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Solvation Dynamics in Nonassociated Polar Solvents

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Ultrafast solvation dynamics in three nonassociated polar solvents, namely, acetonitrile, dimethyl sulfoxide, and acetone, have been studied by using the molecular hydrodynamic theory. For solvation in acetonitrile, the solvent memory function required for this study has been obtained from recent dielectric relaxation measurements of Venabales and Schuttenmaer; earlier theoretical studies used only the Kerr relaxation data. As the latter provides only an indirect information regarding the polar dynamical response of the dipolar liquid, it fails to provide a fully quantitative description of the solvation time correlation function, $S(t)$. The present study with full dielectric data, on the other hand, gives excellent agreement with the experimental results. The theory shows that the ultrafast part of the solvation dynamics originates almost entirely from the high-frequency component of dielectric relaxation (with time constant 0.177 ps), although the latter represents only a small part of the latter. For DMSO and acetone, however, the present theory predicts a decay slower than the experimental observation. It is proposed that for these two solvents specific chromophore−solvent interactions might be responsible for the large discrepancy. On the basis of the theory, two experimental studies have also been proposed.

1. Introduction

Considerable progress has been made in recent years in understanding the solvent energy relaxation after the laser excitation of a chromophore.[1−11] In some solvents, such as water and acetonitrile, the energy relaxation has been found to be very fast, while in others (for example, alcohols and amides), there is a significant slow component. There has been a lot of debate regarding the origin of the ultrafast component in these solvents. It now appears that both the single particle and the collective motions are responsible for the initial fast response of the solvent.[1−8]

Recent discussions, however, do not seem to have adequately addressed the issue of specific chromophore−solvent interactions and their possible effects on the solvation energy relaxation.[1−7] In some solvents consisting of small molecules, such as water and acetonitrile, the specific chromophore−solvent interaction does not appear to constitute any significant component of the total solvation energy. Unfortunately, however, it is rather difficult to distinguish between the energy relaxation due to the passive solvent participation (as assumed in the continuum models and in the wavenumber-dependent theories) and the specific chromophore−solvent interaction where solvent plays a more active role. Note that in many electron transfer reactions of technological importance, the active role of solvent is essential. An idea of the relative importance of the specific chromophore−solvent interaction can be obtained by comparing the theoretical prediction based on passive solvent participation with the available experimental results.

The specific chromophore−solvent interaction can be of different kinds. It may be a strong hydrogen bond (H-bond) formed between the chromophore and the solvent molecules where the chromophore itself can act both as a donor and an acceptor of an electron. It may also be coordination bonds. In all these cases, the common feature is the decrease of entropy of the medium resulting in a greater order of the solvent surrounding the chromophore.

Solvation dynamics in nonassociated polar solvents such as acetonitrile, acetone, dimethyl sulfoxide, and many others have been studied recently with considerable interest.[8−11] These solvents are very important since many of them have potential use in chemical industry. For example, both acetone and dimethyl sulfoxide are commonly used as reaction media for many important organic reactions occurring in solution. Acetonitrile, when mixed with water at desired proportions, acts as a very good solvent in reversed-phase liquid chromatography.[12] The dynamical responses of these nonassociated polar solvents are *distinctly* different from those of the associated liquids such as water, methanol, and formamide. The solvation dynamics in these nonassociated liquids have been found to be rather slow compared to those in water, methanol, and formamide. This is expected because these nonassociated solvents cannot sustain high-frequency librations or vibrations as there is no hydrogen bond network. However, some of them may differ from this trend and can indeed exhibit ultrafast dynamics by virtue of very rapid single particle orientation. One such example is acetonitrile.

The first measurements on solvation dynamics using ultrafast nonlinear laser spectroscopy were carried out for acetonitrile. These experimental studies were performed by Rosenthal et al.[8a] where a big dye molecule, LDS-750, was used as a probe. Their observations were quite fascinating since they reported for the first time the *biphasic* nature of the solvent response. The most interesting outcome of this experiment was the discovery of the presence of an ultrafast component with a time constant less than 100 fs.

Subsequently, theoretical investigations[11,14] and computer simulation studies[9,10] were carried out to understand the origin of the biphasic solvent response and the mechanism which drives

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the ultrafast relaxation in these non-hydrogen bonded solvents. Computer simulation studies of Maroncelli[10] revealed some important aspects of ion solvation dynamics in acetonitrile. A theoretical study[11] on ionic solvation dynamics in acetonitrile was carried out using the Kerr relaxation data. The theoretical results thus obtained[11] were found to be in general good, although but not perfect, agreement with the experimental observations[8a] and simulation studies.[10] However, the use of Kerr relaxation data in studying solvation dynamics is not fully correct because, while the solvation dynamics probes the solvent orientational response of rank one (that is, $l = 1$), the Kerr relaxation[13] measures the collective response of rank, $l = 2$.[2] In addition, the latter often includes contributions from the intermolecular vibrations (hindered translations); these motions influence solvation dynamics in a different manner. Nevertheless, this theoretical study[11] pointed out that the ultrafast solvation in acetonitrile originates from the very fast single particle orientation of a solvent molecule around its principal axis. The theoretical results with Kerr relaxation data as the input predicted a small oscillation at the intermediate time which has not been observed to date.

