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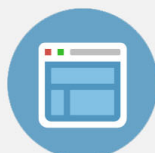
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COMMUNICATIONS

Femtosecond solvation dynamics in acetonitrile: Observation of the inertial contribution to the solvent response

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Recent years have witnessed an explosion of interest in understanding the influence of dynamic solvent properties on charge transfer and other condensed phase chemical reactions.¹⁻³ Theoretical,^{4,5} experimental,^{6,7} and molecular dynamic (MD) simulation studies^{8,9} suggest both activated and activationless electron transfer reactions are most influenced by the fastest part of the solvent response, hence experimental evaluation of dynamic solvation of a femtosecond time scale is critical. The tool for determining the solvent response has been time dependent fluorescence shift measurements.¹⁰ Studies of low barrier electron transfer reactions are now being interpreted using as input for the effective dielectric friction a fluorescent shift measurement of the solvent response, rather than bulk solvent dielectric properties.^{7,10,11} Molecular dynamic simulations of dipolar solvation¹²⁻¹⁵ have shed light on the ultrafast part of the solvent response which previous measurements have been unable to explore due to limited time resolution.^{16,17} Simulations in water,¹² acetonitrile,¹³ and a methyl chloridelikey solvent¹⁴ reveal a 25–150 fs inertial component which contributes 60–80% of the solvent relaxation while simulations in methanol¹⁵ show an inertial contribution with smaller amplitude.

In this Communication we report our efforts to verify the existence and characterize the magnitude of the ultrafast solvent response predicted by MD simulations. Employing the fluorescence upconversion technique we have determined the solvation time correlation function:¹⁸

$$C(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)} \quad (1)$$

for acetonitrile using the dye molecule LDS-750 as a probe. Here ν is either the peak or first moment of the fluorescence spectrum at time t . Previous studies of LDS-750 in polar aprotic solvents¹⁷ have shown structureless, well behaved time resolved spectra, making it a suitable first choice for a probe of dipolar aprotic solvation.¹⁹

Our fluorescence upconversion spectrometer is similar to that of Chesnoy²⁰ and we report here only the salient features. The cavity dumped antiresonant ring dye laser used for these experiments has recently been described in detail.²¹ For this measurement the pulses were typically 75

fs FWHM in duration, 1.4 nJ in energy, had a center wavelength between 605–608 nm and were dumped at a repetition rate of 1 MHz. The dye laser output is directed through a pair of SF-10 prisms in a double pass near retroreflecting geometry which is optimized to compensate for the positive group velocity dispersion of the transmissive optical elements before the upconversion crystal. These precompensated pulses are split by a 50% beam splitter. The gate pulse traverses a fixed delay before being combined with the fluorescence in a 1 mm LiO₃ crystal in a type 1 phase matching geometry while the excitation pulse traverses a variable delay before being focused into a 1 mm sample cell which is positioned at one of the foci of an elliptical reflector (Melles Griot). The distance between the foci of the reflector is 10 cm. The sum frequency is focused directly into an Instruments SA double monochromator and detected by a photon counting PMT (EMI). Auto correlation of the excitation and gate pulse yield an instrument response function of ~ 125 fs FWHM. At long fluorescence wavelengths (750–775 nm) approximately 45 fs is added to the irf due to group velocity mismatch in the LiO₃ crystal.²² The upconversion bandwidth is about 8 nm.

The signal intensity is determined by photon counting using a gated Stanford Research Systems model 400 photon counter. Data sets were collected at 11 fluorescence wavelengths (approx. 1 decay for every 10 or 15 nm of the steady state emission spectrum). A single decay was generated by counting for 2 seconds at each delay setting with a 6.67 fs step size and five such decays comprise an individual data set. An example of an individual data set and instrument response function is shown in Fig. 1. The dye laser intensity was monitored by sampling a portion of the gate pulse with a pmt and boxcar averager. The stability was consistently within a few percent and hence normalization of the raw data was not employed.

The solvation time correlation function, $C(t)$, was constructed from the individual fluorescence decays as described by Maroncelli and Fleming.²³ Briefly, the individual decays are fit to sums of exponentials convoluted with an instrument response function, plus a flat background. The fitted decays are then normalized using the steady state fluorescence spectrum and the spectrum at any time is

