

Millimeter-Wave Rotational Spectrum of CF_3CCD in the Ground and Excited Vibrational States $v_{10} = 1$

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Millimeter-wave rotational spectra of the symmetric top molecule CF_3CCD have been measured in its ground and excited vibrational states, $v_{10} = 1$. Analysis of the ground-state spectra gave the following rotational parameters: $B_0 = 2696.06753$ MHz, $D_J = 0.22759$ kHz, $D_{Jk} = 6.1748$ kHz. H_{Jk} (16.1 mHz) and H_{kJ} (−0.243 mHz) were determined for the first time. In the $v_{10} = 1$ state, $\ell = \pm 1$ series have been assigned and spectroscopic parameters were obtained accurately: $B_1 = 2701.26211$ MHz, $q_t{}^+(2,2) = 3.30887$ MHz, $A\zeta = 3263.93$ MHz. The off diagonal parameter r_t (0.152 MHz) was determined for the first time.

CF_3CCD is a prolate symmetric top molecule. This is an isotopomer of CF_3CCH, and hence, its rotational and vibrational behavior is similar. It has ten fundamental frequencies ($5A_1 + 5E$), all are infrared and Raman active, and they have roughly the same frequencies as in CF_3CCH unless H/D is involved in the vibration.[1] The dipole moment of this molecule is as large as 2.324 Debye,[2] and so, the spectra are intense making it possible to observe its spectra in excited vibrational states. The rotational spectra of this molecule in the ground and $v_{10} = 1$ states have been measured and studied by several authors but only for low J values.[2–4] The lowest vibrational level, $v_{10} = 1$, lies at 163 cm^{-1}; consequently it has a population of 61.8% (including degeneracy) of the ground state at $T = 200$ K.

The aim of this research work was to determine the spectroscopic parameters of this molecule by measuring higher J values.

Experimental

The measurements were made on a Newcastle source-modulated millimeter-wave spectrometer which was described previously.[5] Millimeter waves were generated as harmonics of OKI klystrons, which were phase-locked to a standard crystal frequency. The spectrometer frequency calibration was frequently checked by comparing OCS absorptions with accurately known frequencies listed by Dubrulle et al.[6]

The method used to prepare CF_3CCD was based on that described by Cox et al.[7] During scanning the CF_3CCD spectra; no signal related to CF_3CCH was observed.[8,9]

The spectra for transitions $J \rightarrow J + 1$, where $J = 12$, 13, 17, 21, and 27 (70 to 160 GHz) were recorded at a cell pressure of about 10^{-2} Torr (1 Torr = 133.322 Pa) and with dry ice cooling. Investigation of the rotational spectra of the symmetric top molecule CF_3CCD with high J values yields more precise ground state centrifugal distortion constants.

The signals for all the transitions mentioned above were fairly strong and sharp; weaker lines were also observed that are probably due to rotational spectra of vibrationally excited molecules. For symmetric top molecules like CF_3CCD, the ground vibrational state rotational energies are given up to sextic terms by Eq. 1, and by application of selection rules $\Delta J = +1$ and $\Delta k = 0$, the frequencies are given by Eq. 2.

$$E_{J,k} = BJ(J+1) + (A-B)k^2 - D_J J^2(J+1)^2 - D_{Jk}J(J+1)k^2 - D_k k^4 + H_J J^3(J+1)^3 + H_{Jk}J^2(J+1)^2k^2 + H_{kJ}J(J+1)k^4 + H_k k^6, \quad (1)$$

$$\nu = 2B(J+1) - 4D_J(J+1)^3 - 2D_{Jk}(J+1)k^2 + H_J(J+1)^3[(J+2)^3 - J^3] + 4H_{Jk}(J+1)^3k^2 + 2H_{Jk}(J+1)k^4. \quad (2)$$

The spectra in this state were simple, and so, the different k values ($k = 0, 1, 2, 3, 4, \ldots$) for each J transition were easily assigned. Centrifugal distortion produced a band head at high frequency at $k = 0$, with a spread to lower frequency with higher k.

