Vibrational contributions to the second hyperpolarizability of CF_4

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The frequency dependence of the second hyperpolarizability (γ) of CF_4 has been measured in the visible (488 nm $< \lambda <$ 660 nm) by means of gas-phase electric-field-induced second harmonic generation (ESHG). The results of these experiments are compared with the results of other nonlinear optics experiments which have measured γ by third harmonic generation (THG), ESHG, and the dc Kerr effect. In order to make this comparison, expressions for the vibrational contributions to γ_{CF_4} have been derived and numerically evaluated for each of these optical processes. This comparison indicates that vibrational contributions to γ_{CF_4} are significant for both the dc Kerr effect and ESHG.

INTRODUCTION

The third-order nonlinear susceptibility $\chi^{(3)}$, which mediates a wide range of nonlinear-optical processes, is the macroscopic expression of the microscopic second hyperpolarizability tensor γ.[1–4] 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.[5–7] The underlying unity of the fundamental theoretical description is obscured in practice because γ for each nonlinear optical process has a characteristically different balance of contributions from the electronic, vibrational, and rotational degrees of freedom of each molecule.[8–10] Recently there has been much theoretical interest and activity directed towards gaining an understanding of the various contributions to γ for small molecules by means of *ab initio* calculations.[11–15] On the other hand, since the particular γ tensors mediating the various processes are merely instances of a general γ tensor differing only in their frequency arguments, it should be possible to disentangle the contributions of the various molecular mechanisms by experimentally studying the frequency dependence of γ. Below we will present experimental measurements of the frequency dependence of γ for CF_4 made by means of electric-field-induced second harmonic generation (ESHG), and a comparison of these results with the results of previous measurements from several other nonlinear-optics experiments with the same molecule. In order to interpret the results of this comparison, we have also calculated the vibrational contributions to γ_{CF_4} for the nonlinear-optical processes of third harmonic generation (THG), ESHG, and the dc Kerr effect.

EXPERIMENT

The experimental apparatus is similar to that previously described in detail elsewhere.[16–20] A cw laser beam from a dye laser pumped by an argon-ion laser, or from the argon-ion laser directly, is weakly focused through a sample cell containing the gas in which second-harmonic generation takes place. The static field breaks the symmetry of the system, permitting coherent generation of the second-harmonic signal. The signal is strongly enhanced by means of periodic phase matching, accomplished by arranging the electrodes so that the field alternates in direction every coherence length. The coherence length of the gas is adjusted to match the fixed spacing of the electrodes by varying the gas density. The electrode spacing is 2.69 mm, resulting in optimal pressures in the range of 2.1–5.7 atm (at 20–25 °C) in the experiments reported here. The applied field is typically about 1.8 kV/mm. A double prism spectrometer and glass filters serve to separate the second-harmonic from the fundamental beam. The second-harmonic is detected by a photon counting system with an uncooled photomultiplier tube. The background is usually about 0.5 cps, while the peak signal is around several hundred cps. DCM and Rhodamine-6G are employed in the dye laser. The wavelengths were calibrated by Na or Ne atomic emission lines using spectral lamps and a Jarrell–Ash 1 m spectrometer.

The optical-field and static-field polarizations are parallel in this experiment, so the measurements are related to the *XXXX* component of the orientationally averaged tensor $\gamma_{\alpha\beta\gamma\delta}$. The ratio of hyperpolarizabilities for a sample gas B and a reference gas A is obtained from the relations

$$\gamma_B/\gamma_A = (S_B^{(2\omega)}/S_A^{(2\omega)})^{1/2}(\rho_B n'_B/\rho_A n'_A)^{-1} \qquad (1)$$

and

$$n' = (n_0^4 n_\omega^3 n_{2\omega})^{1/6}, \qquad (2)$$

where $S^{(2\omega)}$ is the peak signal, ρ is the number density and n_ω is the refractive index at frequency ω of the gas at phase match. In the present case $B = CF_4$ and $A = N_2$. Peak signal and optimum density were determined by least squares fitting a polynomial to the measurements of second harmonic power vs sample density, including only data taken symmetrically within about 10% of the peak signal so as to avoid fitting errors. Sample densities were computed from the measured pressures and temperatures using the virial equation of state.[21] Refractive indices were calculated from tables using the measured densities.[22] The local field corrections[20] given by Eq. (2) are very small, of order 0.2%. The purity of the N_2 reference gas is 99.999% while that of the CF_4 sample is better than 99.9%. A Raman spectroscopic assay of the

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TABLE I. Experimental results for $\Delta\alpha$ and γ of CF_4 measured by ESHG over the visible.

λ (nm)	ν (cm^{-1})	$\Delta\alpha_{CF_4}/\Delta\alpha_{N_2}$	$\Delta\alpha_{CF_4}$ (10^{-41} C^2 m^2 J^{-1})	$\gamma_{CF_4}/\gamma_{N_2}$	γ_{CF_4} (10^{-63} C^4 m^4 J^{-3})
659.8	151 52	1.066 ± 0.002	0.823 ± 0.004	1.072 ± 0.004	71.0 ± 0.4
640.2	156 15	1.055 ± 0.002	0.870 ± 0.004	1.067 ± 0.004	71.5 ± 0.4
621.7	160 80	1.045 ± 0.002	0.919 ± 0.005	1.068 ± 0.004	72.4 ± 0.4
589.0	169 73	1.029 ± 0.002	1.019 ± 0.005	1.060 ± 0.002	73.7 ± 0.4
514.5	194 30	0.998 ± 0.002	1.339 ± 0.005	1.046 ± 0.003	78.2 ± 0.4
496.5	201 35	0.991 ± 0.002	1.445 ± 0.006	1.036 ± 0.004	79.2 ± 0.5
488.0	204 86	0.987 ± 0.002	1.498 ± 0.006	1.036 ± 0.003	80.0 ± 0.4

CF_4 found $<0.058\%$ impurities ($CF_3Cl < 0.021\%$, $CHF_3 < 0.005\%$, $N_2 < 0.018\%$, $O_2 < 0.012\%$, and $H_2O < 0.0018\%$). From published measurements of the refractive index dispersion and the third-order susceptibility,[23,24] one may estimate that the effect of the impurities will be to shift the measured hyperpolarizability by less than 0.1% as compared to that of pure CF_4. Measurements were made in coupled triplets (ABABA...) in order to cancel drifts. The estimated total experimental uncertainty of a hyperpolarizability-ratio measurement is obtained by convolving the statistical uncertainty for an average of usually five triplets of runs, with the uncertainty of the density determinations due to the limited accuracy of the pressure gauge. The accuracy of the ratios determined in this experiment is around $\pm 0.4\%$.

In this experiment, one also obtains the ratio of linear polarizability dispersion $\Delta\alpha_{CF_4}/\Delta\alpha_{N_2}$, where $\Delta\alpha(\omega) = \alpha(2\omega) - \alpha(\omega)$, since $\Delta\alpha$ is just proportional to ρ^{-1}, the inverse phase match density. The accuracy of the linear polarizability dispersion ratio has been estimated as about $\pm 0.2\%$, based on the absolute pressure gauge accuracy of $\pm 0.15\%$. The reproducibility of the density ratio is $\pm 0.02\%$.

