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Theoretical Studies of Dielectric Solvation Dynamics

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Abstract. Using a dynamical Gaussian model of solvation, we have developed a phenomenological theory of solvation dynamics. This theory is applied to compute the solvation dynamics correlation function for solutes in various solvents from time-dependent Stokes shift experiments and to compute the peak shift as a function of population period from three-pulse photon-echo experiments. Employing a quantum chemical estimate of the solute's charge distribution, the Richards-Lee estimate of its van der Waals surface, and the measured frequency dependent dielectric constant of the pure solvent, we found the calculated results agree closely with those determined by experiments.

I INTRODUCTION

Many chemical reactions in solution involve a rearrangement of the charge in the reactants. The time-dependent response of the solvent molecules to this change influences reaction dynamics. When light absorption produces an excited electronic state of a solute, the solute charge distribution is suddenly changed and the excited solute is no longer in equilibrium with the solvent. This sudden change of the solute charge distribution forces the solvent to rearrange to a state in equilibrium with the new solute charge distribution. The question that arises is how this relaxation process can be described in terms of the solvent and solute's properties.

With the advent of ultrafast laser techniques, it is now possible to probe these detailed solvent relaxation dynamics. The experimental results, combined with the developments of theoretical models and computer simulations, have led to an appreciation of the linear response features of these processes[1-14]. We review some of our effort to understand the dielectric solvation dynamics in terms of the solvent and solute's properties.

Our approach employs a general model of a linear response solvent and a solute that modifies the response of the solvent via the excluded volume effect. In particular, the solvent is described in terms of a linear responding field, i.e., a Gaussian field, that is expelled from the region of space occupied by the solute. Standard dielectric continuum model is an example of this class of models. The mean spherical

approximation is another example, as it corresponds to approximating a non-linear system by a Gaussian model [15]. We show how the statistical mechanical analysis of solvation dynamics of this class of models can be carried out analytically. The result is a general framework to compute the spectral density of the system with a realistic solute molecular shape and an arbitrary charge distribution change, and thereby, to calculate the experimental observables of linear and non-linear spectroscopy. The inputs to our calculations are the charge distribution change of the solute from the electronic ground state to its first electronically excited state, the solute's molecular surface, and the frequency dependent dielectric constant of the solvent. The first of these is estimated from quantum chemistry calculations; the second is determined from standard atomic van der Waals radii; and the third is determined from experiments. With these ingredients, good agreement is found between our theory and different laser spectroscopy experiments.

In Section II, it is shown that the solvation dynamics can be understood in terms of the spectral density of the system under a linear response approximation. The calculation of this spectral density is related to the dielectric response of the pure solvent, the charge distribution change and the molecular shape of the solute. A particular solvent model, the dielectric continuum model, is considered in Sec.III. The dielectric response function of the solvent is expressed in terms of the frequency-dependent dielectric constant of the solvent. In Sec. IV, a direct comparison between theoretical results and experimental data of various solute-solvent systems is presented. The paper is concluded in Sec. V

II A FORMULATION OF DIELECTRIC SOLVATION DYNAMICS

Consider a solute molecule embedded in a solvent where the solute has two electronic states, the ground state(g) and the excited state(e). Ignoring interstate coupling, the nuclear Hamiltonian of the system can be written as

$$H = H_g |g\rangle\langle g| + H_e |e\rangle\langle e|, \quad (1)$$

where $H_g = H_g^{(0)} + H_s + H_{gs}$, $H_e = H_e^{(0)} + H_s + H_{es}$. $H_g^{(0)}$ and $H_e^{(0)}$ are the gas phase Hamiltonians of the solute molecule at the ground state and the excited state, H_s is the Hamiltonian of the solvent, and H_{gs} and H_{es} are the interactions between the solute and the solvent in the two electronic states.

