DOE/ER/13500--T4

TECHNICAL PROGRESS REPORT

DE-FG02-86ER13500

THE PHOTODISSOCIATION AND REACTION DYNAMICS OF VIBRATIONALLY EXCITED MOLECULES

CONTENTS

ABSTRACT

The goal of our Department of Energy sponsored research is to discover the properties, behavior, and dissociation dynamics of vibrationally energized molecules, which are crucial participants in many chemical reactions. We study vibrationally energized molecules by using an optical excitation scheme to prepare them and a subsequent photon to dissociate them into fragments that we detect with a spectroscopic probe. This technique, vibrationally mediated photodissociation, provides new information on vibrationally energized molecules and even provides a means of controlling the course of a molecular decomposition. During the most recent period of Department of Energy support, we have advanced this work in three directions: we have used vibrational overtone excitation to control the decomposition pathways in the tetra-atomic molecule isocyanic acid (HNCO) and unravelled the decomposition pathways in hydroxylamine (NH_2OH), we have implemented stimulated Raman excitation as the vibrational state preparation technique in vibrationally mediated photodissociation, and we have tested the limits of transient grating spectroscopy as a means of obtaining electronic spectra of vibrationally excited molecules.

DISCLAIMER

INTRODUCTION

This Progress Report describes our Department of Energy sponsored research on the dynamics of vibrationally excited molecules. Unearthing the properties of vibrationally excited molecules, which are the central actors in many chemical reactions, and using those properties to explore and control chemical reactions is a primary goal of our work. Vibrationally excited molecules play crucial roles in a variety of chemical systems, such as those found in the atmosphere, combustion reactions, and plasmas. In addition, a detailed description of vibrationally excited molecules, particularly ones with large amounts of vibrationally energy, challenges and tests theory. Our Department of Energy supported research has explored the chemistry of vibrationally excited molecules broadly over the last several years, during which we have studied unimolecular reaction,[1] photodissociation,[2] and bimolecular reaction[3] in vibrationally excited molecules

One of the ways in which we manipulate vibrationally excited molecules is to prepare a vibrational state and subsequently to excite the vibrationally energized molecule to a dissociative electronic state, where we follow its decomposition with spectroscopic probes. Because the initial vibrational excitation can strongly influence the motion of the vibrationally excited molecule on the electronically excited potential energy surface, we call this process *vibrationally mediated photodissociation.* We have made substantial progress on three different aspects of vibrationally mediated photodissociation during the most recent period of Department of Energy support. The first aspect is the extension our work on *vibrational overtone state control of photodissociation.* We have used vibrational overtone excitation to prepare vibrationally excited hydroxylamine (NH_2OH) and monitor its photodissociation dynamics by laser induced fluorescence detection of the products.[4,5] Applying the same scheme to isocyanic acid (HNCO) and probing either the cleavage of the N-C bond, by detecting NH, or the H-N bond, by detecting NCO, has produced the first example of vibrational state control of the photodissociation yield in two chemically distinct channels.[6] This example in a tetra-atomic molecule builds on our earlier Department of Energy sponsored work demonstrating vibrational state control in the photodissociation of HOD.[7] The second aspect is the introduction of a new technique for vibrational state preparation into our laboratory. We have begun using *stimulated Raman excitation preparation in vibrationally mediated photodissociation.* Our new measurements on HNCO reveal fascinating and complex behavior in photodissociation from the vibrationally excited state and prove that we can apply vibrationally mediated photodissociation to fundamental vibrations of bonds between heavy atoms. The third aspect is the use of *laser induced grating spectroscopy* to explore the electronic spectroscopy of vibrationally excited molecules. Our careful studies have characterized laser induced grating spectroscopy in new detail for weakly absorbing gaseous samples, identifying a limiting background signal[8] and establishing the range over which the technique is useful.[9]

VIBRATIONALLY MEDIATED PHOTODISSOCIATION

The schematic potential energy surfaces on the left of Figure 1 illustrate vibrationally mediated photodissociation of a directly dissociative ABC molecule. The vibrational state preparation photon, λ_1, excites a vibration in the ground electronic state, and the dissociation photon, λ_2, promotes the vibrationally excited molecule to the electronically excited state. In an ideal vibrationally mediated photodissociation experiment, neither photon has sufficient energy to dissociate the molecule from its vibrational ground state, and the combined energy of the two photons is not enough to reach the electronically excited state surface from the equilibrium geometry of the ground electronic state. This later point is the crux of vibrationally mediated photodissociation. Only molecules with vibrations that extend the A-B bond reach configurations where the separation of the excited state surface and the ground state surface is small enough that the dissociation photon λ_2 can connect the two. The third component of our experiment, not shown in the Figure, is a spectroscopic probe of the fragments, such as laser induced fluorescence detection of BC.

The probability of a transition to the excited state surface from a particular initial state depends on the overlap between its wavefunction and that of the dissociative excited state. For a simple, directly dissociative surface, the most important component of this Franck-Condon factor is the overlap between the radial wavefunction along the dissociation coordinate (A-B) in the excited state and the bound state wavefunction along that coordinate in the ground electronic state. There is some optimum amount of A-B stretching excitation that gives the best overlap depending on the wavelength λ_2 of the dissociation photon. A vibrational eigenstate prepared on the ground electronic surface is likely to be a mixture of zero-order states, such as A-B stretches and B-C stretches, and the Franck-Condon factor for these component states controls the excitation efficiency. This picture provides both a model of the dissociation and a means of assessing the character of particular eigenstates.[10] Even though the A-B stretching excitation has the most obvious influence, the overlap integral in the other coordinates is important as well. For example, the excitation in the B-C stretching coordinate determines which B-C stretching states of

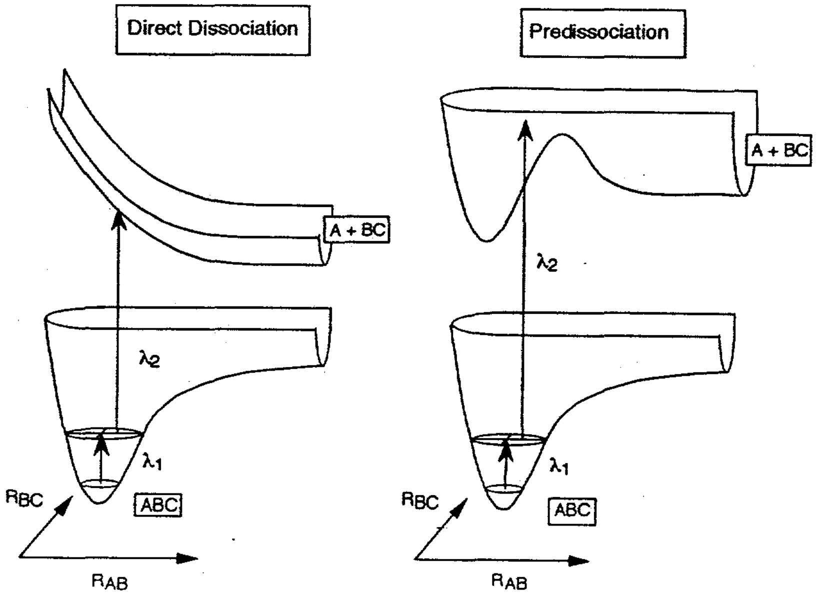


Figure 1

the electronically excited molecule have the largest Franck-Condon factor, and the initial excitation of the B-C stretch in the vibrationally excited state, along with interactions on the excited state surface, determine the amount of vibrational energy in the BC product. This is essentially the situation in our vibrationally mediated photodissociation studies of HOD and H_2O, where the surface is directly dissociative and where we see preservation of the initial excitation in the surviving bond in vibration of the fragment. The key to vibrational control in the bond selective photodissociation of HOD is excitation of a vibrational state that has good Franck-Condon overlap with the wavefunction in one dissociation channel (breaking the O-H bond, for example) compared to the other channel.[7]

