

THE HYPERPOLARIZABILITY OF BENZENE MEASURED IN THE PRESENCE OF ABSORPTION

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The second hyperpolarizability (γ) of benzene has been measured at $\lambda = 514.5$ nm by means of gas-phase electric-field-induced second-harmonic generation (ESHG). Although benzene shows one-photon absorption at the second-harmonic frequency in this experiment, no significant imaginary part is found for γ . This result is reconciled with the result of a recent experiment using a similar method.

1. Introduction

The second hyperpolarizability of a molecule, γ , mediates a wide range of non-linear optical processes [1] as well as providing a sensitive probe into molecular electronic structure [2]. Gas-phase electric-field-induced second-harmonic generation (ESHG) measurements at present provide the most accurate determinations of the non-resonant γ [3–9]. Measurements have usually been made at a single, isolated frequency [3,4] but more recently measurements have also been made systematically as a function of frequency [5–9]. Measurements of frequency dependence allow one to address the mechanisms underlying γ . Since resonant responses in general provide more detailed information about molecular structure than does the non-resonant response, we have attempted to apply our technique to a case where either one-photon or two-photon resonances occur. Benzene was chosen as a suitable candidate because its electronic excitations are sufficiently low-lying to be accessible using a visible laser (for ESHG). We report here the results of measurements of γ for benzene at $\lambda = 514.5$ nm. Benzene shows one-photon absorption at the second harmonic of the laser frequency employed [10] so in general γ will be complex. We outline the special methods used to make measurements for an absorbing vapor sample, and also compare our results with those obtained from a recent, similar experiment [11].

2. Experiment

The experimental technique has been described in detail [5–9]. A cw laser beam from an argon-ion laser 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 electric field. By arranging the electrodes so that the field direction alternates in space every coherence length (adjusted by varying the gas density) periodic phase matching occurs, enhancing the second-harmonic signal generated. The electrode spacing is 2.6924 mm, resulting in optimal pressures of about 2 atm in the experiments reported here. A double-prism spectrometer and glass filter serve to separate the second-harmonic from the fundamental, and a photomultiplier tube is used to count the signal photons. With 2 W of laser power the signal was typically 2000 counts s^{-1} and the background was 0.5 count s^{-1} .

Gas mixtures were used as samples for these experiments in order that the sample pressure at phase match would be high enough to sustain a large static field, and also to keep the absorption of the second-harmonic light manageable. The samples consisted of 10, 20 or 30 Torr of benzene vapor mixed with N_2 as a buffer gas (0.6–2.4 mole% benzene), while the reference was pure N_2 gas. Details of the sample preparation, measurement procedure and calculation of phase-matched gas densities are given elsewhere [9].

In order to extract $\gamma_{C_6H_6}$ one must measure and account for the sample absorption. The sample absorption is measured by placing a crystal quartz plate before the entrance window of the sample cell. A second-harmonic beam is generated in the quartz and attenuated by the sample. Measurement of the ratio of the signals from the quartz before and after evacuation of the sample cell gives the intensity transmission factor t^2 for the sample. The amplitude absorption coefficient of the sample, α , is found from the relation

$$t^2 = \exp(-2\alpha l_0), \quad (1)$$

where l_0 is the sample length (distance between entrance and exit windows; see fig. 1). The absorption measurement is made immediately after passing over the phase match peak. The absorption at phase match is obtained by a short extrapolation which assumes that α is proportional to density.

The absorption of the N_2 reference was also monitored, as a small amount of benzene contamination (about 0.2 Torr) was inevitable (at room temperature) unless the interval between mixture and reference measurements was made so long as to incur a penalty in system drifts. Absorption also provides an independent assay of the benzene content of the sample, calibrated by measuring $t^2(\rho)$ for pure benzene vapor in the same sample cell. The extinction coefficient obtained from this experiment is $\epsilon = \alpha/\rho = 31.9 \pm 0.3$ liter/mole cm. Another check on the mixture composition is possible because the dispersion of the linear polarizability of benzene, deduced from phase match density measurements [9], should remain constant as the sample composition is varied. These assays are important because the accuracy of the final results is to a large extent limited by the accuracy of the sample composition (the small error bar on the 20 Torr benzene result re-

flects the sample reproducibility finally obtained for these, the last measurements).

