Solvation Dynamics in Methanol: Experimental and Molecular Dynamics Simulation Studies

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ABSTRACT

We have investigated the ultrafast dynamics of methanol by time dependent fluorescent shift experiments and molecular dynamic simulations. The experiments were performed with two different probe molecules, 1-aminonaphthalene and coumarin 153. The molecular dynamic simulations employed these probes as well as small atomic and diatomic solutes. We find a previously unobserved fast decay component in the solvation response of methanol. The molecular dynamics results are in good agreement with this experimental result. The origin of this fast response and the linearity of the solvent response are discussed.

I. Introduction

The mechanism and time scale of solvation dynamics in polar liquids has attracted much attention in the past seven years. This attention arises from a fundamental interest in the dielectric properties of liquids and the influence of dynamic solvent properties on charge transfer and other condensed phase chemical reactions. Of particular interest has been the role of solvent dynamics in electron transfer reactions. Theoretical, experimental, and molecular dynamic simulation studies indicate the rate of both activated and activationless electron transfer are most affected by the fastest part of the solvent response, hence experimental determination of dynamic solvation on a femtosecond timescale is critical. The time scale of the solvent response to a
rapid change in the charge distribution of a solute is determined by measuring
the shift in the fluorescence spectrum after short pulse excitation. The
normalized, time-resolved shift in the emission frequency provides a direct
measure of the solvent dynamic response. This shift is characterized by the
solvent response function, $C(t)$, where $^{10}$

$$C(t) = \frac{v(t) - v(\infty)}{v(0) - v(\infty)}$$  \hspace{1cm} \text{(1)}$$

The information contained in the solvent response function, $C(t)$, has been used
by Fonseca, Barbara and coworkers as the effective dielectric friction for
modeling low barrier electron transfer.$^{11-13}$ This was a significant step towards
extracting electron transfer rates from time dependent shift measurements.

Through complimentary experimental$^{14-25}$, theoretical$^{26-37}$, and molecular
dynamic (MD) simulation studies$^{38-49}$ a molecular level understanding of
the solvent response is beginning to emerge. The initial theoretical descriptions
were based on a continuum model$^{10,28}$ and predicted that solvation dynamics
could be described by a single exponential time constant, $\tau_L$, the solvent
longitudinal relaxation time. Time resolved fluorescence experiments
confirmed the approximate correctness of this model but indicated that a range
of timescales was involved. More sophisticated models based on liquid
structure theory followed and have emphasized the importance of dynamics on
molecular length scales and of translational contributions to the relaxation.$^{29a,b}$

With the exception of the work of van der Zwan and Hynes$^{26}$ and Rips and
Jortner,$^{34}$ these early theoretical treatments were based on a diffusion equation
in which the solvent response is always overdamped.

Molecular dynamic simulations of solvation dynamics have contributed
significantly to our understanding of the solvation process. Simulations of
water,$^{38}$ acetonitrile,$^{39}$ methanol$^{41,42}$ and methyl chloride$^{40}$ find that the relaxation
contains a large contribution ($>50\%$) from a very rapid (sub $-100$fs) underdamped, inertial response. Of particular interest to this paper are the simu-
lations of small solutes in methanol by Fonseca and Ladanyi.$^{41}$ Their work
explored the origin of the inertial behavior and the nonlinearity of the solvent
response. The primary inspiration for performing the high time resolution
methanol solvation experiments reported in this paper came from Teresa
Fonseca's simulations. Other simulations studies of methanol have been carved
out by Ando and Kato$^{42}$ and Zhu and Cukier$^{43}$. In both cases larger probes
were employed: dimethyl aniline$^{42}$ and a $\sigma = 6\AA$ anion.$^{43}$ Here a larger probe
molecule, dimethyl aniline, was used. MD simulations of simple model fluids
have also been performed. Perera and Berkowitz$^{46,47}$ and Neria and Nitzan$^{45}$
have simulated the solvation of ions in a Stockmayer fluid (the Stockmayer
potential consists of a Lennard-Jones term and a dipole-dipole term). These
simulations also showed biphasic behavior in the solvent response.
In the absence of high time resolution experimental data for the solvent response function $C(t)$, analytical theories for solvation dynamics have been compared to molecular dynamics simulation results. Chandra and Bagchi developed a theory which includes inertial and viscoelastic contributions to the solvent response. In their analysis of Perera and Berkowitz's Stockmayer simulations Chandra and Bagchi proposed the short time dynamics could be described by a collective solvent excitation. A dielectric theory of ion solvation dynamics in simple model fluids has been presented by Raineri et al. This theory has been used to study the optical-like high frequency mode of TIP4P and SPC/E model water by Resat et al. Most recently a molecular theory of solvation dynamics based on an interaction site model has been described by Raineri et al. Using input from literature MD values for the frequency dependent dielectric constant (or the time correlation function of the total electric polarization), results in good agreement with simulations for ions in water and acetonitrile are obtained. Roy and Bagchi have presented a molecular hydrodynamic theory using experimental dielectric and far infrared data for water which also reproduces the complex structure obtained in the MD simulations. Quite recently Maroncelli and coworkers have proposed the solvent response can be related to the single particle dipole reorientational autocorrelation function by a conversion factor given by the dipole density. The proposed expression shows very good agreement to simulations of water, acetonitrile, and methyl chloride. A derivation of Maroncelli's expression beginning with the direct two particle correlation function has been presented by Roy and Bagchi.

The existence of inertial contributions to $C(t)$ was not apparent in earlier experimental work due to limited time resolution. The method used to follow the time dependent fluorescence shift is to reconstruct the emission spectrum from individual wavelength decays obtained by fluorescence upconversion. In the upconversion technique the emission from the sample is mixed with a “gate” pulse (the laser fundamental) in a nonlinear mixing crystal. When the gate pulse and emission are temporally overlapped, the emission is “upconverted” and light at the sum frequency is produced. The fluorescence decay is mapped out by varying the arrival time of the gate pulse at the mixing crystal. Selection of individual emission frequencies is achieved by tuning the phase matching angle of the mixing crystal. The time resolution of this experiment is determined by the laser pulse width, the dispersion of the experimental optics, and the length of the upconversion crystal. Improvements in generating ultrashort laser pulses and in the fluorescence upconversion technique have provided an experimental window to the ultrashort time scales previously accessible only to MD simulations. With the development of a ~50 fs resolution fluorescence upconversion system we have recently been able to show that a substantial inertial component exists in the solvent response of acetonitrile using the molecule LDS-750 as a probe.
In this paper we compare new experimental results for solvation dynamics in methanol to MD simulations. The molecules 1-aminonaphthalene (1-AN) and Coumarin 153 (C153) were used as probes. These solutes are shown in Figure 1. The MD simulations consider the solvent response to the

![Chemical structures of 1-AN and C153](image)

Figure 1: Structures and charge distributions of the solutes studied. The symbols $q_0$ and $\Delta q$ denote the ESP fitted ground state charge distribution and the charge difference distribution $q(S_1) - q(S_0)$. Darker spheres denote negative charge and the amount of charge is indicated by the volumes of the spheres. (As a calibration, the atoms labeled 11, 15, and 16 in C153($q_0$) have charges of $-0.63$, $+0.21$, and $-0.62$ respectively.)
charge difference between the excited and ground states of 1-AN and C153 (as determined by AMPAC calculations). Following a description of the experimental and simulation methods we present the MD and experimental results. A discussion follows and we conclude by summarizing the main results.

