

Figure 5. Optical Kerr effect (OKE) data from CS₂ liquid. The data are similar in form to those in Figures 4 and 5. Note that the OKE experiment in this case is similar to ISS in that the same type of "impulse" force is exerted by the excitation pulse. The OKE experiment is essentially a forward-scattering ISS experiment.

but rather the first part of the data was ignored during fitting. A more fundamental limitation on our interpretation of the data is the simplicity of the "local oscillator" model used. The wide range of local vibrational frequencies (i.e., inhomogeneous dephasing) has not been accounted for.¹⁸ Moreover, the more slowly relaxing orientational motion may also show "nonrelaxational" short-time behavior since an impulsive torque should produce a delayed, not instantaneous, orientational response. More systematic experimental work currently under way should suggest the proper theoretical description.

These reservations notwithstanding, we close by discussing the important implications of these results. They support basic notions about short-time dynamics in molecular fluids which have been discussed at length but which are difficult to observe directly by

conventional experimental methods. Time-domain methods with sufficient resolution provide the most direct means for observation of these short-time nonrelaxational dynamics. We have observed similar effects in benzene³³ and expect similar results in many liquids. Systematic examination of a variety of pure and mixed fluid systems under different experimental conditions (sample composition, temperature and pressure, laser power, etc.) should further clarify the nature of the short-time motion and may yield configuration-averaged intermolecular potentials, dissipation rates, and additional information fundamental to understanding the forces felt by molecules in a fluid. Determination of absolute electronic and nuclear polarizabilities should also be possible by measurement of absolute diffraction intensities.²⁸ We note finally that the "vibrational" nature of intermolecular motion in liquids may play a major role in electronic excited-state relaxation (e.g. Stokes-shifting dynamics) in fluids and in some liquid-state chemical reactions whose rates are influenced by the solvent.³⁴

Acknowledgment. We acknowledge the participation of Dr. B. I. Greene in the initial stages of this work, and many helpful discussions with Y.-X. Yan and Profs. D. Kivelson and I. Oppenheim. We thank T. Dougherty for assistance with data analysis and presentation. This work was supported in part by NSF Grant No. DMR-8306701 and by NSF and private contributors to a Presidential Young Investigator Award. Contributions from Monsanto, AT&T Bell Labs, Chevron, Perkin-Elmer, and DuPont are gratefully acknowledged. We thank G. A. Kenney-Wallace for inviting us to present our results at the APS Topical Group Meeting²² and for her interest in our results at that time.

Note Added in Proof: We have learned that G. A. Kenney-Wallace et al. have recently reported observations similar to ours in CS₂ and other liquids.³⁵

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Effect of Correlated Proton Jumps on the Zero Field NMR Spectrum of Solid *p*-Toluic Acid

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Zero field NMR spectra of polycrystalline *p*-toluic acid are compared to computer simulations assuming static, uncorrelated, and correlated motions for the protons in the hydrogen-bonded dimers. Correlated jumps seem the most reasonable, in agreement with previous work on single crystals.

Introduction

Small amplitude motions in condensed matter are amenable to study by NMR through their effects on observed chemical shifts and dipolar or quadrupolar couplings. The high-field powder patterns of conventional NMR are generally not very sensitive to these motions. Zero field NMR,¹ however, should be ideal for the study of subtle motions in polycrystalline or disordered ma-

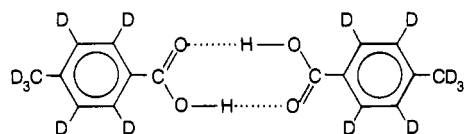
terials since the resulting asymmetry produces line splittings of the dipole spectrum.² An important example of interesting small

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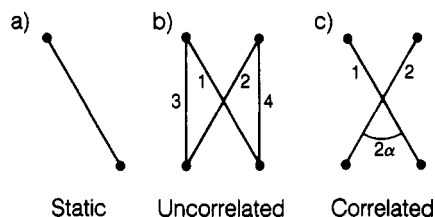
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p-Toluic Acid Dimer



