

Molecular beam infrared spectroscopy and intramolecular dynamics of SF₅CCH in the region of the fundamental and first overtone of the acetylenic CH stretch

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Abstract

We have measured the high resolution spectrum of ethynylsulphurpentafluoride, SF₅CCH, in both the fundamental and the first overtone of the acetylenic CH stretch in a collimated, supersonic molecular beam. The intramolecular redistribution of vibrational energy is discussed in relation to previous experimental results for other similar molecules and theoretical models. The absence of low order anharmonic resonances and the long (> 1 ns) lifetime derived from the spectra support a previously proposed correlation between these two molecular properties.

1. Introduction

The study of intramolecular vibrational energy redistribution and relaxation (IVR) is a problem of fundamental importance for understanding the most elementary steps of chemical reaction dynamics. In the past several years the eigenvalue-resolved spectra of a number of terminal acetylenic compounds have been measured, and have been used to obtain a detailed picture of IVR in this class of molecules [1–8]. This paper represents a further step in the same direction. Previous work has dealt with molecules representing the full range of IVR behaviour: from the small, through the intermediate, to the large molecule statistical limit. The excitation level included energy regions of one to three quanta of CH stretch with the observed IVR lifetimes

spanning three orders of magnitude from ~10 ps to ~10 ns. A major goal is to rationalize (and eventually, to predict) IVR lifetimes from a knowledge of molecular structure and harmonic frequencies.

In earlier work, we compared the compounds (CH₃)₃X–CCH and (CD₃)₃X–CCH (with X = C, Si, Sn) at both the ν_1 and $2\nu_1$ bands [1,2]. In all cases, we found that the lifetime of states for the substituted silanes is considerably longer than for the corresponding hydrocarbon. In addition, the ν_1 lifetime for the substituted stanane (only the CH₃ version was tested) is even longer than that of the Si containing species. This was interpreted as tentative evidence of a “heavy-atom-vibration blocking effect”, though it was recognized that changes in force constants and bond lengths were involved as well as a simple change in mass. Following that work, Stuchebrukhov and Marcus have published a theoretical calculation of the IVR decay

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rates for the carbon and silicon species, which is in excellent agreement with the observed decay rates [9]. Their theoretical model is based upon the assumption that the relaxation occurs through a series of “tiers” of states that are connected to the “bright state” (the CH fundamental or first overtone band) by higher order perturbation theory (based upon the traditional anharmonic expansion of the potential, truncated at the fourth power) [10]. They found that the long lifetime of the Si compounds is due largely to “bottlenecks” in the relaxation process. These are due to the low density of low order, near resonances between the modes that are anharmonically coupled to the CH stretch. This small density of low order resonances for the Si containing species is, to a certain extent, “fortuitous”. In the present work, we extend our work to another species with a second-row atom connecting to the terminal acetylene and find that this also has a long (> 1 ns) lifetime. This lends some support to our hope that IVR lifetimes can be understood, at least on a qualitative level, on the basis of simple models.

Another reason for our interest in the title molecule is that it contains an SF₅ group which is a strong absorber of IR radiation in the region where high power CO₂ lasers are available [11]. It is one of our long term goals to study the effect of “heating the bath” of vibrational modes that ultimately receive the vibrational energy in the IVR process. IR multiphoton pumping provides one attractive route to realize this goal, but one needs to be able to distinguish spectra from different levels of excitation to separate homogeneous and inhomogeneous effects [12]. SF₅CCH, with its long lifetimes and thus sharp vibrational bands, is likely to be a suitable molecule for this type of study.

Finally, we note that, due to the presence of relatively low-frequency oscillators in the SF₅ group, the $2\nu_1$ region presents a sufficiently high density of states, to achieve statistical behaviour without the presence of internal rotors. As discussed in Ref. [9] the presence of such modes make the calculation of the effective density of states substantially less reliable. This is the first molecule without internal rotation that has been found to show IVR at the large molecule limit. The present result supports our earlier conclusion that methyl rotation is not an important factor in the IVR rate of these molecules [2].