Imagine that the solvent is initially in equilibrium with the solute in its ground electronic state. After instantaneous excitation from the ground state to the excited state, the surrounding solvent molecules will relax to a new equilibrium consistent with the excited state. This relaxation can be probed by ultrafast spectroscopy experiments [1-3]. For example, the solvation correlation function,

$$S(t) = \frac{\omega(t) - \omega(\infty)}{\omega(0) - \omega(\infty)}, \quad (2)$$

is measured in a time-dependent Stokes shift experiment. The peak shift is used to probe the solvation dynamics in three-pulse photon-echo experiments [1,2]. In Eq. (2) the time-dependent fluorescence frequency is given by

$$\hbar\omega(t) = \hbar\omega_0 + \Delta E(t). \quad (3)$$

Here, $\hbar\omega_0 = H_e^{(0)} - H_g^{(0)}$ is the gas phase frequency shift, and $\Delta E(t)$ is the solvation energy change due to the charge distribution change between the two electronic states. As such, the solvation correlation function can be rewritten in terms of the time variation of the solvation energy,

$$S(t) = \frac{\Delta E(t) - \Delta E(\infty)}{\Delta E(0) - \Delta E(\infty)}. \quad (4)$$

To estimate the time-dependent solvation energy change we assume that the solvent-solute interactions, H_{gs} and H_{es} , differ only in so far as the charge distributions of the ground and excited states differ. In that case,

$$\Delta E(t) = -\frac{1}{2} \int d\mathbf{r} \mathbf{P}(\mathbf{r}, t) \cdot \Delta \mathcal{E}(\mathbf{r}, t), \quad (5)$$

where $\Delta \mathcal{E}(\mathbf{r}, t) = \theta(t)\Delta \mathcal{E}(\mathbf{r})$ with $\Delta \mathcal{E}(\mathbf{r})$ denoting the change in electric field due to the instantaneous change in charge distribution of the solute at time zero, and $\mathbf{P}(\mathbf{r}, t)$ is the subsequent induced polarization of the solvent. According to linear response theory [16]

$$\mathbf{P}(\mathbf{r}, t) = \int_0^t dt' \int d\mathbf{r}' \chi^{(m)}(\mathbf{r}, \mathbf{r}'; t - t') \cdot \Delta \mathcal{E}(\mathbf{r}', t') \quad (6)$$

where $\chi^{(m)}(\mathbf{r}, \mathbf{r}'; t)$ is the susceptibility tensor of the solution. Thus, to the extent that the linear response description is valid, the solvation energy change can be expressed as

$$\Delta E(t) = -\frac{1}{2} \int_0^t dt' \int d\mathbf{r} \int d\mathbf{r}' \Delta \mathcal{E}(\mathbf{r}, t) \cdot \chi^{(m)}(\mathbf{r}, \mathbf{r}'; t - t') \cdot \Delta \mathcal{E}(\mathbf{r}', t'). \quad (7)$$

Its Fourier-Laplace transform is

$$\begin{aligned} \Delta \tilde{E}(z) &= \int_0^\infty e^{izt} \Delta E(t) \\ &= \frac{1}{2iz} \int d\mathbf{r} \int d\mathbf{r}' \Delta \mathcal{E}(\mathbf{r}) \cdot \tilde{\chi}^{(m)}(\mathbf{r}, \mathbf{r}'; z) \cdot \Delta \mathcal{E}(\mathbf{r}'), \end{aligned} \quad (8)$$

where z is a complex variable.

The time-dependent solvation energy change $\Delta E(t)$ can be related to the dielectric susceptibility, $\tilde{\chi}^{(m)}(\mathbf{r}, \mathbf{r}'; \omega)$, which is the response function of the solution as *modified* by the presence of the solute (hence the superscript m). In fact, using the

inverse transform of $\Delta\tilde{E}(z)$ and the analyticity of the response function [17] we have

$$\begin{aligned}\Delta E(t) &= \frac{1}{2\pi} \int_C dz e^{-izt} \Delta\tilde{E}(z) \\ &= \frac{1}{4} \int d\mathbf{r} \int d\mathbf{r}' \Delta\mathcal{E}(\mathbf{r}) \cdot [\tilde{\chi}^{(m)'}(\mathbf{r}, \mathbf{r}'; 0) - \tilde{\chi}^{(m)'}(\mathbf{r}, \mathbf{r}'; \infty)] \cdot \Delta\mathcal{E}(\mathbf{r}') \\ &\quad - \frac{1}{2\pi} \int_0^\infty d\omega \cos(\omega t) \int d\mathbf{r} \int d\mathbf{r}' \Delta\mathcal{E}(\mathbf{r}) \cdot \frac{\tilde{\chi}^{(m)''}(\mathbf{r}, \mathbf{r}'; \omega)}{\omega} \cdot \Delta\mathcal{E}(\mathbf{r}'),\end{aligned}\quad (9)$$

