

## Submillimeter-Wave Spectra of $^{12}\text{CH}_3\text{F}$ in the $v_2 = 1$ and $v_5 = 1$ Vibrational States

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Transition frequencies of the pure rotational transitions in the  $v_2 = 1$  and  $v_5 = 1$  vibrational states of  $^{12}\text{CH}_3\text{F}$  between 180 and 610 GHz have been measured using the submillimeter-wave spectrometer with acoustic detection RAD3. Twenty-two spectroscopic parameters describing the vibration-rotation interactions within and between the  $v_2 = 1$  and  $v_5 = 1$  states have been fitted using a reduced effective Hamiltonian for interacting vibrational states proposed by Lobodenko *et al.* [*J. Mol. Spectrosc.* **126**, 159–170 (1987)]. © 1991 Academic Press, Inc.

### I. INTRODUCTION

The  $v_2 = 1$  ( $A_1$ ) and  $v_5 = 1$  ( $E$ ) vibrational states of  $^{12}\text{CH}_3\text{F}$  are known to be strongly coupled by the  $x$ - $y$  Coriolis interaction ( $I$ ) ( $\Delta E_v = 8.42 \text{ cm}^{-1}$ ). Vibration-rotation transitions pertaining to these states have been further studied by Betrencourt *et al.* (2) and by Raman spectroscopy (3). The purely rotational transitions within these levels have been studied by microwave spectroscopy (4, 5) and have therefore been limited to the lowest rotational levels ( $J = 1 \leftarrow 0$  and  $2 \leftarrow 1$  transitions).

In the present work, we have extended the measurement of purely rotational transitions within the  $v_2 = 1$  and  $v_5 = 1$  vibrational levels of  $^{12}\text{CH}_3\text{F}$  into the submillimeter-wave region up to 610 GHz, which covers the transitions from  $J = 4 \leftarrow 3$  up to  $J = 12 \leftarrow 11$ . Using a reduced effective Hamiltonian for Coriolis-interacting vibrational states proposed by Lobodenko *et al.* (6), a considerably improved set of molecular parameters has been obtained by fitting the microwave and submillimeter-wave data.

### II. EXPERIMENTAL DETAILS

The spectra were recorded using the third-generation submillimeter-wave spectrometer with acoustic detection RAD3 built in the Institute of Applied Physics in

Nizhnii Novgorod (Gorkii) (7, 8). The sample pressure was kept below 1 Torr in all measurements.

Since a continuous scan is possible with the RAD3 spectrometer, we checked the purity of the sample directly from its spectrum. Besides the ground state rotational lines of  $^{12}\text{CH}_3\text{F}$  and  $^{13}\text{CH}_3\text{F}$  (in natural abundance), the lines of the rotational transitions in the  $v_3 = 1$  excited state of  $^{12}\text{CH}_3\text{F}$  and  $^{13}\text{CH}_3\text{F}$  could be recorded (see Ref. (9) as for  $^{13}\text{CH}_3\text{F}$ ), as well as the lines of rotational transitions in the  $v_6 = 1$  state of  $^{12}\text{CH}_3\text{F}$  (10, 11). The lines of the  $\Delta J = +1$ ,  $\Delta K = 0$ ,  $\Delta l = 0$  rotational transitions in the  $v_2 = 1$  and  $v_5 = 1$  vibrational states appeared as well isolated lines with large frequency separations for a given  $J$  and varying  $K$  because of large  $x$ - $y$  Coriolis interaction between  $v_2 = 1$  and  $v_5 = 1$  states. We could also observe quite distinct lines of the ground state rotational transitions of  $\text{CH}_2\text{DF}$  (in natural abundance of about 0.1%).

