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Difference-Frequency Laser Spectroscopy of the ν_1 and ν_3 Fundamental Bands of H_2Cl^+: Determination of the Equilibrium Molecular Structure

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The gas-phase spectra of the ν_1 and ν_3 fundamental bands of H_2Cl^+ have been observed with a difference-frequency laser spectrometer between 2525 and 2755 cm^{-1}. The ions were generated in a hollow cathode discharge through a gas mixture of HCl and H_2. A simultaneous least-squares analysis of the ν_1 and ν_3 bands with an effective vibration–rotation Hamiltonian including Coriolis interaction between the $v_1 = 1$ and $v_3 = 1$ states yielded the band origins (2643.2200 and 2630.1404 cm^{-1} for the ν_1 and ν_3 of $H_2{}^{35}Cl^+$, and 2641.4931 and 2628.1065 cm^{-1} for the ν_1 and ν_3 of $H_2{}^{37}Cl^+$, respectively), the rotational constants, and the centrifugal distortion constants for the ground and excited states. The equilibrium molecular structure has been determined to be r_e(H–Cl) = 1.30412(17) Å and θ_e(H–Cl–H) = 94.243(27)° for $H_2{}^{35}Cl^+$ and r_e(H–Cl) = 1.30411(17) Å and θ_e(H–Cl–H) = 94.244(26)° for $H_2{}^{35}Cl^+$. © 1988 Academic Press, Inc.

INTRODUCTION

The chloronium ion (H_2Cl^+), which is isoelectronic with H_2S, has been investigated by several experimental techniques such as mass spectroscopy (*1*, *2*), ion cyclotron resonance spectroscopy (*3*), and the molecular beam photoionization method (*4*). These methods provided values for the proton affinities of the hydrogen halides. H_2Cl^+ is expected to be an abundant ion in a discharge through a mixture of H_2 and HCl due to the relatively large proton affinity of HCl, 134.8 kcal/mole (*5*), compared with that of H_2, and due to the fact that the dissociative recombination with electrons is the only significant depletion channel. However, H_2Cl^+ had not been studied with high-resolution spectroscopic methods until the recent observation of the ν_2 fundamental band by Kawaguchi and Hirota (*6*). More recently, Saito *et al.* (*7*) observed rotational transitions of $H_2{}^{35}Cl^+$ in the ground state and obtained more accurate rotational constants for the ground state. Also, the nuclear quadrupole coupling constants have been determined for the first time from the hyperfine structure of the millimeter-wave spectra (*7*).

The cosmic abundance of Cl is estimated to be 5.3 in a logarithmic scale in which the abundance of H is set to be 12.0 (*8*). This abundance is about the same order of magnitude as that of P and about two orders of magnitudes less than those of Si and S. Very few molecules containing P or Cl have been identified in interstellar space so

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far. Turner and Bally (*9*) and Ziurys (*10*) detected PN in several interstellar sources, and PN seems to be the only phosphorus-containing interstellar molecule observed up to the present time. HCl is obviously one of the most likely chlorine-containing molecules expected in interstellar clouds (*11*). Recently Blake *et al.* (*12*) reported a detection of HCl in the Orion Molecular Cloud (OMC-1). According to recent discussions of chlorine chemistry in diffuse (*13*) and dense molecular clouds (*14*), the chloronium ion is supposed to be an important precursor of HCl in interstellar clouds, although the relative abundance is estimated to be 5×10^{-9} (equivalent to a column density of 2.6×10^{12} cm^{-2}) in typical diffuse clouds (*13*) and to be about 3.3×10^{-12} in dense clouds (*14*).

Several ab initio molecular orbital calculations have been performed (*15–17*) to obtain the proton affinity, the molecular structural parameters, and the spectroscopic constants such as the vibrational frequencies and the rotational constants. Botschwina (*16*) employed the self-consistent electron pair method combined with the coupled electron pair method on H_2F^+ and H_2Cl^+ and their deuterated species. More recently he carried out a more extensive CEPA-1 calculation on H_2Cl^+ (*18*).

In this work, the ν_1 and ν_3 fundamental bands of H_2Cl^+ have been observed by a difference-frequency laser system with a hollow cathode discharge modulation technique. From a least-squares analysis of the observed transitions, the molecular constants such as the band origin, the rotational constants, the centrifugal distortion constants, and the Coriolis coupling parameters between the $v_1 = 1$ and $v_3 = 1$ states have been determined. By combining these data with the constants obtained from the analysis of the ν_2 fundamental band (*6*), the equilibrium molecular structure has been determined.

EXPERIMENTAL DETAILS

The experimental apparatus used in this investigation is as described previously (*19, 20*). Frequency-tunable infrared radiation (2.2–4.4 μm) with a spectral purity of a few megahertz is generated by mixing visible radiation from a single-mode tunable dye laser with that of a single-mode Ar^+ laser in a $LiNbO_3$ crystal contained in a temperature-controlled oven. The resulting difference frequency gives continuous coverage from 2400 to 4400 cm^{-1} with a Rh-6G dye laser and a few typical Ar^+ laser lines. The infrared power is proportional to the product of the radiation powers of the two lasers (*21*). About 300 mW of dye laser and about 250 mW of Ar^+ laser power were used, and the resulting infrared power was estimated to be about 5 μW at around 2600 cm^{-1}.

The absorption cell employed in this study was made of Pyrex tube of 70 mm inner diameter fitted with a cylindrical stainless steel of diameter 38 mm and length 80 cm, with copper tubing wound around for the circulation of cooled methanol to cool the discharge. H_2Cl^+ was produced by a modulated discharge at 16 kHz in a flowing gas mixture of H_2 (~700 mTorr) and HCl (~20 mTorr). The optimum peak current was found to be about 500 mA. The signal intensity was not so sensitive to the mixing ratio of the two gases. In order to distinguish the ion signal from that of neutral species, an axial magnetic field of about 150 G was applied to the discharge (*19, 22*), resulting in the suppression of the intensity of the ion signals.

The infrared beam traveled 32 times through the absorption cell, the total effective path length being about 26 m. A part of the infrared beam was directed through a reference gas cell for wavenumber calibration and the infrared power was monitored by an InSb detector operated at liquid nitrogen temperature. The spectra of D_2O (*23*), HDO (*24*), and N_2O (*25, 26*) were used as references, together with frequency markers from a temperature-stabilized étalon of free spectral range 150 MHz. The accuracy of the wavenumber measurement was estimated to be better than 0.001 cm^{-1}.

OBSERVATION AND ANALYSIS OF THE SPECTRA

The band origins of the ν_1 and ν_3 bands of H_2Cl^+ have been estimated on the basis of ab initio calculations by Botschwina (*16*) to be 2676 and 2679 cm^{-1}, respectively, and by DeFrees and McLean (*17*) to be 2669 and 2666 cm^{-1}. Thus, we started the search from 2620 cm^{-1} upward and found many transitions that exhibited the characteristics of ion signals upon application of a magnetic field (*19, 22*). After optimizing the reaction conditions a range of about 100 cm^{-1} up to 2720 cm^{-1} was scanned, and more than 300 lines were observed.

However, the assignment was not straightforward because (1) H_2Cl^+ is a light asym-

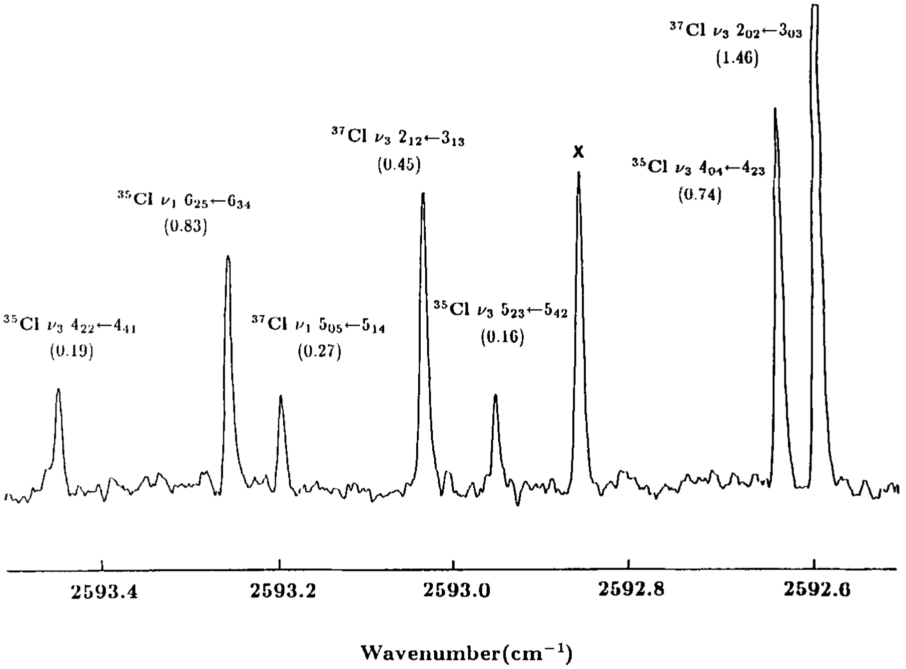

FIG. 1. A portion of the spectrum of H_2Cl^+ recorded with the difference frequency laser spectrometer. ^{35}Cl and ^{37}Cl indicate absorption lines of $H_2{}^{35}Cl^+$ and $H_2{}^{37}Cl^+$, respectively. The values in parentheses represent the relative intensity defined as

$$I = g_I g_{iso} S \exp(-E_{vr}/kT),$$

where S is the linestrength, g_I the spin weight, and g_{iso} the isotopic abundance, calculated at $T = 273$ K. The line marked by X is a transition of an $H^{37}Cl$ hot band ($R(0)$ of $v = 4 \leftarrow 3$).

metric top with no specific regularities in the spectrum over a wide range, (2) the vibration–rotation energy levels are perturbed by Coriolis interaction between the $v_1 = 1$ and $v_3 = 1$ states, and (3) there exist two isotopes (^{35}Cl and ^{37}Cl) of substantial abundance. Nevertheless, the assignment was carried out by sorting the combination differences systematically to be compared with all the possible combination differences for the ground state deduced from the analysis of the ν_2 fundamental band (*6*). The statistical weight of 3:1 for $K_a'' + K_c''$ = odd:even facilitated the assignment. When the several low-J lines had been thus assigned, it was realized that the scanning range was insufficient. The range previously covered included mostly R-branch transitions, and we extended the measurements from 2525 to 2755 cm^{-1}. Eventually more than 1100 transitions were precisely measured. In the course of the measurements, we noticed widely and regularly spaced lines which behaved differently from the ions in the magnetic field. They were identified as the absorption lines of hot bands of HCl (*27*). A section of the spectrum is shown in Fig. 1.