EXPERIMENTAL RESULTS

The ratios $\gamma_{CF_4}/\gamma_{N_2}$ measured at seven wavelengths in this experiment are given in Table I, as well as the values of γ_{CF_4} derived from these measurements. To obtain γ_{CF_4} from the measured ratios, we have employed the previous measurements of γ_{N_2}/γ_{He}[18] and the *ab initio* results for γ_{He}[25] for calibration, as detailed in Ref. 26. Our experimental results for γ_{CF_4} fall on a straight line when plotted vs ν^2, as shown in Fig. 1. The results of previous ESHG measurements are given in Table II, and are also plotted in Fig. 1. The previous results are seen to be in good agreement with the present ESHG measurements for CF_4. The linear polarizability dispersion ratios $\Delta\alpha_{CF_4}/\Delta\alpha_{N_2}$ measured in these experiments are also given in Table I. The value of $\Delta\alpha_{CF_4}$ has been obtained from these ratios using the previously measured values of $\Delta\alpha_{N_2}$ for calibration.[27] Figure 2 shows the values of $\Delta\alpha_{CF_4}/\nu^2$, obtained from our measurements, plotted vs ν^2.

VIBRATIONAL CONTRIBUTIONS TO THE LINEAR POLARIZABILITY

To illustrate our method of analysis we will first apply it to the linear polarizability. The method consists of first calculating the vibrational contribution, in this case α^v, and then of obtaining the electronic contribution $\alpha^e = \alpha - \alpha^v$ from the experimentally measurable α by subtracting α^v. Finally, one compares the value of α^e so obtained with the value obtained from some independent estimate.

The vibrational contribution to the isotropic polarizability $\alpha^v_{CF_4}$ is calculated from the expression[4,8]:

$$\alpha^v(\omega) = \hbar^{-1} \sum_m{}' |\mu^x_{mg}|^2 \frac{2\Omega_{mg}}{\Omega^2_{mg} - \omega^2}, \quad (3)$$

where Ω_{mg} is a vibrational transition frequency, $|\mu^x_{mg}|$ is a matrix element of the transition dipole moment and the primed summation excludes the ground state. Use has been made of the relation $|\mu^x_{mg}| = |\mu^y_{mg}| = |\mu^z_{mg}|$ obeyed by all the nonvanishing dipole matrix elements for CF_4. At optical frequencies ω, one may apply the approximation $\Omega^2_{mg} - \omega^2 \approx -\omega^2$ to obtain

$$\Delta\alpha^v(\omega) = \alpha^v(2\omega) - \alpha^v(\omega)$$

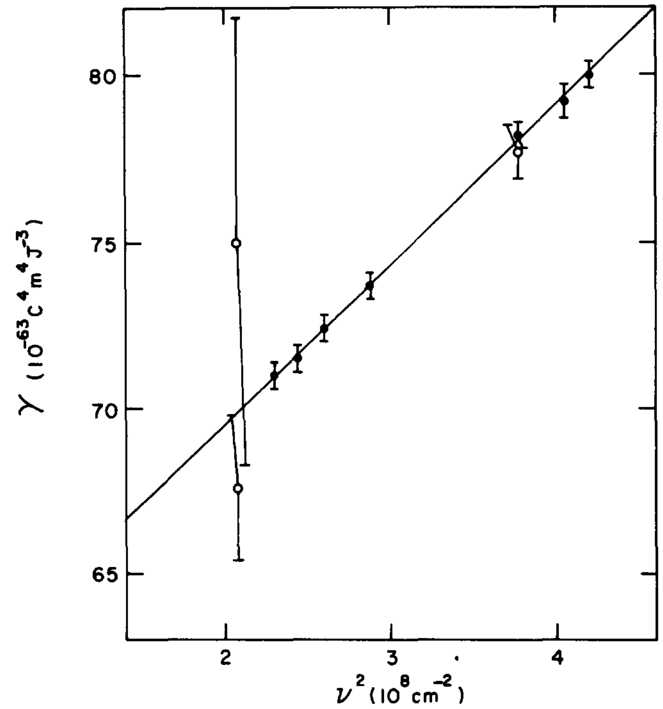

FIG. 1. The values of γ_{CF_4} measured in the present ESHG experiments (filled circles) and in previous experiments (open circles) are plotted vs ν^2. The straight line is a fit of the function $\gamma = A(1 + B\nu^2)$ to the data of the present experiments. The coefficients of the fit are $A = 60.03 \times 10^{-63}$ C^4 m^4 J^{-3} and $B = 7.93 \times 10^{-10}$ cm^2, where ν is given in cm^{-1}.

TABLE II. Hyperpolarizability of CF$_4$ previously measured by several nonlinear optical processes.

Process	λ (nm)	ν_L^2 (10^8 cm^{-2})	γ_{CF_4} (10^{-63} C^4 m^4 J^{-3})
dc Kerr	632.8	4.99	$92.8 \pm 5.2^{\mathrm{a}}$
	632.8	4.99	$77.0 \pm 6.0^{\mathrm{b}}$
ESHG	694.3	12.45	$75.0 \pm 6.7^{\mathrm{c}}$
	694.3	12.45	$67.6 \pm 2.2^{\mathrm{d}}$
	514.5	22.66	$77.7 \pm 0.8^{\mathrm{e}}$
THG	694.3	24.89	$73.5 \pm 3.7^{\mathrm{f}}$

[a] From Ref. 49.
[b] From Ref. 50.
[c] From Ref. 51.
[d] From Ref. 52.
[e] Recalculated from the result given in Ref. 16, using the more accurate value of γ_{CH_4} from Ref. 26 for calibration.
[f] From Ref. 53.

$$\approx -3/4\alpha^v(\omega) \approx 3/2\hbar^{-1}\omega^{-2} \sum_m{}' |\mu_{mg}^x|^2\,\Omega_{mg}, \quad (4)$$

where $\Delta\alpha$ is the quantity actually measured in our experiments. To evaluate $\Delta\alpha^v$ from the above expression, we employ the dipole matrix elements given in Table III. These matrix elements for CF$_4$ are obtained from experimental measurements of infrared absorption[29–31] and Raman scattering [32–35] using the standard theory.[8,36–40] The result for $\Delta\alpha^v$ is simply

$$\Delta\alpha^v(\nu) = (1.360\times10^{-34}\ \mathrm{C^2\,m^2\,J^{-1}\,cm^{-2}})\nu^{-2} \quad (5)$$

where ν is given in cm^{-1}.

Having calculated $\Delta\alpha^v(\omega)$ for CF$_4$, we may extract $\Delta\alpha^e(\omega)$ by subtracting from each data point for $\Delta\alpha$ in Table II the value of Eq. (5) evaluated at the corresponding frequency. The experimental results after removing the vibrational contribution are plotted as the open circles in Fig. 2. These values of $\Delta\alpha^e$ are well represented by a simple polynomial in even powers of the frequency, with the form

$$\Delta\alpha^e(\omega) = a\omega^2 + b\omega^4, \quad (6)$$

as shown by the dashed straight line in Fig. 2. This frequency dependence is of just the form one would expect if $\Delta\alpha^e$ is due to high frequency electronic resonances.

We may check our calculation of $\alpha^v(\omega)$ in two ways. First, we may take the static limit ($\omega = 0$) of Eq. (3):

$$\alpha^v(0) = 2\hbar^{-1} \sum_m{}' |\mu_{mg}^x|^2/\Omega_{mg}, \quad (7)$$

and make use of the matrix elements of Table III to estimate $\alpha_{\mathrm{CF}_4}^v(0) = 1.12\times10^{-40}$ C^2 m^2 J^{-1}. This is in excellent agreement with the value $\alpha_{\mathrm{CF}_4}^v(0) = 1.13 \pm 0.03\times10^{-40}$ C^2 m^2 J^{-1} obtained by Elliott and Ward from the expression

$$\alpha^v(0) = \alpha(0) - \lim_{\omega\to0} \alpha(\omega), \quad (8)$$

where $\alpha(0) = 4.270 \pm 0.003\times10^{-40}$ C^2 m^2 J^{-1} is from a measurement of the static dielectric constant[41] and $\alpha(\omega)$ is from the refractive index measured at optical frequencies.[22,42] Furthermore, from the above data we obtain $\alpha^e(0) = 3.15\times10^{-40}$ C^2 m^2 J^{-1}, and combining this value of $\alpha^e(0)$ with $\alpha^e(\omega) = 3.17\times10^{-40}$ C^2 m^2 J^{-1} from the refractive index at $\lambda = 632.8$ nm,[4] one readily estimates that the leading coefficient of Eq. (6) should be about 3×10^{-50} C^2 m^2 J^{-1} cm^2, again in good agreement with the value 3.13×10^{-50} obtained by analysis of our data (see Fig. 2, frequency in cm^{-1}).