The  $\text{H}_2\text{O}$  lines could be assigned easily. The main impurities of the sample were obviously  $^{12}\text{CH}_3^{35}\text{Cl}$  and  $^{12}\text{CH}_3^{37}\text{Cl}$ ; their concentration was estimated to be less than 0.01%. Very weak lines of  $^{12}\text{CH}_3^{81}\text{Br}$  and  $^{12}\text{CH}_3^{79}\text{Br}$  have also been observed ( $\approx 0.001\%$ ). Only a few lines remained unassigned in the spectrum. They were suspected of belonging to forbidden rotational transitions but their systematic analysis has been postponed until we finish the analysis of the high-resolution Fourier transform spectra of the  $v_2$  and  $v_5$  bands of  $^{12}\text{CH}_3\text{F}$  (12).

The experimental data are reported in Table I. In most cases, transition frequencies have been determined using a heterodyne detection of the signal from the frequency synthesizer (7, 8). In this case, the experimental uncertainty of the frequency was estimated to be 0.1 MHz. In a few cases, the frequency was determined with respect to the  $\text{SO}_2$  calibration standard (7); the experimental uncertainty was then estimated to be 1.0 MHz. Larger experimental uncertainties have been given to a few lines with unresolved  $A_1$ - $A_2$  splittings or weak lines which were found on the wings of much stronger lines.

### III. THEORY

We have used the expression for the diagonal matrix elements of the matrix representation of the reduced vibrational-rotational Hamiltonian describing the interaction between the  $v_2 = 1$  and  $v_5 = 1$  vibrational levels

$$\begin{aligned} E_v(J, K, l)/hc = & E_v/hc + B_v J(J+1) + (A_v - B_v)K^2 - 2(A\zeta_5^v)Kl + \eta_J^5 J(J+1)Kl \\ & + \eta_K^5 K^3 l + \tau_J^5 J^2(J+1)^2 Kl + \tau_{JK}^5 J(J+1)K^3 l + \tau_K^5 K^5 l \\ & - D_J^{(v)} J^2(J+1)^2 - D_{JK}^{(v)} J(J+1)K^2 - D_K^{(v)} K^4 + H_J^{(v)} J^3(J+1)^3 \\ & + H_{JK}^{(v)} J^2(J+1)^2 K^2 + H_{KJ}^{(v)} J(J+1)K^4 + H_K^{(v)} K^6 + \dots, \quad (1) \end{aligned}$$

where the vibrational quantum number  $l = 0$  for the nondegenerate vibrational state  $v_2 = 1$  and  $l = \pm 1$  for the  $\pm l$  sublevels of the doubly degenerate level  $v_5 = 1$ .

From theoretical considerations of Ref. (6) it follows that four parameters of the transformed effective third-order Hamiltonian for Coriolis-interacting  $v_2 = 1$  and  $v_5 = 1$  vibrational states must be constrained in order to eliminate the ambiguity of this Hamiltonian. We have chosen the following constraints:

TABLE I  
Observed and Calculated Transition Frequencies in the  $v_2 = 1$  and  $v_5 = 1$   
Vibrational States of  $^{12}\text{CH}_3\text{F}$  (in MHz Units)

