Very Slow Intramolecular Vibrational Energy Redistribution (IVR) for Molecules in Planar Conformations

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Evidence is presented that shows very slow intramolecular energy redistribution (IVR) in the acetylenic C−H stretch fundamental of molecules in planar conformations. Each molecule,4-chlorobut-1-yne, 4-bromobut-1-yne, 4-fluorobut-1-yne, methyl propargyl ether, 1-pentyne, and pent-1-en-4-yne have a planar trans conformer (except for pent-1-en-4-yne where the planar conformer is cis) that is connected to a nonplanar gauche (skew) conformer by rotation about a C−C bond (C−O for methyl propargyl ether). The planar forms (observed for each molecule except methyl propargyl ether) of these molecules exhibit some of the slowest hydride stretch IVR rates measured, with τ_{IVR} for the acetylenic C−H stretch ranging from 1 to 3 ns. These results are compared to the IVR lifetimes for the nonplanar conformers of 1-pentyne and methyl propargyl ether ($\tau_{\mathrm{IVR}} \approx 300$ ps). Also presented are a series of molecules ((*Z*)-pent-3-en-1-yne, (*E*)-pent-3-en-1-yne, 1-butyne, 3-fluorobut-1-yne, and 2-methyl-1-buten-3-yne) that have a single methyl group substituent and do not form different conformations upon rotation about the C−C bond. The barrier to internal rotation of the methyl tops range from 389 to 2016 cm^{-1}; however, the IVR lifetimes of the acetylenic C−H stretch for each is near 100 ps.

Introduction

The vibrational motion of polyatomic molecules is usually described by the normal-mode, harmonic oscillator approximation.[1] At low total energy, the normal-mode description provides an excellent approximation for the eigenstates of the vibrational Hamiltonian. The connection between specific structural features and their corresponding normal-mode fundamental frequencies, as occurs for the carbonyl and hydride stretches for example, makes vibrational spectroscopy a useful tool for molecular structure determination. Furthermore, this approximation provides an excellent basis for assigning the low-resolution vibrational spectrum of a polyatomic molecule extending to high energies in the overtone regions of the hydride stretches when the diagonal anharmonicity of the hydride stretch vibrations are included. In a low-resolution spectrum, deviations from the expected normal-mode vibrational structure are only observed for strong anharmonic interactions, such as the well-known Fermi resonances in CO_2.[1,2] These results indicate that the normal-mode approximation provides an accurate description for nuclear motion at short times.

When the vibrational spectrum of a highly excited molecule is observed with higher resolution, a qualitatively different picture emerges.[3,4] In these energy regions, the spectrum shows extensive local perturbations. Instead of a single rotation−vibrational transition expected on the basis of the normal-mode/distortable rotor approximation, a set of transitions is observed underneath an overall line shape profile. The fragmentation of the oscillator strength into an "IVR multiplet" indicates that there is flow of vibrational energy between the near-resonant normal-mode vibrational states. This process is called intramolecular vibrational energy redistribution (IVR) and plays a fundamental role in the theory of chemical reaction rates. For example, the validity of statistical theories of chemical kinetics, such as the widely used RRKM theory,[5,6] requires that the rate of IVR exceed the reaction rate and that all energetically accessible states participate in the redistribution process.

The standard model for describing this effect is illustrated in Figure 1.[7,8] The picture represents the case where the full Hamiltonian for the molecular vibrations is separated into a zeroth-order term (the harmonic normal-mode Hamiltonian that provides a good approximation of the nuclear motion) and a collection of the terms not included in the zeroth-order term. This second term includes contributions from the vibrational anharmonicity as well as any rotationally induced mechanisms for coupling between the normal-mode vibrational states (e.g., Coriolis or centrifugal distortion terms)

$$H = H_0 + W \tag{1}$$

In this expression, the interaction matrix elements grouped in the perturbation term, *W*, are responsible for the IVR process. For large systems, often called the statistical limit of IVR, the IVR process leads to a single-exponential decay of the population in the zeroth-order bright state (an eigenstate of H_0) with a rate given by the Fermi Golden Rule expression

$$\Gamma = 2\pi \langle W^2 \rangle \rho \tag{2}$$

where ρ is the density of states coupled to the bright state and *W* is the root-mean-squared interaction matrix element of the bright state with the other near-resonant zeroth-order states (often called the bath). If the spectrum were excited with a short-pulse laser, the initial state prepared by the excitation is the infrared active bright state. With respect to the molecular eigenstates of eq 1, this initial state is a superposition state and, therefore, is nonstationary. The time-dependent population of the bright state can be calculated from the frequency and relative

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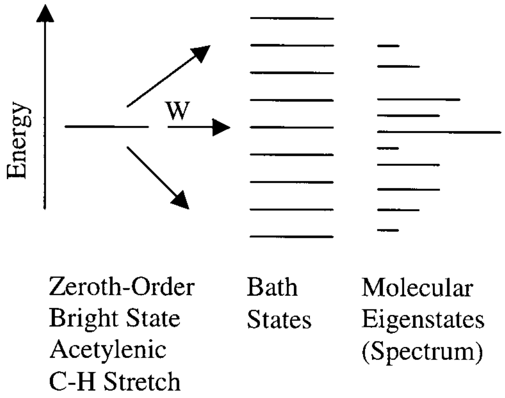

