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Rotational relaxation of rigid dipolar molecules in nonlinear dielectric spectra

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We present complete nonlinear dielectric spectra for a rigid dipolar molecule in dilute solution. The spectra are described theoretically by dispersions of the form as predicted by Coffey and Paranjape [Proc. R. Ir. Acad. **78**, 17 (1978)] and by Alexiewicz and Kasprowicz-Kielich [*Modern Nonlinear Optics*, edited by M. Evans and S. Kielich (Wiley, New York, 1993), Vol. 85, pt. 1, p. 1] and are consistent with linear dielectric measurements. [S1063-651X(98)09602-0]

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Polar molecules exhibit rotational relaxation behavior when exposed to alternating electric fields with increasing frequency. Strong electric fields, on the other hand, will lead to saturation of the orientation. Such nonlinearity in the polarization becomes important for molecules with large dipole moments [1] and in systems near phase transitions (ferroelectric to paraelectric [2] or liquid-crystal [3] phase transitions) as well as in the vicinity of the critical consolute point [4]. Strong electric fields are also used to perturb reactive systems in equilibrium to investigate their kinetic and thermodynamic properties [5]. Most nonlinear dielectric measurements found in the literature are performed at single, fixed frequencies [6] so that the potential of making dynamically revealing studies remains largely unexploited. Today, techniques have been developed that allow nonlinear dielectric spectra to be recorded up to microwave frequencies [7] that are typical for the relaxation of the rotational motion of small molecules in solution. An adequate description of the rotational relaxation in strong electric fields has become indispensable to understand systems where labile chemical equilibria are upset by high fields and competition arises between orientational and fast structural or chemical relaxation as is the case for inverse micelle formation [8], diffusion-controlled reactions [9], and conformational changes. In this paper we report complete nonlinear dielectric spectra for a rigid dipolar molecule in dilute solution and compare them quantitatively with their linear spectra.

The permittivity may conveniently be written as $\varepsilon_0\varepsilon = (\partial \mathbf{D}/\partial \mathbf{E})_E$, with ε_0 the permittivity of free space. In weak fields the electric displacement **D** is directly proportional to the applied electric field **E**. At high field strengths, this linear relation no longer holds. For isotropic systems, **D** can be written as a series in odd powers of the field [10] $\mathbf{D}=\varepsilon_0\varepsilon\mathbf{E}+bE^2\mathbf{E}+\cdots$, giving rise to a dielectric change $\Delta\varepsilon$ defined as $(\partial\mathbf{D}/\partial\mathbf{E})_E-(\partial\mathbf{D}/\partial\mathbf{E})_{E\to 0}$ when switching from low-field to high-field conditions. This leads to the experimental quantity $\Delta\varepsilon/E^2=3b$ characteristic of the nonlinear dielectric effect (NDE). Several contributions to the NDE can be distinguished for dipolar molecules. The most important ones are the anomalous saturation due to chemical and/or structural perturbation and the normal (Langevin) saturation due to realignment of the dipoles in the field. For the system discussed here, only this last contribution to the NDE is of significance.

Theoretical work on the frequency dependence of the third-order nonlinear permittivity has been abundant. Various expressions are given in terms of fundamental and harmonic frequencies depending on the configuration of the electric fields applied. Kasprowicz-Kielich and Kielich [11] treated nonlinear optical and dielectric relaxation processes in terms of changes of the real part of the complex permittivity. Independently, Coffey and Paranjape [12] extended Debye's rotational diffusion approximation to the cases where either a strong alternating electric field is applied to the dielectric or a strong constant field with a superimposed weak ac field is used. More recently, Kimura and Hayakawa [13] reproduced concordant results for the first case. An extension of Coffey's theory to systems containing both permanent and induced moments is given by Déjardin [14]. Finally, Alexiewicz and Kasprowicz-Kielich [15] reviewed the topic and completed the theory developed in Ref. [11] with complex notation.

