Enhanced instability of extreme motion states in propyne: Lifetimes of overtone versus isoenergetic combination states

Joan E. Gambogi, Jozef H. Timmermans, Kevin K. Lehmann, and Giacinto Scolès
Department of Chemistry, Princeton University, Princeton, New Jersey 08544

(Received 28 July 1993; accepted 30 September 1993)

In contrast to the theoretical and experimental evidence for small polyatomic molecules, we demonstrate that in the low overtone region of propyne ($\nu_{CH}=2-4$) pure overtone states are more perturbed by intramolecular vibrational energy redistribution (IVR) than some nearly isoenergetic combination states. We argue that for larger molecules, this is the expected behavior when the combination states have their energy delocalized over modes that interact only weakly by direct low order anharmonic resonances.

INTRODUCTION

Extreme motion states are nonstationary vibrational states of polyatomic molecules that have all the energy localized in a single local or normal mode. Hose and Taylor\(^1\) predicted that the rate of intramolecular vibrational energy redistribution (IVR) will typically be much slower for extreme motion states than for other nearly isoenergetic states. Furthermore, they predicted that extreme motion states, with excitation localized in a CH stretching vibration, would be the most stable of all given their strong adiabatic decoupling from other modes. Brumer and Shapiro\(^2\) reached the same conclusion that adiabatic separation should enhance the stability of extreme motion states. Choi and Moore\(^3\) noted an experimental demonstration of this prediction in the stimulated emission pumping (SEP) spectrum of HFCO. They found that states with all the excitation localized in the out-of-plane vibration showed substantially fewer perturbations, and had longer dissociation lifetimes than nearby states with excitation energy spread between the out-of-plane mode and the CO stretching mode. Another example of this effect is found in the spectrum of acetylene. The visible overtone bands of acetylene show well-defined rotational structure, perturbed occasionally by weak heterogeneous perturbations.\(^4\) In contrast, the SEP spectrum observed in the same energy region, which puts excitation in both the trans-bend and the CC stretching mode, shows highly perturbed spectra with density of observed states on the order of the calculated full density of vibrational states.\(^5\) Recent work by the MIT group\(^6\) also shows that the SEP spectra of acetylene are less perturbed when all of the excitation is initially localized in the trans-bending mode (an extreme motion state). Thus, excitation of the extreme motion states with excitation in either CH or trans-bending modes leads to greatly suppressed IVR. The existence of a firm theoretical basis, supported by several experimental verifications, suggests that the enhanced stability of extreme motion states may represent a common phenomenon in the spectra of polyatomic molecules.

In this Communication we report clear evidence that the excitation of the extreme motion states of the acetylenic CH stretching mode of propyne leads to increased instability (i.e., an increased IVR rate) as compared to states nearby in energy with the energy distributed in more than one normal mode (combination bands). The longer lifetime that we have observed for combination states may be typical for larger molecules that have many vibrational modes and where the initial excitation is spread over "distant" modes. We expect this case to occur in the limit when the modes initially excited are effectively uncoupled, for then each mode relaxes independently at a rate characteristic of a lower energy. A natural question to ask, then, is how the molecular dynamics change from one limit to the other, i.e., when do we expect "small molecule" behavior with extreme motion states most stable, and when do we instead expect "large molecule" behavior with extreme motion states among the most unstable?

INFORMATION OBTAINED FROM THE SPECTRUM OF PROPYNE

In this section, the spectrum of propyne is discussed in the regions of the two, three, and four quanta of CH stretching vibrations, and the relative extent of IVR of pure overtone (extreme motion) states vs that of combination bands is compared in each region. For the three and four CH quanta regions, the densities of states are high enough that we can properly talk about an IVR lifetime, and this will be the principal quantity that we will use to compare the different spectra. For the two quanta region, the density of states is too small relative to the average coupling matrix element to give a true decay of the bright state following excitation, so in a rigorous sense there is no IVR following excitation of the bright states. Still, IVR is driven by couplings between the bright state and the bath, and it is still possible, even in the two quanta region, to compare the mean coupling matrix elements of the bright and bath states in this "sparse molecule limit."

We have studied the overtone spectrum of propyne using the method of optothermal detection of the energy deposited in a collimated molecular beam upon absorption of highly monochromatic infrared IR laser radiation.\(^7\) The spectrometer used was described previously.\(^7\) A few years ago, we studied the first overtone band of the acetylenic CH stretch ($2\nu_1$) by direct excitation with an F-center laser tunable in the 1.5 $\mu$m spectral region.\(^8\) The results of that study will be reported in detail in an-
other paper, but the principal conclusion is that most of the \( K > 0 \) lines in the spectrum are perturbed by a few (one to three) background levels whose vibrational energy is distributed in other modes of the molecule. The \( K = 0 \) lines are unperturbed. Both level spacings and the distribution of coupling matrix elements suggest that the bath states are only weakly mixed with each other, i.e., at most a few normal mode basis functions dominate each eigenstate. The experimentally determined density of perturbers is slightly higher than the calculated density of the vibrational states that have the correct \((A_1)\) symmetry to interact through anharmonic interactions.