However, when the available dielectric relaxation data were used to study the solvation dynamics in this solvent,[11] a poor agreement was observed; the predicted rate was much slower than the experimental observations. This is because the accuracy of the dielectric relaxation data available then was not reliable.[11] In particular, the high-frequency dispersion data were not available. The interesting and detailed work of Raineri, Friedman, and co-workers[14] also seems to suffer from the same limitation of inadequate description of the short-time solvent response of acetonitrile. As already emphasized, this was only because reliable dielectric dispersion data for real acetonitrile was simply not available.

Fortunately, Venables and Schmuttenmaer have recently published dielectric relaxation data of acetonitrile which they obtained by using the femtosecond tera Hertz pulse spectroscopy.[15] Their dielectric relaxation data are expected to be reliable in the high-frequency region. We have used these data in the present calculation. The resulting theoretical predictions are found to be in very good agreement with the experimental results of Rosenthal et al.[8a]

We have also studied the solvation dynamics in acetone (dimethyl ketone) and dimethyl sulfoxide. As discussed earlier, these two solvents are often used as reaction media and therefore possess a potential use in dye and related industries. Preliminary experimental studies on solvation dynamics in these solvents have also been carried out in recent times. This definitely offers an opportunity to explore the role of the specific chromophore–solvent interaction on the solvation dynamics in these reactive solvents. The organization of the rest of the paper is as follows. Section 2 contains the theoretical formulation. The next section contains a brief discussion on calculational details. We present the results on solvation dynamics in acetonitrile, acetone, and dimethyl sulfoxide in section 4. Concluding remarks are given in section 5.

2. Theoretical Formulation

The solvation time correlation function is defined as usual by the following expression[1−11]

$$S(t) = \frac{E_{\mathrm{solv}}(t) - E_{\mathrm{solv}}(\infty)}{E_{\mathrm{solv}}(0) - E_{\mathrm{solv}}(\infty)} \qquad (1)$$

where $E_{\mathrm{solv}}(t)$ is the time-dependent solvation energy of the probe at time t and $E_{\mathrm{solv}}(\infty)$ is the solvation energy at equilibrium. This energy can be obtained by following the time-dependent Stokes shift of the emission spectrum after an initial excitation. The solvent response function, $S(t)$ is a nonequilibrium correlation function. The time-dependent progress of the solvation of a laser-excited dye has also been studied by using other nonlinear spectroscopic techniques which are often sensitive to the total energy–energy time correlation function, $M(t)$ defined as

$$M(t) = \frac{\langle \Delta E(t) \Delta E(0) \rangle}{\langle \Delta E(0) \Delta E(0) \rangle} \qquad (2)$$

where $\Delta E(t)$ is the fluctuation in the energy difference between the ground and the excited state electronic potential energy surfaces. Note that the response function, $M(t)$, is an equilibrium correlation function. When the solvent response is *linear*, $S(t)$ and $M(t)$ are stated to be the *same*. To study the time-dependent progress of solvation in complex systems such as acetonitrile, acetone, and dimethylsulfoxide, we need a theory that properly includes the dynamic response of the solvent and also the coupling of the probe solute to the solvent. In the following discussions, we consider only the polar solvation where the solvation is given by the interaction of the electric field of the polar solute with the polarization field of the dipolar liquid. The present theoretical formulation is based on the well-known density functional theory (DFT) and has been discussed earlier,[7,11] so we give only the bare essentials here. Let us consider a system where the solute ion is translationally mobile and the host dipolar molecules are both rotationally and translationally mobile. All these motions can contribute to the time-dependent progress of solvation of the ion. We then use the DFT to obtain a general free energy functional (of density) from statistical mechanics. The free energy functional leads to the following expression for the time-dependent solvation energy[7]

$$E_{\mathrm{sol}}(r,t) = -k_{\mathrm{B}}Tn_{\mathrm{ion}}(\mathbf{r},t) \int \mathrm{d}\mathbf{r}' \, \mathrm{d}\Omega' c_{\mathrm{id}}(\mathbf{r},\mathbf{r}',\Omega') \, \delta\rho(\mathbf{r}',\Omega',t) \qquad (3)$$