The two most important results of the analysis are illustrated in Fig. 2. First, the vibrational contribution is a significant fraction of the total, and second, after correcting for α^v, the remaining α^e has a very simple frequency dependence.

CALCULATION OF VIBRATIONAL CONTRIBUTION TO γ

Calculations of the vibrational contributions to the second hyperpolarizability are more complicated than those for the linear polarizability. In this section we will first make a relatively rough estimate of the vibrational contributions to γ_{THG}, followed by more precise calculations of the vibrational contributions to γ_{ESHG} and γ_{Kerr}.

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:

$$\gamma_{\alpha\beta\gamma\delta}(-\omega_\sigma;\omega_1,\omega_2,\omega_3) = \hbar^{-3}\sum_P\left\{\sum_m{}'\sum_n{}'\sum_p{}' \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\delta|n\rangle\langle n|\mu_\gamma|p\rangle\langle p|\mu_\beta|g\rangle}{(\Omega_{mg}-\omega_\sigma)(\Omega_{ng}-\omega_1-\omega_2)(\Omega_{pg}-\omega_3)} - \sum_m{}'\sum_n{}' \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\delta|g\rangle\langle g|\mu_\gamma|n\rangle\langle n|\mu_\beta|g\rangle}{(\Omega_{mg}-\omega_\sigma)(\Omega_{ng}-\omega_1)(\Omega_{ng}+\omega_2)}\right\}, \quad (9)$$

where $\omega_\sigma = \omega_1 + \omega_2 + \omega_3$, and Σ_P 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 $|g\rangle$. This expression is valid for nondipolar molecules such as CF$_4$. 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.[9,43]

In the case of THG, the vibrational hyperpolarizability γ^v is obtained by substituting $(-\omega_\sigma;\omega_1,\omega_2,\omega_3) = (-3\omega;\omega,\omega,\omega)$, and writing out the 48 permuted terms

TABLE III. Matrix elements for transitions from the ground state for the CF_4 molecule. The symmetry species for the upper level of each transition are given in the column labeled species. The matrix elements have been deduced from infrared absorption and Raman scattering data as outlined in Refs. 8 and 36–40. The observables in a Raman scattering experiment are the mean polarizability and the anisotropy, usually denoted by "a" and "γ". Summing over degenerate modes, these may be written as $\alpha = 1/3\ (\alpha^{xx} + \alpha^{yy} + \alpha^{zz})$ and $\gamma^2 = (\alpha^{xx} - \alpha^{yy})^2 + 9(\alpha^{xy})^2$ in terms of the independent components of transition polarizability tensor for CF_4.

Assign.	Species	ν_{gm} (cm^{-1})	$\lvert\mu^x_{gm}\rvert$[a] (10^{-32} C m)	$\lvert\alpha^{xy}_{gm}\rvert$[b] ($10^{-42}\ C^2\ m^2\ J^{-1}$)
ν_1	a_1	908	0	0[c]
ν_2	e	435	0	0[d]
ν_3	f_2	1283	112.0	2.20
ν_4	f_2	631	16.0	2.43
$2\nu_2$	$a_1 + e$	869	0	0[e]
$2\nu_3$	$a_1 + e + f_2$	2566	7.66	0.04[f]
$2\nu_4$	$a_1 + e + f_2$	1264	7.98	0.21[g]
$\nu_1 + \nu_3$	f_2	2187	4.43	
$\nu_1 + \nu_4$	f_2	1536	8.86	
$\nu_2 + \nu_3$	$f_1 + f_2$	1718	3.49	
$\nu_2 + \nu_4$	$f_1 + f_2$	1067	3.94	
$\nu_3 + \nu_4$	$a_1 + e + f_1 + f_2$	1915	3.95	
$\nu_1 + \nu_3 + \nu_4$	$a_1 + e + f_1 + f_2$	2819	1.12	
$3\nu_4$	$a_1 + f_1 + 2f_2$	1896	0.18	
$3\nu_3$	$a_1 + f_1 + 2f_2$	3850	0.48	
$\nu_1 + 3\nu_3$	$a_1 + f_1 + 2f_2$	4753	0.19	
$2\nu_3 + \nu_4$	$a_1 + e + 2f_1 + 3f_2$	3198	0.56	
$\nu_1 + 2\nu_3 + \nu_4$	$a_1 + e + 2f_1 + 3f_2$	4102	0.24	
$\nu_3 + 2\nu_4$	$a_1 + e + 2f_1 + 3f_2$	2547	5.10	
$\nu_1 + \nu_3 + 2\nu_4$	$a_1 + e + 2f_1 + 3f_2$	3450	0.69	
$2\nu_1 + \nu_3$	f_2	3091	0.61	
$2\nu_1 + \nu_4$	f_2	2440	1.50	
$\nu_1 + 2\nu_4$	$a_1 + e + f_2$	2168	1.37	
$2\nu_2 + \nu_3$	$f_1 + 2f_2$	2153	1.08	
$\nu_3 - \nu_1$[h]	f_2	373	1.32	
$2\nu_3 - \nu_2$[i]	$a_1 + e + f_2$	2131	0.61	
$3\nu_4 - \nu_2$[i]	$a_1 + f_1 + 2f_2$	1459	3.07	

[a] The matrix elements for the four fundamental transitions are the values calculated by Elliott and Ward from the infrared absorption data of Refs. 28–31. The remaining matrix elements were obtained from the overtone and combination band intensities read from the spectrum given in Ref. 28 and calibrated against the ν_4 band. The accuracy of the latter values is ± 10%–20% at best. The transition dipole $|\mu^x_{gm}|$ is nonzero for the f_2 symmetry species only.

[b] The polarizability matrix elements for the four fundamentals are essentially the values calculated by Elliott and Ward from the Raman scattering data of Refs. 32–35. The overtone intensities were measured in the course of the Raman spectroscopic assay of our sample. The intensities were calibrated against the intensity of the nearest fundamental of the same symmetry. The transition polarizability α^{xy}_{gm} is nonzero for the f_2 symmetry species only.

[c] For this vibration of a_1 symmetry the only nonzero transition polarizability is $1/3\ |\alpha^{xx} + \alpha^{yy} + \alpha^{zz}| = 7.1 \times 10^{-42}\ C^2\ m^2\ J^{-1}$.

[d] For this vibration of e symmetry the only nonzero transition polarizability is $|\alpha^{xx} - \alpha^{yy}| = 6.4 \times 10^{-42}\ C^2\ m^2\ J^{-1}$.

[e] Since the $2\nu_2$ band is strongly polarized and the a_1 symmetry species is in Fermi resonance with ν_1, one may assume that the intensity is dominated by the a_1 species, giving $1/3\ |\alpha^{xx} + \alpha^{yy} + \alpha^{zz}| = 1.44 \times 10^{-42}\ C^2\ m^2\ J^{-1}$.

[f] This is an upper bound arrived at by assuming that the Raman intensity is due to only the f_2 species.