A least-squares program[10] was used to fit the observed frequencies to the parameters of Eq. 2, in which the weights were taken to be $w = 1/(\text{observed error})^2 = 1/(0.1)^2$, where 0.1 in MHz is estimated uncertainty in an observation for each unblended line. A few lines have an observed error of 0.2 MHz to allow for overlapping or broadening.

The results of refinement are shown in Table 1, and the parameters obtained are given in Table 3. If k values are plotted against frequency for this state, the observed Fortrat-like diagram is produced for $J = 21$, which is shown in Fig. 1. In this diagram the splitting increasing as k increases, and this is due to the D_{Jk} parameter.

Because v_{10} state has a high population, the rotational spectra in this state are also strong. It is isolated in frequency from other vibrational states and, thus, not complicated by interactions with nearby states.

Rotational frequencies for transitions $J \rightarrow J + 1$ in the excited degenerate vibrational state $v_t = 1$, $\ell_t = \pm 1$ of molecules with axial symmetry were calculated by Nielsen.[11] Although the Nielsen theory was fairly satisfactory for the rotation spectrum of these types of molecules, some of the calculated frequencies by this method were different from the observed frequencies. This formula was extended to the case of higher J values by Gordy et al.[4] and the frequencies of lines for transition $J \rightarrow J + 1$ were calculated by Amat and Grenier-Besson.[12] The frequency of transition $J \rightarrow J + 1$ for molecules belonging to the point group C_{3v} in singly

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Table 1. The Results of Refinement of Observed Frequencies for CF_3CCD in the Ground State[a)]

J''	k	Observed/MHz	Obs-Calc/MHz	Error/MHz
12	0	70095.750	−0.0059	0.1000
12	1	70095.585	−0.0105	0.1000
12	2	70095.098	−0.0163	0.1000
12	3	70094.317	0.0048	0.1000
12	4	70093.185	−0.0043	0.1000
12	5	70091.737	−0.0084	0.1000
12	6	70089.982	0.0014	0.1000
12	7	70087.890	−0.0046	0.1000
12	8	70085.513	0.0255	0.1000
12	9	70082.790	0.0310	0.1000
12	10	70079.745	0.0358	0.1000
12	11	70076.362	0.0242	0.1000
12	12	70072.657	0.0124	0.1000
13	0	75487.190	−0.2030	excluded
13	1	75487.190	−0.0303	0.2000
13	2	75486.655	−0.0472	0.1000
13	3	75485.788	−0.0505	0.1000
13	4	75484.589	−0.0404	0.1000
13	5	75483.058	−0.0167	0.1000
13	6	75481.171	−0.0033	0.1000
13	7	75478.944	0.0158	0.1000
13	8	75476.360	0.0237	0.1000
13	9	75473.428	0.0296	0.1000
13	10	75470.139	0.0246	0.1000
13	11	75466.494	0.0099	0.1000
13	12	75462.614	0.1066	0.1000
13	13	75458.143	−0.0412	0.1000
17	0	97052.910	−0.2121	excluded
17	1	97052.910	0.0098	0.2000
17	2	97052.200	−0.0344	0.1000
17	3	97051.100	−0.0248	0.1000
17	4	97049.560	−0.0112	0.1000
17	5	97047.570	−0.0036	0.1000
17	6	97045.120	−0.0120	0.1000
17	7	97042.230	−0.0161	0.1000
17	8	97038.920	0.0042	0.1000
17	9	97035.140	−0.0010	0.1000
17	10	97030.900	−0.0216	0.1000
17	11	97026.270	0.0127	0.1000
17	12	97021.180	0.0322	0.1000
17	13	97015.590	−0.0030	0.1000
17	14	97009.490	−0.1026	0.2000
17	15	97003.270	0.1237	0.2000
17	16	96996.270	0.0162	0.1000
17	17	96988.900	−0.0148	0.1000
21	0	118617.284	0.0059	0.1000
21	1	118617.063	0.0559	0.1000
21	2	118616.218	0.0239	0.1000
21	3	118614.866	0.0270	0.1000
21	4	118612.994	0.0523	0.1000
21	5	118610.537	0.0347	0.1000
21	6	118607.508	−0.0125	0.1000
21	7	118603.946	−0.0503	0.1000
21	8	118599.877	−0.0524	0.1000
21	9	118595.314	−0.0056	0.1000
21	10	118590.179	0.0121	0.1000
21	11	118584.511	0.0402	0.1000
21	12	118578.258	0.0269	0.1000
21	13	118571.433	−0.0146	0.1000
21	14	118564.075	−0.0450	0.1000
21	15	118556.197	−0.0507	0.1000
21	16	118547.773	−0.0576	0.1000
21	17	118538.855	−0.0132	0.1000
21	18	118529.391	0.0310	0.1000
21	19	118519.316	0.0103	0.1000
21	20	118508.669	−0.0358	0.1000
21	21	118497.554	−0.0026	0.1000
27	0	150959.880	0.0823	0.1000
27	1	150958.924	−0.5294	excluded
27	2	150958.519	0.0988	0.1000
27	3	150956.721	0.0227	0.1000
27	4	150954.259	−0.0284	0.1000
27	5	150951.148	−0.0396	0.1000
27	6	150947.374	−0.0245	0.1000
27	7	150942.902	−0.0182	0.1000
27	8	150937.735	−0.0173	0.1000
27	9	150931.854	−0.0406	0.1000
27	10	150925.230	−0.1168	0.1000
27	11	150918.130	0.0213	0.1000
27	12	150910.130	−0.0498	0.1000
27	13	150901.560	0.0002	0.1000
27	14	150892.210	−0.0384	0.1000
27	15	150882.250	0.0051	0.1000
27	16	150871.570	0.0209	0.1000
27	17	150860.200	0.0397	0.1000
27	18	150848.200	0.1220	0.1000
27	19	150835.310	0.0083	0.1000
27	20	150821.800	−0.0307	0.1000
27	22	150793.000	0.1977	0.2000
27	24	150760.940	−0.0471	0.1000

