Rotational Spectra of $^{13}CH_3F$ in the $v_2 = 1$ and $v_5 = 1$ Vibrational States

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Millimeter-wave and submillimeter-wave spectra of the rotational transitions in the $v_2 = 1$ and $v_5 = 1$ vibrational states of $^{13}CH_3F$ were measured up to 462 GHz. Far-infrared spectra of these transitions were measured in the region 30–65 cm^{-1} with a resolution of 0.0019 cm^{-1} using an interferometric spectrometer Bruker IFS 120 HR. Almost 700 lines including 14 lines of the $\Delta(k - l_5) = \pm 3$ perturbation-allowed transitions in the $v_5 = 1$ state were assigned. Both vibrational states are strongly perturbed, especially by the x,y-Coriolis resonance and "2, −1" l-type interactions. The corresponding spectroscopical parameters were determined by a nonlinear least-squares fit to the experimental data. © 1994 Academic Press, Inc.

INTRODUCTION

The rotational spectrum of $^{13}CH_3F$ in the excited vibrational states $v_2 = 1$ and $v_5 = 1$ was studied by Hirota *et al.* (*1*) who measured eight $\Delta J = 1$, $\Delta k = 0$ transitions for $J = 0$ and 1, and five direct l-type doubling transitions in the $kl = +1$ sublevel of the $v_5 = 1$ state. They found that both states are strongly perturbed by the x,y-Coriolis interaction, and by using a simple model Hamiltonian of this interaction, they determined approximately the difference between the interacting vibrational levels and some of the diagonal and off-diagonal parameters of the Hamiltonian. Hegelund *et al.* (*2*) reported an analysis of the vibration–rotational structure of the Raman spectrum of the v_2/v_5 band system of $^{13}CH_3F$ measured with 0.30 cm^{-1} resolution. They could determine only the value of E_5 and with a limited accuracy the values of $A_5 - A_0$, $A_2 - A_0$, and $A\zeta_{5a5b}^z$. As far as we know, no high-resolution study has been published so far on the v_2/v_5 system of bands in $^{13}CH_3F$; our high-resolution Fourier transform measurement and analysis of the vibration–rotational transitions to the $v_2 = 1$ and $v_5 = 1$ vibrational states is reported in a subsequent paper (*3*).

In the present paper, we extended the measurements of the frequencies of the rotational transitions in the $v_2 = 1$ and $v_5 = 1$ states of $^{13}CH_3F$ in the millimeter-wave and submillimeter-wave regions up to 462 GHz. Furthermore, we recorded Fourier transform spectra of the pure rotational transitions in the excited vibrational states $v_2 = 1$ and $v_5 = 1$ in the region 30–65 cm^{-1} with an unapodized resolution of 0.0019 cm^{-1}. This made it possible to assign almost 700 lines of the pure rotational transitions and to determine the upper state spectroscopical parameters much more accurately than reported previously (*1, 2*).

Fluoromethane—^{13}CH$_3$F

The sample of ^{13}CH$_3$F was purchased from MSD Isotopes, Montreal, Canada; it contained 99.4 at. % of ^{13}C.

Millimeter-Wave and Submillimeter-Wave Spectra

Rotational spectra in the frequency range 120–300 GHz were measured at the University of Lille, France, with a computer-controlled millimeter-wave spectrometer using heterodyne detection (*4*). The lines between 340 and 470 GHz were measured with a source-modulated and phase-stabilized output frequency of a submillimeter BWOs (Thomson-CSF). The absorption signals were detected with an He-cooled InSb bolometer. The accuracy of the measurements was better than 50 kHz. Forty-eight lines between 158 and 345 GHz were measured with a submillimeter-wave spectrometer with an acoustic detection RAD and with a submillimeter frequency synthesizer built at the Institute of Applied Physics in Nizhnii Novgorod, Russia [Refs. (*5, 6*)]. The experimental uncertainty of the frequency was estimated to be better than 200 kHz. All the spectra were measured at room temperature.

Infrared Spectra

The infrared spectra were measured in Giessen, Germany, in absorption in a heatable cell with an optical path length of 3.00 m using an interferometric spectrometer (Bruker IFS 120 HR) equipped with a mercury lamp as the source and a silicon bolometer operating at 4.2 K as detector. Spectra were recorded at an unapodized resolution 0.0019 cm^{-1} at sample pressures of 1.25 mbar (125 Pa) and an elevated temperature of 360 K. They were calibrated with respect to the lines of the rotational transitions in the ground state of ^{13}CH$_3$F which were previously measured (*7*) at a sample pressure of 0.12 mbar (12 Pa) and calibrated with respect to standard water lines. In this way we avoided pressure-induced shifts of the transition wavenumbers which might not be negligible if the measurement of ^{13}CH$_3$F would be calibrated with respect to standard lines of water [see also Ref. (*8*)]. A segment of the spectrum between 49.0 and 50.5 cm^{-1} is shown in Fig. 1.

Strong vibration–rotational interactions between the closely spaced vibrational levels $v_2 = 1$ (symmetry species A_1) and $v_5 = 1$ (symmetry species E) in ^{13}CH$_3$F require the use of a variational approach in a nonlinear least-squares determination of the parameters of the vibrational states. The situation is analogous to ^{12}CH$_3$F and we used the same reduced vibration–rotational Hamiltonian as that in our previous study of the interactions in the $v_2 = 1$ and $v_5 = 1$ states of ^{12}CH$_3$F (*9, 10*). Thus for the diagonal elements of the matrix representation of the Hamiltonian we used the expression

$$
E_{vr}(J, k, l)/hc = E_v/hc + B_v J(J + 1) + (A_v - B_v)k^2 - 2(A\zeta_5^v)kl + \eta_J J(J + 1)kl
$$

$$
+ \eta_K k^3 l + \tau_J J^2(J + 1)^2 kl + \tau_{JK} J(J + 1)k^3 l + \tau_K k^5 l
$$

$$
- D_J^v J^2(J + 1)^2 - D_{JK}^v J(J + 1)k^2 - D_K^v k^4 + H_J^v J^3(J + 1)^3
$$

$$
+ H_{JK}^v J^2(J + 1)^2 k^2 + H_{KJ}^v J(J + 1)k^4 + H_K^v k^6 + L_J^v J^4(J + 1)^4
$$

$$
+ L_{JJK}^v J^3(J + 1)^3 k^2 + L_{JK}^v J^2(J + 1)^2 k^4 + L_{JKK}^v J(J + 1)k^6 + \cdots \quad (1)
$$
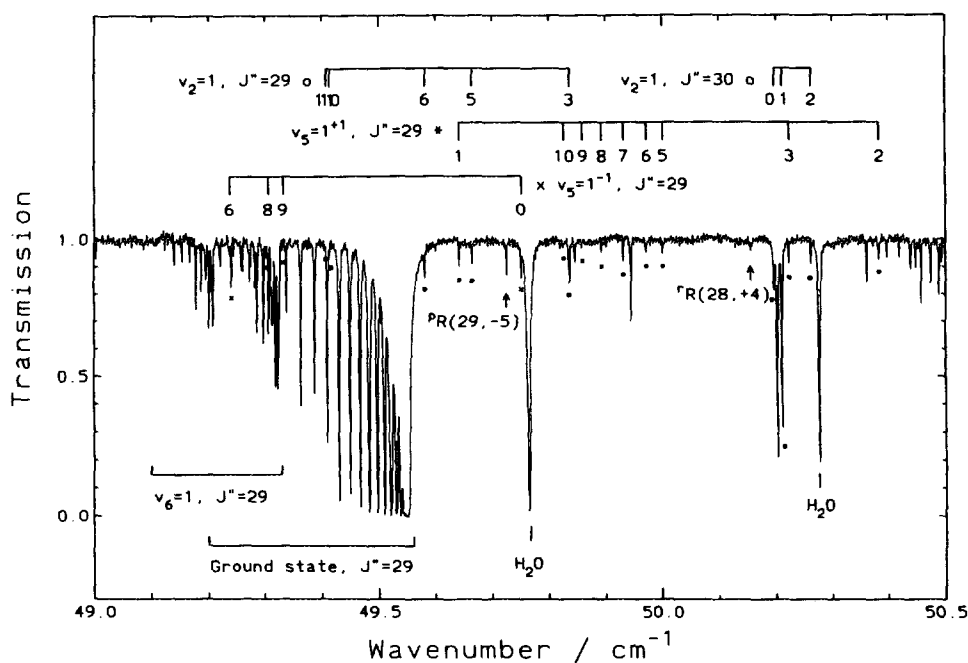
FIG. 1. Part of the far-infrared spectrum of the pure rotational transitions in the $v_2 = 1$ and $v_5 = 1$ vibrational states of $^{13}CH_3F$.

