

Vibrational hyperpolarizability of SF₆

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Expressions are derived for the vibrational second hyperpolarizability γ^v of SF₆, in the static limit and for the nonlinear-optical processes of the dc Kerr effect, electric-field-induced second harmonic generation (ESHG), and third harmonic generation (THG). These expressions give γ^v in terms of vibrational transition dipole, polarizability, and first hyperpolarizability matrix elements (μ, α, β). The matrix elements needed in the numerical evaluation of γ^v are obtained from the literature and from the Raman scattering measurements reported here. In the static limit it is found that $\gamma^v \approx 20 \gamma^e$, where γ^e is the electronic contribution to γ . At optical frequencies γ^v is still comparable to γ^e in magnitude, and it shows significant frequency dependence.

INTRODUCTION

There has been much recent interest in third-order nonlinear optics,^{1,2} and since the nonlinear susceptibility of an optical medium governs its nonlinear response to incident electric fields, the susceptibility has in turn become the focus of much study. In gases, a wide range of third-order nonlinear-optical phenomena may be understood in terms of either the macroscopic susceptibility $\chi^{(3)}$ or the closely related microscopic second hyperpolarizability γ of the constituent atoms or molecules.^{3,4} Fourth-order perturbation theory gives an explicit expression for γ which applies for all third-order nonlinear-optical processes, so all these processes are in fact intimately related.⁵⁻⁷ For atoms, at frequencies far below electronic resonance, the quantitative relation appears to be quite simple.⁸⁻¹⁰ However, for a molecule, in addition to the electronic contribution γ^e there will be contributions to γ arising from vibrational and rotational degrees of freedom of the molecule (γ^v and γ^r),¹¹⁻¹⁶ and this greatly complicates the relations between the different nonlinear-optical processes. For polyatomic molecules it is ex-

pected that γ^v may be as large as γ^e , and though vibrational contributions to nonlinear-optical processes have been recognized for some time,^{17,18} the full expression for γ^v is sufficiently complicated such that accurate evaluations of γ^v for particular molecules are difficult and rare. It would be instructive to examine the relations which actually exist between the vibrational hyperpolarizabilities for different nonlinear-optical processes for some particular polyatomic molecule. The calculations presented below are an attempt at providing such an example. While conceptually this work follows closely the program of Elliott and Ward,¹¹ in order to reliably estimate γ^v we have found it necessary to carry through the calculations in full detail and use better data in the evaluation of the expressions for γ^v .

CALCULATION OF γ^v

Our starting point is the expression for γ due to Orr and Ward,⁵ applicable when damping may be ignored and suitable for use even in the static limit:

$$\gamma_{\alpha\beta\gamma\delta}(-\omega_\sigma; \omega_1, \omega_2, \omega_3) = \hbar^{-3} \sum_P \left\{ \sum_m' \sum_n' \sum_p' \frac{\langle g|\mu_\alpha|m\rangle \langle m|\mu_\delta|n\rangle \langle n|\mu_\gamma|p\rangle \langle p|\mu_\beta|g\rangle}{(\Omega_{mg} - \omega_\sigma)(\Omega_{ng} - \omega_1 - \omega_2)(\Omega_{pg} - \omega_1)} - \sum_m' \sum_n' \frac{\langle g|\mu_\alpha|m\rangle \langle m|\mu_\delta|g\rangle \langle g|\mu_\gamma|n\rangle \langle n|\mu_\beta|g\rangle}{(\Omega_{mg} - \omega_\sigma)(\Omega_{ng} - \omega_1)(\Omega_{ng} + \omega_2)} \right\}, \quad (1)$$

where $\omega_\sigma = \omega_1 + \omega_2 + \omega_3$, and ΣP denotes the sum over terms obtained by permuting the frequencies $-\omega_\sigma, \omega_1, \omega_2$, and ω_3 together with their associated spatial subscripts α, β, γ , and δ . The primed sums over intermediate states exclude the ground state $|g\rangle$. The vibrational contribution to the total γ is the sum of all those terms for which at least one of the intermediate states is a vibrationally excited state in the ground electronic manifold of states.

Calculations have been carried out for the vibrational contributions to the static hyperpolarizability [$\gamma(0,0,0,0)$] as well as to the nonlinear-optical processes of the dc Kerr effect [$\gamma(-\omega; 0,0,\omega,0)$], electric-field-induced second har-

monic generation [ESHG, $\gamma(-2\omega; \omega, \omega, 0, 0)$], and third harmonic generation [THG, $\gamma(-3\omega; \omega, \omega, \omega, 0)$]. The experimentally observable quantity is usually the isotropically averaged hyperpolarizability tensor component $\langle \gamma \rangle_{xxxx}$, where the upper case spatial subscripts refer to the laboratory frame and $\langle \rangle$ denotes the classical isotropic average. For the dc Kerr effect the observable is $\frac{1}{2}(\langle \gamma \rangle_{xxxx} - \langle \gamma \rangle_{xyyx})$. The final results of our calculations are the observable, isotropically averaged vibrational hyperpolarizabilities denoted by γ^v_{static} , γ^v_{Kerr} , γ^v_{ESHG} , and γ^v_{THG} . The present calculation is similar to the treatment previously presented for CF₄,¹⁶ but the results are more complete and systematic.