TABLE I

Fitted Spectroscopic Parameters for $H_2{}^{35}Cl^+$ (in cm^{-1})

	Ground state	v_1=1 state	v_3=1 state
$\tilde{A}$	11.2528817(30)[a]	11.080711(62)	11.025581(60)
$\tilde{B}$	9.1258843(44)	8.981502(58)	9.016378(60)
$\tilde{C}$	4.9401016(20)	4.859978(56)	4.880424(56)
$\Delta_J \times 10^3$	0.66943(23)	0.66226(54)	0.67342(60)
$\Delta_{JK} \times 10^3$	-2.3989(12)	-2.3522(24)	-2.4163(24)
$\Delta_K \times 10^3$	4.4086(19)	4.3174(43)	4.3764(23)
$\delta_J \times 10^3$	0.30040(10)	0.29575(30)	0.30464(32)
$\delta_K \times 10^3$	-0.06365(28)	-0.0568(11)	-0.08210(72)
$\Phi_J \times 10^6$	0.2659(29)	0.2683(51)	0.2451(64)
$\Phi_{JK} \times 10^6$	-1.576(20)	-1.225(30)	-1.259(29)
$\Phi_{KJ} \times 10^6$	1.280(43)	0.377(69)	0.713(47)
$\Phi_K \times 10^6$	2.318(39)	2.355(97)	2.607(39)
$\phi_J \times 10^6$	0.1311(14)	0.1338(26)	0.1330(32)
$\phi_{JK} \times 10^6$	-0.4656(57)	-0.435(15)	-0.4545(89)
$\phi_K \times 10^6$	1.389(16)	1.449(26)	1.360(18)
ν_0		2643.21999(14)	2630.14043(13)
Coupling constants:		h_{13} = -0.1905(19)	
		h'_{13} = 0.17288(31)	

[a] The values in parentheses denote one standard error in units of the last digit in the parameter.

TABLE II

Fitted Spectroscopic Parameters for $H_2{}^{37}Cl^+$ (in cm^{-1})

	Ground state	v_1=1 state	v_3=1 state
$\tilde{A}$	11.219603(55)[a]	11.04754(13)	10.99352(14)
$\tilde{B}$	9.125946(44)	8.98208(12)	9.01627(13)
$\tilde{C}$	4.933638(22)	4.85373(12)	4.87403(13)
$\Delta_J \times 10^3$	0.6719(12)	0.6620(11)	0.6773(11)
$\Delta_{JK} \times 10^3$	-2.4076(41)	-2.3631(45)	-2.4383(42)
$\Delta_K \times 10^3$	4.3885(55)	4.3320(67)	4.3656(51)
$\delta_J \times 10^3$	0.30165(60)	0.29604(60)	0.30556(55)
$\delta_K \times 10^3$	-0.0634(16)	-0.0583(24)	-0.0808(15)
$\Phi_J \times 10^6$	0.297(16)	0.275(12)	0.282(12)
$\Phi_{JK} \times 10^6$	-1.632(70)	-1.500(73)	-1.567(56)
$\Phi_{KJ} \times 10^6$	0.96(13)	0.91(21)	0.946(98)
$\Phi_K \times 10^6$	2.85(15)	2.56(18)	2.81(15)
$\phi_J \times 10^6$	0.1481(79)	0.1361(57)	0.1412(61)
$\phi_{JK} \times 10^6$	-0.493(25)	-0.441(38)	-0.466(16)
$\phi_K \times 10^6$	1.636(65)	1.464(75)	1.506(48)
ν_0		2641.49312(19)	2628.10653(17)
Coupling constants:		h_{13} = -0.1764(48)	
		h'_{13} = 0.17279(72)	

[a] The values in parentheses denote one standard error in units of the last digit in the parameter.

A least-squares fit was carried out with Watson's *A*-reduced vibration–rotation Hamiltonian in a I^r representation (*28*). The Hamiltonian employed is given as

$$
\begin{aligned}
H_{vr} = E_v &+ \frac{1}{2}(\tilde{B}+\tilde{C})J^2 + \left[\tilde{A} - \frac{1}{2}(\tilde{B}+\tilde{C})\right]J_z^2 + \frac{1}{4}(\tilde{B}-\tilde{C})(J_+^2 + J_-^2) \\
&- \Delta_J J^4 - \Delta_{JK} J_a^2 J^2 - \Delta_K J_a^4 - \delta_J J^2 (J_+^2 + J_-^2) \\
&- \frac{\delta_K}{2}[J_a^2, (J_+^2 + J_-^2)]_+ + \Phi_J J^6 + \Phi_{JK} J^4 J_a^2 + \Phi_{KJ} J^2 J_a^4 \\
&+ \Phi_K J_a^6 + \phi_J J^4 (J_+^2 + J_-^2) + \frac{\phi_{JK}}{2} J^2 [J_a^2, (J_+^2 + J_-^2)]_+ + \frac{\phi_K}{2}[J_a^4, (J_+^2 + J_-^2)]_+, \quad (1)
\end{aligned}
$$

where $[A, B]_+ = AB + BA$ and $J_\pm = J_b \pm iJ_c$, for each of the three states involved. In

TABLE III

Observed Transitions of $H_2{}^{35}Cl^+$ (in cm^{-1})