in which $l = 0$ for the nondegenerate vibrational state $v_2 = 1$ and $l = \pm 1$ for the sublevels of the doubly degenerate state $v_5 = 1$.

The strongest vibration–rotational interaction between the $v_2 = 1$ and the $v_5 = 1$ states in CH_3F is the x,y-Coriolis coupling which has the matrix elements

$$\langle 0, 1^{+1}; J, k + 1 |(H_{21} + H_{23})/hc| 1, 0^0; J, k \rangle$$

$$= -\langle 1, 0^0; J, k + 1 |(H_{21} + H_{23})/hc| 0, 1^{-1}; J, k \rangle$$

$$= 2^{1/2}\{C_{11}^{(1)} + C_{11}^{(3a)}J(J + 1) + C_{11}^{(3b)}[k^2 + (k + 1)^2]\}F(J, k), \qquad (2)$$

where

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

The same levels are connected by a matrix element of a quartic term in the expanded Hamiltonian which has, however, a different J, k dependence from that in Eq. (2),

$$\langle 0, 1^{+1}; J, k + 1 |H_{22}/hc| 1, 0^0; J, k \rangle$$

$$= \langle 1, 0^0; J, k + 1 |H_{22}/hc| 0, 1^{-1}; J, k \rangle = 2^{1/2}C_{11}^{(2)}(2k + 1)F(J, k). \qquad (4)$$

The "2, −1" l-type interaction plays an important role in CH_3F because it connects the closely spaced sublevels $+l$; J, K and $-l$; $J, K + 1$ in the $v_5 = 1$ state. It has the following matrix element with determinable parameters q_{12} and f_{12}^K:

$$\langle 0, 1^{-1}; J, k + 1 |(H_{22} + H_{24})/hc| 0, 1^{+1}; J, k \rangle$$

$$= 2\{[q_{12} + f_{12}^J J(J + 1)](2k + 1) + f_{12}^K[k^3 + (k^3 + 1)^3]\}F(J, k). \qquad (5)$$

In order to take into account the A_1–A_2 splittings of the energy levels in a convenient way, the matrix of the Hamiltonian was set up in the fully symmetrized set of basis functions A_+ and A_- obtained by a Wang transformation. In these basis wavefunctions, the matrix of the Hamiltonian factorizes for each value of the rotational quantum number J into three blocks corresponding to the A_1, A_2, and E symmetry species of the C_{3v} group. The dimensions of the A_1, A_2 blocks are $J + 1$ for A_+ and J for A_-, and $2J + 1$ for blocks which correspond to the symmetry species E.

ASSIGNMENT AND ANALYSIS

The results of a least-squares fit of the previously published microwave transition frequencies together with our submillimeter-wave and far-infrared data are given in Tables I–III. The $v_2 = 1$ and $v_5 = 1$ state parameters are given in Table I. The experimental and calculated frequencies (wavenumbers) of the rotational transitions are compared in Tables II and III.

The $v_2 = 1$ and $v_5 = 1$ vibrational states of $^{13}CH_3F$ are strongly perturbed by the x,y-Coriolis interaction because of the large Coriolis coupling coefficient $\zeta^y_{2,5x} = -0.60$ and because the difference $E_2 - E_5$ between the interacting vibrational levels is only 11.918 cm^{-1}. Besides this, there is a strong perturbation in the $v_5 = 1$ vibrational state which is caused by the "2, −1" l-type interaction because of the close resonances and

TABLE I

Parameters of the $v_2 = 1$ and $v_5 = 1$ Vibrational States of $^{13}CH_3F$ (in Units of cm^{-1})

Parameter	Diagonal terms		Parameter	Off-diagonal terms
	$v_2=1$	$v_5=1$		
E_5-E_2	11.918734 (325)[a]		$C^{(1)}_{11}$	0.5039516 (69)
A_v	5.2054072(1462)	5.1376192 (1715)	$C^{(3a)}_{11}$ / 10^{-5}	-0.26178(77)
B_v	0.82728656(26)	0.83102545 (189)	$C^{(3b)}_{11}$ / 10^{-5}	14.153 (499)
D^v_J / 10^{-6}	1.91949 (79)	1.98483(45)	$C^{(2)}_{11}$ / 10^{-3}	1.82377 (472)
D^v_{JK} / 10^{-6}	11.5949 (2316)	12.9085 (1045)	q_{12} / 10^{-3}	2.236009 (123)
D^v_K / 10^{-6}	156.6191 (240761)	141.6605 (312805)	f^K_{12} / 10^{-6}	0.8689 (409)
H^v_J / 10^{-9}	0. [b]	0.00155 [c]		z-Coriolis
H^v_{JK} / 10^{-9}	-0.3544 [c]	-0.0492 (152)	$A\xi^z_5$	-1.2782364 (907)
H^v_{KJ} / 10^{-9}	-35.5992(479)	1.3411 (2401)	η_J / 10^{-4}	-0.51551 (1849)
H^v_K / 10^{-9}	779.14[c]	1.026 [c]	η_K / 10^{-4}	-2.11459 (60360)
L^v_{JK} / 10^{-11} (see [d])	4.70131 [c]	-0.41700 [c]	τ_J / 10^{-6}	-0.003389 (120)
L^v_{JKK} / 10^{-11} (see [d])	49.1929[c]	1.1406[c]	τ_{JK} / 10^{-6}	0.106108 (3602)
			τ_K / 10^{-6}	-0.112194 [c]

Note. Number of data, 711; standard deviation of the fit, 0.427 MHz.

[a] Figures in parentheses are standard errors in units of the last digit stated.

[b] Constrained value.

[c] Constrained to the value obtained by a simultaneous fit of the rotational and vibration–rotational data in Ref. (3).

[d] L^v_J, L^v_{JJK}, and L^v_K constrained to zero.