One begins by classifying the terms of Eq. (1) according to whether one, two, or three of the intermediate states $m, n,$

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and p are vibrationally excited states of the ground electronic manifold. The sums over the remaining excited electronic intermediate states are then approximated by ignoring optical frequencies ω compared to electronic transition frequencies Ω_{eg} in the factors $(\Omega_{eg} - \omega)$, and by replacing the corresponding sums over electronic states by the static Raman or hyper-Raman transition polarizabilities (α or β) between vibrational states:

$$\alpha_{mn}^{\alpha\beta} = \hbar^{-1} \sum_p \sum_e' \langle m | \mu_\alpha | e \rangle \langle e | \mu_\beta | n \rangle / \Omega_{eg}, \quad (2)$$

$$\beta_{mn}^{\alpha\beta\gamma} = \hbar^{-2} \sum_p \sum_e' \sum_{e'}' \times \langle m | \mu_\alpha | e \rangle \langle e | \mu_\beta | e' \rangle \langle e' | \mu_\gamma | n \rangle / \Omega_{eg} \Omega_{e'g}. \quad (3)$$

This approximation ignores the dispersion of α and β . Note that the static $\alpha_{mn}^{\alpha\beta}$ and $\beta_{mn}^{\alpha\beta\gamma}$ have complete permutation symmetry in their spatial superscripts. The numerators are now of the form μ^4 , $\mu^2\alpha$, $\mu\alpha\mu$, $\mu\beta$, or α^2 . With one exception, the denominators contain only optical frequencies and vibrational transition frequencies. The exception arises from the second group of terms in Eq. (1) when $\Omega_{ng} = \Omega_{eg}$. We have approximated this term as $1/2 \sum_m \mu_{gm}^{\alpha} \mu_{mg}^{\delta} \alpha_{gg}^{\gamma\beta} / \Omega_{mg} \Omega_{eg}$, where Ω_{eg} is to be construed as an effective average electronic transition frequency. So far the calculation is quite general. All terms are to be retained in the subsequent treatment.

The next step is to introduce molecular symmetry and specific frequency arguments, write out the permuted versions of each term and rearrange the expressions into a compact form. It is convenient to express molecular properties in the frame where the SF₆ molecule has its S atom at the origin with its F atoms on the x , y , and z axes. The equivalence of the x , y , z directions means that the independent components of $\gamma_{\alpha\beta\gamma\delta}$ are at most γ_{xxxx} , γ_{xxyy} , γ_{xyxy} , and γ_{xyyx} . In fact, $\gamma_{xxyy} = \gamma_{xyxy}$ for the dc Kerr effect and ESHG, and $\gamma_{xxyy} = \gamma_{xyxy} = \gamma_{xyyx}$ in the static limit and for THG. For

each group of terms of μ^4 , $\mu^2\alpha$, $\mu\alpha\mu$, $\mu\beta$, or α^2 we either ignore Ω_{mg} as compared to ω in the denominators or else expand in powers of (Ω_{mg}/ω) as required to obtain the lowest order nonvanishing result. At this point one has expressions for the independent components of the microscopic γ^ν tensor. The final step is to isotropically average γ^ν to obtain the macroscopic observables using

$$\langle \gamma \rangle_{xxxx} = \frac{1}{15} (\gamma_{\alpha\alpha\beta\beta} + \gamma_{\alpha\beta\alpha\beta} + \gamma_{\alpha\beta\beta\alpha}), \quad (4a)$$

$$\langle \gamma \rangle_{xxyy} = \frac{1}{30} (-\gamma_{\alpha\alpha\beta\beta} - \gamma_{\alpha\beta\alpha\beta} + 4\gamma_{\alpha\beta\beta\alpha}), \quad (4b)$$

where summation over repeated greek indices is implied. The resulting expressions are simplified by relabeling dummy indices (m , n , p), summing over degeneracy for each vibrational mode, replacing each matrix element by its equivalent from the standard set of independent matrix elements [μ_g^x , $a = \frac{1}{3}(\alpha^{xx} + \alpha^{yy} + \alpha^{zz})$, $(\alpha^{xx} - \alpha^{yy})$, α^{xy} , β^{xxx} , β^{xxy}],^{19,20} and collecting terms. The following relations, valid for molecules belonging to the cubic point groups, are useful: $\mu_{gm}^x \mu_{mg}^y = 0$, $\mu_{gm}^x \mu_{mn}^y = 0$, $\mu_{gm}^x \mu_{mn}^x \mu_{np}^y \mu_{pg}^y = 0$, and $(\alpha_{gm}^{xx})^2 + (\alpha_{gm}^{yy})^2 + (\alpha_{gm}^{zz})^2 = 3(a_{gm})^2 + (\alpha_{gm}^{xx} - \alpha_{gm}^{yy})^2$, where the last expression is obtained by making use of the explicit form of the α tensor for modes of a and e symmetry species and summing over degeneracy. The distinction between $\mu_{gm}^x \mu_{mn}^x$ and $\mu_{gm}^x \mu_{mn}^y$ must be maintained, since, e.g., the first product is $\sqrt{2}$ times larger than the second in the case that the vibrational level n is an overtone of m .

The actual manipulations are quite lengthy so only the final results for $\gamma_{\text{static}}^\nu$, γ_{Kerr}^ν , γ_{ESHG}^ν , and γ_{THG}^ν will be given here. One-, two-, and threefold degeneracies have already been summed over in these expressions. Since the expressions are in fact valid for molecules of either T_d or O_h symmetry, they may be compared with the more limited results previously derived for CF₄ in Ref. 16. That work is in agreement with the present work except for Eqs. (18) and (23), which are incorrect by factors of 2 and 3. Our results are

$$\gamma_{\text{static}}^\nu = \frac{6}{5} \hbar^{-3} \left\{ \sum_m' \sum_n' \sum_p' \frac{12\mu_{gm}^x \mu_{mn}^x \mu_{np}^x \mu_{pg}^x + 16\mu_{gm}^x \mu_{mn}^y \mu_{np}^x \mu_{pg}^y}{\Omega_{mg} \Omega_{ng} \Omega_{pg}} - \sum_m' \sum_n' \frac{20|\mu_{gm}^x|^2 |\mu_{gn}^x|^2}{\Omega_{mg} (\Omega_{ng})^2} \right\} \quad (5a)$$

