

Dispersion of the nonlinear susceptibility measured for benzene

D. P. Shelton

Department of Physics, University of Toronto, Toronto, Ontario, Canada M5S 1A7

Received June 3, 1985; accepted August 6, 1985

The dispersion of the electronic part of the third-order nonlinear susceptibility of benzene vapor has been measured in the visible by the technique of electric-field-induced second-harmonic generation. The results show rough agreement with phenomenological models used in the literature.

Despite the present intense interest in nonlinear optical processes in general,¹ there have been relatively few accurate measurements of the nonlinear susceptibility (hyperpolarizability) for gases. Those measurements that exist were made at the fixed wavelengths that were available, usually $\lambda = 694.3$ nm (ruby laser), providing little if any information about the frequency dependence of the molecular hyperpolarizabilities involved.²⁻⁵ By taking advantage of recent advances in the technique of electric-field-induced second-harmonic generation (ESHG), which permit accurate measurements of ratios of molecular hyperpolarizabilities using cw lasers, as well as the availability of dye lasers tunable over a wide range, it is possible to address the dispersion properties of molecular hyperpolarizabilities in a systematic manner.⁶⁻¹⁰ Below are reported the results of measurements made for the benzene molecule. Benzene is of particular interest because it is often used as a standard, has relatively low-lying electronic excitations, and is the simplest of the class of conjugated molecules whose extraordinarily large nonlinearities make them candidates for various practical nonlinear optical devices.¹¹⁻¹⁴

The experimental technique has been described in detail elsewhere.⁶⁻¹⁰ A cw laser beam from an argon-ion-pumped R6G or DCM 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 space 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 of 2 to 6 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 detects the signal photons, which are then counted.

The chief technical difference between these experiments and the previously reported experiments⁶⁻¹⁰ is in the matter of sample preparation and handling during the measurements. The sample consisted of a mixture of about 2% benzene vapor in N₂ as a buffer gas, while the reference was pure N₂ gas. A mixture of vapor and buffer gas was used rather than pure vapor (which would phase match at about 0.2 atm) in order to allow a much larger static electric field to

be applied to the sample without electrical breakdown. The ESHG signal is proportional to V^2 . Even in the dilute mixture, the benzene vapor contributes about 30% of the total susceptibility of the sample. High-purity N₂ and reagent-grade benzene were used. The benzene was degassed by repeated freeze-pump-thaw cycles until bubble-free frozen benzene was obtained.

A typical complete run, consisting of sample preparation and measurements for the sample and reference gas, proceeds as follows. First, the cell is filled with benzene vapor at 50 Torr and allowed to come to equilibrium with the cell surfaces for 20 min or more (the saturated vapor pressure is about twice the fill pressure at a room temperature of 22–26°C).¹⁵ Next, the buffer gas is added to make a final mixture whose density is about 1% above the optimum phase-match density. The mixture is allowed to homogenize for 20 min or more, using the second-harmonic signal to monitor the progress of mixing. After mixing is complete, the sample is slowly leaked out and the peak signal and optimum phase-match pressure are determined. Then the cell is pumped and flushed several times to remove residual benzene. Finally, the cell is filled with pure N₂, and the peak signal and phase-match pressure are determined for the reference.

Sample densities are computed from the measured pressures and temperatures using the virial equation of state (virial corrections to the final results are about 0.4%).¹⁶ The benzene density in the sample at phase match is not the same as that measured in the initial fill with pure vapor. Allowance is made for the buffer gas sweeping the benzene vapor from the fill line into the cell (density increase of 0.9%) and subsequently for the effect of the pressure scan over the phase-match peak (density reduced about 1%). The accuracy of the overall measurement is largely determined by the accuracy with which the sample composition is known.