II. Experimental
A. Apparatus

Two different upconversion spectrometers were used to obtain the results discussed here. The fluorescence upconversion apparatus used in the C153 experiments is shown in Figure 2. Excitation at 425 nm was provided by frequency doubling the externally compressed output of a Coherent Mira 900F Ti:Sapphire laser in a 0.4 mm β-barium borate (BBO) crystal. Typical output pulses were 60 fs in duration, 6 nJ/pulse, and the repetition rate was 80 MHz. The sample was excited with <1 nJ pulses, while the gate pulse was ~2 nJ. The doubled excitation pulse is first separated from the fundamental by a dichroic beamsplitter. The gate pulse traverses a variable delay before being combined with the sample fluorescence in a 0.4 mm BBO crystal while the excitation pulse traverses a fixed delay before being focused into a 1 mm pathlength sample flow cell which is positioned at one of the foci of an elliptical reflector. Dispersion of the excitation beam by transmissive optics is compensated for with a set of fused silica prisms in a near retroreflecting geometry. The sample is kept at 20 C. The BBO crystal (type I phase matching) is positioned at the other focus of the elliptical reflector and the sum frequency of the fluorescence and gate pulse is separated from the laser fundamental, fluorescence, and second harmonic by an S1-UV quartz prism, directed into an Instruments SA DH-20 double monochromator and detected by a photon counting photomultiplier. The signal intensity is determined by photon counting using a Stanford Research Systems model 400 photon counter. Gating of the photon counter is not possible because of the high repetition rates and thus dark counts from the photomultiplier tube and some scattered light contribute to the background signal. Cross correlation of the excitation and gate pulse yielded an instrument response function of ~115 fs FWHM. Data sets were collected at 10 fluorescence wavelengths (approximately 1 decay for every 10 or 15 nm of the steady state emission spectrum). A single decay was generated by counting for 1 second at each delay setting with a 6.67 fs step size covering 2.5 ps and five such decays comprise an individual data set. An example of a typical data set with an instrument response function is shown in Figure 3. To explore the long time behavior of the solvent response function an identical upconversion apparatus at Penn State was used. These scans extended for a range of 200 ps. The stability of the Ti:Sapphire laser renders compensation for fluctuations in laser power unnecessary.
Fluorescence Up conversion with Reflective Optics

From Titanium Sapphire Laser

External Chirp Compensation SF 10 Prisms
60 fs pulse, 6 nJ/pulse, 80 MHz rep. rate

0.4mm BBO

425nm

850nm

Elliptical Reflector

Sample Flow Cell

Double Monochromator

Fused Silica Prisms

PMT

Computer

Photon Counter

Variable Optical Delay

Figure 2: Fluorescence upconversion apparatus.

The upconversion apparatus used for the 1-AN experiments has been described in detail elsewhere. Briefly, excitation at 317nm was provided by frequency
doubling the amplified output of a dual jet hybrid Sulforhodamine 640 dye laser in a 1mm BBO crystal. The dye laser was synchronously pumped by the second harmonic of a Quantronix 416 YAG laser. DQTCI was used as the saturable absorber in the dye laser. Amplification was provided by a five-pass bow tie amplifier pumped at 6kHz by an Oxford Copper Vapor Laser. The sample was flown through a 1mm flow cell and maintained at 20 deg. C. 1-AN fluorescence and the laser fundamental were colinearly mixed (Type 1) in a second 1mm BBO crystal. The sum frequency was separated from the laser fundamental, fluorescence, and second harmonic by an S1-UV quartz prism, focused into an Instruments ISA HR 320 monochrometer, and detected by gated photon counting with a solar blind pmt. The system response function, determined by the cross correlation of the laser fundamental and second harmonic, was 400–500fs for these experiments. Individual decays were generated by taking 100 fs steps from –5 to 25ps. The counting time at a given delay setting (~1sec) was normalized to the intensity of the laser fundamental and sample fluorescence. 10 such decays comprised an individual data set.

![Figure 3: Data, fit and residuals for fluorescence upconversion measurements of C153 in methanol. Also shown is the instrument response function. Excitation was at 425 nm and detection was and 303nm, corresponding to a fluorescence wavelength of 470nm + 3nm. The solid line is a fit to sums of exponentials.](image-url)
B. Data Analysis

The spectral reconstruction technique described by Maroncelli and Fleming was used to construct the solvent response function, \( C(t) \), from the individual wavelength decays measured in the fluorescence upconversion experiments. In this procedure the individual decays are first fit to some functional form convoluted with the instrument response function, plus a flat background. For our upconversion data (6.67\,fs steps, 115\,fs instrument response function, \(~3500\, counts per data set\) we have fit the data to two different fitting functions: a sum of exponentials form and a Gaussian plus exponential form. (Simulations show that for data obtained with very high time resolution the true functional form for the individual wavelength decays is poorly represented by sums of exponentials. We will discuss this below) The fit decays are then normalized using the steady state fluorescence spectrum and the spectrum at any time is given by the relative intensities of this normalized, fitted decay series. Finally, the time-resolved spectra are fit to log-normal lineshape functions from which \( C(t) \) is generated.

III. Simulation Methods.

Computer simulations were performed using methods similar to those described previously. The systems investigated consisted of a single solute and \(~256\) solvent molecules. Molecular dynamics were run at constant volume and energy (\( T\sim 298\, K \)) using periodic boundary conditions with application of an approximate Ewald technique to account for the long-range nature of polar interactions. Both the solutes and the solvents were represented as rigid bodies. Propagation of the solvent coordinates was performed using the basic Verlet algorithm with bond lengths and angles constrained by the SHAKE method. For the polyatomic solutes we found it more convenient to employ the quaternion method for propagating the rigid body motion.

