

## High-Resolution Fourier Transform and Submillimeter-Wave Spectroscopy of the $\nu_3$ and $2\nu_3 \leftarrow \nu_3$ Bands of $^{13}\text{CH}_3\text{F}$

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Fourier transform spectra of the  $\nu_3$  band (up to  $J \leq 40$ ,  $954\text{--}1076\text{ cm}^{-1}$ ) and of the  $2\nu_3 \leftarrow \nu_3$  band (up to  $J \leq 29$ ,  $956\text{--}1044\text{ cm}^{-1}$ ) of  $^{13}\text{CH}_3\text{F}$  have been measured with  $0.002\text{--}0.003\text{ cm}^{-1}$  resolution. Submillimeter-wave spectra of the pure rotational transitions in the  $\nu_3 = 0$  and  $\nu_3 = 1$  vibrational states up to  $J \leq 10$  ( $196\text{--}550\text{ GHz}$ ) have been measured using the submillimeter-wave spectrometer with acoustic detection. Improved sets of spectroscopic parameters have been obtained for the  $\nu_3 = 0, 1$ , and  $2$  vibrational states by fitting simultaneously the Fourier transform and submillimeter-wave data. © 1991 Academic Press, Inc.

### I. INTRODUCTION

The  $\nu_3$  band of the  $^{13}\text{CH}_3\text{F}$  molecule is a good test case for the performance of various high-resolution techniques because in the  $P$  and  $R$  branches the lines of transitions having the same rotational quantum number  $J$  and differing in  $K$  are overlapped for  $J \approx 40$  (Fig. 1).

The  $\nu_3$  band of  $^{13}\text{CH}_3\text{F}$  has been studied previously at high resolution by infrared-microwave two-photon spectroscopy (1), infrared laser Stark spectroscopy (2, 3), and by infrared-radiofrequency two-photon Lamb-dip spectroscopy (3, 4). Lee *et al.* (5) have used infrared-microwave sideband laser spectroscopy to record a large number of transitions in the  $\nu_3$  and  $2\nu_3 \leftarrow \nu_3$  bands of  $^{13}\text{CH}_3\text{F}$  at Doppler-limited resolution. They fitted the vibration-rotation parameters of the  $\nu_3 = 0, 1, 2$  states to these vibration-rotation frequencies and to several low- $J$  rotational frequencies in the ground and  $\nu_3 = 1$  states measured by millimeter-wave spectroscopy (6, 7).

The techniques of high-resolution infrared spectroscopy which were used previously (1–5) made it possible to measure only those  $\nu_3$  and  $2\nu_3 \leftarrow \nu_3$  band transition fre-

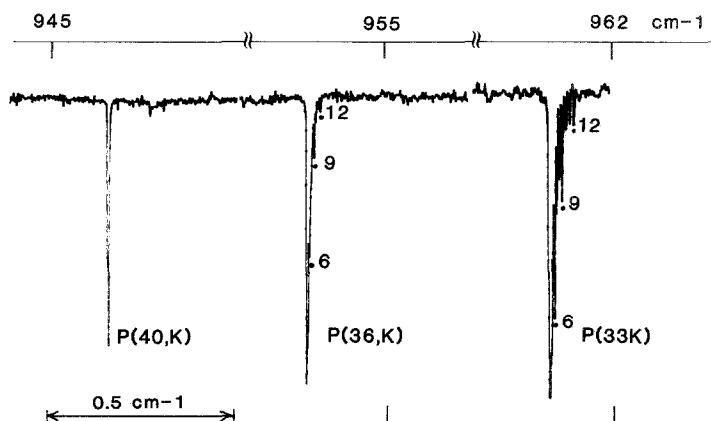


FIG. 1. Part of the Fourier-transform spectrum of the  $\nu_3$  band of  $^{13}\text{CH}_3\text{F}$ .

quencies which were close to the  $\text{CO}_2$  laser lines. Since Fourier-transform spectroscopy approaches the same sensitivity as well as the accuracy of frequency determination in comparison with the previously used techniques (1–5), we have completed these measurements by recording the high-resolution spectra of the  $\nu_3$  and  $2\nu_3 \leftarrow \nu_3$  bands of  $^{13}\text{CH}_3\text{F}$  in the  $920\text{--}1100\text{ cm}^{-1}$  region with  $0.002\text{--}0.003\text{ cm}^{-1}$  resolution using the Fourier-transform spectrometer built at the University of Oulu (8).