Continued.

a) Sigma = 0.047408, Sigma.w = 0.405504, 87 Transitions in fit, 82 Degrees of freedom.

excited vibrational state $v_t = 1$ is given by the approximate perturbation expression, Eq. 3.

$$\nu = 2B(J+1) - 4D_J(J+1)^3 - 2D_{Jk}(J+1)k^2 + 2\eta_J(J+1)k\ell + \Delta\nu, \quad (3)$$

where $\Delta\nu$ has the value $\pm q_t{}^+(J+1)$ if $(k\ell - 1) = 0$ (ℓ-type doubling) or

$$\Delta\nu = -\frac{(q_t{}^+)^2(J+1)^3}{4(B - A + A\zeta)(k\ell - 1)} \quad \text{if } (k\ell - 1) \neq 0 \text{ } (\ell\text{-type resonance}). \quad (4)$$

Because of a degenerate vibrational state, additional parameters were involved in the calculation of the energy levels. The extra parameters, $q_t{}^+$ (ℓ-type coupling constant), $A\zeta$ and η_J which gives the J and k dependence of $A\zeta$, are necessary to determine the frequency of spectra. ℓ is the vibrational angular momentum quantum number and can accept the value $\ell = \pm 1$; therefore, there are two different series in the spectrum. Eq. 3 shows a pattern for doubly degenerate states of a C_{3v} molecule that is predominately due to the splitting of the positive and negative series by ℓ-type resonance. As can be seen in Eq. 4, this resonance is inversely proportional to $(k\ell - 1)$. Thus, one series goes from high fre-

Table 2. The Results of Refinement of Observed Frequencies for CF_3CCD in the $v_{10} = 1$ State[a)]

