Influence of methyl group deuteration on the rate of intramolecular vibrational energy relaxation

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The high resolution spectra of the fundamental and first overtone of the acetylenic C-H stretch in tert.-butylacetylene-d_g and (trimethylsilyl)acetylene-d_g have been measured using optothermal detection of a collimated molecular beam. IVR lifetimes determined from the homogeneously broadened lineshapes are compared to those of their undeuterated analogues. It is found that for both molecules, at both levels of excitation, deuterating the methyl rotors results in an increased rate of IVR. The results indicate that the previously suggested methyl rotor effect, as an enhancer for IVR, plays a secondary role to increasing the number of low order resonances to which the C-H stretch can couple. Although the torsional modes are important for the molecules to exhibit statistical case IVR and contribute to the filled-in homogeneous lineshapes, the rate of energy relaxation seems to be dominated by the number of low order resonances.

INTRODUCTION

High resolution infrared spectroscopy of molecular beams has been recently used to study intramolecular vibrational energy redistribution (IVR) following excitation of a hydride stretching mode in a number of medium to large molecules.¹ These studies have provided quantitative information about the mechanisms and strengths of the vibrational and rovibrational state couplings for individual molecules. Two main conclusions have been extracted from this work so far. First, the observed rates of IVR are often much slower than those observed in earlier work in which Franck–Condon active modes of excited electronic states are accessed² or when high hydrogen overtones are excited.³ Since the observed rates are often comparable to gas phase collision rates for pressures near 1 atm, mode selective chemistry may still be possible upon hydrogen stretching excitation in spite of the presence of IVR. To date, mode specific enhancement of a bimolecular reaction rate following stretching excitation has been observed only for HOD, where IVR does not occur because of the small background density of states.⁴ IVR studies of larger molecules should help to identify other favorable molecules. The second general result is that IVR rates appear to show systematic changes when the molecule undergoes chemical modification.⁵ A major motivation for the current IVR work at Princeton is to extend our understanding of these trends with the long range goal of being able to design molecules to control IVR rates. The present paper examines the effect of deuteration of the methyl groups in two trimethyl substituted acetylenes: the series of trimethyl substituted acetylenes (CH₃)₂X-C≡C-H(X = C, Si, and Sn), were previously studied in our laboratory and exceptionally long lifetimes, up to a few nanoseconds, were measured.⁵ It was found that the lifetimes increase greatly as the central atom is made progressively heavier, despite the fact that the total density of vibrational states increases. One common feature in the structure of these three molecules is the presence of methyl rotors.

The influence of a hindered methyl rotor on IVR has received much experimental and theoretical attention.⁶⁻¹⁰ Most of the experimental results, especially the work of Stone and Parmenter, suggest that the methyl group acts as an IVR enhancer.⁶ This acceleration was attributed to repulsion in the van der Waals' radii of the methyl rotor hydrogens with the ring hydrogens leading to mixing of those states.⁷ We can apply their analysis to our series of trimethyl substituted molecules where there is a threefold, relatively high barrier (1434 cm⁻¹ for tert.-butylacetylene). In the harmonic oscillator limit, the coupling between the torsions should scale as ∆ρ⁶, where ∆ρ is a displacement of the torsional mode, and n is some power that depends upon the order of the coupling. The matrix elements of this operator will scale as ν⁻ⁿ/₂ or m⁻ⁿ/₄. Therefore, as we increase the mass of the rotor, the coupling matrix elements should decrease at least slightly, leading to a decreased rate of IVR upon deuteration of the methyl groups. In a recent paper, Martens and Reinhardt¹⁰ describe a strong anharmonic mixing of the internal rotation with other low frequency modes of the molecule. This results in a chaotically fluctuating bath that leads to relaxation of higher frequency modes, much like multiphonon relaxation in crystals. Deuteration of the methyl group would then decrease the bandwidth of the bath and thus lower the relaxation rate, perhaps substantially.