where ω is the frequency and $\tilde{\chi}^{(m)''}(\mathbf{r}, \mathbf{r}'; \omega)$ is the imaginary part of the dielectric susceptibility. $\tilde{\chi}^{(m)'}(\mathbf{r}, \mathbf{r}'; 0)$ and $\tilde{\chi}^{(m)'}(\mathbf{r}, \mathbf{r}'; \infty)$ are the real parts of the dielectric susceptibility at frequencies zero and infinity respectively. The symbol 'C' under the integral sign denotes the integration contour of the inversion. Therefore, once the dielectric susceptibility function is known at different frequencies the time-dependent solvation energy change $\Delta E(t)$ can be obtained from Eq.(9).

The modified response function generally differs from that of the pure solvent, $\tilde{\chi}(\mathbf{r}, \mathbf{r}'; \omega)$. A conventional way to estimate $\tilde{\chi}^{(m)}(\mathbf{r}, \mathbf{r}'; \omega)$ in terms of $\tilde{\chi}(\mathbf{r}, \mathbf{r}'; \omega)$ is to assume that the solvent outside the volume occupied by the solute remains the same as the bulk solvent, namely, behaves like an unperturbed pure isotropic solvent. The only effect of the solute is on the volume of the integration in Eq.(8). This assumption is the "uniform" or "homogeneous" dielectric approximation used in many solvation dynamics theories; see, for example, discussions of this and alternative approximations in Refs. [9] and [10]. We have shown that this approximation is generally not accurate because the existence of the solute significantly affects dipole-dipole correlations outside the excluded volume [12].

Employing a Gaussian field model of solvation, we are able to derive a general relation between the modified response function $\tilde{\chi}^{(m)}(\mathbf{r}, \mathbf{r}'; \omega)$ and the pure solvent $\tilde{\chi}(\mathbf{r}, \mathbf{r}'; \omega)$ [12],

$$\begin{aligned}\chi^{(m)}(\mathbf{r}, \mathbf{r}'; \omega) &= \chi(\mathbf{r}, \mathbf{r}'; \omega) \\ &\quad - \iint_{\text{in}} d\mathbf{r}'' d\mathbf{r}''' \chi(\mathbf{r}, \mathbf{r}''; \omega) \cdot \chi_{\text{in}}^{-1}(\mathbf{r}'', \mathbf{r}'''; \omega) \cdot \chi(\mathbf{r}''', \mathbf{r}'; \omega).\end{aligned}\quad (10)$$

The 'in' labeling the integration symbol means the integration is limited to the region occupied by the solute and from which the solvent dipole density is expelled. The inverse of the 'in' matrix, $\chi_{\text{in}}^{-1}(\mathbf{r}, \mathbf{r}'; \omega)$, is defined as

$$\int_{\text{in}} d\mathbf{r}'' \chi_{\text{in}}^{-1}(\mathbf{r}, \mathbf{r}''; \omega) \cdot \chi_{\text{in}}(\mathbf{r}'', \mathbf{r}'; \omega) = \delta(\mathbf{r} - \mathbf{r}')\mathbf{I},\quad (11)$$

where \mathbf{I} is the 3×3 identity matrix associated with the Cartesian coordinates of a three-dimensional system, and $\chi_{\text{in}}(\mathbf{r}, \mathbf{r}'; \omega)$ is $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ when both \mathbf{r} and \mathbf{r}' are within the 'in' region, and is zero otherwise.

If the pure solvent response function $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ and the region occupied by the solute are known, the solvation correlation function $S(t)$ can be calculated from

Eqs.(3),(9) and (10). Before a theory of $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ is presented, we show that all linear and non-linear spectroscopic signals can be calculated given the above information as long as the solvent obeys linear response.