TABLE II

Frequencies of the Pure Rotational Transitions in the $v_2 = 1$ and $v_5 = 1$
Vibrational States of $^{13}CH_3F$

J	K	l	Exp[b]	Unc[c]	E-C[d]	Ref[e]	J	K	l	Exp[b]	Unc[c]	E-C[d]	Ref[e]
$v_2 = 1$							2	1	1	158754.880	200	439	N
							2	1	1	149456.600	50	-16	L
0	0		46354.370	200	103	H	2	2	1	152575.463	50	-14	L
1	0		92820.690	*	-2782	H	2	0	-1	(158990.722)			
1	1		89754.250	200	-750	H	2	1	-1	(132567.216)			
2	0		(139503.540)				2	2	-1	(143767.789)			
2	1		(135693.370)				2	2	-1	(143766.806)			
2	2		(163824.298)				3	1	2	211202.970	200	293	N
3	0		186459.210	200	99	N	3	1	1	199268.190	200	-32	N
3	1		182444.660	200	-360	N	(3	1	1	199268.214	50	-8	L)[g]
3	2		(214716.039)				3	2	1	203428.180	200	251	N
3	3		203356.250	200	-365	N	3	3	1	202317.540	200	290	N
4	0		233721.070	200	257	N	3	0	-1	(211517.668)			
4	1		229878.730	200	63	N	3	1	-1	(179400.766)			
4	2		264911.290	200	-642	N	3	2	-1	(191819.157)			
4	3		253993.420	200	-626	N	3	2	-1	(191816.040)			
4	4		250654.910	200	-280	N	3	3	-1	(194981.037)			
5	0		281290.360	200	97	N	4	1	1	263329.520	200	231	N
5	1		277830.000	*	-2088	N	4	1	1	249073.540	200	73	N
5	2		(314736.827)				4	2	1	254273.840	200	18	N
5	3		304519.830	200	-729	N	4	3	1	252875.400	200	273	N
5	4		300737.340	200	-302	N	4	4	1	252085.350	200	199	N
5	5		(299159.501)				4	0	-1	(261971.603)			
6	0		329149.140	200	373	N	4	1	-1	(228304.208)			
6	1		(326164.952)				4	2	-1	(239968.394)			
6	2		364350.000	200	-281	N	4	2	-1	(239959.538)			
6	3		354931.270	200	-750	N	4	3	-1	(243745.878)			
6	4		350794.550	200	-528	N	4	4	-1	(245368.483)			
6	4		350794.520	50	-558	L	5	1	1	315121.440	200	185	N
6	5		348994.324	50	311	L	5	1	1	298870.660	200	114	N
6	6		348036.221	*	1352	L	5	2	1	305109.890	200	23	N
7	0		377266.558	50	461	L	5	3	1	303418.640	200	25	N
7	1		374770.889	50	79	L	5	4	1	302474.340	200	47	N
7	2		413833.991	50	-155	L	5	5	1	301846.700	200	153	N
7	3		(405229.143)				5	0	-1	312361.250	200	479	N
7	4		400823.879	50	-568	L	5	1	-1	277104.140	200	194	N
7	5		398817.203	50	313	L	5	2	-1	288232.010	200	-442	N
7	6		397732.890	*	1270	L	5	2	-1	288206.450	200	411	N
7	7		397055.211	50	-359	L	5	3	-1	292522.930	200	-73	N
8	0		425608.037	50	632	L	5	4	-1	(294437.392)			
8	1		423573.271	50	268	L	5	5	-1	(295477.625)			
8	2		463232.826	50	-56	L	6	1	1	366543.820	200	190	N
8	3		455415.365	50	-751	L	6	1	1	348657.530	200	142	N
8	4		450822.520	50	-580	L	6	2	1	355931.890	200	107	N
8	5		448626.859	50	326	L	6	3	1	353944.820	200	81	N
8	6		447420.336	50	1068	L	6	4	1	352848.260	200	-13	N
8	7		446660.984	*	-1312	L	6	5	1	352120.270	200	93	N
8	8		446138.503	50	-235	L	6	6	1	351587.360	200	206	N
$v_5 = 1$							6	0	-1	362356.790	200	432	N
							6	1	-1	326107.700	200	23	N
0	0	-1	53765.640	200	423	H	6	2	-1	(336664.444)			
1	1	1	106019.990	200	-515	H	6	2	-1	(336558.471)			
1	1	1	99640.600	200	279	H	6	3	-1	341314.180	200	-61	N
1	0	-1	107006.510	200	1622	H	6	4	-1	343503.621	50	-71	L
1	1	-1	(85708.308)[f]				6	5	-1	344707.040	200	113	N
							6	6	-1	(345444.058)			

energy level crossings for certain values of J and kl. As a result, the rotational lines do not appear for a given J in bunches of lines with a rather regular K structure resolved by centrifugal distortion effects, but as a strongly irregular structure which dominates the overall appearance of the rotational spectrum in the $v_2 = 1$ and $v_5 = 1$ states of CH_3F.

TABLE II—*Continued*

J	K	l	Exp[b]	Unc[c]	E-C[d]	Ref[e]		J	K	l	Exp[b]	Unc[c]	E-C[d]	Ref[e]
7	1	1	415118.668	50	126	L		8	0	-1	461568.944	50	355	L
7	1	1	398431.626	50	246	L		8	1	-1	424427.769	50	-84	L
7	2	1	(406734.159)					8	2	-1	430233.141	50	-382	L
7	3	1	(404450.466)					8	2	-1	433573.089	50	-131	L
7	4	1	403204.497	50	-106	L		8	3	-1	438945.921	50	-108	L
7	5	1	402378.077	50	-56	L		8	4	-1	441626.902	50	46	L
7	6	1	401772.640	50	-11	L		8	5	-1	443141.493	50	231	L
7	7	1	401298.200	50	28	L		8	6	-1	444099.297	50	277	L
7	0	-1	412066.657	50	358	L		8	7	-1	444693.474	50	178	L
7	1	-1	375230.954	50	-55	L		8	8	-1	445106.631	50	-354	L
7	2	-1	387766.670	50	-398	L								
7	2	-1	385015.393	50	-37	L		Direct l-type transitions						
7	3	-1	390121.225	50	-80	L								
7	4	-1	392566.974	50	4	L		2	+1		9628.790	200	248	H
7	5	-1	393928.590	50	105	L		3	+1		18926.800	200	433	H
7	6	-1	394766.949	50	170	L		4	+1		30861.450	200	628	H
7	7	-1	395314.495	50	44	L		5	+1		45117.460	200	816	H
8	1	1	472178.716	50	-11	L		6	+1		61368.170	200	817	H
8	1	1	448189.176	50	482	L								
8	2	1	457510.110	50	-156	L		Forbidden rotational transitions [h]						
8	3	1	454932.537	50	-152	L								
8	4	1	453540.680	50	-122	L		rR(7,+1)[i]			421064.075	50	74	L
8	5	1	452618.123	50	-104	L		rR(8,+1)[i]			436178.533	50	-449	L
8	6	1	451941.677	50	-60	L		pR(7,-2)[i]			381821.321	50	-288	L
8	7	1	451410.993	50	1	L		pR(8,-2)[i]			466233.300	50	31	L
8	8	1	450973.311	50	46	L		pR(3,-1)			210703.861	50	129	L

a) In doublets corresponding to transitions between levels with the resolved A_1-A_2 splitting, transitions between the A_+ blocks are given first.

b) Exp is the experimental value in MHz; transition frequencies in parentheses are calculated.

c) E - C = ν_{exp} - ν_{calc} in kHz.

d) Estimated uncertainty of the experiment in kHz. Transitions denoted by asterisk were not included in the fit.

e) H: data taken from Ref. (1), N: our measurements with RAD* spectrometer in Nizhnii Novgorod; L: our measurements at the University of Lille.

f) According to Hirota et al. (1), the experimental value is 85461.32 MHz.

g) The same transition as indicated on the line above.

h) Notation: xR(J,kl) with x = r denoting ΔK = +1 rotational transition, x = p denoting ΔK = -1 rotational transition.

i) Transitions between the A_+ blocks.