[g] Since the $2\nu_4$ band is depolarized and the f_2 species is in Fermi resonance with ν_3, we have assumed that the intensity is dominated by the f_2 species.

[h] Lower level is $\nu_1 = 1$.

[i] Lower level is $\nu_2 = 1$.

from Eq. (9). Each of these terms may be classified according to whether one, two or three of the intermediate states m, n, p are vibrationally excited states of the ground electronic manifold. Thus, seven distinct groups of terms arise from each of the permuted terms of Eq. (9) involving the triple sum over states, while only three groups of terms arise from each of the permuted terms of Eq. (9) involving the double sum over states. The THG signal measured in the lab is related to the $XXXX$ component of the isotropically averaged molecular hyperpolarizability tensor. Since Kleinman sym-

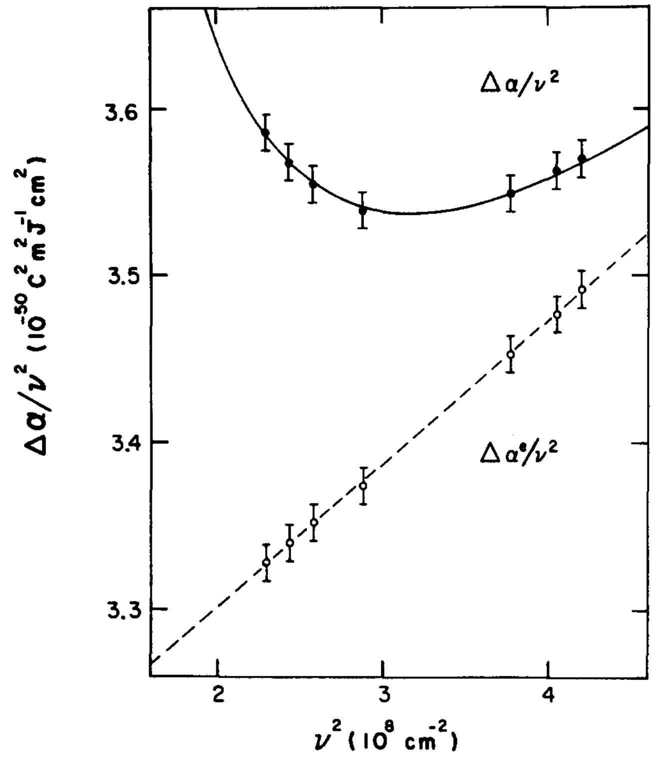

FIG. 2. The frequency dependence of the linear polarizability of CF$_4$ is illustrated. The filled circles are the values of $\Delta\alpha/\nu^2$ measured in this ESHG experiment, while the open circles are the corresponding results for the electronic contribution $\Delta\alpha^e/\nu^2$, obtained from the experimental measurements by subtracting the vibrational contribution calculated in the text [see Eq. (5)]. Plotted vs ν^2, as in this figure, the $\Delta\alpha^e/\nu^2$ data are well represented by a straight line. The dashed straight line through the open circles has the form $\Delta\alpha^e/\nu^2 = A(1 + B\nu^2)$, with the coefficients $A = 3.13\times10^{-50}$ C^2 m^2 J^{-1} cm^2 and $B = 2.74\times10^{-10}$ cm^2, where ν is given in cm^{-1}. The solid curve through the original data points is obtained by adding the calculated vibrational contribution to the dashed straight line. Note that the frequency dependence of $\Delta\alpha^e$ is simpler than that of $\Delta\alpha$.

metry holds for THG,[9] and since the x, y, z, directions are equivalent for the T_d symmetry group, one may write

$$\gamma_{\rm THG} = \langle\gamma\rangle_{XXXX} = \gamma_{xxxx} - 2/5\Delta\gamma, \qquad (10)$$

where $\langle\ \rangle$ denotes the isotropic average, $\Delta\gamma = (\gamma_{xxxx} - 3\gamma_{xxyy})$, and the upper case (lower case) spatial indices refer to the lab (molecular) frame. For an atom $\Delta\gamma = 0$. At the present level of approximation it should be adequate to assume $\Delta\gamma = 0$ for CF$_4$ as well, from which it follows that $\gamma^v_{\rm THG} = \gamma^v_{xxxx}$. By considering only the tensor component γ^v_{xxxx}, the number of distinct terms is reduced from 240 to just 40.

In order to proceed further in evaluating $\gamma^v_{\rm THG}$, one notes that the following approximate relations hold for the transition frequencies and dipole matrix elements of the principal electronic and vibrational transitions for CF$_4$:

$$\Omega_e \approx 10\omega \approx 100\Omega_v, \qquad (11a)$$

$$|\mu_e| \approx 10|\mu_v|, \qquad (11b)$$

$$|\mu_e|^2/\Omega_e \approx |\mu_v|^2/\Omega_v, \qquad (11c)$$

where Ω_e, ω, Ω_v are electronic, optical, and vibrational transition frequencies, and μ_e and μ_v are electronic and vibrational transition matrix elements. Equation (11c) follows from Eqs. (11a) and (11b) and it essentially states that the electronic and vibrational contributions to the static polarizability are about equal, in agreement with the results presented in the previous section. Characterizing all the electronic and vibrational transitions by μ_e, Ω_e and μ_v, Ω_v is a crude approximation, but it allows one to easily obtain a simple result for $\gamma^v_{\rm THG}$. Using Eq. (11a), the denominators of the terms in the expression for $\gamma^v_{\rm THG}$ may be written so as to involve only Ω_v (e.g., $\Omega_v - 3\omega \approx 30\Omega_v$, $\Omega_e - 3\omega \approx 100\Omega_v$, etc.). Similarly, employing Eq. (11b) allows one to write all the numerators so that they involve only μ_v (i.e. $\langle g|\mu|m\rangle \approx 10\mu_v$ if gm is an electronic transition). Then every term of $\gamma^v_{\rm THG}$ is simply proportional to μ_v^4/Ω_v^3. The terms arising from the triple sum over states in Eq. (9) all sum to zero, while the term inside the double sum in Eq. (9) gives just $(-64/1000)\mu_v^4/\Omega_v^3$. Thus, one obtains the following expression for $\gamma^v_{\rm THG}$:

$$\gamma^v_{\rm THG} \approx (64/1000)\left(\sum_m{}' |\mu^x_{mg}|^2\right)^2 / (\hbar\Omega_{\rm v})^3, \qquad (12)$$

where now the sum only extends over vibrationally excited states. The data in Table III allow one to evaluate this expression. For CF$_4$ the sum $\Sigma'_m |\mu^x_{mg}|^2 = 1.3\times10^{-60}$ C^{2}m^2 is dominated (95% contribution) by the ν_3 vibrational fundamental. Using the ν_3 vibrational transition frequency as Ω_v in Eq. (12), one gets

$$\gamma^v_{\rm THG} \approx 1.1\times10^{-63}\ {\rm C^4\ m^4\ J^{-3}}. \qquad (13)$$

This is only about 1% of the total γ. The accuracy of Eq. (13) is difficult to assess, but even if it were in error by a factor of three, $\gamma^v_{\rm THG}$ would still be very small compared to γ^e for CF$_4$.

