Role of Nonpolar Forces in Aqueous Solvation: Computer Simulation Study of Solvation Dynamics in Water Following Changes in Solute Size, Shape, and Charge

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The coupling between solvent fluctuations and the electronic states of solutes is critically important in charge transfer and other chemical reactions. This has piqued enormous interest in solvation dynamics—the study of how solvent motions relax changes in a solute's charge distribution. In nearly every computer simulation of solvation dynamics, the system is modeled by an atomic or molecular solute whose charge (or higher multipole moment) is suddenly changed, and the motions of the solvent molecules that relax the new charge distribution are monitored. Almost none of this work, however, accounts for the fact that most reacting solutes also undergo significant changes in size and shape as well as charge distribution. For the excited states of dye molecules typically used as probes in solvation experiments or for the atoms and molecules that change oxidation state in charge transfer reactions, we expect changes in reactant size on the order of 5–20%. In this paper, we use computer simulation to explore the differences between dielectric solvation, due to changes in charge distribution, and mechanical solvation, due to changes in size and shape, for a Lennard-Jones sphere in flexible water. The solvation energy for the size changes expected in typical reactions is on the same order as that for the appearance of a fundamental unit of charge, indicating that dielectric and mechanical solvation dynamics should participate at comparable levels. For dielectric solvation, solvent librations dominate the influence spectrum, but we also find a significant contribution from the water bending motion as well as low-frequency translations. The influence spectrum for mechanical solvation, on the other hand, consists solely of low-frequency intermolecular translational motions, leading to mechanical solvation dynamics that are significantly slower than their dielectric counterparts. The spectrum of couplings for various mechanical perturbations (size, shape, or polarizability) depends somewhat on the magnitude of the change, but all types of mechanical relaxation dynamics appear qualitatively similar. This is due to the steepness of the solute–solvent interaction potential, which dictates that the majority of the solvation energy for mechanical changes comes from the translational motion of the closest one or two solvent molecules. Finally, we explore the solvation dynamics for combined changes in both size and charge and find that the resulting dynamics depend sensitively on the sign and magnitude of both the size and charge changes. For some size/charge combinations, the translational and rotational motions that lead to relaxation work cooperatively, producing rapid solvation. For other combinations, the key translational and rotational solvent motions for relaxation are antagonistic, leading to a situation where mechanical solvation becomes rate limiting: solvent rotational motions are "frustrated" until after translational relaxation has occurred. All the results are compared with previous experimental and theoretical studies of solvation dynamics, and the implications for solvent-driven chemical reactions are discussed.

I. Introduction

Solvent molecules whose motions are coupled to the energy levels of a solute critically affect the dynamics of chemical reactions in solution. Since all chemical reactions involve the rearrangement of electrons, the time scales over which the solvent acts to stabilize new charge distributions can determine whether (or how rapidly) a particular reaction can cross its transition state. Indeed, solvent fluctuations define the reaction coordinate for electron transfer and many other types of chemical reactions.[1] This has prompted an explosion of recent interest in solvation dynamics—the study of the relaxation of the solvent following a perturbation of the solute.[2–4] The key issue to be understood is the nature of the specific solute motions that lead to relaxation. Over what time scales does solvent relaxation take

place? Are solvent rotational or translational motions more effective at coupling to a reactive solute? For solutes that undergo changes in charge distribution (e.g., oxidation state, dipole or higher multipole moment, etc.), polarizability (van der Waals interactions), or size (Pauli repulsion forces), what are the relative efficiencies of different solvent motions in promoting relaxation? For any solvent, the types of motions available are often characterized by the solvent's spectral density, which is a histogram of all possible solvent motions tabulated by frequency (see, e.g., Figure 1 below). Not all possible solvent motions, however, are equally effective at promoting relaxation. Thus, many of the above questions boil down to finding which of the available solvent motions are strongly coupled to the electronic states of the solute. The weight with which each type of solvent motion participates in solvation dynamics is known as the spectrum of couplings; the spectrum

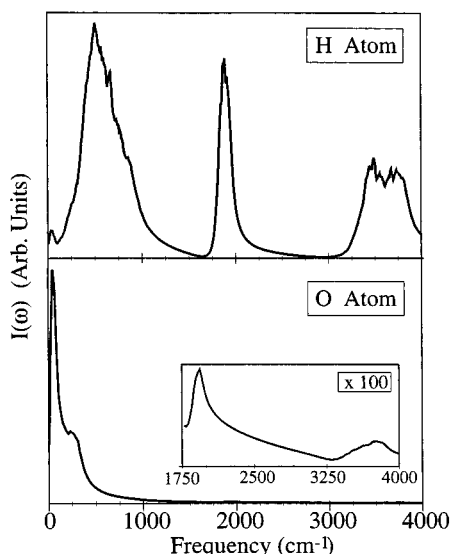* Corresponding author. E-mail: schwartz@chem.ucla.edu.

Role of Nonpolar Forces in Aqueous Solvation

J. Phys. Chem. B, Vol. 103, No. 26, 1999 **5571**

Figure 1. Possible spectral densities for SPC/F water calculated from eq 4 for H atoms (upper panel) and O atoms (lower panel).

of solvent motions that modulates a solute's energy gap is referred to as the influence spectrum.

To get an idea as to what types of solvent motions participate in chemical reactions, we can consider the example of a special class of electron-transfer reaction, that of charge transfer to solvent (CTTS). Because the reaction is photoinitiated, CTTS transitions provide an excellent model system for electron transfer and as such have been the subject of recent experimental[5] and theoretical[6,7] interest. The prototypical example of this class of reactions is that of aqueous iodide: $I^- \xrightarrow{h\nu} I^\bullet + e^-_{aq}$. Initially, the solvent is equilibrated with the iodide anion; the most stable solvent orientation has the water hydrogen bonds pointed radially at the anion.[8] Upon photoexcitation into the CTTS band, solvent fluctuations drive the electron off the iodide anion and into a nearby solvent cavity, producing a neutral iodine atom and hydrated electron.[5-7,9] The motions that drive this reaction must involve rotation of the solvent molecules around the iodine (so that hydrogen bonds are no longer directed toward the solute but instead to neighboring water molecules) to accommodate the now neutral product atom. In addition, the iodine atom has a 15−20% smaller van der Waals radius than parent iodide anion,[10] so the solvent cavity must also change size to conform to the neutral iodine product. At the same time, the initially adjacent nonpolar cavity must undergo both a significant increase in size as well as a change in local molecular orientation to stabilize the newly formed hydrated electron.[6,7] Clearly, the types of solvent fluctuations that drive this type of model reaction are those coupled to changes in both reactant charge distribution and reactant size; both rotational and translational solvent motions must play an important role. Thus, even for electron transfer reactions in a strongly polar solvent like water, it is not clear a priori how the spectrum of couplings should weight translational versus rotational motions.

