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FREQUENCY DEPENDENCE OF THE HYPERPOLARIZABILITY MEASURED FOR SF_6

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The frequency dependence of the hyperpolarizability of SF_6 has been measured in the visible by the technique of electric-field-induced second-harmonic generation (ESHG). The results are consistent with negligible vibrational contributions at optical frequencies for this non-linear process. The relation between these results and the results for other processes is examined.

1. Introduction

The second hyperpolarizability γ of a molecule plays a role in non-linear optical processes [1,2] as well as in intermolecular interactions [3,4]. Usually $\gamma(-\omega_0; \omega_1, \omega_2, \omega_3)$ is measured by optical methods such as the dc Kerr effect, electric-field-induced second-harmonic generation (ESHG) of third-harmonic generation (THG), where these processes differ in the choice of the frequency arguments [2,5–7]. In so far as the relevant γ for intermolecular processes is the zero-frequency limit of the general γ, and because most calculations relate to the static limit, it would be useful to have information about the dispersion of γ. Here we present measurements of the frequency dependence of $\gamma(-2\omega; \omega, \omega, 0)$ (i.e. the ESHG process) for the SF_6 molecule, as well as a discussion of the relation between the various optical hyperpolarizabilities and the static hyperpolarizability.

2. Experiment

The experimental technique has been described in detail [6–10]. A cw laser beam from an argon-ion-pumped dye 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. This is made possible by a symmetry breaking dc field. By arranging the electrodes so that the field direction alternates in direction every coherence length (adjusted by varying the gas density) periodic phase matching results, enhancing the second-harmonic signal generated. The electrode spacing is 2.69 mm, resulting in optimal pressures in the range 1 to 6 atm in the experiments reported here. A double prism spectrometer and glass filter serve to separate the second harmonic from the fundamental beam, and a photomultiplier tube is used to count the signal photons.

The ratio of hyperpolarizabilities for a sample gas A and a reference gas B is obtained from the relation [6]

$$\gamma_A/\gamma_B = (S_A^{(2\omega)}/S_B^{(2\omega)})^{1/2}(\rho_A n_A/\rho_B n_B)^{-1} , \qquad (1)$$

where $S^{(2\omega)}$ is the peak signal, ρ is the number density of the gas at phase match, and in the present case A = SF_6 and B = N_2. The factor $n = (n_0^4 n_\omega^{2+\zeta} n_{2\omega})^{1/6}$, which is obtained by accounting for local-field factors and the refractive index dependence of optical field strength and confocal parameter for a Gaussian beam focused near the center of the electrode array, is essentially a mean refractive index. For focused beams where the ratio of confocal parameter to array half-length satisfies the condition $z_0/L > 0.5$, the parameter ζ falls in the range $\zeta = 1 \pm 1$. Use has been made of $n - 1 \ll 1$ to put the factor in the stated form. (In ref. [6], $n_{2\omega}^2$ should be $n_\omega n_{2\omega}$ in eq. (3), and in eq. (4) the static factor in the local field correction should not be omitted [1].) Sample densities are computed from the measured pressures and temperatures using the virial equa-

Table 1
Experimental results for the second hyperpolarizability γ_{SF_6} measured by ESHG

λ (nm)	$\Delta\alpha_{SF_6}/\Delta\alpha_{N_2}$ [a]	$\gamma_{SF_6}/\gamma_{N_2}$	γ_{SF_6} [b] (10^{-62} C^4 m^4 J^{-3})
694.3	–	–	9.67 ± 0.15 [c]
670.0	1.769 ± 0.003	1.475 ± 0.008	9.75 ± 0.07
650.0	1.758 ± 0.003	1.472 ± 0.008	9.85 ± 0.07
620.0	1.743 ± 0.003	1.455 ± 0.012	9.93 ± 0.09
514.5	1.704 ± 0.003	1.444 ± 0.003	10.84 ± 0.04
488.0	1.696 ± 0.003	1.430 ± 0.005	11.09 ± 0.06
457.9	1.688 ± 0.003	1.401 ± 0.036	11.35 ± 0.30

[a] The dispersion of the linear polarizability $\Delta\alpha(\omega) = \alpha(2\omega) - \alpha(\omega)$ is just proportional to the phase match density ρ measured in obtaining γ; see ref. [6].
[b] Obtained using the smoothed results given in ref. [10].
[c] From ref. [12].

tion of state (the virial corrections for SF_6 are about 2%) [11]. High-purity gases were used (SF_6 99.99%; N_2 99.9995%). The accuracy of the overall measurement is chiefly determined by photon-counting statistics. The large error bar for the λ = 457.9 nm measurement arises because a suitable final optical filter was not available for this wavelength, resulting in a much larger background (200 counts/s) than usual (0.5 counts/s), with a consequent increase in noise even though synchronous photon counting subtracts out the background. The signals $S^{(2\omega)}$ were in the range 50–2000 counts/s, depending on the available laser power (0.3–2.0 W).