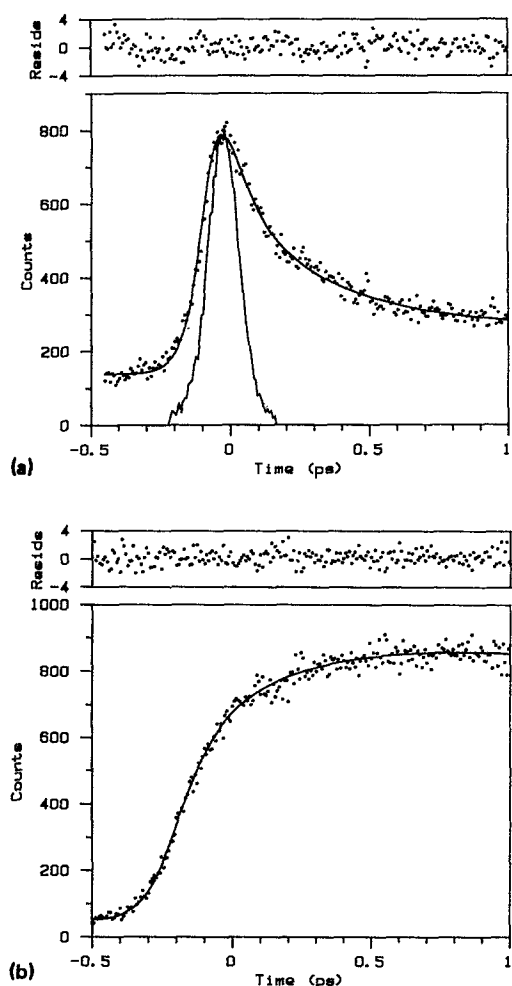


FIG. 1. Upconversion data, fitted curves and residuals for fluorescence from LDS-750 in acetonitrile at 19 °C. Top panel: 654 nm emission. Bottom panel: 779 nm emission. The instrument response function is also shown in the left panel and has a FWHM of 100 fs.

given by the relative intensities of this normalized, fitted decay series. Finally the time resolved spectra are fit to log-normal distribution functions from which $C(t)$ is generated. The result is shown in Fig. 2. The solvation response is clearly two part in character. The fast initial relaxation accounts for $\sim 80\%$ of the amplitude and is well fit by a Gaussian of 120 fs FWHM, giving a decay time of 70 fs. The slower tail is exponential with a decay time of ~ 200 fs. Given the instrument response function of our upconversion spectrometer we can characterize confidently dynamics occurring on a 50 fs time scale. Previous measurements in acetonitrile did not reveal the rapid initial relaxation and $C(t)$ decayed with a ~ 400 fs¹⁷ or ~ 700 fs¹⁶ time constant.

Since our measurements are made with significantly higher time resolution than previous solvation studies it is important to discuss the contribution of vibrational relaxation to the spectral evolution. With excitation at 608 nm the LDS-750 molecules have ~ 1000 cm^{-1} excess vibrational energy. For the dye molecules Oxazine and Nile blue in their first excited state an excess vibrational energy of 500–1000 cm^{-1} leads to a total time dependent spectral

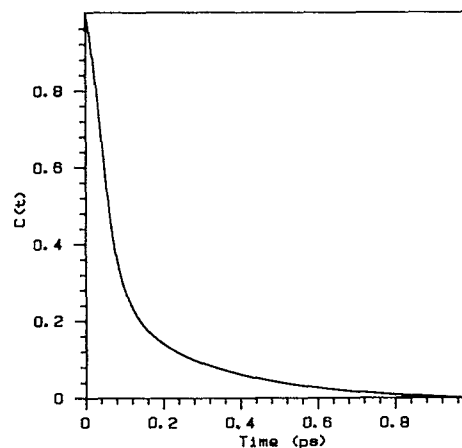


FIG. 2. The solvation time correlation function, $C(t)$, for acetonitrile. $C(t)$ was determined using the peak of the time resolved fluorescence spectra, determined from log normal fits.

shift of ~ 5 nm with relaxation times of 800 and 500 fs, respectively.²⁰ These molecules do not have a change in dipole moment upon excitation and the spectral shift arises primarily from vibrational relaxation. The total spectral shift of LDS-750 is more than 50 nm and most of the relaxation is complete in 150 fs. Given the comparatively slow vibrational relaxation time and the small magnitude of the vibrational spectral shift, the intramolecular vibrational contribution to the ultrafast part of $C(t)$ is expected to be negligible. In addition, the $\nu(0)$ used in calculating $C(t)$ is in good agreement with the peak of the fluorescence spectrum of LDS-750 in frozen acetonitrile, indicating $C(t)$ does not contain a significant intramolecular vibrational relaxation contribution.

The origin of the fast response shown in Fig. 2 can be determined by comparison with simulations of solvation dynamics of spherical solutes in acetonitrile performed by Maroncelli.¹³ The molecular dynamics simulation yields a solvent response which is strikingly similar to the measured response. The initial Gaussian contribution accounts for 80% of the relaxation and decays in ~ 100 fs. The second part of the response occurs on a 0.5 to 1 ps time scale. The simulations also reveal oscillations in $C(t)$ with frequency ~ 30 ps^{-1} which are attributed to librational modes. Molecular dynamics simulations of coumarin 153 in acetonitrile show the same general behavior for $C(t)$, however, the oscillations are far less prominent. This result is shown in Fig. 3. Maroncelli has assigned the fast part of the solvent response to small amplitude inertial rotational motion of molecules in the first solvation shell while the slow tail arises from diffusive restructuring of the first solvent shell. This picture is supported by several observations from the MD simulations. First, $\sim 70\%$ of the solvent relaxation is achieved by the 6–7 molecules which make up the first solvent shell. Secondly, single particle trajectories indicate that rapid fluctuations in the reaction potential are correlated with rapid rotational reorientations and not fluctuations in the distance between the solute and solvent,

