INTRODUCTION

Solvation remains one of the most important issues in chemical physics. Probing the rates and establishing mechanisms for energy transport and molecular motion provides 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,\textsuperscript{1-4} 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 times that have been measured for solution species, such as those for small organic molecules\textsuperscript{5} and metal carbonyls,\textsuperscript{6} 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\textsuperscript{−} in water.\textsuperscript{7} 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 reported\textsuperscript{8} measurement of the vibrational relaxation time of the antisymmetric stretching mode ($\nu_3$) 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\textsuperscript{−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\textsubscript{3}\textsuperscript{−} in the gas phase.\textsuperscript{9} Furthermore, as was shown,\textsuperscript{10} strong Coulomb solvent interactions enhance intermolecular mechanisims.

The previous study employing two-color transient spectroscopy revealed very fast ($T_1\sim 3$ ps) relaxation rates in several protic solvents (H\textsubscript{2}O, D\textsubscript{2}O, methanol, and ethanol).\textsuperscript{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 study\textsuperscript{9} of CN\textsuperscript{−} in H\textsubscript{2}O, which yielded a fast (6–25 ps) $T_1$ time that was dependent on ion concentration. It was the CN\textsuperscript{−} 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 McDonald\textsuperscript{12} have recently performed a molecular dynamics (MD) simulation for azide in water. The N\textsubscript{3}\textsuperscript{−} simulation, similar to that by Ferrario, McDonald, and Symons for CN\textsuperscript{−},\textsuperscript{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,\textsuperscript{14} the energy diffusion into the solvent bath neglecting the high frequency modes of the solvent. These calculations indicate relaxation times of ca. 300
ps would be expected if the transfer of energy was directly into the bath modes. A calculation of the orientational decay \( (P_s) \) 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 \( r(t) \),

\[
\begin{align*}
  r(t) &= \frac{S_\parallel (t) - S_\perp (t)}{[S_\parallel (t) + 2S_\perp (t)]} \\
  &= 0.4 \langle P_2 \cos \theta(t) \rangle,
\end{align*}
\]

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 CO\(^{-}\)—the only previously reported polarized transient infrared pump–probe study is the single-color work by Graener, Seifert, and Laubereau on liquid CH\(_3\)Br.\(^{16}\)

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 D\(_2\)O. These ions also have antisymmetric stretching modes in the 2000 cm\(^{-1}\) region. The dynamics of NCO\(^{-}\) are very similar to those for N\(_2\)T, NCS\(^{-}\) has longer \( T_R \) 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 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 Tejdi 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 \( \mu \)J) which are combined with the other half into a 1 cm LiIO\(_3\) crystal to generate the pump IR pulses (100% photon conversion efficiency, 100 ns 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 LiIO\(_3\) (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 in frared, 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.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Salt</th>
<th>Solvent</th>
<th>Conc. (Molar)</th>
<th>( V_{\text{pump}} ) (cm(^{-1} ))</th>
<th>( V_{\text{probe}} ) (cm(^{-1} ))</th>
<th>Linewidth (cm(^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(_{3}^-)</td>
<td>NaN(_{3}^-)</td>
<td>D(_{2}O)</td>
<td>0.1</td>
<td>2043</td>
<td>2013</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.01</td>
<td></td>
<td></td>
<td>21</td>
</tr>
<tr>
<td>MeOH</td>
<td>0.1</td>
<td>2043</td>
<td>2013</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>2049</td>
<td>2019</td>
<td>26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(_{2}O)</td>
<td>0.01</td>
<td>2193</td>
<td>2163</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>2162</td>
<td>2134</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1</td>
<td>2065</td>
<td>2042</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.01</td>
<td></td>
<td></td>
<td>46</td>
<td></td>
</tr>
<tr>
<td>HMPA</td>
<td>0.3</td>
<td>2065</td>
<td>2042</td>
<td>45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OCN(^-)</td>
<td>KOCN</td>
<td>MeOH</td>
<td>0.13</td>
<td>2162</td>
<td>2134</td>
<td>20</td>
</tr>
<tr>
<td>SCN(^-)</td>
<td>KSCN</td>
<td>D(_{2}O)</td>
<td>0.3</td>
<td>2065</td>
<td>2042</td>
<td>45</td>
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<td></td>
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<td></td>
<td></td>
<td>0.01</td>
<td></td>
<td></td>
<td>45</td>
</tr>
</tbody>
</table>

maining 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 μm 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) (Molektron 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 \( v = 1 \) to \( v = 2 \) 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 \( [S_0(t)] \) and then perpendicular \( [S_1(t)] \) 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 π/4 to this axis. A polarizer in the probe beam generates π/4 or -π/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\(_{2}O\) and methanol, but only methanol solutions of NCO\(^-\) were investigated because of strong D\(_{2}O\) absorption. The transient IR absorption spectrum of N\(_{3}^-\) in D\(_{2}O\) 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\(_{2}O\), D\(_{2}O\), methanol, and hexamethyl-phosphamide (HMPA), for NCO\(^-\) in methanol and for NCS\(^-\) in methanol and D\(_{2}O\). The kinetic transient absorption curves for N\(_{3}^-\) in D\(_{2}O\), H\(_{2}O\), methanol, and HMPA are shown in Fig. 2. The \( T_1 \) times