Figure 1. In the standard model for IVR, the full Hamiltonian is separated into a zeroth-order term (H_0) and an interaction term (W). The zeroth-order bright state (i.e., the acetylenic C−H stretch) carries all of the oscillator strength from the ground state. Nearby in energy there is a dense set of bath states that are combination and overtone bands of the other 3N-6 normal modes of the molecule. The interaction term (W) that connects the bright and bath states includes contributions from vibrational anharmonicity as well as rotationally mediated interactions (Coriolis or centrifugal). The result is a set of molecular eigenstates forming an IVR multiplet spectrum. The intensity of each eigenstate in the high-resolution spectrum (shown) reflects the contribution of the bright state, from which the survival probability of the initial bright state can be determined.

intensities measured in a high-resolution spectrum through the survival probability[9,10]

$$\mathrm{P(t)} = |<\psi(0)\mid\psi(t)|^2 = \sum_i\sum_j I_i I_j \cos\left(\frac{E_i - E_j}{\hbar}\right) \qquad (3)$$

where I_i is the relative intensity of the ith eigenstate such that $\sum_i I_i = 1$ and E_i is the energy of the ith eigenstate. In this way, high-resolution infrared spectroscopy can be used to quantitatively measure the initial rate of vibrational energy redistribution for well-defined prepared states.

The existence of IVR in medium-sized (about 10 atom) molecules in the region of the hydride stretch fundamentals near 3000 cm^{-1} was first demonstrated through the infrared fluorescence dilution measurements of McDonald and co-workers.[11] In a summary of their results, they showed that the onset of IVR occurs when the vibrational state density reaches about 10−100 states/cm^{-1}.[12] This “IVR threshold” was found to be valid independent of the nature of the initial state (e.g., C−H, $=$CH$_2$, and C≡C−H hydride stretch fundamentals). Although the fluorescence dilution experiments clearly demonstrated that IVR occurs at these low energies, the technique cannot directly determine the IVR rate. The universality of this result does strongly suggest, however, that all hydride stretches have approximately the same IVR rates.

The use of high-resolution molecular-beam spectroscopy to measure IVR rates was first demonstrated by deSouza, Kaur, and Perry in their work on the vibrational dynamics of the acetylenic C−H stretch of 1-butyne.[13] Since this measurement, techniques have been developed that provide higher measurement sensitivity.[10,14] Additionally, double-resonance spectroscopy methods have been employed to simplify the complicated spectra that arise for large molecules undergoing IVR.[15−17] In our work, we have developed a microwave-infrared double-resonance technique for molecular-beam bolometer spectroscopy that exploits the unique state-focusing behavior of molecules excited to energies where IVR occurs.[18−21] This method offers the advantages of high-sensitivity and provides spectral simplification through the phase of the detected signal. Using known pure rotational transitions in the double-resonance spectroscopy allows the assignment of spectra for highly asymmetric tops with fast IVR rates where the strong spectral overlap of adjacent rotational states leads to infrared spectra with little discernible rotational structure.

As the number of studies on IVR rates in the region of the hydride stretch fundamentals have increased, there have been many attempts to correlate the IVR rates with structural features in the molecule and, therefore, to develop a structure-based understanding of the intramolecular dynamics. Much of the interest in this direction was spurred by the chemical timing measurement of Moss and Parmenter that shows enhanced IVR in p-fluorotoluene compared to the structurally similar p-difluorobenzene molecule.[22] This result suggests that the presence of a functional group capable of large amplitude internal motion increases the rate of vibrational energy flow. The IVR rate measurements of McIlroy and Nesbitt on isomers of 1-butene further suggest that the presence of large amplitude motions increases IVR rates.[23] Other types of large amplitude motion, such as the flexibility of ring compounds in the study of Li and Philips, appear to support the conjecture.[24] Other structural features, such as the presence of a heavy atom in the framework which slows IVR, have also been found.[25] However, most studies have focused on internal rotation about C−C single bonds.

Perry and co-workers have examined IVR rates for a large number of molecules with methyl groups in the structure. From this data set, they suggest that IVR rates are generally increased by the presence of a methyl rotor.[26] Furthermore, they suggest that the extent of rate enhancement depends on two factors; the proximity of the hydride stretch to the “center of flexibility” and the barrier to internal rotation (with greater rate enhancement found for molecules with low barriers).[27] Of particular importance for the results presented here, they suggest that rate enhancements are not found for the acetylenic C−H stretch due to the fact that this infrared chromophore is always several bonds away from the rotor position due to the −C−C≡CH structure of the functional group.

Below, we present evidence for a new structure correlation for the IVR rates of the acetylenic C−H stretch fundamental. In the course of our work on conformational isomerization,[28] we have found that the planar conformers of acetylenic compounds exhibit extremely slow IVR. Typical IVR lifetimes for these conformers are 1−3 ns, compared to IVR lifetimes of about 100 ps for molecules that cannot exist in distinct conformational structures. In this case, the presence of a large amplitude coordinate appears to slow the IVR rate. Furthermore, these results suggest that the acetylenic C−H stretch vibrational dynamics are sensitive to structural features a few bonds away.

Experimental Section

The IVR rates for the acetylenic C−H stretch of all molecules are determined from the survival probability (eq 3) calculated from the frequencies and intensities in the high-resolution (6 MHz; 0.0002 cm^{-1}) infrared spectrum. The rotation−vibration spectra are assigned using microwave-infrared double-resonance methods to provide unambiguous assignment of the rotational quantum numbers. All spectra were measured using an electric-resonance optothermal spectrometer. The spectrometer, and the mechanism for microwave-infrared double-resonance spectroscopy, have been described previously.[18,21]

The molecular beam is formed by expanding a dilute mixture of the molecule in He (typically a 5% mixture) through a 50

