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The Intermolecular Vibrational Dynamics of Substituted Benzene and Cyclohexane Liquids, Studied by Femtosecond OHD-RIKES

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With femtosecond laser pulses, it is now possible to impulsively excite all of Raman-active intermolecular dynamics in a liquid sample. By using the femtosecond optical-heterodyne detected, Raman-induced Kerr effect spectroscopy (fs-OHD-RIKES) experiment, we have studied the intermolecular dynamics of toluene, benzyl alcohol, benzonitrile, cyclohexane, and methylcyclohexane in both the time and frequency domains. The intermolecular dynamics may be broadly categorized as inertial, or underdamped motions, or diffusive, or overdamped motions. The underdamped motions include the intermolecular collisions, inertial rotations, and libration caging motions arising from torques caused by strong intermolecular electrostatic interactions. The slower diffusive motions that we observe are reorientational motions with the characteristics of Brownian motion. Because of the high signal-to-noise inherent with all OHD techniques, and because the OHD-RIKES signal is linear in the molecular response, we can analyze the third-order molecular response in both the time and frequency domains via Fourier transformation. The measured fs-OHD-RIKES birefringence transients for the five liquids are shown in Figure 1 over a five picosecond time window.

In all of the five liquids, a slower diffusive relaxation is observed on time scales ranging from 1.5 ps in cyclohexane to 63 ps in benzyl alcohol. This diffusive relaxation is shown for benzonitrile in Figure 2. A double-exponential function with time constants of 3.4 and 21.2 ps is required to obtain the best fit to the diffusive relaxation. Though the five solvent molecules are similar in shape and volume, their diffusive reorientation times are related not only to symmetry, but are more strongly correlated with the intermolecular electrostatic interactions. Though methylcyclohexane and toluene have the same molecular symmetry and are of a similar volume, the time constants for diffusive relaxation of 2.64 ps and 5.90 ps, respectively.

In the aromatic liquids, we observe intramolecular bending modes at about 200 cm^{-1}, and a librational feature at about 70 cm^{-1} arising from strong intermolecular dipolar and quadrupolar interactions. The librational feature is absent in the cyclohexanes, as there are no strong intermolecular forces present in these non-polar liquids. Instead, a collision-induced band is clearly observed in cyclohexane and methylcyclohexane, peaked at about 40 cm^{-1}.

To further understand the isolated molecule structure and electrostatic properties of these five molecular liquids, *ab initio* molecular orbital calculations were carried out at the restricted Hartree-Fock level of theory, followed by a density functional correction for electron-correlation and electron-exchange, using the 6-31G** basis set. To briefly summarize the results, we find that even in the most strongly dipolar liquid studied, benzonitrile (μ~4.0 D), that the electrostatic interactions are dominated by quadrupole-quadrupole interactions. Thus, the similarities in the librational lineshapes fitted for toluene, benzyl alcohol, and benzonitrile, should not be surprising. For more than 100 relevant citations, and a much more detailed presentation, please see reference 1.

Reference:

[1] Y. J. Chang and E. W. Castner, Jr., 'The Intermolecular Dynamics Of Substituted Benzene And Cyclohexane Liquids, Studied By Femtosecond Nonlinear-Optical Polarization Spectroscopy', submitted to the Journal of Physical Chemistry.

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Figure Captions:

Figure 1. The OHD-RIKES transients, normalized to unity, are shown in a stacked plot. From the bottom, the data are for cyclohexane, methyl-cyclohexane, toluene, benzonitrile, and benzyl alcohol.

Figure 2. Lower: The longer time delay part of the OHD-RIKES transient for benzonitrile is shown. The data are shown as the large dots, and the solid line is a triple-exponential fit to the data in the range from 0.50 to 119.7 picoseconds. Upper: The residuals for the triple exponential fit are shown in the upper curve. The oscillations in the first picoseconds are the remaining oscillations from the 175 cm^{-1} bending mode, not an improper fit.

