

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231657014>

Nonreactive Dynamics in Solution: The Emerging Molecular View of Solvation Dynamics and Vibrational Relaxation

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY · JULY 1996

Impact Factor: 2.78 · DOI: 10.1021/jp9608483

CITATIONS

516

READS

26

1 AUTHOR:



[Richard M. Stratt](#)

Brown University

122 PUBLICATIONS 4,258 CITATIONS

SEE PROFILE

Nonreactive Dynamics in Solution: The Emerging Molecular View of Solvation Dynamics and Vibrational Relaxation

Richard M. Stratt*

Department of Chemistry, Brown University, Providence, Rhode Island 02912

Mark Maroncelli*

Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania 16802-6300

Received: March 19, 1996[⊗]

Two of the more fundamental ways in which molecules change their behavior when they are dissolved are that they can begin to exchange energy with the surrounding liquid and they can induce their surroundings to rearrange so as to provide a significant stabilizing influence. The first of these is typified by the process of vibrational population relaxation of a vibrationally hot species. The second concept—critical to solution chemistry—is what is known as solvation. Both of these processes are sufficiently fundamental that one would really like to know, at the most mechanical and molecular level possible, just what events are required in order to make them happen. But how difficult is it going to be to extract such molecular detail from the complicated many-body dynamics? The most microscopic level of understanding one could ever hope to possess might seem far removed from the finely detailed dynamical information which is available routinely for individual isolated molecules and for molecule–molecule collisions in molecular beams. It might even seem that the broad, almost featureless character of typical solute spectra would condemn us to never being able to measure anything more than a few paucity tidbits of highly averaged data caricaturing the intriguing processes that can take place in liquids. However, spectroscopists have for some time been able to infer at least some aspects of the dynamics of liquids from the spectroscopy of dissolved molecules, and with the advent of novel ultrafast time-resolved spectroscopies and new theoretical perspectives, the likelihood of resolving solution dynamics into genuinely molecular components has increased dramatically. We discuss a few of these recent developments here for the special, but nonetheless illuminating, cases of solvation dynamics and vibrational relaxation and note a few of the more promising directions that future work might take.

I. Introduction

The elementary events that make chemistry happen in solution are nothing more complicated than the translation, rotation, and vibration of molecules. But precisely how do such processes occur in liquids? Is the dynamics of these degrees of freedom largely the same as it is in isolated molecules, or does the presence of a liquid somehow fundamentally complicate the molecular motion? One of the pivotal realizations in chemical spectroscopy was that the answer to these questions was buried in the shapes of spectral peaks.¹ The very breadth of the peaks and the apparent featurelessness of liquid-state spectra—which sometimes made a depressing contrast with their pristine gas-phase equivalents—were actually expressing vital information about solution-phase dynamics. The idea was quite simple: The molecular events associated with a given kind of spectroscopy have their own natural time scale specified by dividing the energy of the relevant quantum transition into Planck's constant. Thus, NMR experiments probe events on a micro- to nanosecond time scale, whereas IR spectroscopy monitors the pico- to femtosecond regime. If the dynamics of interest to us took place on roughly the natural spectroscopic time scale, then our spectrum would be broadened, but if all of the perturbing activities were either much faster or much slower, the end result would be a sharp peak (although the annoying possibility was always there that there would be so many of these sharp peaks that spectrum would end up being broad for the wrong reason). The cleanest and most familiar example of these phenomena is

that of chemical exchange in NMR.² At low temperatures the spectrum of two interconverting species starts out as two sharp peaks, but as the temperature increases and the rate of interconversion first reaches and then surpasses the NMR time scale, the peaks coalesce into a single broad peak which subsequently sharpens into a single (“motionally narrowed”) peak.

This observation that the frequency spread—the line width—of a spectrum was a powerful dynamical tool provided many of the earliest insights into molecular motion in liquids.³ In formal terms, there was an equivalence between the information being recorded as a function of frequency and the information desired as a function of time. In fact, the measured spectrum was just the Fourier transform of the temporal development.¹ If one wanted to know how much a molecule's orientation (or one of its vibrational normal modes) remembered of its earlier history, the correlation function that expressed that memory, $C(t)$, was the Fourier transform equivalent of the corresponding spectrum, $I(\omega)$.

$$I(\omega) = (1/2\pi) \int_{-\infty}^{\infty} dt e^{-i\omega t} C(t)$$

This kind of relation yielded much of what we now know about the liquid state. In particular, through it and closely related expressions, dielectric, Raman, and infrared spectroscopies provided our first measurements of molecular motion on a picosecond scale.⁴

What became increasingly clear, however, was that simply looking at line widths compressed too much dynamical informa-

* To whom correspondence should be addressed.

[⊗] Abstract published in *Advance ACS Abstracts*, July 1, 1996.

tion into a single number. The line width did yield an immediate value for the characteristic liquid time scale, the so-called T_2 (dephasing) time, precisely as promised, but this single time hid a host of diverse possibilities. If events in the liquid were happening just rapidly enough to cause line broadening, we could never be sure whether we were looking at a simple mechanical interference with the subject molecule's dynamics (pure dephasing, with a time scale T_2^*) or a more serious perturbation capable of causing an actual leakage of energy from the molecule (energy relaxation, with a time scale T_1)—or perhaps a little of both.⁵ Moreover, if some slower liquid process were taking place, it could create the illusion of there being an assortment of different immobile liquid environments, each with its own effect on the energetics of the spectroscopic transition. The resulting spread of transition frequencies would also broaden the spectrum, but via an inhomogeneous broadening mechanism, as opposed to the purely dynamical, homogeneous (T_1 and T_2^*) broadening mechanism of real interest.⁶ To make matters worse, this division into homogeneous and inhomogeneous is no better than an indication of the extreme possibilities open to the liquid. Probably a better way to view things would be to note that as a nearly static liquid environment starts to speed up, a continuum of possibilities opens up, ranging from the classic inhomogeneous broadening one sees in a low-temperature glass, to the sometimes barely noticeable time evolution of the various possible environments (spectral diffusion),⁷ to genuine homogeneous broadening.

Even without these unresolved alternatives, it would have been only natural to wonder whether this limited glimpse of the dynamics was the best one could do. To begin with, if the actual course of time evolution turned out not to be a simple exponential, it was conceivable that there would be no single time that could adequately characterize the dynamics—and as dielectric studies implied early on,⁸ and more recent ultrafast measurements have reemphasized,⁹ such multiple time scales are indeed a common occurrence and are part of what makes liquid dynamics interesting. In fact, there is some evidence that observable events in liquids can be spread over a remarkably large dynamic range, especially in hydrogen-bonded solvents.¹⁰ From a more chemical perspective, line width measurements impose yet a different kind of limitation. What one would eventually like to know is not simply time scales, but which solvent molecules are moving, in what way, and by how much when solvation occurs or when some reactant is thermally activated. Measuring line widths, by contrast, is much the same as measuring reaction rate constants. In the end one has an interesting, yet fundamentally macroscopic, indication of rate that has buried within it all of the myriad mysteries of the process.

What has changed materially since the earliest days of liquid-state dynamics is the arrival of a combination of promising developments in both the experimental and theoretical arenas. On the experimental side, not only has there been considerable progress in extracting more than just simple line widths from frequency-domain spectra,⁴ there is a newfound ability to perform spectroscopy in the picosecond and subpicosecond time domain.¹¹ It is now possible to excite the molecules in a liquid either electronically or vibrationally with one or more femto-second pulses of light and then come in anywhere from femto- to nanoseconds later to probe the results with one or more new pulses. This capability has produced some entirely novel experiments as well as opening up some of the older experiments to new phenomena. The long familiar idea of time-dependent fluorescence, for example, is based on the observation that if one electronically excites some dissolved dye molecule, it will eventually fluoresce back down to its electronic ground state.

Naturally, the very fastest fluorescence would correspond to the dye emitting light of roughly the same characteristics as had just been absorbed. However, if something about the solute–solvent system changed as time evolved, the time profile of the subsequent fluorescence would reveal that dynamics. For example, time-resolved studies have long been used to probe the slow reorientation of polymers and biomolecules on a nanosecond time scale: One excited a dye with light of one polarization and watched for the resulting fluorescence to lose its polarization with time.¹²

It is certainly true that the reorientation times measurable by this technique have gotten faster and faster in recent years,¹³ but as we shall detail in the next section, the majority of the current interest in the technique arises from its striking ability to measure the *dynamics of solvation* in real time. The opportunity to look at solvation comes about because the solute–solvent system changes its energy as the solvation process proceeds; in a time-dependent fluorescence experiment, the solvent, which had been sitting happily around the ground state of the dye, would gradually come to realize that it could lower its free energy by relaxing to conform to the newly created excited state. The fluorescence would thus begin to be more and more red-shifted as the relaxation progressed. These experiments, as with the rotational dynamics study, are no longer novel in concept, but for the first time their time resolution is beginning to be fine enough to resolve the elementary events in solvation¹⁴—and it is there that the really molecular information becomes available. We shall discuss these experiments and their interpretation in section II.

There are yet other kinds of experiments that have been made possible for the first time by other kinds of recent technical developments. The advent of tunable sources of infrared pulses has made explicit measurements of *vibrational relaxation* a reality. Instead of relying on inferences from vibrational line widths to gauge the flow of energy into or out of a dissolved molecule, one can now place a molecule into a specific excited vibrational state and directly monitor the population of that state as a function of time.¹⁵ Moreover, with the aid of properly chosen pulse sequences, one can perform infrared¹⁶ and Raman¹⁷ echo experiments that unambiguously determine the extent to which the solvent influence is homogeneous or inhomogeneous. The lessons being learned from these ongoing experiments will be the subject of section III of this paper.

There are still other noteworthy advances in ultrafast spectroscopy that bear mentioning. Echo experiments analogous to those characterizing the vibrational states of solutes in liquids have also been performed with the electronic states.¹⁸ The issue there is how fast the time scale is over which a solvent perturbs the vibronic dynamics of a solute. In a notably different vein, it has also become possible to probe not just the perspective on a liquid revealed by an individual solute, but the subpicosecond dynamics of a liquid as a whole. These optical Kerr effect¹⁹ (or equivalently impulsive-stimulated-scattering²⁰ or Fourier-transform Raman²¹) spectra measure the relaxation of a transient polarization anisotropy created by some initial optical pump pulses, in effect performing a time-domain version of Raman spectroscopy.

We shall not be discussing these other advances much in this paper, in part because of space limitations, in part because of our own personal predilections, but also because the experimental solvation dynamics and vibrational relaxation studies have begun to make real contacts with some of the parallel developments taking place in theory and have done so at a bit more rapid pace than have, say, electronic dephasing and optical Kerr effect measurements.²² The most dramatic of these theoretical connections are through simulation. It has proven

possible to reproduce not just the general features but the quantitative details of time-dependent fluorescence solvation experiments just by running classical trajectories on the solute–solvent system. One does need to know (or estimate) both the ground- and excited-state solute–solvent potentials for these calculations,²³ but the results have proven reasonably insensitive to such details, reinforcing the idea that such experiments are largely probes of the solvent itself. With the incorporation of new multiple-time-scale methods,²⁴ simulations have also begun to prove their worth in predicting vibrational relaxation, albeit in not quite as quantitative a fashion.²⁵

Of course, simulations, in a sense, are nothing more than exquisitely well-controlled experiments. In their simplest form they are not about providing explanations for the phenomena they display—any more than traditional experiments are. What simulations do do well, though, is provide a rigorous testing ground for our conceptual understanding and for the streamlined analytical models that express our intuition. So, what has been equally important is that recent years have also seen significant progress in developing accurate models for the solvation process.²⁶ Ever more sophisticated liquid-theory techniques have reached the point that some of them can now predict solvation dynamics with something approaching the success enjoyed by comparable theories of equilibrium liquid structure.^{27,28} Moreover, complementary to these developments, a rather different theoretical approach to analyzing liquid dynamics has begun to prove its mettle in the solvation problem. The subpicosecond time scale over which most solvation seems to take place (at least in common solvents) means that the key to thinking about the process is the short-time dynamics. But for times under half a picosecond or so it has proven possible to view the liquid dynamics rigorously as if it arose from certain harmonic normal modes of the solution as a whole.²⁹ When one partitions the solvent's influence through such instantaneous normal modes, it becomes clear that it is indeed meaningful—and even practical—to pose the mechanistic questions of which molecules are doing what moving in a solution process.^{30,31}

The analytical theory of vibrational relaxation is somewhat less well advanced than that of solvation dynamics despite a long history of effort in the area, but here too the comparison with recent simulations and with newer, time-domain experiments has proven stimulating. In a sense that we shall detail later, much of the theory in this field has remained mesmerized by its early success in predicting T_1 times, a success that provided little insight into liquid dynamics.³² But now that higher level information is available, the subject is being revisited. One particularly promising avenue has come from the realization that solute dynamics can be thought of as being governed by an effective equation of motion which includes not only the forces operating inside the molecule itself but also the effective forces arising from the solvent. It is becoming increasingly clear that such generalized Langevin equation descriptions³³ are no longer the theorist's play toys they once were; the *exact* frictional and fluctuating forces that encapsulate the solvent's influence on the solute in this representation can now be extracted from simulations (rather than being simply hypothesized).³⁴ Indeed, the problem of understanding vibrational relaxation has become largely synonymous with understanding this friction.^{24,35} Both simulation methods and instantaneous-normal-mode analysis have revealed that not only can one begin to predict the form of this friction, one can, as with solvation, begin to pose and answer mechanistic questions. This development is a particularly exciting one because the very same friction is also one of the principal ingredients in current models for chemical reaction dynamics in solution.³⁶

Let us turn first, however, to the study of solvation dynamics.

II. Solvation Dynamics: The Time Dependence of Solvent–Solute Interactions

Solute–solvent interactions have both a static and a dynamic aspect. If one observes the interaction energy between a solute molecule and its solvent surroundings as a function of time, $E(t)$, one finds that it fluctuates rapidly about some average value $\langle E \rangle$. As we will discuss in more detail in the next section, the time dependence of these fluctuations, $\delta E(t) = E(t) - \langle E \rangle$, is intimately connected to the frictional forces that mediate a variety of dynamical processes that take place in a solvent environment. In particular, it is the ensemble-averaged ($\langle \dots \rangle$) behavior of these fluctuations, as embodied in the time-correlation function $\langle \delta E(0) \delta E(t) \rangle$, that serves as the time-dependent friction kernel in many dynamical problems. One of the goals of recent research in liquid state dynamics has therefore been to understand the time dependence of such correlations, a phenomenon that has come to be known as “solvation dynamics”. What are some of the questions one would like to ask about such dynamics, and how can one go about answering them? Some of the most important questions are: What are the amplitudes and time scales involved in $\langle \delta E(0) \delta E(t) \rangle$ for a given system? How can these characteristics be understood in terms of the properties of the particular solute/solvent system considered? Furthermore, what are the underlying molecular-level interactions and motions that give rise to such dynamics, i.e., what are the solvation “mechanisms” in particular cases?

