This progress report describes studies of the collisional energy transfer in highly vibrationally excited acetylene ($\text{C}_2\text{H}_2$). It reports state-to-state vibrational and rotational energy transfer rates and pathways in acetylene.
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Energy Transfer Dynamics in Isolated and in Colliding Highly Vibrationally Excited Molecules

Our program explores the nature of highly vibrationally excited molecules and discovers the details of their intramolecular dynamics, both for colliding and isolated molecules. We use the combination of laser preparation of a rovibrational eigenstate and laser induced fluorescence probing of the vibrationally excited molecule to identify and characterize the initially excited vibrational state, determine the state-to-state relaxation pathways and rates of the vibrationally excited molecules, and characterize of the excited electronic state in the probe step. We prepare an initial state by exciting a vibrational overtone transition with a pulsed laser and interrogate the highly vibrationally excited molecule, either immediately after excitation or after a time delay, with a second, ultraviolet laser. The excitation transition reaches a high vibrational level in the ground electronic state, and the probe transition is an electronically excited state from which we observe fluorescence. The state prepared in the first step of our recent experiments is an eigenstate. By characterizing this state, we learn about the couplings in the molecule and, hence, its intramolecular dynamics. By allowing the molecule in this state to have a collision and monitoring the change in its population or the population of the state to which it transfers energy, we are able to discover the pathways of collisional relaxation. Our primary accomplishment during
the period of this report has been an extensive study of rotational and vibrational energy transfer in highly vibrationally excited acetylene.

Our approach prepares an initial state by exciting a vibrational overtone transition with a pulsed laser and interrogates the highly vibrationally excited molecule, either immediately after excitation or after a time delay, with a second, ultraviolet laser. The excitation transition reaches a high vibrational level in the ground electronic state, and the probe transition is to an electronically excited state from which we observe fluorescence. The state prepared in the first step of our recent experiments is an eigenstate. By characterizing this state, we learn about the couplings in the molecule and, hence, its intramolecular dynamics. By allowing the molecule in this state to have a collision and monitoring the change in its population or the population of the state to which it transfers energy, we are able to discover the pathways of collisional relaxation.

Figure 1 is an energy level diagram that illustrates the excitation and detection scheme for the particular case of highly vibrationally excited acetylene probed by laser induced fluorescence. Varying the wavelength $\lambda_2$ of the probe laser generates the laser induced fluorescence excitation spectrum of the highly vibrationally excited molecule, and, by selecting wavelengths corresponding either to initially prepared or collisionally populated states, we can monitor their time evolution. For example, the Figure shows the situation in which collisional energy transfer removes molecules from the initially populated state with bimolecular rate constant $k$. This collisional depopulation appears as a decrease in the LIF signal for longer intervals between the
pulse from the vibrational overtone excitation laser ($\lambda_1$) and that from the probe laser ($\lambda_2$).

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Figure 1}
\end{figure}
Collisional Energy Transfer

The range of states we can excite and interrogate has allowed us to perform a hierarchy of collisional energy transfer measurements in which we have monitored total relaxation, state-to-state rotational energy transfer, and state-to-state vibrational energy transfer in collisions of highly vibrationally excited acetylene molecules with ground state molecules and with Ar atoms. In these experiments, we observe collisional energy transfer from single quantum states of highly vibrationally excited molecules by fixing the vibrational overtone excitation wavelength on a particular rotational transition and selecting a probe laser wavelength that induces fluorescence from the initially populated state. Varying the delay between the two lasers reveals the time-evolution of the initially prepared state. We can tune the probe laser to monitor a collisionally populated state and observe the growth in population of that final state as well. Thus, we have the means of determining state resolved rates and collisional relaxation pathways in molecules containing over 100 kJ mol\(^{-1}\) of vibrational energy, as our measurements on acetylene demonstrate.

Total Relaxation

The simplest measurement is to tune the probe laser to the initially excited state and monitor the decrease in laser induced fluorescence intensity as collisions remove molecules from the initially excited state. Figure 2(a) shows typical data for a relatively high pressure measurement (0.500 Torr), and Figure 2(b) shows them at a low pressure (0.025 Torr). In the latter case, fewer than 10% of the molecules have a
collision during the 150-ns delay between the lasers. Our ability to obtain good data

![Graph (a)](image1)

Self-Relaxation of $^{103}\gamma$, $J=20$

$k' = 12.9 \pm 0.7 \mu s^{-1}$

![Graph (b)](image2)

Self-Relaxation of $^{103}\gamma$, $J=18$

$k' = 0.74 \pm 0.14 \mu s^{-1}$

Pump-Probe Laser Delay (ns)

