Vibrational energy relaxation and reorientation of azide ion pairs in DMSO

2 AUTHORS, INCLUDING:

Jeff Owrutsky
United States Naval Research Laboratory

122 PUBLICATIONS **2,865** CITATIONS

Vibrational energy relaxation and reorientation of azide ion pairs in DMSO

Q. Zhong [1], J.C. Owrutsky *

US Naval Research Laboratory, Chemistry Division Code 6111, 4555 Overlook Ave SW, Washington DC 20375-5342, USA

Abstract

Vibrational energy relaxation (VER) and reorientation times have been measured by ultrafast polarization infrared spectroscopy for the antisymmetric stretching v_3 band of free azide ion and NaN_3, MgN_3^+, and CaN_3^+ ion pairs in dimethyl sulfoxide solutions. The v_3 absorption bands are shifted to higher frequency in the ion pairs relative to the unassociated, dissolved anion, but VER times of the ion pairs are similar, all in the range of 11–18 ps. The reorientation times of the ion pairs are longer (>20 ps) than for free azide (6 ± 2 ps), as expected based on their structures. Ab initio calculations were performed to help interpret the experimental results.
Published by Elsevier B.V.

1. Introduction

There have been numerous experimental studies of the spectroscopy and dynamics of the antisymmetric stretching v_3 vibrational band of azide ion in various media, such as in the gas phase [1], in bulk homogenous solvents [2–8], in reverse micelles [9–11] and in biologically relevant systems [12–15]. The azide v_3 band near 2000 cm^{-1} has a very high IR absorption band strength (of $\sim35\,000$ M^{-1}cm^{-2}) and the linear triatomic azide anion is highly symmetric, so that it provides a sensitive probe for investigating ion solvation properties using frequency and time resolved IR spectroscopy. In solution, the local environment affects the anion structure, charge distribution, normal mode displacements, and other parameters that mediate spectral and dynamical properties, such as solvent induced spectral shifts, vibrational energy relaxation (VER) and rotational reorientation times. Experimental gas phase spectroscopy [1] and high level ab initio [16] and molecular dynamics (MD) [17–19] calculations have provided important details about the isolated and solvated anion that facilitate interpreting experimental solution phase results.

Azide is a prime example of a small ion that exhibits very rapid VER in polar solvents [2–7] due in large part to the role of Coulombic solute–solvent interactions. These electrostatic interactions can accelerate VER either through direct interaction [17–23] or indirectly by drawing the solute and solvent closer together, which increases the strength for other (non-Coulombic) interactions [24–26]. In strongly interacting solvents, the rotational reorientation time (T_R) is comparable to (as in water) or longer than (as in methanol) the VER time (T_1), which represents a clear case in which details of the solute–solvent interaction must be considered within a dynamical theory to account for the persistent nature of the solvent environment during the VER process. The VER rate for azide in different bulk solvents has been found to correlate with the solvent-induced spectral shift and the reorientation time, all of which increase with increasing solute–solvent interaction strength.

In addition to the experimental results, there have been several MD simulations of azide in bulk water that provide valuable insight on how the anion properties affect its solvation characteristics and how the latter can be inferred from dynamical observables such as T_1 and T_R times [17–19]. The terminal nitrogens of azide are negatively charged ($-qe$) and the middle-nitrogen is partially positively charged. MD simulations by the Klein group

* Corresponding author. Fax: +2024048119.
   E-mail address: jeff.owrutsky@nrl.navy.mil (J.C. Owrutsky).
   [1] NRL-NRC Research Associate.

[17,18] were performed for a range of charges ($q = 0.57$–0.952) and the best agreement with the experimental T_1 and T_R times [2,3] was found for $q = 0.952$ in a range of solvents. The MD simulations by Morita and Kato [19] were successful at reproducing the ratio of VER rates in D_2O and H_2O and the absolute predicted rates are very close to those obtained experimentally [3,6,11]. These latter calculations indicate nearly equivalent contributions from IVR and transfer to solvent mechanisms for the v_3 of azide, a result that has not been confirmed (nor ruled out) experimentally.