Static

Uncorrelated

Correlated

Figure 1. Hydrogen bonded dimer of *p*-toluic acid. Jumps of the two hydrogen atoms between molecules in the dimer yield four possible orientations of the dipole-dipole coupling tensor (1, 2, 3, and 4). Shown below are the possible configurations for the two proton dynamics in the carboxylic acid dimer. (a) The static limit. In (b) the uncorrelated motion of the two protons results in all four possible orientations of the internuclear vector. The jumps in (c) are correlated and the proton-proton internuclear vector interchanges between orientations 1 and 2. The jumps between orientations 1 and 2 are described by the angle α . At room temperature, orientations 1 and 2 are assumed to be equally populated and therefore the principal axes of the average dipole coupling tensor will correspond to a frame where the *x* axis is along the carboxyl C-C vector and the *y* axis is also in the plane of the drawing. For either (b) or (c), a motionally induced asymmetry in the averaged dipolar coupling tensor will result.

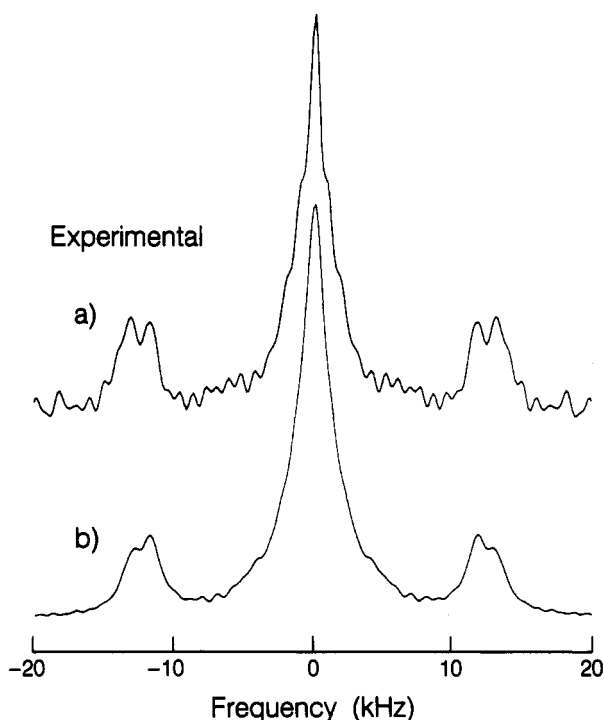


Figure 2. Experimental zero field NMR spectra of *p*-toluic acid ~60% deuteriated on the acid sites and 98% deuteriated elsewhere. Spectrum (a) is the Fourier transform of one FID. The two outer peaks are at 11.5 and 12.9 kHz. To ensure that the sample had not picked up water, it was dissolved in a 60% H₂O/D₂O mixture, recrystallized, and dried. This spectrum is shown in (b), and is the sum of seven FIDs. Here the peaks are at 11.8 and 12.8 kHz. Both spectra are 1024-point Fourier transforms of 50-point FIDs taken with a 25- μ s increment. The predicted low-frequency peak is overwhelmed by the broad zero frequency peak which arises from unpaired protons in the sample. The asymmetry of the average dipolar coupling is reflected in the splitting of the high-frequency lines.

amplitude motions is found in solid *p*-toluic acid which, like many carboxylic acids, forms dimers in the solid state³ as illustrated in

