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New Investigation of Millimeter-Wave Rotational Spectrum of CCl_3CN in Ground, $\nu_7 = 1$ and $\nu_8 = 1$ States

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Abstract: The millimeter-wave rotational spectra of the ground and excited vibrational states $\nu_7 = 1$ and $\nu_8 = 1$ of the symmetric top molecule, CCl_3CN , have been analyzed again. The $B_0 = 1666.80894(13)$ MHz, $D_J = 0.135023(23)$ kHz, $D_{JK} = 0.60596(45)$ kHz, $H_J = -0.0192(10)$ mHz, $H_{JK} = 1.188(34)$ mHz and $H_{KJ} = -1.60(21)$ mHz have been determined for ground state. The $\ell = \pm 1$ series have been assigned and the rotational parameters including $B_7 = 1667.96659(25)$ MHz, $(q^+)_{7} = 1.58855(94)$ MHz for $\nu_7 = 1$ and $B_8 = 1667.08204(31)$ MHz, $(q^+)_{8} = 1.6141(36)$ MHz for $\nu_8 = 1$ states were determined accurately.

Keywords: Millimetre-wave rotational spectra, Excited vibrational state, Symmetric top molecules, CCl_3CN

Introduction

Trichloroacetonitrile, CCl_3CN is a symmetric top molecule and belong to the C_{3v} point group. This molecule has the same symmetry as that of CF_3CN . Selection rules show that there should be $4A_1$ and $4E$ vibrations, all of which should be active both in the infrared and the Raman spectra of CCl_3CN . Several authors have studied the rotational spectra of the ground state and some excited states¹⁻⁵. The lowest doubly degenerate vibrational level, $\nu_8 = 1$, is approximately a $-\text{C}-\text{C}\equiv\text{N}$ bending mode and lies⁶ at 157 cm^{-1} , and occurs at slightly lower wave number than the corresponding vibration⁷ in CF_3CN . The next highest frequency, ν_7 , is found at 268 cm^{-1} (CCl_3 rocking mode). It is still lower than the lowest A_1 fundamental, ν_4 , which is found⁶ at 318 cm^{-1} . There is no doubt about the assignment of the series of lines which lie to high frequency of the ground state rotational transitions. Owing to

the large dipole moment and the large thermal population, the spectra are intense. The aim of this work is study and determination of rotational parameters for the low and high J values in ground and $v_7=1$ and $v_8=1$ states, which are more accurate and reliable.

Ground State

For a non degenerate vibrational state of a prolate C_{3v} molecule, the diagonal part of the rotational Hamiltonian may be written as equation 1.

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

Taking into account the usual selection rule for symmetric top molecules: $\Delta J = \pm 1$ and $\Delta k = 0$, the frequencies are given by Eq (2).

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

In equation 1, the D_J , D_{Jk} , D_k are quartic, H_J , H_{Jk} , H_{kJ} , H_k are sextic centrifugal distortion terms respectively.

$v_7 = 1$ and $v_8 = 1$ 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 Nielsen⁸. Although the 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*⁹. The frequency of transition $J \rightarrow J+1$ for molecules belonging to the point group C_{3v} in singly 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

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

$A\zeta$ 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. q_t^+ is the ℓ -type doubling constant, B and A are rotational constants, and ζ is the z-coriolis constant for the vibrational state v_t . The degree of ℓ -resonance thus largely depends on the ratio of q_t^+ to the resonance denominator $(B-A+A\zeta)$. With low to moderate values of this denominator, the spectrum usually found consists of two extreme outer lines for $(k\ell-1) = 0$ (the ℓ -doublets) and a center group of lines for $(k\ell-1) \neq 0$ whose structure depends very strongly on other parameters such as the centrifugal distortion constants. As the strength of the resonance increase, the lines of the center group spread out until the low $|k\ell-1|$ transitions approach the positions of the ℓ -doublets. So for large q_t^+ and small $(B-A+A\zeta)$ value it is possible to observe direct ℓ -resonance transitions in the microwave range. This is a typical

pattern for C_{3v} doubly degenerate states and is predominantly due to the combinations of the splitting of the positive and negative (kℓ-1) series by ℓ- type resonance [which is inversely proportional to (kℓ-1)] and the shift to low frequency due to D_{JK} [which is proportional to (kℓ-1)²]. 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 (kℓ-1). Thus, one series goes from high frequency 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 Hψ = Eψ and diagonalise to obtain the energy¹⁰⁻¹⁶. The Hamiltonian was set up for a symmetric top molecule like CCl₃CN. This rotation-vibrational Hamiltonian has two different blocks that belong to the different ℓ = + 1 and ℓ = -1 series. k and ℓ are no longer good quantum numbers, but (k - ℓ) or (kℓ - 1) may be used to distinguish between the symmetry species. Those levels with (kℓ - 1) = 3n, where n is an integer, are of species A₁ or A₂. If (kℓ - 1) ≠ 3n the species are E. The q_t⁺ produces a first order splitting of the (kℓ - 1) = 0, A₁A₂ pair, which are the familiar ℓ-doublets, as shown by Grenier-Besson and Amat¹⁰. The main difference from the ground state spectra is the splitting of the |k - ℓ| = 0 into two widely separate ℓ-doublets and the splitting due to ℓ-resonance.

The diagonal matrix elements are given by:

$$\langle v_t, \ell_t, J, k | H/h | v_t, \ell_t, J, k \rangle = BJ(J+1) + (A - B)k^2 - 2A\zeta k\ell - D_J J^2(J+1)^2 - D_{JK} J(J+1)k^2 - D_K k^4 + \eta_J J(J+1)k\ell + \eta_K k^3\ell + H_J J^3(J+1)^3 + H_{JK} J^2(J+1)^2 k^2 + H_{KJ} J(J+1)k^4 + H_K k^6 \quad (5)$$

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

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

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

and hence, the lines can be assigned. The results of refinement of v₇ = 1 and v₈ = 1 states are listed in Tables 3 and 4 respectively. The values of the constants obtained are shown in Table 5.

Results and Discussion

The 255 different measurements of CCl₃CN for ground state were fitted to the Eq (2) by weighted least-squares method¹⁷ in which the weights were taken to be w = 1/(observed error)² = 1/(0.02)², where 0.02 in MHz is estimated uncertainty in an observation for each unblended line. Some of the lines have an observed error of 0.03 to 0.2 MHz to allow for overlapping or broadening. The results of refinement is listed in Table 1, and correlation coefficients of parameters are shown in Table 2. These Tables show that the frequencies of low and high values of CCl₃CN were fitted very well and correlation coefficients of parameters are reasonable. The structural parameters of this compound as shown in Table 5 were obtained with higher accuracy and compared with previous works.

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

If $|k|$ values are plotted against frequency for this state, the Fortrat diagram is produced which is shown in (Fig1). In this diagram the splitting increase as k increases and this is due to the D_{Jk} parameter. In other words the term $-2D_{Jk}(J + 1)k^2$ has the effect of separating the $(J + 1)$ components of each $(J + 1) - J$ transition. This diagram indicates the splitting $k = 3$ lines about 5 MHz for transition $J = 112 \rightarrow 113$.