A. Experimental Measurements. We first consider what experiment has to say about such questions. In contrast to studies of pure fluids, where information about ultrafast dynamics has historically been derived from frequency-domain spectroscopies,³⁷ recent studies of solvation dynamics have mainly employed time-resolved methods. An ultrashort pulse of light is used to resonantly excite a solute molecule from its ground electronic state (S_0) into some other state, usually S_1 ,³⁸ whose interactions with the solvent differ significantly from those of S_0 .³⁹ Solvation dynamics can then be measured in terms of $\langle \delta \nu(0) \delta \nu(t) \rangle$, the spectroscopic equivalent of $\langle \delta E(0) \delta E(t) \rangle$, where the fluctuating frequency $\nu(t)$ reflects the *difference* in solvation energies between the two electronic states involved, $\nu(t) = \Delta E(t)/h$. Virtually all types of electronic spectroscopy in solution contain some information about the function $\langle \delta \nu(0) \delta \nu(t) \rangle$,⁴⁰ and there is considerable effort now being focused on understanding how to derive information on solvation dynamics from multipulse photon-echo and other coherent spectroscopies.⁴¹ But while such methods do promise to provide the ultimate in time resolution (~ 10 – 20 fs range), their connection to solvation is still being clarified. Rather than attempting to describe these most recent developments, we will therefore concentrate on the most widely used and the conceptually simplest approach, which entails measurement of time-resolved spontaneous emission spectra.⁴²

As illustrated in Figure 1, excitation with a short light pulse leads to initial nonequilibrium populations of solute molecules in the electronically excited state. Solvent motions reestablish equilibrium distributions in S_1 on a time scale that is typically much faster than electronic relaxation ($S_1 \rightarrow S_0$). In time-resolved emission spectroscopy the time dependence of the excited-state distribution is monitored via the frequency shift of the emission spectrum after excitation.⁴³ The temporal features of the solvation are captured in the normalized response function,

$$S_r(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)} \quad (2.1)$$

where $\nu(t)$ is some characteristic feature (such as the peak) of

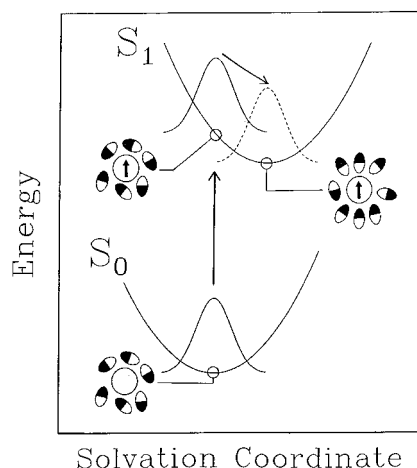


Figure 1. Schematic diagram of how an electronic transition in a solute can be used to study the dynamics of solvation. Shown here is a caricature of a polar solvent's response to excitation of a solute which has zero dipole moment in its ground state (S_0) but a large dipole in its excited electronic state (S_1). A short laser pulse is used to excite the solute from S_0 to S_1 . Since the electronic transition is rapid compared to nuclear motions of the solvent, the excited state is initially prepared with a solvation environment that is characteristic of equilibrium in S_0 , not S_1 . Over time the solvent reorganizes or progresses along the "solvation coordinate", in order to lower the solvation energy in the excited state. This relaxation can be followed by measuring the emission from the solute as a function of time after excitation. Solvation leads to a time-dependent red shift of the emission spectrum that can be used via eq 2.1 as a direct probe of the solvation dynamics.

the emission spectrum at time t . How is this nonequilibrium function connected to the solvent fluctuations $\langle \delta E(0) \delta E(t) \rangle$ that we originally called solvation dynamics? Assuming that the perturbation caused by the electronic transition is not too large, a simple linear response calculation provides the relation

$$S_\nu(t) \cong C_{\Delta E}(t) \equiv \frac{\langle \delta \Delta E(0) \delta \Delta E(t) \rangle}{\langle \delta \Delta E^2 \rangle} = \frac{\langle \delta \nu(0) \delta \nu(t) \rangle}{\langle \delta \nu^2 \rangle} \quad (2.2)$$

Equation 2.2 states that the response ($S_\nu(t)$) of the system when "driven" by the solute perturbation reflects the very same dynamics as the fluctuations of the energy gap $\Delta E = h\nu$ experienced by an unperturbed solute in equilibrium with its solvent environment. The physical content of this "fluctuation-dissipation" connection is that, if the perturbation is not too large (or if the interactions are harmonic), relaxation of the "forced" departure from equilibrium produced by the electronic transition is no different from the relaxation of a naturally occurring fluctuation in the unperturbed system. As we will discuss later, the connection between $S_\nu(t)$ and $C_{\Delta E}(t)$ embodied in eq 2.2 appears to be justified for most of the experimental systems studied to date. In such cases, measuring $S_\nu(t)$ is equivalent to directly measuring the solvation dynamics of interest, with the caveat that it is not the total solvent-solute interaction energy E that is probed, but only that part of the total that differs in the two electronic states (ΔE).

Solvation encompasses a wide range of different intermolecular interactions. Dispersion and other induced-dipole interactions, dipole-dipole or higher-order multipolar interactions, and specific interactions such as hydrogen bonding may all contribute to solvation in a given system. In principle, one can select probe solutes whose electronic transitions are primarily sensitive to only one type of interaction and thereby study the dynamics of these particular interactions in isolation. However, in practice, finding the right probes to achieve this separation can be difficult. To date, only measurements of the solute *s*-tetrazine and its dimethyl derivative⁴⁴ have been

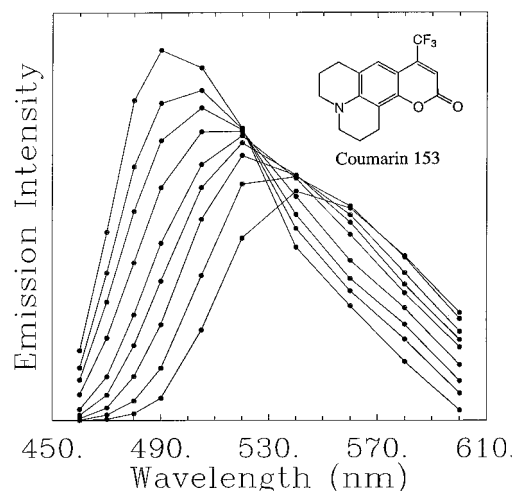


Figure 2. Representative time-resolved emission spectra of C153 (296 K) in formamide showing the continuous red shift with time characteristic of solvation dynamics. The times represented are 0, 0.05, 0.1, 0.2, 0.5, 1, 2, 5, and 50 ps in order of decreasing peak intensity. (See ref 51 for more details.)

interpreted as probing the dynamics of mainly dispersion-type interactions.⁴⁵ While dispersion interactions are present in all solute/solvent systems, the shifts they produce are relatively small (a few hundred cm^{-1}), and very careful characterization of the spectrum in solution and the gas phase is necessary to extract information about their dynamics.⁴⁴ Larger spectral shifts are obtained for stronger interactions such as hydrogen bonding and dipolar interactions, and much more data are available concerning such solvation mechanisms. For example, several molecules used in recent studies, including resorufin,⁴⁶ the benzophenone anion,⁴⁷ and a number of aromatic amines,⁴⁸ appear to mainly report on the energetics of specific solute-solvent hydrogen bonding. What is observed in these systems tends to depend on the particular solute considered, and at this point too little experimental data are available to draw any general conclusions regarding this type of solvation. The situation is much more favorable as regards what we will term nonspecific dipolar solvation. The overwhelming majority of time-dependent solvation studies have concerned this class of systems, which involve solutes that undergo a large change in dipole moment between the S_0 and S_1 states. These are the same sorts of molecules whose equilibrium solvatochromism (spectral shift with solvent) has served as a basis for the empirical scales of solvent polarity widely used in organic chemistry.⁴⁹ While other solvation mechanisms may be present in large dipole solutes, judicious selection allows one to focus on the dynamics of nonspecific solute dipole-solvent dipole (or multipole) interactions. Because so much more is known both experimentally and theoretically about this final type of solvation, in what follows we will mainly focus our attention on describing its features.

A representative "dipolar solvation" probe, which has enjoyed wide use in dynamical solvation studies,^{42,50,51} is coumarin 153 (C153), shown in the inset to Figure 2. Excitation of C153 causes a redistribution of π electron density within the molecule which increases its dipole moment by about 8 D.^{52,53} This dipole change produces a sizable change in the probe's solvation energy and thereby leads to time-dependent emission spectra of the sort illustrated in Figure 2. As can be seen from this figure, the primary change taking place over time is a continuous red shift of the emission band. This shift reflects the continuous evolution of the average solvation environment or solvation energy. Response functions ($S_\nu(t)$, eq 2.1) generated from such time-dependent spectra are provided in Figure 3, which contains

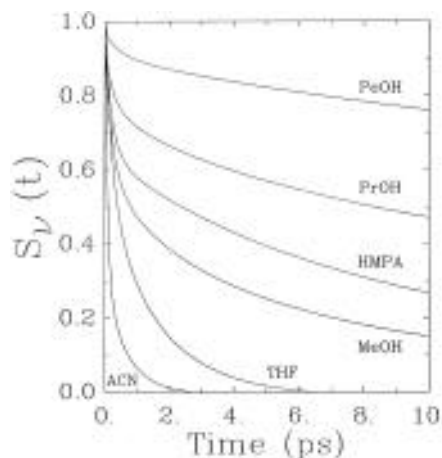


Figure 3. Spectral (or solvation) response functions (eq 2.1) derived from time-resolved emission data on C153 in a variety of solvents at room temperature. The solvents represented are as follows: ACN = acetonitrile, THF = tetrahydrofuran, MeOH = methanol, HMPA = hexamethylphosphoramide, PrOH = 1-propanol, and PeOH = 1-pentanol. (See ref 51 for more details.)

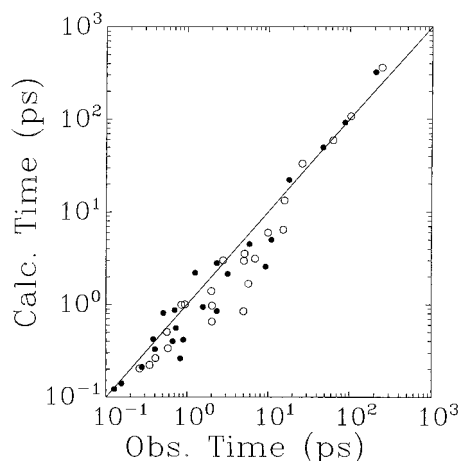


Figure 4. Comparison of characteristic times of the spectral/solvation response functions observed using C153 and calculated on the basis of a simple dielectric continuum theory. The theoretical calculations correspond to the response predicted for a spherical cavity, point-dipole solute using the full dielectric response of the solvent. The two times plotted here are the $1/e$ times (open symbols) and integral (or correlation) times (filled symbols) of the response functions. Data for 24 solvents are shown. (See ref 51 for further details.)

representative results for a number of common room temperature solvents. These data serve to illustrate two important features of the solvation response. The first is that relaxation of the solvation energy takes place on two widely separated time scales. The initial relaxation of $S_v(t)$ is very rapid, such that it is essentially complete within ~ 1 ps. The remainder of the relaxation typically takes place on a much longer time scale. In the case of aprotic solvents, the slower solvation component involves times in the 1–10 ps range, while in associated and/or more viscous solvents, tens to hundreds of picoseconds may be required to fully relax the solvation energy. The second feature to be noted in these data is the impressive range of solvation times observed in different solvents. This point is better illustrated in Figure 4, where we have plotted two characteristic times of the $S_v(t)$ response functions of C153 measured in 24 solvents at room temperature. The solvation times shown here span more than 3 decades in time, ranging from ~ 0.1 ps in acetonitrile to ~ 200 ps in 1-decanol. Even longer times, extending into the nanosecond range, can be observed in highly viscous solvents such as butanediol or glycerol at room temperature.

B. Dielectric Theories. Experimental data of the sort illustrated in Figures 3 and 4 have served to characterize the nature and time scales of solvation in many of the solvents commonly used in “wet” chemistry. Thus, we have an empirical answer to the first question raised above, namely what the main features of the solvation response are, at least for the case of dipolar solvation. We can also answer the question concerning which solute/solvent features serve to determine the dynamics in these systems. To a reasonable first approximation, the dynamics are insensitive to the particular probe solute employed.⁴⁸ It is really the solvent’s attributes that determine the wide range of solvation times illustrated in Figure 4. And, if attention is again confined to nonspecific dipolar solvation, only a single (albeit remarkably complicated) property of the solvent is required in order to model the observed times. This property is the solvent’s dielectric response function, $\epsilon(\omega)$.

We digress momentarily in order to explain the nature of this function.⁵⁴ The dielectric response of a solvent describes the proportionality between an electric field (E) and the polarization (P ; dipole moment per unit volume) it induces in the solvent. For a sinusoidal field of frequency ω , the relationship is $4\pi\vec{P}(\omega) = \{\epsilon(\omega) - 1\}\vec{E}(\omega)$. For ω less than a few megahertz, $\epsilon(\omega) \cong \epsilon_0$, where ϵ_0 is the familiar static dielectric constant of the solvent. As frequency increases through the giga- and terahertz range, $\epsilon(\omega)$ decreases in a stepwise fashion as various molecular motions become too slow to keep up with variations of the applied field. (Ultimately, when only electronic motions can follow the applied field, the limiting value $\epsilon(\omega) \cong n^2$, where n is the optical refractive index, is reached.) For this reason, dielectric dispersion measurements were widely used in the 1950s–1960s in order to learn about motions (mainly rotational) of dipolar molecules in solution.⁵⁴ (However, interpreting the dielectric response of solvents in molecular terms is a difficult task, and one which is still being pursued today.^{55,56})

If one views electronic excitation of the solute as in effect imposing a time-dependent electric field to which the solvent responds, it is easy to see why $\epsilon(\omega)$ should be intimately connected to the dynamics of polar solvation. In fact, a knowledge of $\epsilon(\omega)$ would allow for exact (and relatively simple) prediction of $S_v(t)$ if the solute were of macroscopic size and if only electrostatic interactions were important. Such predictions are termed “continuum theory” predictions, in the sense that they assume that the relative size of the solvent molecules is negligible compared to the solute size, i.e., that the solute effectively views the solvent as a continuous dielectric fluid. Although such a picture cannot be completely correct for molecular solutes like C153, continuum predictions serve as an important benchmark that should be approached in the limit of large solute to solvent size ratio.⁵⁷ Figure 4 shows that, in fact, the solvent dependence of solvation times is reasonably well accounted for by such a naive model. Although the observed solvation times are slower on average than those predicted, and although many predictions are incorrect by more than a factor of 2, the general agreement between observed and calculated times is remarkably good. (It should be noted that simpler solvent properties, viscosity for example, are unable to correlate the wide range of times observed in this set of solvents.)

