

Eigenstate-resolved ν_1 Spectrum of CF_3CCH : Anharmonic Couplings to the Bath

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Using the optothermal technique we have measured the ν_1 fundamental of CF_3CCH in a collimated molecular beam. A linear least-squares fit to the unperturbed K subbands with the band origin fixed at 3329.85 cm^{-1} gives the rotational constants as $B' = 0.0958539(17)\text{ cm}^{-1}$ and $\Delta A = -0.0000088(22)\text{ cm}^{-1}$. The perturbed subbands are best fit by an anharmonic coupling to a background state with an interaction matrix element of ca. 0.005 cm^{-1} . Several other perturbations are noticed in the spectrum.

The sub-doppler infrared spectrum of trifluoropropyne (CF_3CCH) has been measured in a molecular beam and an analysis of the acetylenic stretch (ν_1) near $3.0\text{ }\mu\text{m}$ has been undertaken to examine the nature of the perturbations to the spectrum. A fully resolved, molecular eigenstate study, such as the present one, provides information about the strength and nature of couplings which lead to intramolecular vibrational redistribution in the ground electronic state. The acetylenic group is well suited for studies of this type because: (a) its high frequency allows regions with large density of states to be probed; (b) in contrast to the alkyl C—H chromophore it typically does not exhibit strong stretch-bend couplings; and (c) its linearity does not lower the symmetry of the group attached to the acetylene. Thus, by keeping the symmetry of the attached group the same (C_3 , for example), we obtain the same symmetric-top, parallel band type spectrum but for a number of molecules with very different densities of states at the fundamental. Trifluoropropyne has been studied in the gas phase by FTIR and laser photoacoustic spectroscopy with varying degrees of resolution.^{1,2} Neither of these studies resolved the K structure in the rotational lines. Analysis of the J structure in the gas phase was complicated by the presence of several strong sequence bands due to low-frequency bending modes.¹ Recently fully resolved, jet spectra of both CH_3CCH ^{3a} and butyne^{3b} were reported for the C—H fundamentals. The CH_3CCH spectrum showed an unperturbed acetylenic stretch while the alkyl methyl stretch did show a single anharmonic resonance with a background combination state. The CF_3CCH ν_1 spectrum we now report is first of a series of spectra we are examining of acetylenic groups in larger molecules, both at the fundamental and first overtone, to reveal the nature of vibrational couplings as the density of states and the level of excitation increases.

The spectrum to be analysed here was obtained using the optothermal technique, wherein a collimated molecular beam is crossed by a colour-centre laser and the increase in energy of the beam's molecules due to infrared absorption is measured.⁴ The molecular beam is formed by expanding a 1% CF_3CCH in He gas mixture through a $30\text{ }\mu\text{m}$ nozzle from 5 atm (505 KPa). The F-centre laser (Burlingame FCL 20) output power is ca. 10 mW at $3.0\text{ }\mu\text{m}$ and crosses the molecular beam ca. 25 times using a near-parallel mirror multipass arrangement. Instrumental resolution is ca. 10 MHz, limited by the finite crossing angles of the multipass optics. Frequency calibration is obtained using a scanning etalon with an FSR of ca. 150 MHz. The exact FSR is determined using ground-state combination differences and the reported microwave constants for trifluoropropyne.⁵ The standard deviation

of the fit to ground-state combination differences for $K = 0-6$ is 2.87 MHz. At present we lack an absolute frequency calibration so the band origin is set equal to the FTIR value reported by Dübäl and Quack.¹

The K structure of the $R(5)$ transition is shown in fig. 1. No hot bands were observed in the spectrum. The $K = 0$, $K = 5$ and $K = 6$ sub-branch of the spectrum consist of only one line for each $P(J)$ and $R(J)$, suggesting only minor perturbations, if any, in these subbands. Indeed these three subbands fit a rigid-rotor model quite well yielding the constants listed in table 1. The $R(0)$, $P(1)$ and $P(2)$ lines in the $K = 0$ subband, three out of the nineteen $K = 0$ lines measured, are omitted from the fits since they showed large errors in both the combination differences and rigid ro-vibrator linear least-squares fits; the position errors are most likely due to the low signal-to-noise ratios on these lines. A simultaneous fit of all three subbands has been performed to provide an estimate of ΔA , and the results are also given in table 1.