Recently, Go, Cronin, and Perry\(^7\) used a double resonance method, based upon IR–IR population-modulated absorption, to observe both the \( 2\nu_1 \) and \( \nu_1 + \nu_6 \) bands of propyne (\( \nu_6 \) is the methyl CH asymmetric stretching mode). Their results on the \( 2\nu_1 \) band largely confirmed our previous analysis, including finding a proposed doorway state that appears to act as a virtual intermediate state for the IVR. They found that the \( \nu_1 + \nu_6 \) state is much less perturbed than \( 2\nu_1 \). No perturbations were observed for \( K = 0 \), and for \( K > 0 \), the average coupling matrix element was found to be \( 6.6 \times 10^{-4} \text{ cm}^{-1} \) compared to \( 19.5 \times 10^{-4} \text{ cm}^{-1} \) for the \( 2\nu_1 \) band. To explain the difference, Go et al. pointed out that \( \nu_1 + \nu_6 \) is lower in energy than \( 2\nu_1 \). However, the energy difference is small (6315.8 vs 6568.2 \text{ cm}^{-1} \) and the density of vibrational states of \( E \) symmetry (than can couple with the \( \nu_1 + \nu_6 \) state via anharmonic interactions) is about 15 states/cm\(^{-1} \), which is about 50% higher than the density of vibrational states that can mix with the \( A_1 \) symmetry \( 2\nu_1 \) state. Additional support that the \( \nu_1 + \nu_6 \) state is less perturbed not simply because it is lower in energy is found in the spectrum of the \( 2\nu_6 \) band of propyne near 5920 cm\(^{-1} \), \( \rho(A_1) = 6.1 \text{ states/cm}^{-1} \) that we have recently observed. While the analysis of this band has just begun and will be reported at a later time,\(^{10} \) it is obvious by inspection that its transitions are more heavily perturbed than those of either \( \nu_1 + \nu_6 \) or \( 2\nu_1 \), thus showing that the \( \nu_1 + \nu_6 \) combination band is more stable than either of the two extreme motion states, \( 2\nu_1 \) and \( 2\nu_6 \) that bracket it in energy. The modes \( \nu_1 \) and \( \nu_6 \) interact very weakly, as evidence by the small value of \( X_{16} = -0.11 \text{ cm}^{-1} \) that can be deduced from the energy of the \( \nu_1 + \nu_6 \) band.

In our laboratory, we have recently implemented an IR–IR double resonance method. We use a 3 \( \mu \text{m} \) F-center laser to pump a single \( J,K \) level in the \( \nu_1 \) fundamental, and then further excite the molecules to the 9700 cm\(^{-1} \) region \( \rho(A_1) = 150 \text{ states/cm}^{-1} \) by using a 1.5 \( \mu \text{m} \) F-center laser. Complete details of the experiment will be published at a later time along with a thorough analysis of the \( 3\nu_1 \) absorption band of propyne.\(^{11} \) This band is in a region in which propyne lacks transitions from the ground vibrational state and so any transitions seen when modulating the intensity of the 1.5 \( \mu \text{m} \) radiation have as their lower state the single \( J,K \) level populated by the first pumping step. As a result, the assignments in the spectra are automatic since the spacing of the \( P \) and \( R \) branch transitions from a single \( J,K \) is much larger than the width of the clump of transitions that arise from a single rotational level of the \( 3\nu_1 \) state. Figure 1(a) shows spectra for the \( J_K = 0_6 \) and \( 4_0 \) upper states. The observed spectra are highly fractionated, with the density of lines increasing proportionally.

![FIG. 1. Sequential IR/IR double resonance in 1 propyne. Figure 1(a) shows the \( 3\nu_1 \) band, \( J'=0 \) and 4, where all the lines shown belong to the transition. Shown in Fig. 1(b) is the combination band (\( \nu_1 + 2\nu_6 \), \( J'=0 \) and 4. The lines due to this band are marked with an * and the other lines belong to the \( 2\nu_6 \) band. The energy scale reflects the energy of the scanning laser.](image-url)
to \((2J+1)\) until the dilution of the oscillator strength results in a significant fraction of the lines being lost in the noise. The lifetimes computed from the individual \(JK=0\) features\(^{12}\) are all close to 310 ps, independent of \(J\). For \(K=1\), the signal level is substantially less, likely because of increased fractionation, and the lifetimes appear to be near 210 ps, again largely independent of \(J\). Because of the reduced signal-to-noise ratio of the \(K=1\) spectra, this value should be considered as an upper bound to the real lifetime.