<table>
<thead>
<tr>
<th>Ion</th>
<th>Solvent</th>
<th>( T_1 ) (ps)</th>
<th>( T_2 ) (ps)</th>
<th>Calculated ( T_R ) (ps)(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(_{3}^-)</td>
<td>D(_{2}O)</td>
<td>2.4(0.3)</td>
<td>7.1</td>
<td>9.9</td>
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<tr>
<td></td>
<td>MeOH</td>
<td>2.4(0.3)</td>
<td>12.7</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td>H(_{2}O)</td>
<td>1.2(0.4)</td>
<td>...</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td>HMPA</td>
<td>14.8(0.4)</td>
<td>5.6</td>
<td>31.9</td>
</tr>
<tr>
<td>OCN(^-)</td>
<td>MeOH</td>
<td>2.9(0.3)</td>
<td>6.7</td>
<td>5.0</td>
</tr>
<tr>
<td>SCN(^-)</td>
<td>D(_{2}O)</td>
<td>18.3(0.8)</td>
<td>4.7</td>
<td>13.3</td>
</tr>
<tr>
<td></td>
<td>MeOH</td>
<td>11.0(1.0)</td>
<td>8.7</td>
<td>6.6</td>
</tr>
</tbody>
</table>

\(^a\) \( T_R \) 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 (Ref. 11, 17, and 18). Viscosities are from Ref. 22.
FIG. 2. Transient absorption decay curves measured for N$_3^-$ in H$_2$O, D$_2$O, methanol, and HMPA. The lines are fits to single exponential decays using the indicated values of $T_1$.

Vibrational Relaxation Times of Ions in Solution

FIG. 3. Transient absorption decay curves measured for NCO$^-$ in methanol and for NCS$^-$ in methanol and in D$_2$O.

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$_2$O ($1.2 \pm 0.4$ ps) is somewhat less than that in D$_2$O and methanol ($2.4 \pm 0.3$ 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$_2$O are shown in Fig. 3. While the $T_1$ time for NCO$^-$ ($2.9 \pm 0.3$ 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$_2$O (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...
Transient Anisotropy of Azide ion

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

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

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

In our previous work only results for $S_{\parallel}(t)$ were reported. 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 $T_R$ = 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 ($\nu=0$ to $\nu=1$) bleach and the excited state ($\nu=1$ to $\nu=2$) absorption is approximately 28 cm^{-1}. It agrees with the calculated (ab initio) value (28 cm^{-1}) and earlier measurements. 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 ± 3 cm^{-1} for the bleach ($\nu=0$ to $\nu=1$) and new absorption ($\nu=1$ to $\nu=2$), respectively. The fluctuating forces giving rise to these dephasing widths should also be obtainable from molecular dynamics simulations. The tunability and peak power advantages 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 $T_1$. The...
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.\textsuperscript{21} For example, for $N_3^-$ the values of $T_R$ are comparable in HMPA and D$_2$O while the $T_1$ observed is considerably longer in HMPA. However, the solution structure is the dominating factor in D$_2$O because the viscosity of HMPA is ca. 3 times that of D$_2$O\textsuperscript{22} even though the reorientation times are about the same. The observed value of $T_R$ for $N_3^-$ is much closer to the stick hydrodynamic value\textsuperscript{1} (10 ps) in D$_2$O 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 the molecule in H$_2$O 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.\textsuperscript{12}

The results for $N_3^-$ in the four solvents studied provide estimates of their relative solvent interaction strengths. The very fast $T_1$ time (1.2 ps) in H$_2$O may be partly due to the fact that the solvent forces are somewhat stronger than in D$_2$O or methanol, both of which lead to slightly longer $N_3^-$ $T_1$ 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 D$_2$O is consistent with the slower $T_1$ and faster $T_R$ times for NCS$^-$ in D$_2$O. Also, the $T_R$ time is longer for $N_3^-$ in methanol (13 ps) than in D$_2$O (7 ps), even though the stick boundary prediction is for D$_2$O 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.\textsuperscript{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 $N_3^-$, 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 $N_3^-$ to being essentially a CN stretching mode in NCS$^-$. In the case of these triatomic ions a covalent 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 $N_3^-$, 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 $N_3^-$ 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

\begin{table}[h]
\centering
\caption{Normal modes and atomic charges of pseudohalides.}
\begin{tabular}{cccccc}
Ion & Normal mode & Atomic charges \\
 & $C_1$ & $C_2$ & $C_3$ & $\rho_1$ & $\rho_2$ & $\rho_3$ \\
NNN$^-$ & -0.41 & +0.82 & -0.41 & -0.87 & +0.74 & -0.87 \\
NCO$^-$ & -0.51 & +0.81 & -0.29 & -0.64 & 0.0 & -0.38 \\
NCS$^-$ & -0.66 & +0.75 & -0.09 & -0.46 & 0.0 & -0.54 \\
\end{tabular}
\end{table}

\textsuperscript{a}Defined as $2\sum_{i=1}^{3} C_i q_i$, where $q_i = \sqrt{M_i R_i}$, with $R_i$ the atomic displacement during the antisymmetric stretch.