FTIR studies have shown that azide ion forms contact ion pairs with alkali and alkaline earth metal cations in dimethylsulfoxide (DMSO) solutions [8]. The v_3 band of free azide ion in DMSO is centered at ~ 2000 cm^{-1} and the corresponding band in the ion pairs appears at somewhat higher frequency (20–60 cm^{-1}). The blue shift was found to be roughly proportional to the polarizing power of the metal ion, which is closely related to its ionic potential (z/r) [8,27,28]. Similar spectroscopic results have also been reported for the isoelectronic cyanate anion [29]. Density functional theory (DFT) calculations on these alkali metal-azide ion pairs indicate that the presence of metal cations reduces the symmetry and varies the charge distribution, force constants and band strengths of azide v_3 mode [8]. The DFT calculations predict linear ion pair geometries and qualitatively reproduce the v_3 band shifts observed spectroscopically from ion pairing with the alkali metals. There have also been previous calculations of spectral shifts in related ionic complexes, such as for NCO$^-$ and other anions [30], that show close agreement with experimentally determined values [29]. Previous experimental [2–6,31,32] and theoretical studies [17–25] of VER of charged or polar solutes in polar solvents have shown that Coulombic interactions between solute and solvent play a critical role in accelerating the VER process of high frequency solute modes. The formation of ion pairs could affect the VER dynamics in several ways. It could promote IVR by introducing new internal vibrational modes or reduce the solute–solvent interaction either by restricting access to one of the nitrogens or by changing the charge distribution or normal mode displacement. In this work, we employ time-resolved polarization IR spectroscopy to investigate the influence of contact ion pair formation on the dynamics of azide ion in DMSO solution. Also, DFT calculations similar to those previously reported [8] are extended to alkaline earth metal (Ca, Mg) ion pairs to aid in interpreting the experimental results.

2. Experimental

Details of the experimental methods can be found in our previous publication [10]. Briefly, the laser system consists of an optical parametric amplifier (TOPAS, Light Conversion), pumped by a Ti:sapphire regenerative amplifier (Spitfire, Positive Light). It provides pulses at 1 kHz with a duration of ~ 100 fs and an energy of 150 μJ for the signal (1150–1600 nm) and idler (1600–2700 nm) beams. Difference frequency in the mid–IR range (2.4–11 μm) is generated by mixing the signal and idler pulses in a Type I AgGaS$_2$ crystal (1 mm thick) after traveling through a quartz time-plate. The output is ~ 4 μJ and 200 fs at 5 μm. The mid-IR beam is then split into pump and probe (10%) components. The probe beam has its polarization rotated 45° relative to the pump beam by a wire grid polarizer and is then directed to a translational delay stage. The pump and probe beams are crossed at a small angle at the static sample cell with a 75 mm CaF$_2$ focal lens. The probe beam passes through another wire grid polarizer after the sample, is frequency resolved to ~ 5 cm^{-1} with a monochromator, and is detected with an HgCdTe infrared detector. The pump beam is chopped at 500 Hz and the IR signal is processed with a pair of lock-in amplifiers to determine the pump-induced absorbance change.

NaN$_3$ and N$_3^-$ were prepared by dissolving NaN$_3$ salt in DMSO solution, MgN$_3^+$ and CaN$_3^+$ were prepared by mixing MgCl$_2$ and CaCl$_2$ with NaN$_3$ in DMSO, respectively. Concentrations of N$_3^-$, NaN$_3$, MgN$_3^+$, and CaN$_3^+$ in DMSO solution are less than 0.3, 0.4, 0.1 and 0.1 M, respectively. The sample pathlength was 12–100 μm. Care was taken to keep the samples dry; nevertheless, the FTIR spectra indicate that a small amount of water ($<2\%$) was present in all samples studied. However, the IR bands of all the species are the same as those of the anhydrous samples studied by Le Borgne et al. [6], indicating that the small amount of water present in the system did not cause a significant perturbation in the static IR spectra.