Using the same technique, we have also observed the nearly isoenergetic \(\nu_1+2\nu_3^0\) combination band of propyne [Fig. 1(b)]. Here, the double resonance spectrum occurs in the same region as the single resonance \(2\nu_3^0\) band, but comparison of the spectra with and without the 3 \(\mu\)m pump laser leads to unambiguous assignment of the double resonance features. Transitions to the \(J_K=0_0\) and 1_0 upper states are single lines, while transitions to states 2_0 through 5_0 and 1_1 through 4_1 are each split into narrow clumps of three to six lines, with no apparent systematic increase in the number of lines with \(J\) or \(K\). In each of these cases, the calculated population in the bright state decays to \(e^{-1}\) in a time between 1.2 and 3.2 ns, i.e., four to ten times longer than that found for the 3_1 band. Because of the small number of eigenstates in each clump, strong recurrences follow these decays. The change in density of states, from \(\rho(A_1) = 107\) states/cm\(^{-1}\) for \(\nu_1+2\nu_3^0\) to 150 states/cm\(^{-1}\) for 3_1, is too small to justify the differences in either the extent of state mixing or in the bandwidth over which the spectral intensity is distributed. Thus, the observed eigenstate-resolved spectra show that \(\nu_1+\nu_3\) as reported by Gin et al.\(^{9}\) is less perturbed than the nearly isoenergetic extreme motion states 2_1 and 2_0, and that \(\nu_1+2\nu_3^0\) is even more dramatically less perturbed than 3_1. These results strongly argue that these extreme motion states in propyne have the greatest instability.

An examination of previous, lower resolution studies support the view that this trend continues at the level of the 4_1 band as well. Hall\(^{13}\) and later both Crofton et al.\(^{14}\) and Lin, Boras, and Reilly,\(^{15}\) observed spectra in the 4_1 region and found that most of the absorption strength is in an unresolved 12 713 cm\(^{-1}\) band, near the energy expected for the 4_1 band based upon a Birge-Sponer plot for all the \(n\nu_1\) bands. The lack of \(J\) resolution in this band suggests that the individual \(JK\) transitions split into clumps whose widths exceed the 2B (0.57 cm\(^{-1}\)) spacing between expected rotational lines in this parallel band of a prolate symmetric top. There is a weaker band, 50 cm\(^{-1}\) higher in frequency 3_1+\(\nu_3+\nu_5\), that displays a well resolved J structure. Lin et al.\(^{16}\) simulated the spectrum and extracted an upper limit for the homogeneous width of 0.05 cm\(^{-1}\). This combination band, therefore, has a lifetime at least one order of magnitude longer than the nearby 4_1 band. While using the lack of rotational resolution of the 4_1 band to obtain an upper bound on the lifetime should be viewed with caution, these results are consistent with what we have found for the lower energy states.

Additional experimental evidence for the existence of slow relaxation rates of combination bands has been observed for other terminal acetylenic compounds. In the 2\(\nu_1\) spectrum of \((CD_3)_3SiCH\(_3\)\(^{17}\) we observed a nearly Lorentzian shaped \(Q\) branch centered at 6520 cm\(^{-1}\). This \(Q\) branch has a full width of 1100 MHz, from which we deduced an IVR lifetime of 140 ps. But at slightly lower energy, shifted by 0.084 and 0.12 cm\(^{-1}\), we found two weak but narrow features with full width at half maximum of 170 and 470 MHz, respectively. The natural interpretation of these features is to assign them as \(Q\) branches of two combination bands that gain some intensity via mixing with the 2\(\nu_1\) band. Their narrow widths imply that the IVR lifetimes of these states are in excess of 930 and 340 ps, respectively, far longer than that of the 2\(\nu_1\) state. Previously, we did not have confidence in this interpretation because it contradicted our expectation that IVR rates for combination states should be faster than for extreme motion overtones bands. With the example provided by propyne, this no longer looks like an anomalous result. Lastly, recent work on diacetylene in the \(\nu(CH)=3\) region has shown that the band with local mode assignment \((3,0)^+\) (three quanta in one CH bond) is more fractionated than the higher energy band \((2,1)^+\).\(^{18}\)