For low J values the assignments could be based in principle on the previous results of Hirota *et al.* (*1*), but for higher J's the assignments would be much more difficult without a parallel analysis of the high-resolution infrared bands ν_2 and ν_5 [see Ref. (*3*)]. This was important also for the lower values of J because the frequency of the rotational transition in the ν_5 = 1 state, $J = 2, kl = -1 \leftarrow J = 1, kl = -1$, which was reported by Hirota *et al.* (*1*), is probably obscured by a typographical error in the publication. Attempts to include this frequency in the early stages of the analysis led to considerable difficulties until we decided to exclude it from the fit. Few other frequencies for which the uncertainty of the experimental value was probably larger than the estimated one were also omitted from the analysis (see Tables II and III).

In the final fits, we used 12 frequencies from the data set reported by Hirota *et al.* (*1*), 106 frequencies from our millimeter-wave and submillimeter-wave measurements, and 593 wavenumbers of the rotational transitions from our measurements of the far-infrared spectra. Their statistical weights were taken as $1/UNC^2$, where UNC is the estimated uncertainty of the line as indicated in Tables II and III.

The A_1–A_2 splittings of the rotational energy levels which appear in the kl = +1 states ("giant" *l*-type doubling) could be easily observed in the whole spectrum range

TABLE III

Wavenumbers (in Units of cm^{-1}) of the Pure Rotational Transitions in the $v_2 = 1$ and $v_5 = 1$ Vibrational States of $^{13}CH_3F$[a]

J	K	l	Exp[b]	Unc[c]	E-C[d]	J	K	l	Exp[b]	Unc[c]	E-C[d]	J	K	l	Exp[b]	Unc[c]	E-C[d]
$v_2 = 1$						23	8		39.61979	10	43	29	2		48.62908	10	7
						23	10		39.56981	10	70	29	3		49.83679	100	-95
18	0		30.52956	10	0	23	11		39.56049	66	27	29	3		49.83679	100	47
18	1		30.53469	10	9	24	0		40.37464	16	0	29	5		49.66558	66	-74
18	3		31.78078	10	-11	24	1		40.38746	16	-8	29	6		49.58102	233	-202
18	3		31.78078	10	0	24	2		40.44632	10	9	29	10		49.41419	16	202
18	4		31.64775	10	-12	24	3		41.64927	26	-23	29	11		49.40791	66	85
18	5		31.54353	10	-25	24	3		41.64927	26	19	30	0		50.19709	33	9
19	0		32.17072	10	-3	24	4		41.54859	10	-21	30	1		50.21073	16	-30
19	1		32.17810	16	13	24	5		41.44692	33	-38	30	2		50.26215	10	-5
19	3		33.42895	16	-18	24	6		41.36579	100	-105	30	3		51.47152	100	-17
19	3		33.42895	16	-4	24	10		41.21320	66	145	30	3		51.47152	100	174
19	4		33.30148	10	-5	25	0		42.01401	16	7	30	4		51.39726	16	-31
19	5		33.19691	16	-17	25	1		42.02736	10	4	30	5		51.30516	66	-74
19	6		33.12320	66	-59	25	2		42.08497	16	14	30	6		51.22251	10	0
20	0		33.81215	16	10	25	3		43.29018	33	51	30	10		51.05219	66	281
20	1		33.82104	10	4	25	3		43.29018	33	103	30	11		51.04675	66	149
20	2		33.88326	16	-16	25	4		43.19390	33	-8	31	0		51.83002	10	-29
20	3		35.07582	16	-9	25	5		43.09339	33	-39	31	1		51.84415	33	-12
20	3		35.07582	16	8	25	6		43.01112	166	-130	31	2		51.89409	10	-5
20	4		34.95366	16	-14	25	9		42.87453	166	58	31	3		53.10198	200	-252
20	5		34.84915	16	-21	25	10		42.85502	66	142	31	3		53.10198	200	12
20	6		34.77338	100	-87	25	12		42.85131	166	-81	31	4		53.03337	16	-30
20	7		34.72192	50	76	26	0		43.65256	10	9	31	5		52.94299	66	-97
20	9		34.65490	100	-47	26	1		43.66628	16	10	31	6		52.86024	66	-36
20	10		34.63604	330	-75	26	2		43.72241	16	-5	31	9		52.70874	66	299
20	10		34.63794	330	114	26	3		44.92831	33	-25	32	0		53.46204	10	-33
21	0		35.45309	10	-15	26	3		44.92831	33	41	32	1		53.47591	10	-28
21	1		35.46351	16	-6	26	4		44.83756	33	-14	32	2		53.52467	10	-11
21	2		35.52519	10	-7	26	5		44.73834	33	-62	32	3		54.73622	33	-15
21	3		36.72115	23	-15	26	6		44.65766	100	76	32	3		54.73303	100	50
21	3		36.72115	23	6	26	9		44.51364	333	-146	32	4		54.66778	33	-39
21	5		36.50051	10	-5	26	12		44.49396	10	-122	32	5		54.57953	66	-95
21	6		36.42291	100	-92	27	0		45.29010	16	-2	32	6		54.49847	100	121
21	11		36.27252	100	35	27	1		45.30408	10	4	32	9		54.34317	100	267
21	12		36.27252	100	-149	27	2		45.35921	10	12	32	12		54.33971	16	117
22	0		37.09425	10	8	27	3		46.56596	33	-24	33	0		55.09265	33	-45
22	1		37.10563	16	4	27	3		46.56596	33	60	33	1		55.10651	10	-25
22	2		37.16647	33	9	27	4		46.47986	10	-8	33	2		55.15399	10	-7
22	3		38.36520	33	-14	27	5		46.38243	10	-37	33	3		56.36746	10	-22
22	3		38.36520	33	12	27	6		46.29841	200	-177	33	3		56.36188	33	12
22	4		38.25414	33	0	27	10		46.13740	100	266	33	4		56.30061	10	-44
22	5		38.15031	33	-34	27	11		46.12786	100	-10	33	5		56.21413	100	-127
22	6		38.07161	100	-87	27	12		46.13740	100	-20	34	0		56.72198	10	-43
22	9		37.94652	66	134	28	0		46.92674	10	-8	34	1		56.73561	10	-27
22	10		37.92554	66	-16	28	1		46.94079	10	-5	34	2		56.78185	16	-6
22	11		37.91645	66	-6	28	2		46.99464	10	2	34	3		58.00024	133	61
22	12		37.91645	66	-290	28	3		48.20204	100	-55	34	3		57.98938	10	-12
23	0		38.73462	10	-5	28	3		48.20204	100	53	34	4		57.93262	100	36
23	1		38.74697	16	2	28	4		48.11923	100	-145	34	5		57.84740	66	-126
23	2		38.80679	16	7	28	5		48.02471	33	-57	34	6		57.76261	330	-345
23	3		40.00789	26	-17	28	6		47.94038	200	-187	34	9		57.60823	100	199
23	3		40.00789	26	15	28	9		47.79620	10	165	35	0		58.34983	10	-43
23	4		39.90214	33	-4	28	10		47.77622	66	229	35	1		58.36314	10	-37
23	5		39.79921	33	-36	29	0		48.56242	16	-5	35	2		58.40812	10	-17
23	6		39.71916	*	-101	29	1		48.57651	10	-2	35	3		59.63793	10	179
23	6		39.72165	*	147												

investigated in this paper. The splitting of the $kl = -2$ levels could be well resolved in the millimeter-wave and submillimeter-wave spectra (cf. Table II). In the far-infrared spectrum, we could observe the splitting only for $J = 18$ and 19 (cf. Table III). In the $v_2 = 1$ vibrational state of $^{13}CH_3F$, we were able to resolve the A_1–A_2 splittings only for $K = 3$, $J \geqslant 32$. In some cases, the calculation predicts splittings of lines which

