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Vibrational Energy Redistribution in Polyatomic Liquids: Ultrafast IR−Raman Spectroscopy of Acetonitrile

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Ultrafast anti-Stokes Raman scattering after intense mid-IR excitation is used to study vibrational energy relaxation (VER) and vibrational cooling (VC) in neat liquid acetonitrile. The mid-IR pulse (3000 cm^{-1}) excites a combination of C−H stretching fundamentals and C−H bending overtones, which are coupled by Fermi resonance. Vibrational excitation decays from the pumped C−H stretch in 5 ps. Almost no energy is transferred from C−H stretch to C≡N stretch (2253 cm^{-1}). The C≡N stretch behaves as a VER "blocking group" which keeps vibrational energy in the CH_3−C moiety. A 5 ps buildup, which mirrors the C−H stretch decay, is seen in the C−H bending modes (∼1500 cm^{-1}) at about one-half the C−H stretch energy, and in the lowest energy vibration at 379 cm^{-1}, a C−C≡N bend. By diluting the acetonitrile with CCl_4, it is shown that the buildup of population in the C−C≡N bend mirrors the buildup of excitation of the bath. Monitoring the C−C≡N bend allows us to track the instantaneous fraction of energy which has been transferred from acetonitrile vibrations to the bath. The 5 ps buildup of the C−C≡N bend to about one-half its final value shows C−H stretch decay populates the $v = 1$ C−H bending vibrations, rather than the $v = 2$ C−H bending overtones. The decay of daughter C−H bend excitations to C−C stretching vibrations (918 cm^{-1}) and the decay of the C−C stretching excitation are also observed. Combined with the C−C≡N bending data, a rather complete picture of VER and VC in acetonitrile is obtained. VC in acetonitrile takes about 300 ps. An interesting energy recurrence phenomenon is observed. A C−H bending excitation ($v = 2$) is initially excited by the laser. That excitation is transferred to C−H stretching vibrations, whose decay repopulates the same bending vibration ($v = 1$).

1. Introduction

In this work, ultrafast anti-Stokes Raman spectroscopy following vibrational excitation with an intense mid-infrared (IR) pump pulse[1] was used to investigate neat liquid acetonitrile at ambient temperature. The dynamical processes being studied are redistribution of energy among intramolecular vibrations (vibrational energy relaxation, hereafter VER) and loss of vibrational energy from the molecule (vibrational cooling, hereafter VC). VER of polyatomic molecules in polyatomic liquids and solutions plays an important role in a wide range of chemical phenomena.[2,3] However, VER is not well understood at present, due primarily to the lack of extensive experimental measurements and the difficulties of accurately calculating VER rates and pathways.

VER of polyatomic molecules is fundamentally different from VER of diatomic molecules (diatomic molecule VER in solution has been recently reviewed[6−8]), because there are *several vibrational modes on the same molecule*. Transfer of vibrational energy from one intramolecular vibration to another, with the leftover energy being dissipated to the bath, is generally termed a "ladder process", where the vibrational states are the "rungs" of the ladder. The ladder process is so efficient, that polyatomic molecule VR virtually always occurs on the subnanosecond time scale, whereas in some diatomic systems vibrational excitations live for milliseconds (e.g., liquid O_2)[9] or seconds (e.g., liquid N_2).[10]

Acetonitrile, $CH_3C≡N$, may be regarded as a model system for polyatomic liquids and polar solvation. It has been the object of many theoretical and experimental studies of ultrafast liquid-state dynamics.[2,11,12] In addition, acetonitrile is arguably the simplest molecule to study vibrational dynamics of the unsaturated carbon−carbon linkage, CH_3−C−. Therefore this extensive investigation of VER in acetonitrile may prove helpful in understanding problems in solution-phase chemical reaction dynamics[3], such as the dynamics of C−H bond activation in alkanes.[13]

In our experiments, the pump pulse is tuned to the acetonitrile C−H stretching region. Two important questions addressed here are the mechanism of C−H stretch decay,[5] and the nature and time scales for the loss of all vibrational energy to the bath by VC.[14−16] A sizable literature exists that describes how C−H stretch decay in polyatomic liquids usually takes a few picoseconds,[5] and occurs by exciting daughter C−H bending vibrations.[5,17,18] Since C−H bends have about one-half the energy of the stretch, two quite different C−H stretch decay processes are possible, depending on whether the daughter excitation is the nearly isoenergetic $v = 2$ first overtone of the bend or the $v = 1$ bending fundamental. In the former case, a typical VER process might take the form

$$\nu_{CH} \rightarrow \delta_{CH}(v = 2) \rightarrow \nu_{CC}(v = 2) \rightarrow \delta_{CH}(v = 1) \rightarrow \cdots$$

where for clarity here and immediately below we do not explicitly list the phonons created in each step. Since the first (fast) step dissipates very little energy, all the VC would be

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expected to occur on a time scale somewhat longer than the rather short C−H stretching lifetime.

In the latter case, a typical VER process might take the form

$$\nu_{\mathrm{CH}} \rightarrow \delta_{\mathrm{CH}}(v = 1) \rightarrow \nu_{\mathrm{CC}}(v = 1) \rightarrow \cdots$$

and about one-half the vibrational energy would be dissipated into the bath in the first few picoseconds. The remaining energy would be expected to dissipate on a longer time scale. To distinguish between mechanisms such as these, an experimental method should be used which not only detects energy *leaving the pumped parent vibration*, but also detects energy *transferred to other, daughter vibrations*, as well as *energy buildup in the bath*.

The IR−Raman method directly measures the instantaneous population in all the Raman-active vibrations of a molecule during VER. In earlier works[1,5] using older laser technology (e.g., Nd:glass[1]), the technique was limited mainly to studying energy leaving higher frequency vibrations pumped by mid-IR laser pulses, such as C−H stretching transitions (~3000 cm^{-1}), OH stretching transitions (~3600 cm^{-1}), or metal carbonyl C≡O stretching transitions (~2000 cm^{-1}).[5] In a few cases it was possible to observe the first generation of high-frequency ($h\nu \gg kT$) daughter excitations, e.g., energy transfer from C−H stretch (~3000 cm^{-1}) to C≡C stretch (1968 cm^{-1}) of acetylene,[5,19] energy transfer from N−H stretch of pyrrole[20] (~3400 cm^{-1}) in benzene solution to ring stretching modes of pyrrole (~1400 cm^{-1}) or to the benzene solvent (~1000 cm^{-1}), energy transfer from C−H stretch to C−C stretching (~1400 cm^{-1}) of naphthalene,[21] and energy redistribution among C═O stretching vibrations (~2000 cm^{-1})[22] of W(CO)$_6$.