If the solvent treated as a dielectric medium obeys linear response, the dielectric response of the solvent can be described phenomenologically by a harmonic bath [18]. The Hamiltonian of the solvent assumes the following form [19]:

$$H_s = \frac{1}{2} \sum_i \hbar \omega_i [p_i^2 + q_i^2], \quad (12)$$

and

$$\Delta H = H_e - H_g = \hbar \omega_0 + \frac{1}{2} \sum_i \hbar \omega_i [2q_i d_i + d_i^2], \quad (13)$$

where H_s is the effective harmonic bath of the solvent with dimensionless momentum p_i and coordinate q_i for a mode at frequency ω_i . ΔH is related to the shifted harmonic bath by d_i for mode i due to the interaction with the solute in two different electronic states. As usual, the spectral density is defined as

$$\rho(\omega) = \frac{1}{2} \sum_i d_i^2 \delta(\omega - \omega_i). \quad (14)$$

Given this spectral density, all of the signals from laser spectroscopy experiments can be calculated from the usual line broadening function [19], $g(t)$,

$$\begin{aligned} g(t) &= g'(t) + ig''(t) \\ g'(t) &= \int_0^\infty d\omega (1 - \cos \omega t) \coth\left(\frac{\beta \hbar \omega}{2}\right) \rho(\omega) \\ g''(t) &= \int_0^\infty d\omega \rho(\omega) \sin \omega t. \end{aligned} \quad (15)$$

Furthermore, the reorganization energy is related to the spectral density as

$$\lambda = \int_0^\infty d\omega \rho(\omega) \omega. \quad (16)$$

From Eq.(9), the reorganization energy can also be written as

$$\begin{aligned} \lambda &= \Delta E(0) - \Delta E(\infty) \\ &= \frac{1}{2\pi} \int_0^\infty d\omega \int d\mathbf{r} \int d\mathbf{r}' \Delta \mathcal{E}(\mathbf{r}) \cdot \frac{\tilde{\chi}^{(m)''}(\mathbf{r}, \mathbf{r}'; \omega)}{\omega} \cdot \Delta \mathcal{E}(\mathbf{r}'). \end{aligned} \quad (17)$$

Combining Eqs.(16) and (17) we have

$$\rho(\omega) = \frac{1}{2\pi} \frac{\Delta E''(\omega)}{\omega}, \quad (18)$$

where the imaginary part of the solvation energy (cf Eq.(9)) is

$$\Delta E''(\omega) = \int d\mathbf{r} \int d\mathbf{r}' \Delta \mathcal{E}(\mathbf{r}) \cdot \frac{\tilde{\chi}^{(m)''}(\mathbf{r}, \mathbf{r}'; \omega)}{\omega} \cdot \Delta \mathcal{E}(\mathbf{r}'). \quad (19)$$

This expression has been derived in various contexts for different specific models of the solute [20]. Thus, the calculation of the spectral density is reduced to the calculation of the solvent response function and the solute properties, such as its molecular shape and the electric field change from the ground electronic state to the excited one. From Eqs.(3), (9) and (18) the solvation correlation function can also be written in terms of the spectral density

$$S(t) = \frac{1}{\lambda} \int_0^\infty d\omega \omega \rho(\omega) \cos(\omega t). \quad (20)$$

Now we turn to the theory of the solvent dielectric response for a complete theory of solvation dynamics.

III A DYNAMICAL DIELECTRIC CONTINUUM MODEL OF SOLVATION DYNAMICS

To illustrate the use of the formulation of last section, a theory for $\tilde{\chi}(\mathbf{r}, \mathbf{r}'; \omega)$ is required. For this purpose, we use the simplest, suitably generalized, text book model of a dielectric material [21]. In particular, we imagine that the space is divided into a cubic grid of N polarizable cells. Each cell has volume $v = a^3$, where a is the length of the cell such that the dipole of a cell follows Gaussian statistics. The instantaneous dipole of the cell at discrete position \mathbf{r} is $\mathbf{m}_{\mathbf{r}}(\tau) = \mathbf{m}(\mathbf{r}, \tau)v$, where $\mathbf{m}(\mathbf{r}, \tau)$ is the dipole density at position \mathbf{r} and Euclidean time τ . In this reduced description, the polarizability $\alpha(\tau)$ of each cell is non-local in time, but constant in space, and different cells interact via dipole-dipole interactions. The action of the system can be written as

