

Vibrational and rotational relaxation times of solvated molecular ions

M. Li, J. Owrutsky,^{a)} M. Sarisky, J. P. Culver,^{b)} A. Yodh,^{b)} and R. M. Hochstrasser
Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323

(Received 27 November 1992; accepted 21 December 1992)

Infrared pump-probe and infrared polarization spectroscopy have been used to measure the vibrational relaxation times (T_1) of the antisymmetric stretching mode and the reorientation times (T_R) for N_3^- , NCS^- , and NCO^- in D_2O and/or methanol. For N_3^- , experiments were also conducted in H_2O and hexamethyl-phosphamide (HPMA) solutions. The rapid vibrational relaxation and slow reorientation observed demonstrate strong coupling between the ions and the solvents. Longer vibrational relaxation and shorter reorientation times measured for NCS^- reveal weaker solvent interactions that may be due to the importance of the charge distribution and the form of the normal coordinate. A comparison of the T_1 and T_R times in different solvents permits a determination of the relative interaction strengths for the solvents investigated. The relatively weaker coupling of N_3^- in the aprotic solvent HMPA demonstrates the importance of hydrogen bonding in strong solvent interactions in ionic solutions. The experimental results are compared with recent molecular dynamics simulations of ionic solutions.

INTRODUCTION

Solvation remains one of the most important issues in chemical physics. Probing the rates and establishing mechanisms for energy transport and molecular motion provide important clues to the structure and dynamics of solvation and lead to progress toward a detailed understanding of the influence of the liquid environment on chemical reactions. While there has been significant progress in both experiment and theory, such as investigations concerning ultrafast solvation,¹⁻⁶ there is little experimental data concerning the dynamics of simple systems that are amenable to detailed theoretical treatment.

Studies of vibrational relaxation times (T_1) and reorientation times (T_R) provide important information concerning the structure and dynamics of solvated molecules. The vibrational relaxation rates that have been measured for solution species, such as those for small organic molecules⁷ and metal carbonyls,⁸ were predominantly ascribed to intramolecular vibrational relaxation (IVR) processes and have not yet furnished much clear evidence concerning the role of solvent interactions. Studies on systems with intermolecular relaxation mechanisms provide the most insight into specific molecular solute-solvent interactions. The first solution phase ion whose vibrational relaxation was studied was CN^- in water.⁹ This showed an unexpectedly rapid relaxation, prompting the suggestion that Coulomb forces were involved.

The systemic study of vibrational relaxation in systems demonstrating fast intermolecular (Coulomb-assisted) relaxation prompted our previously reported¹⁰ measurement of the vibrational relaxation time of the antisymmetric stretching mode (ν_3) of the azide ion in various protic solvents. Azide, although triatomic, can be expected to

favor intermolecular relaxation pathways over IVR because of its simple triatomic structure, its relatively low vibrational frequency (near 2000 cm^{-1}) which minimizes the number of nearby modes for Fermi resonance that might enable solvent induced IVR, and the absence of perturbations in the spectrum of N_3^- in the gas phase.¹¹ Furthermore, as was shown,¹⁰ strong Coulombic solvent interactions enhance intermolecular mechanisms.

The previous study employing two-color transient spectroscopy revealed very fast ($T_1 \sim 3\text{ ps}$) relaxation rates in several protic solvents (H_2O , D_2O , methanol, and ethanol).¹⁰ The supporting evidence that the infrared absorption band is isolated and free from intramolecular perturbations induced by solvent forces strongly suggested that the energy is lost through a specific interaction with the solvent. The general notion that ions vibrationally relax through intermolecular routes is most clearly demonstrated by observations of fast relaxation rates for diatomic molecules in which IVR is not possible. Such an observation has been made in the Raman-pump-Raman-probe study⁹ of CN^- in H_2O , which yielded a fast (6-25 ps) T_1 time that was dependent on ion concentration. It was the CN^- result that prompted the suggestion that Coulomb forces must be a key factor in the relaxation of vibrational states of ions.

Essentially infinite dilution T_1 values for a simple molecular system can serve as a benchmark for theoretical and molecular dynamics studies. Prompted by our experimental work, Ferrario, Klein, and McDonald¹² have recently performed a molecular dynamics (MD) simulation for azide in water. The N_3^- simulation, similar to that by Ferrario, McDonald, and Symons for CN^- ,¹³ used a SPC water model and calculated the forces on the antisymmetric stretch coordinate of azide. The trajectories were used to calculate, in the manner described in earlier work on neutrals,¹⁴ the energy diffusion into the solvent bath neglecting the high frequency modes of the solvent. These calculations indicate relaxation times from N_3^- of ca. 200

^{a)}Present address: Naval Research Laboratory, Washington, DC 20375-5000.

^{b)}Physics Department, University of Pennsylvania, Philadelphia, PA 19104

ps would be expected if the transfer of energy was directly into the bath modes. A calculation of the orientational decay (P_2) yielded 500 fs for azide ion in water. In the present work both these parameters have been measured, allowing a direct comparison between experiment and MD simulations.

In order to provide a more detailed comparison with theory and to learn more about the structure and dynamics of the ion-solvent interaction, we have measured reorientation times for solvated ions using transient polarization infrared spectroscopy. The reorientation time provides important insight into the solvation structure of the liquid and suggests answers to such questions as whether the ion rotates within the solvation shell or whether the interaction between the ion and the solvent is strong enough that the rotation is limited by solvent reorientations. An answer emerges by comparing observed reorientation times with those obtained from hydrodynamics.

Polarized infrared spectroscopy is needed to measure reorientation times. From transient signals obtained for parallel, $S_{\parallel}(t)$, and perpendicular, $S_{\perp}(t)$, relative pump-probe polarization geometries, it is possible to obtain the anisotropy $r(t)$,

$$r(t) = [S_{\parallel}(t) - S_{\perp}(t)] / [S_{\parallel}(t) + 2S_{\perp}(t)] \\ = 0.4 \langle P_2[\cos \theta(t)] \rangle, \quad (1)$$

where $\theta(t)$ is the angle of rotation of the axis of the ion within time t . The rotational reorientation time T_R reflects the exponential decay from the initial anisotropy due to the rotational reorientation. While there have been several polarized infrared probe studies to investigate relative bond orientation and transition moment changes induced by optical pulses—such as those performed in this laboratory on hemoglobin CO¹⁵—the only previously reported polarized transient infrared pump-probe study is the single-color work by Graener, Seifert, and Laubereau on liquid CH₃Br.¹⁶

We have extended our earlier studies of vibrational relaxation and reorientation times to solutions of other pseudohalide ions, NCO⁻ in methanol and NCS⁻ in methanol and D₂O. These ions also have antisymmetric stretching modes^{17,18} in the 2000 cm⁻¹ region. While the dynamics of NCO⁻ are very similar to those for N₃⁻, NCS⁻ has longer T_1 and shorter T_R times. In addition, the data demonstrate a correlation between vibrational relaxation and reorientation times.