As energy leaves a higher energy vibration such as a C−H stretch and spreads out among successive generations of daughter vibrations, especially the lower energy ($h\nu \approx kT$) vibrations, it becomes increasingly difficult to detect. Detecting the anti-Stokes signal from energy arriving at the *lowest energy* molecular vibrations is especially problematic due to scattering from the background thermal population. However, the behavior of the lowest energy vibration may be the key evidence needed to understand VER and VC. Dlott and co-workers[16] were the first to observe vibrational energy flow in a polyatomic liquid, from C−H stretching vibrations all the way down to the lowest energy molecular vibrations (656 and 480 cm^{-1}), in nitromethane (CH$_3$NO$_2$), using a 300 Hz Nd:YLF laser system. However, the time resolution of ~50 ps was not good enough to resolve the faster processes. The same authors also studied *intermolecular* vibrational energy transfer between various alcohols and nitromethane.[23] Recently Graener et al. used a 50 Hz Nd:YLF system with 1.5 ps resolution to study VER in dichloromethane[24] (CH$_2$Cl$_2$) and chloroform[25] (CHCl$_3$) after C−H stretch excitation. The latter work[25] is especially notable for being the first where every one of the molecular vibrations was monitored during a VER process in a polyatomic molecule.

We have constructed a 1 kHz Ti:sapphire laser system for IR−Raman spectroscopy, which provides 0.8 ps apparatus time response.[26] Initial experiments with this system observed a vibrational cascade in liquid nitromethane.[26] Here we use that laser to investigate VER in acetonitrile after C−H stretch excitation. The time resolution and signal-to-noise ratio are sufficient to construct a rather complete picture of the VER processes.

2. Experimental Section

The kilohertz Ti:sapphire pumped, two-color optical parametric amplifier (OPA) was described elsewhere.[26] Unlike more conventional femtosecond OPAs with typical frequency bandwidths of 100−200 cm^{-1}, our system gives ~50 cm^{-1} spectral resolution which is needed to distinguish between different Raman transitions of a polyatomic molecule.[26] The experimental setup for acetonitrile measurements is diagrammed in Figure 1. Pump pulses ($\lambda \approx 3000$ cm^{-1}, $\Delta\nu = 35$ cm^{-1}, $E_\mathrm{p} = 45$ μJ, $t_\mathrm{p} \sim 1.0$ ps) tuned to C−H stretching transitions are focused to a diameter of ~200 μm in a flowing jet of spectroscopic grade acetonitrile 150 μm thick, or a mixture of acetonitrile and CCl$_4$ (50:50 by volume). Probe pulses ($\lambda = 532$ nm, $\Delta\nu = 50$ cm^{-1}, $E_\mathrm{p} = 25$ μJ, $t_\mathrm{p} \sim 0.8$ ps) are focused to a slightly smaller diameter in the jet. Backscattered Raman light is collected with *f*/1.2 optics, transmitted through a pair of holographic Raman notch filters (Kaiser Optical) and sharp-cut short pass filters (Omega Optical) to remove Raleigh scattering, and directed into a monochromator/spectrograph equipped with a fast photomultiplier (PMT) and an optical multichannel analyzer (OMA). Raman spectra are obtained with the OMA. Anti-Stokes Raman transients are obtained by scanning the optical delay line while a computer acquires the signal from a PMT and a boxcar integrator. The instantaneous anti-Stokes Raman intensity is proportional to the occupation number of the vibrational transition observed.[1]

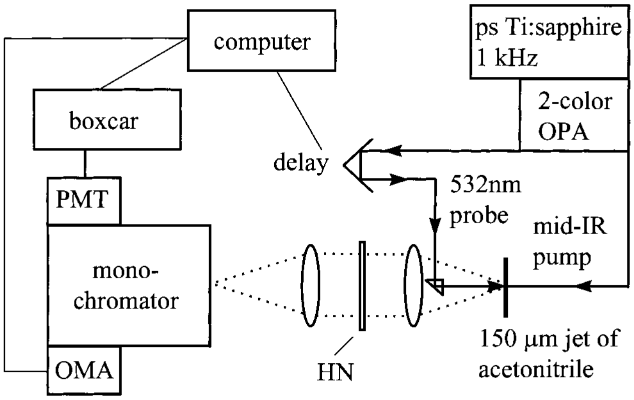

Figure 1. Schematic of experimental apparatus. OPA, optical parametric amplifier; HN, holographic notch filter; OMA, optical multichannel amplifier; PMT, photomultiplier tube.

About 2% of the acetonitrile molecules are excited by the laser, which after VC produces a bulk temperature jump of $\Delta T \sim 7$ (±2) K. This ΔT represents an average over the pumped sample volume.[27,28] The value of ΔT was determined in two consistent ways, either from the anti-Stokes transients, as described previously,[16,27,28] or from knowing the incident fluence, absorption coefficient, and heat capacity.[28]

A method has been proposed[25] to determine the relative fraction Φ of vibrational quanta which are transferred from a higher frequency vibration denoted Ω (e.g., a C−H stretch) to a lower energy vibration denoted ω, using the relative amplitudes of the anti-Stokes transients. The method, however, becomes problematic when several nearby Raman transitions cannot be spectroscopically resolved, which happens in acetonitrile with the C−H stretches and C−H bends. For energy transfer among other acetonitrile vibrations the method works well, given the relative integrated Raman cross-sections σ_R. These cross-sections, measured for acetonitrile with a Raman spectrometer, are listed in Table 1. In some cases, the buildup time of ω will be comparable to its decay time. Allowance must then be made for excitations which decay during the buildup time, which is done with a phenomenological energy transfer model described in ref 16. Φ represents a *quantum transfer efficiency* not an energy transfer efficiency, and it is

TABLE 1: Vibrations of Acetonitrile (C_{3v})

mode	symmetry	type	frequency (cm^{-1})	lifetime (ps)	integrated Raman cross-section σ_r (relative to ν_1)
ν_1	a_1	C−H stretch ν_{CH}	2943	5(±0.4)	1.0
ν_2	a_1	C≡N stretch ν_{CN}	2253	80(±20)	0.47
ν_3	a_1	C−H bend δ_{CH}	1372	30(±7)	0.1
ν_4	a_1	C−C stretch ν_{CC}	917	45(±10)	0.19
ν_5	e	C−H stretch ν_{CH}	3003	5(±0.4)	~0.2
ν_6	e	C−H bend δ_{CH}	1440	30(±7)	0.44
ν_7	e	CH_3 rocking ρ_{CH}	1040	100?	~0
ν_8	e	C−C≡N bending δ_{CCN}	379	<5	0.26

