

High resolution spectroscopic studies of methyl acetylene : analysis of ν_6 band of CD_3CCH

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Abstract : The high-resolution Fourier transform spectrum of the ν_6 band of CD_3CCH has been recorded at an apodized resolution of 0.004 cm^{-1} . The rotational structure in the P and Q subbands of $K = 5$ to 9 have been fitted with a standard deviation of 0.0006 cm^{-1} to evaluate the main localized Fermi resonance between the ν_6 (E) and $(\nu_7 + \nu_8 + \nu_{10})$ (E) levels. The parameters of both levels and the Fermi interaction parameter have been determined.

Keywords : ν_6 band of CD_3CCH , Fermi resonance, vibration-rotation spectra.

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1. Introduction

Propyne (CH_3CCH) has been found to be abundant in several interstellar molecular clouds [1] as well as in the atmospheres of Titan [2], Jupiter and Saturn [3]. Furthermore, optically pumped laser emissions have been observed for this molecule in the far-infrared and midinfrared regions [4,5]. For these reasons, its rotational spectrum has been extensively studied in its vibrational ground state as well as excited states [1,3,6]. The vibration-rotation spectra of propyne and its isotopic molecules provide good examples of various kinds of perturbations as all vibrational levels, except perhaps the lowest lying fundamentals, which are expected to be perturbed to some extent by other vibrational levels. The bands of CD_3CCH studied so far under high resolution are $2\nu_9$ [7], ν_9 [8], ν_5 and ν_8 [9]. Speirs and Duncan [10] studied the ν_6 band of CD_3CCH at medium resolution of $0.2\text{--}0.3\text{ cm}^{-1}$ and the localized perturbation at $\sim 2210\text{ cm}^{-1}$ was identified as a Fermi resonance between the ν_6^{\pm} and $(\nu_7^{\mp} + \nu_8^{\pm} + \nu_{10}^{\mp})$ levels. The resolution that was available to them permitted only a band contour analysis of the Q subband structure and they were unable to determine the Fermi interaction parameter. We have obtained the high-resolution

Fourier transform spectrum of the ν_6 band of CD_3CCH , and the rotational analysis of the spectral region where the Fermi resonance is prominent is carried out and reported in this paper.

2. Experimental details

The infrared absorption spectrum of a commercial sample (Merck, Sharpe & Dohme, Canada) of CD_3CCH (99% purity) in the spectral region of $2040\text{--}2390\text{ cm}^{-1}$ was obtained using a Bomem DA8 Fourier transform spectrometer. The spectrum was taken with a globar source, KBr beam splitter, and InSb detector at an apodized resolution of 0.004 cm^{-1} . A sample pressure of $\sim 33\text{ Pa}$ (0.25 Torr) was used in a folded cell of fixed path length 10 m . A total of 32 scans were coadded. Wavenumber calibration was performed with suitable water vapor [11] lines in the spectrum.

3. Results and discussion

The propyne- d_3 (CD_3CCH) molecule is a symmetric top with C_{3v} symmetry. It has 10 normal modes of vibration, 5 of species A_1 and 5 of species E . The ν_6 band (antisymmetric CD_3 stretching; $\sim 2236\text{ cm}^{-1}$; E symmetry species) of CD_3CCH

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has the typical appearance of a perpendicular type band of a prolate symmetric top with a large rotational constant A : the Q branches are widely separated and the assignment of the rotational quantum number K is straightforward. The Q -branch assignments by Speirs and Duncan [10] were largely confirmed in our present studies. An overview of the ν_6 band of CD_3CCH , taken at a resolution of 0.1 cm^{-1} is shown in Figure 1. A marked localized perturbation occurs between PQ_6 and PQ_7 at $\sim 2210 \text{ cm}^{-1}$. This is evident from the Q -branch separations which diminish markedly on either side of an abnormally large gap. From the very close correspondence to the situation which exists in CD_3CN ,

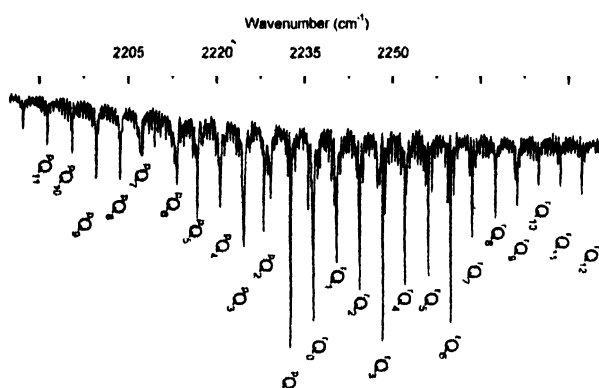


Figure 1. The spectrum of the ν_6 band of CD_3CCH recorded at a resolution of 0.1 cm^{-1} .