On the basis of the above arguments, it is tempting to create a distinction between two classes of solvation: dielectric (or polar) solvation, primarily composed of solvent rotational motions in response to reactant changes in charge distribution, and mechanical (or nonpolar) solvation, comprised of the translational solvent motions that couple to reactant changes in size. Both these limits make sense in terms of continuum theories,[3,11,-13] where the solute can be thought of as a cavity in a dielectric or viscoelastic slab that undergoes relaxation in

response to a change in cavity charge or size. Of course, for solute size changes, the solvent response is expected to be dominated by just a few solvent molecules in the first solvation shell;[14] thus, in this paper, we will take a molecular rather than continuum approach to study the differences between dielectric and mechanical solvation. It is also worth noting that our definitions of dielectric versus mechanical solvation do not depend on the polarity of the solvent. The response of nondipolar solvents to solute charge changes already has been explored in some depth, and the mechanism for solvation is qualitatively the same as that in dipolar liquids.[15] For solute size changes in highly polar solvents, on the other hand, it still might make sense to model the solvent relaxation viscoelastically; nonpolar solvation can occur in water. The details of the distinction between the purely dielectric and purely mechanical solvation limits on the molecular level, however, are not as clear. In this paper, we take a first step toward exploring these two limits microscopically for one of the most important solvents, water. Because the solutes in chemical reactions are expected to undergo changes in both charge and size, the manner in which dielectric and mechanical solvation mix together is expected to be important in ultimately determining solvent control over reaction dynamics. Below, we present the results of molecular dynamics simulations of aqueous solvation in response to changes in solute size, shape, and charge and to simultaneous changes in both size and charge.

In general, the limit of purely mechanical solvation has been much less studied than its dielectric counterpart. Many solutes undergo changes in size on the order of 10% upon excitation;[16] the size changes can be even larger when the solute changes its oxidation state. For solutes that have essentially no change in dipole upon excitation, experiments have established that nonpolar solvation dynamics are qualitatively similar to those in polar solvation.[17-19] In fact, the solvent response in studies using propylene carbonate as a solvent can be equally well fit with either dielectric or viscoelastic continuum theories.[17] Other experiments that have used n-propanol as a solvent (n-propanol has vastly different elastic and dielectric response times), however, indicate that nonpolar solvation occurs primarily on viscoelastic time scales.[19] With only a few exceptions,[20,21] there have been essentially no simulation studies exploring the importance of mechanical forces in solvation dynamics. In their simulations of solvation following photoexcitation of the hydrated electron, Schwartz and Rossky point out that both translational and rotational solvent motions are important.[21] Photoexcitation promotes the hydrated electron from an s-like to p-like state, a perturbation which changes neither the charge nor the dipole but predominantly the quadrupole moment of this solute. In addition to the quadrupole change, the electron nearly doubles in size upon excitation and then shrinks by half in size following nonadiabatic relaxation. The solvent response following nonadiabatic relaxation is qualitatively quite different from that following photoexcitation: the inertial response following nonadiabatic relaxation is both significantly faster and comprises a much higher fraction of the total solvent relaxation than that following photoexcitation.[21] Schwartz and Rossky speculated that this was the result of coupling between mechanical and dielectric solvation: the two types of solvation interact differently depending on whether the electron is growing or shrinking in size.[21] In contrast, Berg has recently modeled these simulation results for the hydrated electron using a purely viscoelastic continuum theory and concluded that mechanical forces alone are sufficient to describe the observed solvation

dynamics.[22] Clearly, a microscopic picture of mechanical solvation and its relation to dielectric relaxation is needed.

For dielectric relaxation, on the other hand, a common molecular-level picture of solvation has emerged.[3,4,23−25] When the solute changes its charge distribution, reorientation of solvent molecules is responsible for the majority of relaxation. The initial relaxation is Gaussian and results from the inertial motions of single molecules in the first solvation shell.[26] In polar solvents such as water[27,28] or acetonitrile,[29] this inertial component can account for 60−80% of the total solvent response. After the inertial phase, the rest of the relaxation occurs exponentially via more collective, diffusive motions of the solvent, usually on the time scale(s) of the solvent's longitudinal dielectric relaxation time(s).[3] Theoretical developments have linked the earliest time motions to an instantaneous normal mode (INM) description of the solvent.[30] In this picture, the global potential energy surface of the solvent is approximated harmonically, and motions of the solvent molecules can then be represented as a set of normal modes. Because the normal modes propagate harmonically in time, a solvation theory can be constructed once the variation of the solvation energy along each normal mode coordinate is known.[23] This provides a natural description of solvation in terms of a spectral density, the spectrum of normal modes, and a spectrum of couplings, the effectiveness of each mode in altering the solvation energy.

Based on such a theory, Ladanyi and Stratt have constructed a scaling argument and concluded that the symmetry of the differential solute−solvent ground and excited-state interactions determines the relative effectiveness of translational versus rotational solvent motions participating in the initial solvent relaxation.[31] The prediction is that translational solvent motions become more important for spherically symmetric differential interactions while rotational solvent motions dominate for interactions with dipolar symmetry. In this analysis, the preference for rotation over translation depends primarily on symmetry and only secondarily on the range of the interaction. This dependence on symmetry has been verified for dielectric relaxation in simulations by Kumar and Maroncelli[24] and by Ladanyi and Maroncelli,[25] who found that both the magnitude and the frequency of the inertial solvation component decrease as the multipole order of the solute's change in charge distribution increases. Another prediction of the scaling argument is that the spectrum of couplings for Coulomb ($1/r$) potentials should have a similar fraction of translational to rotational motions as dispersive ($1/r^6$) or repulsive ($1/r^{12}$) differential interactions, making little distinction between polar and nonpolar solvation.[31] The scaling argument, however, is expected to break down as the range of the difference potential becomes comparable to intramolecular distances, leaving open the question of the relative weights of translational and rotational solvent motions in the spectrum of couplings for the short-ranged forces involved in mechanical solvation.

In this paper, we use molecular dynamics simulation to explore in detail the relationship between dielectric and mechanical solvation for water. In section II, we present the details of the molecular dynamics algorithm and model system used for our simulations. We then start section III.A. by examining different ways to construct a spectral density for water and we argue that the motions available for dielectric and mechanical solvation not only have a different spectrum of couplings but actually arise from different underlying spectral densities. We also point out that expected size changes for species in chemical reactions have comparable solvation energies to typical reactant charge changes so that dielectric and mechanical solvation

should both play a role in solvation dynamics. In section III.B., we examine the solvation dynamics resulting from perturbations of either the solute's charge or size and find that mechanical relaxation is qualitatively different and significantly slower than dielectric relaxation. The solvent response to a variety of mechanical perturbations (size, shape, and polarizability) are compared in section III.C. and found to be different only in detail. Section III.D. explores the issue of the interplay between dielectric and mechanical solvation; solvent response functions for simultaneous changes in solute charge and size are found to differ greatly depending on the sign and magnitude of both the size and charge changes. Finally, we argue that mechanical solvation is inherently a molecular phenomenon in section III.E. We conclude in section IV and point out that mechanical solvation is an important factor in controlling condensed-phase chemical reactions, where size changes are important, including charge transfer reactions polar liquids.