Furthermore, new data on the frequencies of the rotational transitions in the  $\nu_3 = 0$  and  $\nu_3 = 1$  states of  $^{13}\text{CH}_3\text{F}$  have become available since the work of Lee (5): Brown *et al.* (9) have measured frequencies of the rotational transitions in the ground vibrational state of  $^{13}\text{CH}_3\text{F}$  up to  $J \leq 9$  and Sudhakaran *et al.* (10) have measured 10 transitions  $J_K = 18_K \leftarrow 17_K$  using the submillimeter laser Stark technique. We have extended these data by measuring the ground and  $\nu_3 = 1$  state rotational transition frequencies from  $J = 3$  up to  $J = 10$  using the submillimeter-wave spectrometer with acoustic detection RAD 3 which was built at the Institute of Applied Physics in Nizhnii Novgorod (previously Gorkii) (11, 12).

## II. EXPERIMENTAL DETAILS

The sample of  $^{13}\text{CH}_3\text{F}$  has been purchased from MSD Isotopes, Division of Merck Frosst Canada, Incorporated, Ottawa; it contained 94.5 at.% of  $^{13}\text{C}$ . The Fourier-transform spectra have been measured at 0.5 Torr using 1-m optical path. Submillimeter-wave spectra of  $^{13}\text{CH}_3\text{F}$  have been measured at pressures below 1 Torr using a sample with the natural abundance of  $^{13}\text{C}$ .

The estimated uncertainties of the experimental frequencies of the rotational transitions are indicated in Tables I and II. The uncertainty of transition frequencies of the isolated and symmetric vibration-rotation lines was estimated to be  $3 \times 10^{-5}\text{ cm}^{-1}$ . In least-squares fits of the spectroscopic parameters (cf. Tables III–V), each transition was weighted by the inverse square of its experimental uncertainty.

TABLE I

Comparison of Calculated and Observed Frequencies (in MHz) of the Pure Rotational Transitions  
in the Ground Vibronic State of  $^{13}\text{CH}_3\text{F}$

