Study of Millimeter-Wave Rotational Spectra of Trioxane in Ground, $\nu(A)$, $\nu_1(E) = 1$ and $\nu_2(E) = 1$ States

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Received 30 February 2009; Accepted 20 April 2009

Abstract: The millimeter-wave rotational spectra of the ground and excited vibrational states $\nu(A)$, $\nu_1(E) = 1$ and $\nu_2(E) = 1$ of the oblate symmetric top molecule, $(CH_2O)_3$, have been analyzed again. The $B_0 = 5273.25747$ MHz, $D_J = 1.334547$ kHz, $D_{JK} = -2.0206$ kHz, $H_J (-1.01$ mHz), $H_{JK} (-3.80$ mHz), and $H_{KJ} (4.1$ mHz) have been determined for ground state. For non degenerate excited state, $\nu_A(1)$, the $B = 5260.227723$ MHz and D_J and D_{JK} were determined 1.27171 kHz and -1.8789 kHz respectively. The 1 ± 1 series have been assigned in two different excited states $\nu_1(E) = 1$ and $\nu_2(E) = 1$. Most of the parameters were determined with higher accuracy compare with before. For the $\nu_2(E) = 1$ state the $C\zeta = -1940.54(11)$ MHz and $q_J = 0.0753(97)$ kHz were determined for the first time.

Keywords: Millimeter-wave rotational spectra, Excited vibrational state, Symmetric top molecules.

Introduction

1,3,5-Trioxane, $(CH_2O)_3$, is a cyclic trimer of formaldehyde, is an oblate symmetric top molecule belonging to the C_{3v} group. Its vibrational spectrum exhibits 7 type A fundamental absorption bands and 10 type E fundamental bands. Several authors have studied the rotational spectra of the ground state and some excited states¹⁻⁸. In their study observed numerous excited states corresponding to type E and type A vibrational modes. The centrifugal distortion constants are very small and that no structure characteristic of the excited states could be resolved. A more study of the rotational spectrum of this molecule requires the measurement of high J transitions, which are located in the millimeter region and have greater intensity. The microwave spectrum of trioxane was first studied by Oka *et al*¹, who determined the rotational constants for the ground state, for low-lying excited states, and for ¹³C isotopic species. They measured also the dipole moment²⁻⁸, $\mu = 2.07(4)$ D. Cox *et al*³. analyzed also the degenerate excited states $\nu_1(E) = 1$ and $\nu_2(E) = 1$ by direct diagonalization of the Hamiltonian matrix.

If rotational transitions of two degenerate states $v_1(E) = 1$ and $v_2(E) = 1$ are analyzed using the perturbation formula of Grenier-Besson and Amat⁹, the significant discrepancies between calculated and observed frequencies are obtained for these states, particularly for high J , and $Kl - 1$ transitions of the $v_2(E) = 1$ state. The perturbation treatment is only expected to be valid^{3,9} if the following inequalities hold:

$$\frac{1}{2} |q_i| J(J+1) \ll |B - C + C\zeta|,$$

$$|r_i| [J(J+1)]^{1/2} \ll |B - C - 2C\zeta|.$$

Errors arise through the use of the perturbation treatment due to l-type resonance associated with the $\langle 1, K | H_{VR} | 1 \pm 2, K \pm 2 \rangle$ matrix elements, where H_{VR} is the vibration-rotation Hamiltonian. The presence of l-type resonance precludes r-type resonance effects, associated with the $\langle 1, K | H_{VR} | l \pm 2, K \pm 1 \rangle$ elements, arising from inequality $|r_i| [J(J+1)]^{1/2} \ll |B - C - 2C\zeta|$. If the only off-diagonal elements considered are (2,2) elements, the energy matrix can be factored conveniently into a number of tridiagonal submatrices thus facilitating computation (Figure 1).

The aim of this study is determination of rotational parameters for mixing the low and high J values in ground and $v(A)$, $v_1(E) = 1$ and $v_2(E) = 1$ states, which are more accurate and reliable.

Spectra in the ground and nondegenerate states

The rovibrational Hamiltonian for a non-degenerate vibrational state is essentially similar to that of the ground state. For oblate top species:

$$\frac{E_{J,K}}{h} = BJ(J+1) + (C-B)K^2 \quad (1)$$

If centrifugal distortion is taken into account, the energy levels change and so,

$$\frac{E_{J,K}}{h} = BJ(J+1) + (C-B)K^2 - D_J J^2(J+1)^2 - D_{JK} J(J+1)K^2 - D_K K^4$$

$$+ H_J J^3(J+1)^3 + H_{JK} J^2(J+1)^2 K^2 + H_{KJ} J(J+1)K^4 + H_K K^6 + \dots \quad (2)$$

Where D_J , D_{JK} , D_K are quartic centrifugal distortion constants, and H_J , H_{JK} , H_{KJ} , are sextic centrifugal distortion terms, these are small correction terms for non-rigidity. The selection rules are $\Delta J = \pm 1$, $\Delta K = 0$. The $\Delta K = 0$ selection rule means that the C (A in prolate symmetric top molecules) and D_K terms play no part in the spectrum, but the D_{JK} term removes the superposition of the different K components in the spectrum. The transition frequencies for $J \rightarrow (J+1)$ can be expressed as

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

$$+ 4H_{JK}(J+1)^3k^2 + 2H_{KJ}(J+1)k^4 + \dots \quad (3)$$

The frequencies of Refs^{2,8} were mixed in order to improve the accuracy and reliability of the rotational and other centrifugal distortion constants. Then a weighted least-squares method¹⁰ was used to fit the mixed frequencies for low and high J values to the parameters of Eq(3) in which the weights were taken to be $w = \frac{1}{\sigma^2}$ where σ in MHz is estimated

uncertainty in an observation for each unblended line.

The fit to the transitions are given in Tables 1, 2 and obtained parameters are given in Table 5. Some of the lines have an observed error of 0.02 to 0.2 MHz to allow for overlapping or broadening. These tables show that the mixed frequencies of low and high J values of trioxane 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 work.

Table 1. Results of refinement of observed frequencies for (CH₂O)₃ in ground state.

	J	K	Fobs/MHz	Calc/MHz	Obs-Calc/MHz	error/MHz
1.	0	0	10546.4600	10546.5096	-0.0496	0.0200
2.	1	0	21092.9700	21092.9868	-0.0168	0.0200
3.	1	1	21092.9700	21092.9949	-0.0249	0.0200
4.	2	0	31639.4000	31639.3995	0.0005	0.0200
5.	2	1	31639.4000	31639.4116	-0.0116	0.0200
6.	2	2	31639.4000	31639.4480	-0.0480	0.0200
7.	3	0	42185.7900	42185.7153	0.0747	0.0300
8.	3	1	42185.7900	42185.7315	0.0585	0.0300
9.	3	2	42185.7900	42185.7800	0.0100	0.0300
10.	3	3	42185.7900	42185.8608	-0.0708	0.0300
11.	4	0	52731.9200	52731.9020	0.0180	0.0300
12.	4	1	52731.9200	52731.9222	-0.0022	0.0300
13.	4	2	52731.9200	52731.9828	-0.0628	0.0300
14.	4	3	52731.9200	52732.0838	-0.1638	0.0600
15.	4	4	52732.2200	52732.2253	-0.0053	0.0300
16.	5	0	63277.9700	63277.9272	0.0428	0.0300
17.	5	1	63277.9700	63277.9515	0.0185	0.0300
18.	5	2	63277.9700	63278.0242	-0.0542	0.0300
19.	5	3	63278.1600	63278.1454	0.0146	0.0300
20.	5	4	63278.3300	63278.3151	0.0149	0.0300
21.	5	5	63278.5600	63278.5334	0.0266	0.0300
22.	6	0	73823.8000	73823.7587	0.0413	0.0300
23.	6	1	73823.8000	73823.7870	0.0130	0.0300
24.	6	2	73823.8000	73823.8718	-0.0718	0.0300
25.	6	3	73824.0100	73824.0133	-0.0033	0.0300
26.	6	4	73824.2200	73824.2113	0.0087	0.0300
27.	6	5	73824.4700	73824.4658	0.0042	0.0300
28.	6	6	73824.7800	73824.7770	0.0030	0.0300
29.	9	0	105459.8100	105459.7681	0.0419	0.0600
30.	9	1	105459.8100	105459.8085	0.0015	0.0600
31.	9	2	105459.8100	105459.9297	-0.1197	0.0600
32.	9	3	105460.1300	105460.1317	-0.0017	0.0600
33.	9	4	105460.4300	105460.4145	0.0155	0.0600
34.	9	5	105460.7800	105460.7781	0.0019	0.0600
35.	9	6	105461.2300	105461.2226	0.0074	0.0600
36.	9	7	105461.7500	105461.7478	0.0022	0.0600
37.	9	8	105462.3600	105462.3540	0.0060	0.0600
38.	9	9	105463.0500	105463.0409	0.0091	0.0600
39.	10	0	116004.5300	116004.5020	0.0280	0.0600
40.	10	1	116004.5300	116004.5465	-0.0165	0.0600
41.	10	2	116004.5300	116004.6798	-0.1498	0.1000
42.	10	3	116004.9000	116004.9020	-0.0020	0.0600
43.	10	4	116005.2200	116005.2130	0.0070	0.0600
44.	10	5	116005.5900	116005.6130	-0.0230	0.0600
45.	10	6	116006.0800	116006.1018	-0.0218	0.0600
46.	10	7	116006.6500	116006.6795	-0.0295	0.0600
47.	10	8	116007.3200	116007.3462	-0.0262	0.0600
48.	10	9	116008.0700	116008.1018	-0.0318	0.0600
49.	10	10	116008.9300	116008.9464	-0.0164	0.0600
50.	11	0	126548.9500	126548.8809	0.0691	0.0600
51.	11	1	126548.9200	126548.9294	-0.0094	0.0600
52.	11	2	126548.9200	126549.0748	-0.1548	0.2000
53.	11	3	126549.3300	126549.3171	0.0129	0.0600
54.	11	4	126549.6700	126549.6564	0.0136	0.0600
55.	11	5	126550.1100	126550.0927	0.0173	0.0600
56.	11	6	126550.6400	126550.6259	0.0141	0.0600
57.	11	7	126551.2900	126551.2562	0.0338	0.0600