Speirs and Duncan [10] attributed the origin of this effect to a Fermi interaction of the ν_6 state with the combination state ($\nu_7 + \nu_8 + \nu_{10}$) in CD_3CCH . A similar perturbation has been observed in the low resolution spectrum of the ν_6 band of

CD_3CCD [12]. The analyses of the high resolution spectra of the ν_6 band of methyl acetylene (CH_3CCH) or any of its isotopomers have not been reported so far. In this paper we report the analysis of this localized Fermi perturbation in CD_3CCH from our high resolution data by fitting the lines in the ${}^P P_K$ and ${}^P Q_K$ ($K = 5-9$) subbands, which are most affected by this perturbation. The assignment of the J values in these subbands were made with the aid of ground state combination differences using the constants from Ref [9]. The upper state energy levels were determined by the diagonalization of a combined energy matrix of ν_6 and ($\nu_7 + \nu_8 + \nu_{10}$) levels with off-diagonal matrix elements corresponding to Fermi resonance. The diagonal matrix elements are given by the standard polynomial expression,

$$E_{v,J} = G_v + B_v J(J+1) + (A_v - B_v) K^2 - D_v^J J^2 (J+1)^2 \\ \times D_v^{JK} J(J+1) K^2 - D_v^K K^4 - [2(A\zeta^z)_v k \cdot l]$$

where $K = |k|$ and the splitting of the $\pm l$ components through z-axis Coriolis coupling, given by the term in square bracket, is relevant only for degenerate states. The off-diagonal matrix element for Fermi resonance is given by,

$$\langle (v_6^{\pm 1}, K | H | (v_7 + v_8 + v_{10})^{\mp 1}, K \rangle = W$$

The assigned transitions are listed in Table 1, and the parameters derived from the least-squares fit are given in Table 2. The blended lines (with hot band transitions, or other lines) were excluded from the fit. The parameters of the ($\nu_7 + \nu_8 + \nu_{10}$) (E) state, to which transitions are not observed

Table 1. Assigned transitions in the ν_6 band of CD_3CCH .

	Obs	O-C		Obs	O-C		Obs	O-C
	${}^P P_5$							
		34	2199.4993	23°	16	2198.9513		
16	2208.5371	25°	2198.9927	8	17	2198.4484		
17	2208.038	22°	2198.4861	-3	18	2197.9437	0	
18	2207.5352	-13°			19	2197.4371	-13	
19	2207.038	11	${}^P P_6$		20	2196.9343	17	
20	2206.5389	21°	2206.522	1	21	2196.4258	0	
21	2206.0361	-1	2206.0192	13°				
22	2205.5352	-1	2205.5182	-3		${}^P P_8$		
23	2205.0342	0	2205.0154	-5	7	2199.8854	-28	
24	2204.5333	8	2204.5125	0	8	2199.3919	-26	
25	2204.0304	0	2204.0078	-8	9	2198.9004	-1	
26	2203.5295	15°	2203.5031	-9	10	2198.4089	28	
27	2203.0248	-4	2202.9984	-4	11	2197.9173	61	
28	2202.5219	-2	2202.4937	6	12	2197.4126	-31	
29	2202.0191	4	2201.9908	40°	13	2196.9079	-121	
30	2201.5144	-5			14	2196.4145	-95	
31	2201.0115	6	${}^P P_7$		15	2195.9211	-64	
32	2200.5068	2	2199.955	-9	16	2195.4277	-29	
33	2200.0021	1	2199.4522	18°	17	2194.9342	7	

Table 1. (Cont'd.).

