

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 τ_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 (τ_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 τ_2 was found: For $T_1 \ll \tau_2$ 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 (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 (H_2O/D_2O) in the T_1 relaxation of N_3^- .

Table I: T_1 Values for Pseudohalide Ions [1]

Ion	Solvent	T_1 (ps)	τ_2 (ps)
N_3^-	H_2O	1.2	...
	D_2O	2.4	7.1
	MeOH	2.4	12.7
NCO^-	MeOH	3.0	6.7
SCN^-	D_2O	18.3	4.7
	MeOH	11.0	8.7

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 ω 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 μ 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

$Q_\alpha = \sum C_{\alpha k} q_k$, the effective force should take the form:

$$F = \mu^{1/2} \sum_k \bar{F}_k C_{\alpha k} M_k^{-1/2},$$

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 \bar{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:

$$\frac{1}{T_1} = \left(\frac{1}{k_B T} \right) \sum_k (C_{\alpha k}^2 / M_k) G_k(\omega),$$

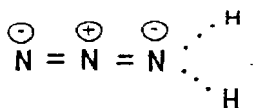
where $G_k(\omega)$ is the spectral density at ω of solvent forces on atom k in direction r .

If the forces are dominated by Coulomb interactions the $G_k(\omega)$ will vary as ρ_k^2 , with ρ_k the charge on the k^{th} atom, and the relaxation rate becomes proportional to $\sum_k C_{\alpha k}^2 \rho_k^2 / M_k$. 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 N_3^- will relax 6.7 times faster than SCN^- when the parameters in Table III of reference [1] are utilized. The observed ratios are 7.6 for D_2O and 4.6 for $MeOH$. Although this suggests that the approach has merit, the significant difference in relaxation predicted from these same data between N_3^- and NCO^- is not observed. Needless to say the results are very sensitive to the charges ρ_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 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 N_3^- in H_2O 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 H_2O molecules on N_3^- is about 10^4 times larger at the combination difference frequencies $\nu_3 - 3\nu_2 = 133 \text{ cm}^{-1}$ and $\nu_3 - (\nu_1 + \nu_2) = 48 \text{ cm}^{-1}$ than at $\nu_3 \sim 2000 \text{ cm}^{-1}$. 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 ν_3 mode resulting from the motions of solvent atoms as before but with the solute atoms moving according to modes ν_2 and ν_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 ν_3 in N_3^- may involve forces that are sufficiently strong to mix the intramolecular modes. In the partial structure:



the ν_3 normal mode of N_3^- is coupled to the ν_1 mode (symmetric stretch) by symmetric stretches and bends of the NH_2 unit while the ν_3 mode couples to ν_2 as a result of asymmetric stretches of the NH_2 group.

The isotope effect showing N_3^- relaxing twice as fast in H_2O compared with D_2O 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_2O 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 metallobonded carbonyls 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

This work was supported by NIH and NSF.

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