The experimental technique used here consists of a stationary relaxation method where a strong but slowly oscillating (<200 Hz) electric field periodically perturbs the system whose permittivity is being measured by a weak probing field of high frequency. The nonlinear dielectric data are obtained by monitoring the modulation of the parameters of a resonant circuit induced by the application of a high field to the dielectric solution enclosed in a capacitor of the circuit. An LC resonance circuit with exchangeable coils [16] covers the frequency range 1–100 MHz, while for frequencies from 100 MHz up to 3 GHz a partially coaxial resonant cavity of adjustable length [7] is used. The experimental setups produce NDE spectra that are theoretically predicted in Refs. [12,15], from which one can deduce that the (complex) NDE corresponding to normal saturation depends on the frequency as

$$\Delta\varepsilon/E^2 = -LN\mu^4\Phi(\omega)/45\varepsilon_0(kT)^3,$$

$$\Phi(\omega)=\frac{1+(1-i\omega\tau)(2-i\omega\tau/3)}{3(1-i\omega\tau)^2(1-i\omega\tau/3)}, \tag{1}$$

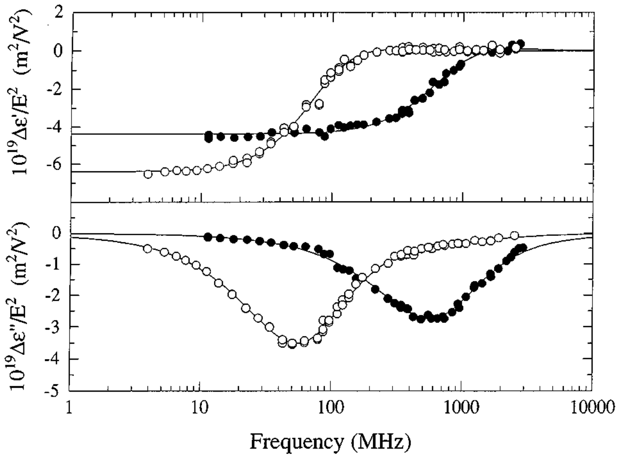

FIG. 1. Real ($\Delta\varepsilon'/E^2$) and imaginary ($\Delta\varepsilon''/E^2$) parts of the NDE spectra (recorded at $E=110$ kV/cm) for solutions of 5CB in cyclohexane (filled circles, 0.037 mol/L) and in squalane (open circles, 0.056 mol/L) at 25 °C. The data for the 5CB/cyclohexane system are fitted with a single NDE relaxation process [Eq. (1)]; the 5CB/squalane system is fitted by the sum of two such dispersions. Contributions due to anisotropy of polarization are not taken into account and $\Delta\varepsilon'/E^2$ is corrected for electrode deformation.

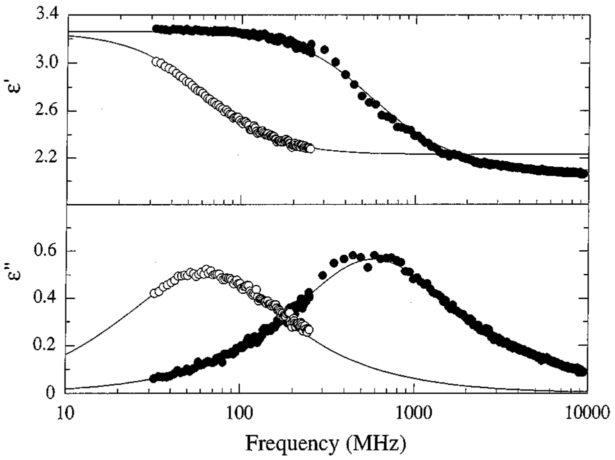

FIG. 2. Real (ε') and imaginary (ε'') parts of the (linear) dielectric spectra for solutions of 5CB in cyclohexane (filled circles, 0.507 mol/L) and in squalane (open circles, 0.486 mol/L) at 25 °C and 22.5 °C, respectively. The data for the 5CB/cyclohexane system are fitted by the sum of two Debye dispersions; the 5CB/squalane system is fitted with a single Debye process.

where τ is the Debye rotational relaxation time, kT the thermal quantum, μ the permanent dipole moment, and N the number density. The factor L is a function of ε and ε_∞ relating the external field to the local field acting on the dipoles [17], with ε_∞ the optical permittivity, and where the dispersion of ε is taken into account.