J	K	Calc	Exp <sup>a</sup>	Unc <sup>b</sup>	Exp-Calc	J	K	Calc	Exp	Unc	Exp-Calc
0	0	49725.07	49725.34 c	0.20	0.27	7	0	397684.06	397684.02 d	0.10	-0.04
1	0	99448.75	99448.74 d	0.10	-0.01	7	1	397677.27	397677.23 d	0.10	-0.04
1	1	99447.05	99447.04 d	0.10	-0.02	7	2	397656.91	397657.04	0.20	0.13
									397656.95 d	0.10	0.04
2	0	149169.66	149169.68 d	0.10	0.02				397623.02	0.20	0.05
2	1	149167.11	149167.14 d	0.10	0.03	7	4	397575.49	397622.92 d	0.10	-0.05
2	2	149159.47	149159.48 d	0.10	0.01				397575.51	0.20	0.02
									397575.50 d	0.10	0.01
3	0	198886.40	198886.38 d	0.10	-0.02	7	5	397514.48	397514.46	0.20	-0.02
			198886.39 e	0.05	-0.01				397514.44 d	0.10	-0.04
3	1	198883.01	198883.07 d	0.10	0.06	7	6	397439.96	397439.95	0.20	-0.01
			198882.98 e	0.05	-0.03				397440.05 d	0.10	0.09
3	2	198872.82	198872.87	0.10	0.05	7	7	397351.97	397352.01	0.20	0.04
			198872.87 d	0.10	0.05				397351.97 d	0.10	-0.00
			198872.80 e	0.05	-0.02	8	0	447359.23	447359.17 d	0.10	-0.06
3	3	198855.85	198855.98	0.10	0.13	8	1	447351.60	447351.50 d	0.10	-0.09
			198855.85 d	0.10	0.00	8	2	447328.69	447328.79	0.20	0.10
			198855.82 e	0.05	-0.03	8	3	447290.53	447290.58	0.20	0.06
									447290.40 d	0.10	-0.12
4	0	248597.60	248597.58 d	0.10	-0.02	8	4	447237.12	447237.12	0.20	0.00
			248597.60 e	0.05	0.00				447237.21 d	0.10	0.09
4	1	248593.36	248593.42 d	0.10	0.07	8	5	447168.49	447168.46	0.20	-0.03
			248593.33 e	0.05	-0.03				447168.41 d	0.10	-0.08
4	2	248580.62	248580.68	0.10	0.06	8	6	447084.67	447084.65	0.20	-0.02
			248580.67 d	0.10	0.05				447084.79 d	0.10	0.12
			248580.61 e	0.05	-0.01	8	7	446985.70	446985.72	0.10	0.02
4	3	248559.41	248559.45	0.10	0.04				446985.51 d	0.20	-0.19
			248559.50 d	0.10	0.09	8	8	446871.62	446871.68	0.20	0.06
			248559.32 e	0.05	-0.09						
4	4	248529.72	248529.75	0.10	0.03	9	0	497021.96	497022.06 d	0.20	0.10
			248529.72 d	0.10	0.00	9	1	497013.47	497013.50 d	0.20	0.03
			248529.69 e	0.05	-0.03	9	2	496988.03	496988.11	0.20	0.08
									496988.11 d	0.20	0.08
5	0	298301.86	298301.85	0.15	-0.01	9	3	496945.63	496945.65	0.20	0.02
			298301.94 d	0.10	0.08				496945.60 d	0.20	-0.03
			298301.93 e	0.05	0.07	9	4	496886.30	496886.28	0.20	-0.02
5	1	298296.77	298296.94	0.15	0.17				496886.13 d	0.20	-0.17
		298296.77	298296.80 d	0.10	0.03	9	5	496810.06	496810.02	0.20	-0.04
			298296.75 e	0.05	-0.02				496809.99 d	0.20	-0.06
5	2	298281.49	298281.57	0.15	0.08	9	6	496716.94	496716.86	0.20	-0.08
			298281.53 d	0.10	0.04				496716.91 d	0.20	-0.04
			298281.49 e	0.05	-0.00	9	7	496607.00	496606.97	0.20	-0.03
5	3	298256.04	298256.09	0.15	0.05	9	8	496480.27	496480.29	0.20	0.02
			298256.04 d	0.10	0.01	9	9	496336.81	496337.02	0.20	0.21
			298256.03 e	0.05	-0.01						
5	4	298220.41	298220.46	0.15	0.05	10	2	546633.54	546633.58	0.30	0.04
			298220.38 d	0.10	-0.03	10	3	546586.91	546586.89	0.30	-0.02
			298220.38 e	0.05	-0.04	10	4	546521.66	546521.59	0.30	-0.07
5	5	298174.64	298174.67	0.15	0.03	10	5	546437.82	546437.69	0.30	-0.13
			298174.64 d	0.10	-0.01	10	6	546335.41	546335.27	0.30	-0.14
			298174.58 e	0.05	-0.06	10	7	546214.50	546214.37	0.30	-0.13
						10	8	546075.12	546075.05	0.30	-0.07
6	0	347997.81	347997.81	0.15	0.00	10	9	545917.35	545917.44	0.30	0.09
			347997.81 d	0.10	-0.00	10	10	545741.25	545741.59	0.30	0.34
6	1	347991.87	347992.06	0.15	0.19						
			347991.89 d	0.10	0.02	17	8	892738.72	892740.50 f	3.99	1.78
6	2	347974.05	347974.14	0.15	0.09	17	9	892481.07	892482.53 f	3.48	1.46
			347974.16 d	0.10	0.11	17	10	892193.48	892194.01 f	2.91	0.53
6	3	347944.35	347944.42	0.15	0.07	17	11	891876.09	891876.94 f	2.29	0.85
			347944.41 d	0.10	0.06	17	12	891529.04	891529.93 f	1.62	0.89
6	4	347902.80	347902.85	0.15	0.05	17	13	891152.49	891153.34 f	0.93	0.85
			347902.78 d	0.10	-0.02	17	14	890746.59	890746.34 f	0.51	-0.25
6	5	347849.41	347849.44	0.15	0.04	17	15	890311.54	890311.15 f	1.03	-0.39
			347849.38 d	0.10	-0.03	17	16	889847.52	889846.42 f	1.89	-1.10
6	6	347784.19	347784.23	0.15	0.04	17	17	889354.75	889366.28 f	(*)	11.53
			347784.14 d	0.10	-0.05						

