



Nitro group asymmetric stretching mode lifetimes of molecules used in energetic materials

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Abstract

Picosecond infrared pump–probe measurements of the vibrational relaxation of the nitro (NO₂) functional group asymmetric stretch ($\sim 1580\text{ cm}^{-1}$) of several molecules used in energetic materials, TNAZ, RDX, HMX, and CL-20 (abbreviations defined in text), and nitromethane, are presented. In addition, a temperature-dependent study was performed between 50 and 298 K on TNAZ. All of the lifetimes fall in the range of 2–6 ps with the exception of nitromethane, which has a lifetime of 16 ps. The temperature dependence of TNAZ is flat and solvent independent, suggesting an intra-molecular relaxation pathway that does not involve low-frequency modes. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The NO₂ group is a common feature of many molecules used in energetic materials [1–3]. Energetic materials are utilized as propellants and explosives. Nitro groups are also found in many other types of organic molecules. They are used as directing groups and reactive intermediates in organic synthesis [4–6], and they are found in molecules with pharmacological applications [7].

The flow of vibrational energy in polyatomic molecules is involved in a wide variety of chemical processes. Vibrational energy flow, i.e., vibrational energy moving into and out of molecular vibrational

modes, can occur through intramolecular and intermolecular interactions among vibrational degrees of freedom [8–10]. For a solute in a solvent, a mode of the solute can be coupled to other internal modes, to vibrations of the solvent, and to the low-frequency (up to a few hundred cm^{-1}) continuum of solvent modes [8–11]. (The low-frequency continuum modes are referred to as phonons although the liquids discussed below are disordered.) An initially excited high-frequency vibration will relax with the excitation of a number of other lower-frequency ‘receiving’ modes to take up the energy. Unless there is accidental degeneracy in which a combination of the receiving modes equals the energy of the initially excited mode, one or more phonons will also be created or annihilated to conserve energy [8–11]. The receiving modes can be modes of the solute molecule or modes of the solvent [8–11]. The lifetime of the initially excited mode depends on the

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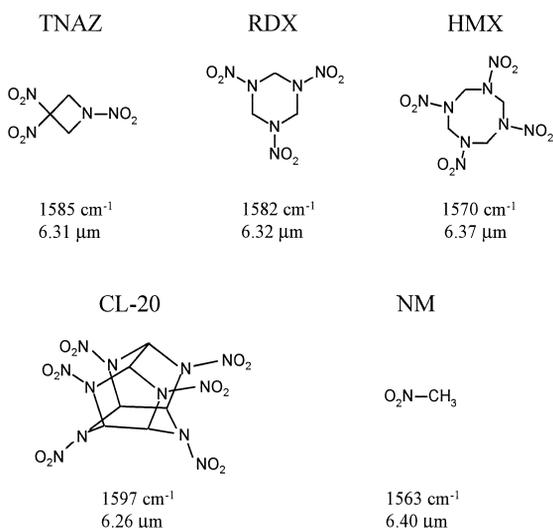


Fig. 1. The structures of the five molecules and the absorption energies and wavelengths of the nitro group asymmetric stretching modes studied with ps infrared pump–probe experiments. The definitions of the abbreviations of the names of the compounds are given in the text.

strength of its coupling to the receiving modes and the phonons and the density of states.

In the experiments presented below, the vibrational lifetime of the asymmetric stretching mode of nitro groups (~ 1580 cm⁻¹) of 1,3,3-trinitroazetidine (TNAZ), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), octahydro-1,3,4,7,8,10-hexanitro-5,2,6-(iminomethenimino)-1*H*-imidazo[4,5-*b*]pyrazine (CL-20), and nitromethane (NM), are measured in deuterated solvents. Fig. 1 shows the structures of the molecules studied and gives the absorption frequency and wavelength of the NO₂ asymmetric stretch of each. These molecules, with the exception of NM, are used in energetic materials. The large molecules have NO₂ lifetimes between 2 and 6 ps, while the much smaller NM has a lifetime of 16 ps. The temperature dependence of the NO₂ vibrational lifetime of TNAZ was measured between 298 and 50 K. The lifetime is independent of temperature over this range. Consideration of the temperature and solvent dependence of the vibrational relaxation suggests that the relaxation in TNAZ involves only relatively high-frequency internal modes of the

