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Experimental and Theoretical Study of the Relaxation of Vibrationally Excited HF by NO and CO, K. J. Rensberger, J. T. Blair, F. Weinhold, and F. F. Crim, J. Chem. Phys. **91**, 1688 (1989).

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Energy Transfer in Highly Vibrationally Excited Acetylene: Relaxation for Vibrational Energies from 6,500 to 13,000 cm^{-1} . A. L. Utz, J. D. Tobiason, E. Carrasquillo M., M. D. Fritz, and F. F. Crim, J. Chem. Phys. (1992) (in press).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The transfer of energy in isolated or colliding molecules is a fundamental process with practical consequences for complex phenomena occurring in atmospheric chemistry, combustion, molecular lasers, plasmas, and a host of other environments containing energetic species. We have developed a technique that combines vibrational overtone excitation, to prepare highly vibrationally excited initial states, and time-resolved spectroscopic detection,

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to probe the evolution of the prepared state, for studying energy transfer in vibrationally energized molecules. We have used this approach to determine directly, for the first time, the frequencies of the three *ungerade* vibrations in the first electronically excited state of acetylene. Using this information we have characterized highly vibrationally excited states of acetylene and directly the frequencies and rotational constants of the perturbing vibrational states at these energies. Combining these spectroscopic insights on the vibrationally and electronically excited states of acetylene has allowed us to determine the energy transfer rates and pathways in the collisional relaxation of a polyatomic molecule containing $10,000 \text{ cm}^{-1}$ of vibrational energy. Rotational energy transfer is very rapid, occurring on about every other collision, but is essentially unaffected by the identity of the vibrational state in which the rotational relaxation occurs.

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TECHNICAL REPORT

We have demonstrated vibrational overtone excitation as a means of preparing highly vibrationally excited polyatomic molecules in single quantum states and have shown that laser induced fluorescence (LIF) is a means of probing the excited molecule during collisional relaxation.^{1,2,3} Because one of the central features of energy transfer in highly energized species is the nature of the vibrationally excited state itself and how its identity affects the relaxation rates and pathways, our work includes characterization of the initially excited state. *The central goal of our effort is the measurement of the rates and pathways from these excited states by monitoring both the initially prepared state and the states into which population relaxes.* Because our detection technique involves an electronically excited state, we also find it both necessary and advantageous to obtain information on the electronically excited molecule. This report describes our AFOSR sponsored research that characterizes vibrationally excited molecules, studies their energy transfer dynamics, and explores the electronically excited states we excite. It also briefly outlines our success in using multiphoton ionization as a selective detection technique for highly vibrationally excited molecules.

Our approach is to prepare an initial state by exciting a vibrational overtone transition with a pulsed laser and to 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 to an electronically excited state from which we observe fluorescence or from which we produce ions by resonant multiphoton ionization (REMPI). Figure 1 is an energy level diagram that illustrates the excitation and detection scheme for the particular

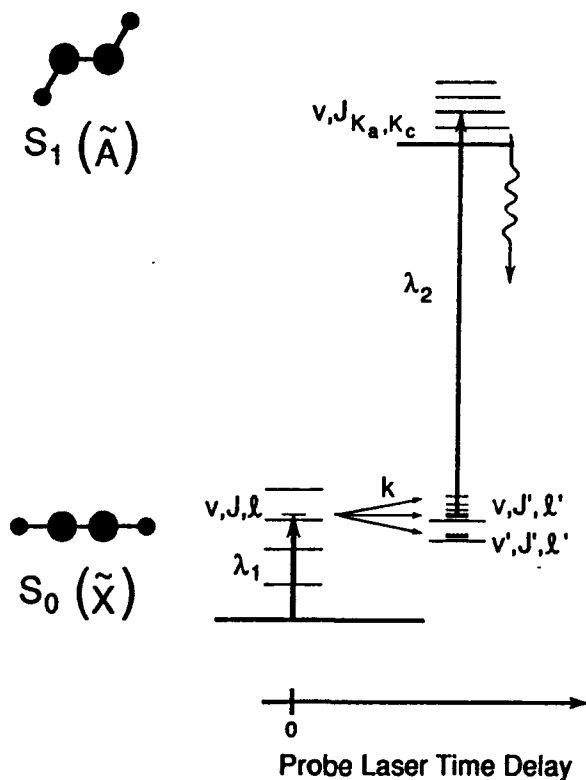


Figure 1

case of highly vibrationally excited acetylene probed by laser induced fluorescence. Varying the wavelength λ_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 (λ_1) and that from the probe laser (λ_2).

