Pulsed Terahertz Spectroscopy of Solutions: Experiment and Memory Function Analysis

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Abstract: The frequency dependent absorption coefficients of mixtures of CCl_4 and $CHCl_3$ are measured by pulsed THz time-domain spectroscopy and analyzed by a Mori memory function formalism.

Understanding the magnitudes and time scales of the intermolecular interactions that occur during a chemical reaction in the liquid phase is a central problem in condensed phase studies. Assuming linear response and validity of the Fluctuation-Dissipation theorem, the spectrum of equilibrium fluctuations of the neat solvent molecules can be directly related to the solvent modes available for acceptance of excess energy during the course of a reaction.[1] Such equilibrium spectra may be obtained from optical Kerr effect studies[2] or far-infrared (i. e. terahertz) dipolar absorption measurements.[3,4] The focus here is terahertz (THz) spectroscopy.

The THz time-domain spectrometer[5] consists of an 80μm antenna, biased with 80V, on a gallium arsenide (GaAs) wafer, optics and a silicon-on-sapphire receiver. The 780nm pulses from a Ti:Sapphire oscillator produce carriers in the source and receiver chips that are accelerated by the applied bias and incident THz field, respectively. The incoming electrical pulse was detected by optically gating the receiver and measuring the current flow driven by the bias from the THz electric field. The THz pulse is shown in Fig. 1.

The frequency dependent absolute absorption coefficients from 0.1 to nearly 4.0 THz (3.3 to 134 cm^{-1}) of neat $CHCl_3$, two weighted Mori curves and the bi-Mori fit are presented in Figure 2. The absorbance spectra for $CHCl_3$ and CCl_4 were fit by third order truncations of Mori's continued fraction[6], equivalent to a second order memory function analysis. When the spectra are fit with a four parameter non-linear least squares routine, the theoretical and experimental curves are nearly overlapped, and are closest for the pure CCl_4 spectrum (not shown). However, when the adjustable parameters are calculated and constrained in a physically meaningful way and nonlinear least squares fitting is performed by varying only one parameter, the exponential relaxation time constant of the intermolecular torques, the fits to the experimental data for pure chloroform are quite poor (not shown). This result indicates that a single Mori function, hence, single type of relaxation process, is not appropriate for chloroform or the mixtures.

Figure 2 illustrates the fit of the sum of two single Mori functions to the data. Curve A (dashed curve) uses Mori parameters that describe diffusive molecular motions and curve B (diamonds) uses Mori parameters that describe inertial motions. The first order memory function related to the angular velocity time correlation function, in curve B is more inertial than in curve A. Furthermore, two parameters associated with torque relaxation are used: τ_D (in curve A) which describes rotational diffusion and τ_L (in curve

B) which is smaller in value. The "bi-Mori" fit suggests that two (or more) types of molecular motion are necessary to describe the FIR spectrum of the liquid.

The assumption of exponential decay of the intermolecular torque correlation function is implicit in the third order truncation of the Mori continued fraction, which may not be rigorously correct.[7] The theory should succeed at frequencies very small relative to the torque decay rate. This prediction originates in the fundamental aim of the Mori theory: the generation of a TCF for an observable variable. Other variables whose correlations decay on comparable time scales cause the observable to behave in a non-Markovian way. In the present case, the two secondary variables, related to the first and second derivatives of the primary variable, are closely related to the angular velocity and the intermolecular torque, respectively. For frequencies much less than the torque decay rate, the fastest process explicitly treated, the torque decay should seem instantaneous, and the lineshape should describe experimental data well. The torque decay rate in Figure 2 is 12.5THz for both curves A and B. Hence for frequencies less than 15% of the torque decay rate (i.e. 2THz and below), the fit is quite good, and the expected condition is observed.

A series of mixtures of $CHCl_3$ and CCl_4 were fit by a mole fraction weighted sum of the fitted curves for $CHCl_3$ and CCl_4. The series of absorption spectra indicate that the problematic behavior of memory function analysis may result from non-exponential relaxation of the intermolecular torques, and consideration of distinct types of relaxation mechanisms of the dipolar correlation functions.
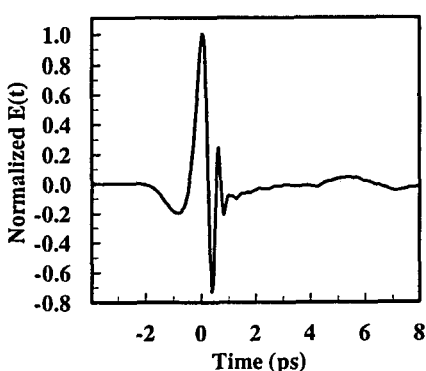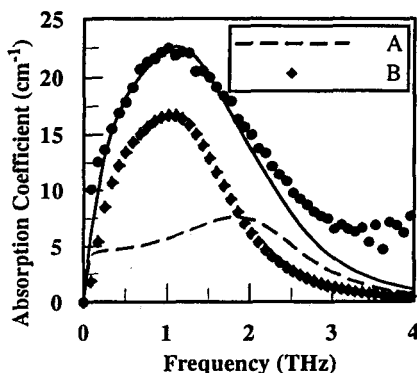

Figure 1: Measured THz Pulse.

Figure 2: Weighted sum of Mori lineshapes.

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