2. Experimental

The sample of ethynylsulphurpentafluoride, SF₅CCH(ESF), was prepared by the method reported in Ref. [13]. The spectrum of the ν_1 and $2\nu_1$ bands was obtained by the method of molecular beam optothermal spectroscopy, using an experimental apparatus described previously [1]. This instrument uses either a 3 or a 1.5 μm color center laser to excite the molecules, and a bolometer to detect the heat deposited in the molecular beam by the IR absorption. The emitted power of the two lasers is of the order of 20 and 150 mW, respectively. Our instrumental resolution, limited by residual Doppler broadening, is 8 MHz in the fundamental region and 16 MHz in the first overtone. The molecular beam was formed by expanding a 0.5% mixture of ESF in He through a 50 μm nozzle with a backing pressure of 430 kPa (65 psi). The gas mixture was stored in a steel cylinder, in which, unfortunately, the ESF decayed over a period of a few days. Therefore, we were not able to extend our study beyond the two spectra obtained on the first run.

Absolute spectral calibration was obtained by means of a home built wavemeter, following the design of Lew et al. [14]. The absolute accuracy of this calibration is about 0.01 cm^{-1} . Relative frequency spacing are determined by reference to a confocal etalon whose precise free spectral range was calibrated by fitting the observed ground state combination differences to values predicted from the microwave spectrum of SF₅-CCH [15].

3. Results

3.1. The ν_1 fundamental spectrum

The ESF molecule has a symmetry described by the point group C_{4v}. The ν_1 fundamental CH stretch is of A₁ symmetry and shows a parallel band spectrum (see Fig. 1). Based upon the peak of the intensity distribution, a rotational temperature of about 5 K can be estimated. As expected for such a heavy symmetric top, we see a series of near-evenly spaced clumps of lines on either side of a strong Q branch. In addition, four other weaker bands are observed with P, Q and R branches. The strong band, which we interpret as the ν_1 fundamental, will be discussed first.

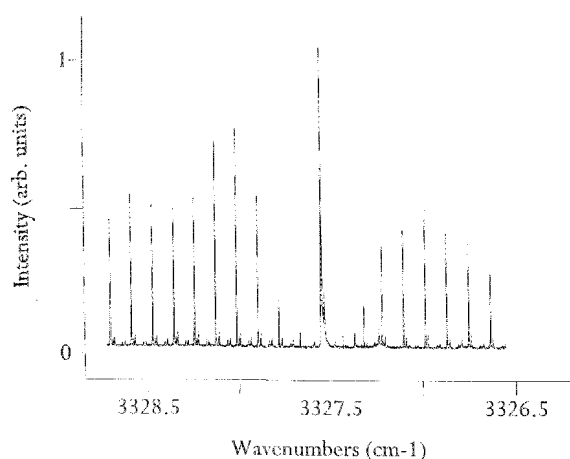


Fig. 1. Fundamental CH stretch of ESF.

Table 1
Fundamental vibration of the CH stretch in ESF

Wavenumber (cm ⁻¹)	Assignment
3328.353	R(6)
3328.238	R(5)
3328.122	R(4)
3328.007	R(3)
3327.891	R(2)
3327.776	R(1)
3327.661	R(0)
3327.545	Q
3327.429	P(1)
3327.313	P(2)
3327.197	P(3)
3327.081	P(4)
3326.965	P(5)
3326.849	P(6)
3326.733	P(7)
3326.616	P(8)

The centers of each clump of lines are listed in Table 1. Table 2 gives the spectroscopic constants that result from a fit to the formula

$$\nu(m) = \nu_0 + (2B'' + \Delta B)m + \Delta B m^2,$$

where $m = J + 1$ for R(J) transitions and $-J$ for P(J) transitions; B'' is the ground state rotational constant (which was fixed at the microwave value) and $\Delta B = B' - B''$ is the change in rotational constant upon vibrational excitation. The standard deviation for the fit of the line positions is 4 MHz.

The individual R and P clumps in the spectrum show both K and IVR structure. The R(0) and P(1) transi-

Table 2
Spectroscopic constants of the fundamental and first overtone of the CH stretch in ESF

	Fundamental	First overtone
center frequency (cm ⁻¹)	3327.545(1)	6552.303(1)
ground state rotational constant B (MHz)	1736.76 [15]	1736.9(2)
ΔB (MHz)	-1.3(1)	-3.0(1)

tions, where only a single $K=0$ transitions is expected, are shown in Fig. 2. It is seen that both transitions are split into two lines, with a separation of 75 and 63 MHz respectively. These splittings reflect the coupling of the bright state with a single bath state. Assuming that the absorption strength reflects the fractional ν_1 character in each eigenstate, one can calculate a coupling matrix element of 1.3×10^{-3} and 1.8×10^{-3} cm⁻¹ for $J'=0$ and 1 respectively. The presence of coupling in the