\textsuperscript{b}Calculated with spectroscopic data from Ref. 18.

\textsuperscript{c}Calculated with spectroscopic data from Ref. 17.

\textsuperscript{d}Estimated 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. DeMichielis, Coordin. Chem. Rev. 1, 7 (1966).
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 \(q_j\) to the antisymmetric stretch \(Q\) at frequency \(\omega\) can be written as \(\Sigma_i \vec{c}_i \cdot q_j \left(\frac{\hbar}{2\omega}\right)^{1/2} \cdot \vec{R}_i\). If the coupling constant \(\vec{c}_i\) is considered proportional to the charge on the \(i\)th atom having Cartesian displacement \(\vec{R}_i\) 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 \((\rho_i^2 C_i/M\omega)\) with \(C_i\) and \(\rho_i\) given in Table III. From the data in Table III, the rates are then predicted to be in ratio \(1.0(N_2^-):0.90(\text{NCO}^-):0.58(\text{NCS}^-)\). 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 \(\nu_3\) mode of all the ions studies studied here.\(^{11,24}\) The solvent shift for \(N_2^-\) [\(\nu_3\text{(gas)}=1986.5\text{ cm}^{-1}\)] is largest for H\(_2\)O (63 cm\(^{-1}\)) and smallest for HMPA (7 cm\(^{-1}\)), and they are the same for D\(_2\)O 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\(_2^-\) 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 \(v=0\to v=1\) transition of N\(_2^-\) between H\(_2\)O and D\(_2\)O of 6 cm\(^{-1}\) is notable and suggests some sort of resonance interaction, perhaps with the bending mode of H\(_2\)O discussed below.

In a recent paper by Whitnell and co-workers\(^{14(b)}\) concerning vibrational relaxation of the neutral molecule CH\(_3\)Cl, a correlation between relaxation time and the charge on Cl and CH\(_3\) was observed by simulations indicating that the relevant forces included the Coulomb 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\(_3\)Cl has \(v=700\text{ cm}^{-1}\) having the normal mode of CH\(_3\)Cl would have been on the order of 10\(^2\) ps with an isotope effect (H\(_2\)O:D\(_2\)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\(_2^-\) 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 hydroxylc. 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\(_2^-\) 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\(_2^-\) in H\(_2\)O\(^{12}\) 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\(_2^-\) showed no clear evidence of an H\(_2\)O:D\(_2\)O isotope effect, but the H\(_2\)O data (reported as 2.7±1.3 ps) was much less accurate than the D\(_2\)O 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 $\text{D}_2\text{O}$ than $\text{H}_2\text{O}$ so an isotope effect from water vibrations would need to involve specific mode coupling; i.e., the correlation function of the relevant forces$^{23}$ is what is required. It is interesting that the reason why the earlier experiments in $\text{H}_2\text{O}$ were so inaccurate was because of the strong IR absorption of $\text{H}_2\text{O}$ compared with $\text{D}_2\text{O}$ in the ions’ antisymmetric stretch region. The $\text{H}_2\text{O}$ mode at 2115 cm$^{-1}$ is a combination of the $\nu_2$ bend with a water librational mode. This band moves to much lower frequency in $\text{D}_2\text{O}$. The closest $\text{D}_2\text{O}$ 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 $\text{D}_2\text{O}$ 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 $\text{ClIFCl}$ by $\text{H}_2\text{O}$ was completed with flexible water. These authors$^{14}$ find a rapid relaxation for $\text{CH}_2\text{Cl}$ 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 $\text{D}_2\text{O}$ but not for $\text{H}_2\text{O}$. Thus the relaxation rate from a Landau–Teller standpoint would be expected to be ca. 8 times faster in $\text{H}_2\text{O}$. Neither the observed rates nor the isotope effect for $\text{N}_2^-$ 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 $\text{I}_2^-$ (Ref. 26) and $\text{I}_2^- \rightarrow \text{I}^-$ and very recent theoretical calculations$^{28}$ on $\text{I}_2^-$ 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 $\text{N}_2^-$ relaxation in $\text{H}_2\text{O}$ at 1.2 ps is still faster than that reported for $\text{I}_2^- \rightarrow \text{I}^-$ 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 $\text{N}_2^-$, $\text{NCO}^-$, and $\text{NCS}^-$ 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.

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