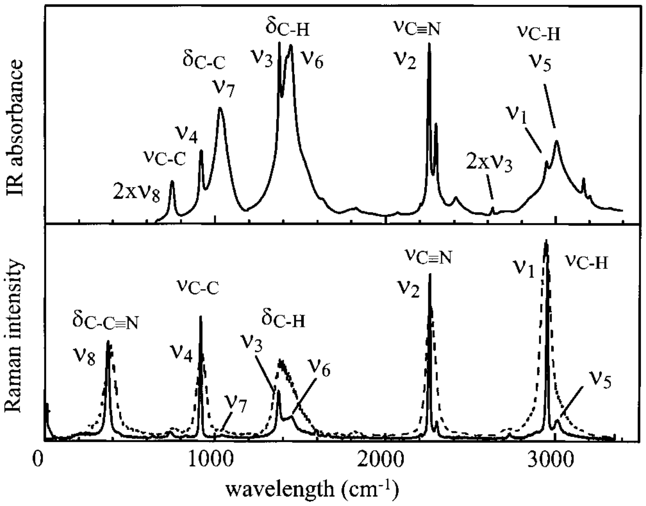

Figure 2. IR (top) and Stokes Raman (bottom) spectra of neat acetonitrile at ambient temperature. The dashed spectrum is taken using the ultrafast laser apparatus, which has ~50 cm^{-1} resolution.

conceivable that Φ may be *much greater* than unity. For a given Ω and ω with energies $h\Omega$ and $h\omega$, at zero temperature Φ must lie in the range $0 \leq \Phi \leq \Omega/\omega$. At finite temperature, Φ could even be a bit greater than Ω/ω, perhaps as large as $(h\Omega + 2kT)/h\omega$.

3. Vibrations of Acetonitrile

Now we review the vibrational spectroscopy and normal mode assignment of acetonitrile. Acetonitrile belongs to the C_{3v} point group.[29] All twelve normal modes are IR and Raman active. There are four nondegenerate vibrations of a_1-symmetry and four doubly degenerate vibrations of e-symmetry. The four a_1 vibrations are ν_1, a symmetric C−H stretch; ν_2, a C≡N stretch; ν_3, a symmetric C−H bend; and ν_4, a C−C stretch. The four doubly degenerate e-symmetry vibrations are ν_5, a C−H stretch; ν_6, a C−H bend; ν_7, a methyl rock (C−C bend); and ν_8, a C−C≡N bending vibration.[29] These assignments and vibrational frequencies are listed in Table 1.

An IR and Stokes Raman spectrum of acetonitrile taken with conventional Raman and FTIR spectrometers are shown in Figure 2. One feature is worth mentioning about the Raman spectrum: in the C−H bending region (1350−1550 cm^{-1}) there is a broader transition at higher energy assigned to the ν_6 (e-symmetry) C−H bend and a sharper transition at lower energy assigned to the ν_3 (a_1-symmetry) C−H bend. The ν_6 transition is broadened by a Fermi resonance between $2\nu_6$ and the ν_5 C−H stretch.[29] There is no Fermi resonance between $2\nu_3$ and ν_1, because $2\nu_3$ is about 200 cm^{-1} below ν_1. The $2\nu_3$ transition can be seen in Figure 2 at about 2730 cm^{-1}. Our 35 cm^{-1} wide mid-IR pulses centered at ~3000 cm^{-1} pump ν_1 and ν_5 and $2\nu_6$ as well (vide infra).

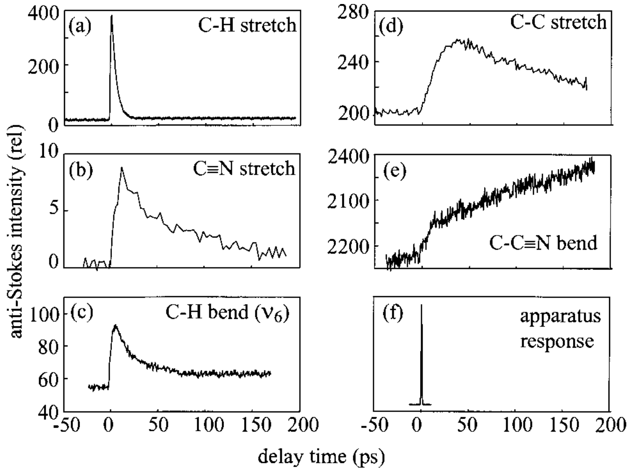

Figure 3. Anti-Stokes transients from acetonitrile with 3000 cm^{-1} pumping in the C−H stretch region. The apparatus response (Figure 3f) is obtained using coherent surface sum-frequency generation. The C−H bending data in Figure 3c refers to the e-symmetry ν_6 mode. The a_1-symmetry ν_3 data are similar, but the rising edge differs (see Figure 4a).

The frequency resolution of the Raman probe pulses plus spectrometer is ~50 cm^{-1}. To illustrate the spectral resolution obtained in ultrafast experiments,[26] a Stokes Raman spectrum taken with the ultrafast system (dashed curve) is shown in Figure 2. With the ultrafast system, the ν_1, ν_2, ν_4, and ν_8 transitions are well resolved. The ν_3 and ν_6 C−H bending transitions are not well resolved. A line shape fitting routine (Microcal Origin) and the known spectral resolution of our apparatus was used to estimate the relative contributions from ν_6 and ν_3 which would be observed in anti-Stokes transients at different monitor wavelengths. To see ν_6, we tune to 1450 cm^{-1}, where the anti-Stokes signal is almost entirely due to ν_6. There is no region of the Raman spectrum where the signal is primarily due to ν_3. The optimal Raman shift to observe ν_3 was found to be 1372 cm^{-1}, where the signal is two parts ν_6 and one part ν_3. An approximation to the ν_3 data may thus be computed by subtracting the ν_6 contribution from the 1372 cm^{-1} transient. We cannot see an anti-Stokes Raman transient from ν_7 because its Raman cross-section is too small.

4. Results

Time-resolved anti-Stokes transients after mid-IR pumping at 3000 cm^{-1} are shown in Figures 3−6. Figure 3 compares anti-Stokes transients for five probed transitions. In each part of Figure 3, the ordinate indicates the relative anti-Stokes signal intensity. The apparatus response in Figure 3f, which has a nearly Gaussian envelope with 0.8 ps fwhm, was obtained using coherent surface sum-frequency generation, as described in ref 26.