The excited state potential does not have to be directly dissociative in vibrationally mediated photodissociation. The right hand side of Figure 1 is a schematic example in which the excited state is bound for low levels of A-B stretching excitation but dissociative for higher ones. This system would show the characteristic change from sharp to diffuse structure with the onset of predissociation and offers the intriguing possibility that excitation from states with large A-B stretching excitation could produce rapid dissociation while isoenergetic states with little A-B excitation could dissociate slowly. It is easy to envision more complex situations in which A-B stretching vibrations promote surface crossings and nonadiabatic effects that the excitation on the ground electronic state could alter dramatically. Electronic spectroscopy[11] and previous photodissociation studies[12,13] suggest that HNCO is such a predissociative molecule in which both dissociation channels are open at our excitation energies. We see strong effects of the initial vibrational excitation on the relative efficiency of dissociation in the two channels, in qualitative accord with our simple picture of vibrationally mediated photodissociation but with the added complication of the more complex excited state potential energy surface.

VIBRATIONAL OVERTONE EXCITATION AND PHOTODISSOCIATION

Vibrational overtone excitation, in which a visible or near infrared photon excites a vibrational state corresponding to several quanta of stretching vibration in a polyatomic molecule, has been the mainstay of our vibrationally mediated photodissociation technique. The molecular eigenstate excited is, in general, a mixture of the stretching excitation of a bond to a light atom, such as C-H, N-H, or O-H bonds, and other vibrations in the molecule. Because the oscillator strength for the vibrational overtone transition comes from the mechanical and electrical anharmonicity of that stretching vibration, the coarse features of the vibrational spectrum reflect the properties of the light atom oscillator.[1,14] In particularly favorable cases such as H_2O, the states are well isolated and virtually unmixed, but this is not typical. In fact, vibrationally mediated photodissociation, which relies on the initial vibrational excitation on the ground electronic state mapping onto a dissociation coordinate, often takes advantage of mixing of the vibrational states to indirectly excite the reaction coordinate. For example, in HOOH, the transition probability comes from the O-H stretching vibration, but the enhanced dissociation into two OH radicals in the electronically excited state comes from the mixture of O-O stretching excitation into the initially prepared state.[2,10]

An important benefit of exciting overtone vibrations of bonds to light atoms is that it deposits the large amounts of energy (100-200 kJ/mol) required to shift the wavelength of the electronic transition, marked with λ_2 in Figure 1, well away from the transition from the ground electronic state. Accessing regions where the ground- and excited-state potentials are close enough that a less energetic photon can effect the transition, as illustrated in the left-hand side of the Figure, suppresses background signal from direct dissociation. We have previously used vibrational overtone excitation in the vibrationally mediated photodissociation of a variety of molecules, including HOD where we were able to control the cleavage of one bond over another.[2] This portion of the Progress Report briefly describes our most recent vibrational overtone excitation and photodissociation experiments on hydroxylamine (NH_2OH) and isocyanic acid (NHCO), the later providing the first example of vibrational state control of the photodissociation of a tetra-atomic molecule.

Hydroxylamine (NH_2OH)

Hydroxylamine (NH_2OH) is an excellent candidate for vibrational overtone excitation in vibrationally mediated photodissociation. It has both O-H and N-H stretching vibrations that are good candidates for vibrational overtone excitation and decomposes to produce a fragment (OH) that we can readily detect by laser induced fluorescence. The first step in our study of hydroxylamine was characterization of its O-H stretching vibrational spectrum. We then performed one-photon dissociation experiments and vibrationally mediated photodissociation experiments in which we observed substantial differences resulting from the initial vibrational excitation.

Vibrational Overtone Spectroscopy[4]

We obtained photoacoustic spectra of hydroxylamine in the regions of the second ($3\nu_{OH}$), third ($4\nu_{OH}$), and fourth ($5\nu_{OH}$) overtones of the O-H stretching vibration using light from a Nd:YAG laser pumped dye laser directly or Raman shifted to longer wavelengths depending on the transition. The left-hand side of Figure 2 shows the photoacoustic spectra in the region of these three transitions. The second and third overtone spectra have sharp, partially resolved rotational structure, but the spectrum for $5\nu_{OH}$ shows none. (The features marked with asterisks are transitions for H_2O, which provide useful wavelength calibration points.) An asymmetric rotor simulation reproduces the rotational structure, as the experimental and simulated spectra for $3\nu_{OH}$ on the right hand side of the figure illustrate, and yields A-axis rotational constants of 6.150(1) and 6.064(1) cm^{-1} for $3\nu_{OH}$ and $4\nu_{OH}$, respectively. The widths of the features in the spectra exceed our largest laser line width of 0.15 cm^{-1}, and we obtain the best fits to the second and third overtone spectra using Lorentzian widths of 0.7 ± 0.2 cm^{-1} and 0.9 ± 0.2 cm^{-1} for the individual rotational transitions, respectively. The individual features are unresolved in the fourth overtone spectrum, where an acceptable fit requires a much larger width of 6 to 10 cm^{-1}, with 7 cm^{-1}

providing the best reproduction of the experimental spectrum. (The best-fit value of the rotational constant is similarly less precise. We used 6.00 cm^{-1} in our simulations.)

All the vibrations we excite lie below the N-O bond dissociation energy of 21,660 cm^{-1},[15] and we conclude that the increase in the widths of individual features in the energy regime between $4\nu_{OH}$ and $5\nu_{OH}$ reflects a sharp increase in the rate of intramolecular vibrational energy redistribution or, in other words, in the coupling of the O-H stretch to other vibrations. This is consistent with infrared-optical double resonance vibrational overtone excitation experiments by Luo, *et al.*[15] that found a width of 14 cm^{-1} for transitions to the sixth vibrational overtone state ($7\nu_{OH}$). This modest increase of a factor of two between the fourth and sixth vibrational overtone states suggests there is no drastic difference in the couplings at these two levels. The changes in line width also