$$+ \frac{6}{5} \hbar^{-2} \left\{ \sum_m' \sum_{n \neq m}' \frac{20\mu_{gm}^x \mu_{mn}^x a_{ng} + 10\mu_{gm}^x a_{mn} \mu_{ng}^x + 16\mu_{gm}^x \mu_{mn}^y \alpha_{ng}^{xy} + 8\mu_{gm}^x \alpha_{mn}^{xy} \mu_{ng}^y}{\Omega_{mg} \Omega_{ng}} + \sum_m' \left[\frac{20\mu_{gm}^x \mu_{mm}^x a_{mg} + 10|\mu_{gm}^x|^2 (a_{mm} - a_{gg})}{(\Omega_{mg})^2} - \frac{10|\mu_{gm}^x|^2 a_{gg}}{\Omega_{mg} \Omega_{eg}} \right] \right\} \quad (5b)$$

$$+ \frac{6}{5} \hbar^{-1} \left\{ \sum_m' \frac{4\mu_{gm}^x (\beta_{mg}^{xxx} + 2\beta_{mg}^{xxy})}{\Omega_{mg}} \right\} \quad (5c)$$

$$+ \frac{6}{5} \hbar^{-1} \left\{ \sum_m' \frac{5(a_{gm})^2 + 2/3(\alpha_{gm}^{xx} - \alpha_{gm}^{yy})^2 + 4(\alpha_{gm}^{xy})^2}{\Omega_{mg}} \right\}, \quad (5d)$$

$$\gamma_{\text{Kerr}}^\nu = \frac{6}{5} \hbar^{-3} \left\{ \sum_m' \sum_n' \sum_p' \left(\frac{1}{\Omega_{mg}} + \frac{1}{\Omega_{pg}} \right) \frac{2\mu_{gm}^x \mu_{mn}^x \mu_{np}^x \mu_{pg}^x + 5\mu_{gm}^x \mu_{mn}^y \mu_{np}^x \mu_{pg}^y}{\omega^2} - \sum_m' \sum_n' \frac{4|\mu_{gm}^x|^2 |\mu_{gn}^x|^2}{\Omega_{mg} \omega^2} \right\} \quad (6a)$$

$$+ \frac{6}{5} \hbar^{-2} \left\{ \sum_m' \sum_{n \neq m}' \left[\frac{6\mu_{gm}^x \mu_{mn}^y \alpha_{ng}^{xy} + 3\mu_{gm}^x \alpha_{mn}^{xy} \mu_{ng}^y}{\Omega_{mg} \Omega_{ng}} + \frac{8\mu_{gm}^x \mu_{mn}^x a_{ng} + 4\mu_{gm}^x \mu_{mn}^y \alpha_{ng}^{xy} + 3\mu_{gm}^x \alpha_{mn}^{xy} \mu_{ng}^y}{\omega^2} \right] + \sum_m' \left[\frac{8\mu_{gm}^x \mu_{mm}^x a_{mg}}{\omega^2} - \frac{5|\mu_{gm}^x|^2 a_{gg}}{\Omega_{mg} \Omega_{eg}} \right] \right\} \quad (6b)$$

$$+ \frac{6}{5} \hbar^{-1} \left\{ \sum_m' \left[1 - \left(\frac{\Omega_{mg}}{\omega} \right)^2 \right] \frac{2\mu_{gm}^x (\beta_{mg}^{xxx} + 2\beta_{mg}^{xyy})}{\Omega_{mg}} \right\} \quad (6c)$$

$$+ \frac{6}{5} \hbar^{-1} \left\{ \sum_m' \left[\frac{\frac{1}{2}(\alpha_{gm}^{xx} - \alpha_{gm}^{yy})^2 + 3(\alpha_{gm}^{xy})^2}{\Omega_{mg}} - \left(\frac{\Omega_{mg}}{\omega} \right) \frac{5(a_{gm})^2 + \frac{1}{2}(\alpha_{gm}^{xx} - \alpha_{gm}^{yy})^2 + (\alpha_{gm}^{xy})^2}{\omega} \right] \right\}, \quad (6d)$$

$$\gamma_{\text{ESHG}}^v = \frac{6}{5} \hbar^{-3} \left\{ \sum_m' \sum_n' \sum_p' \left(\frac{-3\Omega_{mg} + 2\Omega_{ng} - 3\Omega_{pg}}{8\omega} \right) \frac{3\mu_{gm}^x \mu_{mn}^x \mu_{np}^x \mu_{pg}^x + 4\mu_{gm}^x \mu_{mn}^y \mu_{np}^x \mu_{pg}^y}{\omega^3} \right. \\ \left. - \sum_m' \sum_n' \left(\frac{5}{4} \frac{\Omega_{mg}}{\omega} \right) \frac{|\mu_{gm}^x|^2 |\mu_{gn}^x|^2}{\omega^3} \right\} \quad (7a)$$

$$+ \frac{6}{5} \hbar^{-2} \left\{ \sum_m' \sum_{n \neq m} \frac{3}{4} \frac{5\mu_{gm}^x \mu_{mn}^x a_{ng} + 4\mu_{gm}^x \mu_{mn}^y \alpha_{ng}^{xy}}{\omega^2} \right. \\ \left. + \sum_m' \left[\frac{15}{4} \frac{\mu_{gm}^x \mu_{mm}^x a_{mg}}{\omega^2} - \frac{5}{2} \left(\frac{1}{\Omega_{mg} \Omega_{eg}} + \frac{3}{4} \frac{1}{\omega \Omega_{eg}} \right) |\mu_{gm}^x|^2 a_{gg} \right] \right\} \quad (7b)$$

$$+ \frac{6}{5} \hbar^{-1} \left\{ \sum_m' \left[1 - \frac{9}{4} \left(\frac{\Omega_{mg}}{\omega} \right)^2 \right] \frac{\mu_{gm}^x (\beta_{mg}^{xxx} + 2\beta_{mg}^{xyy})}{\Omega_{mg}} \right\} \quad (7c)$$