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58.	11	8	126552.0000	126551.9834	0.0166	0.0600
59.	11	9	126552.8400	126552.8076	0.0324	0.0600
60.	11	10	126553.7800	126553.7289	0.0511	0.0600
61.	11	11	126554.8000	126554.7472	0.0528	0.0600
62.	12	0	137092.9400	137092.8725	0.0675	0.0600
63.	12	1	137092.9400	137092.9250	0.0150	0.0600
64.	12	2	137092.9400	137093.0825	-0.1425	0.1000
65.	12	3	137093.3500	137093.3450	0.0050	0.0600
66.	12	4	137093.7500	137093.7126	0.0374	0.0600
67.	12	5	137094.1900	137094.1851	0.0049	0.0600
68.	12	6	137094.7700	137094.7628	0.0072	0.0600
69.	12	7	137095.4400	137095.4454	-0.0054	0.0600
70.	12	8	137096.2000	137096.2332	-0.0332	0.0600
71.	12	9	137097.1300	137097.1260	0.0040	0.0600
72.	12	10	137098.1300	137098.1239	0.0061	0.0600
73.	12	11	137099.2400	137099.2270	0.0130	0.0600
74.	12	12	137100.4700	137100.4353	0.0347	0.0600
75.	15	0	168722.2800	168722.2012	0.0788	0.0900
76.	15	1	168722.2800	168722.2658	0.0142	0.0900
77.	15	2	168722.2800	168722.4596	-0.1796	0.2000
78.	15	3	168722.8000	168722.7826	0.0174	0.0900
79.	15	4	168723.2500	168723.2348	0.0152	0.0900
80.	15	5	168723.8300	168723.8163	0.0137	0.0900
81.	15	6	168724.5400	168724.5269	0.0131	0.0900
82.	15	7	168725.3800	168725.3669	0.0131	0.0900
83.	15	8	168726.3500	168726.3361	0.0139	0.0900
84.	15	9	168727.4400	168727.4346	0.0054	0.0900
85.	15	10	168728.6700	168728.6624	0.0076	0.0900
86.	15	11	168730.0200	168730.0196	0.0004	0.0900
87.	15	12	168731.5100	168731.5062	0.0038	0.0900
88.	15	13	168733.1400	168733.1222	0.0178	0.0900
89.	15	14	168734.8700	168734.8677	0.0023	0.0900
90.	15	15	168736.7300	168736.7427	-0.0127	0.0900
91.	18	0	200347.1100	200346.8845	0.2255	0.2000
92.	18	1	200347.1100	200346.9612	0.1488	0.2000
93.	18	2	200347.1100	200347.1912	-0.0812	0.0900
94.	18	3	200347.1100	200347.5747	-0.4647	0.2000
95.	18	5	200348.7800	200348.8016	-0.0216	0.0900
96.	18	6	200349.5400	200349.6452	-0.1052	0.0900
97.	18	7	200350.5600	200350.6423	-0.0823	0.0900
98.	18	8	200351.7600	200351.7927	-0.0327	0.0900
99.	18	9	200353.0600	200353.0967	-0.0367	0.0900
100.	18	10	200354.5900	200354.5542	0.0358	0.0900
101.	18	11	200356.1700	200356.1652	0.0048	0.0900
102.	18	12	200357.8800	200357.9298	-0.0498	0.0900
103.	18	13	200359.9100	200359.8481	0.0619	0.0900
104.	18	14	200361.9100	200361.9200	-0.0100	0.0900
105.	18	15	200364.1600	200364.1457	0.0143	0.0900
106.	18	16	200366.5900	200366.5251	0.0649	0.0900
107.	18	17	200369.1200	200369.0584	0.0616	0.0900
108.	18	18	200371.8300	200371.7456	0.0844	0.0900
109.	33	6	358375.2860	358375.1798	0.1062	0.1000
110.	33	7	358376.9730	358376.9586	0.0144	0.1000
111.	33	8	358379.0500	358379.0112	0.0388	0.1000
112.	33	9	358381.4420	358381.3376	0.1044	0.1000
113.	33	10	358383.9930	358383.9379	0.0551	0.1000
114.	33	11	358386.7590	358386.8121	-0.0531	0.1000
115.	33	12	358389.9910	358389.9604	0.0306	0.1000
116.	33	13	358393.3430	358393.3827	-0.0397	0.1000

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117.	33	14	358397.0320	358397.0793	-0.0473	0.1000
118.	33	15	358401.0380	358401.0501	-0.0121	0.1000
119.	33	16	358405.3080	358405.2953	0.0127	0.1000
120.	33	17	358409.7820	358409.8150	-0.0330	0.1000
121.	33	18	358414.5250	358414.6093	-0.0843	0.1000
122.	33	19	358419.5720	358419.6783	-0.1063	0.1000
123.	33	20	358424.9620	358425.0221	-0.0601	0.1000
124.	33	21	358430.6680	358430.6409	0.0271	0.1000
125.	33	22	358436.6430	358436.5348	0.1082	0.1000
126.	33	23	358442.7970	358442.7039	0.0931	0.1000
127.	33	24	358449.1750	358449.1484	0.0266	0.1000
128.	33	25	358455.8290	358455.8685	-0.0395	0.1000
129.	33	26	358462.7530	358462.8643	-0.1113	0.1000
130.	33	27	358470.0380	358470.1361	-0.0981	0.1000
131.	33	28	358477.6290	358477.6839	-0.0549	0.1000
132.	33	29	358485.5110	358485.5079	0.0031	0.1000
133.	33	30	358493.6430	358493.6084	0.0346	0.1000
134.	33	31	358501.9790	358501.9856	-0.0066	0.1000
135.	33	32	358510.6520	358510.6396	0.0124	0.1000
136.	33	33	358519.5530	358519.5708	-0.0178	0.1000
137.	37	6	400478.2110	400478.2333	-0.0223	0.1000
138.	37	9	400485.0010	400485.1081	-0.1071	0.1000
139.	37	12	400494.7950	400494.7348	0.0602	0.1000
140.	37	18	400522.3530	400522.2536	0.0994	0.1000
141.	37	21	400539.9770	400540.1517	-0.1747	0.2000
142.	37	27	400584.3790	400584.2454	0.1336	0.2000
143.	37	30	400610.3610	400610.4508	-0.0898	0.1000
144.	37	33	400639.4730	400639.4360	0.0370	0.1000
145.	37	34	400649.9510	400649.7165	0.2345	0.2000
146.	37	35	400660.4330	400660.3069	0.1261	0.2000
147.	37	36	400671.2680	400671.2074	0.0606	0.1000
148.	37	37	400682.3380	400682.4183	-0.0803	0.1000
149.	47	10	505658.0640	505658.3070	-0.2430	0.2000
150.	47	11	505662.4350	505662.3472	0.0878	0.1000
151.	47	12	505666.7750	505666.7725	0.0025	0.1000
152.	47	13	505671.5200	505671.5831	-0.0631	0.1000
153.	47	14	505676.7640	505676.7791	-0.0151	0.1000
154.	47	15	505682.3700	505682.3606	0.0094	0.1000
155.	47	16	505688.3130	505688.3278	-0.0148	0.1000
156.	47	17	505694.7730	505694.6809	0.0921	0.1000
157.	47	18	505701.2920	505701.4199	-0.1279	0.2000
158.	47	19	505708.5060	505708.5450	-0.0390	0.1000
159.	47	20	505716.0660	505716.0565	0.0095	0.1000
160.	47	21	505723.8880	505723.9545	-0.0665	0.1000
161.	47	22	505732.2390	505732.2392	-0.0002	0.1000
162.	47	23	505740.9520	505740.9108	0.0412	0.1000
163.	47	24	505750.0080	505749.9695	0.0385	0.1000
164.	47	25	505759.4650	505759.4156	0.0494	0.1000
165.	47	26	505769.2340	505769.2493	-0.0153	0.1000
166.	47	27	505779.4120	505779.4707	-0.0587	0.1000
167.	47	28	505790.1280	505790.0803	0.0477	0.1000
168.	47	29	505801.2110	505801.0782	0.1328	0.2000
169.	47	30	505812.4240	505812.4647	-0.0407	0.1000