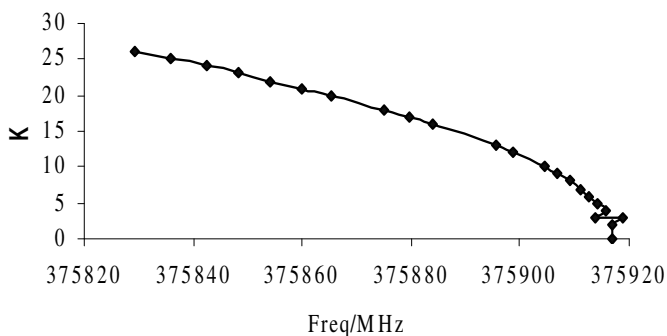


Figure 1. Fortrat diagram of CCl_3CN in ground state. $J = 112 \rightarrow 113$

The $K = 3$ lines of a C_{3v} symmetric top should be split because the rotational Hamiltonian has a nonvanishing off-diagonal matrix element $\langle k|H|k \pm 6 \rangle$. The sextic splitting constant h_3 is very small and normally is less than values of sextic parameters. Cazzoli¹⁸ and colleagues have found a strong correlation between h_3 and $B^4/(A - B)$, the result being (in MHz)

$$h_3 = 2.3 \times 10^{-21} \frac{B^4}{A - B} \tag{8}$$

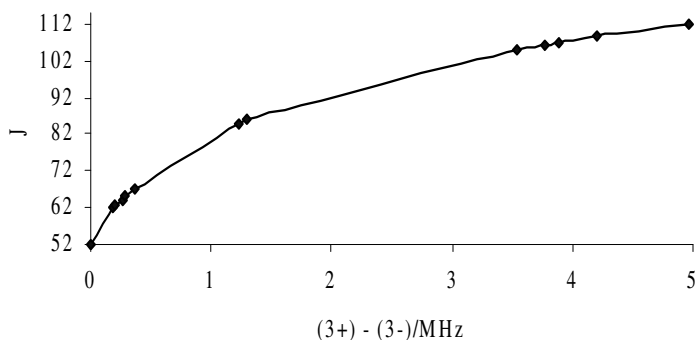


Figure 2. Variation of $K = 3$ splitting with J

This relation can predict known values of h_3 to better than 20%. If rotational parameters A and B are put in Eq (8), the $h_3 = 0.02714$ mHz is obtained for CCl_3CN . while this value has been determined 0.02209 (20) mHz⁴.

The $J = 28 \rightarrow 29$ transition exhibits the usual symmetric top pattern while for $J = 63 \rightarrow 64$

the splitting is well cleared. For $J = 85 \rightarrow 86$ the splitting becomes sufficiently large to result in a missing transition between $k = 2$ and $k = 4$, and for $J = 110 \rightarrow 111$ the higher frequency $k = 3$ component is shifted to high frequency from band origin (Fig 2). The value of D_{jk} for CCl₃CN is low and separations of the low- k lines do not exceed their half width very much. For this reason the close doublet seen for $J = 63 \rightarrow 64$ disappears with increasing J , as the $k = 3$ components move into the neighboring lines.

Table 1. Results of refinement of observed frequencies for CCl₃CN in ground state.

	J	K	Fobs/MHz	Fcal/MHz	O-C/MHz	Err in Obs/MHz
1.	8	0	30002.1200	30002.1670	-0.0470	0.2000
2.	9	0	33335.7400	33335.6384	0.1016	0.2000
3.	10	0	36669.0300	36669.0775	-0.0475	0.2000
4.	26	0	89996.9870	89997.0499	-0.0629	0.0200
5.	26	1	89996.9870	89997.0173	-0.0303	0.0200
6.	26	2	89996.9870	89996.9194	0.0676	0.0200
7.	26	3	89996.7440	89996.7563	-0.0123	0.0200
8.	26	4	89996.5130	89996.5279	-0.0149	0.0200
9.	26	5	89996.2200	89996.2342	-0.0142	0.0200
10.	26	6	89995.8610	89995.8752	-0.0142	0.0200
11.	26	7	89995.4370	89995.4509	-0.0139	0.0200
12.	28	0	96661.7250	96661.7433	-0.0183	0.0200
13.	28	1	96661.7250	96661.7083	0.0167	0.0200
14.	28	2	96661.6030	96661.6032	-0.0002	0.0200
15.	28	3	96661.4220	96661.4280	-0.0060	0.0200
16.	28	4	96661.1790	96661.1828	-0.0038	0.0200
17.	28	5	96660.8620	96660.8675	-0.0055	0.0200
18.	28	6	96660.4850	96660.4821	0.0029	0.0200
19.	28	7	96660.0210	96660.0266	-0.0056	0.0200
20.	28	8	96659.5090	96659.5010	0.0080	0.0200
21.	28	9	96658.9170	96658.9052	0.0118	0.0200
22.	31	0	106658.0690	106658.0700	-0.0010	0.0200
23.	31	1	106658.0690	106658.0314	0.0376	0.0200
24.	31	2	106657.9330	106657.9155	0.0175	0.0200
25.	31	3	106657.7380	106657.7224	0.0156	0.0200
26.	31	4	106657.4630	106657.4520	0.0110	0.0200
27.	31	5	106657.1240	106657.1043	0.0197	0.2000
28.	31	6	106656.6980	106656.6793	0.0187	0.0200
29.	31	7	106656.1970	106656.1771	0.0199	0.0200
30.	31	8	106655.6240	106655.5975	0.0265	0.0200
31.	31	9	106654.9610	106654.9406	0.0204	0.0200
32.	31	10	106654.2130	106654.2063	0.0067	0.0200
33.	31	11	106653.3720	106653.3947	-0.0227	0.0200
34.	41	0	139971.8810	139971.9211	-0.0401	0.0200
35.	41	1	139971.8810	139971.8705	0.0105	0.0200
36.	41	2	139971.7140	139971.7189	-0.0049	0.0200
37.	41	3	139971.4510	139971.4661	-0.0151	0.0200
38.	41	4	139971.1100	139971.1122	-0.0022	0.0200
39.	41	5	139970.6560	139970.6572	-0.0012	0.0200
40.	41	6	139970.1080	139970.1011	0.0069	0.0200
41.	41	7	139969.4570	139969.4438	0.0132	0.0200
42.	41	8	139968.6820	139968.6854	-0.0034	0.0200
43.	41	9	139967.8400	139967.8257	0.0143	0.0200
44.	41	10	139966.8830	139966.8648	0.0182	0.0200
45.	41	11	139965.8170	139965.8026	0.0144	0.0200
46.	41	12	139964.6590	139964.6392	0.0198	0.0200