molecule. The results of the measurements are briefly discussed in the context of shock-induced [12] and crack-propagation-induced [13] multi-phonon vibrational up-pumping that can lead to chemical reaction and detonation of energetic materials.

2. Experimental procedures

Infrared ps pump–probe experiments to measure the vibrational lifetimes were conducted using tunable mid-infrared pulses from the Stanford Free Electron Laser (FEL). The experimental setup has been described in detail previously [14]. The IR pulses had an energy of ~ 0.5 μJ and are nearly transform-limited Gaussians, 1.2 ps in duration. Both the autocorrelation of the IR pulse and the spectrum were monitored continuously during the experiments. The spot size was ~ 100 μm. Pump and probe pulse energies were ~ 300 and ~ 20 nJ, respectively.

Except for NM, the samples were prepared using small quantities (~ 20 mg) of the powdered crystalline form of each material. The powder was dissolved in ethanol-*d*, 99.5%, or acetone-*d*₆, 99.5%. The solvents were purchased from Aldrich and used without further purification. NM, which is a liquid at room temperature, was directly dissolved in the solvent. Deuterated solvents were used because they are more transparent at the NO₂ group absorption frequency. The sample concentrations are given in Table 1. These concentrations are sufficiently low to avoid solute–solute interactions.

The samples were placed a CaF₂ cell with a path length of 200 μm. The temperature study employed a helium flow cryostat. Room-temperature and tem-

Table 1
Nitro group asymmetric stretching mode lifetimes for several molecules at room temperature

Molecule	Solvent	Concentration (M)	Lifetime (ps)
NM	d-acetone	very dilute	15.9 ± 0.5
TNAZ	d-ethanol	0.1	2.4 ± 0.4
TNAZ	d-acetone	0.03	3.0 ± 0.5
RDX	d-acetone	0.05	6.2 ± 0.4
HMX	d-acetone	0.02	4 ± 1
CL-20	d-acetone	0.01	2 ± 1

perature-dependent IR absorption spectra were taken using an FT-IR spectrometer with 0.2 cm^{-1} resolution. For the temperature-dependent study, the laser wavelength was tuned to the peak of the absorption at each temperature.

3. Results

Fig. 2 displays data taken on the smallest of the molecules studied, NM in acetone- d_6 at room temperature (298 K). The decay was taken with the pump and probe beams having parallel polarization, which allows rotational diffusion and vibrational relaxation to be observed. The fast component is the rotational diffusion of the molecule as a whole, while the longer component is the vibrational lifetime. The bi-exponential decay has the form

$$S(t) = S(0)e^{-t/T_1}(1 + 0.8e^{-t/\tau_r}), \quad (1)$$

where T_1 is the vibrational lifetime, and τ_r is the decay time for the orientational correlation function. The data were fit by convolving a bi-exponential decay with the Gaussian instrument response function. The fast-decay component gave $\tau_r = 1 \text{ ps}$, which

is in accord with the Debye–Stokes–Einstein (DSE) equation,

$$\tau_r = \frac{V\eta}{k_B T}. \quad (2)$$

η is the viscosity of acetone at room temperature, k_B is Boltzmann's constant, and V is the NM volume, which was determined using a space filling model. The long-decay component gave $T_1 = 15.8 \text{ ps}$, the vibrational lifetime at room temperature. The lifetimes reported in Table 1 are the average of the results of fitting a number of data sets for each compound. The NM lifetime is consistent with recent measurements in neat NM (see below) [15].