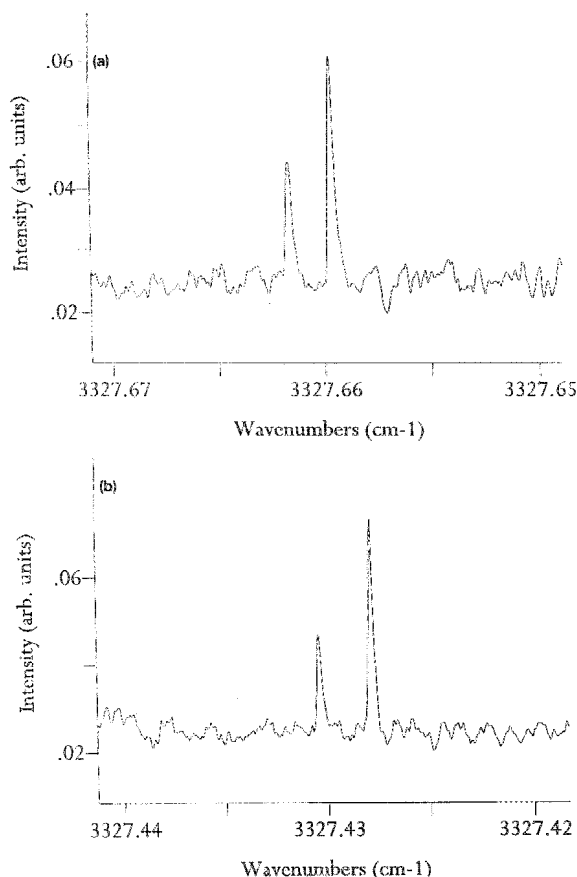


Fig. 2. Fundamental CH stretch of ESF: (a) the R(0) component; (b) the P(1) component.

rotationless level of the upper vibrational state, must arise from anharmonic mixing of the ν_1 fundamental with a background state of A_1 symmetry. The increase in matrix element from $J'=0(K'=0)$ to $J'=1(K'=0)$ reflects either a changing vibrational character of the bath state with rotation, or a second order interaction of the two interacting A_1 symmetry states (through x, y axis Coriolis coupling) with one or more near-resonant E-symmetry states.

Using the normal mode frequencies reported by Zylka et al. [15], a direct count of the harmonic density of states predicts the density of A_1 states as 191 per cm^{-1} at the energy of the ν_1 fundamental. Thus the average spacing of vibrational states of A_1 symmetry should be ~ 150 MHz. The observed perturbing dark state is, most likely, merely the closest state. With only one perturbing state, the time evolution following coherent excitation is a quantum beat between the two levels, not a relaxation. It is possible, however, to define an effective lifetime given by Fermi's Golden Rule (τ_{GR}) if one takes the strength of the single observed perturbation as an estimate for the rms value. Taking $V_{\text{rms}} = 1.5 \times 10^{-3} \text{ cm}^{-1}$ and $\rho = 191 \text{ per cm}^{-1}$, then $\tau_{\text{GR}} = (4\pi^2 c \rho V_{\text{rms}}^2)^{-1} = 2 \text{ ns}$. Because of the fluctuations in coupling matrix elements, and the uncertainties in the density of states, this lifetime must be viewed with a good deal of skepticism, but, as we will see below, it is remarkably consistent with the other information we can extract from the spectrum.

Without perturbations we expect P(2) and R(1) (Figs. 3a and 3b) to each contain only two transitions ($K=0$ and 1) separated by $\Delta A - \Delta B$. Physically, we expect $\Delta A \ll \Delta B$ because the excitation is along the symmetry axis and thus the splitting should only be ~ 2 MHz, which is inside our resolution (8 MHz). However, in a symmetric top, most perturbing levels tune rapidly with K due to first order Coriolis couplings. As discussed in our work on propyne [16], this tuning of levels which are involved in weak long-range perturbations of the bright state, can lead to resolvable, anomalous K splittings in the spectrum. Therefore, the observed spectrum was fitted using a least squares fitting procedure in which the lineshape and the linewidth are determined by our instrumental Gaussian response function. In order to fit the observed clumps, we need to use 6 spectral lines for R(1) and 10 for P(2), spread approximately over 100 MHz in both cases.