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47.	41	13	139963.3910	139963.3744	0.0166	0.0200
48.	41	14	139962.0430	139962.0082	0.0348	0.0200
49.	41	15	139960.5850	139960.5407	0.0443	0.0300
50.	41	16	139958.9730	139958.9716	0.0014	0.0300
51.	41	17	139957.3060	139957.3011	0.0049	0.0300
52.	41	18	139955.5570	139955.5290	0.0280	0.0300
53.	52	0	176601.2370	176601.2918	-0.0548	0.0300
54.	52	1	176601.2370	176601.2283	0.0087	0.0300
55.	52	2	176601.0340	176601.0377	-0.0037	0.0300
56.	52	3	176600.6920	176600.7201	-0.0281	0.0300
57.	52	4	176600.2600	176600.2754	-0.0154	0.0300
58.	52	5	176599.6860	176599.7036	-0.0176	0.0300
59.	52	6	176598.9860	176599.0047	-0.0187	0.0300
60.	52	7	176598.1510	176598.1787	-0.0277	0.0300
61.	52	8	176597.1770	176597.2256	-0.0486	0.0300
62.	52	9	176596.1320	176596.1452	-0.0132	0.0300
63.	52	10	176594.9110	176594.9377	-0.0267	0.0300
64.	52	11	176593.6090	176593.6029	0.0061	0.0300
65.	52	12	176592.1310	176592.1408	-0.0098	0.0300
66.	52	13	176590.5150	176590.5513	-0.0363	0.0300
67.	52	14	176588.8380	176588.8345	0.0035	0.0300
68.	52	15	176586.9830	176586.9902	-0.0072	0.0300
69.	52	17	176582.9610	176582.9190	0.0420	0.0300
70.	52	18	176580.7010	176580.6920	0.0090	0.0300
71.	52	19	176578.3380	176578.3373	0.0007	0.0300
72.	52	20	176575.8480	176575.8547	-0.0067	0.0300
73.	52	21	176573.2340	176573.2443	-0.0103	0.0300
74.	52	22	176570.4980	176570.5060	-0.0080	0.0300
75.	52	23	176567.6510	176567.6396	0.0114	0.0300
76.	52	24	176564.6510	176564.6451	0.0059	0.0300
77.	52	25	176561.5190	176561.5224	-0.0034	0.0300
78.	52	26	176558.3160	176558.2713	0.0447	0.0300
79.	52	27	176554.9180	176554.8918	0.0262	0.0300
80.	52	28	176551.4400	176551.3837	0.0563	0.0300
81.	62	0	209882.7010	209882.7635	-0.0625	0.0300
82.	62	1	209882.7010	209882.6883	0.0127	0.0300
83.	62	2	209882.4890	209882.4628	0.0262	0.0300
84.	62	3	209882.1880	209882.0870	0.1010	0.0300
85.	62	3	209881.9970	209882.0870	-0.0900	0.0300
86.	62	4	209881.5680	209881.5608	0.0072	0.0300
87.	63	0	213209.7810	213209.8385	-0.0575	0.0300
88.	63	1	213209.7810	213209.7622	0.0188	0.0300
89.	63	2	213209.5430	213209.5333	0.0097	0.0300
90.	63	3	213209.2360	213209.1517	0.0843	0.0300
91.	63	3	213209.0290	213209.1517	-0.1227	0.0300
92.	63	4	213208.6060	213208.6174	-0.0114	0.0300
93.	63	5	213207.9160	213207.9305	-0.0145	0.0300
94.	63	6	213207.0680	213207.0909	-0.0229	0.0300
95.	63	7	213206.0940	213206.0985	-0.0045	0.0300
96.	64	0	216536.6440	216536.7055	-0.0615	0.0300
97.	64	1	216536.6440	216536.6281	0.0159	0.0300
98.	64	2	216536.3950	216536.3957	-0.0007	0.0300
99.	64	3	216536.1410	216536.0083	0.1327	0.0300
100.	64	3	216535.8780	216536.0083	-0.1303	0.0300
101.	64	4	216535.4680	216535.4660	0.0020	0.0300
102.	64	5	216534.7420	216534.7687	-0.0267	0.0300
103.	64	6	216533.9130	216533.9164	-0.0034	0.0300
104.	64	7	216532.9090	216532.9091	-0.0001	0.0300
105.	64	8	216531.6950	216531.7467	-0.0517	0.0300

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106.	64	9	216530.3990	216530.4292	-0.0302	0.0300
107.	64	10	216528.9580	216528.9565	0.0015	0.0300
108.	64	11	216527.3150	216527.3287	-0.0137	0.0300
109.	64	12	216525.5300	216525.5457	-0.0157	0.0300
110.	64	13	216523.6010	216523.6073	-0.0063	0.0300
111.	64	14	216521.5400	216521.5136	0.0264	0.0300
112.	64	15	216519.2280	216519.2644	-0.0364	0.0300
113.	64	16	216516.8360	216516.8597	-0.0237	0.0300
114.	64	17	216514.2790	216514.2995	-0.0205	0.0300
115.	64	18	216511.5750	216511.5836	-0.0086	0.0300
116.	64	19	216508.6660	216508.7119	-0.0459	0.0300
117.	64	20	216505.6860	216505.6844	0.0016	0.0300
118.	64	21	216502.5110	216502.5009	0.0101	0.0300
119.	64	22	216499.2150	216499.1614	0.0536	0.0300
120.	64	23	216495.6650	216495.6658	-0.0008	0.0300
121.	64	24	216491.9520	216492.0138	-0.0618	0.0300
122.	64	25	216488.1950	216488.2055	-0.0105	0.0300
123.	64	26	216484.2000	216484.2407	-0.0407	0.0300
124.	64	27	216480.0830	216480.1193	-0.0363	0.0300
125.	64	28	216475.8610	216475.8410	0.0200	0.0300
126.	64	29	216471.3670	216471.4059	-0.0389	0.0300
127.	64	30	216466.7820	216466.8137	-0.0317	0.0300
128.	64	31	216462.0120	216462.0643	-0.0523	0.0300
129.	64	32	216457.1180	216457.1576	-0.0396	0.0300
130.	64	33	216452.0860	216452.0933	-0.0073	0.0300
131.	64	34	216446.8930	216446.8714	0.0216	0.0300
132.	64	35	216441.4760	216441.4916	-0.0156	0.0300
133.	64	36	216435.9640	216435.9538	0.0102	0.0300
134.	64	37	216430.2760	216430.2578	0.0182	0.0300
135.	64	38	216424.4170	216424.4034	0.0136	0.0300
136.	64	39	216418.4260	216418.3905	0.0355	0.0300
137.	64	40	216412.2370	216412.2188	0.0182	0.0300
138.	64	41	216405.8630	216405.8881	-0.0251	0.0300
139.	65	0	219863.4170	219863.3613	0.0557	0.0300
140.	65	1	219863.3270	219863.2827	0.0443	0.0300
141.	65	2	219863.0760	219863.0468	0.0292	0.0300
142.	65	3	219862.8050	219862.6537	0.1513	0.0300
143.	65	3	219862.5190	219862.6537	-0.1347	0.0300
144.	65	4	219862.1070	219862.1033	0.0037	0.0300
145.	66	0	223189.7450	223189.8025	-0.0575	0.0300
146.	66	1	223189.7450	223189.7228	0.0222	0.0300
147.	66	4	223188.5280	223188.5262	0.0018	0.0300
148.	66	5	223187.8200	223187.8082	0.0118	0.0300
149.	66	6	223186.9420	223186.9306	0.0114	0.0300
150.	66	7	223185.8730	223185.8933	-0.0203	0.0300
151.	66	8	223184.7080	223184.6964	0.0116	0.0300
152.	66	9	223183.3760	223183.3399	0.0361	0.0300
153.	66	10	223181.8250	223181.8235	0.0015	0.0300
154.	67	0	226515.9620	226516.0259	-0.0639	0.0300
155.	67	1	226515.9620	226515.9450	0.0170	0.0300
156.	67	2	226515.7370	226515.7023	0.0347	0.0300
157.	67	3	226515.5070	226515.2977	0.2093	0.0300
158.	67	3	226515.1350	226515.2977	-0.1627	0.0300
159.	67	4	226514.7270	226514.7312	-0.0042	0.0300
160.	67	5	226514.0190	226514.0029	0.0161	0.0300
161.	85	0	286347.0170	286347.0661	-0.0491	0.0500
162.	85	1	286347.0170	286346.9649	0.0521	0.0500
163.	85	3	286346.7850	286346.1553	0.6297	0.2000
164.	85	3	286345.5630	286346.1553	-0.5923	0.2000

