

Submillimetrewave spectroscopy of the pure rotational transitions in the $\nu_6 = 1$ vibrational state of $^{12}\text{CH}_3\text{F}$

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Abstract

The $\Delta J = +1$, $\Delta K = 0$, $\Delta l = 0$ pure rotational transition frequencies were measured in the double degenerate $\nu_6 = 1$ vibrational state of $^{12}\text{CH}_3\text{F}$ up to $J \leq 11$ (609 GHz) using a submillimetrewave–microwave RAD spectrometer with acoustic detection. The determinable parameters of the effective rotational Hamiltonian for the degenerate vibrational state of symmetric top molecules were fitted with respect to all available microwave and submillimetrewave transition frequencies.

Keywords: Infrared spectrometry; Fluoromethane; Submillimetrewave spectroscopy

The $\Delta J = +1$, $\Delta K = 0$, $\Delta l = 0$ pure rotational transitions in the double degenerate $\nu_6 = 1$ vibrational state of $^{12}\text{CH}_3\text{F}$ were measured for the first time by Hirota and co-workers [1,2] in the microwave region up to $J \leq 1$ and by Brown et al. [3] in the submillimetrewave region up to $J \leq 7$. Hirota [4] determined the spectroscopic parameters of $^{12}\text{CH}_3\text{F}$ in the $\nu_6 = 1$ state by using diode laser spectrometry to measure the ν_6 vibration–rotation transition wavenumbers. Cho et al. [5] used an infrared–microwave sideband laser spectrometer to determine the $\nu_6 = 1$ parameters by studying the $\nu_3 + \nu_6 - \nu_6$ band of $^{12}\text{CH}_3\text{F}$.

In this work, the measurements of the pure rotational transitions in the doubly degenerate $\nu_6 = 1$ vibrational state of $^{12}\text{CH}_3\text{F}$ up to $J \leq 11$ (609 GHz) were extended using a submillimetrewave–microwave RAD spectrometer built at the Institute of Applied Physics in Gorky [6,7].

The determinable parameters of the effective rotational Hamiltonian for the degenerate vibrational states of symmetric top molecules [8–10] were fitted by using all the available microwave and submillimetrewave transition frequencies.

EXPERIMENTAL

All the transition frequencies in the $\nu_6 = 1$ state of $^{12}\text{CH}_3\text{F}$ were measured at room temperature and at sample pressures varying from 0.2 to 0.4 Torr. The experimental frequencies and their experimental uncertainties are given in Table 1.

RESULTS AND DISCUSSION

A weighted least-squares fit of the the data in Table 1 was made using the following expression

TABLE 1

Experimental ^a and calculated frequencies of the pure rotational transitions in the $v_6 = 1$ vibrational state of $^{12}\text{CH}_3\text{F}$ (in MHz)