II. Methodology

One of the chief advantages of computer simulation is that it allows for description of the solvent at a molecular level. For water in particular, there are many well-characterized models from which to choose. To examine both intramolecular and intermolecular contributions to solvation dynamics, we have selected a flexible version of the simple point charge model (SPC flexible, or SPC/F) due to Toukan and Rahman.[32] Our choice also facilitates comparison to previous studies on the hydrated electron that also employed this same model for the solvent.[21] In SPC/F, intramolecular flexibility is grafted on to the well-known SPC intermolecular potential,[33] which consists of Lennard-Jones (L-J) interactions centered on oxygen sites plus Coulomb interactions between partial charges located at both the oxygen and hydrogen sites. The properties of this model of water have been explored in detail and compared both to other models and to experiment.[34]

The model system in our simulations consists of a cubic cell 24.66 Å on a side containing 500 classical SPC/F molecules (solvent density 0.997 g/mL) and one solute atom which has the same mass as an oxygen atom. For the solute ground state, the water−solute interaction was chosen to be identical to the water−water L-J potential:

$$V_{L-J} = 4\epsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right) \quad (1)$$

This solute−solvent pair potential allows for direct comparison to previous work on dielectric solvation by Maroncelli and Fleming,[27] who also chose an uncharged oxygen atom as a ground-state solute. The various solute excited states in our simulations were constructed simply by changing either σ (size changes) or ϵ (polarizability changes) in eq 1, by using two L-J potentials symmetrically displaced from the ground-state origin (shape changes), by adding a charge or dipole to the solute which interacts with the solvent charges via the Coulomb potential, or by various combinations of all of these. The simulations employ standard periodic boundary conditions, and all interactions were evaluated with a smooth spherical cutoff[35] terminating at a distance of 12 Å. The equations of motion were integrated using the Verlet algorithm with a 1 fs time step in the microcanonical ensemble.[36] Total energy in the simulations was conserved to better than 0.1%, and the average temperature of the equilibrium simulation was 298 K.

The starting point for the simulations was obtained by injecting the Lennard-Jones solute into an equilibrated configuration for neat water. The combined solute−solvent system

Role of Nonpolar Forces in Aqueous Solvation

J. Phys. Chem. B, Vol. 103, No. 26, 1999 **5573**

was equilibrated with velocity rescaling for 10 ps and for an additional 20 ps without rescaling. All the equilibrium ensemble calculation presented below are averaged over at least 100 ps of a ground-state trajectory.

III. Mechanical vs Dielectric Solvation in Water: Linear Response Predictions

The effects of solvent fluctuations on the energy gap of a solute, $U(t) = E_{exc}(t) - E_{gnd}(t)$, are described by the equilibrium solvent response function:

$$C(t) = \frac{\langle \delta U(0) \, \delta U(t) \rangle}{\langle (\delta U)^2 \rangle} \tag{2}$$

where $\delta U(t) = U(t) - \langle U \rangle$ is the fluctuation of the gap from its average value and the angled brackets denote an equilibrium ensemble average. In the limit of linear response, the regression of fluctuations resulting from a nonequilibrium perturbation should relax in the same manner as those present at equilibrium. Thus, for small perturbations, the nonequilibrium solvent response function

$$S(t) = \frac{\bar{U}(t) - \bar{U}(\infty)}{\bar{U}(0) - \bar{U}(\infty)} \tag{3}$$

should be identical to $C(t)$ in eq 1. The overbars in eq 3 denote a nonequilibrium ensemble average. Molecular dynamics simulations of dielectric solvation have found that linear response is obeyed for a wide variety of solute/solvent combinations, although there are a few exceptions.[37] It is the nonequilibrium response function, $S(t)$, that is measured experimentally by monitoring the time-dependent Stokes shift of the solute's fluorescence following excitation.

A. Spectral Densities and Energetics for Polar and Nonpolar Solvation. The solvent motions that modulate the quantum energy gap of the solute can take place only at frequencies present in the solvent's spectral density. For water in particular, there has been a great deal of interest in the spectral density including investigations by infrared absorption,[38] the optical Kerr effect,[39] depolarized Raman scattering,[40] and molecular dynamics simulation.[41,42] For SPC/F water, one way to measure the spectral density is to examine the different frequencies of motion available to the H atoms. This can be done by taking the Fourier transform of the H atom velocity autocorrelation function

$$I(\omega) = \left| \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dt \, e^{-i\omega t} \langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle \right|^2 \tag{4}$$

as shown in the upper panel of Figure 1. As is evident, the spectral density of SPC flexible water is characterized by high-frequency intramolecular symmetric and asymmetric stretching (3200−4000 cm^{-1}) and bending motions (1800−2000 cm^{-1}), as well as lower frequency intermolecular librational (∼400−1000 cm^{-1}) and hindered translational (0 to ∼400 cm^{-1}) motions.[32,38] These lower frequency motions can be loosely characterized as intermolecular H-bond stretching motions (∼300 cm^{-1}) and H-bond bending motions ($\leq$200 cm^{-1}).[40] The librational and intramolecular stretch and bending motions have roughly equal weight in modulating the H atom velocity, whereas translational motions make a significantly smaller contribution. Since dielectric relaxation takes place due to rearrangement of charge, the H atom spectral density represents the possible solvent motions that can participate in dielectric solvation.
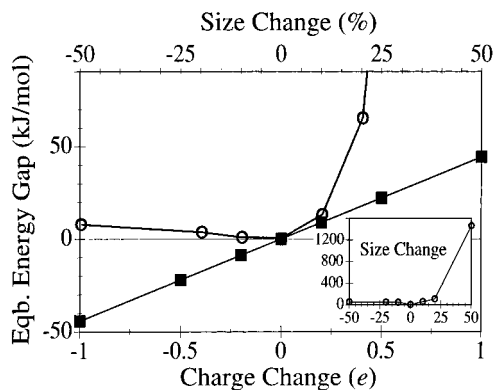

Figure 2. Energy difference between a ground state neutral L-J solute in SPC/F water and excited states with different amounts of charge (squares, lower axis in fundamental units of charge) or with different sizes (circles, upper axis in percent change of the σ parameter in eq 1). Lines connect the data points and are drawn to guide the eye. Inset: energy gap for size changes with an expanded vertical scale.

For mechanical solvation, on the other hand, the types of solvent motions involved in relaxation are expected to be quite different. In our simple model for mechanical solvation, the solvent interacts with the solute only through Lennard-Jones interactions with the O atom; for solute size changes, there are no direct interactions with the solvent H atoms. Thus, we expect the appropriate spectral density for mechanical solvation to consist of the motions available to the solvent O atoms, as seen in the Fourier transform of the solvent O atom velocity autocorrelation (eq 4) shown in the lower panel of Figure 1. Not surprisingly, the intramolecular stretch and bend motions as well as the intermolecular librational motions hardly contribute to the O atom spectral density. This is because the O atom lies essentially on top of the water molecule's center of mass so that motions such as intramolecular vibrations for which the center of mass is conserved lead to little modulation of the O atom velocity. Instead, the O atom velocity is strongly modulated by motions that involve displacement of entire solvent molecules; intermolecular H-bond stretching motions near 300 cm^{-1} and motions of even lower frequency dominate the spectrum. Thus, simply on the basis of the spectral density, we might expect dielectric solvation to have an influence spectrum similar to that in the upper panel in Figure 1, while the influence spectrum for mechanical solvation is expected to more strongly resemble that of the lower panel in Figure 1.