$J'K'_aK'_c$ ←	$J'K''_aK''_c$	Obs.	(O-C) · 10^4	$J'K'_aK'_c$ ←	$J'K''_aK''_c$	Obs.	(O-C) · 10^4
ν_1 fundamental band							
$4_{4\,1}$	$5_{5\,0}$	2531.7710	5	$3_{2\,2}$	$4_{1\,3}$	2588.5596	1
$8_{1\,7}$	$9_{2\,8}$	2531.8130	18^a	$3_{3\,1}$	$4_{2\,2}$	2589.2563	1
$8_{2\,7}$	$9_{1\,8}$	2531.8130	-1	$7_{3\,5}$	$7_{4\,4}$	2591.3159	2
$7_{2\,5}$	$8_{3\,6}$	2531.8730	4	$6_{2\,5}$	$6_{3\,4}$	2593.2583	1
$9_{0\,9}$	$10_{1\,10}$	2531.9175	10	$2_{1\,1}$	$3_{2\,2}$	2593.8540	-2
$9_{1\,9}$	$10_{0\,10}$	2531.9175	10	$7_{2\,5}$	$7_{3\,4}$	2594.1689	2
$7_{3\,5}$	$8_{2\,6}$	2532.1399	7	$6_{1\,5}$	$6_{2\,4}$	2594.1733	7
$4_{4\,0}$	$5_{5\,1}$	2532.5576	8	$5_{1\,5}$	$5_{2\,4}$	2594.6809	-8
$5_{3\,2}$	$6_{4\,3}$	2533.3943	4	$5_{0\,5}$	$5_{1\,4}$	2594.8835	-3
$4_{3\,2}$	$5_{4\,1}$	2533.5200	0	$9_{4\,5}$	$9_{5\,4}$	2596.5234	2
$6_{4\,3}$	$7_{3\,4}$	2537.4736	1	$7_{4\,4}$	$7_{5\,3}$	2596.9485	-3
$6_{2\,4}$	$7_{3\,5}$	2542.6350	6	$3_{0\,3}$	$4_{1\,4}$	2597.3301	-5
$7_{1\,6}$	$8_{2\,7}$	2543.0710	-4	$1_{1\,1}$	$2_{2\,0}$	2597.4468	-4
$7_{2\,6}$	$8_{1\,7}$	2543.0801	-3	$3_{1\,3}$	$4_{0\,4}$	2597.4756	-9
$8_{0\,8}$	$9_{1\,9}$	2543.1838	1^a	$6_{5\,2}$	$6_{6\,1}$	2598.8069	4
$8_{1\,8}$	$9_{0\,9}$	2543.1838	1	$6_{3\,4}$	$6_{4\,3}$	2601.0391	-6
$6_{3\,4}$	$7_{2\,5}$	2543.7185	-9	$7_{5\,2}$	$7_{6\,1}$	2602.2051	3
$4_{3\,1}$	$5_{4\,2}$	2543.7280	-8	$6_{4\,3}$	$6_{5\,2}$	2602.9026	4
$6_{5\,2}$	$7_{4\,3}$	2544.3210	3	$2_{2\,1}$	$3_{1\,2}$	2603.0520	5
$9_{0\,9}$	$9_{1\,8}$	2549.1421	-5	$5_{2\,4}$	$5_{3\,3}$	2603.7693	-2
$5_{2\,3}$	$6_{3\,4}$	2552.3169	1	$1_{1\,0}$	$2_{2\,1}$	2604.2383	0
$3_{2\,2}$	$4_{3\,1}$	2553.0579	5	$4_{1\,4}$	$4_{2\,3}$	2605.4932	-4
$6_{1\,5}$	$7_{2\,6}$	2554.1743	5	$4_{0\,4}$	$4_{1\,3}$	2606.3472	13
$6_{2\,5}$	$7_{1\,6}$	2554.2197	2	$5_{4\,2}$	$5_{5\,1}$	2606.4680	7
$7_{0\,7}$	$8_{1\,8}$	2554.3137	7	$5_{1\,4}$	$5_{2\,3}$	2606.6792	6
$7_{1\,7}$	$8_{0\,8}$	2554.3137	6	$2_{0\,2}$	$3_{1\,3}$	2607.4346	-1
$3_{3\,1}$	$4_{4\,0}$	2554.4832	3	$6_{2\,4}$	$6_{3\,3}$	2607.7971	-4
$5_{4\,2}$	$6_{3\,3}$	2556.0977	-10	$2_{1\,2}$	$3_{0\,3}$	2608.1780	0
$5_{3\,3}$	$6_{2\,4}$	2556.1167	-13	$8_{4\,4}$	$8_{5\,3}$	2608.4333	-1
$3_{3\,0}$	$4_{4\,1}$	2556.3911	3	$7_{3\,4}$	$7_{4\,3}$	2608.8132	-9
$8_{0\,8}$	$8_{1\,7}$	2560.7324	-19^a	$5_{4\,1}$	$5_{5\,0}$	2609.9331	-4
$8_{1\,8}$	$8_{2\,7}$	2560.7324	0	$7_{4\,3}$	$7_{5\,2}$	2611.4453	-2
$4_{2\,2}$	$5_{3\,3}$	2560.7727	3	$4_{2\,3}$	$4_{3\,2}$	2612.7268	-3
$5_{1\,4}$	$6_{2\,5}$	2565.0537	5	$4_{3\,2}$	$4_{4\,1}$	2613.3845	-3
$5_{2\,4}$	$6_{1\,5}$	2565.2781	3	$3_{1\,3}$	$3_{2\,2}$	2615.4644	-2
$6_{0\,6}$	$7_{1\,7}$	2565.3030	9	$1_{0\,1}$	$2_{1\,2}$	2616.9231	-3
$6_{1\,6}$	$7_{0\,7}$	2565.3030	2	$3_{0\,3}$	$3_{1\,2}$	2618.2434	-4
$9_{2\,7}$	$9_{3\,6}$	2568.9275	-4	$6_{3\,3}$	$6_{4\,2}$	2618.2805	-11
$3_{2\,1}$	$4_{3\,2}$	2569.9084	7	$4_{3\,1}$	$4_{4\,0}$	2619.1790	-3
$8_{2\,7}$	$8_{3\,6}$	2570.5073	7	$3_{2\,2}$	$3_{3\,1}$	2619.2095	-2
$8_{1\,7}$	$8_{2\,6}$	2570.5652	4	$4_{1\,3}$	$4_{2\,2}$	2619.2996	-1
$4_{3\,2}$	$5_{2\,3}$	2570.8889	7	$5_{3\,2}$	$5_{4\,1}$	2619.6201	1
$2_{1\,2}$	$3_{2\,1}$	2571.7002	12	$1_{1\,1}$	$2_{0\,2}$	2619.6746	-2
$7_{1\,7}$	$7_{2\,6}$	2572.1965	-6	$5_{2\,3}$	$5_{3\,2}$	2619.7070	-4
$7_{0\,7}$	$7_{1\,6}$	2572.2061	1	$2_{1\,2}$	$2_{2\,1}$	2623.6599	1
$4_{1\,3}$	$5_{2\,4}$	2575.4656	11	$4_{2\,2}$	$4_{3\,1}$	2626.5222	0
$5_{0\,5}$	$6_{1\,6}$	2576.1482	10	$0_{0\,0}$	$1_{1\,1}$	2627.0278	-4
$5_{1\,5}$	$6_{0\,6}$	2576.1482	-32^b	$3_{2\,1}$	$3_{3\,0}$	2628.0464	7
$2_{2\,1}$	$3_{3\,0}$	2576.4558	4	$3_{1\,2}$	$3_{2\,1}$	2628.9897	4
$4_{2\,3}$	$5_{1\,4}$	2576.4741	-2	$2_{0\,2}$	$2_{1\,1}$	2629.4180	2
$4_{4\,1}$	$5_{3\,2}$	2578.0979	0	$2_{1\,1}$	$2_{2\,0}$	2633.3569	1
$8_{3\,6}$	$8_{4\,5}$	2580.2830	-4	$1_{0\,1}$	$1_{1\,0}$	2636.6831	-3
$2_{2\,0}$	$3_{3\,1}$	2580.4409	-7	$1_{1\,0}$	$1_{0\,1}$	2649.2153	-3
$8_{2\,6}$	$8_{3\,5}$	2581.2141	1	$4_{3\,1}$	$4_{2\,2}$	2653.9521	-6
$7_{2\,6}$	$7_{3\,5}$	2582.0288	2	$3_{2\,1}$	$3_{1\,2}$	2654.6433	14
$7_{1\,6}$	$7_{2\,5}$	2582.2683	-2	$3_{3\,0}$	$3_{2\,1}$	2655.2605	-2
$6_{1\,6}$	$6_{2\,5}$	2583.5264	-8	$9_{6\,3}$	$9_{5\,4}$	2655.2964	-1
$6_{0\,6}$	$6_{1\,5}$	2583.5703	-1	$2_{1\,1}$	$2_{0\,2}$	2655.5837	-7
$3_{1\,2}$	$4_{2\,3}$	2584.9106	-6	$6_{4\,2}$	$6_{3\,3}$	2655.7300	0
$4_{0\,4}$	$5_{1\,5}$	2586.8384	-2	$7_{5\,2}$	$7_{4\,3}$	2656.1743	-1
$4_{1\,4}$	$5_{0\,5}$	2586.8638	1	$5_{4\,1}$	$5_{3\,2}$	2656.2607	-2
$8_{4\,5}$	$8_{5\,4}$	2588.4819	-1	$8_{5\,3}$	$8_{4\,4}$	2656.8337	7

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[a] The relative weight is 0.5 due to the weaker component of unresolved K-type doublet in which the S/N ratio of the peak is strong.

[b] The relative weight is 0.1 due to the weaker component of unresolved K-type doublet in which the S/N ratio of the peak is weak.

[c] This transition is omitted from the fit because the S/N ratio of the peak is very weak.