Due to this clear connection between solvation dynamics and the solvent’s dielectric response, a number of more advanced theories have been developed which begin with $\epsilon(\omega)$ as dynamical input, but which also include effects due to the molecular nature of the solvent.^{26–28,58} The most sophisticated of these theories uses fully atomistic representations for both the solute and solvent,^{27,28} and recent comparisons have shown it to be capable of quantitatively reproducing both the static

and dynamic aspects of solvation of C153.⁵⁹ Thus, at least in the case of dipolar solvation, one might be lead to conclude that a "complete" theoretical understanding of solvation has been achieved. However, it must be remembered that much of the success of these theories rests on using the dynamical content of the complicated function $\epsilon(\omega)$, determined from experiment. While there has been some recent progress in formulating "*ab initio*" theories of $\epsilon(\omega)$ for idealized model solvents,⁵⁶ we are a long way from being able to model realistic solvents. Thus, the quantitatively successful theories to date are ones that relate two complex phenomena, solvation dynamics and dielectric relaxation, rather than providing an *ab initio* theory of either one. We do not mean to minimize the importance of these theories, but it is important to keep this distinction in mind.⁶⁰

C. Computer Simulations and the "Mechanisms" of Solvation. We now turn to the question of the molecular "mechanisms" of solvation. Computer simulations have played the leading role in shaping our understanding of this aspect of the problem.⁶¹ Although a variety of levels of sophistication have been applied,⁶² most simulations of solvation dynamics have involved the following simple prescription. First, intermolecular potential functions suitable for modeling the solvent and solute of interest are derived from electronic structure calculations and/or from fitting to empirical information. A single solute is placed in a periodic bath of a few hundred solvent molecules, and the classical equations of motion in the presence of the intermolecular interactions are solved numerically. After a suitable equilibration period, the solvation response can be simulated by making an instantaneous change in the solute-solvent interaction potential and following the ensuing dynamics. Averaging over many such solute "jumps" from independent initial conditions provides the simulation equivalent to $S_V(t)$ as in eq 2.1. An even simpler method is to monitor the temporal behavior of fluctuations in an equilibrium simulation and calculate $C_{\Delta E}(t)$ directly according to eq 2.2. While the former approach corresponds more closely to the time-resolved fluorescence experiment, the latter is more directly tied to theoretical treatments of solvation dynamics. The two are equivalent insofar as the dynamics of interest lies in the linear regime.

One of the first surprises uncovered by computer simulation was the fact that this linear response connection holds true in many cases, even when a relatively severe solute perturbation is applied.⁶³ For example, the act of charging a small atom ($A^0 \rightarrow A^+$) represents a severe test, considering that the difference in solvation energy between the two states is of order $100k_B T$ in a strongly polar solvent. This large difference means that a system in equilibrium with the A^0 solute never samples a fluctuation in energy comparable to the actual change in the $A^0 \rightarrow A^+$ process. For strict adherence to the linear response limit, the two states involved in the perturbation should be "reachable" via equilibrium fluctuations in either state. Nevertheless, in many cases the dynamics of $S_V(t)$ and that of $C_{\Delta E}(t)$ (calculated on the basis of either the A^0 or the A^+ states) are found to be nearly the same. This extended range of linearity probably reflects the fact that, in a highly polar solvent, solvent-solvent interactions are sufficiently strong that (within limits) the solute electronic state and, indeed, even the presence of the solute have little effect on the dynamics of the solvent. This is especially true in the case of polyatomic solutes of the sort studied in experiment. However, it is important to point out that linear behavior is not always observed. In simulations of some systems, significant differences between $S_V(t)$ and $C_{\Delta E}(t)$ have been noted⁶⁴ even for polyatomic solutes.^{52a} These cases all appear to be related to significant changes in the solute-solvent hydrogen bonding in the two solute states considered.

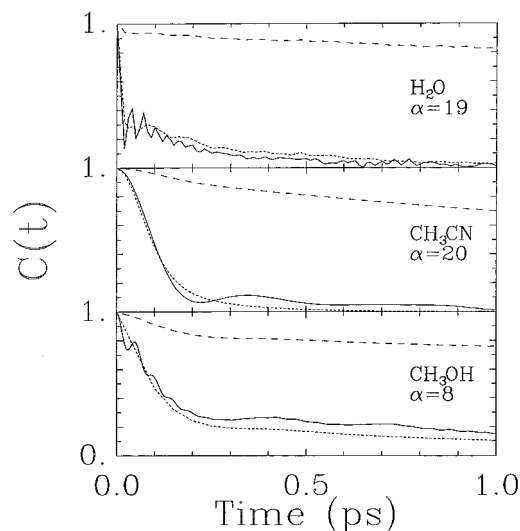


Figure 5. Illustration of the connection between the simulated solvation response in three solvents and the reorientational behavior of individual solvent molecules, as embodied in the dipole autocorrelation function $\langle \hat{\mu}(0) \cdot \hat{\mu}(t) \rangle$. The solid curves in this figure are solvation correlation functions ($C_{\Delta E}(t)$) corresponding to turning on a charge in a small atomic solute. The long-dashed curves are the $\langle \hat{\mu}(0) \cdot \hat{\mu}(t) \rangle$ functions of the solvent (measured in the absence of the solute), and the short-dashed curves are the predictions of eq 2.3 using the α values indicated. (See ref 66 for more details.)

An example of this type of behavior will be considered later. However, we first consider what simulations have to say about nonspecific solvation in the linear regime (i.e., the regime relevant for comparison to the experimental results on C153).

Computer simulations have provided important insight into the origin of the biphasic character of the solvation response. In fact, since time resolution is much easier to come by in computer simulation, the prominent ultrafast component of solvation was actually discovered in simulations well before it was observed experimentally. Initial computer studies focused on the behavior of small atomic or diatomic solutes in small-molecule solvents.⁶³ Examples of the solvation correlation functions [$C_{\Delta E}(t)$] observed in such simulations are provided in Figure 5 (solid curves). In all three of these examples the initial part of the solvation response accounts for well over half of the relaxation. In acetonitrile and methanol the time scale of the fast component is 100–200 fs, whereas in water it is a mere 20 fs! The separation of time scales between the fast and slow portions of the response discussed with respect to experiment is even more obvious in these examples. One feature of the simulated functions, not observed in fluorescence experiments, due to limited time resolution,⁶⁵ is the Gaussian character of the fast response. This Gaussian character is most clearly displayed in the acetonitrile data in Figure 5. In this solvent, virtually all of the rapid part of the response is well approximated by a Gaussian function of time, $\exp(-1/2\omega_s^2 t^2)$, with the "solvation frequency" ω_s determined from the curvature of $C_{\Delta E}(t)$ at $t = 0$. Another difference between these simulated functions and the experimental responses in Figure 3 is the oscillations that are evident in the former, especially in hydroxylic solvents. (Such oscillations are much more subtle in the solvation response to polyatomic solutes, and they are probably too small to be observed experimentally.) The presence of oscillations in the simulated dynamics indicates that it may be better to think of there being in fact three rather than just two phases to the response. Both the initial Gaussian shape and the oscillations in $C_{\Delta E}(t)$ are indicative of the underdamped or "inertial" nature of motions of solvent molecules at early times. At sufficiently short times, the motions of molecules are independent of intermolecular interactions. (That is, if one

expands a coordinate “ x ” of a molecule in a Taylor series, $x(\Delta t) = x(0) + \dot{x}(0)\Delta t + \frac{1}{2}\ddot{x}(0)\Delta t^2 + \dots$, the intermolecular forces ($f = m\ddot{x}$) do not appear until second order in Δt .) The solvation frequency ω_s , which characterizes the initial Gaussian decay of the solvation energy, merely reflects the “free streaming” of solvent molecules uncoupled from one another.^{30,63c,d,66,67} This free-streaming motion represents the first phase of solvation. The oscillations, on the other hand, represent collective dynamics occurring in an intermediate time regime. Within this phase of solvation molecules are colliding with their neighbors (and the solute) and rebounding in a relatively coherent fashion for some length of time, exhibiting behavior similar to that of an underdamped oscillator. However, these oscillations die out relatively quickly. After on the order of 0.5 ps the motions become dissipative in the sense that an individual molecule no longer “remembers” what velocity it had time zero and the oscillations die out. This loss of memory leads to the final phase of solvation, which involves purely diffusive or overdamped behavior. In the cases illustrated here this diffusive component of solvation accounts for only the last 30% or so of the total relaxation.

In the case of the atomic solutes represented in Figure 5, the “mechanism” of solvation is particularly easy to understand. Here the collective dynamics of solvation can be modeled in terms of the rotational motions of individual solvent molecules.^{63c,66} In particular, if the orientation of a solvent molecule is specified by its dipole moment direction $\hat{\mu}$, the solvation response can be approximated by^{66,67}

$$S_\nu(t) \cong C_{\Delta E}(t) \cong \{\langle \hat{\mu}(0) \cdot \hat{\mu}(t) \rangle\}^\alpha \quad (2.3)$$

In this expression $\langle \hat{\mu}(0) \cdot \hat{\mu}(t) \rangle$ is the dipole autocorrelation function of a single solvent molecule in the absence of the solute. This function provides one of the simplest representations of solvent rotational motion, describing it in terms of the average loss of memory of the initial orientation of a solvent molecule. The power α is a function only of the dipole density and dielectric constant of the (pure) solvent.⁶⁶ It contains all information about the effect that *static* correlations between solvent molecules have on the solvation energy.

The long-dashed curves in Figure 5 are the reorientational correlation functions, $\langle \hat{\mu}(0) \cdot \hat{\mu}(t) \rangle$, observed in the pure solvents, and the short-dashed curves are the predictions of eq 2.3, using the values of α shown in the figure. The level of agreement illustrated here (and in a number of other cases^{61a,66} indicates that, at least for solvation of atomic solutes, one can describe the solvation mechanism in terms of rotational motions of single solvent molecules. This observation may seem to be at odds with the fact that there is such a striking difference in time scale between solvation and solvent-molecule orientational relaxation. The difference is accounted for by the conversion factor α , which relates a given amplitude of orientational motion with the effect it has on the solvation energy. α is large for highly polar solvents, and it approaches unity as $\mu \rightarrow 0$. Physically, a large value of α means that a small orientational motion, while it may have little effect on $\langle \hat{\mu}(0) \cdot \hat{\mu}(t) \rangle$, may be sufficient to relax a large fraction of the solvation energy. In this sense, the same inertial and diffusive reorientational motions underlie the decay of both $\langle \hat{\mu}(0) \cdot \hat{\mu}(t) \rangle$ and $C_{\Delta E}(t)$. However, while inertial rotations typically have amplitudes of 10–20° in dense liquids and so are relatively ineffective in causing loss of orientational memory, such motions are all that is required to relax the majority of the solvation energy in highly polar solvents. The reason, and the reason for the appearance of α in eq 2.3, is that the more polar the liquid, the stronger the correlations between solvent molecules that serve to “quench” the solvation response from what it would be in the absence of correlations. The stronger

these correlations, the less solvent motion is required in order to solvate, and therefore the faster the solvation response.^{66,68}

Besides the comparisons just made above, there are other, more direct ways to elucidate the “mechanism” of solvation from simulation data.⁶⁹ One of the most helpful analytical techniques, especially when it comes to the short-time dynamics, involves the use of instantaneous normal mode ideas.^{29,70,71} The essential notion behind the instantaneous-normal-mode (INM) picture of liquid dynamics is that any potential surface—even the notoriously complicated potential surface on which a liquid as a whole evolves—is hardly more complex than one would see with a collection of coupled harmonic oscillators, provided, that is, that one is looking at small enough molecular displacements. Of course, unlike a single vibrating molecule, an entire liquid is not going to be executing small oscillations about some stable arrangement. But if one is concerned with short enough times, even the molecules in a liquid will start to look as if they were vibrating. Much as with the coupled springs that describe the bonds in individual molecules, this harmonic motion can then be dissected into simple, independent pieces called normal modes α , each of which will have its own characteristic frequency ω_α and its own set of specific rules as to which molecule should move in what way to contribute to the mode.⁷⁰

As we can see from the spectrum of such modes portrayed in Figure 6, it is possible to predict the frequencies with which liquid acetonitrile, for example, can move.^{31,72} Simply knowing these frequencies, however, does not tell us anything about its solvation mechanism; we still do not know which of its modes are the most efficient at solvating. The fact that each mode has its own molecular identity, though means that it is possible to compute each mode’s effectiveness in altering the solute–solvent energy ΔE .³⁰ All we have to do is look at derivatives with respect to the INM coordinates q_α

$$c_\alpha = \partial \Delta E / \partial q_\alpha \quad (2.4)$$

We can then use $(c_\alpha)^2$, the efficiency ratings, to reweight the spectrum, giving us what we might call a *solvation spectrum*. By comparing this new spectrum with the librational and the center-of-mass-translational parts of the original INM spectrum, Figure 6 (or better yet, by looking at these components of the new spectrum), we can confirm that the dominant mechanism by which acetonitrile solvates a dipolar solute is indeed librational motion.³¹

Demonstrations of this kind are intriguing, but they do not really tell us what the molecular features are that make a particular solute/solvent system choose a particular solvation strategy. Were we to perform the same kind of analysis on the apparently unrelated example of the solvation of I_2 in liquid CO_2 (Figure 7),³¹ we could find that either 70%, or no more than 19%, of the prompt solvation involved CO_2 libration, depending on whether solvation was defined in terms of a quadrupole–quadrupole ΔE or a dispersion–interaction ΔE , respectively.⁷³ The basis for the selection of libration or translation, in fact, seems to come down to the *symmetry* of the ΔE being probed by a given experiment.³¹ Both dipolar and quadrupolar electrostatic interactions, being orientation dependent, are most easily affected by solvent rotation. Center-of-mass translation, on the other hand, comes to the fore with more spherically symmetric interactions, such as dispersion and excluded-volume forces, as well as with the solvated electron, to which we shall return presently.