<i>J</i>	<i>kl</i>	Exp.	Calc.	Exp.–Calc.	<i>J</i>	<i>kl</i>	Exp.	Calc.	Exp.–Calc.
0	0	50 837.749 (100)A	50 837.566	0.183	6	–1	355 759.460 (100)	355 759.502	–0.042
					6	2	355 786.310 (100)	355 786.408	–0.098
1	0	101 673.770 (100)B	101 673.674	0.096	6	–2	355 724.690 (100)	355 724.734	–0.044
1	1	101 693.870 (100)B	101 693.795	0.075	6	3	355 769.660 (100)	355 769.609	0.051
1	1	101 659.030 (*)B	101 658.583	0.447	6	–3	355 676.810 (100)	355 676.954	–0.144
1	–1	101 667.400 (100)B	101 667.479	–0.079	6	4	355 740.070 (100)	355 740.069	0.001
					6	–4	355 615.939 (100)	355 616.119	–0.180
2	0	152 506.864 (50)C	152 506.865	–0.001	6	5	355 697.727 (100)	355 697.816	–0.089
2	1	152 536.987 (50)C	152 536.985	0.002	6	–5	355 542.130 (100)	355 542.183	–0.053
2	1	152 484.323 (50)C	152 484.307	0.016	6	6	355 642.770 (100)	355 642.895	–0.125
2	–1	152 497.547 (50)C	152 497.567	–0.020	6	–6	355 455.210 (100)	355 455.098	0.112
2	2	152 508.966 (50)C	152 508.920	0.046					
2	–2	152 482.656 (50)C	152 482.719	–0.063	7	0	406 578.130 (100)C	406 578.018	0.112
					7	1	406 656.530 (100)	406 656.554	–0.024
3	0	203 335.707 (50)C	203 335.680	0.027	7	1	406 520.221 (100)	406 520.174	0.047
3	1	203 375.750 (100)	203 375.727	0.023	7	–1	406 552.930 (100)C	406 553.080	–0.150
3	1	203 305.836 (50)	203 305.750	0.086	7	2	406 584.037 (100)C	406 584.006	0.031
3	–1	203 323.280 (100)	203 323.273	0.007	7	–2	406 513.710 (1000)	406 513.292	0.418
3	2	203 338.540 (100)	203 338.453	0.087	7	3	406 564.890 (100)	406 564.829	0.061
3	–2	203 303.455 (50)C	203 303.464	–0.009	7	–3	406 458.490 (100)	406 458.626	–0.136
3	3	203 328.860 (100)	203 328.830	0.030	7	4	406 531.000 (100)	406 531.094	–0.094
3	–3	203 276.136 (50)C	203 276.228	–0.092	7	–4	406 388.870 (100)	406 389.033	–0.163
					7	5	406 482.790 (100)	406 482.827	–0.037
4	0	–	254 158.661	–	7	–5	406 304.390 (100)	406 304.462	–0.072
4	1	254 209.110 (1414)	254 208.537	0.573	7	6	406 419.960 (100)	406 420.077	–0.117
4	1	254 123.500 (1414)	254 121.485	2.015	7	–6	406 204.920 (100)	406 204.857	0.063
4	–1	–	254 143.139	–	7	7	406 342.610 (100)	406 342.897	–0.287
4	2	254 161.980 (100)	254 162.180	–0.200	7	–7	406 090.130 (500)	406 090.166	–0.036
4	–2	254 118.440 (100)	254 118.357	0.083					
4	3	254 150.240 (100)	254 150.159	0.081	8	0	–	457 363.080	–
4	–3	254 084.260 (100)	254 084.289	–0.029	8	1	457 450.720 (100)	457 450.812	–0.092
4	4	254 129.070 (100)	254 129.034	0.036	8	1	–	457 298.808	–
4	–4	254 040.840 (100)	254 040.903	–0.063	8	–1	457 334.960 (100)	457 334.976	–0.016
					8	2	–	457 369.990	–
5	0	–	304 974.350	–	8	–2	–	457 290.146	–
5	1	305 033.920 (100)	305 033.934	–0.014	8	3	457 348.440 (100)	457 348.445	–0.005
5	1	304 932.550 (414)	304 930.086	2.464	8	–3	457 228.390 (100)	457 228.569	–0.179
5	–1	304 955.680 (100)	304 955.702	–0.022	8	4	–	457 310.525	–
5	2	304 978.772 (100)	304 978.649	0.123	8	–4	457 150.000 (100)	457 150.192	–0.192
5	–2	–	304 925.934	–	8	5	457 256.200 (100)	457 256.252	–0.052
5	3	304 964.310 (100)	304 964.235	0.075	8	–5	457 054.790 (100)	457 054.956	–0.166
5	–3	304 884.881 (100)C	304 885.020	–0.139	8	6	457 185.460 (100)	457 185.680	–0.220
5	4	304 938.940 (100)	304 938.899	0.041	8	–6	456 942.760 (1000)	456 942.800	–0.040
5	–4	304 832.820 (100)	304 832.919	–0.099	8	7	457 098.530 (316)	457 098.867	–0.337
5	5	304 902.720 (100)	304 902.668	0.052	8	–7	456 813.860 (1000)	456 813.664	0.196
5	–5	304 769.580 (100)	304 769.593	–0.013	8	8	–	456 995.873	–
					8	–8	456 668.010 (1000)	456 667.488	0.552
6	0	355 781.360 (100)	355 781.288	0.072	9	0	–	508 135.018	–
6	1	355 850.440 (100)	355 850.434	0.006	9	1	508 231.620 (100)	508 231.724	–0.104
6	1	355 730.070 (100)	355 730.125	–0.055	9	1	508 064.430 (100)	508 064.600	–0.170