$\Sigma = 0.076751, 169$ Transitions in fit, $\Sigma.w = 0.837245, 163$ Degrees of freedom

Spectrum in the state $v(A)$

The state indicated by $v_A(E)$ corresponds to the lowest excited non degenerate vibrational state, with an energy 524 cm^{-1} . The population of this state at 298 K has enough population

($\approx 8\%$) relative to ground state to observe the signals. This state shows the characteristic intensity pattern of non-degenerate state in its K structure.

Table 2. Correlation coefficients of obtained parameters for $(\text{CH}_2\text{O})_3$ in ground state.

	B	DJ	DJK	HJ	HJK	HKJ
B	1.0000					
DJ	0.5320	1.0000				
DJK	0.1046	-0.6021	1.0000			
HJ	0.3919	0.9494	-0.6136	1.0000		
HJK	0.0404	-0.5176	0.7276	-0.6960	1.0000	
HKJ	0.1470	-0.2333	0.6831	-0.0985	0.0423	1.0000

The frequencies of Refs^{2,8} were mixed together in order to obtain improved constants. The rotational and quartic constants were obtained with good agreement with previous work. It should be noticed that the distortion constants obtained are different from those of the ground state. The H_J , H_{J_K} , H_{KJ} centrifugal distortions constants are not obtained by these available data. The results of refinements are listed in Tables 3, 4 and derived parameters are given in Table 5.

Table 3. Results of refinement of observed frequencies for $(\text{CH}_2\text{O})_3$ in $\nu(\text{A})$ state.

	J	K	Observed/MHz	Calc/MHz	Obs-Calc/MHz	Error/MHz
1.	0	0	10520.4000	10520.4497	-0.0497	0.6000
2.	1	0	21040.9000	21040.8688	0.0312	0.6000
3.	1	1	21040.9000	21040.8763	0.0237	0.6000
4.	2	0	31561.0000	31561.2269	-0.2269	0.5000
5.	2	1	31561.0000	31561.2382	-0.2382	0.5000
6.	2	2	31561.0000	31561.2720	-0.2720	0.5000
7.	3	0	42081.5400	42081.4935	0.0465	0.0300
8.	3	1	42081.5400	42081.5085	0.0315	0.0300
9.	3	2	42081.5400	42081.5536	-0.0136	0.0300
10.	3	3	42081.5400	42081.6287	-0.0887	0.0300
11.	5	0	63121.7300	63121.6298	0.1002	0.0400
12.	5	1	63121.7300	63121.6523	0.0777	0.0400
13.	5	2	63121.7300	63121.7200	0.0100	0.0400
14.	5	3	63121.7300	63121.8327	-0.1027	0.0400
15.	5	5	63122.2300	63122.1934	0.0366	0.0400
16.	6	0	73641.4700	73641.4385	0.0315	0.0400
17.	6	1	73641.4700	73641.4648	0.0052	0.0400
18.	6	2	73641.4700	73641.5437	-0.0737	0.0400
19.	6	3	73641.4700	73641.6752	-0.2052	0.3000
20.	6	4	73641.7800	73641.8594	-0.0794	0.0400
21.	6	5	73642.0800	73642.0961	-0.0161	0.0400
22.	6	6	73642.3800	73642.3855	-0.0055	0.0400
23.	9	0	105199.5400	105199.4607	0.0793	0.0800
24.	9	1	105199.5400	105199.4983	0.0417	0.0800
25.	9	2	105199.5400	105199.6110	-0.0710	0.0800
26.	9	3	105199.5400	105199.7989	-0.2589	0.3000
27.	9	5	105200.4000	105200.4001	-0.0001	0.0800
28.	9	6	105200.8100	105200.8135	-0.0035	0.0800
29.	9	7	105201.3000	105201.3020	-0.0020	0.0800
30.	9	8	105201.8800	105201.8657	0.0143	0.0800
31.	9	9	105202.4900	105202.5046	-0.0146	0.0800
32.	10	0	115718.2500	115718.2317	0.0183	0.0800
33.	10	1	115718.2900	115718.2730	0.0170	0.0800
34.	10	2	115718.4200	115718.3970	0.0230	0.0800
35.	10	3	115718.6200	115718.6037	0.0163	0.0800

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36.	10	4	115718.9100	115718.8931	0.0169	0.0800
37.	10	5	115719.2800	115719.2651	0.0149	0.0800
38.	10	6	115719.7400	115719.7198	0.0202	0.0800
39.	10	7	115720.2700	115720.2572	0.0128	0.0800
40.	10	8	115720.8900	115720.8772	0.0128	0.0800
41.	10	9	115721.5900	115721.5800	0.0100	0.0800
42.	10	10	115722.3800	115722.3654	0.0146	0.0800
43.	12	0	136754.7900	136754.7360	0.0540	0.0800
44.	12	1	136754.7900	136754.7848	0.0052	0.0800
45.	12	2	136754.7900	136754.9314	-0.1414	0.1000
46.	12	3	136754.7900	136755.1756	-0.3856	0.3000
47.	12	5	136755.9200	136755.9573	-0.0373	0.0800
48.	12	6	136756.5200	136756.4947	0.0253	0.0800
49.	12	7	136757.1400	136757.1297	0.0103	0.0800
50.	12	8	136757.9100	136757.8625	0.0475	0.0800
51.	12	9	136758.7300	136758.6930	0.0370	0.0800
52.	12	10	136759.6000	136759.6212	-0.0212	0.0800
53.	12	11	136760.6600	136760.6471	0.0129	0.0800
54.	12	12	136761.7300	136761.7707	-0.0407	0.0800
55.	33	8	357503.9440	357503.7046	0.2394	0.2000
56.	33	9	357505.9160	357505.8767	0.0393	0.1000
57.	33	10	357508.3580	357508.3043	0.0537	0.1000
58.	33	11	357510.8420	357510.9874	-0.1454	0.1000
59.	33	12	357513.8570	357513.9261	-0.0691	0.1000
60.	33	13	357517.0790	357517.1203	-0.0413	0.1000
61.	33	14	357520.5030	357520.5700	-0.0670	0.1000
62.	33	15	357524.2230	357524.2753	-0.0523	0.1000
63.	33	16	357528.2990	357528.2361	0.0629	0.1000
64.	33	17	357532.4920	357532.4524	0.0396	0.1000
65.	33	18	357536.9460	357536.9243	0.0217	0.1000
66.	33	19	357541.5490	357541.6517	-0.1027	0.1000
67.	33	20	357546.6730	357546.6347	0.0383	0.1000
68.	33	21	357551.8580	357551.8732	-0.0152	0.1000
69.	33	22	357557.5270	357557.3672	0.1598	0.1000
70.	33	23	357563.1860	357563.1167	0.0693	0.1000
71.	33	24	357569.1400	357569.1218	0.0182	0.1000
72.	33	25	357575.6220	357575.3825	0.2395	0.3000
73.	33	26	357581.8790	357581.8986	-0.0196	0.1000
74.	33	27	357588.7540	357588.6703	0.0837	0.1000
75.	33	28	357595.6840	357595.6976	-0.0136	0.1000
76.	33	29	357602.9470	357602.9804	-0.0334	0.1000
77.	33	30	357610.4250	357610.5187	-0.0937	0.1000
78.	33	31	357618.0960	357618.3125	-0.2165	0.3000

Σ = 0.103990, 78 Transitions in fit, $\Sigma.w$ = 0.903378, 75 Degrees of freedom

Table 4. Correlation coefficients of obtained parameters for (CH₂O)₃ in v(A) state.

	B	DJ	DJK
B	1.0000		
DJ	0.6920	1.0000	
DJK	-0.0099	-0.6197	1.0000

Table 5. Results of refinement of observed frequencies for (CH₂O)₃ in ground and $\nu(A) = 1$ states.