Another important issue that needs to be addressed when comparing dielectric to mechanical solvation is that of energetics. How does the strength of the interaction for typical reactant size changes compare to that for typical rearrangements of a reactant's charge distribution? If the energetics associated with the typical 5−20% reactant size change[16] are significantly smaller than those associated with charge changes on the order of a fundamental unit of charge (or vice versa), then we might expect dielectric solvation to dominate over mechanical solvation (or the reverse). Figure 2 compares the differential solvation energy of our Lennard-Jones (L-J) solute with various excited states that are either charged or have undergone a change in size (σ in eq 1). The solid squares show the energy gap for charged excited states that interact with the solvent via the Coulomb potential (in addition to the interaction via the L-J potential whose parameters remain unchanged from those in the ground state). As the magnitude of the charge is increased, the size of the energy gap also increases, and it is clear that for reasonable charge changes, the change in the energy gap is
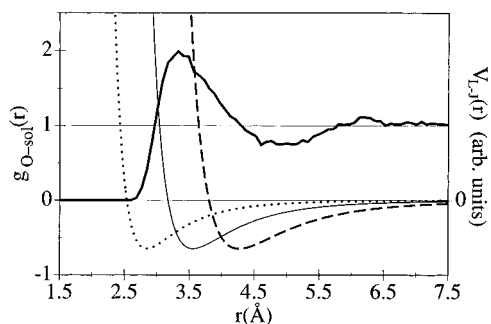
Figure 3. Solute−oxygen pair distribution functions (heavy solid curve, left axis) superimposed on the solute−solvent interaction potential, eq 1 (right axis, thin solid curve), showing that most of the first-shell solvent molecules reside at the minimum of the L-J potential. The dashed and dotted curves show the solute−solvent interaction potential for excited states with a +20% or −20% size change, respectively.
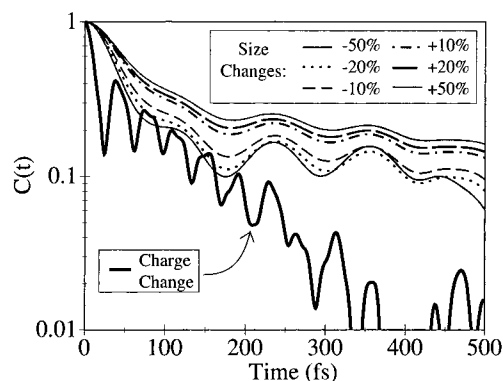

Figure 4. Semilog plot of solvent response functions (linear response predictions, eq 2) for a L-J solute in SPC/F water for various excited states: addition of positive or negative charge (heavy solid curve), alteration of solute size (thin solid and various dotted and dashed curves).

linear. This result is in excellent agreement with the earlier work of Maroncelli and Fleming.[27]

For solute excited states characterized by a change in size, however, the behavior of the energy gap is quite different, as shown by the open circles in Figure 2. When the solute ground and excited states have the same L-J interaction potential with the solvent, there is no size change and the energy gap is zero. As the size of the solute is decreased (upper axis), the energy gap increases due to the fact that the solvent molecules in the first shell no longer reside at the minimum of the solute−solvent L-J potential, as demonstrated explicitly in Figure 3. As the size is further decreased, the solute no longer interacts at all with the first-shell solvent molecules, so the energy gap levels off to a constant value representing the loss of solvation energy present in the ground-state L-J interaction. When the size of the solute is increased, on the other hand, first-shell solvent molecules which were at the L-J potential minimum now find themselves significantly up the $1/r^{12}$ repulsive part of the potential. With a further increase in size, the solute's energy gap increases in a highly nonlinear fashion due to the steepness of the potential (Figure 2, inset). The main point of Figure 2 is that for the typical size changes that we expect of solutes in chemical reactions, the size of the associated energy gap is 25−100% of that for charge changes on the order of a fundamental unit of charge. Thus, on energetic grounds, we expect both size changes and charge changes to participate substantially in the overall solvent response.

It is worth noting that the solute in our simulations is not highly polarizable; the solute−solvent interaction well depth is the same as that between the relatively unpolarizable solvent water molecules. The dye molecules used in solvation experiments and the reactants in electron transfer reactions, however, will generally have much higher polarizabilities than our solute. In addition, most solvents are quite a bit more polarizable than water. This means that the attractive well in the solute−solvent interaction potential is deeper for most systems of chemical interest than for our model system. Thus, even for small size changes where the energetics are dominated by the attractive part of the solute−solvent interaction potential (Figure 3), we anticipate larger mechanical solvation energies for real chemical systems than for those presented in Figure 2. Since the mechanical solvation energy will scale linearly with the well depth (eq 1), we expect that in many chemical reactions mechanical and dielectric relaxation should take place on an equal energetic footing.

B. Solvent Response Functions for Solute Size vs Charge Changes. Given that we expect them to participate about

equally, how do the solvent responses to changes in solute size and charge differ in their dynamics? Figure 4 compares the linear response prediction, eq 2, for solvation dynamics resulting from the addition of charge to the solute (heavy solid curve) to the dynamics resulting from changing the solute's size (thin solid and various dotted and dashed curves). The solvent responses for excited states with different charges are nearly identical (linear response), so only the curve for the excited state with a +1 charge is shown as representative. The initial decay of this response is Gaussian and accounts for over 60% of the total energy relaxation. This Gaussian decay is due to inertial librational motions and the time scale is characteristic of the free-streaming time for a single water molecule to rotate. The remainder of the relaxation decays roughly exponentially with a time constant of 130 fs, in good agreement with other studies of dielectric relaxation in SPC/F water.[34] The parameters for Gaussian + exponential fits to all of the solvent response functions presented in this paper are summarized in Table 1. The postinertial relaxation also shows pronounced recurrences with a ∼35 fs period, characteristic of water librational motion. These results for the solvent response to the appearance of charge on the solute are in excellent agreement with those obtained previously by Maroncelli and Fleming.[27]

The solvent response to solute size changes, in contrast, shows a remarkably different behavior. The inertial component for the size response accounts for a similar fraction of the total solvent response (60−80%), but the inertial frequency is 4−5 times lower than that for the charge change (Table 1). The subsequent decays are also significantly longer than that for the charge change and show oscillations with a much longer period, roughly 100 fs. Neither of the relaxation time scales matches the predictions of continuum theory for the expansion of a spherical cavity in water represented as a viscoelastic medium,[22] as will be discussed further below. Perhaps most striking, however, is the fact that the solvent responses for different size changes are not the same; the solvent response for increases in size is clearly slower than that for size decreases.