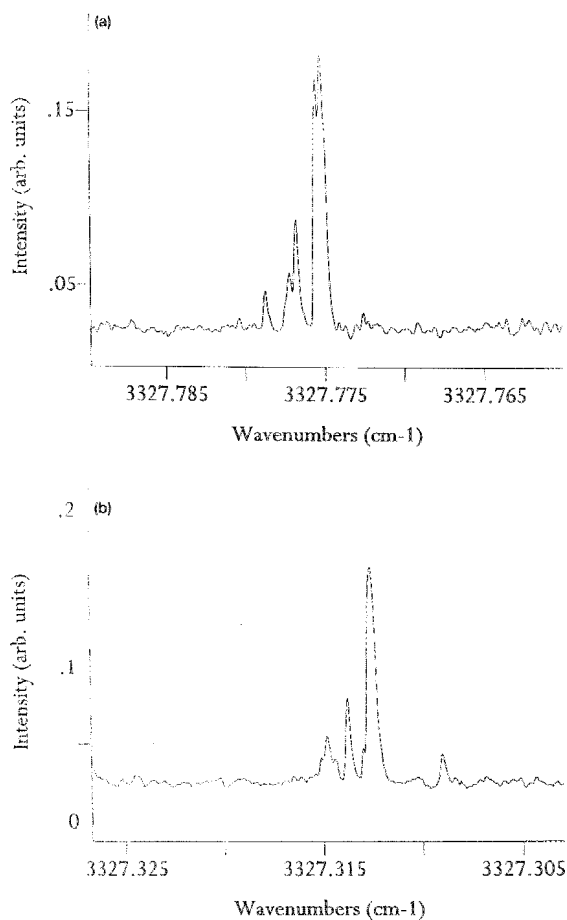


Fig. 3. Fundamental CH stretch of ESF: (a) the R(1) component; (b) the P(2) component.

At higher J' values more lines are needed to simulate the observed bands. Fig. 4 shows the R(4) transitions along with a fit to 13 Gaussian lines. While a good part of this structure is inhomogeneous, if one takes the observed fwhm of the feature (~ 40 MHz) as due to homogeneous broadening, one calculates a lower limit for the lifetime of 4 ns, in good agreement with the value deduced above from the golden rule formula. Table 3 gives the results of fits to all the observed transitions.

Although we have not attempted to assign the spectrum as to K quantum numbers, at the lowest J' s, comparison of the P and R transitions terminating in the same upper state, indicates that the increase in number of components needed to fit each clump can be attributed to an increase in the number of K components.

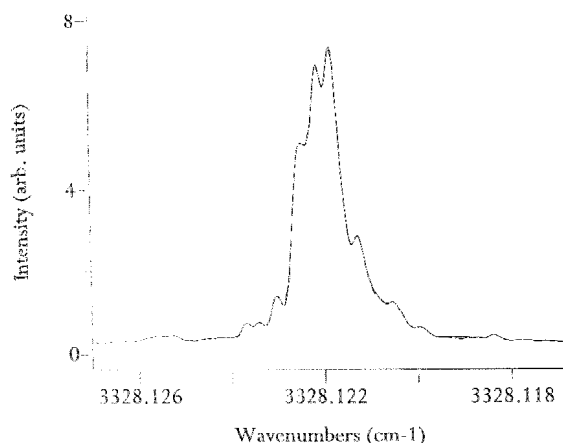


Fig. 4. Fundamental CH stretch of ESF: the R(4) component fitted with a sum of 13 Gaussian instrumental functions.

Thus the dominant interactions at low J 's are probably anharmonic in nature. At higher J 's the increase in the effective density of lines with J cannot be attributed solely to K structure and, therefore, indicates that perpendicular Coriolis interactions are present which cause the breakdown of K as a good quantum number.