TABLE III—*Continued*

$J'K'_aK'_c$ ←	$J''K''_aK''_c$	Obs.	(O-C) × 10^4
$5_{3\,2}$	$5_{2\,3}$	2656.9888	5
$1_{1\,1}$	$0_{0\,0}$	2659.1680	-2
$7_{4\,3}$	$7_{3\,4}$	2660.2185	15
$6_{5\,1}$	$6_{4\,2}$	2660.6990	-3
$4_{4\,0}$	$4_{3\,1}$	2660.8462	-4
$2_{2\,1}$	$2_{1\,2}$	2661.2383	-2
$4_{2\,2}$	$4_{1\,3}$	2662.0247	4
$9_{5\,4}$	$9_{4\,5}$	2662.5469	-3
$3_{3\,1}$	$3_{2\,2}$	2663.7119	-6
$9_{7\,2}$	$9_{6\,3}$	2664.1855	-4
$3_{1\,2}$	$3_{0\,3}$	2665.4687	4
$2_{0\,2}$	$1_{1\,1}$	2665.8979	-2
$7_{6\,1}$	$7_{5\,2}$	2666.3921	0
$4_{4\,1}$	$4_{3\,2}$	2666.9351	-4
$5_{5\,0}$	$5_{4\,1}$	2667.0310	-12
$6_{3\,3}$	$6_{2\,4}$	2667.6677	-3
$3_{2\,2}$	$3_{1\,3}$	2668.1099	-5
$4_{3\,2}$	$4_{2\,3}$	2668.1763	-4
$2_{1\,2}$	$1_{0\,1}$	2668.6372	2
$5_{4\,2}$	$5_{3\,3}$	2669.0063	-9
$5_{5\,1}$	$5_{4\,2}$	2670.6521	25^b
$6_{5\,2}$	$6_{4\,3}$	2670.6521	0
$5_{2\,3}$	$5_{1\,4}$	2672.2917	-3
$7_{5\,3}$	$7_{4\,4}$	2672.9514	2
$7_{6\,2}$	$7_{5\,3}$	2672.9514	6
$8_{6\,3}$	$8_{5\,4}$	2673.1284	3
$6_{4\,3}$	$6_{3\,4}$	2673.6121	-3
$6_{6\,1}$	$6_{5\,2}$	2674.4976	0
$5_{3\,3}$	$5_{2\,4}$	2674.9363	-3
$4_{1\,3}$	$4_{0\,4}$	2675.7676	-1
$3_{0\,3}$	$2_{1\,2}$	2676.4304	-3
$4_{2\,3}$	$4_{1\,4}$	2676.5479	-2
$3_{1\,3}$	$2_{0\,2}$	2677.1953	5
$7_{3\,4}$	$7_{2\,5}$	2677.8252	-1
$7_{4\,4}$	$7_{3\,5}$	2680.2742	2
$3_{1\,2}$	$2_{2\,1}$	2680.9500	0
$2_{2\,1}$	$1_{1\,0}$	2680.9988	2
$9_{4\,5}$	$9_{3\,6}$	2681.9436	-3
$6_{2\,4}$	$6_{1\,5}$	2682.2146	2
$6_{3\,4}$	$6_{2\,5}$	2683.0081	-6
$5_{1\,4}$	$5_{0\,5}$	2685.3372	-1
$5_{2\,4}$	$5_{1\,5}$	2685.5142	2
$4_{0\,4}$	$3_{1\,3}$	2685.8965	-2
$4_{1\,4}$	$3_{0\,3}$	2686.0503	-3
$8_{3\,5}$	$8_{2\,6}$	2687.2104	-1
$2_{2\,0}$	$1_{1\,1}$	2687.8059	4
$3_{2\,2}$	$2_{1\,1}$	2690.0933	-2
$7_{2\,5}$	$7_{1\,6}$	2691.2632	-57^b
$7_{3\,5}$	$7_{2\,6}$	2691.4670	1
$4_{2\,2}$	$3_{3\,1}$	2692.6748	3
$4_{1\,3}$	$3_{2\,2}$	2693.7566	7
$6_{1\,5}$	$6_{0\,6}$	2694.4612	3
$6_{2\,5}$	$6_{1\,6}$	2694.4971	2
$5_{0\,5}$	$4_{1\,4}$	2694.9575	-2
$5_{1\,5}$	$4_{0\,4}$	2694.9846	-4
$9_{3\,6}$	$9_{2\,7}$	2695.6970	-6
$4_{2\,3}$	$3_{1\,2}$	2697.4612	-2
$5_{3\,2}$	$4_{4\,1}$	2699.4854	5
$8_{2\,6}$	$8_{1\,7}$	2699.8369	-12
$8_{3\,6}$	$8_{2\,7}$	2699.8833	-6
$3_{3\,1}$	$2_{2\,0}$	2703.2151	0
$7_{1\,6}$	$7_{0\,7}$	2703.3335	2
$7_{2\,6}$	$7_{1\,7}$	2703.3403	1
$6_{0\,6}$	$5_{1\,5}$	2703.8113	47^b
$6_{1\,6}$	$5_{0\,5}$	2703.8113	0
$5_{1\,4}$	$4_{2\,3}$	2703.9680	9
$5_{2\,4}$	$4_{1\,3}$	2705.0210	-4
$3_{3\,0}$	$2_{2\,1}$	2707.2222	7
$9_{2\,7}$	$9_{1\,8}$	2708.1208	4
$5_{2\,3}$	$4_{3\,2}$	2708.5449	1
$8_{1\,7}$	$8_{0\,8}$	2712.0088	3
$8_{2\,7}$	$8_{1\,8}$	2712.0088	-11
$4_{3\,2}$	$3_{2\,1}$	2712.2544	-4
$7_{0\,7}$	$6_{1\,6}$	2712.4832	-2
$7_{1\,7}$	$6_{0\,6}$	2712.4832	-10
$3_{2\,1}$	$2_{1\,2}$	2712.8298	9
$6_{1\,5}$	$5_{2\,4}$	2712.9915	3
$6_{2\,5}$	$5_{1\,4}$	2713.2334	-1
$5_{3\,3}$	$4_{2\,2}$	2718.7712	-5
$6_{3\,3}$	$5_{4\,2}$	2720.0969	-10
$9_{1\,8}$	$9_{0\,9}$	2720.5002	-2
$6_{2\,4}$	$5_{3\,3}$	2720.7061	0
$8_{0\,8}$	$7_{1\,7}$	2720.9939	-3
$8_{1\,8}$	$7_{0\,7}$	2720.9939	-4
$7_{1\,6}$	$6_{2\,5}$	2721.5583	6
$7_{2\,6}$	$6_{1\,5}$	2721.6084	-3
$6_{3\,4}$	$5_{2\,3}$	2724.6335	-6
$4_{4\,1}$	$3_{3\,0}$	2725.0732	-2
$7_{4\,3}$	$6_{5\,2}$	2725.6450	-6
$4_{4\,0}$	$3_{3\,1}$	2727.0007	19^a
$4_{3\,1}$	$3_{2\,2}$	2728.4089	1
$9_{0\,9}$	$8_{1\,8}$	2729.3394	1
$9_{1\,9}$	$8_{0\,8}$	2729.3394	0
$8_{1\,7}$	$7_{2\,6}$	2729.8923	-1
$8_{2\,7}$	$7_{1\,6}$	2729.9038	10
$7_{2\,5}$	$6_{3\,4}$	2730.3081	3
$7_{3\,5}$	$6_{2\,4}$	2731.4656	-2
$5_{4\,2}$	$4_{3\,1}$	2734.7573	3
$7_{3\,4}$	$6_{4\,3}$	2735.1453	-3
$10_{0\,10}$	$9_{1\,9}$	2737.5181	-4
$10_{1\,10}$	$9_{0\,9}$	2737.5181	-5
$9_{1\,8}$	$8_{2\,7}$	2738.0493	1
$9_{2\,8}$	$8_{1\,7}$	2738.0508	-4
$8_{2\,6}$	$7_{3\,5}$	2738.7864	0
$8_{3\,6}$	$7_{2\,5}$	2739.0811	-1
$6_{4\,3}$	$5_{3\,2}$	2741.0024	-5
$5_{4\,1}$	$4_{3\,2}$	2745.0991	7
$7_{4\,4}$	$6_{3\,3}$	2745.4370	-1
$11_{0\,11}$	$10_{1\,10}$	2745.5315	3
$10_{1\,9}$	$9_{2\,8}$	2746.0381	-3
$5_{5\,1}$	$4_{4\,0}$	2746.1006	5
$8_{3\,5}$	$7_{4\,4}$	2746.3872	2
$8_{4\,4}$	$7_{5\,3}$	2746.4917	10
$9_{2\,7}$	$8_{3\,6}$	2746.8142	2
$5_{5\,0}$	$4_{4\,1}$	2746.8965	-5
$4_{3\,2}$	$3_{0\,3}$	2748.7339	1
$8_{4\,5}$	$7_{3\,4}$	2750.2681	10
$4_{4\,1}$	$3_{1\,2}$	2751.6699	2
$5_{3\,2}$	$4_{2\,3}$	2754.2776	8
$10_{3\,8}$	$9_{2\,7}$	2754.6230	2
$9_{4\,6}$	$8_{3\,5}$	2756.4924	4
$6_{5\,2}$	$5_{4\,1}$	2756.8784	0
ν_3 fundamental band			
$5_{4\,1}$	$6_{4\,2}$	2527.6465	0
$5_{3\,2}$	$6_{3\,3}$	2529.7410	-3
$6_{2\,4}$	$7_{2\,5}$	2530.1904	3
$7_{1\,6}$	$8_{1\,7}$	2530.5413	3
$7_{2\,6}$	$8_{2\,7}$	2530.5459	4
$6_{3\,4}$	$7_{3\,5}$	2530.7236	2
$5_{5\,0}$	$6_{5\,1}$	2530.9077	2
$8_{0\,8}$	$9_{0\,9}$	2531.0396	-4
$8_{1\,8}$	$9_{1\,9}$	2531.0396	-4
$5_{5\,1}$	$6_{5\,2}$	2532.5916	1
$5_{4\,2}$	$6_{4\,3}$	2536.6721	1
$3_{1\,2}$	$4_{3\,1}$	2537.3623	1
$5_{2\,3}$	$6_{2\,4}$	2540.5222	7
$6_{1\,5}$	$7_{1\,6}$	2541.4983	2
$6_{2\,5}$	$7_{2\,6}$	2541.5227	2
$7_{0\,7}$	$8_{0\,8}$	2541.9536	-10
$7_{1\,7}$	$8_{1\,8}$	2541.9536	-11
$5_{3\,3}$	$6_{3\,4}$	2542.2661	-10
$4_{3\,1}$	$5_{3\,2}$	2545.0737	2
$9_{2\,8}$	$9_{2\,7}$	2546.7122	-5
$4_{4\,0}$	$5_{4\,1}$	2547.2192	-4
$8_{0\,8}$	$8_{2\,7}$	2548.5896	9