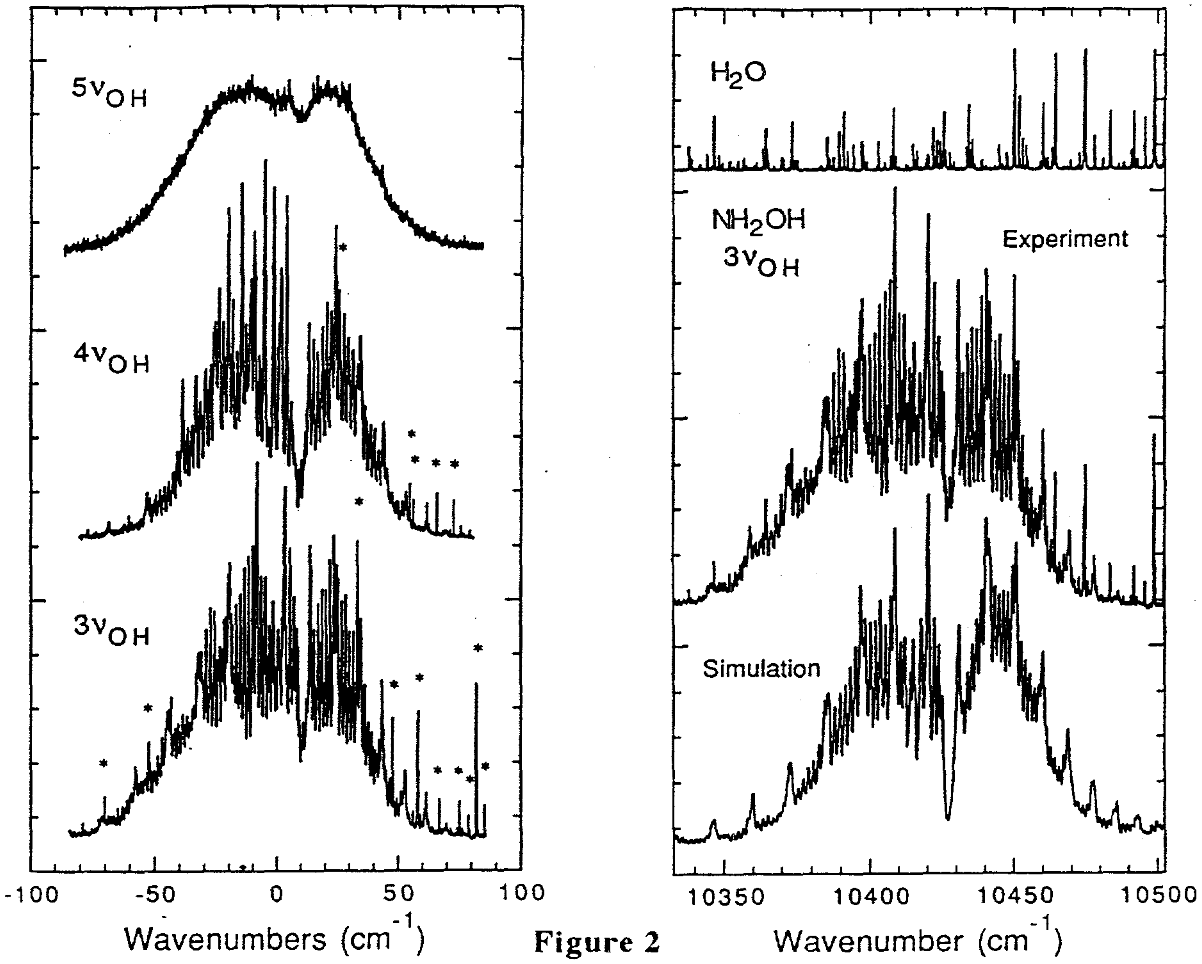


Figure 2

do not simply reflect the total density of states, which grows smoothly from about 10 per cm^{-1} at $3v_{OH}$ to 540 per cm^{-1} at $7v_{OH}$. For example, the density of states increases by a factor of four between the energies of $3v_{OH}$ and $4v_{OH}$ and the line width increases by about 30%, but the density of states increases by about three between the energies of $4v_{OH}$ and $5v_{OH}$ *and the line width increases by almost a factor of ten!* There is clearly an abrupt change at an energy between $4v_{OH}$ and $5v_{OH}$. The change in coupling of the O-H stretching vibration to other vibrations in the molecule that brings about the sharp change in line width may well arise from other isomers becoming energetically accessible. Hydroxylamine can isomerize from the *cis*- to the *trans*-form through a torsional motion or through inversion,[16] and it can isomerize to ammonia oxide, NH_3O, by migration of the hydroxyl hydrogen. Indeed we and others find in *ab initio* calculations that the ammonia oxide isomer is bound,[17,18] and we find the isomerization barrier to lie near the energy of $5v_{OH}$.[18] Hydroxylamine could be very floppy at energies above the isomerization barriers, and isomerization to ammonia oxide is likely to couple the O-H stretching vibration to others particularly well.

One-Photon Photolysis[5]

One-photon dissociation experiments provide the reference point for vibrationally mediated photodissociation measurements, allowing us to separate purely energetic effects from vibrational ones. Our benchmark for the photolysis of vibrationally excited hydroxylamine is the one-photon dissociation at 240 nm to produce NH_2 and OH. By detecting the OH fragment using laser induced fluorescence, we learn about the energy disposal into rotation and vibration of that fragment and, from the Doppler profiles of the transitions, into relative translation of the products. In addition, the populations of the lambda-doublet states reveal details of the motion of the OH fragment during the dissociation. About half (53%) of the 20,460 cm^{-1} of available energy appears in relative translation. The OH fragment receives 6.5% of the available energy, almost entirely as rotation. (Only 2% of the OH fragments are in $v=1$). The NH_2 receives the remaining 40% of the available energy as internal excitation. (The table in the next section summarizes this energy disposal along with that for the vibrationally mediated photodissociation experiments.)

The most striking feature of the one-photon dissociation is the population of the lambda-doublet states. In the limit of high rotation, the $\Pi(A')$ lambda-doublet state of OH, which P-branch transitions probe, has its unpaired electron in an orbital lying in the plane of OH rotation, and the $\Pi(A'')$ state, probed by Q-branch transitions, has its unpaired electron in an orbital perpendicular to the plane of rotation. The rotational distributions for the two states are very different, with the $\Pi(A'')$ state having a maximum at about N=9 and the $\Pi(A')$ state having a maximum at only N=4. Thus, we see that the ratio $\Pi(A'')/\Pi(A')$ increases from 1 to 4 with increasing product rotation. Correlating the unpaired electron in OH with the broken N-O sigma bond in NH_2OH suggests that this strong preference for that electron being in an orbital *perpendicular* to the rotation plane comes from some torsional motion in the electronically excited state. Indeed, our *ab initio* calculations of the electronically excited state of hydroxylamine[19] find that the electronically excited state has a minimum for a torsional angle near $\tau'=90°$ compared to the minimum on the ground state surface at $\tau''=180°$. A vertical transition to this state leaves the excited molecule far away from its equilibrium geometry and produces rotation of the OH fragment perpendicular to the orbital that was originally part of the N-O bond.

Vibrationally Mediated Photodissociation[5]

The vibrationally mediated photodissociation of NH_2OH reveals different dynamics in the dissociation from the vibrationally excited state. The vibrational overtone action spectrum, obtained by fixing the photolysis wavelength λ_2 and the probe wavelength λ_3 and scanning the vibrational overtone excitation wavelength λ_1, is virtually identical to the photoacoustic spectrum for both $4\nu_{OH}$ and $5\nu_{OH}$ excitations. Thus, we fix λ_1 to select an initial rovibrational state and monitor the photodissociation dynamics by probing individual rovibrational states of the OH photolysis products. The key to discovering the differences is to photolyze the vibrationally excited molecule with a photon (λ_2) that leaves the excited molecule with the same total energy as the 240-nm one-photon dissociation. The Table summarizes results of these measurements for dissociation from both $4v_{OH}$ and $5v_{OH}$.