How do we account for the large differences in solvent response for size versus charge changes? Figure 5 shows the influence spectra underlying the solvent relaxation for changes in solute charge and size (and for a change in solute dipole that will be discussed in more detail below in section IV). The spectra presented are the complex-square Fourier transforms of the corresponding energy gap fluctuations,[43] essentially frequency domain versions of the solvent response functions presented in Figure 4. We note here that the O−H stretching

Role of Nonpolar Forces in Aqueous Solvation

J. Phys. Chem. B, Vol. 103, No. 26, 1999 **5575**

TABLE 1: Gaussian + Exponential Fit Parameters to Solvent Response Functions

solute perturbation	Gaussian frequency (ps^{-1})	Gaussian amplitude	exponential decay time (ps)^a	relevant figure
charge only	104	0.62	128	4
dipole only	68	0.67	224	9
+50% size	19	0.61	585	4
+20% size	19	0.65	575	4
+10% size	20	0.67	572	4
−10% size	22	0.74	615	4
−20% size	23	0.79	680	4
−50% size	26	0.82	872	4
L-J ϵ change	25	0.79	525	6
shape change	19	0.64	459	6
−20% size/−1 charge	104	0.61	146	7
−20% size/−0.5 charge	102	0.61	164	7
−20% size/+0.5 charge	103	0.62	126	7
−20% size/+1 charge	104	0.62	132	7
+20% size/−1 charge	70	0.53	140	7
+20% size/−0.5 charge	41	0.33	61 (0.45); 660 (0.22)	7
+20% size/+0.5 charge	26	0.27	59 (0.44); 670 (0.31)	7
+20% size/+1 charge	90	0.26	70 (0.50); 665 (0.24)	7
Coumarin 343	38.5	0.48	126 (0.2); 880 (0.35)	9; ref 28
dipole + 15% size	41	0.45	110 (0.38); 815 (0.12)	9

^{a} Response functions which were not well described by a Gaussian + single exponential were fit to a Gaussian + two exponentials; for these cases, both exponential times are quoted with the relevant amplitudes in parentheses.
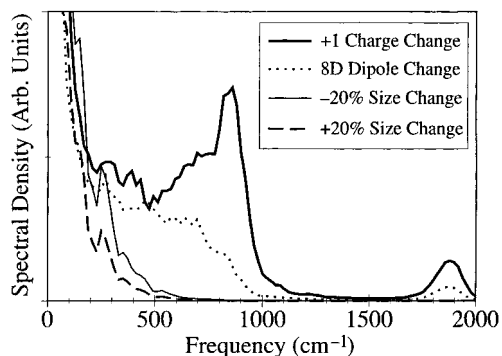

Figure 5. Influence spectra for solute charge changes (heavy solid curve), a 20% increase in size (thin solid curve) and a 20% decrease in size (dashed curve); cf. time domain response functions presented in Figure 4. The dotted curve shows the influence spectrum for an 8 D dipole change (cf. Figure 9, below).

motions are not found to participate in any of the solvation dynamics explored in this paper, so we present the various influence spectra only for frequencies up to 2000 cm^{-1}.

The heavy solid curve in Figure 5 shows the influence spectrum when a +1 charge is placed on the solute. Not surprisingly, water librational motions dominate the spectrum; reorientation of the solvent molecule dipoles is, as expected, the most effective method for solvating the appearance of a charge on the solute. It is interesting to note, however, that the spectrum of couplings is not uniform: high frequency librations are better at promoting solvation than lower frequency librations, leading to a fairly sharp peak in the influence spectrum near 900 cm^{-1}; cf. Figure 1a. The ∼900 cm^{-1} peak is also visible in the time-domain solvent response function in Figure 4 as the ∼35 fs period oscillations. The influence spectrum in Figure 5 also shows a notable amount of the intramolecular water bending motion. Since the primary mechanism for solvation is reorienta-

tion of water H-bonds, the water bending motion can be quite effective at rapidly moving one of the water H atoms closer to or farther from the solute as needed to promote solvation. To the best of our knowledge, no one has previously explored the role of intramolecular solvent motions in solvation dynamics. The presence of the water bending motion in the influence spectrum indicates it is strongly displaced upon excitation of the solute; thus, the water bending motion should be significantly enhanced in the solute's resonance Raman spectrum. Enhancement of solvent motions has been seen in the resonance Raman spectrum of small molecules undergoing dissociation,[44] so the idea of intramolecular modes participating directly in solvation dynamics should be directly testable by experiment. Finally, low-frequency translational motions are also seen to play an important role in the influence spectrum of Figure 5. This is the result of electrostriction, the net attraction of the dipolar solvent molecules to the newly charged solvent ion. This Coulombic attraction causes nearby solvent molecules to "crawl" part way up the $1/r^{12}$ repulsive part of the solute−solvent interaction potential, leading to a net inward translational motion of the first shell solvent molecules. The importance of electrostriction in the solvation dynamics of charged solutes was also noted by Marconelli and Fleming, who found different solvent responses for charging a neutral solute compared to neutralizing a charged solute.[27]

The dashed and thin solid curves in Figure 5 show the influence spectra for solute size changes of +20% and −20%, respectively. As argued above, these influence spectra should contain only those frequencies present in the O atom spectral density presented in Figure 1b. Indeed, the highest frequency (fastest) motion that plays a significant role in solvating the new solute size is the intermolecular H-bond stretch near 300 cm^{-1}. The spectra clearly indicate that this motion is more effective at promoting solvation when the solute shrinks compared to when the solute grows in size. For decreases in solute size, the first-shell molecules find themselves out of the minimum in the solute−solvent interaction potential (cf. Figure 3); equilibrium is re-established by inward translational motion of these molecules. Since the shrunken solute exerts essentially no force on the first-shell molecules, pressure from the second shell directs the first-shell molecules inward, and the inertial motion of molecules undergoing H-bond stretching is highly effective (albeit slow relative to rotational motions) at lowering the solvation energy. For the solute size increase, on the other hand, the nearby solvent molecules find themselves on a highly repulsive part of the solute−solvent interaction potential so that outward motion is needed to re-establish equilibrium. This outward motion, however, is hindered by the fact that the first-shell molecules can only translate so far before encountering second-shell molecules. This limits the effectiveness of intermolecular H-bond stretching motion in promoting solvation, leading to smaller amplitude of this motion in the influence spectrum. This explains why the linear response prediction for solvation dynamics for size decreases is faster than that for size increases: the amplitude of the fastest solvent motions that cause relaxation is reduced when the solute grows in size, leading to a slower overall solvent response (see also Table 1).

C. Mechanical Solvation Dynamics for Solute Size and Shape Changes. In addition to simple size changes, there are many other types of solute perturbations that result in mechanical solvation dynamics. Depending on the nature of the excitation, reacting solutes can undergo significant changes in polarizability or shape as electron density rearranges or as chemical bonds are broken or formed. What types of solvent motions couple to
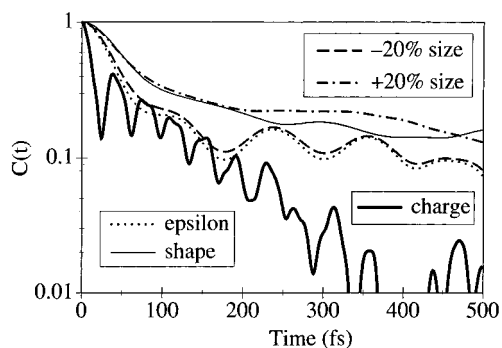
Figure 6. Solvent response functions (eq 2) for solute perturbations with spherical symmetry (charge change, heavy solid curve; +20% size change, dot-dashed curve; −20% size change, dashed curve; polarizability change, dotted curve) and for a shape change with quadrupolar symmetry (thin solid curve; see text for details).

these different types of mechanical perturbations? As mentioned in the Introduction, Ladanyi and Stratt constructed a scaling argument which predicts that the influence spectrum should be similar for spherically symmetric solute−solvent difference potentials, including charge changes (Coulomb interaction), size changes (L-J σ parameter), and changes in polarizability (L-J ϵ parameter).[31] In Figure 5, we have already compared the influence spectrum for a change in solute charge to that for changes in solute size. Clearly, the spectra are both quantitatively and qualitatively different: the charge change influence spectrum shows a large mix of translational and rotational solvent motions, while the size change influence spectra consist solely of translational motions. This indicates that the conditions of the scaling argument, which assumes the range of the difference potential is large compared to the size of the solvent and solute molecules, are not met for mechanical solvation.

