Intramolecular vibrational dynamics of diacetylene and diacetylene- d 1 via eigenstate-resolved overtone spectroscopy

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Intramolecular vibrational dynamics of diacetylene and diacetylene-d_1 via eigenstate-resolved overtone spectroscopy

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Abstract

The high resolution spectra of several CH overtone bands in diacetylene and diacetylene-d_1 were measured using optothermally detected excitation of a collimated molecular beam. The first overtone of the acetylenic CH stretches in these two molecules were recorded in a single resonance scheme using a 1.5 μm color center laser. The second overtone spectra were taken using sequential infrared/infrared double resonance with a 3.0 and a 1.5 μm color center lasers. The perturbations in the spectra have been analyzed to obtain information about the nature and timescales of the underlying intramolecular vibrational redistribution processes. The uncovered dynamical features appear to be dominated by anharmonic couplings and exhibit regular, not chaotic, behavior. The first and second overtone spectra of diacetylene-d_1 are consistent with a coupling model which involves coupling through a doorway state and then subsequent coupling to the bath. In diacetylene, a combination band was also recorded which, in the local mode picture, is equivalent to putting two quanta in one acetylenic CH stretch and one quanta at the other end of the molecule. Comparison of this spectrum with the spectrum obtained by putting three quanta in the same CH stretch, is consistent with earlier observations that delocalized combination bands are less perturbed than nearly isoenergetic pure overtone states.

1. Introduction

During the past decade, several research groups have used high resolution, infrared spectroscopy of jet-cooled samples to study intramolecular vibrational energy redistribution (IVR) in a large number of molecules (for a recent review see Ref. [1]). In some cases several different vibrational states of the same molecule have been studied. Analysis of the spectra gives the coupling strengths of the initial (bright) state with the nearly isoenergetic vibrational states that have no direct absorption strength from the ground state (dark states), and allows the calculation of the population decay of the bright state. These experiments, however, give only limited direct information about the characteristics of and the couplings between the dark states. In order to extract the maximum information from the experiments, extensive theoretical modeling of the bath levels, including important anharmonic interactions must be carried out. Such an analysis requires that the molecule be well characterized spectroscopically.

While many molecules have been thoroughly studied by vibrational spectroscopy, most have too small a density of vibrational states to show extensive IVR in states that can be reached by excitation in the near-IR. A particularly interesting exception is diacetylene. The high symmetry of this molecule dramatically reduces the number of important low order anharmonic reso-

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nances. The fundamentals and many hot band transitions have been studied by high resolution spectroscopy, leading to a wealth of spectroscopic data [2–7]. Botschwina has carried out a high level ab initio calculation of the anharmonic potential function for the stretching modes, and this potential does an excellent job at predicting the fundamental spectrum, including the unexpected ordering of the symmetric and antisymmetric CH stretching modes [8]. Perhaps most importantly, diacetylene could provide an important test for the utility of transferring knowledge gained about IVR from a given molecule to another that may show a higher degree of complexity. IVR in the spectrum of acetylene has been thoroughly studied by both near-IR [9] and SEP [10] spectroscopies, and a complex set of interacting resonances have been analyzed. Given the great similarity of the normal modes of acetylene and diacetylene, one can hope that the acetylene results can be used to determine the most important low order resonances in diacetylene. These can then be used to calculate the IVR dynamics in diacetylene, similar to what has been done previously in some larger systems [11], where the potentials are however much less known, and the available spectroscopic information far less detailed.

In this paper we have studied the high resolution spectra of several overtone bands in diacetylene and diacetylene-d_1 with the goal of elucidating the effects on IVR of varying both the distribution of energy within the molecule by exciting different transitions and the distribution of dark states by substituting a terminal deuterium. For diacetylene and diacetylene-d_1, the first overtone spectra of the CH stretch were measured using a 1.5 μm color center laser and the second overtones were recorded by infrared/infrared double resonance. By sequential excitation with 2 infrared photons, the $v = 3$ spectra can be reached with less overall power than by direct $3 \leftarrow 0$ excitation, since $3 \leftarrow 0$ is more "forbidden" than $3 \leftarrow 1$. Furthermore, with two photon excitations new vibrational states can be reached which are not allowed, or only weakly allowed, with one photon excitation. These include the symmetric, or gerade, stretches in molecules with a center of inversion and delocalized combination bands. As an added advantage, the rotational quantum numbers assigned in the first step in the sequential excitation restrict the number of states accessible at the final level of excitation. This reduces the possibility of misassign-

ing lines as a result of the finite precision in the experiment.

Room temperature spectra in the region of the second overtone of the CH stretch of diacetylene were previously studied using photographic plates at 0.2 cm^{-1} resolution [12], and more recently using a Fourier transform spectrometer with an instrumental linewidth of 0.002 cm^{-1} [3]. In the higher resolution study, the spectrum contained at least three perturbations caused by resonant crossings, making a fit for the upper state constants impossible. Here we have recorded the spectra of several overtone bands near 6565, 9685 and 9896 cm^{-1} in diacetylene and near 6561 and 9686 cm^{-1} in diacetylene-d_1 at 0.0005 cm^{-1} resolution. It is our hope that besides yielding additional information about the wide variation in IVR dynamics of acetylenic CH stretches, the results of this study can be used for later comparison with theory. The relatively low number of atoms present in diacetylene allows, in principle, the accurate a priori calculation of all intramolecular couplings, presenting an opportunity for making real progress towards a fully predictive theory of IVR in isolated polyatomic molecules.

2. Experimental

Diacetylene was synthesized via the method of Armitage et al. [13]. 1,4-dichloro-2-butyne (Aldrich), aqueous potassium hydroxide, and dioxane were heated between 80 and 90°C under reflux. The evolved gas was dried over $CaCl_2$ and collected in a liquid nitrogen trap without further purification. Diacetylene-d_1 was made by washing diacetylene with a 50/50 mixture of D_2O/H_2O and Na at 0°C for a few hours [14]. This resulted in a statistical mixture of diacetylene, diacetylene-d_1, and diacetylene-d_2. However, no attempts were made to separate the species. Therefore the single resonance spectra of diacetylene-d_1 also contained many transitions due to diacetylene which were easily assigned and were then used for additional frequency calibration. The diacetylene-d_2 impurity did not interfere since its absorptions are in a different frequency region. For beam formation, the molecules were used diluted in helium at concentrations between 0.5 and 1%.

The spectra were recorded in a high resolution, bolometer based, molecular beam spectrometer which

has been described previously [15]. In brief, the technique consists of a supersonic expansion through a 50 μm pinhole nozzle, followed by collimation of the beam through a 0.5 mm diameter conical skimmer, interaction with the laser radiation, and final detection by a liquid helium cooled bolometer. The laser interaction region consists of two plane parallel gold mirrors in which both lasers cross the molecular beam about 20 times. Both lasers are Burleigh color center lasers which have been set up to scan under computer control. The laser frequency is continuously monitored using two external scanning etalons (150 MHz and 8 GHz) and a custom built comparator circuit [16]. The circuit consists of an analog sample and hold which monitors the positions of the etalon transmission peaks with respect to their external ramping voltages. The first laser is a Burleigh FCL-20, lasing at 3.0μm with about 18 mW of power. The linewidth resulting from slightly nonorthogonal crossings in the multipass cell is about 8 MHz. The second laser, a Burleigh FCL-220, has about 180 mW of power around 1.6 μm and generates a final linewidth of 16 MHz.

