Three pulse stimulated photon echo experiments as a probe of polar solvation dynamics: Utility of harmonic bath models

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I. INTRODUCTION

The interaction of a solute with its solvent bath is often modeled via a Hamiltonian in which the bath is represented by a set of harmonic oscillators which are linearly coupled to the electronic transition of the solute. The multimode Brownian oscillator is one such model, as is the equivalent spin boson approach. The system dynamics can be described by means of spectral density,

$$\rho(\omega) = \sum_a \frac{c_a^2}{2m_a\omega_a^2} \delta(\omega - \omega_a),$$

where \(c_a^2/(2m_a\omega_a^2)\) is the displacement of the \(a\)th mode. The spectral density, \(\rho(\omega)\), captures both the frequency distribution of the oscillators and the strength of coupling of the oscillators to the observable; for instance, the optical transition frequency. The linearly coupled harmonic bath model has found most use in the analysis of nonlinear spectroscopic measurements. In a parallel development, much progress has been made over the past decade in developing molecular descriptions of the dynamics of polar solvation with particular reference to time-dependent fluorescence Stokes shift studies. These models, including the simple continuum model which works quite well when appropriate high-frequency dielectric data are included, are intrinsically anharmonic in nature.

There are several ways to regard the spectral density obtained from experiment, simulation, or theory. The most literal reading is that the oscillators represent the actual motions of the system, and thus the spectral density, \(\rho_{INM}(\omega)\) (or influence spectrum in the terminology of Stratt), is simply the actual density of states weighted by the coupling constants of the individual modes. This approach is taken in the instantaneous normal mode (INM) model. It appears to provide a reasonable description of the ultrafast solvation dynamics in room temperature acetonitrile. However, in the harmonic INM model the solvation time correlation function, \(S(t)\), does not decay to zero and thus \(\rho_{INM}(\omega)\) cannot, at present, describe long time solvation dynamics.

A second approach is to regard the spectral density, \(\rho_{HO}(\omega)\), as simply representing a basis set for the dynamics. In this case, the domain of validity might be expected to extend to significantly longer times than when \(\rho_{INM}(\omega)\) is used, since there is no requirement for modes to retain their identity or even directly represent the actual motions of the bath nuclei. Thus this model appears to be an extremely flexible approach. However, once one considers transferring the spectral density to other systems or circumstances, for example, to different temperatures, the issue of whether the
II. THEORETICAL BACKGROUND

A. General background

The basis of the 3PEPS experiment has been described in detail elsewhere, and only a brief sketch of the background will be given here. The key quantity involved is the system bath coupling potential \( V_{SB} \{ q_a \}, Q \) which is a function of both bath \( \{ q_a \} \) and system \( Q \) coordinates. We partition \( V_{SB} \) into an average component and a fluctuating component

\[
\delta V_{SB}(t) = V_{SB}(t) - \langle V_{SB} \rangle. \tag{1}
\]

Now, both linear and nonlinear spectroscopies are calculated from the line broadening function which is most generally defined as

\[
g(t) = \int_0^\infty d\tau (\delta V_{SB}(\tau') \delta V_{SB}(0)) - \langle \delta V_{SB}(\tau') \delta V_{SB}(0) \rangle, \tag{2}
\]

where \( \delta V_{SB}(t) \) is the Heisenberg operator of \( \delta V_{SB} \). In general, the single sided correlation function, \( \langle \delta V_{SB}(t) \delta V_{SB}(0) \rangle \), is complex, and is expressible in terms of the antisymmetrized correlation function, \( G(t) \), which is defined as

\[
G(t) = \frac{i}{\hbar} \langle [\delta V(t), \delta V(0)] \rangle, \tag{3}
\]

and the symmetrized correlation function, \( C(t) \), which is

\[
C(t) = \frac{1}{\hbar} \langle [\delta V(t), \delta V(0)] \rangle. \tag{4}
\]

In terms of the spectral density, the line shape function is

\[
g(t) = -\frac{i\lambda t}{\hbar} + \int_0^\infty d\omega \rho(\omega) \coth \left( \frac{\hbar \omega}{2} \right) (1 - \cos \omega t)
+ i \int_0^\infty d\omega \rho(\omega) \sin \omega t, \tag{5}
\]

where \( \lambda \) is the reorganization energy defined as the first moment of the spectral density

\[
\lambda = \hbar \int_0^\infty d\omega \omega \rho(\omega), \tag{6}
\]

and \( \beta = 1/k_B T \).

Linear and nonlinear optical spectroscopic signals can be calculated via Eq. (5). For example, the absorption spectrum profile is given by

\[
\sigma_\lambda(\omega) = \text{Re} \left[ \int_0^\infty dt \exp(-i(\omega - \omega_{eg})t) \exp[-g(t)] \right], \tag{7}
\]

with \( \omega_{eg} \) being the 0'–0'' vibronic transition frequency, and third-order nonlinear spectroscopy are calculated via the response functions \( R_1 \sim R_8 \). Two equivalent models for the coupling potential operators have been used: the Brownian oscillator model and the harmonic bath model. In a following section, we derive a relationship between various models of solvation and the spectral density. New coupling

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potential operators are proposed which are generated from intrinsically anharmonic potential energy surfaces of the relevant nuclear degrees of freedom. In any case, a spectral density representation is able to represent an arbitrary bath model. In other words, all the strengths and time scales of the system-bath interaction are contained in the function $\rho(\omega)$.

Echo signals are most often discussed in terms of the harmonic Bohr frequency correlation function, $M(t)$, defined as

$$M(t) = \frac{\langle \Delta \omega(t) \Delta \omega(0) \rangle}{\langle \Delta \omega^2 \rangle} = \frac{1}{\langle \Delta \omega^2 \rangle} \int_0^\infty d\omega \, \omega^2 \rho(\omega) \coth \left( \frac{\hbar \beta \omega}{2} \right) \cos \omega t, \quad (8)$$

where $\langle \Delta \omega^2 \rangle$, the mean square fluctuation amplitude, is commonly referred to as the coupling strength

$$\langle \Delta \omega^2 \rangle = \int_0^\infty d\omega \, \omega^2 \rho(\omega) \coth \left( \frac{\hbar \beta \omega}{2} \right). \quad (9)$$

In Eq. (8), the real, or symmetrized, part of $\langle \Delta \omega(t) \Delta \omega(0) \rangle$ defines $M(t)$. Note that for a temperature independent $\rho(\omega)$, the only temperature dependence in the dynamics arises from the hyperbolic cotangent term [Eqs. (5), (8), and (9)].

Fluorescence Stokes shift studies are characterized by the Stokes shift function $S(t)$ defined as

$$S(t) = \frac{\Delta \overline{E}(t) - \Delta \overline{E}(\infty)}{\Delta \overline{E}(0) - \Delta \overline{E}(\infty)}, \quad (10)$$

where $\Delta \overline{E}(t)$ is the nonequilibrium energy difference between ground and excited states. In terms of the spectral density, $S(t)$ corresponds to the time dependence of the first moment of $\rho(\omega)$ (i.e., the time-dependent reorganization energy):

$$S(t) = \frac{\hbar}{\lambda} \int_0^\infty d\omega \omega \rho(\omega) \cos \omega t. \quad (11)$$

Note that Eqs. (8) and (11) are equivalent in the high-temperature limit resulting in

$$\langle \Delta \omega^2 \rangle = \frac{2\lambda k_B T}{\hbar^2}. \quad (12)$$

B. Spectral densities from various models of polar solvation

In Sec. V, we compare our experimental 3PEPS results to numerical simulations which used spectral densities obtained from SC, DMSA, and XRISM models of polar solvation. The observable in each model is the relaxation of the solvation energy, which is assumed to be the electrostatic interaction between the solute and the solvent. That is, the spatially fixed solute acquires a change in the multipole magnitude, but not direction, at time=0, and the response of the solvent to this perturbation results in the solvation energy relaxation. A detailed discussion of the more complex (and more realistic) XRISM model of Raineri and Friedman is beyond the scope of this paper. Briefly, the fluctuating polarization charge density of the solvent is related to the fluctuating vertical energy gap through a "surrogate" electrical potential field that drives the solvent relaxation. The beauty of this theory results from the ability to obtain equilibrium (ground or excited state) structural information through solute-solvent site-site correlation functions. For XRISM model spectral densities we started with time correlation functions provided to us by Raineri and Friedman, and used Eq. (11) to obtain $\rho_{XRISM}$.