where $n_{\mathrm{ion}}(\mathbf{r},t)$ is the probability that the solute is at position $\mathbf{r}$ at time t and $\delta\rho(\mathbf{r},\Omega,t)$ is the fluctuation in the position- ($\mathbf{r}$), orientation- (Ω), and time- (t) dependent number density of the dipolar solvent. $c_{\mathrm{id}}(\mathbf{r},\mathbf{r}',\Omega')$ is the ion–dipole direct correlation function (DCF). Note that in this expression, the coupling between the ionic solute and the dipolar solvent enters through $c_{\mathrm{id}}(\mathbf{r})$. At large distance from the solute this term gives the usual coupling between the electric field of the ion and the dipole moment density. At small distances, it includes the molecular aspects and the distortion of the solvent due to the polar solute.

Note that eq 2 *includes the effects of self-motion of the ion*. Subsequent algebra leads to the following expression for the normalized solvation energy time correlation function[7]

$$S(t) = \frac{\int_0^\infty \mathrm{d}k \, k^2 \, S_{\mathrm{ion}}(k,t) |c_{\mathrm{id}}^{10}|^2 \, S_{\mathrm{solvent}}^{10}(k,t)}{\int_0^\infty \mathrm{d}k \, k2 \, S_{\mathrm{ion}}(k,t{=}0) \, |c_{\mathrm{id}}^{10}|^2 \, S_{\mathrm{solvent}}^{10}(k,t{=}0)} \qquad (4)$$

where $S_{\mathrm{ion}}(k,t)$ is the self-dynamic structure factor of the ion and $S_{\mathrm{solvent}}^{10}(k,t)$ is the orientational dynamic structure factor of the solvent. Also, note here that the $l = 1$, $m = 0$ component (that is, the longitudinal component) only survives for the ionic solute. The following expression for the ion dynamic structure factor is used

$$S_{\mathrm{ion}}(k,t) = \exp[-D_{\mathrm{ion}}k^2t] \qquad (5)$$

where D_{ion} is the translational diffusion coefficient of the solute ion. This is calculated self-consistently.[7]

The expression for the orientational solvent dynamic structure factor, on the other hand, is complex and involves both the rotational and translational memory (frictional) kernels. This is given by[7,11]

$$S^{10}_{\text{solvent}}(k,t) = \frac{N}{4\pi 3Y}\left[1 - \frac{1}{\epsilon_{\text{L}}(k)}\right] L^{-1}\left[\frac{1}{z + \sum(k,z)}\right] \qquad (6)$$

Here, L denotes Laplace inversion with respect to the frequency z and N represents the total number of molecules present in the system. $3Y$ is the polarity parameter of the pure solvent which can be calculated from the number density (ρ) and dipole moment (μ) of the solvent as follows: $3Y = (4\pi/3)(k_{\text{B}}T)^{-1}\mu^2\rho$. $\sum(k,z)$ stands for the wavenumber- and frequency-dependent generalized rate of solvent polarization relaxation which was shown to be given by[7,11]

$$\sum(k,z) = \frac{2k_{\text{B}}Tf_{\text{L}}(k)}{I\,[z + \Gamma_{\text{R}}(k,z)]} + \frac{k_{\text{B}}Tk^2 f_{\text{L}}(k)}{m\sigma^2[z + \Gamma_{\text{T}}(k,z)]} \qquad (7)$$

where I is the average moment of inertia of a solvent molecule of diameter σ and mass m. $\Gamma_{\text{R}}(k,z)$ and $\Gamma_{\text{T}}(k,z)$ are the rotational and the translational dissipative kernels, respectively.

The longitudinal component of the static structural correlations of the pure solvent is expressed by[7]

$$f_{\text{L}}(k) = 1 - \left(\frac{\rho_0}{4\pi}\right)c(110;\,k) \qquad (8)$$

where $c(110;k)$ denotes the 110th component of the direct correlation function in the intermolecular frame with **k** parallel to the z axis. $f_{\text{L}}(k)$ is also related to the longitudinal part of the wavenumber-dependent dielectric function, $\epsilon_{\text{L}}(k)$, by the following exact relation[7,11]

$$1 - \frac{1}{\epsilon_{\text{L}}(k)} = \frac{3Y}{f_{\text{L}}(k)} \qquad (9)$$

Equation 4 is essentially a mode coupling theory expression.[16] The solvation energy is seen to be driven by the collective density modes of the solvent and the self-motion of the ion. Note further that the solvent density mode involved for ionic solvation is the longitudinal component of the orientational density.

