Determination of Rotational Parameters of CH₃CN, CD₃CN and their Different Isotopic Species in the Ground and $\nu_4 = 1$ States

MOTAMEDI, MASOUD* and MORADI, PARINAZ

Department of Chemistry, Faculty of Science,
University of Kurdistan, Sanandaj, Iran.

motamedimas@yahoo.co.uk

Received 2 September 2008; Revised 18 October 2008; Accepted 1 November 2008

Abstract: The millimeter-wave rotational spectra of the symmetric top molecules CH₃CN, ¹³CH₃CN, CH₃¹³CN, CH₃C¹⁵N, CD₃CN, ¹³CD₃CN, CD₃¹³CN and CD₃C¹⁵N have been investigated again in their ground and $\nu_4 = 1$ states. The analysis of spectra and fitting the frequencies in these states give rotational parameters with higher accuracy compare with previous works. The parameter $H_J = -0.107(96)$ mHz was determined for CH₃C¹⁵N for the first time.

Keywords: Millimeter-wave rotational spectra, Ground state, Symmetric top molecules, CH₃CN, CD₃CN

Introduction

Methyl Cyanide, CH₃CN is a symmetric top molecule and belongs to the C_{3v} point group. The symmetry species for this point group are A₁, A₂, and E. This compound has 8 different fundamental frequencies and $4 + 4 \times 2 = 12$ modes of vibration. All of these vibrations are both infrared and Raman active. The infrared spectrum of CD₃CN is similar to that of CH₃CN in many respects. Following the Pauli principle and the symmetries of the rovibronic states, the rotational levels are separated into two symmetry modifications, distinguished by their nuclear spin states. Levels where K is a multiple of 3 ($K = 0, 3, 6, \dots$) belong to the A symmetry state while those with K not a multiple of 3 ($K = 1, 2, 4, 5, \dots$) belong to the E species. The A symmetry modifications have twice the spin statistical weight of the E states. The lowest doubly degenerate vibrational level, $\nu_8 = 1$, is approximately a $-C-C \equiv N$ bending mode and lies at 361 cm^{-1} (331 cm^{-1} for CD₃CN)¹ and consequently has a population which is 6% of the ground state (ignoring degeneracy) at the temperature of 298 K. The next highest frequency is C-C stretch $\nu_4(A_1) = 1$ and lies at 920 cm^{-1} (831.3 cm^{-1} for CD₃CN)¹, so there is no doubt about the assignment of the series of lines which lie to high frequency of the ground state rotational

transitions. Symmetric top molecules such as CF_3CCH , CF_3CN and CH_3CN have been investigated in different vibrational excited states before. The authors showed that resonance can take place in these molecules in different k value which is dependent on their rotational parameters²⁻¹⁴. The aim of this study is determination of rotational parameters for mixing the low and high J values, which are more accurate and reliable.

Rotational Spectra in Ground and non-degenerate vibrational States

For ground and non degenerate vibrational states 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 equation 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.

CH_3CN , Ground State

The 185 different measurements of CH_3CN for ground state were combined to each other¹⁸⁻²⁰. A weighted least-squares method²¹ was used to fit the mixed frequencies for low and high J values to the parameters of equation 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 to 0.5 MHz to allow for overlapping or broadening. The result of refinement is listed in Table 1, and correlation coefficients of parameters are shown in Table 2. These tables show that the mixed frequencies of low and high values of CH_3CN were fitted very well and correlation coefficients of parameters are reasonable. The structural parameters of this compound as shown in Table 3 were obtained with higher accuracy and compared with previous works.

Table 1. Results of refinement of observed frequencies for CH_3CN in the ground state¹⁸⁻²⁰.

S.No.	J	K	Observed/MHz	Obs-Calc/MHz	Error/MHz
1.	4	0	91987.0700	-0.0076	0.2000
2.	4	1	91985.3500	0.0447	0.2000
3.	4	2	91980.0000	0.0108	0.1000
4.	4	3	91971.3500	0.2187	0.2000
5.	4	4	91958.7800	0.0451	0.2000
6.	5	0	110383.4700	-0.0178	0.2000
7.	5	1	110381.3900	0.0287	0.1000
8.	5	2	110375.0100	0.0272	0.1000
9.	5	3	110364.5200	0.1655	0.2000
10.	5	4	110349.6800	0.1993	0.2000
11.	5	5	110330.7900	0.4231	0.5000
12.	6	0	128779.4300	0.0804	0.2000
13.	6	1	128777.0200	0.1509	0.2000
14.	6	2	128769.5200	0.0915	0.2000
15.	6	3	128757.0300	-0.0007	0.2000
16.	6	4	128739.9100	0.2296	0.3000

Contd...

17.	6	5	128717.6900	0.3058	0.3000
18.	6	6	128690.5700	0.4193	0.5000
19.	7	0	147174.7200	0.1483	0.2000
20.	7	1	147171.9500	0.2127	0.2000
21.	7	2	147163.4600	0.2248	0.2000
22.	7	3	147149.2800	0.2114	0.2000
23.	7	4	147129.4100	0.1671	0.2000
24.	7	5	147104.0700	0.3042	0.3000
25.	9	0	183962.6200	-0.1111	0.2000
26.	9	1	183959.0800	-0.1095	0.2000
27.	9	2	183948.4900	-0.0761	0.2000
28.	9	3	183930.7900	-0.0748	0.2000
29.	9	4	183906.0500	-0.0426	0.2000
30.	9	5	183874.2100	-0.0488	0.2000
31.	10	0	202355.6100	0.1244	0.2000
32.	10	1	202351.4500	-0.1407	0.2000
33.	10	3	202321.5400	1.0992	excluded
34.	10	4	202293.7800	0.5823	0.4000
35.	10	5	202257.8700	-0.3186	0.3000
36.	11	0	220747.2400	0.0053	0.2000
37.	11	1	220742.9900	0.0031	0.2000
38.	11	2	220730.2700	0.0251	0.2000
39.	11	3	220709.0800	0.0662	0.2000
40.	11	4	220679.3200	0.0185	0.2000
41.	11	5	220641.1200	0.0004	0.2000
42.	17	0	331071.5900	0.0901	0.2000
43.	17	1	331065.1700	0.0292	0.2000
44.	17	9	330557.5710	-0.1560	0.2000
45.	17	12	330159.7000	-0.2683	0.2000
46.	21	3	404519.5340	0.0156	0.2000
47.	21	6	404310.2880	-0.0457	0.2000
48.	21	12	403477.0540	-0.1596	0.2000
49.	21	15	402855.9600	-0.2136	0.2000
50.	24	0	459707.0000	0.0944	0.2000
51.	24	6	459390.2660	-0.0975	0.2000
52.	24	12	458444.7160	-0.4078	0.2000
53.	25	1	478065.8840	0.0497	0.2000
54.	25	3	477992.6920	0.0336	0.2000
55.	25	6	477745.8820	-0.0847	0.2000
56.	25	9	477335.6190	-0.1453	0.2000
57.	25	12	476763.3230	-0.1540	0.2000
58.	28	0	533164.5790	-0.0172	0.2000
59.	28	1	533154.4820	0.0724	0.2000
60.	28	2	533123.9140	0.0605	0.2000
61.	28	3	533072.9560	0.0162	0.2000
62.	28	4	533001.7190	0.0309	0.2000
63.	28	5	532910.1350	0.0091	0.2000
64.	28	6	532798.2780	-0.0105	0.2000
65.	28	7	532666.1610	-0.0582	0.2000
66.	28	8	532513.8910	-0.0779	0.2000
67.	28	9	532341.4980	-0.0985	0.2000
68.	28	10	532149.0630	-0.1059	0.2000
69.	28	11	531936.6420	-0.1186	0.2000
70.	28	12	531704.3290	-0.1250	0.2000
71.	28	13	531452.2410	-0.0985	0.2000
72.	28	14	531180.4360	-0.0792	0.2000
73.	28	15	530889.0300	-0.0571	0.2000
74.	28	16	530578.1630	-0.0062	0.2000
75.	28	17	530247.9150	0.0320	0.2000
76.	28	18	529898.4330	0.0748	0.2000