Both SC and DMSA models treat the solute as a stationary nonpolarizable sphere which contains a centered multipole. The solvents' properties enter through the frequency and wave vector-dependent complex relative permittivities, $\epsilon(k,\omega) = \epsilon'(k,\omega) - i \epsilon''(k,\omega)$, where $\epsilon'(k,\omega)$ and $\epsilon''(k,\omega)$ represent the dispersive and dissipative couplings of the electric field to its electric displacement. $\epsilon(k,\omega)$ is assumed to be known through experiment or theory. For the SC model, the solvent is assumed to be a dielectric continuum completely described by $\epsilon(k=0,\omega)$; hence, the SC model is a macroscopic model of solvation. For the microscopic DMSA model, the solvent is treated as a hard sphere fluid, and even the size of the solute may be incorporated into the DMSA model. We loosely refer to the SC and DMSA models as susceptibility models of solvation, because, with the above assumptions, the Laplace transform of $S(t)$, $L^{-1}[S(t)]$, is a function of susceptibilities which are functions of the complex relative permittivities, i.e.,

$$L^{-1}[S(t)] = \int d^3k \frac{[\chi(\epsilon(k,0)) - \chi(\epsilon[k,\omega])]}{i\omega[\chi(\epsilon[k,\omega]) - \chi(\epsilon[k,\infty])]}.$$  

Comparing Eqs. (13) and (14) results in

$$\frac{\hbar \pi \omega^2 \rho_{SM}(\omega)}{2\lambda} = \text{Im} \left[ \int d^3k \frac{[\chi(\epsilon(k,0)) - \chi(\epsilon[k,\omega])]}{[\chi(\epsilon[k,\infty]) - \chi(\epsilon[k,0])]} \right].$$  

and constitutes the main result of this section. The subscript SM, emphasizes the susceptibility model origin of the spectral density. Both $\rho_{SM}$ and $\rho_{XRISM}$ are intrinsically anharmonic in nature, temperature dependent, and independent of harmonic bath models.

As noted by Marcus and Sutin, the assumption that the dielectric polarization responds linearly is much less drastic than the assumption that the potential energy of the solvent molecules is a quadratic function of their coordinates. From Eqs. (3) and (4), the line shape function in Eq. (2) is expressible as

$$g(t) = \frac{1}{2\hbar} \int_0^\tau d\tau' \int_0^\tau d\tau'' (C(\tau') - iG(\tau')).$$  

In general, the quantum fluctuation-dissipation theorem, which was used to generate the line shape dissipation function in Eq. (5), requires a complete knowledge of the spectral density function to relate $C(t)$ to $G(t)$ or visa versa. In the high-temperature limit, which applies to classical systems and for all of our spectral densities discussed in this manuscript, $G(t)$ and $C(t)$ are related by a simple time derivative and temperature is the only parameter determining the classical fluctuation-dissipation relationship. Therefore, using the spectral densities from various models of solvation avoids the assumption that the potential energy of the solvent molecules $V_{SM}(q_{s},Q)$ is a quadratic function of their coordinates, as was assumed in the Hamiltonian of the MBO and INM models.

The solute could have any multipole, but we will confine our discussion to the ionic (‘‘i’’) or dipole (‘‘d’’) solutes. The SC-i, SC-d, DMSA-i, and DMSA-d susceptibility models of solvation have analytic $\chi(\varepsilon[k,\omega])$. Hence, we could obtain an analytic expression for $\rho(\varepsilon[k,\omega])$ for these susceptibility models; however, this provides little physical insight. The fastest route to a spectral density is to generate $S(t)$ by solving Eq. (13), and then use Eq. (11) to obtain the spectral density. Now the line shape function, $g(t)$, is generated via Eq. (5) and from this line and nonlinear optical signals without assuming a harmonic bath model. Figure 1 shows a flowchart of our calculation procedure. For our $\rho_{SM}$, we used experimentally determined $\varepsilon[k=0,\omega]$ as input for Eq. (13). The manipulation of $\varepsilon[k=0,\omega]$ to generate $S(t)$ is essentially the same as described by Horng et al. For completeness, this procedure is outlined in the Appendix. Additionally, we assume only the continuum limit ($k=0$). Hence, the integration over $k$ space in Eq. (15) was not required for spectral densities in this manuscript.

III. EXPERIMENTAL APPARATUS

A cavity-dumped Kerr lens mode-locked Ti:sapphire laser operating at a center wavelength of 780 nm generated 22 fs nearly transform-limited pulses at $\sim 250$ kHz. The laser output was split into three roughly equal power rectilinear beams with parallel polarization, and aligned in an equilateral triangle with each side about 8 mm to enable simultaneous detection of two equally phase matched integrated three pulse photon echo (3PE) signals (see Fig. 2). Two of three beams were independently delayed by stepper motor driven translation stages. We refer to the delay between the first two pulses as $\tau$, and the delay between the second and third pulse, which remained constant throughout the 3PE scan, as $T$. $T$ is sometimes called the population period, because during this interval the system propagates via a diagonal (ground and excited state) density matrix. All beams were focused by a 10-cm singlet lens onto the sample, which was circulated ($\sim 2$ mL/s) through a 0.1-mm quartz flow cell. The pulse energy before the antireflection coated lens never exceeded 200 pJ for each beam to avoid undesirable effects such as thermal grating and other higher order phenomena. Additionally, the repetition rate of the laser was varied between 20 kHz and 253 kHz; this did not affect the peak shifts.

The time-reversed image 3PE signals at $k_{1}-k_{3}+k_{3}$ and $-k_{1}+k_{2}+k_{3}$ ($B$ and $B'$ in Fig. 2, respectively) were spatially filtered, imaged onto separate 10-ns rise-time photodiodes, and detected over the period $t=-\infty$ to $\infty$. Three typical integrated 3PE signals with different population periods are shown in Fig. 3 for 1R144 in benzonitrile, with the circles and triangles representing $B'$ and $B$, respectively. The integrated echo signals are quite symmetric and were fit to Gaussian functions. Half the separation of the center of the two fitted Gaussians accurately specifies the delay of the echo signal from zero delay on the $\tau$ axis. This quantity, $\tau^{\#}(T)$, is the primary variable of interest here; measurement of $\tau^{\#}$ for a series of different values of $T$, the population period, constitutes what we have called a 3PEPS measurement. The experimental reproducibility of peak shift values is $\pm 0.3$ fs. About 80 sets of $\tau$ scans for differing values of $T$ are used to construct a typical 3PEPS data set. The maximum value of $T$ was typically 300–500 ps, because of the relatively short $S_1$ population lifetime of 1R144 ($\sim 600$ ps) and the modulus squared nature of the 3PE signal.

We expect no static inhomogeneity for systems with solvents like methanol, acetonitrile, and ethylene glycol, since the longest dielectric relaxation time (vide infra Table IV)
much shorter than our experimental timescale (300–500 ps). Therefore, we expect the long time value of \( \tau^* \), \( \tau^*(\infty) \), to be zero. However, use of the 10-cm singlet focusing lens results in a small (~1.5 fs) value of \( \tau^*(T) \) at large values of \( T \) where the signal is constant. Using a 20-cm achromatic lens reduces \( \tau^*(\infty) \) to zero, suggesting the finite asymptotic value is an artifact and results either from chromatic aberration and/or the larger crossing angle in the 10-cm case. Nevertheless, the 3PEPS relaxation is the same when measured with either lens. Since all of the data discussed here were collected with a 10-cm singlet lens, the constant long time value was subtracted from each individual \( \tau^*(T) \) vs \( T \) curve to make the final value zero, as is expected for systems with no dynamical timescales longer than a few tens of ps.