<sup>a</sup> Our submillimeter-wave measurement unless stated otherwise.

<sup>b</sup> Estimated experimental uncertainties.

<sup>c</sup> Ref. (6). <sup>d</sup>Ref. (9). <sup>e</sup>Ref. (7). <sup>f</sup>Ref. (10).

TABLE II

Comparison of Calculated and Observed Frequencies (in MHz) of the Pure Rotational Transitions in the  $\nu_3 = 1$  State of  $^{13}\text{CH}_3\text{F}$

J	K	Calc	Exp <sup>a</sup>	Unc <sup>b</sup>	Exp-Calc	J	K	Calc	Exp	Unc <sup>c</sup>	Exp-Calc
0	0	49084.00	49084.30 c	0.20	0.30	7	0	392561.38	-	-	-
						7	1	392553.75	-	-	-
1	0	98166.69	-	-	-	7	2	392530.87	392531.01	0.20	0.14
1	1	98164.78	-	-	-	7	3	392492.71	392492.75	0.20	0.04
						7	4	392439.23	392439.30	0.20	0.07
2	0	147246.74	-	-	-	7	5	392370.41	392370.49	0.20	0.08
2	1	147243.88	-	-	-	7	6	392286.16	392286.13	0.20	-0.03
2	2	147235.30	-	-	-	7	7	392186.44	-	-	-
3	0	196322.84	196322.95 d	0.05	0.11	8	0	441597.96	-	-	-
3	1	196319.03	196319.08 d	0.05	0.06	8	1	441589.39	-	-	-
3	2	196307.58	196306.75	0.10	-0.83	8	2	441563.64	441563.77	0.20	0.13
		196307.58	196307.67 d	0.05	0.09	8	3	441520.71	441520.65	0.20	-0.06
3	3	196288.50	196288.35	0.10	-0.15	8	4	441460.55	441460.63	0.20	0.08
		196288.50	196288.53 d	0.05	0.02	8	5	441383.12	441383.05	0.20	-0.07
						8	6	441288.35	441288.43	0.20	0.08
4	0	245393.67	245393.73 d	0.05	0.07	8	7	441176.16	441176.27	0.20	0.11
4	1	245388.90	245388.90 d	0.05	-0.00	8	8	441046.45	441046.34	0.20	-0.11
4	2	245374.60	245374.12	-0.10	-0.48						
		245374.60	245374.65 d	0.05	0.05	9	0	490622.70	-	-	-
4	3	245350.75	245350.46	0.10	-0.29	9	1	490613.16	-	-	-
		245350.75	245350.79 d	0.05	0.04	9	2	490584.56	490584.46	0.20	-0.10
4	4	245317.33	245317.97	0.10	0.64	9	3	490536.85	490536.64	0.20	-0.21
		245317.33	245317.30 d	0.05	-0.03	9	4	490470.01	490469.92	0.20	-0.09
						9	5	490383.98	490384.11	0.20	0.13
5	0	294457.91	294457.99 d	0.05	0.07	9	6	490278.68	-	-	-
5	1	294452.20	294452.16 d	0.05	-0.04	9	7	490154.02	-	-	-
5	2	294435.03	294435.20	0.15	0.17	9	8	490009.90	490010.06	0.20	0.16
		294435.03	294434.98 d	0.05	-0.05	9	9	489846.20	489845.89	0.20	-0.31
5	3	294406.41	294406.32	0.15	-0.09						
		294406.41	294406.40 d	0.05	-0.01	10	0	539634.25	-	-	-
5	4	294366.30	294366.79	0.15	0.49	10	1	539623.77	-	-	-
		294366.30	294366.11 d	0.05	-0.20	10	2	539592.30	539591.93	0.30	-0.37
5	5	294314.68	294315.03	0.15	0.34	10	3	539539.83	539539.53	0.30	-0.30
						10	4	539466.30	539466.70	0.30	0.40
6	0	343514.26	-	-	-	10	5	539371.67	539371.68	0.30	0.01
6	1	343507.58	-	-	-	10	6	539255.83	539256.06	0.30	0.23
6	2	343487.56	343487.56	0.15	0.00	10	7	539118.71	539119.17	0.30	0.46
6	3	343454.17	343454.27	0.15	0.10	10	8	538960.18	538960.15	0.30	-0.03
6	4	343407.38	343407.38	0.15	0.00	10	9	538780.11	538780.41	0.30	0.30
6	5	343347.16	343347.13	0.15	-0.03	10	10	538578.35	-	-	-
6	6	343273.44	343273.28	0.15	-0.16						