The methodology for the double resonance experiments has been described in Ref. [17]. A sequential process is used to deposit three quanta of vibrational energy into a CH stretch. The 3.0 μm laser is held resonant with a particular ro-vibrational transition in the $1 \leftarrow 0$ spectrum. The 1.5 μm laser is then scanned over the region of the $3 \leftarrow 1$ spectrum. Only $\Delta J = \pm 1$ transitions are allowed, making the resultant spectra unequivocally assigned by the quantum numbers of the first step. In the case of the combination band $(\nu_1 + 2\nu_4)$, there are $2 \leftarrow 0$ transitions in the same region as the $3 \leftarrow 1$ spectrum. The latter is compared with the one photon $(2 \leftarrow 0)$ spectrum, and the new features attributed to double resonance signals.

Absolute frequencies were obtained using a home built wavemeter [18], except for the ν_1 spectra of diacetylene where literature values were used [2]. The wavemeter has a relative accuracy of about 0.005 cm^{-1} and is corrected for absolute accuracy against known acetylene transitions. Because of the nature of the double resonance experiments, the spectrum is not obtained continuously but piece-wise. Absolute frequencies are determined by using the wavemeter readings to identify the correct 150 MHz etalon order to within ± 1 order. The relative frequency of the clump on the identified 150 MHz etalon trace is then used to position the frequencies of the clumps relative to each other. The 150 MHz etalon used in conjunction with the 1.5 μm laser is temperature stabilized to within 0.01 °C and hermetically sealed. It is assumed not to drift significantly during the time required to record a band (about 10 hours).

3. Results

Both diacetylene and diacetylene-d_1 are linear molecules with all stretches showing parallel type transitions with the usual selection rule $\Delta J = \pm 1$. Since diacetylene is a symmetric molecule ($D_{\infty h}$), it imposes the added u ← g selection rule. With two photons, i.e. in a double resonance experiment, the sequence is g ← u ← g and so the final state is of g vibrational symmetry. The bands we have recorded in this study are summarized in Table 1 along with the $v = 1$ bands of diacetylene (ν_1 and ν_4) for which literature values are shown [2].

The overtones of diacetylene are better described in the local mode picture as discussed by Child and Halonen [19]. These authors define a dimensionless parameter equal to the bond anharmonicity over the net coupling between equivalent bonds ($\omega\chi_e/\lambda$). In the limit $\omega\chi_e/\lambda \gg 1$, the molecule displays local mode dynamics while for the other extreme, $\omega\chi_e/\lambda \ll 1$, the molecule is in the normal mode limit. This parameter is about 70 for diacetylene indicating that the local mode picture should apply. The first overtone spectrum, $v = 2 \leftarrow 0$, is thus more accurately described as the asymmetric combination of 2 quanta in one acetylenic bond plus 0 quanta in the other. In double resonance, the first laser, at 3.0 μm, deposits one quantum into a CH stretch. The second laser, near 1.6 μm, can either put two quanta of vibration into the same CH stretch, resulting in the $(3, 0)^+$ band, or put two quanta into the opposite end of the molecule, resulting in the $(2, 1)^+$ band.

The density of background states listed in Table 1 were calculated by a direct count, constraining the total vibrational angular momentum to zero. The normal modes listed in Refs. [2] and [14] were used for diacetylene and diacetylene-d_1, respectively. Diagonal anharmonicities for the stretching modes were obtained from Ref. [8] except for the CH stretches for which the value obtained in this work was used. The bending

Table 1
Classifications of CH stretch excitations in diacetylene and diacetylene-d_1

	Number of vibrational quanta	Normal mode	Local mode	Symmetry	Energy (cm^{-1})	Density of symmetry allowed states (/cm^{-1}) (partial anharmonic count)
diacetylene	1	ν_1	$1,0^+$	Σ_g^+	3332.155 [2]	
		ν_4	$1,0^-$	Σ_u^+	3333.665 [2]	0.5
	2	$2\nu_1$	$2,0^+$	Σ_g^+	–	
		$(\nu_1 + \nu_4)$	$2,0^-$	Σ_u^+	6565.472	14.6
		$2\nu_4$	$1,1^+$	Σ_g^+	–	
	3	$3\nu_1$	$3,0^+$	Σ_g^+	9684.566	173
		$(2\nu_1 + \nu_4)$	$3,0^-$	Σ_u^+	9683.810 [3]	
		$(\nu_1 + 2\nu_4)$	$2,1^+$	Σ_g^+	9895.983	197
		$3\nu_4$	$2,1^-$	Σ_u^+	–	
diacetylene-d_1	1	ν_1		Σ^+	3331.931	1.2
	2	$2\nu_1$		Σ^+	6561.141	41.8
	3	$3\nu_1$		Σ^+	9685.878	535

modes X_{ij} and g_{ij} were estimated from those reported for cyanoacetylene [20]. The only off diagonal anharmonicities used were between the CH stretches and C–C≡C bends, which is very large in cyanoacetylene (-20 cm^{-1}) [20]. The anharmonicity of the CD stretch was estimated to be -25 cm^{-1}.

The calculated density of states indicates that, at $v = 1$, both molecules fall in the sparse regime of IVR where perturbations to the expected distortable rigid-rotor Hamiltonian spectra should be nonexistent or very small and local in nature. At $v = 2$, the spectra are moving from the sparse to the intermediate regime where more perturbations in the spectrum are typically observed. By $v = 3$, both molecules are well into the intermediate regime and perturbations become the rule instead of isolated occurrences. If Coriolis, or rotational, forces are present, the effect is to increase the density of available background states even further than that allowed by vibrational symmetry alone.