Table 3

Observed and predicted width of the R(J) and P(J) clumps in the fundamental vibration of the CH stretch in SF₅CCH: calculated and measured dispersion

Transition clump	Calculated width ^a (10 ⁻³ cm ⁻¹)	Observed width ^b (10 ⁻³ cm ⁻¹)	Fitted width ^c (10 ⁻³ cm ⁻¹)	Number of K values in clump	Observed number of transitions
R(6)	1.56	8.0	1.9	7	> 20
R(5)	1.08	7.5	1.8	6	> 20
R(4)	0.69	3.8	1.0	5	13
R(3)	0.39	3.6	0.8	4	12
R(2)	0.17	3.8	0.8	3	13
R(1)	0.04	4.1	^d	2	6
R(0)	0.00	2.3	^d	1	2
P(1)	0.00	1.9	^d	1	2
P(2)	0.04	5.8	^d	2	10
P(3)	0.17	6.3	^d	3	9
P(4)	0.39	3.6	0.9	4	13
P(5)	0.69	3.2	0.8	5	12
P(6)	1.08	3.6	1.0	6	12
P(7)	1.56	8.5	1.8	7	> 20
P(8)	2.12	7.6	2.0	8	> 20

^a Calculated by rigid rotor formula: $\nu \sim (\Delta A - \Delta B)K^2$ ($0 \leq K \leq J'$), assuming $\Delta A \ll \Delta B$ and using ΔB given in Table 2. Since SF₅CCH is a slightly prolate top ($A \approx 1.57B$ based upon standard bond lengths), the high J, K levels will have low Boltzmann population.

^b These are the experimentally observed spreads in frequency.

^c These are the fwhm values obtained for each clump by fitting to a single Lorentzian line.

^d The spectrum is too sparse for these clumps to define a meaningful full width at half maximum (fwhm).

The modest increase in clump width with J , argues that the coupling of the bright state to the bath is dominated by anharmonic interactions, and thus that the slight K mixing must arise primarily from bath–bath Coriolis interactions.

Table 4 lists the spectroscopic constants for the four other bands observed in the region of the ν_1 fundamental. It is seen that the strength of these bands varies approximately from 1 to 5 percent of the ν_1 fundamental. These bands can arise from (1) the existence of isotopomers, (2) the presence of hot bands, or (3) from the presence of near-resonant states that steal intensity from the ν_1 fundamental. We will consider each of these possibilities in succession.

Table 5 lists the calculated change of ground state rotational constant for the isotopomers that are expected to lie close in energy to the ν_1 fundamental. Rigid rotor rotational constants are calculated from the structural constants given in Ref. [15]. It is seen that isotopic substitution at the S atom should produce a negligible shift in rotational constant because of the proximity of the center of mass. Isotopic change of the C atom bound to the S atom produces a relatively large

Table 4
Spectroscopic constants for the spectral components observed in the region of the fundamental vibration of the CH stretch of ESF

	Center frequency (cm^{-1})	Intensity (arb. units)	B ground (MHz)	ΔB (MHz)
CH-stretch	3327.545	100	1736.76 ^a	-1.3(1)
band A	3327.531	1.4	1736.8(1.0)	-0.7(1.3)
band B	3327.528	5.5	1728.4(4)	-1.3(3)
band C	3327.365	3.0	1735.4(3)	-0.2(5)
band D	3327.237	3.9	1736.1(2)	-5.3(2)

^a Adjusted to agree with the microwave value given in Ref. [15].

Table 5
Calculated frequency shift of the fundamental CH stretch and ground state rotational constants for the more common isotopomers of ESF

	$\Delta \nu$ (cm^{-1})	ΔB ground (MHz)	Relative abundance (%)
³² SF ₅ ¹² C ¹² CH	0	0	~93
³⁴ SF ₅ ¹² C ¹² CH	-0.001	-0.4	~4
³² SF ₅ ¹³ C ¹² CH	-1.4	-13.9	~1
³³ SF ₅ ¹² C ¹² CH	-0.0006	-0.2	~1

change in B'' . Shifts in the ν_1 fundamental are also calculated based upon the harmonic force field of Zylka et al. [15]. While anharmonic effects can be expected to make a significant contribution to the shift as well, particularly when the harmonic shift is very small, we can take these values as rough lower bounds of the expected shift. None of the bands have a shift anywhere as large as in the case of the ¹³C isotopic substitution and the only band with approximately the correct rotational constant is the band B, which has much too large

an intensity to be due to a ¹³C isotopomer. Thus we rule out this isotopomer as contributing to our spectrum. Based upon relative intensity and position, the most likely explanation for bands A and B appears to be the ³³S and ³⁴S isotopomers. One would expect twice the shift for the ³⁴S substitution as compared to ³³S but, given the tiny shift, it is certainly possible that a weak anharmonic push (by a band with significant S motion and thus isotopic shift) could dominate the harmonic shift, which is calculated to be negligible. The main difficulty with these assignments is the rotational constant of band B, which is about 8 MHz too low. Given the fact that the rotational constant is extracted from bands without K resolution, the observed $R(J-1) - P(J+1)$ separation is not a true ground state combination difference; high K lines have higher relative strength in the P compared with the R branch. As a result, perturbed K structure in the band can affect the fitted lower state rotational constant.