Intermolecular potential functions for the simulations consisted of Lennard-Jones plus Coulomb interactions placed at atomic sites. The methanol potential used was the "H1" potential developed by McDonald and coworkers, which has been shown to provide a good representation of many static and dynamic properties of bulk methanol. (In this model the methyl group is treated as a united atom.) The monatomic solutes, \( S^0 \), \( S^+ \), and \( S^- \) were modeled with LJ parameters \( \epsilon/k_B = 38\, K \) and \( \sigma = 3.1\, \text{Å} \) (those of an oxygen atom in ST2 water). These solutes were used as fixed probes of the solvent's dynamics and were not allowed to translate during the simulations. The diatomic solutes considered were the "small" solutes studied originally by Fonseca and Ladanyi. These consisted of two atoms of mass 30 amu having LJ parameters \( \epsilon/k_B = 87.9 \) and \( \sigma = 3.083\, \text{Å} \). The atoms were separated by 1.43\,Å and carried either zero charge (nonpolar pair, NP) or \( \pm 1 \) electronic charge (dipolar pair, DP).
For the polyatomic solutes, l-AN and C153, the Lennard-Jones parameters were those recommended by Jorgensen. Atom-centered charges were obtained from electrostatic potential fits to semi-empirical MNDO wavefunctions calculated using the AMPAC program package. Such calculations (after a modest scaling) have been shown to provide good representations of the ground-state charge distributions of molecules obtained from ab initio calculations at the 6-31G* level. As described below, equilibrium simulations were run in the presence of the ground state solute charges, which should be accurately represented by these calculations. To simulate the experimental dynamics, which involves excitation to S1, the charge differences between S1 and S0 are also required. These differences were obtained from analogous MNDO calculations using the "EXCITED" option, which entails very limited configuration interaction. For this reason, and because the MNDO hamiltonian is not parameterized for excited-state calculations, we only consider the calculated charge differences to be illustrative of what might be expected upon electronic excitation. Fortunately, the simulated dynamics are not highly sensitive to the details of the excited state charge distribution in most cases. The ground-state charges and charge differences used for the l-AN and C153 simulations are illustrated in Figure 1.

The dynamics of interest here is the solvation energy relaxation subsequent to a step-function change in the solute charge distribution {q}0 → {q}1. To monitor solvation we will use the electrostatic solute-solvent interaction energy, E_{el}. The normalized response function to be compared to the results of time-resolved fluorescence experiments (Eq. 1) is:

$$S_{\Delta}(t) = \frac{\Delta E_{el}(t) - \Delta E_{el}(\infty)}{\Delta E_{el}(0) - \Delta E_{el}(\infty)}$$

where ΔE_{el}(t) refers to the difference in solute-solvent interaction energies between solutes in the two charge states, ΔE_{el}=E_{el}(q1)-E_{el}(q0), and the dynamics is propagated in the presence of the final state charge distribution.

In the present work we will consider mainly the results of equilibrium simulations. Under the assumption of a linear solvation response, the non-equilibrium response functions described above are computed from certain time-correlation functions (tcfs) of electrical properties of the system in equilibrium. In particular, the tcf corresponding to the observable response $S_{\Delta}(t)$ is $^{38,40}$:

$$C_{\Delta}(t) = \frac{\langle \delta \Delta E_{el}(0) \delta \Delta E_{el}(t) \rangle(0)}{\langle \delta \Delta E_{el}^2 \rangle(0)}$$

(3)
where \( \langle X \rangle^{(0)} \) denotes an average of the quantity \( X \) over an ensemble in equilibrium with the solute in the initial charge state \( q_0 \), and \( \delta X \) a fluctuation, \( \delta X = X - \langle X \rangle \). For solutes composed of discrete atomic charges \( q_i \) this function can be written,

\[
C_\Delta(t) = \frac{\sum_{i,j} \Delta q_i \Delta q_j \langle \delta v_i(0) \delta v_j(t) \rangle^{(0)}}{\sum_{i,j} \Delta q_i \Delta q_j \langle \delta v_i \delta v_j \rangle^{(0)}}
\]

(4)

where \( v_i \) is the electrical potential and \( \Delta q_i \) the \( (S_1-S_0) \) charge difference at site \( i \). The latter form allows one to consider decomposition of the total response into contributions from individual atomic sites,

\[
C_i(t) = \frac{\langle \delta v_i(0) \delta v_i(t) \rangle^{(0)}}{\langle \delta v_i^2 \rangle^{(0)}}
\]

(5)

For future reference we note that for a monatomic solute that undergoes a charge jump the relevant tcf is identical to this single-site correlation function. In the case of a monatomic solute we will refer to this sort of tcf of the electrical potential as \( C_V(t) \).

It will also be useful to compare the \( C_\Delta(t) \) tcfs defined above to similar tcfs of the electrostatic solvation energy in the ground state,

\[
C_0(t) = \frac{\langle \delta E_{el}(0) \delta E_{el}(t) \rangle^{(0)}}{\langle \delta \Delta E_{el}^2 \rangle^{(0)}}
\]

(6)

Here \( E_{el} \) is that calculated for the ground state charge distribution (i.e. \( C_0(t) \) is calculated from Eq. 4 with \( q_0 \) replacing \( \Delta q_i \)). Although \( C_0(t) \) is not experimentally measurable, its comparison with \( C_\Delta(t) \) helps in understanding how the nature of the charge change determines the dynamics of solvation.

Simulations were performed with a 3 fs time step. Each solute was equilibrated for a period of 100 ps prior to collecting equilibrium information. Simulation lengths were 300 ps for the atomic and diatomic solutes and 450 and 750 ps for the 1-AN and C153 solutes respectively.

IV. Molecular Dynamic Simulation Results

A. Small Atomic and Diatomic Solutes

In previous studies we have simulated the solvation response of small, immobile monatomic solutes ("S") in water, acetonitrile, and a series of
The behavior of such solutes in methanol is illustrated in Figs. 4 and 5 and further characterized in Table 1. The curves plotted here are time correlation functions of the electrical potential at the center of three solutes of varying charge. These functions are the linear response predictions \( C_V(t) \); Eq. 5) for the solvation response \( S_S(t) \); Eq. 2) to a charge jump in the solute. These linear response predictions show many features in common with the results observed in other solvents as well as simulations of other solutes in methanol. One is the pronounced bimodal character of the solvation response. All of the atomic solutes show a large-amplitude (±70%) component that decays on a ~100 fs time scale.