EXPERIMENT

The experiments involve two-color transient infrared spectroscopy incorporating optical gating for the infrared detection. For this work improvements have been made by generating the probe IR as a quasi-cw pulse and developing the capability of performing polarized infrared spectroscopy as well as magic angle pump-probe spectroscopy.

In the experiments the IR detection is accomplished using optical gating of an IR source as in previous transient infrared studies from this laboratory in which a cw or modulated cw infrared laser was the IR source.¹⁰ Although

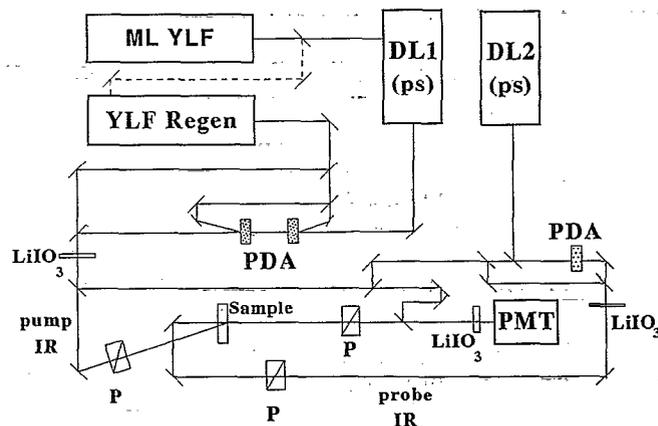


FIG. 1. Schematic of the infrared pump-probe and infrared polarization spectroscopy: ML YLF, cw mode-locked Nd:YLF laser; YLF Regen, Nd:YLF regenerative amplifier; DL1, synchronously pumped hybrid mode-locked dye laser (0.5–3 ps); DL2, synchronously pumped dye laser (30 ps); PDA, pulse dye amplifier cells; P, wire grid polarizer; PMT, photomultiplier tube.

this technique has a number of advantages, such as separating the frequency and time resolution which are determined by the probe and gating pulse, respectively, it has limitations imposed by the characteristics (coverage, tunability, peak power, etc.) of cw infrared lasers. Diode laser and CO lasers have been used so far. One method to overcome these limitations is to generate a relatively long, narrow-band infrared pulse as the infrared source while still using the optical gating scheme. We have employed a quasi-cw source obtained from mixing the amplified output of a second dye laser with the green doubled Nd:YLF laser pulse (DL2 in Fig. 1). The pulse from the second dye is relatively long (30 ps) in time compared with the gating pulse (0.5–3.0 ps) and narrow in frequency (2 cm⁻¹). It therefore serves the same purpose as a cw laser without the tunability limitations associated with diode and CO lasers. A similar scheme was introduced by Jedju and Rothberg.¹⁹ The long pulse reduces noise in the up-conversion signal from jitter of the two dye lasers.

Briefly, the laser system consists of a frequency doubled cw ML Nd:YLF laser pumping a hybrid mode-locked dye laser that generates 3 ps pulses in the range 580–594 nm. One-half the radiation from a doubled Nd:YLF regenerative amplifier (1 mJ at 1 kHz, 527 nm, and 50 ps) is used to amplify the dye laser pulses (to ca. 10 μJ) which are combined with the other half into a 1 cm LiIO₃ crystal to generate the pump IR pulses (10% photon conversion efficiency, 100 nJ of IR). For some of the experiments a 1.0 ps dye pulse was obtained by using a different one plate birefringent filter and the IR pulse was generated with a 5 mm LiIO₃ (yielding 3% photon conversion efficiency, 30 nJ of IR). The dye and doubled Nd:YLF pulses are then recovered for optical gating and generating the probe infrared, respectively. Some of the doubled ML Nd:YLF radiation is used to synchronously pump a second dye laser which operates with a single jet, a 3-plate birefringent filter and two étalons, producing 30 ps, 2 cm⁻¹ pulses. The re-

TABLE I. Relevant data concerning solution samples investigated.

Ion	Salt	Solvent	Conc. (Molar)	ν_{pump} (cm^{-1})	ν_{probe} (cm^{-1})	Linewidth (cm^{-1}) ($\pm 2 \text{ cm}^{-1}$) = $2/T_2$		
N_3^-	NaN_3	D_2O	0.1	2043	2013	20		
			0.01			21		
		MeOH	0.1	2043	2013	20		
			0.01			21		
			0.01			27		
		H_2O	0.6	2049	2019	26		
			0.1			28		
				0.01			27	
				HMPA	0.01	1993	1963	15
		OCN^-	KOCN	MeOH	0.13	2162	2134	20
SCN^-	KSCN	D_2O	0.5	2065	2042	45		
			0.01			46		
		MeOH	0.3	2065	2042	45		
			0.5			45		
			0.01			45		

maintaining regeneratively amplified Nd:YLF pulse is used to amplify and mix the second dye pulses as the source of probe IR. The probe IR polarization is rotated 45° relative to the pump pulses and focused through the sample with a $100 \mu\text{m}$ spot size at a small angle relative to the pump pulses. The probe IR is directed through a wire grid polarizer (P in Fig. 1) (Molelectron IGP-225, extinction ca. 50) after the sample and then onto a 3 mm LiIO_3 crystal along with the dye laser DL1 pulses for the optical gating. The difference frequency signal near 670 nm was detected through a double monochromator on a photomultiplier tube (PMT). The pump IR pulses are chopped at 500 Hz, one-half the repetition rate of the regenerative amplifier (1 kHz), and a double lock-in amplifier scheme is used to measure the transient absorbance change.