IR144, acetonitrile, benzonitrile, methanol, and ethylene glycol were used as received from the Exciton Company or Aldrich Company. Experiments were conducted at ambient temperatures of approximately 297 K unless otherwise noted. For temperatures above 297 K, the solutions were purged with dry nitrogen gas and the temperature was measured by a copper-constantan thermocouple located at the outlet of the flow cell. Peak sample o.d.s of approximately 1, as determined by an absorption spectra obtained from a Shimadzu UV-1601 UV-visible spectrophotometer, were typical. The absorption spectra of heated samples were identical before and after cooling.

IV. RESULTS

A. 3PE

From sets of measurements of the type shown in Fig. 3, the peak shift \( \tau^*(T) \) is constructed as a function of \( T \). 3PEPS data discussed in this work were collected for IR144 in the following solvents and temperatures: methanol at 297 and 323 K, ethylene glycol at 297 and 397 K, acetonitrile at 297 K. \( \tau^*(T) \) scans for the protic solvents are shown in Fig. 4. In all cases, the peak shift decreases by ~75% in the first 0.2 ps. Weak oscillations (clearly evident at 0.19 ps) result from intramolecular vibrational modes of IR144. On the picosecond timescale, where \( \tau^*(T) \) corresponds directly to the solvation dynamics, the differences between the solvents become strikingly clear.

We fit the peak shift data to sums of exponentials, because this procedure gives time constants directly related to the solvation correlation function for population times longer than the bath correlation time which is about 0.3 ps for our systems. The shortest timescales (i.e., those less than the bath correlation time) do not correspond to time scales in the underlying correlation function and appear exponential in the peak shift curve even if they are, for example, Gaussian in \( S(t) \). There are three distinct phases in the decay of \( \tau^*(T) \) in all cases: (1) an initial very rapid decay arising from intramolecular vibrations giving a component of ~6 fs; (2) an ~60-fs component which we believe arises mainly from the inertial component of solvation; (3) picosecond timescale components that vary significantly from solvent to solvent. In the case of acetonitrile the picosecond region can be fit by a single exponential component; methanol and ethylene glycol at 397 K can be resolved into two exponential decays; and ethylene glycol at 297 K can be resolved into three exponential decays. Since intramolecular vibrational contributions of the solute to the dynamics are not of concern here, Table I presents exponential fits to the peak shift data with the fastest component removed.

In contrast to the slower timescales, noted above, the fastest timescales (<~0.1 ps) are not directly related to the solvent correlation function. Following the discussion of Joo et al., we note that the amplitude of the inertial component is overestimated and its time constant underestimated by exponential fits of \( \tau^*(T) \) vs \( T \). Numerical simulations, which
TABLE I. Peak shift fits excluding the fastest decaying component.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$a_2$</th>
<th>$r_2$</th>
<th>$a_3$</th>
<th>$r_3$</th>
<th>$a_4$</th>
<th>$r_4$</th>
<th>$a_5$</th>
<th>$r_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>0.813</td>
<td>0.073</td>
<td>0.187</td>
<td>2.23</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>0.698</td>
<td>0.050</td>
<td>0.120</td>
<td>4.04</td>
<td>0.057</td>
<td>33.1</td>
<td>0.125</td>
<td>284</td>
</tr>
<tr>
<td>Ethylene glycol$^a$</td>
<td>0.633</td>
<td>0.057</td>
<td>0.217</td>
<td>1.36</td>
<td>0.150</td>
<td>16.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>0.729</td>
<td>0.062</td>
<td>0.167</td>
<td>1.47</td>
<td>0.104</td>
<td>9.47</td>
<td>0.065</td>
<td>284</td>
</tr>
</tbody>
</table>

$^a$Solvent at 397 K. All other solvents are at 297 K. For methanol at 323 K (not shown), the fit parameters were almost exactly the same as at room temperature. The fitting function is a sum of exponentials. All inverse decay rates, $r_i$, are in ps and the amplitudes are normalized. The fastest ($\leq 0.01$ ps) component is not shown; therefore subscripts start at 2. These fit parameters should not be confused with the experimentally determined parameters for $M(t)$ shown in Table III.

include finite excitation pulse duration, must be performed to determine timescales, amplitudes, and spectral distribution, of these components. Thus the entries, $r_i$, in Table I and their relative amplitudes should be directly comparable to, for example, the time-dependent fluorescence Stokes shift picosecond relaxation times of Horng et al.,$^{22}$ only for $i \geq 3$. The fitting parameters in Table I are not the same as the parameters used for numerical simulations of the 3PEPS data (which are listed in Table III vide infra).

Figure 4(a) shows the 3PEPS of the IR144 in methanol at 297 and 323 K on two distinct timescales. As is evident, the modest change in temperature was insufficient to change the appearance or timescales of the relaxation of the 3PEPS signal. In contrast, Fig. 4(b) shows the dependence of $r_{\text{osc}}(T)$ on the temperature for ethylene glycol. The upper panel of Fig. 4(b) shows that the two fast phases of the relaxation are essentially independent of temperature over this range. The decrease in the initial value of the peak shift at high temperature presumably reflects the increase in amplitude of the fluctuations ($\langle \Delta \omega^2 \rangle$). The temperature independence of the inertial solvent component is in accord with our assumption that 297 K is already in the high-temperature limit for the solvation spectral density. We illustrate this in more detail below in terms of a spectral density ($\rho_{\text{HO}}$). Figure 4(b) shows the effect of temperature on the picosecond components is dramatic for ethylene glycol. We see three components for the 297-K data and only two at 397 K. Even if the slowest component of the 297-K data is ignored (i.e., treated as static inhomogeneity), the remaining components are quite different at the two temperatures. To investigate this further, we simulated our 3PEPS signals using both harmonic “basis set” spectral densities and spectral densities based on dielectric theories.

B. Spectral densities, $\rho_{\text{HO}}$, from simulation of 3PEPS data

Our original strategy for simulation of 3PEPS signals is shown schematically in Fig. 5. As described elsewhere in more detail,$^{10,12,26,27}$ $M(t)$ is the sum of several terms reflecting the distinct phases of solvent relaxation. Each contribution possesses its own reorganization energy, and the total reorganization energy is determined from steady state Stokes shift measurements. Resonance Raman spectra and transient grating experiments resolve the same intramolecular oscillation frequencies of the solute (all the modes within the bandwidth of the excitation pulses for the transient grating measurement). However, the intramolecular oscillations were determined directly from the transient grating data as described previously,$^{10,12,26,27}$ since the phases, inverse damping times, and reorganization energies are recoverable from these measurements. The intramolecular vibrational: frequencies, phases, inverse damping rates, and reorganization energies are listed in Table II. Other simulation parameters are listed in Table III. The constants $a_{\text{gau}}^2\tau_{\text{gau}}$ and $a_i^4/\tau_i$ represent the relative weights/timescales of solvent librational and diffusive contributions to solvation, respectively. Due to the lengthy computation required when including finite electric fields, our fitting criterion is visual inspection. It is important to note that the simulation parameters in Table III represent the dynamics of solvation, while the parameters in Table I only represent relaxation rates of the peak shift.