TABLE III—*Continued*

J	K	l	Exp[b]	Unc[c]	E-C[d]	J	K	l	Exp[b]	Unc[c]	E-C[d]	J	K	l	Exp[b]	Unc[c]	E-C[d]
35	3		59.61585	10	12	19	4	1	33.52850	10	-10	21	3	-1	35.83905	33	9
35	4		59.56129	33	-48	19	5	1	33.47163	10	-22	21	4	-1	36.17470	16	-16
35	5		59.47879	100	-146	19	6	1	33.42894	66	70	21	5	-1	36.08696	10	11
35	6		59.40137	333	325	19	7	1	33.39304	10	5	21	6	-1	36.14793	16	19
35	8		59.27679	66	276	19	9	1	33.33719	33	0	21	7	-1	36.18818	433	-460
36	0		59.97589	33	-69	19	10	1	33.31378	66	-8	21	10	-1	36.26076	33	-43
36	1		59.98914	16	-45	19	11	1	33.29211	66	-42	22	1	1	38.99463	10	3
36	2		60.03275	33	-40	19	12	1	33.27282	33	-3	22	1	1	38.12673	10	-7
36	3		(61.29663)			19	0	-1	33.40919	10	-7	22	3	1	39.45549	166	28
36	3		61.24000	10	-39	19	1	-1	33.50406	10	1	22	4	1	38.51070	10	1
36	4		61.18873	10	-84	19	2	-1	32.39778	33	25	22	5	1	38.45598	16	20
36	5		61.10853	100	-157	19	2	-1	32.39840	33	-29	22	6	1	38.40822	166	-97
36	6		61.02448	433	-406	19	3	-1	32.58105	33	25	22	7	1	38.37068	16	4
36	9		60.86964	100	301	19	4	-1	32.74775	10	4	22	8	1	38.33757	33	-6
37	0		61.60070	33	-62	19	5	-1	32.81260	10	6	22	10	1	38.28222	33	0
37	1		61.61346	33	-61	19	6	-1	32.87237	16	-19	22	12	1	38.23566	33	7
37	3		62.50405	200	-188	19	10	-1	32.97664	100	-113	22	0	-1	38.31408	16	5
37	3		62.86345	66	-1	19	11	-1	32.98371	166	-225	22	1	-1	38.41402	10	-5
37	4		62.81435	66	-124	20	1	1	35.68921	10	0	22	2	-1	37.30297	33	38
37	7		62.58885	100	222	20	1	1	34.82579	10	9	22	2	-1	37.30297	100	-7
38	0		63.22369	33	-72	20	2	1	35.45718	33	34	22	3	-1	37.46882	10	0
38	1		63.23620	33	-71	20	3	1	35.21859	10	7	22	4	-1	36.77794	50	99
38	3		(64.63097)			20	4	1	35.19202	10	-3	22	5	-1	37.72497	16	8
38	3		(64.48488)			20	5	1	35.13482	10	0	22	6	-1	37.78432	16	1
38	4		64.88426	100	210	20	6	1	35.08976	33	-23	22	7	-1	37.83128	100	81
38	6		64.28511	100	86	20	7	1	35.05351	10	-2	22	8	-1	37.86308	33	-28
						20	8	1	35.02261	10	-3	22	9	-1	37.88582	66	-38
$v_5 = 1$						20	9	1	34.99329	233	-226	22	10	-1	37.90191	66	46
						20	10	1	34.97135	100	15	22	11	-1	37.91089	100	12
18	1	1	32.37632	10	0	20	11	1	34.94912	10	20	23	1	1	40.64449	16	-13
18	1	1	31.52004	16	4	20	0	-1	35.04423	10	8	23	1	1	39.77573	16	5
18	2	1	32.10446	16	-20	20	1	-1	35.14137	10	6	23	2	1	40.45590	16	-2
18	3	1	31.93549	10	-5	20	2	-1	34.03345	83	78	23	3	1	40.10366	16	12
18	4	1	31.86302	10	0	20	2	-1	34.03345	10	-3	23	4	1	40.16406	10	3
18	5	1	31.80736	16	-1	20	3	-1	34.20938	10	0	23	5	1	40.11355	33	5
18	6	1	31.76461	66	-52	20	4	-1	34.41967	16	10	23	6	1	40.06656	10	6
18	7	1	31.73106	10	-11	20	5	-1	34.44957	10	-1	23	7	1	40.02706	10	0
18	8	1	31.70105	166	-153	20	6	-1	34.51048	10	-1	23	8	1	39.99447	133	137
18	9	1	31.67783	16	15	20	9	-1	34.60602	16	6	23	10	1	39.93627	33	48
18	10	1	31.65529	33	-7	20	10	-1	34.62027	66	30	23	0	-1	39.94898	10	6
18	11	1	31.63342	166	-160	20	11	-1	34.62846	66	-7	23	1	-1	40.04951	10	-2
18	12	1	31.61805	166	176	21	1	1	37.34188	166	-92	23	2	-1	38.93736	33	23
18	0	-1	31.77463	10	16	21	1	1	36.47680	10	-1	23	2	-1	38.93736	33	-11
18	1	-1	31.86613	10	-10	21	2	1	37.12631	10	9	23	3	-1	39.09875	16	14
18	2	-1	30.76242	100	-5	21	3	1	36.76168	10	21	23	4	-1	39.42200	10	10
18	2	-1	30.76427	100	3	21	4	1	36.85294	10	-2	23	5	-1	39.36497	10	15
18	3	-1	30.95539	10	0	21	5	1	36.79612	10	-5	23	6	-1	39.42016	33	-12
18	4	-1	31.09878	33	-30	21	6	1	36.74895	100	-138	23	7	-1	39.46650	100	-73
18	5	-1	31.17554	16	16	21	7	1	36.71277	16	-1	24	1	1	42.29303	10	9
18	6	-1	31.23400	10	6	21	8	1	36.68112	33	31	24	1	1	41.42335	16	0
18	8	-1	31.30107	166	-160	21	9	1	36.65223	200	-45	24	2	1	42.11672	10	2
18	10	-1	31.33514	100	47	21	10	1	36.62723	10	-11	24	3	1	41.87905	16	23
18	11	-1	31.34216	50	-30	21	12	1	36.58287	10	32	24	4	1	41.81076	10	6
18	12	-1	31.34433	100	-206	21	0	-1	36.67909	16	0	24	5	1	41.76897	16	-16
19	1	1	34.03335	50	-40	21	1	-1	36.77794	16	-4	24	6	1	41.72195	16	-18
19	1	1	33.17337	10	-7	21	2	-1	35.66810	100	37	24	7	1	41.68176	10	-19
19	2	1	33.78365	10	-1	21	2	-1	35.66810	100	-22	24	8	1	41.64713	10	0
19	3	1	33.58977	10	0												

were within the range of the significant digits of the experimental transition frequencies or wavenumbers, but the splittings could not be resolved in the spectrum. In these cases, the experimental frequencies were compared in the fit with both calculated values but their weights were decreased by taking into account the predicted splitting and the quality of the blended lines.