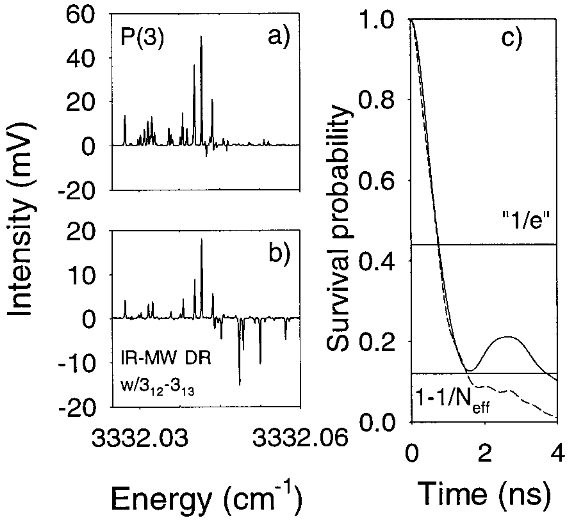

Figure 2. Basic IVR measurement is shown for 4-fluorobut-1-yne. (a) The single-photon infrared spectrum of P(3) of the acetylenic C−H stretch. (b) IR-MW double resonance spectrum of P(3) monitoring the $3_{12}-3_{13}$ ($J_{\text{Ka,Kc}}$ notation) pure rotational transition at 728.92 MHz showing the $2_{11}-3_{12}$ IR multiplet (positive) and the $2_{12}-3_{13}$ multiplet (negative). (c) The corresponding survival decay determined from (b) and eq 3 (2_{11} solid line and 2_{12} dashed line). The IVR lifetime is defined as the time it takes the decay to drop to a value of 1/e of the equilibrium probability ($1-1/N_{\text{eff}}$).

μm pinhole nozzle. Purification of the sample is unnecessary because the spectra are measured in double resonance with known pure rotational transitions of the molecule of interest. Several of the molecules discussed here were obtained from commercial sources (1-butyne, 1-pentyne, methyl propargyl ether, 2-methyl-1-buten-3-yne, isobutene, allyl fluoride, and methyl vinyl ether). Others were prepared using standard literature methods (4-chlorobut-1-yne,[29] 4-bromobut-1-yne,[29] 4-fluorobut-1-yne,[30] 3-fluorobut-1-yne,[30] pent-1-en-4-yne,[31] (*Z*)-pent-3-en-1-yne,[29] and (*E*)-pent-3-en-1-yne,[29]).

The basic measurement procedure is illustrated in Figure 2. The high-resolution infrared spectrum of a single rotational level of the acetylenic C−H bright state is obtained through microwave-infrared double-resonance spectroscopy using a known pure rotational transition of the molecule (Figure 2b). The double-resonance measurement ensures that the homogeneous spectrum of a single rovibrational bright state is obtained and removes the possibility of including vibrational transitions from “hot bands” in the spectrum. From the eigenstate resolved spectrum, the survival probability of the bright state is calculated using eq 3. In all cases, the survival probability shows an initial decay toward an equilibrium value given by the effective number of states coupled in the dynamics[11]

$$N_{\text{eff}} = \frac{(\sum_i I_i)^2}{\sum_i I_i^2} \tag{4}$$

The lifetime of the bright state is calculated in two ways: (1) by the time it takes the probability to drop to 1/*e* of its full decay to equilibrium (defined as $1-1/N_{\text{eff}}$), and (2) by a fit to a single-exponential decay for the fall of the probability from 0.9 to 0.8 (i.e., in the smooth region of the decay).[32] In most cases, these two determinations are in good agreement (Figure 2c). The second method is useful in cases where the level structure leads to recurrences before the 1/*e*-point is reached. The IVR rate is the reciprocal of the reported lifetimes.

In all spectra, we find that the IVR rate is independent of the initial rotational state. This result indicates that anharmonic interactions dominate the coupling of the acetylenic C−H stretch to the other near-resonant normal-mode basis states. The lifetimes reported come from the IVR multiplets with the highest signal-to-noise ratio since low sensitivity often leads to longer measured lifetimes when weak transitions in the wings of the spectrum go undetected. Although the IVR rates are found to be independent of the rotational state, we find that the density of coupled states increases with increasing value of the total angular momentum. This increase is found to follow the form expected for full participation of all rotational states with the same total angular momentum

$$\rho(J) = \rho_0\,(2J + 1) \tag{5}$$

where ρ_0 is the density of states permitted for anharmonic coupling. These two effects indicate that rotationally mediated coupling of the acetylenic C−H stretch to the bath is weaker than the anharmonic term and/or that the rotationally mediated interactions occur most strongly between the bath states as described by Perry’s “keyhole” model.[33] These observations are typically found in high-resolution studies of IVR dynamics.[3] State densities are reported as the ρ_0 value determined by the measured state densities and eq 5.

Results

We compare IVR measurements of the acetylenic C−H stretch, all made on the same spectrometer, for two classes of molecules. We first present results for molecules that can exist in two distinct conformations through rotation about a C−C (or C−O, in one case) single bond. The IVR results for this series of molecules are compared to a second set where the molecule contains only a symmetric rotor group (i.e., a methyl rotor). Finally, we briefly examine previous IVR measurements of other hydride stretches to assess the generality of the results found for the acetylenic C−H stretch.

A. Molecules with Two Conformations. *Ab Initio Potentials and Molecular Beam Populations*. The ab initio potentials for internal rotation of 1-pentyne, methyl propargyl ether, 4-fluorobut-1-yne, 4-chlorobut-1-yne, 4-bromobut-1-yne, and pent-1-en-4-yne are shown in Figure 3. The potentials are calculated using Gaussian 98W[34] at the HF/6-311G** level. The conformational potential is determined by varying the torsional angle in steps of 15° and performing an optimization of the remaining structural parameters at each point. Previous experimental studies of torsional vibrational spectra in the far-infrared have shown that the ab initio potentials are highly accurate.[35,36] This set of energies is then fit to a Fourier series to obtain the smooth curves shown in Figure 3. For the first five molecules in this series, the two stable conformations are the planar trans conformer (with the acetylene opposite to the internal rotation substituent) and the nonplanar gauche conformer (where the acetylene and the internal rotation group are approximately ±60° apart). For pent-1-en-4-yne, the planar conformation adopts a cis configuration.