TABLE 1 (continued)

J	kl	Exp.	Calc.	Exp.–Calc.	J	kl	Exp.	Calc.	Exp.–Calc.
9	–1	508 103.560 (100)	508 103.728	–0.168	10	–7	558 219.110 (100)	558 219.187	–0.077
9	2	508 142.540 (100)	508 142.908	–0.368	10	8	558 445.070 (100)	558 444.441	0.629
9	–2	508 053.860 (100)	508 053.833	0.027	10	–8	558 040.150 (100)	558 040.195	–0.045
9	3	508 118.910 (100)	508 119.005	–0.095	10	9	558 300.300 (1000)	558 298.862	1.438
9	–3	507 985.070 (100)	507 985.318	–0.248	10	–9	557 840.540 (1000)	557 840.280	0.260
9	4	–	508 076.912	–	10	10	558 133.730 (1000)	558 133.635	0.095
9	–4	507 897.890 (100)	507 898.126	–0.236	10	–10	–	557 619.366	–
9	5	508 016.480 (100)	508 016.644	–0.164					
9	–5	507 792.040 (100)	507 792.912	–0.152	11	0	609 633.730 (100)	609 633.690	0.040
9	6	507 938.040 (100)	507 938.257	–0.217	11	1	609 746.693 (100)	609 747.583	–0.890
9	–6	507 667.350 (100)	507 667.450	–0.100	11	1	609 551.689 (100)	609 551.946	–0.257
9	7	507 841.480 (100)	507 841.817	–0.337	11	–1	609 595.696 (100)	609 595.965	–0.269
9	–7	507 523.750 (100)	507 523.832	–0.082	11	2	609 643.095 (100)	609 643.737	–0.642
9	8	507 726.960 (100)	507 727.390	–0.430	11	–2	609 536.203 (500)	609 535.855	0.348
9	–8	507 361.410 (1000)	507 361.270	0.140	11	3	609 614.958 (100)	609 615.158	–0.200
9	9	507 595.610 (1000)	507 595.043	0.567	11	–3	609 453.084 (100)	609 453.370	–0.286
9	–9	507 180.070 (100)	507 179.697	0.373	11	4	609 564.408 (100)	609 564.758	–0.350
					11	–4	609 348.181 (100)	609 348.444	–0.263
10	0	558 896.860 (*)	558 892.374	4.486	11	5	609 492.287 (100)	609 492.532	–0.245
10	1	558 998.670 (100)	558 997.809	0.861	11	–5	609 220.813 (100)	609 221.001	–0.188
10	1	–	558 816.121	–	11	6	609 398.327 (100)	609 398.542	–0.215
10	–1	558 858.950 (100)	558 857.878	1.072	11	–6	609 070.752 (100)	609 070.963	–0.211
10	2	–	558 901.308	–	11	7	609 282.596 (100)	609 282.866	–0.270
10	–2	558 804.830 (*)	558 802.890	1.940	11	–7	608 898.005 (100)	608 898.248	–0.243
10	3	558 876.100 (100)	558 875.060	1.040	11	8	609 145.356 (100)	609 145.582	–0.226
10	–3	558 728.460 (100)	558 727.407	1.053	11	–8	608 702.393 (100)	608 702.777	–0.384
10	4	558 828.460 (100)	558 828.807	–0.347	11	9	608 986.767 (100)	608 986.770	–0.003
10	–4	558 632.290 (100)	558 631.366	0.924	11	–9	608 483.866 (100)	608 484.466	–0.600
10	5	558 763.830 (100)	558 762.553	1.277	11	10	608 806.416 (100)	608 806.513	–0.097
10	–5	558 515.670 (100)	558 514.698	0.972	11	–10	–	608 243.236	–
10	6	558 677.200 (100)	558 676.360	0.840	11	11	–	608 604.890	–
10	–6	558 377.830 (100)	558 377.330	0.500	11	–11	–	607 979.005	–
10	7	558 571.130 (100)	558 570.299	0.831					

