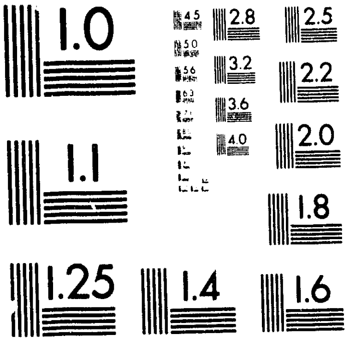
1.0
4.5
2.8
2.5
5.0
3.2
2.2
5.6
6.3
3.6
2.0
4.0
1.1
1.8
1.25
1.4
1.6

1 of 1

Conf-9306203--1

BNL-49234

2

Femtosecond Raman-Induced Kerr Effect Study of Polar Solvent Dynamics: Amides.

RECEIVED

JUL 27 1993

OSTI

Yong Joon Chang and Edward W. Castner, Jr.

Chemistry Department
Brookhaven National Laboratory
Building 555A
Upton, NY 11973-5000, U.S.A.

Abstract. We have measured the ultrafast pure solvent dynamics of highly polar liquids, formamide (FA), N-methylformamide (NMF), N-methylacetamide (NMA), N-methylpropionamide (NMP) and N,N'-dimethylformamide (DMF) using femtosecond optical-heterodyne-detected Raman-induced Kerr effect spectroscopy (OHD-RIKES). The effects of deuteration and temperature-dependence were studied to characterize in detail both the inertial (or non-diffusive) and diffusive intermolecular motions in these liquids.

1. Introduction

Detailed characterization of neat solvent dynamics is an important step in elucidating the role that the solvent plays in determining condensed phase chemical reaction dynamics. Time-resolved degenerate four-wave mixing techniques such as optical Kerr effect [1-5] and impulsive stimulated Raman scattering [6] spectroscopies have been used recently to observe directly the ultrafast intermolecular motions in various solvent systems.

We have studied the pure solvent dynamics of the amides FA, NMF, NMA, NMP and DMF using the electronically non-resonant femtosecond OHD-RIKES technique. These amides are highly polar molecules, and all except DMF form highly structured liquids that have an extensive intermolecular H-bonding network. DMF liquid is less structured because of the absence of intermolecular H-bonds. We present the results of temperature-dependent and deuterium-substitution OHD-RIKES experiments on the formamide liquid.

The time-resolved OHD-RIKES is a Fourier-transform nonlinear optical polarization spectroscopy that measures the decay of a transient birefringence induced in a transparent liquid sample by an intense ultrashort optical pulse. Through the Fourier transform relationship, the heterodyne detection provides a linear relationship between the measured signal decay and the third order nonlinear susceptibility, $\chi^{(3)}$, and spontaneous Raman cross section, σ_r, of the sample [7]. We have taken advantage of the nearly transform-limited 50 fs optical pulses to analyze our data both in the time and frequency domains. The details of our experimental set-up have been discussed previously [5].

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

2. Results and Discussion

The nonlinear optical response of a sample detected in the OHD-RIKES experiment is separable into electronic and nuclear contributions. The former originates from the electronic hyperpolarizability of the sample and is effectively instantaneous. The time delayed response arises from nuclear dynamics that include both the inertial and diffusive types of molecular motions. The electronic and nuclear responses for FA are illustrated in Figure 1. The surprising finding is that in addition to the long diffusive nuclear response caused by molecular reorientation, we observe inertial responses that have both oscillatory and exponentially-decaying components on the sub-ps timescale. We have further analyzed the data in the frequency domain using the Fourier transform/deconvolution procedure described previously by McMorrow and Lotshaw [1]. The low frequency spectrum obtained for FA is shown in Figure 2(A). We were able to adequately fit the frequency data using two anti-symmetrized Gaussian lineshapes and an Ohmic lineshape of the form

$$I(\omega)=\omega\cdot\exp(-\omega/\omega_0). \qquad (1)$$

The inhomogeneously broadened Gaussian bands centered at about 100 and 190 cm^{-1} have been observed previously in the low-frequency Raman study by Faurskov-Nielsen et al. [8], and are assigned to out-of-plane intermolecular H-bond bending motions in the FA liquid. The oscillatory responses we observe in the time domain are correlated exactly to these Raman band frequencies, and we assign these responses to the underdamped intermolecular H-bond librational dynamics. The sub-ps exponentially-decaying component has been observed previously in other liquids and is assigned to collisional interaction-induced effects such as multipole-induced multipole interactions. These collision-induced dynamics correspond to the lowest frequency band peaking at about 30 cm^{-1} in the spectrum. The rotational diffusion response is found to decay biexponentially (τ_1=1.45, τ_2=11.30ps @ 299K), and we attribute this to the rotations about the dissimilar inertial axes of the FA molecule [5].