To account for the effect of absorption of the second-harmonic light by the sample we have numerically integrated eq. (3) of ref. [5], generalized to include sample absorption and an arbitrary position for the waist of the focused laser beam with respect to the center of the electrode array. The signal is proportional to the factor $I^2(\Delta k)$, which may be approximated to sufficient accuracy from the sum:

$$I(\Delta k) = \frac{\Delta k}{K} \frac{1}{2N} \sum_{n=-N}^{N-1} \frac{\exp[-\alpha(x_c - x')/K]}{(1 + u^2)^{1/2}} \\ \times \{(1 - \Delta k/K) \cos \phi + (\cos \phi + u \sin \phi) \\ \times [x_0(1 + u^2)]^{-1}\}, \quad (2a)$$

where

$$\phi = \frac{K + \Delta k}{K} (x' - x_w) - \arctan u, \quad (2b)$$

$$u = (x' - x_w)/x_0, \quad (2c)$$

$$x' = (n + \frac{1}{2})\pi, \quad (2d)$$

and $\Delta k/K$ is the wavevector mismatch in units of the array spatial frequency $K = \pi/l'$ (note that $\Delta k/K$ is negative), $x_0 = Kz_0$ is the normalized laser beam confocal parameter, $x_w = Kz_w$ and $x_c = Kz_c$ are the positions of the focus and the array center (see fig. 1) and $2N$ is the number of electrode pairs of spacing l' [5, 12]. The confocal parameter and waist position (z_0 and z_w) of the laser beam were obtained by fitting a hyperbola [5, 13] to measurements of spot size versus position obtained by scanning a wire through the beam.

The sum giving $I^2(\Delta k)$ for a given set of parameters describing the experiment (N, l', z_0, z_w, z_c and α) was evaluated as a function of Δk to obtain its maximum value $I^2(\Delta k_{opt})$. The ratio of the values of $I^2(\Delta k_{opt})$ so obtained, for the measured value of α and then for $\alpha = 0$, is just the factor A^2 by which the ESHG signal is reduced due to absorption. Dividing the ESHG signal by the appropriate factor A^2 gives the signal that would be seen if absorption could be switched off. The values of A^2 for the mixed samples in these experiments were in the range 0.33–0.71, and after correcting for absorption the ratio of signals from sample and reference was near unity.

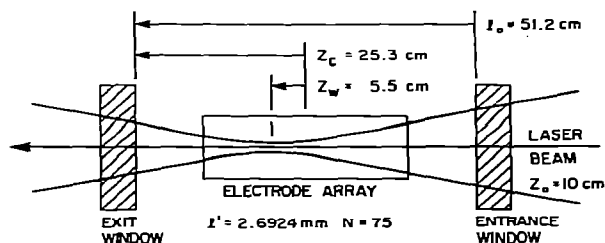


Fig. 1. Schematic diagram showing the disposition of the focused laser beam and electrode array inside the sample cell.

After correcting for absorption the experimental observations are R^2 , ρ_A^0 , ρ_A and ρ_B , where $R^2 = S_{A+B}^{(2\omega)} / S_A^{(2\omega)}$ is the absorption-corrected ratio of signals for the mixture A+B and for the reference gas A, ρ_A^0 is the density of the reference gas at phase match, and ρ_A and ρ_B are the partial densities of buffer gas A and sample gas B in the mixture at phase match. The hyperpolarizability γ_A of the reference molecule A is assumed to be pure real, but since the sample molecule is near resonance its hyperpolarizability will in general be complex:

$$\tilde{\gamma}_B = \gamma'_B + i\gamma''_B.$$

Thus we may write

$$R^2 = \frac{(\rho_A \gamma_A + \rho_B \gamma'_B)^2 + (\rho_B \gamma''_B)^2}{(\rho_A^0 \gamma_A)^2}, \quad (3)$$

which may be rearranged to give

$$F \equiv \frac{(\rho_A^0 / \rho_A)^2 R^2 - 1}{2\rho_B / \rho_A} = \frac{\gamma'_B}{\gamma_A} + \frac{1}{2} \left| \frac{\tilde{\gamma}_B}{\gamma_A} \right|^2 \frac{\rho_B}{\rho_A}. \quad (4)$$

Furthermore, if F is evaluated from experimental measurements made using a different reference and buffer gas C, eq. (4) may be transformed to give

$$\frac{\gamma_C}{\gamma_A} F = \frac{\gamma'_B}{\gamma_A} + \frac{1}{2} \left| \frac{\tilde{\gamma}_B}{\gamma_A} \right|^2 \frac{\gamma_A}{\gamma_C} \frac{\rho_B}{\rho_C}. \quad (5)$$

In the present context $A = N_2$ and $B = \text{benzene}$, while $C = N_2, \text{Ar}$ or CO_2 in order to encompass the recent experiments [11] done using Ar and CO_2 as buffer gases. Plotting $(\gamma_C / \gamma_A) F$ versus $(\gamma_A / \gamma_C)(\rho_B / \rho_C)$ will result in a straight line whose intercept gives the real part of $\tilde{\gamma}_B$ and whose slope gives the magnitude of $\tilde{\gamma}_B$.