Our experimental measurements are in good agreement with the relative stability of the isomers indicated in Figure 3. For example, the two conformers of 1-pentyne are predicted to have approximately the same energy. McIlroy and Nesbitt have previously shown,[10] and we also find, that both conformers give strong infrared spectra. In methyl propargyl ether, the gauche conformation is favored due to the stability associated with placing the lone pair of the oxygen trans to the acetylene.[37] In

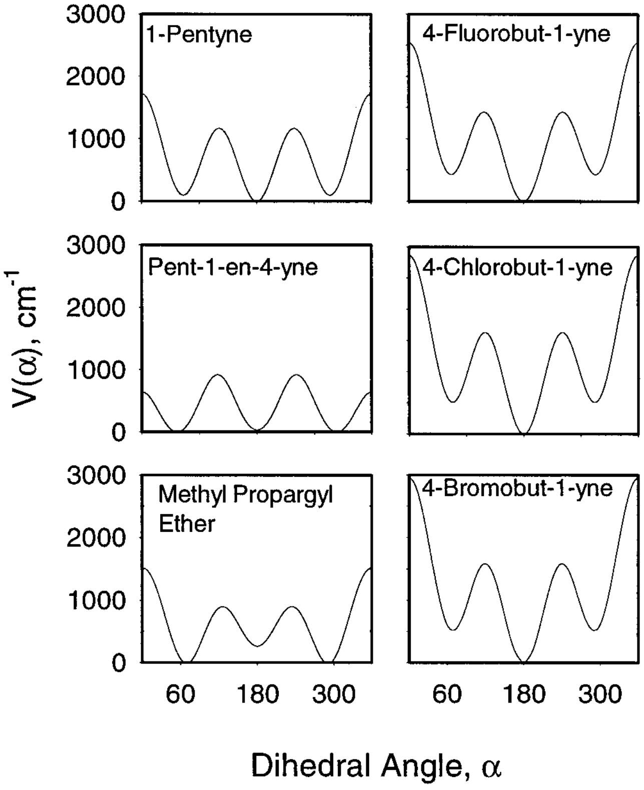

Figure 3. Potential functions due to internal rotation are determined by ab initio calculations using the HF/6-311G** basis set. All of these molecules have a planar form (180°) and a degenerate nonplanar form.

our infrared measurements, we observe only the spectrum of the gauche conformer. Furthermore, we have been unable to observe any pure rotational spectra of trans methyl propargyl ether using the pure rotational spectroscopy capabilities of the spectrometer.

For the three halobutynes, the trans conformer is favored in all cases, and only the infrared spectrum of this conformation is observed. However, in all three cases, we have observed the pure rotational spectrum of both conformers, although with a lower signal-to-noise ratio for the gauche compared to the trans conformer. Because the rotational intensities depend strongly on the state-focusing properties of the rotational levels, it is impossible to use the relative intensities of the rotational spectra to determine the relative populations in the beam. The case of pent-1-en-4-yne shows the largest discrepancy with the ab initio potential. On the basis of the potential, we expect both conformers to be nearly equally populated, as in 1-pentyne, and both conformers are observed in the pure rotational spectroscopy. However, we have only been able to observe the infrared spectrum for the planar cis form of the molecule. Our sensitivity in the infrared spectrum is low for this measurement, compared to the halobutynes, and may be insufficient to detect the other conformer.

IVR Measurements of the Acetylenic C−H Stretch: Planar Conformers. For all of the planar conformers, we find exceptionally slow IVR, some of the slowest IVR rates measured for the hydride stretch fundamentals.[3] The average IVR lifetimes for this series are reported in Table 1. Also included in this table are the measured and calculated anharmonic state densities (ρ_0) and the average intensity for a typical IVR multiplet (to indicate the measurement sensitivity). The state densities are calculated using a direct counting algorithm,[38] where all of the normal modes except for the torsion (isomerization coordinate) are taken to be harmonic. The energy levels for the torsion are calculated explicitly from the torsional barrier and the reduced rotational constant, F. The normal modes used are scaled from the HF calculations. The IVR rate for 1-pentyne has been previously determined by McIlroy and Nesbitt.[10] We have remeasured this spectrum using microwave-infrared double-resonance spectroscopy to remove the rotational inhomogeneity in the spectrum. An example of the double-resonance measurement for 1-pentyne is shown in Figure 4. The IVR lifetime determined from the rotationally resolved measurement is about a factor of 3 longer than the previous estimate based on a contour analysis. In general, the IVR lifetimes of the planar conformers are >1 ns in all cases. For 4-chloro- and 4-bromobut-1-yne, the IVR lifetimes for both isotopes of the halogen are the same. Some individual IVR multiplets, especially in the halobutyne series, show extremely long lifetimes with very little fragmentation of the oscillator strength. Two examples are shown in Figure 5.

TABLE 1: IVR Lifetimes for the Acetylenic C−H Stretch in Molecules with conformational isomers

molecule	$\tau_{\mathrm{IVR\,(ps)}}$	average intensity (mV)	measured state density (states/cm^{-1})	calculated state density (states/cm^{-1})
4-fluorobut-1-yne	1480	70	120	137
4-chlorobut-1-yne	3480	20[a]	135	164
4-bromobut-1-yne	1990	10[a]	145	214
cis-pent-1-en-4-yne	1200	10	170	194
trans−1-pentyne (gauche)	1000 (325)	25	1200	2400
gauche-methyl propargyl ether	300	35	400	750

[a] Intensity for a single hyperfine component (and isotope).