Figure 6 explores the role of symmetry in the solvation dynamics by comparing the solvent response functions (eq 2) for a variety of solute perturbations. For comparison, the heavy solid, dashed, and dot−dashed curves for the charge, −20% and +20% size changes, respectively, are reproduced from Figure 4. The dotted curve shows the solvent response when the polarizability of the solute in the excited state (ϵ in eq 1) is 1.5 times that of the ground state. Inspection of eq 1 shows that the solute−solvent interaction potential is linear in this parameter. Thus, the solute energy gap increases linearly with increasing polarizability by construction, and not surprisingly, the solvent response functions for changes in polarizability of different magnitude are identical. The solvation dynamics for the polarizability change bear a strong resemblance to those for the 20% decrease in solute size (Table 1). This is because the first-shell molecules need only undergo small amounts of translational motion to re-establish equilibrium when the well depth of the solute−solvent interaction potential has changed. Since there is nothing to hinder this motion, the effectiveness of the solvent intermolecular H-bond stretch in promoting relaxation is similar to the case of the solute size decrease, resulting in similar solvent response functions.

The thin solid curve in Figure 6 shows the solvation dynamics resulting from a change in solute shape. In this case, the solute excited state is dumbbell shaped, consisting of two Lennard-Jones spheres each with the same parameters as the ground state but with their centers displaced symmetrically from the ground-state center by 0.2 σ. Thus, the excited-state solute has increased in length by ~40% along the direction connecting the two L-J spheres but remains roughly the same size in the other two directions. (Actually, there is a small size decrease in the plane

perpendicular to the long axis at the location of the former center of the ground state). This is a quadrupolar change in shape, similar to that which takes place upon photoexcitation of the hydrated electron.[21] For this shape change, the solvent response function bears a strong resemblance to that of the 20% size increase. The bulk of the solvation energy comes from the repulsive interactions between the solute and the one or two solvent molecules at the ends of the lobes of the excited-state shape. The small increase in attraction between the solvent molecules near the equator of the dumbbell and the solute provides a relatively negligible amount of solvation energy. Thus, the best solvent motions to re-establish equilibrium are translational motions of solvent molecules away from the solute lobes, essentially the same fluctuations as for the case of the solute size increase. Also like the case of the size increase, the intermolecular H-bond stretch which carries the solvent molecules away from the solute is somewhat hindered due to the presence of the second shell. Thus, even though solvation of the dumbbell solute involves faster, inward motion of the equatorial solvent molecules, the overall of solvent response is limited by the slower outward motion of the solvent molecules responsible for the majority of the relaxation.

Finally, Figure 6 shows that the INM-based scaling argument also does not work for the case of solute shape changes. The scaling argument would predict a higher degree of rotational motions in the relaxation for the quadrupolar shape change relative to spherical size changes. Instead, the influence spectra for the size increases and shape change are nearly identical. The reason all the different mechanical solvation responses presented in Figure 6 are so similar is that the underlying solvation dynamics are dominated by the one or two solvent molecules that are closest to the solvent,[14] discussed further in subsection E below. The important conclusion of Figure 6 is that, for changes of solute polarizability, dispersion, size, or shape, the only solvent motions that can participate in the influence spectrum are translational in nature. Thus, with only minor differences in detail, the solvent response functions for all forms of mechanical solvation are similar. This is in sharp contrast to dielectric solvation where solvent rotations play a substantial role and where the details of the charge distribution change are important in changing the relative weights of the different solvent motions involved.[24,25,28]

D. Coupling of Mechanical and Dielectric Solvation. Given that the solutes in most chemical reactions undergo simultaneous changes in size, shape, and charge distribution, the logical question to explore next is how the solvent responses for mechanical and dielectric relaxation mix together. Will the faster rotational motions in dielectric relaxation dominate the solvation dynamics when both size and charge are changed, or will the slower translational motions associated with size changes prevent equilibration from occurring on the time scales of dielectric relaxation? The answer to this question is presented in Figure 7, which shows the equilibrium solvent response functions (eq 2) for simultaneous changes in both size and charge that are typical of solutes in charge-transfer reactions. The excitations considered here consist of a ±20% change in size combined with various charge changes ranging from −1 to +1 unit of fundamental charge, about what is expected for the CTTS transitions mentioned in the Introduction. A glance at Figure 2 indicates that the solvation energies of each component of the +20% size and charge change are comparable; the solvation energy of the −20% size change is about 1/4 that of the charge change. Thus, we might expect both mechanical and dielectric solvent responses to play a role, leading to
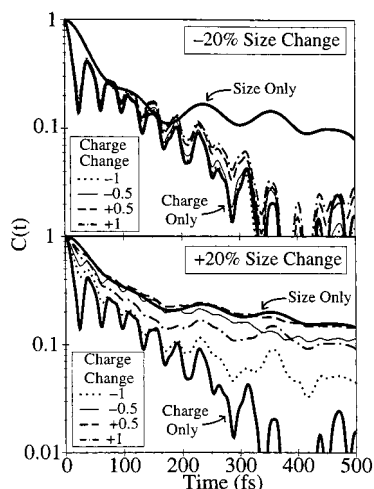
Role of Nonpolar Forces in Aqueous Solvation

J. Phys. Chem. B, Vol. 103, No. 26, 1999 **5577**

Figure 7. Solvation dynamics for L-J solute in SPC/F water undergoing combined changes in both size and charge. The upper panel shows solvent response functions (eq 2) for various charges (-1, dotted curve; -0.5, thin solid curve; $+0.5$, dashed curve; $+1$, dot-dashed curve) with a simultaneous 20% size decrease. The lower panel shows solvent response functions for the same charge changes combined with a 20% size increase (same symbols as upper panel). The heavy solid curves in each panel show the solvent response for the charge-only and relevant size-only changes (reproduced from Figure 4 for comparison).

influence spectra containing both translational and rotational solvent motions. Instead, Figure 7 shows that either purely dielectric or purely mechanical solvation can dominate the total relaxation depending on the circumstances.

The upper panel in Figure 7 displays the equilibrium solvent response functions (eq 2) for a 20% decrease in size of the solute with the simultaneous appearance of charge (various dotted and dashed curves). The solvation dynamics for the corresponding size-only and charge-only changes (heavy solid curves, same as in Figure 4) are also shown for reference. Clearly, the presence of the -20% size change makes little difference in the solvent response; the charge-only relaxation dynamics are nearly identical to those for the combined size and charge. There are two reasons that account for the relative lack of importance of the size decrease in these response functions. First, for our relatively unpolarizable solute, the amount of energy relaxation that can be obtained from mechanical solvent motions is roughly 4 times less than that for dielectric motions (Figure 2). Second, when the solute shrinks, the first-shell solvent molecules can freely translate and rotate into the space formerly occupied by the solute to relax the newly appeared charge. Thus, the fastest solvent motions that lead to relaxation are the rotational motions associated with dielectric solvation. The solvation process is also aided by the fact that the driving force for the translational motions associated with mechanical solvation are aided by electrostriction; the L-J and Coulomb forces work together to help the first-shell molecules translate inward to re-establish equilibrium.