^a Values in parentheses are estimated experimental uncertainties in units of the last digit quoted; asterisks denote the data which were not included in the fit. Our measurements unless stated otherwise: A [1]; B [2]; C [3].

for the frequencies of the $J + 1 \leftarrow J$, $\Delta(kl) = 0$ transitions [3,11,12] (the notation is clarified further in Table 2):

$$\begin{aligned}
 \nu = & 2B^*(J+1) - 4D_J^*(J+1)^3 \\
 & - 2D_{JK}^*(J+1)(kl-1) \\
 & + H_J^*(J+1)^3[(J+2)^3 - J^3] \\
 & + 4H_{JK}^*(J+1)^3(kl-1)^2 \\
 & + 2H_{KJ}^*(J+1)(kl-1)^4 \\
 & + 2\eta_J^*(J+1)(kl-1)
 \end{aligned}$$

$$\begin{aligned}
 & + 4\tau_J^*(J+1)^3(kl-1) \\
 & + 2\tau_{JK}^*(J+1)(kl-1)^3 + \Delta\nu
 \end{aligned} \tag{1}$$

where $\Delta\nu$ is the frequency correction due to the “2, 2” l -type operator which is off-diagonal in the vibrational quantum number l (see, e.g., [11]):

$$\begin{aligned}
 \langle 1^{+1}; J, k+2 | (H_{22} + H_{24}) / h | 1^{-1}; J, k \rangle \\
 = 2 \left\{ q_{22} + f_{22}^{(J)} J(J+1) + f_{22}^{(K)} [k^2 + (k+2)^2] \right\} \\
 \times F(J, k) F(J, k+1)
 \end{aligned} \tag{2}$$

TABLE 2

Relationships $X^* = \sum X_i$ for the determinable parameters in Eqn. 1

X^*	$\sum X_i$
B^*	$B - D_{JK} + H_{KJ} + \eta_J + \tau_{JK}$
D_J^*	$D_J - H_{JK} - \tau_J$
D_{JK}^*	$D_{JK} - 6H_{KJ} - 3\tau_{JK}$
H_J^*	H_J
H_{JK}^*	H_{JK}
H_{KJ}^*	H_{KJ}
η_J^*	$\eta_J - 2D_{JK} + 4H_{KJ} + 3\tau_{JK} - 2(q_{22}^{*2} + q_{22}^* f_{22}^{(J)}) / (A - B - A\xi)$
τ_J^*	$\tau_J + 2H_{JK} + 4(q_{22}^* f_{22}^{(K)} - q_{22}^* f_{22}^{(J)}) / (A - B - A\xi)$
τ_{JK}^*	$\tau_{JK} + 4H_{KJ} - 2(4q_{22}^* f_{22}^{(K)} - q_{22}^* f_{22}^{(J)}) / (A - B - A\xi)$
q_{22}^*	$q_{22} + 2f_{22}^{(K)}$
$f_{22}^{*(J)}$	$f_{22}^{(J)}$

where

$$F(J, k) = [J(J+1) - k(k+1)]^{1/2} \quad (3)$$

Thus, for $kl = +1$, we have a diagonal contribution to $\Delta\nu$:

$$\Delta\nu_D = \pm 4 [q_{22}^*(J+1) + 2f_{22}^{(J)}(J+1)^3] \quad (4)$$

For $kl \neq +1$, the second-order correction to energy can be written as

$$E_c(J, kl)/h = \frac{[q_{22}^* + f_{22}^{(J)}J(J+1) + 2f_{22}^{(k)}(kl-1)^2]^2}{(kl-1)(A-B-A\xi)} \times [J(J+1) - kl(kl-1)] \times [J(J+1) - (kl-1)(kl-2)] \quad (5)$$