Equation 4 is appropriate only for ionic solvation. For dipolar solvation, one requires a different, a bit more complicated expression which has been discussed elsewhere.[16] When the size of the chromophore is smaller than that of the solvent molecules, ionic solvation is found to be significantly different (that is, faster) than the dipolar solvation. However, this difference is less significant when the chromophore size is larger than the solvent, as in the present case. Nevertheless, this difference should be kept in mind when comparing with experimental results.

The important ingredients to calculate $S(t)$ from eq 4 are the wavenumber-dependent ion−dipole direct correlation function ($c_{\text{id}}(k)$), the static orientational correlation function ($\epsilon_{\text{L}}(k)$), and the memory functions. We shall discuss the calculational procedure of these quantities in the next section.

3. Method of Calculation

3.1. Calculation of the Wavenumber-Dependent Ion−Dipole Direct Correlation Function, $c_{\text{id}}(k)$. This has been calculated from the MSA solution of Chan et al. for strong electrolytes.[17] We have of course used it in the limit of zero ion concentration. The details have been discussed in refs 7 and 16. The analytical solution provided by MSA is correct in the long-wavelength (that is, $k \to 0$) limit. At intermediate wavenumbers (that is, when the value of $k\sigma$ is around 2π), MSA tends to underestimate the effects of the ion on solvent structure.

TABLE 1: Solvent Parameters Needed for the Theoretical Calculation (Room-Temperature Data)

solvent	diameter (Å)	R^a	μ (D)	ρ (g/cc)	η (cp)
acetonitrile	4.48	1.74	3.5	0.7857	0.341
acetone	5	1.56	2.7	0.79	0.337
DMSO	5.27	1.48	4.1	1.014	1.1

[a] R is the solute−solvent size ratio, calculated for coumarin 153.

3.2. Calculation of the Static Orientational Correlations. For acetonitrile, this has been taken from the XRISM results of Raineri et al.[14] For acetone and DMSO, where we are not aware of any XRISM calculation, we have obtained the static orientational correlation functions from the mean spherical approximation (MSA) model, *after correcting the values both at* $k \to 0$ and $k \to \infty$ limits.[7,16] This gives us an accurate estimation of $\epsilon_{\text{L}}(k)$. In all the cases, the solvent molecules are approximated as hard spheres with diameter σ. Note that approximating them as Lennard−Jones spheres will not change the results significantly, as the long-wavelength limit is not affected by these molecular details. We would also like to stress that this point is often missed in scientific discussions. The relevant static parameters are summarized in Table 1.

3.3. Calculation of the Rotational Memory Kernel, $\Gamma_{\text{R}}(k,z)$. The calculation of the rotational memory kernel, $\Gamma_{\text{R}}(k,z)$ is somewhat involved and complex. The steps are the following. First, one uses the molecular hydrodynamic theory to relate the wavenumber (k) dependent memory function exactly to the relevant dynamical correlation function. In the limit of $k = 0$, this reduces to the dielectric relaxation function. Thus, the k dependence of the rotational memory kernel is neglected and $\Gamma_{\text{R}}(k,z)$ was replaced by $\Gamma_{\text{R}}(k{=}0,z)$. This approximation was found to be valid for polar solvation dynamics since the polar solvation energy relaxation is dominated by the large-wavelength polarization density fluctuations. The latter has been calculated from the experimentally determined frequency-dependent dielectric function, $\epsilon(z)$. The relevant expressions and the procedure have been described in detail elsewhere,[11,16] and therefore, we give only the bare essentials here. The frequency-dependent dielectric function, $\epsilon(z)$, for these solvents is often described by the following rather general expression[14]

$$\epsilon(z) = \epsilon_\infty + \sum_{i=1}^{m} \frac{(\epsilon_i - \epsilon_{i+1})}{[1 + (z\tau_i)^{1-\alpha}]^{\beta}} \qquad (10)$$

where z is the Laplace frequency, ϵ_1 is the static dielectric constant, ϵ_i, $i = 2$, m are the intermediate values of the dielectric constant, $\epsilon_{m+1} = \epsilon_\infty$ is its limiting value at high frequency, m is the number of distinct relaxation processes, τ_i are their relaxation time constants, and β is the fitting parameter to describe the deviation from Debye behavior. For acetonitrile, $\alpha = 0$, $\beta = 1$, and $m = 2$,[15] that is, dielectric relaxation of acetonitrile is described by Debye processes. For acetone, $\alpha = 0.02$, $\beta = 1.0$, and $m = 1$.[2,18] For DMSO, $\alpha = 0$, $\beta = 0.888$,[2,19] and $m = 1$. The dielectric relaxation data of these solvents are summarized in Table 2.