$$+ \frac{6}{5} \hbar^{-1} \left\{ \sum_m' \left(-\frac{3}{4} \frac{\Omega_{mg}}{\omega} \right) \frac{5(a_{gm})^2 + 2/3(\alpha_{gm}^{xx} - \alpha_{gm}^{yy})^2 + 4(\alpha_{gm}^{xy})^2}{\omega} \right\}, \quad (7d)$$

$$\gamma_{\text{THG}}^v = \frac{6}{5} \hbar^{-3} \left\{ \sum_m' \sum_n' \sum_p' \left(\frac{-2\Omega_{mg} + 3\Omega_{ng} - 2\Omega_{pg}}{9\omega} \right) \frac{3\mu_{gm}^x \mu_{mn}^x \mu_{np}^x \mu_{pg}^x + 4\mu_{gm}^x \mu_{mn}^y \mu_{np}^x \mu_{pg}^y}{\omega^3} \right. \\ \left. - \sum_m' \sum_n' \left(\frac{16}{9} \frac{\Omega_{mg}}{\omega} \right) \frac{|\mu_{gm}^x|^2 |\mu_{gn}^x|^2}{\omega^3} \right\} \quad (8a)$$

$$+ \frac{6}{5} \hbar^{-2} \left\{ \sum_m' \sum_{n \neq m} \frac{2}{3} \frac{5\mu_{gm}^x \mu_{mn}^x a_{ng} - 5\mu_{gm}^x a_{mn} \mu_{ng}^x + 4\mu_{gm}^x \mu_{mn}^y \alpha_{ng}^{xy} - 4\mu_{gm}^x \alpha_{mn}^y \mu_{ng}^y}{\omega^2} \right. \\ \left. + \sum_m' \frac{10}{3} \left[\frac{\mu_{gm}^x \mu_{mm}^x a_{mg} - |\mu_{gm}^x|^2 (a_{mm} - a_{gg})}{\omega^2} - \frac{2|\mu_{gm}^x|^2 a_{gg}}{\omega \Omega_{eg}} \right] \right\} \quad (8b)$$

$$+ \frac{6}{5} \hbar^{-1} \left\{ \sum_m' \left(-\frac{28}{9} \frac{\Omega_{mg}}{\omega} \right) \frac{\mu_{gm}^x (\beta_{mg}^{xxx} + 2\beta_{mg}^{xyy})}{\omega} \right\} \quad (8c)$$

$$+ \frac{6}{5} \hbar^{-1} \left\{ \sum_m' \left(-\frac{1}{4} \frac{\Omega_{mg}}{\omega} \right) \frac{5(a_{gm})^2 + 2/3(\alpha_{gm}^{xx} - \alpha_{gm}^{yy})^2 + 4(\alpha_{gm}^{xy})^2}{\omega} \right\}. \quad (8d)$$

RAMAN INTENSITY MEASUREMENTS

We have made Raman scattering measurements to obtain the transition polarizability matrix elements needed to evaluate γ^v . The usual 90° scattering geometry was employed,¹⁹ with the incident polarization perpendicular to the observation direction for the scattered light. A polarization scrambler was placed before the entrance slit of the spectrometer. Usually both polarizations of the scattered light were collected, but polarization analysis was also used for some of the bands to dissect overlapping components. Spectra were obtained using a laser power of about 1 W at $\lambda = 514.5$ nm to excite samples of high purity (> 99.99%) gas. The scattered light was dispersed by a 1 m double monochromator and detected by a photon counting photomultiplier tube. All measurements were made at room temperature ($T = 22$ °C). The scattered light signal ranged from 10 cps for the weaker bands to about 10⁴ cps for the fundamentals, for measurements made on SF₆ samples at pressures in the range of 2–10 atm using a spectral slit width of 3–10 cm⁻¹.

The scattered intensity of the SF₆ fundamental bands was calibrated by comparison with the scattered intensity of the rotational Raman lines of H₂ gas at 3 atm as a reference.²¹ The weaker bands of SF₆ were calibrated by comparison with the nearest fundamental band in the same sample. Small deadtime corrections were made for the stronger bands. The relative spectral response of the spectrometer was measured using a calibrated tungsten ribbon lamp.²² Bands due to modes of a_{1g} symmetry will be narrow and totally polarized, while e_g and f_{2g} symmetry modes will give wide, totally depolarized bands (we cannot distinguish between e_g and f_{2g} experimentally).^{19,20} We have tried to separate the contributions from the various symmetry species for each transition wherever possible, using bandwidth and depolarization ratio as criteria for the decomposition. The dissection of the overlapping $2\nu_1$ and $\nu_1 + \nu_5$ bands is fairly reliable because the bands are partially resolved, but since $2\nu_1$ and $\nu_3 + \nu_4$ (and also $\nu_1 - \nu_5$ and $\nu_4 - \nu_6$) are completely unresolved we can in this case only estimate upper bounds for the intensities of the separate bands.

In Table I are given the values of the scattering cross section (in terms of the ratio of the numbers of scattered and incident photons) per molecule for the observed bands of SF₆ (decomposed into isotropic and anisotropic contributions). These cross sections have been calibrated in terms of the scattering cross section per molecule for the H₂ S(*J*) lines calculated from^{21,23}

$$\left(\frac{d\sigma}{d\Omega}\right)_{H_2} = (2\pi)^4 \nu (\nu - \nu_{J,J+2})^3 n(J) \times \frac{3}{2} \frac{(J+1)(J+2)}{(2J+1)(2J+3)} \frac{7}{45} \times (\alpha_{||} - \alpha_1)^2_{J,J+2}, \quad (9)$$