We have carried out deuteration effect and temperature dependence studies to further characterize the inertial and diffusive nuclear motions occurring in FA liquid. In Fig. 2(B), we observe that the low-frequency bands of $HCOND_2$ red-shift relative to those of $HCONH_2$. We would expect a factor of ~1.4 red-shift with deuteration for intramolecular stretching vibrations. However, the bands are observed to red-shift by a factor of ~1.1. We attribute this to the fact that the nuclear motions that give rise to these bands are intermolecular in nature and therefore involve complex motions including librations and translations.

The temperature dependence of the longer rotational diffusion time constant, τ_2, shows an Arrhenius behavior, and we obtain an enthalpy of activation, ΔH_a, of 4.3±0.2 kcal/mol. This is in excellent agreement with the ΔH_a of 4.2 kcal/mol obtained from the temperature dependent study of depolarized Rayleigh linewidths carried out by Whittenburg, et al. [9]. In view of the fact that this ΔH_a is correlated with the ΔH_a obtained from the temperature dependence of viscosity and to the enthalpy of H-bond formation, ΔH_f=-5.2 kcal/mol [10], we conclude that the diffusive rotational motions in FA liquid are strongly correlated with the making and breaking of the intermolecular H-bonds.

All three low-frequency intermolecular Raman bands in Fig. 2(A) are also observed to red-shift upon increasing the temperature, and this is shown in Fig. 2(C). The local minima in the intermolecular interaction potential become less pronounced with increasing temperature, and this is reflected in the lowering of the frequencies of these bands. We are currently analyzing the results we have obtained for the amides. Future work will involve pressure-dependent OHD-RIKES studies on these highly polar liquids.

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.

3. References

[1] D. McMorrow and W. T. Lotshaw, J. Phys. Chem., **95**, 10395 (1991).

[2] T. Hattori, A. Terasaki, T. Kobayashi, T. Wada, A. Yamada and H. Sasabe, J. Chem. Phys., **95**, 937 (1991).

[3] K. Wynne, C. Galli and R. M. Hochstrasser, Chem. Phys. Lett.,**193**, 17 (1992).

[4] M. Cho, M. Du, N. F. Scherer, G. R. Fleming and S. Mukamel, J. Chem. Phys., submitted, 1993.

[5] Y. J. Chang and E. W. Castner, Jr., J. Chem. Phys., **99**, 113 (1993); ibid., submitted May, 1993.

[6] S. Ruhman, A. G. Joly and K. A Nelson, IEEE J. Quant. Elect., **24**, 46 (1988).

[7] G. L. Eesley, M. D. Levenson and W. M. Tolles, IEEE J. Quant. Elect., **14**, 45 (1978).

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

[9] S. L. Whittenberg, V. K. Jain and S. J. McKinnon, J. Phys. Chem.,**90**,1004 (1986).

[10] 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-RIKES data for FA at 299K shown with various sub-component responses: —— total response, • • • electronic, - - diffusive rotational. Inset: ····· 100 cm^{-1} librational, ---- 190 cm^{-1} librational, –·· collisional interaction-induced responses.

Figure 2. Frequency domain data for: (A) FA at 299K fit with two anti-symmetrized Gaussian lineshapes at ~100 and 190 cm^{-1} and an Ohmic lineshape peaked at ~30 cm^{-1}, (B) —— FA and ······ deuterated FA, both at 299K, (C) FA at —— 299K and at - - 350K.

