega_2, \omega_3) = \sum_{P} \sum_{\substack{vJv'J' \\ (v \neq v')}} \sum_{K} \frac{\rho(v, J)}{4\hbar} \frac{2J'+1}{2K+1}$$

$$\times \begin{pmatrix} J' & K & J \\ 0 & 0 & 0 \end{pmatrix}^2 |\alpha_0^{(K)}|^2 \frac{\theta_{\alpha\delta\gamma\beta}^K}{(\omega_{vJv'J'} - \omega_1 - \omega_2)}, \tag{10}$$

where $\theta_{\alpha\delta\gamma\beta}^K$ is the angular factor evaluated for electric field polarizations along the $\alpha\beta\gamma\delta$ Cartesian axes. The usual Raman selection rule $\Delta J = 0$, ± 2 is embodied in the Wigner $3 - j$ symbol appearing in equation (10). Substituting the values of

the $3 - j$ symbols [15] and evaluating the sums over J' and K in equation (10), one obtains

$$\gamma^v_{\alpha\beta\gamma\delta}(-\omega_\sigma; \omega_1, \omega_2, \omega_3) = \sum_P \sum_{\substack{v, v' \\ (v \neq v')}} \sum_J (4\hbar)^{-1}$$

$$\times \left\{ \left[\frac{(J+1)(J+2)}{(2J+1)(2J+3)} \frac{\rho(v, J)(\alpha_\| - \alpha_\perp)^2_{vJ, v'J+2}}{(\omega_{vJ, v'J+2} - \omega_1 - \omega_2)} \right. \right.$$

$$+ \frac{(J+1)(J+2)}{(2J+3)(2J+5)} \frac{\rho(v, J+2)(\alpha_\| - \alpha_\perp)^2_{vJ+2, v'J}}{(\omega_{vJ+2, v'J} - \omega_1 - \omega_2)}$$

$$+ \left. \frac{2}{3} \frac{J(J+1)}{(2J-1)(2J+3)} \frac{\rho(v, J)(\alpha_\| - \alpha_\perp)^2_{vJ, v'J}}{(\omega_{vJ, v'J} - \omega_1 - \omega_2)} \right] \frac{\theta^2_{\alpha\delta\gamma\beta}}{5}$$

$$+ 3 \left. \frac{\rho(v, J)}{(\omega_{vJ, v'J} - \omega_1 - \omega_2)} \left(\frac{\alpha_\| + 2\alpha_\perp}{3} \right)^2_{vJ, v'J} \theta^0_{\alpha\delta\gamma\beta} \right\}. \quad (11)$$

4. Sum over permutations

As well as summing over molecular states, one must also sum over all permutations of the paired electric field frequencies and polarizations in order to evaluate γ^v. One may interchange the order of summation in equation (11), and then split each term into a factor invariant under the permutation operator multiplied by a factor of the form

$$\mathbb{D}^K(\Omega) \equiv \frac{1}{4} \sum_P \frac{\theta^K_{\alpha\delta\gamma\beta}}{(\Omega - \omega_1 - \omega_2)} \quad (12)$$

where Ω is the transition frequency $\omega_{vJ, v'J'}$. Given an expression for θ^K one may explicitly perform the summation in equation (12). The factors $\mathbb{D}^K(\Omega)$ contain essentially all the frequency and polarization dependence of γ^v.

The angular factors θ^K defined by equation (6) have, in the case where the polarization vectors are all coplanar, the explicit expression

$$\theta^0 = \tfrac{1}{3}(\mathbf{e}_0 \cdot \mathbf{e}_3)(\mathbf{e}_2 \cdot \mathbf{e}_1), \quad (13\,a)$$

$$\theta^2 = \tfrac{1}{6}\{(\mathbf{e}_0 \cdot \mathbf{e}_3)(\mathbf{e}_2 \cdot \mathbf{e}_1) + 3(\mathbf{e}_0 \cdot \mathbf{e}_1)(\mathbf{e}_2 \cdot \mathbf{e}_3) + 3(\mathbf{e}_0 \times \mathbf{e}_1) \cdot (\mathbf{e}_2 \times \mathbf{e}_3)\}. \quad (13\,b)$$

