Measurements of molecular hyperpolarizabilities for ethylene, butadiene, hexatriene, and benzene[a]

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Third-order polarizabilities are measured in the gas phase using dc electric-field induced optical second-harmonic generation and are found to be positive in each case.

We report measurements of third-order nonlinear electric polarizabilities (hyperpolarizabilities) for ethylene, 1,3-butadiene, 1,3,5-hexatriene and benzene molecules in the gas phase using dc electric-field induced optical second-harmonic generation.[1,2] The hyperpolarizabilities of conjugated molecules have been of interest for some time.[3-6] Because of the delocalized π electrons these hyperpolarizabilities are quite large, and increase faster than the size of the molecule. Recent theoretical work[7-10] makes these measurements timely. We were also intrigued to investigate three of these molecules, ethylene, butadiene, and hexatriene, for which there is evidence that the third-order hyperpolarizability might be negative.[9-11]

The dc electric-field induced optical second-harmonic generation experiments reported here are similar in method to those described previously.[1] Optical second harmonic generated by a focused 694.3 nm ruby laser beam in a vapor-phase sample subjected to a dc electric field is measured to determine the effective third-order hyperpolarizability χ^e. This hyperpolarizability can be measured with dc and fundamental optical electric fields parallel $\chi_{||}^e$ or perpendicular $\chi_\perp^e$. In general, two processes contribute to the effective hyperpolarizability: the intrinsic third-order process; and, in the case of dipolar molecules, harmonic generation rendered observable by the temperature-dependent partial alignment of the molecules by the dc electric field:

$$\chi_{||,\perp}^e = \chi_{||,\perp}^{(3)} + (\mu/9kT)\chi_{||,\perp}^{(2)} . \tag{1}$$

$\chi_{||,\perp}^{(3)}$ and $\chi_{||,\perp}^{(2)}$ all represent averages over molecular orientations and are, therefore, well defined linear combinations of molecular hyperpolarizabilities. Detailed definitions of these hyperpolarizabilities are given in Ref. 12. Butadiene and hexatriene each include *cis*- and *trans*-isomers in poorly known proportions. The temperature dependence of $\chi_{||}^e$ for these gases, shown in Fig. 1, yields an average over the isomeric mixture for $\chi_{||}^{(2)}$ which is small and of little interest here, and for $\chi_{||}^{(3)}$ which we assume is similar for both isomers. Ethylene and benzene are nondipolar and were studied at one temperature only. Absolute magnitudes for coefficients, shown in Table I, are established by comparing harmonic generation in pairs of gases and using a calculated value for $\chi_{||}^{(3)}$ (helium).[13] To deduce χ^e from harmonic generation observations it is necessary to know the wave vector mismatch Δk_0 (quoted here at a density of Loschmidt's number cm^{-3})

$$\Delta k_0 = 2k^\omega - k^{2\omega} .$$

Δk_0 is measured as in previous experiments.[14] The ruby laser beam passes in succession through a quartz plate, air, a cell containing the gas under observation and a second quartz plate. The dependence of interference between second harmonic generated in each of the quartz plates as a function of gas density in the cell yields values for $|\Delta k_0|$ (see Table I). A technique to determine the sign of Δk_0 was introduced here: if increasing the air path length (by increasing the quartz crystal separation) has the same effect on the harmonic interference signal as increasing the cell gas density then the sign of Δk_0 for the gas is the same as that for air, namely negative. This was found to be the case for all four gases studied here. The relative sign for $\chi_{||}^e$ for two species is established by measuring harmonic generation in binary mixtures as a function of proportion. Data for hexatriene/nitrogen mixtures shown in Fig. 2 together with curves calculated for both positive and negative relative χ^e's indicate unambiguously that the two χ^e's have the same sign. Knowledge of the sign of Δk_0 is helpful in this respect since it eliminates two further possibilities which would otherwise have to be considered. Signs are put on an absolute basis by binary comparisons linked to helium[2] for which the calculated sign of $\chi_{||}^{(3)}$ is positive[13] or equivalently to argon where the same positive sign can be inferred as has been established for the Kerr hyperpolarizability.[15] Signs, other results, and data on experimental condi-
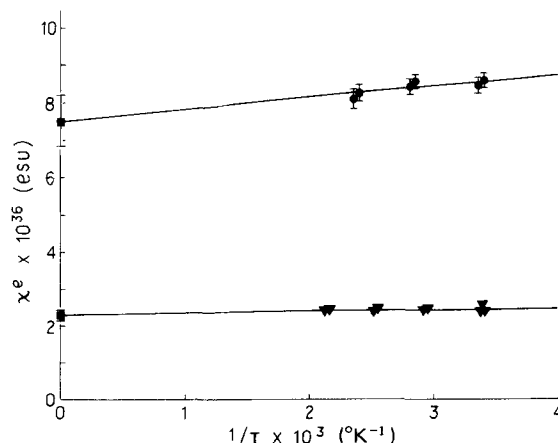