**DISCUSSION AND A GENERAL MODEL**

The previously proposed enhanced stability of extreme motion states can be understood by both classical and quantum pictures of the interaction of modes coupled by strong anharmonic interactions. Hose and Taylor\(^{19}\) were led to their proposal by the common observation that in classical trajectory calculations on few mode systems, the last regions of quasiperiodic motion to survive are often localized around periodic orbits that have all the action localized in a well-defined mode. Quantum states localized in these quasiperiodic regions would decay via tunneling over an adiabatic barrier into the chaotic regions of phase space. The extreme motion quantum states have the longest distance to tunnel, and thus would be expected to have the longest lifetimes. If one looks at a purely quantum picture for an anharmonic resonance between two modes, one finds that the coupling matrix elements are smallest when one of the modes has zero quanta of excitation. For a Fermi resonance (2 to 1) between modes \(\nu_j\) and \(\nu_\omega\), the state \((N,0)\) is coupled to \((N-1,2)\) by a matrix element proportional to \(\sqrt{N}\), while the state \((\frac{1}{2}N,0)\) is coupled to \((\frac{1}{2}N-1,N+2)\) by a matrix element proportional to \(\sqrt{N(N+1)}(N+2)\sim N^{1.5}\). For higher order anharmonic interactions, the matrix elements grow faster as quanta are distributed among the interacting modes. The larger the coupling matrix elements, the faster the expected rate of IVR.

Recent theoretical calculations by Stuchebrukhov and Marcus\(^{19}\) have demonstrated that, in several of the terminal acetylene molecules that we have been studying, the IVR rate is dominated by cubic and quartic interactions, which only directly couple states differing by at most three and four quanta, respectively. Because the density of states observed in our spectra is always close to the calculated density of states, we know that essentially every mode
throughout the molecule must be active in receiving excitation in the relaxation. In the Stuchebrukhov and Marcus model, however, the calculated lifetime is independent of the exact nature of the states that receive the vibrational excitation. Instead, the lifetime is determined by the coupling strength and the positions of the levels in the first several tiers of states (each tier representing levels coupled to the bright state at a given order in perturbation theory) and not the total density of states.

The importance of low order of resonances for the relaxation shows why the arguments for the stability of the extreme motion states, which are valid for smaller molecules, are not relevant when the excitation is shared between distant parts of a molecule. Anharmonic coupling between modes is normally expected to be small except when these modes share motion in at least one common atom (though exceptions could exist for conjugated systems, for example). Exciting delocalized combination bands will increase the coupling matrix elements between these modes, but given the small size of these coupling terms, it is expected that these will have a negligible contribution to the IVR rate. Instead, each model in the combination band would be expected to relax independently, through its own chain of tiers determined by the important near resonances for each mode. In this relaxation, the amplitude of each mode of the combination band is typically lower and thus more harmonic than for an isoenergetic extreme motion state, and therefore the anharmonic coupling matrix elements will be less for the combination band. All else being equal, as far as the distribution of levels in the tiers is concerned, the relaxation rate of the combination band will then be smaller.

The tier model predicts, and our experiments have confirmed, substantial variations in the rate of IVR upon subtle changes in the molecule and excitation, due to nearly random changes in the resonance detuning of levels in the first several tiers. On the other hand, in our experimental work on terminal acetylene compounds we have seen evidence of clear trends in the changes of IVR rate with chemical substitution. These are most likely due to systematic changes in the strength of resonances and in the coarse frequency distribution of modes. The enhanced stability of delocalized combination bands should be a similar change in the average rate of IVR, about which substantial fluctuations are still expected.

If this enhanced IVR rate for extreme motion states is common in larger molecules, it has important implications for statistical theories of unimolecular reactions. Spectroscopic experiments initially populate states much closer to extreme motion states than the highly delocalized states that dominate the phase space of a polyatomic molecule at chemically interesting energies. Up to now, it was largely assumed that the IVR rates measured for such localized states represented a lower limit for the rates of IVR of a molecule with delocalized excitation. If extreme motion states that are directly populated by a spectroscopic pumping process decay into combination states that are even longer lived, then the time required for IVR to thermalize a molecule is increased. This improves the possibility of observing nonstatistical effects since reactions need not be as fast to compete with IVR.

ACKNOWLEDGMENTS

We thank Eric Kerstel for assistance and Professor James Reilly for providing unpublished details of their simulation of the propyne \(3\nu_1 + \nu_3 + \nu_5\) spectrum. This work was supported by the National Science Foundation.

12Lifetimes represent population decay of the localized "bright" state which is assumed to carry all of the transition strength. They are determined as the 1/e decay point of the Fourier transform of the spectral autocorrelation function which is calculated using the formula given by K. F. Freed and A. Nitzan, J. Chem. Phys. 73, 4765 (1980).
16Z. Lin, K. Boras, and J. P. Reilly (private communication).