Parameter	G.S. (Ref ⁸ .)	G.S. this work	$\nu(A) = 1$ (Ref ⁸)	$\nu(A) = 1$ (this work)
C _v /MHz	2950*	2950*	2950*	2950*
B _v /MHz	5273.257670(207)	5273.25747 (27)	5260.22746 (99)	5260.22737 (49)
D _J /kHz	1.34622 (34)	1.34547 (38)	1.27160 (48)	1.27171 (32)
D _{JK} /kHz	-2.02435 (155)	-2.0206 (20)	-1.87820 (97)	-1.8789 (11)
H _J /mHz	1.189 (100)	1.01 (10)	-	-
H _{JK} /mHz	-4.30 (40)	-3.80 (45)	-	-
H _{KJ} /mHz	3.12 (101)	4.1 (11)	-	-

*constrained at this value

Spectrum in the $\nu_1(E) = 1$ state

The $\nu_1(E)$ and $\nu_2(E)$ degenerate modes are at 307 cm⁻¹ and 472 cm⁻¹. These two vibrations come from the COC and OCO bending vibration. These have populations at 298 K relative to the ground state of ($\approx 22.7\%$) and ($\approx 10\%$) respectively.

The theory for the rotational spectrum of an E degenerate vibrational state of a C_{3v} molecule is well known⁹. Essentially the two components of the vibration each give rise to a series of K levels which are coupled to each other by *l*-resonance. This results in two series of transitions which are best labeled by the pseudo-quantum number K_l-1. The *l*-resonance splitting is greatest for levels with low values of this label. Perturbation theory yields the approximate frequency expression

$$\nu = \frac{(q_l^+)^2 (J+1)[(J+1)^2 - (K_l-1)^2]}{4(B-C+C\zeta_l)(K_l-1)} \quad \text{when } (K_l-1) \neq 0 \quad (4)$$

where q_l^+ is the *l*-type doubling constant, B and C are rotational constants, and ζ_l is the z-coriolis constant for the vibrational state ν_l . The degree of *l*-resonance thus largely depends on the ratio of q_l^+ to the resonance denominator $(B-C+C\zeta_l)$. With low to moderate values of this denominator, the spectrum usually found consists of two extreme outer lines for K_l-1 = 0 (the *l*-doublets) and a center group of lines for K_l-1 $\neq 0$ whose structure depends very strongly on other parameters such as the centrifugal distortion constants. As the strength of the resonance increases, the lines of the center group spread out until the low |K_l-1| transitions approach the positions of the *l*-doublets.

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 energy¹¹⁻¹⁸. The Hamiltonian was set up for a symmetric top molecule like (CH₂O)₃. This rotation-vibrational Hamiltonian has two different blocks that belong to the different $l = +1$ and $l = -1$ series Figure 1. K and *l* are no longer good quantum numbers, but (K - *l*) or (K_l - 1) may be used to distinguish between the symmetry species. Those levels with (K_l - 1) = 3n, where n is an integer, are of species A₁ or A₂. If (K_l - 1) $\neq 3n$ the species are E. The q_l^+ produces a first order splitting of the (K_l-1) = 0, A₁A₂ pair, which are the familiar *l*-doublets, as shown by Grenier-Besson and Amat⁹. 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.

Figure 1. The Hamiltonian matrix for $v_t 1$ state, $J = 3$.

The diagonal matrix elements are given by:

$$\begin{aligned}
 \langle J, l, K | \hat{H} | J, l, K \rangle = & CK^2 + B[J(J+1) - K^2] - D_J J^2(J+1)^2 \\
 & - D_{JK} J(J+1)K^2 - D_K K^4 + H_J J^3(J+1)^3 \\
 & + H_{JK} J^2(J+1)^2 K^2 + H_{KJ} J(J+1)K^4 \\
 & + H_K K^6 - 2C\zeta Kl + \eta_J J(J+1)Kl + \eta_K K^3 l \\
 & + \eta_{JJ} J^2(J+1)^2 Kl + \eta_{JK} J(J+1)K^3 l + \eta_{KK} K^5 l \\
 & \text{and} \quad 4q_l^+ = q_v
 \end{aligned} \quad (5)$$

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

$$\begin{aligned}
 \langle J, l, K | \hat{H} | J, l \pm 2, K \pm 2 \rangle = & \frac{1}{4} [q_v - q_J J(J+1)] \{ [J(J+1) - K(K \pm 1)] \\
 & \times [J(J+1) - (K \pm 1)(K \pm 2)] [(v+1)^2 - (l \pm 1)^2] \}^{1/2}
 \end{aligned} \quad (6)$$

$$\text{and } \langle v_t, l, J, K | \hat{H} | v_t, l \pm 2, J, K \mp 1 \rangle = -r_l [(v_t + 1)^2 - (l \pm 1)^2]^{1/2} [J(J+1) - K(K \mp 1)]^{1/2} (2K \mp 1) \quad (7)$$

and hence, the lines can be assigned.

The 273 frequencies of Refs^{2,3-8} for this state were mixed together in order to improve the accuracy of the parameters in this state, then a weighted least-squares method¹⁰ was used to fit these frequencies to Eq(5), 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. Some of the lines have uncertainty between 0.2 to 0.5 MHz due to overlapping or blending lines. The fit to the transitions are given in Tables 6,7 and the constants obtained are given in Table 10.

Table 6. Results of Refinement of Observed Frequencies for (CH₂O)₃ in $\nu_1(\text{E}) = 1$ State.

	J	K l-1	K l sym	Observed/MHz	Obs-Calc/MHz	Error/MHz
1.	2	0	1, 1 A+	31633.1000	0.9904	0.5000
2.	2	1	2, 1 E	31609.4000	0.8393	0.5000
3.	2	-1	0, 1 E	31609.4000	0.3956	0.5000
4.	2	-2	1, -1 E	31609.4000	0.5439	0.5000
5.	2	-3	2, -1 A+	31609.4000	0.5777	0.5000
6.	3	-1	0, 1 E	42145.4300	-0.0396	0.1000
7.	3	1	2, 1 E	42144.2800	-0.0362	0.1000
8.	3	2	3, 1 E	42144.7100	-0.0411	0.1000
9.	4	-1	0, 1 E	52682.0200	-0.0261	0.0600
10.	4	-2	1, -1 E	52681.2000	-0.1980	0.0600
11.	4	-3	2, -1 A+	52681.2000	-0.0079	0.0600
12.	4	-4	3, -1 E	52681.2000	0.0374	0.0600
13.	4	-5	4, -1 E	52681.2000	0.0006	0.0600
14.	4	1	2, 1 E	52679.7200	0.0179	0.0600
15.	4	2	3, 1 E	52680.4600	-0.0111	0.0600
16.	4	3	4, 1 A+	52680.8400	-0.0227	0.0600
17.	-5	0	-1, -1 A-	63169.9700	-0.0246	0.1000
18.	5	-1	0, 1 E	63218.7600	-0.0011	0.1000
19.	5	-2	1, -1 E	63217.6700	0.0163	0.1000
20.	5	0	1, 1 A+	63263.3700	0.0251	0.1000
21.	5	1	2, 1 E	63214.6200	-0.0068	0.1000
22.	5	2	3, 1 E	63215.8800	0.0007	0.1000
23.	5	3	4, 1 A+	63216.4500	-0.0095	0.1000
24.	5	4	5, 1 E	63216.8700	-0.0376	0.1000
25.	-6	0	-1, -1 A-	73697.8700	0.0305	0.0300
26.	6	-1	0, 1 E	73755.7000	0.0590	0.0300
27.	6	-2	1, -1 E	73753.9400	0.0440	0.0300
28.	6	-3	2, -1 A+	73753.1600	-0.1894	0.0300
29.	6	-4	3, -1 E	73753.1600	0.0144	0.0300
30.	6	-5	4, -1 E	73753.1600	0.0472	0.0300
31.	6	-6	5, -1 A+	73753.1600	-0.0339	0.0300
32.	6	-7	6, -1 E	73753.1600	-0.2041	0.0900
33.	6	0	1, 1 A+	73806.7900	0.0455	0.0300
34.	6	1	2, 1 E	73749.0400	0.0406	0.0300
35.	6	2	3, 1 E	73750.9600	0.0463	0.0300
36.	6	3	4, 1 A+	73751.7400	-0.0025	0.0300
37.	6	4	5, 1 E	73752.3400	-0.0013	0.0300
38.	6	5	6, 1 E	73752.7700	-0.1118	0.0300
39.	-9	0	-1, -1 A-	105279.8900	-0.0050	0.0600
40.	9	-1	0, 1 E	105367.5100	0.0061	0.0600
41.	9	-2	1, -1 E	105362.5000	-0.0158	0.0600
42.	9	-3	2, -1 A+	105360.8900	0.0017	0.0600
43.	9	-4	3, -1 E	105360.1800	0.0078	0.0600
44.	9	-5	4, -1 E	105359.8200	-0.0501	0.0600
45.	9	-6	5, -1 A+	105359.8200	0.0045	0.0600
46.	9	-7	6, -1 E	105360.1800	0.2430	0.0600
47.	9	-8	7, -1 E	105360.1800	-0.0188	0.0600
48.	9	-9	8, -1 A+	105360.8900	0.3091	0.0600
49.	9	0	1, 1 A+	105435.4300	-0.0236	0.0600
50.	9	1	2, 1 E	105347.8900	-0.0353	0.0600
51.	9	2	3, 1 E	105353.1900	0.0347	0.0600
52.	9	3	4, 1 A+	105355.2200	0.0342	0.0600
53.	9	4	5, 1 E	105356.4700	0.0038	0.0600
54.	9	5	6, 1 E	105357.4800	-0.0138	0.0600
55.	9	6	7, 1 A+	105358.4000	-0.0352	0.0600
56.	9	7	8, 1 E	105359.3200	-0.0416	0.0600
57.	9	8	9, 1 E	105360.1800	-0.1291	0.0600