The reader may have noticed that thus far our discussion of solvation mechanism has not been very “mechanistic” in the usual sense of the word. That is, we have not yet presented any “who-done-it” endings, pointed the finger at one or two solvation “perpetrators”, and detailed their modus operandi. The

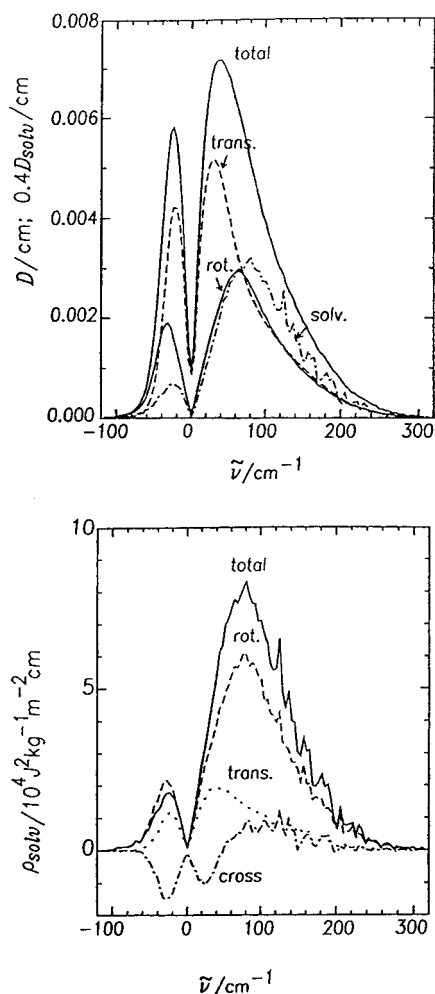


Figure 6. Instantaneous-normal-mode spectrum $D(\omega)$ of liquid CH_3CN (top panel) and the corresponding solvation spectrum $\rho_{\text{solv}}(\omega)$ for a dipolar solute dissolved in liquid CH_3CN (bottom panel). In the both panels, the spectra are partitioned into their respective components arising from the translational and rotational motions of the CH_3CN (and, in the case of the solvation spectrum, from the translational/rotational cross-term as well). In addition, the top panel shows how the solvation spectrum would compare with the rotational portion of $D(\omega)$ if the two were identically normalized. Reproduced with permission from ref 31.

reason is that, for the most part, the sorts of mechanisms one thinks about in organic chemistry are not really applicable to solvation. At least within the realm where linear response is valid, solvation is a collective process, involving many solvent molecules. While it is true that most of the energy of solvation comes from the first shell of solvent molecules surrounding the solute, there are still usually 10–30 such molecules involved in the action. Thus, rather than analyzing the behavior of one or two individuals, solvation can only be described in terms of the much more complex psychology of a fairly large gang. Moreover, there is hardly any difference to be found in the behavior of the individual member of this gang when it is caught in the act of solvating (i.e., responding to a solute perturbation) versus when it is merely loitering in the presence of the solute, i.e., when equilibrium solvation prevails. (Just how subtle the differences between these two situations was nicely highlighted in a recent simulation of 3-methylindole solvation in water.^{61d}) Thus, the above descriptions of average behavior of molecules and of the rotational versus translational mechanisms of solvation is really the best one can do in most cases.

However, one *can* obtain much more mechanistic detail when one leaves the linear response regime. In cases where only one or two solvent molecules play a dominant role in the solvation

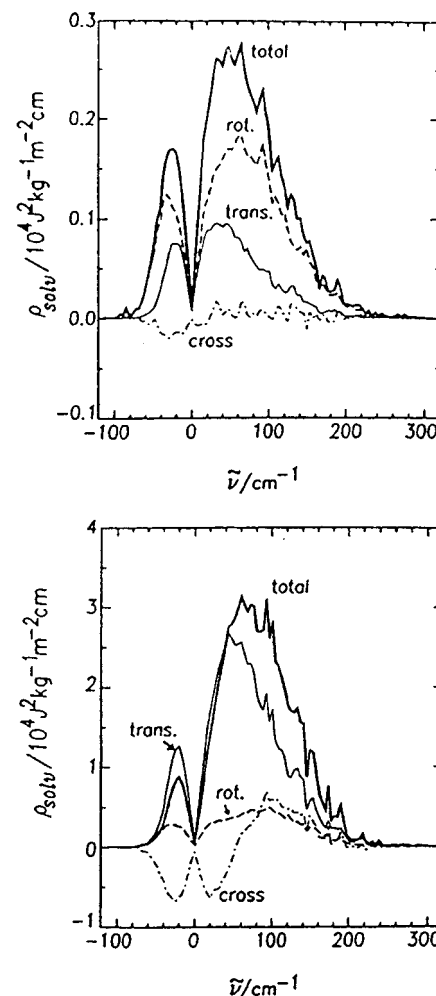


Figure 7. Solvation spectra of I_2 dissolved in liquid CO_2 . The top panel gives the spectrum that would arise from a purely electrostatic solute–solvent interaction, and the bottom panel gives the spectrum expected from purely dispersive (van der Waals) interactions. On decomposing the spectra into their respective translational, rotational, and cross-terms, one finds that the electrostatic solvation is controlled by solvent libration, as in Figure 6, whereas the dispersive situation is dominated by solvent translation. Reproduced with permission from ref 31.

process, as happens when strong, specific hydrogen-bonding interactions are important, one can be more definite in describing who is doing the solvating and how. As an example, we consider one of the most thoroughly studied cases: solvation of diatomic solutes in methanol.⁶⁴ Figure 8 shows an example of the structural changes that occur when a unit negative charge is transferred between two ends of a diatomic molecule in methanol.^{64b} Initially, there are several solvent molecules strongly hydrogen bonded to the negatively charged end of the solute. Once the charge is transferred to the opposite end of the solute, these molecules experience a strong repulsion from one another which causes the O–H bonds quickly rotate away from their initial orientation. As shown in Figure 8b, in the 64–92 fs time window the very sharp spike in the radial distribution function g_{NH} that signaled the presence of these strong hydrogen bonds before $t = 0$ (as in the $t = \infty$ curve in panel a) has all but disappeared. About 30–40% of the solvation energy is relaxed by the inertial O–H rotation that takes place before the first snapshot depicted here. The remainder of the solvation energy builds in more slowly (over hundreds of femtoseconds) as a result of the formation of new hydrogen bonds to the nascent negative site by the solvent molecules that happened to be closest to this site at $t = 0$. The slower dynamics here in part involves reorganization of the

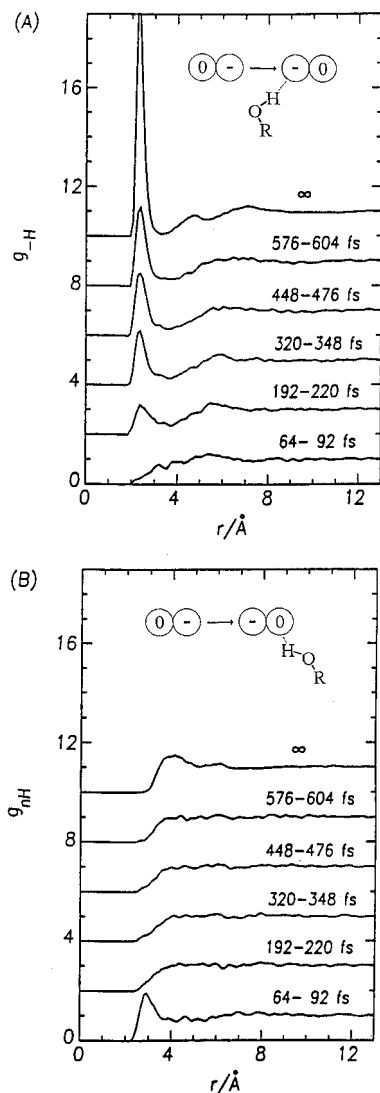


Figure 8. Time-dependent radial distribution functions (rdf's) illustrating the evolution of hydrogen-bonding structure subsequent to a charge transfer in a small diatomic solute in methanol. Panel A shows the rdf of the hydroxyl hydrogen atoms of methanol molecules and the nascent negative charge site of the solute. Panel B shows the rdf of the hydroxyl hydrogen with the neutralized solute site. Radial distribution functions were collected over the time windows indicated. (See ref 64b for more details.)

initial hydrogen bonding among these molecules and the (translational) exchange of molecules between the first and second solvation shells. Similarly detailed dynamics can be followed when one examines a charge shift in a positive–neutral pair.^{64b} What one finds is that the solvation response can be quite varied depending on the nature and size of the charge jump imposed. Such differences with respect to solute perturbation are in sharp contrast to the situation prevailing in the linear response regime, where similar dynamics are observed for many different solutes and perturbations. It is, of course, no coincidence that the systems just discussed are ones where linear response approaches (eq 2.2) break down. It appears that if one wants clear mechanistic pictures of solvation, one must be in the nonlinear regime. Unfortunately, here the dynamics are expected to be system specific, and theoretical modeling is difficult. Within the linear response realm, which seems to apply to the majority of systems studied to date, our theoretical understanding of the way solvation works is highly developed. But in this case one must be satisfied with the more statistical sorts of descriptions of mechanism discussed previously.

D. Electron Solvation Dynamics. Before closing this section on solvation dynamics, we pause to mention closely related work on a rather unusual solute, the solvated electron. Since the initial ultrafast observations of electrons in preequilibrium states nearly a decade ago,⁷⁴ there has been a great deal of interest in elucidating the nature of the ultrafast events involved in electron solvation. When an electron is injected into water, either by photoionization or electron beam methods, a complex sequence of events involving thermalization, electronic relaxation, trapping, and solvation dynamics occurs.⁷⁵ It has only been recently, due to the synergistic interplay between sophisticated three-pulse transient absorption experiments⁷⁶ and nonadiabatic molecular dynamics computer simulations,^{75,77} that the role of solvation dynamics in the overall process has been clarified. While it may be impossible to differentiate between solvation and electronic relaxation via experiment alone, experiments combined with simulation are beginning to provide a detailed picture of the nature of the solvation response to this “simplest” of solutes. In the ground electronic state (an “s-like” state), equilibrium hydration structure of an electron in water is similar to that of an atomic anion such as Cl^- or Br^- . Electronic excitation to the lowest-lying excited state (of “p-like” character) leads to nonequilibrium solvation analogous to that produced by electronic excitation of the atomic or molecular solutes described previously.^{61b,d,63a,b} Indeed, many of the outward features observed with these latter solutes in water appear to be shared by the case of electron hydration. However, one important difference that has been noted is the larger role played by translational (as compared to rotational) solvent motions in electron solvation. The greater importance of translation arises here from the fact that there is a large difference in the solvent-excluded volume between the s and p states of the electron. (There is roughly a 50% difference in the extension of the longest dimension of the solvent cavity in the two states.⁷⁷) Since the solute’s energy in this example is so sensitive to the size of the cavity, much of the solvation response reflects a translational “flow” of solvent molecules that reshapes the electron’s cavity. Curiously, this solvation mechanism is less similar to the rotation-dominated case of dipolar solvation dynamics which we have discussed extensively above than it is to “nonpolar solvation” dynamics,^{44,45} wherein the solvent mainly modulates the dispersion interactions with the solute. In the few examples available on this latter type of solvation,³¹ the dynamics are also believed to be more tied to translational dynamics of solvent molecules, or to the mechanical relaxation of the liquid,⁴⁵ rather than to the rotational/dielectric response of central importance in the dipolar solvation case. Further experiments and simulations of electron solvation in solvents other than water, both of which are currently in progress,^{76b,78} should help to clarify whether this conclusion is a general one.

III. Vibrational Relaxation

Up until relatively recently, it would have been fair to say that vibrational relaxation in liquids was interesting largely because of its implications for other problems. The relaxation process seemed straightforward, both phenomenologically and in terms of theoretical modeling. On the experimental side, one inevitably found that vibrational population lifetimes seen in small molecules were numbingly long on a molecular scale. Molecular oxygen dissolved in liquid Ar and neat liquid CO both, for example, had T_1 times on the order of milliseconds¹⁵—far too long, it would seem, to inform us about any but the most highly averaged and most macroscopic of dynamical events.

From a theoretical perspective, matters were somewhat disappointing as well, though in an opposite sense. Early on, it became clear that vibrational relaxation rates often correlated

beautifully with the predictions of a model called independent-binary-collision (IBC) theory.^{32,79} The central notion of the model was that vibrational relaxation was extraordinarily sensitive to how far up on the repulsive intermolecular potential the colliding species were and should therefore be dominated by the colliding partners who managed to make unusually close approaches.⁸⁰ In a liquid context, this model appeared to have the striking implication that the many-body character of the liquid state was largely irrelevant: it was unlikely that more than a single solvent molecule would be having such a close encounter with a solute at any given instant, nor would we expect these infrequent events to be all that highly correlated. Presumably, then, one could accurately regard the relaxation as proceeding through a series of independent pairwise collisions, just as had to be the case in the gas phase, though the collisions would no doubt be taking place with a somewhat greater frequency in the liquid.

This simple picture suggested, once again, that there was no obvious microscopic information to be extracted from the relaxation studies. The success of the model was a little puzzling, however. Numerous authors began to point out how unlikely it was that this model could survive the translation from the gas phase, at least in any literal fashion.⁸¹ For one thing, the very notion of a collision seemed foreign to the liquid state. If collisions were defined by the existence of a significant intermolecular interaction, then the high density present in a liquid meant that molecules were continuously involved in multiple collisions. If, on the other hand, one adopted a minimum intermolecular distance criterion for a collision, the predicted collision rates could be wildly uncertain. In a study of I₂ in liquid Xe, for example, the simulated collision rate could be made to vary from 0.86 to 15.3 ps⁻¹ just by choosing different critical distances in the range 3.9 ± 0.25 Å.⁸² Nonetheless, some of the trappings of the IBC theory, if not the microscopic interpretation, seemed hard to dispute. Simulated vibrational energy relaxation in both noble-gas liquids^{79c} and liquid CS₂⁸³ seem to have the scaling with solvent density one would expect from such a theory. Moreover, with I₂ in liquid Xe, experimental studies of the vibrational relaxation from near the dissociation limit of the I₂ ground electronic state, spanning a considerable range of iodine vibrational frequencies, saw a solvent density dependence quite consistent with an IBC picture.^{82,84}

Still, the latest viewpoints, while not disputing all of these empirical facts, have begun to take a rather different perspective on vibrational relaxation. As a result of some new experimental and theoretical findings, there are now real prospects for molecular-level insights, far more so than one ever would have suspected a few years back.