The C−H stretch data in Figure 3a give the time dependence of ν_1 with a small contribution from ν_5. The population of ν_1

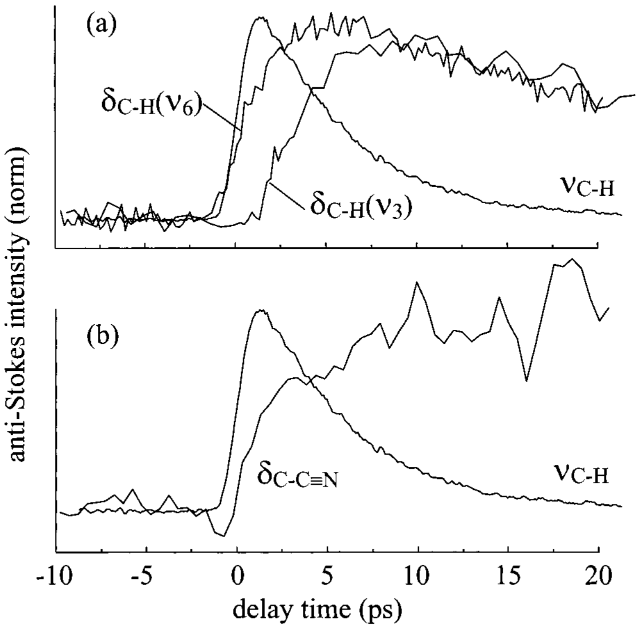

Figure 4. (a) Anti-Stokes transients from C−H stretching (ν_1) and C−H bending vibrations ν_3 and ν_6. The ν_6 data are obtained with the detection band centered at 1450 cm^{-1}. The ν_3 data are obtained with the detection band centered at 1372 cm^{-1} and subtraction of the ν_6 contribution. At first the ν_6 data track the instantaneous rise of the C−H stretch excitation, which indicates direct laser pumping of 2ν_6. Then the rise of ν_6 slows down. This slower rise of ν_6 occurs on the time scale of C−H stretch decay. After ∼10 ps, the decays of both ν_3 and ν_6 C−H bending vibrations are identical. (b) Comparison of C−H stretch data with ν_8 low-frequency C−C≡N bending vibration data show the initial fast jump in ν_8 population occurs on the same time scale as the decay of C−H stretch excitation.

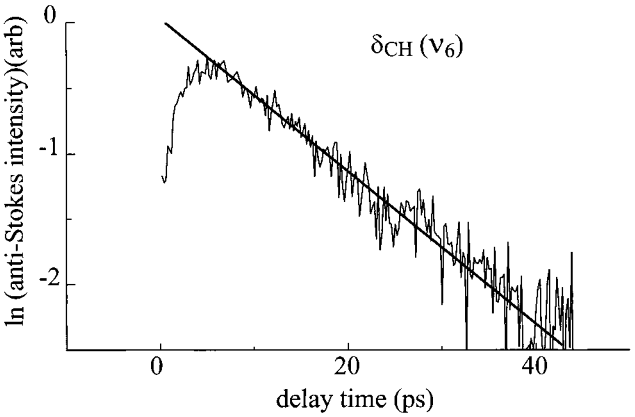

Figure 5. Semilog plot of ν_6 C−H bending population shows a decay which is a single exponential in time.

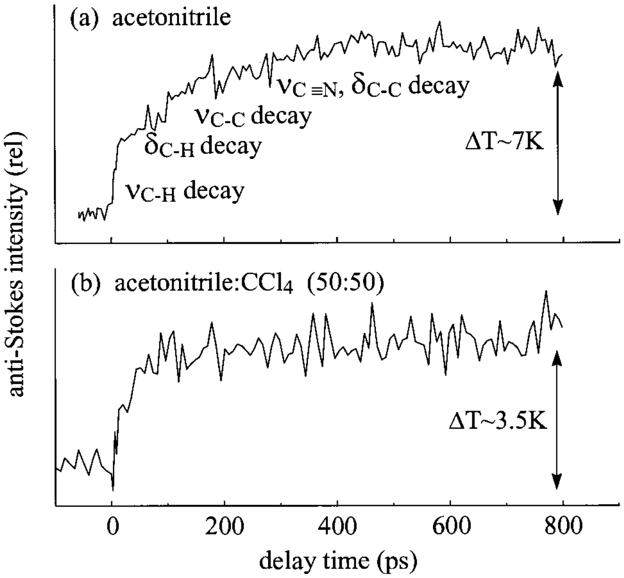

Figure 6. (a) Rise of excitation of the acetonitrile low-frequency bending vibration ν_8, which mirrors the rise of excitation in the bath. The fast initial jump is associated with C−H stretch decay. The slower rise is due to up-pumping by phonons produced by subsequent VER processes such as C−H bend decay, C−C stretch decay, etc., as indicated. At equilibrium there is a 7 K temperature jump. (b) Rise of ν_8 excitation (solid line) in a solution of acetonitrile diluted with CCl$_4$ (50:50). The temperature jump decreases by a factor of ∼2 in solution. The amplitude of the fast jump decreases by a factor of ∼2 as well, which can happen only if ν_8 has a lifetime much shorter than the 5 ps time scale for C−H stretch decay, so that ν_8 remains in equilibrium with the bath at all times.

rises instantaneously (with the apparatus time response) and then decays exponentially with a lifetime of 5 ps.

The ν_2 C≡N stretch signal in Figure 3b has a quite small amplitude, showing the efficiency of energy transfer from ∼3000 cm^{-1} C−H stretch to C≡N stretch is quite small, $\Phi \approx 0.02$. The C≡N stretch data do not rise instantaneously. As best we can discern, the C≡N stretch rise time mirrors the 5 ps fall time of the C−H stretch. The C≡N stretch lifetime is quite long, ≈80 ps.

Figures 3c, 4a, and 5 show data for C−H bending vibrations. The data for ν_6 (observed at 1450 cm^{-1}) are shown in Figure 3c. The time dependence of ν_3 population in Figure 4a was computed as described above, by subtracting the ν_6 contribution from the 1372 cm^{-1} transient. The ν_6 rise seen in Figure 4a is interesting. The first half of the rise is instantaneous (i.e., it exactly tracks the rise of the C−H stretch pumped by the laser). Subsequently, the rise of ν_6 stops following the rise of C−H stretch excitation and becomes much slower (Figure 4a). The second half of the rise occurs on the 5 ps time scale of C−H stretch decay. In contrast, we cannot discern an instantaneous rise of ν_3 rise, which is admittedly noisy. The ν_3 rise occurs on the 5 ps time scale of C−H stretch decay. After about 5 ps, the decays of ν_3 and ν_6 become identical. Later we will need to show that C−H bending decay is a single exponential in time, which is seen from the semilog plot in Figure 5. Because ν_3 and ν_6 have different Raman cross-sections, and we cannot individually resolve their anti-Stokes transients, it is not possible to accurately determine the fraction Φ of C−H stretch population transferred to C−H bends on the basis of the C−H bending data alone. However, we will be able to estimate Φ using ν_8 data as discussed below.

The ν_4 C−C stretch rise time (Figure 3d) mirrors the ∼30 ps decay time of the C−H bend, and its fall time gives a lifetime of 45 ps. The quantum efficiency for transfer from C−H bend to C−C stretch was quite large, $\Phi \approx 0.7$.

The ν_8 bend is the lowest energy vibration. It has a large background thermal occupation number of ∼0.37 at ambient temperature, and the population increase produced by the mid-IR pulse is only ∼0.02, so the anti-Stokes transient is noisy. Figure 6a shows the anti-Stokes signal rises from its initial value to a final plateau representing the ∼7 K temperature jump. About one-half of the jump occurs in 5 ps, mirroring the 5 ps decay of the C−H stretch, as seen in Figure 3e. Subsequently, there is a gradual nonexponential rise, as seen in Figure 6a. The signal reaches ∼75% of its final value at ∼100 ps and ∼95% of its final value at ∼300 ps.