3.1. Spectroscopy of diacetylene

3.1.1. The (2, 0)⁻ band

The first overtone of the acetylenic CH stretch in diacetylene was recorded from P(17) to R(15). The spectrum, particularly at low J, is characterized by the presence of 3 strong lines for each transition and many weak lines. The three lines are split by a total of 0.49 cm^{-1}, while $2B$ is only 0.29 cm^{-1} (Fig. 1). Ground state combination differences were calculated using the

ground state constants reported by Guelachvili et al. [2]. The average deviation from the calculated combination differences was 3 MHz for the strong lines in the spectrum. Many weak lines throughout the spectrum fit correctly to the combination differences but could not be followed with J. For example, over the whole spectral range recorded, R(0) and P(2) had 16 lines that matched combination differences to within 8 MHz and had the correct intensity ratios. In the energy region of the three stronger lines, there were about 7 other weak lines, with intensity less than 10%, that could be assigned to R(0) and P(2). With the degree of overlap between neighboring J clumps, the possibility of accidental coincidences, and the inability to
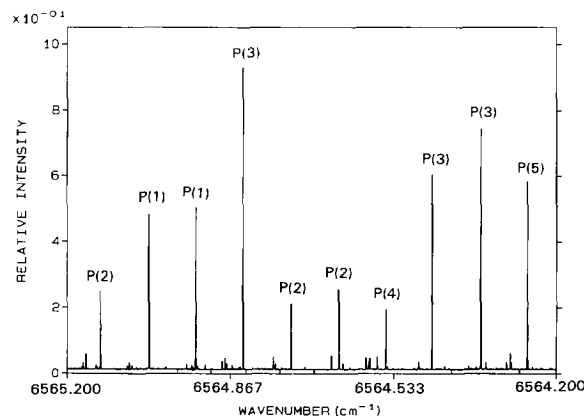

Fig. 1. A 1 cm^{-1} portion of the P branch in the spectrum of the (2, 0)⁻ band of diacetylene.

follow each line with J, it is difficult to definitively assign these small lines.

Attempts to fit the center of gravity of the spectral features to a standard distortable rigid rotor formula while including just the 3 strong lines at each J or all the reasonable lines that have the correct combination differences, were not successful. The center frequency for the band was determined to be $6565.466(16)$ cm^{-1}; however, ΔB was indeterminate, and the standard deviation of the fit was 488 MHz. Most of the problems of the fit can be attributed to the magnification of intensity errors in the spectrum by the extremely large spacing of the transition. Estimating the error in frequency to be 3 MHz and the error in intensity to be 5% for each line results in an error in the centers of gravity of 190 MHz.

Each of the three strong lines could be fit individually over a limited region of J, however. The lowest and the middle frequency line of each clump were fit from R(5) to P(7) with a standard deviation of 5 and 8 MHz, respectively. After this point a fourth line begins to gain intensity and it appears that the three states interact. The higher frequency line was fit from R(8) to P(10) with a standard deviation of 10 MHz. Results of these fits are summarized in Table 2. The fits for the 3

Table 2
Spectroscopic constants determined for the three strong eigenstates in the $2\nu_1$ band of diacetylene (cm^{-1}) [a]

lowest frequency line (R(5)–P(7))	
ν_0	6565.26313 (24) [b]
B'	0.1469723 (296)
ΔB	16.830 MHz
D'_J	3.418 (658) $\times 10^{-6}$
σ of the fit	5.4 MHz
middle frequency line (R(5)–P(7))	
ν_0	6565.35853 (26)
B'	0.1476952 (114)
ΔB	38.50 MHz
D'_J	–
σ of the fit	8.2 MHz
highest frequency line (R(8)–P(10))	
ν_0	6565.75111 (23)
B'	0.1465898 (197)
ΔB	5.363 MHz
D'_J	$- 1.80$ (22) $\times 10^{-7}$
σ of the fit	9.7 MHz

[a] Lower state constants were constrained to $B_0 = 0.1464109$ and $D_{J0} = 1.565 \times 10^{-8}$ cm^{-1} [2].
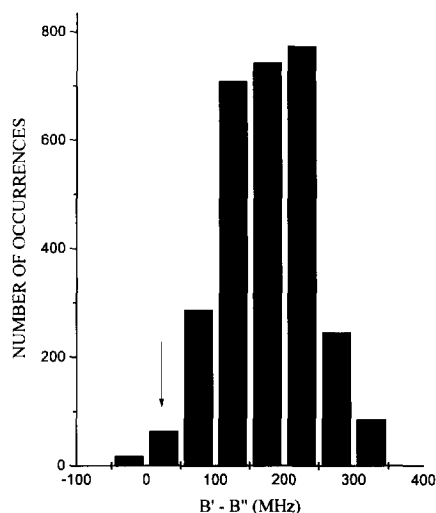[b] Error reported in parenthesis represent 2σ of the fit.

Fig. 2. Histogram of ΔB values expected between 6540 and 6590 cm^{-1}. States located by a direct count including diagonal anharmonicities and rotational constants estimated as discussed in the text. The arrow marks the positions of the ΔB's of the three strong eigenstates.

states yielded unexpected values for D'_J. For the middle frequency line, D'_J could not be determined. The 2σ error in the calculated value was greater than the value itself and including the extra parameter did not improve the standard deviation of the fit. The lowest frequency line had a D'_J value 2 orders of magnitude larger than that of the ground state and the highest frequency line produced a negative value. These are both indications of the presence of nonresonant perturbations acting on the spectrum as the interacting state tunes with J'.

A modified version [21] of the Lawrence–Knight deconvolution method [22] was used to extract the position of the bath states and their coupling strengths by deconvoluting the energies and intensities of the eigenstates. The root mean square coupling matrix element between the three strong lines was calculated to be 0.15 cm^{-1} through $J' = 6$.

The calculated density of states for this band is about 15 symmetry-allowed vibrational states per cm^{-1}, or 3000 states in a 50 cm^{-1} region around the band center. It is difficult to identify the exact perturbing state or states; however, we do have some information. Fig. 2 shows a histogram of ΔB's for all the states calculated between 6540 and 6590 cm^{-1}. The energy and number of vibrational quanta in each mode were determined by a direct count using the anharmonicities described earlier. The vibration–rotational interaction constants,

α_i's, for modes ν_4 through ν_9 were obtained from Ref. [2]. The constants for the parity doublet levels of the bending modes were averaged together. The values for α_1 and α_2 were assumed to be the same as for α_4 and α_5, and α_3 was estimated from cyanoacetylene [23]. As seen from the arrow marking the position in the histogram of the three eigenstates, they fall well to one side of the distribution. The perturbing states must contain some bend character, as shown by the positive ΔB values. However a significant portion of stretch character must also be present since the final ΔB's are relatively close to zero. Instead of a statistical mixture of all possible perturbing modes causing the perturbations, specific states appear to be responsible. If we assume the fraction of bright state character in each of the three lines to be about 1/3 and subtract the contribution of the bright state to ΔB by estimating it to be twice that of the ν_1 band [2], we obtain a $\Delta B = +31.81$, 64.32 and 14.61 MHz for the three eigenstates. Considering only ΔB's for the bath states within ± 7 MHz and a range of energies around the bright state $(6565.466 \text{ cm}^{-1})$ of $\pm 10 \text{ cm}^{-1}$, there are still several bath states that may be causing each perturbation. For example, for the lowest frequency line at 6565.2631 cm^{-1} there is a calculated state at 6563.980 cm^{-1} with a $\Delta B = +31.98$ MHz comprised of $(3\nu_3 + \nu_5 + \nu_7 + \nu_8 + 4\nu_9)$ and a second state at 6563.400 cm^{-1} with a $\Delta B = +33.32$ MHz corresponding to $(3\nu_3 + \nu_5 + \nu_6 + \nu_7 + 4\nu_9)$. Considering that we have made several approximations and that there is no evidence that a single state is causing the perturbation, it is impossible to identify the perturbing states. All of the realistic possibilities contain a fair number of quanta, in the region of 7 to 10, with no energy in ν_1 or ν_4 (CH stretch modes). The average number of quanta for all the bath modes calculated in the region between 6540 and 6590 cm^{-1} is 14.2 with a standard deviation of 3.7, so the 7 to 10 quanta comprised in the possible perturbing states are a little below average.

