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# Rotational hyperpolarizability of a homonuclear diatomic molecule

D. P. Shelton
*Department of Physics, University of Manitoba, Winnipeg, Manitoba, Canada R3T 2N2*

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The rotational hyperpolarizability of a homonuclear diatomic molecule is calculated for all off-resonance third-order nonlinear optical processes. The treatment of rotations is fully quantum mechanical. The classical limit of the expression obtained for the dc Kerr effect agrees with the classical calculation in the static limit, but differs by a factor of $\frac{3}{4}$ at optical frequencies.

Nonlinear optical phenomena have attracted much interest in recent years.[1–4] The third-order nonlinear susceptibility $\chi^{(3)}$ mediates a wide range of nonlinear optical processes, and is the macroscopic expression of the microscopic second hyperpolarizability tensor $\gamma$. Perturbation theory gives a single expression for $\gamma$, 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 has a characteristically different balance of contributions from the electronic, vibrational, and rotational degrees of freedom of each molecule. In order to compare and combine the results of experiments based on different nonlinear optical processes, it is necessary to disentangle the various contributions to $\gamma$. A basis for the comparison of the nonresonant electronic contributions to the hyperpolarizabilities of atoms and molecules has been presented,[8] and the vibrational contributions to $\gamma$ have been considered for homonuclear diatomic[9,10] and linear[11] molecules. Below we will obtain and examine expressions for the off-resonance rotational contributions to $\gamma$ for homonuclear diatomic molecules. The derivation follows closely that presented in Ref. 9.

The starting point is the quantum-mechanical perturbation-theoretic expression due to Orr and Ward,[5] appropriate when damping may be ignored and suitable even in the static limit

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

where $\sum_P$ denotes the sum of the 24 terms generated by permuting the frequencies and their associated spatial subscripts, $\omega_\sigma=\omega_1+\omega_2+\omega_3$, $|\,g\,\rangle$ is the initial (ground) state of the system and $\mu_\alpha$ is the $\alpha$ Cartesian component of the electric dipole-moment operator.

The separation of $\gamma$ into rotational, vibrational, and electronic contributions is as follows: (a) $\gamma^r$ is all terms which involve a pure rotational level of the ground electronic manifold as an intermediate state, (b) $\gamma^v$ is all terms which involve a vibration-rotation level of the ground electronic manifold as an intermediate state, and (c) $\gamma^e$ is everything else. Making use of the fact that the dipole matrix elements vanish for the pure rotational transitions of a nondipolar molecule, the rotational hyperpolarizability of a homonuclear diatomic molecule is given by

$$\gamma^r_{\alpha\beta\gamma\delta}(-\omega_\sigma;\omega_1,\omega_2,\omega_3)=\sum_P\sum_{n(\neq g)}\frac{1}{4\hbar}\frac{\alpha^{gn}_{\alpha\delta}\alpha^{ng}_{\gamma\beta}}{(\Omega_{ng}-\omega_1-\omega_2)}, \tag{2}$$

where $g\to n$ is a pure rotational transition, and where

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

is the static limit of the Raman transition polarizability. Equation (2) is a good approximation for field frequencies small compared to electronic transition frequencies, and is exact in the static limit.[9]

The $\gamma^r$ for a molecule in a particular free-rotor state $|\,JM\,\rangle$ may be related to the experimentally observable quantity by performing an ensemble average. This is most easily done by expressing Eq. (2) in spherical tensor form, averaging over the degenerate $M$ sublevels with the aid of the Wigner-Eckart theorem, and averaging over $J$ by introducing the normalized population distribution function $\rho(J)$.[12] Proceeding as in Ref. 9 one obtains