TABLE III—*Continued*

$J'K'_aK'_c$ ←	$J''K''_aK''_c$	Obs.	(O-C) × 10^4	$J'K'_aK'_c$ ←	$J''K''_aK''_c$	Obs.	(O-C) · 10^4
8_{18}	8_{17}	2548.5896	-10	7_{53}	7_{52}	2616.2012	-46^c
4_{41}	5_{42}	2550.5764	3	8_{81}	8_{80}	2616.3860	-7
4_{22}	5_{23}	2550.9453	-7	8_{80}	8_{81}	2616.4048	-3
5_{14}	6_{15}	2552.2952	1	2_{12}	2_{11}	2617.0098	-1
5_{24}	6_{25}	2552.4192	1	8_{72}	8_{71}	2617.9429	0
6_{06}	7_{07}	2552.7556	-1	8_{71}	8_{72}	2618.5747	4
6_{16}	7_{17}	2552.7556	-5	3_{22}	3_{21}	2618.7244	3
4_{32}	5_{33}	2554.5703	-4	7_{71}	7_{70}	2619.4629	5
9_{37}	9_{36}	2556.6375	-1	7_{70}	7_{71}	2619.5166	4
2_{11}	3_{30}	2557.1418	-9	4_{32}	4_{31}	2620.3206	1
2_{02}	3_{21}	2558.0959	7	7_{62}	7_{61}	2620.3672	-3
8_{17}	8_{36}	2558.1558	4	6_{52}	6_{51}	2621.9170	-3
8_{27}	8_{26}	2558.2163	-1	7_{61}	7_{62}	2621.9307	3
7_{07}	7_{26}	2559.8379	-5	6_{61}	6_{60}	2622.1438	3
7_{17}	7_{16}	2559.8469	-7	6_{60}	6_{61}	2622.2964	-3
4_{13}	5_{14}	2562.7974	13	5_{42}	5_{41}	2622.8982	-1
3_{30}	4_{31}	2563.2317	1	8_{62}	8_{63}	2623.6599	-34^b
4_{23}	5_{24}	2563.3489	3	5_{51}	5_{50}	2624.3645	-2
5_{05}	6_{06}	2563.4438	22^a	5_{50}	5_{51}	2624.7842	1
5_{15}	6_{16}	2563.4438	-2	6_{51}	6_{52}	2625.4619	2
3_{21}	4_{22}	2563.8213	7	1_{11}	1_{10}	2625.6707	8
8_{26}	8_{45}	2567.7646	8	3_{31}	3_{30}	2626.0244	13^a
3_{31}	4_{32}	2567.8845	-6	4_{41}	4_{40}	2626.0244	-21^a
9_{46}	9_{45}	2568.7070	2	2_{21}	2_{20}	2626.3665	-4
8_{36}	8_{35}	2568.7856	3	4_{40}	4_{41}	2627.0837	-7
7_{26}	7_{25}	2569.7434	6	3_{30}	3_{31}	2629.3840	1
6_{06}	6_{25}	2570.9812	11	5_{41}	5_{42}	2629.4634	5
6_{16}	6_{15}	2571.0247	3	2_{20}	2_{21}	2631.7910	-1
8_{44}	8_{63}	2572.3594	-11	4_{31}	4_{32}	2633.9109	-1
3_{12}	4_{13}	2572.8652	9	1_{10}	1_{11}	2633.9868	-5
4_{04}	5_{05}	2574.0068	7	6_{42}	6_{43}	2636.2029	-2
4_{14}	5_{15}	2574.0220	5	3_{21}	3_{22}	2638.2773	4
3_{22}	4_{23}	2574.6465	5	8_{53}	8_{54}	2638.3491	-42^c
8_{35}	8_{54}	2575.2236	-1	2_{11}	2_{12}	2641.9263	5
7_{25}	7_{44}	2578.5024	-2	5_{32}	5_{33}	2642.6499	0
2_{20}	3_{21}	2579.8308	5	1_{01}	0_{00}	2644.0256	-2
6_{15}	6_{34}	2580.5366	-2	7_{43}	7_{44}	2646.7388	7
6_{25}	6_{24}	2581.5208	-5	4_{22}	4_{23}	2648.2341	-4
7_{35}	7_{34}	2581.7517	-7	2_{21}	2_{02}	2648.5940	-5
5_{05}	5_{24}	2581.9722	4	3_{12}	3_{13}	2652.4150	-2
5_{15}	5_{14}	2582.1799	-7	3_{31}	3_{12}	2652.6189	-3^a
1_{01}	2_{20}	2582.3040	-8	2_{12}	1_{11}	2653.4900	0
6_{33}	6_{52}	2583.2256	-7	6_{33}	6_{34}	2653.9363	0
2_{11}	3_{12}	2583.7390	0	2_{02}	1_{01}	2655.0332	0
3_{03}	4_{04}	2584.4202	-3	3_{22}	3_{03}	2655.2029	-2
3_{13}	4_{14}	2584.5110	-3	4_{32}	4_{13}	2655.8220	-6
2_{21}	3_{22}	2586.8638	-5	8_{44}	8_{45}	2658.6836	-7
6_{24}	6_{43}	2587.5100	-4	5_{23}	5_{24}	2659.3401	0
5_{14}	5_{33}	2590.7869	1	5_{42}	5_{23}	2660.2671	6
4_{04}	4_{23}	2592.6360	1	6_{43}	6_{24}	2661.4336	7
5_{23}	5_{42}	2592.9514	-1	2_{11}	1_{10}	2661.6853	-6
4_{22}	4_{41}	2593.4419	-7	5_{33}	5_{14}	2662.2417	-6
4_{14}	4_{13}	2593.5286	-2	4_{13}	4_{14}	2662.8704	4
5_{24}	5_{23}	2594.0444	-1	3_{13}	2_{12}	2663.6118	4
2_{02}	3_{03}	2594.5740	-2	4_{23}	4_{04}	2663.6516	-3
2_{12}	3_{13}	2595.0269	1	3_{03}	2_{02}	2664.1387	0
6_{34}	6_{33}	2595.8867	1	7_{34}	7_{35}	2665.0703	-2
1_{10}	2_{11}	2597.5063	-8	8_{54}	8_{35}	2665.7000	-4
7_{44}	7_{43}	2598.8306	-9	7_{44}	7_{25}	2667.8420	-7
4_{13}	4_{32}	2599.0486	-4	6_{24}	6_{25}	2669.4795	1
3_{03}	3_{22}	2602.4084	-1	6_{34}	6_{15}	2670.3037	2
3_{12}	3_{31}	2603.5142	-3	3_{22}	2_{21}	2670.6853	4
1_{01}	2_{02}	2604.5320	-4	9_{55}	9_{36}	2672.0620	-2
3_{13}	3_{12}	2605.4253	7	5_{14}	5_{15}	2672.5315	2
1_{11}	2_{12}	2605.9102	5	5_{24}	5_{05}	2672.7029	-3
4_{23}	4_{22}	2607.1831	-6	4_{14}	3_{13}	2673.0793	-3
5_{33}	5_{32}	2609.6567	-8	4_{04}	3_{03}	2673.1936	6
2_{02}	2_{21}	2610.0559	0	3_{12}	2_{11}	2674.3982	-1
6_{43}	6_{42}	2612.0464	-2	8_{35}	8_{36}	2674.7114	-8
9_{91}	9_{90}	2612.9561	1	2_{20}	1_{01}	2676.7683	0
9_{90}	9_{91}	2612.9626	3	3_{21}	2_{20}	2677.7800	5
9_{82}	9_{81}	2614.8875	-3	7_{25}	7_{26}	2678.6543	6
9_{73}	9_{72}	2614.9600	11	7_{35}	7_{16}	2678.8518	-8
0_{00}	1_{01}	2616.0771	1	4_{23}	3_{22}	2681.6399	-1
8_{63}	8_{62}	2616.0771	-27^b	6_{15}	6_{16}	2681.7751	-4

TABLE III—*Continued*

$J'K'_aK'_c$ ←	$J''K''_aK''_c$	Obs.	(O-C) $\times 10^4$	$J'K'_aK'_c$ ←	$J''K''_aK''_c$	Obs.	(O-C) $\times 10^4$
$6_{2\,5}$	$6_{0\,6}$	2681.8098	1	$6_{4\,2}$	$5_{4\,1}$	2722.4292	-1
$5_{1\,5}$	$4_{1\,4}$	2682.2551	7	$7_{4\,4}$	$6_{4\,3}$	2725.1633	3
$5_{0\,5}$	$4_{0\,4}$	2682.2756	4	$10_{0\,10}$	$9_{0\,9}$	2725.8752	4
$4_{1\,3}$	$3_{1\,2}$	2683.7837	5	$10_{1\,10}$	$9_{1\,9}$	2725.8752	4
$4_{3\,2}$	$3_{3\,1}$	2686.4724	-4	$9_{2\,8}$	$8_{2\,7}$	2725.9094	6
$8_{2\,6}$	$8_{2\,7}$	2687.3652	8	$9_{1\,8}$	$8_{1\,7}$	2725.9094	-10
$7_{1\,6}$	$7_{1\,7}$	2690.8015	7	$4_{4\,0}$	$3_{2\,1}$	2725.9541	-3
$7_{2\,6}$	$7_{0\,7}$	2690.8081	5	$8_{3\,6}$	$7_{3\,5}$	2726.3584	6
$6_{0\,6}$	$5_{0\,5}$	2691.2632	-11	$8_{2\,6}$	$7_{2\,5}$	2726.5623	5
$6_{1\,6}$	$5_{1\,5}$	2691.2632	26[b]	$4_{2\,2}$	$3_{0\,3}$	2728.7915	-1
$5_{2\,4}$	$4_{2\,3}$	2691.3325	-5	$7_{6\,2}$	$6_{6\,1}$	2728.8230	-2
$5_{1\,4}$	$4_{1\,3}$	2692.0388	1	$7_{6\,1}$	$6_{6\,0}$	2729.4878	0
$4_{3\,1}$	$3_{3\,0}$	2692.0488	-2	$7_{3\,4}$	$6_{3\,3}$	2730.2339	2
$4_{2\,2}$	$3_{2\,1}$	2692.3125	-1	$7_{5\,3}$	$6_{5\,2}$	2730.4060	2
$9_{3\,7}$	$9_{1\,8}$	2695.8301	-2	$10_{2\,9}$	$9_{2\,8}$	2734.1313	2
$5_{3\,3}$	$4_{3\,2}$	2698.4956	4	$10_{1\,9}$	$9_{1\,8}$	2734.1313	-2
$8_{1\,7}$	$8_{1\,8}$	2699.6594	6	$11_{0\,11}$	$10_{0\,10}$	2734.1665	5
$8_{2\,7}$	$8_{0\,8}$	2699.6594	-7	$11_{1\,11}$	$10_{1\,10}$	2734.1665	5
$3_{2\,1}$	$2_{0\,2}$	2700.0071	1	$9_{3\,7}$	$8_{3\,6}$	2734.5237	2
$7_{0\,7}$	$6_{0\,6}$	2700.1252	-5	$9_{2\,7}$	$8_{2\,6}$	2734.5740	3
$7_{1\,7}$	$6_{1\,6}$	2700.1252	2	$8_{4\,5}$	$7_{4\,4}$	2734.7051	3
$3_{3\,0}$	$2_{1\,1}$	2700.2681	4	$8_{3\,5}$	$7_{3\,4}$	2737.0090	4
$6_{2\,5}$	$5_{2\,4}$	2700.3401	2	$7_{4\,3}$	$6_{4\,2}$	2737.5022	5
$6_{1\,5}$	$5_{1\,4}$	2700.5120	-1	$5_{4\,1}$	$4_{2\,2}$	2739.6870	3[b]
$5_{4\,2}$	$4_{4\,1}$	2702.7629	-3	$8_{5\,4}$	$7_{5\,3}$	2739.9475	-3
$5_{2\,3}$	$4_{2\,2}$	2703.1755	3	$8_{7\,2}$	$7_{7\,1}$	2741.4297	2
$5_{4\,1}$	$4_{4\,0}$	2704.9138	4	$8_{7\,1}$	$7_{7\,0}$	2741.7036	-4
$9_{2\,8}$	$9_{0\,9}$	2708.3594	-8	$11_{1\,10}$	$10_{1\,9}$	2742.2092	2
$5_{3\,2}$	$4_{3\,1}$	2708.3992	-5	$11_{2\,10}$	$10_{2\,9}$	2742.2092	2
$6_{3\,4}$	$5_{3\,3}$	2708.7952	0	$12_{0\,12}$	$11_{0\,11}$	2742.3030	-4
$8_{0\,8}$	$7_{0\,7}$	2708.8506	0	$12_{1\,12}$	$11_{1\,11}$	2742.3030	-4
$8_{1\,8}$	$7_{1\,7}$	2708.8506	1	$10_{3\,8}$	$9_{3\,7}$	2742.5100	2
$7_{2\,6}$	$6_{2\,5}$	2709.0322	2	$10_{2\,8}$	$9_{2\,7}$	2742.5227	8
$7_{1\,6}$	$6_{1\,5}$	2709.0698	5	$8_{6\,3}$	$7_{6\,2}$	2742.9893	-2
$3_{3\,1}$	$2_{1\,2}$	2710.8059	-2[a]	$9_{4\,6}$	$8_{4\,5}$	2743.1533	-1
$6_{2\,4}$	$5_{2\,3}$	2711.1050	3	$5_{3\,2}$	$4_{1\,3}$	2743.9021	2
$6_{4\,3}$	$5_{4\,2}$	2713.8635	6	$9_{3\,6}$	$8_{3\,5}$	2743.9309	-2
$6_{5\,2}$	$5_{5\,1}$	2715.7939	0	$8_{6\,2}$	$7_{6\,1}$	2745.8037	-3
$10_{1\,9}$	$10_{1\,10}$	2716.9045	-11	$8_{4\,4}$	$7_{4\,3}$	2748.4719	12
$6_{5\,1}$	$5_{5\,0}$	2717.2351	2	$12_{1\,11}$	$11_{1\,10}$	2750.1392	4
$9_{0\,9}$	$8_{0\,8}$	2717.4355	6	$11_{3\,9}$	$10_{3\,8}$	2750.3472	-6
$9_{1\,9}$	$8_{1\,8}$	2717.4355	6	$9_{5\,5}$	$8_{5\,4}$	2750.4597	2
$8_{2\,7}$	$7_{2\,6}$	2717.5430	-11	$10_{3\,7}$	$9_{3\,6}$	2751.2686	0
$8_{1\,7}$	$7_{1\,6}$	2717.5510	-7	$8_{5\,3}$	$7_{5\,2}$	2751.3672	4
$7_{3\,5}$	$6_{3\,4}$	2717.8909	-5	$9_{8\,2}$	$8_{8\,1}$	2753.6997	-7[b]
$4_{3\,1}$	$3_{1\,2}$	2718.6453	1	$9_{7\,3}$	$8_{7\,2}$	2755.4070	-5[a]
$7_{2\,5}$	$6_{2\,4}$	2718.6526	1	$9_{4\,5}$	$8_{4\,4}$	2755.6240	-1[a]
$6_{3\,3}$	$5_{3\,2}$	2721.3269	0	$5_{4\,2}$	$4_{2\,3}$	2757.5549	0
				$13_{1\,13}$	$12_{1\,12}$	2750.2805	0