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165.	85	2	286346.6530	286346.6613	-0.0083	0.2000
166.	85	4	286345.5630	286345.4468	0.1162	0.0500
167.	85	5	286344.5730	286344.5359	0.0371	0.0500
168.	85	6	286343.4520	286343.4226	0.0294	0.0500
169.	85	7	286342.1080	286342.1067	0.0013	0.0500
170.	85	8	286340.6250	286340.5882	0.0368	0.0500
171.	86	0	289668.4760	289668.5282	-0.0522	0.2000
172.	86	1	289668.4760	289668.4259	0.0501	0.2000
173.	86	3	289668.2750	289667.6074	0.6676	0.2000
174.	86	3	289666.9810	289667.6074	-0.6264	0.2000
175.	86	2	289668.1090	289668.1190	-0.0100	0.0500
176.	86	4	289666.9810	289666.8913	0.0897	0.0500
177.	86	5	289665.9880	289665.9704	0.0176	0.0500
178.	86	6	289664.8750	289664.8449	0.0301	0.0500
179.	86	7	289663.5280	289663.5146	0.0134	0.0300
180.	86	8	289662.0340	289661.9796	0.0544	0.0500
181.	105	3	352719.3590	352717.5853	1.7737	0.2000
182.	105	3	352715.8140	352717.5853	-1.7713	0.2000
183.	105	0	352718.4050	352718.6905	-0.2855	0.0500
184.	105	1	352718.4050	352718.5677	-0.1627	0.0500
185.	105	2	352718.4050	352718.1993	0.2057	0.0500
186.	105	4	352716.9220	352716.7257	0.1963	0.0500
187.	105	5	352715.7060	352715.6204	0.0856	0.0500
188.	105	6	352714.3990	352714.2694	0.1296	0.0500
189.	105	7	352712.7220	352712.6727	0.0493	0.0500
190.	105	8	352710.8950	352710.8301	0.0649	0.0500
191.	106	3	356034.6520	356032.7416	1.9104	0.0500
192.	106	3	356030.8830	356032.7416	-1.8586	0.0500
193.	106	0	356033.4870	356033.8562	-0.3692	0.0500
194.	106	1	356033.4870	356033.7324	-0.2454	0.0500
195.	106	2	356033.4870	356033.3608	0.1262	0.0500
196.	106	4	356032.0890	356031.8746	0.2144	0.0500
197.	106	5	356030.9070	356030.7599	0.1471	0.0500
198.	106	6	356029.4600	356029.3973	0.0627	0.0500
199.	106	7	356027.8190	356027.7869	0.0321	0.2000
200.	107	3	359349.4790	359347.5483	1.9307	0.0500
201.	107	3	359345.5990	359347.5483	-1.9493	0.0500
202.	107	0	359348.2920	359348.6724	-0.3804	0.0500
203.	107	1	359348.2920	359348.5475	-0.2555	0.0500
204.	107	2	359348.2920	359348.1728	0.1192	0.0500
205.	107	4	359346.8590	359346.6740	0.1850	0.0500
206.	107	5	359345.6520	359345.5498	0.1022	0.0500
207.	107	6	359344.3000	359344.1757	0.1243	0.0500
208.	107	7	359342.6480	359342.5518	0.0962	0.0500
209.	107	8	359340.7700	359340.6778	0.0922	0.0500
210.	107	9	359338.5760	359338.5537	0.0223	0.0500
211.	107	10	359336.1830	359336.1796	0.0034	0.0500
212.	107	11	359333.6100	359333.5552	0.0548	0.0500
213.	107	12	359330.7660	359330.6805	0.0855	0.0500
214.	107	13	359327.5300	359327.5555	-0.0255	0.0500
215.	107	14	359324.2120	359324.1799	0.0321	0.0500
216.	107	16	359316.7010	359316.6769	0.0241	0.0500
217.	107	17	359312.5760	359312.5491	0.0269	0.0500
218.	107	18	359308.1690	359308.1704	-0.0014	0.0500
219.	109	3	365978.1640	365976.0998	2.0642	0.0500
220.	109	3	365973.9590	365976.0998	-2.1408	0.0500
221.	109	0	365976.7810	365977.2426	-0.4616	0.0500
222.	109	1	365976.7810	365977.1156	-0.3346	0.0500
223.	109	2	365976.7810	365976.7347	0.0463	0.0500

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224.	109	4	365975.4560	365975.2109	0.2451	0.0500
225.	109	5	365974.1450	365974.0679	0.0771	0.0500
226.	109	6	365972.7390	365972.6709	0.0681	0.0500
227.	109	7	365971.0650	365971.0198	0.0452	0.0500
228.	109	8	365969.1120	365969.1146	-0.0026	0.0500
229.	109	9	365966.9680	365966.9551	0.0129	0.0500
230.	109	10	365964.5850	365964.5413	0.0437	0.0500
231.	109	11	365961.8730	365961.8731	-0.0001	0.0500
232.	109	13	365955.7890	365955.7732	0.0158	0.0500
233.	109	14	365952.4060	365952.3413	0.0647	0.0500
234.	109	16	365944.7440	365944.7130	0.0310	0.0500
235.	109	17	365940.4890	365940.5164	-0.0274	0.0500
236.	109	19	365931.2490	365931.3574	-0.1084	0.0500
237.	109	20	365926.3540	365926.3948	-0.0408	0.0500
238.	110	3	369292.0530	369289.8379	2.2151	0.2000
239.	110	3	369287.5960	369289.8379	-2.2419	0.2000
240.	110	0	369290.6060	369290.9900	-0.3840	0.0500
241.	110	1	369290.6060	369290.8620	-0.2560	0.0500
242.	110	2	369290.6060	369290.4780	0.1280	0.0500
243.	110	4	369289.1690	369288.9417	0.2273	0.0500
244.	110	5	369287.8820	369287.7894	0.0926	0.0500
245.	110	6	369286.4500	369286.3810	0.0690	0.0500
246.	110	7	369284.8220	369284.7164	0.1056	0.0500
247.	110	8	369282.7720	369282.7956	-0.0236	0.0500
248.	110	9	369280.6470	369280.6185	0.0285	0.0500
249.	110	10	369278.1400	369278.1849	-0.0449	0.0500
250.	110	11	369275.4680	369275.4950	-0.0270	0.0500
251.	110	12	369272.6120	369272.5484	0.0636	0.0500
252.	110	13	369269.3380	369269.3452	-0.0072	0.0500
253.	110	14	369265.8870	369265.8853	0.0017	0.0500
254.	110	15	369262.1050	369262.1685	-0.0635	0.0500
255.	110	16	369258.1400	369258.1947	-0.0547	0.0500

Σ = 0.416454 255 Transitions in fit
 $\Sigma.w$ = 6.593633 249 Degrees of freedom

Table 2. Correlation coefficients

	B	DJ	DJK	HJ	HJK	HKJ
B	1.0000					
DJ	0.9000	1.0000				
DJK	0.2383	-0.0041	1.0000			
HJ	0.8162	0.9777	-0.1154	1.0000		
HJK	0.1513	-0.0025	0.7893	-0.1345	1.0000	
HKJ	0.2248	0.0593	0.7367	0.0284	0.2244	1.0000

For the $v_7 = 1$ state the important parameters in determining form of the spectrum are the ℓ -type doubling constant q_7^+ and the value of A_{ζ_7} . As Table 5 shows, the B_7 is slightly larger than the B_8 value and this means that the spectrum lies amongst the transitions due to $v_8 = 2$. The parameter η_J , which is to be regarded as a type of centrifugal distortion constant, has a negative value. As can be seen from Eq (3) this results in the positive series being displaced to lower frequency and the negative series to higher frequency (Fig 4).