J	K	Exp	Calc	Exp-Calc	Unc <sup>a</sup>	J	K	Exp	Calc	Exp-Calc	Unc
$v_2 = 1$						8	0	434781.13	434781.19	-0.06	0.1
0	0	46743.28 <sup>b</sup>	46743.26	0.02	0.2	8	1	433276.34	433276.35	-0.01	0.1
						8	2	472636.35	472636.35	0.00	1.0
						8	3	465468.52	465468.52	0.00	0.1
1	0	93716.88 <sup>b</sup>	93716.62	0.26	0.2	8	4	461854.18	461854.08	0.10	0.1
1	1	87009.99 <sup>b</sup>	87010.24	-0.25	0.2	8	5	460071.59	460071.67	-0.08	0.1
						8	6	459057.26			
2	0		141093.25			8	7	458399.40	458399.38	0.02	0.1
2	1		134162.30			8	8	457922.77	457923.04	-0.27	0.1
2	2		161876.39								
3	0	188961.67	188961.78	-0.11	1.0	9	0	484809.79	484809.71	0.08	1.0
3	1		182819.44			9	1	483821.94	483821.86	0.08	0.1
3	2	214689.00	214688.79	0.21	1.0	9	2	523586.82	523586.99	-0.17	0.1
3	3	207425.93	207425.51	0.42	1.0	9	3	516858.30	516858.46	-0.16	1.0
						9	4	513084.06	513084.14	-0.08	1.0
4	0	237333.07	237333.37	-0.30	1.0	9	5	511149.49	511149.75	-0.26	1.0
4	1	232299.48	232299.40	0.08	1.0	9	6	510032.12			
4	2	266953.56	266953.55	0.01	0.1	9	7	509302.14	509302.44	-0.30	0.1
4	3	259172.36	259172.19	0.17	0.1	9	8	508772.43	508772.54	-0.11	0.1
4	4	256719.35	256719.05	0.30	0.1	9	9	508351.51	508351.29	0.22	0.1
5	0	286167.58	286167.63	-0.05	0.1	10	0	534998.81	534998.83	-0.02	0.1
5	1	282235.14	282234.97	0.17	0.1	10	1	534416.96	534416.97	-0.01	0.1
5	2	318784.80	318784.97	-0.17	0.1	10	2	574436.07	574436.93	-0.86	1.0
5	3	310854.61	310854.33	0.28	0.1	10	3	568176.21	568176.34	-0.13	1.0
5	4	308030.78	308030.63	0.15	0.1	10	4	564288.49	564288.74	-0.25	1.0
5	5	306772.22	306772.35	-0.13	0.1	10	5	562214.13	562214.69	-0.56	0.5
						10	6	560996.75			
6	0	335399.13	335399.65	-0.52	1.0	10	7	560195.57	560195.74	-0.17	0.1
6	1	332436.79	332436.65	0.14	0.1	10	8	559612.29	559612.14	0.15	0.1
6	2	370289.45	370289.64	-0.19	0.1	10	9	559147.58	559147.66	-0.08	0.1
6	3	362466.26	362466.22	0.04	0.1	10	10	558749.84			
6	4	359325.34	359325.21	0.13	0.1	11	0	585311.66	585311.62	0.04	0.1
6	5	357881.59	357881.63	-0.04	0.1	11	1	585046.22	585046.30	-0.08	0.1
6	6	357081.37	357081.30	0.07	0.1	11	2	625209.68	625209.55	0.13	0.1
						11	3	619424.84	619424.89	-0.05	0.1
7	0	384959.14	384959.21	-0.07	1.0	11	4	615466.21	615466.20	0.01	0.2
7	1	382803.03	382802.98	0.05	0.1	11	5	613264.84	613265.11	-0.27	0.2
7	2	421552.17	421552.41	-0.24	0.1	11	6	611949.98			
7	3	414004.37	414004.65	-0.28	0.1	11	7	611078.37	611078.18	0.19	0.1
7	4	410600.47	410600.43	0.04	0.1	11	8		610440.75		
7	5	408981.83	408981.85	-0.02	0.1	11	9		609932.79		
7	6		408073.28			11	10		609497.71		
7	7	407487.89	407487.62	0.27	0.1	11	11		609102.93		

<sup>a</sup> Estimated experimental uncertainty (in MHz units).

<sup>b</sup> Data from Refs. (4, 5).

<sup>c</sup> The first transitions in the  $A_1$ - $A_2$  split pairs correspond to transitions between levels in the larger  $A$  blocks.