For the other molecules, calculations using the DSE equation showed that the rotational relaxation times are too long to contribute to the signal. This was tested by comparing the decay of TNAZ in d-ethanol with the probe polarization at the magic angle to remove the orientational relaxation component to the decay with the probe polarization parallel. The lifetime results were the same. However, the signal-to-noise ratio was better for parallel probing, so it was used for the experiments. (With parallel probing, there is a very fast component of the decay,

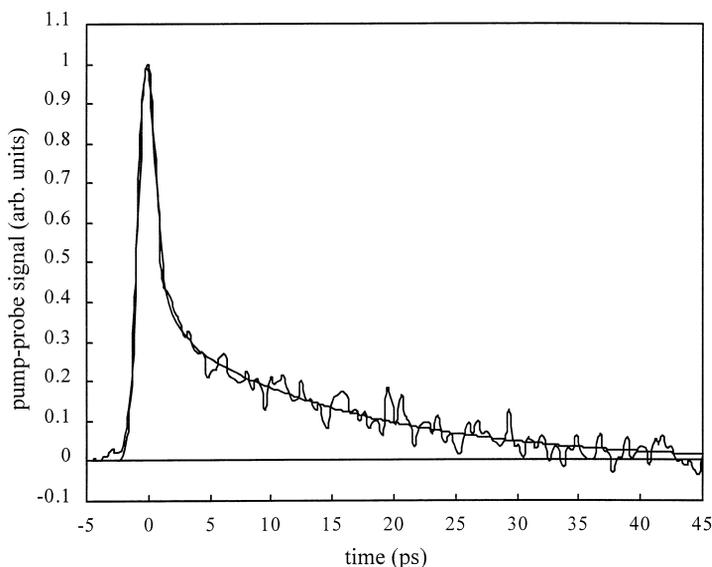


Fig. 2. ps infrared pump–probe data taken on nitro group asymmetric stretching mode of nitromethane in d-acetone at 298 K. The fast component is due to rotational diffusion of the molecule (1 ps), and the slow component is the vibrational lifetime (16 ps). The line through the data is a fit to a bi-exponential decay (see text).

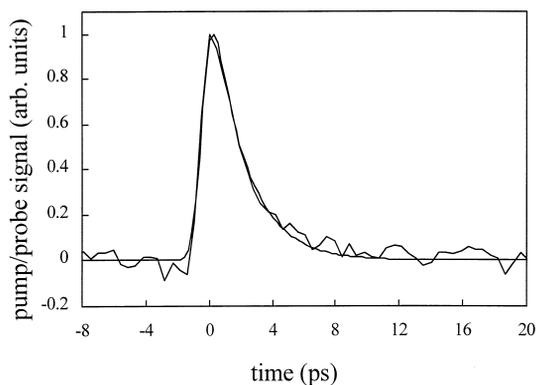


Fig. 3. ps infrared pump-probe data taken on nitro group asymmetric stretching mode of TNAZ in d-ethanol at 250 K. The solid line through the data is a single-exponential fit (2.6 ps).

< 500 fs, which was not measurable with the pulse durations used. This may be caused by wobbling of the NO_2 groups.) The results of the lifetime measurement on all samples at room temperature are given in Table 1. The signal-to-noise ratios for HMX and CL-20 were poor, giving rise to the large error bars in Table 1.

A temperature-dependent study of the vibrational lifetime for TNAZ in ethanol-d was performed between 298 and 50 K. Fig. 3 shows a decay for TNAZ

in ethanol-d at 250 K. The lifetime is 2.6 ps. The fit is a single exponential convolved with the instrument response. Fig. 4 displays the temperature dependence. Each point is the average of a number of decay curves. The data show that, within experimental error, the lifetime has no temperature dependence. The glass transition temperature, T_g , is 110 K. The lifetime does not change as the solvent passes from the liquid to the glassy state.