Probing Highly Vibrationally Excited Molecules: Observation of State Mixing

The intensity of a transition in the laser induced fluorescence excitation spectrum depends on the Franck-Condon overlap integral between the highly vibrationally excited, ground electronic state and the particular rovibrational level of the excited electronic state to which the probe laser is tuned. One of the keys to our measurements, in which the vibrational overtone transition excites fewer than 10^{-5} of the molecules, is efficient discrimination against vibrationally unexcited species. As Figure 1 illustrates, we use probe laser photons that have only enough energy to reach the few lowest levels of the electronically excited state in transitions from highly vibrationally excited molecules. Because these photons are unable to excite molecules from low vibrational levels of the ground state, our detection scheme favors "off-diagonal" probe transitions in which a large geometry change produces good Franck-Condon factors between the vibrationally excited molecule in the ground electronic state and the vibrationally unexcited molecule in the excited electronic state. The Franck-Condon factors for off-diagonal transitions of vibrations involving light atoms are often small, since the bond lengths change little upon electronic excitation, but those for lower frequency vibrations can be larger. The amount of the bright zero-order state $|s\rangle$ in an eigenstate determines its vibrational overtone excitation probability, but, in the systems we study, the amount of a dark zero-order state $|l\rangle$ controls the intensity of its transitions in the probe step. This situation provides an experimental window on the nature of the initially prepared state in frequency-domain experiments. The intensity in the probe spectrum reflects the extent to which the eigenstate resembles the zero-order states that have favorable Franck-Condon factors in the electronic transition.

Our measurements on acetylene illustrate the means by which we probe highly vibrationally excited states in the frequency domain.^{1,4} The lower portion of Figure 2 is the