We show the inertial and diffusive components of our normalized spectral densities, $\omega^2\rho_{\text{HO}}$, for ethylene glycol at 397 K (solid line) and 297 K (dashed line) simulations in

<table>
<thead>
<tr>
<th>$\omega$ (cm$^{-1}$)</th>
<th>$\lambda$ (cm$^{-1}$)</th>
<th>$\gamma$ (fs)</th>
<th>$\phi$ (rad)</th>
</tr>
</thead>
<tbody>
<tr>
<td>85</td>
<td>4.83</td>
<td>630</td>
<td>0.32</td>
</tr>
<tr>
<td>138</td>
<td>25.4</td>
<td>320</td>
<td>0.45</td>
</tr>
<tr>
<td>204</td>
<td>3.39</td>
<td>500</td>
<td>0.96</td>
</tr>
<tr>
<td>302</td>
<td>5.47</td>
<td>890</td>
<td>0.42</td>
</tr>
<tr>
<td>317</td>
<td>63.4</td>
<td>110</td>
<td>0.16</td>
</tr>
<tr>
<td>437</td>
<td>3.75</td>
<td>1000</td>
<td>0.88</td>
</tr>
<tr>
<td>479</td>
<td>9.07</td>
<td>260</td>
<td>-0.10</td>
</tr>
<tr>
<td>571</td>
<td>4.57</td>
<td>580</td>
<td>2.90</td>
</tr>
<tr>
<td>645</td>
<td>0.323</td>
<td>1600</td>
<td>2.55</td>
</tr>
<tr>
<td>709</td>
<td>0.346</td>
<td>1800</td>
<td>1.51</td>
</tr>
</tbody>
</table>
Fig. 6. Normalizing the spectral densities makes the coupling strengths equal to unity in the integration range [Eq. (7)]. For our systems, ρ_HO should be nonzero only for ω < 300 cm⁻¹ in this system if the intermolecular IR144 vibrational modes are ignored. The spectral density as defined in the introduction is temperature independent. The influence of temperature in this model is only on Bose occupation numbers of the system-bath modes and appears in the coupling strength t_HO accurately describes the inertial (0–100 cm⁻¹) temperature dependence of our 3PEPS relaxation with ωt_HO as input. The decrease in the initial peak shift, t* (0), observed experimentally presumably results from an increase in coupling strength with temperature, although its magnitude is not predicted by our simulations. Thus we show the calculated t* minus 0.3 fs to facilitate a comparison of the simulation to the experimental signal. Evidently, our 297-K ω²t_HO predicts the inertial phase of the relaxation reasonably well at 397 K. This suggests the inertial (solvent librational) dynamics is well represented by a harmonic model, since the spectral density is essentially temperature independent in the range 10–250 cm⁻¹. Conversely, the picosecond experimental components change dramatically over this temperature range; so much so that we cannot predict the low-frequency (0–10 cm⁻¹) temperature dependence of our 3PEPS relaxation with t_HO, because t_HO is strongly temperature dependent in this frequency range. To our knowledge, this represents the first direct experimental study of the frequency region over which the harmonic bath models adequately describe the solvent.

Experimental 3PEPS data (circles) for IR144 in ethylene glycol at 297 K are shown in Fig. 7(a) along with the results of simulation (solid line) with the 297-K ρ_HO from Fig. 6. Clearly, our model ‘basis set type’ ρ_HO accurately describes the 297-K 3PEPS for IR144 in ethylene glycol from 0.03 to 10 ps. The disagreement at very early times (<0.03 ps) arises because we were unable to resolve the rapid destructive interference of the intramolecular vibrational coherence.26 ρ_HO serves well as a fitting function, but Fig. 7(b) shows the difficulty of using ρ_HO to predict 3PEPS data at a different temperature. We simulated (solid line) the experimental (triangles) 397-K ethylene glycol 3PEPS relaxation using the 297-K ω²ρ_HO as input. The decrease in the initial peak shift, t* (0), observed experimentally presumably results from an increase in coupling strength with temperature, although its magnitude is not predicted by our simulations. Thus we show the calculated t* minus 0.3 fs to facilitate a comparison of the simulation to the experimental signal. Evidently, our 297-K ω²ρ_HO predicts the inertial phase of the relaxation reasonably well at 397 K. This suggests the inertial (solvent librational) dynamics is well represented by a harmonic model, since the spectral density is essentially temperature independent in the range 10–250 cm⁻¹. Conversely, the picosecond experimental components change dramatically over this temperature range; so much so that we cannot predict the low-frequency (0–10 cm⁻¹) temperature dependence of our 3PEPS relaxation with ρ_HO, because ρ_HO is strongly temperature dependent in this frequency range. To our knowledge, this represents the first direct experimental study of the frequency region over which the harmonic bath models adequately describe the solvent.

Fig. 6. Basis set spectral densities, ρ_bas(ω), determined from simulations of 3PEPS relaxation for IR144 in ethylene glycol at 397 (solid line) and 297 K (dashed line).
V. DISCUSSION

The results of the previous section indicate harmonic bath models are not adequate to describe the diffusive solvation dynamics, i.e., for frequencies less than $\sim 25$ cm$^{-1}$. In an attempt to describe our experimental results, we simulated our experimental 3PEPS results using spectral densities obtained from three different models of polar solvation, which vary in complexity. Each spectral density, which was calculated as discussed in Sec. II, is intrinsically anharmonic in nature. For the SC and DMSA models of polar solvation, we used complex relative permittivities, $\varepsilon[k=\mathbf{0},\omega]$, calculated from far-infrared absorption$^{57,58}$ and dielectric dispersion data$^{59,60}$ Tables IV and V show the parameters used in Eqs. (A1)–(A4) to generate $\varepsilon[k=\mathbf{0},\omega]$ and spectral densities for methanol, acetonitrile at 297 K, and ethylene glycol at 297 K and 397 K. The solute-solvent size ratio was set to unity; increasing this ratio made the DMSA-$i$ dynamics faster, while all the other models were insensitive to the size ratio.$^{18,19}$ For the more sophisticated XRISM model, we start with $S(t)$’s for methanol and acetonitrile that were provided to us by Raineri and Friedman.$^{14,15}$ At this point our nomenclature used for the various spectral densities becomes difficult to follow. We summarize our nomenclature in Table VI for easy reference. The subscripts define the solvation model, or models, which were used to calculate the spectral density. For example, $\rho_{SC-d}$ specifies the simple continuum-dipole spectral density. We use $\rho_{SM}$ to represent all susceptibility model spectral densities and $\rho_{XRISM}$ to represent all XRISM spectral densities.

A. Temperature dependence of $\omega_n^2\rho(\omega)$ from susceptibility models of solvation

$\rho_{PHO}$ is intrinsically temperature independent, but the spectral densities for susceptibility models (SM) of solvation, $\rho_{SM}$, change with temperature because the relative permittivities change with temperature.$^{20,21}$ This is especially true from 0 to 3 cm$^{-1}$ and, by analogy with temperature-dependence measurements of reduced Raman spectra,$^{22}$ presumably not so pronounced for $> 20$ cm$^{-1}$. In Fig. 8(a) we show the normalized ambient temperature $\omega_n^2\rho_{SM}$ for ethylene glycol$^{60}$ using the experimentally determined $\varepsilon[k=\mathbf{0},\omega]$. The input dielectric relaxation data in Table IV spans 0.2–70 GHz (6.6×10$^{-3}$–2.3 cm$^{-1}$): i.e., the frequencies lower than the arrow. The longitudinal relaxation time of $\sim 300$ ps should appear below 0.2 GHz, and thus we show the fastest two diffusive components of our experimental 297-K $\omega_n^2\rho_{PHO}$ from Fig. 6 (lower panel) for comparison. The SC-$i$, SC-$d$, and our fastest two diffusive components of 297-K $\omega_n^2\rho_{PHO}$ from Fig. 6 (lower panel) for comparison. The SC-$i$, SC-$d$, Acetonitrile & 1.43 & 41.65 & 3.95 & 0.905 & 0.095 & 122.5 & 11 \\
Etgl & 24.3 & 4.0 & 0.374 & 0.626 & 6.7 & 1.0 \\

*The values in this table were inserted into Eqs. (A1)–(A4) to generate the spectral density by a procedure outlined in the text. For ethylene glycol at 297 (etgl) and 397 K (etgl$^b$) we interpolated and extrapolated temperature-dependent measurements (Ref. 60). With the exception of $\epsilon_i$, the parameters for ethylene glycol at 397 K are rough estimates (see the Appendix). $n_D$ was not needed for ethylene glycol. The values for methanol (Ref. 60) and acetonitrile (Ref. 59) are at ambient temperature. All quantities, with the exception of ethylene glycol at 397 K, were reported elsewhere in Tables I and IV of Horng et al. (Ref. 22).