view of the fact that the $v_1 = 1$ and $v_3 = 1$ states lie close together ($E(v_1 = 1) - E(v_3 = 1) \simeq 13$ cm^{-1}) and the accuracy of the measurements, the Coriolis interaction between the two states given as (*29, 30*)

$$H_C^{13} = h_{13} i J_c + h'_{13}[J_b, J_a]_+ \qquad (2)$$

was taken into account explicitly so that the matrix was set up for each symmetry species for the $v_1 = 1$ and $v_3 = 1$ states in terms of the symmetrized base functions. The possible Fermi resonance between the $v_1 = 1$ and $v_2 = 2$ states and Coriolis interaction between the $v_3 = 1$ and $v_2 = 2$ states were neglected. Gillis and Edwards (*31*) concluded that the Fermi resonance is negligibly small in H_2S. The energy level structure and molecular constants of H_2Cl^+ are very similar to those of H_2S, and we expect that the Fermi resonance can also be safely neglected in H_2Cl^+. However, it

TABLE IV

Observed Transitions of $H_2{}^{37}Cl^+$ (in cm^{-1})

$J'K'_aK'_c$ –	$J'K''_aK''_c$	Obs.	$(O-C)\cdot 10^4$	$J'K'_aK'_c$ –	$J'K''_aK''_c$	Obs.	$(O-C)\cdot 10^4$
ν_1 fundamental band							
$8_{2\,7}$	$9_{1\,8}$	2530.2183	10	$5_{4\,1}$	$5_{5\,0}$	2608.5491	-13
$7_{2\,5}$	$8_{3\,6}$	2530.3000	-6	$4_{2\,3}$	$4_{3\,2}$	2611.0962	-3
$9_{0\,9}$	$10_{1\,10}$	2530.3093	0	$4_{3\,2}$	$4_{4\,1}$	2611.8540	-6
$9_{1\,9}$	$10_{0\,10}$	2530.3093	0	$3_{1\,3}$	$3_{2\,2}$	2613.7954	-5
$4_{4\,1}$	$5_{5\,0}$	2530.3093	-27^b	$7_{4\,3}$	$7_{5\,2}$	2614.3464	-34^c
$4_{4\,0}$	$5_{5\,1}$	2531.1252	8	$1_{0\,1}$	$2_{1\,2}$	2615.2495	-3
$4_{3\,2}$	$5_{4\,1}$	2531.8955	4	$3_{0\,3}$	$3_{1\,2}$	2616.5061	-6
$6_{4\,3}$	$7_{3\,4}$	2535.6624	-6	$6_{3\,3}$	$6_{4\,2}$	2616.6194	-11
$6_{2\,4}$	$7_{3\,5}$	2541.0750	1	$4_{1\,3}$	$4_{2\,2}$	2617.5378	6
$7_{1\,6}$	$8_{2\,7}$	2541.4673	5	$3_{2\,2}$	$3_{3\,1}$	2617.6121	-5
$7_{2\,6}$	$8_{1\,7}$	2541.4753	2	$1_{1\,1}$	$2_{0\,2}$	2617.9492	4
$8_{0\,8}$	$9_{1\,9}$	2541.5674	-3	$5_{2\,3}$	$5_{3\,2}$	2617.9683	2
$8_{1\,8}$	$9_{0\,9}$	2541.5674	-3	$5_{3\,2}$	$5_{4\,1}$	2621.1155	-12
$6_{3\,4}$	$7_{2\,5}$	2542.0918	-8	$2_{1\,2}$	$2_{2\,1}$	2622.0095	-4
$4_{3\,1}$	$5_{4\,2}$	2542.2473	-5	$4_{2\,2}$	$4_{3\,1}$	2624.8904	1
$5_{2\,3}$	$6_{3\,4}$	2550.7917	-8	$0_{0\,0}$	$1_{1\,1}$	2625.3413	1
$3_{2\,2}$	$4_{3\,1}$	2551.3860	-2	$3_{2\,1}$	$3_{3\,0}$	2626.4060	1
$6_{1\,5}$	$7_{2\,6}$	2552.5598	-2	$3_{1\,2}$	$3_{2\,1}$	2627.2878	4
$6_{2\,5}$	$7_{1\,6}$	2552.6023	0	$2_{0\,2}$	$2_{1\,1}$	2627.6909	12
$7_{0\,7}$	$8_{1\,8}$	2552.6873	-1	$2_{1\,1}$	$2_{2\,0}$	2631.7104	0
$7_{1\,7}$	$8_{0\,8}$	2552.6873	-3	$1_{0\,1}$	$1_{1\,0}$	2634.9836	-4
$3_{3\,1}$	$4_{4\,0}$	2552.9592	15	$1_{1\,0}$	$1_{0\,1}$	2647.4624	-1
$5_{3\,3}$	$6_{2\,4}$	2554.4202	7	$4_{3\,1}$	$4_{2\,2}$	2652.1001	5
$3_{3\,0}$	$4_{4\,1}$	2554.9087	12	$3_{2\,1}$	$3_{1\,2}$	2652.8142	8
$4_{2\,2}$	$5_{3\,3}$	2559.2649	1^b	$3_{3\,0}$	$3_{2\,1}$	2653.3657	3
$5_{1\,4}$	$6_{2\,5}$	2563.4341	4	$2_{1\,1}$	$2_{0\,2}$	2653.8623	3
$5_{2\,4}$	$6_{1\,5}$	2563.6440	2	$6_{4\,2}$	$6_{3\,3}$	2653.8799	7
$6_{0\,6}$	$7_{1\,7}$	2563.6672	11	$7_{5\,2}$	$7_{4\,3}$	2654.1953	9
$6_{1\,6}$	$7_{0\,7}$	2563.6672	4	$5_{4\,1}$	$5_{3\,2}$	2654.3040	2
$3_{2\,1}$	$4_{3\,2}$	2568.3010	12	$1_{1\,1}$	$0_{0\,0}$	2657.4009	-3
$8_{2\,7}$	$8_{3\,6}$	2568.8435	6	$5_{3\,2}$	$5_{2\,3}$	2658.3005	-3
$4_{3\,2}$	$5_{2\,3}$	2569.0789	-3	$6_{5\,1}$	$6_{4\,2}$	2658.5933	-9
$2_{1\,2}$	$3_{2\,1}$	2570.0142	2	$4_{4\,0}$	$4_{3\,1}$	2658.8391	-7
$7_{0\,7}$	$7_{1\,6}$	2570.5498	9	$2_{2\,1}$	$2_{1\,2}$	2659.4304	-7
$4_{1\,3}$	$5_{2\,4}$	2573.8501	0	$4_{2\,2}$	$4_{1\,3}$	2660.3423	-1
$5_{0\,5}$	$6_{1\,6}$	2574.5024	15	$3_{3\,1}$	$3_{2\,2}$	2661.8455	-8
$5_{1\,5}$	$6_{0\,6}$	2574.5024	-23^b	$3_{1\,2}$	$3_{0\,3}$	2663.7549	-8
$4_{2\,3}$	$5_{1\,4}$	2574.8108	3	$7_{6\,1}$	$7_{5\,2}$	2664.1577	-28^c
$2_{2\,1}$	$3_{3\,0}$	2574.8613	0	$2_{0\,2}$	$1_{1\,1}$	2664.1697	-6
$2_{2\,0}$	$3_{3\,1}$	2578.8943	-7	$5_{5\,0}$	$5_{4\,1}$	2664.9307	-1
$6_{1\,6}$	$6_{2\,5}$	2581.8601	-4	$4_{4\,1}$	$4_{3\,2}$	2664.9937	2
$6_{0\,6}$	$6_{1\,5}$	2581.9014	1	$6_{3\,3}$	$6_{2\,4}$	2666.0349	-12
$3_{1\,2}$	$4_{2\,3}$	2583.3125	6	$3_{2\,2}$	$3_{1\,3}$	2666.3147	-5
$4_{0\,4}$	$5_{1\,5}$	2585.1819	3	$4_{3\,2}$	$4_{2\,3}$	2666.3364	-4
$4_{1\,4}$	$5_{0\,5}$	2585.2051	-2	$2_{1\,2}$	$1_{0\,1}$	2666.8545	2
$3_{2\,2}$	$4_{1\,3}$	2586.8384	-2	$5_{4\,2}$	$5_{3\,3}$	2667.1003	0
$6_{2\,5}$	$6_{3\,4}$	2591.5840	-1	$6_{5\,2}$	$6_{4\,3}$	2668.6602	4
$2_{1\,1}$	$3_{2\,2}$	2592.2485	-4	$5_{2\,3}$	$5_{1\,4}$	2670.6108	9
$7_{2\,5}$	$7_{3\,4}$	2592.3879	4	$6_{4\,3}$	$6_{3\,4}$	2671.7639	4
$6_{1\,5}$	$6_{2\,4}$	2592.4551	-6	$6_{6\,1}$	$6_{5\,2}$	2672.3884	2
$5_{0\,5}$	$5_{1\,4}$	2593.1978	-6	$5_{3\,3}$	$5_{2\,4}$	2673.1353	-12
$3_{0\,3}$	$4_{1\,4}$	2595.6653	3	$4_{1\,3}$	$4_{0\,4}$	2674.0259	0
$3_{1\,3}$	$4_{0\,4}$	2595.8035	-1	$3_{0\,3}$	$2_{1\,2}$	2674.6687	-1
$6_{3\,4}$	$6_{4\,3}$	2599.4158	4	$4_{2\,3}$	$4_{1\,4}$	2674.7671	-11
$2_{2\,1}$	$3_{1\,2}$	2601.2693	5	$3_{1\,3}$	$2_{0\,2}$	2675.4082	-8
$6_{4\,3}$	$6_{5\,2}$	2601.3928	6	$8_{5\,4}$	$8_{4\,5}$	2675.8301	-8
$5_{2\,4}$	$5_{3\,3}$	2602.1079	-5	$7_{3\,4}$	$7_{2\,5}$	2676.1750	-7
$1_{1\,0}$	$2_{2\,1}$	2602.6174	-4	$2_{2\,1}$	$1_{1\,0}$	2679.1658	4
$4_{1\,4}$	$4_{2\,3}$	2603.8147	-7	$3_{1\,2}$	$2_{2\,1}$	2679.2830	-4
$4_{0\,4}$	$4_{1\,3}$	2604.6348	-6	$6_{3\,4}$	$6_{2\,5}$	2681.2305	-1
$5_{1\,4}$	$5_{2\,3}$	2604.9199	2	$5_{1\,4}$	$5_{0\,5}$	2683.5674	3
$5_{4\,2}$	$5_{5\,1}$	2605.0088	-14	$5_{2\,4}$	$5_{1\,5}$	2683.7312	-11
$2_{0\,2}$	$3_{1\,3}$	2605.7659	2	$4_{0\,4}$	$3_{1\,3}$	2684.1123	1
$2_{1\,2}$	$3_{0\,3}$	2606.4832	10	$4_{1\,4}$	$3_{0\,3}$	2684.2590	-2
$7_{3\,4}$	$7_{4\,3}$	2607.0100	3	$2_{2\,0}$	$1_{1\,1}$	2686.0022	-1