J	$k\ell - 1$	k	ℓ		Observed /MHz	Obs-Calc /MHz	Error /MHz
12	0	−1	−1	A1	70188.173	−0.0204	0.1000
12	1	2	1	E	70210.500	−0.0157	0.1000
12	2	3	1	E	70219.868	0.0230	0.1000
12	3	4	1	A2	70223.168	0.0177	0.1000
12	4	5	1	E	70224.345	−0.0213	0.1000
12	5	6	1	E	70224.540	0.0275	0.1000
12	6	7	1	A2	70223.955	0.0003	0.2000
12	7	8	1	E	70222.860	0.0051	0.1000
12	8	9	1	E	70221.315	0.0197	0.1000
12	9	10	1	A2	70219.335	0.0128	0.1000
12	10	11	1	E	70216.943	−0.0206	0.1000
12	11	12	1	E	70214.235	−0.0021	0.1000
12	−13	12	−1	E	70200.638	−0.0354	0.1000
12	−12	11	−1	A2	70205.198	−0.0365	0.1000
12	−11	10	−1	E	70209.458	−0.0459	0.1000
12	−10	9	−1	E	70213.470	−0.0199	0.1000
12	−9	8	−1	A2	70217.190	−0.0143	0.1000
12	−8	7	−1	E	70220.678	0.0129	0.1000
12	−7	6	−1	E	70223.995	0.0948	0.2000
12	−6	5	−1	A2	70226.948	−0.0076	0.1000
12	−5	4	−1	E	70229.910	−0.0039	0.1000
12	−4	3	−1	E	70232.925	−0.0118	0.1000
12	−3	2	−1	A2	70236.375	−0.0152	0.1000
12	−2	1	−1	E	70241.295	0.0012	0.1000
12	−1	0	1	E	70251.593	0.0110	0.1000
17	0	−1	−1	A1	97181.090	0.0246	0.1000
17	1	2	1	E	97197.300	0.0280	0.1000
17	2	3	1	E	97212.670	0.0349	0.1000
17	3	4	1	A2	97220.230	0.0029	0.1000
17	4	5	1	E	97223.910	0.0157	0.1000
17	5	6	1	E	97225.580	0.1588	0.2000
17	6	7	1	A2	97225.580	0.0000	0.2000
17	7	8	1	E	97224.640	−0.1029	0.2000
17	8	9	1	E	97223.210	0.1022	0.1000
17	9	10	1	A2	97220.800	0.0109	0.1000
17	10	11	1	E	97217.900	0.0429	0.1000
17	11	12	1	E	97214.390	0.0328	0.1000
17	12	13	1	A2	97210.330	0.0100	0.1000
17	13	14	1	E	97205.780	0.0128	0.1000
17	14	15	1	E	97200.710	−0.0039	0.2000
17	15	16	1	A2	97195.190	0.0184	0.1000
17	16	17	1	E	97189.150	0.0011	0.1000
17	0	1	1	A2	97300.170	−0.0146	0.1000
17	−1	0	1	E	97283.530	−0.0054	0.1000
17	−2	1	−1	E	97266.800	−0.0445	0.1000
17	−3	2	−1	A2	97257.030	−0.0097	0.1000
17	−4	3	−1	E	97250.280	0.0056	0.1000
17	−5	4	−1	E	97244.780	0.0156	0.1000
17	−6	5	−1	A2	97239.730	−0.0072	0.1000
17	−7	6	−1	E	97234.810	−0.0108	0.1000
17	−8	7	−1	E	97229.820	0.0028	0.2000