$$S[\mathbf{m}_{\mathbf{r}}(\tau)] = \frac{\beta}{2} \int_0^{\beta\hbar} \frac{d\tau}{\beta\hbar} \int_0^{\beta\hbar} \frac{d\tau'}{\beta\hbar} \sum_{\mathbf{r}} \alpha^{-1}(\tau - \tau') \mathbf{m}_{\mathbf{r}}(\tau) \cdot \mathbf{m}_{\mathbf{r}}(\tau') - \frac{\beta}{2} \int_0^{\beta\hbar} \frac{d\tau}{\beta\hbar} \sum_{\mathbf{r} \neq \mathbf{r}'} \mathbf{m}_{\mathbf{r}}(\tau) \cdot \mathbf{T}_{\mathbf{r}, \mathbf{r}'} \cdot \mathbf{m}_{\mathbf{r}'}(\tau), \quad (21)$$

where $\beta = 1/k_B T$ and T is temperature. $\mathbf{T}_{\mathbf{r}, \mathbf{r}'}$ is the dipole-dipole interaction tensor given by

$$\mathbf{T}_{\mathbf{r}, \mathbf{r}'} = 3 \frac{(\mathbf{r} - \mathbf{r}')(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^5} - \frac{\mathbf{I}}{|\mathbf{r} - \mathbf{r}'|^3}. \quad (22)$$

Using the spatial Fourier transform and an analytical continuation from Matsubara frequency to the real frequency ω , this model can be solved under the continuum limit [22,23,12]. The response function $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ is given by

$$\chi(\mathbf{r} - \mathbf{r}'; \omega) = \frac{\epsilon(\omega) - 1}{4\pi\rho\epsilon(\omega)} \left[\frac{2\epsilon(\omega) + 1}{3} \delta(\mathbf{r} - \mathbf{r}') \mathbf{I} + \frac{\epsilon(\omega) - 1}{4\pi\rho} \mathbf{T}_{\mathbf{r},\mathbf{r}'} \right], \quad (23)$$

where the dielectric constant $\epsilon(\omega)$ is related to the dimensionless polarizability $y(\omega) = 4\pi\alpha(\omega)/3v$ through Clausius-Mossotti equation,

$$\frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2} = y(\omega). \quad (24)$$

$\delta(\mathbf{r} - \mathbf{r}')$ is the usual Dirac delta-function and $\rho = 1/v$. Under the continuum limit, the dielectric response is completely specified by the dielectric constant function $\epsilon(\omega)$, which can be obtained from experiments.

Now apply the above pure solvent response function to our theory of solvation dynamics formulated in Sec. II. Consider a charge distribution change created at time $t = 0$ inside a dielectric cavity due to the solute. The Fourier-Laplace transform of the time dependent solvation energy change [13] is

$$\Delta E(\omega) = -\frac{1}{\omega} \sum_{\mathbf{r}_i, \mathbf{r}_j} \oint_S da_{\mathbf{R}} q_i \sigma(\mathbf{r}_i, \mathbf{R}; \omega) \frac{q_j}{|\mathbf{R} - \mathbf{r}_j|}, \quad (25)$$

where \mathbf{r}_i is the position of the i th charge, q_i . And $da_{\mathbf{R}}$ is the normal area element at position \mathbf{R} of the surface S . The surface charge $\sigma(\mathbf{r}, \mathbf{R}; \omega)$ satisfies the following integral equation:

$$\begin{aligned} \sigma(\mathbf{r}, \mathbf{R}_0; \omega) - \frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 1} \frac{1}{2\pi} \oint_S da_{\mathbf{R}} \sigma(\mathbf{r}, \mathbf{R}; \omega) \nabla_n \frac{1}{|\mathbf{R} - \mathbf{R}_0|} \\ - \frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 1} \frac{1}{2\pi} \nabla_{\mathbf{n}_0} \frac{1}{|\mathbf{r} - \mathbf{R}_0|} = 0, \end{aligned} \quad (26)$$

where $\nabla_{\mathbf{n}_0}$ denotes the outward normal gradient at \mathbf{R}_0 . The spectral density of the system follows from Eq.(18) by taking the imaginary part of $\Delta E(\omega)$.