In most cases, the observed lines correspond to transitions with the usual selection rules for the purely rotational transitions in a symmetric top molecule $\Delta J = 1$, ΔK

TABLE III—*Continued*

J	K	l	Exp[b]	Unc[c]	E-C[d]	J	K	l	Exp[b]	Unc[c]	E-C[d]	J	K	l	Exp[b]	Unc[c]	E-C[d]
24	10	1	41.58814	33	15	27	2	1	47.08390	10	7	29	6	-1	49.23761	33	38
24	11	1	41.56144	133	-53	27	3	1	46.91123	10	0	29	8	-1	49.30667	100	85
24	0	-1	41.58370	10	5	27	4	1	46.62376	10	21	29	9	-1	49.33223	100	-97
24	1	-1	41.68433	16	0	27	5	1	46.72048	16	18	30	1	1	(52.14676)		
24	2	-1	40.57137	16	16	27	6	1	46.67825	33	10	30	1	1	51.28255	13	-1
24	2	-1	40.57137	16	-11	27	7	1	46.63691	16	0	30	2	1	52.02936	10	4
24	3	-1	40.72814	33	0	27	9	1	46.56596	100	-60	30	3	1	51.87391	16	26
24	4	-1	40.93733	10	5	27	12	1	46.47986	200	-58	30	4	1	51.55768	10	20
24	5	-1	41.00886	10	6	27	0	-1	46.48611	10	10	30	5	1	51.63167	16	11
24	6	-1	41.05605	10	27	27	1	-1	46.58430	10	-6	30	6	1	51.61488	16	15
24	7	-1	41.10363	100	53	27	1	-1	(46.58436)			30	7	1	51.57555	10	-6
24	10	-1	41.17821	33	-55	27	2	-1	45.47007	16	23	30	8	1	51.53781	33	13
24	12	-1	41.19324	100	-53	27	2	-1	45.47007	10	9	30	10	1	51.46967	66	15
25	1	1	43.93957	10	3	27	3	-1	45.61396	10	0	30	0	-1	51.38324	10	10
25	1	1	43.06977	16	-6	27	4	-1	45.76032	10	6	30	1	-1	51.47699	33	13
25	2	1	43.77487	16	-2	27	5	-1	46.05217	166	64	30	2	-1	50.36126	10	17
25	3	1	43.57567	16	11	27	6	-1	45.96196	33	41	30	2	-1	50.36126	10	9
25	4	1	43.44595	10	6	27	7	-1	46.00684	166	147	30	3	-1	50.49365	33	-12
25	5	1	43.42226	16	-14	27	12	-1	46.10180	66	-100	30	4	-1	50.62677	16	13
25	6	1	43.37612	33	7	28	1	1	48.86851	83	-64	30	7	-1	50.90063	10	-17
25	7	1	43.33506	10	-21	28	1	1	48.00163	100	5	30	11	-1	50.99477	166	-17
25	9	1	43.26746	50	-34	28	2	1	48.73470	33	3	30	12	-1	50.99889	50	-182
25	10	1	43.23917	10	40	28	3	1	48.56884	10	1	31	1	1	53.78255	23	-14
25	0	-1	43.21822	10	7	28	4	1	48.10092	10	10	31	1	1	52.92081	16	-5
25	1	-1	43.31849	10	4	28	5	1	48.36370	16	15	31	2	1	53.67332	16	15
25	2	-1	42.20492	16	16	28	6	1	48.32629	16	22	31	3	1	53.52224	16	30
25	2	-1	42.20492	16	-5	28	7	1	48.28494	10	-13	31	4	1	53.30341	10	21
25	3	-1	42.35798	66	70	28	8	1	48.24830	66	65	31	5	1	53.25041	33	31
25	4	-1	42.52856	16	8	28	9	1	48.21364	16	10	31	6	1	53.25534	66	44
25	5	-1	42.66174	10	13	28	10	1	48.18202	50	-3	31	7	1	53.21773	16	-7
25	6	-1	42.69138	33	45	28	12	1	48.12467	200	-33	31	8	1	53.17987	16	-3
25	7	-1	42.73738	66	-67	28	0	-1	48.11923	16	10	31	0	-1	53.01376	16	2
25	8	-1	42.77372	66	6	28	1	-1	48.21593	10	-15	31	1	-1	53.10578	33	17
25	9	-1	42.79918	66	33	28	2	-1	47.10143	16	24	31	2	-1	51.98954	10	4
25	11	-1	42.82655	66	37	28	2	-1	47.10143	10	13	31	2	-1	51.98954	10	-1
25	12	-1	42.83091	66	-37	28	3	-1	47.24139	10	6	31	3	-1	52.11908	16	12
26	1	1	45.58443	10	-2	28	4	-1	47.38218	10	19	31	4	-1	52.24845	16	10
26	1	1	44.71513	10	7	28	5	-1	47.85372	100	3	31	5	-1	52.47102	16	-17
26	2	1	45.43061	10	3	28	6	-1	47.59855	33	36	31	6	-1	52.53340	16	51
26	3	1	45.24833	10	6	28	7	-1	47.63970	200	189	32	1	1	(55.41645)		
26	4	1	45.05871	10	14	28	9	-1	47.69949	200	-190	32	1	1	54.55753	10	-11
26	5	1	45.07307	10	8	28	10	-1	47.71767	200	-214	32	2	1	55.31482	10	6
26	6	1	45.02799	16	-8	29	1	1	50.50885	10	-2	32	3	1	55.16798	10	23
26	7	1	44.98706	10	10	29	1	1	49.64277	16	-2	32	4	1	54.99805	166	138
26	9	1	44.91832	16	35	29	2	1	50.38324	10	9	32	5	1	54.85044	50	34
26	0	-1	44.85253	16	22	29	3	1	50.22284	10	10	32	6	1	54.89207	100	28
26	1	-1	44.95175	16	-4	29	5	1	50.00152	16	12	32	7	1	54.85744	10	-33
26	2	-1	43.83779	33	12	29	6	1	49.97199	33	31	32	8	1	54.82006	10	-10
26	2	-1	43.83779	33	-5	29	7	1	49.93127	10	-6	32	9	1	54.78401	16	-9
26	3	-1	43.98607	10	16	29	8	1	49.89326	16	-30	32	0	-1	54.64368	66	52
26	5	-1	44.33427	10	13	29	10	1	49.82671	33	8	32	1	-1	54.73303	16	-40
26	6	-1	44.32630	33	26	29	0	-1	49.75169	10	13	32	2	-1	53.61685	16	8
26	7	-1	44.37360	166	146	29	1	-1	49.84688	16	-2	32	2	-1	53.61886	200	203
26	8	-1	44.40781	66	-51	29	2	-1	48.73184	10	21	32	3	-1	53.74316	33	-5
26	9	-1	44.43385	66	-34	29	2	-1	48.73184	10	12	32	4	-1	53.86925	16	-1
27	1	1	47.22821	66	54	29	3	-1	48.86877	100	79	32	5	-1	54.04456	16	-6
27	1	1	46.35896	10	-2	29	4	-1	49.00434	16	-3	32	6	-1	54.20089	66	67

$= 1$, $\Delta l = 0$. However, we were able to observe 14 lines of purely rotational transitions in the $v_5 = 1$ state, which are allowed by the "2, -1" l-type interaction described by Eq. (5). They have the selection rules $\Delta J = \pm 1$, $\Delta(k - l_5) = \pm 3$, as illustrated by Fig. 2. Such perturbation-allowed rotational transitions can have a significant intensity only if there is a large difference between the mixing of the wavefunctions in the upper and lower rotational levels. This is illustrated by Table IV, in which the coefficients of the mixing of the vibration–rotational wavefunctions are given. The mixing of the