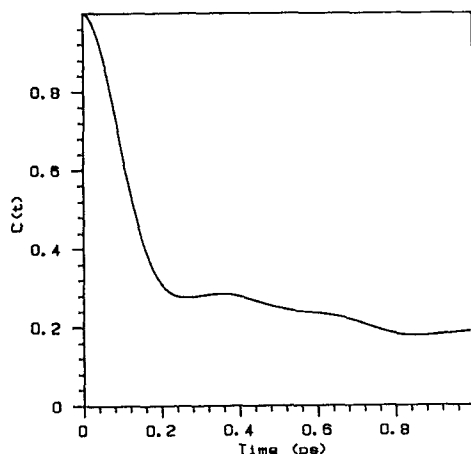


FIG. 3. Equilibrium molecular dynamics simulation result for coumarin 153 in acetonitrile. The ground state charge distribution for Cu153 was determined by a AMPAC calculation (Ref. 23). This simulation result was graciously provided by M. Maroncelli. Full details of the simulation methods are given in Ref. 13.

indicating rotational motion is primarily responsible for the solvent relaxation. For the first solvent shell, small angular displacements of only 10–20° are required to relax the solvation energy created by a charge jump. The small amplitude of this motion leads to the rapid relaxation. By a series of “rigid cage” simulations in which all but one solvent molecule is frozen in orientation, Maroncelli shows that the rapid Gaussian contribution to the relaxation results from independent single molecule motion. The equilibrium dynamics of the single free molecule are followed and the appropriate correlation function is constructed. The results are then averaged over all choices of the free solvent molecule. The rigid cage $C(t)$ is indistinguishable from the normal liquid $C(t)$ for the first 100 fs after which the agreement is quite poor, indicating uncorrelated dynamics are responsible for the rapid relaxation while correlated motions are responsible for the slow exponential tail of the solvent response.

Carter and Hynes¹⁴ MD simulation of an ion pair instantaneously created from a neutral pair in a methylchloridelike solvent also indicates the short time solvation dynamics are dominated by inertial Gaussian behavior. Hynes and co-workers have further demonstrated the inertial solvent response dominates the time dependent friction on electron transfer,^{8,9} proton transfer,²⁴ and ion pair reactions,²⁵ and hence controls the reaction rate. Both Maroncelli¹³ and Carter and Hynes¹⁴ point out most current theoretical treatments of solvation dynamics do not incorporate inertial solvent motion. A notable exception is the approach of van der Zwan and Hynes.²⁶ Recently, Chandra and Bagchi have included inertial motion of the solvent by using a generalized hydrodynamic equation.²⁷ This result shows reasonable agreement with the acetonitrile MD simulations.²⁸

Our observation of a substantial inertial contribution to the solvent response should not be surprising as important inertial effects have been previously observed in opti-

cal Kerr effect experiments. In these experiments the amplitude of the nuclear response continues to increase after the perturbation (laser pulse) is turned off. Thus the existence of inertial motion is particularly clear. In the solvation dynamics the perturbation remains on and the underdamped motion leads to a rapid return to equilibrium. An inertial delay in the appearance of the nuclear response has been observed in optical Kerr studies of CS₂,^{29–31} benzene and benzene derivatives,^{32,33} and acetonitrile.^{34,35} The solvent motions contributing to the solvation dynamics $C(t)$ should likewise contribute to the decay in the nuclear response of the Kerr experiment. A similar view has been recently expressed by McMorro and Lotshaw.³⁶ We have connected the results of the two experiments by using a Langevin equation description for a collection of solvent oscillators described by a inhomogeneous frequency distribution. Starting from the $C(t)$ result we determine the frequency distribution and damping constant representing the dynamical aspects of acetonitrile and simulate the nuclear contribution to the optical Kerr effect signal. The calculated Kerr signal is very similar to our recent measurements.³⁴ We should not expect exact agreement since some perturbation of the acetonitrile by the solute is expected.

The existence of a large amplitude, rapid inertial Gaussian component in the solvent response has substantial implication for theoretical descriptions of chemical reaction dynamics in solution. Theories invoking continuum or overdamped approximations are likely to be inappropriate in many applications. Barbara and Fonseca^{7,10,11} have included a full description of the time dependent friction for low barrier electron transfer reactions while Hynes and co-workers^{8,9,26} have shown the connection between $C(t)$ and the time dependent friction in the rate determining barrier region for reactions with a substantial barrier. Both descriptions require an experimental measurement of the solvent response which includes the inertial contribution. Clearly further measurements exploring the magnitude and time scale of the inertial component in heavier polar aprotic solvents, alcohols, and water are warranted.

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