In order to check the theory we choose to study the rotational relaxation of the nematogen 4,4′-*n*-pentyl-cyanobiphenyl (5CB) in dilute solution in the presence of strong electric fields. The dipolar molecule promised to be a good test case for the shape of the rotational relaxation of the NDE as predicted for rigid dipoles in solution. Indeed, Davies *et al.* [18] had reported linear dielectric spectra for concentrated solutions of 7CB in benzene and found a single Debye-type relaxation process confirming the dipole moment to coincide with the long molecular axis. In the present study, NDE measurements have been performed on solutions of 5CB both in cyclohexane and in squalane (2,6,10,15,19,23-hexamethyltetracosane) within a concentration range 0.01–0.1 mol/L at 25 °C. Figure 1 shows the real and imaginary parts of the NDE spectra for solutions of 5CB in both solvents. Squalane has a viscosity $\eta=28$ cp at 25 °C compared to 0.9 cp for cyclohexane explaining the slower relaxation in squalane. The accessible frequency window was not wide enough to register complete relaxation for solutions in cyclohexane. The nonlinear spectra for solutions in squalane, however, are best described by the sum of two relaxation processes as in Eq. (1) resulting in the components μ_1^4 and μ_2^4.

For the sake of comparison, linear dielectric spectra have been measured for solutions of 5CB in cyclohexane (0.2–1.2 mol/L) and in squalane (0.06–0.5 mol/L). The complex linear dielectric spectra in the frequency range of 30–250 MHz were recorded using a high-precision rf vector analyzer [19]. Additional high-frequency measurements were made with a Hewlett-Packard 85070M Dielectric Probe Measurement System [20], which is operational from 200 MHz to 20 GHz. The low-frequency measurements were performed at room temperature (22 °C) while the high-frequency spectra were recorded at 25 °C. Figure 2 shows the real and imaginary parts of the linear dielectric spectra for solutions of 5CB in cyclohexane and in squalane. The linear permittivity spectra of the 5CB/cyclohexane system can be decomposed into two separate Debye [21] relaxation processes as described by

$$\varepsilon=\varepsilon_\infty+\sum \Delta\varepsilon_k/(1+i\omega\tau_k), \tag{2}$$

with $k=1,2$ and where $\Delta\varepsilon_k$ and τ_k are the dielectric relaxation strength and relaxation time for the kth process, respectively. To each dielectric relaxation strength $\Delta\varepsilon_k$ corresponds a component μ_k^2 computed according to Onsager's equation [22].

Because the experimental setup for NDE measurements is limited to frequencies below 3 GHz, only the slower relaxation process was noticeable in the nonlinear spectra for solutions in cyclohexane. For solutions of 5CB in squalane the linear spectra, on the other hand, could only be recorded partially because the Dielectric Probe Measurement System is not sensitive enough. Accordingly, only one relaxation process is observed, while the corresponding NDE spectra clearly show two distinct relaxation steps. Therefore, the amplitude of the second relaxation step was estimated by subtracting the first amplitude $\Delta\varepsilon_1$ from the static permittivity value determined at $\omega\rightarrow 0$. The dipole moment values derived for the two relaxation processes in the two systems studied are plotted against concentration in Fig. 3, where also the components from the NDE measurements are represented.

The figure illustrates that the linear and nonlinear results are perfectly consistent, strengthening the appropriateness of Eq. (1) to describe the NDE spectra. It is concluded here that dielectric saturation operates on the separate rotational modes individually. The slight decrease of the components

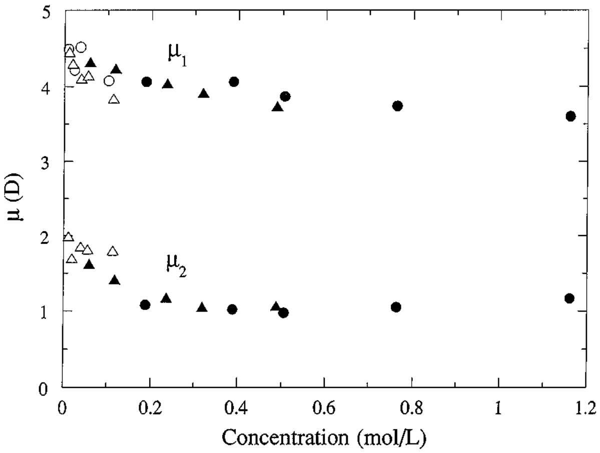

FIG. 3. Dipole moment components vs concentration for the 5CB/cyclohexane (circles) and 5CB/squalane (triangles) systems. Open symbols represent values obtained with the NDE method; filled symbols represent values extracted from the linear dielectric measurements.