3.4. Calculation of the Translational Memory Kernel, $\Gamma_{\text{T}}(k,z)$. This has been calculated by using the isotropic dynamic

TABLE 2: Dielectric Relaxation Data for Acetonitrile, Acetone, and Dimethyl Sulfoxide (DMSO) at Room Temperature

solvent	ϵ_0	τ_1 (ps)	ϵ_1	τ_2 (ps)	ϵ_∞
acetonitrile	35.77	3.506	3.323	0.177	1.439
acetone	20.67	3.06		2.29	
DMSO	46.40	20.5		4.16	

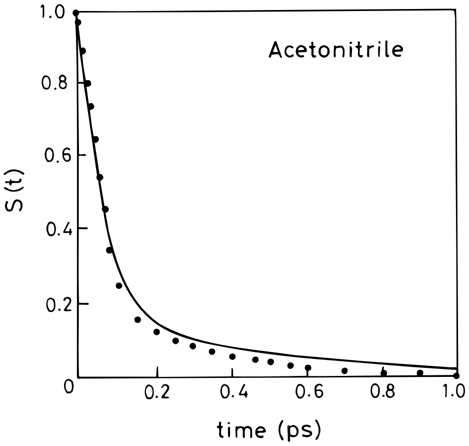

Figure 1. Calculated solvation time correlation function, $S(t)$, compared with the experimental data of Rosenthal et al.[8a] in liquid acetonitrile. The theoretical results are represented by the solid line and the experimental observations by solid circles. The solvation time correlation function has been obtained by using the dielectric relaxation data of Venabales and Schuttenmayer[15] in the calculation of the rotational memory function; the details are discussed in the text. The chromophore−solvent size ratio is 1.74.

structure factor of the liquid. The calculational details regarding the calculation of $\Gamma_T(k,z)$ have been described in ref 7. For acetone and DMSO, this is obtained from the translation diffusion coefficient by using the well-known Einstein relation.

4. Results

4.1. Ion Solvation Dynamics in Acetonitrile. Figure 1 displays the theoretical solvation time correlation function obtained by using the most recent dielectric relaxation data of Venables and Schmuttenmaer.[14] The agreement with experiment is very good and somewhat better than what was obtained earlier by using the Kerr data.[11] The advantage of the present scheme is that we can easily explore the origin of the ultrafast solvation by selectively turning off the relaxation channels. This is demonstrated in Figure 2 where we compare the solvation time correlation function obtained with and without the fast component of the dielectric relaxation (DR) data. Note that when the fastest component of the DR data of acetonitrile is removed, the solvation becomes substantially slower than that calculated with the full DR data. The interesting observation here is that the removal of the fastest component not only slows down the initial rate of solvation, substantially, but decelerates the rate rather strongly even at long time. Thus, we conclude that the ultrafast component is driven mostly by the fastest component of the dielectric relaxation data which is the rotation of the cyanide group (−CN) around the CH_3-CN bond of the acetonitrile molecule.

The dominance of the collective solvent polarization relaxation in ion solvation dynamics in acetonitrile is shown in Figure 3 where contribution of *only* the $k\sigma \cong 0$ polarization mode is included. This is equivalent to the continuum model result, of course with the full dielectric response included. The agreement with the relevant experimental results is almost the same as that when contributions from all wavenumbers were included (see Figure 1). This particular feature again highlights the fact that the long-wavelength polarization mode does govern much of the ionic solvation dynamics in ultrafast liquids. This is also the reason different theoretical approaches often succeed in providing a reliable description,[7,14,20] as all the theories/models reproduce the continuum limit correctly. This also explains why the solvation dynamics in acetonitrile seems to be insensitive to the shape and the size of the chromophore. However, $S(t)$ probed by different experimental techniques can still be rather different.

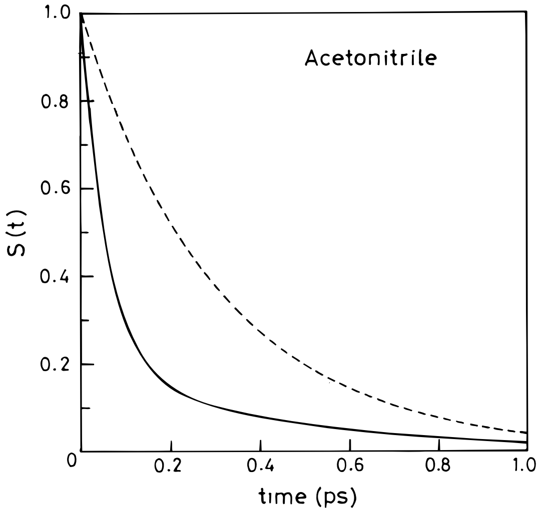

Figure 2. Effect of the removal of faster component of the dielectric relaxation on the solvation dynamics in acetonitrile. The calculated solvation time correlation function, $S(t)$, is plotted against time. The solid line represents the result with two Debye relaxation (full data) and the dashed line with only the first, that is, with the slower Debye relaxation time constant.