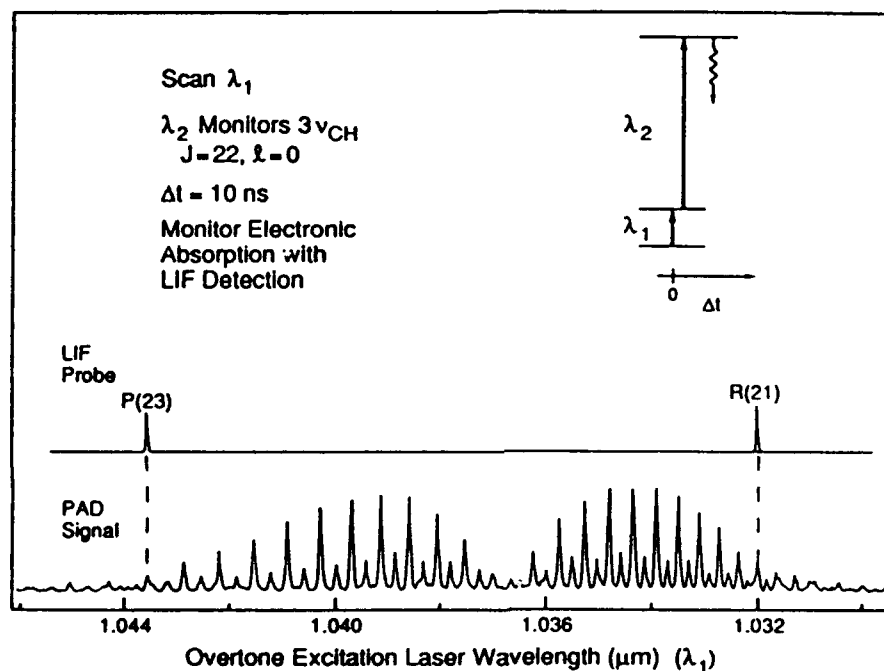


Figure 2

photoacoustic absorption spectrum for acetylene showing transitions to single rotational states in the region of the second overtone of the C-H stretching vibration ($3\nu_{CH}$). (The spectrum also contains small contributions from other vibrational transitions. We can simulate the complete spectrum using known band centers and rotational constants for C_2H_2 .)⁵ The upper trace in the figure illustrates selective detection. In this case, the probe laser is tuned to an electronic transition that interrogates only those highly vibrationally excited molecules in $J=22$, which we can identify because we have analyzed the electronic spectroscopy as

described below. The action spectrum obtained by scanning the vibrational overtone excitation wavelength shows only transitions that populate $J = 22$ of the selected vibrational state since we are selectively interrogating that level. This is the key to the state resolution in our experiment. Having identified the electronic transitions for the highly vibrationally excited molecule, we can probe the populations of the rovibrational state we choose.

The complementary measurement is to set the wavelength (λ_1) of the vibrational overtone excitation light, which comes from stimulated Raman scattering of pulses from a Nd:YAG/dye laser in H_2 , to a particular rotational line, such as the R(17) transition. Scanning the wavelength (λ_2) of the frequency-doubled, excimer/dye probe laser produces the LIF excitation spectrum for $C_2H_2(3\nu_{CH})$ shown in Figure 3. We obtain these data at low total pressures (≈ 50 mTorr) and short delays (≈ 10 ns) between the laser pulses to ensure that we observe only the initially prepared state.

The sharp features in the LIF excitation spectrum are transitions between single rotational states in the highly vibrationally excited molecule and those in the electronically excited molecule. Because the ground electronic state ($X^1\Sigma_g^+$) of acetylene is linear and the excited electronic state (A^1A_u) that we access is *trans*-bent,⁶ the *trans*-bending vibration has particularly good off-diagonal Franck-Condon factors that lead to progressions in this vibration in resolved emission spectra.⁷ In addition, the increased length of the carbon-carbon bond in the A state produces a similar progression in that stretching vibration. Thus, we expect that these are the two zero-order states $|l\rangle$ that lead to the largest signal in the probe step, and we infer that the states we observe must possess significant *trans*-bending or C=C stretching character.

The selectivity of our detection scheme allows us to probe state mixing by observing eigenstates that have very little bright ($|s\rangle$) state character but a large component of dark ($|l\rangle$)

