

Correspondence

Nonlinear Third-Order Polarizability of Some Molecules in the Liquid State

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Abstract—By comparison of optical Kerr effect and depolarized Rayleigh scattering data, both measured by laser techniques, we have determined the mean value of the nonlinear third-order polarizability of ten molecules in the liquid state.

Information about the third-order nonlinear polarizability of anisotropic molecules is usually obtained by two main different methods.

The first method uses extrapolation toward $T \rightarrow \infty$ of the curve $B_s = f(1/T) + g$. Here B_s is the molar static Kerr effect (SKE) constant and f and g are, respectively, its temperature-dependent and independent part [1]. It is, however, very difficult to perform the required extended extrapolation and the determination of the molecular third-order polarizability tensor $C_{\alpha\beta\gamma\delta}^{-\omega_A, \omega_A, 0, 0}$ (second hyperpolarizability) is rather inaccurate. The experimental g value is related to $C_{\alpha\beta\gamma\delta}^{-\omega_A, \omega_A, 0, 0}$ by

$$g = \frac{\pi N}{45} (3c_{\alpha\beta\alpha\beta}^{-\omega_A, \omega_A, 0, 0} + 3c_{\alpha\beta\beta\alpha}^{-\omega_A, \omega_A, 0, 0} - 2c_{\alpha\alpha\beta\beta}^{-\omega_A, \omega_A, 0, 0}), \quad (1)$$

where N is the Avogadro number and $C_{\alpha\beta\gamma\delta}^{-\omega_A, \omega_A, 0, 0}$ is the third-order nonlinear polarizability tensor defined by

$$C_{\alpha\beta\gamma\delta}^{-\omega_A, \omega_A, 0, 0} = \partial^3 m_\alpha^{-\omega_A} / \partial \epsilon_\beta^{\omega_A} \partial E_\gamma^0 \partial E_\delta^0. \quad (2)$$

ω_A is the frequency of the analyzing optical wave of wavelength

λ_A , $m_\alpha^{-\omega_A}$ and $\epsilon_\beta^{\omega_A}$ are the α and β components of the induced dipole m and of the electric field \mathcal{E} of the optical wave, E_γ^0 and E_δ^0 are the γ and δ components of the inducing static field E .

The second method uses evaluation of the difference $B_s - f(1/T)$ at room temperature [2]. B_s is then determined by dc Kerr investigations and $f(1/T)$ by measurements of the isotropic Rayleigh constant R_{in} of the depolarization ratio D at wavelength λ_R and of the index of refraction n_R . f is given by

$$f\left(\frac{1}{T}\right) = \frac{\lambda_R^4 V}{2\pi^3 kT} \left(\frac{3}{\eta_R^2 + 2}\right)^2 \frac{R_{in} D}{6 - 7D}, \quad (3)$$

where V is the molar volume and R_{in} is connected to the mean first-order polarizability α by

$$R_{in} = 8 \left(\frac{\pi}{\lambda_R}\right)^4 \frac{N}{V} \left(\frac{\eta_R^2 + 2}{3}\right)^2 \bar{\alpha}^2. \quad (4)$$

This is an *indirect* method and unfortunately suffers from two fundamental limitations.

So far there exists no experimental proof that f and g really give the main contributions to B_s . In fact, molecular reorientation and redistribution (f) and nonlinear deformation (g) can be totally or partially obscured by slow kinetic effects (electrostriction, electrocaloric effect, etc.). On the other hand, these two investigations are performed at very different frequencies: in the optical range for the Rayleigh scattering and at the limit $\omega \rightarrow 0$ for the dc Kerr experiment. Consequently, it is difficult to relate the two effects.

Determination of the anisotropic component f of the Rayleigh constant makes use of two separate measurements and the above relation (3). This equation, however, is based on phenomenological models whose applicability is not entirely proved. (See for instance, discussion of the validity of Gans' theory, from which relation (3) is deduced and its correction in [2].)