Furthermore, the following symmetries apply in the case that the polarization vectors are linear, coplanar and oriented along cartesian axes

$$\theta^K_{\alpha\beta\gamma\delta} = \theta^K_{\alpha\beta\delta\gamma} = \theta^K_{\beta\alpha\gamma\delta} = \theta^K_{\delta\gamma\beta\alpha}. \quad (14)$$

The sum in equation (12) is evaluated by writing down all the terms formed by simultaneous permutations of $(-\omega_\sigma, \omega_1, \omega_2, \omega_3)$ and $(\alpha, \beta, \gamma, \delta)$, applying the symmetries of equation (14), and regrouping to obtain

$$\mathbb{D}^K(\Omega) = \theta^K_{\alpha\delta\gamma\beta} D_1 + \theta^K_{\alpha\gamma\beta\delta} D_2 + \theta^K_{\alpha\beta\gamma\delta} D_3 \quad (15)$$

where

$$D_1 = \mathscr{D}(\Omega; \omega_1 + \omega_2), \quad (16\,a)$$

$$D_2 = \mathscr{D}(\Omega; \omega_1 + \omega_3), \quad (16\,b)$$

Table 1.   The frequency factors $\mathbb{D}^K(\Omega)$ defined by equation (12) have been evaluated for the four combinations of field polarizations needed to completely describe a general isotropic fourth rank tensor. Note that only three of these components are independent because of the relation $T_{xxxx} = T_{xxyy} + T_{xyxy} + T_{xyyx}$ which holds for isotropic tensors [19]. The terms D_1, D_2, D_3 are defined by equation (16).

$\alpha\beta\gamma\delta$	$3\mathbb{D}^0(\Omega)$	$6\mathbb{D}^2(\Omega)$
$xxxx$	$(D_1 + D_2 + D_3)$	$4(D_1 + D_2 + D_3)$
$xxyy$	D_3	$3(D_1 + D_2 + D_3) - 5D_3$
$xyxy$	D_2	$3(D_1 + D_2 + D_3) - 5D_2$
$xyyx$	D_1	$3(D_1 + D_2 + D_3) - 5D_1$

$$D_3 = \mathscr{D}(\Omega;\ \omega_2 + \omega_3) \qquad (16\,c)$$

and

$$\mathscr{D}(\Omega;\ \omega) = \frac{2\Omega}{\Omega^2 - \omega^2} \qquad (16\,d)$$

The values of $\mathbb{D}^K(\Omega)$ in the specific case of colinear light beams propagating along z, with linear polarization vectors along x and y, are obtained by combining equations (13) and (15). The results for $\mathbb{D}^K(\Omega)$ are given in table 1. In terms of $\mathbb{D}^K(\Omega)$, equation (11) may be written as

$$\gamma^v_{\alpha\beta\gamma\delta}(-\omega_\sigma;\ \omega_1,\ \omega_2,\ \omega_3)$$

$$= \hbar^{-1} \sum_{\substack{v,\,v' \\ (v \neq v')}} \sum_J$$

$$\times \left\{ \frac{1}{30} \left[\frac{(J+1)(J+2)}{(2J+1)(2J+3)} \rho(v,\,J)(\alpha_\| - \alpha_\perp)^2_{vJ,\,v'J+2}\, 6\mathbb{D}^2(\omega_{vJ,\,v'J+2}) \right. \right.$$

$$+ \frac{(J+1)(J+2)}{(2J+3)(2J+5)} \rho(v,\,J+2)(\alpha_\| - \alpha_\perp)^2_{vJ+2,\,v'J}\, 6\mathbb{D}^2(\omega_{vJ+2,\,v'J})$$

$$\left. + \frac{2}{3} \frac{J(J+1)}{(2J-1)(2J+3)} \rho(v,\,J)(\alpha_\| - \alpha_\perp)^2_{vJ,\,v'J}\, 6\mathbb{D}^2(\omega_{vJ,\,v'J}) \right]$$

$$\left. + \rho(v,\,J)\left(\frac{\alpha_\| + 2\alpha_\perp}{3}\right)^2_{vJ,\,v'J} 3\mathbb{D}^0(\omega_{vJ,\,v'J}) \right\}. \qquad (17)$$

5. Further approximations

The principal approximation made in the derivation of equation (17) has been the use of the Raman transition polarizability in equation (4). However, molecular polarizabilities are not usually known in the detail required to evaluate equation (17) as it stands. Therefore, to obtain a more convenient expression for γ^v, we will employ several further approximations. The adequacy of these approximations will be assessed when γ^v is calculated for the diatomic molecules H_2, D_2, N_2 and O_2. The approximations to be made are fourfold.

