

# INTRAMOLECULAR VIBRATIONAL REDISTRIBUTION ON THE NANOSECOND TIME SCALE: $\nu_1$ AND $2\nu_1$ SPECTRA OF SUBSTITUTED ACETYLENE COMPOUNDS

K.K. LEHMANN, B.H. PATE AND G. SCOLES

Department of Chemistry  
Princeton University  
Princeton, NJ 08544-1009 USA

**ABSTRACT.** Intramolecular vibrational energy redistribution (IVR) continues to be a subject of wide interest to chemical physics. Most previous work has found that IVR is rapid (on the time scale of 10 psec or less) whenever the density of ro-vibrational states is on the order of 100 states per wavenumber or greater. We have been studying IVR in a series of substituted acetylene compounds using optothermal detection of the acetylenic C-H stretch or its first overtone absorption spectrum in a cold (few degrees K), collimated molecular beam. This gives a resolution of 10 MHz, which allows us to study IVR on times scales up to 30 nsec. Our results show that these molecules undergo statistical IVR (energy spreads over all vibrational modes) but with lifetimes of 200 psec or greater. This is clearly long enough to allow bimolecular collisions before reactions, and thus possible mode specific chemistry even in the gas phase at modest pressure. Chemical modification is allowing us to make interesting correlations between structure and relaxation lifetime.

## 1. Introduction

Intramolecular vibrational energy redistribution (IVR) is one of the most elementary and common transformations of a molecular system. The highly successful statistical theories of molecular reactions assume that IVR is both fast and complete (producing a microcanonical distribution in vibrational phase space) on a time scale short compared to intra and intermolecular chemical reactions<sup>1</sup>. What would be desirable, but so far lacking, is a general understanding of what aspects of a molecule's structure and its potential energy surface determine the time scale and the extent of IVR following excitation in a localized coordinate of the molecule. Earlier work, by Sibert et al<sup>2</sup>, and Quack and coworkers<sup>3</sup>, has demonstrated that Fermi resonances control the fastest IVR that has been observed. The time scale for interchange of vibrational excitation between a localized hydrogen stretch and its own bending vibration, ~50 fsec, are remarkably similar in a number of related  $CX_3H$  compounds. This similarity of rates reflects the similar strength of the equivalent bend-stretch anharmonic coupling in these molecules.

Specific low order resonances are known to determine the rate of IVR in a number of other molecules undergoing subpicosecond IVR<sup>4</sup>. Such IVR is now well understood, at least at modest energy levels compared to dissociation. Much less well understood is how IVR proceeds even in the absence of low order resonances. In particular, the IR emission experiments of McDonald and coworkers<sup>5</sup> has shown that essentially all molecules will undergo IVR when their hydrogen stretching fundamentals are excited as long as the density of ro-vibrational levels exceeds 10-100

per  $\text{cm}^{-1}$ . A similar "universal threshold" for the onset of IVR has been observed on the  $S_1$  surface of many aromatic molecules<sup>6</sup>. Such work argues that there are sufficient anharmonic couplings between essentially all ro-vibrational levels to produce IVR lifetimes on the order of 100 psec or less whenever there are isoenergetic states to relax into. Isoenergetic is defined by the homogeneous width for the IVR lifetime.

A theoretical understanding of such behavior is seriously lacking. The most fundamental question, whether or not the same physical model used to describe fast IVR is appropriate here, has not been established in our opinion. Given the highly averaged nature of most of the previous measurements, the phenomenon has not been well characterized experimentally either. Of the many methods that have been used, we believe that when it is practical, eigenstate resolved, high resolution spectroscopy provides the greatest insight into this problem as the pioneering work of Perry and coworkers has demonstrated<sup>7</sup>.