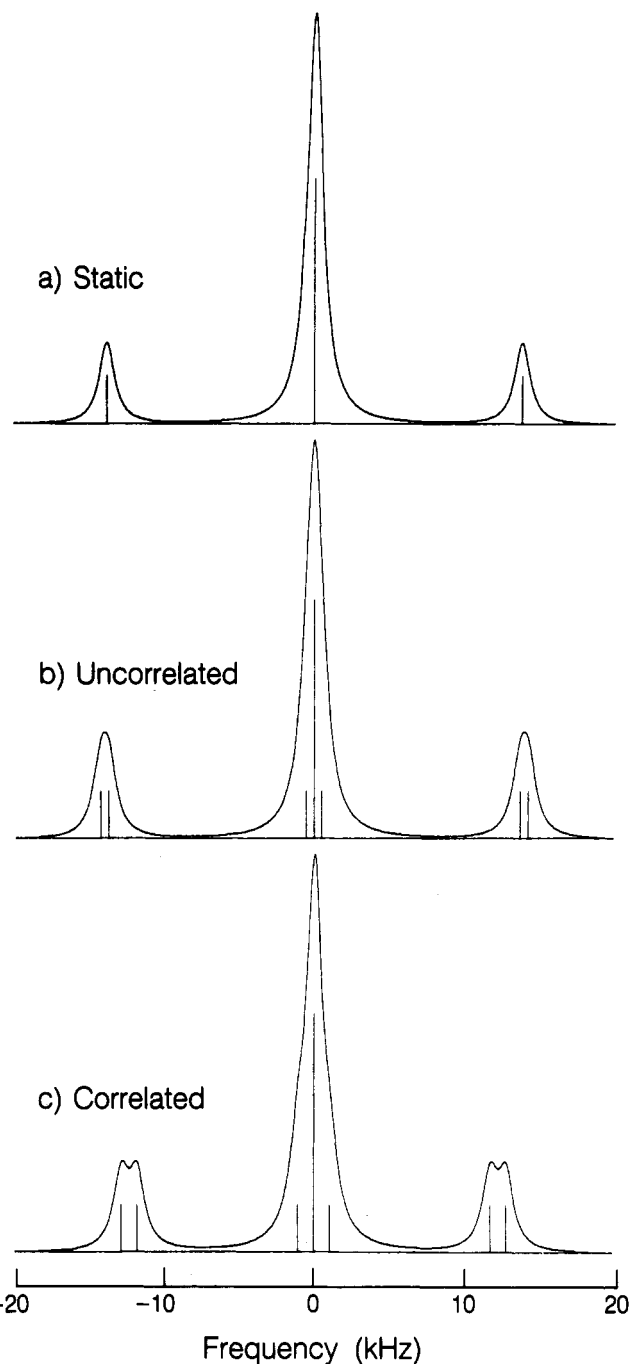


Figure 3. Simulated spectra for *p*-toluic acid. (a) Computer-simulated spectrum for the static limit of the two protons with $r_1 = 2.33$ Å. (b) Computer-simulated spectrum for the uncorrelated jump model ($P_1 = P_2 = P_3 = P_4 = 0.25$) of the two protons with $\alpha = 16^\circ$, $r_1 = 2.33$ Å and $r_3 = 2.23$ Å. (c) Computer-simulated spectrum for the correlated jump model ($P_1 = P_2 = 0.5$, $P_3 = P_4 = 0$) with the same α and r_1 values as in (b). Note that the asymmetry is more pronounced in the average over orientations 1 and 2 alone. In (b) the outer lines are shifted to higher frequency due to the added contributions of the larger dipolar couplings of orientations 3 and 4.

Figure 1. As shown previously in single-crystal studies by X-ray crystallography³ and NMR,⁴ the carboxylic protons in this crystalline solid are in a state of dynamic disorder at room temperature. Additionally, ¹⁷O NQR experiments⁵ have demonstrated, through an averaging of the quadrupolar tensor, that the hydrogens jump between oxygens rather than undergoing 180°

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flips about the C-C vector. In their single-crystal NMR study, Meier et al.⁴ concluded that the hydrogen bond protons undergo correlated jumps. Such correlated motions should be readily observable in the zero field NMR spectrum even for a polycrystalline sample, and we have performed a study to observe such motions.

Results and Discussion

Details of the zero field NMR experiment^{1a} and the spectrometer⁶ have been presented elsewhere. The *p*-toluic acid sample used was ~60% deuteriated on the acid sites and 98% deuteriated elsewhere. By diluting the acid site protons, coupling between dimers is reduced and the splitting of the lines is better resolved. The room temperature proton zero field NMR spectrum of *p*-toluic acid appears in Figure 2. Simulated zero field spectra for the case of static protons as well as correlated and uncorrelated jumps were produced for comparison to the experimental spectrum as follows. In the most general case, the average dipole coupling tensor is written

$$\mathbf{D} = P_1\mathbf{D}_1 + P_2\mathbf{D}_2 + P_3\mathbf{D}_3 + P_4\mathbf{D}_4 \quad (1)$$

where P_n is the fractional population of orientation n . The tensors, \mathbf{D}_n , describe the dipole coupling for the two protons in a particular orientation, as explained in the caption to Figure 1. A few simplifications to this expression can be made immediately. First, when the tensor is viewed in the molecular based frame of Figure 1, the interproton vectors 3 and 4 are equivalent and thus $\mathbf{D}_3 = \mathbf{D}_4$, unlike the interproton vectors 1 and 2 which have a different dependence on the jump angle α . Additionally, at room temperature, sites 1 and 2 are assumed to be equally populated,⁴ as are 3 and 4.