17	−9	8	−1	A2	97224.640	0.0279	0.2000
17	−10	9	−1	E	97219.080	−0.0552	0.1000
17	−11	10	−1	E	97213.360	0.0190	0.1000
17	−12	11	−1	A2	97207.220	0.0212	0.1000
17	−13	12	−1	E	97200.710	0.0227	0.2000
17	−14	13	−1	E	97193.810	0.0191	0.1000
17	−15	14	−1	A2	97186.400	−0.0984	0.1000
17	−16	15	−1	E	97178.810	0.0087	0.1000
17	−17	16	−1	E	97170.680	−0.0128	0.1000
17	−18	17	−1	A2	97162.170	0.0020	0.1000
20	0	−1	−1	A1	113375.572	−0.0594	0.1000
20	0	1	1	A2	113514.553	−0.0507	0.1000
20	1	2	1	E	113387.831	−0.0467	0.1000
20	2	3	1	E	113404.147	0.0060	0.1000
20	3	4	1	A2	113414.143	0.0034	0.1000
20	4	5	1	E	113419.643	0.0104	0.1000
20	5	6	1	E	113422.382	0.0183	0.1000
20	6	7	1	A2	113423.292	0.0233	0.1000
20	7	8	1	E	113422.779	−0.0657	0.1000
20	8	9	1	E	113421.391	0.0202	0.1000
20	9	10	1	A2	113418.999	−0.0143	0.1000
20	10	11	1	E	113415.807	−0.0698	0.1000
20	11	12	1	E	113412.034	0.0041	0.1000
20	12	13	1	A2	113407.510	−0.0093	0.1000
20	13	14	1	E	113402.351	−0.0269	0.1000
20	14	15	1	E	113396.583	−0.0467	0.1000
20	15	16	1	A2	113390.320	0.0278	0.1000
20	16	17	1	E	113383.329	−0.0498	0.1000
20	17	18	1	E	113375.947	0.0472	0.1000
20	18	19	1	A2	113367.886	0.0229	0.1000
20	19	20	1	E	113359.251	−0.0242	0.1000
20	−3	2	−1	A2	113471.479	0.0313	0.1000
20	−4	3	−1	E	113462.373	0.0319	0.1000
20	−5	4	−1	E	113454.989	0.0260	0.1000
20	−6	5	−1	A2	113448.398	0.0198	0.1000
20	−7	6	−1	E	113442.107	0.0172	0.1000
20	−8	7	−1	E	113435.835	0.0164	0.1000
20	−9	8	−1	A2	113429.416	0.0178	0.1000
20	−10	9	−1	E	113422.658	−0.0663	0.1000
20	−11	10	−1	E	113415.737	0.0089	0.1000
20	−12	11	−1	A2	113408.320	−0.0429	0.1000
20	−13	12	−1	E	113400.599	0.0033	0.1000
20	−14	13	−1	E	113392.412	0.0092	0.1000
20	−15	14	−1	A2	113383.783	0.0166	0.1000
20	−16	15	−1	E	113374.697	0.0238	0.1000
20	−17	16	−1	E	113365.153	0.0400	0.1000
20	−18	17	−1	A2	113355.145	0.0672	0.1000
20	−19	18	−1	E	113344.579	0.0179	0.1000
20	−20	19	−1	E	113333.590	0.0320	0.1000
20	−21	20	−1	A2	113321.982	−0.0822	0.1000