<sup>a</sup> Our submillimeter-wave measurement unless stated otherwise.

<sup>b</sup> Estimated experimental uncertainties.

<sup>c</sup> Ref. (6). <sup>d</sup>Ref. (7).

### III. THEORY

The  $\nu_3 = 1$  vibrational state of  $^{13}\text{CH}_3\text{F}$  has the symmetry species  $A_1$  (the C-F stretching mode) and it can therefore interact with the  $\nu_6 = 1$  and  $\nu_5 = 1$  vibrational levels of symmetry species  $E$  through the  $x$ - $y$  type Coriolis interaction. As  $\nu_6 - \nu_3 \approx 134 \text{ cm}^{-1}$  and  $\nu_5 - \nu_3 \approx 411 \text{ cm}^{-1}$ , the more important interaction between  $\nu_3$  and  $\nu_6$  is still so small that it can be described by the effective parameters in the standard polynomial expression for the rotational energy levels of a nondegenerate vibrational state of a symmetric top molecule [cf. (13, 14)]:

$$\begin{aligned}
 E_v(J, K)/hc = & E_v/hc + B_v J(J+1) + (A_v - B_v)K^2 - D_J^{(v)} J^2(J+1)^2 \\
 & - D_{JK}^{(v)} J(J+1)K^2 - D_K^{(v)} K^4 + H_J^{(v)} J^3(J+1)^3 + H_{JK}^{(v)} J^2(J+1)^2 K^2 \\
 & + H_{KJ}^{(v)} J(J+1)K^4 + H_K^{(v)} K^6 + L_J^{(v)} J^4(J+1)^4 + L_{JK}^{(v)} J^3(J+1)^3 K^2 \\
 & + L_{JK}^{(v)} J^2(J+1)^2 K^4 + L_{KK}^{(v)} J(J+1)K^6 + L_K^{(v)} K^8 + \dots \quad (1)
 \end{aligned}$$

We assume that Eq. (1) holds also for  $\nu_3 = 2$ .