TABLE 3

Spectroscopic parameters of the $\nu_6 = 1$ state of $^{12}\text{CH}_3\text{F}$

Parameter	This work ^a	Brown et al. [3]	Cho et al. [5]
B^* (MHz)	25 419.5322 (55)	25 419.5427 (23)	25 419.6207 (231)
D_J^* (kHz)	60.620 (26)	60.754 (42)	61.606 (419)
D_{JK}^* (kHz)	458.779 (315)	461.238 (165)	458.213 (4225)
H_J^* (Hz)	-5.81 (124)	-	7.231 (8791)
η_J^* (kHz)	168.02 (132)	173.37 (99)	231.25 (464)
τ_J^* (Hz)	90.1 (62)	-	-
τ_{JK}^* (Hz)	568 (16)	632 (33)	-
q_{22}^* (MHz)	2.2054 (51)	2.2043 (21)	2.1801 (990)
$f_{22}^{*(J)}$ (kHz)	-0.5816 (256)	-0.5885 (41)	-0.5369 (645)

^a Number of data 134. Standard deviation of the fit 0.312 MHz. Values in parentheses are one standard deviation in units of the last digit quoted. Calculated for $A_6 - B_6 - A\xi = 84178$ MHz.

According to Eqn. (5), the correction to transition frequencies for $kl \neq 1$ can be approximated as

$$\Delta\nu_{\text{OFF}} = [E_c(J+1) - E_c(J)]/h = [E_c^*(J+1) - E_c^*(J)]/h + \Delta\nu_{\text{cor}} \quad (6)$$

where

$$E_c^*(J)/h = \frac{[q_{22}^* + f_{22}^{(J)}J(J+1)]^2}{(kl-1)(A-B-A\xi)} [J(J+1)]^2 \quad (7)$$

and $\Delta\nu_{\text{cor}}$ are those terms which are completely correlated with other terms in Eqn. 1 (cf. Table 2). Note that $f_{22}^{(K)}$ is not a determinable parameter.

The “2, -1” l -type operator is purely off-diagonal in l :

$$\langle 1^{-1}; J, k+1 | (H_{22} + H_{24})/h | 1^{+1}; J, k \rangle = 2 \{ [q_{12} + f_{12}^{(J)}J(J+1)](2k+1) + f_{12}^{(K)}[k^3 + (k+1)^3] \} F(J, k) \quad (8)$$

Following the procedure described above for the “2, 2” l -type interaction, it can be shown that q_{12} and $f_{12}^{(J)}$ are not determinable parameters. We have constrained them to zero, thus completing the reduction of the Hamiltonian [10]. The parameter $f_{12}^{(K)}$ can be shown to be determinable but it is so small [12] that we have neglected it.

The $\Delta k = \pm 4$ interaction due to the H_{24} term,

$$\langle 1^{-1}; J, k+4 | H_{24}/h | 1^{+1}; J, k \rangle$$

$$= 2f_{42}F(J, k)F(J, k+1)F(J, k+2)$$

$$\times F(J, k+3) \quad (9)$$

has a diagonal contribution for $kl = -2$. It was determined that $|f_{42}| = 0.2096$ kHz by analysing the high-resolution Fourier transform spectra of the ν_6 band of $^{12}\text{CH}_3\text{F}$ [12]. This gives a splitting of the frequencies for the $J, kl = -2$ levels which could not be resolved in the present experiment.

The values of the fitted parameters are compared in Table 3 with those obtained by previous workers [3,5]. Although the agreement between our results and those of Brown et al. [3] is satisfactory, the discrepancy in the B^* value obtained by us and Cho et al. [5] is large.

The fit of the experimental data is not completely satisfactory for the highest J values. This is probably related to the limited theoretical accuracy of our effective Hamiltonian, which does not take into account explicitly the x - y Coriolis interaction between ν_3 and ν_6 [12]. Hence the purpose of this paper is to provide reliable experimental data rather than the final values of spectroscopic parameters; a simultaneous analysis of the precise

microwave, submillimetrewave and high-resolution vibration-rotation data [12] using an extended theoretical model Hamiltonian should give the final result.

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