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Pressure Dependence of Solvation Dynamics of Coumarin 480 in Ethanol

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The effect of the pressure on the solvation dynamics of coumarin 480 in ethanol has been studied by means of time-resolved emission using the time-correlated single-photon-counting technique with 20-ps resolution. The solvation dynamics slow with pressure. The pressure was varied from atmospheric pressure to about 1.8 GPa, the liquid−solid phase transition. At low pressures, <0.5 GPa, the solvation correlation function is nearly exponential, whereas, at pressures higher than about 0.5 GPa, it is nonexponential and can be fitted to a biexponential function whose short component is about 110 ps at pressures above 1 GPa. In the solid phase, solvation dynamics occurs at a relatively fast rate, similar to the liquid phase and at about the same pressure.

Introduction

Solvation statics and dynamics have been extensively studied.[1−6] The spectral shifts of both the static absorption and fluorescence spectra of many probe molecules have been measured in different neat solvents. Ultrashort laser pulses, of pico- and femtosecond time duration, have been used during the past 2 decades to study solvation processes on a femto- to picosecond time scale. In these studies, the solvation dynamics was monitored via the time-dependent spectral shift of the fluorescence band of a probe molecule dissolved in the solvent under study. The solvation dynamics of probe molecules in polar liquids is bimodal. The short component (<100 fs) is attributed to the inertial rotation of the solvent molecules. The long component is about 10 times longer in nonassociative liquids and arises from the diffusive rotational motion of the solvent molecules. Recently, studies of solvent dynamics have also been conducted in mixtures of nonpolar and polar solvents,[7−11] as well as complex environments.[12−16]

In the condensed phase, pressure is known to influence chemical reaction rates. External hydrostatic pressure in solution changes such properties of the medium and reactants as the reaction free volume, potential energy profile along the reaction path, compressibility, viscosity, dielectric relaxation, and energy of reorganization of the medium.[17] The absolute value of the reaction rate constant and its temperature dependence depend on all of these parameters.

In 1988, Huppert and Rentzepis[18] studied the dynamics of the intramolecular charge-transfer (ICT) process in the excited state of *p*-(9-anthryl)-*N*,*N*-dimethylaniline (ADMA) as a function of pressure up to 0.7 GPa in pentanol, 1-octanol, and 3-octanol on the picosecond time scale. They found that the ICT dynamics at various pressures is nonexponential. The long component of the dynamics follows both the viscosity change with pressure and the longitudinal dielectric relaxation time, $\tau_L = (\epsilon_\infty/\epsilon_S)\tau_D$, where ϵ_∞ and ϵ_S are the high- and low-frequency dielectric constants, respectively, and τ_D is the slow component of the dielectric spectrum.

Hara and co-workers[19] studied the solvation dynamics of coumarin 153 in several alcohols, including propanol, butanol, and pentanol, as a function of pressure up to about 0.4 GPa. As

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in the Huppert and Rentzepis[18] study, they also found that the average solvation time correlates well with the longest longitudinal relaxation time. Values of τ_D as a function of pressure for these liquids are not available at the studied pressures. The viscosities of these liquids as a function of pressure are known.[20] To estimate the value of τ_D at a certain pressure, Hara and coworkers used the values of τ_D of these liquids at low temperatures for which the viscosity is equal to the desired pressure.

In this study, we used the time-correlated single-photon-counting technique to measure the time-resolved emission of coumarin 480 in ethanol as a function of pressure. We used a diamond anvil cell to increase the hydrostatic pressure up to 1.8 GPa, the liquid−solid phase-transition pressure at room temperature.

Experimental Section

The pressurized time-resolved emission was measured in a compact gasketed diamond anvil cell[21] (DAC) purchased from D'Anvil[22,23] with 0.3-carat low-fluorescence high-UV transmission diamonds.