Energy Disposal for NH_2OH Photodissociation*

	E_{avail}	Translation	OH Rotation	OH Vibration	NH_2 Internal
240 nm	20460	10890 (53%)	1260 (6.2%)	70	8240 (40%)
$4v_{OH}$+ 355 nm	20500	9180 (45%)	770 (3.8%)	150	10400 (51%)
$5v_{OH}$+ 400 nm	20240	9150 (45%)	1270 (6.3%)	270	9550 (47%)
$4v_{OH}$+ 532 nm	11100	8530 (77%)	720 (6.5%)	65	1785 (16%)
$5v_{OH}$+ $5v_{OH}$	11680	8510 (73%)	1070 (9.2%)	90	2010 (17%)
$4v_{OH}$+ $4v_{OH}$	5820	4750 (82%)	730 (12%)	-	340 (5.8%)

*The energy is in cm^{-1}, and the numbers in parenthesis are the fraction of the available energy.

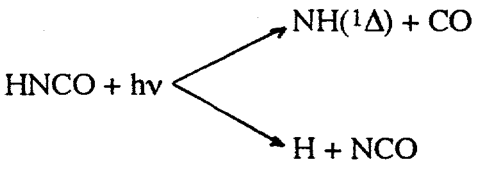
Both the one-photon dissociation with a 240-nm photon and the isoenergetic vibrationally mediated photodissociations for $4v_{OH}$ and $5v_{OH}$ produce qualitatively similar results: little energy goes into internal excitation of the OH fragment, and roughly equal amounts appear in relative translation and internal energy of the NH_2 fragment. A more subtle difference seems to reflect the role of initial vibrational excitation. Although the energy deposition into vibration of the OH is small for all cases, it doubles in going from the one-photon dissociation to the isoenergetic photodissociation from the $4v_{OH}$ state, and it doubles again in going to the isoenergetic dissociation from $5v_{OH}$. Thus, the fraction of the OH molecules born in v=1 increases from about 2% to almost 8%, reflecting some retention of the initial vibrational excitation in the vibration that provides the oscillator strength for the vibrational overtone transition. This retention is in keeping with the general behavior we observe in vibrationally mediated photodissociation in molecules such as HOOH and t-BuOOH.[2]

Another notable feature of the OH product from the vibrationally mediated photodissociation is that *it shows no preference for one lambda doublet state over another.* This is in sharp contrast to the situation for the one-photon dissociation and points to the difference in reaching the electronically excited surface from a vibrationally excited state. It is likely that the vibrational excitation in the first step places some energy in vibrations that alter the excited state dynamics. For example, torsional excitation on the ground electronic surface could carry the molecule into a geometry from which a vertical transition to the excited state surface reaches regions where the torque on the fragments is smaller. Another possibility is that coupling of O-H stretching excitation and N-O-H bending excitation could lead to enhanced rotation of the OH fragment in the plane of the orbital containing the unpaired electron that originates in the broken N-O bond. Both of these speculations are consistent with the *ab initio* surface we have begun calculating.

The table shows that the fraction of the available energy deposited in relative translation increases with decreasing total energy and is independent of the form of excitation, being roughly the same for different combinations of electronic and vibrational excitation. This suggests that the topology of the excited state surface controls the energy release, with relatively large amounts always entering translation at the expense of internal excitation of NH_2 because portions of the excited state surface are directly repulsive. Indeed, our calculations find a steep repulsion in the N-O coordinate at long bond lengths but also indicate a barrier at lengths less than the equilibrium bond length on the ground state surface. It seems likely that at the highest excitation energies the excited molecule samples the region above the well, where coupling of excitation into the NH_2 moiety is greater and, consequently, a larger fraction of the energy appears in the NH_2 fragment.

ISOCYANIC ACID (HNCO)

Isocyanic acid offers a new possibility in vibrationally mediated photodissociation. It has two chemically distinct photodissociation channels,



$$HNCO + h\nu \rightarrow \begin{cases} NH(^1\Delta) + CO \\ H + NCO \end{cases},$$

that form products (NH and NCO) that are both observable by laser induced fluorescence. The challenge and opportunity with this tetra-atomic molecule is to discover and control the dissociation dynamics in the two chemically distinct channels that have different energy thresholds. (Our first bond selected vibrationally mediated photodissociation studies (on HOD) probed the two isotopically distinct products OH and OD, which have only a modest energy difference.) Figure 3 shows the energetics for the photodissociation of vibrationally excited HNCO. The NH($^1\Delta$) product comes from the lowest spin allowed channel and is the only one we detect in either one-photon or vibrationally mediated photodissociation. As with hydroxylamine, comparison to the one-photon dissociation is an important part of our measurements. We focus on measuring the relative yields in the two channels for isocyanic acid and find that *excitation in the region of the 4*ν_{OH} *vibration changes the relative yields in the two channels by a factor of 20.*

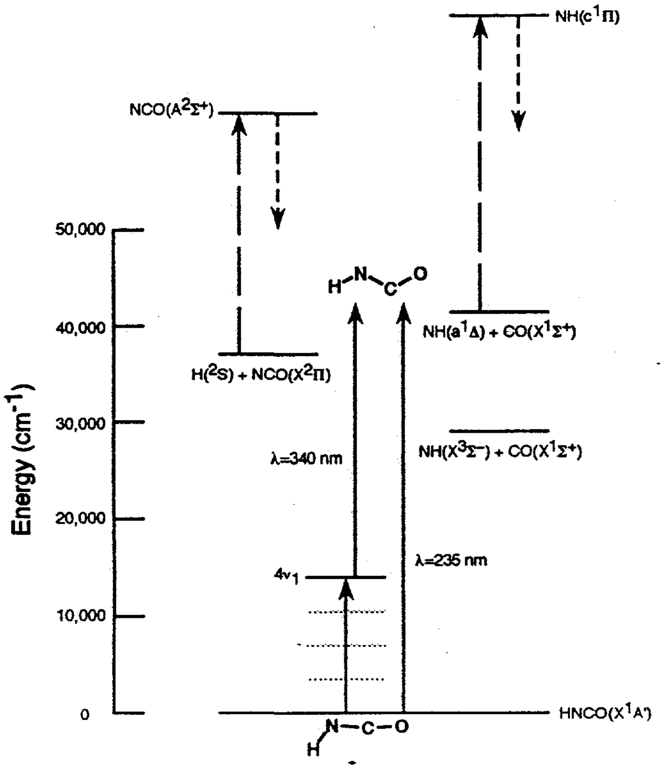


Figure 3

Vibrational Overtone Spectroscopy

The vibrational overtone photoacoustic spectrum in the region of $4\nu_{OH}$, shown in Figure 4, has partially resolved rotational structure that we can model by analogy to the fundamental N-H stretching vibration in HNCO.[20] Isocyanic acid is nearly an accidental prolate symmetric top (κ=0.9996) with the N-H bond bent away from the nearly linear N-C-O moiety by 57°, as shown schematically on the energy level diagram of Figure 3. The displacement of the hydrogen atom from the axis produces a large *a*-axis rotational constant ($A \approx 30$ cm^{-1}) with its attendant large spacing of the K_a subbranches of the spectrum. The fundamental vibrations of HNCO have an irregular spacing of the subbranches that we also find for the vibrational overtone transitions, and, following the analysis for the fundamentals, we assign each a different *a*-axis rotational constants. The simulation at the bottom of Figure 4 reproduces the spectrum and allows us to identify the transition that we excite in the vibrational overtone excitation step. (The transition, marked with an arrow in the middle panel, excites K_a=1 and $J \approx 12$.)