In general, the formulation of this section is not confined to the continuum theory of a non-ionic dielectric. For example, in place of Eq.(23), one may use a response function matrix appropriate to a homogeneous ionic solution. Short length scales with molecular detail could also be included. Equation (26) could be written, but the integral equation for $\sigma(\mathbf{r}, \mathbf{r}'; \omega)$ will be modified due to the features in $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ referring to ionic strength and molecular detail. For the applications given in this paper, however, we confine ourselves to the case of a non-ionic dielectric continuum solvent.

IV COMPARISON WITH ULTRAFAST SPECTROSCOPY EXPERIMENTS

We now discuss how to solve the integral Eq.(26) numerically and combine it with Eq.(18) to calculate the spectral density of a charge distribution inside a dielectric

cavity spanned by the solute. Comparisons with experiments are made for four experimental systems: the solvation correlation functions of coumarin 343⁻ (C343⁻) in water [24], coumarin 153 (C153) in methanol and C153 in acetonitrile [25] measured by time-dependent Stokes shift experiments and the peak shift of eosin in water measured by three-pulse photon-echo experiments [14].

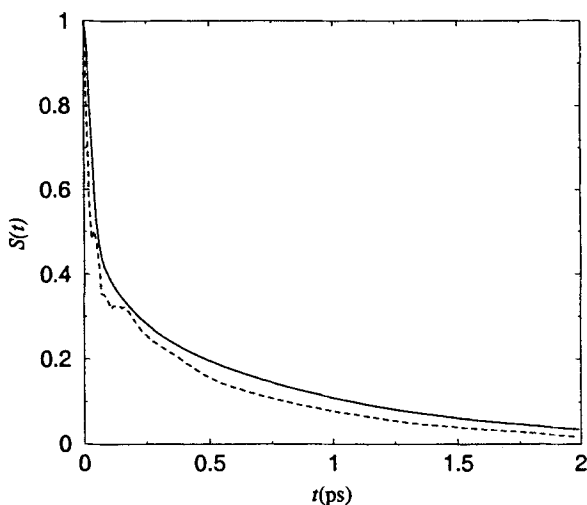


Figure 1. The comparison of the solvation correlation function between theory and experiments for C343⁻ in water. The solid curve is from experiments [24], the dashed curve is from our calculation. The dielectric data are from Ref. [26].

The numerical method to solve the integral Eq.(26) over a surface is based on collocation methods by Atkinson and coworkers [27]. Basis functions prescribed in Ref. [27] are set up over the surface by triangulation, and the integral equation is converted to a system of linear equations. Then, the spectral density of the system can be calculated. For a molecule like C343⁻, we use the Lee and Richards molecular surface [28], and triangulation over this surface is done by Zauhar's method [29]. The van der Waals radii of the atoms are taken from the CHARMM parameter package [30]. The atomic charge distribution and its change due to electronic excitation of C343⁻, C153 and eosin are obtained from electrostatic fits to semi-empirical MNDO wave-functions [31] calculated using the AMPAC program package. The frequency dependent dielectric constant functions of various solvents, $\epsilon(\omega)$, are taken from Refs. [26,32]. With this information, the solvation correlation function can be obtained from Eq.(20). The results are shown in Figs.1-3. It is clear that all of the major features observed in experimental results, the initial inertial decay and the multiple exponential long time relaxation, are reproduced almost quantitatively by these calculations.