FIG. 1. Temperature dependence of the effective hyperpolarizability for butadiene ($\blacktriangledown$) and hexatriene ($\bullet$). Each point represents an average of at least 200 laser shots. The standard deviation in the case of butadiene is smaller than the size of the triangle. $\chi^{(3)}$ is given by the $1/T = 0$ intercept ($\blacksquare$).

TABLE I. Experimental parameters and hyperpolarizabilities.

		μ (D)	E^0 (esu cm⁻¹)	T (°K)	ρ_0[a]	$-\Delta k_0$ (cm⁻¹)	$10^{36}\,\lim_{T^{-1}\to 0}\chi_\parallel^e$ (esu)	$10^{36}\,\partial\chi_\parallel^e/\partial T^{-1}$ (esu °K)	$R^{(3)}$
Ethylene		···	0	9	295	0.483	10.3±0.1	0.758±0.017	···	2.83±0.20
1,3-Butadiene *cis*	<1%[b]	···	8.5	295–465	0.140	35.6±0.3	2.30±0.13	54±45	2.84±0.37
trans	99+%	0							
1,3,5-Hexatriene *cis*	40–10%[c]	···	7	295–353	0.0499	100±2.5	7.53±0.70	315±225	2.91±0.14
trans	60–90%	0							
Benzene		···	0	9	334	0.144	34.6±0.1	2.06±0.05	···	3.03±0.17

[a]Optimum density given in Loschmidt's number cm⁻³. Virial data taken from the following sources: Ethylene and benzene; J. H. Dymond and E. B. Smith, *The Virial Coefficients of Gases* (Clarendon, Oxford, 1969). Butadiene; R. B. Scott, C. H. Meyers, R. D. Rands, Jr., F. G. Brickwedde, and N. Bekkedahl, J. Res. Natl. Bur. Stand. **35**, 39 (1945). Hexatriene; no correction applied, virial data not available. Correction would be expected to increase Δk_0 and χ by not more than a few per cent.

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tions are summarized in Table I. It may be noted that intermolecular interactions and differences between local and applied fields are negligible in these gas-phase experiments whereas additional uncertainties are introduced in extracting molecular hyperpolarizabilities from liquid-phase measurements.

The measured ratios $R^{(3)} = \chi_\parallel^{(3)}/\chi_\perp^{(3)}$ are shown in Table I to differ insignificantly from 3. This is true for all molecules for which data is currently available and may be interpreted to imply that in this process the molecule does not draw a significant distinction between optical and dc fields (see Ref. 16 for a detailed discussion). Further discussion here will be limited to $\chi_\parallel^e$ and we omit the ∥ subscript for brevity.

Table II, in addition to our measured values, shows various other experimental and calculated hyperpolarizabilities for these four molecules. In comparing third-order polarizabilities for different processes involving different frequencies there is no reason to believe that these quantities should be identical. Howev-

TABLE II. Third-order polarizabilities ×10³⁶ esu.

	$\chi_\parallel^{(3)}$[a] exptl	$\chi_\parallel^{(3)}$ exptl	$\chi_\parallel^{(3)}$[h] calc	$\chi_\parallel^{(3)}(\sigma)$[i] calc	$\chi_\parallel^{(3)}$ calc	
Ethylene	+0.758±0.017	−0.05±0.34[b] +0.88±0.22[c]		+0.5		
Butadiene	+2.30±0.13		+1.4	+1.0	−0.32[j]	−0.32[l]
Hexatriene	+7.53±0.70		+10	+1.6	−1.11[j]	−1.01[l]
Benzene	+2.06±0.05	+1.1±0.5[d] +2.34±0.35[e] +2.2[f] +2.4±0.72[g]		+1.7	+6.15[k]	+0.08[l]