In the case of ESHG, the situation is rather different from that of THG. Substituting $(-\omega_\sigma;\omega_1,\omega_2,\omega_3) = (-2\omega;\omega,\omega,0)$, one may again write out the 48 permuted terms. One finds that more than half the terms have, in the denominator, a factor $(\Omega_v - \omega')$ with $\omega' = 0$. Since for typical vibrational and optical frequencies $\Omega_v \ll \omega$, terms with a factor of the form $(\Omega_v - 0)$ in the denominator will be strongly enhanced over all the other terms. Retaining only enhanced terms one obtains the following expressions for the relevant tensor components of $\gamma^v_{\rm ESHG}$:

$$\begin{aligned}\gamma^v_{\alpha\beta\beta\alpha}&(-2\omega;\omega,\omega,0)\\ &= \hbar^{-1}\sum_m{}' \frac{2\mu^\alpha_{gm}(\beta_{\alpha\beta\beta})_{mg}}{\Omega_{mg}}\\ &\quad + \hbar^{-3}\sum_m{}'\sum_n{}' \left\{\frac{\mu^\alpha_{gm}\mu^\alpha_{mg}\mu^\beta_{gn}\mu^\beta_{ng} + 2\mu^\alpha_{gm}\mu^\beta_{mg}\mu^\beta_{gn}\mu^\alpha_{ng}}{\omega^3}\right.\\ &\quad \left. + \frac{2\mu^\alpha_{gm}\mu^\alpha_{mg}\mu^\beta_{gn}\mu^\beta_{ng} - 2\mu^\alpha_{gm}\mu^\beta_{mg}\mu^\beta_{gn}\mu^\alpha_{ng}}{\Omega_{mg}\omega^2}\right\} \qquad (14a)\end{aligned}$$

and

$$\begin{aligned}\gamma^v_{\alpha\beta\alpha\beta}&(-2\omega;\omega,\omega,0)\\ &= \gamma^v_{\alpha\alpha\beta\beta}(-2\omega;\omega,\omega,0)\\ &= \hbar^{-1}\sum_m{}' \frac{\mu^\beta_{gm}(\beta_{\alpha\alpha\beta})_{mg} + \mu^\beta_{gm}(\beta_{\beta\alpha\alpha})_{mg}}{\Omega_{mg}}\end{aligned}$$

$$+\hbar^{-3}\sideset{}{'}\sum_{m}\sideset{}{'}\sum_{n}\left\{\frac{2\mu^{\beta}_{gm}\mu^{\alpha}_{gm}\mu^{\alpha}_{gn}\mu^{\beta}_{ng}+\mu^{\beta}_{gm}\mu^{\beta}_{mg}\mu^{\alpha}_{gn}\mu^{\alpha}_{ng}}{\omega^{3}}\right.$$

$$\left.+\frac{\mu^{\beta}_{gm}\mu^{\alpha}_{mg}\mu^{\alpha}_{gn}\mu^{\beta}_{ng}-\mu^{\beta}_{gm}\mu^{\beta}_{mg}\mu^{\alpha}_{gn}\mu^{\alpha}_{ng}}{\Omega_{mg}\omega^{2}}\right\}, \qquad (14b)$$

where $|m\rangle$, $|n\rangle$ are vibrationally excited states of the ground electronic manifold, and $(\beta_{\alpha\beta\beta})_{gp}$ are components of the hyper-Raman transition hyperpolarizability tensor defined by[44]

$$(\beta_{\alpha\beta\gamma})_{gp}=2\hbar^{-2}\sideset{}{'}\sum_{m}\sideset{}{'}\sum_{n}\left\{\frac{\langle g|\mu_{\beta}|m\rangle\langle m|\mu_{\alpha}|n\rangle\langle n|\mu_{\gamma}|p\rangle}{(\Omega_{mg}+\omega)(\Omega_{ng}-\omega)}\right.$$

$$+\frac{\langle g|\mu_{\beta}|m\rangle\langle m|\mu_{\gamma}|n\rangle\langle n|\mu_{\alpha}|p\rangle}{(\Omega_{mg}+\omega)(\Omega_{ng}+2\omega)}$$

$$\left.+\frac{\langle g|\mu_{\gamma}|m\rangle\langle m|\mu_{\beta}|n\rangle\langle n|\mu_{\alpha}|p\rangle}{(\Omega_{mg}-2\omega)(\Omega_{ng}-\omega)}\right\}. \qquad (15)$$

The experimentally measured quantity in our ESHG experiment is $\langle\gamma\rangle_{XXXX}$. The isotropically averaged γ tensors for ESHG and the dc Kerr effect have only two independent components, since $\langle\gamma\rangle_{XXYY}=\langle\gamma\rangle_{XYXY}$ for these processes in particular, and $\langle\gamma\rangle_{XXXX}=\langle\gamma\rangle_{XXYY}+\langle\gamma\rangle_{XYXY}+\langle\gamma\rangle_{XYYX}$ in general. Making use of the equivalence of the x, y, z directions for a tetrahedral molecule, one may write the independent components of $\langle\gamma\rangle$ in terms of the three independent components of γ as follows:

$$\langle\gamma\rangle_{XXXX}=1/5(3\gamma_{xxxx}+4\gamma_{xxyy}+2\gamma_{xyyx}), \qquad (16a)$$

$$\langle\gamma\rangle_{XYYX}=1/5(\gamma_{xxxx}-2\gamma_{xxyy}+4\gamma_{xyyx}), \qquad (16b)$$

where the lower case indices denote components in the molecule fixed frame. Substituting Eqs. (14a) and (14b) into Eq. (16a), and considering that for the spherical top molecule CF_4 the following relations are satisfied[45–47]:

$$\beta_{xxx}=\beta_{yyy}=\beta_{zzz}, \qquad (17a)$$

$$\beta_{xyy}+\beta_{zzx}=\beta_{yzz}+\beta_{xxy}=\beta_{zxx}+\beta_{yyz}, \qquad (17b)$$

$$\beta_{xyy}=\beta_{yyx},\quad \beta_{xzz}=\beta_{zzx},\quad \beta_{yzz}=\beta_{zzy}, \qquad (17c)$$

one obtains the following expression for $\gamma^{v}_{\mathrm{ESHG}}$ for CF_4:

$$\gamma^{v}_{\mathrm{ESHG}}=\frac{12}{5}\hbar^{-1}\sideset{}{'}\sum_{m}\frac{\mu^{x}_{gm}(\beta_{xxx}+\beta_{xyy}+\beta_{zzx})_{mg}}{\Omega_{mg}}$$

$$+\frac{27}{5}\hbar^{-3}\sideset{}{'}\sum_{m}\sideset{}{'}\sum_{n}\frac{|\mu^{x}_{gm}|^{2}|\mu^{x}_{gn}|^{2}}{\omega^{3}}. \qquad (18)$$

At optical frequencies, the second term of Eq. (18) should be very small and the first term is expected to be dominant. Numerical estimation and discussion will be deferred until the next section.

The procedure for calculation of $\gamma^{v}_{\mathrm{Kerr}}$ is similar to that used in the calculation of $\gamma^{v}_{\mathrm{ESHG}}$. Substituting $(-\omega_{\sigma};\omega_{1},\omega_{2},\omega_{3})=(-\omega;0,0,\omega)$ in Eq. (9) and writing out the 48 frequency permuted terms for $\gamma^{v}_{\mathrm{Kerr}}$, one finds there appear terms with two of the factors $(\Omega_{v}-\omega')$ in the denominator having $\omega'=0$. These terms are expected to be greatly enhanced over all other terms and, therefore, to dominate the expression for $\gamma^{v}_{\mathrm{Kerr}}$. Retaining only the doubly enhanced terms results in the following expression for the relevant tensor components of $\gamma^{v}_{\mathrm{Kerr}}$:

$$\gamma^{v,\alpha}_{\alpha\beta\beta\alpha}(-\omega;0,0,\omega)$$

$$=2\hbar^{-2}\left\{\sideset{}{'}\sum_{m}\sideset{}{'}\sum_{n}\frac{2\alpha^{\alpha\alpha}_{gm}\mu^{\beta}_{mn}\mu^{\beta}_{ng}+\mu^{\beta}_{gm}\alpha^{\alpha\alpha}_{mn}\mu^{\beta}_{ng}}{\Omega_{mg}\Omega_{ng}}\right.$$