TABLE III—*Continued*

J	K	l	Exp[b]	Unc[c]	E-C[d]	J	K	l	Exp[b]	Unc[c]	E-C[d]	J	K	l	Exp[b]	Unc[c]	E-C[d]
32	7	-1	54.16314	66	45	35	1	1	60.29166	33	-245	36	8	-1	60.69961	166	146
32	8	-1	54.19497	66	129	35	1	1	59.45832	10	-4	37	1	1	(63.92569)		
33	1	1	57.04701	33	-55	35	2	1	60.22614	16	13	37	1	1	62.71691	10	-13
33	1	1	(56.19285)			35	3	1	60.09097	16	-4	37	2	1	63.48909	10	13
33	2	1	56.95416	10	7	35	4	1	59.96798	33	25	37	3	1	63.36180	33	19
33	3	1	56.81131	16	15	35	5	1	59.43079	100	26	37	4	1	63.24891	16	23
33	4	1	56.66512	10	25	35	6	1	59.77627	166	102	37	5	1	62.39325	100	19
33	6	1	56.52537	100	60	35	7	1	59.76251	33	-25	37	7	1	63.01716	16	-90
33	7	1	56.49530	10	-7	35	0	-1	59.52119	66	59	37	1	-1	62.85364	33	-44
33	0	-1	56.27136	16	20	35	1	-1	59.60950	10	-23	37	2	-1	61.73371	33	-13
33	1	-1	56.35990	16	-18	35	2	-1	58.49127	10	13	37	2	-1	61.73371	33	-14
33	2	-1	55.24289	10	4	35	2	-1	58.49127	10	11	37	4	-1	61.95735	33	-10
33	2	-1	55.24289	10	0	35	3	-1	58.61286	100	-67	37	5	-1	62.07512	33	-33
33	3	-1	55.36807	133	126	35	4	-1	58.72571	100	-13	37	7	-1	62.35049	166	213
33	4	-1	55.48926	33	2	35	5	-1	58.85356	100	-35	38	1	1	(65.04588)		
33	5	-1	55.63983	33	-14	35	6	-1	59.40137	100	5	38	1	1	64.34338	33	-45
33	6	-1	55.89494	50	92	35	7	-1	59.06429	166	196	38	4	1	64.88426	66	38
33	7	-1	55.79398	100	-21	35	8	-1	59.07297	33	-8	38	7	1	64.63904	66	-123
34	1	1	58.67359	33	-119	35	9	-1	59.09681	166	-117	38	0	-1	64.29069	33	202
34	1	1	57.82649	16	4	36	1	1	(61.88627)			38	1	-1	64.47364	33	-46
34	2	1	58.59145	33	28	36	1	1	61.08852	16	-6	38	2	-1	63.35349	33	54
34	3	1	58.45246	16	20	36	2	1	61.85871	16	10	38	2	-1	63.35349	33	54
34	4	1	58.32033	10	22	36	3	1	61.72737	16	-10						
34	5	1	57.94768	83	32	36	4	1	61.61021	16	3	Forbidden rotational transitions[e]					
34	6	1	58.15393	166	92	36	6	1	61.39150	266	185						
34	7	1	58.12989	33	-55	36	7	1	61.39150	16	-58	rR(21,+3)			38.08079	33	72
34	0	-1	57.89775	33	49	36	0	-1	61.13994	133	112	rR(22,+3)			38.09562	33	8
34	1	-1	57.98551	33	-3	36	1	-1	61.23238	16	-22	rR(28,+4)			50.15584	33	-79
34	2	-1	56.86760	10	-5	36	2	-1	60.11398	66	75	rR(29,+4)			49.50451	33	10
34	2	-1	56.86760	10	-7	36	2	-1	60.11398	66	74	pR(21,-4)			34.85645	100	18
34	4	-1	57.10804	50	-8	36	3	-1	60.23838	166	-121	pR(22,-4)			38.13675	100	13
34	5	-1	57.24489	100	0	36	4	-1	60.34189	100	-41	pR(23,-4)			41.46334	100	14
34	7	-1	57.42607	100	-95	36	5	-1	60.46417	66	-36	pR(28,-5)			45.80018	100	230
34	9	-1	57.47416	100	51	36	7	-1	60.70219	16	28	pR(29,-5)			49.72669	10	18

a) In doublets corresponding to transitions between levels with the A_1-A_2 splitting (J,K = 3 in the $v_2 = 1$ state, J,kl = +1 and J,kl = -2 in the $v_5 = 1$ state), transitions between the A_+ blocks are given first.

b) Transition frequencies in parentheses are calculated. Transitions denoted by asterisk were not included in the fit.

c) Estimated uncertainty of the experiment in units 10^{-5} cm^{-1}.

d) E - C = v_{exp} - v_{calc} in units 10^{-5} cm^{-1}.

e) See footnote h) in Table II.

symmetrized zeroth-order wavefunctions $| v_2, v_5; J, kl \rangle_0$ which are involved in these rotational transitions can be described as

$$| 0, 1^{\pm 1}; J, kl \rangle_{perturbed} = c_1 | 0, 1^{\pm 1}; J, kl = +1 \rangle_0 + c_2 | 0, 1^{\pm 1}; J, kl = -2 \rangle_0$$

$$+ c_3 | 1, 0^0; J, k = 0 \rangle_0 + c_4 | 1, 0^0; J, k = 3 \rangle_0 + c_5 | 0, 1^{\pm 1}; J, kl = +4 \rangle_0, \quad (6)$$

where on the left-hand side of Eq. (6), kl is either +1 or -2 depending on the values of the mixing coefficients c_i (see further discussion).

There is almost a complete mixing of the wavefunctions of the $kl = +1$ and $kl = -2$ unperturbed states for $J = 8$, while the mixing is relatively small for $J = 7$ and $J = 9$. It should be noted that for $J = 8$, both perturbed wavefunctions have the largest contributions from the unperturbed wavefunction $| 0, 1^{\pm 1}; J = 8, kl = -2 \rangle_0$ (see Table IV). Thus, formally both states should be assigned as the $kl = -2$ states of $v_5 = 1$, but this is certainly not convenient. In cases such as this the assignment is rather arbitrary but certainly the choice of a label which we decide to attach to a particular line is a matter of convenience. This fact has no effect on the calculation of the pa-
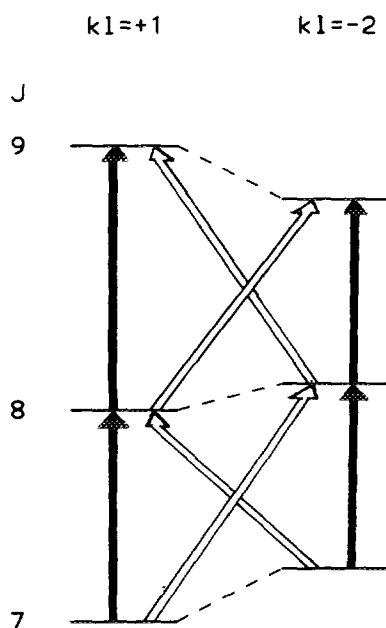
$kl = +1$ $kl = -2$

J

9

8

7

FIG. 2. Illustration of the allowed rotational transitions (filled arrows) and "forbidden" rotational transitions (empty arrows) in the $v_5 = 1$ vibrational state of $^{13}CH_3F$.

rameters by fitting the experimental data. A situation like this occurs also in other states of CH_3F, especially in states which are strongly mixed by the x,y-Coriolis interaction ($3, 10$). For example, this occurs for all the pairs of energy levels which are related to the unperturbed energy levels $|1, 0^0; J, K = 3\rangle_0$ and $|0, 1^{\pm1}; J, kl = -2\rangle_0$ for $J \geqslant 31$. In this case both perturbed states have a maximum contribution from the $|0, 1^{\pm1}; J, kl = -2\rangle_0$ state and their assignment is rather arbitrary.

