Vibrational Dynamics of Condensed-Phase Molecules Studied by Ultrafast Infrared Spectroscopy

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Abstract. Infrared pump/probe measurements of $T_1$ relaxation and orientational relaxation of ions in hydrogen bonding solvents are discussed in terms of solvent induced anharmonic coupling.

Introduction

Transient IR spectroscopy was used to measure $T_1$ vibrational energy relaxation times and orientational ($P_2$) relaxation times $\tau_2$. The results of such measurements on simple ions and on FeCO groups in proteins provide insight into solvent dynamics.

Experimental Methods

The experiments involve IR spectroscopy of molecules in excited vibrational states. An intense, tunable IR pulse in 2000 cm$^{-1}$ range was used to excite the samples. Probing was effected by a tunable IR pulse (duration ca. 20 ps) which was gated before the detector by a 300 fs optical pulse. By this technique sub-picosecond IR pump/IR probe experiments could be carried out [1].

Pseudohalide Ions: Results Summary

The observation that high frequency vibrational states of diatomic [2] and triatomic ions [1, 3] relax on the few picosecond timescale in hydroxylic solvents demonstrates the importance of Coulomb forces in the coupling to the solvent. Infrared pump/probe experiments with tunable pulses have enabled measurements of $T_1$ relaxation and orientational relaxation ($\tau_2$) of a number of simple pseudohalogen ions, N$_3^-$, NCO$^-$ and NCS$^-$. These ions have an asymmetric stretch mode near 2000 cm$^{-1}$ which is studied in this work. The principal results were as follows and in Table I:

- An inverse relation between $T_1$ and $\tau_2$ was found: For $T_1 <\tau_2$ Vibrational relaxation occurs within a well-defined solvent structure - i.e. supermolecule relaxation. For $T_1 > \tau_2$ Vibrational relaxation averaged over a broad range of structures.
The $T_1$ relaxation is charge related indicating importance of Coulombic forces. This may mean that not only the nearest neighbor solvent atoms are involved. Relaxation rates are roughly consistent with being proportional to $(\text{charge})^2$.

The $T_1$ relaxation depends on the extent of motion of the end atoms in the asymmetric stretch coordinate.

Hydrogen bonding is a crucial factor in ultrafast relaxation. In nonhydroxylic solvents the rates are much slower.

A possible role seen for internal modes of water is inferred from isotope effects ($\text{H}_2\text{O}/\text{D}_2\text{O}$) in the $T_1$ relaxation of $\text{N}_3^-$.

Table I: $T_1$ Values for Pseudohalide Ions [1]

<table>
<thead>
<tr>
<th>Ion</th>
<th>Solvent</th>
<th>$T_1$ (ps)</th>
<th>$\tau_2$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{N}_3^-$</td>
<td>$\text{H}_2\text{O}$</td>
<td>1.2</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>$\text{D}_2\text{O}$</td>
<td>2.4</td>
<td>7.1</td>
</tr>
<tr>
<td></td>
<td>$\text{MeOH}$</td>
<td>2.4</td>
<td>12.7</td>
</tr>
<tr>
<td>$\text{NCO}^-$</td>
<td>$\text{MeOH}$</td>
<td>3.0</td>
<td>6.7</td>
</tr>
<tr>
<td>$\text{SCN}^-$</td>
<td>$\text{D}_2\text{O}$</td>
<td>18.3</td>
<td>4.7</td>
</tr>
<tr>
<td></td>
<td>$\text{MeOH}$</td>
<td>11.0</td>
<td>8.7</td>
</tr>
</tbody>
</table>

Pseudohalide Ions: Discussion

A conceptually useful approach to describing vibrational relaxation processes involves the Landau-Teller method which incorporates the Zwanzig [4] notion that the fluctuations in forces exerted by the solvent on the mode of vibration with characteristic frequency $\omega$ is what causes the dissipation of vibrational energy. According to this idea which has been taken much further by a number of different groups [5], the $T_1$ relaxation is given by:

$$
\frac{1}{T_1} = \frac{G(\omega)}{\mu k_B T}
$$

where $\mu$ is a reduced mass for the vibration and $G(\omega)$ is the power spectrum (i.e. the cosine Fourier transform of the autocorrelation function) of the forces acting on the vibrational coordinates. The power spectrum will incorporate forces from all types of solvent motion. When translational, rotational or librational fluctuations determine $G(\omega)$, the dissipation mechanism is $V \rightarrow T, R$ and $L$; when internal modes of solvent molecules determine $G(\omega)$ the relaxation is mainly of $V \rightarrow V$ type. In general, the molecular (solute) vibrational energy relaxes into a distribution of solvent motions. It is important to note that $G(\omega)$ contains the forces on the oscillator. This means specifically that to be effective, the collisions should involve the solute atoms that are involved in the vibrational motion. Then if this mode has the form
Q_{a} = \sum C_{x,a} q_{k}, the effective force should take the form:

\[ F = \mu^{1/2} \sum_{k} \bar{F}_{k} C_{a,k} M_{k}^{-1/2}, \]

where \( \bar{F}_{k} \) is the force in the \( k \)-th atom in the direction \( r \) (= \( x_{k}, y_{k}, z_{k} \)). In principle the forces \( F_{k} \) can be obtained from a dynamics simulation [5, 6] and if the forces on different atoms are uncorrelated the relevant spectral density reduces to:

\[ \frac{1}{T_{1}} = \left( \frac{1}{k_{B}T} \right) \sum_{k} \left( \frac{C_{z_{k}}^{2}}{M_{k}} \right) G_{k}(\omega) \]

where \( G_{k}(\omega) \) is the spectral density at \( \omega \) of solvent forces on atom \( k \) in direction \( r \).

