

Polarization-Resolved Ultrafast Polarizability Relaxation in Aromatic Liquids

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Abstract. The ultrashort time resolved decay of the isotropic and anisotropic components of the polarizability of three polar aromatic liquids have been measured as a function of temperature using a diffractive optic based heterodyne detection method. The isotropic spectral density, which contains only interaction induced components of the liquid's collective polarizability, is contrasted with the anisotropic response to unravel the interaction induced and molecular contributions to the latter. These data are discussed in relation to some existing molecular dynamics simulations.

Knowledge of the structure and dynamics of molecular liquids is central to an understanding of chemical reactivity in solution.¹ The rate coefficient for reactions as diverse as isomerization, electron transfer and solvation are all influenced, and even controlled, by solvent dynamics. Among various methods to investigate dynamics ultrafast optically heterodyne detected optical Kerr effect (OHD-OKE) has been widely used and produced important results.²

Planar aromatic liquids have been the subject of theoretical and experimental investigations because of their somewhat complex low frequency behaviour.^{3,4} Like small molecule liquids they have a low frequency peak that is well represented by the SED equation, but when this is subtracted a broad bimodal or 'flat topped' reduced spectral density is recovered.⁵

In this work we shed further light on the origin of this structure through measurements of both the isotropic and anisotropic polarizability relaxation of the aromatic liquids toluene, nitrobenzene and benzonitrile as a function of temperature. The isotropic spectral density, which contains only interaction induced components of the liquid's collective polarizability, is contrasted with the anisotropic response to unravel the interaction induced and molecular contributions to the latter. Very similar behaviour was observed for the three different aromatic liquids (see Figure 1b). The fast damping of the isotropic response in the time domain confirms the assignment of the prominent slow exponential relaxation in the anisotropic response to diffusive molecular orientational relaxation. The isotropic response in the frequency domain is found to be asymmetric and peaked at low frequency, as can be seen on Figure 1a, but extending to higher frequencies as well, thus contributing over a rather wide frequency range. The relatively low mean frequency of the isotropic spectral density supports the assignment of the highest frequency part of the anisotropic response to molecular librational motion. Finally a number of affinities are noted between the interaction induced (isotropic) response and the low frequency shoulder in the anisotropic spectral density which is so characteristic of the dynamics of aromatic liquids. These data are discussed in relation to some existing molecular dynamics simulations.

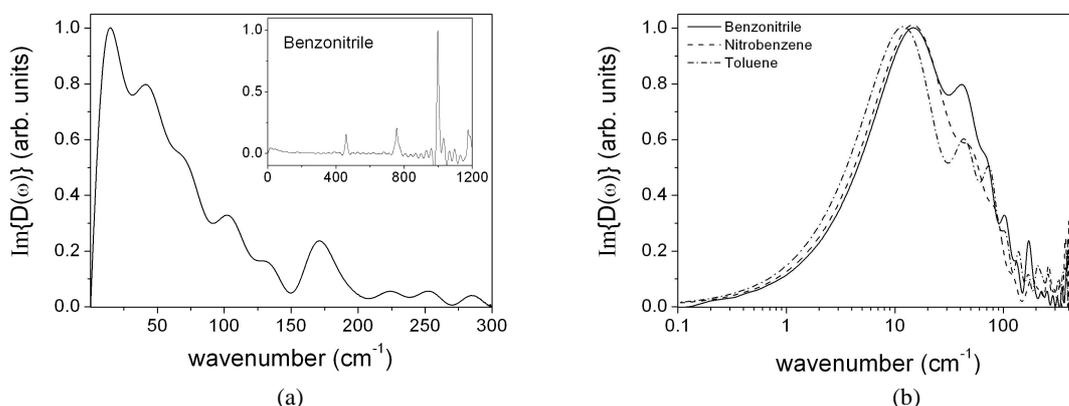


Fig. 1. (a) Representative deconvoluted isotropic spectral density obtained for benzonitrile. Inset shows the same result over a broader frequency scale showing the intramolecular vibrational modes contribution to the measured signal; (b) Comparison of the isotropic spectral densities at room temperature for the three liquids on a semilog scale.

References

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