The first approximation to be made is that of assuming only the ground vibrational state is populated, and that only the fundamental $v = 0 \rightarrow 1$ vibrational transition contributes significantly. For a fundamental vibrational frequency above $1400 \, cm^{-1}$, the population of the excited vibrational levels is readily calculated to be less than $0 \cdot 1$ per cent at room temperature [16], which is negligible. The $v = 0 \rightarrow 2$ overtone Raman transition intensities, which are proportional to the corresponding overtone contribution to γ^v, have been measured for D_2, N_2 and O_2 [17]. The overtone intensities are measured to be in the range $0 \cdot 03$–$0 \cdot 12$ per cent of the fundamental intensities, which is again negligible.

The second approximation is to ignore the J dependence of the transition polarizability matrix elements $\alpha_{vJ, v'J'}$ and to replace them by a single representative value for the $v = 0 \rightarrow 1$ transition. Such an average Raman polarizability α_{01} is usually all that is available from experimental measurements.

The third approximation is to ignore the rotational transition frequencies compared to the fundamental vibrational frequency. This is justified because $(6 + 4J)B_0 \ll \omega_{01}$, where B_0 is the ground state rotational constant, and also because the $\Delta J = \pm 2$ transitions are usually much weaker than the $\Delta J = 0$ transitions in vibration–rotation Raman spectra.

The fourth and final approximation is to take the limit $J \gg 1$ in order to simplify the sums over J. This approximation is valid when $\hbar B_0 \ll kT$ because then most of the population is in fact in high J levels.

Applying the above four approximations to equation (17) results in the following simple expression

$$\gamma^v_{\alpha\beta\gamma\delta}(-\omega_\sigma; \omega_1, \omega_2, \omega_3)$$

$$= \hbar^{-1}\left\{\frac{(\alpha_\parallel - \alpha_\perp)^2_{01}}{45} 6\mathbb{D}^2(\omega_{01}) + \left(\frac{\alpha_\parallel + 2\alpha_\perp}{3}\right)^2_{01} 3\mathbb{D}^0(\omega_{01})\right\}. \quad (18)$$

In obtaining equation (18), all four approximations are applied to the $\mathbb{D}^2$ terms, while only the first two approximations need to be applied to the $\mathbb{D}^0$ term. Since the $\mathbb{D}^2$ term of equation (18) accounts for only about 10 per cent of the total γ^v, one may expect that the effects of the last two approximations will be correspondingly reduced. Equation (18) is in agreement with the result previously derived by means of a classical orientation average in terms of Cartesian tensors in the special case of ESHG [18, 19].

6. Static limit

The relative contributions of the various terms in γ^v and the effects of the approximations made in deriving the expressions for γ^v may be assessed most readily in the static limit, because the expressions simplify and because there is only a single independent tensor component to consider [19]. At $\omega = 0$, Kleinman symmetry requires that

$$\gamma^v_{xxyy} = \gamma^v_{xyxy} = \gamma^v_{xyyx} = \tfrac{1}{3}\gamma^v_{xxxx}. \quad (19)$$

The data required to evaluate γ^v_{xxxx} for the molecules H_2, D_2, N_2 and O_2 have been obtained from *ab initio* calculations [20] and experimental measurements [11, 21], and are presented in table 2. In order to evaluate γ^v_{xxxx} from equation

Table 2. Molecular parameter values used to evaluate γ^v.

Molecule	ν_{01} (cm^{-1})	$\left(\dfrac{B_0}{2\pi c}\right)$ (cm^{-1})	$g_{ns}(J)$ $J = \dfrac{\text{even}}{\text{odd}}$	$\left(\dfrac{\alpha_{\parallel} + 2\alpha_{\perp}}{3}\right)_{01}$ (10^{-42} C^2 m^2 J^{-1})	$(\alpha_{\parallel} - \alpha_{\perp})_{01}$ (10^{-42} C^2 m^2 J^{-1})
H$_2$†	4156	59·32	1/3	12·21	10·09
D$_2$‡	2988	29·91	2/1	10·18	8·28
N$_2$§	2331	1·990	2/1	6·13	4·04
O$_2$§	1555	1·438	0/1	5·89	5·89

 † *Ab initio* values for the $J = 1$ state, from [20].
 ‡ *Ab initio* values for the $J = 2$ state, from [20].
 § From Raman intensity measurements of [11] and depolarization ratios of [21].