If the forces are dominated by Coulomb interactions the \( G_{k}(\omega) \) will vary as \( \rho_{k}^{2} \), with \( \rho_{k} \) the charge on the \( k \)-th atom, and the relaxation rate becomes proportional to \( \sum_{k} C_{z_{k}}^{2} \rho_{k}^{2}/M_{k} \). This notion was introduced in our earlier paper [1]. Of course if the Coulomb interactions become less important than the forces from other sources this simple rule will not hold. This relation predicts \( \text{N}_{3}^{+} \) will relax 6.7 times faster than \( \text{SCN}^{-} \) when the parameters in Table III of reference [1] are utilized. The observed ratios are 7.6 for \( \text{D}_{2} \text{O} \) and 4.6 for \( \text{MeOH} \). Although this suggests that the approach has merit, the significant difference in relaxation predicted from these same data between \( \text{N}_{3}^{+} \) and \( \text{NCO}^{-} \) is not observed. Needless to say the results are very sensitive to the charges \( \rho_{k} \) which must be subject to considerable uncertainty as to their values in solution.

The effect of anharmonicity needs careful consideration. In our first paper on \( \text{N}_{3}^{+} \) [3] we suggested that the coupling between the asymmetric stretch and combination modes is sufficiently small in the isolated ion that its contribution to the relaxation likely would be small. From another standpoint, the existence of anharmonic coupling large enough to generate a \( T_{1} \) in the range 1 ps would be likely to have spectral manifestations (e.g. a splitting) even in solution phase. However we observe a single Lorentzian lineshape in the 2000 cm\(^{-1}\) spectral region with no trace of combination bands. However we wish to emphasize here that the role of \( G(\omega) \) should be crucial in determining the importance of weak anharmonicity effects. As an illustration of the effect of the energy gap, according to the simulation by Klein, Ferrario and McDonald [6] the value of \( G(k_{B} T/hc) / G (2000 \text{ cm}^{-1}) \) for \( \text{N}_{3}^{+} \) in \( \text{H}_{2} \text{O} \) is approximately \( 10^{4} \) and \( G(k_{B} T/hc) / G (1000 \text{ cm}^{-1}) \) is ca. \( 10^{2} \) at 300 k. Thus the spectral density for the forces of \( \text{H}_{2} \text{O} \) molecules on \( \text{N}_{3}^{+} \) is about \( 10^{4} \) times larger at the combination difference frequencies \( v_{3} - 3v_{2} = 133 \text{ cm}^{-1} \) and \( v_{3} - (v_{1} + v_{2}) = 48 \text{ cm}^{-1} \) than at \( v_{3} - 2000 \text{ cm}^{-1} \). Whenever there exists strong interactions between solute and solvent there will be frequency regimes where \( G(\omega) \) is very large. In order to describe a solvent induced anharmonic pathway in the Landau-Teller picture it seems necessary to calculate the forces on the \( v_{3} \) mode resulting from the motions of solvent atoms as before but with the solute atoms moving according to modes \( v_{2} \) and \( v_{1} \). In other words the very high frequency part of the fluctuating force would
be needed. Any intrinsic anharmonicity of the solute ion potential function might be dominated by this solvent effect in polar and ionic systems.

For example, the ion water hydrogen bonded structure that must persist throughout the decay of $v_3$ in $N^+_3$ may involve forces that are sufficiently strong to mix the intramolecular modes. In the partial structure:

```
  O  O  O  H
N = N = N  
    H
```

the $v_3$ normal mode of $N^+_3$ is coupled to the $v_1$ mode (symmetric stretch) by symmetric stretches and bends of the $NH_2$ unit while the $v_3$ mode couples to $v_2$ as a result of asymmetric stretches of the $NH_2$ group.

The isotope effect showing $N^+_3$ relaxing twice as fast in H$_2$O compared with D$_2$O suggests an internal mode of water is involved in the relaxation, arguing against solvent modification of the surfaces. However, the correlation observed between the relaxation times and the solvent shifts of the vibrational spectra do evidence the involvement of solvent forces in the relaxation mechanism. The idea of the persistence of a supermolecule structure throughout the $T_1$ relaxation of $N^+_3$ and NCO in water does argue in favor of "polyatomic" behavior, incorporating mode mixing as suggested above.

Proteins

The results on the $T_1$ relaxation of the carbonyl $\nu=1$ state in myoglobin, hemoglobin and protoporphyrin in D$_2$O using the same approach showed much slower relaxation times of 18, 18 and 31 ps respectively. These relaxations are nevertheless much faster than normally found for metallocarbonyls and are proposed to involve anharmonic coupling to the modes of the heme-CO group, mediated by the iron atom.

Further development of these ideas will require both new experiments and theory.

Acknowledgements

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References