Based upon these arguments, methyl deuteration in the (CH₃)₃XC≡CH molecules should lead to a measurable decrease in the IVR rate. To test this prediction, the high resolution spectra of 3,3-dimethylbutylene-d₉ (tert.-butylacetylene-d₉) and (trimethylsilyl)acetylene-d₉ were measured. The relaxation of these molecules falls in the statistical limit, so the IVR lifetime can be directly ob-

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tained from the observed Lorentzian linewidth of the spectral features, assuming that inhomogeneous effects are negligible. In contrast to the theoretical predictions, the IVR rates obtained for the deuterated compounds were found to be substantially faster than those of the undeuterated isotopomers. It is perhaps useful to add that when we began our experiments no unambiguous examination of the effect of methyl deuteration had been reported. Recent results by Parmenter and co-workers comparing para-fluorotoluene (pFT) to pFT-$d_3$ showed the undeuterated compound to have a lifetime of 3.4 ps, while the deuterated pFT had a lifetime of 1.5 ps for the $3^1S^1$ vibrational band. The authors claim that this difference is within the error of their model, however, and conclude that deuteration has no effect on IVR lifetimes for this molecule. While absolute lifetimes determined by the chemical timing technique are likely to show considerable uncertainties, it is not at all clear why the relative accuracy, when comparing two isotopomers, should not be better than a factor of 2. The fact that the results of Parmenter and co-workers show a trend which is the same as the one reported here is likely to be significant.

**EXPERIMENT**

\[ [4, 4, 4', 4', 4', 4', 4', 4', 4'-2H_2]-3, 3-dimethyl-1-butyne \text{(tert-Butylacetylene-$d_5$)} \] was synthesized by the method of Negishi, King, and Tour from \[ [1, 1, 1, 4, 4, 4', 4', 4', 4', 4', 4'-2H_2]-3, 3-dimethyl-butane-2-one \text{(pinacolone-$d_{12}$)} \]. Pinacolone-$d_{12}$ was prepared by standard methods from acetone-$d_6$ (Cambridge Isotopes). Ethynyl tri-$[^2H_3]$-methyl silane \text{(trimethylsilylacetylene-$d_6$)} was synthesized by the method of Holmes and Sporikou from ethynylmagnesium chloride (Aldrich) and chloro tri-$[^2H_3]$-methylsilane (MSD isotopes).

Absorption spectra in the region of the $v_1$ and $2v_1$ (the acetylenic hydrogen stretch) were observed using the method of optothermal spectroscopy in a cold, collimated molecular beam with the apparatus described in Ref. 5. A 1% mixture of the sample gas in He is expanded through a 50 $\mu$m diameter nozzle at a backing pressure of 5 atm. Two commercial color center lasers are used as the source of infrared radiation. The first is a Burleigh FCL-20 color center laser pumped by 2 watts of the 647.1 nm line from Spectra-Physics model 171 Kr$^+$ laser. In the acetylenic C–H region this yields 25 mW of single mode, continuous wave power. The second laser is a Burleigh FCL-120, pumped by 1.9 W of a Spectra-Physics 3460, continuous-wave Nd:YAG laser resulting in 150 mW of power at the acetylenic C–H first overtone region. The infrared radiation is crossed almost perpendicular to the beam through a multipass arrangement resulting in slightly Doppler broadened linewidths. The instrumental resolution of 8 and 16 MHz at 3 and 1.5 $\mu$m, respectively, is much higher than the width of the observed features and can be neglected when determining the linewidths and thus the IVR rates from observed transitions.