<i>J</i>	Obs	O-C		Obs	O-C		Obs	O-C
18	2194.4333	-24*	24	2216.7914	-3			
19	2193.9361	-16	25	2216.7801	4			
20	2193.4389	-5	26	2216.767	-1	20	2203.7366	38*
21	2192.9399	-8	27	2216.7538	-5	21	2203.7235	-4
22	2192.4427	10	28	2216.7406	-4	22	2203.714	-6
23	2191.9436	13	29	2216.7274	0	23	2203.7065	14*
24	2191.437	-54*	30	2216.7123	-11	24	2203.6971	20*
25	2190.9436	12*	31	2216.6992	1	25	2203.6858	11
26	2190.4464	44*	32	2216.6841	-2	26	2203.6764	24*
27	2189.9417	5	33	2216.669	-2	27	2203.6632	4
28	2189.4407	6	34	2216.654	1	28	2203.6519	6
29	2188.9379	-7	35	2216.6389	7	29	2203.6406	11*
30	2188.437	0	36	2216.622	-1	30	2203.6255	-16*
31	2187.9341	-8				31	2203.6123	22*
32	2187.4294	-32*		ⁿ Q ₆		32	2203.5973	-43*
33	2186.9247	-53*	13	2213.3884	6	33	2203.5973	89*
	^{pp} Q ₉		14	2213.3771	3	34	2203.5822	74*
			15	2213.3639	-11*	35	2203.5671	63*
24	2187.4671	-15*	16	2213.3526	0	36	2203.5483	18*
25	2186.97	-7	17	2213.3394	0	37	2203.5295	-22*
26	2186.4727	0	18	2213.3244	-12*	38	2203.5295	126*
27	2185.9737	-5	19	2213.3112	0	39	2203.5031	15*
28	2185.4765	7	20	2213.2961	0	40	2203.4824	-35*
29	2184.9774	4	21	2213.281	5		ⁿ Q ₉	
30	2184.4783	2	22	2213.2679	37*			
31	2183.9793	4	23	2213.249	17*	23	2199.7253	-9
32	2183.4802	6	24	2213.2358	60*	24	2199.7177	-6
33	2182.9793	-7				25	2199.7102	1
34	2182.4783	-21*		ⁿ Q ₇		26	2199.7008	-6
35	2181.9792	-14*				27	2199.6933	6
36	2181.4802	-5	16	2207.2866	0	28	2199.6838	2
	ⁿ Q ₅		17	2207.2734	2	29	2199.6744	1
			18	2207.2583	-6	30	2199.665	3
19	2216.8461	5	19	2207.2433	-6	31	2199.6556	7
20	2216.8366	9	20	2207.2282	2	32	2199.6462	14*
21	2216.8253	0	21	2207.2113	1	33	2199.633	-14
22	2216.814	-5	22	2207.1943	8	34	2199.6217	-22*
23	2216.8027	-6	23	2207.1755	7			

^aThe observed values are in cm⁻¹ and the residuals (O-C) are in cm⁻¹ × 10⁻⁴. Lines marked with asterisks were excluded from the fit.

Table 2. Molecular parameters for ν_6 and ($\nu_7 + \nu_8 + \nu_{10}$) states of CD₃CCH^a

	Ground State	ν_6 state	$\nu_7 + \nu_8 + \nu_{10}$ state
<i>G</i>	0.0 ^b	2235 05887 (178)	2192.67747 (195)
<i>B</i>	0.24536128 ^b	0.24509854 (256)	0.2439885 (130)
<i>A - B</i>	2.4116 ^b	2.398583 (142)	2.376696 (394)
<i>D</i> ^c × 10 ⁷	0.7237 ^b	0.6088 (131)	0.7237 ^b
<i>D</i> ^k × 10 ⁵	0.341774 ^b	0.27867 (206)	0.341774 ^b
<i>D</i> ^k × 10 ⁴	0.225 ^b	0.20491 (871)	0.225 ^b
(2 <i>A</i> ζ ²)		0.846464 (965)	8.70093 (191)
<i>H</i>			0.216537 (372)
No. of lines assigned		150	
No. of lines used		98	
RMSD (cm ⁻¹) × 10 ⁴		5.7	

^aAll values are in cm⁻¹. The standard deviation of the parameters given in parantheses are in the units of the least significant digit.

^bConstrained parameter. ^cFrom Ref. [9].

in the spectrum, are not completely determinable. The ζ^2 values for the fundamentals given by Speirs and Duncan [10] were used and for the combination band $\zeta^2(\nu_7 + \nu_8 + \nu_{10}) = -\zeta_7 + \zeta_8 + \zeta_{10}$. In the least-squares analysis, the starting values for $(2A\zeta^2)$ used were 0.8343 cm^{-1} and 8.7 cm^{-1} for the ν_6 (*E*) and $(\nu_7 + \nu_8 + \nu_{10})$ (*E*) states, respectively, which are very close to the values obtained from the fit as seen from Table 2.

4. Conclusion

This study explains the major localized Fermi resonance between the ν_6 and $(\nu_7 + \nu_8 + \nu_{10})$ band of CD_3CCH . About 150 lines in the pP_K ($K = 5-7$) subbands could be fitted to a standard deviation of 0.0006 cm^{-1} , which is comparable to the precision of the measurements. The molecular parameters for the ν_6 and $(\nu_7 + \nu_8 + \nu_{10})$ combination states and the Fermi interaction parameter have been obtained with statistical significance. Efforts are being made to assign the lines of all the subbands, with the inclusion of additional perturbations in the least-squares fit for complete analysis of this band and the results will be reported soon.

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