To provide a larger volume of the sample for sufficient fluorescence intensity, a 1-mm hole was drilled in the 1-mm-thick stainless gasket. The low-fluorescence-type diamonds served as anvils. The anvil seats had suitable circular apertures for the entry and exit of the exciting laser beam and the excited fluorescent intensity. With this cell, pressures of up to 30 kbar were reached without detriment to the diamond anvils. The pressure generated was calibrated using the well-known ruby fluorescence technique.[24]

Time-resolved fluorescence was detected using a time-correlated single-photon-counting (TCSPC) technique. As a sample excitation source, we used a CW mode-locked Nd:YAG-pumped dye laser (Coherent Nd:YAG Antares and a cavity-pumped 702 dye laser), which provided a high repetition rate of short pulses [2 ps at full width at half-maximum (fwhm)]. The TCSPC detection system is based on a multichannel plate Hamamatsu 3809 photomultiplier and a Tennelec 864 TAC and 454 discriminator. A personal computer was used as a multichannel analyzer and for data storage and processing. The overall instrumental response was about 40 ps (fwhm). Measurements were taken at 10 or 20 ns full scale. The samples were excited at 310 nm (the second harmonic of the Rhodamine 6G dye laser). At this wavelength, a sample is excited to S_2, the second excited electronic state. The transition dipole moment S_0-S_2 is perpendicular to S_0-S_1. Therefore, a polarizer set at an angle complementary to the "magic angle" was placed in the fluorescence collection system.

Coumarin 480 was purchased from Exciton and used without further purification. Ethanol was purchased from Aldrich and used without further purification. All experiments were performed at room temperature (23 ± 2 °C).

Results and Discussion

Figure 1a shows, on a semilogarithmic plot, the viscosity dependence on pressure $\eta(P)$ of ethanol at 303 K normalized to its value at atmospheric pressure, η_0, taken from ref 20. At low pressure, the logarithm of the viscosity increases linearly with the pressure. At high pressure (>8 kbar), the slope decreases. Figure 1b shows the dependence of the compressibility of ethanol on pressure.[20] At 12 kbar, the volume decreases by about 25%. The pressure dependence data of the dielectric constant of ethanol are given in ref 25. The dielectric constant increases with pressure. Figure 1c shows the static dielectric constant of ethanol at various pressures. The pressure dependence, $\partial\epsilon_S/\partial P$, decreases as the pressure increases. At 12 kbar, $\epsilon_S = 33$ as compared with $\epsilon_S = 24$ at 1 atm and 298 K.