3.1.2. The (3, 0)$^+$ band

The second overtone of the CH stretch in diacetylene was recorded in double resonance by first exciting and locking on a particular rovibrational transition of the fundamental CH stretch spectrum, ν_1, and then scanning the second laser in the $3 \leftarrow 1$ region. Transitions with $J' = 0$ through 8 were recorded. The transitions of the $3 \leftarrow 1$ step were fitted using the lower state constants

Table 3
Spectroscopic constants determined from a linear least squares fit for $(3, 0)^+$ band of diacetylene (cm^{-1}) [a]

ν_0	9684.5656 (10) [b]
B'	0.145903 (27)
D'_J	–
σ of the fit	27 MHz

[a] Lower state constants and D'_J were constrained to those reported in Ref. [2] for the ν_1 band, as described in the text.
[b] Error reported in parentheses represent 2σ of the fit.

determined by Guelachvili et al. [2] for the ν_1 band and determining the relative frequencies between the transitions as described in the experimental section. Results of the fit are listed in Table 3. D'_J was not statistically determined since the 2σ error was greater than the actual value and so was constrained to the lower state value. The standard deviation of the fit was 27 MHz. An estimate of the error in the centers of gravity based on an energy error of 3 MHz and an intensity error on the order of 10% is 44 MHz. Since the error of the fit is well within this limit we obtain an indication that, despite the limited signal to noise ratio particularly at high J, most transitions of significant intensity have been accounted for correctly.

Fig. 3 shows two of the J's recorded. The appearance of $J' = 2$ and $J' = 6$ (not shown) indicates a smaller number of perturbations than the other rotational transitions. Table 4 summarizes some of the information obtained from the band as is typically determined from a highly fractionated, intermediate case IVR spectrum. First, the experimental density of states is determined by counting the number of eigenstates in the clump minus one (the bright state) and dividing by the energy region over which the states are seen. Comparing the experimentally observed density of states to the calculated one (173/cm^{-1}), one sees that for most J's the observed value is less than the calculated. There are large fluctuations around the average, however.

Next, listed in Table 4, is the dilution factor σ_d. This is defined by McDonald to be a factor by which the infrared fluorescence is diluted by IVR relative to what is expected for the unperturbed level [24]. It is calculated from the spectrum by taking the sum of the squared intensities of the individual transitions in a clump divided by the square of the sum of their intensities. $J' = 2$ and 6, which appear to be less perturbed, exhibit above average dilution factors.
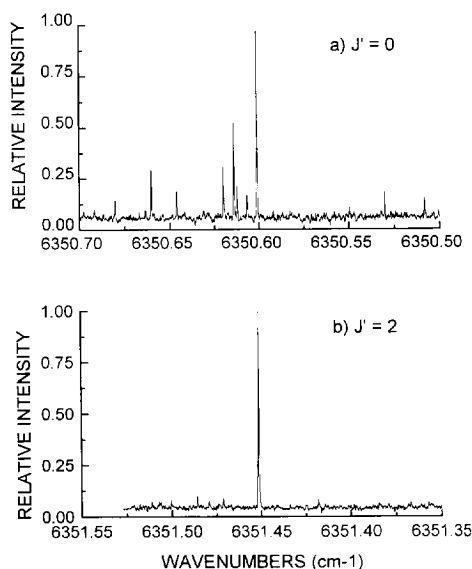
Fig. 3. The $(3, 0)^+$ band in diacetylene recorded using sequential infrared/infrared double resonance. The energy scale represents the frequency of the scanning laser. (a) $J' = 0$ is reached by a R(0) (at 3333.9571 cm^{-1}) followed by a P(1) sequence. (b) $J' = 2$ is reached with a R(0) (at 3333.9571 cm^{-1}) followed by a R(1) sequence.

Lifetimes can be calculated from a frequency resolved spectrum using the fluorescence theorem which determines the survival probability of the bright state [25]. Use of this theorem necessitates considering IVR in the time domain. A hypothetical, infinitely short pulse is used to coherently prepare the bright state at time $t = 0$. This bright state decays in time by transfer-

ring vibrational energy to the other modes of the molecule. This time decay is what we call the lifetime of the state at some characteristic point, typically the 1/e point. In the frequency domain, there is no actual time decay since we are exciting the molecular eigenstates, or the admixtures of the bright state and dark states. However, a Fourier transform of the autocorrelation function of the frequency domain spectrum puts us into the time domain picture. Bethardy, Wang and Perry have suggested that a more realistic reference point for comparing lifetimes, particularly for spectra which are not highly fractionated, is not the 1/e point but instead is $(\sigma_d + (1/e^*)(1 - \sigma_d))$ where σ_d is the dilution factor [26]. This is because the probability of remaining in the bright state for spectra that are not very fractionated decays, or oscillates, around the dilution factor instead of zero. States which are only slightly fractionated often do not show a real decay at all; instead they exhibit quantum beats representing energy flow between a few states. For these clumps an "effective" lifetime can be calculated using Fermi's golden rule. This estimate is only accurate in the limit of statistical IVR where there is a continuum of bath states. However, it can be useful to represent an "effective" lifetime for comparing the dynamics of different spectra. Listed in Table 4 are lifetimes calculated by these two methods. The calculations do not yield identical results, but they only differ by a factor of 2 at the most. Averaging all lifetimes from both calculations yields an average lifetime for this band of approximately 165 ps.

The experimental density of states and the root mean square coupling matrix elements show a slight J

Table 4
Summary of information obtained from the $(3, 0)^+$ band of diacetylene

J'	Pathway $(1 \leftarrow 0, 3 \leftarrow 1)$	Number of eigenstates	$\Delta E (\text{cm}^{-1})$	ρ_{exp} $(/\text{cm}^{-1})$	σ_d	W_{rms} (cm^{-1})	$\tau_{\text{golden rule}}$ [a] (ps)	τ_σ [b] (ps)
0	R(0), P(1)	10	0.172	52	0.191	1.17×10^{-2}	120	144
1	R(1), P(2)	24	0.230	100	0.113	1.09×10^{-2}	71	90
2	R(0), R(1)	10	0.144	62	0.337	7.96×10^{-3}	215	$-$[c]
3	R(1), R(2)	19	0.273	66	0.142	8.76×10^{-3}	168	$-$[c]
4	R(2), R(3)	12	0.135	82	0.121	8.86×10^{-3}	131	180
5	R(5), P(6)	24	0.081	285	0.062	3.73×10^{-3}	213	305
6	R(6), P(7)	7	0.048	125	0.223	6.71×10^{-3}	150	260
7	R(5), R(6)	25	0.144	167	0.059	7.07×10^{-3}	102	222
8	R(6), R(7)	20	0.135	141	0.061	8.41×10^{-3}	85	140

[a] $\tau_{\text{golden rule}} = (4\pi^2 c \rho_{\text{exp}} V_{\text{rms}}^2)^{-1}$.
[b] Lifetimes determined from the fluorescence theorem as discussed in the text.
[c] Does not decay, or shows very strong recurrences.

dependence; however, the fluctuations from J to J outweigh any trends. Therefore it appears that, at least through $J' = 8$, Coriolis coupling plays a minor role in the dynamics of this band. The average root-mean-square coupling matrix element for this band is 8.3×10^{-3} cm^{-1}. The fluctuations in coupling matrix elements *within* each J clump are very large with some elements reaching values a factor of 20 from the average (not shown).