where *n*(*J*) is the fractional population of the level *J* (calculated including nuclear statistical weights)^{19,21} and where the H₂ rotational transition matrix elements at $\lambda = 514.5$ nm for the S(0) and S(1) lines are taken as $(\alpha_{||} - \alpha_1)_{J,J+2} = 35.19$ and 35.46×10^{-42} C² m² J⁻¹, respectively [conversion from SI to esu: 8.98756×10^{15} α (C² m² J⁻¹) = α (cm³); Eq. (9) is in esu with ν in cm⁻¹]. These values were deduced by considering the results of three recent *ab initio* calculations for H₂,²⁴⁻²⁶ and are probably accurate to better than 0.2%. The reproducibility of the measured intensities is better than 1% for the fundamentals and about 10% for the other, weaker bands. An indication of the residual systematic errors in the intensity measurements of the fundamental bands is given by the 1.5% discrepancy between the measured and calculated intensity ratios for the S(0) and S(1) lines of H₂. We estimate that the accuracies of our cross sections are about 2% for the fundamentals, and about 10% for the summed components of other isolated bands. The scattering cross sections previously measured for SF₆ with about 10% accuracy by Holzer and Ouillon²⁷ (calibrated in terms of the N₂ cross section²¹) are also given in Table I for comparison. Except for the weakest bands, the two sets of cross sections agree to within their combined uncertainties.

If all the SF₆ molecules were initially in the ground vibrational state, then the scattering cross section per SF₆ molecule would be simply^{21,23}

$$\left(\frac{d\sigma}{d\Omega}\right)_{SF_6} = (2\pi)^4 \nu (\nu - \nu_{gm})^3 \left\{ (a_{gm})^2 + \frac{7}{45} (\Delta a_{gm})^2 \right\}, \quad (10)$$

where $(\Delta a_{gm})^2 = \frac{3}{2} (\alpha_{gm}^{xx} - \alpha_{gm}^{yy})^2$ or $9 (\alpha_{gm}^{xy})^2$ for e_g or f_{2g} vibrational modes, respectively, when summed over degeneracy.^{19,20} In fact, for SF₆ at room temperature the ground state population is only 31%, with 17% in $\nu_6 = 1$ and 52% spread over various higher levels. The harmonic oscillator matrix element for an upward transition from an initial state with vibrational quantum number ν is proportional to $(\nu + 1)^{1/2}$ for a fundamental, $(\nu + 1)^{1/2} (\nu + 2)^{1/2}$ for an overtone, and $(\nu_a + 1)^{1/2} (\nu_b + 1)^{1/2}$ for a combination transition. Due to the thermal population of excited vibrational levels the scattering cross section for a band will be increased by a multiplicative "hot band correction factor" *F*. To evaluate *F* for a given transition one sums the contributions from each initial level (weighted by the fractional population of the level) taking account of the multiplicity of

possible transitions from each state of the initial level and the increase in the magnitude of the matrix element for more highly excited levels. The calculated correction factors *F* are given in Table I along with the values of $\{a^2 + \frac{7}{45} (\Delta a^2)\}$, deduced from the measured cross sections using Eq. (10) and *F*, for transitions from the ground state (*g* → *m*).

NUMERICAL EVALUATION AND DISCUSSION

The μ and α matrix elements needed for the evaluation of Eqs. (5)–(8) for γ^ν have been collected in Table II. The Raman transition polarizabilities have been extracted from $(a_{gm})^2 + 7/45 (\Delta a_{gm})^2$ given in Table I, while the transition dipole moments come from infrared absorption measurements and calculations.²⁸⁻³¹ Since the hyper-Raman spectra for other small spherical top molecules show a single dominant band^{32,33} we have assumed that β_{gm} is negligible except for the ν_3 transition. The assumed value $(\beta_{gm}^{xxx} + 2\beta_{gm}^{xyy}) = 3 \times 10^{-52}$ C³ m³ J⁻² for this transition in SF₆ is an estimate based on the *ab initio* value $\beta_{gg}^{xyz} = 2.8 \times 10^{-52}$ C³ m³ J⁻² for CH₄³⁴ and the measured value $(\beta_{gm}^{xxx} + 2\beta_{gm}^{xyy}) = 2.6 \times 10^{-52}$ C³ m³ J⁻² for CF₄¹⁶ [2× larger than the value reported in Ref. 16 because of the factor of 2 error in Eq. (18) there].

In evaluating Eqs. (5)–(8) we will assume for simplicity that all the molecules are in the ground vibrational state, even though this is not the case at room temperature. Since the size of the matrix elements increases for hot band transitions of all types, one may expect that the effect of an excited initial population distribution will be to increase γ^ν and to impart a significant temperature dependence to γ^ν . Though Eqs. (5)–(8) are applicable when the initial state |*g*⟩ is an excited vibrational state, and there is reason to believe that the room temperature value of γ^ν may be substantially larger than the zero temperature value, we feel that the added complexity of dealing with an initial population distributed over many excited levels is not warranted at present.

Several aspects of the evaluation of Eqs. (5)–(8) must be considered to estimate the reliability of the numerical results obtained. Therefore we will examine each of the four types of terms for Eqs. (5)–(8) in turn, starting first with the simplest type. One finds that the values of the α^2 terms [parts (d) of Eqs. (5)–(8)] are determined almost entirely by the matrix elements for the Raman fundamentals. While there is a cancellation of terms in Eq. (6d) for γ_{Kerr}^ν , the first term is 100× larger than the second term so that the cancellation has no significant effect on the accuracy of the computed result. Thus, the numerical results for the α^2 terms are expected to be quite reliable because only a few positive definite terms dominate and because those terms contain only the fundamental transition matrix elements (which are most accurately known). This is in contrast to the situation for some of the other contributions to γ^ν , which is less favorable. For example, the summations for the $\mu\beta$ terms [parts (c) of Eqs. (5)–(8)] contain essentially a single term but we have only an educated guess as to the magnitude and sign of β .