3. Results

Fig. 1 shows FTIR spectra in the 2000 cm^{-1} region of the v_3 band of N$_3^-$ for DMSO solutions containing NaN$_3$, MgN$_3^+$, and CaN$_3^+$. In all the samples some free N$_3^-$ ion can be seen with a peak centered at about 2000 cm^{-1}. The v_3 bands of NaN$_3$, MgN$_3^+$, and CaN$_3^+$ are blue shifted relative to the free ion band, with NaN$_3$ centered at 2024 cm^{-1}, MgN$_3^+$ at 2058 cm^{-1}, and CaN$_3^+$ at 2048 cm^{-1}, in agreement with the earlier measurements by Le Borgne et al. [8].

VER times (T_1) and reorientation times (T_R) for NaN$_3$ and CaN$_3^+$ were obtained from transient bleach measurements, since transient absorption decay measurements were precluded due to spectral overlap with the bleach signal of the free azide ion. T_1 and T_R times of N$_3^-$ and MgN$_3^+$ were obtained from both transient
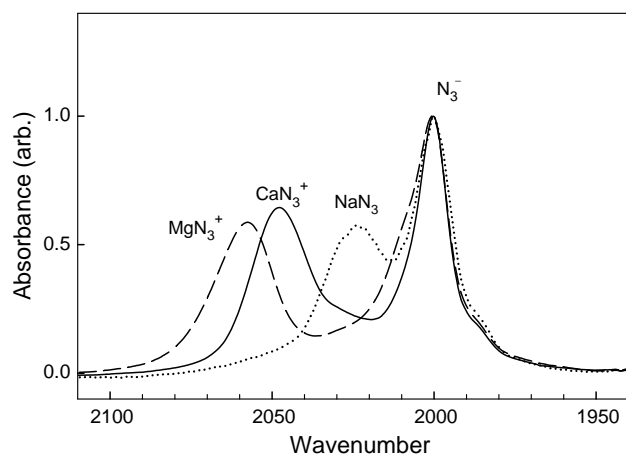
Fig. 1. FTIR spectra in the region of the antisymmetric stretching band (v_3) of N_3^- in NaN$_3$, MgN$_3^+$, and CaN$_3^+$ in DMSO, normalized to the intensity of the free N_3^- band intensity.

Table 1
Vibrational frequency, energy relaxation time (T_1) and reorientation time (T_R) for N_3^-, NaN$_3$, MgN$_3^+$, and CaN$_3^+$ in DMSO

	N_3^-	NaN$_3$	CaN$_3^+$	MgN$_3^+$
Frequency (cm^{-1})				
Observed[a]	2000	2024	2048	2058
Calculated[b]	2075[a]	2196[a]	2260	2321[c]
T_1 (ps)	11 ± 2	15 ± 2	18 ± 2	13 ± 1
T_R (ps)	6 ± 2	>20	>20	>20

[a] Ref. [8] and this work.
[b] DFT harmonic frequency for the isolated species at B3LYP/6–311+G(d) level.
[c] For the linear ion pair structure; for the minimum, bent structure (with a Mg–N–N angle of 137°), the frequency is 2227 cm^{-1}.