It is one of the purposes of the present paper to verify to what extent this is true up to  $J$  approaching 40. We have not introduced corrections due to the terms off-diagonal in the rotational quantum number  $k$  which lead to the  $A_1$ - $A_2$  splitting and/or to shifts of energy levels (15, 16). The negligibly small effects of these interactions in the ground as well as in the  $\nu_3 = 1$  vibrational states of  $^{13}\text{CH}_3\text{F}$  have been indicated by previous measurements (1-7) and will be confirmed also in our paper.

The transition frequencies used for fitting of experimental data have been generated as appropriate differences of energies calculated from Eq. (1) using the usual selection rules  $\Delta J = +1$ ,  $\Delta K = 0$  for the purely rotational transitions and using  $\Delta J = 0, \pm 1$ ,  $\Delta K = 0$  for vibrational-rotational transitions.

#### IV. RESULTS

Three sets of the ground state spectroscopic parameters were determined by fitting only the ground state transition frequencies, by fitting only the vibrational-rotational transition frequencies, and by fitting simultaneously the submillimeter-wave and infrared data (Table III).

The  $\nu_3 = 1$  state parameters obtained by various fits are given in Table IV. The calculated frequencies of the pure rotational transitions in the  $\nu_3 = 0$  and  $\nu_3 = 1$  states of  $^{13}\text{CH}_3\text{F}$  are compared with the experimental data in Tables I and II.

The  $\nu_3$  band transitions have been measured up to  $J \leq 36$  in the  $P$  branch,  $J \leq 25$  in the  $Q$  branch, and  $J \leq 40$  in the  $R$  branch. They are not listed in this paper, but they are available upon request.

The  $2 \nu_3 \leftarrow \nu_3$  "hot" band transitions have been measured up to  $J \leq 29$  in the  $P$  branch,  $J \leq 12$  in the  $Q$  branch, and  $J \leq 22$  in the  $R$  branch. The  $2 \nu_3 \leftarrow \nu_3$  band

TABLE III  
Ground State Parameters of  $^{13}\text{CH}_3\text{F}$  (in MHz Units)

Parameter	I <sup>a</sup>	II <sup>b</sup>	III <sup>c</sup>	IV <sup>d</sup>	V <sup>e</sup>
$B''$	24862.65090 (129) <sup>f</sup>	24862.66448 (3166)	24862.64442 (212)	24862.65456 (191)	24862.6460 (34)
$D_J'' \times 10^3$	57.8368 (260)	57.7200 (275)	57.7243 (113)	57.8211 (185)	57.7386 (156)
$D_{JK}'' \times 10^3$	424.6040 (654)	425.5933 (4854)	424.8293 (1089)	424.886 (185)	424.736 (285)
$H_J'' \times 10^6$	0.476 (169)	-0.0218 (110)	-0.0214 (73)	-0.0212 <sup>g</sup>	-0.0172 (100)
$H_{JK}'' \times 10^6$	2.073 (721)	1.533 (163)	1.536 (87)	4.86 (159)	1.582 (143)
$H_{KJ}'' \times 10^6$	15.54 (129)	26.09 (199)	21.49 (77)	13.89 (283)	20.38 (138)

<sup>a</sup> Fit to the pure rotational transition frequencies of the ground state (cf. Table I); number of data : 122, standard deviation of the fit : 0.057 MHz.

<sup>b</sup> Obtained from the fit of the vibration-rotation transition frequencies of the  $\nu_3$  band (see also Table IV).

<sup>c</sup> Obtained from the simultaneous fit of the  $\nu_3 = 0$  and  $\nu_3 = 1$  state pure rotational transition frequencies (Tables I and II) together with the vibration-rotation transition frequencies of the  $\nu_3$  band (see also Table IV).

<sup>d</sup> Ref. (9); fit to the pure rotational transition frequencies of the ground state.

<sup>e</sup> Ref. (5); see also Table IV.

<sup>f</sup> Numbers in parentheses are standard errors in units of the last digit quoted.