In this work, all of the frequencies selected from Ref (4) and refined them by least square method¹². If all the sextic constants were included in the fit, these were not only strongly correlated but also had standard deviations which were of about the same absolute magnitudes as the quantities themselves. This means that actual values are not significant, hence H_{KJ} was set to zero. In this case H_{JK} and H_J were determined with reasonable standard deviations. The results of fitting are given in Table 3 and obtained results are shown in Table 5.

For $v_8 = 1$ state a least-squares refinement of the 172 observations was carried out using the programme¹⁷. The results of fitting are given in Table 4 and obtained results are shown in Table 5. For this state the sextic parameters are not determinable by this data. The Fortrat-like diagram in this state is shown in (Fig 4). This diagram shows that the ' ℓ ' doublet splitting is smaller than this term in the $v_7 = 1$ state (Fig 3). η_J can be determined precisely from the mm-wave spectrum, while η_K is not determined. In this molecule, the term $(A - B - A\zeta) = 854$ MHz and -1269 MHz for $v_8 = 1$ and $v_7 = 1$ states respectively, so the l-resonance is observable and $A\zeta$ can be determined from mm-wave spectrum which has positive and negative values for these two states (Table 5). ζ_{JJ} parameter was obtained with negative value for $v_7 = 1$ and with positive value for $v_8 = 1$ states but this parameter has different signs in these two states⁵.

Table 3. Results of refinement of observed frequencies for CCl_3CN in $v_7 = 1$ state

	J	Kl-l	K	l	sym	Fobs/MHz	O-C/MHz	Err in Obs/MHz
1.	20	5	6,	1	E	70049.3390	0.0068	0.0500
2.	20	4	5,	1	E	70050.0330	0.1518	0.0500
3.	20	3	4,	1	A+	70050.5630	0.0297	0.0500
4.	20	2	3,	1	E	70051.5380	0.0218	0.0500
5.	21	5	6,	1	E	73384.5540	-0.0408	0.0500
6.	21	4	5,	1	E	73385.1780	-0.0155	0.0500
7.	21	3	4,	1	A+	73385.8740	-0.0415	0.0500
8.	21	2	3,	1	E	73386.9900	-0.0324	0.0500
9.	21	0	1,	1	A+	73419.6150	0.0028	0.0500
10.	22	6	7,	1	A+	76719.2050	0.0117	0.1000
11.	22	5	6,	1	E	76719.7900	-0.0089	0.0500
12.	22	4	5,	1	E	76720.4290	-0.0214	0.0500
13.	22	3	4,	1	A+	76721.2170	-0.0308	0.0500
14.	22	2	3,	1	E	76722.4570	-0.0320	0.0500
15.	26	2	3,	1	E	90063.9130	-0.0083	0.0500
16.	26	3	4,	1	A+	90062.0330	0.0024	0.0500
17.	26	4	5,	1	E	90060.8670	-0.0070	0.0500
18.	26	5	6,	1	E	90059.9630	-0.0129	0.0500
19.	26	6	7,	1	A+	90059.1040	-0.0718	0.0500
20.	26	7	8,	1	E	90058.4300	0.0255	0.0500
21.	26	8	9,	1	E	90057.6730	0.0458	0.0500
22.	26	12	13,	1	A+	90054.2650	0.0959	0.0500
23.	26	13	14,	1	E	90053.1110	-0.0729	0.0500
24.	26	15	16,	1	A+	90050.9580	-0.0887	0.0500
25.	26	16	17,	1	E	90049.7860	-0.1056	0.0500
26.	26	17	18,	1	E	90048.5890	-0.0883	0.0500
27.	26	-15	14,-1	A+	90053.5360	0.0906	0.0500	
28.	26	-14	13,-1	E	90054.2650	0.0625	0.0500	
29.	26	-13	12,-1	E	90054.9290	0.0405	0.0500	
30.	26	-4	3,-1	E	90056.9210	-0.0592	0.0500	
31.	26	-3	2,-1	A+	90056.2740	0.0029	0.0500	
32.	26	-2	1,-1	E	90054.6690	-0.0310	0.0500	
33.	-26	0	-1,-1	A-	90016.5850	-0.0086	0.0500	
34.	28	2	3,	1	E	96734.3320	-0.0168	0.0500
35.	28	3	4,	1	A+	96732.0360	-0.0256	0.0500
36.	28	4	5,	1	E	96730.6600	-0.0279	0.0500
37.	28	5	6,	1	E	96729.6180	-0.0255	0.0500

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38.	28	6	7,	1	A+	96728.6850	-0.0456	0.0500
39.	28	7	8,	1	E	96727.8600	-0.0038	0.0500
40.	28	8	9,	1	E	96727.0210	0.0210	0.0500
41.	28	9	10,	1	A+	96726.1170	0.0015	0.0500
42.	28	10	11,	1	E	96725.2440	0.0480	0.0500
43.	28	11	12,	1	E	96724.3350	0.1029	0.0500
44.	28	12	13,	1	A+	96723.2780	0.0600	0.0500
45.	36	5	6,	1	E	123405.0000	-0.0070	0.0500
46.	36	6	7,	1	A+	123403.5130	-0.0106	0.0500
47.	36	7	8,	1	E	123402.2250	0.0366	0.0500
48.	36	8	9,	1	E	123400.9130	-0.0007	0.0500
49.	36	-3	2,-	1	A+	123393.7250	-0.0409	0.0500
50.	41	2	3,	1	E	140086.0840	0.0576	0.0500
51.	41	3	4,	1	A+	140079.9420	0.0276	0.0500
52.	41	4	5,	1	E	140076.4560	0.0332	0.0500
53.	41	5	6,	1	E	140073.9970	0.0137	0.0500
54.	41	6	7,	1	A+	140072.0590	0.0250	0.0500
55.	41	7	8,	1	E	140070.3940	0.0676	0.0500
56.	41	8	9,	1	E	140068.6950	-0.0391	0.0500
57.	41	9	10,	1	A+	140067.1420	-0.0443	0.0500
58.	41	10	11,	1	E	140065.6070	-0.0330	0.0500
59.	41	11	12,	1	E	140063.9950	-0.0730	0.0500
60.	41	15	16,	1	A+	140057.3020	0.0731	0.0500
61.	41	-13	12,-	1	E	140060.1270	-0.0852	0.0500
62.	41	-6	5,-	1	A+	140062.1560	-0.0190	0.0500
63.	41	-5	4,-	1	E	140061.2800	-0.0389	0.0500
64.	41	-4	3,-	1	E	140059.7590	-0.0148	0.0500
65.	41	-3	2,-	1	A+	140056.9700	-0.0078	0.0500
66.	41	-2	1,-	1	E	140051.3840	0.0212	0.0500
67.	-41	0	-1,-	1	A-	140002.4160	0.0686	0.0500
68.	52	3	4,	1	A+	176745.8810	-0.0290	0.0500
69.	52	4	5,	1	E	176739.6930	0.0620	0.0500
70.	52	5	6,	1	E	176735.4320	0.1005	0.0500
71.	52	6	7,	1	A+	176732.0400	0.0170	0.0500
72.	52	7	8,	1	E	176729.2740	0.0271	0.0500
73.	52	8	9,	1	E	176726.8070	0.0428	0.0500
74.	52	9	10,	1	A+	176724.4760	0.0375	0.0500
75.	52	10	11,	1	E	176722.1910	0.0044	0.0500
76.	52	11	12,	1	E	176719.9580	0.0028	0.0500
77.	52	12	13,	1	A+	176717.6810	-0.0271	0.0500
78.	52	14	15,	1	E	176713.1520	0.0780	0.0500
79.	52	-16	15,-	1	E	176707.0450	0.0581	0.0500
80.	52	-14	13,-	1	E	176709.5670	-0.0208	0.0500
81.	52	-12	11,-	1	A+	176711.4300	-0.0403	0.0500
82.	52	-10	9,-	1	E	176712.5080	0.0021	0.0500
83.	52	-9	8,-	1	A+	176712.5080	-0.1271	0.0500
84.	52	-8	7,-	1	E	176712.5080	0.0682	0.0500
85.	52	-7	6,-	1	E	176711.8570	0.0201	0.0500
86.	52	-5	4,-	1	E	176708.7900	0.0301	0.0500
87.	52	-4	3,-	1	E	176705.5680	-0.0203	0.0500
88.	52	-3	2,-	1	A+	176700.1490	-0.0376	0.0500
89.	-52	0	-1,-	1	A-	176639.7510	-0.0162	0.0500
90.	64	4	5,	1	E	216716.3560	-0.1746	0.0500
91.	64	5	6,	1	E	216709.4070	-0.1305	0.0500
92.	64	6	7,	1	A+	216704.2430	0.0272	0.0500
93.	64	7	8,	1	E	216699.9380	0.0814	0.0500