A. New Phenomenology. The intuition about vibrational relaxation that had been built up over the years was based almost entirely on simple neutral molecules in nonpolar solvents. It therefore came as a bit of a surprise when experiments and simulations began to look at ions dissolved in polar solvents. Population relaxation times that were in the milli-, micro-, and nanosecond, range began to be replaced by times in the tens of picoseconds—and a few examples, such as N₃⁻ in H₂O and NCO⁻ in MeOH, had T₁'s on the order of a picosecond or two.¹⁵

More generally, it became clear that when long-ranged electrostatic forces were involved then a variety of the truisms about vibrational relaxation could change—in a way that illuminated the older results. For example, a crucial quantity in this problem (and one to which we shall return) is the correlation function $\langle F(0)F(t) \rangle$, which measures the dynamics of the solvent force $F(t)$ felt on a solute bond. One particularly compelling piece of evidence supporting the binary-collision

model was that when the power spectrum of this correlation function was broken into a binary part (coming from the motion of just one solvent molecule at a time) and a remainder, the binary part always seemed to dominate, at least in rare-gas fluids.^{79c} However, when an aqueous solution containing a dipolar solute (mimicking Me-Cl) was simulated, the interparticle cross-terms turned out to be significant at certain frequencies.⁸⁵ In particular, binary behavior was observed for frequencies of the order of those seen in intramolecular water vibrations, whereas a signature of distinctly nonbinary character was seen at frequencies closer to those associated with librations in liquid water.

The interpretation that has been offered for this disparity between ionic and dipolar systems and others is not simply that the Coulombic forces can exert stronger forces on the vibrating bonds. That might account for the diminution in T₁'s, but it would not address the dependence of binary behavior on frequency. Rather, it seems that one also needs to postulate the existence of some sort of solvent modes that could be thought of as coupling to the vibrating bond. These modes, were they to exist, would have to be highly collective at frequencies near those affiliated with intermolecular dynamics (such as libration), but single molecule in character at the higher, intramolecular, frequencies.⁸⁵

Actually, these electrostatic examples are not the only places where it has been tempting to conjure up the spirit of liquid modes. In a variety of instances the interesting question has been not the rate of energy transfer from a solute to a solvent but the rate of intramolecular transfer within the solute. That a solvent can influence—and even control—such an occurrence was demonstrated dramatically by the recent observation of “vibrational up-pumping”.⁸⁶ On exciting the T_{1u} vibration of W(CO)₆ (or, equivalently, of Cr(CO)₆) dissolved in organic solvents using an IR pulse, subsequent anti-Stokes Raman probing disclosed that an IR-forbidden E_g vibration (a state 32 cm⁻¹ higher in energy) had become excited. By contrast, another IR-forbidden vibration, an A_{1g} mode with a slightly higher frequency, 136 cm⁻¹ above the T_{1u} mode, was apparently not excited. It is by no means indisputable, but a logical interpretation would be that some solvent mode, or modes, had just the right coupling characteristics to combine with the T_{1u} vibration, producing enough energy to populate a higher-lying state. Within this scenario, there were simply no solvent modes of a high enough frequency to which the T_{1u} mode could couple strongly enough to populate the A_{1g} mode.⁸⁷

Simultaneous with this kind of state-specific probing of the fate of a single quantum of solute vibration, a number of experiments have started to appear which get directly at the time scale of the solvent's interaction.^{16,17,88–90} As with NMR spectroscopy, solvent perturbations of vibrations that are slow compared to the intrinsic vibrational time scale can be literally erased by applying a carefully chosen sequence of pulses; the original unperturbed response of the solute then appears as an echo of the original pulse. Conversely, any failure of this perfect rephasing of the original signal is an indication that there are solvent perturbations fast enough to interfere with the vibrational dynamics, that is, the echo measures of the extent of homogeneous broadening.⁹¹

What has been found is that, barring exceptional circumstances, the solvent always seems to be capable of dephasing the solute on the solute's own time scale, even on the 16 fs time scales required for 2000 cm⁻¹ vibrations (Figure 9). Almost all of the broadening in the examples studied, in neat acetonitrile,^{88a} benzonitrile,^{88d} and ethanol^{88c} and in dilute solutions of W(CO)₆,⁸⁹ has turned out to be homogeneous. In order to obtain significant inhomogeneous broadening, one

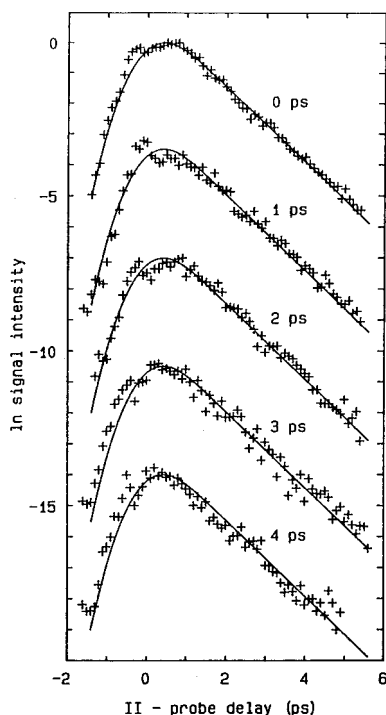


Figure 9. Raman echo results for the symmetric methyl stretching vibration in neat liquid CH_3CN (symbols). Shown here is the logarithm of the echo signal as function of second delay time t_2 at five different values of the first delay time t_1 ($= 0, 1, \dots, 4$ ps). If the vibrational dephasing were completely homogeneous, all five of these curves would be identical to each other and to the solid $t_1 = 0$ curve—as they apparently are. Reproduced with permission from ref 88a. Copyright 1991 American Institute of Physics.

actually had to take special steps to ensure that there were slow fluctuations in the systems—by making the solvent a mixture for example^{88b} or by cooling the liquid until it became a glass.⁹² Apparently, the ultrafast dynamics of the liquid are vital to understanding the solvent's perturbation, notwithstanding the ultraslow T_1 times. Parenthetically, the instances in which inhomogeneous broadening did assert itself were interesting in themselves. The ability to follow a substance's vibrational dynamics from its behavior as a low-temperature glass may very well lead (as with the comparable solvation dynamics⁴⁴ and optical Kerr effect⁹³ studies) into a deeper view of the glass transition and the nature of the glassy state. In a purely liquid context, however, the noteworthy feature is the newfound relevance of microscopic dynamics to the process of vibrational relaxation.

We might also note that yet another avenue into this dynamics is being provided by studies involving solutes excited with more than a single quantum of vibration. It has become clear from theoretical modeling that the relaxation of highly vibrationally excited solutes such as I_2 looks different to the solvent as the system relaxes from the highly asymmetric, low-frequency quanta characteristic of a near-dissociation vibrator to the almost harmonic, higher frequencies found near the well bottom.⁸⁴ Indeed, as we have noted, some recent experimental work has taken advantage of these differences to demonstrate the robustness of the independent-binary-collision form for vibrational relaxation rates.⁸² What is clearly needed, though, are some further *state-specific* probes of vibrational states beyond $v = 0$ and $v = 1$. Some early success in this area has been reported with an experiment in which a coherence was created involving the $v = 0, 1$, and 2 levels simultaneously—and the 1–2 transition displayed a dephasing rate 10 times that of the 0–1 transition,

despite there being no more than a small difference in frequency between the transitions.⁹⁰

B. Vibrational Relaxation as an Example of Liquid Friction. From a theoretical perspective, the ideal way in which to view vibrational dynamics in liquids (and, for that matter, to think of solvation dynamics) would be to find some probabilistic and highly summarized description of the many-body solvent's influence. As has long been appreciated, it is possible to carry out such a program by deriving a formal equation of motion in which the forces governing the vibration in the isolated molecule are supplemented by some forces that summarize the effect of the solvent. The basic content of the classical version of this equation, a generalized Langevin equation (GLE),³³

$$m \, d^2x/dt^2 = F_0(x) + \mathcal{F}(t) - \int dt' \, \eta(t-t') \, v(t') \quad (3.1)$$

is that a solute coordinate x , subject to an intramolecular force $F_0(x)$, feels both an instantaneous fluctuating force $\mathcal{F}(t)$ from the solvent and another, indirect, solvent force. This latter, so-called friction force, is a time-delayed response from the solvent that comes from the solute's own velocity v having an effect on the dynamics of the solvent, which, in turn, responds by affecting what the solute feels. The notion of friction is, of course, a common one at the macroscopic level; a particle moving through a viscous fluid feels a drag force proportional to the particle's velocity. But, what was recognized early on about GLE's is that the friction kernel $\eta(t)$ is in principle a well-defined, fully microscopic quantity, albeit one that might be difficult to obtain.⁹⁴

Two points have become increasingly clear in recent years, though they were amply foreshadowed by earlier work: One is that the relaxation rate $1/T_1$ is given remarkably well by the Fourier component of the friction at the frequency of the oscillator⁹⁵—so the friction is the essential quantity of interest in understanding population relaxation. The second is that it has become clear how to extract accurate friction kernels governing vibrational relaxation.³⁴ To within an excellent approximation, the friction kernel is just the correlation function of the force a hypothetically rigid vibration would feel from the solvent. This point has been confirmed by explicit simulations in which the exact friction was constructed (from the exact vibrational dynamics in the liquid) and the results compared with the “rigid-bond” friction.²⁴

Though these developments do not themselves explain precisely which molecular processes give rise to the friction, they have fermented an understanding of what kinds of considerations are relevant. In situations with electrostatic forces, for example, the dominance of those forces over shorter-range, nonelectrostatic, forces is revealed by the preeminence of the Coulombic contribution to the force autocorrelation function.⁸⁵ Still, having to rely on simulated correlation functions alone would leave a sizable gap in our knowledge of the dynamics at the ultimate level of the motions of individual solvent molecules. But what may help to fill in this gap is some progress being made in understanding how the instantaneous normal modes of a liquid can be thought as the basic molecular ingredients in friction kernels^{96,97}—and how these same modes can serve as the liquid modes currently being postulated as essential ingredients in vibrational relaxation.

These new developments are based on the realization that even events with long “incubation” times, such as vibrational relaxation, can be controlled by short-time dynamics. Simulated liquid frictions are, in fact well-known to lose almost all of their memory within a few hundred femtoseconds (Figure 10).⁹⁸ What allows such transient behavior to have an influence far beyond its ultrashort lifetime is the time-delayed fashion in which friction enters eq 3.1. Indeed the shortest-time approximation

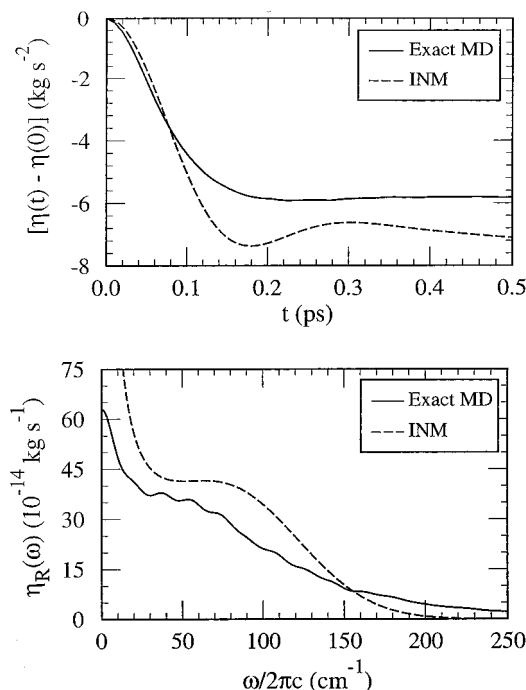


Figure 10. Friction felt by a diatomic molecule dissolved in supercritical fluid Ar, reported both as a function of time (top panel) and (as a cosine transform) as a function of frequency (bottom panel). The solid lines in both panels are the frictions inferred from numerically exact molecular dynamics simulation (data taken from Berne et al., ref 34). Note how the friction decays to its asymptotic value within 100–200 fs. The corresponding dashed lines are instantaneous-normal-mode predictions for the same quantities (ref 97).

to the friction imaginable, a simple Gaussian ansatz, has been a workhorse in the field.^{35,98,99} The instantaneous-normal-mode approach, though, goes beyond such modeling. If one simply writes down an equation of motion for a solute under the assumption that the short-time contributions from the solvent are all that is relevant to the dynamics, the solvent trajectory will enter only through its $3N$ instantaneous normal modes α (N being the number of atoms in the system). If effects of these trajectories are then folded into the solute equation of motion, the end result will actually be a GLE, but one in which the friction kernel has been specified microscopically in terms of the instantaneous-normal-mode frequencies ω_α and the coupling constants c_α , both of which are given explicitly in terms of derivatives of the intermolecular potentials.⁹⁷

Once the critical short-time assumption has been made, the mathematics of this procedure traces the now familiar connection between GLEs and solutes linearly coupled to hypothetical harmonic baths.¹⁰⁰ This formal analogy has proven extraordinarily helpful when it has been applied to the general problem of reaction dynamics in liquids,¹⁰¹ and even to vibrational relaxation,¹⁰² because it provides us with an explicit Hamiltonian with which to work. The difference here, though, is that the INM harmonic bath is not a formal construct—it is fully molecular. Within the standard analogy, none of the details of the solvent enter, except for a specially combined probability distribution of the harmonic frequencies and coupling constants commonly called the spectrum of coupling, $J(\omega)$.¹⁰¹ The cosine transform of the friction, for example, is just $J(\omega)/\omega$. Although one can work backward from simulations or estimates of the friction to compute what the precise form of $J(\omega)$ has to be (Figure 11), the analogy by itself provides no physical identification of the postulated harmonic modes; in fact, it does not even uniquely specify what the (non-coupling-weighted) spectrum of these modes is.¹⁰³ When modes start to mean the particular motions of particular atoms, however, the possibility

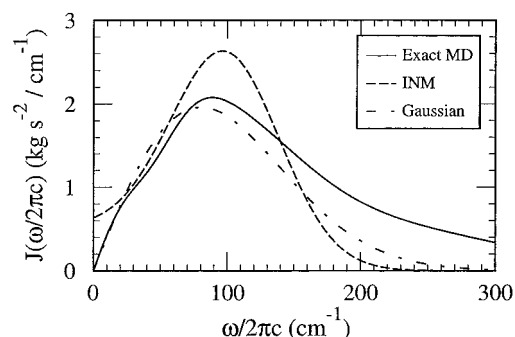


Figure 11. Spectrum of couplings of solvent modes to a solute vibration in supercritical fluid Ar. Shown here as a solid line the exact spectrum inferred from numerically exact simulations (derived from data taken from Berne et al., ref 34). The dash-dot curve is the prediction of a simple Gaussian fit to the very short-time dynamics, and the dashed curve is the fully microscopic instantaneous-normal-mode prediction (ref 97).

is there for discerning the real mechanisms by which liquid friction causes vibrational energy relaxation.

