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Dieter Bingemann, Michael P. Gorman, Andrew M. King, and F. Fleming Crim

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COMMUNICATIONS

Time-resolved vibrationally mediated photodissociation of HNO₃: Watching vibrational energy flow

Dieter Bingemann, Michael P. Gorman, Andrew M. King, and F. Fleming Crim Department of Chemistry, University of Wisconsin-Madison, Madison, Wisconsin 53706

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Ultrafast excitation of an O–H stretching vibrational followed by photodissociation of the energized molecules allows direct observation of the time for intramolecular energy redistribution in isolated nitric acid. We excite the first overtone of the O–H stretch vibration in HNO₃ with a 100 fs laser pulse. A second, time-delayed pulse preferentially photodissociates molecules having vibrational excitation in modes orthogonal to the O–H stretch. The photodissociation yield increases as a function of time because energy flows out of the initially excited O–H bond into other more efficiently dissociated vibrations. The single exponential time constant for this intramolecular vibrational relaxation is 12 ps, consistent with moderate coupling of the O–H stretch to states close in energy. © *1997 American Institute of Physics*. [S0021-9606(97)02426-4]

INTRODUCTION

The redistribution of vibrational energy within a molecule is at the heart of reaction dynamics. Not surprisingly, intramolecular vibrational energy redistribution (IVR) has attracted many experimental studies, mostly in the frequency domain.¹ The absorption frequencies and intensities in high resolution spectra of isolated molecules reveal the energies of molecular eigenstates and coupling constants between zero-order bright and dark states, respectively. The analysis of such spectra allows one to infer the dynamics of an initially localized excitation, if it were prepared, by calculating the time evolution of the zero-order bright state wave function.²

There is less work on IVR in the time domain. Typically in time-domain experiments, a short laser pulse prepares a vibrationally excited state in the first electronically excited state S_1 through an electronic transition to a Franck–Condon bright state, and a second short pulse probes the IVR dynamics by fluorescence depletion,³ pulsed field ionization,^{4–7} or other spectroscopic techniques.^{8,9} The molecules investigated in such studies are fairly large. Smaller molecules with fewer normal modes and lower densities of states potentially allow a more specific modeling of their IVR dynamics. Further, comparing the results for molecules of different size could reveal trends that help establish a detailed molecular description of IVR.

We have studied the IVR dynamics of a small molecule, HNO₃, on its ground state surface in the time domain using the technique of vibrationally mediated photodissociation¹⁰ to monitor the vibrational energy redistribution. Vibrationally mediated photodissociation allows one to specify the nature of the initial vibrational excitation and to monitor *di*- *rectly* the flow of energy from the initially excited vibration to other vibrational modes of the molecule.

VIBRATIONALLY MEDIATED PHOTODISSOCIATION

Vibrationally mediated photodissociation is a double resonance technique: one laser pulse prepares a vibrationally excited molecule in its electronic ground state, and a second laser pulse, tuned to an electronic transition, photodissociates the molecule. In an ideal vibrationally mediated photodissociation experiment (see Fig. 1), the photodissociation laser pulse has too little energy to dissociate molecules with no initial vibrational excitation. However, since the excited state surface is repulsive and its potential energy decreases along the dissociation coordinate, the energy difference between the electronic ground state and the excited state decreases along this coordinate. Therefore, a less energetic photolysis photon can transfer vibrationally excited molecules that are elongated along the dissociation coordinate to the excited state surface. Even in less than ideal vibrationally mediated photodissociation experiments, vibrational excitation produces a substantial increase in dissociation yield.^{11–14} For the same photolysis energy, the excitation of the vibration along the dissociation coordinate improves the Franck-Condon overlap of the ground state wave function with the wavefunction of the dissociative state.