a) Sigma = 0.038915, Sigma.w = 0.339152, 101 Transitions in fit, 95 Degrees of freedom.

quency at low k to low frequency at high k, while the other is at low frequency.

In order to obtain more accuracy in rotational energies for singly excited vibrational states than can be obtained from perturbation theory, it is necessary to set up a rotational Hamiltonian as a matrix (H) in equation $H\psi = E\psi$ and diagonalise to obtain the energy.[13,14] The Hamiltonian was set up for a symmetric top molecule like CF_3CCD. This rotation–vibrational Hamiltonian has two different blocks that belong to the different $\ell = +1$ and $\ell = -1$ series. k and ℓ are no longer good quantum numbers, but $(k - \ell)$ or $(k\ell - 1)$ may be used to distinguish between the symmetry spe-

Table 3. Comparison of Rotation–Vibration Parameters for CF_3CCD in Ground, $v_{10} = 1$ and $v_{10} = 2$ States

Parameter	Ground State[4]	Ground State (this work)	$v_{10} = 1$[8,9]	$v_{10} = 1$ (this work)	$v_{10} = 2$[8]
A/MHz	5737.6[a)]	5712.446[a)18]	5737.6[a)]	5712.446[a)18]	5718.8436[a)19]
B/MHz	2696.073	2696.06753(39)	2701.26157(49)	2701.26212(39)	2706.46204(46)
$A\zeta$/MHz	—	—	3289.25987(19)	3263.93(16)	3270.8306(23)
$q^+{}_t$/MHz	—	—	3.30877(85)	3.30887(78)	3.30878[a)]
r_t/MHz	—	—	—	0.152(34)	0.158(51)
D_J/kHz	0.2(6)	0.22759(34)	0.23030(87)	0.23181(53)	0.23831(72)
D_{Jk}/kHz	6.2	6.1748(30)	6.14841(139)	6.14689(87)	6.11343(72)
D_k/kHz	—	0.0[a)]	0.0[a)]	0.0[a)]	−5.2300[a)]
η_J/kHz	—	—	22.75398(1)	22.74725(3)	22.82807(3)
η_k/kHz	—	—	0.0[a)]	0.0[a)]	0.0[a)]
H_J/mHz	—	0.0[a)]	0.0[a)]	0.0[a)]	0.0[a)]
H_{Jk}/mHz	—	16.1(23)	0.0[a)]	0.0[a)]	0.0[a)]
H_{kJ}/mHz	—	−24.3(51)	0.0[a)]	0.0[a)]	0.0[a)]
q_J/Hz	—	—	0.0[a)]	0.0[a)]	0.0[a)]
g_{ll}/kHz	—	—	—	—	−22.72094(13)
x_{ll}/MHz	—	—	—	—	7716.97486(275)
η_{JJ}/Hz	—	—	—	—	−0.11047(23)
η_{Jk}/Hz	—	—	—	—	−15.46839(5)

a) Constrained at this value.

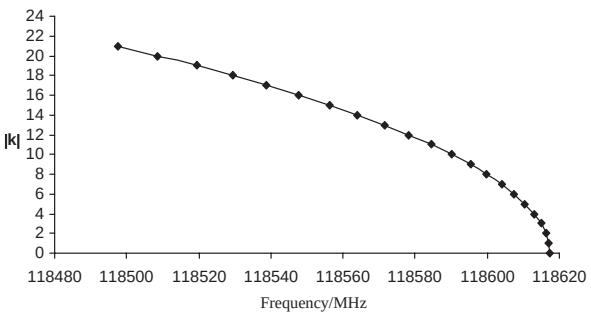

Fig. 1. Fortrat-like diagram of CF_3CCD in ground state. $J = 21 \rightarrow 22$.

cies. Those levels with $(k\ell - 1) = 3n$, where n is an integer, are of species A_1 or A_2. If $(k\ell - 1) \neq 3n$ the species are E. The $q_t{}^+$ produces a first-order splitting of the $(k\ell - 1) = 0$, A_1A_2 pair, which are the familiar ℓ-doublets, as shown by Grenier-Besson and Amat.[12] The main difference from the ground-state spectra is the splitting of the $|k - \ell| = 0$ into two widely separate ℓ-doublets and the splitting due to ℓ-resonance.

The diagonal matrix elements are given by:

$$\begin{aligned}\langle v_t, \ell_t, J, k|H/h|v_t, \ell_t, J, k\rangle &= BJ(J+1) + (A-B)k^2 \\ &- 2A\zeta k\ell - D_J J^2(J+1)^2 - D_{Jk}J(J+1)k^2 \\ &- D_k k^4 + \eta_J J(J+1)k\ell + \eta_k k^3\ell + H_J J^3(J+1)^3 \\ &+ H_{Jk}J^2(J+1)^2k^2 + H_{kJ}J(J+1)k^4 + H_k k^6. \end{aligned} \quad (5)$$

In addition, there are off-diagonal terms that arise from the transformation. The major one of these gives rise to the ℓ doubling:

$$\begin{aligned}&\langle v_t, \ell, J, k|H/h|v_t, \ell \pm 2, J, k \pm 2\rangle \\ &= -\frac{1}{4}q_t{}^+\{(v_t \mp \ell)(v_t \pm \ell + 2)[J(J+1) \\ &\quad - k(k \pm 1)][J(J+1) - (k \pm 1)(k \pm 2)]\}^{1/2}, \end{aligned} \quad (6)$$

and

$$\begin{aligned}&\langle v_t, \ell, J, k|H/h|v_t, \ell \pm 2, J, k \mp 1\rangle \\ &= -r_t[(v_t+1)^2 - (\ell \pm 1)^2]^{1/2}[J(J+1) \\ &\quad - k(k \mp 1)]^{1/2}(2k \mp 1), \end{aligned} \quad (7)$$

and hence, the lines can be assigned. The results of refinement are listed in Table 2, and the values of the constants obtained are shown in Table 3.