4. Discussion

As can be seen from Table 1, all of the lifetimes are in the range 2–6 ps except for NM, which has a lifetime of 16 ps. NM is substantially smaller than the other molecules and has many fewer vibrational modes. NM has 15 normal modes, while the next smallest molecule, TNAZ has 45. Thus, NM has many fewer internal pathways that can contribute to relaxation. Clearly, the number of modes is not the sole determining factor in the relaxation of the nitro group asymmetric stretch. RDX has 57 normal modes but has a lifetime which is ~ 2.5 times longer than TNAZ. The fact that TNAZ, which is the smallest of the molecules used in energetic materials, has one of the fastest lifetimes shows that a complex interplay between anharmonic interactions and den-

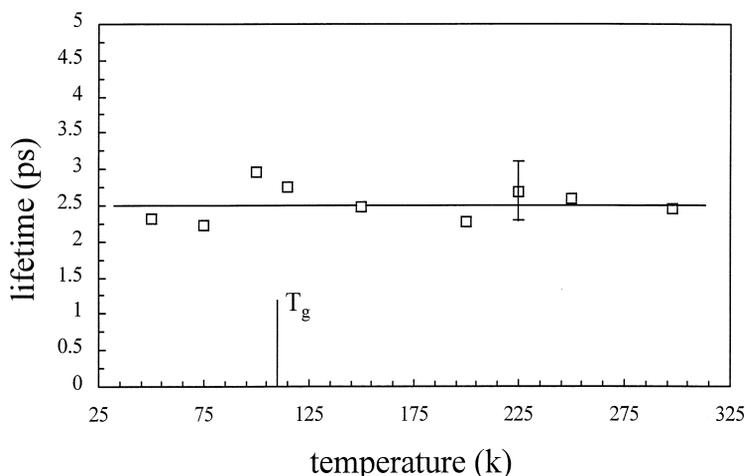


Fig. 4. Temperature-dependent ps infrared pump-probe data taken on nitro group asymmetric stretching mode of TNAZ in ethanol-d between 298 and 50 K. Within experimental error, the lifetime is temperature independent. T_g marks the ethanol glass transition temperature. A representative error bar is shown.

sity of states determines the relaxation rate. It is interesting to note that TNAZ and CL-20, which exhibit the fastest lifetimes, have highly strained structures. The TNAZ four-member ring has a great deal of strain, and CL-20 has steric strain. The strain may contribute to increased anharmonic coupling among modes.

For TNAZ, the lack of temperature dependence and the lack of a solvent dependence (see Table 1), within experimental error, strongly indicates that no low-frequency modes are involved in the NO₂ asymmetric stretch relaxation and that the relaxation pathways use internal modes only; no solvent vibrations or phonons are excited or annihilated. The evidence supporting internal relaxation pathways involving high-frequency modes is obtained from the following arguments.

The rate of vibrational relaxation, $K = 1/T_1$, of the initially excited mode can be expressed in terms of Fermi's Golden Rule [8–10],

$$K = \frac{2\pi}{\hbar} \sum_{r, r'} \rho_{r, r'} |\langle \sigma', r' | V | \sigma, r \rangle|^2. \quad (3)$$

where σ and σ' denote the initial and final state of the initially excited vibration, respectively, and r and r' refer to the receiving modes. The ket $|\sigma, r\rangle$ is the initial state, described by thermal occupation numbers of the various modes of the system, in addition to unit occupation of the state initially excited by the IR pump. The bra $\langle \sigma', r'|$ is the final state after relaxation with the initially excited state having occupation number 0 and two or more other states having increased occupation numbers. V is the anharmonic potential that couples the initially excited vibration and the receiving modes. The receiving modes can include internal vibrations, solvent vibrations, and phonons [8–10]. The low-frequency solvent continuum can be described in terms of instantaneous normal modes (INMs) [16–18]. ρ is the density of states of the receiving modes for the relaxation step. V in Eq. (3) is written as a harmonic term and a sum of anharmonic terms, $V^{(i)}$ [10]. The terms with $i \geq 3$, govern relaxation processes involving the coupling of the initially excited mode to two or more other modes, i.e., relaxation of the energy into a combination of two or more modes.