bleach and transient absorption measurements, which yielded results that were indistinguishable within the experimental uncertainties. Fig. 2 shows the bleach recovery VER curves for N_3^-, NaN$_3$, MgN$_3^+$, and CaN$_3^+$ in DMSO measured at the magic angle, i.e., with the pump and probe polarizations at an angle of 54.7°, which eliminates polarization and orientational contributions to the signal. The data were fitted to a single exponential decay convoluted with a Gaussian pulse. In some cases, an additional, instrument-limited component of the signal was observed due to coherence or multiphoton processes. When necessary, another Gaussian pulse term was included in the model for the data. The fitting results show that the T_1 times of N_3^- NaN$_3$, MgN$_3^+$, and CaN$_3^+$ are 11 ± 2, 15 ± 2, 13 ± 1, and 18 ± 2 ps, respec-
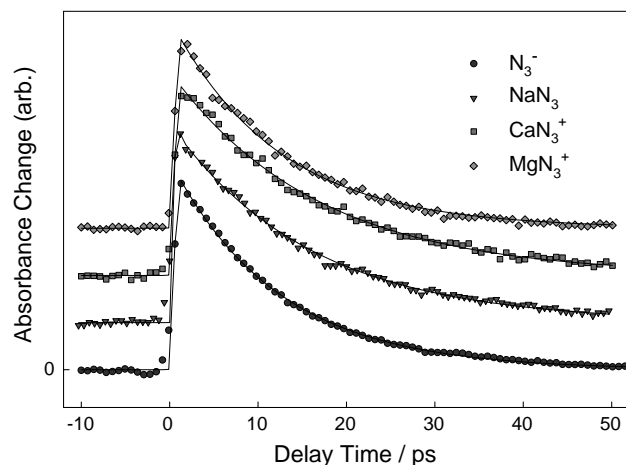
tively, which are listed in Table 1. The T_1 times measured for N_3^- did not depend on concentration over the range 0.05–0.5 M. There was no evidence that the signals were affected by using broadband excitation that overlaps the free ion and ion pair bands.

Fig. 3 shows the anisotropy ($r(t)$) decay measured for N_3^-, NaN$_3$, MgN$_3^+$, and CaN$_3^+$ in DMSO. Here, $r(t) = (I_\parallel(t) - I_\perp(t))/(I_\parallel(t) + 2I_\perp(t))$, where $I_\parallel(t)$ and $I_\perp(t)$ are the transient signals measured with the polarization of the probe beam parallel and perpendicular, respectively, to that of the pump beam. The T_R time of N_3^- is about 6 ± 2 ps. The anisotropy decays of NaN$_3$, MgN$_3^+$, and CaN$_3^+$ are similar and decay on the order of several tens of picoseconds, which is significantly longer than for N_3^-. The measured T_R times are listed in Table 1.

The experimental vibrational frequencies measured for the ion pairs are consistent with the previous study [8] and they suggest that the ion pairs are linear. DFT calculations were reported previously for N_3^- and ion pairs with Li, Na, and K using B3LYP/6–311+G(d) [8]. We calculated structures, vibrational frequencies, atomic normal mode displacements and charge distributions
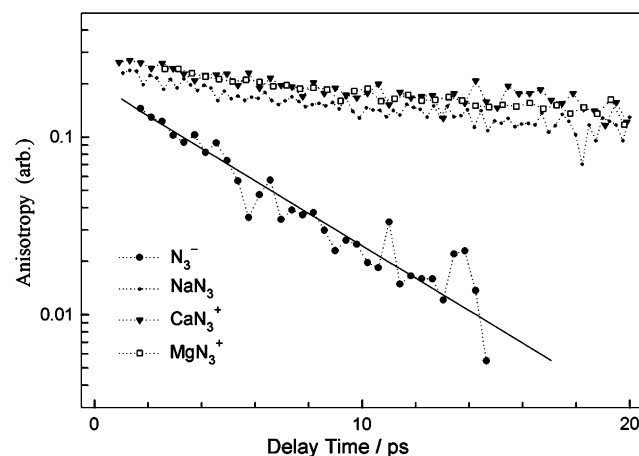

Fig. 2. Transient bleach decay curves measured for the v_3 band of N_3^-, NaN$_3$, MgN$_3^+$, and CaN$_3^+$ in DMSO. The probe wavelengths are at the static absorption maxima, which are listed in Table 1. The curves are normalized and offset for clarity. The maximum absorbance changes are in the range −(60–120 mOD).