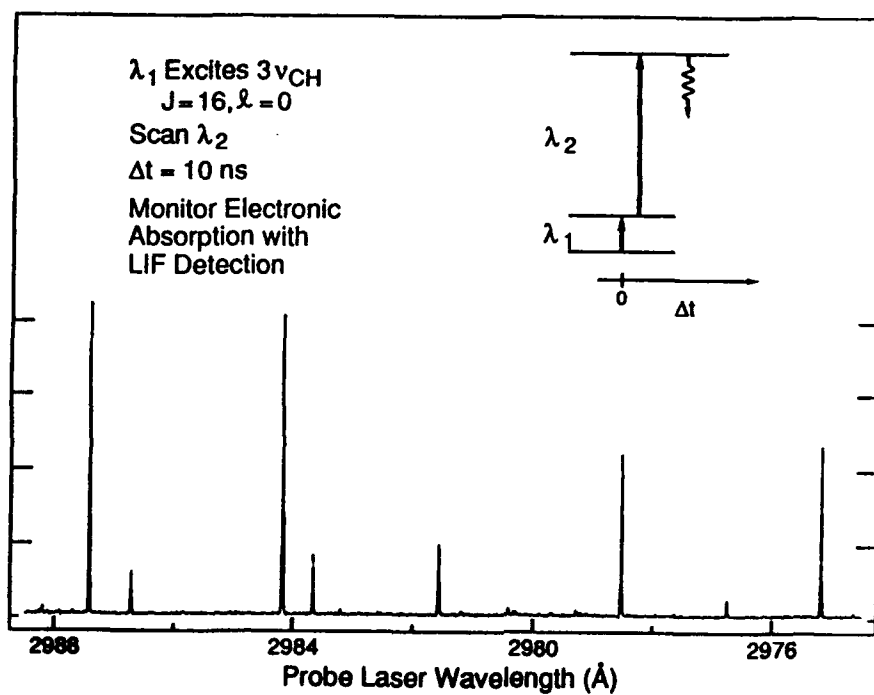


Figure 3

state character. Transitions to these eigenstates are too weak to be observed in absorption, since they contain so little of the bright zero-order state, but they are prominent in our two-photon detection scheme. Figure 4 illustrates the trade between excitation and detection efficiency in our experiments. The upper panel shows a portion of the photoacoustic vibrational overtone absorption spectrum in the region of the R(21) transition to the vibrational eigenstate that contains substantial bright state character as a broken line and the laser induced fluorescence signal obtained with the probe laser tuned to interrogate that same state as a solid line. The R(21) features are the same, but the LIF action spectrum does not have the R(22) transition (on the right) or the hot band transition (on the left) since we are interrogating only $J=22$ states with our probe laser. The lower panel shows another

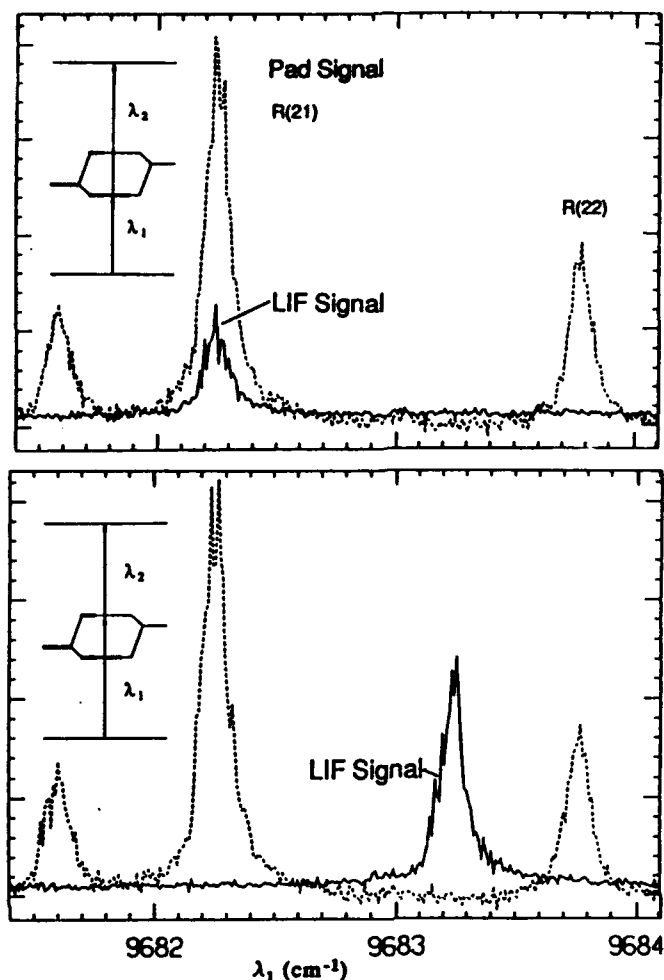


Figure 4

photoacoustic spectrum (broken line) taken simultaneously with an LIF action spectrum (solid line) for which the probe laser is tuned to the $J=22$ rotational state of a different vibrational state that has mostly dark state character. The transition to this mostly dark eigenstate occurs at a different wavelength than the transition to the mostly bright state that appears in the photoacoustic spectrum. The energy level diagram in the figure illustrates the situation schematically. In absorption we see only one of the mixed pair of states, but in the LIF action spectrum, which is sensitive to dark state character, we can see both. (We are confident of the assignments because we have independently characterized the electronic spectroscopy, and we obtain equivalent results using the P(23) transition to reach the same, $J=22$,

vibrationally excited state. The locations of the probe transitions for the mostly dark eigenstates come from a two-dimensional search.)