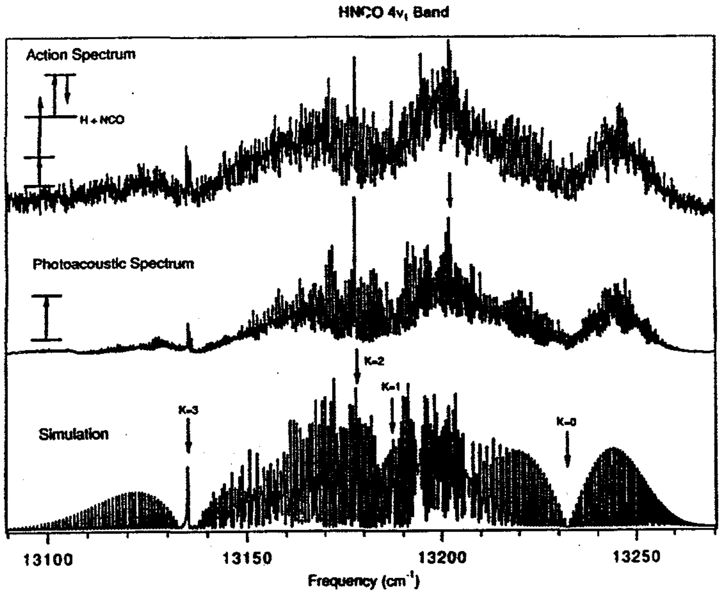
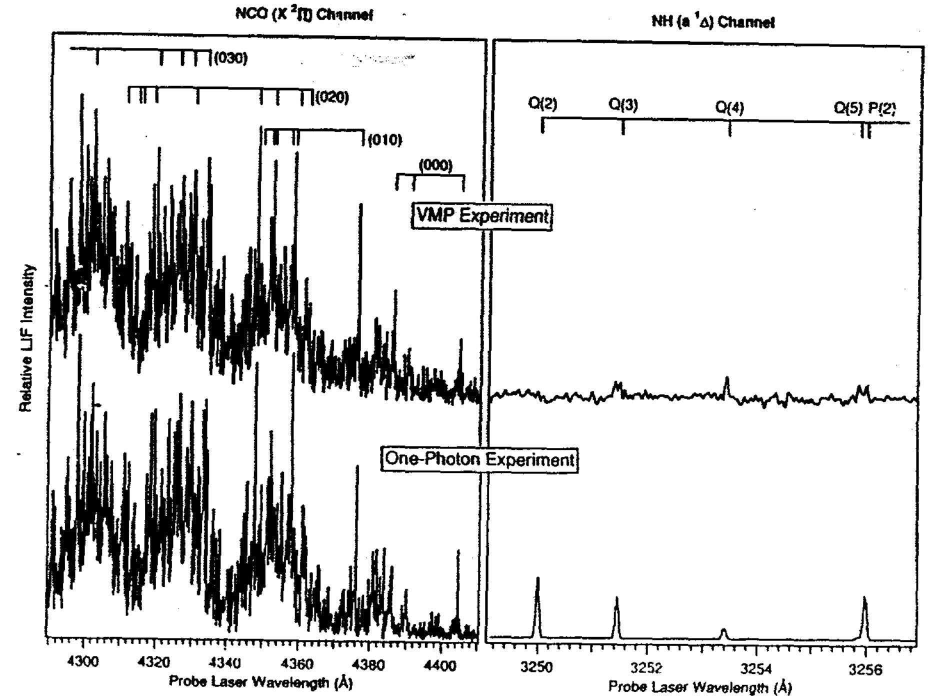


Figure 4

Vibrationally Mediated and One-Photon Dissociation: Controlling the Products

The comparison between one-photon and vibrationally mediated photodissociation for HNCO rests on isoenergetic dissociation at a total energy of 42,550 cm^{-1}, produced either by one-photon excitation at 235 nm or two-photon excitation through $4\nu_{OH}$ using a 340-nm second photon, as Figure 3 illustrates. The action spectrum obtained monitoring the NCO product, shown in the upper panel of Figure 4, is virtually identical to the absorption spectrum, showing that there is little rotational state influence on the yield in the NCO channel. The key question is the relative yields in the two different channels, one producing NH and the other NCO. Figure 5 summarizes the results of such a comparison. It contains the LIF excitation spectra for both NCO and NH produced in the vibrationally mediated and one-photon dissociation of NHCO. The lower trace on the left-hand side of the figure is the LIF excitation spectrum for the NCO fragment formed in the one-photon photolysis. The progression in the NCO bending mode, ν_2, dominates the spectrum,

Figure 5



which Renner-Teller and spin-orbit interactions complicate by producing numerous vibronic states separated by only about 500 cm^{-1} [21,22]. Both one- and two-photon dissociations form products with up to at least five quanta of bending excitation although we only show the spectrum to $v_2=3$. (The combs in the spectrum mark the band heads for the various transitions.[21]) Both spectra have very good signal levels, and the many features are transitions, not noise.

The NH($^1\Delta$) product, by contrast, has little internal energy, as the right-hand side of Figure 5 shows. The lower portion is the LIF excitation spectrum for NH($^1\Delta$) from the one-photon photolysis. We find products only in v=0 with rotational excitation only up to J=5, a result consistent with there being only 1000 cm^{-1} of energy available to the products in that channel. The most important observation is that there is virtually no NH($^1\Delta$) product in the vibrationally mediated photodissociation. The relative detection efficiency for NCO and NH is the same in the one-photon photolysis and the vibrationally mediated photodissociation. Thus, the change in the ratio of the NCO signal to the NH signal in going from the one-photon to the two-photon dissociation directly measures the change in branching ratio between the two channels resulting from excitation of the N-H stretch. This quantitative analysis supports our qualitative observation that the N-H yield is much smaller in the vibrationally mediated photodissociation that in the one-photon process. *We find more than a factor of 20 increase in the relative yield of NCO, $\Phi_{NCO}/\Phi_{NH}>20$, for HNCO with four quanta of N-H stretching excitation.* (The data actually allow us to estimate, very approximately, the branching ratio in the absence of vibrational excitation. We find that the NCO channel dominates by about a factor of 20 and, thus, that the ratio changes to 400 upon vibrational excitation.)

The important message in this result is that exciting the N-H stretch dramatically changes the product branching ratio in this tetra-atomic molecule. We know that excitation of the N-H stretch gives access to different portions of the excited state surface by changing the Franck-Condon factor and the regions sampled on the ground state surface. The N-H stretching excitation provides the oscillator strength for the vibrational overtone transition, and, although it may be substantially mixed with other vibrations, we certainly expect it to enhance transitions that have good Franck-Condon overlap with wavefunctions in the channel that breaks the N-H bond, leading to enhanced NCO formation.

STIMULATED RAMAN EXCITATION

The experiments described above on HNCO and our earlier measurements on HOD show that vibrational overtone excitation can alter the relative product yields in photodissociation. Vibrational control of photodissociation does not always require the high levels of energy provided by vibrational overtone excitation. For example, Rosenwaks, Valentini, and coworkers[23] demonstrated that stimulated Raman excitation of the O-H and O-D stretches of HOD followed by 193-nm photolysis causes one bond to break preferentially. One of the principle goals during our current period of Department of Energy support has been the application of stimulated Raman excitation to lower frequency, skeletal motions in order to expand the scope and detail of vibrationally mediated photodissociation. Indeed, we have used stimulated Raman excitation of three different fundamental vibrations in HNCO to alter its dissociation efficiency.