Contd...

77.	28	19	529529.8290	0.0967	0.2000
78.	28	20	529142.2400	0.0896	0.2000
79.	29	0	551522.7200	0.0986	0.2000
80.	29	12	550013.0450	-0.0804	0.2000
81.	30	0	569877.9820	0.0773	0.2000
82.	30	3	569780.0770	0.0190	0.2000
83.	30	6	569486.8180	-0.0397	0.2000
84.	30	9	568999.1820	-0.1419	0.2000
85.	31	1	588219.1970	0.0597	0.2000
86.	32	0	606579.9560	0.0755	0.2000
87.	32	1	606568.3610	0.0402	0.2000
88.	32	2	606533.6900	0.0440	0.2000
89.	32	3	606475.8990	0.0294	0.2000
90.	32	4	606395.0200	0.0060	0.2000
91.	32	5	606291.0900	-0.0203	0.2000
92.	32	6	606164.1010	-0.0979	0.2000
93.	32	7	606014.2990	-0.0298	0.2000
94.	32	8	605841.4860	-0.0721	0.2000
95.	32	9	605645.9300	-0.0240	0.2000
96.	32	10	605427.4730	-0.1192	0.2000
97.	32	11	605186.4510	-0.1067	0.2000
98.	32	13	604636.7610	-0.0939	0.2000
99.	32	14	604328.3830	-0.0181	0.2000
100.	32	15	603997.7220	0.0186	0.2000
101.	32	16	603644.9690	0.0774	0.2000
103.	32	17	603270.2210	0.1169	0.2000
104.	32	18	602873.6360	0.1477	0.2000
105.	32	19	602455.3670	0.1664	0.2000
106.	32	20	602015.5340	0.1276	0.2000
107.	32	21	601554.3680	0.0882	0.2000
108.	32	22	601071.8320	-0.1721	0.2000
109.	33	3	624819.3430	0.0355	0.2000
110.	33	6	624498.4440	0.0115	0.2000
111.	34	1	643257.5510	0.0003	0.2000
112.	34	3	643159.6850	0.0398	0.2000
113.	34	6	642829.5600	-0.0276	0.2000
114.	34	9	642280.7090	-0.0618	0.2000
115.	35	1	661597.4610	0.0466	0.2000
116.	35	3	661496.8230	0.0314	0.2000
117.	36	0	679946.9720	0.0627	0.2000
118.	36	3	679830.6760	0.0206	0.2000
119.	36	6	679482.3460	0.0466	0.2000
120.	38	0	716610.1610	-0.3390	0.3000
121.	38	1	716596.9430	0.0386	0.2000
122.	38	2	716556.2120	0.0894	0.2000
123.	38	3	716488.1810	0.0104	0.2000
124.	38	4	716393.1180	0.0432	0.2000
125.	38	5	716270.9030	0.0310	0.2000
126.	38	6	716121.4140	-0.1960	0.2000
127.	38	7	715945.3250	-0.0216	0.2000
128.	38	8	715742.1230	-0.0276	0.2000
129.	38	9	715512.0870	-0.0142	0.2000
130.	38	10	715255.2650	-0.0232	0.2000
131.	38	11	714971.8090	-0.0028	0.2000
132.	38	12	714661.8000	0.0171	0.2000
133.	38	13	714325.3290	0.0059	0.2000
134.	38	14	713962.8330	0.2687	excluded
135.	38	15	713573.7720	0.1230	0.2000
136.	39	0	734937.0510	0.0564	0.2000
137.	39	1	734923.0970	0.0343	0.2000

Contd...

138.	39	2	734881.3250	0.0527	0.2000
139.	39	3	734811.6570	0.0173	0.2000
140.	39	4	734714.2260	0.0341	0.2000
141.	39	5	734589.0040	0.0371	0.2000
142.	39	6	734436.0330	0.0196	0.2000
143.	39	7	734255.3840	-0.0070	0.2000
144.	39	8	734047.1570	-0.0131	0.2000
145.	39	9	733811.4370	0.0051	0.2000
146.	39	10	733548.2570	-0.0115	0.2000
147.	39	11	733257.7960	0.0132	0.2000
148.	39	12	732940.0900	0.0015	0.2000
149.	39	13	732595.3540	0.0438	0.2000
150.	39	14	732224.0830	0.4998	0.2000
151.	39	15	731825.2020	0.1482	0.2000
152.	39	16	731400.0450	0.1659	0.2000
153.	39	17	730948.4290	0.2021	0.2000
154.	39	18	730470.4450	0.1690	0.2000
155.	40	1	753245.6610	0.0948	0.2000
156.	40	3	753131.3940	-0.0674	0.2000
157.	40	6	752746.8650	0.0701	0.2000
158.	41	3	771447.4920	-0.0527	0.2000
159.	41	6	771053.8890	0.0251	0.2000
160.	42	1	789879.2720	0.0285	0.2000
161.	42	3	789759.7670	-0.0314	0.2000
162.	42	6	789357.1010	-0.0288	0.2000
163.	42	9	788687.5830	-0.0044	0.2000
164.	43	0	808205.4800	-0.0218	0.2000
165.	43	1	808190.1770	-0.0574	0.2000
166.	43	2	808144.4360	-0.0023	0.2000
167.	43	3	808068.1150	-0.0163	0.2000
168.	43	4	807961.2930	-0.0501	0.2000
169.	43	5	807824.0830	-0.0325	0.2000
170.	43	6	807656.4730	-0.0292	0.2000
171.	43	7	807458.5240	-0.0445	0.2000
172.	43	8	807230.3110	-0.0811	0.2000
173.	43	9	806971.9910	-0.0711	0.2000
174.	43	10	806683.6180	-0.0620	0.2000
175.	43	11	806365.3020	-0.0569	0.2000
176.	43	12	806017.1850	-0.0388	0.2000
177.	43	13	805639.4260	0.0141	0.2000
178.	43	15	804795.4060	0.0410	0.2000
179.	43	16	804329.5190	0.0553	0.2000
180.	43	18	803310.8510	0.0225	0.2000
181.	43	19	802758.4270	-0.0728	0.2000
182.	43	21	801568.4300	-0.4922	0.2000
183.	46	1	863098.7460	0.0257	0.2000
184.	46	3	862968.6560	-0.0370	0.2000
185.	49	1	917968.5930	0.0361	0.2000
Sigma =			0.132825	182 Transitions in fit	
Sigma.w =			0.572735	177 Degrees of freedom	