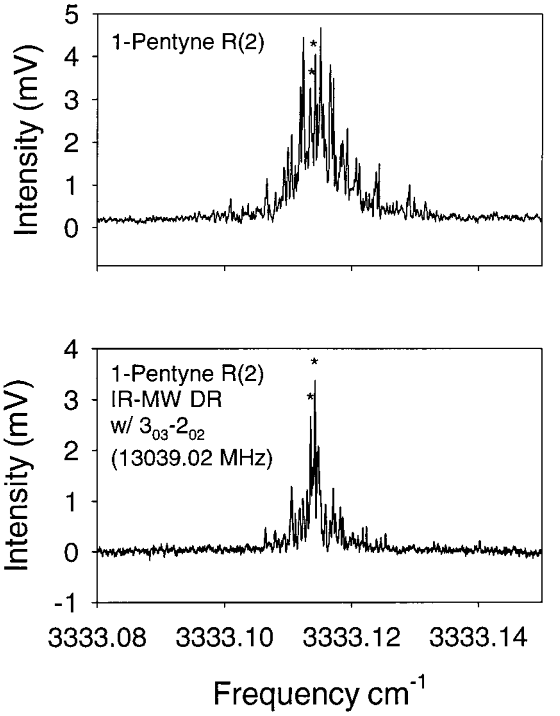

Figure 4. Example of a MW−IR measurement for 1-pentyne. A single photon IR spectrum of R(2) (top). This spectrum has an inhomogeneous width due to the overlap of different asymmetric rotor transitions. The MW−IR DR spectrum (bottom) extracts the IVR multiplet for a single rotational level ($3_{03}-2_{02}$) from which the (narrower) homogeneous width can be determined.

IVR Measurements of the Acetylenic C−H Stretch: Nonplanar Conformers. In their previous work on 1-pentyne, McIlroy and Nesbitt determined that the IVR rate for the nonplanar

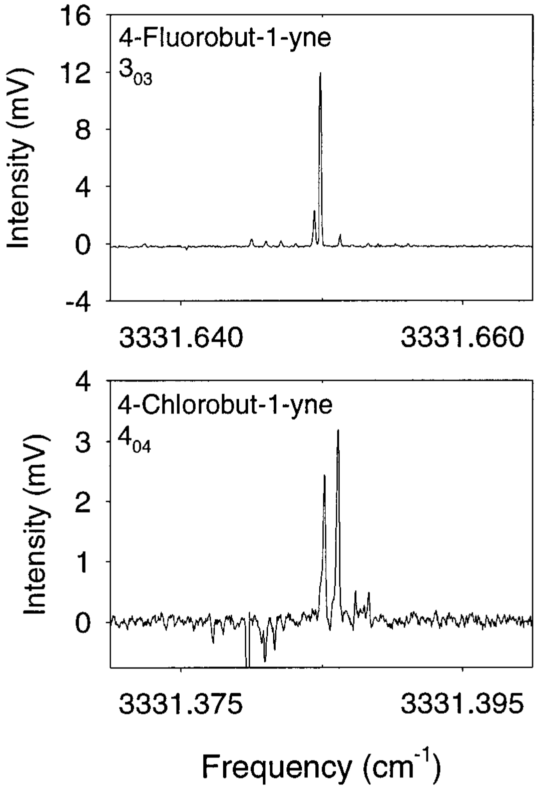

Figure 5. The 3_{03} IVR multiplet from 4-fluorobut-1-yne and the 4_{04} multiplet of 4-chlorobut-1-yne displayed here have extremely long lifetimes and very little fragmentation of the oscillator strength.

conformer was faster than that of the planar form.[10] We have had limited success in obtaining infrared spectra of the nonplanar conformers and, so far, have only two measurements (1-pentyne and methyl propargyl ether), also reported in Table 1. Both nonplanar conformers have an IVR lifetime of about 300 ps, a factor of 3 shorter than the planar forms. The apparent faster IVR rate of the nonplanar conformers may contribute to our inability to observe the spectra of the gauche conformers of the halobutynes and pent-1-en-4-yne.

B. Molecules with Symmetric Internal Rotation Groups. We have measured the IVR lifetimes of the acetylenic C−H stretch of several molecules with single methyl group substituents. The IVR lifetimes for these molecules, along with measured state densities, representative total IVR multiplet intensities, and the angle that the internal rotation axis makes with the *a*-principal axis, are presented in Table 2. In this case, the state densities reflect the anharmonic density of states with A-symmetry from the internal rotation. The barrier heights (V_3) for internal methyl group rotation are also listed in Table 2. These barrier heights have been determined previously through internal rotation splittings in the pure rotational spectrum for all molecules[39−42] except 3-fluorobut-1-yne which has been determined through far-IR measurements.[43] Of these molecules, only 1-butyne has been previously studied by high-resolution infrared spectroscopy.[10,13] The IVR lifetime we report for 1-butyne is considerably shorter than found in previous work. We find significantly broader multiplets with the higher sensitivity and double resonance capabilities of our measurements. A full presentation of the infrared spectrum of this molecule will be published elsewhere.