The ν_8 bending vibration was studied in a solution of acetonitrile diluted with CCl_4 (50:50 volume percent). Both neat and diluted samples are optically thick with respect to the mid-IR pump pulses and optically thin with respect to the visible probe pulses. Thus in both samples, *the same number of C−H stretch excitations are produced and probed*, but in the diluted sample, *the bulk heating of the solution is reduced by approximately a factor of 2,* to $\Delta T \approx 3.5$ K. Dilution at this level is observed to have no effect on the C−H stretch decay lifetime. The ν_8 data are noisier with dilution, but Figure 6b shows that dilution has no appreciable effect on the *functional form* of the ν_8 anti-Stokes data. In other words, dilution reduces the amplitude of the fast jump as well as the amplitude of bulk heating. The principal concern in interpreting this dilution experiment is understanding the fast jump in ν_8 excitation (see Section 5.3.1.) and determining whether the lifetime of ν_8 is fast enough to maintain an equilibrium between the bath and ν_8 at all times. The CCl_4 has little effect on the ∼5 ps decay of the C−H stretching vibration, so we believe the mechanisms of C−H stretch decay are essentially unchanged in neat and diluted acetonitrile, but we do not rule out the possibility that CCl_4 (where the highest energy vibration[30] is at 790 cm^{-1}) might affect the decay of lower energy acetonitrile vibrations by intermolecular[4] vibrational energy transfer.

5. Discussion

If an isolated acetonitrile molecule were pumped by our mid-IR pulses, the molecule would not lose energy at all, except by extremely inefficient radiative processes. However, one might expect rapid dephasing (often termed IVR[31]) due to intramolecular redistribution among a manifold of isoenergetic states consisting primarily of three C−H stretches and the first overtone of the two e-symmetry C−H bends. All the VER processes seen here are a consequence of condensed phase interactions with a bath[4] consisting of a continuum of lower energy collective vibrations often termed instantaneous normal modes.[34−38] It is convenient simply to call these collective vibrations phonons. An excellent theoretical treatment of ultrafast VER of polyatomic molecules in polyatomic liquids or solutions is given by Kenkre et al.,[4] which we will follow in subsequent discussions.

In this section, we first summarize the relevant results. Then we present a brief overview of what theory leads one to expect VER in a polyatomic liquid, which is used to provide a framework for discussing the results.

5.1. Time Constants. Our measurements reveal several different time constants in the VER process initiated by mid-IR pumping.

1 ps Time Constant. Pumping by the mid-IR pulse produces a 1 ps rise of excitation. This time constant is seen in two places: in the rise of the pumped C−H stretch ν_1 and in the rise of the e-symmetry C−H bend ν_6 (Figure 4a). The pump pulse evidently directly pumps the first overtone $2\nu_6$, as well as the C−H stretch. With our present spectral resolution, excitation of the first overtone of ν_6 appears as excitation of the fundamental with twice the amplitude.[25]

5 ps Time Constant. The ν_1 C−H stretch decays on the 5 ps time scale. A 5 ps transient is observed in three other places: in the rise of the C≡N stretch, in the rise of C−H bending vibrations ν_3 and ν_6 (Figure 4a), and in the rise of the low-frequency bending vibration ν_8 (Figure 4b).

30 ps Time Constant. The decay of ν_3 and ν_6 C−H bending vibrations occurs with identical 30 ps time constants (Figure 4a). A 30 ps time constant is also observed in the rise of the C−C stretch ν_4 (Figure 3d).

45 ps Time Constant. The decay of the ν_4 C−C stretch occurs with a 45 ps time constant (Figure 3d).

80 ps Time Constant. The decay of the ν_2 C≡N stretch occurs with an 80 ps time constant.

∼100−150 ps Time Constant. The ν_8 bending vibration data in Figure 6a shows a gradual rise which extends out to almost 300 ps, suggesting the presence of an unseen VER process with this quite long time constant.

5.2. Mechanisms of Vibrational Energy Relaxation (VER). The acetonitrile vibrations and bath excitations interact via anharmonic coupling.[4] At the 3000 cm^{-1} energy of the C−H stretch, the total density of states is relatively large, so there are a vast number of energy-conserving pathways for C−H stretch decay as discussed in ref 4. For purposes of the present discussion, let us consider an illustrative example, one of the simplest possible VER processes: the zero temperature decay via cubic anharmonic coupling, of a higher energy vibration Ω with normal coordinate Q_Ω, by a ladder process. The decay of Ω excites a lower energy vibration ω with normal coordinate Q_ω and a bath excitation (phonon) ω_{ph} with normal coordinate q_{ph}. In this case, the lifetime T_1 of vibration Ω is given by[4,39]

$$(T_1)^{-1} = 36\pi^2 \sum_{\omega,\omega_{ph}} \langle V^{(3)}{}_{\Omega,\omega,\omega_{ph}} \rangle^2 \delta(\Omega - \omega - \omega_{ph}) \qquad (1)$$

where $\langle V^{(3)} \rangle$ is the matrix element of the cubic anharmonic Hamiltonian

$$V^{(3)} = \frac{1}{3!} \frac{\partial^3 V(\mathbf{Q})}{\partial Q_\Omega \partial Q_\omega \partial q_{\omega_{ph}}} \bigg|_{\mathbf{Q}} Q_\Omega Q_\omega q_{\omega_{ph}} \qquad (2)$$

and $V(\mathbf{Q})$ is the potential energy surface. Quartic and higher order interactions give similar zero temperature results, except that the vibration Ω decays by emitting three (quartic) or more lower energy excitations.[4]

Theory provides general guidelines for VER of polyatomic molecules, which are considered as a framework for discussing our results:

(1) Most VER processes involve at least one phonon,[4] otherwise energy conservation (represented by the δ-function in eq 1) is difficult or impossible. Equation 1 is derived in the zero temperature limit where only spontaneous phonon emission may occur. At finite temperature,[4,39] stimulated phonon emission and phonon absorption (up-conversion) are also possible for phonon energies $h\omega_{ph}$ on the order of kT.

(2) Phonons are ordinarily more anharmonic than molecular vibrations.[4,39] All things being equal, anharmonic coupling is greater if the derivative in eq 2 contains more phonon coordinates and fewer vibration coordinates.[4,39] For example, a cubic matrix element of the form $Q_\Omega q_{ph} q_{ph}$ ($\Omega \rightarrow 2\omega_{ph}$) is ordinarily larger than $Q_\Omega Q_\omega q_{ph}$ ($\Omega \rightarrow \omega + \omega_{ph}$).