$$\left.-\sideset{}{'}\sum_{m}\frac{\alpha^{\alpha\alpha}_{gg}\mu^{\beta}_{gm}\mu^{\beta}_{mg}}{\Omega_{mg}\Omega_{mg}}\right\} \qquad (19a)$$

and

$$\gamma^{v,\alpha}_{\alpha\beta\alpha\beta}(-\omega;0,0,\omega)$$

$$=\gamma^{v,\alpha}_{\alpha\alpha\beta\beta}(-\omega;0,0,\omega)$$

$$=\hbar^{-2}\left\{\sideset{}{'}\sum_{m}\sideset{}{'}\sum_{n}\frac{2\alpha^{\alpha\beta}_{gm}\mu^{\beta}_{mn}\mu^{\alpha}_{ng}+2\alpha^{\beta\alpha}_{gm}\mu^{\alpha}_{mn}\mu^{\beta}_{ng}}{\Omega_{mg}\Omega_{ng}}\right.$$

$$+\sideset{}{'}\sum_{m}\sideset{}{'}\sum_{n}\frac{\mu^{\alpha}_{gm}\alpha^{\beta\alpha}_{mn}\mu^{\beta}_{ng}+\mu^{\beta}_{gm}\alpha^{\alpha\beta}_{mn}\mu^{\alpha}_{ng}}{\Omega_{mg}\Omega_{ng}}$$

$$\left.-\sideset{}{'}\sum_{m}\frac{2\alpha^{\alpha\beta}_{gg}\mu^{\alpha}_{gm}\mu^{\beta}_{mg}}{\Omega_{mg}\Omega_{mg}}\right\}, \qquad (19b)$$

where

$$\alpha^{\alpha\beta}_{mn}=\hbar^{-1}\sideset{}{'}\sum_{p}\langle m|\mu_{\alpha}|p\rangle\langle p|\mu_{\beta}|n\rangle\frac{2\Omega_{pg}}{\Omega^{2}_{pg}-\omega^{2}} \qquad (20)$$

is the Raman transition polarizability.

The dc Kerr effect birefringence measured in the lab is related to the isotropically averaged molecular hyperpolarizability tensor through the definition

$$\gamma_{\mathrm{Kerr}}=3/2[\langle\gamma\rangle_{XXXX}-\langle\gamma\rangle_{XYYX}], \qquad (21)$$

where the notation is the same as in the calculations for $\gamma^{v}_{\mathrm{THG}}$ and $\gamma^{v}_{\mathrm{ESHG}}$. Substituting Eqs. (19a) and 19(b) into Eqs. (16a) and (16b) and Eq. (21), and recalling that $\mu^{x}_{gm}=\mu^{y}_{gm}$, $\alpha^{xy}_{gg}=0$, and $\alpha^{xy}_{gm}=\alpha^{yx}_{gm}$, one gets the following expression for $\gamma^{v}_{\mathrm{Kerr}}$ of CF_4:

$$\gamma^{v,\alpha}_{\mathrm{Kerr}}=\frac{18}{5}\hbar^{-2}\sideset{}{'}\sum_{m}\sideset{}{'}\sum_{n}\frac{2\alpha^{xy}_{gm}\mu^{y}_{mn}\mu^{x}_{ng}+\mu^{x}_{gm}\alpha^{xy}_{mn}\mu^{y}_{ng}}{\Omega_{mg}\Omega_{ng}}. \qquad (22)$$

If one carefully retains those terms with only one of the factors $(\Omega_{v}-\omega')$ in the denominator having $\omega'=0$, as well as the doubly enhanced terms which gave rise to Eq. (22), one obtains an additional contribution to $\gamma^{v}_{\mathrm{Kerr}}$ which involves the hyper-Raman β:

$$\gamma^{v,\beta}_{\mathrm{Kerr}}=\frac{4}{15}\hbar^{-1}\sideset{}{'}\sum_{m}\frac{2\mu^{x}_{gm}(\beta_{xxx}+\beta_{xyy}+\beta_{zzx})_{mg}+\mu^{z}_{gm}(\beta_{xyy}+\beta_{zzx})_{mg}}{\Omega_{mg}}. \qquad (23)$$

The relations of Eq. (17) have been employed in obtaining this result.

The expressions given in Eqs. (18), (22), and (23) allow one to calculate γ^{v} for ESHG and the dc Kerr effect. The

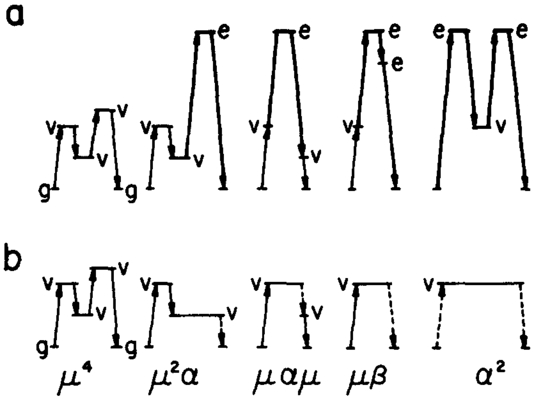

FIG. 3. Diagrams for the five essential types of term which contribute to γ^v. (a) The arrows denote transition dipole matrix elements between states of the molecule. The states are labeled v or e according to whether they are vibrationally or electronically excited. All diagrams start and end at the molecular ground state g. Heavier arrows are drawn for electronic transitions. (b) Summing over the sequences of electronic transitions in (a) gives diagrams involving transition matrix elements of the Raman or hyper-Raman polarizabilities α or β (dashed arrows). Thus, the diagrams for γ^v may be expressed in terms of vibrational transitions only, at the expense of containing matrix elements for all lower order processes.

infrared and Raman data in Table III is essentially sufficient for this purpose, although some further assumptions still have to be made in the numerical evaluation, as will be discussed in the next section.

The nature of the final expressions for γ^v and the manner in which they were derived may be clarified by reference to Fig. 3. The terms of Eq. (9) have been classified in Fig. 3(a) according to possible sequences of the vibrationally or electronically excited intermediate states $|m\rangle$, $|n\rangle$, and $|p\rangle$ in the terms which contribute to γ^v. Making use of Eqs. (15) and (20) allows sequences of electronic transition dipoles in Fig. 3(a) to be collapsed into vibrational transition polarizabilities and hyperpolarizabilities as shown in Fig. 3(b). Eqs. (18), (22), and (23) result when the calculation is done with due regard for spatial subscripts in the numerator and frequency arguments in the denominator, account is taken of molecular symmetry, and the microscopic molecular result is isotropically averaged. Note that the various diagrams in Fig. 3(b) do not contribute equally to γ^v. For N_2 only the α^2 terms are nonvanishing. For CF_4 all terms are allowed, but the $\mu^2\alpha$, $\mu\alpha\mu$, and $\mu\beta$ terms are dominant for the nonlinear optical processes that we have considered.

NUMERICAL ESTIMATION AND DISCUSSION

Before proceeding with the numerical evaluation of γ^v it is useful to compare the experimental measurements for several different third-order optical processes, for the moment ignoring the contribution due to γ^v. It has been suggested in previous work that far below resonance the electronic contributions to γ for the various third-order nonlinear optical processes will obey the relation[10,48]

$$\gamma^e(-\omega_\sigma;\omega_1,\omega_2,\omega_3) = \gamma^e(0;0,0,0)\,[1 + C\omega_L^2\,], \qquad (24)$$

where

$$\omega_L^2 = \omega_\sigma^2 + \omega_1^2 + \omega_2^2 + \omega_3^2 \qquad (25)$$

is the effective laser frequency. If it is the case that the electronic contributions to γ_{CF_4} are dominant, the values of γ_{CF_4} experimentally determined by means of different nonlinear optical processes should all fall on the same straight line when plotted vs ν_L^2.