## 2. Experimental

In the last two years, we have been studying the  $\nu_1$  and  $2\nu_1$  absorption spectra of a number of substituted acetylene compounds<sup>8</sup>. The  $\nu_1$  mode is the acetylenic CH stretching fundamental near  $3330 \text{ cm}^{-1}$ . The spectra are obtained in a collimated molecular beam using the optothermal detection method<sup>9</sup>. This has given us a substantially better signal-to-noise ratio and resolution than direct absorption, even in a slit jet<sup>10</sup>. For the fundamental spectrum of butyne ( $\text{CH}_3\text{CH}_2\text{CCH}$ ), for example, we have recently obtained spectra with a S/N ratio of 250 to 1 and a resolution of 6 MHz. Resolution is important in these studies since one often has dense, overlapping spectra from many rotational transitions and because the resolution determines the length of time we can follow the dynamics. Sensitivity is important because it determines how fractionated a spectrum can become and still be observed. Many transitions also have small intensities and may be missed without sufficient signal-to-noise. We have chosen to study substituted acetylene compounds for several reasons, some practical, some theoretical. One interesting reason is that the frequency of the  $\nu_1$  and  $2\nu_1$  absorptions hardly changes as we change molecules. This supports our view that the initial excitation is essentially the same as we change molecule, only the "bath" of dark states and their couplings to the "bright" state change. Table 1 shows the calculated density of states at  $\nu_1$  and  $2\nu_1$  for a number of molecules which we have studied or are studying. We see that we can, in principle, compare similar molecules with the same density of states but different levels of excitation which should allow us to isolate the effects of vibrational amplitude, density of states, and molecular complexity. Another advantage of these molecules is that the observed spectroscopic structure due to IVR is less than  $2B$ , the spacing of the symmetric top rotational lines. This dramatically simplifies the interpretation of the spectrum since, at least for symmetric tops, we can rather cleanly separate inhomogeneous structure, due to rotations, from the interesting homogeneous structure, which relates to the dynamics. Even for asymmetric tops, the close clustering of lines makes spectral assignments by combination-differences easier and more secure.

## 3. Discussion

Our discussion here will focus on the IVR lifetimes observed for molecules in the intermediate or large molecule limits where a lifetime can be defined. We refer the reader to reference 8c for a more complete discussion of the theoretical issues involved in what we mean by a lifetime in the present context. The operational definition is that

each bright ro-vibrational state must be split into at least 5-10 transitions so that the power spectrum of the observed spectrum (which gives the survival probability) has a decay at early times instead of just ringing. Table 2 presents the lifetimes we have thus far determined. Many other molecules that have been studied are in the sparse to intermediate limit; for them we obtain a wealth of information about the couplings, but not an unambiguous lifetime. In a few cases, such as the overtone of butyne, we have failed to observe spectra that we had expected to see with high sensitivity, likely reflecting a much more rapid IVR that obliterates the high resolution structure in the spectrum.

Several general comments need to be made about our results. First, the lifetimes given in Table 2 are equivalent to  $T_1$  times, i.e. they describe the decay of the excited state population. In the statistical limit, Lorentzian lines are observed the width of which directly gives  $T_2$  (which we incorrectly gave as "the lifetime" in our preliminary publication<sup>8b</sup>), but in the present case just as in spontaneous emission,  $T_2=2T_1$ .

Secondly, our lifetime results are consistent with the relaxation rate having no dependence on rotational state (with a possible exception of  $\text{CF}_3\text{CCH } 2\nu_1$ ) and clearly rules out a strong rotational dependence. The lack of a systematic decrease in the IVR lifetime with rotational excitation demonstrates that it is determined by anharmonic interactions, not Coriolis or centrifugal couplings, for at least the range of rotational energy ( $0\text{-}20\text{ cm}^{-1}$  typically) that we have explored in our beam spectra. However, it may well be that at  $300\text{ cm}^{-1}$  of rotational energy, typical of a room temperature molecule, the rotationally induced couplings may become more important and even dominate the relaxation rate. Saturation spectroscopy (in the frequency or time domain) could easily resolve this issue. A further point is that while Coriolis interactions do not contribute to the linewidth, we do have evidence of Coriolis interactions in some of the smaller molecules we have studied. Thus, our results are consistent with K scrambling of the eigenstates (the so called IVRET)<sup>11</sup>, as long as the time scale for tumbling is longer than the IVR lifetimes we have observed. Because the IVR lifetime is long compared to (A-B) in these molecules it is clear that each eigenstate can have significant contributions from at most one bright ro-vibrational basis state, thus K scrambling can only be directly observed by measurements that are sensitive to the nature of the dark states that make up each eigenstate. Resonance fluorescence would be expected to be as polarized as if there was no IVRET.

What is perhaps the most surprising result is that for the molecules with a large density of states, the trimethyl substituted molecules<sup>8b,d</sup>, we do not even observe fluctuations in the linewidth as a function of J or K, while our work on molecules with a small to intermediate density of states shows large changes in the spectrum as a function of rotational state<sup>8c</sup>. As a function of J, different dark vibrational states will tune through resonance with the bright state because of different effective B values. For the symmetric tops, the tuning as a function of K is due largely to parallel Coriolis interactions, which are on the order of the A rotational constant itself causing new states to be in resonance for each single value of K. In the same molecule, therefore, the observation that the IVR rate appears independent of J and K appears to imply that the relaxation rate is independent of the states that the energy relaxes into!