### Table 1: Characteristics of the Simulated Dynamics in Methanol

<table>
<thead>
<tr>
<th>Solute</th>
<th>(-E_{el})</th>
<th>(&lt;\Delta E_{el}^2&gt;)</th>
<th>(\omega_X^{(b)})</th>
<th>(\omega^{(c)})</th>
<th>(\tau^{(c)})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(10^{-2} au)</td>
<td>(10^{-4} au)</td>
<td>(ps^{-1})</td>
<td>(ps^{-1})</td>
<td>(ps)</td>
</tr>
<tr>
<td>S^0</td>
<td>0</td>
<td>1.8</td>
<td>30</td>
<td>14(68%)</td>
<td>2.4</td>
</tr>
<tr>
<td>S^+</td>
<td>25</td>
<td>2.0</td>
<td>30</td>
<td>23(60%)</td>
<td>2.9</td>
</tr>
<tr>
<td>S^-</td>
<td>30</td>
<td>1.8</td>
<td>32</td>
<td>30(67%)</td>
<td>4.2</td>
</tr>
<tr>
<td>NP(fixed)</td>
<td>0</td>
<td>.21</td>
<td>30</td>
<td>13(45%)</td>
<td>2.4[0.22(25%)+4.1(31%)]</td>
</tr>
<tr>
<td>DP(fixed)</td>
<td>3.8</td>
<td>.59</td>
<td>30</td>
<td>20(63%)</td>
<td>3.0</td>
</tr>
<tr>
<td>C153; (q_0)</td>
<td>2.4</td>
<td>.43</td>
<td>26</td>
<td>17(20%)</td>
<td>5.0[0.43(17%)+6.4(60%)]</td>
</tr>
<tr>
<td>C153; (\Delta q)</td>
<td>.073</td>
<td>23</td>
<td>16(16%)</td>
<td>3.8[0.30(29%)+5.8(53%)]</td>
<td></td>
</tr>
<tr>
<td>1-AN; (q_0)</td>
<td>2.5</td>
<td>.053</td>
<td>18</td>
<td>19(20%)</td>
<td>4.3[0.33(16%)+5.4(63%)]</td>
</tr>
<tr>
<td>1-AN; (\Delta q)</td>
<td>.060</td>
<td>31</td>
<td>19(23%)</td>
<td>2.2[0.17(33%)+3.9(40%)]</td>
<td></td>
</tr>
</tbody>
</table>

a) The quantity \( E_{el} \) is the average electrostatic solute-solvent interaction energy calculated for the solute in its initial charge state. With the exception of the rows labelled \( q_0 \), \(<\Delta E_{el}^2>\) is the average squared fluctuation in the energy difference between the two solute charge states considered. For the atomic solutes the change is a ±1e jump. For the diatomic solutes the change is dipole creation or destruction of a charge pair \((00)->(+-)\) and for the larger solutes it is the \( S_0\rightarrow S_1 \) change. For the solutes labelled \( q_0 \) the value is the fluctuation in the ground state electrostatic energy.

b) Solvation frequencies calculated according to Eq. 8.

c) Fits of the tcf's to the empirical form:

Amplitudes are given in parenthesis. The column marked \( \tau \) gives the average of the exponential time constants and the biexponential parameters (if applicable).
followed by a much slower component decaying on a few picosecond time scale. In simpler solvents the fast component can be well fit to a Gaussian function of the form,

$$C_V(t) = \exp\left(-\frac{1}{2} \omega_s^2 t^2\right)$$

(7)

where $\omega_s$ is termed the solvation frequency, related to the t=0 curvature of the response by

$$\omega_s^2 = \left. \frac{\partial^2 C_V}{\partial t^2} \right|_{t=0}$$

(8)

Figure 4: Solvation time correlation functions corresponding to the response to a charge jump ($C_V(t)$, Eq. 5) in three atomic solutes in methanol (solid curves). The curves have been vertically displaced for clarity with their respective zero levels indicated at the right. The dashed curves on the top two panels are the fits to Eq. 9. The curve with points marked is the longitudinal dipole density autocorrelation function calculated for pure methanol by Skaf et al. (see text).

The same is not true in methanol however. While the bimodal nature of $C_V(t)$ can be conveniently characterized (see Figure 1 and Table 1) by fits of the sort
\[ C(t) = a_1 \exp\left(-\omega_1^2 t^2 / 2\right) + a_2 \exp\left(-t / \tau_2\right) + a_3 \exp\left(-t / \tau_3\right), \]  

(9)

the best-fit frequency of the fast component is not the initial curvature defined by Eq. 8. As can be seen from Table 1 the initial frequencies \( \omega_s \) given by Eq. 8 are much higher than the effective Gaussian frequencies \( \omega_g \) used to characterize the 100 fs decay component. The reason for this difference will be discussed shortly. Another feature of the data displayed in Figs. 4 and 5 is the presence of oscillations in \( C_v(t) \). Such oscillations have previously observed in simulations of small solutes in a number of different solvents.38–41,45–47,60–64

We have not yet performed a complete analysis of the molecular mechanisms responsible for the above features of the solvation response in methanol. However, such investigations have been performed for these solutes in other solvents38–39 and detailed analyses have already been performed for similar solutes in methanol.41,62,65 These studies lead to the following interpretations. The long-time part of the response involves large amplitude reorientation and translation of solvent molecules that is diffusive in nature. In contrast, the fast part of the response and the oscillations in \( C(t) \) are a result of small-amplitude, underdamped solvent motions. Oscillations result from

Figure 5: Correlation functions of Fig. 4 plotted on a logarithmic scale. Successive curves have been vertically displaced for clarity.
intermolecular vibrational motions of solvent molecules within their nearest-neighbor cage. In the case of the S0 and S+ solutes oscillations appear with a frequency of 21 ps\(^{-1}\) (720 cm\(^{-1}\)). In the response of the S\(^{-}\) solute there is still an oscillation of this frequency but it is overshadowed by a more pronounced oscillation at 5.0 ps\(^{-1}\) (170 cm\(^{-1}\)). Based on the H/D isotope comparisons made by Fonseca and Ladanyi\(^{41,62}\) it is clear that the 21 ps\(^{-1}\) oscillations result from librational motions of the hydroxyl hydrogen about the C-O bond. The pronounced lower frequency oscillations in the S\(^{-}\) solute most likely reflect an ion-solvent vibrational mode in which the solvent motion is largely translational in character. Finally, interpretation of the fast decay component in methanol is slightly more complex than in most solvents thus far simulated. In simple solvents such as acetonitrile the fast component of C\(_v(t)\) can be well fit to a Gaussian function with a frequency given by Eq. 8 for well over half of its decay. In such cases the motion involved has been shown to be a "free-streaming" of molecules.\(^{39-40,47}\) What is meant by this terminology is the following. Prior to perturbation of the solute charge distribution, solvent molecules are moving with velocities distributed according to a Maxwell-Boltzmann distribution. These velocities depend only on the temperature and the inertial properties of the solvent. For sufficiently short times after the solute perturbation, the dynamics contained in the response involves nothing more than propagation of these initial velocities. Since the velocity distribution is independent of molecular interactions, the initial molecular motion is free-particle motion, even though the effect that such motion has on the solvation energy is strongly dependent upon intermolecular correlations.\(^{52}\) In the case of methanol this free-streaming phase only strictly holds for the short period (<40 fs) before the first velocity reversal of the hydroxyl librator. It is only during this brief period that C\(_v(t)\) decays with the inertial frequency determined by Eq. 8. But this initial relaxation only accounts for one quarter to one half of the fast part of the dynamics in methanol. What is the remainder due to? As Fonseca and Ladanyi\(^{41,62}\) pointed out, methanol is unique among the solvents thus far simulated in that the inertial moment for rotation of the hydroxyl proton is a factor of 5 smaller than its other two principal moments. Since rotations about all three inertial axes cause rotation of the dipole moment, all three contribute to the solvation dynamics, and therefore there are two rather distinct frequencies involved in the inertial component of this dynamics. Thus we ascribe the remainder of the fast component of the dynamics to something analogous to the "free-streaming" motions used to describe quasi-linear molecules such as methyl chloride\(^{40,60}\) and acetonitrile.\(^{39}\) That is, while the hydroxyl rotation is obviously undergoing hindered libration after 40 fs, rotations about the other inertial axes may still be described as relatively free in the same sense that the motion in a solvent like acetonitrile may be considered free.\(^{67}\) We note that if one calculates an effective average moment of inertia for methanol and
calculates an effective inertial solvation frequency from it, this frequency (-17 ps⁻¹) is close to the Gaussian frequency needed to approximately fit the fast part of the decays in all but the S⁻ solute.