The previously published values of γ_{CF_4} from dc Kerr effect,[49,50] ESHG[16,51,52] and THG[53] experiments have been collected in Table II and have been plotted vs ν_L^2 in Fig. 4. The straight line drawn there is the least squares fit of Eq. (24) to the experimental ESHG results of the present work. Two discordant values of γ_{CF_4} from dc Kerr effect experiments are given in Table II, but only one has been plotted in Fig. 4. The earlier measurement[49] was made on a sample of relatively low purity, only 98%, the chief impurity being air. The effect of 2% air as an impurity will be to increase the apparent value of γ_{CF_4} by 10%. A similar systematic error would arise from as little as 0.1% of typical fluoromethane impurities. The effect of the impurities would be revealed by a spurious temperature dependence of the measured γ_{CF_4}, but the measurement was made at only a single temperature. The later measurements,[50] on the other hand, used a sample of 10×higher purity (99.7%) and demonstrated temperature independence of the measured value of γ_{CF_4} over the temperature range 269–322 K. On the basis of these considerations, we have rejected the result of Ref. 49 in favor of the result of Ref. 50, which alone has been plotted in Fig. 4.

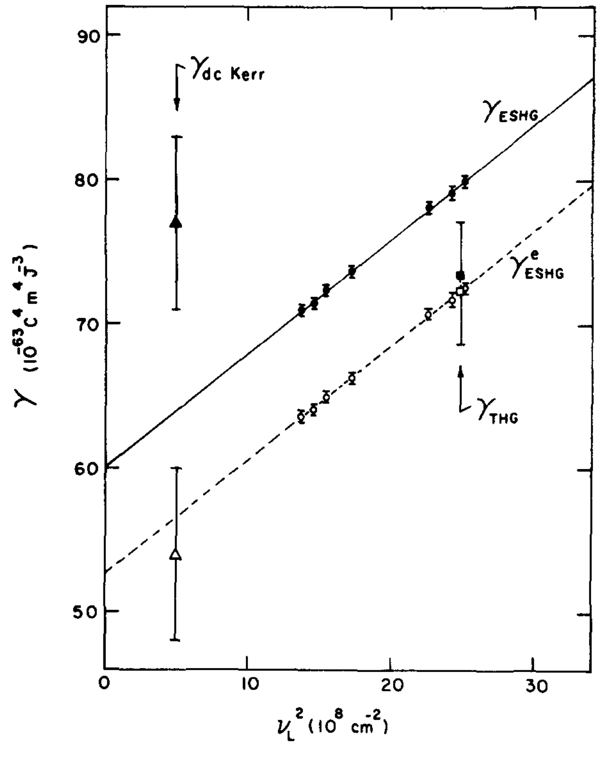

FIG. 4. Experimental values of γ_{CF_4} measured by the dc Kerr effect (triangles), ESHG (circles) and THG (squares) are plotted vs ν_L^2 [defined by Eq. (25)]. The filled symbols are the directly measured values of γ, while the open symbols are the corresponding results after subtracting the calculated vibrational contributions to obtain the purely electronic contribution γ^e. Note that the vibrational contribution is very small for THG. The solid line is the straight line which was fit to the ESHG data in Fig. 1, while the dashed line is the corresponding straight line fit to the vibrationally corrected ESHG data points. All the measurements of γ^e (open symbols) fall on the dashed straight line to within the error bars, as predicted by Eq. (24).

Comparing the dc Kerr and THG measurements with the straight line fitted to the ESHG measurements, one finds that the dc Kerr measurement falls about 20% above, while the THG measurement falls about 7% below the straight line. These differences are well outside the error bars of the various measurements, which clearly indicates that vibrational contributions to γ are significant.

The estimate of the vibrational contribution to γ_{THG} made in the last section indicates that γ^v_{THG} is almost negligible in comparison to the electronic contribution, and suggests that the vibrationally corrected γ_{THG} may be used to calibrate the electronic contributions to the other processes for CF_4. Following this idea and taking γ^v_{ESHG} as the vertical distance between the ESHG line and the vibrationally corrected THG point, the vibrational contribution to γ_{ESHG} is estimated to be 7.1×10^{-63} C^4 m^4 J^{-3}. It may be seen from Eq. (18) that there is a term of γ^v_{ESHG} which varies as ω^{-3}. However, evaluating this term using the matrix elements given in Table III, one finds that it is negligibly small (0.14×10^{-63} C^4 m^4 J^{-3}). Therefore, at optical frequencies the vibrational contribution to γ_{ESHG} is nearly independent of ω, and so subtracting the value of γ^v_{ESHG} from the γ_{ESHG} data to obtain γ^e_{ESHG} only causes a parallel translation of the solid straight line shown in Fig. 4. The estimate of γ^e obtained by a parallel translation of the γ_{ESHG} line until it passes through the γ^e_{THG} point is shown as the dashed line in Fig. 4. Deviations of the measured values of γ from this dashed line are to be interpreted as vibrational contributions. If this analysis is correct, γ^v calculated from Eq. (18) for ESHG and from Eqs. (22) and (23) for the dc Kerr effect must agree with the experimental values which are obtained from Fig. 4.

Evaluation of γ^v_{ESHG} using Eq. (18) would be straightforward except that, while there have been measurements of the hyper-Raman spectra of various other CX_4 compounds,[54–56] there have been no measurements of the hyper-Raman β for CF_4. Therefore, we will use the measurements[55] and calculations[57] which have been made for CH_4 for guidance. The hyper-Raman spectrum of CH_4 shows that the intensities of the hyper-Rayleigh line and the ν_3 Stokes hyper-Raman line are of the same order, and that all other transitions are much weaker. The experiment measures the XXX component of the isotropically averaged β^2, which may be expressed in terms of the hyperpolarizability components in the molecule fixed frame by the expression[45]:

$$\langle\beta^2\rangle_{XXX}=\frac{1}{35}\Bigg\{5\sum_{a}\beta^2_{\alpha\alpha\alpha}+6\sum_{\alpha\neq\beta}\beta_{\alpha\alpha\alpha}\beta_{\alpha\beta\beta}+9\sum_{\alpha\neq\beta}\beta^2_{\alpha\alpha\beta}+6\sum_{\substack{\alpha,\beta,\gamma\\ \text{cyclic}}}\beta_{\alpha\alpha\beta}\beta_{\beta\gamma\gamma}+12\beta^2_{\alpha\beta\gamma}\Bigg\}. \tag{26}$$