C. The Mechanisms of Vibrational Energy Relaxation.

When a molecular solute is dissolved in a molecular solvent, the most likely sequence of events is not that a large quantum of solute vibrational energy is turned directly into solvent translational motion. Rather, the energy to be dissipated works its way through a sequence of discrete, but successively lower frequency, vibrations, releasing (relatively) small quantities of energy with each step, until the energy is completely dispersed.¹⁰⁴ That means, of course, that one should be able to follow the relaxation pathway by monitoring the spectroscopy of each possible acceptor mode in the system. Just such an experiment has already been undertaken: if the N–H stretching vibration in pyrrole is excited, one can monitor both the excitation of other pyrrole modes and any excitation that might take place within the solvent by looking at the spontaneous anti-Stokes Raman spectra.¹⁰⁵ The results seem to imply that there really are identifiable pathways involving specific solvent acceptor modes. A small fraction of the initial excitation seems to wind up in the C=C stretch of benzene when benzene is the solvent, and when pyrrole is its own solvent there is strong evidence that one is populating the ring-stretching vibrations of pyrroles *other* than the ones originally excited. The quantum of ring-stretching vibration generated in neat liquid pyrrole disappears in dilute Et₂O solutions, for example.

Lacking any particularly promising high-frequency slots within the solvent molecules with which to absorb the energy, a solute will turn of necessity to its own normal modes, in the hopes that they will find an easier time of disposing of the energy to the solvent. As several theoretical and experimental studies have pointed out though, the solvent need not be entirely innocent in such a process.^{106,107} One of the more intriguing observations was made during an echo study of the temperature dependence of dephasing mechanisms.^{88c} Unlike the usual situation in which vibrational line broadening progresses from purely homogeneous to inhomogeneous as the temperature is lowered, in a study of the methyl group symmetric stretch in neat EtOH, the dephasing was shown to remain purely homogeneous to temperatures as low as 12 K, with T_2 only changing (in fact, decreasing) from (roughly) 700 to 500 fs on cooling the liquid from room temperature. The obvious question was, what relaxation processes could be so rapid—and could remain so even when the liquid was frozen into a glass? Direct solvent-to-solute energy transfer could be ruled out because the T_1 was on the order of 22 ps even at room temperature, and normal pure dephasing seemed an unlikely candidate because it should slow significantly as the temperature dropped.

Perhaps, the suggestion was advanced, what was being seen was solvent-assisted *intramolecular* vibrational relaxation. This process could in principle be quite rapid, even at low temperatures because of the high density of (relatively) high-frequency *intermolecular* solvent modes one would expect to be available in a hydrogen-bonded solvent.

The notion that specific solvent modes could play a well-defined role in relaxation was not made lightly. This same study actually offered some fairly compelling evidence for the need for at least some kind of molecular-level analysis of the intermolecular solvent dynamics.^{88c} It has frequently been suggested that the rate of vibrational relaxation ought to correspond to some bulk transport coefficient of the solvent, say its diffusion constant or its viscosity. But the viscosity of ethanol varies over 15 decades during the same temperature interval that sees T_2 change by less than 30%. Admittedly, there is a certain amount of support for correlations of relaxation times with bulk quantities in other, less extreme cases,^{79c,108} but the quest for a more molecular picture of the intermolecular dynamics remains. In fact, a number of studies have begun to single out the important and unimportant solvent motions for certain kinds of relaxations.

A Raman echo investigation of $\text{CH}_3\text{I}-\text{CDCl}_3$ mixtures,^{88b} for example, found that the symmetric Me stretch of the MeI was inhomogeneously broadened with a time scale on the order of 4–7 ps. Since this inhomogeneous broadening was apparently a direct result of the solvent being a mixture, the inhomogeneity almost certainly reflected a diffusional process in which CH_3I and CDCl_3 solvent molecules slowly replaced one another in the first solvation shell. The more general conclusion, though, was that solvent *translational* motion had to be the key element in this relaxation. Reinforcing this idea was that the times involved were far too long to involve solvent dynamics that was largely rotational in character. On the other hand, the simulation of a dipolar solute in water that we had alluded to earlier seemed to be almost completely controlled by the *librational* motions of the water.⁸⁵ So what is it that governs this choice?

As with solvation dynamics, one approach to answering this kind of question is to perform an instantaneous-normal-mode analysis, generating an appropriate distribution of liquid modes weighted by their respective contributions to the process at hand.^{96,97,106} Since the instantaneous-normal-mode friction needed here can be broken down into its separate components from a variety of different solvent motions, we can show in Figure 12 the projection of the INM friction spectrum in much the same way that Figure 7 displayed the projections of the INM solvation spectrum.⁹⁷ The calculation illustrated here is for a nonpolar homonuclear diatomic molecule dissolved in an atomic liquid. There is obviously no analog of the solvent rotation/translation dichotomy in this system, but one can still ask which solvent motions are the most efficient in leading to population relaxation. As one can see from the upper panel, there is no more than a statistical difference between solvent motion parallel to the solute bond and that perpendicular to the bond; in three dimensions there are always twice as many perpendicular directions as there are parallel ones, and this trivial 2:1 ratio is just about what one sees. However, when one considers solvent motion parallel (longitudinal) and perpendicular (transverse) with respect to the solute–solvent line of centers, the lower panel shows that the former clearly wins out, despite its statistical disadvantage. In retrospect it is clear on geometrical grounds alone why this distinction should obtain. Most solvent atoms in the first solvation shell (which includes virtually all of the solvent contributing directly to the relaxation) are not collinear with the solute. But except for collinear solvent

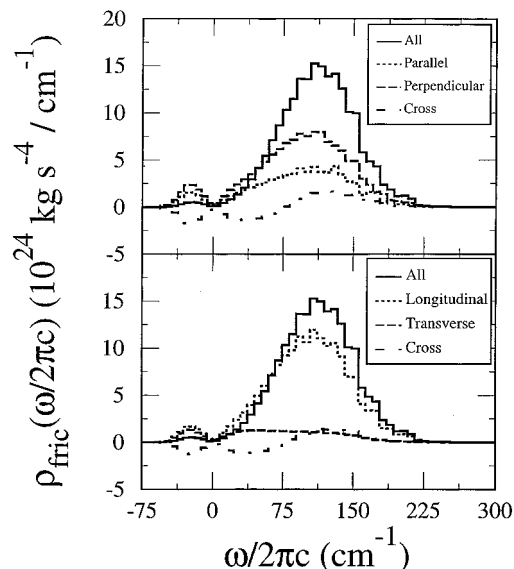


Figure 12. Resolution of the friction spectrum of a vibrating diatomic dissolved in supercritical fluid Ar into components from various kinds of solvent dynamics. The top panel compares the contributions of solvent motion parallel and perpendicular to the diatomic bond. The bottom panel contrasts the contributions of solvent motion longitudinal and transverse to the center of mass of the diatomic. Since on purely statistical grounds one would expect the perpendicular curve to be twice the parallel curve and the transverse curve to be twice the longitudinal curve, only the bottom panel shows a significant geometrical preference to the solvent dynamics. Reproduced with permission from ref 97. Copyright 1996 American Institute of Physics.

atoms, motion parallel to the solute bond is not *along* the bond. In fact, for a typical solvent atom, a good way to produce a force along the bond is actually for the solvent to move toward (or away from) the center of mass of the solute, pushing the solute atoms apart or pulling them together. Hence, it is quite plausible that we should end up seeing such motions contributing a disproportionate share to the friction.⁹⁷

All of these examples have their own special features and peculiarities, but the broader message is that some fairly well-defined solvent dynamics really can come into play in vibrational relaxation. There can indeed be an identifiable mechanism. Moreover, it is evident that by considering the frequencies and geometries of the available solvent motions, it should eventually be possible to figure out not only whether a given mechanism should dominate, but why.

IV. Prospectus

This article has certainly not attempted to present a definitive picture of just how much was known—or was thought to be known—about the subject of liquid-state chemical physics in the spring of 1996. The problems, the puzzles, and the techniques discussed here represent but a small subset of the recent developments that we thought could be the most illustrative and stimulating to nonspecialists. There are, however, a number of reasonably far-reaching themes suggested by our discussion, some of which may apply equally well to topics besides the two we chose to focus on here.

One of the more powerful unifying notions we would like to suggest is that all of the myriad degrees of freedom of a solute—be they vibrational, rotational, or electronic—see the dynamics of the surrounding solvent filtered through the solute's own idiosyncratic, but well-defined and fully molecular, perspective(s). A solvent may have a characteristic set of time scales, discernible perhaps by dielectric studies, or far-IR spectroscopy, or optical Kerr effect measurements, or via instantaneous-normal-mode analysis, but what a given experi-

ment sees is not a generic spectrum, but a specific spectrum of couplings. It sees each time scale—each mode—of the liquid weighted according to how efficiently that mode couples to the phenomenon in question. It is therefore possible to think about 100 ps vibrational relaxation and 100 fs solvation dynamics (to name just two examples) as both responding to the dynamics of the same solvent, but with different geometrical requirements for solvent involvement and with emphases on entirely different solvent frequencies.

From a theorist's viewpoint, a natural way to make this language precise is to make use of something we mentioned here only in the context of vibrational relaxation: one can write a generalized Langevin description in which the solute's equations of motion correctly incorporate the solvent's spectrum of coupling in the guise of some effective solvent friction. However, there is nothing unique to vibrational relaxation in this regard; nothing stops us from appealing to these same ideas for help in understanding a much wider set of solution problems. Just as it has been traditional to calculate the friction for vibrational and rotational relaxation by looking at the time correlation functions for solvent forces and torques,¹⁰⁹ it is possible to think of the frictions relevant to solvation dynamics and to optical Kerr spectra as correlation functions for the solute-solvent potentials and for (particular components) of the local solvent polarizability. And just as with vibrational relaxation, one is no longer compelled to interpret such frictions in terms of a few pieces of bulk information. Advances in simulation and in more analytical computational methods, along with progress in fleshing out the molecular contributions of liquid modes, make it seem likely that the microscopic information content of these kinds of data are well within our reach.

Nor, for that matter, is likely that these data are all that we will have to rely on to get at friction at its most molecular level. The echo experiments that we alluded to earlier are rapidly becoming more sophisticated: echoes with ever more pulses are being discussed in the literature, as are experiments in which echo signals themselves are time resolved into their own fine details.⁴¹ These kinds of experiments offer the promise of not just passively observing the consequences of a solvent's spectrum of coupling, but of actually mapping out real spectra of couplings. Indeed, there are some even more tantalizing possibilities that recent experiments have given us a glimpse at. If one is really most interested in how a solvent manages to influence a solute, one might argue that the ultimate target of the spectroscopy ought to be the *solvent* in the vicinity of the solute and not the solute itself. Indeed, studies attempting to look at just such dynamics are taking their first, tentative steps in this direction. Several experiments, for example, have begun to measure the changes in the vibrational and electronic spectra of the solvent that take place on electronic excitation of a solute.^{110–112} In most (though apparently not all)^{112b} of these cases, the solvent is responding to the energy relaxation of the solute—to a sudden release of heat. But what is intriguing is not simply that the relaxation is being monitored from an unusual perspective, that of the solvent, it is that one is seeing precisely how a molecule absorbs heat. In other words, one is measuring how molecules becomes thermally activated—the triggering event in chemical reactions.

The open questions in liquid dynamics, of course, go well beyond the phenomena of energy relaxation and flow. Yet, the kinds of efforts described in this paper may still prove to be of some help in answering a much wider range of questions than they initially set out to. To close with just one example, both solvation and the vibrational relaxation studies have been extended beyond the liquid state into the glassy regime, where relaxation times suddenly become so lengthy that dynamics is

effectively no longer reversible. The key question, though, is *how* does irreversibility makes it's appearance? In a sense, solvation dynamics should provide a piece of the answer, because it is a small-scale case study in the onset of irreversibility. The progress from ballistic (free streaming) motion of individual molecules at the earliest times, to collective, but deterministic, normal-mode dynamics a little later, to fundamentally diffusive motion at still longer times all takes place within the observation window of the newer experiments and theoretical models. Part of the challenge that remains is to begin to forge these connections between macroscopic chemical dynamics and our emerging molecular insight.

Acknowledgment. R.M.S. gratefully acknowledges the National Science Foundation for support of work on instantaneous normal modes, and M.M. is pleased to acknowledge the Office of Naval Research for an equipment grant and the Office of Basic Energy Sciences for support of studies on solvation dynamics. We both are delighted to be able to acknowledge numerous collaborations and discussions with students and other colleagues concerning many of the topics discussed in this paper.