Bands C and D do not have reasonable assignments as due to isotopomers, and thus are likely to be due to either hot bands or to anharmonic resonances. Given that they are almost equal in intensity, it is unlikely that they are both hot bands since one would expect the hot band arising from the lowest frequency mode ($\nu_{15} = 144 \text{ cm}^{-1}$) to be significantly higher in intensity than that from its overtone or the next lowest frequency mode ($\nu_{14} = 375 \text{ cm}^{-1}$) [15]. In addition for a hot band we expect to see an increase in the rotational constant and a red shift in the band origin due to the cross anharmonicity. For CF₃CCH, the increase in the rotational constant for the lowest bending mode ($\nu_{10} = 171 \text{ cm}^{-1}$) is 5.48(2) MHz, and the shift of the hot bands $-0.86(3) \text{ cm}^{-1}$ [17]. Since the lowest mode in both CF₃CCH and SF₅CCH involve primarily bending of the CCH group, we can expect these values

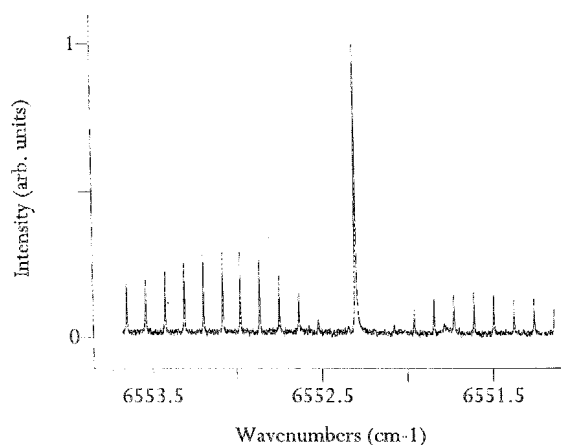


Fig. 5. First overtone of the CH stretch of ESF.

to provide rough predictions also for SF₅CCH. Band D, with a change in ground state rotational constant of +3.5(1.5) MHz and band origin shift of -0.316 cm⁻¹ is the only reasonable feature to assign as a hot band. The corresponding hot band in the overtone spectrum (see below) would be expected to have twice as large a shift. The only feature in the overtone spectrum that could possibly be the Q branch of a hot band is broadened and has a shift of -0.53 cm⁻¹. Given the uncertainties in the fitted lower state B constant for band D, one cannot rule out the ground state as the origin of this band. In principle, we could use microwave-IR double resonance or a temperature dependence study (by varying the source conditions) to resolve this issue. However, with the present data, the ambiguity of assignment of band D as either a hot band or as an originally dark band that has borrowed intensity from the ν_1 fundamental can not be resolved. Band C however can only be assigned as a dark state which appears only because of its interaction with ν_1 . Based upon their shifts and relative intensities, the calculated interaction strengths of the C and possibly D upper state levels with the ν_1 fundamental are 0.03 and 0.06 cm⁻¹ respectively. The fact that both Q branches are so sharp imply that these bands (which are likely high order combination bands) are less significantly coupled to the bath than the ν_1 fundamental itself. This is consistent with our recent observations on the lifetimes of a few delocalized states of propyne [18].

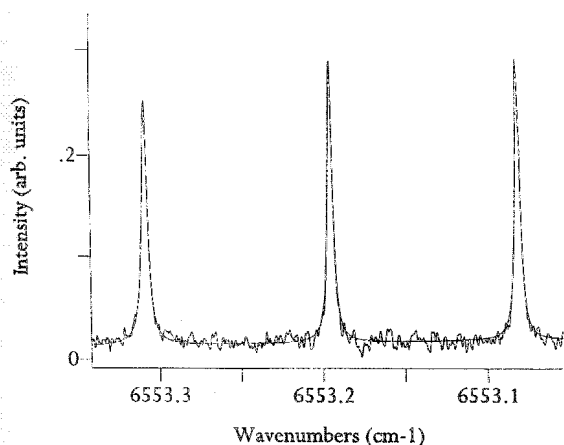


Fig. 6. First overtone of the CH stretch of ESF: components R(6) to R(8) fitted with Lorentzian functions.