The $K = 1$, $K = 3$ and $K = 4$ subbands show a perturbation resulting in avoided crossing behaviour of two vibrational states. For a given K the perturbing (or dark) state moves off to higher frequency with increasing J , indicating that it has a larger rotational constant than ν_1 . At $J = 1$ the $K = 1$ eigenstates are already beyond the avoided crossing. The $K = 3$ subband crosses between $J = 6$ and 7. The $K = 4$ subband first shows two eigenstates at $J = 7$ as it begins to enter the avoided crossing. Two coupling schemes were used to fit the $K = 1$ and $K = 3$ perturbed subbands. One assumed a constant, anharmonic coupling between ν_1 and an unknown 'dark' state, d_1 . The second had the two states interacting via a $\Delta K = -1$ Coriolis interaction where the matrix element of the coupling is given by $W_{\text{Cor}}[J(J+1) - K(K-1)]^{1/2}$. Since the $K = 1$ splitting appears in $P(2)$

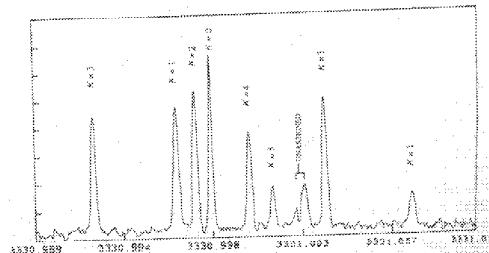


Fig. 1. Optothermal molecular beam spectrum of the $R(5)$ transition for the ν_1 acetylenic stretch of CF_3CCH showing the K structure for this parallel band transition. The FWHM of the individual lines is machine limited to ca. 10 MHz. The $K = 0$, $K = 4$ and $K = 5$ lines are unperturbed. The perturbations to the $K = 1$, $K = 2$ and $K = 3$ lines are discussed in the text.

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Table 1. Spectroscopic constants from linear least-squares fitting to rigid ro-vibrator^a

A Fits to individual K subbands				
K sub-band	subband origin/cm ⁻¹	B /cm ⁻¹	ΔB /cm ⁻¹	σ /MHz
$K = 0$	3329.850 07 (06)	0.095 854 3 (12)	-0.000 143 7 (12)	2.08
$K = 2$	3329.848 74 (11)	0.095 862 0 (26)	-0.000 136 0 (26)	3.01
$K = 5$	3329.853 66 (12)	0.095 852 7 (19)	-0.000 145 3 (19)	1.68
$K = 6$	3329.854 99 (09)	0.095 852 3 (12)	-0.000 143 7 (12)	0.81

B Multiband fit to the $K = 0$, $K = 5$ and $K = 6$ subbands	
band origin/cm ⁻¹	3329.850 11 (08)
B /cm ⁻¹	0.095 853 9 (17)
ΔB /cm ⁻¹	-0.000 144 1 (17)
ΔA /cm ⁻²	-0.000 008 8 (22)
σ /MHz	2.85

^a All ground-state constants are held at the reported microwave values.⁵ The fitting is made to the change in the constants, that is ΔB , for example, is fit. Owing to the low J values populated in the molecular beam, the values of ΔB , and ΔD_{JK} could not be determined and were held at zero for all fits. The values in parentheses are 2σ uncertainties in the last digits and the reported σ is the standard deviation for the fit.

and the $K = 3$ splitting in P(4) a $\Delta K = +1$ Coriolis interaction can be eliminated. A $\Delta K = 0$ (A axis) Coriolis interaction would lead to a constant interaction for each K subband that would be proportional to K , therefore, since only single subbands are fit, this type of interaction has the same functional form as the anharmonic interaction. Intensities were also calculated from the results of the two fits by assuming that v_1 carries all the transition moment. For these fits the band origin and B rotational constant of v_1 were fixed to the values obtained from the fit of the unperturbed subbands. The results, given in table 2, indicate that the anharmonic coupling model gives a better fit to the data. The $K = 3$ matrix element is clearly not three times as large as the $K = 1$ matrix element so a $\Delta K = 0$ (A axis) Coriolis interaction can also be eliminated. For both the $K = 1$ and $K = 3$ fits the anharmonic interaction also gives a better prediction of the observed intensities, in particular, for the $K = 3$ data the anharmonic fit correctly puts the crossing between $J' = 6$