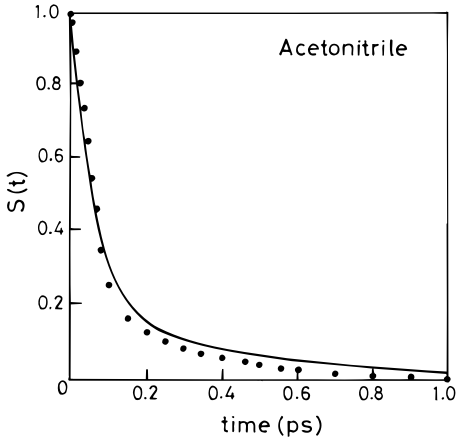

Figure 3. Dominance of the $k\sigma = 0$ polarization mode in ionic solvation dynamics. The theoretical results (solid line) are calculated from eq 4 by considering *only* the $q\sigma \cong 0$ solvent polarization mode. Note the agreement with the experiment data (solid circles). The other static parameters remain the same as those used for Figure 1.

Recently, Ernsting and co-workers[21] have investigated the solvation dynamics of aminonitrofluorene (ANF) in acetonitrile by using the transient hole burning spectroscopy. The dynamics has been found to be biphasic as before but with one extra feature, a weak oscillation in the $S(t)$ versus time curve at intermediate time. Although such oscillations in $S(t)$ have neither been detected in experiments of Rosenthal et al.[8a] nor been reproduced by the present extended molecular hydrodynamic theory, they always seem to be present in simulations.[10] This point deserves further study.

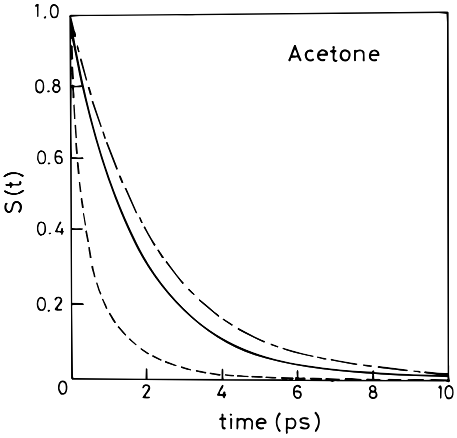

Figure 4. Calculated solvation time correlation function, $S(t)$, compared with the experimental one for ionic solvation of excited coumarin 152 in acetone. The experimental results are denoted by the small dashed line. The theoretical results (solid line) are obtained by using eq 4 after adding a libration of 60 cm^{-1} in $\epsilon(z)$ of acetone. The large dashed line denotes the theoretical result *without* any librational contribution. Note that the experimental decay is much faster than the theoretical prediction. The chromophore−solvent size ration is 1.56.

4.2. Ion Solvation Dynamics in Acetone.

The calculated solvation time correlation function ($S(t)$) of coumarin 152 in acetone is shown in Figure 4. The solute−solvent size ratio here is 1.56. We have attributed the calculated ($\epsilon_\infty - n^2$) dispersion to a libration with frequency 60 cm^{-1}.[18] This librational mode of acetone at that frequency has been detected in the far-infrared (FIR) studies of Gadzhiev.[18] The experimental results of Horng et al.[19] are also presented in the same figure. The comparison shows that the theoretically predicted decay of $S(t)$ is much slower than what has been observed in experiments.[19] We have earlier pointed out that in the interesting experimental results of Joo et al.[22] on solvation dynamics in alcohols, the faster decay observed in experiment may arise from the chromophore−solvent specific interaction.[23] This specific interaction coupled with solute−solvent binary cage dynamics may provide an extra channel for faster energy relaxation. This mechanism can be nonpolar and driven by short-range interactions and can provide a energy relaxation on the time scale of a few hundred femtoseconds (200−400 fs), as discussed earlier by Sevan and Skinner,[24] Larsen et al.,[25] and also by us.[26] The present calculation does not include this contribution.

The effects of the specific solute−solvent interaction will be more pronounced if the solvent is reactive and tends to coordinate with the probe solute. Such might be the case for dimethyl sulfoxide (DMSO). The high reactivity of DMSO to a large variety of organic chromophores may be the reason this solvent did not attract as much attention of the experimentalists as acetonitrile did. We have carried out a theoretical study of solvation dynamics in this solvent. The results are presented next.

