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Femtosecond Dynamics in Hydrogen-Bonding Solvents: Formamides

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We report the results of temperature-dependent optical Kerr effect experiments for formamide (FA) and N-methylformamide (NMF). Binary solutions of FA and NMF were also studied with water, acetonitrile, and N,N-dimethylformamide as cosolvents.

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The series formamide (FA), N-methylformamide (NMF), and N,N-dimethylformamide (DMF) have been studied using the optical-heterodyne-detected optical Kerr effect (OHD-OKE). The formamides are of great interest because of their high polarity, large dielectric constants, and strong intermolecular hydrogen-bonding interactions. The amides are frequently used in synthetic chemistry as solvents, and are valued as model compounds for studying hydrogen-bonding interactions between proteins and water.

We have studied neat FA and NMF as a function of temperature. In addition we have studied binary solutions of both FA and NMF with water, DMF, and acetonitrile as cosolvents at room temperature. Our data reveals an underdamped librational motion (previously assigned to an out-of-plane libration between hydrogen-bonded amide pairs [1]) that changes dramatically with temperature and also with concentration in a binary solution.

The experiments were carried out using the same geometry as McMorrow et al. [2] , with the exception that a femtosecond mode-locked Ti:Sapphire laser was used instead of a dye laser. Results for the FA and NMF temperature-dependent experiments are shown in Figures 1 and 2, respectively. Careful analysis shows that the bump apparent in the signal at ~400 fs delay is the second period of the underdamped librational motion with a frequency of ~100 cm^{-1}. The longer tail of the signal arises from the Brownian rotational diffusion of the molecules. This rotational reorientation component of the signal could not be fit well to a single or stretched exponential decay, but acceptable fits were obtained using a bi-exponential model.

The temperature data for formamide fits well to a 3-term model for the nonlinear optical response. The three terms include the underdamped libration at ~100 cm^{-1}, the bi-exponential slower component arising from diffusive reorientational motion, and the component that tracks the femtosecond laser autocorrelation response arising from the electronic hyperpolarizability. For all other samples of NMF and binary solutions of FA, a four-term model was required to achieve the best fits. This model included all of the components in the three-term model, with an additional intermediate overdamped librational term, similar to the analysis of McMorrow, et al. [2] .

The longer of the two exponential lifetimes for both FA and NMF decreased significantly with increasing temperature. Using an Arrhenius analysis, we found activation energies for the slowest reorientational diffusion component of 4.52 and 1.81 kcal/mol for FA and NMF, respectively. These values correspond well to the published values of hydrogen-bond formation enthalpies for FA and NMF of Spencer, et al. [3] . Thus, we find that the slowest motions resolved in our experiment correspond to the making and breaking of individual hydrogen bonds in the formamides.

Acknowledgments

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References

[1] O. Faurskov Nielsen, P.-A. Lund and E. Praestgaard, J. Chem. Phys. **77**, 3878 (1982).

[2] D. McMorrow, W. T. Lotshaw and G. A. Kenney-Wallace, IEEE J. Quantum Electron. **24**, 443 (1988).

[3] J. N. Spencer, S. K. Berger, C. Powell, B. D. Henning, G. S. Furman, W. M. Loffredo, E. M. Rydberg, R. A. Neubert, C. E. Shoop and D. N. Blauch, J. Phys. Chem. **85**, 1236 (1981).

Figure Captions

Figure 1. OHD-OKE birefringence anisotropy transients for neat formamide as a function of temperature. Decays are all normalized to the same amplitude, and offset by a constant factor for clarity.

Figure 2. OHD-OKE birefringence anisotropy transients for neat N-methylformamide as a function of temperature. Decays are all normalized to the same amplitude, and offset by a constant factor for clarity.