**RESULTS**

The $Q$-branch of the fundamental acetylenic C–H stretch for \((CD_3)_2C≡CCH\) (TBA-$d_6$) and \((CH_3)_2C≡CCH\) (TBA) are shown in Fig. 1. For the deuterated compound the line shape is Lorentzian with a linewidth of 4 GHz which corresponds to an IVR lifetime of 40 ps. With such a broad linewidth, and the estimated rotational constant of 2.3 GHz, the rotational structure in the P and R branches are expected to be unresolved, and indeed no structure was observed. Because the line shape is symmetric and is accurately fit by a single Lorentzian we conclude that inhomogeneous contributions can be neglected. Broadening due to individual ro-vibrational transitions would produce an asymmetry on the low frequency side of the branch. The TBA $Q$-branch [Fig. 1(b)] is in fact slightly asymmetric revealing a rotational inhomogeneous broadening of about 90 MHz. Since the rotational constants decrease upon deuteration, the inhomogeneous component of the deuterated compound is expected to be smaller. Therefore, for TBA-$d_6$ the homogenous linewidth dominates the spectrum. We also point out the presence of a 2.8 cm$^{-1}$ blueshift of the band origin upon deuteration (from 3329.4 cm$^{-1}$ for TBA to 3332.2 cm$^{-1}$ for TBA-$d_6$). Deuteration must result in a lowering of the vibrational
The overtone region of TBA-d₉ was scanned under the same conditions as the fundamental and no evidence of any absorption was found, indicating that the linewidth is so broad to place the peak height of the Q branch below the noise level of our spectrometer. Based on signal-to-noise estimates, this corresponds to a lifetime in the overtone shorter than 20 ps.

The full spectrum of (CD₃)$_3$SiC≡CH (TSA-d₅) was measured from R(8) to P(9). Each of the P and R branch features fits to a single Lorentzian. The linewidths obtained from these fits are plotted in Fig. 2 as a function of J', the rotational quantum number of the upper state. Contrary to the case of TSA, the linewidths appear to narrow slightly at higher J's. For the undeuterated silicon compound, the linewidths of the features in the fundamental showed a slow but steady increase as a function of J, with a shoulder developing at the high frequency side. This was consistent with the expected increase in inhomogeneous broadening from unresolved K structure and was not taken as evidence of a Coriolis coupling mechanism. Since the deuterated compound shows a slight decrease with J from about 215 MHz for R(1) to 170 MHz for R(8), we conclude that at least part of the linewidth is due to the anharmonic mixing of ν₁ with a doorway state that detunes from near resonance with increasing J.

The spectra of the R(5) lines of the ν₁ fundamental of TSA-d₅ and TSA are compared in Fig. 3. For both molecules the linewidths are considerably narrower than those of the carbon analogues and corresponds to an IVR lifetime of 850 ps for the deuterated silicon compound and 2000 ps for the undeuterated one. Table I gives the spectroscopic constants determined in a fit to the observed line positions. The band origin for the silicon compound is only slightly redshifted (0.05 cm⁻¹) upon deuteration.

In the overtone region of TSA-d₅ the Q branch was observed at 6520 cm⁻¹ (Fig. 4). This absorption is asymmetric and the low energy side of the branch does not fit to a Lorentzian. (See Table II) However, for all of the trimethyl substituted compounds measured previously, it was found that obtaining the linewidth from the high energy half of the Q branch provided an excellent estimate (within 10%) of the linewidth of the individual rotational features of the spectrum. By fitting the high energy half of the line shape in Fig. 4, a lifetime of 140 ps was obtained. Contrary to TSA, the lifetime does not increase from the fundamental to the overtone excitation for the deuterated silicon compound. The P and R branch features were observed for this molecule with a very low signal to noise ratio and provided no additional information. The broad weak feature on the low frequency side of the Q branch is likely due to a hot band. The two sharp features near 6519.88 and 6519.92 cm⁻¹ are reproducible and it is very probable that they are the Q branches of resonantly coupled states. If these features were due to a chemical impurity or to hot bands, they would have also been seen in the ν=1 spec-

![FIG. 2. Linewidths (fwhm) as a function of the upper state rotational quantum number, J, for the fundamental of (CD₃)$_3$SiC≡CH.](image)

![FIG. 3. R(5) of the fundamental acetylenic C-H stretch of (CD₃)$_3$SiC≡CH (upper) and (CH₃)$_3$SiC≡CH (lower) and their fits to a single Lorentzian.](image)
A very broad region was scanned for \( v = 1 \) and no evidence of other features was seen.