$$\langle \gamma^r(-\omega_\sigma;\omega_1,\omega_2,\omega_3)\rangle_{\alpha\beta\gamma\delta}=\frac{1}{4\hbar}\sum_P\sum_J\rho(J)\sum_{J'}\sum_K\frac{2J'+1}{2K+1}\begin{pmatrix}J' & K & J\\ 0 & 0 & 0\end{pmatrix}^2\frac{|\alpha_0^{(K)}|^2\Theta^K_{\alpha\delta\gamma\beta}}{(\omega_{J,J'}-\omega_1-\omega_2)}\ , \tag{4}$$

where ${\alpha_Q}^{(K)}$ is the $Q$th component of the $K$th-rank spherical tensor and $\Theta^K_{\alpha\delta\gamma\beta}$ is a scalar angular factor (as previously defined[9]) evaluated for electric field polarizations along $\alpha\beta\gamma\delta$ Cartesian axes. For a linear rotor the polarizability tensor is diagonal and the only nonvanishing spherical tensor components are ${\alpha_0}^{(0)}$ and ${\alpha_0}^{(2)}$. Furthermore, one may show that the only nonvanishing matrix elements for $\Delta J=0$ transitions are just those for the $JM \rightarrow JM$ transitions, which are excluded from the $n(\neq g)$ summation in Eq. (2). Therefore $\Delta J=0$ transitions do not contribute to $\gamma^r$. The only contribution to $\gamma^r$ comes from $\Delta J=\pm 2$ transitions mediated by ${\alpha_0}^{(2)}=(\frac{2}{3})^{1/2}(\alpha_\parallel-\alpha_\perp)$, where $\alpha_\parallel$ and $\alpha_\perp$ are the polarizabilities parallel and perpendicular to the molecular axis, respectively. Aside from the additional simplification for the rotational case, the substitution of the values of the Wigner $3j$ symbols and the summation over $J'$, $K$, and permutations $P$ follows exactly the same pattern as given in Ref. 9. The final result is

$$\langle \gamma^r(-\omega_\sigma;\omega_1,\omega_2,\omega_3)\rangle_{\alpha\beta\gamma\delta}=\frac{1}{30\hbar}\sum_J(\alpha_\parallel-\alpha_\perp)^2_{J,J+2}\left[\rho(J)-\frac{2J+1}{2J+5}\rho(J+2)\right]\times\frac{(J+1)(J+2)}{(2J+1)(2J+3)}6\mathbb{D}^2(\Omega_{J,J+2})\ , \tag{5}$$

where the frequency factors $6\mathbb{D}^2(\Omega)$, evaluated in Table I for various combinations of the field polarizations, are expressed in terms of the function

$$\mathcal{D}(\Omega;\omega)=\frac{2\Omega}{\Omega^2-\omega^2}\ . \tag{6}$$

To delineate the region of validity of Eq. (5) we have also repeated the derivation including damping (using another expression given by Orr and Ward,[5] valid when there is no "proper dephasing" in the sense of Ref. 7). One finds that the final result is the same as in Eq. (5) except that $\mathcal{D}(\Omega;\omega)$ of Eq. (6) is replaced by

$$\mathcal{D}(\Omega,\Gamma;\omega)=\frac{2\Omega}{\Omega^2-\omega^2+\Gamma^2}\left[\frac{1+iy}{1+y^2}\right]\ , \tag{7a}$$

$$y=2\omega\Gamma/(\Omega^2-\omega^2+\Gamma^2)\ , \tag{7b}$$

where $\Gamma_{gm}$ is the half width at half maximum (HWHM) of the transition with frequency $\Omega_{gm}$. The difference between Eqs. (6) and (7) is not significant unless $\Gamma \gtrsim \Omega$. This condition will be satisfied for pressures above 300 atm. in $N_2$, for example, at which point the rotational Raman spectrum begins to collapse and the free-rotor description becomes inappropriate. For less extreme conditions Eq. (5) should be a good approximation.

