

INTRAMOLECULAR VIBRATIONAL ENERGY RELAXATION (IVR) IN LARGE MOLECULES: HOMOGENEOUS IVR LIFETIMES AND THE MECHANISM OF ENERGY RELAXATION

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ABSTRACT

Using an optothermal molecular beam spectrometer we have measured the high resolution infrared spectra of a number of molecules of the form $(CX_3)_3YC\equiv CH$ in the regions of the acetylenic C-H stretch fundamental and first overtone. We find that all of these spectra consist of quantitatively Lorentzian transitions, as expected for statistical case intramolecular vibrational energy relaxation (IVR). The IVR lifetime is determined by the linewidth of these spectral features. We discuss the correlation of the IVR lifetime with the number of bath states that are able to couple to the acetylenic C-H stretch through low order interactions. We also discuss analogous lifetime results that have been found for vibrational relaxation of molecules in non-polar solvents.

1. Introduction

Intramolecular vibrational energy redistribution (IVR) is a process of fundamental importance in chemical physics. Accordingly, there has been extensive experimental and theoretical work in this field over the past two decades. The theoretical description of the IVR process in terms of the vibrational couplings of a single, optically active bright state with the near-resonant bath states is well developed.¹ Also the connection between the frequency resolved spectrum and the time evolution of a coherent superposition of the rovibrational eigenstates (created by a short, weak excitation pulse) is well understood.² In the last few years we have been studying the frequency resolved infrared spectra of rather large molecules (> 6 atoms) which exhibit the extensive vibrational couplings that characterize IVR.³ Since the first contribution to this field by Perry *et al.*,⁴ there has been a growing number of investigations that have been able to obtain much quantitative information about the vibrational couplings that lead to IVR.⁵

In addition to providing information about the vibrational coupling (i.e. the strength of the coupling, coupling mechanism, and the extent to which a state is coupled to the bath states), frequency resolved techniques have been able to determine homogeneous lifetimes for the IVR process in a number of studies.^{3,4d} The ability to measure *homogeneous* IVR lifetimes is one of the benefits of frequency resolved studies over time dependent measurements. Here we consider how the information contained in a *series of homogeneous lifetime data* can be used to elucidate the pathway for energy redistribution in a certain class of molecules and to guide theoretical descriptions of the IVR process.

2. Experimental

The full details of our optothermal spectrometer have been presented previously and only a brief description is given here.^{3b,d} A bolometer is used to measure a laser induced photon absorption by detecting an increase in the thermal content of a collimated molecular beam.⁶ The laser output makes >50 crosses of the molecular beam by passing through a parallel plate multipass cell. The resolution of the spectrometer (8 MHz at 3330 cm^{-1} and 16 MHz at 6550 cm^{-1}) is limited by the crossing angle of the laser beam with the molecular beam. Two cw lasers are used in our experiments. Both are Burleigh color center lasers: One laser operates in the 3.0 μm region providing about 20 mW of single mode power and the other operates near 1.5 μm with about 150 mW output power. Since the bolometer measures the internal energy of the molecular beam, it is possible to measure weak transitions (such as the overtones reported here) provided there is a sufficiently powerful laser available in the desired frequency region. Using these two laser sources we are able to measure both the fundamental and first overtone of the acetylenic C-H stretch. To a large extent, this unique capability has motivated our interest in the acetylenic C-H stretches.

3. The Measurement of IVR Lifetimes for Large Substituted Acetylenes

Here we will consider only the lifetimes that we have measured for molecules of the form $(CX_3)_3Y-C\equiv CH$. The results are summarized in Table I. These molecules are all quite large in terms of the density of states in the region of the acetylenic C-H stretch which is shown in the first row of Table 1. All of these molecules have spectra that are in the statistical limit of IVR.¹ Specifically, the spectrum consists of a series of individual Lorentzian lines. In this case, the corresponding time domain measurement will show only a simple exponential decay of the localized vibrational energy. The lifetime of this decay can be determined from the linewidth of the features in the frequency resolved spectrum. In Figure 1 we show the measurement of $R(7)$ of $(CD_3)_3Si-C\equiv CH$ acetylenic C-H stretch fundamental at $3.0 \mu m$. The solid line through the data is a fit to a Lorentzian lineshape. The transition is quantitatively Lorentzian.