[a]Present work. dc induced second-harmonic generation, 694 nm, gas phase.
[b]Ref. 11. Kerr effect, 633 nm, gas phase.
[c]Ref. 18. Third-harmonic generation, 694 nm, gas phase.
[d]Ref. 17. Kerr effect, 633 nm, gas phase.
[e]Ref. 19. dc induced second-harmonic generation, 1.06 μm, liquid phase.
[f]Ref. 20 as reported in Ref. 19. Three wave mixing, liquid phase.
[g]Ref. 21 as reported in Ref. 19. Third-harmonic generation, 1.89 μm, liquid phase.
[h]Ref. 5. dc hyperpolarizability, calculated using free electron model. The number quoted here is γ_{xxxx} from this reference multiplied by the factor 16/45.
[i]σ-electron contributions based on bond additivity using data from Refs. 1, 6, 11, 19.
[j]Ref. 9. dc hyperpolarizability calculated using Hückel wavefunctions.
[k]Ref. 8. CNDO calculation, dc hyperpolarizability, σ-electron contributions included.
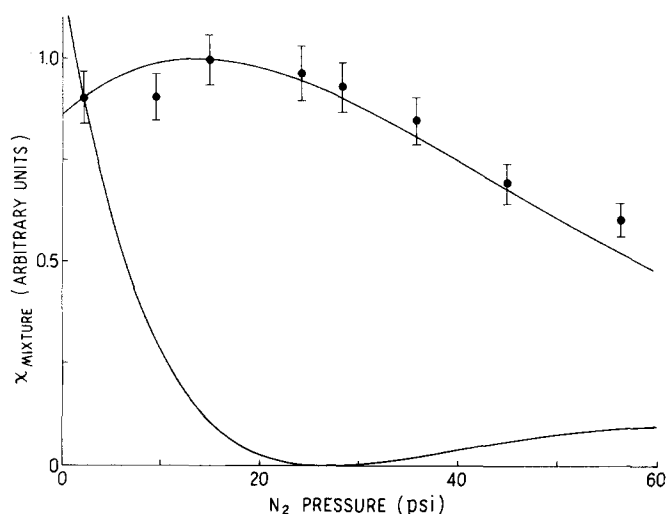[l]Ref. 10. SCF calculation, dc hyperpolarizability.

FIG. 2. The dependence of χ^e on the proportions of a mixture of hexatriene and nitrogen. The upper and lower curves are calculated plots for positive and negative relative χ^e's, respectively, fitted to the first data point. The unambiguous conclusion is that χ^e for hexatriene and for nitrogen are of the same sign.

er, in the absence of resonances, we would be surprised if differences of more than 20% were to arise from dispersion.

The uncertainties in results presented here are substantially smaller than those of previous measurements for ethylene and benzene. Uncertainties in Kerr effect results are large because $\chi^{(3)}$ has to be determined in the presence of a large contribution arising from linear polarizability anisotropy. These results[11,17] differ from ours by about two standard deviations. A result for $\chi_{\shortparallel}^{(3)}$ for ethylene from third-harmonic generation in the gas[18] is consistent with our value. There is good agreement between the value presented here for $\chi^{(3)}$ in benzene and that measured by dc electric-field induced second-harmonic generation in the liquid[19] at 1.06 μm. $\chi^{(3)}$ in benzene has also been measured by three-wave mixing[20] and third-harmonic generation.[21] Levine and Bethea have adjusted these results for dispersion and shown them to be in good agreement also.[19]

Most of the theoretical results presented in Table II are for the π-electron contribution to $\chi^{(3)}$. We therefore include estimates of the σ-electron contribution derived from experimental $\chi^{(3)}$ for a number of alkanes.[1,6,11,19] It is assumed that this contribution for a given bond (carbon—carbon or carbon—hydrogen) is equivalent to $\chi^{(3)}$ for the same bond in an alkane and that bond additivity applies. The estimated σ contribution is not negligibly small compared to the measured $\chi^{(3)}$ for any of these molecules. Although Hameka has cast some doubt on the additivity of π and σ contributions,[8] it is of interest to compare $\chi^{(3)} - \chi^{(3)}(\sigma)$ with the calculated π contributions. Looked at from this viewpoint the modified free electron results for butadiene and hexatriene

are close[5] whereas the results based on Hückel wavefunctions are of the wrong sign and quite small.[9,10] (However, Hameka and McIntyre note the possibility of considerable uncertainty in an overall multiplicative factor.) In the case of benzene the author of both theoretical results regards the smaller as the preferred value, and as he remarks the result for "benzene seems much too small."[10] We conclude that the theory for small conjugated molecules is not yet adequate.

Previous evidence which indicated that $\chi^{(3)}$ was negative for ethylene, butadiene, and hexatriene was weak, depending on an experimental result with low significance[11] or on conflicting theoretical calculations.[5,9,10] The $\chi^{(3)}$ measured are, however, unambiguously positive for all these molecules. It may be noted that this result does not depend on the choice of molecular coordinate system. Whereas we know of no fundamental reason why this polarizability must be positive, there is no known case of measured negative low frequency third-order polarizability.

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