Table 2. Correlation coefficients of CH₃CN for the ground state

	B	DJ	DJK	HJK	HKJ
B	1.0000				
DJ	0.9303	1.0000			
DJK	0.5775	0.4414	1.0000		
HJK	0.5432	0.5823	0.7391	1.0000	
HKJ	0.2257	0.0384	0.6760	0.0573	1.0000

Table 3. Comparison of rotational parameters of CH₃CN in the ground state with previous works

Rotational parameters	References			
	Ref ¹⁸	Ref ¹⁹	Ref ²⁰	This work
B(MHz)	9198.89	9198.8994(64)	9198.89914(77)	9198.89816(54)
D _J (KHz)	3.8	3.80834(64)	3.80074 (57)	3.80804(17)
D _{JK} (KHz)	176.9	177.3924(33)	177.4048(17)	177.2809(51)
H _{KJ} (Hz)	-	5.939(32)	6.0589(74)	5.6413(92)
H _{JK} (Hz)	-	1.004(21)	1.0224(72)	0.9768(12)
H _J (Hz)	-	0.0*	-0.264(15)	0.0*

*Fixed value

¹³CH₃CN, CH₃¹³CN and CH₃C¹⁵N Spectra

The refinements of different frequencies²² for different species ¹³CH₃CN, CH₃¹³CN and CH₃C¹⁵N are listed in Tables 4 to 6. The obtained parameters are shown in Table 7 and compared with previous works.

Table 4. Results of refinement of observed frequencies for ¹³CH₃CN in the ground state²².

S.No.	J	K	Observed/MHz	Obs-Calc/MHz	Error/MHz
1.	0	0	17866.6000	-0.0127	0.1000
2.	3	0	71465.5200	-0.0493	0.1000
3.	3	1	71464.1400	-0.0882	0.1000
4.	5	0	107196.5700	-0.0214	0.1000
5.	5	1	107194.5500	-0.0296	0.1000
6.	5	2	107188.5000	-0.0443	0.1000
7.	5	3	107178.5000	0.0146	0.1000
8.	5	4	107164.4800	0.0769	0.1000
9.	6	0	125061.3000	-0.0533	0.1000
10.	6	1	125058.9800	-0.0262	0.1000
11.	6	2	125051.9000	-0.0650	0.1000
12.	6	3	125040.2000	-0.0297	0.1000
13.	6	4	125023.8600	0.0598	0.1000
14.	6	5	125002.8000	0.1234	0.1000
15.	7	0	142925.6000	0.1018	0.1000
16.	7	1	142922.8400	0.0241	0.1000
17.	7	2	142914.8500	0.0812	0.1000
18.	7	3	142901.4000	0.0430	0.1000
19.	7	4	142882.6300	0.0495	0.1000
20.	7	5	142858.4700	0.0308	0.1000
21.	7	6	142828.9000	-0.0333	0.1000
22.	8	0	160788.9500	0.0119	0.1000
23.	8	1	160785.9000	-0.0205	0.1000
24.	8	2	160776.8200	-0.0475	0.1000
25.	8	3	160761.7900	0.0108	0.1000
26.	8	4	160740.5200	-0.1357	0.1000
27.	8	5	160713.3700	-0.1268	0.1000
28.	8	6	160680.3000	-0.0026	0.1000
29.	8	7	160641.1500	0.0769	0.1000
30.	9	0	178651.6200	0.0352	0.1000
31.	9	1	178648.2400	0.0081	0.1000
32.	9	2	178638.2400	0.0670	0.1000
33.	9	3	178621.3900	-0.0183	0.1000
34.	9	4	178597.9800	0.0423	0.1000
35.	9	5	178567.6900	-0.0711	0.1000
36.	9	6	178530.8400	-0.0387	0.1000
Sigma =	0.062499		36 Transitions in fit		
Sigma.w =	0.624994		33 Degrees of freedom		

Table 5. Results of refinement of observed frequencies for CH₃¹³CN in the ground state²².

S.No.	J	K	Observed/MHz	Obs-Calcd/MHz	Error/MHz
1.	1	0	36777.1800	-0.0962	0.1000
2.	3	0	73553.8200	0.0014	0.1000
3.	3	1	73552.3600	-0.0494	0.1000
4.	4	0	91941.5800	-0.0055	0.1000
5.	4	1	91939.7900	-0.0339	0.1000
6.	4	2	91934.6000	0.0608	0.1000
7.	5	1	110326.8700	0.0901	0.1000
8.	5	2	110320.4000	-0.0382	0.1000
9.	5	3	110309.8000	-0.0687	0.1000
10.	5	4	110295.2000	0.1285	0.1000
11.	6	0	128715.6500	-0.0018	0.1000
12.	6	1	128713.1100	-0.0756	0.1000
13.	6	2	128705.7400	-0.0470	0.1000
14.	6	3	128693.3800	-0.0759	0.1000
15.	6	4	128676.2900	0.0975	0.1000
16.	7	0	147101.7800	0.0121	0.1000
17.	7	1	147099.0400	0.0906	0.1000
18.	7	2	147090.5400	0.0462	0.1000
19.	7	3	147076.4000	-0.0012	0.1000
20.	7	4	147056.5600	-0.1115	0.1000
21.	7	5	147031.2900	-0.0147	0.1000
22.	7	6	147000.3500	0.0490	0.1000
23.	9	0	183871.7400	0.0327	0.1000
24.	9	1	183868.2400	0.0558	0.1000
25.	9	2	183857.5900	-0.0247	0.1000
26.	9	3	183839.9800	-0.0189	0.1000
27.	9	4	183815.2800	-0.0568	0.1000
28.	9	5	183783.6000	-0.0284	0.1000
29.	9	6	183744.8900	0.0164	0.1000
Sigma =			0.063729	29 Transitions in fit	
Sigma.w =			0.637292	26 Degrees of freedom	

Table 6. Results of refinement of observed frequencies for CH₃C¹⁵N in the ground state²².