3.2. The $2\nu_1$ overtone band

Fig. 5 shows the spectrum of ESF in the region of the $2\nu_1$ overtone band, from R(11) through P(8). The spectrum is dominated by a single parallel band which is assigned to the $2\nu_1$ upper state. In this band, instead of the complex fine structure present in the fundamental, we observe that each line fits quantitatively to a Lorentzian lineshape (Fig. 6). The density of A₁ vibrational states, calculated by a harmonic count, is about 1×10^5 cm⁻¹ at this energy. As in other ‘‘large-molecule limit’’ spectra obtained previously [1,2], we interpret the Lorentzian lineshape as resulting from an effectively irreversible decay of the $2\nu_1$ state into the dense bath of closely spaced vibrational states, with ~ 50 states in any interval equal to our instrumental resolution of 16 MHz. Given the inhomogeneous K structure in the spectrum, we would need to increase our instrumental resolution by at least 100 times before we could expect to resolve the individual eigenstates, each of which should have a lifetime limited by radiative decay (> 1 ms). Looking at the problem in the

Table 6
First overtone of the CH stretch of ESF

Wavenumber (cm ⁻¹)	fwhm (cm ⁻¹)	Lifetime (ns)	Assignment
6553.678	0.0036	1.47	R(11)
6553.564	0.0037	1.43	R(10)
6553.451	0.0038	1.40	R(9)
6553.337	0.0037	1.43	R(8)
6553.223	0.0034	1.56	R(7)
6553.109	0.0034	1.56	R(6)
6552.994	0.0031	1.71	R(5)
6552.879	0.0032	1.66	R(4)
6552.764	0.0036	1.47	R(3)
6552.649			R(2) ^a
6552.534			R(1) ^a
6552.303			Q
6552.072			P(2) ^a
6551.955	0.0036	1.47	P(3)
6551.838	0.0037	1.43	P(4)
6551.722	0.0039	1.36	P(5)
6551.605	0.0036	1.47	P(6)
6551.488	0.0042	1.26	P(7)
6551.370	0.0037	1.43	P(8)
6551.253	0.0037	1.43	P(9)
6551.135	0.0039	1.36	P(10)

^a Due to the poor S/N ratio the values of fwhm (and lifetime) of these features could not be determined.

time domain, our instrumental resolution of 16 MHz means that we can follow the molecular relaxation up to a time of ~ 10 ns, while the density of vibrational states implies that the relaxation should have recurrences on a times scale of ~ 1 μ s. One consequence of the washing out in the overtone spectrum of the perturbations that dominate the fundamental is the much smoother J dependence of the intensities in the P and R branches of the former spectrum as compared to the latter.

Table 6 gives the positions and widths that result from fits to the individual R and P lines and shows that the linewidths are independent of J , except for the lower J levels where the signal to noise ratio is low. The independence of the width on rotational excitation demonstrates that the relaxation is dominated by anharmonic interactions. From the average width of 3.6×10^{-2} cm^{-1} (108 MHz) we calculate an excited state lifetime of 1.5 ns. If both the fundamental and overtone levels are undergoing relaxation due to anharmonic terms that are linear in the ν_1 coordinate, then one expects the allowed coupling matrix elements to be proportional to $\sqrt{n_1 + 1}$, where n_1 is the ν_1 vibrational quantum number. According to the golden rule, the lifetime for the overtone level should be one half that of the fundamental. It is interesting to note that the true statistical limit lifetime of the overtone (1.5 ns) is just one half the average of the two approximate lifetimes we deduced earlier for the fundamental, despite the fact that the latter spectrum was found to belong to the small-to-intermediate molecule case of IVR. This nearly exact agreement, which must be viewed as somewhat fortuitous, gives support to the view that, despite the large anharmonic shift of the overtone (which is observed in all the acetylenic CH stretches), the relaxation is similar in both cases.