For highly fractionated spectra, those containing many eigenstates, statistical analysis of the spectrum provides additional information about the dynamics present. The usual procedure is to compare properties of the spectrum with a Gaussian orthogonal ensemble (GOE) model which has properties similar to those of a system experiencing chaotic dynamics [27]. For such statistical analysis as energy level spacings, a Poisson distribution is indicative of regular dynamics [28] while a Wigner or GOE distribution is characteristic of chaotic dynamics [27]. The level spacings in this band indicate even more clustering than would appear in a Poisson distribution and could be called "super-Poisson". Realistically, 10 to 20 lines are not enough transitions with which to reliably compute level spacing statistics. Furthermore, there is an experimental bias towards observing levels more readily when they are close enough in energy to another state to borrow sufficient intensity. In spite of this, a Poisson or regular spectrum is consistent with the large fluctuations observed in the density of states, dilution factor and coupling matrix elements. Fluctuations in coupling matrix elements are expected in the GOE model. However, because they fluctuate within a Gaussian distribution [27], very few elements should have values more than a few times the average. This condition is clearly not satisfied for this band.

3.1.3. The (2, 1)$^+$ band

The (2, 1)$^+$ band of diacetylene was recorded in double resonance by depositing one quantum of vibrational energy into a CH stretch and 2 quanta in the opposite CH stretch. For this band, $2 \leftarrow 0$ transitions occur in the same energy region as the $3 \leftarrow 1$ transitions, consequently spectra taken with and without the first laser ($1 \leftarrow 0$) were compared. The results of a fit for this band are shown in Table 5 and the fit has a standard deviation of 19 MHz. Since the transitions in a clump are quite close together, the error in the centers of grav-

Table 5
Spectroscopic constants determined from a linear least squares fit for (2, 1)$^+$ band of diacetylene (cm^{-1}) [a]

ν_0	9895.9831 (8) [b]
B'	0.145867 (83)
D'_J	1.92 (149) $\times 10^{-6}$
σ of the fit	19 MHz

[a] Lower state constants were constrained to those reported in Ref. [2] for the ν_1 band, as described in the text.
[b] Error reported in parentheses represent 2σ of the fit.

ity is estimated to be only 7 MHz. Although the deviation of the fit is slightly larger, the fit appears to be good and most lines are properly assigned. The $D_{J'}$ calculated from the fit is about 2 orders of magnitude larger than the lower state value and is, as before, indicative of a nonresonant state perturbing the band slightly.

Fig. 4 shows two of the J's recorded for this band and a summary of information obtained from the spectrum is located in Table 6. The band lies 214 cm^{-1} higher in energy than the (3, 0)$^+$ band and consequently has a larger calculated density of states (Table
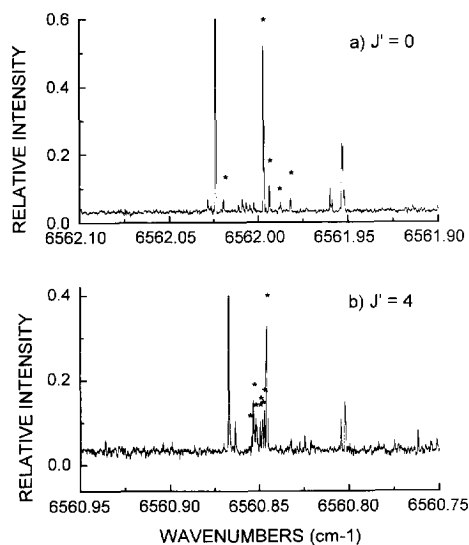

Fig. 4. The (2,1)$^+$ band in diacetylene recorded using sequential infrared/infrared double resonance. Only the lines marked with an asterisk are seen in double resonance, the unmarked lines belong to the (2, 0)$^-$ spectrum. The energy scale represents the frequency of the scanning laser. (a) $J' = 0$ is reached by a R(0) (at 3333.9571 cm^{-1}) followed by a P(1) sequence. (b) $J' = 4$ is reached with a R(4) (at 3335.1222 cm^{-1}) followed by a P(5) sequence.

Table 6
Summary of information obtained from the $(2, 1)^+$ band of diacetylene

J'	Pathway $(1 \leftarrow 0, 3 \leftarrow 1)$	Number of eigenstates	ΔE (cm^{-1})	ρ_{exp} (/cm^{-1})	σ_d	W_{rms} (cm^{-1})	$\tau_{golden\ rule}$ [a] (ns)
0	R(0), P(1)	5	0.0377	106	0.56	3.31×10^{-3}	0.39
1	R(1), P(2)	6	0.0117	427	0.25	1.79×10^{-3}	1.34
2	R(0), R(1)	3	0.0179	112	0.49	2.45×10^{-3}	1.00
3	R(1), R(2)	4	0.0064	470	0.63	8.07×10^{-4}	6.58
4	R(4), P(5)	10	0.0086	1043	0.15	1.05×10^{-3}	3.88
5	R(5), P(6)	10	0.0160	561	0.17	3.14×10^{-3}	4.04
6	R(4), R(5)	5	0.0151	265	0.32	3.14×10^{-3}	0.435
7	R(5), R(6)	9	0.0157	510	0.34	6.14×10^{-4}	4.04

[a] $\tau_{Golden\ rule} = (4\pi^2 c \rho_{calc} V_{rms}^2)^{-1}$

1). In spite of this, the clumps are consistently fractionated into less lines and spread over a smaller energy region. Both of these factors indicate a longer lifetime for the $(2, 1)^+$ band. Averaging the values calculated at each J results in a lifetime of 2.7 nsec, which is a factor of 16 longer than that calculated for the $(3, 0)^+$ band! The average value of the root-mean-square coupling matrix element for the band is 2.04×10^{-3} cm^{-1}. As in the case of the $(3, 0)^+$ band, the $(2, 1)^+$ band shows large fluctuations in density of states, lifetimes and coupling matrix elements within a J clump. These fluctuations are again indicative of regular dynamics in the spectra with specific states tuning in and out of resonance, as opposed to a statistical mixture of all bath states interacting with the bright state.