μ_k with concentration can be ascribed to orientational correlation with increasing preference for opposite moment directions as a result of dipole-dipole interactions. This was also concluded from static dielectric measurements on 5CB in benzene [23] and in p-xylene [24], and for 7CB in octane solutions [25].

The unobserved component μ_2 in the NDE measurements of the 5CB/cyclohexane systems seems to be identical to μ_2 observed for the solutions in squalane. Indeed, the calculation of the total dipole moment $\mu_{\mathrm{total}}=(\mu_1^2+\mu_2^2)^{1/2}$ at infinite dilution in cyclohexane, borrowing the μ_2 value from the 5CB/squalane system, leads to a value of 4.95 D in perfect agreement with the literature: Megnassan and Proutiere [26] calculated the dipole moment of 5CB in cyclohexane at infinite dilution to be 4.92 D and Gueu, Megnassan, and Proutiere reported values between 4.85 and 5.08 D for 5CB in four nonpolar solvents [27].

The relaxation times obtained from the linear and nonlinear spectra cannot be compared directly with each other because the NDE spectra for the solutions in cyclohexane are incomplete and because the linear spectra for the solutions in squalane do not cover the entire relaxation region. Moreover, the difference in measuring temperature of 3 °C for the 5CB/squalane system leads to an appreciable change in viscosity: η(squalane) varies from 28 cp (25 °C) to 32 cp (22.5 °C). A similar change in temperature, however, does not lead to a significant change in viscosity for the 5CB/cyclohexane systems. Comparing the slowest relaxation process in the NDE spectra for 5CB in squalane with the (visible) one in cyclohexane, it appears that the 30-fold increase in viscosity leads to an increase in relaxation time by a factor of about 10. For the fastest relaxation process (only visible in the NDE spectra of 5CB in squalane and in the linear dielectric spectra of 5CB in cyclohexane) this factor is found to be no more than 3. For each solvent series individually, the longer relaxation times are consistent when taken from either the linear or nonlinear data [28].

These observations lead to the conclusion that for the isolated molecule of 5CB in solution the dipole vector does not coincide with the long molecular axis. Consequently, the low-frequency process bears on the rotation of the molecule around its short axis while the high-frequency process reflects that around the long molecular axis, where less of the solvent has to be displaced, making it less dependent on the viscosity of the medium. Recent linear dielectric spectra of 7CB and 8CB in benzene solutions led Yagihara *et al.* to a similar conclusion [29]. Dielectric measurements on the pure nCB ($n=4-8$) liquids [25,30–33] in the isotropic phase also showed a second (faster) relaxation with smaller amplitude.

The complete nonlinear dielectric spectra presented here are consistent with linear dielectric measurements and lead to experimental values of the dipole moment of 5CB in perfect agreement with literature. The dispersion is accurately predicted by Coffey and Paranjape [12] and Alexiewicz and Kasprowicz-Kielich [15]. The NDE measurements are very sensitive and constitute an accurate tool to reveal dynamic properties of polar molecules.

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[28] 5CB in cyclohexane: $\tau_1 = 177 \pm 6$ ps for 0.103 mol/L from NDE and $\tau_1 = 186 \pm 6$ ps for 0.189 mol/L from linear spectra. 5CB in squalane: $\tau_1 = 2.05 \pm 0.09$ ns for 0.0562 mol/L from NDE and $\tau_1 = 2.27 \pm 0.09$ ns for 0.0595 mol/L from the linear spectrum; the ratio of these τ_1 values corresponds closely to the ratio $\eta^{25\,°\mathrm{C}}/\eta^{22.5\,°\mathrm{C}} = 0.88$.

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