From the experimental measurements one may extract two pieces of information: the dispersion of the linear polarizability, $\Delta\alpha$, and the value of the hyperpolarizability, γ . Neglecting local field corrections (of order 10^{-4} here),^{1,6} one may express $\Delta\alpha$ and γ in terms of the experimental measurements as

$$\Delta\alpha_{C_6H_6}/\Delta\alpha_{N_2} = (\rho_{N_2} - \rho_{N_2})/\rho_{C_6H_6}, \quad (1)$$

Table 1. Experimental Results for the Linear and Nonlinear Susceptibilities of Benzene Measured by ESHG

λ (nm)	$\Delta\alpha_{C_6H_6}/\Delta\alpha_{N_2}$	$\gamma_{C_6H_6}/\gamma_{N_2}$	$\gamma_{C_6H_6}^a$ ($10^{-60} C^4 m^4 J^{-3}$)
514.5	21.9 ± 0.2	—	—
590.0	18.2 ± 0.3	25.2 ± 0.5	1.76 ± 0.04
620.0	17.5 ± 0.3	24.4 ± 0.4	1.67 ± 0.03
670.0	16.9 ± 0.3	23.1 ± 0.4	1.53 ± 0.03
694.3	$16.7 \pm 0.3^{(b,c)}$	—	$1.53 \pm 0.04^{(c)}$
1064.	$16.2^{(d)}$	—	$1.16 \pm 0.17^{(e)}$
∞	—	—	$0.73 \pm 0.09^{(f)}$

^a Obtained using Ref. 10; conversion factors are 1 a.u. = $6.2353 \times 10^{-65} C^4 m^4 J^{-3}$; 1 esu = $7.4279 \times 10^{-25} C^4 m^4 J^{-3}$.

^b From Ref. 3.

^c From Ref. 4; $-\Delta k_0$ should read 31.6 ± 0.4 rather than 34.6 ± 0.1 .

^d From Ref. 18.

^e From Ref. 5; their definition of γ differs from ours by a factor of 3/2.

^f Obtained by extrapolation to $\omega = 0$.

$$\gamma_{C_6H_6}/\gamma_{N_2} = (\rho_{N_2} [S_{mix}^{(2\omega)}/S_{N_2}^{(2\omega)}]^{1/2} - \rho_{N_2})/\rho_{C_6H_6}, \quad (2)$$

where ρ_{N_2} and $S_{N_2}^{(2\omega)}$ are the phase-match density and peak signal for the pure N_2 reference, ρ_{N_2} and $\rho_{C_6H_6}$ are the partial densities of N_2 and benzene in the mixture at phase match, and $S_{mix}^{(2\omega)}$ is the peak signal for the mixture. The dispersion of the polarizability is defined by $\Delta\alpha(\omega) = [\alpha(2\omega) - \alpha(\omega)]$, while the hyperpolarizability $\gamma(\omega)$ that we measure is in fact the $zzzz$ component of the isotropically averaged molecular hyperpolarizability tensor $\gamma_{\alpha\beta\gamma\delta}(-2\omega; \omega, \omega, 0)$. There is an ambiguity in the sign of γ in Eq. (2) because of the square root. This ambiguity may be resolved by comparison of various binary mixtures^{3,4} or by Kerr measurements¹⁷; γ is found to be positive for both N_2 and C_6H_6 .

The results of the experiments for benzene are presented in Table 1 as ratios to N_2 at several wavelengths. The error bars include both the statistical uncertainties and as an estimate of the possible systematic errors in the benzene density estimate. The hyperpolarizability $\gamma_{C_6H_6}$ has also been extracted in absolute units by use of Ref. 10. Only $\Delta\alpha$ is given at $\lambda = 514.5$ nm because strong one-photon absorption of the second-harmonic radiation in this case does not allow the data to be analyzed simply by using Eq. (2). The tabulated values at $\lambda = 694.3$ nm are from gas-phase measurements by Ward and Elliott.⁴ The tabulated value of $\gamma_{C_6H_6}$ at $\lambda = 1064$ nm comes from liquid-phase measurements by Levine and Bethea,⁵ while the $\Delta\alpha$ at this wavelength has been evaluated using published refractive-index data.¹⁸ The results of the experiment are also presented graphically in Fig. 1. Since α and γ are expected to be expressible as power series in even powers of ω far below resonance,⁷ the results have been plotted versus ω^2 .