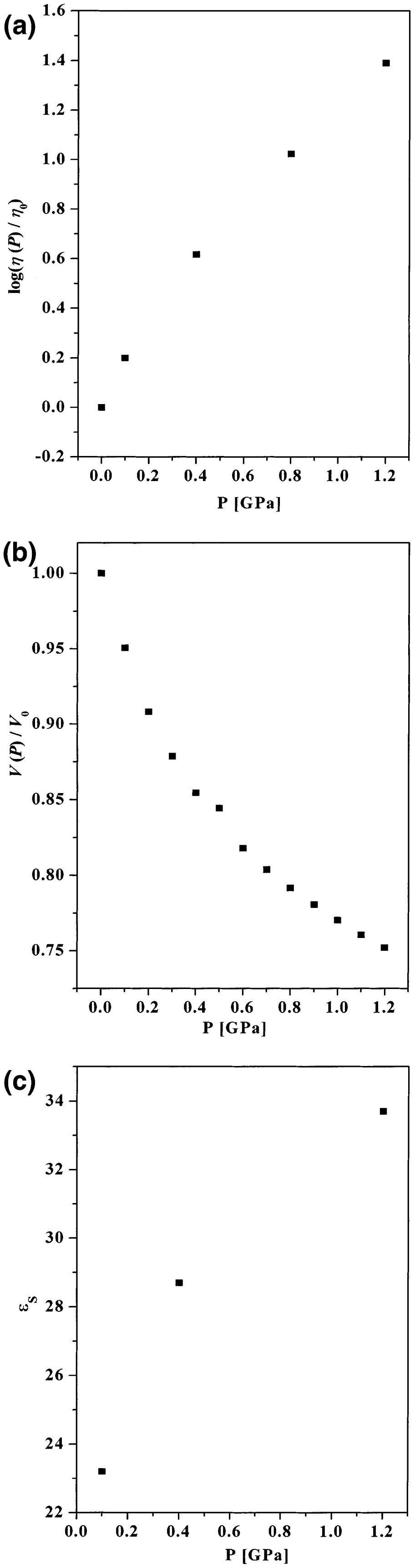

Figure 1. (a) Viscosity dependence on pressure of ethanol at 303 K taken from ref 20. (b) Pressure dependence of V_P/V_0 of ethanol. (c) Pressure dependence of the dielectric constant of ethanol.

TABLE 1: Relevant Parameters for Time-Resolved Measurements of Coumarin 480 in Ethanol at Different Pressures.

Liquid Phase						
	$C(t)$ fitting parameters[b]					
pressure[a] (GPa)	a_1	τ_1 (ps)	a_2	τ_2 (ps)	$<\tau_1>$[c] (ps)	$\Delta\nu$[d] (cm^{-1})
atmospheric	1	35			35	900
0.2	1	50			50	900
0.52	0.85	65	0.15	200	85	900
0.77	0.8	90	0.2	250	120	900
1.07	0.65	110	0.35	300	180	1000
1.29	0.6	110	0.4	350	210	1200
1.55	0.22	110	0.78	500	410	1200

Solid Phase								
	$C(t)$ fitting parameters[e]							
	a_1	τ_1 (ps)	a_2	τ_2 (ps)	a_3	τ_3 (ps)	$<\tau>$[c] (ps)	$\Delta\nu$[d] (cm^{-1})
1.8	0.3	90	0.4	380	0.3	600	360	1400

[a] The error in the determination of pressure is ±0.075 GPa. [b] Biexponential fit to the experimental data. [c] Average solvation time ($<\tau>$). [d] Spectral shift ($\Delta\nu$ from $\tau = 10$ ps to $\tau = 1$ ns). [e] Three-exponential fit to the experimental data.

Johari and Danhauser studied the pressure dependence of the dielectric relaxation of isomeric octanols.[26] The dielectric relaxation time, τ_D, of isomeric octanols decreases with increasing pressure in the range of 0.001−4 kbar. The pressure dependence of τ_D of 2-methyl-3-heptanol is close to exponential in the temperature range of 215−250 K. At 250 K, τ_D increases by about 3 orders of magnitude as the pressure is increased to 4 kbar. For 3-octanol, τ_D exhibits nonexponential behavior as a function of pressure. The slope, $[\partial (\ln \tau_D)/\partial P]_T$, decreases as the pressure increases. Johari and Danhauser also studied the viscosity dependence of isomeric octanols[27] and compared it with the dielectric relaxation pressure dependence. They found good correspondence between the pressure dependence of the viscosity and dielectric relaxation times. In general, the viscosity dependence on pressure is larger than that of the dielectric relaxation.

In alcohols, the long component of the solvation correlation function, $S(t)$, of excited fluorophore correlates well with τ_D. Therefore, a dependence of $S(t)$ on the pressure is expected because the dielectric relaxation of alcohols exhibit a strong pressure dependence. The larger the pressure, the slower the relaxation time of $S(t)$.

Time-correlated single-photon counting has a limited instrument response function (IRF) of ∼40 ps, which limits the time resolution to about 20 ps. The time-resolved emission of coumarin 480 in ethanol at atmospheric pressure measured by time-correlated single-photon counting cannot provide the fast solvation components of less than <20 ps because of its poor time resolution. To estimate the contribution to the solvation energy of the ultrafast components of solvation we used Maroncelli's procedure[1] to find the band position at "$t = 0$" immediately after the laser pulse excitation. The emission spectrum at about $t = 10$ ps is determined from the constructed time-resolved spectra. The difference in the band position at $t = 0$ and its position at $t = 10$ ps is attributed to the fast solvation components. We find that the fast components, which we cannot observe, contribute about 1000 cm^{-1} to the spectral shift.