In the cases of 1-butyne, 2-methyl-1-buten-3-yne, and 3-fluorobut-1-yne, the IVR lifetime is obtained from the full infrared spectrum that contains transitions for both the *A*- and *E*-symmetry states (in the G_6 molecular symmetry group).[44] For the two pentenynes, the internal rotation splittings in the pure rotational spectrum are sufficient to separately assign the IR spectra for the two spin symmetries. The lifetime for the *A*-symmetry spectrum is reported; however, the lifetimes for the *E*-symmetry spectrum are the same. Also, in the case of 1-butyne, we have been able to make a partial separation of the spin symmetries through an infrared correlation method.[45] From this analysis, we find the IVR rates for both *A*- and *E*- spectra match the IVR rate determined from the measured composite spectrum. Therefore, we expect that the inhomogeneity caused by the overlap of the spectra from the two spin species cause only small effects in the rate determination for 2-methyl-1-buten-3-yne and 3-fluorobut-1-yne.[46]

The IVR lifetimes for this set of molecules falls into a well-defined range around 100 ps. Additionally, the IVR lifetimes are independent of the barrier height, which ranges from about 400−2000 cm^{-1}, as indicated in Figure 6. This result supports the previous conclusions of Perry based on a proximity hypothesis that the barrier to internal rotation has no effect on the IVR lifetime of the acetylenic C−H stretch.[27] Also, the IVR lifetime is largely independent of the orientation of the methyl group with respect to the principal axes: 1-butyne and (*E*)-pent-3-en-1-yne have the rotor axis oriented predominantly along the *a*-inertial axis, 2-methyl-1-buten-3-yne and (*Z*)-pent-3-en-1-yne have large projections on the *b*-axis, and 3-fluorobut-1-yne has projections along all three inertial axes. Tan and Pratt have suggested that the variation of the top orientation can be used to assess the importance of internal rotation contributions to the IVR dynamics because this orientation determines the relative strengths of different Coriolis terms that couple internal rotation to overall rotation of the frame.[47] The independence of the IVR lifetimes on this parameter, however, along with the fact that the IVR lifetimes show no dependence on the rotational quantum numbers, suggests that the methyl rotor dynamics do not play a significant role in the IVR process for the acetylenic C−H stretch. In a full analysis of the infrared spectra of the pentenynes we will further describe the role that the rotor plays in IVR.[48]

The set of molecules with methyl rotors in this study were chosen for their similarity to the molecules that can exist as conformers. For example, 1-butyne can be considered to be a member of the series $HC{\equiv}C{-}CH_2{-}CH_2X$ (with X = H, F, Cl, Br, CH_3). 2-Methyl-1-buten-3-yne, (*Z*)-pent-3-en-1-yne, and (*E*)-pent-3-en-1-yne are structural isomers of pent-1-en-4-yne, although they do differ in the bonding of the third carbon atom in the $H{-}C{\equiv}C{-}C$ functional group.

3-Fluorobut-1-yne, a structural isomer of 4-fluorobut-1-yne, was prepared explicitly for this study. We also synthesized and measured the infrared spectrum of 3-chlorobut-1-yne. Because of the large spread of infrared intensity resulting from the existence of two isotopes and the hyperfine induced dilution of the rotational spectrum, a complete analysis of 3-chlorobut-1-yne was not performed. The Q branch was identified, however, and an IVR rate of 105 ps was determined from the leading edge of the Q branch, giving a lower bound to the IVR rate.[49] This value agrees well with the results for the other nonconformer molecules in this study. A direct comparison of the two fluorobutyne spectra is shown in Figure 7. This demonstrates the disparity in IVR lifetimes for these two systems and illustrates our general conclusion that planar conformers, as a class, are highly resistant to IVR.

C. Other Hydride Stretch Chromophores. A natural question is whether the hierarchy of IVR lifetimes observed for the acetylenic C−H stretch occurs for other infrared

TABLE 2: IVR Lifetimes for the Acetylenic C−H Stretch for Molecules with a Single Methyl Rotor

molecule	τ_{IVR} (ps)	average intensity (mV)	measured state density[a] (states/cm^{-1})	calculated state density (states/cm^{-1})	barrier height[b] (cm^{-1})	methyl angle[c]
(*Z*)-pent-3-en-1-yne	150	20[e]	85	75	389	76.8°
(*E*)-pent-3-en-1-yne	90	35[e]	75	84	666	15.3°
1-butyne	70	150	15	17	1090	47.55°
3-fluorobut-1-yne	140	110	130	116	1441	61.4°[d]
2-methyl-1-buten-3-yne	105	25	40	36	2016	59.2°

[a] Measured and calculated state densities are for A_1 symmetry. [b] The barrier to internal methyl rotation has been measured by the pure rotational spectrum (References 39−42 except for 3-fluorobut-1-yne which has been determined by far-IR measurements (ref 43)). [c] Angle of the internal rotation with respect to the principal axis. [d] Determined by ab initio structure. The others are from the structures determined from the pure rotational spectrum. [e] A-symmetry only. The other totals are expected to have equal contributions from the A- and E- symmetry spectra.

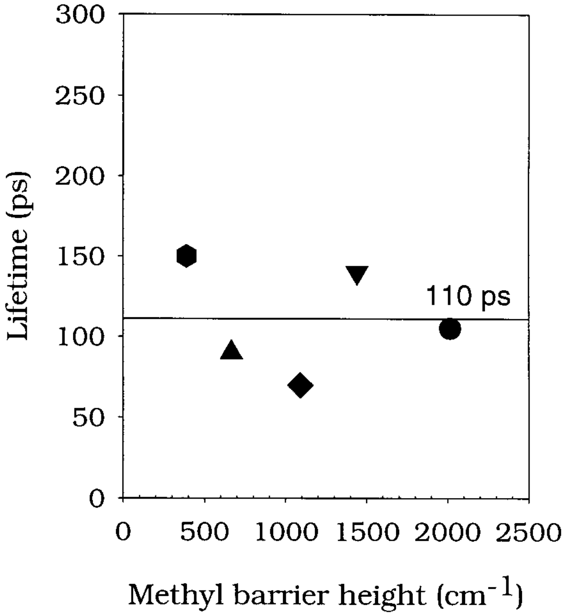

Figure 6. Acetylenic C−H stretch IVR lifetime of different molecules is shown as a function of methyl barrier height. The values fluctuate around 100 ps with no correlation between barrier height and IVR lifetime. ⬢-(*Z*)-pent-3-en-1-yne, ▲- (*E*)-pent-3-en-1-yne, ◆-1-butyne, ▼−3-fluorobut-1-yne, ●-2-methyl-1-buten-3-yne.