Figure 3. The results of the lineshape analysis of the frequency-domain OHD-RIKES spectra are shown. The solid lines are the OHD-RIKES frequency-domain data, and the dashed and dot-dashed lines are the fits to anti-symmetrized Gaussian, Eq. (7), and collisional, Eq. (6), lineshapes, respectively. From bottom to top, the data sets are for cyclohexane, methylcyclohexane, toluene, benzonitrile, and benzyl alcohol.

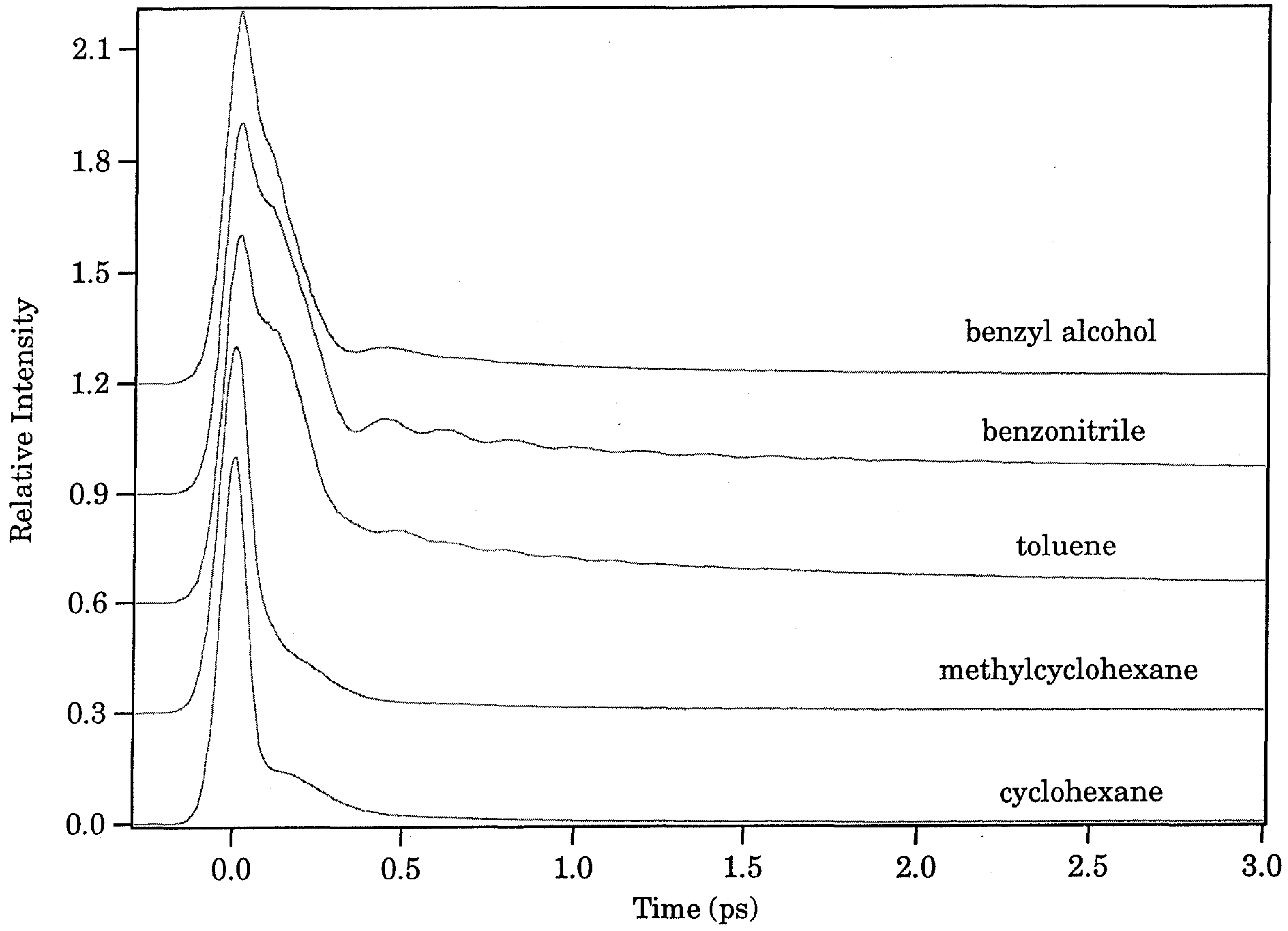

Figure 1
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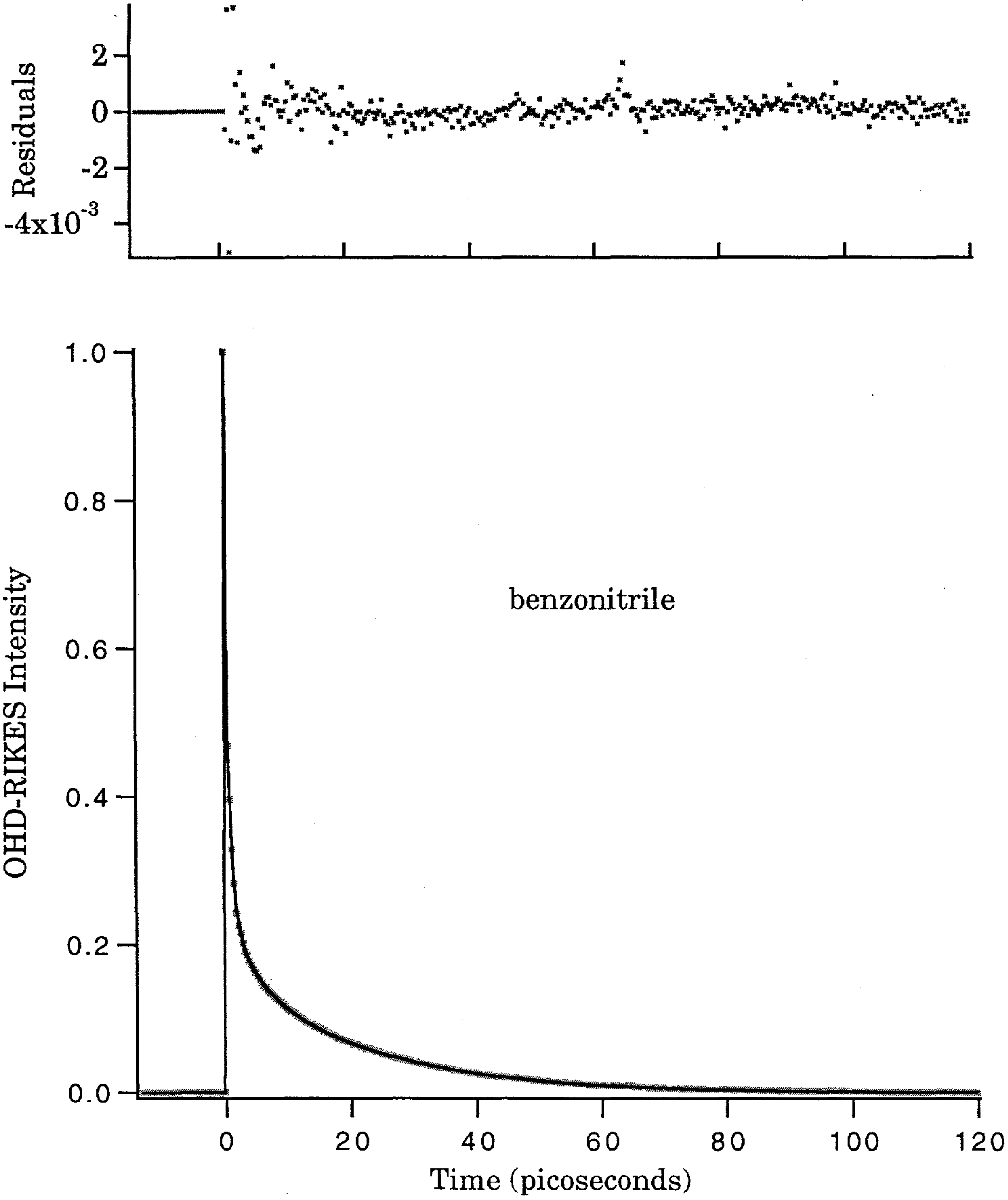