Table 2. Non-linear least-squares fits to the perturbed subbands using an anharmonic and coriolis interaction between two states^a

A $K = 1$ subband		
	anharmonic interaction	Coriolis $\Delta K = -1$ interaction
dark-state subband origin/cm ⁻¹	3329.851 50 (52)	3329.854 8 (20)
dark-state B /cm ⁻¹	0.096 046 (16)	0.095 991 (70)
$ W_{12} $ /cm ⁻¹	0.005 27 (18)	0.001 77 (18)
σ /MHz	11.6	56.1

B $K = 3$ subband		
	anharmonic interaction	Coriolis $\Delta K = -1$ interaction
dark-state subband origin/cm ⁻¹	3329.8336 (16)	3329.830 9 (24)
dark-state B /cm ⁻¹	0.096 180 (37)	0.096 217 (58)
$ W_{12} $ /cm ⁻¹	0.007 07 (46)	0.001 04 (12)
σ /MHz	27.7	46.7

^a In all fits the constants for the bright state (v_1 of CF₃CCH) were fixed to the values obtained in the multisubband fit of the unperturbed $K = 0$, $K = 5$ and $K = 6$ subbands. The energy of the dark state was calculated as $E_{\text{dark}} = v_{\text{dark sub-origin}} + B_{\text{dark}} J(J+1)$. The values in parentheses are 2σ in the last digits.

and 7, whereas the Coriolis fit would place the crossing between $J' = 7$ and 8.

In addition to the anharmonically coupled state responsible for the avoided crossings observed for $K = 1$ and $K = 3$ there also exists at least one additional state perturbing the spectrum. The presence of this state is indicated because the $K = 2$ subband does not show an avoided crossing, expected near $J' = 3$, it does not fit accurately as an unperturbed subband, and its effective origin is shifted to the red. The anomalous origin for the $K = 2$ subband indicates that the $K = 2$ levels of the dark state, d_1 , are shifted to higher frequency, presumably by yet another dark state, d_2 . This results in the v_1-d_1 crossing becoming a virtual crossing at negative J . Given the K selectivity of this second perturbation (and the similar size of A and B in this molecule), it is likely that the d_1-d_2 coupling is a perpendicular Coriolis interaction. Furthermore, there exist weak lines in the $J' = 4, 5, 6$ and 7 regions that belong to $K = 2$ and/or $K = 3$, although the specific assignments are not yet known. It is this additional coupling in the $K = 3$ case which most likely causes the goodness of the anharmonic fit to be inferior to that of the $K = 1$ subband and gives slightly different effective constants for $K = 1$ and $K = 3$. These extra eigenstates may be due to d_2 or may represent yet other states with much weaker coupling constants.

In summary, the spectrum clearly reveals a multistate mixing of the v_1 fundamental that is dominated by a single anharmonic interaction with a background state with a coupling matrix element of ca. 0.005 cm⁻¹. This coupling is more than an order of magnitude weaker than the 0.096 cm⁻¹ coupling found for propyne in the methyl stretch near 3000 cm⁻¹,³ suggesting that a higher-order perturbation is present in the trifluoropropene spectrum. A harmonic vibrational state count gives a vibrational density of states of 57 cm⁻¹ at 3300 per cm⁻¹ above the ground state. Matrix elements of ca. 0.1 cm⁻¹, as are often invoked, would lead, in our case, to a much more complex spectrum than is observed. The CF₃CCH spectrum shows that at a ro-vibrational density of states of several hundred per cm⁻¹ multistate mixing, the precursor of intramolecular vibrational redistribution, is present, but not yet statistical and involves coupling to only a few levels with relatively small coupling matrix elements. The trifluoropropene fundamental is similar to the visible spectrum of acetylene in the extent of perturbation observed.⁶ A more detailed analysis of the v_1 trifluoropropene fundamental will appear in a later publication together with the measurement and analysis of its first overtone.

The authors thank the NSF for support of this work.

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