Figure 2

under these single collision conditions is important in the state-to-state measurements described below. The total relaxation rates that we measure for the first (2νCH), second (3νCH), and third (4νCH) C–H stretching overtone vibrations, whose energies range from 6500 to 13,000 cm⁻¹, are all the same within the uncertainty of the measurement. The rate constant of about $9 \times 10^{-10}$ cm³/molecule·s⁻¹ is about twice the Lennard-Jones collision rate constant and corresponds to an average energy transfer cross section of 120Å². Figure 3(b) shows the rate constants for these states along with the results of
pressure broadening measurements, which give the same total rate as our direct population transfer measurements. As Figure 3(a) shows, the relaxation rate constant decreases slightly with increasing initial rotation, in agreement with the pressure broadening data for the same state (2vCH). (This is the only state where there are both population transfer and pressure broadening data.) The magnitude of the cross section, its constancy with vibrational level, and its decrease with increasing rotational level all hint at the relaxation occurring mostly by rotational energy transfer. The test of this inference is a direct measurement of the fate of the excited molecules during the relaxation.
State-to-State Rotational Energy Transfer

The relatively small energy separation between adjacent rotational levels, even in a light molecule like acetylene, makes a number of energy transfer pathways available out of any single initial state. To extract state-to-state rotational energy transfer rates without an involved and, usually, model dependent kinetic analysis, we work under single collision conditions, where the increase in signal from a particular destination state reflects the arrival of population in that state directly from the initial state, without the complication of transfer through other rotational states in multiple collisions. We observe state-to-state rotational energy transfer by fixing the interrogating laser on a particular destination state and scanning the vibrational overtone excitation laser through different initial rotational states, as the left hand side of Figure 4 illustrates.

**Figure 4**

![Diagram showing state-to-state rotational energy transfer](image)
This avoids an involved calibration of probe laser sensitivity since all the transfer is into the same final state, and it produces an excitation spectrum that shows the pathways and relative rates of rotational energy transfer at a glance. The right hand side of Figure 4 shows the spectrum obtained by fixing the probe laser on J=20 of $3\nu_{CH}$ and scanning the vibrational overtone excitation laser through different rotational states. The bottom trace (c) is the photoacoustic spectrum showing the location of all of the rotational transitions to $3\nu_{CH}$ of acetylene. The middle trace (b) is the spectrum under single collision conditions and the top trace (a) shows the spectrum when there are essentially no collisions during the time between the vibrational overtone excitation laser pulse and that from the probe laser.

The intensities in the photoacoustic spectrum reflect the thermal population and absorption strength of the different initial rotational states. Those in the action spectrum (b) reflect both of those factors as well as the rate of collisional transfer out of the different initial states into the final state (in this case J=20). The action spectrum immediately shows two features of the rotational energy transfer in acetylene. One is that collisions produce only even changes in the rotational quantum number. The action spectrum contains only transitions from even rotational states into J=20, as required by conservation of nuclear spin. The second is that the transitions extend over a broad range of angular momentum states. The presence of the P(1) transition, corresponding to transfer from J=0 to J=20, shows that a single collision occasionally changes the rotational angular momentum by 20 units. Using this approach we extract quantitative values of the state-to-state rotational energy transfer rate constants for a
range of initial and final states. The resulting set of 50 rate constants permit some
detailed comparisons. In particular, the largest state-to-state rate is one-third of the
Lennard-Jones collision rate. Using detailed balance, we can obtain a complete set of
rate constants for state-to-state transfer from a particular initial state into all final states.
Summing these rate constants for rotational energy transfer and comparing them to
our measured total relaxation rate constant, shows that rotational relaxation accounts
for 70% of the total relaxation of an initial state. Thus, we infer that rapid, collision
induced intramolecular vibrational energy transfer accounts for the rest. Monitoring
different final vibrational states allows us to test this conclusion as well.

State-to-State Vibrational Energy Transfer

Monitoring a single rotational state in a different final vibrational state under
single collision conditions gives the fully state-resolved vibrational energy transfer rate
constant. The approach, shown in Figure 5,
is identical to the rotational energy transfer measurements except we fix our probe laser on a rotational state ($J_f=4$) in the $|012>-|20>^0$ vibrational state and scan our excitation laser through the different rotational states of the $|03>^-$ state. (The final vibrational state has two quanta of C-H stretch, one of C-C excitation, and two of trans-bending while the latter has three quanta of C-H stretching excitation. In normal mode notation the final and initial states are (111200) and (00100) respectively.) For a single rotational level, the vibrational energy transfer occurs in about 160 collisions. The total transfer, obtained by summing the rates into all of the final states, has a rate constant of 1.3 $\mu$s$^{-1}$Torr$^{-1}$, corresponding to only 13 collisions. This very fast relaxation appears to reflect a Fermi resonance that couples the two vibrational levels. Because we obtain the vibrational energy transfer rate for each rotational state, we also uncover a few states that relax even faster. Transfer from $J_i=16$ and $J_i=20$ is particularly efficient, probably because of particularly strong intramolecular couplings that mix the initial state with other vibrations, which themselves promote vibrational energy transfer. Our spectroscopic studies point to these special couplings for $J=16$ and 20, and the energy transfer measurements find them as well.

Future Directions

During the next year we will use our knowledge of the electronically excited state to probe the intramolecular vibrational dynamics of the isolated vibrationally
excited molecule by double resonance spectroscopy that builds on our knowledge of
the electronically excited state.

Supported Students and Post-Doctoral Associates

Students:

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Cumulative List of AFOSR Sponsored Publications (from 1989)

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