The situation is quite different, however, when charge appears on the solute with a simultaneous increase in size. The lower panel in Figure 7 shows that, for smaller charge changes (dashed and thin solid curves for change of $\pm 0.5e$), the solvation dynamics for the combined change strongly mirror those of the size only change. The first-shell solvent molecules that participate in mechanical relaxation are translating away from the solute and thus tend to be in contact with the second-shell molecules. As a result, the rotation of these molecules is hindered, and indeed, rotational solvent motions do not appear in the influence spectrum for the combined size increase and

appearance of charge. For the larger charge changes (of $\pm 1e$, dot−dash and dotted curves), the influence spectrum for the combined charge and size change shows a bit more rotational character. With the larger driving force for dielectric solvation, smaller amplitude rotational motions become effective at promoting a significant amount of relaxation. One interesting feature of this combination of mechanical and dielectric solvation is that the degree to which rotational motion participates depends on the sign of the charge change. For the appearance of a negative charge, dielectric solvation takes place by rotating the H atoms on the solvent molecules toward the solute; motion which also rotates the O atom away from the solute. This rotational motion works cooperatively with the fact that the O atom is already being pushed away from the solute by the size increase. For the appearance of a negative charge, on the other hand, dielectric solvation takes place by rotation of first-shell solvent molecules to point their O atoms toward the solute. This motion is antagonistic to the outward translational motion induced by the size change; solvent molecules whose O atoms are translating away from the solute tend not to be rotating to point their O atoms toward the solute. In other words, the molecular rotations that are effective for dielectric solvation are essentially frustrated until after solvent molecule translation has occurred. Thus, the net solvent response follows that of the mechanical relaxation, which has become the rate-limiting step for re-establishing equilibrium.

E. The Molecular Nature of Mechanical Solvation. As pointed out above, the changes in the solute−solvent interaction that give rise to mechanical solvation are inherently short ranged, unlike the longer ranged Coulomb interaction responsible for dielectric solvation. In addition to implying that the assumptions underlying the INM-based scaling argument[31] should break down for mechanical relaxation, the short interaction range implies that only a few first-shell molecules are responsible for all of mechanical solvation dynamics. Figure 3 above shows that only a few solvent molecules are present in the range of the difference potential for solute size changes. Solvent molecules that are just a few percent closer to the solute will have significantly higher interaction energies due to the steepness of the $1/r^{12}$ repulsive part of the solute−solvent interaction potential. Indeed, for the results presented in Figure 2, essentially all of the solvation energy for solute size decreases is accounted for by the first solvation shell, and only the closest molecule is needed to account for $\geq 50\%$ of the solvation energy when the solute's size increases. This leads to inherently different microscopic mechanisms for dielectric and mechanical solvation. Following the inertial response in dielectric relaxation, solvation dynamics in polar fluids can be well described by simple continuum theories and hence must be an essentially collective phenomenon.[3,15] For the case of mechanical solvation, on the other hand, the short range of interaction leads us to expect that just a few molecules dominate not only the inertial regime but also the entire dynamics of solvation.

The ability of only a few first-shell solvent molecules to describe mechanical solvent relaxation is explored in more detail in Figure 8. The dotted curves show the influence spectra for a change in solute charge (upper panel), for a 20% solute size decrease (center panel), and for a 20% increase (lower panel) (same as in Figure 5). The heavy solid curves show the influence spectra resulting from the fluctuations in the energy gap produced by only the closest solvent molecule. The single-molecule spectra at very low frequencies (≤ 200 cm^{-1}) are expected to be inaccurate and are not shown in Figure 8 because the identity of the closest solvent molecule changes every few
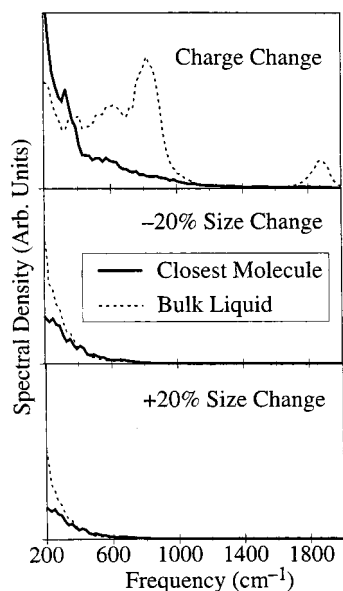
Figure 8. Influence spectra for various solute perturbations from the single molecule closest to the solute (heavy solid curves) and for the entire solvent (dotted curves, same as in Figure 5) for a 20% size increase (lower panel), a 20% size decrease (center panel), and a change in charge (upper panel).

Figure 9. Solvent response functions (eq 2) for an L-J solute in SPC/F water for the appearance of an 8 D dipole (heavy solid curve) and for the appearance of the dipole with a simultaneous 15% increase in size (dashed curve). The experimental solvent response for Coumarin 343 in water, reproduced from the fitting parameters given in ref 28, is shown as the thin solid line for comparison.

hundred femtoseconds: memory of the low-frequency fluctuations is lost every time a new solvent molecule becomes closest to the solute. As is clear for the mechanical solute changes, the fastest solvent motions leading to relaxation are those of the closest molecule. The rest of the solvent makes a contribution only at lower frequencies, confirming that the initial relaxation is the result of solute interactions with predominantly a single solvent molecule. For the charge change, on the other hand, the closest molecule provides only a small fraction of the total influence at librational frequencies and makes almost no contribution at the bending frequency; motions of a single molecule are inadequate to describe the relaxation dynamics for dielectric solvation. The results in Figure 8 are in excellent agreement with the previous work of Ladanyi and Stratt, who also found that the motions of a single molecule dominate the influence spectrum for mechanical processes such as Lennard-Jones solvation, dispersive solvation, and vibrational relaxation and that the single-molecule description fails for dielectric solvation.[14]

The fact that both the energetics and dynamics of mechanical solvation are the result of just one or two first-shell solvent molecules is directly responsible for the similarity of the different solvent response functions presented in Figure 6. For a wide variety of mechanical perturbations, translational motions of the 1 or 2 closest solvent molecules accomplish the bulk of the relaxation. Since the motions of those molecules responsible for relaxation are the same independent of whether the solute has changed size, shape, or polarizability, the solvent response functions are qualitatively the same. The small differences in the response functions presented in Figure 6 are the result of subtle changes in the effectiveness of the motions of the closest solvent molecules in promoting solvation. This difference in effectiveness is evident as small changes in the amplitude of different motions in the corresponding influence spectrum, like those seen in Figures 4 and 8. The key point is that both the energetics and dynamics of all forms of mechanical solvation can be understood on the basis of the translational motions available to the closest solvent molecule or two.
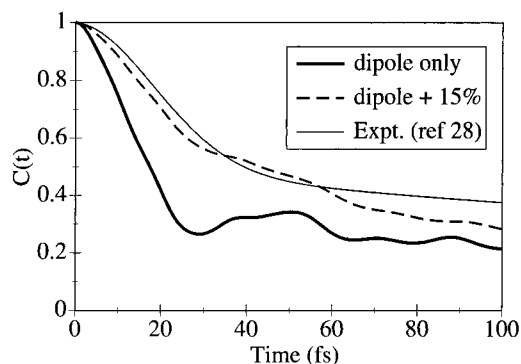
IV. Discussion

In this paper, we have explored the molecular differences between mechanical and dielectric solvation in water by molecular dynamics simulation. While water librational motions dominate the dielectric response to changes in charge distribution, the mechanical response to solvent size or shape changes consists solely of low-frequency solvent translations. This implies that mechanical solvation should be significantly slower than dielectric solvation; the inertial translational motions in mechanical solvation have a lower frequency then their librational counterparts in dielectric solvation (Figures 4 and 6, Table 1). Moreover, the energetics of typical solute size changes are comparable to those of typical solute charge changes, indicating that the magnitude of the mechanical component of solvation dynamics in chemical reactions is not negligible (Figure 2). This means that even for polar solutes in polar solvents such as water, the dynamics of nonpolar (mechanical) solvation are of critical importance in solution-phase chemical reactions, such as charge-transfer reactions, which are driven by changes in both reactant size and charge.