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58.	-10	0	-1, -1	A-	115806.5600	-0.0867	0.0600
59.	10	-1	0, 1	E	115905.3100	0.0491	0.0600
60.	10	-2	1, -1	E	115898.6200	-0.0554	0.0600
61.	10	-3	2, -1	A+	115896.5100	0.0050	0.0600
62.	10	-4	3, -1	E	115895.5700	0.0444	0.0600
63.	10	-5	4, -1	E	115894.9200	-0.1579	0.0600
64.	10	-6	5, -1	A+	115894.9200	-0.0208	0.0600
65.	10	-7	6, -1	E	115894.9200	-0.0994	0.0600
66.	10	0	1, 1	A+	115977.7700	0.0179	0.0600
67.	10	1	2, 1	E	115879.1600	-0.0666	0.0600
68.	10	2	3, 1	E	115886.1200	0.0419	0.0600
69.	10	3	4, 1	A+	115888.7200	0.0281	0.0600
70.	10	4	5, 1	E	115890.2800	-0.0120	0.0600
71.	10	5	6, 1	E	115891.5400	0.0022	0.0600
72.	10	6	7, 1	A+	115892.6600	0.0097	0.0600
73.	10	7	8, 1	E	115893.6800	-0.0445	0.0600
74.	10	8	9, 1	E	115894.9200	0.1120	0.0600
75.	-11	0	-1, -1	A-	126333.0100	-0.0347	0.0600
76.	11	-1	0, 1	E	126443.3800	0.1094	0.0600
77.	11	-2	1, -1	E	126434.7100	-0.0942	0.0600
78.	11	-3	2, -1	A+	126431.9100	-0.0754	0.0600
79.	11	-4	3, -1	E	126430.8300	0.1413	0.0600
80.	11	-5	4, -1	E	126430.0200	-0.0428	0.0600
81.	11	-6	5, -1	A+	126430.0200	0.1987	0.0600
82.	11	-7	6, -1	E	126430.0200	0.1787	0.0600
83.	11	-8	7, -1	E	126430.0200	-0.0409	0.0600
84.	11	0	1, 1	A+	126519.6600	-0.0344	0.0600
85.	11	1	2, 1	E	126409.5500	-0.0152	0.0600
86.	11	2	3, 1	E	126418.3100	-0.0118	0.0600
87.	11	3	4, 1	A+	126421.8000	0.1757	0.0600
88.	11	4	5, 1	E	126423.6900	0.0919	0.0600
89.	11	5	6, 1	E	126425.1500	0.0553	0.0600
90.	11	6	7, 1	A+	126426.4500	0.0497	0.0600
91.	11	7	8, 1	E	126427.6800	0.0421	0.0600
92.	11	8	9, 1	E	126428.8500	-0.0192	0.0600
93.	11	9	10, 1	A+	126430.0200	-0.1086	0.0600
94.	-12	0	-1, -1	A-	136859.0600	0.0030	0.1000
95.	12	-1	0, 1	E	136981.5000	-0.0331	0.1000
96.	12	-2	1, -1	E	136970.8300	-0.0662	0.1000
97.	12	-3	2, -1	A+	136967.3000	-0.0163	0.1000
98.	12	-4	3, -1	E	136965.5600	-0.0840	0.1000
99.	12	-5	4, -1	E	136964.8900	0.0857	0.1000
100.	12	-9	8, -1	A+	136964.8900	-0.0409	0.1000
101.	12	-11	10, -1	E	136966.2500	0.0939	0.1000
102.	12	-13	12, -1	E	136968.0700	0.1326	0.1000
103.	12	0	1, 1	A+	137061.2300	-0.0180	0.1000
104.	12	1	2, 1	E	136938.9100	0.0334	0.1000
105.	12	2	3, 1	E	136949.8300	0.0021	0.1000
106.	12	3	4, 1	A+	136953.9200	-0.0118	0.1000
107.	12	4	5, 1	E	136956.3300	-0.0077	0.1000
108.	12	5	6, 1	E	136958.1300	0.0094	0.1000
109.	12	6	7, 1	A+	136959.6600	0.0170	0.1000
110.	12	7	8, 1	E	136961.0700	0.0089	0.1000
111.	12	8	9, 1	E	136962.4600	0.0069	0.1000
112.	12	9	10, 1	A+	136963.8300	-0.0326	0.1000
113.	14	-1	0, 1	E	158058.6100	-0.1574	0.1000
114.	14	-2	1, -1	E	158042.8500	-0.0887	0.1000
115.	14	-11	10, -1	E	158034.0100	-0.1108	0.1000
116.	14	-13	12, -1	E	158036.0800	0.0216	0.1000

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117.	14	1	2, 1	E	157994.2600	0.0513	0.1000
118.	14	2	3, 1	E	158010.5300	0.1299	0.1000
119.	14	3	4, 1	A+	158016.4700	0.0002	0.1000
120.	14	4	5, 1	E	158019.9900	0.0590	0.1000
121.	14	5	6, 1	E	158022.4100	0.0066	0.1000
122.	14	6	7, 1	A+	158024.5300	0.0917	0.1000
123.	14	7	8, 1	E	158026.3500	0.0761	0.1000
124.	14	8	9, 1	E	158028.0200	-0.0098	0.1000
125.	14	9	10, 1	A+	158029.7500	-0.0228	0.1000
126.	14	10	11, 1	E	158031.5200	-0.0229	0.1000
127.	14	11	12, 1	E	158033.4700	0.1043	0.1000
128.	15	-1	0, 1	E	168597.6800	-0.0062	0.0900
129.	15	-2	1, -1	E	168578.8400	-0.0288	0.0900
130.	15	-3	2, -1	A+	168572.2300	-0.0408	0.0900
131.	15	-4	3, -1	E	168569.0500	-0.0321	0.0900
132.	15	-5	4, -1	E	168567.4000	0.0378	0.0900
133.	15	-6	5, -1	A+	168566.3900	-0.0569	0.0900
134.	15	-7	6, -1	E	168565.9900	-0.0584	0.0900
135.	15	-9	8, -1	A+	168566.3900	0.1033	0.0900
136.	15	-10	9, -1	E	168566.8100	0.0159	0.0900
137.	15	-11	10, -1	E	168567.8700	0.3566	0.0900
138.	15	0	1, 1	A+	168683.2900	0.0368	0.0900
139.	15	1	2, 1	E	168520.1500	-0.0033	0.0900
140.	15	2	3, 1	E	168539.3600	0.0024	0.0900
141.	15	3	4, 1	A+	168546.5800	-0.0205	0.0900
142.	15	4	5, 1	E	168550.6900	-0.0021	0.0900
143.	15	5	6, 1	E	168553.5300	-0.0428	0.0900
144.	15	6	7, 1	A+	168555.8900	-0.0169	0.0900
145.	15	7	8, 1	E	168558.0100	0.0278	0.0900
146.	15	8	9, 1	E	168559.9500	0.0066	0.0900
147.	15	9	10, 1	A+	168561.8500	-0.0213	0.0900
148.	15	10	11, 1	E	168563.8300	0.0156	0.0900
149.	15	11	12, 1	E	168565.9900	0.1862	0.0900
150.	15	12	13, 1	A+	168567.8700	0.0100	0.0900
151.	15	13	14, 1	E	168570.0100	0.0126	0.0900
152.	18	-1	0, 1	E	200214.9700	-0.0957	0.1000
153.	18	-2	1, -1	E	200186.0400	-0.0776	0.1000
154.	18	-3	2, -1	A+	200175.4500	0.1070	0.1000
155.	18	-4	3, -1	E	200170.0300	0.0422	0.1000
156.	18	-5	4, -1	E	200166.9300	-0.0502	0.1000
157.	18	-6	5, -1	A+	200165.1000	-0.1419	0.1000
158.	18	-11	10, -1	E	200165.1000	0.0901	0.1000
159.	18	0	1, 1	A+	200300.4000	-0.1948	0.1000
160.	18	1	2, 1	E	200090.8000	-0.1102	0.1000
161.	18	2	3, 1	E	200120.1800	-0.1378	0.1000
162.	18	3	4, 1	A+	200131.7500	-0.1082	0.1000
163.	18	4	5, 1	E	200138.1900	-0.0956	0.1000
164.	18	5	6, 1	E	200142.5900	-0.0816	0.1000
165.	18	6	7, 1	A+	200146.0700	-0.0248	0.1000
166.	18	7	8, 1	E	200148.9300	-0.0977	0.1000
167.	18	8	9, 1	E	200151.6400	-0.0697	0.1000
168.	18	9	10, 1	A+	200154.2700	-0.0044	0.1000
169.	18	10	11, 1	E	200156.7800	-0.0226	0.1000
170.	18	11	12, 1	E	200159.3500	0.0042	0.1000
171.	18	12	13, 1	A+	200161.8700	-0.0684	0.1000
172.	19	-2	1, -1	E	210721.5900	-0.0290	0.1000
173.	19	1	2, 1	E	210612.1800	0.0236	0.1000
174.	19	2	3, 1	E	210645.1500	-0.0364	0.1000
175.	19	3	4, 1	A+	210658.4400	0.0291	0.1000