Consider an example in which the initially excited NO₂ relaxes into two lower energy vibrations, which almost equal the initial energy, and a mode of the continuum to conserve energy. This relaxation path is a 4th-order process. The initially excited mode is annihilated and two vibrations and a phonon are created. The matrix element can be written as a magnitude times a product of raising and lowering operators [10]. An annihilation operator brings out a factor of \sqrt{n} , and a creation operator brings out a factor of $\sqrt{n+1}$. When the matrix element is squared, these become n and $n+1$, respectively. The rate constant for this 4th-order process is then

$$K = \frac{2\pi}{\hbar} \rho |\langle V^{(4)} \rangle|^2 n_1 (n_A + 1) (n_B + 1) (n_{\text{ph}} + 1), \quad (5)$$

where $|\langle V^{(4)} \rangle|^2$ is the square of the magnitude of the 4th-order matrix element, n_1 is the occupation number of the initially excited mode, n_A , n_B , and n_{ph} respectively are the occupation numbers of the receiving modes, labeled A and B, and of the phonon with energy E_{ph} , such that $E_A + E_B + E_{\text{ph}} = E_1$. $n_1 = 1$, since this is the mode that is excited by the IR pulse. If modes A and B are both of sufficiently high energy such that $E_A, E_B \gg k_B T$, then, n_A and n_B are both $\ll 1$, and the first and second terms in parentheses in Eq. (5) equal 1. Usually $E_{\text{ph}} \leq \sim 200 \text{ cm}^{-1}$, so n_{ph} is significant. Its temperature dependence is given by

$$n_{\text{ph}} = \frac{1}{e^{E_{\text{ph}}/k_B T} - 1}. \quad (6)$$

If $E_{\text{ph}} < k_B T$, then $n_{\text{ph}} \cong k_B T/E_{\text{ph}}$. If only one phonon is involved in the relaxation process, putting n_{ph} into Eq. (5) gives the minimum temperature dependence that can occur. If more than one phonon is involved, the temperature dependence will be steeper. If a phonon is not involved because $E_A + E_B = E_1$, and if, for example, E_B is small (comparable to $k_B T$), then there will still be a temperature dependence, but E_B is used in Eq. (6) instead of E_{ph} .

From the above considerations, given the substantial temperature range covered in the experiments it is clear that a significant temperature dependence would be observed if either a phonon or a low-

frequency vibration were involved in the vibrational relaxation. Taking into account the size of the error bars in Fig. 4, any mode involved in the relaxation must have $E > 400 \text{ cm}^{-1}$. Modes of the hydrogen bonding network of ethanol-d can have energies $> 400 \text{ cm}^{-1}$, but the considerations discussed below would seem to rule these out as well.

The experiments also indicate that intermolecular modes, solvent vibrations or high-frequency phonons, are not involved in the relaxation. In addition to the explicit temperature dependence contained in the occupation numbers, vibrational relaxation can also be influenced by changes in density [11,19,20]. When the temperature of the sample is lowered at constant pressure, the density of the sample increases. In Eq. (3) both the magnitude of the matrix element and the density of states will change with density. Changes in the solvent density will change the region of the intermolecular potential that is sampled, giving rise to a change in the intermolecular contribution to the vibrational lifetime. As the density is increased (temperature is lowered), in general, vibrational relaxation will become faster because the strength of the intermolecular interactions increase [11,20]. Also, the density of states will increase as the density increases. It is possible that, by coincidence, as the temperature is lowered, an increase in the vibrational relaxation rate with increasing density is exactly cancelled by a decrease caused by reduced occupation numbers of low-frequency modes. However, within experimental error, the vibrational lifetime of TNAZ in d-ethanol and d-acetone are the same (see Table 1). These two solvents have vastly different phonon structures as well as different vibrational mode frequencies in the range below the NO_2 frequency, $\sim 1580 \text{ cm}^{-1}$. The lack of a solvent dependence supports the proposition that neither solvent vibrations nor phonons are involved in the relaxation. An additional piece of information is provided by recent experiments on NM [15]. The vibrational lifetime of the NO_2 asymmetric stretch of neat NM was measured to be 16 ps, and was found to remain constant when significant amounts of CCl_4 were added. Table 1 gives the same value for NM in d-acetone, also suggesting that the NO_2 relaxation in NM does not involve intermolecular modes. Therefore the combined experimental evidence of the lack of a temperature dependence and the lack of a