The separation between the mostly bright and mostly dark eigenstates depends on the rotational state since they have different rotational constants. The separation scales as $\Delta B J(J+1)$ where ΔB is the difference in rotational constants of the two states, and Figure 5 is a plot of the energy difference for pairs of states as a function of $J(J+1)$ from which we can extract the difference in the rotational constants. Each of the three lines in the figure comes from a different perturbing vibrational state. (The isolated point on the left is from a

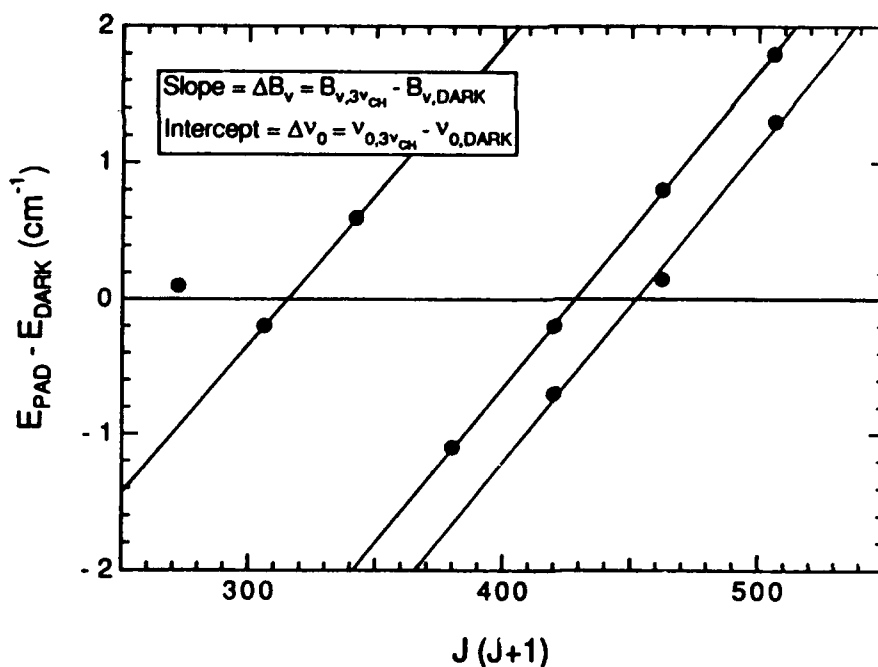


Figure 5

fourth interaction.) The rotational constants for the mostly dark eigenstate are consistently

larger than for the mostly bright eigenstate that contains largely C-H stretching character. The smaller moment of inertia associated with the larger rotational constant is consistent with the dark state containing significant amounts of *trans*-bending excitation, which lowers the moment of inertia.

Collisional Energy Transfer

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.^{2,3}

Figure 6 shows the LIF signal from an initially populated vibrational state of $\text{C}_2\text{H}_2(3\nu_{\text{CH}})$ having $J = 20$ for increasing delay times between the excitation and probe lasers. Fitting the decrease as a single exponential provides a pseudo-first order decay constant from which we extract the bimolecular relaxation rate constant for a single rotational state. Measurements on several different rotational states ($J = 8, 17, 18, 20$) show that C_2H_2 molecules containing 9600 cm^{-1} of vibrational energy relax at about 1.5 times the Lennard-Jones collision rate. With rare gases the rate is only about one-third smaller, comparable to the Lennard-Jones collision rate, indicating that the relaxation is not *intermolecular* vibrational energy transfer,