For population decays, the maximum transient absorption corresponding to the $\nu=1$ to $\nu=2$ transition of the ion was located by tuning the probe frequency. The probe polarizer was adjusted for the "magic angle," 54.7° , relative to the pump polarization. In the polarization experiments the signal at each delay is collected with the polarizer oriented parallel [$S_{\parallel}(t)$] and then perpendicular [$S_{\perp}(t)$] to the pump polarization and the anisotropy obtained from Eq. (1). The crystal (LiIO_3 , type I) for up-conversion is oriented with the ordinary axis parallel to the initial probe

polarization direction. The pump polarization is $\pi/4$ to this axis. A polarizer in the probe beam generates $\pi/4$ or $-\pi/4$ polarization to yield the parallel and perpendicular signals.

The experiments were performed using static cells containing the sample solutions. The salts used, concentrations, and pump and probe frequencies are listed in Table I. N_3^- and NCS^- were studied in D_2O and methanol, but only methanol solutions of NCO^- were investigated because of strong D_2O absorption. The transient IR absorption spectrum of N_3^- in D_2O was also measured. Transient signals were measured as a function of the probe IR frequency with ca. 3 cm^{-1} increments at a delay of 4 ps. The probe IR frequency was varied by changing the long-pulse dye laser frequency.

RESULTS

The results of this work are summarized in Table II, which lists the vibrational population relaxation times and reorientation times measured for N_3^- in H_2O , D_2O , methanol, and hexamethyl-phosphamide (HMPA), for NCO^- in methanol and for NCS^- in methanol and D_2O . The kinetic transient absorption curves for N_3^- in D_2O , H_2O , methanol, and HMPA are shown in Fig. 2. The T_1 times

TABLE II. Summary of transient infrared results for ions in solution.

Ion	Solvent	T_1 (ps)	T_R (ps)	Calculated T_R (ps) ^a	
				Stick	Slip
N_3^-	D_2O	2.4(0.3)	7.1	9.9	1.7
	MeOH	2.4(0.3)	12.7	4.9	0.9
	H_2O	1.2(0.4)	...	8.0	1.4
	HMPA	14.8(0.4)	5.6	31.9	5.6
OCN^-	MeOH	2.9(0.3)	6.7	5.0	0.8
SCN^-	D_2O	18.3(0.8)	4.7	13.3	2.6
	MeOH	11.0(1.0)	8.7	6.6	1.3

^a T_R was calculated by assuming the ions were prolate symmetric rotors viscosities are from Ref. 22. Bond lengths and van der Waals radii were obtained from the literature (Refs. 11, 17, and 18). Viscosities are from Ref. 22.

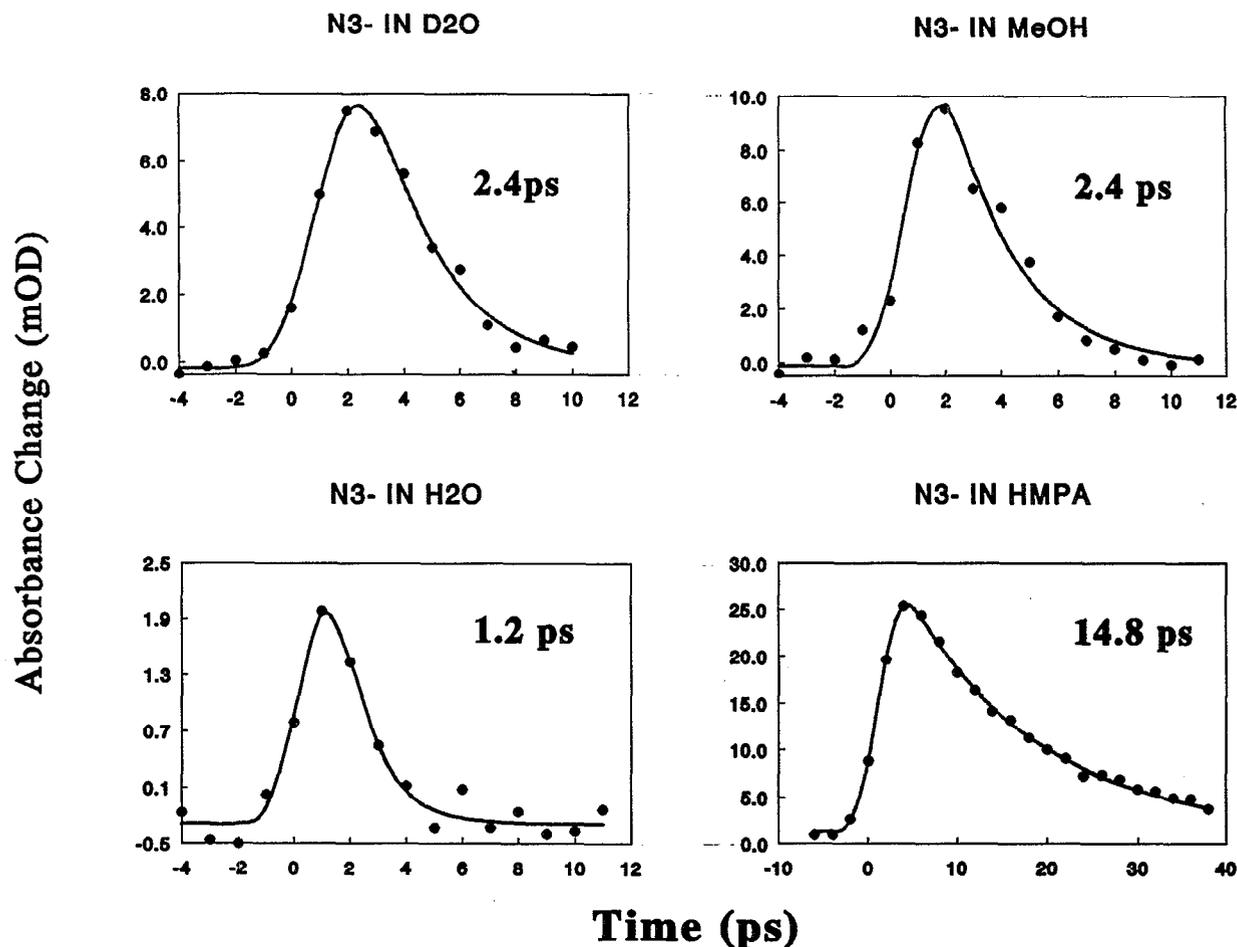


FIG. 2. Transient absorption decay curves measured for N_3^- in H_2O , D_2O , methanol, and HMPA. The lines are fits to single exponential decays using the indicated values of T_1 .

were determined by a least squares analysis to a single exponential in convolution with a Gaussian pulse. The T_1 times for N_3^- in the first three solvents are more accurate than, but within the uncertainties of the previously reported results. With the improved precision which has allowed magic angle methods to be used to separate rotational and population effects, we now discern that the relaxation time in H_2O (1.2 ± 0.4 ps) is somewhat less than that in D_2O and methanol (2.4 ± 0.3 ps). In addition, the 15 ps T_1 time observed in the aprotic solvent HMPA is significantly longer than found in protic solvents, demonstrating the importance of hydrogen bond interactions in the relaxation pathway.