Writing the average dipole coupling tensor in the molecule based frame (x, y, z) of Figure 1 yields eq 2, where α is the jump angle shown in Figure 1 and $D_n = \hbar\gamma^2/r_n^3$. The value of D_3 is based

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$$\mathbf{D} = D_1 \times \begin{bmatrix} 2P_1(1 - 3 \sin^2 \alpha) + \frac{2D_3P_3}{D_1} & 0 & 0 \\ 0 & 2P_1(1 - 3 \cos^2 \alpha) - \frac{4D_3P_3}{D_1} & 0 \\ 0 & 0 & 2P_1 + \frac{2D_3P_3}{D_1} \end{bmatrix} \quad (2)$$

on the internuclear distances taken from X-ray crystallographic data for pentafluorobenzoic acid.⁷

The normalized zero field signal is calculated^{1a} to be

$$S(t_1) = \frac{1}{3}[\cos \omega_{12}t_1 + \cos \omega_{13}t_1 + \cos \omega_{23}t_1] \quad (3)$$

Thus one expects three lines of equal intensity at the frequencies corresponding to the differences in eigenvalues derived from eq 2. Simulated spectra were produced for the static ($P_1 = 1.0$), correlated ($P_1 = P_2 = 0.5$, $P_3 = P_4 = 0$), and uncorrelated ($P_1 = P_2 = P_3 = P_4 = 0.25$) cases and appear in Figure 3. Comparison to the experimental spectra indicates that correlated jumps between two orientations is the most plausible situation. The values of r_1 and α derived from the experimental spectrum are $r_1 = 2.33 \pm 0.05$ Å and $\alpha = 16.0 \pm 2^\circ$ which are in good agreement with results previously reported by Meier et al.⁴ from single crystal experiments in high field. More complex dynamics are also accessible with zero field NMR and have been treated theoretically.^{2b,d}

Acknowledgment. We thank H. Zimmermann for the synthesis of the deuteriated *p*-toluic acid. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the U.S. Department of Energy under Contract DE-AC03-76SF00098.

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Antiferroelectric Stacking in Lead Phthalocyanine Columnar Mesophases

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(Received: December 23, 1986)

Experimental evidence is presented for the first example of columnar mesophase (1) observed far below room temperature, (2) obtained with flat discotic molecules possessing a strong dipole moment normal to the molecular plane, and (3) showing an intramolecular antiferroelectric coupling of the molecules along the columns.

Introduction

In a series of recent papers,¹⁻³ octakis(alkoxymethyl) derivatives of phthalocyanine were shown to produce columnar liquid-crystalline structures upon heating. The crystal/mesophase transition occurred in a range from 40 to about 80 °C. The mesophase/isotropic liquid transition was generally difficult to detect: most of the products studied remained in the mesomorphic state up to temperatures of the order of 300 °C, where they started to de-

compose. The structure of the mesophases was studied by optical microscopy and X-ray diffraction. It was described as corresponding to the stacking of the flat aromatic cores of the phthalocyanine molecules in columns, surrounded by the aliphatic chains in disordered conformations, and laterally assembled in a two-dimensional hexagonal lattice. The majority of the phthalocyanine derivatives were studied with a metal ion (Cu, Zn, Mn) included in the empty central cavity of the charged aromatic core. Because they are smaller size than the cavity, and because of their electrostatic interactions with the phthalocyanine moiety, these metal ions lie in the average plane of the molecule.

Among the metal ions which are known to form complexes with phthalocyanine (Pc), lead (Pb²⁺) is of particular interest, because its diameter (2.4 Å) is larger than that (1.6 Å) of the Pc cavity to which it tends to be attracted. In both monoclinic and triclinic

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