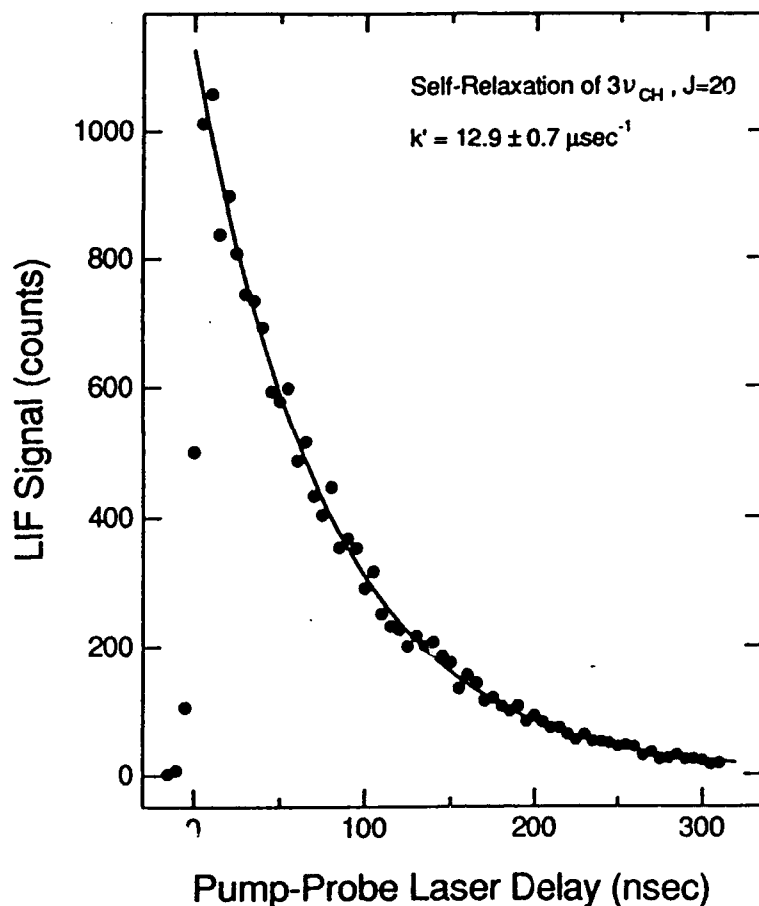


Figure 6

since it is relatively insensitive to the internal structure of the partner, but is either *intramolecular* or rotational energy transfer. By monitoring other states, we are able to observe the relative population growth into various final states to demonstrate that rotational relaxation is the dominant relaxation path, with $|\Delta J| = 2$ transitions accounting for almost half of the total relaxation rate constant. We observe changes in rotational quantum number that are as large as $\Delta J = 8$. There is also a small, but observable, amount of *intramolecular* vibrational energy transfer during rotational relaxation. We can explore this process in substantive detail now that we have unravelled the initial states and can prepare nearly isoenergetic states with rather different vibrational character.

Vibrations in the Electronically Excited State

The involvement of an electronically excited state in our detection scheme creates both a complication and an opportunity. In some cases, we must sort out new electronic spectroscopy to completely analyze our measurements, but we have an opportunity to observe vibrations in the electronically excited state that are often inaccessible. Two features of our experiment make this possible. One is that the excitation in the probe step (see Figure 1) comes from states in a molecule that contain far more vibrational energy than available in a room-temperature sample. Thus, transitions that appear only as very weak hot-bands in a conventional experiment might be quite strong in our measurement. The other differentiating feature is that we reach the electronic state by a two-photon process, one for vibrational overtone excitation and one for the subsequent electronic excitation. In molecules of high symmetry, this makes available a set of vibrations of the excited state that are unobservable in the one-photon electronic excitation. Because the first transition is solely on the ground electronic surface, we can easily perform two-photon measurements on the lowest electronically excited state. The excitation goes through a real state of known vibrational symmetry and, hence, reaches a limited subset of the available vibrations in the excited state.