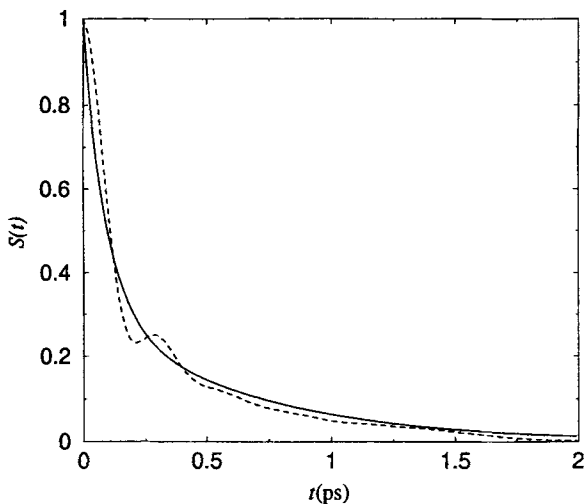


Figure 2. The comparison of the solvation correlation function between theory and experiments for C153 in acetonitrile. The solid curve is from experiments [25], the dashed curve is from our calculation. The dielectric data are from Ref. [32].

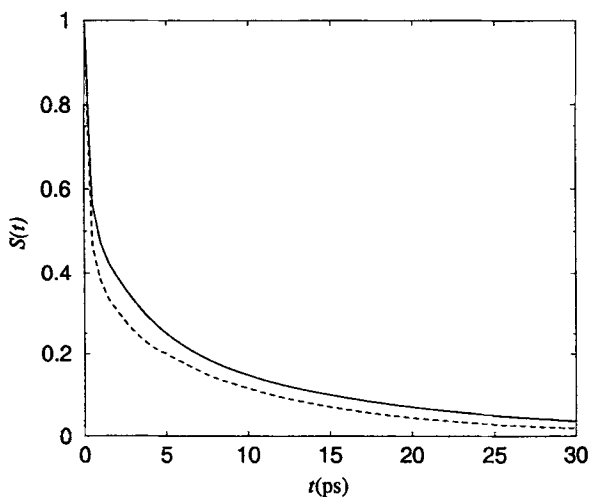


Figure 3. The comparison of the solvation correlation function between theory and experiments for C153 in methanol. The solid curve is from experiments [25], the dashed curve is from our calculation. The dielectric data are from Ref. [32].

For the photon-echo experiment, combining the spectral density calculations described above and the experimental laser pulse width, the peak shift of the echo signal can be obtained [14]. The comparison with experiments is shown in Fig. 4.

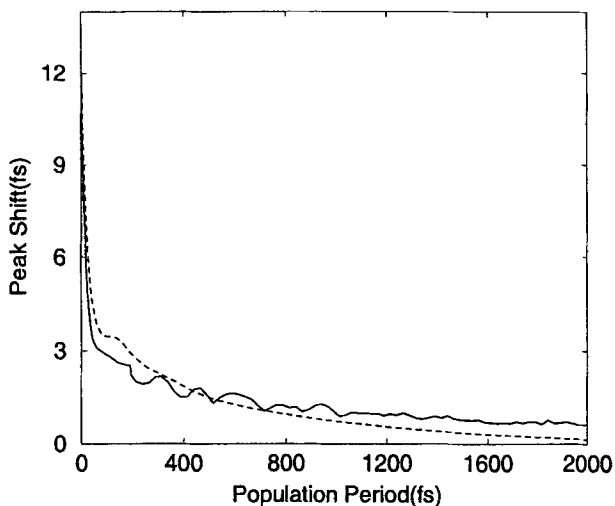


Figure 4. The comparison of the three-pulse photo-echo peak shift between theory and experiments for eosin in water. The solid curve is from experiments [14], the dashed curve is from our calculation. The first point of the calculated peak shift data is normalized to the experimental first point. The dielectric data are from Ref. [26].

Without the contribution of intramolecular vibrations, we were able to capture almost all of the features of the experimental results. Especially, the low-frequency hindered translation band (180 cm^{-1}) resulting from dipole-induced-dipole interactions in water is responsible for the sudden change in the slope of the peak shift between 40 and 80 fs. If the intramolecular vibrational modes contribution is accounted for, the oscillatory features in the peak shift can be simulated almost quantitatively [14].

V CONCLUDING REMARKS

In this report, we briefly reviewed our effort to develop a theory of solvation dynamics from solute properties and experimentally accessible dielectric constant functions of solvents. With this formulation, we have derived a practical algorithm to calculate the spectral density of the system for an arbitrary charge distribution in a dielectric cavity with realistic molecular shape.

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