If we compare the series of molecules: butyne, cis and trans pentyne (work of McIlroy and Nesbitt<sup>10b</sup>) and t-butyl acetylene, which all have the C-C-C $\equiv$ CH linkage, we find a remarkable consistency of linewidth as well. Any specific resonance must detune by orders of magnitude more than the observed linewidth ( $0.02\text{ cm}^{-1}$ ) as we move in this series, yet the relaxation rate stays the same. We see systematic variation in linewidths in the series  $(\text{CH}_3)_3\text{XC}\equiv\text{CH}$ , X=C, Si, Sn suggesting a heavy atom blocking effect<sup>12</sup> (though the blocking may reflect longer bond length and decrease in

bond stiffness as much as increased mass). It is easy to rationalize that the strength of anharmonic coupling should decrease in this series, but in a resonance model the relaxation rate depends upon the specific resonance that is involved and its detuning. Given the complexity of these molecules one would expect that the near resonances would be completely different from one molecule to another. Once again, one would expect erratic linewidths.

Both the J,K and the molecule independence of the IVR rate in these molecules appear to be difficult to rationalize with the idea of a chain of specific resonance as controlling the IVR process. One is tempted to try to rescue the resonance picture by invoking a specific "doorway state" as discussed by McIlroy and Nesbitt for some of these molecules<sup>10b</sup>. The difficulty is that if the doorway state is localized on the acetylene end of the molecule (which is required for it not to be completely detuned as the substituted part of the molecule is changed), then we have only changed the problem to why the coupling of the doorway state to the bath of states does not depend upon the vibrational character of the specific states of the bath. In a formal sense, a doorway state can always be defined<sup>13</sup> but unless this is dominated by some specific normal mode state, nothing appears to be gained by its introduction into the theory.

Perhaps the bath states are chaotically mixed over an interval that is much larger than the width of our ultra-narrow resonance. There are both experimental and theoretical reasons for supposing this, although the matter has not been conclusively demonstrated. Our own work on  $\text{CF}_3\text{CCH}$  argues that the bath states are not strongly mixed at  $\nu_1$ , but are at  $2\nu_1$ <sup>8c</sup>. This model implies that couplings of the bright state to the bath should fluctuate, but with a constant mean square matrix element over the width of the resonance. This model is consistent with our observations of molecules with intermediate to dense spectra. In order to relate this to the resonance model, however, we must assume that coupling between the bright state and the bath states comes from coupling to one or a few specific states that are strongly mixed with all the others. But the spectral density of these doorway, or "first tier", states will change over a frequency interval of their own relaxation rates. This could rationalize the observed stability to changes in rotational quantum numbers if the lifetimes of the doorway states are on the 1 psec or less time scale. However, this model does not predict the stability of our observed lifetime to changes in the molecule. We would likely need to invoke unreasonably short lifetimes in order that the resonances not completely detune (relative to the linewidth of the doorway states) when we change from one molecule to another. Instead, we are presently of the opinion that the long lifetimes of the acetylene chromophore is due to the absence of any low order resonances. The bath states isoenergetic with  $\nu_1$  are found (based upon harmonic frequencies) to be made up of a total of at least 7-10 quanta distributed in other modes. We expect weak, high order couplings to these states which should be completely different when we change molecules.

Resonances between states in quantum mechanics are really of two distinct kinds. Some of these resonances are the quantum mechanical equivalent of classical resonances between modes. The bend-stretch Fermi resonance case has been shown to be of this form. If we ran classical trajectories we would expect to find IVR on a similar time scale. But specific state resonances in quantum mechanics can also reflect quantum tunneling through a potential or a dynamical barrier. The local mode doubling observed in many symmetric hydrides<sup>14</sup> and asymmetry doubling of the rotational levels of an asymmetric top<sup>15</sup> are familiar examples of the latter. While in the language of quantum mechanics it is difficult to distinguish between the two, they are qualitatively different when we attempt to understand what is happening in the dynamics. The fastest of our observed lifetimes is still four orders of magnitude longer

than the vibrational period and thus it is unlikely that this can be a classically allowed relaxation. However, extremely small rates could naturally be expected if the rate limiting step is quantum tunneling through a dynamical barrier.