One interesting observation to be made about these simulations of atomic solutes is that the solvation tcf Cₜ(t) is very similar to the simple continuum prediction for solvation dynamics. This fact is illustrated in the bottom pair of curves in Figure 4. The dotted curve there is the longitudinal dipole density tcf,68

$$\Phi_{L}(k,t) = \frac{\langle M_z(k,t)M_z(-k,0) \rangle}{\langle |M_z(k,0)|^2 \rangle}$$

recently determined by Skaf et al.69 The curve shown is for the smallest k value attainable in their simulations (k=0.24Å⁻¹) and should provide a reasonable estimate for the k→0 limit, which is the simple continuum prediction for charge solvation dynamics.1 Apart from a modest difference in the relative amplitudes of the fast and slow decay components, Φₜ(t) is virtually identical to Cₜ(t) for the S⁰ solute. (Actually, Skaf et al. point out that at the value of k used here Φₜ(t) has not completely converged to the k=0 limit and in the limit the agreement between the two curves should be even better.) Not only is the overall shape of the solvation Cₜ(t) reflected in the simple continuum prediction but the appearance of fast and slow oscillations are also well reproduced. Thus, at least in the case of this relatively non-perturbing solute (and when inertial components are included in the solvent description), the finite size of the solute and other aspects of the solute-solvent structure have very minor effect on determining the dynamics of ionic solvation. Similar observations have been previously made concerning other solvents.39

Another interesting aspect of the solvation dynamics in methanol concerns the linearity of the solvation response. In the above discussion and in much of what follows we rely on linear response predictions (C(t)) to tell us about the non-equilibrium solvation response (S(t)). This approach is valid only for sufficiently small perturbations of the solute charge distribution. Somewhat unexpectedly, previous simulations of water,38,63,64 acetonitrile,39 and other solvents,44 have shown that the linear-response treatment often provides reasonably accurate predictions for solvation dynamics, even for jumps as large as a full electronic charge on a small solute. One observes such linearity in spite of the fact that the change in solvation energy resulting from such a charge jump amounts to ~200kT. The linear response results displayed in Figs. 4 and 5 indicate that the situation in methanol is probably not unlike that of these other cases. Since the tcfs for these three solutes are different, a linear response calculation of a full charge jump S⁰→S⁺ or S⁰→S⁻ cannot be quantitatively accurate. However, we note that Cₜ(t) of the S⁰ and S⁺ solutes are fairly similar
and a linear response prediction for the dynamics of $S^0 \leftrightarrow S^+$ might be expected to be good to about the $\pm 20\%$ level. This estimate is based on the fact that the long time decays of $S^0$ and $S^+$ differ by only that amount (see Table 1) and the fact that the change in the solvation energy calculated via a linear response calculation,

$$\Delta E_{el}(0) - \Delta E_{el}(\infty) = \frac{\langle \delta E_{el}^2 \rangle}{kT}$$

is also correct to within $15-25\%$ (depending on direction). The case with respect to jumps of the sort $S^0 \leftrightarrow S^-$ is not as satisfactory. There is a $60\%$ difference between the time constants of the slow component and the prediction of the total energy change is in error by $\sim 35\%$. Evidently, the solvation structure around a small negative ion is sufficiently different from that around a cation or neutral species that the dynamics of adding a full negative charge to a small neutral solute can be only roughly predicted by a linear response calculation.

Although the above results indicate some breakdown of linear response predictions for small atomic solutes in methanol, the departures observed here are not as dramatic as those observed by Fonseca and Ladanyi in their original simulations of diatomic solutes. In order to help understand why not, we have also performed a few equilibrium simulations of a diatomic solute of the sort employed in their work. We have examined the smaller of the two solutes in their original study and have calculated the linear response predictions $C(t)$ (Eq. 4) corresponding to dipole creation and extinction $(00)\leftrightarrow(+-)$. Figure 6 illustrates the results. The top panel shows the solvation tcfs observed in the presence of the nonpolar and dipolar solutes when the latter are free to rotate and translate. These curves reproduce the results already reported by Fonseca and Ladanyi. One sees a marked difference between the NP curve and that of the DP solute, and in fact, between the NP solute and any of the other solutes discussed thus far. The most striking difference is that $C(t)$ of the NP appears to lack any of the slow (2-4 ps) component that makes up 30-40% of the relaxation observed with the DP and other solutes. This difference implies that a linear response calculation based on $C(t)$ of the NP should provide a rather poor approximation for the actual non-equilibrium dynamics subsequent to dipole creation—a fact directly confirmed in non-equilibrium simulations by Fonseca and Ladanyi. This large departure from linear behavior is not surprising except that it appears to set methanol apart from other solvents studied previously. It also appears that interactions between methanol and the NP are somehow unique so as to give rise to special behavior of this solute relative to all other solutes thus far studied in methanol.
A partial explanation for these observations is provided by the results shown in the lower panel of Figure 6. In this panel we plot $C_\Delta(t)$ obtained when we freeze all motion of the solutes during the course of the simulation, as we have done with atomic solutes.\cite{38,39,48} Comparing the top and bottom panels it is apparent that solute motion contributes substantially to relaxing $C_\Delta(t)$. In the DP case, immobilizing the solute increases the amplitude of the slow component of the decay from 40% to 65%. In the NP solute the change is more than just quantitative. Whereas the slow component is virtually absent in the free NP solute it makes up about 45% of the relaxation in the immobile solute case. We are still in the process of understanding the detailed basis of these differences, however it seems reasonable to conjecture that rotational motions of the solute account for the faster relaxation in the mobile solute simulations. The fact that the free NP relaxes without any substantial slow component probably reflects a much greater rotational mobility for this solute compared to the DP solute. For the latter, structural studies of Ladanyi and coworkers\cite{62,65} suggest the presence strong hydrogen bonding between the solute and methanol that would inhibit rotation of even the "free" DP solute.
Whatever the explanation, these observations have important implications for thinking about the linear or non-linear character of methanol solvation dynamics. First, it may or may not be the case that methanol is substantially different from other solvents as regards the non-linearity of its solvation response. Since most of the solutes previously studied in methanol have been small mobile diatomics, and since we have seen that solute motion significantly affects the overall solvation response, it is misleading to compare these results in methanol with results on different solutes in other solvents, especially the fixed atomic solutes used many studies. Small mobile solutes do show substantial non-linear dynamics in methanol but it would not be surprising to find similarly large non-linear effects in water and less pronounced effects in non-associated solvents for these same solutes. Second, we note that in past theoretical descriptions of solvation dynamics the role of solute motion has been largely neglected. The above results suggest that, when small solutes are involved, such neglect is inappropriate. It will therefore be useful to undertake further simulations in order to explore how solute motion affects the dynamics in the linear response limit as well as how it contributes to the non-linear behavior displayed situations of the sort illustrated by some of the methanol simulations.