(17) one needs the normalized population distribution function $\rho(v, J)$. To a sufficiently good approximation, $\rho(v, J)$ factors as $\rho(v)\rho(J)$ where $\rho(v) = \delta_{0v}$ and

$$\rho(J) = \rho'(J) \Big/ \sum_J \rho'(J) \qquad (20\,a)$$

$$\rho'(J) = g_{ns}(J)(2J + 1) \exp\left(-J(J + 1)\hbar B_0/kT\right) \qquad (20\,b)$$

with $g_{ns}(J)$ the nuclear statistical weight factor. Alternatively, equation (18) in the static limit becomes simply

$$\gamma^v_{xxxx}(0; 0, 0, 0) = \frac{6}{\hbar\omega_{01}}\left[\frac{4}{45}(\alpha_{\parallel} - \alpha_{\perp})^2_{01} + \left(\frac{\alpha_{\parallel} + 2\alpha_{\perp}}{3}\right)^2_{01}\right]. \qquad (21)$$

The values of γ^v calculated using equations (17) and (18) are compared in table 3, where the results of the more approximate expression equation (18) are seen to differ very little from the results obtained by explicitly summing over rotational levels in equation (17). This good agreement is obtained because the terms arising from the second rank irreducible spherical tensor part of γ^v (i.e. terms involving $(\alpha_{\parallel} - \alpha_{\perp})^2_{vJ, v'J'}$) account for only about 5 per cent of the total γ^v. While the terms

Table 3. Calculated values of the static γ^v at 293 K.

		$\gamma^v_{xxxx}(0; 0, 0, 0)/10^{-62}$ C^4 m^4 J^{-3}		
Molecule	Equation (17)	Equation (18)	$\dfrac{\text{Equation (18)}†}{\text{Equation (17)}}$	$\dfrac{\frac{4}{45}(\alpha_{\parallel} - \alpha_{\perp})^2_{01}‡}{(\alpha_{\parallel} + 2\alpha_{\perp}/3)^2_{01}}$	$\dfrac{\gamma^v_{xxxx}(0; 0, 0, 0)§}{\gamma^e_{xxxx}(0; 0, 0, 0)}$
H$_2$	1·140‖	1·149	0·993	0·061	0·292
D$_2$	1·104‖	1·110	0·994	0·059	0·286
N$_2$	0·506¶	0·506	1·000	0·039	0·094
O$_2$	0·734¶	0·734	1·000	0·089	0·141

 † Equation (18) is essentially the classical limit of the quantum mechanical expression given by equation (17), so this ratio is a measure of the size of quantum effects.
 ‡ This ratio measures the relative size of the second and zeroth rank tensor components contributing to γ^v.
 § The electronic contribution γ^e is obtained from [18] and [22].
 ‖ The *ab initio* transition polarizabilities $\alpha_{vJ, v'J'}$ from [20] have been used.
 ¶ The J-averaged transition polarizabilities given in table 2 have been used.

in $(\alpha_{\parallel} - \alpha_{\perp})^2_{01}$ evaluated by equation (18) are in error by $+8$, $+5$, $+0.5$ and $+0.3$ per cent for H_2, D_2, N_2 and O_2, respectively, as compared to the results of equation (17), these terms only make a small contribution to the total. Thus, no significant error is incurred by using equation (18) in place of equation (17) unless the term in $(\alpha_{\parallel} - \alpha_{\perp})^2_{01}$ is required in particular.

Also shown in table 3 is a comparison of the vibrational contribution and the electronic contribution [18, 22] to γ, in the static limit. Typically, the vibrational contribution is about 10 per cent of the total, which is significant but not dominant. However, *ab initio* calculations for the H_2^+ molecule [23–25] show that the vibrational contribution is dominant in this case, amounting to more than 90 per cent of the total γ. For H_2^+ the internuclear bond is much less stiff than for H_2, which accounts for the large enhancement of γ^v.