<sup>d</sup> Not in the fit.

$$q_{22}^5 = \eta_K^5 = C_{21}^{(2)} = \alpha^5 = 0. \quad (2)$$

Thus we have fitted the Coriolis interaction parameters in the expression for the corresponding matrix element

$$\begin{aligned}
 &\langle 0, 1^{+1}; J, k+1 | (H_{21} + H_{23})/hc | 1, 0^0; J, k \rangle \\
 &= -\langle 1, 0^0; J, k+1 | (H_{21} + H_{23})/hc | 0, 1^{-1}; J, k \rangle \\
 &= \sqrt{2} \{ C_{11}^{(1)} + C_{11}^{(3a)} J(J+1) + C_{11}^{(3b)} [k^2 + (k+1)^2] \} F(J, k), \quad (3)
 \end{aligned}$$

TABLE I—Continued

J	K	<i>l</i>	Exp	Calc	Exp-Calc	Unc	J	K	<i>l</i>	Exp	Calc	Exp-Calc	Unc
$v_5 = 1$													
0	0	-1	58585.86 <sup>b</sup>	58585.50	0.36	0.2	6	1	1	378945.45	378945.37	0.08	0.1
							6	1	1	358172.92	358172.90	0.02	0.1
							6	2	1	366801.87	366801.76	0.11	0.1
							6	3	1	364260.51	364260.39	0.12	0.1
1	1	1	110528.46 <sup>b,c</sup>	110528.36	0.10	0.2	6	4	1	362921.39	362921.06	0.33	0.1
1	1	1	102360.58 <sup>b</sup>	102360.24	0.34	0.2	6	5	1	362058.48	362058.21	0.27	0.1
1	0	-1	114740.31 <sup>b</sup>	114739.99	0.32	0.2	6	6	1	361440.72	361440.56	0.16	0.1
1	1	-1	94021.23 <sup>b</sup>	94020.96	0.27	0.2	6	0	-1	373625.44	373625.34	0.10	0.1
							6	1	-1	338261.61	338261.35	0.26	0.1
2	1	1		165265.52			6	2	-1	347710.60	347709.87	0.73	2.0
2	1	1		153536.30			6	2	-1	347359.80	347359.66	0.14	0.1
2	2	1		157266.66			6	3	-1	351254.11	351254.37	-0.26	0.1
2	0	-1		168510.68			6	4	-1	353166.61	353166.93	-0.32	0.1
2	1	-1		141756.38			6	5	-1	354265.13	354265.03	0.10	0.1
2	2	-1		148615.47			6	6	-1	354956.46	354956.38	0.08	0.1
2	2	-1		148613.94									
3	1	1	219499.72	219499.28	0.44	1.0	7	1	1		432795.14		
3	1	1	204706.43	204707.43	-1.00	1.0	7	1	1	409304.51	409304.67	-0.16	0.1
3	2	1	209676.71	209676.06	0.65	1.0	7	2	1	419119.26	419119.31	-0.05	0.1
3	3	1	208232.79	208232.09	0.70	1.0	7	3	1	416221.99	416221.69	0.30	0.1
3	0	-1	220634.55 <sup>d</sup>	220637.64	-3.09	1.0	7	4	1	414706.19	414705.90	0.29	1.0
3	1	-1	190253.04 <sup>d</sup>	190249.47	3.57	1.0	7	5	1	413728.96	413728.91	0.05	0.1