B. Molecular Solutes 1-AN and C153

We now turn to simulations on polyatomic solutes in methanol performed for the purpose of direct comparison to experiment. As above, most of our results consist of linear response predictions, $C_{\Delta}(t)$, for the non-equilibrium dynamics subsequent to a change in the electronic charge distribution accompanying the $S_0 \rightarrow S_1$ transition. Figure 7 compares the tcfs observed with 1-AN, C153, and the uncharged atomic solute $S^0$. There are substantial differences in the solvation dynamics predicted for these three solutes. Both molecular solutes show a much smaller fraction of the response coming from the fast inertial component compared to the atomic solutes. The molecular solutes also differ in this regard, with 1-AN showing a significantly larger amplitude fast component than C153. The long time decay of $C(t)$ also appears to be slower in the molecular solutes as compared to $S^0$. Some attempt at quantifying various aspects of the dynamics observed with all of these solutes is provided in Table 1. Here we list the initial frequencies $\omega_s$ along with the parameters required to best fit these data to a Gaussian plus exponential form (Eq. 9). The rows labeled "$\Delta q$" in this table pertain to the linear response predictions for the changes in solute charge distribution expected upon electronic excitation, i.e. the predictions to be compared to experimental time-resolved fluorescence results. Also shown are analogous tcfs of the electrostatic solvation energy in the ground state($C_0(t)$; Eq. 6), labeled "$q_0$".

There are several reasons why the molecular solvation tcfs shown in Figure 7 differ from those observed with atomic solutes. These are best
discussed with the aid of Figs. 8 and 9 which illustrate the differences between the "q_0" and "Δq" tcfs and also show several of the individual site tcfs defined in Eq. 5. First, consider the behavior of the individual sites within the polyatomic solutes. In the molecular solutes there are typically one or more sites that form relatively strong hydrogen bonds to the methanol solvent. In the 1-AN case the sites involved are the amino N and H atoms and in C153 the main site for strong solvent interaction is the carbonyl O(#16). In the ground electronic state these interactions account for 31% and 18% of $E_{el}$ respectively. The individual site tcfs at these positions have fast components with much smaller amplitude than do the solvation tcfs of any of the atomic solutes. The long-time portion of the response at these sites is similar to or somewhat slower than that of the slowest atomic solute, $S^-$. Apart from these few "special" sites, the $c_i(t)$ tcfs at most sites (represented in Figure 8 by the curves labeled "typ" and in Figure 9 by $N_{11}$ and $H_{15}$) are much faster, and are all fairly similar to $C_s(t)$ of the $S^0$ solute. From these observations one concludes that how the overall molecular tcf differs from those calculated for monatomic solutes will depend in part on how these two sorts of sites are mixed in the overall response. If one calculates the tcf of the ground state electrostatic solvation energy, $C_0(t)$, 

Figure 7: Comparison of the time correlation functions corresponding to the solvation response to electronic excitation in C153 and 1-AN and for an uncharged atomic solute ($S^0$).
the strongly interacting, slow site tcfs play a large role and the calculated response is relatively slow. In calculating the charge difference tcfs, $C_A(t)$, which are based on $\Delta q$ rather than $q_0$, the slow sites may or may not contribute importantly to the overall tcf. In the 1-AN case, the $S_0\rightarrow S_1$ electronic transition is calculated to be largely localized on the naphthalene carbon atoms (Figure 1). Neglecting cross terms between different sites in Eq. 4 one finds that nearly 90% of the overall tcf comes from these carbon atoms and only 4% from the amino group. Thus, the difference between $C_0(t)$ and $C_A(t)$ shown in Figure 8 is understandable. In contrast to 1-AN, in C153 the $q_0$ and $\Delta q$ tcfs are similar to one another. Both are comparable to that of the carbonyl O site tcf and show much smaller fast components than the tcfs of the other sites or that of a monatomic solute. It is true that the charge redistribution in C153 is calculated to be less localized on the aromatic ring system than in 1-AN. However, even here if one ignores cross terms in Eq. 4 one finds only a 6% contribution to $C_A(t)$ from the slow carbonyl O16. Thus the similarity between $C_0(t)$, $C_A(t)$, and $c_{O16}(t)$ is not so readily understood in this case. Given only a
6% contribution to $C_{\Delta}(t)$ it is clear that the similarity between $C_{\Delta}(t)$ and $c_{O16}(t)$ is largely coincidental. The fact that $C_{\Delta}(t)$ is much slower than the atomic sites that account for ~94% of its amplitude means that important cross correlations between sites in Eq. 4 must be causing the slowdown. In simulations on a variety of simple solutes in acetonitrile and methanol we have observed that the collective response of a number of correlated sites is typically slower and shows a fast component of smaller amplitude than the response of any individual atomic site. The extent of the difference between the atomic and molecular responses (in the linear limit) appears to depend on the symmetry of the charge perturbation considered. This observation is in keeping with our previous finding that in monatomic solutes the solvation response becomes slower and more single-particle like as one progresses from ion to dipole to quadrupole solvation. A similar principle must operate in these molecular solutes and further analysis is in progress to better understand how cross correlations between sites lead to such differences in the molecular solvation response.