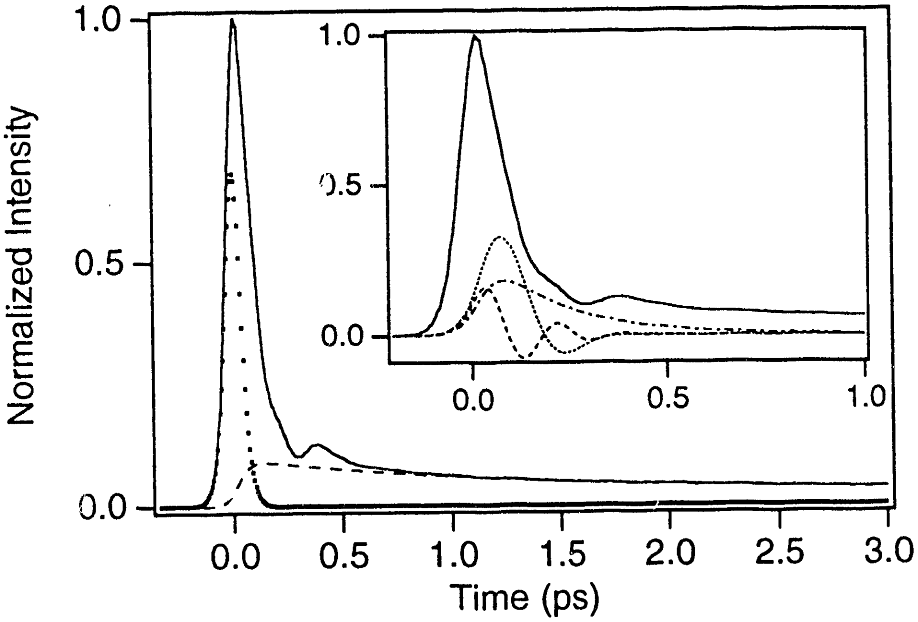

Figure 1
Chang and Castner

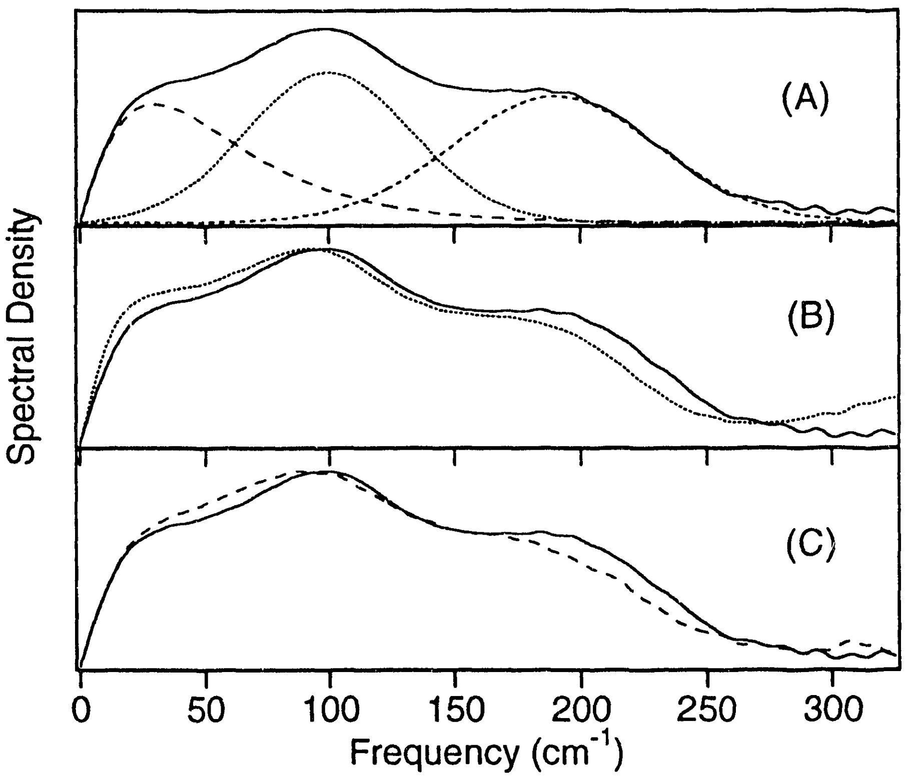

Figure 2
Chang and Castner

DATE
FILMED

11/4/93

END