3. Results and discussion

The results of the experiments for SF_6 are presented in table 1 as the ratio $\gamma_{SF_6}/\gamma_{N_2}$ at several wavelengths. The value of γ_{SF_6} has also been extracted in absolute units by use of ref. [10]. The error bars given for γ_{SF_6} include allowance for ±0.4% uncertainty in the calibration values of γ_{N_2}. (The values at λ = 514.5 nm in ref. [6] are systematically low by 1.5% [10]; when corrected, γ_{SF_6} from ref. [6] coincides with the value reported here.) The tabulated value at λ = 694.3 nm comes from the work of Ward and Miller [12]. The results are also presented graphically in fig. 1, plotted versus ν^2. Far below resonance the electronic contribution to γ is expressible as a power series in even powers of ν [7], and would appear as a straight line in this plot. A straight line, obtained by a weighted-least-squares fit of a function of the form $\gamma = A(1 + B\nu^2)$, is seen to represent the data very well. The parameter values obtained in the fit are $A = (8.21 \pm 0.09) \times 10^{-62}$ C^4 m^4 J^{-3} and $B = (8.44 \pm 0.03) \times 10^{-10}$ cm^2, where ν is in cm^{-1}. The ν^2 dependence seen in these experiments substantiates the usual assumption that vibra-

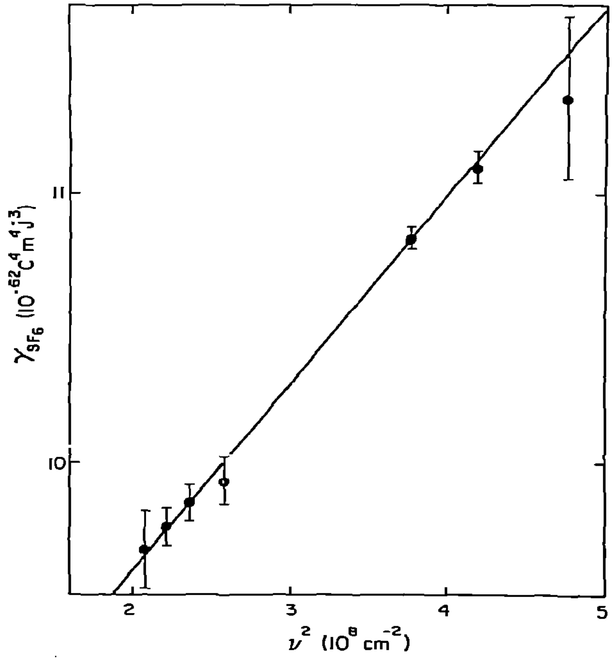

Fig. 1. Dispersion of the second hyperpolarizability of SF_6. The frequencies employed are far from resonance, so the electronic contribution to γ_{SF_6} is expected to give a straight line when plotted versus ν^2.

tional contributions to γ are negligible at optical frequencies for ESHG.

The electronic contribution is also believed to dominate γ for THG [5]. The dispersion of γ^{elec} may be expressed by

$$\gamma^{\mathrm{elec}} = \gamma_0^{\mathrm{elec}}[1 + C(\omega/\omega_0)^2] \tag{2}$$

for $\omega \ll \omega_0$, where ω_0 is some effective resonance frequency and γ_0^{elec} is the static electronic hyperpolarizability (the same for all processes). Furthermore, the coefficients C for the different processes may be evaluated by an approximate method due to Dawes [13] and subsequently extended by Finn [14], and are found to be [5] in the ratios

$$C^{\mathrm{THG}} : C^{\mathrm{ESHG}} : C^{\mathrm{Kerr}} = 6 : 3 : 1 \,. \tag{3}$$

The same result is obtained from a model due to Owyoung [15], and is supported by experimental results for Ar and H_2 [16] and by ab initio results for He [17]. Assuming these ratios are exact and that ω_0 is the same for all the γs of a given molecule, and having measured the frequency dependence of γ^{ESHG}, it should be possible to predict the frequency dependence of all the other γs (provided the electronic contribution dominates). The ratio of the measured values of γ^{THG} and γ^{ESHG} for SF_6 at $\lambda = 694.3$ nm is 1.14 ± 0.07 [5,18] while from our dispersion data one predicts $\gamma^{\mathrm{THG}}/\gamma^{\mathrm{ESHG}} = 1.15$ at this wavelength. The good agreement in this case supports eqs. (2) and (3) as an adequate description of γ^{elec}.

Applying the same procedure for $\gamma^{\mathrm{ESHG}}/\gamma^{\mathrm{Kerr}}$ predicts the ratio 1.11, in poor agreement with the measured ratio of 0.65 ± 0.06 at $\lambda = 694.3$ nm [5]. It has been suggested [5] that the experimentally observed enhancement of γ^{Kerr} over γ^{ESHG} and γ^{THG} at optical frequencies is due to vibrational contributions to γ^{Kerr}. The magnitude of the vibrational contribution is thought to be greatly enhanced when subsets of the applied frequencies sum to zero [5]. In that case, the distance off resonance for many of the terms in the expression for γ is of the order of the vibrational frequency rather than of the optical frequency, resulting in an increase by nearby two orders of magnitude for those terms. A possible experimental test of this theory would involve comparison of γ^{Kerr} dispersion measurements with the measured frequency dependence of γ^{ESHG}.

In the static limit, where all the applied field frequencies go to zero, the γs for all processes converge to the same value: $\gamma_0 = \gamma(0; 0, 0, 0)$. The electronic contribution to γ_0 is readily estimated by extrapolating γ^{ESHG} to $\omega = 0$, but the vibrational contribution is more difficult to assess. In the case of H_2, where the expressions are simpler and the required matrix elements have been calculated, it is possible to calculate γ_0^{vib} and measure γ_0^{elec}, obtaining the ratio $\gamma_0^{\mathrm{vib}}/\gamma_0^{\mathrm{elec}} = 0.28$ [9]. For SF_6 there are many more vibrational modes, including infrared-active modes, than for H_2, and the vibrational frequencies are about 5 times lower. Thus, γ_0^{vib} may dominate over γ_0^{elec} for SF_6.

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