3	2	-1	198219.76 <sup>d</sup>	198222.29	-2.53	1.0	7	6	1	413028.35	413028.53	-0.18	0.1
3	2	-1	198219.76 <sup>d</sup>	198217.28	2.48	1.0	7	7	1	412488.70	412488.94	-0.24	0.1
3	3	-1	200689.02	200689.01	0.01	1.0	7	0	-1	424112.41	424112.37	0.04	0.1
							7	1	-1	388203.57	388203.88	-0.31	1.0
4	1	1	273210.48	273210.92	-0.44	0.1	7	2	-1	396176.71	396176.62	0.09	0.1
4	1	1	255871.60	255871.87	-0.27	0.2	7	2	-1	397201.14	397200.92	0.22	0.1
4	2	1	262072.59	262072.39	0.20	0.1	7	3	-1	401458.79	401459.03	-0.24	1.0
4	3	1	260262.15	260261.75	0.40	0.1	7	4	-1	403604.55	403604.85	-0.30	0.1
4	4	1	259291.05	259290.60	0.45	0.1	7	5	-1	404849.47	404849.53	-0.06	0.1
4	0	-1	272051.00	272051.18	-0.18	0.1	7	6	-1	405636.48	405636.40	0.08	0.1
4	1	-1	239172.34	239172.13	0.21	1.0	7	7	-1	406159.73	406159.70	0.03	0.1
4	2	-1	247885.52	247886.70	-1.18	1.0							
4	2	-1	247872.58	247871.58	1.00	1.0	8	1	1		483724.32		
4	3	-1	250870.41	250870.80	-0.39	0.1	8	1	1	460418.98	460419.31	-0.33	0.1
4	4	-1	252276.78	252276.93	-0.15	0.2	8	2	1	471392.26	471392.44	-0.18	0.1
							8	3	1	468152.64	468152.42	0.22	0.1
5	1	1	326416.40	326417.59	-1.19	2.0	8	4	1	466466.73	466466.57	0.16	1.0
5	1	1	307027.72	307027.75	-0.03	0.1	8	5	1	465378.85	465379.03	-0.18	0.1
5	2	1	314450.26	314449.96	0.30	0.1	8	6	1	464597.57	464598.06	-0.49	0.1
5	3	1	312272.96	312272.46	0.50	1.0	8	7	1	463994.92	463995.41	-0.49	0.1
5	4	1	311115.49	311114.97	0.52	0.1	8	8	1	463504.89	463504.57	0.32	0.1
5	5	1	310369.58	310369.43	0.15	0.1	8	0	-1	474495.88	474495.70	0.18	0.1
5	0	-1	322973.30	322973.32	-0.02	0.1	8	1	-1	438318.31	438318.60	-0.29	0.1
5	1	-1	288554.81	288555.21	-0.40	0.1	8	2	-1		447340.24		
5	2	-1	297636.15	297635.89	0.26	0.1	8	2	-1	447109.82	447109.53	0.29	0.1
5	2	-1	297584.18	297584.12	0.06	0.1	8	3	-1	451675.02	451675.14	-0.12	0.1
5	3	-1	301058.62	301058.82	-0.20	0.1	8	4	-1	454037.27	454037.42	-0.15	1.0
5	4	-1	302723.94	302724.10	-0.16	0.1	8	5	-1	455424.30	455424.36	-0.06	0.2
5	5	-1	303671.88	303671.95	-0.07	0.1	8	6	-1	456305.57	456305.35	0.22	0.1
							8	7	-1	456892.45	456892.60	-0.15	0.1
							8	8	-1		457293.26		