The kinetic absorption decays for NCO^- in methanol and for NCS^- in both methanol and D_2O are shown in Fig. 3. While the T_1 time for NCO^- (2.9 ± 0.3 ps) is close to that for N_3^- in the same solvents, the vibrational population decay in NCS^- is considerably slower and it exhibits a significant solvent dependence. The T_1 time of NCS^- in D_2O (18 ps) is almost twice that in methanol (11 ps) with both times approximately 10 times those for N_3^- . This is an important result when considering whether very fast vibrational relaxation is a general property of ions in protic

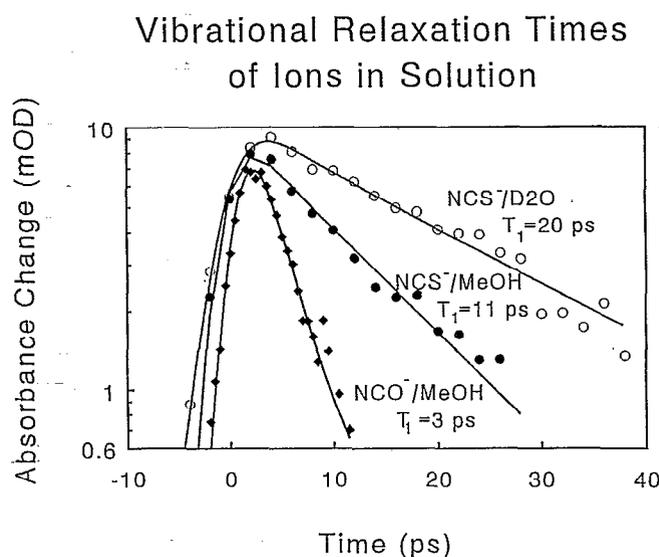


FIG. 3. Transient absorption decay curves measured for NCO^- in methanol and for NCS^- in methanol and in D_2O .

Transient IR Anisotropy of Azide Ion

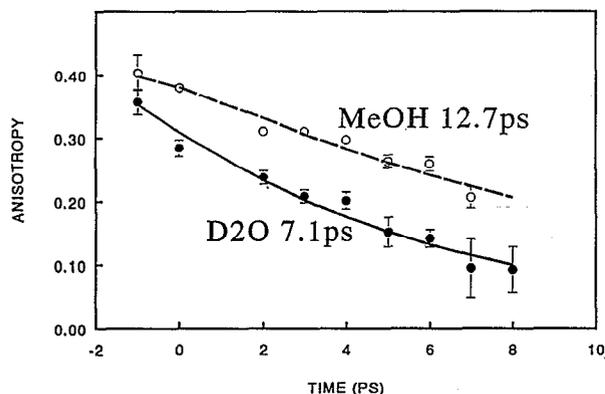


FIG. 4. Anisotropy decay of ν_3 measured using polarized transient spectroscopy for N_3^- in methanol and D_2O .

solvents. The form of the normal coordinate in NCS^- is more localized than in N_3^- and NCO^- and the charge distribution is also different. These are both factors that should influence the relaxation as is discussed later in the paper.

The anisotropy decay has been measured with polarized infrared spectroscopy and the results for N_3^- in methanol and D_2O are shown in Fig. 4. These have been modeled as the combination of parallel [$S_{\parallel}(t)$] and perpendicular [$S_{\perp}(t)$] signals in Eq. (1), which are convoluted with the pulse, where

$$S_{\parallel}(t) = [1 + 0.8 \exp(-t/T_R)] \exp(-t/T_1) * I(t),$$

$$S_{\perp}(t) = [1 - 0.4 \exp(-t/T_R)] \exp(-t/T_1) * I(t).$$

In our previous work only results for $S_{\parallel}(t)$ were reported.¹⁰ The reorientation times (T_R) determined for N_3^- in methanol and D_2O are 12.7 and 7.1 ps, respectively. For the other solutions, reorientation times were determined by carefully measuring the anisotropy at one or several delay times, typically near time zero and at 6 ps, and then assuming the above form for the decay. For example, the anisotropy measured for NCO^- at 6 ps was 0.16, indicating that $T_R = 6.7$ ps. Similarly, for N_3^- in HMPA, T_R was found to be 5.6 ps, and for NCS^- in methanol and D_2O , T_R was measured to be 8.7 and 4.7 ps, respectively.

The transient absorption spectrum was measured for N_3^- in D_2O as shown in Fig. 5. The separation between the fundamental band ($\nu=0 \rightarrow \nu=1$) bleach and the excited state ($\nu=1 \rightarrow \nu=2$) absorption is approximately 28 cm^{-1} . It agrees with the calculated (*ab initio*) value (28 cm^{-1})²⁰ and earlier measurements.¹⁰ Similar anharmonicities were also observed for NCO^- (ca. 28 cm^{-1}) and NCS^- (ca. 23 cm^{-1}). The fits in Fig. 5 lead to bandwidths full-width at half maximum (FWHM) of 25 ± 3 and $21 \pm 3 \text{ cm}^{-1}$ for the bleach ($\nu=0 \rightarrow \nu=1$) and new absorption ($\nu=1 \rightarrow \nu=2$), respectively. The fluctuating forces giving rise to these dephasing widths should also be obtainable from molecular dynamics simulations. The tunability and peak power ad-