Figure 9: Various time correlation functions measured in C153 simulations. The curves labeled "N11", "H15", and "O16" are tcfs of the electrical potential at the atomic sites ($c_i(t)$; Eq. 5; see Fig. 1 for atom definitions). S0 labels the $C_p(t)$ tcf of an uncharged monatomic solute and q and Dq denote the composite molecular tcfs defined by Eqs. 3b and 3, respectively.
Finally, some comment should be made regarding the expected accuracy of the above calculations for comparison to the experimental data. There are two factors of concern. First, as illustrated by the comparisons between $C_0(t)$ and $C_D(t)$, the calculated dynamics in methanol depend somewhat on the charge differences utilized. As mentioned earlier we do not expect the AMPAC charges to be particularly accurate representations of the excited state charge distribution and this will be reflected in the dynamics. Some appreciation of the quality of the charge differences employed can be obtained by comparing the predicted magnitude of the time-resolved spectral shift (obtained from Eq. 11) and the observed shift. The calculated and observed values are 1390 compared to 3500 cm$^{-1}$ in the case of 1-AN, and 1700 versus 2200 cm$^{-1}$ in the C153 case. Thus, while the C153 calculation appears to yield reasonable predictions (within 25%), the calculations greatly underestimate the polarity change in 1-AN, possibly due to an indole-like $L_a - L_b$ state reversal in polar solvents compared to the gas phase calculation.\cite{72,73} We are in the process of trying to improve the excited state charge representation in 1-AN, but in the meantime the calculated $C_D(t)$ should be viewed as rather approximate. The second aspect of the above results that could be questioned is the validity of the linear response approach in these molecules. As there is important non-linear behavior displayed by diatomic solutes in methanol it is possible that such effects could also be present in these molecular solutes. We are currently performing non-equilibrium dynamics to test this possibility. However, it seems reasonable to expect that any deviations from linear behavior here should be much more mild than what is observed in the small, highly charged solutes described in part A. We note that whereas the charge jumps discussed there involved changes in solvation energies of the order of 40 kT (diatomics) and 200 kT (atomic solutes), the charge changes for the polyatomics amount to only about 10 kT.

V. Experimental Results

Given the timescale of the inertial contribution suggested by molecular dynamics simulations, ultrafast fluorescence upconversion spectrometers are required to experimentally explore the magnitude and timescale of this contribution to the solvent response. Previous studies of methanol have been performed by Kahlow et al.\cite{19} and Castner et al.\cite{15} These experiments had an instrument response functions of \~250 fs and ~700 fs respectively, which are insufficient to explore the inertial regime. With the development of a \~50 fs upconversion apparatus we have shown that a substantial inertial component exists in acetonitrile.\cite{24} This experiment employed the large, charged, non-rigid probe molecule LDS-750. Using the probe Coumarin 153 we have verified this result for acetonitrile.\cite{25}

One of the difficulties in determining the magnitude of the fast part of the solvent response is determining the position of the t=0 emission spectrum. What is meant by the true t=0 spectrum with respect to the solvation problem is
the emission spectrum of a solute that is completely relaxed internally (i.e. vibrationally) but whose solvent environment has undergone no relaxation. This is illustrated by the case of 1-AN in methanol. With a 400fs instrument response function we can reconstruct the emission spectra back to ~150fs. In order to construct the entire response function we must have an estimate of the position of the initial emission spectrum. Without going into details, which are discussed elsewhere, comparison of the spectra in polar and non-polar solvents allows one to estimate the position of the “true” $t=0$ spectrum of probes like C153 and 1-AN to an accuracy of ~300 cm$^{-1}$. The estimated $t=0$ spectrum determined for 1-AN in methanol is shown with the reconstructed spectra in the inset of Figure 10. In this experiment we miss approximately half of the shift. Figure 10 compares the experimental solvent response function to the MD simulation result.

Figure 10: Comparison of experimental (dashed line) to molecular dynamics results for $C(t)$ for 1-AN in methanol. $C(t)$ is constructed from the peak of the reconstructed spectra. Inset: Reconstructed, time resolved spectra for 1-AN in methanol at $t=0.0, 0.5, 2.0, 5$, and 10 ps. The thick solid lines are the $t=0$ and $t=\infty$ spectra. Frequency range 20,000–30,000 cm$^{-1}$.

For the relatively low time resolution 1aminonaphthalene data, the individual wavelength decays were adequately fit to sums of exponentials. For our high time resolution (110 fs instrument response function) C153 data we explored fitting the individual wavelength decays to both sums of exponentials and a Gaussian plus exponential terms. That sums of exponentials are not the correct functional form for the individual wavelength decays was suggested by
Figure 11: Simulations of individual wavelength decays in acetonitrile. The left side was simulated using a 5fs instrument response function, the right side employed a 115fs instrument response function. From top to bottom the wavelengths are 470nm, 490nm, 540nm and 600nm.
the simulation of individual fluorescence decays for acetonitrile shown in Figure 11. Beginning with a MD result for the time evolution of the spectral shift, the magnitude of the total shift, and the shape of the emission spectrum we calculated individual wavelength decays. The decays are then convoluted with an instrument response function and statistical noise is added. Figure 11 shows data convoluted with a 5fs instrument response function and a time step size of 1 fs. The panels on the left compare simulated data at 470nm, 490nm, 540nm, and 600nm to experimental data (110 fs instrument response function, 6.67fs step size). Clearly some of the structure seen in the simulations is hidden in the type of data that we are able to collect.

For the case of C153 in methanol, including a Gaussian component in the fitting of the individual wavelength decays did not significantly improve the fitting results. This is not surprising given the time resolution of our experiment. The reconstructed spectra using purely exponential fitting or a Gaussian term with exponentials are shown in Figure 12 along with the estimated t=0 spectrum. The effect of the Gaussian fitting in this case is to redshift the peak of the experimental t=0 spectrum in comparison to the exponential fitting results. The magnitude of this effect depends on which measure of the emission energy is used—the fitted peak frequency or the first moment of the fitted spectrum. For the peak frequency the response functions are very similar in shape for the exponential and Gaussian fitting (i.e. there is an

![Figure 12: Time resolved reconstructed spectra for C153 in methanol. Left: Gaussian plus exponential fitting. Right: exponential fitting.](image-url)
almost constant displacement between them) whereas the initial slopes and magnitudes of the ultrafast portion differ significantly for the first moment plotted from the two fitting methods. These results are summarized in Figure 13. There are a number of possible reasons for the variations shown in Figure 14. The lack of a determination of the high frequency side of the $t=0$ spectrum compromises our ability to locate $v(0)$. The error could well be different in the two measures of $v$—certainly the initial frequencies are very sensitive to the two bluest wavelength points in the $t=0$ spectrum, which are the least well determined. In addition there may be real changes in the shape of the spectrum resulting, for example, from vibrational relaxation.