References and Notes

- (1) Gordon, R. G. *Adv. Magn. Reson.* **1968**, 3, 1. For a more recent review, see: Madden, P. A. In *Liquids, Freezing, and the Glass Transition*; Hansen, J. P., Levesque, D., Zinn-Justin, J., Eds.; North-Holland: Amsterdam, 1991.
- (2) Kubo, R. *Adv. Chem. Phys.* **1969**, 15, 101.
- (3) *Molecular Liquids. Dynamics and Interactions*; Barnes, A. J., Orville-Thomas, W. J., Yarwood, J., Eds.; Reidel: Dordrecht, 1984.
- (4) Indeed, modern frequency domain techniques continue to teach us much about the dynamics of liquids. Some recent reviews include: *Spectroscopy and Relaxation of Molecular Liquids*; Steele, D., Yarwood, J., Eds.; Elsevier: Amsterdam, 1991; pp 174–273. Neilsen, O. F. *Annu. Rep. Prog. Chem.* **1993**, C90, 3.
- (5) Burns, M. J.; Liu, W. K.; Zewail, A. H. In *Spectroscopy and Excitation Dynamics of Condensed Molecular Systems*; Agranovich, V. M., Hochstrasser, R. M., Eds.; North-Holland: Amsterdam, 1983.
- (6) Sevan, H. M.; Skinner, J. L. *Theor. Chim. Acta* **1992**, 82, 29.
- (7) Stein, A. D.; Fayer, M. D. *J. Chem. Phys.* **1992**, 97, 2948.
- (8) Cole, R. H. *Annu. Rev. Phys. Chem.* **1989**, 40, 1.
- (9) Pshenichnikov, M. S.; Dupen, K.; Wiersma, D. A. *Phys. Rev. Lett.* **1995**, 74, 674. Cong, P.; Yan, Y. J.; Deuel, H. P.; Simon, J. D. *J. Chem. Phys.* **1994**, 100, 7855. Jarzeba, W.; Walker, G. C.; Johnson, A. E.; Barbara, P. F. *Chem. Phys.* **1991**, 152, 57.
- (10) Joo, T.; Jia, Y.; Fleming, G. R. *J. Chem. Phys.* **1995**, 102, 4063. Yu, J.; Berg, M. J. *Chem. Phys.* **1992**, 96, 8741. Yu, J.; Earvolino, P.; Berg, M. J. *Chem. Phys.* **1992**, 96, 8750. Sasai, M.; Ohmine, I.; Ramaswamy, R. *J. Chem. Phys.* **1992**, 96, 3045. Luzar, A.; Chandler, D. *Phys. Rev. Lett.* **1996**, 76, 928.
- (11) Fleming, G. R. *Chemical Applications of Ultrafast Spectroscopy*; Clarendon Press: Oxford, 1986. *Ultrafast Dynamics of Chemical Systems*; Simon, J. D., Ed.; Kluwer: Amsterdam, 1994.
- (12) See, for example: Barkley, M. D.; Kowalczyk, A. A.; Brand, L. J. *Chem. Phys.* **1981**, 75, 3581.
- (13) Pereira, M. A.; Share, P. E.; Sarisky, M. J.; Hochstrasser, R. M. In *Ultrafast Phenomena VII*; Harris, C. B., Ippen, E. P., Mourou, G. A., Zewail, A. H., Eds.; Springer-Verlag: Berlin, 1990.
- (14) A particularly striking example is a recent study of solvation dynamics in water: Jimenez, R.; Fleming, G. R.; Kumar, P. V.; Maroncelli, M. *Nature* **1994**, 369, 471.
- (15) Owrutsky, J. C.; Raftery, D.; Hochstrasser, R. M. *Annu. Rev. Phys. Chem.* **1994**, 45, 519.
- (16) Tokmakoff, A.; Zimdars, D.; Sauter, B.; Francis, R. S.; Kwok, A. S.; Fayer, M. D. *J. Chem. Phys.* **1994**, 101, 1741.
- (17) Vanden Bout, D.; Berg, M. J. *Raman Spectrosc.* **1995**, 26, 503.
- (18) An overview of the dephasing of electronic transitions and of optical photon echoes is given by: Nibbering, E. T. J.; Wiersma, D. A.; Duppen, K. *Chem. Phys.* **1994**, 183, 167. Some noteworthy theoretical studies include those of: Shemetulskis, N. E.; Loring, R. F. *J. Chem. Phys.* **1992**, 97, 1217. Cho, M.; Fleming, G. R. *J. Chem. Phys.* **1993**, 98, 2848. Rosenthal, S. J.; Schwartz, B. J.; Rossky, P. J. *Chem. Phys. Lett.* **1994**, 229, 443.
- (19) McMorro, D.; Lotshaw, W. T.; Kenney-Wallace, G. A. *IEEE J. Quantum Electron.* **1988**, 24, 443.
- (20) Ruhman, S.; Joly, A. G.; Nelson, K. A. *IEEE J. Quantum Electron.* **1988**, 24, 460.
- (21) McMorro, D.; Lotshaw, W. T. *J. Phys. Chem.* **1991**, 95, 10395.

- (22) It might be mentioned, though, that the somewhat more sophisticated, heterodyned, version of optical Kerr effect spectroscopy discussed in ref 21 seems to lend itself nicely to physical interpretation. Some more recent applications and developments include: Chang, Y. J.; Castner, E. W., Jr. *J. Chem. Phys.* **1993**, *99*, 113, 7289. Vöhringer, P.; Scherer, N. F. *J. Phys. Chem.* **1995**, *99*, 2684. Moreover, recent theoretical studies of optical Kerr spectra have pointed out some close connections between these spectra and solvation dynamics: Ladanyi, B. M.; Liang, Y. Q. *J. Chem. Phys.* **1995**, *103*, 6325. Ladanyi, B. M.; Klein, S. *J. Chem. Phys.*, submitted, a connection anticipated by: Cho, M.; Rosenthal, S. J.; Scherer, N. F.; Ziegler, L. D.; Fleming, G. R. *J. Chem. Phys.* **1992**, *96*, 5033.
- (23) See for example: Jimenez, R.; *et al.* (ref 14) and Muino, P. L.; Callis, P. R. *J. Chem. Phys.* **1994**, *100*, 4093.
- (24) Tuckerman, M.; Berne, B. J. *J. Chem. Phys.* **1993**, *98*, 7301.
- (25) State-of-the-art simulations of vibrational relaxation can have difficulties reproducing experimental results quantitatively because of, among other matters, extreme sensitivity to the details of the solution-phase interactions. Some recent efforts at making direct connections with experimental relaxation data include: Benjamin, I.; Whitnell, R. M. *Chem. Phys. Lett.* **1993**, *204*, 45. Ferrario, M.; Klein, M. L.; McDonald, I. R. *Chem. Phys. Lett.* **1993**, *213*, 537.
- (26) See, for example: Biswas, R.; Bagchi, B. *J. Phys. Chem.* **1996**, *100*, 1238. Chandra, A.; Wei, D.; Patey, G. N. *J. Chem. Phys.* **1993**, *99*, 4926.
- (27) Friedman, H. L.; Raineri, F. O.; Hirata, F.; Perng, B.-C. *J. Stat. Phys.* **1995**, *78*, 239.
- (28) Raineri, F. O.; Resat, H.; Perng, B.-C.; Hirata, F.; Friedman, H. L. *J. Chem. Phys.* **1994**, *100*, 1477. Raineri, F. O.; Perng, B.-C.; Friedman, H. L. *Chem. Phys.* **1994**, *183*, 187.
- (29) Stratt, R. M. *Acc. Chem. Res.* **1995**, *28*, 201.
- (30) Stratt, R. M.; Cho, M. *J. Chem. Phys.* **1994**, *100*, 6700.
- (31) Ladanyi, B. M.; Stratt, R. M. *J. Phys. Chem.* **1995**, *99*, 2502. Ladanyi, B. M.; Stratt, R. M. *J. Phys. Chem.* **1996**, *100*, 1266.
- (32) The so-called isolated binary collision (or isolated binary interaction) model for vibrational population relaxation in liquids can be written in a number of different guises, depending on how literally some of its tenets are taken. At its most literal, only equilibrium information about the solution is required. The basic ideas are reviewed in: Chesnoy, J.; Gale, G. M. *Adv. Chem. Phys.* **1988**, *70* (part 2), 297.
- (33) The basic features of Langevin equations and the formal approach by which one can develop generalized Langevin equations are reviewed by: Friedman, H. L. *A Course in Statistical Mechanics*; Prentice-Hall: Englewood Cliffs, NJ, 1985; Chapters 12 and 14.
- (34) The requisite ingredients have long been available from simulation in solid-state examples. Vibrational relaxation in solid matrices, for example, was studied by: Shugard, M.; Tully, J. C.; Nitzan, A. *J. Chem. Phys.* **1978**, *69*, 336. The analogous development is much more recent in a liquid context: Berne, B. J.; Tuckerman, M. E.; Straub, J. E.; Bug, A. L. *R. J. Chem. Phys.* **1990**, *93*, 5084.
- (35) Adelman, S. A.; Stote, R. H.; Muralidhar, R. *J. Chem. Phys.* **1993**, *99*, 1320. Adelman, S. A.; Muralidhar, R.; Stote, R. H. *J. Chem. Phys.* **1993**, *99*, 1333. Adelman, S. A.; Ravi, R.; Muralidhar, R.; Stote, R. H. *Adv. Chem. Phys.* **1993**, *84*, 73.
- (36) Hynes, J. T. In *Theory of Chemical Reaction Dynamics*; Baer, M., Ed.; CRC Press: Boca Raton, FL, 1985.
- (37) Note, in particular, the studies of ion-solvent vibrations pursued in the 1970s and 1980s. Examples include: Barker, C.; James, P. L.; Yarwood, J. *Faraday Discuss. Chem. Soc.* **1977**, *64*, 188. Schmidt, P. P. *J. Chem. Soc., Faraday Trans. 2* **1980**, *76*, 1026.
- (38) For studies of processes occurring over times of microseconds to seconds one can use excitation to longer-lived states such as T₁. See for example: Richert, R.; Wagener, A. *J. Phys. Chem.* **1991**, *95*, 10115.
- (39) Electronic excitation is not the only way to prepare nonequilibrium electronic states on an ultrafast time scale. One can also attempt create a "new" solute either as a product of a photoinduced reaction [Ernsting, N. P. In *Ultrafast Phenomena VIII*; Martin, L.-J., Migus, A., Mourou, G. A., Zewail, A. H., Eds.; Springer-Verlag: Berlin, 1993; pp 638–640] or via electron injection into a pure solvent or solution. In the photoinduced case, one produces a brand new solute, the electron, whose solvation dynamics can be monitored spectroscopically, as will be discussed later. In the case of electron injection into solutions, one can use the fact that electrons will attach themselves rapidly to preexisting solutes (such as benzophenone, ref 47) and thereby create a negative ion, whose solvation can be observed spectroscopically.
- (40) See, for example: Mukamel, S. *Principles of Nonlinear Optical Spectroscopy*; Oxford: New York, 1995.
- (41) An entry into this rapidly developing literature is provided by the recent papers: (a) Joo, T.; Jia, Y.; Yu, J.-Y.; Lang, M. J.; Fleming, G. R. *J. Chem. Phys.*, in press. (b) Joo, T.; Jia, Y.; Fleming, G. R. Reference 10. (c) Fainberg, B. D.; Huppert, D. *J. Mol. Liq.* **1995**, *64*, 123. (d) Vöhringer, P.; Arnett, D. C.; Yang, T.-S.; Scherer, N. F. *Chem. Phys. Lett.* **1995**, *237*, 387. (e) de Boeij, W. P.; Pshenichnikov, M. S.; Weirsmas, D. A. *Chem. Phys. Lett.* **1995**, *238*, 1. (f) Cong, P.; Yan, Y. J.; Deuel, H. P.; Simon, J. D. Reference 9. (g) Bardeen, C. J.; Shank, C. V. *Chem. Phys. Lett.* **1994**, *226*, 310.
- (42) Reviews of time-resolved emission studies of solvation dynamics are: Maroncelli, M. *J. Mol. Liq.* **1993**, *57*, 1. Barbara, P. F.; Jarzaba, W. *Adv. Photochem.* **1990**, *15*, 1.
- (43) The ground state population can be followed by time-resolved absorption spectroscopy, which is typically referred to as "dynamic hole burning spectroscopy" in this context. See for example: Murakami, H.; Kinoshita, S.; Hirata, Y.; Okada, T.; Mataga, N. *J. Chem. Phys.* **1992**, *97*, 7881 and ref 44. Closely related are measurements using stimulated rather than spontaneous emission, for example: Bingemann, D.; Ernsting, N. P. *J. Chem. Phys.* **1995**, *102*, 2691.
- (44) Ma, J.; Bout, D. V.; Berg, M. *J. Chem. Phys.* **1995**, *103*, 9146. Fourkas, J. T.; Berg, M. *J. Chem. Phys.* **1993**, *98*, 7773. Fourkas, J. T.; Benigno, A.; Berg, M. *J. Chem. Phys.* **1993**, *99*, 8552.
- (45) (a) Berg, M. *Chem. Phys. Lett.* **1994**, *228*, 317. (b) Bagchi, B. *J. Chem. Phys.* **1994**, *100*, 6658.
- (46) Benigno, A. J.; Ahmed, E.; Berg, M. *J. Chem. Phys.*, in press.
- (47) Lin, Y.; Jonah, C. D. In *Ultrafast Dynamics of Chemical Systems*; Simon, J. D., Ed.; Kluwer Academic Publishers: Dordrecht, 1994; pp 137–162.
- (48) Chapman, C. F.; Fee, R. S.; Maroncelli, M. *J. Phys. Chem.* **1995**, *99*, 4811.
- (49) See, for example: Laurence, C.; Nicolet, P.; Dalati, M. T.; Abboud, J.-L. M.; Notario, R. *J. Phys. Chem.* **1994**, *98*, 5807. Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319.
- (50) Jarzaba, W.; Walker, G. C.; Johnson, A. E.; Barbara, P. F. Reference 9. Chapman, C. F.; Fee, R. S.; Maroncelli, M. *J. Phys. Chem.* **1990**, *94*, 4929. Maroncelli, M.; Fleming, G. R. *J. Chem. Phys.* **1987**, *86*, 6221.
- (51) Horng, M. L.; Gardecki, J. A.; Papazyan, A.; Maroncelli, M. *J. Phys. Chem.* **1995**, *99*, 17311.
- (52) (a) Kumar, P. V.; Maroncelli, M. *J. Chem. Phys.* **1995**, *103*, 3038. (b) Reynolds, L.; Gardecki, J. A.; Frankland, S. J. V.; Horng, M. L.; Maroncelli, M. *J. Phys. Chem.*, in press.
- (53) Baumann, W.; Nagy, Z. *Pure Appl. Chem.* **1993**, *65*, 1729.
- (54) A complete discussion of dielectric dispersion measurements and their interpretation can be found in: Böttcher, C. J. F.; Bordewijk, P. *Theory of Electric Polarization*; Elsevier: Amsterdam, 1978; Vol. II.
- (55) Skaf, M. S.; Fonseca, T.; Ladanyi, B. M. *J. Chem. Phys.* **1993**, *98*, 8929.
- (56) Bagchi, B.; Chandra, A. *Chem. Phys.* **1993**, *173*, 133. Chandra, A.; Wei, D.; Patey, G. N. *J. Chem. Phys.* **1993**, *99*, 2068.
- (57) We note that in the cases of tetrazine and dimethyltetrazine, where the solvation dynamics being observed appears to be mainly related to dispersion interactions, the dynamics of solvation has also been modeled using a continuum solvent approach (ref 45a). Rather than focusing on dielectric behavior, the model instead treats the solvent as an elastic continuum and relates the observable dynamics to relaxation of shear waves in the fluid.
- (58) A number of these theories have been reviewed by Maroncelli (ref 42) and by Raineri *et al.* (Raineri, F. O.; Zhou, Y.; Friedman, H. L. *Chem. Phys.* **1991**, *152*, 201).
- (59) Raineri, F. O. Private communications.
- (60) The distinction is apparent, for example, when one attempts to model solvation dynamics in solvents such as benzene or dioxane. While these solvents are nondipolar, they nevertheless have significant polarity, as attested to by their position in solvatochromically based polarity scales. Experiments with C153 (ref 52b) have uncovered substantial time-dependent solvation in these solvents which is in all ways analogous to that found in dipolar solvents. While the energetics of solvation can be accurately modeled by fully atomistic representations of such solvents (ref 59), the dynamical input needed to model solvation dynamics is not available in $\epsilon(\omega)$. For these solvents, $\epsilon(\omega) \approx n^2$ because of the long-wavelength nature of bulk dielectric measurements.
- (61) Some of the more recent simulation studies are: (a) Olender, R.; Nitzan, A. *J. Chem. Phys.* **1995**, *102*, 7180. (b) Bursulaya, B.; Zichi, D. A.; Kim, H. J. *J. Phys. Chem.* **1995**, *99*, 10069. (c) Brown, R. *J. Chem. Phys.* **1995**, *102*, 9059. (d) Muino, P. L.; Callis, P. R. Reference 23. (e) Benjamin, I. *Chem. Phys.* **1994**, *180*, 287.
- (62) More sophisticated modeling has been performed in which the electronic structure of the solute has been allowed to equilibrate in response to the solvent. For example, refs 61b and 61d have considered the behavior of a solute whose charge distribution reacts to the state of the classical solvent via a quantum mechanical polarizability (see also ref 52a for a classical analog). The dynamics observed with these quantum-mechanical solutes are not substantially different from the behavior observed with classical solutes. (See also the discussion of electron solvation and refs 75 and 77.)
- (63) See for example: (a) Maroncelli, M.; Fleming, G. R. *J. Chem. Phys.* **1988**, *89*, 5044. (b) Bader, J. S.; Chandler, D. *Chem. Phys. Lett.* **1989**, *157*, 501. (c) Maroncelli, M. *J. Chem. Phys.* **1991**, *94*, 2084. (d) Carter, E. A.; Hynes, J. T. *J. Chem. Phys.* **1991**, *94*, 5961.
- (64) (a) Fonseca, T.; Ladanyi, B. M. *J. Mol. Liq.* **1994**, *60*, 1. (b) Phelps, D. K.; Weaver, M. J.; Ladanyi, B. M. *Chem. Phys.* **1993**, *176*, 575. (c) Fonseca, T.; Ladanyi, B. M. *J. Phys. Chem.* **1991**, *95*, 2116.
- (65) Photon echo measurements (Joo, T.; Jia, Y.; Fleming, G. R. Reference 10) do appear to have sufficient resolution to detect the Gaussian character of the initial solvation response in some solvents.