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176.	19	4	5, 1	E	210665.8300	0.0592	0.1000
177.	19	5	6, 1	E	210670.7500	-0.0081	0.1000
178.	19	6	7, 1	A+	210674.5800	-0.0330	0.1000
179.	19	7	8, 1	E	210677.8900	0.0081	0.1000
180.	19	8	9, 1	E	210680.8600	0.0180	0.1000
181.	19	9	10, 1	A+	210683.6700	0.0212	0.1000
182.	19	10	11, 1	E	210686.4300	0.0339	0.1000
183.	19	12	13, 1	A+	210691.8900	-0.0415	0.1000
184.	20	-1	0, 1	E	221293.1000	-0.0078	0.1000
185.	20	-2	1, -1	E	221256.9000	-0.0530	0.1000
186.	20	-4	3, -1	E	221235.5300	-0.0596	0.1000
187.	20	-8	7, -1	E	221226.8500	-0.0112	0.1000
188.	20	-16	15, -1	E	221234.5500	-0.0291	0.1000
189.	20	1	2, 1	E	221132.2400	-0.0290	0.1000
190.	20	2	3, 1	E	221168.8900	-0.0416	0.1000
191.	20	3	4, 1	A+	221183.9900	0.0339	0.1000
192.	20	4	5, 1	E	221192.3000	-0.0265	0.1000
193.	20	5	6, 1	E	221197.9700	0.0030	0.1000
194.	20	6	7, 1	A+	221202.3000	0.0099	0.1000
195.	20	7	8, 1	E	221205.9100	-0.0118	0.1000
196.	20	8	9, 1	E	221209.1700	-0.0107	0.1000
197.	20	9	10, 1	A+	221212.2500	0.0044	0.1000
198.	20	10	11, 1	E	221215.2400	0.0152	0.1000
199.	20	11	12, 1	E	221218.1200	-0.0673	0.1000
200.	20	12	13, 1	A+	221221.1100	-0.0695	0.1000
201.	20	13	14, 1	E	221224.2500	0.0167	0.1000
202.	20	16	17, 1	E	221233.9200	-0.0459	0.1000
203.	20	17	18, 1	E	221237.4000	-0.0440	0.1000
204.	20	18	19, 1	A+	221241.3200	0.2665	0.2000
205.	33	0	-1, -1	A-	357759.3130	0.0597	0.1000
206.	33	-1	0, 1	E	358241.9330	-0.0396	0.1000
207.	33	-2	1, -1	E	358180.2230	-0.2406	0.2000
208.	33	-3	2, -1	A+	358140.4610	0.1746	0.1000
209.	33	-6	5, -1	A+	358088.1720	-0.2358	0.2000
210.	33	-20	19, -1	E	358086.3590	-0.0035	0.1000
211.	33	-24	23, -1	A+	358104.9830	-0.0083	0.1000
212.	33	-28	27, -1	E	358128.8060	-0.1278	0.1000
213.	33	-29	28, -1	E	358135.5920	-0.1129	0.1000
214.	33	-30	29, -1	A+	358142.8500	0.0678	0.1000
215.	33	-32	31, -1	E	358157.7580	-0.0856	0.1000
216.	33	-33	32, -1	A+	358165.8520	0.0294	0.1000
217.	33	-34	33, -1	E	358174.0520	-0.0455	0.1000
218.	33	0	1, 1	A+	358286.6760	-0.0683	0.1000
219.	33	1	2, 1	E	357804.3270	0.0279	0.1000
220.	33	2	3, 1	E	357866.4550	-0.1754	0.1000
221.	33	3	4, 1	A+	357908.2650	0.0870	0.1000
222.	33	4	5, 1	E	357935.0730	0.0606	0.1000
223.	33	5	6, 1	E	357953.6470	0.0507	0.1000
224.	33	6	7, 1	A+	357967.5860	0.1292	0.1000
225.	33	7	8, 1	E	357978.5390	0.0571	0.1000
226.	33	8	9, 1	E	357987.6650	-0.0713	0.1000
227.	33	9	10, 1	A+	357995.8200	-0.0361	0.1000
228.	33	10	11, 1	E	358003.2790	0.0373	0.1000
229.	33	11	12, 1	E	358010.2110	0.0548	0.1000
230.	33	12	13, 1	A+	358016.8310	0.0517	0.1000
231.	33	13	14, 1	E	358023.2310	-0.0066	0.1000
232.	33	14	15, 1	E	358029.5210	-0.1018	0.1000
233.	33	15	16, 1	A+	358035.7780	-0.2247	0.1000
234.	33	16	17, 1	E	358042.1640	-0.2648	0.2000

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235.	33	17	18, 1	E	358048.9340	-0.0065	0.1000
236.	33	18	19, 1	A+	358055.3020	-0.2668	0.2000
237.	33	19	20, 1	E	358062.3520	0.0137	0.1000
238.	33	25	26, 1	E	358106.8560	0.0522	0.1000
239.	33	28	29, 1	E	358131.9190	-0.0264	0.1000
240.	33	31	32, 1	E	358159.3540	0.1248	0.1000
241.	33	32	33, 1	E	358168.9010	0.0854	0.1000
242.	-37	0	-1, -1	A-	399789.9470	0.0126	0.1000
243.	37	-1	0, 1	E	400344.0520	0.0653	0.1000
244.	37	-5	4, -1	E	400188.7150	0.2844	0.2000
245.	37	-18	17, -1	A+	400153.3770	0.0061	0.1000
246.	37	-25	24, -1	E	400186.6660	0.0127	0.1000
247.	37	-29	28, -1	E	400214.4060	0.1737	0.1000
248.	37	-31	30, -1	E	400230.1030	-0.0471	0.1000
249.	37	-35	34, -1	E	400266.0210	-0.0565	0.1000
250.	37	0	1, 1	A+	400379.1290	0.0751	0.1000
251.	37	1	2, 1	E	399825.2700	-0.0379	0.1000
252.	37	2	3, 1	E	399885.1330	0.0835	0.1000
253.	37	3	4, 1	A+	399931.9780	0.1275	0.1000
254.	37	4	5, 1	E	399964.4460	-0.1936	0.1000
255.	37	5	6, 1	E	399988.2770	0.0611	0.1000
256.	37	6	7, 1	A+	400006.2420	0.1733	0.1000
257.	37	7	8, 1	E	400020.3600	0.0508	0.1000
258.	37	8	9, 1	E	400032.1790	-0.0301	0.1000
259.	37	9	10, 1	A+	400042.4680	-0.0919	0.1000
260.	37	10	11, 1	E	400051.7760	-0.0965	0.1000
261.	37	11	12, 1	E	400060.5040	0.0147	0.1000
262.	37	12	13, 1	A+	400068.6210	-0.0260	0.1000
263.	37	13	14, 1	E	400076.4680	-0.0460	0.1000
264.	37	14	15, 1	E	400084.3730	0.1599	0.1000
265.	37	15	16, 1	A+	400091.8470	0.0111	0.1000
266.	37	16	17, 1	E	400099.3460	-0.1061	0.1000
267.	37	17	18, 1	E	400106.9030	-0.2124	0.2000
268.	37	18	19, 1	A+	400114.7220	-0.1459	0.1000
269.	37	19	20, 1	E	400122.6480	-0.0953	0.1000
270.	37	20	21, 1	E	400130.7950	0.0265	0.1000
271.	37	21	22, 1	A+	400139.0340	0.0685	0.1000
272.	37	29	30, 1	E	400212.3580	-0.0204	0.1000
273.	37	31	32, 1	E	400233.3330	0.1130	0.1000

$\text{Sigma} = 0.131052$, 273 Transitions in fit, $\text{Sigma.w} = 1$, 132693, 266 Degrees of freedom.