S.No.	J	K	Observed/MHz	Obs-Calcd/MHz	Error/MHz
1.	0	0	17844.1700	0.1022	0.1000
2.	1	0	35688.0800	0.0295	0.1000
3.	1	1	35687.3700	-0.0043	0.1000
4.	2	0	53531.9200	0.0570	0.1000
5.	2	1	53530.8800	0.0313	0.1000
6.	2	2	53527.8700	0.0636	0.1000
7.	3	0	71375.4500	0.0301	0.1000
8.	3	1	71374.0700	0.0024	0.1000
9.	3	2	71370.0300	0.0185	0.1000
10.	3	3	71363.2600	0.0063	0.1000
11.	4	0	89218.7000	0.0644	0.1000
12.	4	1	89216.9700	0.0245	0.1000
13.	4	3	89203.4100	-0.0195	0.1000
14.	4	4	89191.5900	-0.0206	0.1000
15.	5	0	107061.4100	-0.0143	0.1000
16.	5	1	107059.3400	-0.0564	0.1000
17.	5	2	107053.2700	-0.0437	0.1000
18.	5	3	107043.1400	-0.0392	0.1000
19.	5	4	107028.9400	-0.0583	0.1000
20.	5	5	107010.7700	-0.0083	0.1000

Contd...

21.	6	0	124903.6600	-0.0398	0.1000
22.	6	1	124901.2900	-0.0442	0.1000
23.	6	2	124894.2500	0.0113	0.1000
24.	6	3	124882.4100	-0.0070	0.1000
25.	6	4	124865.8600	-0.0150	0.1000
26.	6	5	124844.6000	-0.0214	0.1000
27.	6	6	124818.6600	-0.0070	0.1000
28.	7	0	142745.3600	-0.0153	0.1000
29.	7	1	142742.6700	-0.0023	0.1000
30.	7	2	142734.5700	0.0055	0.1000
31.	7	3	142721.1000	0.0438	0.1000
32.	7	4	142702.1800	0.0257	0.1000
33.	7	5	142677.8800	0.0115	0.1000
34.	7	6	142648.2300	0.0186	0.1000
35.	7	7	142613.2100	0.0118	0.1000
36.	11	4	214039.6400	0.0904	0.1000
37.	12	0	231941.7100	0.0336	0.1000
38.	12	1	231937.2800	-0.0091	0.1000
39.	12	2	231924.1000	-0.0295	0.1000
40.	12	3	231902.2300	0.0256	0.1000
41.	12	4	231871.4900	-0.0350	0.1000
42.	12	5	231832.0100	-0.0972	0.1000
43.	12	6	231784.0300	0.0586	0.1000
44.	12	9	231587.5200	-0.0068	0.1000
<hr/>					
Sigma =			0.042838	44 Transitions in fit	
Sigma.w =			0.428377	38 Degrees of freedom	

Table 7. Comparison of ground rotational parameters of $^{13}\text{CH}_3\text{CN}$, $\text{CH}_3^{13}\text{CN}$ and $\text{CH}_3\text{C}^{15}\text{N}$ with previous works.

Parameters	$^{13}\text{CH}_3\text{CN}$		$\text{CH}_3^{13}\text{CN}$		$\text{CH}_3\text{C}^{15}\text{N}$	
	Ref. ²²	This work	Ref. ²²	This work	Ref. ²²	This work
B(MHz)	8933.313(23)	8933.3136(23)	9194.349(22)	9194.3496(22)	8922.043 (97)	8922.0409 (21)
D _J (KHz)	3.674(16)	3.672(15)	3.817(17)	3.821(15)	3.5788 (48)	3.544 (29)
D _{Jk} (KHz)	167.650(55)	167.647(48)	176.146(80)	176.157(71)	169.043 (6)	169.069 (72)
H _{kj} (Hz)	0.0*	0.0*	0.0*	0.0*	7.2 (11)	7.24 (91)
H _{jk} (Hz)	0.0*	0.0*	0.0*	0.0*	0.89 (26)	0.948 (27)
H _J (mHz)	0.0*	0.0*	0.0*	0.0*	0.0*	-0.107 (96)

* constrained at this value

$v_4 = 1$ state

The frequencies of rotational transitions^{19,23} of CH_3CN for $v_4 = 1$ state mixed together and were fitted in equation 1. The results of refinement are shown in Table 8.

Table 8. Results of refinement of observed frequencies for CH_3CN in the $v_4 = 1$ state^{19,23}.

S.No.	J	K	Observed/MHz	Obs-Calc/MHz	Error/MHz
1.	6	0	128131.8700	0.1295	0.3000
2.	6	1	128129.1900	0.0284	0.2000
3.	6	2	128121.4800	0.0573	0.2000
4.	6	3	128108.5900	0.0724	0.2000
5.	6	4	128090.4800	0.0443	0.2000
6.	7	0	146434.4900	0.0405	0.2000
7.	7	1	146431.5300	0.0272	0.2000
8.	7	2	146422.6300	-0.0305	0.2000
9.	7	3	146407.9300	0.0149	0.2000

Contd...