3.2. Spectroscopy of diacetylene-d_1

3.2.1. The ν_1 band

The fundamental CH stretch in diacetylene-d_1 was recorded primarily to obtain the constants needed for the analysis of the double resonance spectrum. The sample contained approximately 25% of undeuterated diacetylene from which arose extra lines which were assigned and used for absolute calibration. There were two checks on the relative frequencies of the spectrum: ground state combination differences using constants determined from microwave spectroscopy [29] and the undeuterated diacetylene lines. Unfortunately, in analyzing this spectrum we encountered an unexpected problem which make it impossible for the spectrum to accurately meet either of the above criteria. Deviations from the combination differences and the known diacetylene lines increased dramatically and almost linearly

from their expected values, indicating that the frequency scale of the spectrum was nonlinear. The deviations from the combination differences for R(5) minus P(7) was 220 MHz. Because of the manner in which we process the data using the traces of the 2 external scanning etalons, such deviations can only occur if the free spectral range of the 150 MHz etalon is not constant over the length of the scan (3333.6 through 3329.5 cm^{-1}). A possible cause for this inconsistency is temperature drifts of the etalon. There is no active temperature stabilization on our 150 MHz etalon for the 3 μm laser. However, the etalon is insulated, and we have not encountered this problem before. At this point, we do not have an explanation for the problem.

Over a short distance, R(1) through P(3) or 3332.47 through 3331.11 cm^{-1}, the spectrum was linear and had an average deviation over the two combination differences of 0.06 MHz. The five diacetylene-d_1 lines in this region were fit and the results are listed in Table 7.

3.2.2. The $2\nu_1$ band

The first overtone of the CH stretch in diacetylene-d_1 was recorded from R(9) through P(11). Results of a fit for the spectroscopic constants are listed in Table 8.

The density of Σ^+ states for this band is calculated to be 41.8/cm^{-1}. This is greater than that for diacetylene (14.6/cm^{-1}) because of the reduced symmetry restrictions and the lower frequency of the CD stretch (ν_4) and bend (ν_8) compared to those of the CH's. This spectrum has a dramatically different appearance than the first overtone of the CH stretch in diacetylene.

Table 7
Spectroscopic constants determined from a linear least squares fit of
the ν_1 band in diacetylene-d_1 (cm^{-1}) [a]

ν_0	3331.930558 (74) [b]
B'	0.1360619 (187)
D'_J	–
σ of the fit	1.5 MHz

[a] Lower state constants and D'_J were constrained to $B_0 = 0.13624274$
and $D_{J0} = 1.3409 \times 10^{-8}$ cm^{-1} [30].
[b] Error reported in parentheses represent 2σ of the fit.

Table 8
Spectroscopic constants determined from a linear least squares fit of
the $2\nu_1$ band in diacetylene-d_1 (cm^{-1}) [a]

ν_0	6561.14149 (24) [b]
B'	0.1358374 (44)
D'_J	–
σ of the fit	10.8 MHz

[a] Lower state constants and D'_J were constrained to $B_0 = 0.13624274$
and $D_{J0} = 1.3409 \times 10^{-8}$ cm^{-1} [30].
[b] Error reported in parentheses represent 2σ of the fit.

A portion of the P branch is shown in Fig. 5. At $J' = 0$
there is a single unperturbed state; then a resonance
appears in the spectrum at $J' = 1$ and is gone again by
$J' = 3$. At $J' = 6$ through 8 the transition becomes shat-
tered into 6 and 7 lines and by $J' = 9$ the spectrum is
back to that of an unperturbed spectrum. For $J' = 6–8$,
the root mean square coupling matrix element is
2.2×10^{-3} cm^{-1} and is constant for the 3 J' values.
The experimental density of states for $J' = 6$, 7, and 8
is 163, 319 and 269/cm^{-1} respectively (4 to 6.5 times
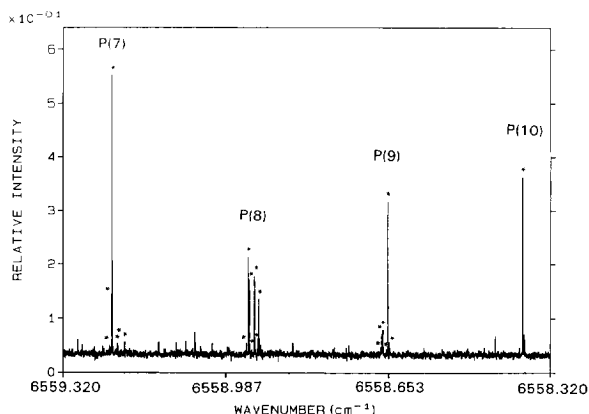the calculated density of Σ^+ levels).

Fig. 5. A 1 cm^{-1} portion of the P branch in the spectrum of the $2\nu_1$
spectrum of diacetylene-d_1.

The behavior of this band clearly is consistent with
the previously proposed model of a doorway state act-
ing as an intermediate step in the dynamics [30]. Only
when a certain state or states are resonant with the bright
state is coupling allowed to occur. At this point the
"door" is open to the full density of bath states and the
original bright state becomes fractionated into many
eigenstates. In this case, the bath is likely highly mixed
and given the very high density of states observed may
represent all possible bath states. The experimental
density of states is actually considerably higher than
the calculated value (41.8/cm^{-1}) and may correspond
to a Coriolis mixed bath as observed in the 3 ν_1 band in
propyne [17], but could also derive from fluctuations
in the density of the bath states. A considerably higher
density of states than calculated has been observed pre-
viously for spectra in this low state density regime
[31,32].

3.2.3. The 3 ν_1 band

Sequential double resonance was used to record the
second overtone of the CH stretch in diacetylene-d_1
through $J' = 6$. This band is the most fractionated of
the bands recorded here and therefore has the lowest
signal to noise ratio. The fit for the upper state constants
shown in Table 9, has a relatively large standard devi-
ation of 55 MHz. An estimate of the error in the deter-
mination of the centers of gravity due to the intensity
fluctuations and energy uncertainty, is only 19 MHz.
In addition, the ΔB determined from the fit has a posi-
tive value. The above mentioned problems indicate that
something is not accounted for properly in the spec-
trum. Most likely transitions are missing from the anal-
ysis, either due to being lost in the noise or due to a
nonresonant (out of our scanning region) perturbation
pushing on the band. In spite of this apparent incom-

Table 9
Spectroscopic constants determined from a linear least squares fit of
the 3 ν_1 band in diacetylene-d_1 (cm^{-1}) [a]

ν_0	9685.8776 (10) [b]
B'	0.1362546 (960)
D'_J	–
σ of the fit	55 MHz

[a] D''_J and D'_J were constrained to the microwave value [30] of
$D_{J0} = 1.3409 \times 10^{-8}$ cm^{-1} and B'' was constrained to that determined
for the ν_1 band of $B = 0.13606194$.
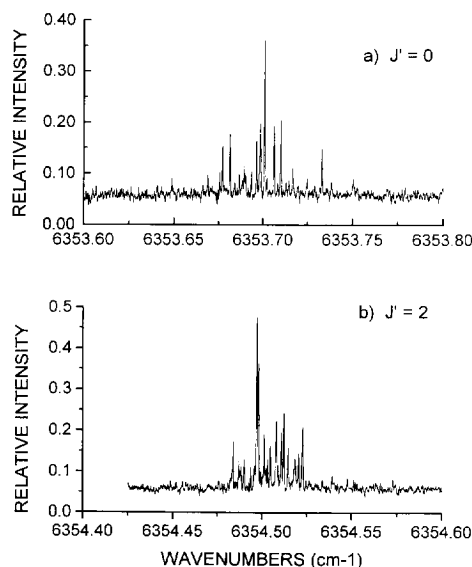[b] Error reported in parentheses represent 2σ of the fit.