Assuming that the hyper-Rayleigh and the Stokes hyper-Raman scattering have equal intensities and that $\beta_{xxx}=\beta_{xyy}=\beta_{zzx}$, Eq. (26) may be applied to obtain the following relation between the magnitudes of the hyper-Raman and hyper-Rayleigh hyperpolarizability components:

$$|\beta_{xxx}|_{\nu_3}\approx 1/3|\beta_{xyz}|_{\mathrm{Rayleigh}}. \tag{27}$$

Hyper-Rayleigh scattering by a tetrahedral molecule is mediated by the single nonvanishing hyperpolarizability component β_{xyz}, whose magnitude was estimated theoretically by Buckingham and Stephen to be about 7.8×10^{-52} C^3 m^3 J^{-2} for CH_4.[57] Hyper-Raman scattering is mediated by several components of the transition hyperpolarizability. Equation (18) for γ^v_{ESHG} involves the following combination of transition hyperpolarizability components:

$$\beta_{\mathrm{eff}}=\beta_{xxx}+\beta_{xyy}+\beta_{zzx}, \tag{28}$$

which may be evaluated by means of Eq. (27) to obtain $|\beta_{\mathrm{eff}}|\approx|\beta_{xyz}|=7.8\times 10^{-52}$ C^3 m^3 J^{-2} for CH_4. With this value of β_{eff}, and using the transition matrix elements given in Ref. 8, one obtains from Eq. (18) the estimate $\gamma^v_{\mathrm{ESHG}}=3\times 10^{-63}$ C^4 m^4 J^{-3} for CH_4. This is only 1% of the total γ_{ESHG} of CH_4. In a similar fashion, using Eq. (18) and the matrix elements of Table III and the observed difference $\gamma_{\mathrm{ESHG}}-\gamma^e_{\mathrm{THG}}=7.1\times 10^{-63}$ C^4 m^4 J^{-3}, one deduces

$$|\beta_{\mathrm{eff}}|\approx 1.3\times 10^{-52}\ \mathrm{C^3\,m^3\,J^{-2}} \tag{29}$$

for the ν_3 mode of CF_4, 6× smaller than the corresponding value for CH_4.

Before attempting to evaluate γ^v_{Kerr}, it is useful to consider in more detail the nature of the vibrations for CF_4. As a spherical top molecule, CF_4 has fundamentals ν_1, ν_2, ν_3, and ν_4 with the symmetry assignments a_1, e, f_2 and f_2 in the T_d point group, respectively. All four of the fundamentals are Raman active, while only ν_3 and ν_4 with f_2 symmetry are infrared active. The symmetry species of a combination or overtone level are obtained from the direct product of irreducible representations, and will be a sum of a_1, a_2, e, f_1 and f_2 terms. The transitions with nonvanishing dipole matrix elements are just those for which the symmetry species f_2 appears at least once in the direct product of the representations of the initial and final levels of the transition. The three degenerate components of a mode of f_2 symmetry may be taken as vibrations in the x, y, and z directions, in which case only a single transition dipole matrix element and a single pair of transition polarizability matrix elements are nonvanishing for each vibrational component. The vibrational components and the corresponding nonvanishing matrix elements are $(x,\mu^x,\alpha^{yz}=\alpha^{zy})$, $(y,\mu^y,\alpha^{zx}=\alpha^{xz})$ and $(z,\mu^z,\alpha^{xy}=\alpha^{yx})$. The nonvanishing matrix elements also satisfy $\mu^x=\mu^y=\mu^z$ and $\alpha^{yz}=\alpha^{zx}=\alpha^{xy}$. Note that only vibrations of f_2 symmetry contribute to the final expressions for γ^v_{ESHG} and γ^v_{Kerr}, Eqs. (18), (22), and (23), and that the three-fold degeneracy of such vibrations has already been accounted for by making use of Eq. (16) for the isotropic averages. However, when the symmetry species f_2 appears n times in the representation of a particular vibrational overtone or combination transition, then one must multiply the matrix element by an extra degeneracy factor n. Furthermore, in the harmonic approximation, the matrix element for the hot band transition $v_i,v_j\rightarrow v_i,v_j+1$ is proportional to $(v_j+1)^{1/2}$. Such a simple result is not obtained for overtone and combination transitions, which are not allowed in the harmonic approximation, so for simplicity we have assumed that an overtone or combination transition starting from an excited level has the same matrix element as the same transition starting from the ground state.

The evaluation of $\gamma^{v}_{\rm Kerr}$ from Eqs. (22) and (23) makes use of the matrix elements given in Table III and the hyper-Raman β deduced when considering $\gamma^{v}_{\rm ESHG}$. Evaluation of Eq. (22) is done by writing out diagrams with three successive transitions $g \rightarrow m \rightarrow n \rightarrow g$, using matrix elements selected from Table III (about 100 diagrams altogether, with the 30 diagrams arising from just 12 of the largest matrix elements accounting for 98% of the final result). Taking all the matrix elements to be positive when computing the diagrams, and noting that many of the required matrix elements correspond to hot band transitions, one obtains:

$$\gamma^{v,\alpha}_{\rm Kerr} = 20.2\times 10^{-63}\ {\rm C^4\ m^4\ J^{-3}}. \qquad (30)$$

When Eq. (23) is evaluated and added, the final result is:

$$\gamma^{v}_{\rm Kerr} = 23.0\times 10^{-63}\ {\rm C^4\ m^4\ J^{-3}}. \qquad (31)$$

One sees that Eq. (23) involving the hyper-Raman β makes only a small contribution to the total. Subtracting Eq. (31) from the measured value of $\gamma_{\rm Kerr}$ to get $\gamma^{e}_{\rm Kerr}$, and plotting this as the open triangle in Fig. 4, one finds that the error bar of the plotted point overlaps the dashed line representing γ^{e}, just as required by our analysis.

The calculated value of $\gamma^{v}_{\rm Kerr}$ finally permits a clear test of our calculations of γ^{v}. We had proceeded by attributing the difference between the $\gamma^{e}_{\rm THG}$ and $\gamma_{\rm ESHG}$ measurements to $\gamma^{v}_{\rm ESHG}$. However, the theoretical expression for $\gamma^{v}_{\rm ESHG}$ is proportional to the unknown hyper-Raman β for CF_4, so the calculation for $\gamma^{v}_{\rm ESHG}$ ends up being used to determine the free parameter β. For $\gamma^{v}_{\rm Kerr}$, no further unknown parameters enter the calculation and so one may carry through the comparison of theory and experiment in order to judge the accuracy of the calculation. Thus, the fact that all the vibrationally corrected measurements fall on the same line supports the adequacy of our analysis. We note, however, that the calculated $\gamma^{v}_{\rm Kerr}$ is likely to be an overestimate since all matrix elements were assumed to be positive in the evaluation of the theoretical expressions. There will be a cancellation of terms if some matrix elements are negative. If six of the largest matrix elements are assumed to be positive but the signs of the other matrix elements are chosen at random, then $\gamma^{v,\alpha}_{\rm Kerr}$ is reduced by about 2× on average. Good agreement between theory and experiment seems to require that the largest matrix elements are all positive. In any case, the numerical results obtained here are much more reliable than those previously obtained by Elliott and Ward. Their calculation gave $\gamma^{v}_{\rm Kerr} \approx 3\gamma^{e}$, which is about 10× too large (note that an extra factor of 1/6 is included in the definition of γ in Ref. 8).

In summary, we have presented experimental measurements of γ made by ESHG and a method for combining these measurements with those from other nonlinear-optics experiments. All the experimental data is consistent with the decomposition of γ into electronic and vibrational parts, where γ^{e} is strongly frequency dependent but γ^{v} is essentially constant for each nonlinear optical process. Combining measurements and calculations, for CF_4 we find that $\gamma^{v}/\gamma^{e} \approx 1\%$, 10%, and 30% for THG, ESHG, and the dc Kerr effect, respectively. Accurate data on the frequency dependence of $\gamma_{\rm THG}$ and $\gamma_{\rm Kerr}$ would allow a better test of the calculations and analysis that have been presented here. The estimate of the value of the hyper-Raman β of CF_4 which is obtained as a byproduct of this work allows one to predict that the hyper-Raman spectrum of CF_4 will be 40× weaker than that of CH_4. A measurement of the hyper-Raman spectrum of CF_4 would provide another test of the above analysis. Ultimately, a measurement of $\gamma^{v}_{\rm ESHG}$ may provide a means for the accurate absolute calibration of the hyper-Raman β.

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