4.3. Ion Solvation Dynamics in Dimethyl Sulfoxide (DMSO).

Figure 5 shows the comparison between the theoretical predictions and experimental results of ion solvation dynamics in DMSO. The solute−solvent size ratio is 1.5. Here, the difference between ϵ_∞ and n^2 is 1.9755. This dispersion is attributed to a libration of 40 cm^{-1}. Castner and Maroncelli[2] have observed a peak at this frequency in DMSO in their studies of the polarizability anisotropy response using the optical heterodyne detected Raman-induced Kerr effect spectroscopy (OHD-RIKES). It is clear from Figure 5 that the disparity between the theory and the experiment is quite large in this case. The origin of this pronounced disagreement may again be the enhanced chromophore−solvent specific interaction.

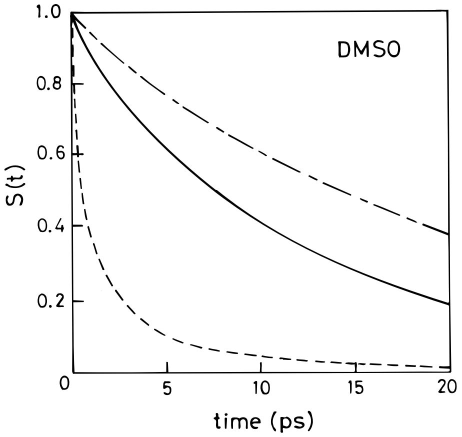

Figure 5. Ion solvation dynamics of coumarin 152 in dimethyl sulfoxide (DMSO). The theoretical results are shown by the solid line. This is obtained after adding a libration of 40 cm^{-1} in $\epsilon(z)$ of DMSO. The large dashed line represents the calculation *without* any libration. The small dashed line denotes the experimental observations. The chromophore−solvent size ratio is 1.48. As discussed in the text, the poor agreement may be due to the presence of specific chromophore−solvent interaction.

5. Conclusion

Let us first summarize the main results of this article. The ionic solvation dynamics of acetonitrile, acetone, and dimethyl sulfoxide have been studied by using the molecular hydrodynamic theory.[7] These solvents represent a particular class—the nonassociated polar solvent. In all the cases, the rotational memory function required to evaluate the solvation time correlation function has been obtained from the available dielectric relaxation data. For acetonitrile, an excellent agreement between the theory and the experimental results have been observed. On the basis of this work, we conclude that the ultrafast component observed in this solvent seems to arise from the fast rotation of the cyanide group around the CH_3−CN bond. This fast orientation is further intensified by the large value of the collective force constant.[7] It is shown that because of the dominance of the long-wavelength mode, a continuum model description for the solvation dynamics should be reliable here. Another result is that we did not observe any oscillations in the solvation time correlation function. The present calculation is to be contrasted with the earlier one by Roy et al.[11] who calculated the memory function from the Kerr relaxation. The present work provides a more direct calculation.

For acetone and DMSO, the theoretical predictions of $S(t)$ are much slower than the experimental observations. The specific solute−solvent interaction may play a significant role in determining the initial part of the solvent response in these liquids. A systematic inclusion of this particular aspect in any dynamic theory is a nontrivial task. However, this needs further attention.

Here, we note that the effects of the specific chromophore−solvent interaction is more pronounced in acetone and DMSO than that in acetonitrile. There could be several reasons for this. First, the solvent response is much faster in acetonitrile than those for the two other liquids. This is because acetonitrile possesses a very rapid single particle orientation (<200 fs) which leads to a faster polar solvation energy relaxation through this rotational mode. This fast component is absent in acetone and DMSO. Second, the presence of two methyl groups in acetone and DMSO may enhance the coordinating tendency of the oxygen via hyperconjugation. This part of solvation energy is distinct from the polar solvation energy and is additional energy which is not present in acetonitrile. When this enhanced coordinating ability couples with the relatively large viscosity of DMSO, the effect of the specific interaction may become large. This is probably the reason for the largest deviations observed between the theoretical predictions and experimental results for DMSO.

The role of the specific chromophore–solvent interaction on solvation dynamics can be assessed semiquantitatively by designing some ingenious experiments. One such suggestion is to study the solvation dynamics in halogen-substituted DMSO. The presence of the halo atom (F or Cl atom) in the methyl carbon atom will reduce the coordinating tendency of the carbonyl oxygen. This should in turn reduce the degree of specific interaction. Second, it would be very interesting to study ultrafast solvation dynamics in binary mixtures. Here, one can also tune the magnitude of the specific interactions. Third, one requires accurate dielectric relaxation data both for acetone and DMSO, the existing data are rather old. Thus, several interesting problems remain for future study.