Table 7. Correlation coefficients of obtained parameters for $(\text{CH}_2\text{O})_3$ in $v_1(\text{E}) = 1$ state.

	B	DJ	DJK	Azeta	nJ	qv	qj
B	1.0000						
DJ	0.6864	1.0000					
DJK	0.0049	-0.5200	1.0000				
Azeta	0.0118	0.2908	-0.2256	1.0000			
nJ	-0.0754	0.0841	-0.1657	-0.1507	1.0000		
qv	0.0304	0.1418	-0.1071	0.5186	0.0021	1.0000	
qj	0.0541	0.1450	-0.1033	0.0768	0.0405	0.7905	1.0000

Spectrum in $v_2(\text{E}) = 1$ state

This state shows the characteristic intensity pattern of doubly degenerate state in its k structure as $v_1(\text{E}) = 1$ state. This state has enough population ($\approx 10\%$) relative to ground state to observe the signals.

The frequencies of Refs^{2,3,8} were mixed together in order to obtain improved constants. The results of refinements are listed in Tables 8, 9 and derived parameters are given in Table 10. The H_J , H_{Jk} , H_{kj} , H_k centrifugal distortions constants are not obtained with these available data.

Table 8. Results of refinement of observed frequencies for $(CH_2O)_3$ in $v_2(E) = 1$ state.

	J	K l -1	K l	sym	Observed/MHz	Obs-Calc/MHz	Error/MHz
1.	1	-1	0, 1	E	21108.3000	-0.0562	0.6000
2.	1	-2	1, -1	E	21108.3000	0.5818	0.6000
3.	2	-2	1, -1	E	31661.9000	-0.4152	0.6000
4.	2	-3	2, -1	A+	31661.9000	0.3528	0.6000
5.	5	-1	0, 1	E	63344.0400	-0.0145	0.0400
6.	5	-2	1, -1	E	63332.5000	-0.0012	0.0400
7.	5	-3	2, -1	A+	63328.0700	-0.0212	0.0400
8.	5	-4	3, -1	E	63325.6400	0.0048	0.0400
9.	5	-5	4, -1	E	63324.0400	0.0349	0.0400
10.	5	-6	5, -1	A+	63322.8300	0.0139	0.0400
11.	5	1	2, 1	E	63300.0500	-0.0170	0.0400
12.	5	2	3, 1	E	63311.7700	-0.0001	0.0400
13.	5	3	4, 1	A+	63316.4400	0.0102	0.0400
14.	5	4	5, 1	E	63319.2300	-0.0053	0.0400
15.	-6	0	-1, -1	A-	73784.2100	-0.0059	0.0400
16.	6	-1	0, 1	E	73909.2800	0.0348	0.0400
17.	6	-2	1, -1	E	73892.1700	-0.0266	0.0400
18.	6	-3	2, -1	A+	73885.5600	0.0170	0.0400
19.	6	-4	3, -1	E	73881.8500	-0.0317	0.0400
20.	6	-5	4, -1	E	73879.4700	-0.0220	0.0400
21.	6	-6	5, -1	A+	73877.7500	-0.0259	0.0400
22.	6	-7	6, -1	E	73876.4600	-0.0128	0.0400
23.	6	0	1, 1	A+	73966.2100	0.0124	0.0400
24.	6	1	2, 1	E	73841.2200	-0.0066	0.0400
25.	6	2	3, 1	E	73858.4800	0.0300	0.0400
26.	6	3	4, 1	A+	73865.4100	0.0152	0.0400
27.	6	4	5, 1	E	73869.4600	-0.0039	0.0400
28.	6	5	6, 1	E	73872.3800	0.0021	0.0400
29.	-9	0	-1, -1	A-	105403.2700	-0.0179	0.0800
30.	9	-1	0, 1	E	105616.2300	-0.0182	0.0800
31.	9	-2	1, -1	E	105581.8900	-0.0235	0.0800
32.	9	-3	2, -1	A+	105565.5600	-0.0277	0.0800
33.	9	-4	3, -1	E	105556.3100	-0.0213	0.0800
34.	9	-5	4, -1	E	105550.3600	0.0212	0.0800
35.	9	-6	5, -1	A+	105546.0800	-0.0310	0.0800
36.	9	-7	6, -1	E	105542.9600	0.0040	0.0800
37.	9	-8	7, -1	E	105540.5300	0.0161	0.0800
38.	9	0	1, 1	A+	105663.1200	0.0118	0.0800
39.	9	1	2, 1	E	105450.2200	-0.0111	0.0800
40.	9	2	3, 1	E	105484.8100	-0.0055	0.0800
41.	9	3	4, 1	A+	105501.5600	0.0026	0.0800
42.	9	4	5, 1	E	105511.4100	0.0137	0.0800
43.	9	5	6, 1	E	105518.1600	0.0223	0.0800
44.	9	6	7, 1	A+	105523.2700	-0.0110	0.0800
45.	9	7	8, 1	E	105527.5600	0.0421	0.0800
46.	9	8	9, 1	E	105531.2400	0.0318	0.0800
47.	10	0	-1, -1	A-	115942.4000	0.0219	0.0800
48.	10	-1	0, 1	E	116186.6400	-0.0116	0.0800
49.	10	-2	1, -1	E	116148.4400	0.0415	0.0800
50.	10	-3	2, -1	A+	116128.3800	0.0380	0.0800
51.	10	-4	3, -1	E	116116.5700	-0.0644	0.0800
52.	10	-5	4, -1	E	116108.9500	-0.0378	0.0800
53.	10	-6	5, -1	A+	116103.6100	0.0269	0.0800

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54.	10	-7	6,-1	E	116099.5400	-0.0119	0.0800
55.	10	-8	7,-1	E	116096.4300	-0.0043	0.0800
56.	10	-9	8,-1	A+	116093.9800	0.0141	0.0800
57.	10	-10	9,-1	E	116092.0200	0.0358	0.0800
58.	10	0	1, 1	A+	116228.1100	-0.0007	0.0800
59.	10	1	2, 1	E	115983.9200	-0.0087	0.0800
60.	10	2	3, 1	E	116022.4800	0.0236	0.0800
61.	10	3	4, 1	A+	116043.1200	0.1494	0.0800
62.	10	4	5, 1	E	116055.2600	-0.0591	0.0800
63.	10	5	6, 1	E	116063.8600	0.0705	0.0800
64.	10	6	7, 1	A+	116070.2300	0.0289	0.0800
65.	10	7	8, 1	E	116075.4800	0.0577	0.0800
66.	10	8	9, 1	E	116079.9400	0.0270	0.0800
67.	10	9	10, 1	A+	116083.9300	-0.0077	0.0800
68.	-11	0	-1,-1	A-	126481.2200	0.1057	0.0800
69.	11	-1	0, 1	E	126756.6500	-0.0114	0.0800
70.	11	-2	1,-1	E	126716.0400	-0.0178	0.0800
71.	11	-3	2,-1	A+	126692.3800	-0.0197	0.0800
72.	11	-5	4,-1	E	126668.5400	-0.0240	0.0800
73.	11	-6	5,-1	A+	126661.9900	0.1744	0.0800
74.	11	-7	6,-1	E	126656.6600	-0.1131	0.0800
75.	11	-8	7,-1	E	126652.8500	-0.0207	0.0800
76.	11	-9	8,-1	A+	126649.7000	-0.0781	0.0800
77.	11	-10	9,-1	E	126647.2000	-0.0909	0.0800
78.	11	-11	10,-1	E	126645.2400	-0.0359	0.0800
79.	11	-12	11,-1	A+	126643.6700	0.0268	0.0800
80.	11	0	1, 1	A+	126792.7500	0.0106	0.0800
81.	11	1	2, 1	E	126517.2000	-0.0922	0.0800
82.	11	2	3, 1	E	126558.1800	-0.0154	0.0800
83.	11	3	4, 1	A+	126582.2700	-0.0828	0.0800
84.	11	4	5, 1	E	126597.5100	0.1200	0.0800
85.	11	5	6, 1	E	126607.7600	-0.0262	0.0800
86.	11	6	7, 1	A+	126615.5200	-0.1132	0.0800
87.	11	7	8, 1	E	126621.9700	-0.0038	0.0800
88.	11	8	9, 1	E	126627.3500	-0.0242	0.0800
89.	11	9	10, 1	A+	126632.1300	-0.0344	0.0800
90.	-12	0	-1,-1	A-	137019.4400	-0.0244	0.0800
91.	12	-1	0, 1	E	137325.9100	0.0196	0.0800
92.	12	-2	1,-1	E	137284.5000	0.0084	0.0800
93.	12	-3	2,-1	A+	137257.6800	0.0647	0.0800
94.	12	-4	3,-1	E	137240.6200	0.0398	0.0800
95.	12	-5	4,-1	E	137229.0200	-0.0583	0.0800
96.	12	-6	5,-1	A+	137220.8200	-0.0151	0.0800
97.	12	-7	6,-1	E	137214.6700	0.0193	0.0800
98.	12	-8	7,-1	E	137209.8700	0.0161	0.0800
99.	12	-9	8,-1	A+	137206.0300	-0.0156	0.0800
100.	12	-10	9,-1	E	137202.9700	-0.0057	0.0800
101.	12	-11	10,-1	E	137200.5000	0.0199	0.0800
102.	12	-12	11,-1	A+	137198.5000	0.0529	0.0800
103.	12	-13	12,-1	E	137196.8800	0.0820	0.0800
104.	12	0	1, 1	A+	137356.9300	-0.0304	0.0800
105.	12	1	2, 1	E	137050.6400	-0.0026	0.0800
106.	12	3	4, 1	A+	137119.8000	0.0169	0.0800
107.	12	4	5, 1	E	137137.5900	0.0144	0.0800
108.	12	5	6, 1	E	137150.0600	0.0089	0.0800
109.	12	6	7, 1	A+	137159.5100	0.0257	0.0800
110.	12	7	8, 1	E	137167.0400	-0.0351	0.0800
111.	12	8	9, 1	E	137173.4600	-0.0347	0.0800
112.	12	9	10, 1	A+	137179.1300	-0.0121	0.0800
113.	12	10	11, 1	E	137184.2500	-0.0175	0.0800
114.	12	11	12, 1	E	137189.0000	-0.0349	0.0800