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[a] The relative weight is 0.5 due to the weaker component of unresolved K-type doublet in which the S/N ratio of the peak is strong.

[b] The relative weight is 0.1 due to the weaker component of unresolved K-type doublet in which the S/N ratio of the peak is weak.

[c] This transition is omitted from the fit because the S/N ratio of the peak is very weak.

TABLE IV—*Continued*

$J'K'_aK'_c$ ←	$J''K''_aK''_c$	Obs.	(O-C) × 10^4
$8_{4\,5}$	$8_{3\,6}$	2686.2019	-2
$3_{2\,2}$	$2_{1\,1}$	2688.2400	5
$7_{2\,5}$	$7_{1\,6}$	2689.5059	-4
$4_{1\,3}$	$3_{2\,2}$	2692.0183	-2
$6_{1\,5}$	$6_{0\,6}$	2692.6709	-1
$6_{2\,5}$	$6_{1\,6}$	2692.7046	6
$5_{0\,5}$	$4_{1\,4}$	2693.1572	11
$5_{1\,5}$	$4_{0\,4}$	2693.1831	10
$4_{2\,3}$	$3_{1\,2}$	2695.6108	8
$8_{3\,6}$	$8_{2\,7}$	2698.0925	-12
$3_{3\,1}$	$2_{2\,0}$	2701.3074	-3
$7_{1\,6}$	$7_{0\,7}$	2701.5261	-6
$7_{2\,6}$	$7_{1\,7}$	2701.5261	-70[c]
$6_{0\,6}$	$5_{1\,5}$	2701.9932	36[b]
$6_{1\,6}$	$5_{0\,5}$	2701.9932	-8
$5_{1\,4}$	$4_{2\,3}$	2702.1775	2
$5_{2\,4}$	$4_{1\,3}$	2703.1855	-5
$3_{3\,0}$	$2_{2\,1}$	2705.3616	1
$5_{2\,3}$	$4_{3\,2}$	2706.8967	8
$8_{1\,7}$	$8_{0\,8}$	2710.1858	3
$8_{2\,7}$	$8_{1\,8}$	2710.1858	-9
$4_{3\,2}$	$3_{2\,1}$	2710.3125	0
$7_{0\,7}$	$6_{1\,6}$	2710.6511	2
$7_{1\,7}$	$6_{0\,6}$	2710.6511	-5
$3_{2\,1}$	$2_{1\,2}$	2710.9768	11
$6_{1\,5}$	$5_{2\,4}$	2711.1724	-2
$6_{2\,5}$	$5_{1\,4}$	2711.4016	1
$5_{3\,3}$	$4_{2\,2}$	2716.8232	-2
$6_{3\,3}$	$5_{4\,2}$	2718.5884	-1
$6_{2\,4}$	$5_{3\,3}$	2718.9517	5
$8_{0\,8}$	$7_{1\,7}$	2719.1453	-3
$8_{1\,8}$	$7_{0\,7}$	2719.1453	-5
$7_{1\,6}$	$6_{2\,5}$	2719.7200	-6
$7_{2\,6}$	$6_{1\,5}$	2719.7673	-8
$6_{3\,4}$	$5_{2\,3}$	2722.7173	7
$4_{4\,1}$	$3_{3\,0}$	2723.0994	0
$4_{4\,0}$	$3_{3\,1}$	2725.0659	-2
$4_{3\,1}$	$3_{2\,2}$	2726.5811	4
$9_{0\,9}$	$8_{1\,8}$	2727.4741	2
$9_{1\,9}$	$8_{0\,8}$	2727.4741	2
$8_{1\,7}$	$7_{2\,6}$	2728.0386	-3
$8_{2\,7}$	$7_{1\,6}$	2728.0486	0
$7_{2\,5}$	$6_{3\,4}$	2728.4883	2
$7_{4\,3}$	$6_{5\,2}$	2728.7324	-1
$7_{3\,5}$	$6_{2\,4}$	2729.5845	5[a]
$5_{4\,2}$	$4_{3\,1}$	2732.7261	3[a]
$7_{3\,4}$	$6_{4\,3}$	2733.4995	10
$10_{0\,10}$	$9_{1\,9}$	2735.6353	-3
$10_{1\,10}$	$9_{0\,9}$	2735.6353	-3
$9_{2\,8}$	$8_{1\,7}$	2736.1807	8
$8_{2\,6}$	$7_{3\,5}$	2736.9336	-2[c]
$8_{3\,6}$	$7_{2\,5}$	2737.2107	14
$6_{4\,3}$	$5_{3\,2}$	2738.9407	15
$5_{4\,1}$	$4_{3\,2}$	2743.2319	4
$7_{4\,4}$	$6_{3\,3}$	2743.3940	2[b]
$11_{0\,11}$	$10_{1\,10}$	2743.6301	4
$11_{1\,11}$	$10_{0\,10}$	2743.6301	4
$5_{5\,1}$	$4_{4\,0}$	2744.0669	-5
$10_{1\,9}$	$9_{2\,8}$	2744.1472	0
$10_{2\,9}$	$9_{1\,8}$	2744.1472	-4
$5_{5\,0}$	$4_{4\,1}$	2744.8904	4
$9_{2\,7}$	$8_{3\,6}$	2744.9399	-1
$8_{4\,5}$	$7_{3\,4}$	2748.2898	6
$12_{0\,12}$	$11_{1\,11}$	2751.4556	-11[b]
$12_{1\,12}$	$11_{0\,11}$	2751.4556	-11[b]
$6_{5\,2}$	$5_{4\,1}$	2754.7771	1
ν_3 fundamental band			
$6_{2\,4}$	$7_{2\,5}$	2528.3125	-8
$7_{2\,6}$	$8_{2\,7}$	2528.6580	2
$6_{3\,4}$	$7_{3\,5}$	2528.8186	3
$5_{4\,2}$	$6_{4\,3}$	2531.6804	0
$5_{2\,3}$	$6_{2\,4}$	2538.6399	-12
$6_{1\,5}$	$7_{1\,6}$	2539.5935	4
$6_{2\,5}$	$7_{2\,6}$	2539.6157	1
$7_{0\,7}$	$8_{0\,8}$	2540.0576	4
$7_{1\,7}$	$8_{1\,8}$	2540.0576	3
$5_{3\,3}$	$6_{3\,4}$	2540.3271	-1
$4_{3\,1}$	$5_{3\,2}$	2543.0444	0
$4_{4\,0}$	$5_{4\,1}$	2545.1433	3
$4_{4\,1}$	$5_{4\,2}$	2548.5957	1
$4_{2\,2}$	$5_{2\,3}$	2549.0217	2
$5_{1\,4}$	$6_{1\,5}$	2550.3755	3
$5_{2\,4}$	$6_{2\,5}$	2550.4924	2
$6_{0\,6}$	$7_{0\,7}$	2550.8386	1
$6_{1\,6}$	$7_{1\,7}$	2550.8386	-3[a]
$4_{3\,2}$	$5_{3\,3}$	2552.5935	-5
$2_{1\,1}$	$3_{3\,0}$	2555.3437	1
$4_{1\,3}$	$5_{1\,4}$	2560.8672	-2
$3_{3\,0}$	$4_{3\,1}$	2561.1675	4
$4_{2\,3}$	$5_{2\,4}$	2561.3984	4
$5_{0\,5}$	$6_{0\,6}$	2561.5083	22[a]
$5_{1\,5}$	$6_{1\,6}$	2561.5083	0
$3_{2\,1}$	$4_{2\,2}$	2561.8213	1
$3_{3\,1}$	$4_{3\,2}$	2565.9563	-1
$7_{2\,6}$	$7_{2\,5}$	2567.7734	0
$3_{1\,2}$	$4_{1\,3}$	2570.9236	10
$4_{0\,4}$	$5_{0\,5}$	2572.0540	7
$4_{1\,4}$	$5_{1\,5}$	2572.0684	6
$3_{2\,2}$	$4_{2\,3}$	2572.6660	6
$2_{2\,0}$	$3_{2\,1}$	2577.7898	-2
$6_{1\,5}$	$6_{3\,4}$	2578.5745	-4
$7_{3\,5}$	$7_{3\,4}$	2579.6648	11
$5_{1\,5}$	$5_{1\,4}$	2580.2053	-3
$1_{0\,1}$	$2_{2\,0}$	2580.3816	-8
$2_{1\,1}$	$3_{1\,2}$	2581.7507	-4
$3_{0\,3}$	$4_{0\,4}$	2582.4514	-11
$3_{1\,3}$	$4_{1\,4}$	2582.5388	-8
$2_{2\,1}$	$3_{2\,2}$	2584.8535	-5
$6_{2\,4}$	$6_{4\,3}$	2585.6360	-1
$5_{1\,4}$	$5_{3\,3}$	2588.8401	1
$4_{0\,4}$	$4_{2\,3}$	2590.6628	-7
$5_{2\,4}$	$5_{2\,3}$	2591.9778	-6
$2_{0\,2}$	$3_{0\,3}$	2592.5942	-4
$2_{1\,2}$	$3_{1\,3}$	2593.0347	-4
$1_{1\,0}$	$2_{1\,1}$	2595.4800	-5
$7_{4\,4}$	$7_{4\,3}$	2596.5862	-10
$4_{1\,3}$	$4_{3\,2}$	2597.1528	-4
$1_{0\,1}$	$2_{0\,2}$	2602.5352	12
$3_{1\,3}$	$3_{1\,2}$	2603.3811	-3
$1_{1\,1}$	$2_{1\,2}$	2603.8962	-2
$4_{2\,3}$	$4_{2\,2}$	2605.0850	-2
$5_{3\,3}$	$5_{3\,2}$	2607.5020	-9
$2_{0\,2}$	$2_{2\,1}$	2608.1221	-3
$9_{9\,1}$	$9_{9\,0}$	2611.0715	-1
$9_{8\,2}$	$9_{8\,1}$	2612.9846	-23[c]
$0_{0\,0}$	$1_{0\,1}$	2614.0500	4
$8_{8\,1}$	$8_{8\,0}$	2614.4741	1
$8_{8\,0}$	$8_{8\,1}$	2614.4941	5
$3_{2\,2}$	$3_{2\,1}$	2616.6411	-1
$8_{7\,1}$	$8_{7\,2}$	2616.6675	-6
$7_{7\,1}$	$7_{7\,0}$	2617.5232	-2
$7_{7\,0}$	$7_{7\,1}$	2617.5796	-4
$4_{3\,2}$	$4_{3\,1}$	2618.2190	-3
$7_{6\,2}$	$7_{6\,1}$	2618.3982	-16
$6_{5\,2}$	$6_{5\,1}$	2619.9319	2
$7_{6\,1}$	$7_{6\,2}$	2620.0159	13
$6_{6\,1}$	$6_{6\,0}$	2620.1809	0
$6_{6\,0}$	$6_{6\,1}$	2620.3396	0
$8_{6\,2}$	$8_{6\,3}$	2621.8437	8
$5_{5\,1}$	$5_{5\,0}$	2622.3821	-3
$5_{5\,0}$	$5_{5\,1}$	2622.8120	4
$6_{5\,1}$	$6_{5\,2}$	2623.5457	7
$1_{1\,1}$	$1_{1\,0}$	2623.6309	1
$4_{4\,1}$	$4_{4\,0}$	2624.0400	1
$3_{3\,1}$	$3_{3\,0}$	2624.0618	-5
$2_{2\,1}$	$2_{2\,0}$	2624.3152	-3
$4_{4\,0}$	$4_{4\,1}$	2625.1025	3