10.	7	4	146387.2700	0.0153	0.2000
11.	7	5	146360.7500	0.0876	0.2000
12.	7	6	146328.1500	0.0335	0.2000
13.	8	0	164736.4500	0.0216	0.2000
14.	8	1	164733.0700	-0.0442	0.2000
15.	8	2	164723.1700	0.0009	0.2000
16.	8	3	164706.5300	-0.0549	0.2000
17.	8	4	164683.3200	-0.0279	0.2000
18.	8	5	164653.5300	0.0907	0.2000
19.	8	6	164616.7600	-0.0745	0.3000
20.	9	0	183037.5200	-0.0658	0.2000
21.	9	1	183033.8300	-0.0745	0.2000
22.	9	2	183022.8500	-0.0076	0.2000
23.	9	3	183004.4100	-0.0259	0.2000
24.	9	4	182978.5800	-0.0446	0.2000
25.	9	5	182945.4300	0.0277	0.2000
26.	9	6	182904.6900	-0.0520	0.3000
27.	18	0	347696.0300	0.0498	0.2000
28.	18	3	347633.1500	-0.0950	0.2000
29.	18	4	347584.2900	-0.1075	0.2000
30.	18	5	347521.7500	0.2252	0.3000
31.	18	6	347444.2600	-0.3153	excluded
32.	18	7	347361.2900	7.8041	excluded
33.	18	8	347250.1000	1.9178	excluded
34.	18	9	347128.6400	0.0619	0.2000
35.	18	10	346994.5600	-0.0162	0.2000
36.	18	12	346682.8600	-0.0720	0.2000
37.	19	0	365983.9800	0.0762	0.2000
38.	19	1	365976.7400	0.1652	0.3000
39.	19	2	365954.6100	0.0285	0.2000
40.	19	3	365917.7600	-0.1461	0.3000
41.	19	4	365866.3100	-0.2082	0.3000
42.	19	5	365800.3000	-0.0756	0.2000
43.	19	6	365718.9600	-0.4641	excluded
44.	19	7	365631.4200	7.8228	excluded
45.	19	8	365514.9300	2.1134	excluded
46.	19	9	365387.0600	0.0683	0.2000
47.	19	10	365245.9500	-0.0700	0.2000
48.	19	11	365089.7800	-0.0067	0.2000
49.	19	12	364918.2400	0.0747	0.2000
50.	20	0	384270.0600	0.0579	0.2000
51.	20	3	384200.7100	-0.0378	0.2000
52.	20	4	384146.7000	-0.1242	0.2000
53.	20	5	384077.4800	0.0622	0.2000
54.	20	6	383992.1000	-0.3717	excluded
55.	20	7	383899.8500	7.9339	excluded
56.	20	8	383777.8900	2.2214	excluded
57.	20	9	383643.6900	0.0557	0.2000
58.	20	10	383495.6500	-0.0555	0.2000
59.	20	11	383331.7500	-0.0117	0.2000
60.	20	12	383151.7000	0.0300	0.2000
61.	23	0	439116.5300	0.0979	0.2000
62.	23	1	439107.7300	0.0692	0.2000
63.	23	2	439081.2800	-0.0598	0.2000
64.	23	3	439037.3400	-0.1073	0.2000
65.	23	4	438975.8000	-0.1472	0.2000
66.	23	5	438896.9000	0.1113	0.3000
67.	23	6	438799.4200	-0.4867	excluded
68.	23	7	438693.1800	7.9585	excluded
69.	23	8	438555.3800	2.7409	excluded

Contd...

70.	23	9	438402.1600	0.1093	0.2000
71.	23	10	438233.3300	-0.0034	0.2000
72.	23	11	438046.1900	-0.1596	0.3000
73.	23	12	437840.9200	-0.0271	0.2000
74.	24	0	457394.3800	0.0638	0.2000
75.	24	1	457385.2500	0.0637	0.2000
76.	24	2	457357.8000	0.0108	0.2000
77.	24	3	457311.9300	-0.1721	0.3000
78.	24	4	457247.9200	-0.1674	0.3000
79.	24	5	457165.7900	0.0977	0.2000
80.	24	6	457064.3200	-0.5289	excluded
81.	24	7	456953.4800	8.0058	excluded
82.	24	8	456810.3300	2.8597	excluded
83.	24	9	456650.7900	0.0662	0.2000
84.	24	10	456475.0200	-0.0868	0.2000
85.	24	11	456280.5100	0.0342	0.2000
86.	24	12	456066.7000	0.0276	0.2000
Sigma =			0.087165	71 Transitions in fit	
Sigma.w =			0.366816	66 Degrees of freedom	

Table. 8 shows that, differences between observed and calculated values in $k = 6, 7$ & 8 are very high especially for $k = 7$ Figure 1. This deviation is due to Fermi resonance^{19,23}. For obtaining the reasonable fitting, the $k = 6, 7$ and 8 were excluded from fitting. In this case the values of sigma and sigma.w show that the result of fitting is satisfactory. The result of refinement of frequencies are listed in Table 9 and compared with previous works.

Table. 9. Comparison of rotational parameters of CH_3CN in $v_4 = 1$ state with previous works.

Rotational parameters	References		
	Ref ¹⁹	Ref ²³	This work
B(MHz)	9152.6413 (12)	9152.6397(11)	9152.63985(99)
D _J (KHz)	3.8047(23)	3.8029(11)	3.80282(99)
D _{Jk} (KHz)	184.351(70)	184.534(32)	184.332(27)
H _{Jk} (Hz)	1.33(11)	1.399(22)	1.397(19)
H _{kj} (Hz)	-11.96(47)	-11.18(18)	-12.570(145)
H _J (Hz)	0.0*	0.0*	0.0*

*constrained at this value

Figure 1. Differences between observed and calculated rotational frequencies of CH_3CN for $v_4 = 1$ state .

CD₃CN and its isotopes

A weighted least-squares method²¹ was used to fit the 103 fixed frequencies of CD_3CN in the ground state for low and high J values^{22,24}. The result of fitting are listed in Table 10. The values of the parameters obtained are shown in Table 11 and compared with pervious works. Sextic parameters H_{kj} and H_{Jk} were determined with more accuracy compared with previous works

Table 10. Results of refinement of observed frequencies for CD₃CN in the grounds state^{22,24}.

S.No.	J	K	Observed/MHz	Obs-Calc/MHz	Error/MHz
1.	0	0	15715.9600	0.0025	0.1000
2.	2	0	47147.6000	-0.0075	0.1000
3.	2	1	47146.9000	-0.0436	0.1000
4.	2	2	47144.9100	-0.0421	0.1000
5.	4	0	78578.5200	0.0576	0.1000
6.	4	1	78577.3100	-0.0461	0.1000
7.	4	2	78574.0200	-0.0174	0.1000
8.	4	3	78568.5100	0.0029	0.1000
9.	5	0	94293.4300	0.0040	0.1000
10.	5	2	94288.1500	0.0334	0.1000
11.	5	3	94281.4700	-0.0110	0.1000
12.	5	4	94272.1200	-0.0733	0.1000
13.	8	0	141435.6900	0.0237	0.1000
14.	8	1	141433.6800	0.0039	0.1000
15.	8	2	141427.7100	0.0040	0.1000
16.	8	3	141417.7200	-0.0374	0.1000
17.	8	4	141403.8600	0.0275	0.1000
18.	8	5	141386.0100	0.0754	0.1000
19.	8	6	141364.0600	-0.0076	0.1000
20.	8	7	141338.2200	-0.0166	0.1000
21.	9	0	157148.6200	-0.0220	0.1000
22.	9	1	157146.4000	-0.0312	0.1000
23.	9	2	157139.7800	-0.0191	0.1000
24.	9	3	157128.7400	-0.0073	0.1000
25.	9	4	157113.2500	-0.0284	0.1000
26.	9	5	157093.3900	-0.0057	0.1000
27.	9	6	157069.0900	-0.0140	0.1000
28.	9	7	157040.4000	-0.0087	0.1000
29.	9	8	157007.2900	-0.0264	0.1000
30.	9	9	156969.8300	-0.0046	0.1000
31.	13	0	219993.2300	-0.0261	0.1000
32.	13	1	219990.1500	-0.0141	0.1000
33.	13	2	219980.9000	0.0113	0.1000
34.	13	3	219965.4000	-0.0320	0.1000
35.	13	4	219943.7900	-0.0077	0.1000
36.	13	5	219915.9500	-0.0405	0.1000
37.	13	6	219881.9700	-0.0469	0.1000
38.	13	7	219841.9000	0.0153	0.1000
39.	13	8	219795.5900	-0.0129	0.1000
40.	13	9	219743.1900	0.0077	0.1000
41.	13	10	219684.6600	0.0253	0.1000
42.	13	11	219619.9300	-0.0437	0.1000
43.	13	12	219549.2500	0.0361	0.1000
44.	14	0	235702.2400	-0.0161	0.1000
45.	14	1	235698.8800	-0.0643	0.1000
46.	14	2	235688.9400	-0.0694	0.1000
47.	14	3	235672.4400	-0.0138	0.1000
48.	14	4	235649.2800	-0.0013	0.1000
49.	14	5	235619.4400	-0.0572	0.1000
50.	14	6	235583.0400	-0.0682	0.1000
51.	14	7	235540.1400	0.0173	0.1000
52.	14	8	235490.5200	-0.0305	0.1000
53.	14	10	235371.6300	-0.0628	0.1000
54.	14	11	235302.3700	-0.0647	0.1000
55.	14	14	235055.5100	-0.0277	0.1000
56.	24	0	392726.7650	0.1082	0.1000
57.	24	1	392721.2880	0.1274	0.1000