where

$$F(J, k) = [J(J+1) - k(k+1)]^{1/2}. \quad (4)$$

Analogously, the following coefficients of the “2, -1” *l*-type interaction are determinable parameters:

$$\begin{aligned} \langle 0, 1^{-1}; J, k+1 | (H_{22} + H_{24})/hc | 0, 1^{+1}; J, k \rangle \\ = 2 \{ q_{12}^5 (2k+1) + f_{12}^5 K [k^3 + (k+1)^3] \} F(J, k) \end{aligned} \quad (5)$$

TABLE I—Continued

J	K	<i>l</i>	Exp	Calc	Exp-Calc	Unc	J	K	<i>l</i>	Exp	Calc	Exp-Calc	Unc
9	1	1	535903.57 <sup>d</sup>	535906.67	-3.10	0.1	11	1	1	639348.58	639349.12	-0.54	1.0
9	1	1	511510.09	511510.40	-0.31	0.2	11	1	1	613538.78	613538.90	-0.12	0.2
9	2	1	523607.97	523608.42	-0.45	0.1	11	2	1	627781.29	627781.19	0.10	0.1
9	3	1	520048.65	520048.55	0.10	0.1	11	3	1	623720.13	623719.66	0.47	0.1
9	4	1	518200.22	518200.15	0.07	1.0	11	4	1	621574.70	621574.40	0.30	0.1
9	5	1	517005.04	517006.09	-1.05	0.1	11	5	1	620180.91	620181.21	-0.30	1.0
9	6	1	516147.33	516146.92	0.41	0.1	11	6	1	619172.77	619173.70	-0.93	1.0
9	7	1	515482.94	515482.69	0.25	0.1	11	7	1	618390.10	618391.41	-1.31	1.0
9	8	1	514940.98	514940.86	0.12	0.1	11	8	1	617750.02	617750.93	-0.91	1.0
9	9	1	514482.47 <sup>d</sup>	514479.74	2.73	0.1	11	9	1		617204.19		
9	0	-1	524814.40	524814.17	0.23	0.2	11	10	1		616721.39		
9	1	-1	488558.61	488558.85	-0.24	0.1	11	11	1		616282.97		
9	2	-1	497083.05 <sup>d</sup>	497077.51	5.54	0.1	11	0	-1	625355.07	625354.44	0.63	1.0
9	2	-1		497087.97			11	1	-1	589289.70	589289.78	-0.08	1.0
9	3	-1		501907.05			11	2	-1	597101.03	597101.71	-0.68	1.0
9	4	-1	504464.09	504464.36	-0.27	0.2	11	2	-1	597317.24	597315.43	1.81	1.0
9	5	-1	505988.42	505988.47	-0.05	1.0	11	3	-1	602471.84	602471.83	0.01	0.1
9	6	-1	506962.05	506961.94	0.11	0.1	11	4	-1	605301.89	605302.03	-0.14	1.0
9	7	-1		507612.54			11	5	-1	607080.99	607080.91	0.08	0.1
9	8	-1		508057.08			11	6	-1	608235.61	608233.10	2.51	1.0
9	9	-1		508361.07			11	7	-1	609007.80	609008.13	-0.33	1.0
							11	8	-1	609532.85	609539.57		
10	1	1	587716.36	587717.41	-1.05	1.0	11	9	-1		609903.82		
10	1	1	562563.49	562564.00	-0.51	0.5	11	10	-1		610147.67		
10	2	1	575748.75	575749.17	-0.42	0.1	11	11	-1		610301.68		
10	3	1	571906.08	571905.84	0.24	1.0	Direct <i>l</i> -doubling transitions						
10	4	1	569903.91	569903.73	0.18	1.0							
10	5	1	568607.31	568607.63	-0.32	0.1							
10	6	1	567672.07	567672.86	-0.79	1.0							
10	7	1	566947.60	566948.72	-1.12	1.0							
10	8	1		566356.98									
10	9	1		565852.65									
10	10	1		565407.90									
10	0	-1	575094.55	575094.15	0.40	1.0	2	+1		12368.54 <sup>b</sup>	12368.11	0.43	0.2
10	1	-1	538890.63	538890.81	-0.18	0.1	3	+1		24097.91 <sup>b</sup>	24097.33	0.58	0.2
10	2	-1	547052.42	547052.42	0.00	1.0	4	+1		38889.59 <sup>b</sup>	38889.18	0.41	0.2
10	2	-1	547146.44	547144.94	1.50	1.0	5	+1		56228.47 <sup>b</sup>	56228.22	0.25	0.2
10	3	-1	552164.23	552164.24	-0.01	0.1	6	+1		75617.30 <sup>b</sup>	75618.07	-0.77	0.2
10	4	-1	554886.21	554885.72	0.49	0.1	7	+1			96390.54		
10	5	-1	556541.13	556540.93	0.20	0.1	8	+1			119881.00		
10	6	-1		557604.92			9	+1			143186.01		
10	7	-1	558317.94	558318.16	-0.22	0.1	10	+1			167582.28		
10	8	-1		558806.31			11	+1			192735.69		
10	9	-1		559140.48			12	+1			218545.91		
10	10	-1		559363.98									

and also

$$\begin{aligned}
 &\langle 0, 1^{+1}; J, k+1 | H_{22}/hc | 1, 0^0; J, k \rangle \\
 &= \langle 1, 0^0; J, k+1 | H_{22}/hc | 0, 1^{-1}; J, k \rangle = \sqrt{2} C_{11}^{(2)}(2k+1)F(J, k). \quad (6)
 \end{aligned}$$