No extra P and R branches are observed in the overtone spectrum. While the signal to noise ratio (the peak of the Q branch is about 25 times larger than the peak to peak noise) is lower in the overtone spectrum than in the fundamental, Q branches with 3–5% relative intensity should have been evident if they were just as sharp. In fact, the only extra feature in the spectrum is a weak and broad feature near 6551.78 cm^{-1} (seen between P(4) and P(5) in Fig. 5) which has an intensity of only $\sim 1\%$ of the main peak. This may be the hot band discussed earlier in the assignment of band D observed in the region of the fundamental. The absence

of other Q branches with a smaller shift, implies that the extra bands due to isotopic S substitution are unresolved. A shift of twice that observed in the fundamental spectrum (which would be expected if the shift was due to a change in the effective ν_1 harmonic frequency) would be clearly resolved. Thus this supports the assignment of the bands observed in the fundamental as due to long range anharmonic perturbations that shift the isotopomer's band centers. In the high density of state region of the overtone, such fluctuations are greatly reduced resulting in immeasurably small, shifts.

4. Discussion

The spectrum of SF_5CCH shows a lifetime in the $2\nu_1$ state of 1.5 ns, and an effective lifetime about twice this long in the fundamental. These lifetimes are similar

Table 7
Comparison of lifetimes (ns) of the excitation in the CH acetylenic stretch with previous results

Molecule	Lifetimes		Reference
	fundamental	overtone	
$(\text{CH}_3)_3\text{C}-\text{C}\equiv\text{C}-\text{H}$	0.2	0.11	[1]
$(\text{CH}_3)_3\text{Si}-\text{C}\equiv\text{C}-\text{H}$	2.0	4.0	[1]
$\text{CF}_3-\text{C}\equiv\text{C}-\text{H}$	> 15	2	[3]
$(\text{CF}_3)_3\text{C}-\text{C}\equiv\text{C}-\text{H}$	0.06	< 0.015	[4]
$\text{SF}_5-\text{C}\equiv\text{C}-\text{H}$	> 15	1.4	present work

Table 8
The vibrational fundamentals of the ESF molecule (from Ref. [15])

		Wavenumber (cm^{-1})	Symmetry
CH stretch	ν_1	3327.6	a_1
CC stretch	ν_2	2123	a_1
SF stretch	ν_3	907	a_1
SF stretch	ν_4	889	e
	ν_5	718	e
	ν_6	714	a_1
	ν_7	630	b_1
	ν_8	611	a_1
	ν_9	613	e
	ν_{10}	552	e
	ν_{11}	518	b_2
	ν_{12}	510	a_1
	ν_{13}	371	b_1
	ν_{14}	375	e
	ν_{15}	144	e

to those observed earlier for both the ν_1 and $2\nu_1$ states of $(\text{CH}_3)_3\text{SiCCH}$ and for the $2\nu_1$ state of CF_3CCH , but much longer than for the corresponding states of $(\text{CH}_3)_3\text{CCCH}$ and $(\text{CF}_3)_3\text{CCCH}$ (see Table 7). Earlier work had shown a correlation of the observed lifetime with the density of low order resonances [9], though this correlation had failed to predict the rapid decay observed for $(\text{CF}_3)_3\text{CCCH}$ [4]. As apparent from Table 8, ESF has no states coupled by cubic (3rd order interactions), and only a handful of states coupled by fourth order interactions. This is due to the fact that except for the CH and CC modes (2123 cm^{-1}), all the normal modes have fundamental frequencies below 907 cm^{-1} . In fact the density of low order resonances is considerably smaller than even for the Si compounds, and quite similar to that of CF_3CCH , which has almost the same overtone lifetime. Like ESF, CF_3CCH has too low a density of states in the fundamental to give a true decay, but based upon the $K=1$ spectrum, where 3 perturbers are observed, we can estimate $V_{\text{rms}}=4\times 10^{-3}\text{ cm}^{-1}$, which combined with the calculated density of A_1 states (10 per cm^{-1}), gives a $\tau_{\text{GR}}=5\text{ ns}$. Thus we see that the effective lifetimes are quite comparable for EPS and CF_3CCH .

In conclusion, the present results fit well in the trends previously identified for the lifetime of terminal acetylene compounds. The predictive success of such trends, supports our hope that IVR rates are largely determined by coarse spectral features, such as the fundamental vibrations of the molecule, that are transferable between closely related molecules. The observed rapid decay of $(\text{CF}_3)_3\text{CCCH}$ now stands out as even more anomalous than before, and we encourage our theoretical colleagues to seek an explanation for that result.

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