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94.	64	10	11, 1	E	216689.4550	0.0717	0.0500
95.	64	11	12, 1	E	216686.1210	-0.1263	0.0500
96.	64	-11	10,-1	E	216668.6870	0.0451	0.0500
97.	64	-10	9,-1	E	216668.6870	-0.0434	0.0500
98.	64	-6	5,-1	A+	216663.7510	0.0263	0.0500
99.	64	-5	4,-1	E	216660.0010	-0.0910	0.0500
100.	64	-4	3,-1	E	216654.4660	-0.0148	0.0500
101.	64	-3	2,-1	A+	216645.5440	0.0411	0.0500
102.	64	-2	1,-1	E	216630.3880	0.0495	0.0500
103.	74	0	1, 1	A+	250084.6470	0.0279	0.0500
104.	74	1	2, 1	E	250068.9610	0.0103	0.0500
105.	74	2	3, 1	E	250043.6420	-0.0161	0.0500
106.	74	3	4, 1	A+	250024.5240	-0.0190	0.0500
107.	74	4	5, 1	E	250011.3620	0.0472	0.0500
108.	74	6	7, 1	A+	249994.4470	0.0239	0.0500
109.	74	8	9, 1	E	249983.2750	-0.0242	0.0500
110.	74	9	10, 1	A+	249978.7050	0.0045	0.0500
111.	74	10	11, 1	E	249974.4360	-0.0054	0.0500
112.	74	14	15, 1	E	249958.7640	0.0772	0.0500
113.	74	15	16, 1	A+	249954.7170	-0.0574	0.0500
114.	74	16	17, 1	E	249950.8580	0.0537	0.0500
115.	74	17	18, 1	E	249946.7450	-0.0108	0.0500
116.	74	18	19, 1	A+	249942.5740	-0.0388	0.0500
117.	74	20	21, 1	E	249934.0050	0.0099	0.0500
118.	74	21	22, 1	A+	249929.5260	0.0245	0.0500
119.	74	22	23, 1	E	249924.9270	0.0517	0.0500
120.	74	23	24, 1	E	249920.0200	-0.0906	0.0500
121.	74	-3	2,-1	A+	249906.7320	-0.0611	0.0500
122.	74	-4	3,-1	E	249918.8280	0.0457	0.0500
123.	74	-5	4,-1	E	249926.7790	0.0389	0.0500
124.	74	-6	5,-1	A+	249932.1000	-0.0341	0.0500
125.	74	-18	17,-1	A+	249932.9960	0.0266	0.0500
126.	74	-19	18,-1	E	249930.6350	-0.0357	0.0500
127.	74	-21	20,-1	A+	249925.3810	0.0088	0.0500
128.	74	-22	21,-1	E	249922.4050	0.0174	0.0500

Σ = .054806

128 Transitions in fit

$\Sigma.w$ = 1.095954

118 Degrees of freedom

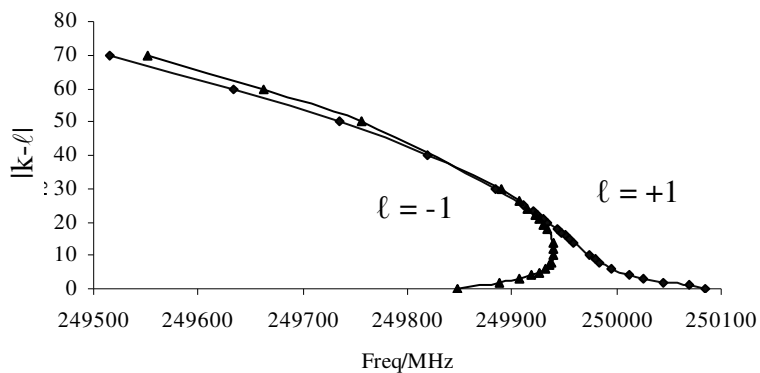


Figure 3. Fortrat diagram of CCl_3CN in $\nu_7=1$ state. $J = 74$

Table 4. Results of refinement of observed frequencies for CCl₃CN in $v_8 = 1$ state.