The main features of the experimental results are as follows. The results for $\Delta\alpha_{C_6H_6}/\Delta\alpha_{N_2}$ (Fig. 1A) show a marked effect that is due to the 260-nm absorption band of benzene. Far below resonance $\Delta\alpha_{C_6H_6}/\Delta\alpha_{N_2}$ versus ω^2 should tend to a nearly horizontal straight line, but the experimental curve veers sharply upward instead. In contrast, the data for $\gamma_{C_6H_6}$ are represented well by a linear function of ω^2 (Fig. 1B). The 260-nm absorption band seems to have little or no

effect on the hyperpolarizability of the molecule. A weighted least-squares fit of a function of the form $\gamma = A(1 + B\omega^2)$ has been made to the present experimental data and is shown by the straight line in Fig. 1B. The parameter values obtained in the fit are $A = 0.73 \pm 0.09 \times 10^{-60} C^4 m^4 J^{-3}$ and $B = 0.49 \pm 0.06 \times 10^{-8} cm^2$, where ω is given in reciprocal centimeters. The quality of the fit supports the belief that the error estimates for the present measurements are, if anything, too conservative. However, the measurement of Ward and Elliott⁴ falls 3% high, and while this is within the combined error bars, further experiments to address the possibility of a small systematic error are perhaps in order.

One may ask whether there are any models or calculations that are able to represent adequately the experimental results. The dispersion of γ may be calculated on the basis of single-resonance models, which, far below resonance, give

$$\gamma = A[1 + C(\omega/\omega_0)^2], \quad (3)$$

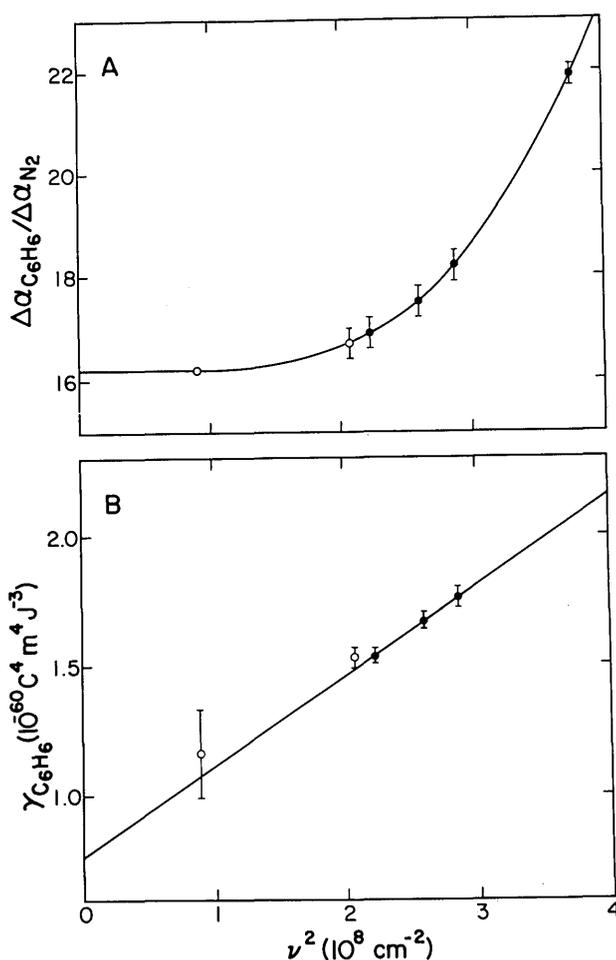


Fig. 1. Dispersion of the linear and nonlinear susceptibilities of benzene. A, Experimental results for the dispersion of $\alpha_{C_6H_6}$ expressed as the ratio ($\Delta\alpha_{C_6H_6}/\Delta\alpha_{N_2}$) and plotted versus ω^2 , where $\Delta\alpha = [\alpha(2\omega) - \alpha(\omega)]$. The lowest-order expression for the dispersion ratio $\Delta\alpha_{C_6H_6}/\Delta\alpha_{N_2}$ would give a horizontal straight line on this plot. B, Experimental results for $\gamma(\omega)$ for benzene plotted versus ω^2 . The lowest-order expression for the dispersion of γ would give a straight line on this plot. In each case, the filled circles are the results of the present experiments, whereas the open circles are the results of previous measurements.