The spectra we measure are all parallel bands of symmetric top molecules.⁷ Therefore, all of the rotational transitions contain inhomogeneity due to unresolved K structure. In addition, the presence of three methyl rotors produces a number of torsional states.⁸ The measured spectrum is actually the superposition of a spectrum from each individual torsional state, thereby adding an additional inhomogeneous component. Still, even considering these inhomogeneous contributions we believe the reported lifetimes to be the true homogeneous lifetimes. This conclusion is based on the fact that the measured transitions, with the exception of $(CH_3)_3Sn-C\equiv CH$, are quantitatively Lorentzian and show no evidence of asymmetric K structure or torsional structure. Generally, the linewidths we measure are much broader than the widths expected from these inhomogeneous contributions indicating that the homogeneous lifetime is dominating the lineshape. The spectrum of $(CH_3)_3Sn-C\equiv CH$, which has the longest lifetime of this series, shows a fine structure which is consistent with that expected for transitions originating in each of the

ground state torsional levels.⁸ For this molecule the reported lifetime is determined by the linewidth of the individual components of this fine structure.

4. IVR Lifetimes and Energy Relaxation Models

One limitation of frequency resolved techniques is that the spectrum does not provide direct information on the pathway of the energy relaxation. That is, we cannot determine the time dependence of the populations of the individual bath states. Time domain techniques could measure this probability flow, thereby providing direct information on the energy relaxation pathway. Experiments of this type have been reported for liquid phase samples but extending this method to gas phase samples still remains a large experimental challenge.⁹ Alternatively, if the vibrational states observed in the high resolution spectrum can be assigned, a model Hamiltonian for the system can be developed. From this Hamiltonian the time dependent probability flow following laser excitation can be calculated that will be valid up to times determined by the resolution of the spectrum.¹⁰ We now consider how the availability of lifetime data can help elucidate the state-to-state relaxation pathways for IVR.

The lifetimes reported in Table I display a variety of trends. For example, the lifetime of $(\text{CH}_3)_3\text{Si-C}\equiv\text{CH}$ is actually longer in the overtone than it is in the fundamental. Also the lifetimes increase as the size of the molecule increases in the series $(\text{CH}_3)_3\text{Y-C}\equiv\text{CH}$, showing that a higher total density of states does not necessarily imply a shorter IVR lifetime. We also find that deuteration of the methyl groups results in a decreased lifetime compared to that of its nondeuterated companion. This observation contradicts a number of previous experimental results¹¹ and theoretical predictions.¹²

The IVR lifetime is a quantity of fundamental importance. The prospect of performing laser induced, bond selective chemistry rests on the ability to find molecular systems where the IVR lifetime is on the order of the mean collision time.¹³ This time scale is on the order of a nanosecond for reasonable pressures. The lifetimes presented

here are sufficiently long that bond specific reactions could be observed. Clearly, major theoretical goals are a) to understand the factors determining the IVR lifetime and b) to be able to calculate this quantity for individual molecules. The wide variety of behavior of this series seems to make it suitable for evaluating proposed energy relaxation models and methods of lifetime calculation.

Together with the lifetime data, in Table I we also give the total density of states near the acetylenic stretch and the number of low order resonances. First of all, as mentioned above, there is no correlation between decreasing lifetimes and increasing total density of states. In fact, our longest lifetimes are found for our largest molecules. This result makes us optimistic that long vibrational lifetimes can be found for very large molecules that are more important in practical chemistry.

We do find a correlation between the lifetimes and the number of low-order states near the excited vibration. For example, the molecules with $-\text{CH}_3$ rotors have rather different numbers of the lowest order coupled states. The longer the lifetime the fewer these resonances are. We also note that when comparing the fundamental results with the overtone results, there is a unique behavior for $(\text{CH}_3)_3\text{Si}-\text{C}\equiv\text{CH}$; it is perhaps significant that, for this molecule, there is a substantial decrease in the number of fourth order resonances in the overtone. This molecule is the only one we have measured that actually has a longer lifetime in the overtone. This correlation is also successful in interpreting the results of deuteration. For these molecules deuteration results in an increase in low order couplings.

The success of this correlation in explaining the whole set of lifetime measurements suggests that the appropriate physical model for the vibrational energy redistribution is a tier model¹⁴, where the coupling is envisioned to proceed through successive low order resonances. In this way the excitation probability flows through tiers of levels of increasing total vibrational quanta. The lifetime is largely determined by the relaxation rate at the slowest tier coupling (the rate determining step). In the case of the acetylenes this is

apparently the rate for the initial coupling into the first one or two tiers. The subsequent tier-to-tier flow into the bath states is much faster than the flow into the first tiers.