Figure 1

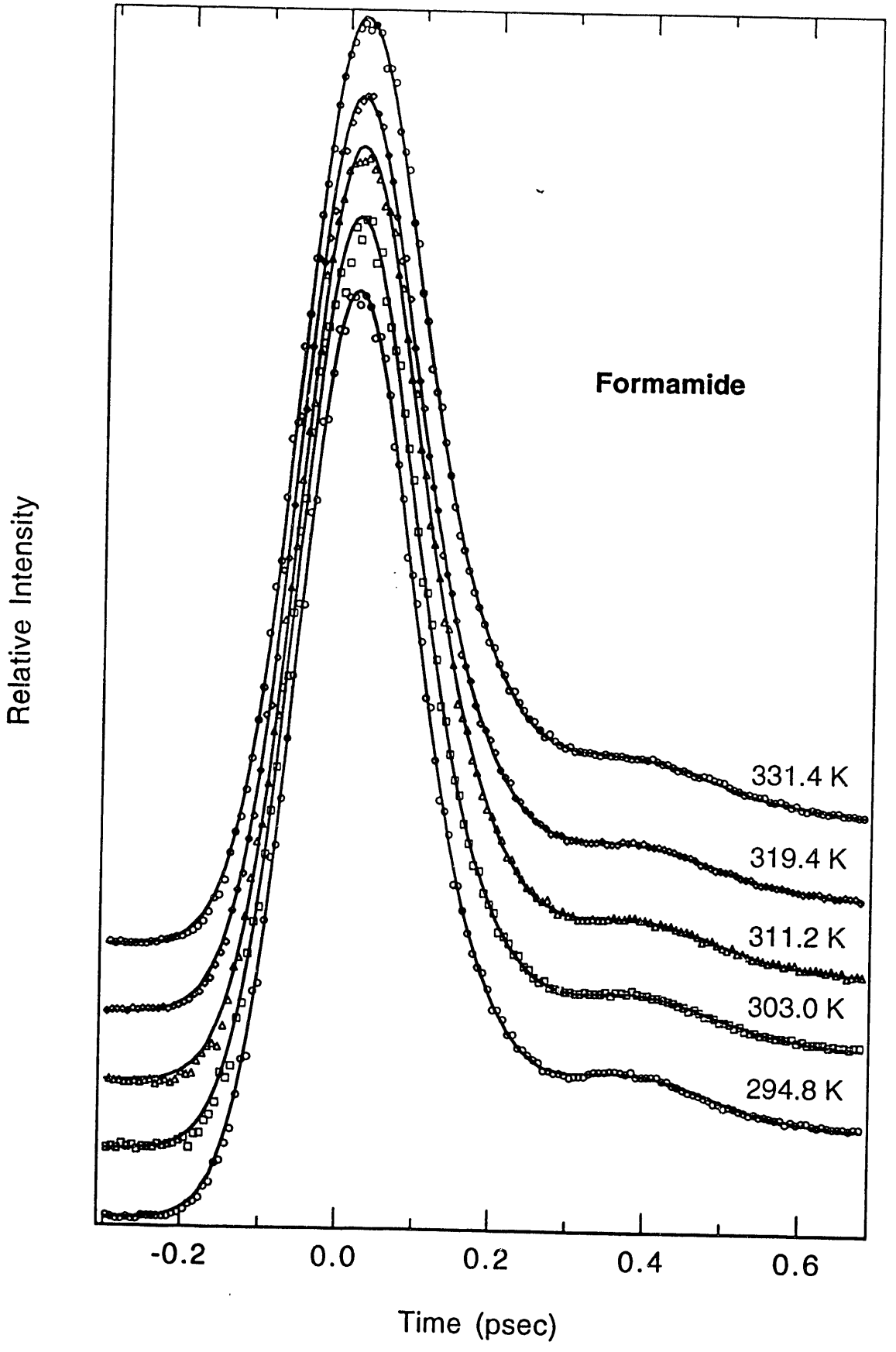
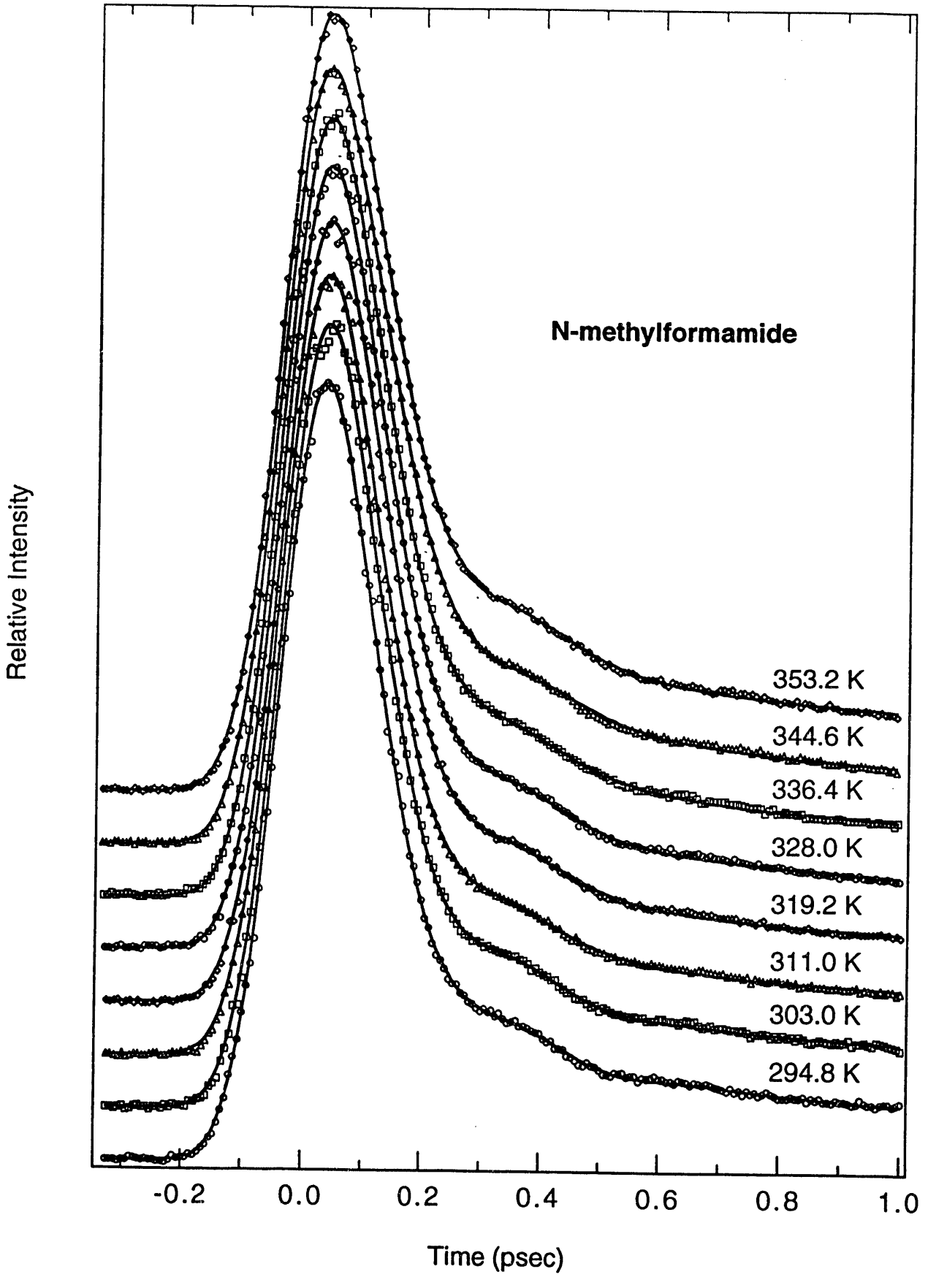

Formamide
331.4 K
319.4 K
311.2 K
303.0 K
294.8 K
Relative Intensity
-0.2
0.0
0.2
0.4
0.6
Time (psec)

Figure 2


N-methylformamide
353.2 K
344.6 K
336.4 K
328.0 K
319.2 K
311.0 K
303.0 K
294.8 K
Relative Intensity
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
Time (psec)

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