7. VIBRATIONAL HYPERPOLARIZABILITIES AT OPTICAL FREQUENCIES

One may make use of equation (18) to compare the various nonlinear optical processes at optical frequencies. By direct substitution of the appropriate frequency arguments, the following result is obtained for the frequency dependence of the vibrational contribution for CARS

$$\gamma^v_{xxxx}(-2\omega_1 + \omega_2; \omega_1, \omega_1, -\omega_2) = \gamma^v_{xxxx}(0; 0, 0, 0)$$
$$\times \frac{1}{3} \left\{ 2\left[1 - \left(\frac{\omega_1 - \omega_2}{\omega_{01}}\right)^2 \right]^{-1} + \left[1 - \left(\frac{2\omega_1}{\omega_{01}}\right)^2 \right]^{-1} \right\}. \quad (22)$$

Several other processes of interest may be evaluated by simply choosing suitable values of ω_1 and ω_2. For example, for ESHG one takes $\omega_1 = \omega$ and $\omega_2 = 0$, while for THG one chooses $\omega_1 = \omega$ and $\omega_2 = -\omega$ in equation (22). At optical frequencies such that ω_1, $\omega_2 \gg \omega_{01}$ the value of γ^v will be reduced by a factor of order $(\omega_{01}/\omega_1)^2$ compared to its static value, unless pairs of field frequencies sum to zero or near to it. In the later case γ^v will have a value near its static limiting value.

The expression for the dc Kerr hyperpolarizability doesn't fit the pattern of equation (22) because $\gamma^v_{dc\,Kerr}$ is defined as the difference between two tensor components. The definition reflects the fact that the experimental observable is an induced birefringence. The expression for $\gamma^v_{dc\,Kerr}$ is

$$\gamma^v_{dc\,Kerr} \equiv \tfrac{3}{2}[\gamma^v_{xxxx}(-\omega; 0, 0, \omega) - \gamma^v_{xyyx}(-\omega; 0, 0, \omega)]$$
$$= \frac{6}{\hbar\omega_{01}} \left\{ \frac{(\alpha_{\parallel} - \alpha_{\perp})^2_{01}}{45} \left[3 + \left[1 - \left(\frac{\omega}{\omega_{01}}\right)^2 \right]^{-1} \right] \right.$$
$$\left. + \left(\frac{\alpha_{\parallel} + 2\alpha_{\perp}}{3}\right)^2_{01} \left[1 - \left(\frac{\omega}{\omega_{01}}\right)^2 \right]^{-1} \right\}. \quad (23)$$

The value of $\gamma^v_{dc\,Kerr}$ is much smaller than $\gamma^v_{xxxx}(0; 0, 0, 0)$, even though a pair of frequencies sums to zero, because of a cancellation of terms. Also for this reason, the dc Kerr hyperpolarizability has the peculiar property that the $(\alpha_{\parallel} - \alpha_{\perp})^2_{01}$ term will dominate $\gamma^v_{dc\,Kerr}$ for optical frequencies $\omega \gg \omega_{01}$. Therefore, if an accurate estimate of $\gamma^v_{dc\,Kerr}$ is desired one must use equation (17) for the calculation, rather than equation (18) from which equation (23) has been obtained. Similar considerations apply to the ac Kerr effect [$\gamma(-\omega_2; \omega_1, -\omega_1, \omega_2)$].

Table 4. Vibrational contributions to the hyperpolarizability at optical frequencies. The fundamental optical field frequency is $v_1 = 15\,800\,\text{cm}^{-1}$ ($\lambda = 633\,\text{nm}$). For the CARS case the second optical field frequency is $v_2 = v_1 - 2500\,\text{cm}^{-1}$. The γ^v are calculated using equation (18). For comparison, $\gamma^e \approx 5 \times 10^{-62}\,\text{C}^4\,\text{m}^4\,\text{J}^{-3}$ for the molecules considered.

| Molecule | v_{01}/cm^{-1} | $\gamma^v/10^{-62}\,\text{C}^4\,\text{m}^4\,\text{J}^{-3}$ | | | | |
		dc Kerr†	DFWM‡	CARS§	ESHG‖	THG¶
H_2	4156	−0·032*	+0·759	+1·194	−0·042	−0·020
D_2	2998	+0·007*	+0·737	+2·426	−0·020	−0·010
N_2	2331	+0·003*	+0·336	−2·231	−0·006	−0·003
O_2	1555	+0·038*	+0·489	−0·310	−0·004	−0·002