We have previously proposed (3) a new method and applied it to the determination of the mean third-order polarizability of carbon tetrachloride. In this work, we investigated ten new

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TABLE I

Compounds	Measured Anisotropy of First-Order Effective Polarizability $(3a_{ij}^*n_{ij}^*n - a_{ij}^*n_{ij}^*n)/2$ (in 10^{-16} cm ³)	Measured Contribution of Third-Order Non-linear Polarizability to the Optical Kerr Constant g/B_{OKE} (%)	Measured Values of Mean Third-Order Polarizability $-\omega_A, \omega_A, -\omega_L, \omega_L$ c (in 10^{-36} erg ⁻¹ cm ³)
Carbon tetrachloride	1.57 ± 0.01	31	3.5 ± 0.9
Cyclohexane	1.57 ± 0.01	34	4.0 ± 1.2
n-pentane	2.48 ± 0.02	31	5.5 ± 1.3
Methyl cyclohexane	2.81 ± 0.03	35	7.5 ± 1.9
Trimethyl pentane	2.96 ± 0.03	29	6.0 ± 2.0
n-hexane	3.26 ± 0.03	31	7.2 ± 2.1
Cis-decahydronaphthalene	4.48 ± 0.04	14	3.6 ± 1.8
Transdimethylcyclohexane 1-4	5.79 ± 0.06	22	8.1 ± 3.6
Transdecahydronaphthalene	6.27 ± 0.06	17	6.3 ± 3.1
Noctane	6.40 ± 0.06	23	9.5 ± 3.6
Freon 113	9.8 ± 0.1	29	19.8 ± 6.1

Measured values of mean third-order polarizability for $\lambda_R = 0.5461 \mu$, $\lambda_A = 0.53 \mu$, $\lambda_L = 1.06 \mu$, and at temperature $t = 20^\circ\text{C}$. The anisotropy of the first-order polarizability was measured from depolarized Rayleigh scattering in our experiments.

liquids by this method. Note that our method may be viewed as an adaptation to laser techniques of the second method mentioned above. The dc Kerr effect is replaced by the optical Kerr effect (OKE), i.e., by induced birefringence [4] due to Q -switched laser radiation. $f(1/T)$ is determined directly from depolarized Rayleigh scattering (DRS) [5]. The main advantage is obviously that all measurements are performed in the optical range and the dispersion of refractive index and of molecular polarizability can easily be taken into account. Moreover, the OKE constant is determined 30 ns after the electric field begins to act on the sample, thus avoiding all difficulties from slow kinetic disturbance, which are bound to occur in dc Kerr experiments. The calculated difference $B_{\text{OKE}} - f(1/T)$ directly gives information on $c(-\omega_A, \omega_A, -\omega_L, \omega_L) = (1/5)c_{\alpha\alpha\beta\beta}^{-\omega_A, \omega_A, -\omega_L, \omega_L}$, where ω_L is the frequency of inducing laser of wavelength λ_L . Let us point out that B_{OKE} is defined by

$$B_{\text{OKE}} = \frac{2}{3} \frac{n_A \Delta n V}{\langle E^2 \rangle} \left(\frac{3}{n_A^2 + 2} \right)^2 \left(\frac{3}{n_L^2 + 2} \right)^2, \quad (5)$$

where Δn is the induced anisotropy and n_A the index of refraction. The direct measurement of depolarized scattered light obviates the use of (3), of which many versions have already been proposed in the literature. All our results are referred to the well-known "high" value [6] of the benzene Rayleigh constant $R = 16.3 \cdot 10^{-6}$ cm⁻¹.

The results are listed in Table I, which also quotes our experimental accuracy of typically 1 percent for DRS investigations and 30 percent for the OKE ones.

In Table I, column 1 gives the DRS measured values of the anisotropy of the first-order effective polarizability. ω_R is the frequency of the incident light wave (0.5461 μ). Column 2 shows that the nonlinear contribution to the OKE constant is, for all the compounds studied, in the range 0.14-0.35. Column 3 gives the mean value of the nonlinear third-order polarizability measured at frequency ω_A ($\lambda_A = 0.53 \mu$) and induced by the laser frequency ω_L ($\lambda_L = 1.06 \mu$).

While in some cases good agreement is found between our values and those from static Kerr investigations [2] (e.g., in the case of n-hexane and n-octane), the difference between the two methods is very significant in the case of carbon tetrachloride, namely

$$C_{\text{OKE}} = (3.5 \pm 0.9) 10^{-36} \text{ CGS};$$

$$C_{\text{SKR}} = (7.2 \pm 1.0) 10^{-36} \text{ CGS}.$$

This discrepancy cannot be explained by experimental error

For molecules of larger first-order polarizability anisotropy, the difference between DRS and OKE is not significant, i.e., the nonlinear part of the OKE constant is progressively obscured by the reorientational contribution. This may in particular, explain the unexpected negative value of the mean third-order polarizability of benzene as recently reported [2]. This result is valid within the experimental error and quite consistent with the small ratio of g/B_A in this case.

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