Time-resolved spectra were constructed and analyzed by a procedure given by Maroncelli and co-workers.[1] The time-resolved emission data, collected at 10-nm intervals, were analyzed using a convolution procedure with the system IRF and a sum of exponentials. Figure 2 shows the reconstructed time-resolved emission spectra of coumarin 480 in ethanol at a pressure of 1.07 GPa (10.7 kbar). The total measured peak shift is about 1000 cm^{-1}. The band shape at time t was fitted to a log-normal function. The bandwidth and asymmetry at various times did not change in a systematic way as a function of pressure. From the time-dependent spectral shift of the fluorescence band maximum of coumarin 480, we calculated the solvation correlation function given by

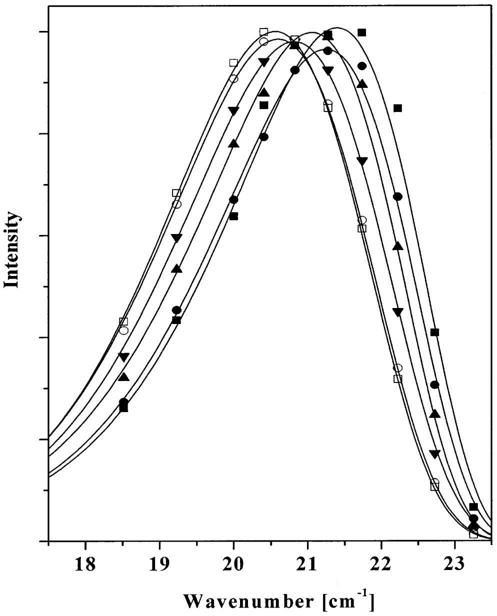

Figure 2. Time-resolved emission spectra of coumarin 480 in ethanol at 1.07 GPa at various times: 20 (■), 50 (●), 100 (▲), 200 (▼), 500 (○), and 1000 (□) ps. Solid lines are computer fit.

$$S(t) = \frac{\bar{\nu}_0 - \bar{\nu}(t)}{\bar{\nu}_0 - \bar{\nu}_\infty} \tag{1}$$

where $\bar{\nu}(t)$, $\bar{\nu}_0$, and $\bar{\nu}_\infty$ are the band maximum positions at time t, time zero, and long times, respectively. We fit $S(t)$ to a sum of exponentials.

Figure 3 shows plots of the solvation correlation function $S(t)$ of coumarin 480 in liquid ethanol as a function of pressure with a limited time resolution of 20 ps. At low pressure, $S(t)$ is nearly exponential, whereas at high pressure, $S(t)$ is nonexponential. Table 1 shows the relaxation parameters of $S(t)$ as a function of pressure. As the pressure increases, the average relaxation time gets longer. Above 0.5 GPa, the decay of $S(t)$