Time domain vibrationally mediated photodissociation experiments use short, broadband laser pulses for the vibrational overtone excitation and photodissociation. Information about the molecular dynamics comes from varying the time delay between the two laser pulses while their frequencies remain constant. The vibrational overtone excitation initially prepares the zero-order bright state. Because the bright state is not an eigenstate of the molecular Hamiltonian, it evolves

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FIG. 1. Schematic drawing of ground and excited state potential energy surfaces of nitric acid (HNO3) illustrating time-resolved vibrationally mediated photodissociation. λ_{ovt} is the vibration overtone excitation laser wavelength (1.44 $\mu m),~\lambda_{diss}$ is the photolysis wavelength (266 nm), and Δt is the time delay between excitation pulse and photolysis pulse. In this schematic, the HO-NO2 stretch coordinate represents all vibrational modes with a strong increase in photodissociation yield after vibrational excitation.

in time as vibrational energy leaks into dark background states. The vibrational wave packet spreads, and probability moves into vibrationally excited states other than the zeroorder bright state. Some of these states have a higher photolysis yield from the second laser pulse than the initially prepared state. Varying the time delay between vibrational overtone excitation laser and photolysis laser pulses directly measures the time for energy to flow out of the zero-order bright state.

EXPERIMENTAL DETAILS

Using nitric acid (HNO₃) as a model system has several advantages in a time-resolved vibrational mediated photodissociation experiment. Its photodissociation yields a small amount of electronically excited NO2 , which we can detect using its spontaneous fluorescence. Furthermore, the vibrationally mediated photodissociation of HNO3 is well studied in the frequency domain.¹⁴ Figure 1 schematically shows a potential energy surface for the time-resolved vibrationally mediated photodissociation of HNO₃. In this simple picture, the N-O stretch coordinate represents modes with a strong increase in photodissociation yield after vibrational excitation. A 100 fs pulse at 1.44 μ m prepares the zero-order bright state, the O–H stretch (v=2) local mode, via its first overtone absorption, and a second short laser pulse at 266 nm subsequently photolyzes the vibrationally excited molecules.

We generate the two pulses by nonlinear frequency conversion in an optical parametric amplifier (OPA) and a frequency tripling stage, respectively, starting with 80 fs Ti:Sapphire laser pulses. The regeneratively amplified Ti:Sapphire laser system (Clark MXR, CPA 1000) produces 800 nm pulses at a repetition rate of 1 kHz and an energy of 1 mJ. We frequency double 100 μ J of the 800 nm pulses in a 0.3 mm BBO crystal (type I, $\theta = 29^{\circ}$) and mix the generated 400 nm pulses with leftover 800 nm light in a 0.2 mm BBO crystal (type I, θ =42°) to make 1 μ J pulse at 266 nm. The remaining Ti:Sapphire output pumps a continuum seeded, double pass OPA (Ref. 15) (5 mm BBO, type II, θ =27°), which gives 90 μ J pulses at 1.44 μ m. These roughly 100 fs pulses have a bandwidth of approximately 280 cm^{-1} (1.9 times the Fourier limit). A 500 mm lens focuses the 4 mm diameter infrared beam to a diameter of about 250 μ m in the center of a fluorescence cell, where it overlaps with the ultraviolet pulses, which are focused down from a 1.5 mm diameter with a 300 mm lens. The polarizations of the two laser pulses are perpendicular to each other.

A photon counting photomultiplier (EMI 9813QB) detects the fluorescence of the electronically excited NO₂ product in the range of 480-580 nm through a Schott GG475 cutoff filter. The signal passes to a gated photon counter (SR400) with a 1.2 μ s wide gate that opens 40 ns after the laser pulses arrive. An externally synchronized chopper (PAR, Super Chopper 300) blocks every other infrared pump pulse for separate background detection. We average 5000 shots per time delay step and record up to about 5000 signal counts on top of a background of about 15 000 counts. The HNO₃ vapor flows through the room temperature fluorescence cell at a pressure of 250 mTorr and an approximate rate of 200 scc/h. We prepare the anhydrous HNO₃ by mixing concentrated HNO3 and H2SO4 in a 1:3 ratio and collecting the HNO₃ vapor in a trap at dry ice temperature.

RESULTS

Our primary observation is the time evolution of the photodissociation yield as a function of time delay between the vibrational excitation pulse and the photolysis pulse. Figure 2 shows the increase in the fluorescence from the NO_2 product of the vibrationally mediated photodissociation signal of HNO₃ for the first 80 ps (circles). From 80 ps through 1 ns there is no statistically significant change in the signal level. A single exponential rise with a time constant of $\tau=12$ ps (solid line) fits these data well.