TABLE IV

Coefficients of the Mixing of Wavefunctions in the $+l; J, K = 1$ and $-l; J, K = 2$ States of the $v_5 = 1$ Vibrational Level of $^{13}CH_3F$

Assignment	Coefficient					Energy (cm^{-1})
	c_1	c_2	c_3	c_4	c_5	
$\|0, 1^{\pm1}; J=7, kl = +1\rangle_{pert}$	0.94080	-0.07740	0.32927	-0.02206	0.00154	1521.608
$\|0, 1^{\pm1}; J=7, kl = -2\rangle_{pert}$	0.07637	0.95333	0.02542	0.29026	-0.02066	1522.719
$\|0, 1^{\pm1}; J=8, kl = +1\rangle_{pert}$	0.65689	-0.67166	0.25347	-0.22969	0.01893	1535.455
$\|0, 1^{\pm1}; J=8, kl = -2\rangle_{pert}$	0.66325	0.66513	0.25367	0.23021	-0.01903	1535.654
$\|0, 1^{\pm1}; J=9, kl = +1\rangle_{pert}$	0.91972	0.08401	0.38190	0.03451	-0.00328	1551.206
$\|0, 1^{\pm1}; J=9, kl = -2\rangle_{pert}$	-0.08324	0.93001	-0.03646	0.35457	-0.03313	1550.005

TABLE V

Comparison of the Parameters (in Units of cm^{-1}) in the $v_2 = 1$ and $v_5 = 1$ States of ^{13}CH$_3$F

Parameter	Ref. (1)	Ref. (2)	Our work
$E_5 - E_2$	11.94 (4)[a]		11.918734 (325)
B_5	0.831415 (43)		0.83102545 (189)
$A\zeta_5^z$	-1.264 (25)	-1.273 (8)	-1.2782364 (907)
B_2	0.826345 (25)		0.82728656 (26)
$A_5 - A_0$		-0.044 (3)	-0.0448108 (1715)
$A_2 - A_0$		0.021 (4)	0.0229772(1462)
$C_{11}^{(1)}$	0.5015 (15)		0.5039516 (69)
$q_{12} / 10^{-3}$	2.63 (120)		2.236009 (123)
$\eta_J / 10^{-4}$	-0.60 (40)		-0.51551 (1849)

[a] Number in parentheses are standard errors in units of the last digit.

DISCUSSION

Such a rich purely rotational spectrum (including many "forbidden" transitions) in an excited vibrational state of a symmetric top molecule has been probably observed for the first time. This demonstrates that with the use of highly sensitive millimeter-wave and submillimeter-wave spectrometers, and Fourier transform spectrometers with excellent signal to noise ratios in the far-infrared region, one can now observe spectra of purely rotational transitions in the excited vibrational states, from which almost the same information can be obtained on the spectroscopic parameters of the upper vibrational states as is possible from the high-resolution infrared spectra of the vibration–rotational transitions (apart, of course, from the band origin which is the exclusive feature of infrared measurements).

For ^{13}CH$_3$F, this can be seen in Table I. It should be noted that because of the $\Delta k = 0$ selection rule for the usual purely rotational transitions, information which can be obtained, for example, on the difference $E_5 - E_2$ or on the coefficients A, $A\zeta_5^z$, D_K^v or the Coriolis parameters C_{11}, etc., depends on the magnitude of the vibration-rotational interactions between the states $v_2 = 1$ and $v_5 = 1$. For CH$_3$F, this interaction is so strong that most of these parameters could be determined very accurately, except D_K^2 and D_K^5 which are influenced by their smaller sensitivity to the available experimental data. It was also not possible to determine from the rotational data the values of the coefficients H_K^2, H_K^5, and τ_K. We constrained them to the values obtained in the subsequent paper [Ref. (3)] by fitting the rotational data simultaneously with the wavenumbers of the vibration–rotational transitions to the states $v_2 = 1$ and $v_5 = 1$. We also constrained the coefficients H_J^v, L_{JK}^v, and L_{JKK}^v, to the values obtained in Ref. (3). Sextic and octic centrifugal distortion coefficients for the $v_2 = 1$ and $v_5 = 1$ states of CH$_3$F are effective parameters which partially absorb interactions that have not been explicitly taken into account in this paper. As is discussed in more detail in Ref. (3), it seems that that for $J > 30$ and for certain values of the rotational quantum numbers, the interaction between the lower lying vibrational state $v_6 = 1$ and the

states $v_2 = 1$ and $v_5 = 1$ cannot be completely absorbed into the effective spectroscopical parameters of the $v_2 = 1$ and $v_5 = 1$ states. A future variational analysis of the interactions between the $v_2 = 1$, $v_5 = 1$, $v_3 = 1$, and $v_6 = 1$ states is expected to improve the situation.

The values of some of the parameters which were obtained in the present paper are compared with the previously determined parameters [Refs. (1, 2)] in Table V. A simultaneous analysis of the vibration–rotational transition wavenumbers with the wavenumbers of the purely rotational transitions in the ground and excited vibrational states should of course provide more accurate parameters.

Note added in proof. E. Hirota, A. Taleb-Bendiad, and T. Amano (*J. Mol. Spectrosc.*, in press), remeasured the $J = 2 \leftarrow 1$ $kl = -1$ transition and found its frequency at 85 710.095 MHz (see footnote f of Table II).

REFERENCES

1. E. HIROTA, S. SAITO, AND Y. ENDO, *J. Mol. Spectrosc.* **70**, 469–471 (1978).
2. F. HEGELUND, S. BRODERSEN, AND I. M. MILLS, *J. Mol. Spectrosc.* **70**, 386–393 (1978).
3. D. PAPOUŠEK, J. DEMAISON, G. WLODARCZAK, P. PRACNA, S. KLEE, AND M. WINNEWISSER, *J. Mol. Spectrosc.* **164** (1994).
4. J. BURIE, D. BOUCHER, J. DEMAISON, AND A. DUBRULLE, *J. Phys. (Paris)* **43**, 1319–1325 (1982).
5. S. P. BELOV, A. V. BURENIN, L. I. GERSHTEIN, V. V. KOROLIKHIN, AND A. F. KRUPNOV, *Opt. Spectrosc.* **35**, 172–176 (1973).
6. S. P. BELOV, V. M. DEMKIN, V. I. PUCENKIN, AND M. YU. TRETYAKOV, Third Generation Submillimeterwave Spectrometer, Institute for Applied Physics, Gorkii, 1988, unpublished report.
7. P. PRACNA, S. KLEE, M. WINNEWISSER, D. PAPOUŠEK, YEN-CHU HSU, AND HANN-SEN CHEN, *J. Mol. Spectrosc.* **156**, 217–226 (1992).
8. D. PAPOUŠEK, YEN-CHU HSU, HANN-SEN CHEN, P. PRACNA, S. KLEE, M. WINNEWISSER, AND J. DEMAISON, *J. Mol. Spectrosc.* **159**, 33–41 (1993).
9. P. PRACNA, D. PAPOUŠEK, S. P. BELOV, M. YU. TRETYAKOV, AND K. SARKA, *J. Mol. Spectrosc.* **146**, 120–126 (1991).
10. D. PAPOUŠEK, Z. PAPOUŠKOVÁ, J. F. OGILVIE, P. PRACNA, S. CIVIS, AND M. WINNEWISSER, *J. Mol. Spectrosc.* **153**, 145–166 (1992).