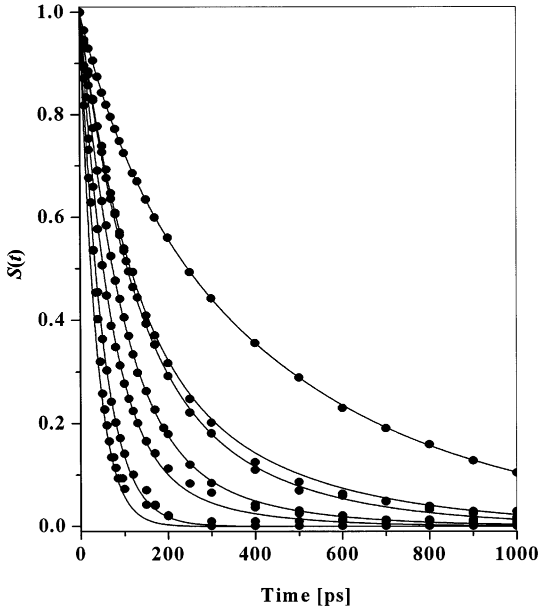

Figure 3. Normalized solvation response function, $S(t)$ of coumarin 480 in ethanol at different pressures. Top to bottom: $P = 1.55$, 1.29, 1.07, 0.77, 0.52, and 0.2 GPa and atmospheric pressure. Circles are experimental data, and solid lines are fits to the experimental data.

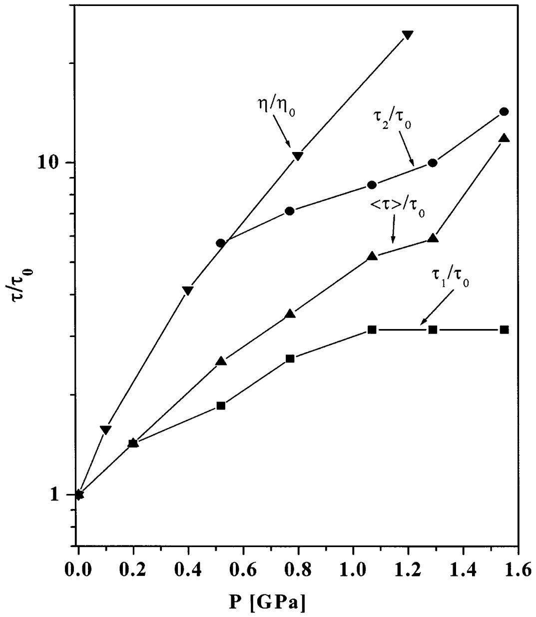

Figure 4. Solvation relaxation times as a function of pressure; short-lifetime component (■), long-lifetime component (●), $<\tau>$ (▲), normalized viscosity (▼).

reasonably fits a biexponential function. At relatively low pressures, i.e., 0.5−1.0 GPa, the two decay times differ only by about a factor of 3, which is too small of a difference to provide good criteria for defining biexponential fitting to well-defined values of the three parameters τ_1, τ_2, and a. We used a fit in which the relative amplitude between the two components varies as a function of pressure, and the correlation of the fit was $R = 0.998 \pm 0.001$. The short-time component, τ_1, of $S(t)$ is almost independent of pressure. Its relative amplitude, a_1, at 0.52 GPa is about 0.85. As the pressure further increases, its amplitude decreases (see Table 1). At 1.3 GPa, a_1 is 0.6, and at 1.55 GPa, it reduces to 0.22. The amplitude, $a_2 = 1 - a_1$, as well as the decay time of the long component, τ_2, of $S(t)$ increases with pressure. At 0.52 GPa, $\tau_2 = 200$ ps and $a_2 = 0.15$, whereas at 1.55 GPa, $\tau_2 = 500$ ps and $a_2 = 0.78$. Figure 4 shows, on a semilogarithmic scale, the relaxation times τ_1 and τ_2 of $S(t)$, normalized to τ_0, the value at atmospheric pressure, as a function of pressure. Also displayed in the figure are the normalized values of both $<\tau>/\,\tau_0$ and viscosity, $\eta(P)/\eta_0$. As seen in Figure 4, the average solvation time, $<\tau>$, follows the change in viscosity as a function of pressure. The dependence of the average relaxation time on pressure is smaller than that of the viscosity, $\eta(P)$.