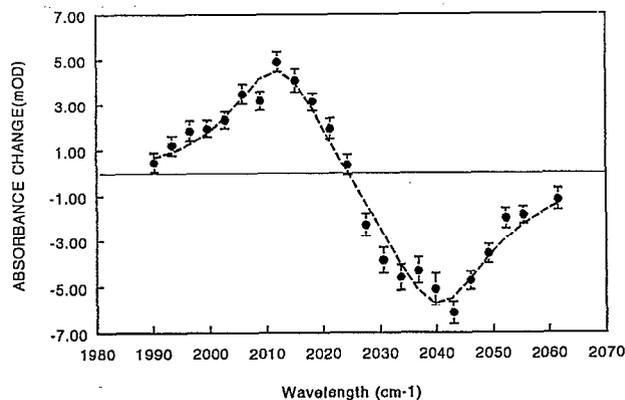
N3- IN D2O
IR Pump-Probe

FIG. 5. Transient spectrum of azide ν_3 band in D_2O at 4 ps.

vantages of the independently generated probe IR combined with the optical gating method used in this work are evident. Few cw infrared lasers operate in the region slightly above 2050 cm^{-1} . Also, the high peak power of the quasi-cw probe beam permits measurements even at frequencies where there is moderately high steady state absorbance by the solvent.

DISCUSSION

There are several major new conclusions from the results of the present work summarized in Table II. (1) There is evidence for a correlation between rotational reorientation times and vibrational relaxation times. Stronger solvent interaction is indicated by faster vibrational relaxation times and slower reorientation times. (2) For the ions studied, the solvent coupling strength increases in the order HMPA, D_2O , methanol, H_2O . The importance of hydrogen bonds in the ion-solvent interaction can be seen in the slower T_1 and faster T_R of N_3^- in aprotic HMPA. (3) While in general we have proven that molecular ions exhibit fast vibrational relaxation, the rate depends on details of the interaction and the mode as indicated by the slower T_1 time of NCS^- compared to N_3^- and NCO^- . (4) Qualitatively the trends in the solvation strength are more strongly correlated with the solvent shifts of the vibrational transitions than with their linewidths. (5) The rotational reorientation times in protic solvents are mostly observed to be approximately equal to or slower than the stick boundary hydrodynamic values. (6) The T_1 relaxation of N_3^- is faster in H_2O than in D_2O . Each of these points will now be discussed in more detail.

The results demonstrate that rotational reorientational times are inversely correlated with vibrational relaxation times. This is intuitively appealing because stronger solvent coupling is expected to increase the rate of relaxation and perhaps open new (inter- and/or intramolecular) vibrational relaxation pathways while increasing the mean lifetime of the ion-solvent complex. For NCS^- , T_R is slower in methanol than in D_2O while the opposite is true for T_1 .

TABLE III. Normal modes and atomic charges of pseudohalides.

Ion	Normal mode ^a			Atomic charges		
	C_1	C_2	C_3	ρ_1	ρ_2	ρ_3
NNN ⁻	-0.41	+0.82	-0.41	-0.87	+0.74	-0.87 ^e
NCO ⁻	-0.51	+0.81	-0.29 ^b	-0.64	0.0	-0.38 ^e
NCS ⁻	-0.66	+0.75	-0.09 ^d	-0.46	0.0	-0.54 ^f

^aDefined as $\sum_{i=1}^3 C_i q_i$ where $q_i = \sqrt{M_i} R_i$ with R_i the atomic displacement during the antisymmetric stretch. The atoms in the ion column are ordered 123, left to right.

^bReference 17.

^cT. Gora and P. J. Kemmey, *J. Chem. Phys.* **57**, 3579 (1972).

^dCalculated with spectroscopic data from Ref. 18.

^eCalculated from INDO wave functions reported by F. J. Owens and J. Sharma, *Chem. Phys. Lett.* **74**, 72 (1980).

^fEstimated from data given in work cited in (d) above. The IR spectra show only a small amount of double bond character in the CS stretch. See also L. DiSipio, L. Oleari, and G. DeMichelis, *Coord. Chem. Rev.* **1**, 7 (1966).

When comparing T_R in different solvents, it is useful also to compare the observed T_R values with those calculated by stick hydrodynamic theory for the ion, i.e., the T_R obtained by assuming an ellipsoid having the dimensions of the ion is undergoing rotational diffusion determined by the solvent viscosity.²¹ For example, for N₃⁻ the values of T_R are comparable in HMPA and D₂O while the T_1 observed is considerably longer in HMPA. However, the solvation structure is the dominating factor in D₂O because the viscosity of HMPA is ca. 3 times that of D₂O,²² even though the reorientation times are about the same. The observed value of T_R for N₃⁻ is much closer to the stick hydrodynamic value²¹ (10 ps) in D₂O than it is in HMPA (32 ps) where there are no hydrogen bonds formed. The rotational diffusion appears adequately described by slip hydrodynamics in that case. The inverse relation between T_R and T_1 values appears to be a clear manifestation of the solvent interaction strength in these ionic solutions. The molecular dynamics simulation of azide in H₂O mentioned earlier used smaller end-atom charges than those given in Table III and underestimated the ion-solvent interaction; it yielded longer T_1 and shorter T_R times than the experimental values measured here. It did predict the observed trend of T_1 , T_R , and the coupling to the solvent and showed a strong effect of the charge on the end atoms on the calculated T_R time.¹²

The results for N₃⁻ in the four solvents studied provide estimates of their relative solvent interaction strengths. The very fast T_1 time (1.2 ps) in H₂O may be partly due to the fact that the solvent forces are somewhat stronger than in D₂O or methanol, both of which lead to slightly longer N₃⁻ T_1 times (2.4 ps), but the spectral density of accepting modes is also likely to be different, a point that will be discussed further below. The evidence that methanol couples more strongly to the ion than does D₂O is consistent with the slower T_1 and faster T_R times for NCS⁻ in D₂O. Also, the T_R time is longer for N₃⁻ in methanol (13 ps) than in D₂O (7 ps), even though the stick boundary prediction is for D₂O to have a longer T_R . In contrast to the other solvents, the T_1 time for azide in the aprotic solvent HMPA is much longer (15 ps), clearly demonstrating that

proton interactions with the charged terminal nitrogens play an important role in the relaxation pathway.