<sup>g</sup> Constrained value [cf. Ref. (9)].

TABLE IV  
Parameters of the  $\nu_3$  Band of  $^{13}\text{CH}_3\text{F}$  (in  $\text{cm}^{-1}$  Units)<sup>c</sup>

Parameter	I <sup>a</sup>	II <sup>b</sup>	III <sup>c</sup>	IV <sup>d</sup>
$\nu_3$	1027.49316 (2)	1027.49320 (2)		1027.49325 (3)
B	0.81863864 (102)	0.81863738 (9)	0.81863670 (14)	0.81863715 (12)
$\Pi_J' \times 10^6$	1.837671 (909)	1.836917 (351)	1.830640 (1629)	1.836717 (490)
$D_{JK}' \times 10^6$	15.9746 (171)	15.9368 (46)	15.8974 (135)	15.9296 (105)
$H_J' \times 10^{10}$	-0.0371 (33)	-0.0401 (22)	0. <sup>f</sup>	-0.0465 (32)
$H_{JK}' \times 10^{10}$	3.4202 (859)	3.2364 (504)	0. <sup>f</sup>	3.2888 (630)
$H_{KJ}' \times 10^{10}$	-11.028 (679)	-12.816 (378)	-11.227 (1845)	-13.425 (565)
$L_J' \times 10^{14}$	0. <sup>f</sup>	0. <sup>f</sup>		0.026 (5)
$L_{JJK}' \times 10^{14}$	-3.140 (260)	-2.579 (198)		-2.554 (144)
$L_{JK}' \times 10^{14}$	39.95 (212)	44.36 (168)		37.82 (167)
$L_{JJK}' \times 10^{14}$	-290.4 (110)	-299.1 (91)		-272.5 (92)
$(D_K' - D_K'') \times 10^6$	-2.2066 (148)	-2.1932 (130)		-2.3302 (356)
$(H_K' - H_K'') \times 10^{10}$	26.501 (535)	27.182 (460)		18.679 (2078)
$[ (A' - B') - (A'' - B'') ] \times 10^3$	1.05470 (114)	1.05461 (103)		1.04567 (216)
B''	0.82932922 (106)	0.82932855 (7)		0.82932860 (11)
$D'' \times 10^6$	1.925330 (917)	1.925477 (376)		1.925952 (520)
$D_J'' \times 10^6$	14.1963 (162)	14.1708 (36)		14.1678 (95)
$H_J'' \times 10^{10}$	-0.00726 (366)	-0.00712 (243)		-0.00574 (334)
$H_{JK}'' \times 10^{10}$	0.5113 (544)	0.5125 (291)		0.5275 (475)
$H_{KJ}'' \times 10^{10}$	8.702 (663)	7.170 (255)		6.798 (461)
Type of data	No. St.Dev. ( $\text{cm}^{-1}$ )	No. St.Dev. ( $\text{cm}^{-1}$ )	No. St.Dev. ( $\text{cm}^{-1}$ )	
GS ROT	- -	122 6.3 $\times 10^{-6}$	- -	
$\nu_3$ ROT	- -	55 2.7 $\times 10^{-6}$	55 5.7 $\times 10^{-6}$	
VIB ROT	555 8.6 $\times 10^{-6}$	555 8.7 $\times 10^{-6}$	- -	

<sup>a</sup> Fit to the transition frequencies obtained by our Fourier transform measurement of the  $\nu_3$  band.

<sup>b</sup> Simultaneous fit of the pure rotational transition frequencies in the  $\nu_3 = 0$  and  $\nu_3 = 1$  vibrational states (Tables I and II) and our Fourier transform data on the  $\nu_3$  band.

<sup>c</sup> Fit to the pure rotational transition frequencies in the  $\nu_3 = 1$  vibrational state (cf. Table II).