FIG. 8. (a) Susceptibility model spectral densities, $\rho_{SM}(\omega)$, for ethylene glycol at 297 K using experimentally determined $\varepsilon[k=\mathbf{0},\omega]$ (Table IV and the Appendix) and our fastest two diffusive components of $\rho_{PHO}(\omega)$ for ethylene glycol at 297 K (circles) from Fig. 7(a). (b) Susceptibility model spectral densities, $\rho_{SM}(\omega)$, for ethylene glycol at 397 K using extrapolations of experimental dielectric measurements to determine $\varepsilon[k=\mathbf{0},\omega]$ (Table IV) and our diffusive components of $\rho_{PHO}(\omega)$ for ethylene glycol at 397 K (circles) from Fig. 7(a). In both (a) and (b) frequencies lower than the arrow correspond to the frequency range of the reported experimental dielectric dispersion measurements (Ref. 60).
and DMSA- models predict faster dynamics than expected from our 3PEPS experiment, and seem to resolve only the higher-frequency solvent relaxation. Additionally, these three spectral densities are quite similar, which is true of all the \( \omega^2 \rho_{SC,i} \), \( \omega^2 \rho_{SC,d} \), and \( \omega^2 \rho_{DMSA,i} \) we have calculated. Notice the presence of a shoulder at \( \sim 0.1 \text{ cm}^{-1} \) in the \( \omega^2 \rho_{DMSA,d} \) and \( \omega^2 \rho_{DMSA,i} \) and the absence of a shoulder in \( \omega^2 \rho_{SC,d} \) and \( \omega^2 \rho_{SC,i} \); presumably, this results from treating the solvent at the molecular level, via the dynamical mean spherical approximation, as opposed to an electric continuum. The consistency between the \( \omega^2 \rho_{DMSA,d} \) and our experimental \( \omega^2 \rho_{PHO} \) is remarkable, as we only used the experimentally determined \( \{ \mathbf{k} = 0, \omega \} \) as input; i.e., there were no adjustable parameters in the calculation of the normalized \( \omega^2 \rho_{SM} \).

Figure 8(b) compares our normalized diffusive experimental components at 397 K (\( \omega^2 \rho_{PHO} \) from Fig. 6 (bottom panel)) and the susceptibility model, \( \omega^2 \rho_{SM} \), which we calculated with experimental temperature-dependent (283–313 K) dielectric dispersion data\textsuperscript{60} extrapolated to 397 K (see Table IV and the Appendix). As was the case in Fig. 8(a), the frequencies where experimental dielectric dispersion data exists are approximately the frequencies lower than the arrow. The SC-\( i \), SC-\( d \), and DMSA-\( i \) models predict much faster dynamics than observed in our 3PEPS experiment, and seem unable to generate the lower-frequency diffusive solvent relaxation. The DMSA-\( d \) spectral density does seem to contain the lower-frequency diffusive solvent relaxation, but the level of agreement between the experimental \( \omega^2 \rho_{PHO} \) and \( \omega^2 \rho_{DMSA,d} \) is clearly not as good as at ambient temperature. The \( \sim 0.5 \text{ cm}^{-1} \) component seen in our experimental 3PEPS relaxation is visible in the \( \omega^2 \rho_{DMSA,d} \) and barely in the \( \omega^2 \rho_{DMSA,i} \), but not in the \( \omega^2 \rho_{SC,d} \) and \( \omega^2 \rho_{SC,i} \). The level of agreement between experimental \( \omega^2 \rho_{PHO} \) and \( \omega^2 \rho_{DMSA,d} \) is likely to improve if dielectric relaxation data for ethylene glycol are available at 397 K and we did not have to rely on large extrapolations from near ambient temperature data. Additionally, the higher-frequency peak in \( \omega^2 \rho_{PHO} \) extends to higher frequencies than those reported in the experimental dielectric dispersion measurements\textsuperscript{50} and at frequencies where we would expect deviations from the “Debye type” models to appear.\textsuperscript{20,21}

B. Simulation of 3PEPS relaxation with solvation model \( \omega^2 \rho(\omega) \)

The failure of our \( \omega^2 \rho_{PHO} \) to describe the temperature dependence of the diffusive 3PEPS relaxation for IR144 in ethylene glycol clearly suggests the need for an improved approach which avoids a harmonic assumption. In the previous subsection we showed that susceptibility model spectral densities, \( \omega^2 \rho_{SM} \), represented the diffusive 3PEPS relaxation of IR144 in ethylene glycol quite well at ambient temperatures [Fig. 8(a)] and displayed promise at 397 K [Fig. 8(b)], but our discussion was restricted to the diffusive relaxation processes (\( 0 \sim 3 \text{ cm}^{-1} \)), because we were unable to find far-infrared absorption measurements above \( \sim 3 \text{ cm}^{-1} \) for ethylene glycol in the literature. In this subsection, we show \( \omega^2 \rho_{SM} \) for acetonitrile\textsuperscript{58} and methanol\textsuperscript{57,60} two solvents with dielectric relaxation data extending to at least 250 cm\(^{-1} \), to see if they are able to reproduce our 3PEPS data for these solvents. The input parameters are given in Tables IV and V (see the Appendix).

Figure 9(a) shows area normalized \( \omega^2 \rho_{SM} \) for acetonitrile which were calculated with the experimentally determined \( \{ \mathbf{k} = 0, \omega \} \).\textsuperscript{58,59} Clearly, the DMSA-\( d \) spectral density differs strongly from that of the DMSA-\( i \), SC-\( d \), and SC-\( i \) models, with DMSA-\( d \) being weighted more heavily at lower frequencies. The molecular nature of the solvent is more noticeable for the dipole solute in the higher-frequency part of the spectral density (\( \sim 3 \text{ cm}^{-1} \)). Interestingly, \( \omega^2 \rho_{DMSA,i} \), \( \omega^2 \rho_{SC,d} \), and \( \omega^2 \rho_{SC,i} \) are only slightly different and will predict similar dynamics, as shown in Fig. 9(c).

Next, we compare these \( \omega^2 \rho_{SM} \) to the XRISM model spectral densities, \( \omega^2 \rho_{XRISM} \), shown in Fig. 9(b). The \( \omega^2 \rho_{XRISM} \) were determined in two different ways: the first (solid line) uses an impressive 19 interaction sites to simulate the laser dye coumarin-153 (C153),\textsuperscript{56} a theoretically based \( \{ \mathbf{k}, \omega \} \), and is called \( \omega^2 \rho_{XRISM,1} \);\textsuperscript{14,15} the second (dashed line) uses an experimentally determined \( \{ \mathbf{k} = 0, \omega \} \) for acetonitrile\textsuperscript{58,59} and methanol\textsuperscript{57,60} that was converted to \( \{ \mathbf{k}, \omega \} \) by the reference memory function approximation,\textsuperscript{52,63} and is called \( \omega^2 \rho_{XRISM,2} \).\textsuperscript{14,15} The simulated \( \omega^2 \rho_{XRISM,1} \) resembles all the \( \omega^2 \rho_{SM} \) to a certain degree, but \( \omega^2 \rho_{XRISM,2} \) with its bimodal appearance,\textsuperscript{64,65} is unique among these spectral densities. For acetonitrile all of the calculated solvation model spectral densities span the frequencies of our \( \omega^2 \rho_{PHO} \) for acetonitrile reported elsewhere,\textsuperscript{12} but they are shifted to significantly higher frequencies than the inertial and diffusive components of our experimentally determined \( \omega^2 \rho_{PHO} \).