- (66) Maroncelli, M.; Kumar, V. P.; Papazyan, A. *J. Phys. Chem.* **1993**, *97*, 13. Maroncelli, M.; Kumar, P. V.; Papazyan, A.; Horng, M. L.; Rosenthal, S. J.; Fleming, G. R. In *Ultrafast Reaction Dynamics and Solvent Effects*; Gauduel, Y., Rossky, P. J., Eds.; American Institute of Physics: New York, 1994; pp 310–333.
- (67) Raineri, F. O.; Friedman, H. L. *J. Chem. Phys.* **1994**, *101*, 6111.
- (68) See also the related discussion in: Kivelson, D.; Friedman, H. *J. Phys. Chem.* **1989**, *93*, 7026.
- (69) For example: Reference 63c and Neria, E.; Nitzan, A. *J. Chem. Phys.* **1992**, *96*, 5433 deliberately used various sorts of artificial constraints in order to demonstrate that rotational motion is the dominant relaxation mechanism.
- (70) Buchner, M.; Ladanyi, B. M.; Stratt, R. M. *J. Chem. Phys.* **1992**, *97*, 8522.
- (71) Moore, P.; Keyes, T. *J. Chem. Phys.* **1994**, *100*, 6709.
- (72) The possibility of getting at spectral densities directly through experimental means has been explored in a number of papers: Cho, M.; Rosenthal, S. J.; Scherer, N. F.; Ziegler, L. D.; Fleming, G. R. Reference 22. Vöhring, P.; Arnett, D. C.; Westervelt, R. A.; Feldstein, M. J.; Scherer, N. F. *J. Chem. Phys.* **1995**, *102*, 4027. Yang, T.-S.; Vöhringer, P.; Arnett, D. C.; Scherer, N. F. *J. Chem. Phys.* **1995**, *103*, 8346.
- (73) Perhaps the way to envision these possibilities is to imagine conducting a series of experiments in which we successively populate different excited electronic states of the solute, thereby allowing us to switch between various different interactions with the solvent.
- (74) Migus, A.; Gauduel, Y.; Martin, J. L.; Antonetti, A. *Phys. Rev. Lett.* **1987**, *58*, 1559.
- (75) See the descriptions and references in: Keszel, E.; Murphrey, T. H.; Rossky, P. J. *J. Phys. Chem.* **1995**, *99*, 22.
- (76) (a) Kimura, Y.; Alfano, J.; Walhout, P.; Barbara, P. *J. Phys. Chem.* **1994**, *98*, 3450. (b) Walhout, P. K.; Alfano, J. C.; Kimura, Y.; Silva, C.; Reid, P. J.; Barbara, P. F. *Chem. Phys. Lett.* **1995**, *232*, 135.
- (77) Schwartz, B. J.; Rossky, P. J. *J. Chem. Phys.* **1994**, *101*, 6902. Schwartz, B. J.; Rossky, P. J. *J. Chem. Phys.* **1994**, *101*, 6917.
- (78) Rossky, P. J. Personal communications.
- (79) (a) Davis, P. K.; Oppenheim, I. *J. Chem. Phys.* **1972**, *57*, 505. (b) Oxtoby, D. *Mol. Phys.* **1977**, *34*, 987. (c) Chesnoy, J.; Weis, J. J. *J. Chem. Phys.* **1986**, *84*, 5378. (d) Russell, D. J.; Harris, C. B. *Chem. Phys.* **1994**, *183*, 325.
- (80) For a discussion of some of the issues involved in gas-phase vibrational energy transfer, see: Shin, H. K. In *Dynamics of Molecular Collisions*, Part A; Miller, W. H., Ed.; Plenum: New York, 1976. The role of the potential shape is explored by: Maricq, M. M.; Gregory, E. A.; Simpson, C. J. S. M. *Chem. Phys.* **1985**, *95*, 43.
- (81) Fixman, M. *J. Chem. Phys.* **1961**, *34*, 369. Zwanzig, R. *J. Chem. Phys.* **1961**, *34*, 1931. Zwanzig, R. *J. Chem. Phys.* **1962**, *36*, 2227. Dardi, P. S.; Cukier, R. I. *J. Chem. Phys.* **1988**, *89*, 4145. Dardi, P. S.; Cukier, R. I. *J. Chem. Phys.* **1991**, *95*, 98.
- (82) Paige, M. E.; Harris, C. B. *Chem. Phys.* **1990**, *149*, 37.
- (83) Rejto, P. A.; Chandler, D. *J. Phys. Chem.* **1994**, *98*, 12310.
- (84) The first liquid-state experiments on the geminate recombination dynamics of photodissociated I₂ were pointed mainly at providing an experimental look at the role of solvent cages in solution-phase chemical reactions, but it soon became clear that these experiments were actually intriguing case studies in vibrational relaxation. Nesbitt, D. J.; Hynes, J. T. *J. Chem. Phys.* **1982**, *76*, 6002. Nesbitt, D. J.; Hynes, J. T. *J. Chem. Phys.* **1982**, *77*, 2130.
- (85) Whitnell, R. M.; Wilson, K. R.; Hynes, J. T. *J. Phys. Chem.* **1990**, *94*, 8625. Whitnell, R. M.; Wilson, K. R.; Hynes, J. T. *J. Chem. Phys.* **1992**, *96*, 5354.
- (86) Tokmakoff, A.; Sauter, B.; Kwok, A. S.; Fayer, M. D. *Chem. Phys. Lett.* **1994**, *221*, 412.
- (87) There is yet other evidence that solvent energy reservoirs have some fairly well-defined preferences with regard to the amounts of energy they care to transfer. Vibration-to-vibration energy transfer between small molecules in liquids has been compared carefully with the equivalent transfer in gases. The results display a pronounced dependence on the frequency mismatch between the molecules, the shape of which is suggestive of a spectrum of liquid modes capable of making up the energy difference. See, for example: Andrew, J. J.; McDermott, D. C.; Mills, S. P.; Simpson, C. J. S. M. *Chem. Phys.* **1991**, *153*, 247. Evans, G. T.; Madden, P. A. *Mol. Phys.* **1991**, *74*, 1171.
- (88) Raman echo experiments have been presented in: (a) Vanden Bout, D.; Muller, L. J.; Berg, M. *Phys. Rev. Lett.* **1991**, *67*, 3700. (b) Muller, L. J.; Vanden Bout, D.; Berg, M. *J. Chem. Phys.* **1993**, *99*, 810. (c) Vanden Bout, D.; Freitas, J. E.; Berg, M. *Chem. Phys. Lett.* **1994**, *229*, 87. (d) Inaba, R.; Tominaga, K.; Tasumi, M.; Nelson, K. A.; Yoshihara, K. *Chem. Phys. Lett.* **1993**, *211*, 183.
- (89) Infrared echo experiments include: Zimdars, D.; Tokmakoff, A.; Chen, S.; Greenfield, S. R.; Fayer, M. D.; Smith, T. I.; Schwettman, H. A. *Phys. Rev. Lett.* **1993**, *70*, 2718. Tokmakoff, A.; Zimdars, D.; Sauter, B.; Francis, R. S.; Kwok, A. S.; Fayer, M. D. Reference 16.
- (90) Tokmakoff, A.; Kwok, A. S.; Urdahl, R. S.; Francis, R. S.; Fayer, M. D. *Chem. Phys. Lett.* **1995**, *234*, 289. See, in addition: Tominaga, K.; Yoshihara, K. *Phys. Rev. Lett.* **1996**, *76*, 987.
- (91) An especially physical description of echo experiments is given by: Ma, S.-K. *Statistical Mechanics*; World Scientific: Philadelphia, 1985; Chapter 24. See also: Mayer, J. E.; Mayer, M. G. *Statistical Mechanics*, 2nd ed.; Wiley: New York, 1977; pp 133–137. The reader may be amused to note this latter (classic) text's prediction that "it is very likely ... that similar echo effects will remain pretty well limited to nuclear spin systems."
- (92) Tokmakoff, A.; Fayer, M. D. *J. Chem. Phys.* **1995**, *103*, 2810.
- (93) Halalay, I. C.; Nelson, K. A. *J. Chem. Phys.* **1992**, *97*, 3557.
- (94) For harmonic vibrations these equations can be derived quite rigorously by projection operator techniques: Zwanzig, R. *Lect. Theor. Phys.* **1961**, *3*, 106. Mori, H. *Prog. Theor. Phys.* **1965**, *33*, 423. The purely formal expressions that result are rarely used in their exact form, however; while there is a set of rules for how the necessary projection operators work, there is no explicit microscopic prescription for constructing them.
- (95) When the friction is approximated by its equivalent on a rigid bond, this result is the just the Landau–Teller theory for vibrational relaxation, though the rigid-bond version can be regarded more generally as direct consequence of low-order perturbation theory: Oxtoby, D. W. *Adv. Chem. Phys.* **1981**, *47*, 487. For a derivation from the generalized Langevin equation *not* assuming rigid bonds, see ref 24. Simulation evidence for how well these expressions do is presented in refs 24 and 85.
- (96) Schvaneveldt, S. J.; Loring, R. F. *J. Chem. Phys.* **1995**, *102*, 2326.
- (97) Goodyear, G.; Larsen, R. E.; Stratt, R. M. *Phys. Rev. Lett.* **1996**, *76*, 243. Goodyear, G.; Stratt, R. M. *J. Chem. Phys.*, submitted.
- (98) Grote, R. F.; van der Zwan, G.; Hynes, J. T. *J. Phys. Chem.* **1984**, *88*, 4676. Bergsma, J. P.; Reimers, J. R.; Wilson, K. R.; Hynes, J. T. *J. Chem. Phys.* **1986**, *85*, 5625. Berne, B. J.; Tuckerman, M. E.; Straub, J. E.; Bug, A. L. R. Reference 34.
- (99) For recent example, see: Reese, S. K.; Tucker, S. C.; Schenter, G. K. *J. Chem. Phys.* **1995**, *102*, 104.
- (100) Zwanzig, R. *J. Stat. Phys.* **1973**, *9*, 215.
- (101) Pollak, E. *J. Chem. Phys.* **1986**, *85*, 865. Gertner, B. J.; Wilson, K. R.; Hynes, J. T. *J. Chem. Phys.* **1989**, *90*, 3537. Tucker, S. C. *J. Phys. Chem.* **1993**, *97*, 1596.
- (102) Levine, A. M.; Shapiro, M.; Pollak, E. *J. Chem. Phys.* **1988**, *88*, 1959. Georgievskii, Yu. I.; Stuchebrukov, A. A. *J. Chem. Phys.* **1990**, *93*, 6699.
- (103) A spectrum of couplings $J(\omega)$ irreversibly combines two different kinds of information—time scale information (a set of frequencies) and liquid-structure information (a coupling constant for each frequency)—into a single, aggregate function. Thus, even if there is some genuinely fundamental set of frequencies for a liquid, each new experiment conducted on the liquid will still have its own set of coupling constants and therefore its own spectrum of couplings. Unfortunately, without any molecular information as to what goes into the coupling constants, such $J(\omega)$'s cannot possibly tell us what the fundamental spectrum is.
- (104) Nitzan, A.; Mukamel, S.; Jortner, J. *J. Chem. Phys.* **1975**, *63*, 200. Kenkre, V. M.; Tokmakoff, A.; Fayer, M. D. *J. Chem. Phys.* **1994**, *101*, 10618.
- (105) Ambroseo, J. R.; Hochstrasser, R. M. *J. Chem. Phys.* **1988**, *89*, 5956.
- (106) Moore, P.; Tokmakoff, A.; Keyes, T.; Fayer, M. D. *J. Chem. Phys.* **1995**, *103*, 3325.
- (107) Heilweil, E. J.; Casassa, M. P.; Cavanagh, R. R.; Stephenson, J. C. *Annu. Rev. Phys. Chem.* **1989**, *40*, 143.
- (108) Oxtoby, D. W. *Annu. Rev. Phys. Chem.* **1981**, *32*, 77.
- (109) Steele, W. A. *Adv. Chem. Phys.* **1976**, *34*, 2.
- (110) Scherer, P. O. J.; Seilmeier, A.; Kaiser, W. *J. Chem. Phys.* **1983**, *83*, 3948. Sukowski, U.; Seilmeier, A.; Elsaesser, T.; Fischer, S. F. *J. Chem. Phys.* **1990**, *93*, 4094.
- (111) Lingel, Jr., R.; Xu, X.; Yu, S.-C.; Chang, Y. J.; Hopkins, J. B. *J. Chem. Phys.* **1990**, *92*, 4628.
- (112) (a) Lian, T.; Locke, B.; Kholodenko, Y.; Hochstrasser, R. M. *J. Phys. Chem.* **1994**, *98*, 11648. (b) Lian, T.; Kholodenko, Y.; Hochstrasser, R. M. *J. Phys. Chem.* **1995**, *99*, 2546.