	J	Kl -1	K l	sym	Fobs/MHz	O-C/MHz	Err in Obs/MHz
1.	-20	0	-1, -1	A-	69978.7020	0.0423	0.1000
2.	20	3	4, 1	A+	70010.1590	-0.0021	0.0500
3.	20	-9	8, -1	A+	70010.6270	0.0717	0.0500
4.	20	-8	7, -1	E	70011.2510	0.0981	0.1000
5.	20	-6	5, -1	A+	70012.3200	0.0228	0.1000
6.	20	-5	4, -1	E	70012.9500	0.0671	0.1000
7.	20	-4	3, -1	E	70013.6250	0.0892	0.1000
8.	20	-3	2, -1	A+	70014.4500	0.0781	0.1000
9.	20	-2	1, -1	E	70015.7360	0.0004	0.1000
10.	20	0	1, 1	A+	70046.3830	0.0642	0.1000
11.	21	2	3, 1	E	73341.9900	0.0468	0.0500
12.	21	-9	8, -1	A+	73344.0600	0.1021	0.0500
13.	21	-8	7, -1	E	73344.6900	0.0961	0.0500
14.	21	-7	6, -1	E	73345.1550	-0.0552	0.0500
15.	21	-6	5, -1	A+	73345.8380	0.0153	0.0500
16.	21	-5	4, -1	E	73346.4600	-0.0001	0.0500
17.	21	-4	3, -1	E	73347.2100	0.0302	0.0500
18.	21	-3	2, -1	A+	73348.1250	0.0103	0.0500
19.	21	-2	1, -1	E	73349.6630	0.0042	0.0500
20.	21	0	1, 1	A+	73381.3260	-0.0166	0.0500
21.	22	2	3, 1	E	76674.7840	0.0621	0.0500
22.	22	3	4, 1	A+	76676.2810	0.0905	0.1000
23.	22	-8	7, -1	E	76677.9740	-0.0019	0.1000
24.	22	-7	6, -1	E	76678.6910	0.0567	0.1000
25.	22	-6	5, -1	A+	76679.3470	0.0537	0.1000
26.	22	-5	4, -1	E	76680.0020	0.0163	0.0500
27.	22	-4	3, -1	E	76680.8290	0.0520	0.1000
28.	22	-3	2, -1	A+	76681.8580	0.0394	0.0500
29.	22	-2	1, -1	E	76683.5900	0.0317	0.0500
30.	22	-1	0, 1	E	76688.1610	0.0478	0.0500
31.	22	0	1, 1	A+	76716.2950	0.0006	0.1000
32.	33	2	3, 1	E	113326.0920	0.0257	0.1000
33.	33	3	4, 1	A+	113330.6400	0.0310	0.1000
34.	33	4	5, 1	E	113332.8360	-0.0198	0.1000
35.	33	-11	10, -1	E	113336.7480	-0.0694	0.0500
36.	33	-10	9, -1	E	113338.0560	-0.0031	0.0500
37.	33	-9	8, -1	A+	113339.2800	-0.0005	0.0500
38.	33	-8	7, -1	E	113340.4680	-0.0358	0.0500
39.	33	-7	6, -1	E	113341.7640	0.0001	0.0500
40.	33	-6	5, -1	A+	113343.1200	0.0016	0.0500
41.	33	-5	4, -1	E	113344.6800	0.0099	0.0500
42.	33	-4	3, -1	E	113346.5640	-0.0571	0.0500
43.	33	-3	2, -1	A+	113349.4320	0.0031	0.0500
44.	33	-2	1, -1	E	113354.4000	0.0277	0.0500
45.	34	2	3, 1	E	116657.1120	0.0525	0.0500
46.	34	3	4, 1	A+	116661.9720	-0.0015	0.0500
47.	34	4	5, 1	E	116664.3600	-0.0618	0.0500
48.	34	5	6, 1	E	116665.7520	-0.0211	0.0500
49.	34	6	7, 1	A+	116666.5080	-0.0133	0.0500
50.	34	7	8, 1	E	116666.8920	0.0066	0.1000
51.	34	8	9, 1	E	116666.8920	-0.0851	0.1000
52.	34	-12	11, -1	A+	116667.6600	-0.1203	0.0500
53.	34	-11	10, -1	E	116669.1600	0.0513	0.1000

Contd...

54.	34	-10	9,-1	E	116670.3720	-0.0316	0.0500
55.	34	-9	8,-1	A+	116671.6680	-0.0131	0.0500
56.	34	-8	7,-1	E	116672.9640	-0.0016	0.0500
57.	34	-7	6,-1	E	116674.2720	-0.0228	0.0500
58.	34	-6	5,-1	A+	116675.6880	-0.0435	0.0500
59.	34	-5	4,-1	E	116677.3680	-0.0192	0.0500
60.	34	-4	3,-1	E	116679.4800	-0.0010	0.0500
61.	34	-3	2,-1	A+	116682.5160	0.0092	0.0500
62.	34	-2	1,-1	E	116687.8320	-0.0013	0.0500
63.	35	2	3, 1	E	119987.8880	0.0087	0.0500
64.	35	3	4, 1	A+	119993.1630	-0.0146	0.0500
65.	35	4	5, 1	E	119995.8130	-0.0240	0.0500
66.	35	5	6, 1	E	119997.2500	-0.0665	0.0500
67.	35	-11	10,-1	E	120001.3130	0.0126	0.1000
68.	35	-10	9,-1	E	120002.6880	0.0382	0.0500
69.	35	-9	8,-1	A+	120003.9630	-0.0222	0.0500
70.	35	-8	7,-1	E	120005.3500	0.0171	0.0500
71.	35	-7	6,-1	E	120006.7880	0.0541	0.0500
72.	35	-6	5,-1	A+	120008.2880	0.0317	0.0500
73.	35	-5	4,-1	E	120010.0640	0.0432	0.0500
74.	35	-4	3,-1	E	120012.2750	0.0109	0.0500
75.	35	-3	2,-1	A+	120015.5880	0.0705	0.0500
76.	35	-2	1,-1	E	120021.3250	0.0849	0.0500
77.	35	-1	0, 1	E	120034.7700	-0.0252	0.0500
78.	36	2	3, 1	E	123318.5600	0.0372	0.0500
79.	36	3	4, 1	A+	123324.2300	0.0125	0.0500
80.	36	4	5, 1	E	123327.1300	0.0326	0.0500
81.	36	6	7, 1	A+	123329.5900	-0.0405	0.0500
82.	36	8	9, 1	E	123330.2100	-0.0657	0.0500
83.	36	9	10, 1	A+	123330.2100	0.0038	0.0500
84.	36	11	12, 1	E	123329.5900	0.0720	0.0500
85.	36	-1	0, 1	E	123368.8400	-0.0334	0.0500
86.	36	-2	1,-1	E	123354.5800	-0.0090	0.0500
87.	36	-3	2,-1	A+	123348.4800	0.0218	0.0500
88.	36	-4	3,-1	E	123344.9400	-0.0278	0.0500
89.	36	-5	4,-1	E	123342.5900	0.0216	0.0500
90.	36	-6	5,-1	A+	123340.6900	-0.0003	0.0500
91.	36	-7	6,-1	E	123339.0600	-0.0187	0.0500
92.	36	-8	7,-1	E	123337.6000	-0.0031	0.0500
93.	36	-9	8,-1	A+	123336.1900	0.0000	0.0500
94.	36	-10	9,-1	E	123334.7900	-0.0050	0.0500
95.	36	-11	10,-1	E	123333.3900	0.0004	0.0500
96.	36	-12	11,-1	A+	123331.9800	0.0254	0.0500
97.	-36	0	-1,-1	A-	123277.2500	0.0300	0.1000
98.	41	-2	1,-1	E	140020.3420	0.0171	0.0500
99.	41	-3	2,-1	A+	140012.0600	0.0459	0.0500
100.	41	-4	3,-1	E	140007.2320	0.0286	0.0500
101.	41	-5	4,-1	E	140003.9750	0.0511	0.0500
102.	41	-6	5,-1	A+	140001.4700	0.0650	0.0500
103.	41	-7	6,-1	E	139999.3130	0.0210	0.0500
104.	41	-8	7,-1	E	139997.4270	0.0262	0.0500
105.	41	-9	8,-1	A+	139995.6490	0.0223	0.0500
106.	41	-10	9,-1	E	139993.9120	0.0060	0.0500
107.	41	-11	10,-1	E	139992.2240	0.0264	0.0500
108.	41	-12	11,-1	A+	139990.4300	-0.0440	0.0500
109.	41	-13	12,-1	E	139988.7340	0.0179	0.0500

Contd...