Discussion

In this experiment B_0, D_J, D_{Jk}, H_{Jk}, and H_{kJ} were determined for the ground state of CF_3CCD with high accuracy because they were determined for high J values, Table 3. In this table they are compared to parameters derived by Gordy et al.[4] The parameters H_{Jk} and H_{kJ} were determined in the ground state for the first time. H_{Jk} appears to be more important than H_{kJ} in analysis of high J rotational spectrum of this particular molecule, and it seems that the H_J parameter is important for this molecule only at very high J values. The H_J parameters in the ground state and η_k in $v_{10} = 1$ state were constrained to zero since their inclusion in the fit did not improve the sum of weighted squares of errors and resulted in a value not significantly different from zero. $A\zeta$ and η_J (which gives the J and k dependence of $A\zeta$) are necessary to reproduce the frequencies of the recorded transitions. Off diagonal parameters r_t and $q_t{}^+$ were determined together with high accuracy for this state for the first time. Other parameters are fairly similar to reported values,[8,9] except $A\zeta$. In this experiment, $A\zeta$ could not be determined with high accuracy from the available data.

For CF_3CCD, in the observed Fortrat-like diagram for $J = 12$ (Fig. 2), $|k - \ell| = (k\ell - 1)$ was plotted rather than k against ν which are the positive and negative $(k\ell - 1)$ series. This diagram shows the "ℓ" doublet and two different series $\ell = \pm 1$. So, the spectrum is more complex than the ground-state spectrum.

If B_v values of CF_3CCH, CF_3CCD, and CF_3CN[15–17] are plotted against vibrational quantum number v_t, roughly parallel lines are produced. Extrapolation of CF_3CCD line gives B_3

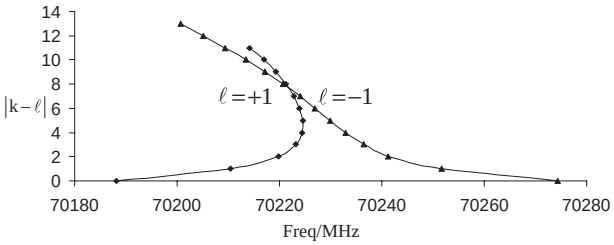

Fig. 2. Fortrat-like diagram of CF_3CCD in $v_{10} = 1$ state, $J = 12 \rightarrow 13$.

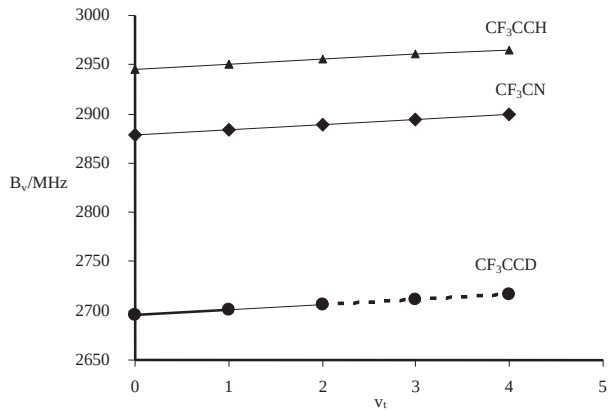

Fig. 3. Comparison of B value with vibrational quantum number for CF_3CCD, CF_3CCH, and CF_3CN.

and B_4 values of 2711.7 and 2716.8 MHz, respectively (Fig. 3). Finally the values of rotational parameters in these different vibrational states show that these levels are free of interactions with any other vibrations and act as isolated levels.

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