#### IV. RESULTS AND DISCUSSION

Parameters of the reduced Hamiltonian obtained by a least-squares fit to the microwave and submillimeter-wave data are compared in Table II with those determined by Betrencourt *et al.* (2) by fitting their  $\nu_2$  and  $\nu_5$  vibration-rotation transition frequencies. It is obvious that the higher accuracy of our submillimeter-wave data leads to an improved set of parameters which describe the data practically within their experimental accuracy except for a few data with the highest values of  $J$  and  $K$ . This is especially true for the difference  $\Delta E_v = E_5 - E_2$ . However, parameters on whose values the  $\Delta K = 0$  selection rule for the pure rotational transitions provides limited

TABLE II

Spectroscopic Parameters of the  $\nu_2 = 1$  and  $\nu_5 = 1$  Vibrational States of  $^{12}\text{CH}_3\text{F}$ 

Parameter ( $\text{cm}^{-1}$ )	Our work	Ref. (2)
$B_2$	0.849645900 (526) <sup>a</sup>	0.8496303 (77)
$A_2$	5.2034734 (797)	5.204882 (63)
$D_J^2 \times 10^6$	1.99456 (372)	1.9665 (96)
$D_{JK}^2 \times 10^6$	13.220 (136)	13.83 (21)
$D_K^2 \times 10^6$	70.33 <sup>b</sup>	70.33 <sup>b</sup>
$H_{JK}^2 \times 10^9$	1.0668 (587)	
$H_{KJ}^2 \times 10^9$	-0.849 (161)	
$E_5 - E_2$	8.421095 (132)	8.4207 (16)
$B_5$	0.85369922 (439)	0.8536710 (34)
$A_5$	5.135641 (125)	5.137524 (16)
$A_5^{\zeta_z}$	-1.2974247 (776)	-1.295676 (42)
$D_J^5 \times 10^6$	2.08205 (199)	2.0916 (45)
$D_{JK}^5 \times 10^6$	12.7980 (626)	12.752 (46)
$D_K^5 \times 10^6$	70.33 <sup>b</sup>	70.33 <sup>b</sup>
$H_{JK}^5 \times 10^9$	-0.0709 (628)	
$H_{KJ}^5 \times 10^9$	6.060 (243)	
$\eta_J^5 \times 10^4$	-0.3745 (448)	
$\eta_K^5 \times 10^4$	0.0	-0.904 (17)
$\tau_{JK}^5 \times 10^6$	0.28890 (735)	
$C_{11}^{(1)}$	0.5181731 (164)	0.518374 (26)
$C_{11}^{(3a)} \times 10^5$	-0.29153 (166)	-0.2907 (41)
$C_{11}^{(3b)} \times 10^5$	10.58 (124)	
$C_{11}^{(2)} \times 10^3$	1.81333 (504)	-1.7506 (34)
$q_{12}^5 \times 10^3$	2.349301 (808)	2.4079 (22)
$f_{12}^{5,K} \times 10^6$	8.029 (233)	

<sup>a</sup> Values in parentheses represent a standard deviation in units of the least significant digit.<sup>b</sup> Constrained to the ground state value [see Ref. (13)].

information (e.g.,  $A_2$ ,  $A_5$ , or  $A_5^{\zeta_z}$ ) were determined less precisely.

A simultaneous fit to all the pure rotational and  $\nu_2$ ,  $\nu_5$  vibration-rotation transition frequencies should lead to a final set of highly precise parameters of the  $\nu_2$  and  $\nu_5$  bands as well as of the ground and upper vibrational states parameters.

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