(3) Lower order (i.e., cubic or quartic) processes are expected to dominate. For example, the multiphonon process $\Omega \rightarrow 10\omega_{ph}$ is thought to be less likely than the ladder process $\Omega \rightarrow \omega + \omega_{ph}$.[4]

(4) The coupling between Ω and a lower energy vibration ω is ordinarily greater for intramolecular VER than intermolecular VER.[4] Because of the stronger coupling, one usually expects intramolecular VER to dominate intermolecular VER. Experiments on a neat liquid do not tell whether the daughter vibrations are on the same or on adjacent molecules.[25] To further investigate intermolecular processes, experiments need to be

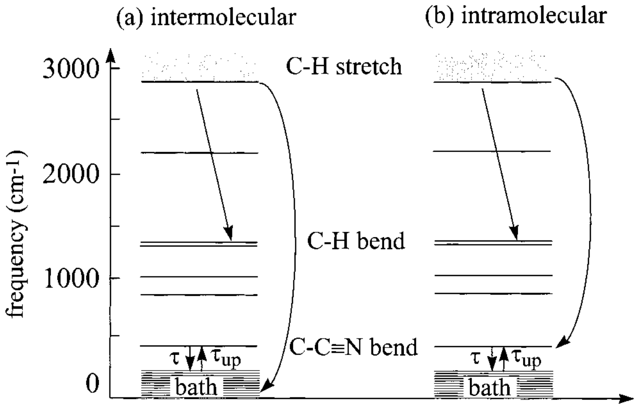

Figure 7. The ν_8 C−C≡N bend might be populated by C−H stretch decay in two ways. C−H stretch decay excites a C−H bend at about one-half its energy. (a) The rest of the energy appears as bath excitations (phonons) which up-pump ν_8 with time constant τ_{up} by an intermolecular process. (b) The rest of the energy directly excites ν_8 via an intramolecular process. When the ν_8 lifetime τ is less than the C−H stretch lifetime, ν_8 is in equilibrium with the bath at all times.

done on binary mixtures as in refs 20 and 23. Right now, we have only a little bit of data. We do know the decay rate for C−H stretching excitations is not affected by adding 50% CCl_4, suggesting the daughter vibrations of C−H stretch decay are on the same molecule.

(5) As proposed by Nitzan and Jortner,[42] one ordinarily expects three energy regimes for VER. *Regime I*: The lowest energy vibrations have short lifetimes because they are strongly coupled to the anharmonic bath by low-order anharmonic interactions (e.g., of the form $Q_\Omega q_{ph} q_{ph}$). *Regime II*: The intermediate energy vibrations have the longest lifetimes, because few lower energy vibrations ω are accessible by low-order coupling (e.g., of the form $Q_\Omega Q_\omega q_{ph}$), and coupling directly to the bath requires smaller, higher order matrix elements (e.g., of the form $Q_\Omega q_{ph} q_{ph} q_{ph} q_{ph}$). *Regime III*: High-energy vibrations have short lifetimes because even though the coupling may be high-order and quite weak, the density of states grows exponentially with increasing energy and inevitably becomes very large at high energies.

5.3. Dynamics of the Individual Vibrations. *5.3.1. C−C≡N Bend ν_8.* Understanding the C−C≡N bend ν_8 is the key to understanding VER in acetonitrile. Because this bend is the lowest energy vibration, it should be in Regime I and closely coupled to the bath. The lowest frequency vibration is often called a "doorway mode", since it serves as the doorway for vibrational energy leaving the molecule (VC) or entering the molecule from the bath (multiphonon up-pumping).[43,44]

During the acetonitrile VER process, energy is dissipated into the bath on times ranging from 5 ps (C−H stretch decay) to ~300 ps, and these time scales are all seen in the rise of ν_8 excitation (Figure 6a). If the lifetime τ of ν_8 were shorter than all these time scales, ν_8 would *always be in equilibrium with the bath during VER*, and the time-dependent buildup of population in ν_8 would *mirror the* buildup *of bath excitation*.

To demonstrate this is true, we have to consider two possible ways that (intermolecular and intramolecular) C−H stretch decay could populate ν_8, which are shown in Figure 7. We know that C−H stretch decay produces a daughter C−H bend excitation. The rest of the energy (~1500 cm^{-1}) might be transferred to ν_8 by an *intermolecular* process (Figure 7a) where bath excitations (phonons) are produced with a 5 ps time constant, and then the phonons excite ν_8 by up-pumping, e.g., $\nu_{CH} \rightarrow \delta_{CH} + (\text{phonons} \rightarrow \delta_{C-C\equiv N})$. Since the fast jump in ν_8 occurs with a 5 ps time constant, the up-pumping time constant τ_{up} must be less than 5 ps. Fast up-pumping implies a short ν_8 lifetime, since $\tau = \tau_{up} \exp(-h\nu/kT)$.

The rest of the energy of C−H stretch relaxation might instead be transferred directly to ν_8 via an *intramolecular* process, e.g., $\nu_{CH} \rightarrow \delta_{CH} + 4\delta_{C-C\equiv N}$ diagrammed in Figure 7b. If this mode of decay occurred, we can use the results of the dilution experiment to show that ν_8 must have a short lifetime. To show this, we need to consider the dilution experiment in more detail.

In neat acetonitrile (Figure 6a), ν_8 shows a fast jump which (in the case being considered) would be due to intramolecular transfer from C−H stretch to ν_8 (see Figure 7b). ν_8 also shows a slower rise which is due to intermolecular processes, namely up-pumping from phonons which build up during VC (the temperature jump is $\Delta T \sim 7$ K). The amplitudes of these two processes are about equal.

Diluting the acetonitrile will reduce the amplitude of intermolecular processes such as up-pumping, but it should have little effect on intramolecular processes. In dilute acetonitrile, the amplitude of the bulk temperature increase is reduced by a factor of ~2 (to $\Delta T \sim 3.5$ K), so the amplitude of the *slower* rise of ν_8 excitation will be reduced by a factor of ~2. Since the data in Figure 6a,b have exactly the same time dependence, *the amplitude of the fast jump of* ν_8 excitation is reduced by a factor of ~2 upon dilution. This is the critical observation which proves the point. Dilution hardly affects the fast intramolecular transfer from C−H stretch to ν_8, so if the amplitude of the fast jump of ν_8 excitation is reduced upon dilution, it can only be because there is an intermolecular process involved, namely that ν_8 has a short lifetime and is in fast equilibrium with the bath.

Whether ν_8 is populated by an intermolecular or an intramolecular process, our results show the lifetime of ν_8 must be short. In other words, ν_8 is a molecular thermometer[28,45] which provides a measure of the instantaneous bath temperature. It should be mentioned that interconversion among bath excitations is thought to be faster than VER,[43,44] so the bath itself should remain approximately in thermal equilibrium during VER.