Figure 9(b) and 9(a) shows the \( S(t) \) obtained from these solvation models. Besides the very fast initial decay and diffusive tail, the underdamped intermolecular solvent modes are a prominent feature of these correlation functions. Although underdamped solvent modes are present in various

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**TABLE V.** Relative permittivity constants used to generate spectral densities for methanol and acetonitrile from FIR data (\( \sim 3 \text{ cm}^{-1} \)). The values in this table were inserted into Eqs. (A1)-(A4) to generate the spectral density by a procedure outlined in the text. We used the numbers reported in Ref. 54 of Horng et al. (Ref. 22), which resulted from fits to far-infrared absorption data for acetonitrile (Ref. 58) and methanol (Ref. 57).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( b_1 )</th>
<th>( b_2 )</th>
<th>( b_3 )</th>
<th>( \omega_1 )</th>
<th>( \omega_2 )</th>
<th>( \omega_3 )</th>
<th>( \gamma_1 )</th>
<th>( \gamma_2 )</th>
<th>( \gamma_3 )</th>
<th>( \varphi_1 )</th>
<th>( \varphi_2 )</th>
<th>( \varphi_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>0.555</td>
<td>0.662</td>
<td>0.125</td>
<td>6.75</td>
<td>24.1</td>
<td>648</td>
<td>21</td>
<td>126</td>
<td>134</td>
<td>2</td>
<td>7</td>
<td>0</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>1.31</td>
<td>0.555</td>
<td>1.57</td>
<td>111</td>
<td>19</td>
<td>40</td>
<td>-21</td>
<td>4</td>
<td></td>
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</tr>
</tbody>
</table>

---

models of solvation dynamics\textsuperscript{16,17,22} and molecular dynamics simulations,\textsuperscript{34–36} they are yet to be observed experimentally. In reference to the beat in our experimental 3PEPS decay at ~0.2 ps; IR144 intramolecular vibrations will make it very difficult to definitely identify underdamped solvent modes if they are present.

A similar discussion can be given for the methanol spectral densities which are shown in Fig. 10. Notice $\rho_{\text{XRISM,2}}$ for methanol [Fig. 10(b)] has a large amplitude diffusive peak ($<3 \text{ cm}^{-1}$) which manifests itself as an offset in the XRISM,2 time correlation function when compared to its XRISM,1 counterpart [Fig. 10(d)].

The spatially varying electric potential in the solvent resulting from the newly created solute multipole provides the force driving solvation. Gradients in the electric potential of a SC solvent (i.e., when the solvent is a dielectric continuum.) are easy to visualize. When examining the ethylene glycol, acetonitrile, and methanol spectral densities in Figs. 9 and 10, notice that the SC spectral densities do not contain the lowest diffusive frequency components of solvation that are present in the other spectral densities. Additionally, SC spectral densities are only slightly dependent upon whether the solute is a monopole or a dipole, in strong contrast to the mean spherical approximation treatment of the solvent which is very sensitive to the multipole of the solute. Although visualizing the gradients in the molecular case is more difficult than for the SC treatment of the solvent, the lower-frequency diffusive relaxation seem to be the result of the solvent packing of dipolar hard spheres. These observations are consistent with our previous discussion of the increase in solvation frequency with increasing solvent/solute size ratio. (The analytical expressions for the DMSA-d spectral densities that we used were derived with the assumption that solvent/solute size ratio is unity.\textsuperscript{18,19}) XRISM model spectral densities are too complex to discuss briefly, but their relationship to “cavity” theories was discussed elsewhere.\textsuperscript{16,66}

To simulate 3PEPS data we needed to include the effects of intramolecular vibrational quantum beats of IR144. We added the intramolecular vibrational modes of IR144 listed in Table II to the spectral densities shown in Figs. 9 and 10 (see Table II for reorganization energies.). In Fig. 11(a), we show simulation of 3PEPS relaxation for IR144 in acetonitrile keeping the total reorganization energy, $\lambda_{\text{tot}}$, equal to 1064 cm$^{-1}$, what we expect from the “basis set” spectral density.\textsuperscript{12} The pulse duration was 22 fs for all numerical simulations in this manuscript and the value of $\lambda_{\text{tot}}$ was the only adjustable parameter. Four distinct phases of 3PEPS relaxation are present in both experimental and numerical simulations of 3PEPS signals. The fastest relaxation, which is due to the destructive interference of intramolecular vibrational wave packets of IR144, is not particularly interesting.

<table>
<thead>
<tr>
<th>Model type</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_{\text{SRM}}$</td>
<td>instantaneous normal mode</td>
</tr>
<tr>
<td>$\rho_{\text{SM}}$</td>
<td>all susceptibility models</td>
</tr>
<tr>
<td>$\rho_{\text{SC}}$</td>
<td>simple continuum, ion</td>
</tr>
<tr>
<td>$\rho_{\text{DMSA-d}}$</td>
<td>dynamical mean sphere approx., dipole</td>
</tr>
<tr>
<td>$\rho_{\text{DMSA-i}}$</td>
<td>all XRISM models</td>
</tr>
<tr>
<td>$\rho_{\text{XRISM}}$</td>
<td>theory with simulated $\varepsilon(k,\omega)$</td>
</tr>
<tr>
<td>$\rho_{\text{XRISM,1}}$</td>
<td>$^a$ theory with experimental $\varepsilon(k,\omega)$</td>
</tr>
</tbody>
</table>

$^a$ $\varepsilon(k,\omega)$ was generated from an experimentally determined $\varepsilon(k,\omega)$ for acetonitrile (Refs. 58,59) and methanol (Refs. 57,60) by the reference memory function approximation (Refs. 62,63).

Table VI. Nomenclature for spectral densities used in this manuscript.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig9.pdf}
\caption{Susceptibility model spectral densities (a), $\rho_{\text{SRM}}(\omega)$, and $S(\tau)$ (c) for ambient temperature acetonitrile using experimentally determined $\varepsilon(k=0,\omega)$, and XRISM model spectral densities (b), $\rho_{\text{XRISM}}(\omega)$, and $S(\tau)$ (d) for ambient temperature acetonitrile.}
\end{figure}
from a solvent dynamics perspective. The amplitudes of the inertial component (0.03–0.19 ps) are larger and their decay rates are more rapid than experiment for all simulations except with $\rho_{\text{DMSA-d}}$. The recurrence at $-0.19$ ps is due exclusively to the intramolecular IR144 modes in the experimental signal, but an underdamped solvent motion (Fig. 9) enhances this recurrence in the simulated signals. The diffusive relaxation of the experimental 3PEPS signal is much slower than in any of the simulations with $\rho_{\text{SM}}$.

The agreement between simulation using $\rho_{\text{DMSA-d}}$ and experiment (triangles) in acetonitrile is reasonable at early times (0.03 $<$ $T$ $<$ 0.3 ps), but the simulations predict a very fast diffusive relaxation when compared to experiment. Figure 11(b) shows that increasing $\lambda_{\text{tot}}$ to 1370 cm$^{-1}$ results in better agreement between DMSA-d and experiment for the initial relaxation of the 3PEPS signal, but the diffusive tail is still too fast. However, 1370 cm$^{-1}$ $\times$ 2 is much larger than the actual steady state Stokes shift (1750 cm$^{-1}$).$^{67}$ Simulations with $\rho_{\text{DMSA-i}}$ require a slightly smaller $\lambda_{\text{tot}}$ to align the numerical simulation with experiment in the 0.03–0.3 ps range than does $\rho_{\text{DMSA-d}}$, but the overall agreement (0.03–1 ps) is less satisfying than for $\rho_{\text{DMSA-d}}$. Simulations using $\rho_{\text{SC-i}}$ and $\rho_{\text{SC-d}}$ predict much faster dynamics than observed experimentally for any reasonable reorganization energy.

Figure 11(c) shows the 3PEPS simulation for acetonitrile using XRISM model spectral densities $\rho_{\text{XRISM}}$. As expected from the spectral densities, the simulations with $\rho_{\text{XRISM,1}}$ and $\rho_{\text{XRISM,2}}$ are very similar. Clearly, the agreement between experiment and simulation is striking at early times (0.03 $<$ $T$ $<$ 0.3 ps), with the timescales of the experimental 3PEPS relaxation being reproduced quantitatively by $\rho_{\text{XRISM,1}}$ (solid line in Fig. 9(b)). The disagreement between calculated and experimental curves results mainly from including the intramolecular IR144 vibrations with a large ad hoc relative displacement, but the solvent features are captured. The diffusive portion of the relaxation, although slower than that calculated from $\rho_{\text{DMSA-d}}$, is still a little too fast. The $\lambda_{\text{tot}}$ values from the simulations based on $\rho_{\text{XRISM,1}}$ and $\rho_{\text{XRISM,2}}$ are more consistent with the experimental steady state Stokes shift than the values obtained via susceptibility model spectral densities. Better agreement may be achieved by remodeling the solute to resemble IR144, but the overall agreement between numerical simulation and experiment is still satisfying.