We obtained additional information about the initially prepared zero-order state by changing the wavelength of the vibrational overtone excitation laser while recording the vibrationally mediated photodissociation signal with the time delay fixed at 50 ps. The result is plotted in Fig. 3 as filled circles. For comparison, we also include a photoacoustic spectrum of HNO₃ recorded with the same fs pulses (open circles) and a conventional infrared absorption spectrum of



FIG. 2. Increase in fluorescence signal from the NO₂ product of the vibrationally mediated photodissociation of nitric acid (HNO₃) as a function of time delay Δt between the vibrational excitation laser pulse and the photodissociation laser pulse (filled circles). The solid line is a single exponential rise with a time constant of 12 ps.

HNO₃ vapor (dotted line). The widths of the action and photoacoustic spectra reflect the bandwidth of our infrared laser pulse. Both spectra have the same wavelength dependence, consistent with our simple picture of the first overtone of the O–H stretch vibration as the zero-order bright state in this time-resolved vibrationally mediated photodissociation experiment. The rise of the signal establishes a characteristic time of 12 ps for relaxation of the initially excited O–H stretch in a HNO₃ molecule at an energy level of 7000 cm⁻¹.

ANALYSIS

A count of vibrational states in HNO₃ (Ref. 16) assuming the vibrations are harmonic oscillators gives a vibrational state density of $\rho(E) \approx 10$ states/cm⁻¹ near the 7000 cm⁻¹



FIG. 3. Dependence of the vibrationally mediated photodissociation (VMP) signal on the vibrational excitation wavelength at a delay of 50 ps between excitation and photolysis laser pulse (filled circles). A photoacoustic spectrum of nitric acid recorded with the same infrared laser pulses (open circles) and a conventional infrared absorption spectrum (dashed line) are plotted for comparison.

energy of the first O–H stretch overtone. A simple analysis of the data treats all states equally and uses Fermi's Golden Rule^{17} (energies in cm⁻¹),

$$1/\tau = 4 \pi^2 c |V|^2 \rho(E)$$

to relate the observed lifetime τ to the coupling strength |V| in the molecule. Using the measured time constant of $\tau=12$ ps and the calculated state density $\rho(E)\approx 10$ states/ cm^{-1} , we find an average coupling matrix element of |V|= 0.08 cm^{-1} . For a state density of 10 vibrational states/ cm⁻¹, this matrix element mixes only a few dark states with the zero-order bright state. In that situation, the vibrational energy should beat back and forth between these few coupled zero-order states,² producing oscillations ("quantum beats") in the time-resoled vibrationally mediated photodissociation signal. Instead, we observe a simple exponential rise. The excitation laser bandwidth in our experiment (280 cm^{-1}), which spans the entire thermal rotational bandwidth of the overtone absorption band (50 cm^{-1}) , could explain the absence of quantum beats. This pulse initially prepares an ensemble of molecules with a thermal distribution of rotational quantum numbers and two quanta of O-H stretch vibration. Because the rotational constants depend on the vibrational state, the energy differences between the rovibronic eigenstates that mix to form the zero-order bright state are slightly different for each rotational state. Molecules with different rotational quantum numbers will therefore beat at different frequencies. In our ensemble with a broad distribution of rotational excitation, these beats add destructively, and we observe an unstructured time evolution reflecting the average rate.

Absorption of a linearly polarized laser pulse leads to a preferred orientation of excited molecules. For the thermal distribution of rotational states in our experiment, this initial anisotropy decays rapidly compared to the observed signal rise time, but an orientational recurrence should occur after about 40 ps. The absence of such a recurrence in Fig. 2 suggests that orientational effects are unimportant in our experiments.

Time-resolved IVR experiments performed thus far used larger probe molecules such as stilbene,⁸ fluorene,³ or *p*-difluorobenzene⁶ with considerably higher state densities at much lower vibrational excitation energies. These measurements found IVR time constants on the order of 10–20 ps for excitation energies around 1500 cm⁻¹ at a density of states of several 100 states/cm⁻¹. The much lower density of states (10 states/cm⁻¹) necessary to yield an IVR time constant of 12 ps in HNO₃ could be the consequence of larger coupling constants in nitric acid. It could equally well reflect the participation of only a portion of the available states in the initial IVR. Such selective coupling of a subset of all the available states is consistent with results from frequency domain IVR experiments such as those on acetylene homologs.^{18–21}

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