Contd...

58.	24	2	392704.7350	0.0618	0.1000
59.	24	3	392677.2370	0.0387	0.1000
60.	24	4	392638.7580	0.0156	0.1000
61.	24	5	392589.2160	-0.0982	0.1000
62.	24	6	392528.9370	0.0120	0.1000
63.	24	9	392282.1430	-0.0001	0.1000
64.	24	12	391937.3780	0.0150	0.1000
65.	24	14	391653.3740	-0.0365	0.1000
66.	24	15	391495.2650	-0.0341	0.1000
67.	24	18	390957.0190	0.1488	0.4000
68.	24	21	390323.1870	-0.0122	0.1000
69.	43	0	690562.2000	0.3273	0.4000
70.	43	1	690552.5000	0.1648	0.1000
71.	43	2	690523.7000	-0.0251	0.1000
72.	43	3	690476.4000	0.3511	0.4000
73.	43	4	690409.7000	0.3822	0.4000
74.	43	5	690323.7000	0.1527	0.4000
75.	43	6	690219.1000	0.3427	0.4000
76.	43	7	690095.6000	0.6277	0.4000
77.	43	8	689952.9000	0.6790	0.4000
78.	43	9	689791.2000	0.6632	0.4000
79.	43	10	689610.7000	0.7427	0.4000
80.	43	11	689411.7000	1.1753	0.5000
81.	43	12	689192.8000	0.5144	0.4000
82.	43	13	688956.0000	0.7090	0.4000
83.	45	13	720183.2000	-0.0958	0.1000
84.	45	14	719916.6000	0.0947	0.1000
85.	45	15	719630.3000	0.0336	0.1000
86.	48	0	768782.4000	-0.7826	0.4000
87.	48	1	768771.8000	-0.8151	0.4000
88.	48	2	768740.5000	-0.4148	0.4000
89.	48	3	768687.7000	-0.3893	0.4000
90.	48	4	768613.6000	-0.5509	0.4000
91.	48	5	768518.4000	-0.7168	0.4000
92.	48	6	768402.4000	-0.6094	0.4100
93.	48	7	768265.4000	-0.4557	0.4000
94.	48	8	768107.1000	-0.5880	0.4000
95.	48	9	767928.2000	-0.3431	0.4000
96.	48	12	767265.0000	-0.6908	0.5000
97.	65	7	1033397.0400	0.0385	0.4000
98.	65	8	1033188.9000	0.3809	0.4000
99.	65	9	1032952.4000	0.0101	0.1000
100.	65	10	1032689.0000	0.3296	0.4000
101.	65	11	1032397.2000	-0.2238	0.4000
102.	65	12	1032078.2000	-0.5201	0.4000
103.	65	13	1031732.2000	-0.4357	0.4000
Sigma =			0.309662	103 Transitions in fit	
Sigma.w =			0.841528	98 Degrees of freedom	

Table 11. Comparison of rotational parameters of CD₃CN in the ground state with previous works

Rotational parameters	References		
	Ref. ²⁵	Ref. ²²	This work
B(MHz)	7857.98361(28)	7857.98222(13)	7857.98428(54)
D _r (KHz)	2.76083(28)	2.4751(11)	2.76091(15)
D _{JK} (KHz)	110.6635(60)	110.661(27)	110.6628(95)
H _K (Hz)	2.115(22)	2.107(76)	2.100(21)
H _{JK} (Hz)	0.5882(28)	0.586(72)	0.589(17)
H _r (Hz)	0.0*	-0.041(26)	0.0*

* constrained at this value

Table 12. Results of refinement of observed frequencies for ¹³CD₃CN in the grounds state^{22,25}.

S.No.	J	K	Observed/MHz	Obs-Calc/MHz	Error/MHz
1.	8	0	138507.6900	138507.7644	0.2000
2.	8	1	138505.8600	138505.8420	0.2000
3.	8	2	138500.1200	138500.0753	0.2000
4.	8	3	138490.4600	138490.4657	0.2000
5.	8	4	138476.9800	138477.0160	0.2000
6.	8	5	138459.8000	138459.7297	0.2000
7.	9	0	153895.4800	153895.4981	0.2000
8.	9	1	153893.3600	153893.3625	0.2000
9.	9	2	153886.9600	153886.9562	0.2000
10.	9	3	153876.3200	153876.2809	0.2000
11.	9	4	153861.3600	153861.3396	0.2000
12.	9	5	153842.1400	153842.1363	0.2000
13.	9	6	153818.7700	153818.6760	0.2000
14.	9	7	153791.0400	153790.9652	0.2000
15.	9	8	153759.0000	153759.0114	0.2000
16.	9	9	153722.7800	153722.8231	0.2000
17.	13	0	215439.4300	215439.4230	0.2000
18.	13	1	215436.4900	215436.4360	0.2000
19.	13	2	215427.4600	215427.4758	0.2000
20.	13	3	215412.5500	215412.5447	0.2000
21.	13	4	215391.6100	215391.6468	0.2000
22.	13	5	215364.7800	215364.7877	0.2000
23.	13	6	215331.9800	215331.9748	0.2000
24.	13	7	215293.2200	215293.2167	0.2000
25.	14	0	230823.3000	230823.3332	0.2000
26.	14	1	230820.0900	230820.1338	0.2000
27.	14	2	230810.5400	230810.5363	0.2000
28.	14	3	230794.5100	230794.5433	0.2000
29.	14	4	230772.1400	230772.1592	0.2000
30.	14	5	230743.4400	230743.3899	0.2000
31.	14	7	230666.6400	230666.7288	0.2000
32.	25	0	399969.1100	399969.2385	0.2000
33.	25	1	399963.6600	399963.7177	0.2000
34.	25	3	399919.7000	399919.5598	0.2000
35.	25	4	399881.0300	399880.9348	0.2000
36.	25	6	399770.7600	399770.6448	0.2000
37.	25	7	399698.9100	399699.0098	0.2000
38.	25	9	399522.7900	399522.8567	0.2000
39.	25	10	399418.3500	399418.3865	0.2000
40.	25	12	399176.8900	399176.8008	0.2000
41.	25	13	399039.7200	399039.7511	0.2000
Sigma =			0.062119	41 Transitions in fit	
Sigma.w =			0.310596	36 Degrees of freedom	