As indicated above, the experiments do not indicate whether C−H stretch decay populates ν_8 by a high-order multiphonon process (e.g., $\nu_{CH} \rightarrow \delta_{CH} + 15\omega_{ph}$) or an intramolecular process (e.g., $\nu_{CH} \rightarrow \delta_{CH} + 4\delta_{C-C\equiv N}$). However, theory predicts such high-order multiphonon processes to be unlikely. The rate of the multiphonon process should be *extremely sensitive* to temperature[4] (e.g., rate $\propto T^{15}$) and also to the phonon density of states. Our dilution experiments show the rate of C−H stretch decay is virtually unaffected by dilution with CCl_4. The multiphonon process should be highly sensitive to dilution,[46] which is a strong indication that the bending vibration is populated by intramolecular transfer from ν_{CH} to $\delta_{C-C\equiv N}$.

5.3.2. C−H Stretch. The ν_8 bend data in Figure 6 show that about one-half of all the C−H stretch energy is dissipated to the bath on the 5 ps time scale of C−H stretch decay. This observation greatly constrains the possible C−H stretch decay mechanisms. Since we believe high-order multiphonon emission to be unlikely,[4] the remaining possibilities are (1) $\nu_{CH} \rightarrow \delta_{CH} + (\delta_{C-C\equiv N} \leftrightarrow \text{bath})$, which since C−H bending vibrations have about one-half the energy of C−H stretching vibrations, dissipates about one-half the C−H stretching energy in the bath, or (2) a roughly equal competition between two parallel processes, one, $\nu_{CH} \rightarrow 2\delta_{CH}$, which dissipates practically no energy to the bath, and another, $\nu_{CH} \rightarrow (8\delta_{C-C\equiv N} \leftrightarrow \text{bath})$, which dissipates *all* the C−H stretching energy to the bath.

If the second possibility (2) above were correct, then C−H stretch decay would populate the first overtone of the C−H bending vibrations. Then the decay of ν_6 C−H bending population seen in Figure 5 would at early times represent the decay of $2\nu_6$. However, quantum mechanics shows[4] the decay rate of the first overtone must be *at least twice as fast* as the decay rate of the fundamental. Therefore if we were seeing $2\nu_6$ and ν_6 decay in Figure 5, we should see a biexponential decay with the earlier part due to $2\nu_6$ decay and the later part due to ν_6 decay. However, Figure 5 shows that the decay of ν_6 C−H bending population is a single exponential in time. In addition, one-half of the C−H stretch decay would involve a high-order or multiphonon process which theory predicts to be unlikely and which would be strongly affected by dilution with CCl_4. CCl_4 dilution experiments show the rate of C−H stretch decay is virtually unaffected by dilution. Therefore C−H stretch decay does not significantly populate C−H bending overtones. *C−H stretch decay in acetonitrile populates C−H bending fundamentals.*

5.3.3. C−H Bend. As concluded above, the decay of C−H bending excitation represents decay of the bending fundamentals. Both ν_3 and ν_6 apparently have the same decay rate. Spectral overlap of the three C−H bending and three C−H stretching transitions keeps us from directly measuring the quantum yield for C−H stretch to C−H bend transfer. But knowing the energy of a C−H bend is about one-half the energy of a C−H stretch, and that the ν_8 data in Figure 6 show that about one-half of the C−H stretch energy goes into the bath, we can estimate the quantum yield for C−H stretch to C−H bend transfer to be $\Phi \approx 1$. Our data are consistent with the idea that every C−H stretch decay excites one C−H bend fundamental.

The decay of the C−H bending vibrations (~1450 cm^{-1}) must in part occur by exciting lower energy ν_4 C−C stretching vibrations (918 cm^{-1}), since the C−H bend population decay matches the C−C stretch buildup (Figure 3c,d). The quantum efficiency of transfer from C−H bend to C−C stretch $\Phi \approx 0.7$, so most of the C−H bend energy is transferred to the C−C stretch. As discussed below, we surmise the remaining C−H bend energy is transferred to the ν_7 CH_3 rocking vibration (1040 cm^{-1}). Therefore the bath temperature increase due to C−H bend decay should be about one-sixth of the total increase (~500 cm^{-1} out of a total of 3000 cm^{-1}) during the time range of 5−50 ps. That expectation is consistent with the magnitude of ν_8 population growth in that time range (Figure 6a).

Although both ν_3 and ν_6 evidence the expected 5 ps rise which corresponds to the 5 ps decay of the C−H stretch, there is an instantaneous part to the rise of ν_6 seen in Figure 4a which is quite interesting, and which requires a somewhat more complicated picture than the simple C−H stretch to C−H bend decay. We must include the bending overtones and the Fermi resonance between ν_5 and $2\nu_6$. The energy level diagram needed to discuss this picture is shown in Figure 8.

The laser at 3000 cm^{-1} pumps a superposition of ν_1, ν_5, and $2\nu_6$. The pumping of $2\nu_6$ is seen from the instantaneous rise of the ν_6 population in Figure 4a. Recall that in a low-resolution ultrafast experiment, excitation of the overtone appears as excitation of the corresponding fundamental with twice the amplitude.[25] There is no direct laser pumping of $2\nu_3$, which Figure 2 shows lies well below the laser pump wavelength. Nor do we see any evidence for energy transfer from C−H stretch to $2\nu_3$. The fact that no $2\nu_6$ population remains after 5 ps leads us to postulate a fast (compared to 5 ps) interconversion between the C−H stretching vibrations and $2\nu_6$, as indicated in Figure 8. Therefore the decay of $2\nu_6$ population would follow the path of the 5 ps C−H stretch decay.

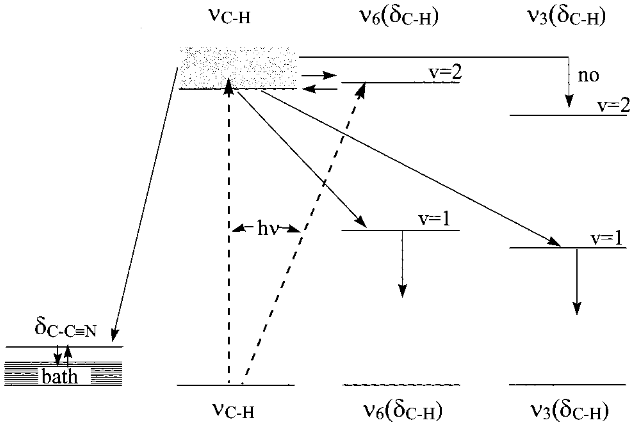

Figure 8. Energy level diagram for the early stages of acetonitrile VER. The laser (dashed arrows) pumps C−H stretches and the $2\nu_6$ bend overtone. Interconversion between C−H stretch and $2\nu_6$ is fast, so $2\nu_6$ and C−H stretch decay occur simultaneously. C−H stretch decay populates C−H bending fundamentals and the low-energy C−C≡N stretch, which rapidly exchanges energy with the bath. A rapid recurrence of ν_6 excitation occurs. The ν_6 mode ($v = 2$) is first excited by the laser. It loses energy as C−H stretching excitations decay, and then becomes excited again ($v = 1$) by C−H stretch decay.