Figure 2
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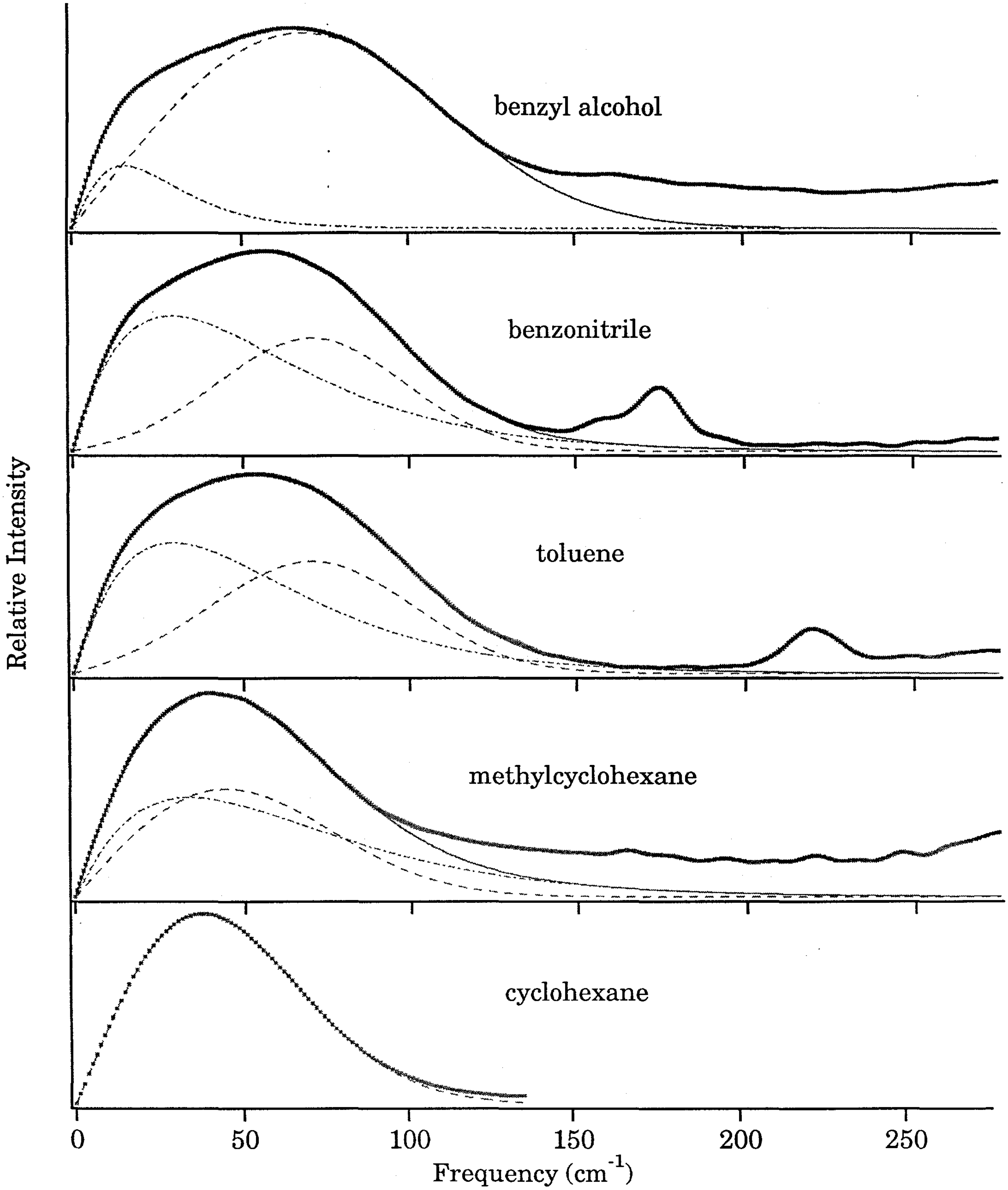

Figure 3
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