Femtosecond Dynamics in Hydrogen-Bonding Solvents: Temperature-Dependence of the Inertial and Diffusive Relaxation of Liquid Acetic Acid

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Abstract

Acetic acid ultrafast dynamics were measured using femtosecond optical-Kerr spectroscopy for temperatures ranging from near the melting to boiling points of the liquid.

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Femtosecond nonlinear optical spectroscopy has proven to be a powerful tool with which to probe both the inertial and diffusive dynamics of molecular liquids.¹ Only very recently have these techniques been applied to the study of dynamics in complex, strongly-interacting Hydrogen-bonding (H-bonding) liquids.² We present here new results on the study of neat liquid acetic acid, CH₃CO₂H. The measurements of the inertial and diffusive dynamics were made using the optical-heterodyne-detected, optical-Kerr-effect (OHD-OKE) technique, which is an electronically non-resonant polarization spectroscopy providing a signal linear in the third-order nonlinear-optical response.^{1a} Our measurements have been made as a function of sample temperature, with data taken at 19 and 108 °C. The melting and boiling points of acetic acid are *ca.* 16.2 and 117 °C, respectively, so our measurements have probed the extremes of the liquid phase. One of the most important uses for such ultrafast solvent relaxation data is to predict the rate of solvent-limited chemical reactions in solution, particularly adiabatic electron-transfer reactions.

Because of a two-fold H-bond, acetic acid forms a cyclic dimer of C₂ symmetry in the crystalline, liquid, and gas phases, as shown below.

Unlike other complex H-bonding liquids such as the amides^{2a} or water^{2b,2c}, which may form linear chains and tetrahedrally coordinated networks, liquid acetic acid is only observed as a monomer or dimer. Turi and Dannenberg³ used high level *ab initio* and semi-empirical molecular-orbital calculations to explain this observation as resulting from the increased stability of 3.1 kcal/mole, of the doubly H-bonded configuration relative to the singly H-bonded dimer. Thus, the acetic acid liquid is a simpler system in which to study the dynamics of H-bonding liquid interactions.

Our raw transient birefringence data for acetic acid are shown in Figure 1, for temperatures near the melting and boiling points. The rising edge of the transient tracks the non-resonant electronic hyperpolarizability response, while the fall from the peak of the transient immediately indicates the inertial nuclear dynamics. On a longer time scale (not shown), the diffusive relaxational regime dominates. After many molecular collisions, on a 0.5-1.0 picosecond time scale, the transient becomes a multi-exponential decay, with the longest time constant being 22 picosecond at room temperature. This molecular relaxation process is a measure of the diffusive rotational correlation function of the molecule. The dynamics occurring in the inertial regime, before the dephasing resulting from molecular collisions has occurred, is best studied in the frequency domain representation of our data.

By doing a Fourier-transform deconvolution on the birefringence transients shown in Figure 1,^{1a} we obtain a frequency domain representation of the nonlinear-optical susceptibility, shown in Figure 2A, which we call $\text{Im}[R_{\text{OHD-OKE}}(\nu)]$. Lineshape analysis resolves this low-frequency spectrum into three intermolecular vibrational bands. The low-frequency Raman work of Faurskov-Nielsen and Lund shows that the three intermolecular vibrational (or librational) frequencies of liquid acetic acid have peaks at 55, 115, and 165 cm^{-1} in the $R(\nu)$ representation of their data. They have assigned these bands to a symmetric stretch, an out-of-plane bend, and a librational motion, respectively.⁴ The $R(\nu)$ representation of the Raman spectrum, $I_{\text{Raman}}(\nu)$ is commonly used in low-frequency Raman and Rayleigh-wing spectroscopy to enable observation of the intermolecular dynamics from underneath the large, Lorentzian peaks arising from the diffusive rotational relaxation. This nonlinear-optical susceptibility is related to the low-frequency Raman spectrum by a Boltzman factor, i.e.,

$$\text{Im}[R_{\text{OHD-OKE}}(\nu)] \propto I_{\text{Raman}}(\nu)[1-\exp(-h\nu/kT)], \quad (1)$$

and the $R(\nu)$ representation is thus connected to our frequency domain representation by:

$$R(\nu) = \nu \cdot I_{\text{Raman}}(\nu)[1-\exp(-h\nu/kT)]. \quad (2)$$

The inter-relationships between the three spectral representations are presented graphically in Figure 2. Precisely because we can analyze the rotational correlation function directly from our measured transients, we are then able to analyze the inertial intermolecular dynamics in the frequency domain, without resorting to the $R(\nu)$ representation that distorts the low-frequency spectrum.

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