Figure 7 illustrates this aspect of our technique for acetylene. The first excitation from the vibrationally unexcited molecule prepares a vibration of B_u symmetry in the A_g ground electronic state. (The ground Σ_g^+ electronic state is A_g in the reduced symmetry of the C_{2h} point group of the bent electronically excited state.) In the absence of collisions, the second transition reaches a ungerade vibration in the A_u electronically excited state, compared to one-photon transitions that can excite only gerade vibrations. In the absence of Coriolis coupling,

Symmetry Allowed Transitions

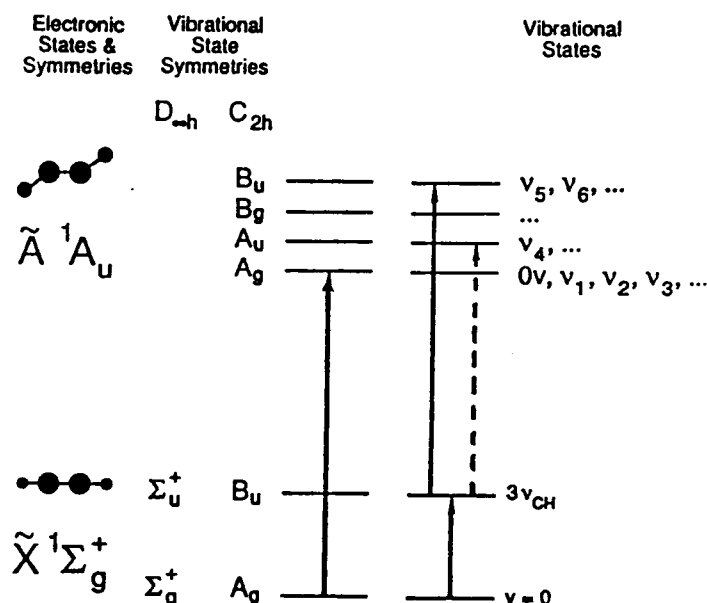


Figure 7

which can mix states of A and B symmetry, the second photon excites only B_u vibrations (the antisymmetric C-H stretch ν_5 and the *cis* bend ν_6), but Coriolis coupling can mix the states to permit transitions to the A_u vibration (the out-of-plane torsion ν_4). Our approach allows us to unravel the complicated spectrum and directly observe these three vibrations for the first time. This not only provides new information on the electronically excited state but also is also the basis of our vibrational analysis in the state mixing experiments. Exploiting the J selection of our double resonance experiment, we have analyzed the spectra to obtain vibrational frequencies of 760, 2858, and 771 cm^{-1} for the ungerade vibrations, ν_4 , ν_5 , and ν_6 .⁷ We obtain rotational constants and, through the Coriolis coupling analysis, coupling constants for the electronically excited state. The antisymmetric C-H stretching vibration ν_5

has never been observed, and our measurement is about 400 cm^{-1} smaller than the *ab initio* prediction. The values for ν_4 and ν_6 differ by about 80 cm^{-1} from assignments based on a two-quantum deperturbation analysis in resolved laser induced emission experiments.³⁸ Direct observation of these states is an important ancillary benefit of using laser induced fluorescence to probe highly vibrationally excited molecules. Our detection scheme, which requires extensive information about the electronically excited state from independent spectroscopic studies, can also add to that body of knowledge.

Multiphoton Ionization Detection

The experiments on acetylene demonstrate the utility of our approach using vibrational overtone excitation and laser induced fluorescence detection to explore the dynamics of highly vibrationally excited molecules. A number of molecules are likely candidates for LIF detection, but we have also developed a scheme that potentially broadens the scope of our measurements. We have used resonant multiphoton ionization to detect highly vibrationally excited ammonia, $\text{NH}_3(3\nu_{\text{NH}})$, following its preparation by vibrational overtone excitation. The selectivity in this detection technique again depends on the electronic transition and favorable Franck-Condon factors, but we detect the ion formed by the subsequent absorption of additional photons. This technique has been demonstrated for lower levels of excitation,^{8,9} but implementing it for the small fraction of excited molecules that we prepare requires considerable care to avoid an overwhelming background signal. Using a well prepared and maintained high vacuum system and very pure gases allows us to observe the highly vibrationally excited molecules quite well.

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