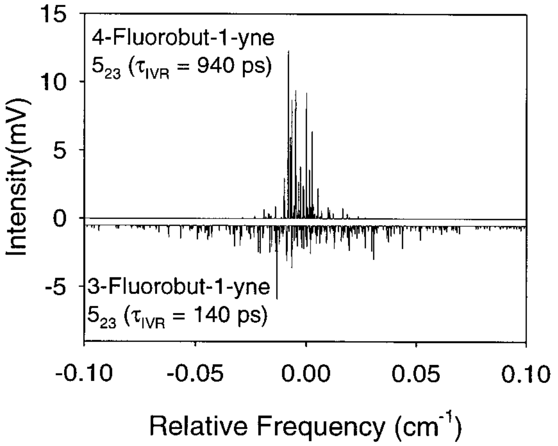

Figure 7. Infrared spectrum of the 5_{23} IVR multiplets for 4-fluorobut-1-yne (top) and 3-fluorobut-1-yne (bottom). These molecules differ only by the placement of the fluorine atom; however, there are large differences in the observed spectra. The top spectrum corresponds to an IVR lifetime of 940 ps, whereas the bottom has a lifetime of 140 ps.

chromophores. The data set for other systems is small at present, however, in part because the oscillator strength for other C−H stretches is weaker than for the acetylenic C−H. In our laboratory, we have studied the spectra of a few molecules with the $=CH_2$ chromophore, and the trend appears to be the same. For example, we have obtained the IVR lifetimes for both the planar cis and nonplanar gauche conformers of allyl fluoride.[50] The lifetime for the cis conformer is in the range of 1−3 ns and the gauche conformer has a lifetime of 100 ps. However, as we have discussed previously, the state density for this system places it close to the IVR threshold and may lead to an underestimate of the rate for cis conformer. We have also measured the IVR lifetime of the planar cis conformer of methyl vinyl ether.[32] Unfortunately, this spectrum contains a strong resonant interaction that complicates the dynamics. In our attempt to deconvolute the IVR rates through a two-state analysis, we found that the cis $=CH_2$ bright state was long-lived, with a lifetime of about 700 ps, and maybe longer. Also in methyl vinyl ether, we were able to obtain the pure rotational spectrum of the less stable (nonplanar) conformer but could find no evidence of its infrared spectrum. This result is similar to our experiences for the halobutynes and pent-1-en-4-yne.

By comparison, the IVR lifetime of isobutene ($(CH_3)_2C=CH_2$), where conformers do not exist, was determined to be about 100 ps, in agreement with the lifetimes we have observed for the methyl rotor series in this work. A possible counter example to the general trend is that we find relatively slow IVR for the ethylenic $=CH_2$ stretch of 2-methyl-1-buten-3-yne (420 ps). This lifetime is longer than the one we report for the acetylenic C−H stretch in Table 2. However, this lifetime may be underestimated due to the lower signal-to-noise ratio in the ethylenic $=CH_2$ stretch measurement.

The trend of slow IVR in planar conformers, compared to molecules without conformational freedom, does not appear to hold for the methyl C−H stretches. For example, in the study of 1-pentyne by McIlroy and Nesbitt[10] there was no discernible structure in the methyl stretch region of the spectrum indicating fast IVR compared to the acetylenic C−H stretch. Also in their work on butene, McIlroy and Nesbitt found a discrete spectrum for the C−H stretch of *trans*-2-butene, indicating slow IVR, whereas the C−H stretch spectrum of 1-butene, which has an isomerization coordinate, displayed continuous absorption.[23] We have determined the IVR lifetime for the methyl C−H stretch in the planar cis conformer of methyl vinyl ether (70 ps).[51] This lifetime is much shorter than our estimated lifetime of 700 ps for the ethylenic C−H stretch. Furthermore, the methyl C−H stretch lifetime for 1-butyne measured by Bethardy and Perry is comparatively long at 275 ps.[52] Finally, the methyl C−H stretch lifetime in the planar trans conformation of ethanol, also determined by Bethardy and Perry, is 59 ps.[53] For this chromophore, a different mechanism appears to control the IVR rates, perhaps the proximity effect proposed by Perry.