Consider the following model, the outline of which was proposed to us by Howard Taylor. Each of these molecules has a stable periodic orbit that is essentially a pure  $\equiv\text{C}-\text{H}$  stretch with a rapidly decreasing motion of atoms as one goes down the chain. Quantization along this periodic orbit is the state referred to as  $\nu_1$ . Excitation in the directions perpendicular to this periodic orbit produces combination states with the other, lower frequency modes of the molecule. But this periodic orbit is the center of a small island of stability, moving away we will come to a separatrix and a chaotic sea beyond. Taylor has stressed the fact that "extreme motion states", where all the action is localized along a single mode, are often the last regions of periodic motion to be destroyed classically<sup>16</sup>. Getting to that separatrix requires excitation in one or more perpendicular modes without taking energy out of  $\nu_1$ , thus producing a dynamical barrier. Beyond the separatrix, motion in  $\nu_1$  is unstable and energy will flow from  $\nu_1$  into other modes of the molecule. If the total volume of phase space in the molecule (the density of states) is too small, amplitude will reflect back to the well, and destructive interference will prevent most of the amplitude of  $\nu_1$  from leaving the well. In this case, one eigenstate of the molecule will be mostly  $\nu_1$ . As the density of states increases, we will first get an intermediate and then a large molecule limit spectrum as the  $\nu_1$  state converts into a resonance. To get relaxation we need a high density of states, but the rate of relaxation is determined by tunneling through the dynamical barrier. If this barrier does not change, then the relaxation rate will be the same.

Ultimately, the separatrix and thus the dynamical barrier are related to classical resonances between the modes. But since the periodic orbit is presumed stable, the important resonance could be a low order (and therefore broad) resonance of a highly anharmonically shifted mode. Arguments based upon the need for precise matching of energy within a narrow resonance no longer apply. Presently, what is needed is a way to turn this "cartoon" into a real calculation. This picture is attractive because if we can learn how to locate and calculate the dynamical barrier we may be able to make a semiclassical estimate of the rate without the need to run trajectories (or worse, quantum wavepackets!) for  $10^5$  periods.

#### 4. Conclusion

Our present results raise fundamental questions about the nature of intramolecular dynamics. Our experimental work is continuing and we hope to have a more complete empirical picture in the near future. One key feature we want to continue to explore is the relationship of chemical structure to relaxation lifetimes. We would also like to perform experiments that use the nsec lifetimes to do laser selective chemistry of the type Crim and coworkers<sup>17</sup> have been doing on HDO, where IVR is not an issue. In many of molecules, we can truly heat one bond of a large molecule for a chemically significant time, something everything but hope told us was impossible until recently. Our theoretical understanding of IVR on the nsec time scale is poorly developed and calls out for more help. In this talk we have presented our own speculations on this matter, which are admittedly very crude. I hope some members of the theoretical community will take up the fight!

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Table I.

Density of States<sup>a</sup> for Several Substituted Acetylenes at the Fundamental and First Overtone

Molecule	$\rho(\nu=1)$	$\rho(\nu=2)$
propyne	0.3	10
trifluoropropyne	10	$10^3$
tertbutylacetylene	$1 \times 10^4$	$2 \times 10^7$
trimethylsilylacetylene	$4 \times 10^5$	$1 \times 10^9$
trimethylstannylacetylene	$1 \times 10^7$	$6 \times 10^{10}$
propynal	1.5	49
propiolyl fluoride	4	193
vinyl acetylene	4	320
propargylamine	16	$1.8 \times 10^3$
Propargyl alcohol	20	$1.5 \times 10^3$
1-butyne	75	$3. \times 10^3$

<sup>a</sup> The reported density of states are the number of vibrational states per  $\text{cm}^{-1}$  expected in transitions from the ground state, calculated in the harmonic approximation through a direct count algorithm. By ground vibrational state, we include all tunneling components and assume that the same are resolved in the excited state. Selection rules have been used to reduce the density of states where some symmetry species should not mix with the bright states and states degenerate by symmetry are only counted once.

Table II.

IVR Lifetimes for Some Substituted Acetylenes Determined by High Resolution Infrared Spectroscopy

Molecule	Vibrational Level	Lifetime (nsec)
1-butyne	$\nu = 1$	0.2
tertbutylacetylene	$\nu = 1$	0.2
trimethylsilylacetylene	$\nu = 1$	2.0
trimethylstannylacetylene	$\nu = 1$	6.0
propynal	$\nu = 2$	1.2
trifluoropropyne	$\nu = 2$	2.0
tertbutylacetylene	$\nu = 2$	0.1
trimethylsilylacetylene	$\nu = 2$	>4.
trimethylstannylacetylene	$\nu = 2$	>5.