where ω_0 is the effective single-resonance frequency obtained from refractive-index data.^{7,10} The value of the coefficient C derived for the isotropic classical anharmonic oscillator is $C = 6$,¹⁹ whereas for an approximate calculation starting from the full expression for γ one obtains $C = 10$.^{20,21} Taking $\omega_0 = 82\,000\text{ cm}^{-1}$ (from refractive-index data in the visible for benzene¹⁸), the experimental data for $\gamma_{\text{C}_6\text{H}_6}$ give $C = 33$. Thus for the atoms and molecules He, Ar, H₂, D₂, N₂, O₂, and C₆H₆ the value of C obtained experimentally falls in the range $13 < C < 33$, approximately 2–3 times larger than estimated on the basis of the simple models.^{9,10} Note that the value of γ for these same molecules varies by a factor of 600. A single-resonance model with $C = 20$ would seem to provide a crude but useful estimate of the dispersion of γ for the ESHG process.

An important open question is whether there is a simple relation between the dispersion coefficient C for ESHG and the corresponding dispersion coefficients for other nonlinear processes such as third-harmonic generation (THG) or the Kerr effect. For THG the classical anharmonic oscillator¹⁹ model gives $C = 12$, whereas the approximate quantum calculation^{20,21} gives $C = 20$. Both models predict that the dispersion coefficient C will be exactly twice as large for THG as for ESHG. An *ab initio* calculation for He also gives a low-frequency dispersion coefficient that is twice as large for THG as for ESHG.²² This agreement suggests that it may be possible to describe accurately the frequency dependence of all the third-order off-resonant nonlinear optical processes for a given molecule in terms of the same effective resonance frequency (which, however, would differ from the ω_0 derived from the dispersion of the linear polarizability). Such a result, if valid, would produce a quantitative unification of the disparate experimental results for third-order optical processes.

Also of interest is the question of whether *ab initio* calculations of γ can be made with usefully high accuracy. Even the largest possible configuration-interaction calculations for the simplest molecule (H₂) seem to be accurate to no better than 5%.⁹ Since the difficulty of the calculation increases rapidly with molecular size, what can be expected for a molecule as large as benzene or even larger? A static variational calculation of the π -electron contribution for benzene has been performed by Schweig.¹¹ Taking the isotropic average of Schweig's results (assuming the components not calculated are equal to zero) one gets $\gamma_{\text{calc}}^\pi = 0.41 \times 10^{-60}\text{ C}^4\text{ m}^4\text{ J}^{-3}$. Levine and Bethea,⁵ from measurements of a series of conjugated ring compounds, have estimated that γ^π accounts for 41% of the total γ for benzene. Extrapolating to $\omega = 0$, the experimental estimate of the π -electron contribution to $\gamma_{\text{C}_6\text{H}_6}$ is thus $\gamma_{\text{expt}}^\pi = 0.30 \times 10^{-60}\text{ C}^4\text{ m}^4\text{ J}^{-3}$. Even though the wave function used by Schweig is of simple form, his calculation falls within 30% of the experimental estimate. It may be that the contributions from delocalized π electrons may be calculated with relatively high accuracy compared with the contribution of the rest of the electrons of a molecule. This would indicate that calculations for large, complicated donor-acceptor compounds may be much more reliable than extrapolation of the results of *ab initio* calculations for H₂ would indicate. However, this conclusion must be treated with caution since more recent calculations for benzene seem to give results either five times larger²³ or five times smaller²⁴ than the experimental results.

ACKNOWLEDGMENTS

This research was supported by grants from the Natural Sciences and Engineering Research Council of Canada and from the Research Corporation (New York).

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