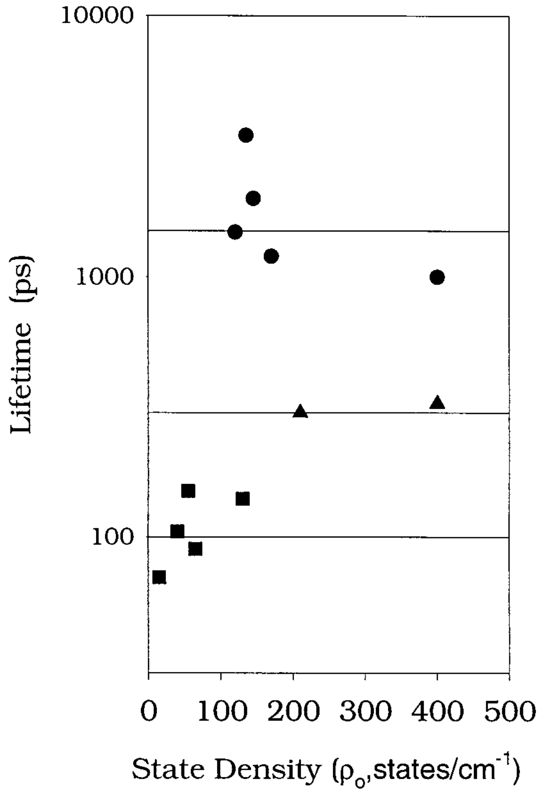

Figure 8. IVR lifetimes for the acetylenic C−H stretch. The planar conformers (●) all have lifetimes greater than 1 ns, the nonplanar conformers (▲) both have a lifetime near 300 ps, and the molecules with methyl rotors (■) have IVR lifetimes around 100 ps.

Conclusions

We have presented a series of IVR lifetime measurements for the acetylenic C−H stretch that shows a strong structural correlation. A summary of the IVR lifetime results for the acetylenic C−H stretch is shown in Figure 8. One conclusion from Figure 8 is that the IVR lifetime is independent of the total state density, a point that has been emphasized previously.[3] However, the second feature of this figure is that there are apparently three distinct classes of IVR lifetimes: planar conformers >1000 ps, nonplanar conformers ~300 ps, and methyl rotors ~100 ps. This result further supports the idea that features of the molecular structure can influence the vibrational dynamics of the molecule.

One possible explanation for the relatively slow rates of the planar conformers is that the region of the torsional potential sampled by their ground torsional state is less anharmonic than for the gauche conformer and in the 3-fold-symmetric methyl rotor potential. However, comparison of the potentials for the set of molecules studied here show minimal differences. For example, the potential surfaces for the two fluorobutynes are compared in Figure 9. The similarity reflects the fact that the Fourier expansion of the isomerization potential is dominated by the $n = 3$ term.

For the methyl rotor series, the internal rotation barrier height appears to play no role in the dynamics (for the isomerization potentials, there is less variation in the barriers than for the methyl rotor series so it is harder to determine whether there is a height effect). In terms of the proximity hypothesis of Perry, the internal rotation dynamics are assumed to have no effect on the IVR rate because the rotor coordinate is several bonds away from the acetylenic C−H stretch.[27] This argument is frequently made based on the physical grounds that the initial IVR rate is determined by the direct coupling of the acetylenic C−H stretch to the rest of the vibrational states. As the molecule is extended, it is not expected that vibrational motion at the “far end” of the molecule can couple to the excited vibrational mode. However, the results presented here show that the structure beyond the C−C≡CH substituent can have a large impact on the dynamics. This idea is illustrated in Figure 7 where the position of the fluorine atom in the structure significantly modifies the IVR rate.

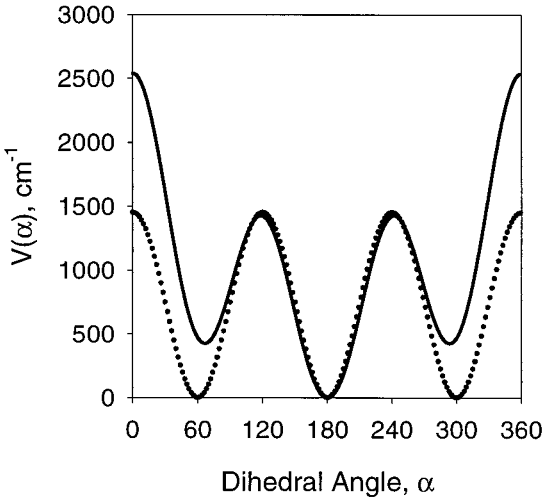

Figure 9. Comparison between the isomerization potential for 4-fluorobut-1-yne (from ab initio calculation) and the barrier for methyl rotation of 3-fluorobut-1-yne (ref 43) is shown. The potentials are not different in the region of the planar (trans) conformer (180°)

As a whole, this data set will provide a challenging benchmark for theoretical methods of calculating IVR rates because of the large range of time scales observed for structurally similar molecules. Previous theoretical studies based on an artificial intelligence algorithm that identifies important low-order anharmonic resonances have successfully accounted for the very different IVR rates of $(CH_3)_3C{-}CCH$ (200 ps) and $(CH_3)_3Si{-}CCH$ (2000 ps).[54,55] Further developments that define relationships between the interaction matrix elements have led to the successful modeling of the IVR dynamics of propyne.[56] Alternatively, this series might be useful for testing new ideas for explaining IVR rates. For example, the coupling between internal rotation of methyl groups and other vibrational motions of the molecule has been shown to arise through electronic interaction.[57,58] These effects suggest that the shapes of the molecular orbitals for different conformers could play a role in determining the IVR rate, perhaps leading to the conformer-specific rates observed in the present study.

The main weakness of this data summary is the data set that is missing. To completely address the problem, a study measuring the IVR lifetimes of molecules with no internal rotors is needed. For example, we are unsure whether the IVR lifetimes of the planar conformers should be considered significantly longer than expected, or whether the methyl rotor series is significantly shorter than expected (as suggested by the original work of Parmenter and Stone).[59] The main difficulty is finding a molecule without a large amplitude coordinate that has a state density above the IVR threshold in the region of the hydride stretch fundamentals. Extension of this work to the first overtone, which might now be possible due to the significant sensitivity improvements achieved using laser build-up cavities,[60] would potentially be able to make this final comparison and would show whether the basic effect we have presented is still operative at higher energies.

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