The vibrational energy relaxation in these ions must depend on the forces exerted by the solvent molecules on the antisymmetric stretch coordinate of the ion.²³ As far as the properties of the ion are concerned, three factors would seem to be of primary importance: One is the nature of the normal coordinate describing the antisymmetric stretch and the others are the charge distribution and polarizability of the ion. Through the isovalent, pseudohalide series N₃⁻, NCO⁻, and NCS⁻ each of these factors changes. The normal modes for the antisymmetric stretch and the atomic charges for the three ions are shown in Table III.

The normal modes illustrate that the antisymmetric stretching frequency tends from being delocalized over the molecule in N₃⁻ to being essentially a CN stretching mode in NCS⁻. In the case of these triatomic ions a colinear force on one end of the molecule, from a solvent collision, couples the solvent to the antisymmetric stretch mode and it couples the antisymmetric, translational and symmetric stretches. Forces acting towards the center of mass at the same instant at each end of the molecule couple to the symmetric stretch. If the forces acting at each end of the molecule are uncorrelated, then the rate of relaxation would have equal contributions from each end. Model calculations have indicated that negatively charged solvent oxygen atoms cannot get too close to the central N atom, which is positively charged in N₃⁻, because of repulsive interactions with the negatively charged terminal atoms. Thus a qualitative reason for the slower T_1 relaxation in NCS⁻ could be that the similar solvent forces are effective on only one end (the N end) of the molecule. Again qualitatively, this effect might be expected to increase the T_1 relaxation time by as much as a factor of 2, assuming there is no correlation between the forces at either end of the molecule.

The charge distributions for the three pseudohalides are significantly different (see Table III). In N₃⁻ there is almost one extra electron on each end nitrogen. Presumably this charge greatly facilitates coupling to the solvent because of the Coulomb potential. In NCO⁻ the charge is

more localized on the single end N atom. This effect would further reduce the coupling to the solvent by the O end of NCO^- . There appears to be considerable charge on the S end of NCS^- .

These properties of the distribution of displacements and charge qualitatively account for the trends in T_1 relaxation rate that are observed. The potential due to the coupling of solvent motions $\{q_s\}$ to the antisymmetric stretch Q at frequency ω can be written as $\sum_{i,s} \xi_{si} q_s (\hbar/2\omega)^{1/2} 2R_i$. If the coupling constant ξ_{si} is considered proportional to the charge on the i th atom having Cartesian displacement R_i , as expected for a Coulomb potential, then the relative rates of T_1 relaxation for each atom might be given roughly by the relative values of $(\rho_i^2 C_i^2 / M_i \omega)$ with C_i and ρ_i given in Table III. From the data in Table III, the rates are then predicted to be in ratio $1.0(\text{N}_3^-):0.90(\text{NCO}^-):0.58(\text{NCS}^-)$. Certainly the trend is in agreement with experiment but the proper model probably requires knowledge of the whole solvent structure around the ion. Nevertheless, it makes clear that if the solvent induced S atom motions do not push on the antisymmetric stretch coordinate, then shifting charge to S will reduce the overall coupling to the solvent. The importance of protons interacting with the terminal atoms of the ion is strongly implicated by the weaker coupling to HMPA as discussed above.

The trends in vibrational relaxation times correlate with the solvent shifts (see Table I), but less so with the linewidths of the vibrational transition: Although NCS^- has the broadest absorption line, it has the longest T_1 . It is possible to deduce gas-to-solution solvent shifts by comparing solution Fourier-transform IR (FTIR) spectra with the high resolution gas phase studies available for the ν_3 mode of all the ions studied here.^{11,24} The solvent shift for N_3^- [$\nu_3(\text{gas})=1986.5 \text{ cm}^{-1}$] is largest for H_2O (63 cm^{-1}) and smallest for HMPA (7 cm^{-1}), and they are the same for D_2O and methanol (57 cm^{-1}). This is the same ordering as observed for the vibrational relaxation rates. The same correspondence occurs when comparing different ions in the same solvent. There is almost no shift in NCS^- [for NCS^- , $\nu_3(\text{gas})=2065.9 \text{ cm}^{-1}$], which exhibits the weakest coupling, and the larger shifts for N_3^- and NCO^- [$\nu_3(\text{gas})=2124.3 \text{ cm}^{-1}$] are comparable. These solvent shifts signal properties of the amplitude of the force-force autocorrelations also needed to account for the dynamics and should represent another benchmark for theoretical calculations. At least in part the shifts are related to the parts of the solvent-solute potential that are quadratic in the normal mode of the ion. The shift of the $\nu=0 \rightarrow \nu=1$ transition of N_3^- between H_2O and D_2O of 6 cm^{-1} is notable and suggests some sort of resonance interaction, perhaps with the bending mode of H_2O discussed below.

In a recent paper by Whitnell and co-workers^{14(b)} concerning vibrational relaxation of the neutral molecule CH_3Cl , a correlation between relaxation time and the charge on Cl and CH_3 was observed by simulations indicating that the relevant forces included the Coulombic part of the potential used in the calculation. For that example the Landau-Teller rates for a vibration of 2000 cm^{-1} (of

course CH_3Cl has $\nu=700 \text{ cm}^{-1}$) having the normal mode of CH_3Cl would have been on the order of 10^2 ps with an isotope effect ($\text{H}_2\text{O}:\text{D}_2\text{O}$) of ca. 8:1 on the rates, according to their calculation of the frequency dependent friction exerted on the C-Cl bond [see Fig. 2 of Ref. 14(b)]. The energy diffusion calculated from this simulation did include internal motions of water. While these results explain the relaxation of low frequency modes that shift partial charges, it will be interesting to see whether similar potentials can predict relaxation of modes far above 1000 cm^{-1} .