**DISCUSSION**

The fact that the IVR rate is increased upon deuteration is contrary to previous experimental observations and theoretical predictions. A gas phase FTIR study of the fundamental and first overtone of several carbonyl compounds suggested that deuteration of the methyl rotor reduces the IVR rate.\(^7\) In that study, a substantial simplification in the spectrum of acetyaldehyde was noted upon deuteration. However, at the low density of states for this molecule (3 states per cm\(^{-1}\) in the carbonyl overtone region), IVR alone could not be responsible for the observed spectral congestion. The results probably reflect a changing hot band structure or the detuning of a single anharmonic resonance. Another study probed the fourth overtone of the O–H stretch in several simple alcohols.\(^8\) Deuterating the alcohols resulted in spectra with sharpened band features. This was attributed possibly to a loss of vibrational congestion, however it could also indicate a change in the IVR rate since the energies were high enough for IVR to play a role.

To explain our results the theory of Moss et al., which explains the IVR enhancement as a result of overlap of the methyl hydrogens with the rest of the framework of the molecule, can be considered.\(^9\) This theory can mechanistically account for the fact that a remote change in chemical structure (remote from the initially excited bond) may have such a large effect on the relaxation of the acetylenic chromophore. Increased overlap of van der Waals’ radii leads to an increased IVR rate which is consistent with the comparison between the carbon compound and its silicon analogue, since the C–CH\(_3\) bonds are shorter than the Si–CH\(_3\) bonds. As mentioned earlier however, decreasing the methyl rotor torsional frequency (a consequence of deuteration) should reduce the IVR rate and this is not consistent with our results.

Martens and Reinhardt have proposed an alternative explanation of the methyl rotor effect based on dividing the molecule’s multidimensional phase space into two subsystems.\(^10\) The methyl rotor and other low frequency modes are included in the first subset and their dynamics is strongly chaotic leading to rapid energy redistribution. The second subset consists of the high frequency modes which do not couple to the methyl rotor directly due to a large energy mismatch. These modes are induced to relax by the low frequency modes producing a stochastic perturbation on the high frequency modes which leads to a diffusion-like relaxation. Evaluation of the IVR rate depends on the closeness of the torsional frequencies and the low frequency skeletal vibrations. For the substituted trimethyl acetylenes, as shown in Table III, the torsional modes are often in near resonance with a low frequency mode. The chaotic bath that Martens and Reinhardt describe could exist in these molecules however, as mentioned earlier, one would predict from this theory a reduction in the relaxation rate upon deuteration.

As an alternative approach to the interpretation of the IVR lifetimes one can consider a tier model. This type of model treats the relaxation of the initial excitation as occurring through a set of sequential couplings to the background states. The initial state first couples to a set of low order background states which subsequently couple to more background states, through low order anharmonic couplings. The process continues to fan out and drives the relaxation. This model of sequential couplings has proven useful in the analysis of IVR for several polyatomic molecules.\(^15\)–\(^19\) Sibert, Reinhardt, and Hynes have been able to describe quite well the overtone spectrum of benzene using a tier model.\(^15\) In their calculations they found that the rate is only sensitive to the first (or first few) steps. Quack and co-workers have quantitatively modeled the C–H overtone.
TABLE III. Normal modes of the trimethyl substituted acetylenes.