Figure 12(a) shows experimental (triangles) and calculated 3PEPS signals for IR144 in methanol keeping $\lambda_{\text{tot}}$ = 1064 cm$^{-1}$. Of the susceptibility model spectral densities, $\rho_{\text{DMSA-i}}$ best resembles our experimental data especially at long times (>0.5 ps). Unlike for acetonitrile, $\rho_{\text{DMSA-d}}$ does not accurately represent our experimental methanol data, even with a very large $\lambda_{\text{tot}}$. Decreasing the value of $\lambda_{\text{tot}}$ to 1020 cm$^{-1}$ results in a better agreement between the simulation with $\rho_{\text{DMSA-i}}$ and our experimental signal from 0.5–10 ps. As was the case with acetonitrile, the value of $\lambda_{\text{tot}}$ is inconsistent with twice the steady state the Stokes shift of IR144 in methanol (1150 cm$^{-1}$).$^{67}$ Similarly to acetonitrile, simulations with $\rho_{\text{SC-d}}$ and $\rho_{\text{SC-i}}$ cannot be made to resemble our experimental methanol data by varying the value of $\lambda_{\text{tot}}$.

Figure 12(b) shows the 3PEPS simulation for methanol with $\rho_{\text{XRISM,1}}$ (solid line) and $\rho_{\text{XRISM,2}}$ (dashed line). Clearly, the agreement between experiment and simulation for $\rho_{\text{XRISM,1}}$ is the best of all models considered. The value of $\lambda_{\text{tot}}$ from the XRISM,1 calculations are in reasonable agreement with the experimental steady state Stokes shift again in contrast to the susceptibility models. The 3PEPS simulation using $\rho_{\text{XRISM,2}}$ (dashed line) is only quantitative at population times greater than $\sim$ 3 ps when using a reasonable value of $\lambda_{\text{tot}}$.
The XRISM model clearly provides more realistic spectral densities than do the DMSA and SC models. Additionally, theoretical investigations of the temperature dependence of XRISM model spectral densities are consistent with our observed temperature dependence of our ethylene glycol 3PEPS data. For example, the initial decay rate in XRISM model $S(t)$ for TIP4P water is almost unaffected by temperature for times less than 0.05 ps, as we observed in our ethylene glycol 3PEPS data. Furthermore, the amplitude of the initial component increases with increasing temperature, and is inconsistent with predictions based on harmonic bath models. Additionally, solute (and solvent) size and charge distribution are included into XRISM model spectral densities making them amenable for studying specific multipole (ion, dipole, quadrupole, etc.) solute-solvent interactions.

Although they did not compare their fluorescence Stokes shift time correlation functions, $S_D(t)$, with XRISM model time correlation functions, Horng et al. reported their experimental time-dependent fluorescence Stokes shift time correlation function, $S_D(t)$, were closest to the DMSA-i $S(t)$ for most solvents (including methanol), but for acetonitrile, their $S_D(t)$ was closest to the DMSA-d $S(t)$. These findings are consistent with our methanol and acetonitrile simulations above. As mentioned previously, our long time (>0.3 ps) 3PEPS relaxation components are directly related to the solvation time correlation function and should compare well to their long time $S_D(t)$ relaxation; direct comparisons of our shortest 3PEPS timescales (<0.3 ps) to time-dependent fluorescence Stokes shift timescales cannot be made. There are at least three major differences between the time-dependent fluorescence Stokes shift experiments of Horng et al. and our 3PEPS experiments which may explain the discrepancy in the diffusive components: the solute, the

FIG. 11. Experimental (triangles) 3PEPS signals for IR144 in acetonitrile and simulations with (a) susceptibility model spectral densities $\rho_{SM}(\omega)$ and (b) XRISM model spectral densities $\rho_{XRISM}(\omega)$.

FIG. 12. Experimental (triangles) 3PEPS signals for IR144 in methanol and simulations with (a) susceptibility model spectral densities $\rho_{SM}(\omega)$ and (b) XRISM model spectral densities $\rho_{XRISM}(\omega)$.
steady state Stokes shift magnitude, and the system evolution during the population period. C153 is a rigid solute that is much smaller than the less rigid tricarbocyanine, IR144, and the differences in solute charge distribution following excitation may contribute to observed differences. Additionally, the steady state Stokes shift for IR144 varies from 850 cm$^{-1}$ in chloroform to 1750 cm$^{-1}$ in acetonitrile; more typically, we expect $\sim$1100 cm$^{-1}$ from solvents like benzonitrile, methanol, ethanol, and ethylene glycol. C153 is much more strongly coupled to solvation: the steady state Stokes shift is nominally 5000–6000 cm$^{-1}$. The smaller perturbation generated by IR144 compared to C153 may account for some of the observed differences. Third, for time-dependent fluorescence Stokes shift the system evolves exclusively in the excited state. However, the system propagates on both the ground state and the excited state during the population period of the 3PEPS experiment. The population period interference makes 3PEPS experiments sensitive to breakdowns in the linear response approximation, which is almost always assumed in the interpretation of experimental data. The breakdown of the linear response approximation is well documented in respect to molecular dynamics simulations and the solvation time correlation functions, but it is currently uncertain if the nonlinear dynamics represent real systems or only the potential energy model used to calculate the dynamics.

C. Relationship between solvation and polarizability $\alpha^2 \rho(\omega)$

The sparseness of experimental far-infrared absorption data from 0 to 200 cm$^{-1}$ might limit the application of continuum model spectral densities, but reduced Raman spectra line shapes may substitute for the unavailable absorption spectra for some solvents. Cho and Fleming hypothesized the solvent polarizability spectral density would be similar to the solvation spectral density. This was verified for acetonitrile by numerical simulations of Ladanyi and Klein, who showed the INM density of states of acetonitrile that couple the solvent polarizability, $\rho_{\text{INM,pol}}$ is almost indistinguishable (experimentally) from the INM density of liquid states that couples to the solvating chromophore $\rho_{\text{INM,solv}}$.

Experimentally, Nagasawa et al. demonstrated the $\rho_{\text{HO}}$ for PMMA as determined from 3PEPS and transient grating experiments were quite similar to the reduced Raman spectra of PMMA in the temperature range 30–300 K, and subsequent optical Kerr effect measurements of Kinoshita et al. Scherer et al. demonstrated that two pulse photon echo signals were reasonably well-simulated with the polarizability spectra density ($\rho_{\text{HO}}$) obtained from optical Kerr effect measurements. Lund et al. showed the spectra of the depolarized Raleigh wing scattering and the FIR absorption are similar (3–150 cm$^{-1}$) for symmetric top solvents. This indicates the same motions responsible for $\rho_{\text{solv}}$ generate $\rho_{\text{pol}}$ in the case of symmetric tops. The ability of $\rho_{\text{pol}}$ to predict photon echo signals and the ability of $\rho_{\text{solv}}$ to predict reduced Raman spectra demonstrate that relationships often may exist between photon echoes and other resonance enhanced experiments to optical Kerr effect measurements. However, the generality of this connection should not be overstated.

VI. CONCLUSIONS

Photon echo measurements reflect the ability of a system to retain its memory of an optical transition frequency. In the 3PE experiments, solvation dynamics are probed by providing a population during which the system evolves on both ground and excited states. A very useful quantity is the 3PE peak shift, which has been shown to reflect the decay of the solvation time correlation function for times greater than the bath correlation time. For times less than the bath correlation time, the solvation time correlation function is obtained by numerical fitting of the three pulse photon echo peak shift relaxation using finite-temporal duration optical fields.