Raman Spectroscopy of HNCO

Our stimulated Raman excitation apparatus uses 50 mJ of 532-nm light from an injection seeded Nd:YAG laser as the first photon in the Raman excitation process and roughly the same amount of tuneable light from a dye laser pumped by the same Nd:YAG laser as the second (Stokes) photon. The bottom trace in Figure 6 shows the Raman photoacoustic spectrum obtained by scanning the wavelength of the Stokes photon to produce Raman transitions in the region of the N-H stretching normal mode, ν_1. The spectrum shows only the strong Q-branch transitions although we can observe other, weaker branches using increased sensitivity. Infrared spectroscopy identifies P- and R-branches for many of these same transitions,[20] and, using those assignments, we are able to identify many of the transitions we observe. The spacing of transitions originating in different K_a states is irregular, reflecting perturbations that are probably from aharmonic couplings.[20] The K_a=2 features are a particularly notable example of these interactions, where the coupling mixes a pair of states that we designate as a Fermi resonance pair $(\nu_1/\nu_x)_I$ and $(\nu_1/\nu_x)_{II}$. (Yamada, *et al.*[20] suggest several possible states as the perturber of ν_1. The most significant feature, in the present context, is that they almost all include bending excitation.) Stimulated Raman spectra for the antisymmetric N-C-O stretch, ν_2, and the symmetric N-C-O stretch, ν_3, have a similar irregular pattern for the K_a states. We can use the partially analyzed infrared spectra to guide our assignments for ν_2. Our photolysis results combined with our stimulated Raman excitation spectrum may help the analysis of the most poorly characterized stretching vibration, ν_3, which we observe particularly well since it is the analog of the Raman active symmetric stretching vibration in CO_2.

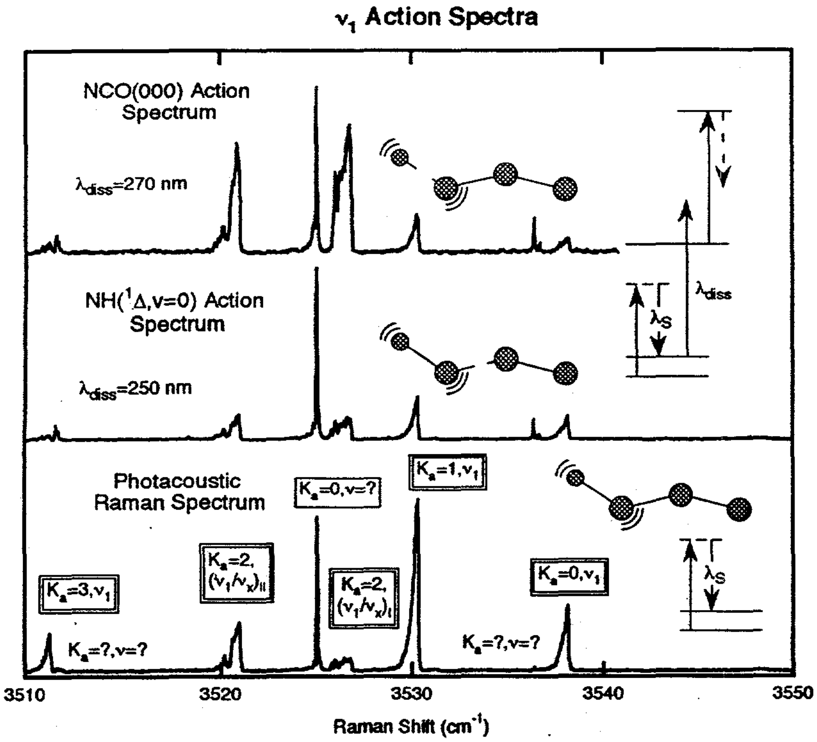


Figure 6

Raman Driven Vibrationally Mediated Photodissociation of HNCO

The top two spectra in Figure 6 show the influence that vibrational excitation of fundamental vibrations has on the photodissociation of HNCO. The upper trace is the action spectrum obtained by monitoring the NCO product from the photodissociation of HNCO at 270 nm while varying the wavelength of the Stokes photon in the stimulated Raman excitation. The key is the comparison of the action spectrum to the photoacoustic spectrum. The later reflects only the excitation efficiency, and the former reflects *both* the excitation and photodissociation efficiencies. The substantial difference in the relative intensities in the photoacoustic and action spectra point to the influence that different initial state has on the dissociation efficiency. For example, the Fermi resonance pair with K_a=2, which has relatively modest intensity in the photoacoustic spectrum, grows to become the second most prominent set of features in the NCO action spectrum. This growth reflects, at least in part, the presence of bending excitation in the vibrational eigenstates, excitation that enhances the photodissociation efficiency by increasing the Franck-Condon factor between the ground and excited electronic states. The other aspect to enhancing the dissociation is that the dissociating state on the electronically excited surface must correlate to the interrogated products, H + NCO. Apparently, the mixed vibrational state has a good combination of bending excitation, to promote the electronic excitation, and N-H stretching excitation to put the system in the exit channel for breaking the N-H bond to make NCO.

The NH action spectrum, which probes the channel making NH + CO, supports this picture. In the simplest picture, N-C stretching excitation should promote the dissociation but bending excitation should still enhance the electronic transition. Indeed, the Fermi resonant pair does not grow compared to the photoacoustic spectrum, but another transition, which we assign as a K_a=0 state with a presently unknown vibrational identity, dominates. (The shading on the Q-branch transitions gives us some hint to the identity of the vibrations. Those shaded to lower energy probably access primarily stretching states, which necessarily have smaller rotational constants, and those shaded to higher energy probably access states with substantial bending character and, hence, larger rotational constants. The very sharp features may be transitions to states that have a combination of both.) A striking feature of both the NH and NCO action spectra is the prominence of some small features that barely appear in the photoacoustic Raman spectrum. For example, the feature near 3538 cm^{-1} is just visible in the photoacoustic spectrum but is almost an order of magnitude larger in both action spectra. This transition, which we intend to identify, is special in the context of vibrationally mediated photodissociation. It is clearly a weak Raman transition to a state that promotes dissociation very efficiently.

The action spectra for the asymmetric (ν_2) and symmetric (ν_3) stretching vibrations show similar strong effects. One example is in the spectrum in the region of ν_2. A transition to a bending state, which falls in the same region, appears clearly in the photoacoustic Raman spectrum but is invisible in the NH action spectrum. The N-C-O stretching excitation promotes dissociation while the bending state does not. The insights we can obtain into the dissociation dynamics do not come from the Raman excitation spectra alone. We also monitor the NH and NCO products by laser induced fluorescence to learn about *energy disposal* in the dissociation, and, perhaps most significantly, we acquire *dissociation spectra* by varying the energy of the dissociation photon with the vibrational excitation and probe wavelengths fixed. These structured spectra have resolved rotational features, which we have used to assign the K_a quantum number of the vibrationally excited molecule in some cases, as well as vibrational structure that teaches us about the predissociative excited state. Our first molecule, HNCO, is proving to be rich and informative. More important, the combination of stimulated Raman excitation and vibrationally mediated photodissociation has given us access to entirely new classes of molecules and vibrational excitation to study.