Fig. 3. Anisotropy decay curves measured for N_3^-, NaN$_3$, MgN$_3^+$, and CaN$_3^+$ in DMSO. The points are the data and the line is the result of a fit to the N_3^- data with a decay time of 6 ps.

for N_3^-, NaN_3, CaN_3^+, and MgN_3^+ with the same method and basis set [33]. Our data for N_3^- and NaN_3 agree with the earlier results. We extended these to include the alkaline earth metal (Mg^{2+}, Ca^{2+}) ion pairs with azide to compare with our experimental results. The calculated frequencies are listed in Table 1 and they reproduce the trend observed experimentally of shifting to higher frequency in the ion pairs compared to the free ion. For the isolated ion pairs, the most stable structures were found to be linear for NaN_3 and CaN_3^+, but for MgN_3^+ it was bent. Previous ab initio studies of ion pairs involving pseudohalide ions [34] indicate that the ν_3 frequency is higher for linear than for bent or cyclic isomers. This helps explain why the MgN_3^+ frequency from our calculations is lower than for CaN_3^+, which is the opposite of what is observed. A calculation of MgN_3^+ constrained to a linear structure results in a frequency higher than CaN_3^+. The experimental frequencies suggest that the ion pairs in solution, including MgN_3^+, are linear. Including solvent effects in the calculations may improve their agreement with experiment for the most stable MgN_3^+ isomer.

4. Discussion

VER of a polyatomic solute molecule in bulk homogenous solvent can occur by intermolecular energy transfer to the solvent modes or intramolecular vibration redistribution (IVR) to other solute modes, with or without solvent coupling. The VER rate can be affected by many factors, such as excitation energy, frequency and anharmonicity of the solute vibrational mode, the solute–solvent interaction strength, and specific solute–solvent vibrational resonances. Vibrational and rotational dynamics of CN^-, N_3^-, NCO^-, and NCS^- have been studied in several bulk solvents including H_2O, D_2O, methanol, and hexamethyl phosphamide (HMPA) [2–7,11,31,32]. VER rates as well as T_R times increase with increasing solvent polarity and degree of hydrogen bonding, i.e, with increasing solute–solvent interaction strength: $H_2O > D_2O \approx$ Methanol $>$ HMPA. In more polar solvents, such as H_2O, stronger coupling promotes VER and also increases friction or resistance to reorientation. DMSO is a polar aprotic solvent similar to HMPA, and our measured T_1 and T_R times of N_3^- in DMSO are similar to those in HMPA solution [3], consistent with this trend.

Previous FTIR studies have shown that azide ion can form contact ion pairs with alkali and alkaline earth metal cations in DMSO. (The most stable species for LiN_3 in water is a solvent stabilized ion pair.) The ν_3 band of free azide ion in DMSO is centered at $\sim$2000 cm^{-1}, and blue shifts by 24 cm^{-1} in NaN_3, 48 cm^{-1} in CaN_3^+, and 58 cm^{-1} in MgN_3^+ [8]. The blue shift was found to be approximately proportional to the polarizing power of the metal

cations, P; $P = \frac{IP}{5z^{0.27}\sqrt{r}}$, where IP is the ionization potential of $M^{(z-1)+}$, z is the charge of the metal ion, and r is the cation radius [8,27,28]. In sharp contrast to the case of free azide solvated in various solvents, the blue frequency shift upon ion pair formation is not reflected in the VER dynamics. For the free azide ion in solution, including in reverse micelles [10,11], the magnitude of the spectral shift correlates with the VER rate. A larger blue shift, such as the 62 cm^{-1} shift in water compared to the gas phase frequency, reflects a strong solute–solvent interaction. The latter is also evident in the fast VER ($T_1 = 0.8$ ps for water). In contrast, the smaller solvent shift (13 cm^{-1}) in DMSO is associated with a VER rate that is at least 10 times slower. The spectral shift in MgN_3^+ is similar to that of free azide in aqueous solution, but the VER is about the same as free azide in DMSO. Clearly the mechanisms for the solvent shift and VER are not the same or there are some other counteracting factors for the ion pairs.