solvent dependence strongly suggests that the vibrational relaxation in TNAZ occurs through a pathway involving a combination of high-frequency ($> 400 \text{ cm}^{-1}$) internal modes. It is likely that the relaxation in the other molecules occurs in a similar manner.

The four molecules used in energetic materials, TNAZ, RDX, HMX, and CL-20, have NO_2 asymmetric stretching mode lifetimes between ~ 2 and ~ 6 ps. In energetic materials, shock-initiated molecular reactions occur through the transfer of mechanical energy from a shock front to internal molecular vibrational states. A model has been developed that describes the flow of energy into the internal vibrational states of a molecule [12]. A shock wave produces a bath of highly excited phonons, which flow into the lowest vibrational modes of the molecules that make up a crystal. Continued absorption of phonons leads to higher and higher levels of vibrational excitation, heating the molecules to temperatures at which chemical bonds break. In energetic materials used in explosives, strong shocks lead to the initiation of substantial chemistry and detonation.

In detailed modeling of shock-induced multi-phonon up-pumping, it was assumed that the rate-limiting step was the excitation of low-frequency modes (doorway modes) by phonons [12]. Once energy enters the system of internal vibrational degrees of freedom, the model states that equilibration among internal modes is rapid compared to the excitation of doorway modes. Using realistic values of a wide variety of physical parameters, the rate of shock-induced up-pumping was calculated to be tens of ps [12]. These results have been supported by subsequent experiments [21,22] and simulations [23–25]. The measurements reported here bolster the assumption of rapid internal equilibration since the time scale for equilibration with the NO_2 asymmetric stretching mode is ps, substantially faster than the tens of ps required for flow of energy into the molecule. Model calculations on naphthalene also support the assumption of rapid equilibration [26], but these are the first supporting measurements on molecules actually used in energetic materials.

The assumption of rapid equilibration means that mode selective chemistry caused by multi-phonon up-pumping will not occur. If rapid equilibration takes place among all modes, the final internal

molecular temperature resulting from multi-phonon up-pumping is

$$T_{\text{vib}}^{\text{eq}} = T_{\text{ph}}^{\text{m}} \frac{C_{\text{ph}}}{C_{\text{ph}} + C_{\text{vib}}}, \quad (7)$$

where T_{ph}^{m} is the maximum phonon quasi-temperature induced by the shock or a propagating crack [13], C_{ph} is the phonon heat capacity, C_{vib} is the vibrational heat capacity, and $T_{\text{vib}}^{\text{eq}}$ is the internal molecular vibrational temperature once the phonons and the vibrations have reached equilibrium. C_{vib} is

$$C_{\text{vib}} = k_{\text{B}} \sum_{i=1}^N \frac{\left(\frac{\phi_i}{T}\right)^2 \exp\left(\frac{\phi_i}{T}\right)}{\left[1 - \exp\left(\frac{\phi_i}{T}\right)\right]^2}, \quad (8)$$

where ϕ_i is the characteristic temperature of the i th molecular vibration. If the equilibration time of one or more modes is long compared to the time scale for the inflow of energy into the molecule, then, for some period of time, these modes essentially drop out of the sum in the heat capacity. Thus, there will be an interval during which the other modes overshoot the final equilibrium temperature. The overshoot could lead to reaction pathways that would not occur under thermal equilibrium conditions. The nitro group results show that they will contribute to the vibrational heat capacity at both short and long times.