The evaluation of the $\mu^2\alpha + \mu\alpha\mu$ terms [parts (b) of Eqs. (5)–(8)] is somewhat complicated. The double summed terms are essentially determined by about a dozen combinations of four dipole matrix elements ($\nu_3, \nu_4, \nu_1 + \nu_3$,

TABLE I. Raman scattering cross sections measured for SF₆. Bandwidth and polarization analysis have been employed to separate each band into a narrow, totally polarized (*N*) component and a wide, totally depolarized (*W*) component. Where the separation has not been carried out, the total (*T*) cross section is given for the band. The results from Ref. 27 are included for comparison, but the values of $\{(a_{gm})^2 + 7/45(\Delta\alpha_{gm})^2\}^{1/2}$ in the last column are based on our measurements alone (except in the first two lines of the table). The scattering cross section is proportional to $F\{(a_m)^2 + 7/45(\Delta\alpha_{gm})^2\}$, where *F* is the hot band correction factor which accounts for the intensity enhancement due to the thermal population of excited vibrational levels at room temperature for SF₆. For each band, the *N* and *W* components correspond to the $(a_{gm})^2$ and $(\Delta\alpha_{gm})^2$ polarizability invariants, respectively.

Mode	ν_{mg} (cm ⁻¹)	Species	$\frac{d\sigma}{d\Omega}$ (10 ⁻³³ cm ² sr ⁻¹)	$\frac{d\sigma^a}{d\Omega}$ (10 ⁻³³ cm ² sr ⁻¹)	<i>F</i>	$\{(a_{gm})^2 + 7/45(\Delta\alpha_{gm})^2\}^{1/2}$ (10 ⁻⁴² C ² m ² J ⁻¹)
$\nu_1 - \nu_5$	268	f_{2g}		2.0 <i>W</i> ^b	0.087 ^c	1.10 <i>W</i> ^b
$\nu_4 - \nu_6$	268	$a_{2g} + e_g + f_{1g} + f_{2g}$		2.0 <i>W</i> ^b	0.238 ^c	0.66 <i>W</i> ^b
ν_5	524	f_{2g}	532 <i>W</i>	605 <i>W</i>	1.08	5.45 <i>W</i>
ν_2	643	e_g	778 <i>W</i>	872 <i>W</i>	1.05	6.77 <i>W</i>
$2\nu_6$	694	$a_{1g} + e_g + f_{2g}$	24.4 <i>N</i>	21.8 <i>N</i>	1.50	1.01 <i>N</i>
ν_1	775	a_{1g}	2177 <i>N</i>	2335 <i>N</i>	1.02	11.57 <i>N</i>
$2\nu_5$	1049	$a_{1g} + e_g + f_{2g}$	0.93 <i>N</i>	0.7 <i>N</i>	1.17	0.23 <i>N</i>
$2\nu_4$	1230	$a_{1g} + e_g + f_{2g}$	1.02 <i>N</i>	0.62 <i>N</i>	1.10	0.25 <i>N</i>
$2\nu_2$	1285	$a_{1g} + e_g$	0.79 <i>N</i>	0.62 <i>N</i>	1.05	0.23 <i>N</i>
			1.00 <i>W</i>		1.05	0.26 <i>W</i>
$\nu_1 + \nu_5$	1298	f_{2g}	0.97 <i>W</i>	1.48 <i>W</i>	1.11	0.24 <i>W</i>
$\nu_1 + \nu_2$	1415	e_g	1.10 <i>W</i>	0.78 <i>W</i>	1.12	0.27 <i>W</i>
$2\nu_1$	1558	a_{1g}	0.99 <i>N</i> ^d	2.02 <i>T</i> ^e	1.05	0.26 <i>N</i> ^d
$\nu_3 + \nu_4$	1558	$a_{1g} + e_g + f_{1g} + f_{2g}$	0.99 <i>N</i> ^d		1.06	0.27 <i>N</i> ^d
			1.10 <i>W</i>		1.13	0.26 <i>W</i>
$2\nu_3$	1887	$a_{1g} + e_g + f_{2g}$	1.35 <i>N</i>	2.5 <i>T</i>	1.02	0.32 <i>N</i>
			1.51 <i>W</i>		1.02	0.33 <i>W</i>

^a Reference 27.^b Upper bounds for the unresolved components of the overlapping bands.^c *F* is small because only excited initial levels contribute for these bands.^d Upper bounds for the unresolved polarized components of the overlapping bands.^e Sum of $2\nu_1$ and $\nu_3 + \nu_4$ bands.

TABLE II. Transition dipole and polarizability matrix elements for the SF₆ molecule. The uncertainties of the matrix elements are near 1% for the fundamental transitions and 10%–100% for the other transitions. The first line of the table gives the ground state mean polarizability a_{gg} and the effective electronic transition frequency ν_{eg} derived from refractive index data. The other polarizabilities are derived from the $\{(a_{gm})^2 + 7/45(\Delta\alpha_{gm})^2\}^{1/2}$ values in Table I. Where both e_g and f_{2g} symmetry species occur for a vibration, the corresponding matrix elements are upper bounds obtained assuming that either the e_g or f_{2g} species could give the dominant contribution to $(\Delta\alpha_{gm})^2$. The dipole matrix elements are from infrared absorption data.

Mode	ν_{mg} (cm ⁻¹)	$ \mu_{gm}^x $ (10 ⁻³² C m)	$ a_{gm} $	$ \alpha_{gm}^{xx} - \alpha_{gm}^{yy} $	$ \alpha_{gm}^{xy} $
				(10 ⁻⁴² C ² m ² J ⁻¹)	
0	167 000 ^a		500 ^a		
ν_1	775		11.6		
ν_2	643			14.0	
ν_3	948	146 ^b			
ν_4	615	42 ^b			
ν_5	524				4.60
ν_6	347				
$2\nu_1$	1 558		0.26		
$2\nu_2$	1 285		0.23	0.53	
$2\nu_3$	1 887		0.32	0.69	0.28
$2\nu_4$	1 230		0.25		
$2\nu_5$	1 049		0.23		
$2\nu_6$	694		1.01		
$\nu_1 + \nu_2$	1 415			0.55	
$\nu_1 + \nu_3$	1 721	5.0 ^c			
$\nu_1 + \nu_4$	1 388	1.7 ^c			
$\nu_1 + \nu_5$	1 298				0.19
$\nu_2 + \nu_4$	1 257	4.2 ^c			
$\nu_2 + \nu_6$	988	9.4 ^c			
$\nu_3 + \nu_4$	1 558		0.26	0.56	0.22
$\nu_5 + \nu_6$	869	7.3 ^c			
$\nu_1 - \nu_5$	268				0.9
$\nu_4 - \nu_6$	268			1.4	0.6

^a References 4 and 35.^b Reference 29.^c Reference 28.