Coupling potential operators [Eq. (2)] based on our “basis set” spectral densities and, presumably, instantaneous normal mode spectral densities, capture the inertial phase of solvation from our temperature-dependent experimental 3PEPS data. These coupling potential operators seem to be transferable to different temperatures for the inertial part of the spectral density $[\alpha^2 \rho(\omega)]$ from 10 to 250 cm$^{-1}$, in which temperature is manifested only in the hyperbolic cotangent terms of Eqs. (5), (8), and (9). However, for the diffusive part of the spectral density $[\alpha^2 \rho(\omega)]$ from 0 to 3 cm$^{-1}$ (which the instantaneous normal mode approach does not contain), the basis set harmonic spectral densities are mainly fitting functions, and are incapable, for example, of predicting the temperature dependence of our experimental 3PEPS relaxation for ethylene glycol.

Using expressions derived by Cho, new coupling potential operators based on SC and DMSA theories of polar solvation were proposed to supply temperature dependence to the spectral density. Unlike harmonic “basis set” spectral densities, susceptibility model spectral densities change with temperature, because their input, $\phi_r$, changes with temperature. When using experimentally determined values for $\phi_r=0$, the DMSA-d spectral density accurately represents our harmonic “basis set” spectral density for ethylene glycol at 297 K. The DMSA-d spectral density obtained using extrapolations from experimentally determined $\phi_r=0$ qualitatively followed to our harmonic “basis set” spectral density for ethylene glycol at 397 K. Unfortunately, our discussion was limited to the diffusive motions, because we are unaware of any resonant far-infrared absorption measurements ($>3$ cm$^{-1}$) of ethylene glycol in the literature.

Susceptibility model spectral densities were calculated for acetonitrile and methanol: two solvents with published far-infrared absorption measurements well above $3$ cm$^{-1}$. Additionally, spectral densities were calculated from XRISM solvation time correlation functions for acetonitrile and methanol. Simulations with susceptibility model and XRISM model spectral densities were compared to the experimental 3PEPS relaxation of both methanol and acetonitrile. The XRISM model spectral densities describe both methanol and acetonitrile better than the DMSA and SC spectral densities,
and predict reasonable values of the total reorganization energy. Although DMSA model spectral densities predicted the 3PEPS relaxation of methanol (DMSA-i) and acetonitrile (DMSA-d) reasonably well, the value of the total reorganization energy required is inconsistent with the experimental (IR144) steady state Stokes shift measurements. Thus the XRISM should be preferred for studies of this type. Indeed, the type of 3PEPS data reported here allows for sensitive tests of models of solvation dynamics and of the frequency and wave vector dependence of the dielectric constant.

ACKNOWLEDGMENTS

We thank Professor Mark Maroncelli for his useful comments and for sharing his computer programs which calculate simple continuum and dynamical mean spherical approximation time correlation functions from relative permittivity constants. We thank Professors Harold L. Friedman and Fernando O. Raineri for providing the time correlation functions in Figs. 9(d) and 10(d). We thank Professor M. Cho for access to his unpublished results and for helpful comments on this manuscript. We thank T. Joo, F.O. Raineri, and A. Tokmakoff for helpful discussions. This work was supported by the NSF; Y.N. was supported in part by donors to the ACS-Petroleum Research Fund, and in part by JSPS. S.A.P. was a GAANN Fellow during the course of this work.

APPENDIX

Spectral densities derived from susceptibility models of polar solvation (SC and DMSA) rely upon experimentally determined complex relative permittivities, \( \epsilon(k=0,\omega) \), which were calculated from far-infrared absorption \(^{57,58} \) and microwave dielectric dispersion data.\(^ {59,60} \) Here, we state only what is necessary to understand our work, because complete introductions to far-infrared absorption\(^ {25} \) and microwave dielectric dispersion\(^ {20,21} \) measurements exist in the literature. Our procedure is adapted from the work of Horng et al.;\(^ {22} \) for simplicity, we use their notation.

The frequency- and wave vector-dependent complex relative permittivity is

\[
\epsilon(k,\omega) = \epsilon'(k,\omega) - i \epsilon''(k,\omega),
\]

where \( \epsilon'(k,\omega) \) and \( \epsilon''(k,\omega) \) represent the dispersive and dissipative couplings of the electric field to its electric displacement. Orientational dipole relaxation results in characteristic microwave absorption and dispersion in the 0–3 cm\(^{-1} \) region of the electromagnetic spectrum. From experimental measurements, if the continuum approximation is made, \( \epsilon(k=0,\omega) = \epsilon(\omega) \) is usually well represented by

\[
\epsilon(\omega) = \epsilon^\infty + (\epsilon_0 - \epsilon^\infty) \sum_j a_j f_j(\omega), \tag{A1}
\]

where \( \epsilon_0 \) is the static frequency permittivity constant, \( \epsilon^\infty \) is the infinite frequency permittivity constant, and \( a_j \) is the percent drop in \( \epsilon'(\omega) \) (from \( \epsilon_0 \) to \( \epsilon^\infty \)) for a particular dielectric relaxation. \( f_j(\omega) \) is

\[
f_j(\omega) = \frac{1}{(1 + (i\omega \tau_j)^{\gamma})^\rho}, \tag{A2}
\]

and recognizable as a general function that could represent the Debye (\( \alpha=0, \beta=1 \)), Cole–Cole (\( \alpha>0, \beta=1 \)), or Cole–Davidson (\( \alpha=0, \beta<1 \)) models of dielectric dispersion with relaxation time \( \tau_j \). Temperature-dependent dielectric dispersion measurements show the relaxation times have Arrhenius lawlike behavior over appreciable temperature ranges and activation enthalpies of a few kcal/mol for hydrogen bonding solvents. For example, to extrapolate near ambient temperature ethylene glycol\(^ {60} \) (Table IV) to 397 K, we used

\[
\log(\tau_1) = 1508.7 \text{ K/temperature} \times 2.976, \\
\text{and, for } \tau_2 \text{ we used}
\]

\[
\log(\tau_2) = 1258.7 \text{ K/temperature} \times 3.161.
\]

\( \epsilon_0 \) is temperature dependent, but its temperature dependence is readily inferable from the literature. The value of \( \alpha_2(\epsilon_0 - \epsilon^\infty) \) seems to be temperature independent;\(^ {60} \) therefore we kept this value constant in our simulation. Because of the magnitude of the extrapolation, the relaxation times and \( \alpha_2(\epsilon_0 - \epsilon^\infty) \) should be considered only as crude estimates of the true values at 397 K.

Far-infrared data exist for some liquids where Debye type models fail to describe \( \epsilon(\omega) (\sim 3 \text{ cm}^{-1}) \).\(^ {20,21} \) This allows us to develop a more realistic spectral density as described in the text. For these solvents, we splice the dielectric dispersion data to the resonant absorption by

\[
\epsilon(\omega) = n_D^2 + (\epsilon_0 - \epsilon^\infty) \sum_j a_j f_j(\omega) + \sum_j b_j f_i(\omega), \tag{A3}
\]

where \( n_D \) is the refractive index value, \( b_j \) is the weight of \( f_i(\omega) \), and

\[
f_i(\omega) = 1 - \frac{i\omega(i\omega + \gamma_j^i) + i\omega\omega_j \tan \varphi_j}{(i\omega + \gamma_j^i)^2 + \omega_j^2}. \tag{A4}
\]

Here \( \gamma_j \) is the width of the resonant FIR absorption, \( \omega_i \) is its frequency, and \( \varphi_j \) is a fitting parameter for the far-infrared absorption data. These parameters are obtained by fitting experimental \( \epsilon'(\omega) \) and \( \epsilon''(\omega) \). If the continuum limit is assumed, \( \epsilon(k=0,\omega) \) can be calculated from experimental far-infrared absorption and dielectric dispersion data. In principle, one could approximate \( \epsilon(k,\omega) \) from \( \epsilon(k=0,\omega) \) by the reference memory function approximation,\(^ {64,65} \) but we did not take this last step for the simple continuum and dynamical mean spherical model spectral densities in this manuscript.

\(^{1}\) S. Mukamel, Principles of Nonlinear Optical Spectroscopy (Oxford University Press, New York, 1995).