The rise of ν_6 seen in Figure 4a thus represents an extremely interesting vibrational energy recurrence phenomenon which we believe has not been observed previously. At short times, the ν_6 mode ($v = 2$) is excited by the laser pulse. Then the ν_6 energy is transferred to the isoenergetic C−H stretch, and subsequently returned back to ν_6 ($v = 1$). This process may be viewed as an *incoherent population oscillation* of the ν_6 mode, since the rates of these energy transfer processes are quite a bit slower than the rates for vibrational dephasing in acetonitrile.[11]

5.3.4. C−C Stretch. The ν_4 C−C stretch at 918 cm^{-1} is populated mainly by C−H bend decay. The decay of C−C stretch excitation is complete by about 150 ps, as shown in Figure 3d. The C−C stretch can decay only by exciting C−C≡N bends or phonons. Since the quantum yield $\Phi \approx 0.7$ for transfer from C−H stretch to C−H bend to C−C stretch, and since C−C stretch decay dissipates ~900 cm^{-1} of energy during the time period of C−C stretch decay (say 30−150 ps), the bath temperature rise due to C−C stretch decay should be about $0.7 \times (900/3000)$ or about 20% of the total rise, which is consistent with the rise in ν_8 population in the 30−150 ps time range seen in Figure 6a.

5.3.5. CH_3 Rocking. The data in Figure 3 do not explain the slowest part of the rise in bath temperature (100−300 ps) seen in the ν_8 data in Figure 6a. The 80 ps time scale decay of C≡N stretch excitation cannot account for this rise since it represents less than 2% of the available energy. The only vibration not seen in our experiments is the ν_7 CH_3 rocking vibration, so conservation of energy leads us to conjecture that this slow buildup of bath excitation is due to the decay of ν_7. We know that 70% of the C−H bend quanta are transferred to C−C stretching excitations, so up to 30% of the C−H bending quanta might be transferred to ν_7. To account for the time scale of ν_8 buildup, the ν_7 lifetime would have to be in the 100−150 ps range.

5.3.6. C≡N Stretch. Decay of the laser-excited C−H stretch (~3000 cm^{-1}) to the C≡N stretch (~2250 cm^{-1}) can occur by a relatively low-order anharmonic process (e.g., $\nu_{CH} \rightarrow \nu_{C\equiv N} + 2\delta_{C-C\equiv N}$. Since only ~2% of the C−H stretching excitation is transferred to the C≡N stretch in 5 ps, we can estimate the time constant for $\nu_{CH} \rightarrow \nu_{C\equiv N}$ to be quite slow, on the order of 250 ps. Evidently the anharmonic coupling between C−H and

C≡N stretches is quite small. In addition, the ~80 ps lifetime of the C≡N stretch fundamental is quite long for such a high-frequency excitation of a polyatomic molecule. In the present experiments, we pump ~3000 cm^{-1} of energy into ambient temperature molecules. At this level of excitation, the C≡N stretch appears to be a highly harmonic vibration in the sense that it couples quite poorly to other vibrations of acetonitrile and to the bath. However, it is worth noting a small peak seen in the IR absorption spectrum at ~3150 cm^{-1}, which is assigned to a combination of C≡N + C−C stretch.[29] We have seen that pumping acetonitrile at ~3150 cm^{-1} produces vastly more excitation of the C≡N stretch and some intriguing population dynamics as well.[47]

6. Summary and Conclusions

The VER process which results from laser pumping of the C−H stretching region of acetonitrile was studied by ultrafast anti-Stokes Raman spectroscopy. The lowest energy vibration of acetonitrile, the ν_8 C−C≡N bend, has a short lifetime of less than 5 ps, and it is strongly coupled to the bath. It is thus possible to monitor the buildup of bath excitation by observing the rise of population of this state. This vibration serves as a molecular thermometer which monitors the rise in bath temperature. Knowing what fraction of the initial ~3000 cm^{-1} of vibrational energy is dissipated at each instant provides constraints needed to distinguish among many possible VER pathways allowed by energy conservation.

C−H stretch decay (~3000 cm^{-1}) mainly involves exciting the C−H bending fundamentals at about one-half the energy (~1500 cm^{-1}), rather than the almost isoenergetic C−H bending overtones. The remaining one-half of the vibrational energy is transferred to the bath in just a few picoseconds, probably via the C−C≡N bend. Only a small fraction of C−H stretch quanta are transferred to the C≡N stretch (2253 cm^{-1}). The C≡N stretch has a long lifetime of ~80 ps. We can think of the C≡N stretch as a vibrational relaxation "blocking group" which keeps vibrational energy in the CH_3−C moiety, at least at energies ≤3000 cm^{-1}. (At 3150 cm^{-1}, energy flows rapidly between C−H stretch and C≡N stretch[47]). The C−H bending vibrations relax mainly (~70%) by exciting C−C stretching vibrations (918 cm^{-1}). The fate of the remaining 30% of the C−H bending quanta was not directly observed, but it is suggested that they are transferred to the ν_7 vibration (1040 cm^{-1}) which was not seen in our experiments. Because there is a slow component of the buildup of bath temperature indicated by ν_8 which continues out to ~300 ps, of approximately the correct amplitude (~30% of the C−H bending quanta), we infer that decay of the CH_3 rocking vibration occurs with a rather slow lifetime in the 100−150 ps range.

Our picture of VC is summarized in Figure 8 as follows. About one-half, or ~1500 cm^{-1}, of the vibrational energy is dissipated during the 5 ps decay of the C−H stretch, probably from the C−C≡N stretch to the bath. The ~1500 cm^{-1} energy in C−H bending excitations is ultimately dissipated by other VER steps in the 5−300 ps time range. The most important of these other steps, which accounts for ~70% of the C−H bending quanta is $\delta_{CH} \rightarrow \nu_{CC} \rightarrow (\delta_{CC\equiv N} \leftrightarrow \text{bath})$. Although we cannot directly observe the methyl rocking vibration, the slowest part of the bath temperature buildup leads us to conjecture the rest of the dissipation process follows the path $\delta_{CH} \rightarrow \rho_{CH_3} \rightarrow (\delta_{CC\equiv N} \leftrightarrow \text{bath})$.

An interesting vibrational energy recurrence phenomenon is observed as a result of the Fermi resonance between ν_5 and $2\nu_6$, which is manifested in the rise of the ν_6 anti-Stokes transient. The ν_6 C−H bending mode is initially excited ($\upsilon = 2$) by direct laser pumping. Then the C−H bending energy is transferred to C−H stretching. Decay of C−H stretching subsequently repopulates the ν_6 mode ($\upsilon = 1$). This process may be thought of as an incoherent population oscillation, since it occurs slower than vibrational dephasing in acetonitrile.

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