$\nu_1 + \nu_4$) and four polarizability matrix elements (ν_1 , $2\nu_3$, $2\nu_4$, $\nu_3 + \nu_4$). The reliability of the numerical result in this case is compromised by the possibility of cancellations if not all the matrix elements are positive in sign, and by the large uncertainty in magnitude for the overtone and combination matrix elements. The situation is saved by the fact that the singly summed $|\mu_{gm}^x|^2 a_{gg}/\Omega_{eg}$ terms are positive definite, determined by fundamental transitions, and dominant, though this is tempered by the uncertainty as to the appropriate value of Ω_{eg} to use (we have used the effective frequency characterizing the refractive index dispersion³⁵). We can show that the other singly summed terms are small or negligible in comparison as follows. To estimate the size of $\mu_{gm}^x \mu_{mm}^x a_{mg}$ and $|\mu_{gm}^x|^2 (a_{mm} - a_{gg})$ we recall that a matrix element of α may be expressed as an integral of the form $\alpha_{mn} \approx \int d^3R \alpha(R) \psi_m(R) \psi_n(R)$, where $\psi_m(R)$ is just a harmonic oscillator wave function to first approximation and $\alpha(R)$ is to be expanded in a Taylor series about the equilibrium position R_0 : $\alpha(R) = \alpha_0 + (d\alpha/dR)\Delta R + \dots$ (with analogous expressions for μ_{mn}).¹⁹ The magnitude of α_{mn} for an allowed fundamental is proportional to $d\alpha/dR$, while for an overtone α_{mn} is proportional to $d^2\alpha/dR^2$ or $(d\alpha/dR)|\delta\psi|$, where $|\delta\psi|$ is the perturbation of the vibrational wave function due to mechanical anharmonicity. For a forbidden fundamental $d\alpha/dR = 0$ and α_{mn} is proportional to $d^3\alpha/dR^3$ or $(d^2\alpha/dR^2)|\delta\psi|$. Compared to $a_{gg} = 1$, the matrix elements a_{gm} for fundamentals, overtones, and forbidden fundamentals have magnitudes about $(40)^{-1}$, $(40)^{-2}$, and $(40)^{-3}$, respectively. Similar arguments apply for μ_{mn} , except that for symmetry forbidden transitions $\mu_{mn} = 0$ is exact [$\mu(R) = 0$ for any amplitude of vibration]. Now consider $\mu_{gm} \mu_{mm} a_{mg}$ and note that this product vanishes unless $g \rightarrow m$ is infrared allowed, in which case a_{mg} will have the magnitude of a forbidden fundamental, $a_{mg} \approx (40)^{-3} a_{gg}$, and also $\mu_{mm} \lesssim 10^{-1} \mu_{gm}$. Since $\Omega_{eg}/\Omega_{mg} \approx 200$, one sees that $\mu_{gm} \mu_{mm} a_{mg}/\Omega_{mg} \approx 10^{-4} |\mu_{gm}|^2 a_{gg}/\Omega_{eg}$ so that the $\mu_{gm} \mu_{mm} a_{mg}$ terms may be neglected. Similarly, $g \rightarrow m$ must be infrared allowed to make $|\mu_{gm}|^2 (a_{mm} - a_{gg})$ nonvanishing, in which case $(a_{mm} - a_{gg})$ has the magnitude of an overtone, and $(a_{mm} - a_{gg})/\Omega_{mg} \approx 10^{-1} a_{gg}/\Omega_{eg}$. Detailed consideration of the singly summed terms containing $(a_{mm} - a_{gg})$ shows

that they comprise a 10% correction to the a_{gg}/Ω_{eg} terms in the static case and a 1% correction for THG.

Finally, there are the μ^4 terms to consider [parts (a) of Eqs. (5)–(8)]. The cancellation of terms evident in the expressions for the μ^4 terms may be dealt with exactly, and when the dust settles one finds that the numerical results are dominated by sums of positive definite terms containing $|\mu_{gm}|^4$ or $|\mu_{gm}|^2 |\mu_{gn}|^2$, with the dipole matrix elements for the two fundamental infrared transitions almost completely determining the final result. One may show that terms with $m = n \neq p$ or $m \neq n = p$ vanish, and that the contribution of the terms with $m = n = p$ (containing $|\mu_{gm}|^2 |\mu_{mm}|^2$) is only 0.1% of the final result for the μ^4 terms. The terms which are constructed from a sequence of four different dipole matrix elements are the only ones which are sensitive to the sign of the matrix elements, but these terms contribute only 1% of the total for the μ^4 terms.

Our discussion of the evaluation of Eqs. (5)–(8) may be summarized as follows. Numerical results for the μ^4 and α^2 terms should be quite accurate, results for the $\mu^2\alpha + \mu\alpha\mu$ terms will be less reliable, and the accuracy of results for the $\mu\beta$ terms may be quite poor. The expected uncertainty ranges from a few percent at best to perhaps a factor of 2 at worst.