Table 13. Results of refinement of observed frequencies for CD₃¹³CN in the ground state^{22,25}.

S.No.	J	K	Observed/MHz	Obs-Calc/MHz	Error/MHz
1.	8	0	141265.5400	141265.5571	0.2000
2.	8	1	141263.6100	141263.5832	0.2000
3.	8	2	141257.6000	141257.6616	0.2000
4.	8	3	141247.7400	141247.7934	0.2000
5.	8	4	141234.0200	141233.9801	0.2000
6.	8	5	141216.2400	141216.2239	0.2000
7.	9	0	156959.6000	156959.6308	0.2000
8.	9	1	156957.3200	156957.4380	0.2000
9.	9	4	156924.4600	156924.5525	0.2000
10.	9	6	156880.8500	156880.7258	0.2000

Contd...

11.	9	7	156852.3200	156852.2510	0.2000
12.	9	8	156819.3300	156819.4077	0.2000
13.	9	9	156782.1900	156782.2012	0.2000
14.	13	0	219728.5300	219728.6328	0.2000
15.	13	1	219725.6400	219725.5661	0.2000
16.	13	2	219716.4700	219716.3666	0.2000
17.	13	3	219701.0300	219701.0356	0.2000
18.	13	4	219679.6000	219679.5756	0.2000
19.	13	5	219652.0000	219651.9901	0.2000
20.	14	0	235418.7600	235418.7287	0.2000
21.	14	1	235415.4700	235415.4441	0.2000
22.	14	2	235405.6000	235405.5905	0.2000
23.	14	3	235389.2000	235389.1697	0.2000
24.	14	5	235336.6400	235336.6379	0.2000
25.	14	7	235257.8400	235257.8823	0.2000
26.	24	0	392254.0200	392254.0550	0.2000
27.	24	1	392248.5900	392248.6048	0.2000
28.	24	3	392204.9400	392205.0087	0.2000
29.	24	5	392118.0200	392117.8445	0.2000
30.	24	7	391987.1400	391987.1685	0.2000
31.	24	9	391812.9900	391813.0648	0.2000
32.	24	10	391709.7500	391709.7616	0.2000
33.	24	11	391595.6700	391595.6457	0.2000
34.	24	12	391470.7500	391470.7357	0.2000
Sigma = 0.068348			34 Transitions in fit		
Sigma.w = 0.341740			29 Degrees of freedom		

Table 14. Results of refinement of observed frequencies for CD₃C¹⁵N in the ground state^{22,25}

S.No	J	K	Observed/MHz	Obs-Calc/MHz	Error/MHz
1.	3	0	60953.7000	60953.8049	0.2000
2.	3	2	60950.2800	60950.4299	0.2000
3.	3	3	60946.2000	60946.2116	0.2000
4.	8	0	137139.9700	137140.0311	0.2000
5.	8	1	137138.1300	137138.1341	0.2000
6.	8	2	137132.4600	137132.4433	0.2000
7.	8	3	137122.9400	137122.9597	0.2000
8.	8	4	137109.6700	137109.6846	0.2000
9.	8	5	137092.5600	137092.6199	0.2000
10.	8	6	137071.8000	137071.7682	0.2000
11.	9	0	152375.8400	152375.8539	0.2000
12.	9	1	152373.7600	152373.7466	0.2000
13.	9	2	152367.4000	152367.4250	0.2000
14.	9	3	152356.9600	152356.8900	0.2000
15.	9	4	152342.1200	152342.1433	0.2000
16.	9	5	152323.2000	152323.1870	0.2000
17.	9	6	152300.0500	152300.0238	0.2000
18.	9	7	152272.7200	152272.6573	0.2000
19.	9	8	152241.1200	152241.0914	0.2000
20.	9	9	152205.4400	152205.3308	0.2000
21.	13	0	213312.2900	213312.3419	0.2000
22.	13	1	213309.3700	213309.3952	0.2000
23.	13	2	213300.5000	213300.5553	0.2000
24.	13	3	213285.8800	213285.8236	0.2000
25.	13	4	213265.2000	213265.2023	0.2000
26.	13	6	213206.3300	213206.3040	0.2000
27.	13	7	213168.0400	213168.0356	0.2000
28.	13	8	213123.8700	213123.8951	0.2000

Contd...

29.	13	9	213073.9900	213073.8890	0.2000
30.	14	0	228544.4400	228544.4539	0.2000
31.	14	1	228541.3200	228541.2978	0.2000
32.	14	3	228516.0000	228516.0515	0.2000
33.	14	4	228494.0200	228493.9651	0.2000
34.	14	5	228465.5400	228465.5739	0.2000
35.	14	6	228430.8600	228430.8820	0.2000
36.	14	7	228389.9200	228389.8948	0.2000
37.	14	8	228342.7500	228342.6181	0.2000
38.	14	9	228289.1200	228289.0591	0.2000
39.	14	12	228090.5400	228090.7719	0.2000
40.	25	0	396022.9500	396022.8525	0.2000
41.	25	1	396017.5900	396017.4120	0.2000
42.	25	3	395973.7500	395973.8924	0.2000
43.	25	5	395886.8900	395886.8792	0.2000
44.	25	6	395826.9600	395827.0777	0.2000
45.	25	8	395674.8400	395674.9293	0.2000
46.	25	9	395582.4800	395582.6052	0.2000
47.	25	10	395479.5400	395479.4655	0.2000
48.	25	11	395365.5600	395365.5258	0.2000
49.	25	12	395240.8800	395240.8029	0.2000
Sigma =			0.080223	49 Transitions in fit	
Sigma.w =			0.401116	44 Degrees of freedom	

Table 15. Comparison of rotational parameters of ¹³CD₃CN, CD₃¹³CN and CD₃C¹⁵N with previous work²² in the ground state.