This idea of the importance of nonpolar solvation also has implications for many of the solvation studies in the literature, which for the most part have ignored changes in solute size or shape. For example, Jimenez et al. measured the time-dependent Stokes shift of an excited Coumarin dye in water by fluorescence upconversion and experimentally determined water's solvent response function.[28] The inertial component was found to have a frequency of 38.5 ps^{-1} with an amplitude of 48%, followed by exponential relaxation on longer time scales (Table 1). Both the experimental inertial frequency and amplitude are smaller than those predicted by simple computer simulations where a charge (Figure 4) or dipole (Figure 9) appears on a L-J solute (see also Table 1 and ref 27). Better agreement between simulation and experiment can be obtained by using a more realistic solute model that accounts for the complexity of the change in charge distribution of the Coumarin dye.[28] The improvement in agreement is the result of the dependence of the solvation response on the details of the change in charge distribution, as mentioned above.[24,25,31] We note, however, that, even with a realistic model solute, the MD simulations which incorporate only a change in charge distribution still overestimate the frequency of the inertial response seen experimentally.[28]

In Figure 9, we show that a simple model including mechanical solvation can capture the essential physics of this

Role of Nonpolar Forces in Aqueous Solvation

J. Phys. Chem. B, Vol. 103, No. 26, 1999 **5579**

experiment. For photoexcitation of Coumarin 343, the leading order change in charge distribution is a dipole moment change of ∼8 D. In addition, we expect the Coumarin dye to undergo a size increase of 10−15% as characteristic for excited aromatic molecules.[16,45] The solid curve in Figure 9 shows the solvent response function, eq 2, for the appearance of an 8 D dipole on our L-J solute; the corresponding influence spectrum was presented earlier in Figure 5. While this dipole-only change has a lower inertial frequency than the charge-only change (as summarized in Table 1 and seen in previous work),[24,25,27,31] the inertial frequency is still too high and has too large an amplitude to be consistent with experiment. When we couple the 8 D dipole change with a 15% size increase, however, the simulated solvent response shows parameters much closer to experiment (thin dotted curve in Figure 9, Table 1). Our purpose here is not to suggest that the experiments in ref 28 are best described by a simple L-J solute with a size and dipole change. Rather, the point is that the mechanical solvation due to the solute size change, a factor that has been ignored in previous analyses, plays an important role in the physics of solvation even for large solute dipole changes in polar solvents such as water.

Another important aspect of mechanical solvation is the fact that it is largely single molecule in character (Figure 8). As noted above, this result agrees with the work of Ladanyi and Stratt who found that just one or two molecules dominate the influence spectrum for vibrational relaxation and for solvation resulting from changes in L-J or dispersion interactions.[14] The forces involved are simply too short-ranged (Figure 3) for collective effects to be important, indicating that continuum theories of mechanical solvation[12] are not likely to prove accurate. As mentioned in the Introduction, Berg has recently constructed such a theory and used it to explore the solvation dynamics of the hydrated electron.[13] In this theory, the electron is represented as a spherical cavity in a viscoelastic slab with parameters appropriate for water and the relaxation dynamics resulting from an increase in cavity size are calculated. The size change simulations presented above in Figure 4 are for exactly this situation and thus should provide the best molecular-level test of the continuum theory. The solvent response function calculated from the continuum theory agrees well with that computed for the hydrated electron[13,21] but looks nothing like the size increase response functions presented above: neither the inertial nor subsequent relaxation is well described. In fact, the continuum theory predicts a solvent response function that is not like any of the mechanical solvation functions presented in Figure 6 but instead is quite similar to the dipole-only solvent response function shown in Figure 9.[22] As expected, the continuum theory does not correctly describe the single-molecule nature of the mechanical solvation process, leading to errors in the calculated relaxation dynamics.

Given that the continuum theory does do an excellent job of reproducing the solvation dynamics for the hydrated electron,[13] it is worth exploring why the hydrated electron's dynamics are different from the classical changes in size and shape studied here. Photoexcitation of the hydrated electron leads to a quadupolar shape change similar to that studied in Figure 6, although for the electron, the excited state increases in size in the long direction by nearly a factor of 2 instead of only 40%.[21] The size change for the electron, however, does not occur instantaneously; it takes nearly the entire duration of the solvent response for the electron to reach its equilibrium size in the excited state.[21] This is a result of the highly polarizable nature of the hydrated electron.[46] Upon photoexcitation, the molecules comprising the solvent cavity have not moved and the quantum

mechanical electron is still confined as a particle in a more-or-less spherical box that has not changed in size. The quadrupolar change in charge distribution, however, couples to motions of solvent molecules which change the cavity's shape and which allow the electron to expand in size. This expansion in turn drives further solvent motion that causes an additional size increase, and the feedback continues until equilibrium is achieved. Thus, for the case of photoexcitation of the hydrated electron, the solvation dynamics drive the mechanical size change which drives solvation dynamics, a situation quite different than the simple size changes considered here.[47]

Finally, we have yet to address the issue of linear response: the agreement of the equilibrium (eq 2) and nonequilibrium (eq 3) solvent response functions. As pointed out in the Introduction, nearly every (but not all)[37] molecular dynamics simulation of dielectric solvation has found that linear response is obeyed. The Coulomb force responsible for dielectric relaxation is long ranged, so a wide variety of fluctuations in the solvent couple to the charge distribution on the solute. If the number of molecules that couple is large, the central limit theorem dictates that the force fluctuations will be Gaussian in nature, thereby leading to linear response. For the case of mechanical solvation however, the forces are inherently short ranged and the important fluctuations for relaxation are those of only one or two molecules interacting with the solute via the highly nonlinear L-J potential. Thus, we might expect that linear response will not be obeyed for mechanical solvation.[20] The data above give several other indications that linear response fails for nonpolar solvation: (1) unlike the linear variation of solvation energy with solute charge, the solvation energy changes in a highly nonlinear way with size (Figure 2); (2) unlike the case for charge changes of different magnitude, the equilibrium solvent response functions for different size changes are not identical (Figure 4); (3) for combined size and charge changes, the solvent response depends on both the magnitude and sign of the charge (Figure 7). Preliminary results from nonequilibrium simulations show that this expectation is borne out: linear response is not obeyed for solute size changes, even when the size changes are relatively small.[48] A full exploration as to which solvent motions are responsible for the nonlinearity will be presented in future work.[48]

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