The results of evaluating the various terms in Eqs. (5)–(8), for a molecule in the ground state and assuming $\nu = 20000 \text{ cm}^{-1}$, are given in Table III. The most striking result is that $\gamma_{\text{static}}^\nu$ is more than $20\times$ the estimated value of $\gamma_{\text{static}}^\epsilon$.³⁶ The dominant contribution to $\gamma_{\text{static}}^\nu$ is from the μ^4 terms. The large value of $\gamma_{\text{static}}^\nu$ may make it important in intermolecular interactions. Examining the expressions for the microscopic, molecular-frame tensor components γ_{xxxx}^ν and γ_{xyyx}^ν (before isotropic averaging, expressions not given here), one finds the interesting result that $\gamma_{xyyx}^\nu \approx 10\gamma_{xxxx}^\nu$ in the static limit.

At optical frequencies, one sees from Table III that $\gamma^\nu < \gamma^\epsilon$ for the various nonlinear-optical processes. Note that the contributions from all four terms may be comparable and that they tend to cancel. Due to this cancellation of terms one gets the surprising result $|\gamma_{\text{ESHG}}^\nu| > |\gamma_{\text{THG}}^\nu| > |\gamma_{\text{Kerr}}^\nu|$ at $\nu = 20000 \text{ cm}^{-1}$. This result may be put into perspective by calculating γ^ν as a function of frequency,

TABLE III. Vibrational contributions to the isotropically averaged hyperpolarizabilities γ^ν are given for the SF₆ molecule in the static limit and for the dc Kerr effect, ESHG, and THG, evaluated at the optical frequency $\nu = 20000 \text{ cm}^{-1}$ using Eqs. (5)–(8). As well as the total γ^ν for each process, the separate contributions of the μ^4 , $\mu^2\alpha + \mu\alpha\mu$, $\mu\beta$, and α^2 terms [parts (a), (b), (c), and (d) of Eqs. (5)–(8)] are given for each process. For comparison, the measured value of $\gamma = \gamma^\epsilon + \gamma^\nu$ for ESHG at $\nu = 20000 \text{ cm}^{-1}$ is $\gamma = 11 \times 10^{-62} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$.

Term	$\gamma^\nu (10^{-62} \text{ C}^4 \text{ m}^4 \text{ J}^{-3})$			
	Static	dc Kerr	ESHG	THG
μ^4	227.5	3.6	-1.9×10^{-3}	1.9×10^{-4}
$\mu^2\alpha + \mu\alpha\mu$	-6.6	-10.4	-6.0	-0.71
$\mu\beta$	11.2	5.6	2.8	-2.0×10^{-2}
α^2	7.2	1.5	-7.3×10^{-3}	-2.5×10^{-3}
Total	239.4	0.3	-3.2	-0.73

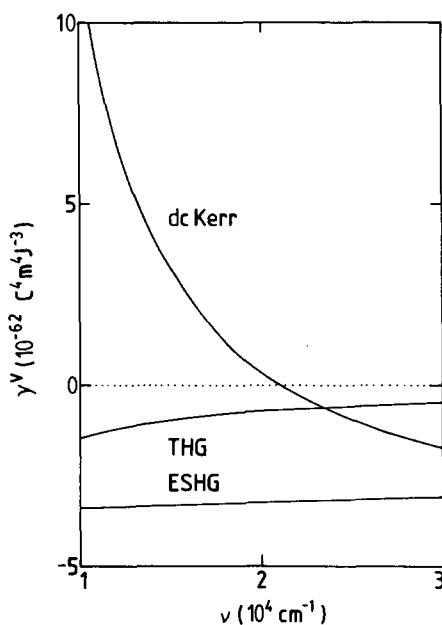


FIG. 1. Vibrational contributions to the isotropically averaged hyperpolarizabilities γ^v for the SF₆ molecule are plotted as functions of optical frequency ν for the dc Kerr effect, ESHG, and THG [evaluated using Eqs. (6)-(8)].

as shown in Fig. 1. There one sees that the frequency dependence of γ_{ESHG}^v and γ_{THG}^v is weak while the frequency dependence of γ_{Kerr}^v is very strong. At low frequencies γ_{Kerr}^v becomes much larger than γ_{ESHG}^v or γ_{THG}^v , as expected. If we ignore the dispersion of γ^v we may use the experimental measurements of γ for the dc Kerr effect,³⁷ ESHG,^{36,38} and THG³⁹ as a rough test of our calculations ($\gamma_{\text{Kerr}} = 15 \times 10^{-62} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$ at $\lambda = 632.8 \text{ nm}$, $\gamma_{\text{ESHG}} = 10 \times 10^{-62} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$ at $\lambda = 632.8 \text{ nm}$, and $\gamma_{\text{THG}} = 11 \times 10^{-62} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$ at $\lambda = 694.3 \text{ nm}$). If γ^v is constant then we may expect the observed difference $\gamma_{\text{Kerr}} - \gamma_{\text{ESHG}} = 5 \times 10^{-62} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$ to equal the calculated difference $\gamma_{\text{Kerr}} - \gamma_{\text{ESHG}}^v = 5.6 \times 10^{-62} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$, and also $\gamma_{\text{THG}} - \gamma_{\text{ESHG}}^v = 1 \times 10^{-62} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$ to equal $\gamma_{\text{THG}} - \gamma_{\text{ESHG}}^v = 2.4 \times 10^{-62} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$. The observed agreement is about as good as can be expected in view of the accuracy of the experimental data ($\pm 1 \times 10^{-62} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$) and the systematic errors due to the neglect of the dispersion of γ^v and the temperature dependence of γ^v .

In summary, we have derived expressions for vibrational contributions to the hyperpolarizabilities of spherical top molecules and have shown that these expressions may be accurately evaluated in the case of the SF₆ molecule. For SF₆ we find that γ^v may be as large as γ^e at optical frequencies, and that γ^v is much larger than γ^e in the static limit. The size and frequency dependence of γ^v is very different for the dc Kerr effect, ESHG, and THG. Further experimental study of γ^v for SF₆ should be interesting because γ^v is large enough (compared to γ^e) that it may be reliably estimated by com-

parison of measurements made by several nonlinear-optical processes, and because the high population in low-lying vibrational levels may result in significant temperature dependence for γ^v .

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