The measured reorientation times are further evidence of strong solvent coupling for the ions studied. Strong solvent interactions will hold the solute in place long enough so that rotational relaxation may require rotation of both the ion and its associated solvent structure. Therefore the reorientation time is a sensitive indicator of the solvation structure dynamics. In particular, quantitative information regarding the residence time of the solvent molecules on the ion might be obtained from such measurements. For N_3^- in methanol, the observed reorientation time (12.7 ps) is substantially longer than predicted by hydrodynamic stick boundary conditions (4.9 ps), indicating that specific molecular interactions need to be considered to successfully account for the rotational motion. The general trend of orientational relaxation parameters is that they are in the range of stick boundary condition predictions when the solvent is hydroxylic. This suggests that the rotational diffusion is a result of the ion moving within its solvent cage, perhaps undergoing stochastic jumps as a result of H-bond breaking and making. Only in the case of N_3^- in HMPA is the reorientation better described by slip boundary conditions. This again dramatizes the role of hydrogen bonding in determining the dynamics. On the other hand, the observed parameters for the ionic solutions differ markedly with those that emerge from the recent MD simulation on N_3^- in H_2O ¹² when the charge on the end nitrogen is -0.25 . The simulation results in longer T_1 and shorter T_R times, closer to the slip hydrodynamic predictions, which indicates that the coupling has been underestimated. The experimental values obtained here provide an opportunity for critically testing the accuracy of MD calculations of simple solvated systems. On the basis of our results, it is suggested that there is a rather persistent ion-solvent structure, persistent over the T_1 time scale, that undergoes the vibrational relaxation. It is therefore evident that aspects of the *electronic* and *vibrational* structure of this unit be incorporated in calculations of the ion dynamics. The simplest characteristic of the electronic structure to incorporate would be the ion and solvent polarizabilities: For example, the distribution of charge in the solvated ion needs to be considered since it may not be the same as found from vacuum calculations and indeed it may fluctuate. The specific inclusion of internal vibrational motions of the solvent also appear indicated for reasons discussed below concerning isotope effects.

The earlier study of N_3^- showed no clear evidence of an $\text{H}_2\text{O}/\text{D}_2\text{O}$ isotope effect, but the H_2O data (reported as $2.7 \pm 1.3 \text{ ps}$) was much less accurate than the D_2O data (reported as 2.7 ± 0.5). In this work we have narrowed the

errors on these measurements considerably and conclude that the isotope effect on the T_1 rate is $k(\text{H}_2\text{O})/k(\text{D}_2\text{O}) = 2.1 \pm 0.7$. This could be signaling the involvement of internal modes of water and is more consistent with our idea that the relaxation should be considered as occurring within an ion–water super molecule structure. The gross density of vibrational states near 2000 cm^{-1} is ca. 2 times larger for D_2O than H_2O so an isotope effect from water vibrations would need to involve specific mode coupling; i.e., the correlation function of the relevant forces²³ is what is required. It is interesting that the reason why the earlier experiments in H_2O were so inaccurate was because of the strong IR absorption of H_2O compared with D_2O in the ions' antisymmetric stretch region. The H_2O mode at 2115 cm^{-1} is a combination of the ν_2 bend with a water libration.²⁵ This band moves to much lower frequency in D_2O . The closest D_2O band to the 2050 cm^{-1} region is $2\nu_2$ at 2360 cm^{-1} . Thus the existence of an isotope effect prompts the suggestion that this water bending mode should be considered as a candidate for inducing the relaxation. Such an identification is consistent with the isotope effect on the solvent shifts as discussed above. Although we have considered near resonance (quantum) effects in this discussion, even the classical forces from H and D atoms on the ion should be different. However, the average momentum exchanged in a hard sphere collision is likely to be somewhat larger for D_2O , which is opposite to the observed effect. At this point we do not know how the vibrational spectra of the water molecules in the ion–solvent complex (super molecule) are modified from those of the bulk, and clearly such information is needed to resolve the detailed source of the isotope effect.

In the recent paper by Whitnell and co-workers^{14(b)} the force–force autocorrelation for end-on impacts on CH_3Cl by H_2O was completed with flexible water. These authors¹⁴ find a rapid relaxation for CH_3Cl in water but the vibrational frequency falls into the region where the effective spectral density in water is at least 2 orders of magnitude larger than at 2000 cm^{-1} . The reported power spectrum shows a pronounced minimum at ca. 2000 cm^{-1} for D_2O but not for H_2O . Thus the relaxation rate from a Landau–Teller standpoint would be expected to be ca. 8 times faster in H_2O . Neither the observed rates nor the isotope effect for N_3^- relaxation appear to fit this power spectrum well. One possible reason for this, discussed in our earlier paper,⁹ is that the solvent collisions actually couple the antisymmetric with the symmetric stretch. While we have found no evidence of this in the spectrum (i.e., solvent induced Fermi resonances), the possibility cannot be completely ruled out on the basis of the present experiments. The occurrence of the collision induced mixing of internal modes would have the effect of dramatically reducing the frequency of the relevant part of the power spectrum of solvent forces needed in the Landau–Teller calculation, thereby greatly increasing the rate.

Recently, there were additional indications that ions undergo ultrafast vibrational relaxation. Experiments with I_3^- (Ref. 26) and I_2^- ,²⁷ and very recent theoretical calculations²⁸ on I_2^- have indicated ultrafast relaxation. While

these results further corroborate our idea that Coulomb forces are important in ion relaxation, it should be realized that the low frequency of the iodine stretch vibration places it in a region of the water power spectrum where ultrafast rates are not unexpected even from theory involving simple nonflexible water force fields.¹² Nevertheless, the N_3^- relaxation in H_2O at 1.2 ps is still faster than that reported for I_2^- ,²⁷ even though the latter has a frequency of only 115 cm^{-1} , which is less than kT and amidst the most intense region of the water spectral density.

In summary, we have measured vibrational relaxation times and rotational reorientation times for N_3^- , NCO^- , and NCS^- in a variety of solvents using IR pump–probe and IR polarization spectroscopy. The experiments were performed using optically gated IR detection involving independently generated probe IR pulses and with the capability of varying the pump–probe polarization geometry. The results of the present work provide the most comprehensive study to date of vibrational and rotational dynamics for simple ionic molecular systems in dilute solution and are intended to serve as a benchmark for theoretical investigations of solvation. The structures of polyatomic ions in solutions have been studied both experimentally by various spectroscopic methods and theoretically by means of MD simulations.^{29–35} A major issue that remains as an open question is the extent to which the water structure is modified by polyatomic ions. Even with simple monatomic ions in water, this question is not fully answered as recent simulations have indicated.³⁶ Another crucial caveat in the present discussion concerns the role, if any, of counter ions in the relaxation processes. This clearly merits systematic study. On the experimental side it will be important to devise methods to investigate the possibility of solvent induced internal energy flow. It seems clear that transient IR experiments of the type discussed herein can contribute significantly to this debate, particularly in as much as the experiments directly challenge simulations of the dynamics in frequency regimes where the direct coupling to the bath (rigid solvent) modes is small.