The solvation correlation function, $S(t)$, could also be reasonably fitted to a biexponential function with a fixed relative amplitude of the two time components. We chose amplitudes of $a_1 = 0.8$ and $a_2 = 0.2$ to fit the complete set of the solvation dynamics as a function of pressure from 0.52 to 1.55 GPa. When we use such a fit, we find that, unlike the previous fit, the short decay time, τ_1, varies from 60 ps at 0.52 GPa to about 145 ps at 1.3 GPa, while τ_2 is about 300 ± 50ps. For a particular pressure, the average relaxation time, $<\tau>$, is about the same as in the previous analysis. Thus, our fit of the nonexponential decay of $S(t)$ is not unique, and the set of values of the short and long components and their relative amplitudes can be set at a relatively large range of values.

Bagchi and co-workers[28] carried out a detailed theoretical study to investigate the time-dependent solvation process of a dipolar solute in monohydroxy straight-chain alcohols (C_1-C_4) and compared it with the experimental results of solvation of coumarin 153[1] and other probe solutes.[29,30] They found a good agreement between the excited-state solvation experimental results and the frequency-dependent dielectric function measured by dielectric methods and, more recently, terahertz (THz) spectroscopy.[31,32] They used the dielectric response for methanol, ethanol, and propanol measured by femtosecond terahertz pulse transmission[32] to characterize the three dispersion region of these alcohols. For ethanol, the fastest dielectric relaxation component, $\tau_1 = 0.22$, is followed by two longer components of 3.3 and 160 ps. For methanol, Bagchi and co-workers[28] found that the solvation is primarily governed by an ultrashort-time, 70-fs, Gaussian component of about 50% of the total solvation energy. However, for the other longer-chain alcohols, from ethanol to butanol, they did not find an ultrashort Gaussian component but rather found a relatively long component of about 200 fs with an amplitude of about 15%. The solvation correlation function of coumarin 153 in ethanol at room temperature and ambient pressure were measured by Maroncelli and co-workers and can be reconstructed by a four-exponential function.[1] The two fast components, $\tau_f \leq 400$ fs, have a combined amplitude of approximately 0.32, and the two subsequent longer components, of 5 and 30 ps, have amplitudes a_3 and a_4 of 0.18 and 0.5, respectively.

The short-time behavior of solvation, $\tau \leq 200$ fs, is attributed to single-molecule frictionless inertial reorientations. The long-time decay components are associated with collective motion. However, the individual long-time components are not assigned to a particular solvent motion. Therefore, it is not a simple task to assign physical meaning to each decay time or relative amplitude of the parameter derived from the analysis of the $S(t)$ of coumarin in ethanol as a function of pressure.

Our current results of the pressure dependence of solvation dynamics are similar to Hara those of and co-workers[19] who studied the solvation dynamics of coumarin 153 in several alcohols, including propanol, butanol, and pentanol, as a function of pressure up to about 0.4 GPa. As in the Huppert and Rentzepis study,[18] they too found that the average solvation time correlates well with the longest longitudinal relaxation time.

The total frequency shift due to solvation dynamics that should be observed in time-resolved emission experiments is 2060 cm^{-1} for coumarin 153,[1] and for coumarin 480, it should be larger by about 10%. From about 10 ps to about 1 ns, we observe only about a 1000 cm^{-1} shift, which is about one-half of the total band shift. A 1000 cm^{-1} shift fits the contribution of the longest solvation component $a_4 = 0.5$.[1] At high pressures, >1 GPa, the total observed band shift increases to about 1200 cm^{-1}. The increase in the band shift at high pressures might arise from stronger interactions between the solvent and solute due to the decrease in volume, $V(P)$ (at 12 kbar, the volume decreases by 25%), and the increase in the dielectric constant, $\epsilon(P)$. An approximation to the spectral shift of the absorption and emission band based on the continuum model is given by Lippert[33] and Mataga[34]

$$\Delta\nu_{\mathrm{a}} - \Delta\nu_{\mathrm{f}} = \frac{2(\mu_{\mathrm{e}} - \mu_{\mathrm{g}})^2}{cha^3}\left[\frac{\epsilon_{\mathrm{S}} - 1}{2\epsilon_{\mathrm{S}} + 1} - \frac{n^2 - 1}{2n^2 + 1}\right] \qquad (2)$$