TRANSIENT GRATING SPECTROSCOPY[8,9]

Our third major goal during this period of Department of Energy support has been the implementation of laser induced grating techniques to observe the electronic spectroscopy of highly vibrationally excited molecules. In applying laser induced grating spectroscopy (LIGS) to highly vibrationally excited water molecules, we have sorted out the details of a wavelength independent background, the "nonresonant background", that often appears in transient grating experiments at high pressure. We have also found that using laser induced grating spectroscopy to monitor electronic transitions from vibrationally excited molecules does not have the broad applicability we had hoped. Even very modest amounts of collisional relaxation of the vibrationally excited molecule can produce a thermal background signal that overwhelms that from transitions to the electronically excited state.

Buntine, Hayden, and Chandler[24] pioneered the application of LIGS to vibrational overtone excitation in polyatomic molecules. They used LIGS to monitor the vibrational excitation of water in the region of the third overtone of the O-H stretching vibration and obtained a vibrational overtone excitation spectrum by scattering 266-nm radiation from the grating formed by crossing the vibrational overtone excitation beams in a gaseous sample. The key to LIGS is the creation of a periodic modulation in a population or density, usually by crossing a pair of identical laser beams having wavelengths that are resonant with a transition in the molecule of interest. This periodic variation is the grating that scatters the probe laser light. In the first application to water[24] and in our experiments,[8,9] the vibrational overtone excitation beams form the grating and an ultraviolet light pulse scatters from it.

The $|13\rangle^-$ state of water was the target of our laser induced grating experiments. (This state is the antisymmetric linear combination of the local mode vibration having one quantum of vibrational excitation in one O-H oscillator and three in the other.) We obtained vibrational overtone excitation spectra, analogous to those of Buntine, *et al.*, by exciting the vibration with 700-nm photons in a grating configuration and probing with a 266-nm photons. The significance of the probe wavelength is that it is too long to reach the electronically excited state of water even from the $|13\rangle^-$ vibrational state. Thus, the probe beam diffracts only from the spatial variations in the index of refraction of the sample. Such an index of refraction grating is a phase grating. The other type of grating, in which the absorption coefficient of the sample varies periodically, is an amplitude grating. By choosing a wavelength that the sample does not absorb, we eliminate amplitude gratings and simplify our analysis. The most striking feature of the diffraction that we observe is that, although it increases when the vibrational overtone excitation laser is resonant with a transition in water, there is a constant component that depends on the presence of the excitation laser but *not on its wavelength.* This nonresonant background potentially limits the grating technique. Careful analysis of the temporal evolution of the signal and its pressure dependence showed that its origin is electrostriction (Brillouin scattering). The electric field of the excitation laser produces a change in the density of the sample from which the laser scatters. The essential clue to this behavior is the time evolution of the acoustical wave that the laser pulse launches through electrostriction. Miller, *et al.*[25] have observed and carefully analyzed electrostriction in liquid samples, and, carrying their analysis over to our gaseous samples at pressures up to one atmosphere, we find good agreement with our observed behavior. Figure 7 shows the resonant and nonresonant signal as a function of the delay between the pulse that creates the grating and the one that probes it. The damped oscillations are characteristic of acoustical waves in the one atmosphere total pressure sample produced either by thermal relaxation for the resonant case or electrostriction for the nonresonant case. The striking feature is that the oscillations are *twice as fast* in the nonresonant case. A result that agrees quantitatively with our prediction[8] using the analysis of Miller, *et al.*[25], as the solid lines in the Figure show.

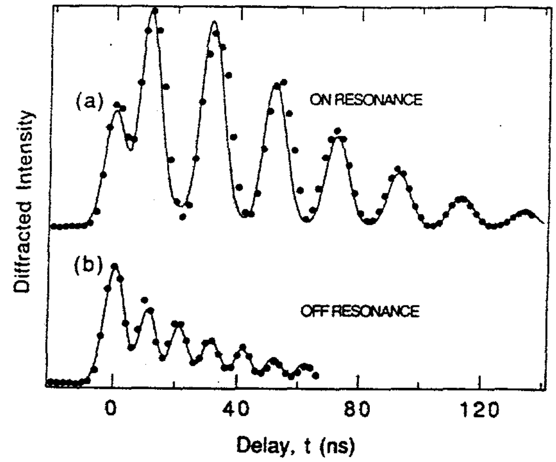


Figure 7

The most important application of laser induced grating spectroscopy for our purposes is to use the probe laser beam to obtain the electronic spectrum of a vibrationally excited molecule. Because we have previously determined the variation in the cross section for electronic excitation from the $|04\rangle^-$ state by detecting the OH product of the decomposition of the electronically excited water, we set out to test this approach on that state and then to extend it to make the same measurement on the $|13\rangle^-$ state. The nonresonant electrostriction signal is very useful in this context since it provides an internal calibration of the excitation and interrogation pulse energies at each wavelength. Careful measurements showed essentially no change in the diffraction efficiency as we changed the probe wavelength over a range where our earlier measurements found that the electronic excitation cross section changes by a factor of ten. This constancy of diffraction efficiency signals the presence of a probe-wavelength independent diffraction that, nonetheless, depends on the presence of vibrationally excited molecules. Our calculations show that even a few percent of collisional relaxation of the vibrationally excited molecules accounts for the probe-wavelength independent signal, which completely obscures the signal arising from the electronic excitation out of the vibrationally excited state. An even more interesting possibility is that the difference between the polarizability of the vibrationally excited molecules and that of vibrationally unexcited molecules produces a variation in the index of refraction between excited and unexcited regions that accounts for the diffraction we observe. Our best estimate, from calculations and analyzing our data, is that the two effects are roughly comparable.[9] For molecules with large enough electronic excitation cross sections, there are ranges of pressures where it is possible to detect the electronic excitation from a vibrationally excited molecule, but water is apparently not one of them.

SUMMARY

Vibrationally mediated photodissociation is a means of understanding and controlling molecular decomposition pathways and the nature of vibrationally energized molecules. During the last period of Department of Energy support, we have advanced our work in three areas: the use of vibrational overtone excitation to influence decomposition paths, the use of stimulated Raman excitation as the first step in vibrationally mediated photodissociation, and the use of laser induced grating spectroscopy to explore electronic transitions from vibrationally excited molecules.

Our *vibrational overtone excitation* experiments on hydroxylamine (NH_2OH) and isocyanic acid (HNCO) have revealed new dissociation dynamics as reflected in distribution of the products among their quantum states. In the case of HNCO, we can use initial vibrational excitation to alter the branching ratio between chemically distinct channels, one producing H + NCO and one producing NH + CO, by at least a factor of 20. Our *stimulated Raman excitation* measurements show its utility for exciting skeletal vibrations in the initial step of vibrationally mediated photodissociation and point to using relatively low frequency bending and stretching vibrations as a means of altering photodissociation dynamics. The *laser induced grating* measurements revealed the source of a previously unexplained background contribution and defined the limits of the applicability of laser induced grating spectroscopy in weakly absorbing systems. Our experiments showed that even very modest collisional relaxation of the initially excited molecule can produce a signal that overwhelms the small diffraction from vibrationally excited molecules. All of these accomplishments set the stage for future developments in understanding and using vibrational excitation in molecular decomposition dynamics.