Rotational parameters	¹³ CD ₃ CN		CD ₃ ¹³ C ¹⁴ N		CD ₃ C ¹⁵ N	
	Ref. ²⁵	This work	Ref. ²⁵	This work	Ref. ²⁵	This work
B(MHz)	7695.30617 (66)	7695.30594 (84)	7848.53388 (109)	7848.5340 (10)	7619.30697 (61)	7619.3080 (10)
D _J (KHz)	2.65605 (130)	2.65519 (86)	2.76196 (221)	2.7623 (11)	2.57515 (122)	2.5769 (10)
D _{Jk} (KHz)	106.886 (22)	106.889 (30)	109.748 (40)	109.764 (37)	105.464 (21)	105.494 (30)
H _{kl} (Hz)	2250 (27)	2395. (141)	1250 (53)	1462. (233)	1890 (30)	1298.(201)
H _{jk} (Hz)	547. (31)	530. (26)	611 (52)	607. (34)	560 (25)	641. (19)
H _J (mHz)	0.0*	0.0*	0.0*	0.0*	0.0*	0.0*

*Constrained at this value

Results and Discussion

The spectra in ground and v_4 states are simple, so the different k values ($k = 0, 1, 2, 3, 4, \dots$) for each J transition are easily assigned. The centrifugal distortion produces a band head at high frequency at $k = 0$, with a spread to lower frequency with higher k .

If $|k|$ values are plotted against frequency for ground state, the Fortrat diagram is produced which is shown in Figure 2. 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. Due to negative value¹³ (-2.512 kHz) of D_{Jk} for CHCl₃, this situation is different Figure 3.

Most of the rotational constants for CH₃C¹⁵N molecule were determined with higher accuracy compare to parameters derived by previous works. The H_J parameter was obtained - 0.107(96) mHz for this molecule for the first time (Table 7). But this parameter was not determinable for other species and 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. H_{jk} appears to be more important than H_{kj} in analysis of high J rotational spectra all of the isotopic species of CH_3CN molecule. D_k has no influence on the quality of the fit.

Figure 2. Fortrat diagram of CH_3CN for $J = 20$ in the ground state.

Figure 3. Fortrat diagram of CHCl_3 in ground state for $J = 18$.

Table 11 shows that most of the parameters of CD_3CN were determined with more accuracy and reliability. Investigation in Tables 7 and 15 shows that relationship between rotational constants and other different parameters are:

$$\begin{aligned} B(\text{CD}_3\text{CN}) &> B(\text{CD}_3^{13}\text{C}^{14}\text{N}) > B(^{13}\text{CD}_3\text{CN}) > B(\text{CD}_3\text{C}^{15}\text{N}) \\ D_J(\text{CD}_3\text{CN}) &> D_J(^{13}\text{CD}_3\text{CN}) \approx D_J(\text{CD}_3^{13}\text{C}^{14}\text{N}) > D_J(\text{CD}_3\text{C}^{14}\text{N}) \\ D_{Jk}(\text{CD}_3\text{CN}) &> D_{Jk}(\text{CD}_3^{13}\text{C}^{14}\text{N}) > D_{Jk}(^{13}\text{CD}_3\text{CN}) > D_{Jk}(\text{CD}_3\text{C}^{15}\text{N}) \\ H_{kj}(^{13}\text{CD}_3\text{CN}) &> H_{kj}(\text{CD}_3\text{C}^{14}\text{N}) > H_{kj}(\text{CD}_3\text{C}^{15}\text{N}) > H_{kj}(\text{CD}_3^{13}\text{C}^{15}\text{N}) \end{aligned}$$

References

1. Fletcher W H and Shoup C S, *J Mol Spectrosc.*, 1963, **10**, 300.
2. Carpenter J H, Motamedi, M and Smith J G, *J Mol Spectrosc.*, 1995, **171**, 468.
3. Carpenter J H, Motamedi M and Smith J G, *J Mol Spectrosc.*, 1995, **174**, 106.
4. Motamedi M, Carpenter J H and Smith J G, *J Mol Spectrosc.*, 2003, **221**, 23.
5. Motamedi M and Haseli A, *J Mol Spectrosc.*, 2006, **236**, 91.
6. Motamedi M and Haseli A, *Bull Chem Soc Jpn.*, 2006, **79**(12), 1876.
7. Masoud Motamedi and Bahram Vahabzadeh Zargari, *E J Chem.*, 2007, **4**(1), 67.
8. Masoud Motamedi and Prinaz Moradi, *E J Chem.*, 2008, **5**(2), 201.
9. Masoud Motamedi and Tahere Zohrevand, *E J Chem.*, 2008, **5**(4), 946.
10. Friedrich A, Greke C, Harder H, Mäder H, Cosléau J, Wlodarczak G and Demaison, *J Mol Phys.*, 1997, **91**, 697.
11. Wötzel U, Mäder H, Harder H, Pracna. P and Sarka K, *Chemical Physics*, 2005, **312**, 159.

12. Seo P Ja, Carpenter J H and Smith J G, *J Mol Spectrosc.*, 1997, **184**, 362.
13. Carpenter J H, Seo P Ja and Whiffen D H, *J Mol Spectrosc.*, 1995, **170**, 215.
14. Bauer A and Maes S, *J. Mol Spectrosc.*, 1971, **40**, 207.
15. Bauer A, *J Mol Spectrosc.*, 1971, **40**, 183.
16. Chen W, Bocquet R, Boucher D, Demaison J and Wlodarczak G, *J Mol Spectrosc.*, 1991, **150**, 470.
17. Wötzel U, Mäder H, Harder H, Pracna P and Sarka K, *J Molecular Structure*, 2006, **780-781**, 206.
18. Venkateswarlu P, Baker J G and Gordy W, *J Mol Spectrosc.*, 1961, **6**, 215.
19. Bocquet. R, Wlodarczak. G, Bauer. A and Demaison. J, *J Mol Spectrosc.*, 1988, **127**, 382.
20. Šimečková, M, Urban Š, Fuchs U, Lewen F, Winnewisser G, Morino I. and Yamada K., *J Mol Spectrosc.*, 2004, **226**, 123.
21. <http://info.ifpan.edu.pl/~Kisiel/prospe.html>.
22. Demaison J, Dubrulle A, Boucher D, Burie J and Typke V, *J Mol Spectrosc.*, 1979, **76**, 1.
23. Cosleou J, Wlodarczak G, Boucher D and Demaison J. *J Mol Spectrosc.*, 1991, **146**, 49.
24. Brown F X, Cosleau J, Dangoisse D, Demaison J and Wlodarczak G, *J Mol Spectrosc.*, 1989, **134**, 234.
25. Cosleau J, Wlodarczak G, Burie J and Demaison J. *J Mol Spectrosc.*, 1989, **137**, 47.