In this expression, $\Delta\nu_{\mathrm{a}}$ and $\Delta\nu_{\mathrm{f}}$ are the shifts (in cm^{-1}) of the absorption and fluorescence frequencies, respectively, relative to their gas-phase values. The solute parameters are the excited- and ground-state dipole moments μ_{e} and μ_{g} and the probe molecule cavity radius, a, which might be affected by pressure. According to eq 2, even a small decrease in the value of a will increase the spectral shift. The static dielectric constant, ϵ_{S}, increases from 24 to 33 at about 1.2 GPa. Using $\epsilon_{\mathrm{S}} = 33$ instead of 24 in eq 2 increases the calculated total shift by less than 4%. This contribution is too small compared with the actual increase in the band shift of about 20%. Another source that might contribute to the increase of the spectral shift is the second slow component of $S(t)$, the amplitude of which is $a_3 = 0.18$ at ambient pressure and the relaxation time of which is $\tau_3 = 5$ ps. This is too fast to observe at atmospheric pressure. It is expected that the relaxation time of this component also increases with pressure. At high pressures, we find a short-time component with a relaxation of about 100 ps, which might arise from this component of $S(t)$.

We compare the results of the two previous studies[18,19] that measured the effect of hydrostatic pressure on solvation dynamics with the current one. The three studies used time-resolved emission techniques to measure the solvation dynamics of a fluorescent probe molecule in several monols from the small-chain ethanol to the long-chain 3-octanol. The main finding of all three studies is that the average solvation relaxation follows the long component of the longitudinal dielectric relaxation time. In all three studies, the normalized solvation correlation function, $S(t)$, is nonexponential. In the current study, we find that only at relatively high pressures (above 0.5 GPA) does $S(t)$ deviate from being exponential. $S(t)$ could easily be fitted to a biexponential function with a very good correlation, whereas our effort to use a single stretched exponential failed. Surprisingly, we find that the short-component relaxation time is almost independent of pressure ($\tau_1 \approx 110$ps) and its amplitude decreases as a function of pressure.

Solid-State Dynamics

Anderson et al.[35] studied the IR spectra of the liquid and crystalline phases of ethanol at high pressures. They found that the freezing pressure is at 1.8 ± 0.1GPa, and unlike methanol, the resulting solid is crystalline rather than glassy. Viewing the frozen coumarin 480 ethanol sample at 1.8 GPa through a microscope showed a crystalline structure. Figure 5 shows the solvation correlation function of coumarin 480 in ethanol, $S(t)$, as a function of time in the solid phase at 1.8 GPa. Surprisingly, the solvation correlation dynamics is rather fast. $S(t)$ could be fit to a three exponent function with average solvation time $<\tau>$ of 360 ps. Richert et al.[36] measured the solvation dynamics of several dyes in the glass-forming solvent 2-methyl tetrohydrofuran (2MTHF) at low temperatures. They found a relatively good correspondence of $S(t)$ with the dielectric relaxation time in the time range between 100 ps and 100 s and the dielectric covering 10 decades in frequency for 2MTHF. The study of slow solvation dynamics by fluorescence is limited by the excited-state lifetime, τ_{F}, which is about 5 ns for coumarin dyes. At low enough temperatures, the solvation dynamic is slow, and the average relaxation time extends to tens of nanoseconds, beyond the fluorescence measurement limit. As the temperature decreases further, near the glass transition, where both τ_{D} and $S(t)$ are much longer than τ_{F}, Richert et al.[36] used phosphorescence with a radiative lifetime of seconds to monitor $S(t)$.