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References and Notes

(1) Fleming, G. R.; Joo, T.; Cho, M. *Adv. Chem. Phys.* **1997**, *101*, 141. Fleming, G. R.; Cho, M. *Annu. Rev. Phys. Chem.* **1996**, *47*, 109. Jimenez, R.; Fleming, G. R.; Kumar, P. V.; Maroncelli, M. *Nature* **1994**, *369*, 471.

(2) Castner, E. W., Jr.; Maroncelli, M *J. Mol. Liq.* **1998**, *77*, 1.

(3) Stratt, R. M.; Maroncelli, M. *J. Phys. Chem.* **1996**, *100*, 12981. Maroncelli, M. *J. Mol. Liq.* **1993**, *57*, 1.

(4) Barbara, P. F.; Jarzeba, W. *Adv. Photochem.* **1990**, *15*, 1.

(5) Rossky, P. J.; Simon, J. D. *Nature* **1994**, *370*, 263.

(6) Ladanyi, B. M.; Stratt, R. M. *J. Phys. Chem.* **1995**, *99*, 2502; **1996**, *100*, 1266.

(7) Bagchi, B.; Biswas, R. *Adv. Chem. Phys.,* in press. Bagchi, B. *Annu. Rev. Phys. Chem.* **1989**, *40*, 115. Bagchi, B.; Chandra, A. *Adv. Chem. Phys.* **1991**, *80*, 1.

(8) (a) Rosenthal, S. J.; Xie, X.; Du, M.; Fleming, G. R. *J. Chem. Phys.* **1991**, *94*. 4715. (b) Maroncelli, M., et al. In *Ultrafast Reaction Dynamics and Solvent Effects*; AIP Conference Proceedings 298; Gauduel, Y., Rossky, P. J., Eds.; 1993; p 310.

(9) Bader, J. S.; Chandler, D. *Chem. Phys. Lett.* **1989**, *157*, 501.

(10) Maroncelli, M. *J. Chem. Phys.* **1991**, *94*, 2084.

(11) Roy, S.; Komath, S.; Bagchi, B. *J. Chem. Phys.* **1993**, *99*, 3139.

(12) Guillaume, Y. C.; Guinchard, C. *Anal. Chem.* **1997**, *69*, 183.

(13) McMorrow, D.; Lotshaw, W. T. *J. Phys. Chem.* **1991**, *95*, 10395.

(14) Raineri, F. O.; Friedman, H. L. *J. Chem. Phys.* **1993**, *98*, 8910. Friedman, H. L.; Raineri, F. O.; Resat, H. In *Molecular Liquids*; NATO-ASI Series; Teixeira-Diaz, J., Ed.; Kluwer: Amsterdam, 1992. Raineri, F. O.; Resat, H.; Friedman, H. L. *J. Chem. Phys.* **1992**, *96*, 3068.

(15) Venables, D. S.; Schmuttenmaer, C. A. *J. Chem. Phys.* **1998**, *108*, 4935.

(16) Biswas, R.; Bagchi, B.: *J. Phys. Chem.* **1996**, *100*, 4261; **100**, *100*, 1238.

(17) Chan, D. Y. C.; Mitchell, D. J.; Ninham, B. W. *J. Chem. Phys.* **1979**, *70*, 2946.

(18) Gadziev, A. Z. *Russ. J. Phys. Chem.* **1982**, *56*, 1660.

(19) Horng, M. L.; Gardecki, J. A.; Papazyan, A.; Maroncelli, M. *J. Phys. Chem.* **1995**, *99*, 17311.

(20) Hsu, C. P.; Song, X.; Marcus, R. *J. Phys. Chem. B* **1997**, *101*, 2546. Song, X.; Chandler, D. *J. Chem. Phys.* **1998**, 2594.

(21) (a) Ernsting, N. Private communication. (b) Kovalenko, S. A.; Ruthmann, J.; Ernsting, N. P. *J. Chem. Phys.* **1998**, *109*, 1894.

(22) Joo, T. et al. *J. Chem. Phys.* **1996**, *104*, 6089.

(23) Biswas, R.; Nandi, N.; Bagchi, B.: *J. Phys. Chem. B* **1997**, *101*, 2968.

(24) Sevan, J. G.; Skinner, J. L. *J. Chem. Phys.* **1993**, 4391 and private communication.

(25) Larsen, R. E.; David, E. F.; Goodyear, G.; Stratt, R. M. *J. Chem. Phys.* **1997**, 524.

(26) Biswas, R.; Bhattacharyya, S.; Bagchi, B. *J. Chem. Phys.* **1998**, *108*, 4963. Bagchi, B. *J. Chem. Phys.* **1994**, *100*, 6658.