Fig. 6. Two rotational clumps from the 3 ν_1 band of diacetylene-d_1. The energy scale represents the frequency of the scanning laser. (a) $J'=0$ is reached by a P(2) (at 3331.3852 cm^{-1}) followed by a P(1) transition. (b) $J'=2$ is reached by a P(2) (at 3331.3852 cm^{-1}) followed by a R(1) transition.

pleteness, it is still reasonable to assume that many of the intense transitions have been accounted for, so that quantitative analysis is useful for comparison with the other bands.

Two of the J clumps recorded for this band are shown in Fig. 6. As listed in Table 10, most clumps are split into 20 to 25 transitions. Indeed while the density of observed states increases with increasing J', this pattern is not due to increased fractionation but rather arises from the clumps becoming compressed over a smaller

energy window. The general trend, albeit with fluctuations, is that the energy window becomes smaller with increasing J'. On average, the root-mean-square coupling matrix element decreases with increasing J' and the lifetimes increase. Normally, Coriolis coupling is invoked to explain increasing density of states and decreasing lifetimes with increasing J', but the predicted trend contrasts with what is observed here. Instead, the mechanism is more likely that of a doorway state or states that tune out of resonance with the bright state due to a difference in rotational constant. The first step in the relaxation process is anharmonic coupling of the bright state to the doorway state. The second step is coupling of the doorway state to the bath. The combination of the two steps is an effective coupling between the bright state and isoenergetic bath states that is given by the product of the two coupling matrix elements, divided by the energy separation between the bright and doorway states. Such a model was invoked to explain the near resonant perturbations in the propyne 2 ν_1 spectrum [33]. As the separation between the bright and doorway states increases with increasing J, the effective coupling of the bright state to the bath decreases, and thus the rate of IVR decreases. Given the limited range of data, we can not exclude a direct coupling as well, which would persist even after the doorway state has tuned far off resonance. In this case, since the experimental density of states is close to (or slightly greater than) the calculated density of Σ^+ vibrational levels, it is likely that the bath is a statistical mixture of all possible modes of the molecule. There is no real evidence in this spectrum of Coriolis mixing.

The normalized moments of the energy level spacings from a frequency resolved spectrum are typically

Table 10
Summary of information obtained from the 3 ν_1 band of diacetylene-d_1

J'	Pathway ($1 \leftarrow 0, 3 \leftarrow 1$)	Number of eigenstates	ΔE (cm^{-1})	ρ_{exp} (/cm^{-1})	σ_d	W_{rms} (cm^{-1})	$\tau_{golden\ rule}$ [a] (ps)	τ_σ [b] (ps)
0	P(2), P(1)	25	0.0894	268	0.075	3.25×10^{-3}	298	330
1	P(3), P(2)	27	0.0653	398	0.073	3.66×10^{-3}	159	255
2	P(2), R(1)	24	0.0390	590	0.064	2.18×10^{-3}	301	470
3	P(3), R(2)	21	0.0256	781	0.071	1.53×10^{-3}	462	710
4	R(4), P(5)	17	0.0313	511	0.132	2.15×10^{-3}	357	545
5	R(3), R(4)	18	0.0220	771	0.171	1.19×10^{-3}	774	930
6	R(4), R(5)	23	0.0363	607	0.073	1.69×10^{-3}	487	640

[a] $\tau_{golden\ rule} = (4\pi^2 c \rho_{exp} V_{rms}^2)^{-1}$.
[b] Lifetimes determined from the fluorescence theorem as discussed in the text.

what is compared with a Wigner or GOE (chaotic) distribution or a Poisson's (regular) distribution. The limits for the two distributions for the second moment are 2.00 for a Poisson's and 1.21 for a GOE distribution [34]. Second moments falling between these two limits can be thought of as resulting from missing transitions [35] which can be correlated to the ratio of the experimental to the expected density of states. Intermediate moments have also been interpreted as reflecting "weak" chaos, leading to a spacing distribution intermediate between Poisson and GOE [36]. The normalized moments determined from this spectrum (not shown) fluctuate over the range from slightly greater than 2.0 to 1.3 and exhibit no consistent correlation with any of the other properties calculated from the spectrum. As in the case of the $(3, 0)^+$ band in diacetylene, there are large fluctuations in the coupling matrix elements within each J clump. Therefore, the dynamics again appear to be regular, showing none of the usual signatures of chaos.

4. Discussion

The deuteration of one end of diacetylene has a major effect on the IVR dynamics. This effect appears despite the strongly local mode motion expected in diacetylene, which would imply that the corresponding zeroth order states in both molecules should be almost identical. At $v = 2$, where the spectra are in a relatively low state density region, the differences are most pronounced. In diacetylene, the root-mean-square coupling matrix element for the strongly perturbing states is 0.15 cm^{-1} and the states persist through the spectral region recorded. This very strong coupling and slow detuning indicates perturbing states with similar B constants to the bright state, located relatively far away from it. The effect of deuterating one acetylene group is to totally remove these strong resonances. Since most likely the dark state perturbing the diacetylene $v = 2$ band contains no CH stretch mode, it is possible that the H–C≡C bend (ν_8) is an important component to the perturbing state which is removed upon deuteration. All the normal modes experience small shifts upon deuteration, however. In diacetylene-d_1 the root-mean-square coupling matrix element is 2×10^{-3} cm^{-1} for $J' = 6, 7$, and 8. All other lines are unperturbed or only weakly perturbed. It would be very interesting to compare the

IVR dynamics of the two other first overtone bands in diacetylene: $(2, 0)^+$ and $(1, 1)^+$. These bands can be reached by infrared/infrared double resonance with two 3.0 μm lasers [37].

At $v = 3$, the pure overtone bands are also different in the undeuterated and deuterated species, although both spectra are highly fractionated and the differences not as dramatic. The $(3, 0)^+$ band shows large fluctuations in density of states, lifetimes, and coupling matrix elements as a function of J'. The average lifetime for this band is 165 psec. Although the state density increases to 535/cm^{-1} for diacetylene-d_1 compared to 173/cm^{-1} for the undeuterated species, the lifetimes of the former are longer (500 to 600 ps) and actually show an increase with J'.