† $3/2[\gamma^v_{xxxx}(-\omega; 0, 0, \omega) - \gamma^v_{xyyx}(-\omega; 0, 0, \omega)]$, see equation (23).
‡ $\gamma^v_{xxxx}(-\omega; \omega, \omega, -\omega)$, see equation (22).
§ $\gamma^v_{xxxx}(-2\omega_1 + \omega_2; \omega_1, \omega_1, -\omega_2)$, see equation (22).
‖ $\gamma^v_{xxxx}(-2\omega; \omega, \omega, 0)$, see equation (22).
¶ $\gamma^v_{xxxx}(-3\omega; \omega, \omega, \omega)$, see equation (22).
* The dc Kerr hyperpolarizability is particularly sensitive to the approximations made in order to obtain equation (18) from equation (17). Using equation (17) one obtains $\gamma^v/10^{-62}\,\text{C}^4\,\text{m}^4\,\text{J}^{-3} = -0\cdot041$, $+0\cdot001$, $+0\cdot003$ and $+0\cdot038$ for H_2, D_2, N_2 and O_2, respectively, at 293 K. The calculation uses the *ab initio* $\alpha_{vJ,v'J'}$ and $\omega_{vJ,v'J'}$ of [20] for H_2 and D_2 and the J-averaged transition polarizabilities given in table 2 for N_2 and O_2.

In table 4 are presented the values of γ^v calculated for five representative nonlinear optical processes, for light of wavelength 633 nm incident on the molecules H_2, D_2, N_2 and O_2. As expected, γ^v is negative and very small for ESHG and THG. We note in passing that the calculated γ^v for ESHG has been experimentally verified for H_2 and D_2 [18]. The calculated γ^v for the dc Kerr effect is also of about the same magnitude, but it has the opposite sign. In contrast, the γ^v for degenerate four wave mixing (i.e. the nonlinear refractive index) DFWM, is nearly as large as the static value of γ^v. Finally, one sees from table 4 that γ^v for CARS may be larger than the static value of γ^v even when the frequency difference $\omega_1 - \omega_2$ is tuned more than $1000\,\text{cm}^{-1}$ off resonance. Even far off resonance the value of γ^v_{CARS} may be quite comparable to γ^e. It has been suggested [8] that the resonant CARS amplitude could be calibrated against the nonresonant background. The above considerations indicate that care must be taken in dealing with the broad, strong wings of the vibrational resonance if such a procedure is to be implemented.

8. Discussion

So far we have restricted our consideration to homonuclear diatomic molecules for reasons of simplicity. The question naturally arises as to whether the above derivation may be extended to more complicated molecules, and as to whether the behaviour of γ^v for homonuclear diatomic molecules illustrates the essential features and relationships which exist in the more general case. The special features of homonuclear diatomic molecules which make the treatment especially simple are that the vibrations are totally symmetric, there is no permanent dipole moment and the angular momentum vector has a fixed orientation with respect to the molecular axes. Provided one considers only those vibrations

for which there is no nonvanishing dipole matrix element between states of the ground rotation–vibration manifold (i.e. infrared inactive vibrations), the extension to symmetric top molecules is straightforward [10]. Thus, the γ^v for the breathing vibrational mode (only) of CO_2 or CH_4 would be quite similar in form to the expressions obtained above.

However, for an infrared active molecular vibration the transition polarizability of equation (3) will no longer be a good approximation to the factors in equation (2 *a*), especially if the optical field frequencies are near vibrational transition frequencies. Furthermore, for a molecule with a permanent dipole moment equation (1) is no longer adequate [5]. In these cases one expects γ^v to be enhanced, perhaps dramatically, as compared to γ^v for a homonuclear diatomic molecule. This is consistent with the results of the approximate calculations that have been done for the series of fluorinated methanes [9], and which suggest that in the static limit γ^v may dominate γ^e for many polyatomic molecules. In order to quantitatively assess the effect of the restriction to homonuclear diatomic molecules in our derivation, an extension is warranted. An extension of the above treatment to consider more general linear molecules is probably the most tractable alternative. The two cases of particular interest would be the symmetric, linear triatomic molecule (e.g. CO_2), which would show the effect of infrared active vibrations in the absence of a permanent dipole moment, and the heteronuclear diatomic molecule (e.g. HCl), which is the simplest molecule with a permanent dipole moment. In fact, a detailed calculation of γ^v for the dc Kerr effect in CO_2 has recently been performed [26] which demonstrates that the additional terms which arise for γ^v of CO_2 are at least as large as those given by equation (23).

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