VER studies of azide ion pairs provide a way to investigate the possible role of IVR in vibrational relaxation. As noted above, ab initio calculations of azide in water by Morita and Kato [19] indicated comparable rates, i.e., significant contributions, from both direct (transfer to solvent) and IVR pathways. There has been no direct evidence of this experimentally, such as measuring different excited state decay (k_1) and ground state recovery (k_0) rates. But, if the relaxation rate from the intermediate to ground state were very rapid, it would be difficult to experimentally resolve the difference between k_1 and k_0 and to discern that the mechanism involves IVR. Another observation that supports the idea that azide VER involves IVR is that the azide relaxes more rapidly than cyanide. (The T_1 times for cyanide are 30–128 ps for various isotopomers in D_2O and H_2O [32].) Since the latter is a diatomic and incapable of IVR, the faster VER rates for azide and other triatomic anions, cyanate and thiocyanate (T_1 is <30 ps for all), may be due to IVR. An alternative explanation for the relatively slower VER rate in cyanide is its weak transition moment. Associating a metal ion to azide to form ion pairs could increase the VER rate through IVR by increasing the number of internal vibrational modes. But our results provide no evidence to support this since the ion pair rates are not faster than those for the free ion. Also, the rotational reorientation times for the ion pairs are >4 times longer than for the free ion, which qualitatively agrees with the relative lengths of the molecules, i.e, their rotational constants. Furthermore, in free azide in DMSO, the VER rate is somewhat slower than the rotational reorientation, so that the solvent environment is orientationally averaged during the VER processes. The opposite is true for the ion pairs but the VER rates are very similar. This suggests that the VER mechanism is not very sensitive to orientational averaging or there are several processes or factors in the ion pairs that effectively cancel each other out, so that there is no net effect of the metal ion on the VER rate.

There are several ways to account for the observation that VER in the ion pairs is comparable if not slower, particularly for CaN_3^+, relative to the free anion. An obvious difference is that the metal ion reduces the ability of the bonded nitrogen to interact with the solvent, which would lower the overall solute–solvent interaction and the VER rate. Also, the effects in the ion pairs on the atomic charges and normal mode displacements offset one another. If a direct Coulomb mechanism were responsible for the VER process, the azide ion/ion pair–DMSO interaction might be dominated by charge-dipole coupling terms. In this case, a rough estimate of the relative VER rates might be estimated based on the sum of squares of the product of the solute atomic charges and normal coordinate displacements [3,4]. Our DFT results indicate that compared to the free anion, charge shifts in the ion pair ($MN_1N_2N_3$) from the terminal (N_3) to the bonded (N_1) nitrogen, whereas the atomic normal mode displacement is larger for the former and smaller for the latter. These charge and displacement effects offset one another in a manner that might explain the similarity of T_1 times observed experimentally for azide both free and in the ion pairs.

In summary, we have used ultrafast IR spectroscopy to determine VER and reorientational times for free azide and several ion pairs in DMSO. As demonstrated previously, the contact ion pair formation results in a blue shift of the azide v_3 frequency [8]. For free azide in DMSO the spectral shifts and VER rates are consistent with the trends measured previously for azide in other solvents [3,4,6]. Our results indicate that there is little effect on the T_1 time of azide in DMSO (11 ± 2 ps) as a result of ion pair formation with Na^+, Mg^{2+} and Ca^{2+} (for which the T_1 times are 15 ± 2 ps, 13 ± 1 ps, and 18 ± 2 ps, respectively). This suggests that different mechanisms and molecular properties dominate the spectral shifts and VER, and that for latter, the higher number of vibrational modes in the ion pairs does not seem to accelerate IVR. It is not surprising that the ion pair formation reduces the reorientation time. The presence of a metal cation reduces the free rotor time and the Coulombic interaction between the metal cation and DMSO solvent creates additional friction to reorientation. DFT calculations reproduce the observed spectral shifts and may account for the weak dependence on the associated metal atom due to counterbalancing effects on the charge and atomic normal mode displacements.

Acknowledgements

References

[1] M. Polak, M. Gruebele, R.J. Saykally, J. Am. Chem. Soc. 109 (1987) 2884.

[2] J.C. Owrutsky, Y.R. Kim, M. Li, M. Sarisky, R.M. Hochstrasser, Chem. Phys. Lett. 184 (1991) 368.

[3] M. Li, J.C. Owrutsky, M. Sarisky, J.P. Culver, A. Yodh, R.M. Hochstrasser, J. Chem. Phys. 98 (1993) 5499.