In the absence of a much more detailed examination of the origin of the trends in Figure 13 we have chosen to average the exponential and Gaussian fitting results separately for the first moment and the peak frequency. These $C(t)$ functions are compared with the simulation for C153 in methanol in Figure 13. In view of the discussion above the almost perfect correspondence of $v_{FM}$ and the simulation should be viewed with some caution. Only further analysis will tell whether $v_{pk}$ is simply shifted by a constant amount, or reflects a real discrepancy. As a first step in this direction we used the simulation results

![Figure 13: Solvent response functions for C153 in methanol generated from Gaussian plus exponential fitting. $v_{av}$ indicates $C(t)$ was constructed from the first moment of the time resolved spectra and $v_{pk}$ indicates $C(t)$ was generated from the peak of the spectra. The solid line is the molecular dynamics result for C153 in methanol. Inset: Long time comparison between experimental and MD simulation result for C153 in methanol. Note the logarithmic ordinate.](image-url)
along with estimates for the $t=0$ and $t=\infty$ spectra to predict the individual experimental decay curves. The comparison in Figure 14 provides additional assurance that the $t=0$ spectrum is reasonable extracted by the fits and that a substantial ultrafast component does indeed exist. Clearly, however, the comparison is not particularly good for the shortest wavelength curve.

To examine the solvent response function at later times, we patched the high time resolution 0–2\,ps scans together with lower time resolution (210\,fs instrument response) 0–200\,ps scans (1\,ps steps). The solvent response function and comparison to the MD results is shown as an inset in Figure 13 on a logarithmic scale. The 210\,fs measurements themselves miss the fast component in $C(t)$ seen in Figure 13, providing further evidence that these experiments require rather high time resolution to explore the fastest dynamics.

![Figure 14: Simulated individual wavelength decays (curves with noise) for C153 in methanol, compared with fit results (smooth lines) obtained from experimental data. The simulated curves were convoluted with an experimental instrument function and had statistical noise added. The fluorescence wavelengths (from bottom) are 470\,nm, 490\,nm, 515\,nm, 540\,nm, 575\,nm, 605\,nm.](image)

VI. Discussion

The biphasic nature of the solvent response in methanol is clearly evident in Figure 13. For the first moment the agreement with simulation is quantitative, for the peak frequency the shape is also in excellent agreement with simulation. For the purposes of discussion only we have further combined the two $C(t)$ curves and fit to the form $C(t) = a_0\exp(-t/\tau_0) + a_1\exp(-t/\tau_1) + a_2\exp(-t/\tau_2)$. The parameters obtained are $a_0 = 0.22$, $\omega = 12.8\,\text{ps}^{-1}$.
(corresponding to ~ 100fs HWHM for the ultrafast decay); $a_1 = 0.23$, $\tau_1 = 0.56$ps; $a_2 = 0.34$, $\tau_2 = 8.1$ps. The Gaussian component compares well with the Cl53 ($\Delta t$) values listed in Table 1, while the long time data is in excellent agreement with the results of Kahlow et al.\textsuperscript{19} using the probe Coumarin 152.

Fonseca and Ladanyi explored the solvent motions that give rise to the solvent response in methanol for the first 30fs of the decay (which accounts for 20\% of the solvent relaxation in their simulation). They performed simulations for CH$_3$OH, CH$_3$OD, and CH$_3$OH with artificially heavy methyl and oxygen groups, such that the CH$_3$–O motion is frozen during the simulation. The initial ultrafast response is slower in CH$_3$OD than CH$_3$OH and is the same for both the heavy and normal solvent. They thus conclude that O–H librational motion is responsible for the first 30fs of the decay. They did not explore the molecular motions which give rise to the remainder of the Gaussian response. Ando and Kato\textsuperscript{42} and Zhu and Cukier\textsuperscript{43} have also discussed solvation dynamics in methanol. They find a significant contribution of O–H librational motion in the spectrum of the solvent coordinate velocity autocorrelation function. We have previously explored the molecular origin of the inertial response for solvation experiments (obtained with a 170fs instrument response) by using a Brownian oscillator model for methanol.\textsuperscript{25} This model requires a spectral density of solvent modes responsible for the solvation and a damping parameter which separates underdamped and overdamped modes. As a rough approximation we used the spectral density obtained from optical Kerr measurements of pure methanol. Our preliminary conclusion was that frequencies associated with both O–H librational motion and hindered molecular rotation are responsible for the total initial decay. This is consistent with the discussion of the MD results given above, however a more quantitative discussion requires improved optical Kerr data.

Consistent with the simulation results, the initial decay in C(t) is faster and comprises a larger portion of the response for IAN than Cl53. The implication from the simulation is that extensive cancellations between the responses for individual atomic sites in Cl53 are responsible for the comparatively low amplitude of the inertial component. To what extent this is a general phenomenon in large polyatomic solutes remains to be investigated.

VII. Conclusions

The agreement between the simulation and experiment over the whole time range for Cl53 in methanol (Figure 15) is better than can be reasonably expected given (a) the sensitivity of the simulations to details of the electronic charge distribution and (b) the complexity of analyzing experimental data containing a sizable inertial (Gaussian) contribution. Nonetheless comparison of the two results shows that a sizable ultrafast component does exist in the solvation response of methanol. Classical molecular dynamics simulations, combined with semi-empirical quantum chemical calculations appear to give
quite accurate predictions, whereas simulations based on atomic solutes do not. In the case of C153 (but not 1AN) the simulations show that cross correlations between the response functions of individual atomic sites play a major role in reducing the amplitude of the inertial contribution and slowing the overall response function.

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References
55. See, for example, M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon, Oxford, 1987) for a description of these techniques.
58. AMPAC 4.5, distributed by A. J. Holder, Semichem Inc.
Note that Eqs. 10 and 11 in Ref. 39 contain typographical errors.

Actually, one could question how appropriate it is to call the entire Gaussian part of the response "free-streaming" even in a solvent such as acetonitrile. However, the fact that the initial frequency $\omega_0$ suffices to determine the shape of the entire Gaussian component, as well as the results of independent-molecule simulations [47], suggest that this simple dynamics accounts for much of the solvation energy relaxation in a number of systems.

The fields here are assumed to be directed along the $z$ direction. For this comparison we have used what Skaf et al. term the reorientational part of the longitudinal tcf.


P. V. Kumar and M. Maroncelli, manuscript in preparation.

See for example the recent discussion by P. R. Callis, J. Chem. Phys. 95, 4230 (1991).


R. S. Fee and M. P. Maroncelli, manuscript in preparation.