Both diacetylene-d_1 overtone bands, $2\nu_1$ and $3\nu_1$, show clear evidence that a doorway state or tier model dominates the IVR dynamics. The bright state is anharmonically coupled to a doorway state, or small number of states, which controls the lifetime of redistribution. This state or states is then coupled sequentially to other tiers, finally reaching the full density of symmetry allowed states. Most likely the doorway state or first tier of levels are of low order, meaning that they have shifted only a few quanta into other modes of the molecule. Evidence of this type of relaxation has been seen previously in the spectra of other acetylenic CH stretches. In the spectrum of $3\nu_1$ in propyne, for $K' = 0$ the lifetimes were all constant as a function of J', although the density of states observed in the spectrum increased dramatically [17]. This behavior was interpreted as a sign of a doorway state controlling the initial relaxation which in turn was coupled to a highly Coriolis mixed bath. A tier model was used very successfully by Stuchebrukov and Marcus to explain the different relaxation rates in the series $(CX_3)_3YC≡CH$, where $X = H$ or D and $Y = C$ or Si [15,38]. In their study they were able to accurately calculate the lifetimes for relaxation out of the acetylenic CH stretch and found IVR rates to be dominated by cubic and quartic interactions which directly couple states differing by at most 3 or 4 quanta. The calculated lifetimes were found to be determined, not by the total density of states in the molecule, but by the coupling strengths and positions of the levels in the first few tiers of states. Further evidence that this is an appropriate picture of IVR relaxation was seen in the ν_1 and $2\nu_1$ spectra of $SF_5C≡CH$ [39]. At the energy of these two excitations

this molecule has very few low order resonances. The lifetimes, as expected, were found to be very long – around 3 ns at ν_1 and 1.4 ns at $2\nu_1$. A tier model of low order resonances or sequential excitation through doorway states that control the relaxation is likely to be a general mechanism in the IVR of larger polyatomics.

When the density of states in the spectrum is very high or the coupling is very strong, GOE-type statistics are observed and the fluctuations in the spectrum appear to be greatly reduced. It is difficult to separate, at least in an experimental spectrum, the difference between direct high order coupling and sequential coupling through a chain of off resonant states. For spectra, such as those of diacetylene examined in this paper, with a sparse, weakly coupled bath of levels, the effect of the low order resonances becomes apparent in the enhanced fluctuations of the observed statistical properties of the spectrum. It is also possible, such as in the case of the $(2, 0)^-$ spectrum of diacetylene, for specific states, coupled in an intermediate to high number of quanta (8–10), to ''light up'' due to accidental degeneracies.

Both of the second overtone bands in diacetylene and diacetylene-d_1 appear to behave in a regular fashion, exhibiting no sign of quantum chaos. The energy levels in a chaotic spectrum are regularly spaced due to the mutual repulsion of nearby states (GOE model) [27]. Regular, non-chaotic dynamics results in a random spacing or Poisson distribution [28]. Moments of the spacing distribution for both the $(3, 0)^+$ band in diacetylene and the $3\nu_1$ band in diacetylene-d_1 vary at different J's but do not coincide with the predictions of the GOE model. Also the large fluctuations in the coupling matrix elements within each J clump indicate regular rather than GOE dynamics.

Another consistent feature in the spectra is the absence of significant Coriolis coupling. All the spectra presented here appear dominated by anharmonic coupling. Even the $3\nu_1$ band in diacetylene-d_1 which has relatively slow relaxation, on time scales much longer than the rotational motion of the molecule (for $J' = 3$, $(2BJ)^{-1} = 41$ ps), does not show evidence that Coriolis coupling plays an important role. This is contrary to what has been found for many other molecules, which show an increase in density of observed states at increasing J' [17,30].

The two second overtone bands in diacetylene, $(3, 0)^+$ and $(2, 1)^+$, lend support to our earlier observa-

tions for propyne that the delocalized combination bands are less perturbed than the nearly isoenergetic pure overtone states [40]. In propyne, we have excited the acetylenic CH stretch, ν_1, in combination with the overtone of the asymmetric methyl CH stretch ($2\nu_6^0$) as well as the $(2\nu_1 + \nu_6)$ combination band [41]. These two combination bands excite opposite ends of the molecule, that interact only weakly as evidenced by the small value of $X_{16} = -0.11$ cm^{-1}. These two spectra are much less perturbed than the nearly isoenergetic $3\nu_1$ band [17] where all the energy is initially deposited in the acetylenic CH stretch. This can be understood in terms of the fact that the combination bands that we have excited in propyne involve vibrations which share no common atoms. Direct anharmonic coupling between the modes is expected to be small. Therefore, each mode in the combination band is expected to relax independently of the other and behave more like a lower energy (more harmonic) state. This is contrary to previous experimental and theoretical evidence for *small* polyatomic molecules. In the SEP spectra of HFCO [42] and the visible [9a] and SEP spectra of acetylene [10] it was found that the combination bands were more perturbed than the pure overtone states. Hose and Taylor proposed pure overtone, or extreme motion, states to be more stable based on classical trajectory calculations using only a few mode system [43]. In these cases the combination states are exciting neighboring bonds.

In the $(3, 0)^+$ band in diacetylene, in which 3 quanta of vibration are deposited into a single CH stretch, we found an average lifetime of 165 ps and an average root mean square coupling matrix element of 8.3×10^{-3} cm^{-1}. For the $(2, 1)^+$ band, where two quanta are deposited into one CH stretch and the third quanta in the opposite end of the molecule, the average lifetime over the J's recorded was 2.7 ns with an average root mean square coupling matrix element of 2.0×10^{-3} cm^{-1}. The calculated density of states for the $(2, 1)^+$ band of 197/cm^{-1} is slightly higher than that of the $(3, 0)^+$ band of 173/cm^{-1}.

5. Conclusions

The several overtone bands recorded in diacetylene and diacetylene-d_1 illustrate the varied IVR dynamics that can occur just by making subtle structural changes

or by exciting slightly different modes in the molecule. Since these molecules are linear and contain only 6 atoms, they should be feasible cases for theoretical calculations. The underlying dynamics in both the second overtone bands of diacetylene and diacetylene-d_1 appear not to be chaotic, and show no signs of significant Coriolis coupling. In diacetylene, the second overtone band with all three vibrational quanta in the same CH stretch was found to be more perturbed than the combination band of one quanta in one CH stretch and two quanta at the other end of the molecule. Our results for these two bands in diacetylene, in conjunction with the results for propyne [40,41], suggest that the dramatically different behavior in the relaxation of combination bands as compared to pure overtone bands may be a general phenomenon occurring in larger molecules when vibrations are excited which do not share common atoms. This hypothesis can be tested on more molecules and different types of stretches (O–H, N–H or =C–H) using infrared/infrared double resonance techniques. If the conclusion is found to be general, it will represent an important step in the understanding of unimolecular reactions and will enhance the possibility of achieving mode selective chemistry in large polyatomic molecules.

Acknowledgement

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