110.	41	-14	13,-1	E	139986.8530	-0.0571	0.0500
111.	41	-16	15,-1	E	139982.9900	-0.1259	0.0500
112.	41	13	14, 1	E	139984.3270	0.0438	0.0500
113.	41	11	12, 1	E	139985.5630	0.0092	0.1000
114.	41	7	8, 1	E	139985.5630	-0.0246	0.1000
115.	41	5	6, 1	E	139983.3570	0.0253	0.0500
116.	41	4	5, 1	E	139981.0060	0.0627	0.0500
117.	41	3	4, 1	A+	139976.8580	0.0325	0.0500
118.	52	-2	1,-1	E	176676.5320	-0.0554	0.0500
119.	52	-3	2,-1	A+	176663.4170	-0.0202	0.0500
120.	52	-4	3,-1	E	176655.1130	-0.0447	0.0500
121.	52	-5	4,-1	E	176649.3900	-0.0279	0.0500
122.	52	-6	5,-1	A+	176645.0670	-0.0004	0.0500
123.	52	-7	6,-1	E	176641.5350	0.0167	0.0500
124.	52	-8	7,-1	E	176638.4480	0.0009	0.0500
125.	52	-9	8,-1	A+	176635.6700	0.0065	0.0500
126.	52	-10	9,-1	E	176633.0330	-0.0159	0.0500
127.	52	-11	10,-1	E	176630.5870	0.0612	0.0500
128.	52	-12	11,-1	A+	176628.0110	-0.0307	0.0500
129.	52	-13	12,-1	E	176625.5300	-0.0296	0.0500
130.	52	-14	13,-1	E	176623.0190	-0.0338	0.0500
131.	52	-15	14,-1	A+	176620.4770	-0.0248	0.0500
132.	52	-16	15,-1	E	176617.8700	-0.0214	0.0500
133.	52	-17	16,-1	E	176615.2710	0.0605	0.0500
134.	52	-19	18,-1	E	176609.5170	-0.0856	0.0500
135.	52	-20	19,-1	E	176606.5020	-0.1610	0.0500
136.	52	19	20, 1	E	176605.6930	0.0516	0.0500
137.	52	18	19, 1	A+	176607.2530	-0.1636	0.0500
138.	52	16	17, 1	E	176610.1700	-0.3004	0.0500
139.	52	15	16, 1	A+	176611.6280	-0.1049	0.0500
140.	52	13	14, 1	E	176613.8610	0.1898	0.0500
141.	52	11	12, 1	E	176614.6270	-0.0747	0.0500
142.	52	10	11, 1	E	176614.7520	-0.0501	0.0500
143.	52	9	10, 1	A+	176614.6270	0.0658	0.0500
144.	52	8	9, 1	E	176613.8610	-0.0404	0.0500
145.	52	6	7, 1	A+	176610.7460	-0.0332	0.0500
146.	52	5	6, 1	E	176607.8470	0.0440	0.0500
147.	52	4	5, 1	E	176603.1390	-0.0485	0.0500
148.	64	-2	1,-1	E	216644.7590	-0.0981	0.0500
149.	64	-3	2,-1	A+	216628.2520	-0.0791	0.0500
150.	64	-4	3,-1	E	216616.2840	-0.0505	0.0500
151.	64	-7	6,-1	E	216594.9900	-0.0645	0.0500
152.	64	-8	7,-1	E	216590.3160	0.0241	0.0500
153.	64	-9	8,-1	A+	216586.0720	0.0106	0.0500
154.	64	-10	9,-1	E	216582.1960	0.0192	0.0500
155.	64	-11	10,-1	E	216578.5720	0.0599	0.0500
156.	64	-12	11,-1	A+	216574.9740	-0.0061	0.0500
157.	64	-13	12,-1	E	216571.4380	-0.0802	0.0500
158.	64	-14	13,-1	E	216568.0600	-0.0207	0.0500
159.	64	-15	14,-1	A+	216564.7280	0.0944	0.0500
160.	64	-16	15,-1	E	216561.2400	0.0892	0.0500
161.	64	-17	16,-1	E	216557.8470	0.2348	0.0500
162.	64	-18	17,-1	A+	216553.9770	-0.0249	0.0500
163.	64	-19	18,-1	E	216550.3600	0.0525	0.0500
164.	64	12	13, 1	A+	216547.3430	0.3277	0.0500
165.	64	11	12, 1	E	216547.3430	0.3358	0.0500

Contd...

166.	64	10	11,	1	E	216546.6520	0.0919	0.0500
167.	64	9	10,	1	A+	216545.6130	0.0264	0.0500
168.	64	8	9,	1	E	216543.9010	-0.0598	0.0500
169.	64	7	8,	1	E	216541.3250	-0.1714	0.0500
170.	64	6	7,	1	A+	216537.9310	0.0232	0.0500
171.	64	4	5,	1	E	216525.1000	-0.1726	0.0500
172.	64	2	3,	1	E	216498.4230	-0.1657	0.0500

Σ = 0.073848 172 Transitions in fit
 $\Sigma.w$ = 1.435948 164 Degrees of freedom

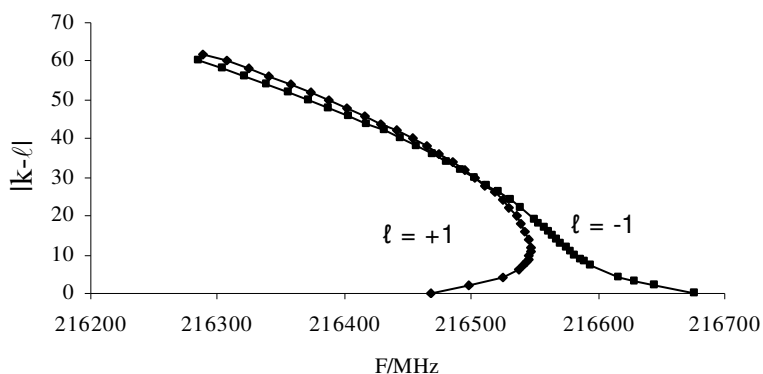


Figure 4. Fortrat diagram of CCl_3CN in $v_8=1$ State, $J = 64$

Table 5. Comparison of rotation-vibration parameters for CCl_3CN in ground, $v_7 = 1$ and $v_8 = 1$ states

Parameter	gs (Ref 4)	gs this work	$v_7=1$ (Ref 5)	$v_7=1$ (this work)	$v_8 = 1$ (Ref 5)	$v_8 = 1$ (this work)
A/MHz	1732.20*	1732.20*	1732.20*	1732.20*	1732.20*	1732.2*
B/MHz	1666.808922 (56)	1666.80892 (43)	1667.96648 (19)	1667.96659 (25)	1667.08229 (32)	1667.08145 (17)
A ζ /MHz	-	-	-1204.857 (0.873)	-1204.9 (10)	918.47 (1.80)	918.9 (20)
q_t^+ /MHz	-	-	1.58815 (69)	1.58855 (94)	1.6118 (17)	1.6121 (19)
D_J /kHz	0.1350194 (100)	0.135920 (79)	0.13567 (6)	0.135701 (25)	0.13585 (14)	0.135501 (28)
D_{JK} /kHz	0.605692 (173)	0.6059 (15)	0.59291 (126)	0.5922 (16)	0.58943 (70)	0.58929 (76)
H_J /mHz	-0.01906 (46)	-0.0193 (36)	0.0485 (64)	0.0505 (74)	0.0*	0.0*
H_{JK} /mHz	1.1338 (91)	1.19 (11)	0.251 (121)	0.20 (15)	0.0*	0.0*
H_{KJ} /mHz	-1.478 (94)	-1.61 (74)	0.0*	0.0*	0.0*	0.0*
η_J /kHz	-	-	-0.8119 (122)	-0.821 (17)	2.6964 (227)	2.666 (24)
η_{JJ} /Hz	-	-	0.0224 (13)	-0.0214 (17)	-0.0109 (36)	0.0171 (39)
η_K /kHz	-	--	-	0.0*	0.0*	0.0*
q_J /kHz	-	-	0.00112 (8)	0.001169 (98)	0.00138 (16)	0.00137 (138)

*constrained at this value.

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