Equation (5) describes $\langle\gamma^r\rangle$ for any off-resonance third-order nonlinear optical process. To illustrate its application we will consider the hyperpolarizability mediating the dc Kerr effect,

$$\gamma_{\text{dc Kerr}}\equiv\frac{3}{2}[\langle\gamma(-\omega;0,0,\omega)\rangle_{xxxx}-\langle\gamma(-\omega;0,0,\omega)\rangle_{xyyx}]\ . \tag{8}$$

Using Eq. (5), the rotational contribution to $\gamma_{\text{dc Kerr}}$ may be expressed as

$$\gamma^r_{\text{dc Kerr}}=\sum_J\frac{(\alpha_\parallel-\alpha_\perp)^2_{J,J+2}}{5kT}\frac{kT}{\hbar B}\left[\rho(J)-\frac{2J+1}{2J+5}\rho(J+2)\right]\frac{(J+1)(J+2)}{(2J+1)(2J+3)^2}\frac{1}{2}\left\{3+\left[1-\left[\frac{\omega}{\Omega_{J,J+2}}\right]^2\right]^{-1}\right\}\ , \tag{9}$$

where rigid rotor energy levels and transition frequencies $E(J)=J(J+1)\hbar B$ and $\Omega_{J,J+2}=(6+4J)B$ have been assumed, and damping has been ignored. It is especially instructive to consider the classical limit of this expression, obtained when $\hbar B/kT \ll 1$ and $J \gg 1$. Assuming a thermal population distribution, expanding in powers of $\hbar B/kT$, and neglecting the weak $J$ dependence of $(\alpha_\parallel-\alpha_\perp)$, one obtains the following simple result for the classical limit of Eq. (9):

$$\gamma^r_{\text{dc Kerr}}=\frac{(\alpha_\parallel-\alpha_\perp)^2}{5kT}\left\{\frac{3}{4}+\frac{1}{4}\left[1-\left[\frac{\omega}{\Omega_m}\right]^2\right]^{-1}\right\}\ , \tag{10}$$

where the mean effective transition frequency is $\Omega_m=4B(kT/\hbar B)^{1/2}$ when $\omega \gg \Omega$. For comparison, ignoring the dispersion of $\alpha$ the classical result is just $\gamma^r_{\text{dc Kerr}}=(\alpha_\parallel-\alpha_\perp)^2/5kT$.[13–15] The zero-frequency limit of Eq. (10) agrees exactly with the classical result. However, at optical frequencies where $\omega \gg \Omega$, Eq. (10) gives $\frac{3}{4}$ times the classical result. Thus, Eqs. (9) and (10) disagree with the classical dc Kerr result and also with the previously calculated quantum result for the dc Kerr effect.[14] The linear rotor is not a pathological special case, since the classical limit of a calculation (similar to that presented here) for the more general case of a sym-

TABLE I. The frequency factors $6\mathbb{D}^2(\Omega)$ have been evaluated for the four combinations of field polarizations needed to completely describe a general isotropic fourth rank tensor. The terms $D_1$, $D_2$, and $D_3$ are defined as $\mathcal{D}(\Omega;\omega_1+\omega_2)$, $\mathcal{D}(\Omega;\omega_1+\omega_3)$, and $\mathcal{D}(\Omega;\omega_2+\omega_3)$, respectively, where $\mathcal{D}(\Omega;\omega)$ is defined by Eq. (6).

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

metric top molecule also disagrees with the classical result. On this basis it appears that Buckingham's ansatz for calculating the dc Kerr birefringence in terms of a perturbed refractive index is only valid in the static limit.[14,15] Further investigation to determine the precise reason for the discrepancy is warranted, as well as an experimental test to establish which calculation is in fact correct.

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[10] Table 4 of Ref. 9 contains several numerical errors. Line 2 should read $D_2$, 2988, $+0.007^*$, $+0.737$, $+2.464$, $-0.031$, $-0.010$. Column 6 should read ESHG, $-0.064$, $-0.031$, $-0.008$, $-0.005$.

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