$\Sigma = 0.089051$ 114 Transitions in fit, $\Sigma.w = 0.600169$, 107 Degrees of freedom

Table 9. Correlation coefficients of obtained parameters for $(\text{CH}_2\text{O})_3$ in $v_2(E) = 1$.

	B	DJ	DJK	Azeta	nJ	qv	qj
B	1.0000						
DJ	0.8551	1.0000					
DJK	-0.0374	-0.4169	1.0000				
Azeta	-0.0108	-0.0665	0.1289	1.0000			
nJ	-0.0173	0.0281	-0.0877	-0.3116	1.0000		
qv	-0.0142	-0.0270	0.0248	0.5750	-0.0101	1.0000	
qj	-0.0172	-0.0260	0.0137	0.2562	0.0328	0.8906	1.0000

Table 10. Comparison of rotation-vibration parameters for $(\text{CH}_2\text{O})_3$ in $v_1(E) = 1$ and $v_2(E) = 1$ states.

Parameters	$v_1(E) = 1$		$v_2(E) = 1$	
	This work	Ref ⁸	This work	Ref ³
C/MHz	2950*	2950*	2950*	2950*
B/MHz	5268.15146 (27)	5268.15125 (27)	5276.93598 (49)	5276.936 (2)
C ζ /MHz	-810.40 (71)	-810.50 (54)	-1940.54 (11)	-
D _J /kHz	1.34451 (16)	-1.34448 (14)	1.3782 (21)	1.382 (1)
D _{JK} /kHz	-2.01532 (58)	-2.01537 (41)	-2.0804 (54)	-2.11 (1)
η_J /kHz	-0.863 (11)	-0.8644 (82)	-2.516 (37)	-2.34 (9)
q _v /MHz	7.7798 (17)	7.7787 (17)	13.0060 (26)	13.008 (3)
q _j /kHz	0.00980 (75)	-0.00936 (68)	0.0753 (97)	-

*constrained at this value

Results and Discussion

Ignoring sextic term in Eq(3) for $K = 0$ the frequency expression becomes

$$v = 2B(J + 1) - 4D_J(J + 1)^3 \quad (8)$$

Eq (8) has enough accuracy for practical works. From a series of lines, D_J can be evaluated and therefore B is obtained very accurately. Plotting $\frac{v}{(J+1)}$ against $(J+1)^2$ gives a

straight line with slope $-4D_J$ and intercept $2B$ Figure 2.

Figure 2. Diagram of $v/(J + 1)$ against $(J + 1)^2$ for trioxane for ground state, from $J = 0$ to $J = 19$. Abbreviation of equation Eq(3) gives Eq(9).

$$\nu = 2B(J+1) - 4D_J(J+1)^3 - 2D_{JK}(J+1)K^2 \quad (9)$$

The constant D_{JK} is obtained from the slopes of $\nu = f(K^2)$ plotted for each group of transitions $J \rightarrow (J+1)$ Figure 3.

Figure 3. Diagram of frequencies of different K values against K^2 for trioxane in ground state, $J = 18$.

By this method it is possible to determine the rotational constant and other two quartic constants D_J and D_{JK} which are very important to predict these values for fitting the data of ground and other excited states.

Since ^{12}C and ^{16}O are Bose particles with spin zero, the symmetry of the spin-wave function of trioxane is determined solely from the hydrogen atoms. Table 5 shows that rotational constants, obtained quartic parameters for ground and $\nu(\text{A})=1$ states are in good agreement with the previous results and have more accuracy compare with them. For the ground state, it is possible to determine the tree sextic centrifugal distortion constants. The H_{JK} and H_J are well determined, but H_{KJ} is obtained with lower accuracy.

For the $\nu(\text{A})$ state, all of the sextic parameters were constrained to zero since there inclusion in the fit did not improve the sum of weighted squares of errors and resulted in a values not significantly different from zero and not well determined by the data. Probably these parameters are important in analysis of high J rotational spectrum of this particular molecule.

The oblate symmetric top $(\text{CH}_2\text{O})_3$ shows a strong $\Delta J=+1, \Delta K=0$ ground state spectrum. The spectra in ground and $\nu(\text{A})=1$ states are 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 ground and $\nu(\text{A})=1$ states, the Fortrat diagram is produced which is shown in (Figures 4, 5). In these diagrams 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.

Figure 4. Fortrat diagram of $(\text{CH}_2\text{O})_3$ in ground state for $J = 18$.

Figure 5. Fortrat diagram for calculated frequencies of $(\text{CH}_2\text{O})_3$ in $\nu(\text{A})$ state for $J = 12$

Table 10 shows that our D_J parameter for $\nu_1(\text{E})$ state is obtained with positive value but its value in Ref⁸ is negative. The parameters $C\zeta = -1940.54(11)$ MHz and $q_J = 0.0753(97)$ kHz were determined for the $\nu_2(\text{E}) = 1$ state for the first time.

For the $\nu_1(\text{E}) = 1$ and $\nu_2(\text{E}) = 1$ states the important parameters in determining form of the spectra are the l-type doubling constant q_v and the value of $A\zeta$. 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(5) this results in the positive series being displaced to lower frequency and the negative series to higher frequency. If $|K - l|$ values are plotted against frequency for $\nu_1(\text{E}) = 1$ and $\nu_2(\text{E}) = 1$ states, the Fortrat diagrams are produced which are shown in Figures 6 & 7.

Figure 6. Fortrat diagram for $(\text{CH}_2\text{O})_3$ in $\nu_1(\text{E}) = 1$ state for $J = 9$.

Figure 7. Fortrat diagram for $(\text{CH}_2\text{O})_3$ in $v_2(\text{E}) = 1$ state for $J = 9$.

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 in this state and constrained at the zero value.

Investigations in Ref² and Tables 5 and 10 shows that D_{JK} (-1.87 ± 0.02 kHz) for the $v(\text{A})$ state in trioxane was significantly lower in magnitude than the ground state value (-2.03 ± 0.01 kHz). From the present analysis D_{JK} for the $v_2(\text{E}) = 1$ state ($-2.080(54)$ kHz) is significantly greater than the ground state while the lowest E state $v_1(\text{E}) = 1$ is essentially the same as the ground state. These changes in D_{JK} probably arise through a Coriolis interaction between the $v_2(\text{E}) = 1$ and $v_1(\text{A})$ states.

If B_v values of $(\text{CH}_2\text{O})_3$ are plotted against vibrational quantum number v_t , the straight line is obtained Figure 6. Extrapolating of this line gives roughly $B_4 = 5253.5$ MHz. It seems these different vibrational states show that these levels are free of interaction with any other vibrations and act as isolated levels.

Figure 8. Variation of B value with vibrational quantum number v_t for trioxane in different excited states of $v_1(\text{E}) = \text{state}$.

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