<table>
<thead>
<tr>
<th>Mode</th>
<th>TBA(^{20})</th>
<th>TBA-(d_9)(^{21})</th>
<th>TSA(^{22})</th>
<th>TSA-(d_9)(^{22})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\nu_{\text{C-H}})</td>
<td>3329(^a)</td>
<td>3332(^a)</td>
<td>3312(^b)</td>
<td>3312(^b)</td>
</tr>
<tr>
<td>(\nu_{\text{C-H}})</td>
<td>2977</td>
<td>2227</td>
<td>2966</td>
<td>2220</td>
</tr>
<tr>
<td>(\nu_{\text{C-H}})</td>
<td>2889</td>
<td>2081</td>
<td>2900</td>
<td>2120</td>
</tr>
<tr>
<td>(\delta_{\text{C-H}})</td>
<td>2017</td>
<td>2161</td>
<td>2037</td>
<td>2037(^b)</td>
</tr>
<tr>
<td>(\delta_{\text{C-H}})</td>
<td>1475</td>
<td>1031</td>
<td>1420</td>
<td>1060</td>
</tr>
<tr>
<td>(\delta_{\text{C-H}})</td>
<td>1363</td>
<td>1028</td>
<td>1265</td>
<td>995</td>
</tr>
<tr>
<td>(\nu_{\text{X-C}})</td>
<td>1748</td>
<td>1110</td>
<td>654</td>
<td>570</td>
</tr>
<tr>
<td>(\nu_{\text{X-C}})</td>
<td>691</td>
<td>645</td>
<td>557</td>
<td>515</td>
</tr>
<tr>
<td>(\rho_{\text{C-H}})</td>
<td>885</td>
<td>740</td>
<td>860</td>
<td>745</td>
</tr>
<tr>
<td>(\delta_{\text{X-C}})</td>
<td>382</td>
<td>319</td>
<td>218</td>
<td>185</td>
</tr>
</tbody>
</table>

\(^{a}\) Taken from our spectra.

The low frequency torsional modes have been reported only for TBA; the torsional modes for the others are estimated from similar molecules.\(^{23}\)

In Table III the fundamental frequencies for the four molecules discussed in this paper are listed. Neither IR nor Raman spectrum of TBA-\(d_9\) has been reported; the fundamentals for this molecule (listed in Table III) were calculated by Crowder, using force constants adjusted to fit the observed fundamentals of TBA.\(^{20,21}\) The fundamental frequencies of TSA-\(d_9\) were obtained from those of TSA-\(d_{10}\) with minor adjustments.\(^{22}\) The low frequency torsional modes have been reported only for TBA; the torsional modes for the others are estimated from similar molecules.\(^{23}\)

Density of states values were calculated by a direct count for the fundamental and first overtone, treating all modes as harmonic vibrations. Calculations carried out for the hydrogen compounds showed that treating the torsional modes as uncoupled hindered rotors increased the density of \(A_1\) symmetry vibrational states by a factor of 1.7. A lifting of the torsional degeneracy is predicted to increase the density of observed lines by as much as a factor of 24.\(^{24}\) Table IV summarizes the total density of states calculations, the density of states with the torsional modes excluded, and the number of low order resonances for each molecule in the harmonic approximation. It is evident from the calculated density of states without the torsional modes that, at least for TBA and TBA-\(d_9\), the number of background states is too sparse to support "statistical" IVR. Some energy must flow into the torsional modes from the initially excited C-H stretch.

The low order resonances, listed in Table IV, are for a 100 cm\(^{-1}\) window around the acetylenic stretch fundamen-

TABLE IV. Density of states and low order resonances.