3. Results and discussions

The results of the experimental measurements for benzene are given in table 1. The results obtained with N_2 as buffer gas are each the average of three separate measurements; the error bars are chiefly determined by the reproducibility of the measurements. The results with Ar or CO_2 as buffer gas are computed from the data obtained in a similar experiment done by Pantinakos et al. [11]. The results are also plotted in

Table 1
Experimental measurements for benzene-buffer gas mixtures, made at $\lambda = 514.5 \text{ nm}$ using ESHG

C	$\frac{\gamma_C}{\gamma_{N_2}}$ a)	$\frac{\gamma_{N_2} \rho_{C_2H_6}}{\gamma_C \rho_C}$ b)	$\frac{\gamma_C}{\gamma_{N_2}} F$ c)
	N_2	1	0.62×10^{-2}
N_2	1	1.31×10^{-2}	34.0 ± 0.6
N_2	1	2.38×10^{-2}	37.2 ± 2.4
Ar	1.295	0.97×10^{-2} d)	31.0 ± 11 d)
CO_2	1.378	1.95×10^{-2} d)	42.2 ± 9 d)

a) From refs. [5,8].

b) Uncertainties about $\pm 1\%$.

c) F is defined by eq. (4) with C substituted for A.

d) Computed from the data given in ref. [11].

fig. 2. If one assumes that $\tilde{\gamma}_{C_6H_6}$ is pure real, then a weighted least-squares fit to the data gives the estimate $\gamma'_{C_6H_6} / \gamma_{N_2} = 28.6 \pm 0.2$. The straight line shown in fig. 2 follows from this estimate and is clearly consistent with all the data. However, the error bars are not small enough to exclude the possibility of a small imaginary part to $\tilde{\gamma}_{C_6H_6}$. The steepest line which passes through all the error bars corresponds to $\tilde{\gamma}_{C_6H_6}$.

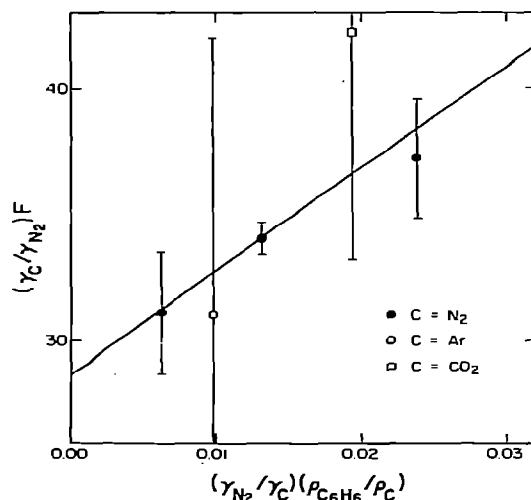


Fig. 2. Experimental results for benzene-buffer gas mixtures. The straight line is the best fit to all the data shown, assuming that $\tilde{\gamma}_{C_6H_6}$ is real.

$\gamma_{N_2} = 26.4 + 20i$. On the basis of the present data, and obeying the constraint $|\tilde{\gamma}| \geq \gamma'$, we deduce that the values of the real and imaginary parts of $\tilde{\gamma}_{C_6H_6}$ fall in the ranges $\gamma'_{C_6H_6}/\gamma_{N_2} = 27.6 \pm 1.2$ and $\gamma''_{C_6H_6}/\gamma_{N_2} = 10 \pm 10$.

We may compare the results of these measurements with the results of experiments done far below resonance for benzene [9]. Extrapolating the low-frequency results to $\lambda = 514.5$ nm gives $\gamma'_{C_6H_6}/\gamma_{N_2} = 27.7 \pm 0.5$, in excellent agreement with the present result. This implies that the dispersion of the hyperpolarizability of benzene has only a weak contribution from the lowest excited singlet electronic state giving rise to the absorption seen at $\lambda = 514.5$ nm. This is not unreasonable in view of the fact that this transition is only allowed as a result of vibrational mixing with a higher-lying electronic state of different symmetry [10]. Furthermore, the second harmonic of $\lambda = 514.5$ nm happens to fall at the absorption minimum between two successive vibronic bands of this absorption system [10]. This is consistent with the imaginary part of $\tilde{\gamma}_{C_6H_6}$ being small. A clear demonstration of a non-zero $\gamma''_{C_6H_6}$ would seem to require more accurate measurements and preferably the ability to scan over the resonance.

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