Ours is not an attempt to make this correlation quantitative. A full calculation of the lifetimes will involve calculating the strengths of the couplings to the low order resonances and this is a formidable task. However, recent advances in *ab initio* methods may make it possible to perform the type of calculation necessary to make the tier model quantitative.¹⁵ We do believe, though, that the availability of more homogeneous lifetime information can provide insight into which models are most appropriate for a description of the IVR process. Furthermore, this information can possibly point out how structural modification of the molecules (for example isotope substitution or heavy atom substitution) can be used to influence the vibrational couplings, leading to the ability to design molecules with long IVR lifetimes.

5. Connection with Condensed Phase Studies

Finally, we discuss some implications that a low order resonance model for the vibrational relaxation has for condensed phase IVR. The low order resonances are typically a very sparse set of states that are detuned by several wavenumbers from the excited vibrational state. In the case where the coupling to these levels determines the IVR lifetime, the dynamics of molecules in lightly perturbing solvents should be similar to the dynamics of gas phase molecules. A solvent which does not cause much shifting of the vibrational energy levels, is expected to allow the tier structure of the sparse low order states to remain largely intact. If the vibrational excitation lifetime in the condensed phase is determined by intramolecular dynamics, and not by interactions with the solvent, we might expect to observe similar lifetime effects to those we have found in our isolated molecule studies. Solvents that cause large shifting of the vibrational levels will produce in a very different low order tier structure, possibly resulting in very different relaxation dynamics.

The vibrational relaxation behavior of phenylacetylene in nonpolar solvents has been studied previously.⁹ In these experiments a time delayed Raman spectrum was obtained which allowed the measurement of the vibrational excitation probability flow to the bath states. It was found that the excitation flowed into states containing the acetylenic C≡C stretch on a time scale of about 10 ps. It was noted that, surprisingly, there was no evidence of population of the states with ring C-H excitation. However, examining the low-order states resonant with the acetylenic C-H stretch (states in a 100 cm⁻¹ window around 3300 cm⁻¹), it is found that none of them have excitation in the ring C-H modes. Instead all three of the lowest order coupled states (coupled by 3rd order coupling terms) have the acetylenic C≡C stretch excited. In the next tier, that composed of the 4th order coupled states it is again found that none of the states involve ring C-H stretching modes. In this tier 10% of the levels (17 of 189) have excitation in the acetylenic C≡C stretch. The rest of the states involve ring C-C stretch modes that would be weak in the time dependent Raman spectrum. The experimental observation is in agreement with the predictions of the tier model.

There is also a corresponding condensed phase result for our observation of lifetime increase upon substitution of silicon in the central atom position of large molecules. The lifetimes of the two molecules, (CH₃)₃C-OH and (CH₃)₃Si-OH, following excitation of the O-H stretch have been measured in a nonpolar solvent.¹⁶ It was found that the silanol, such as trimethyl silylacetylene in the gas phase, has a longer lifetime than the analogous carbon compound. Again, this would be attributed to the general frequency lowering accompanying silicon substitution reducing the number of near-resonant states that can couple through low-order interactions.

Lastly, a series of lifetime measurements of the series CX_3H ($X = Cl, Br, I$) in nonpolar solvents has been recently reported.¹⁷ It was found that the heavier the substituent, the longer the lifetime and this was attributed to the larger frequency mismatch between the C-H stretch and the other normal modes of the molecule. Again, the key result is that the total density of vibrational states does not determine the lifetime. Our interpretation of these results in terms of the tier model is slightly different. It would not be the frequency mismatch of the normal modes that reduces the IVR rate, but the fact that for this molecular structure the heavy atom substitution necessarily results in the near resonant bath states being of higher order. This condensed phase result is analogous to our deuteration results. In our case, deuteration provided vibrational states that, in spite of being in larger frequency mismatch with the acetylenic C-H stretch, happened to provide an increased number of "platforms" for making low order combination states that were near resonant, resulting in an increased IVR rate.

It is definitely true that the condensed phase results are more complex than we may seem to be making them in the above discussion. However, it does appear that there is an extremely good agreement in the basic results. Gas phase results can then be important for making further progress in the study of condensed phase phenomena. If the intramolecular dynamics can be understood from isolated molecule studies, then it will be possible to differentiate the intramolecular effects from the intermolecular effects in the condensed phase relaxation. This will allow a better understanding of the very important solvent effects that are so basic to the dynamics of the majority of important chemical systems.