<sup>d</sup> Ref. (5); simultaneous fit of the vibration-rotation transition frequencies of the  $\nu_3$  band (infrared-microwave sideband laser spectroscopy) and of the  $\nu_3 = 0$  and  $\nu_3 = 1$  pure rotational transition frequencies from Refs. (6,7).

<sup>e</sup> Numbers in parentheses are standard errors in units of the last digit quoted

<sup>f</sup> Constrained value.

parameters (Table V) have been obtained by fitting these data with the  $\nu_3 = 1$  state parameters constrained to the values which were obtained in the simultaneous fit of the  $\nu_3$  band data (Set II in Table IV).

It is obvious from the results (Tables III-V) that the simple polynomial expression for the energy levels of the  $\nu_3 = 0, 1$ , and 2 vibrational states of  $^{13}\text{CH}_3\text{F}$  can be used to reproduce the data quantitatively within the experimental uncertainties up to rel-

TABLE V  
Parameters of the  $2 \nu_3 \leftarrow \nu_3$  Band of  $^{13}\text{CH}_3\text{F}$  (in  $\text{cm}^{-1}$  Units)

Parameter	I <sup>a</sup>	II <sup>b</sup>
$2 \nu_3 \leftarrow \nu_3$	1012.17695 (9) <sup>c</sup>	1012.17684 (10)
$B'$	0.80829058 (76)	0.80829188 (120)
$D'_J \times 10^6$	1.75549 (233)	1.76149 (644)
$D'_{JK} \times 10^6$	17.2345 (223)	17.2307 (653)
$H'_J \times 10^{10}$	-0.556 (26)	-0.481 (139)
$H'_{JK} \times 10^{10}$	7.984 (321)	7.983 (1665)
$H'_{KJ} \times 10^{10}$	-17.65 (167)	-18.13 (798)
$L'_{JJJJ} \times 10^{14}$	5.33 <sup>d</sup>	8.60 (101)
$L'_{JJJK} \times 10^{14}$	-58.60 <sup>d</sup>	-58.60 (1336)
$L'_{JJKK} \times 10^{14}$	216.8 <sup>d</sup>	216.8 (778)
$L'_{JXXX} \times 10^{14}$	-1177.4 <sup>d</sup>	-1177.4 (3388)
$(D'_K - D'_K) \times 10^6$	-0.991 (202) <sup>e</sup>	-1.53 (27) <sup>f</sup>
$(H'_K - H'_K) \times 10^{10}$	77.3 (151) <sup>e</sup>	51.0 (226) <sup>f</sup>
$[(A' - B') - (A'' - B'')] \times 10^3$	0.88145 (761) <sup>e</sup>	0.86592 (1197) <sup>f</sup>

<sup>a</sup> Fit to our Fourier transform data on the  $2 \nu_3 \leftarrow \nu_3$  band; number of data : 97, standard deviation of the fit :  $1.25 \times 10^{-4} \text{ cm}^{-1}$ .

<sup>b</sup> Ref. (5).

<sup>c</sup> Values in parentheses are standard deviations in units of the last digit.

<sup>d</sup> Constrained value.

<sup>e</sup>  $D'_K$ ,  $H'_K$ , and  $(A'' - B'')$  are related to the  $\nu_3$  state (cf. set II in Table IV).

<sup>f</sup> Calculated from data in Table IV of Ref. (5).

atively high  $J$  values indicated in this paper. We have not attempted to fit our data simultaneously with the  $\nu_3$  and  $2 \nu_3 \leftarrow \nu_3$  bands transition frequencies obtained by previous authors (1-5) because we wished to check the internal consistency of our measurements with the previous data by comparing the values of the spectroscopic parameters obtained in various fits. Except for a few parameters with large dispersions, the values of parameters in Tables III-V agree within their error intervals. By fitting our submillimeter-wave and Fourier-transform data, improved sets of spectroscopic parameters for the  $\nu_3 = 0, 1$ , and 2 vibrational states of  $^{13}\text{CH}_3\text{F}$  have been obtained.

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