[4] J.C. Owrutsky, D. Raftery, R.M. Hochstrasser, Annu. Rev. Phys. Chem. 45 (1994) 519.

[5] P. Hamm, M. Lim, R.M. Hochstrasser, Phys. Rev. Lett. 81 (1998) 5326.

[6] P. Hamm, M. Lim, R.M. Hochstrasser, in: T. Elsaesser, J.G. Fujimoto, D.A. Wiersma, W. Zinth (Eds.), Ultrafast Phenomena XI, Springer, Berlin, 1998.

[7] M.C. Asplund, M. Lim, R.M. Hochstrasser, Chem. Phys. Lett. 323 (2000) 269.

[8] C. Le Borgne, B. Illien, M. Beignon, M. Chabanel, Phys. Chem. Chem. Phys. 1 (1999) 4701.

[9] Q. Zhong, D.A. Steinhurst, E.E. Carpenter, J.C. Owrutsky, Langmuir 18 (2002) 7401.

[10] Q. Zhong, A.P. Baronavski, J.C. Owrutsky, J. Chem. Phys. 118 (2003) 7074.

[11] Q. Zhong, A.P. Baronavski, J.C. Owrutsky, J. Chem. Phys. 119 (2003) 9171.

[12] M.H. Lim, P. Hamm, R.M. Hochstrasser, P. Natl. Acad. Sci. USA 95 (1998) 15315.

[13] M. Vamvouka, M. Leone, A. Cupane, V. Militello, M.E. Stroppolo, A. Desideri, Biochemistry 37 (1998) 4459.

[14] M. Vamvouka, W. Muller, B. Ludwig, C. Varotsis, J. Phys. Chem. B 103 (1999) 3030.

[15] C. Varotsis, M. Vamvouka, J. Phys. Chem. B 103 (1999) 3942.

[16] P. Botschwina, J. Chem. Phys. 85 (1986) 4591.

[17] M. Ferrario, M.L. Klein, I.R. McDonald, Chem. Phys. Lett. 213 (1993) 537.

[18] D.A. Yarne, M.E. Tuckerman, M.L. Klein, Chem. Phys. 258 (2000) 163.

[19] A. Morita, S. Kato, J. Chem. Phys. 109 (1998) 5511.

[20] R.M. Whitnell, K.R. Wilson, J.T. Hynes, J. Phys. Chem. 94 (1990) 8625.

[21] R.M. Whitnell, K.R. Wilson, J.T. Hynes, J. Chem. Phys. 96 (1992) 5354.

[22] R. Rey, J.T. Hynes, J. Chem. Phys. 108 (1998) 142.

[23] S. Okazaki, Adv. Chem. Phys. 118 (2001) 191.

[24] M. Bruehl, J.T. Hynes, Chem. Phys. 175 (1993) 205.

[25] S. Gnanakaran, R.M. Hochstrasser, J. Chem. Phys. 105 (1996) 3486.

[26] B.M. Ladanyi, R.M. Stratt, J. Chem. Phys. 111 (1996) 2008.

[27] N. Cartledge, J. Amer. Chem. Soc. 50 (1928) 2855.

[28] M.H. Brooker, M.A. Bredig, J. Chem. Phys. 58 (1973) 5319.

[29] C. Le Borgne, M. Chabanel, J. Mol. Liq. 73–4 (1997) 171.

[30] P.W. Schultz, G.E. Leroi, J.F. Harrison, Mol. Phys. 88 (1996) 217.

[31] E.J. Heilweil, F.E. Doany, R. Moore, R.M. Hochstrasser, J. Chem. Phys. 76 (1982) 5632.

[32] P. Hamm, M. Lim, R.M. Hochstrasser, J. Chem. Phys. 107 (1997) 10523.

[33] M.J. Frisch et al., GAUSSIAN 03, Revision A. 1, Gaussian Inc., Pittsburgh, PA, 2003.

[34] T. Veszpremi, T. Pasinszki, M. Feher, J. Am. Chem. Soc. 116 (1994) 6303.