ACKNOWLEDGMENTS

This research was supported by grants from the NSF and the National Institute of Health. Dr. Y.-R. Kim contributed significantly in setting up the probe dye laser. We are indebted to M. Klein and co-workers (see Ref. 12) for sharing their simulation results with us, prior to publication; and to R. M. Whitnell for a preprint (Ref. 28).

¹B. Bagchi and A. Chandra, *J. Chem. Phys.* **97**, 5126 (1992), and references therein.

²L. Perera and M. L. Berkowitz, *J. Chem. Phys.* **96**, 3092 (1992).

³E. Neria and A. Nitzan, *J. Chem. Phys.* **96**, 5433 (1992).

⁴G. A. Kenney-Wallace, S. Paone, and C. Kalpouzos, *Faraday Discuss. Chem. Soc.* **85**, 185 (1988).

⁵M. A. Kahlou, W. Jarzeba, T. J. Kang, and P. F. Barbara, *J. Chem. Phys.* **90**, 151 (1989).

⁶S. J. Rosenthal, X. Xie, M. Du, and G. R. Fleming, *J. Chem. Phys.* **95**, 4715 (1991), and references therein.

⁷A. Laubereau and W. Kaiser, *Rev. Mod. Phys.* **50**, 607 (1978); A. Seilmeier and W. Kaiser, in *Ultrasfast Light Pulses and Their Applications*, edited by W. Kaiser (Springer, Berlin, 1988).

- ⁸E. J. Heilweil, M. P. Casassa, R. P. Cavanagh, and J. C. Stephenson, *Annu. Rev. Phys. Chem.* **40**, 143 (1990).
- ⁹E. J. Heilweil, F. E. Doany, R. Moore, and R. M. Hochstrasser, *J. Chem. Phys.* **76**, 5632 (1982); E. J. Heilweil, R. Moore, G. Rothenberger, S. Velsko, and R. M. Hochstrasser, in *Photochemistry and Photobiology*, edited by A. H. Zewail (Harwood-Academic, New York, 1983), Vol. 1, p. 493; *Laser Chemistry* (Harwood-Academic, New York, 1983), Vol. 3, p. 109.
- ¹⁰J. C. Owruksy, Y. R. Kim, M. Li, M. J. Sarisky, and R. M. Hochstrasser, *Chem. Phys. Lett.* **184**, 368 (1991).
- ¹¹M. Polak, M. Gruebele, and R. J. Saykally, *J. Am. Chem. Soc.* **109**, 2884 (1987).
- ¹²M. Ferrario, I. R. McDonald, and M. L. Klein (unpublished).
- ¹³M. Ferrario, I. R. McDonald, and M. C. R. Symons, *Mol. Phys.* (submitted); G. Eaton, A. S. Pena-Nunez, M. C. R. Symons, M. Ferrario, and I. R. McDonald, *Faraday Discuss. Chem. Soc.* **85**, 237 (1988).
- ¹⁴(a) R. M. Whitnell, K. R. Wilson, and J. T. Hynes, *J. Phys. Chem.* **94**, 8625 (1990); (b) *J. Chem. Phys.* **96**, 5354 (1992).
- ¹⁵J. N. Moore, P. A. Hansen, and R. M. Hochstrasser, *Proc. Natl. Acad. Sci. U.S.A.* **85**, 5062 (1988); B. Locke, T. Lian, and R. M. Hochstrasser, *Chem. Phys.* **158**, 409 (1991).
- ¹⁶H. Graener, G. Seifert, and A. Laubereau, *Chem. Phys. Lett.* **172**, 435 (1990).
- ¹⁷V. Schettino and I. C. Hisatsune, *J. Chem. Phys.* **52**, 9 (1970).
- ¹⁸L. H. Jones, *J. Chem. Phys.* **25**, 1069 (1956).
- ¹⁹T. M. Jedju and L. Rothberg, *Appl. Opt.* **26**, 2877 (1987).
- ²⁰P. Botschwina, *J. Chem. Phys.* **85**, 4591 (1986).
- ²¹G. R. Fleming, in *Chemical Applications of Ultrafast Spectroscopy* (Oxford University, New York, 1986), Chap. 6.
- ²²*Lange's Handbook of Chemistry*, 12th ed., edited by J. A. Dean (McGraw-Hill, New York, 1979).
- ²³R. Zwanzig, *J. Chem. Phys.* **34**, 1931 (1960).
- ²⁴M. Gruebele, M. Polak, and R. J. Saykally, *J. Chem. Phys.* **86**, 6631 (1987); M. Polak, M. Gruebele, and R. J. Saykally, *ibid.* **87**, 3352 (1987).
- ²⁵G. E. Walrafen, *J. Chem. Phys.* **36**, 1035 (1962); **40**, 3249 (1964).
- ²⁶U. Banin, A. Waldman, and S. Ruhman, *J. Chem. Phys.* **96**, 2416 (1992).
- ²⁷A. E. Johnson, N. E. Levinger, and P. F. Barbara, *J. Phys. Chem.* **96**, 7841 (1992).
- ²⁸I. Benjamin, and R. M. Whitnell (unpublished).
- ²⁹T. H. Lilley, in *Water: A Comprehensive Treatise*, edited by F. Franks (Plenum, New York, 1973), Vol. 3, Chap. 6.
- ³⁰H. G. Hertz, in *Water: A Comprehensive Treatise*, edited by F. Franks (Plenum, New York, 1973), Vol. 3, Chap. 7.
- ³¹G. Licheri, G. Piccaluga, and G. Pinna, *J. Chem. Phys.* **64**, 2437 (1976).
- ³²J. E. Enderby, *Annu. Rev. Phys. Chem.* **34**, 155 (1983).
- ³³W. Jarzeba, G. C. Walker, A. E. Johnson, M. A. Kahlow, and P. F. Barbara, *J. Phys. Chem.* **92**, 7039 (1988).
- ³⁴B. Bagchi, *Annu. Rev. Phys. Chem.* **40**, 115 (1989).
- ³⁵K. Heinzinger, in *Ions and Molecules in Solution, Studies in Physical and Theoretical Chemistry*, edited by N. Tanaka, H. Ohtaki, and R. Tamamushi (Elsevier, Amsterdam, New York, 1983).
- ³⁶S. B. Zhu and G. W. Robinson, *J. Chem. Phys.* **97**, 4336 (1992), and references therein.