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References

- [1] J.P. Agrawal, *Prog. Energy Combust. Sci.* 24 (1998) 1.
- [2] P.J. Haskins, *J. Phys. (Paris) IV* 5 (1995) 595.
- [3] G.A. Olah, R. Malhotra, S.C. Narang, in: H. Feuer (Ed.), *Nitration Methods and Mechanism*, VCH, New York, 1989.
- [4] T. Urbanski, in: H. Feuer (Ed.), *The Chemistry of the Nitro and Nitroso Groups Part 2*, Interscience, New York, 1970.
- [5] H.H. Baer, L. Urbas, in: H. Feuer (Ed.), *The Chemistry of the Nitro and Nitroso Groups Part 2*, Interscience, New York, 1970.
- [6] T.J. de Boer, I.P. Dirkx, *The Chemistry of the Nitro and Nitroso Groups Part 1*, Interscience, New York, 1969.
- [7] J. Venulet, R.L. Van Etten, in: H. Feuer (Ed.), *The Chemistry of the Nitro and Nitroso Groups Part 2*, Interscience, New York.
- [8] D.W. Oxtoby, *Adv. Chem. Phys.* 47 (1981) 487.
- [9] D.W. Oxtoby, *Annu. Rev. Phys. Chem.* 32 (1981) 77.
- [10] V.M. Kenkre, A. Tokmakoff, M.D. Fayer, *J. Chem. Phys.* 101 (1994) 10618.
- [11] P. Moore, A. Tokmakoff, T. Keyes, M.D. Fayer, *J. Chem. Phys.* 103 (1995) 3325.
- [12] A. Tokmakoff, M.D. Fayer, D.D. Dlott, *J. Phys. Chem.* 97 (1993) 1901.
- [13] W. Holmes, R.S. Francis, M.D. Fayer, *J. Chem. Phys.* (1999, to be published).
- [14] K.D. Rector, M.D. Fayer, *J. Chem. Phys.* 108 (1998) 1794.
- [15] D.D. Dlott, private communication (to be published).
- [16] T. Keyes, *J. Phys. Chem.* 101 (1997) 2921.
- [17] B.C. Xu, R.M. Stratt, *J. Chem. Phys.* 92 (1990) 1923.
- [18] T.M. Wu, R.M. Loring, *J. Chem. Phys.* 97 (1992) 8568.
- [19] A. Tokmakoff, B. Sauter, M.D. Fayer, *J. Chem. Phys.* 100 (1994) 9035.
- [20] R.S. Urdahl, D.J. Myers, K.D. Rector, P.H. Davis, B.J. Cherayil, M.D. Fayer, *J. Chem. Phys.* 107 (1997) 3747.
- [21] X. Hong, S. Chen, D.D. Dlott, *J. Phys. Chem.* 99 (1995) 9102.
- [22] S. Chen, X. Hong, J.R. Hill, D.D. Dlott, *J. Phys. Chem.* 99 (1995) 4525.
- [23] C.M. Tarver, L.E. Fried, A.J. Ruggiero, D.F. Calef, 10th Int. Detonation Symp., Off. Naval Res., Boston, MA, 1993, ONR 33395-12.
- [24] L.E. Fried, C. Tarver, in: S.C. Schmidt, W.C. Tao (Eds.), *Shock Compression of Condensed Matter – 1995*, Am. Inst. Phys., New York, 1996, p.179.
- [25] C.M. Tarver, *J. Phys. Chem. A* 101 (1997) 4845.
- [26] J. Hill, D.D. Dlott, *J. Phys. Chem.* 96 (1988) 10000.