REFERENCES

1. F. F. Crim, Ann. Rev. Phys. Chem. **35**, 657-91 (1984); F. F. Crim, Science **249**, 1387 (1990).

2. F. F. Crim, Ann. Rev. Phys. Chem. **44**, 397 (1993).

3. A. Sinha, M. C. Hsiao, and F. F. Crim, J. Chem. Phys. **92**, 6333 (1990); A. Sinha,M. C. Hsiao, and F. F. Crim, J. Chem. Phys. **94**, 4928 (1991); M. C. Hsiao, A. Sinha, and F. F. Crim J. Phys. Chem. **95**, 8263 (1991); A. Sinha, J. D. Thoemke, and F. F. Crim, J. Chem. Phys. **96**, 372 (1992); R. B. Metz, J. D. Thoemke, J. M. Pfeiffer, and F. F. Crim, J. Chem. Phys. **99**, 1744-1751 (1993); R. B. Metz, J. M. Pfeiffer, J. D. Thoemke and F. F. Crim, Chem. Physics Lett. **221**, 347-352 (1994).

4. J. L. Scott, D. Luckhaus, and F. F. Crim, J. Chem. Phys. (1995) (to be submitted).

5. J. L. Scott, D. Luckhaus, Steven S. Brown and F. F. Crim, J. Chem. Phys. (1995) (in press).

6. S. S. Brown, H. L. Berghout, and F. F. Crim, J. Chem. Phys. (1995) (submitted).

7. R. L. Vander Wal and F. F. Crim, J. Phys. Chem. **92**, 5331-3 (1989); J. L. Scott, and F.F. Crim R.L. Vander Wal, J. Chem. Phys. **92**, 803 (1990); V. Engel, V. Staemmler, R. L. Vander Wal, F. F. Crim, R. J. Sension, B. J. Hudson, P. Andresen, S. Hennig, K. Weide and R. Schinke, J. Phys. Chem. **96**, 3201-13 (1992); R. L. Vander Wal, J. L. Scott, F. F. Crim, K. Weide and R. Schinke, J. Chem. Phys. **94**, 3548-55 (1991); R. Schinke, R. L. Vander Wal, J. L. Scott and F. F. Crim, J. Chem. Phys. **94**, 283-8 (1991); R. L. Vander Wal, J. L. Scott and F. F. Crim, J. Chem. Phys. **94**, 1859-67 (1991).

8. D. E. Govoni, J. A. Booze, A. Sinha, and F. F. Crim, Chem. Phys. Lett. **216**, 525 (1993).

9. J. A. Booze, D. E. Govoni, and F. F. Crim, J. Chem. Phys. (1995) (to be submitted).

10. D. T. Colbert and E. L. Sibert, J. Chem. Phys. **94**, 6519 (1991).

11. R. N. Dixon and G. H. Kirby, Trans. Faraday Soc. **64** 2002 (1968).

12. A. Spiglanin, R. A. Perry and D. W. Chandler, J. Phys. Chem. **90** 6184 (1986); T. A. Spiglanin, R. A. Perry and D. W. Chandler, J. Chem. Phys. **87**, 1568 (1987); T. A. Spiglanin, R. A. Perry and D. W. Chandler, J. Chem. Phys. **87**, 1577 (1987); T. A. Spiglanin and D. W. Chandler, Chem. Phys. Lett. **141**, 428 (1987).

13. W. K. Yi and R. Bersohn, Chem. Phys. Lett. **206**, 365-368 (1993); B. Bohn and F. Stuhl, J. Phys. Chem. **97**, 4891-4898 (1993).

14. M. S. Child and L. Halonen, Adv. Chem. Phys. **57**, 1-58 (1984).

15. X. Luo, P. R. Fleming, T. A. Seckel, and T. R. Rizzo, J. Chem. Phys. **93**, 9194 (1990).

16. K. Tamagake, Y. Hamada, J. Yamaguchi, A. Hirakawa, and M. Tsuboi, J. Molec. Spect. **49**, 232 (1974); J. Tyrrell, W. Lewis-Bevan, and D. Kristiansen, J. Phys. Chem. **97**, 12768 (1993); C. Trindle and D. D. Shillady, J. Amer. Chem. Soc. **95**, 703 (1973).

17. D. Luckhaus, J. L. Scott, J. M. Pfeiffer, and F. F. Crim, (to be published).

18. Y.-Z. Han, D.-Z. Zhu, and C.-D. Zhao, Chin. J. Chem. **5**, 405 (1990).

19. D. Luckhaus, J. L. Scott, and F. F. Crim, (in preparation).

20. K. M. T. Yamada, M. Winnewisser and J. W. C. Johns, J. Mol. Spec. **140**, 353 (1990).

21. D. Patel-Misra, D. G. Sauder and P. J. Dagdigian, J. Chem. Phys. **93**, 5448 (1990)

22. R. N. Dixon, Phil. Trans. R. Soc. London A., **252**, 165 (1960); P. S. H. Bolman, J. M. Brown, A. Carrington, I. Kopp and D. A. Ramsay, Proc. R. Soc. London A., **343**, 17 (1975).

23. I. Bar, Y. Cohen, D. David, S. Rosenwaks and J. J. Valentini, J. Chem. Phys. **93**, 2146 (1990); I. Bar, Y. Cohen, D. David, T. Arusi-Parapr, S. Rosenwaks and J. J. Valentini, J. Chem. Phys. **95**, 3341 (1991).

24. M. A. Buntine, D. W. Chandler, and C. C. Hayden, J. Chem. Phys. (1995) (in press).

25. R. J. D. Miller, R. Casalegno, K. A. Nelson, and M. D. Fayer, Chem. Phys. **72**, 371 (1982).

DEPARTMENT OF ENERGY SPONSORED PUBLICATIONS SINCE 1992

Manuscripts Published, In Press, or Submitted

The Photodissociation of Water in the First Absorption Band: A Prototype for Dissociation on a Repulsive Potential Energy Surface. V. Engel, V. Staemmler, R. L. Vander Wal, F. F. Crim, R. J. Sension, B. Hudson, P. Andresen, S. Hennig, K. Weide, and R. Schinke, J. Phys. Chem. **96**, 3201 (1992).

Vibrationally Mediated Photodissociation: Exploring Excited State Surfaces and Controlling Decomposition Pathways, F. F. Crim, Ann. Rev. Phys. Chem. **44**, 397 (1993).

The Non-Resonant Signal in Laser-Induced Grating Spectroscopy of Gases, D. E. Govoni, J. A. Booze, A. Sinha, and F. F. Crim, Chem. Phys. Lett. **216**, 525 (1993).

Overtone Spectroscopy of the Hydroxyl Stretch Vibration in Hydroxylamine (NH_2OH). Jacqueline L. Scott, David Luckhaus, Steven S. Brown and F. Fleming Crim, J. Chem. Phys. (1995) (in press).

Vibrational State Controlled Bond Cleavage in the Photodissociation of Isocyanic Acid (HNCO). Steven S. Brown, H. Laine Berghout, and F. Fleming Crim, J. Chem. Phys. (1995) (submitted)

Diffraction Mechanisms in Gas-Phase Laser Induced Grating Spectroscopy using Vibrational Overtone Transitions. J. A. Booze, D. E. Govoni, and F. F. Crim, J. Chem. Phys. (1995) (submitted)

Manuscripts of Completed Work Now in Preparation

The Vibrationally Mediated Photodissociation Dynamics of Hydroxylamine (NH_2OH). Jacqueline L. Scott, David Luckhaus, and F. Fleming Crim, J. Chem. Phys. (1995) (in preparation).

The Photodissociation of Isocyanic Acid (HNCO) in Selected Vibrational States: Stimulated Raman Excitation in Vibrationally Mediated Photodissociation. Steven S. Brown, H. Laine Berghout, and F. Fleming Crim, J. Chem. Phys. (1995) (in preparation).