6. Conclusion

Frequency resolved infrared studies of large polyatomic molecules have provided homogeneous IVR lifetimes for a number of molecules. Here we have discussed how a set of lifetime data can be used to guide the development of theoretical models for the IVR process. We find that our results for the series of molecules $(CX_3)_3Y-C\equiv CH$ suggest that

the vibrational energy redistribution is occurring through the subset of low-order resonances: the tier model.¹⁴ We also find that there are analogous results in condensed phase studies for many of the lifetime effects that we have observed. The condensed phase results can also be successfully interpreted in terms of the tier model. It is possible that the quantitative understanding of the IVR process that can be achieved from gas phase studies can be transferred in certain cases to condensed phase studies, allowing the separation of intramolecular dynamics from the intermolecular dynamics of these systems.

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Table I. The Number of Low Order Coupled States, the Total Density of States, and the IVR Lifetime for the Trimethyl Substituted Acetylenes

a) Acetylenic C-H Stretch Fundamental

	(CH ₃) ₃ CCCH	(CH ₃) ₃ SiCCH	(CH ₃) ₃ SnCCH	(CD ₃) ₃ CCCH	(CD ₃) ₃ SiCCH
Total Density ^a	7 x 10 ²	2 x 10 ⁴	5 x 10 ⁵	3 x 10 ³	1 x 10 ⁵
Lifetime (ns)	0.2	2.0	6.0	0.04	0.75
3 rd Order States ^b	25	15	3	96	6
4 th Order States	285	266	271	229	561
5 th Order States	1176	2228	1923	2765	3074

b) Acetylenic C-H Stretch First Overtone

	(CH ₃) ₃ CCCH	(CH ₃) ₃ SiCCH	(CH ₃) ₃ SnCCH	(CD ₃) ₃ CCCH	(CD ₃) ₃ SiCCH
Total Density	1 x 10 ⁶	5 x 10 ⁷	3 x 10 ⁹	7 x 10 ⁶	6 x 10 ⁸
Lifetime (ns)	0.11	4.0	~6.0	<0.05	0.14
3 rd Order States	17	21	21	21	51
4 th Order States	259	135	308	581	276
5 th Order States	1835	2106	1723	2465	3229

^a This is the density of A₁ states in states per cm⁻¹.

^b These are the total number of states in a 100 cm⁻¹ region around the C-H stretch.

FIGURE 1

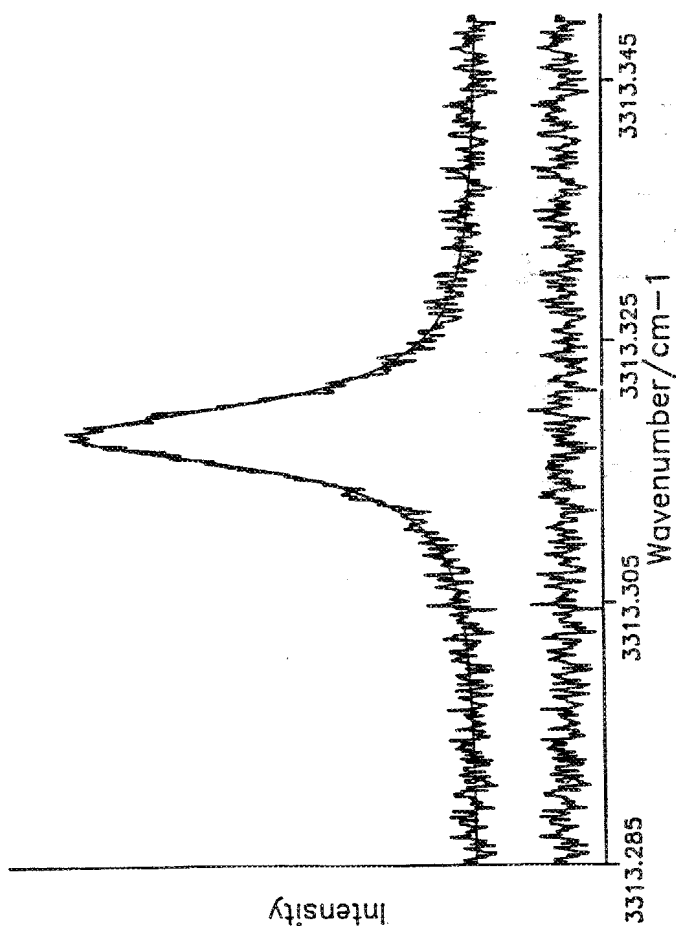


Figure 1. The R(7) transition in the acetylenic C-H stretch fundamental of $(\text{CD}_3)_3\text{Si-C}\equiv\text{CH}$. The transition is quantitatively Lorentzian, as expected for a simple, exponential relaxation of the vibrational excitation into the near-resonant bath states. Below the transition the residuals of the fit to a single Lorentzian lineshape are shown. The linewidth of the feature is about 180 MHz, corresponding to an IVR lifetime of about 0.86 ns.