**Temperature-Dependence of the Ultrafast Intermolecular Dynamics of Amides:
Formamide, N-Methylformamide, N,N-Dimethylformamide, N-Methylacetamide, and
N-Methylpropionamide from 290-370 K.[‡]**

Edward W. Castner, Jr. and Yong Joon Chang
Chemistry Department
Brookhaven National Laboratory
Building 555
Upton, NY 11973-5000
Tel. (516) 282-4362
344

Using the femtosecond optical-heterodyne detected, Raman-induced Kerr effect spectroscopic technique^{1,2} (fs-OHD-RIKES), we have characterized the full spectrum of the intermolecular vibrational and diffusive dynamics for a series of five amides. The OHD-RIKES birefringence transients of the neat liquids formamide (FA), N-methylformamide (NMF), N,N-dimethylformamide (DMF), N-methylacetamide (NMA), and N-methylpropionamide (NMP) were measured in at temperatures in the range 290-370 K. Because we have used 50 fs, transform-limited pulses to perform the experiments, we impulsively excite all of the intermolecular motions in the 0 to 400 cm^{-1} range. Use of optical-heterodyne detection permits observation of a response linear in the molecular response; thus we can analyze the data in both the time and frequency domains by Fourier-transformation.²

Collectively, the amides are among the most interesting organic solvents. All are highly polar liquids, not just because of their substantial gas-phase dipole moments of about 3.5 Debyes, but more importantly because they contain very strong hydrogen-bond (H-bond) donor and acceptor groups in the N-H protons and carbonyl oxygens, respectively. Because of the strong H-bonding that occurs in the protic amides, these liquids are highly structured. Evidence for this structure in our work is provided by the existence of intermolecular vibrational bands across the H-bonds at about 100 and 190 cm^{-1} . Also, the extraordinarily high dielectric constants of the N-methylamides (of about $\epsilon \sim 190$ for NMA at 32°C) indicate a substantial local ordering among the polar molecules in their liquid state.

The intermolecular motions observed include librations, arising from strong intermolecular dipole-dipole interactions, as well as other intermolecular vibrations between and librations about the hydrogen-bonded (transient) structures in the liquid. These higher frequency motions are the liquid state analogs of the phonons present in the glassy and crystalline states, but are of course less extended in space because of the more rapid diffusive reorganization occurring in the liquid relative to the solid state. The slower diffusive motions appear in the time-domain as a multi-exponential decay on the fs-OHD-RIKES transient, or as a narrow Lorentzian line in the frequency domain at small wavenumber values.

The raw fs-OHD-RIKES birefringence data are shown below in Figure 1 for each of the five amides, observed near room temperature. The rising edge of the OHD-RIKES transient exactly tracks the rise of the laser pulse cross-correlation. Substantial shoulders and oscillations are observed in the time regime from 100 to 500 fs, arising from the underdamped intermolecular vibrations. After about 1.0 ps, the diffusive reorientational dynamics dominate the time domain response.

The first step in our data analysis is to fit the reorientational diffusion response in the time domain. Figure 2 shows the Arrhenius plot of the inverse of the longest diffusive exponential lifetime versus inverse temperature. We obtain the activation enthalpy for the diffusive relaxation from the slope of these plots. We find that these enthalpies obtained from the diffusive relaxation lifetimes correlate well with the measured hydrogen-bond enthalpy for the protic amides. In the case of non-H-bonding DMF, the activation enthalpy indicates the energy required for overcoming the strong dipole-dipole correlations.

Although the OHD-RIKES transient data can be fit exactly in the time domain using the same model functions,³ we find that there is considerable benefit to doing some of the analysis in the frequency domain. We begin by subtracting the reorientational diffusion decay law obtained in the long-time fits to the raw data. Fourier-transform deconvolution is then performed to obtain the nuclear-coordinate response free from the hyperpolarizability background, and to deconvolve the effect of the non-delta-function laser pulse on the measured molecular response.² We then obtain an OHD-RIKES spectrum in the frequency domain, proportional to the low-frequency Raman spectrum, and to the density of states.

[‡] This research was carried out at Brookhaven National Laboratory under contract DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

We find a clear differences in the OHD-RIKES response as a function of temperature. The DMF liquid shows collisional and librational dynamics with bands centered at about 20 and 55 cm^{-1} , respectively. The N-methylamide, NMA, NMF, and NMP, also have a vibration that occurs along the trans-linear H-bonds between molecules, with a frequency of $\sim 100 \text{ cm}^{-1}$. Formamide liquid displays the above collisional, librational, and H-bond vibrations, with the addition of a mode at about 190 cm^{-1} arising from the doubly-H-bonded cyclic dimer.⁴ For each of the five amide liquids, the inertial (or vibrational, or underdamped) motions show a weak red-shift, and a moderate shift in amplitude, with increasing temperature. The simple explanation is that at higher temperature, the average number of H-bonds in the liquid is decreasing, and the lifetime of such H-bonds is also decreasing, as indicated by the longer-time rotational diffusion response. The diffusive reorientation of DMF is hindered by strong dipolar interactions, while the protic amides have even slower diffusive reorientation because H-bonds must break and re-form before configurational relaxation can occur.

Figure 1

Figure 2

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