<table>
<thead>
<tr>
<th>Mode</th>
<th>(CH(_3))(_3)C-C=C-H</th>
<th>(CD(_3))(_3)C-C=C-H</th>
<th>(CH(_3))(_3)Si-C=C-H</th>
<th>(CD(_3))(_3)Si-C=C-H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total density of (A_1) states (10(^{15}))</td>
<td>4.9x10(^2)</td>
<td>2.8x10(^2)</td>
<td>1.0x10(^4)</td>
<td>1.0x10(^5)</td>
</tr>
<tr>
<td>Density of (A_1) states without torsional</td>
<td>50.0</td>
<td>1.7x10(^2)</td>
<td>7.8x10(^2)</td>
<td>4.1x10(^3)</td>
</tr>
<tr>
<td>3rd order states</td>
<td>24.0</td>
<td>34.0</td>
<td>15.0</td>
<td>6.0</td>
</tr>
<tr>
<td>4th order states</td>
<td>293.0</td>
<td>373.0</td>
<td>250.0</td>
<td>540.0</td>
</tr>
<tr>
<td>5th order states</td>
<td>1819.0</td>
<td>3623.0</td>
<td>1415.0</td>
<td>2932.0</td>
</tr>
<tr>
<td>IVR Rate (s(^{-1}))</td>
<td>5.0x10(^6)</td>
<td>25.0x10(^6)</td>
<td>0.5x10(^9)</td>
<td>1.2x10(^9)</td>
</tr>
</tbody>
</table>

\(^{a}\) Total number of states in a 100 cm\(^{-1}\) region around the C-H stretch.
A second piece of evidence implicating the importance of low order resonances is the blue shift of the TBA-d_{9} band origin, which can only be explained by resonant couplings. Almost all of the low order resonances in the TBA-d_{9} window fall below the acetylenic C-H stretch. The ignored off diagonal anharmonicity will most likely not change this. A blue push is therefore expected. Lastly, there are the other two features in the overtone spectrum of TSA-d_{9}. If they are, as it assumed, Q branches of resonantly coupled states, then this shows that some background states are well defined and have a state identity making it proper to consider their couplings separately. These states appear to have dramatically different IVR rates, which demonstrates the difficulty in the tier model for quantitative interpretation since coupling out of the first tier can show large fluctuations (the tier model arguments assume an “average” coupling at each tier). A further indication that without a knowledge of coupling strengths predictions can be hazardous is provided by the fact that the recently measured fast IVR rate for (CF_{3})_{3}C=C=C-H does not agree with the calculated small number of low order resonances.25 On the other hand, the force constants for this molecule are very different and therefore any comparison with the hydrogen containing molecules may be invalid.

The evidence that the low order resonances are relevant to the dynamics gives a rationalization for the lack of success of the existing theories on methyl rotors to predict the increase in IVR rate upon deuteration. In the present series of molecules most of the low order resonances do not involve rotor excitation. According to the tier model these interactions only occur later in time. If the rate is largely determined by the initial coupling out of the C-H stretch, our results should be mainly independent of the methyl rotor properties.

Going beyond simple correlations to a full quantitative model which would include coupling strengths is a formidable task, but is being attempted by Stuchebrukhov.26 Quantitative predictions require estimations of size of cubic and quartic anharmonic force constants for large molecules, for which there is little spectroscopic guidance. There is evidence that anharmonic constants calculated from ab initio methods are of good accuracy.27 Hopefully coupling matrix elements for larger molecules will be available in the near future and thus allow for quantitative models for predicting IVR lifetimes.

Note added in proof. Stuchebrukhov26 has made predictions of the IVR lifetimes of these molecules which are in excellent agreement with our experimental results discussed above.

ACKNOWLEDGMENTS

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(a) A. M. de Souza, D. Kaur, and D. S. Perry, J. Chem. Phys. 88, 4569 (1988); (b) A. McIlroy and D. J. Nesbitt, ibid. 92, 2229 (1990); (c) B. H. Pate, K. K. Lehmann, and G. Scoles, ibid. 95, 3891 (1991).


21 G. A. Crowder (private communication).


24 K. K. Lehmann and B. H. Pate, J. Mol. Spectrosc. 144, 443 (1990). The density of observed lines is 24 times the density of $A_1$ states as opposed to 27 times because one of the irreducible representations of the molecular symmetry group $G_{162, 14}$ is separably 6-fold degenerate and thus has a density of only three times the density of $A_1$, as opposed to the 6-fold degeneracy for the other $I$ representations.


26 A. Stuchebrukhov (private communication).