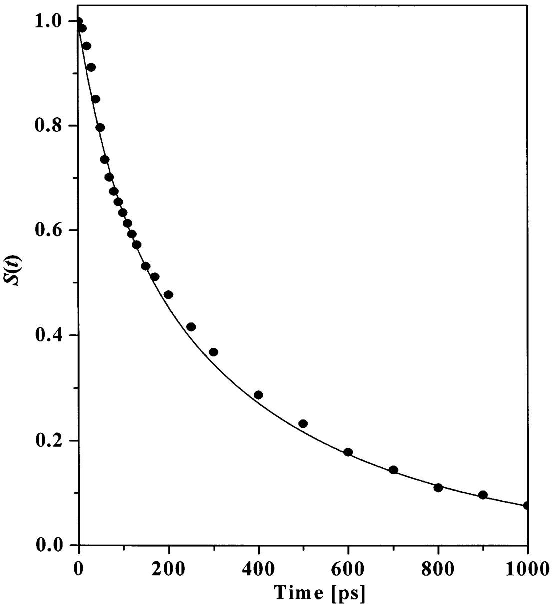

Figure 5. Normalized solvation response function, $S(t)$, of coumarin 480 in solid ethanol at 1.8 GPa. Circles are experimental data, and solid lines are fits to the experimental data.

In most molecular crystals, the molecules cannot reorientate. Therefore, these crystals do not have an orientational polarization, and dielectric relaxation phenomena are not observed. This holds for crystals in the low-temperature phase, but when heated above a certain temperature, a number of compounds, especially those with rigid molecules, enter what is called the solid rotator phase in which reorientation of the molecules is possible so that, for these crystals, dielectric relaxation phenomena can be observed. Various types of dielectric relaxation behaviors are known for solid rotator phases,[37] and no general rule can be given as to which type of relaxation behavior is observed for which compound.

In a previous study, Bart and co-workers[38−40] used combined steady-state and time-resolved measurements to study solvation statics and dynamics of electronically excited dye molecules in solid melts of organic quaternary ammonium salts. They found that solvation processes occur on short time scales when various fluorophores are excited in solid melts at room temperature. It was found that the solvation process in solid electrolytes at about 10−50 °C below the melting point is qualitatively similar but slower by a factor of 3−10 than the solvation dynamics in molten organic electrolytes, at a few degrees centigrade above the melting point. The time-dependent spectral shifts observed in the solid melts at room temperature are explained in terms of ion transport that takes place in solid electrolytes even at room temperature, about 100 °C below the melting point.

When ethanol at atmospheric pressure is cooled at a fast rate to a supercooled liquid and then warmed slowly, it can form a plastic crystal. In plastic crystals the centers of mass of the molecules form a crystalline lattice, but the molecules are orientationally disordered. Studies[41] in both disordered phases of ethanol have shown the importance of orientational degrees of freedom in the super cooled state of matter. Recently, Lunkenheimer and co workers[42] systematically studied the dielectric relaxation dynamics in plastic crystals of several compounds including ethanol. The dielectric spectra and relaxation times as a function of temperature of plastic crystals are very similar to those of solvents that are known to form glasses. Ethanol in the plastic crystal phase exhibits relaxation times that are somewhat lower than those obtained in the liquid state at the same temperature. As the temperature increases, the relaxation times in the plastic phase approach values nearly identical to those of a supercooled liquid.

At room temperature and high pressures, we find that the solvation correlation function, $S(t)$, of coumarin 480 in the solid phase is similar to that in the liquid phase at about the same pressure. Our finding can be explained by comparing it to the dielectric relaxation properties of plastic crystals, which are similar to the relaxation properties of the liquid phase. We do not have evidence of the formation of a plastic crystal at high pressure, but it is known that mixed crystals form an orientationally disordered state, which is believed to be caused by frustrated interactions due to substitutional disorder. Close to the coumarin molecule in the high-pressure ethanol crystal, we expect that the ethanol molecules are not in an ordered structure. In this region, the ethanol molecules are capable of reorienting themselves to accommodate the abrupt change in the charge distribution of a photoexcited coumarin molecule. The reorientation relaxation time we find in this study is similar to that detected in the liquid state at about the same pressure.

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