TABLE IV—*Continued*

$J'K_a'K_c' \leftarrow$	$J''K_a''K_c''$	Obs.	(O-C) · 10^4	$J'K_a'K_c' \leftarrow$	$J''K_a''K_c''$	Obs.	(O-C) · 10^1
3_{30}	3_{31}	2627.3933	-2	6_{25}	5_{24}	2698.2278	-3
5_{41}	5_{42}	2627.5439	4	6_{15}	5_{14}	2698.3923	-1
2_{20}	2_{21}	2629.7871	13	5_{23}	4_{22}	2701.0452	-1
1_{10}	1_{11}	2631.9609	-1	5_{41}	4_{40}	2702.9885	8
4_{31}	4_{32}	2631.9724	1	5_{32}	4_{31}	2706.3845	-3
6_{42}	6_{43}	2634.3660	-2	6_{34}	5_{33}	2706.6948	4
3_{21}	3_{22}	2636.3022	-2	8_{08}	7_{07}	2706.7424	3
2_{11}	2_{12}	2639.9133	1	8_{18}	7_{17}	2706.7424	4
5_{32}	5_{33}	2640.7598	3	7_{26}	6_{25}	2706.9119	5
1_{01}	0_{00}	2641.9861	0	7_{16}	6_{15}	2706.9475	8
4_{22}	4_{23}	2646.2795	3	6_{24}	5_{23}	2708.9373	1
3_{12}	3_{13}	2650.3999	6	6_{43}	5_{42}	2711.8369	-8
3_{31}	3_{12}	2650.4700	1	6_{52}	5_{51}	2713.8999	2
2_{12}	1_{11}	2651.4392	-6	9_{09}	8_{08}	2715.3245	-4
6_{33}	6_{34}	2652.0496	2	9_{19}	8_{18}	2715.3245	-4
2_{02}	1_{01}	2652.9673	5	6_{51}	5_{50}	2715.3401	15
3_{22}	3_{03}	2653.1086	-7	8_{27}	7_{26}	2715.4165	-7
4_{32}	4_{13}	2653.6709	-4	8_{17}	7_{16}	2715.4241	-4
5_{42}	5_{23}	2654.9822	4	7_{35}	6_{34}	2715.7639	-6
5_{23}	5_{24}	2657.3606	25[a]	4_{31}	3_{12}	2716.4868	7
2_{11}	1_{10}	2659.6477	0	7_{25}	6_{24}	2716.4927	-3
5_{33}	5_{14}	2660.1445	-3	6_{33}	5_{32}	2719.2244	-7
4_{13}	4_{14}	2660.8250	-2	6_{42}	5_{41}	2720.4832	-2
3_{13}	2_{12}	2661.5435	-3	7_{44}	6_{43}	2723.0762	1
4_{23}	4_{04}	2661.5730	-7	10_{010}	9_{09}	2723.7661	-6
3_{03}	2_{02}	2662.0586	5	10_{110}	9_{19}	2723.7661	-6
7_{44}	7_{25}	2665.7527	-5	9_{18}	8_{17}	2723.7778	-8
6_{24}	6_{25}	2667.4514	1	9_{28}	8_{27}	2723.7778	6
6_{34}	6_{15}	2668.2292	-6	8_{36}	7_{35}	2724.2156	-1
3_{22}	2_{21}	2668.6372	2	8_{26}	7_{25}	2724.4087	-1
5_{14}	5_{15}	2670.4636	0	7_{62}	6_{61}	2726.9351	-7
5_{24}	5_{05}	2670.6265	6	7_{34}	6_{33}	2728.0386	9
4_{14}	3_{13}	2670.9988	7	10_{19}	9_{18}	2731.9963	2
4_{04}	3_{03}	2671.1079	6	10_{29}	9_{28}	2731.9963	5
3_{12}	2_{11}	2672.3237	2	11_{011}	10_{010}	2732.0654	4
2_{20}	1_{01}	2674.6306	1	11_{111}	10_{110}	2732.0654	4
3_{21}	2_{20}	2675.7656	17	9_{37}	8_{36}	2732.3728	2
7_{35}	7_{16}	2676.7820	-6	9_{27}	8_{26}	2732.4202	5
4_{23}	3_{22}	2679.5654	-7	8_{45}	7_{44}	2732.5745	5
6_{15}	6_{16}	2679.6948	0	8_{35}	7_{34}	2734.7922	2
5_{15}	4_{14}	2680.1638	2	7_{43}	6_{42}	2735.4641	-2
5_{05}	4_{04}	2680.1831	0	8_{54}	7_{53}	2737.9199	1[c]
4_{13}	3_{12}	2681.6667	-2	11_{210}	10_{29}	2740.0715	-3
4_{32}	3_{31}	2684.4451	-6	12_{012}	11_{011}	2740.2173	-1
7_{26}	7_{07}	2688.7180	3	10_{28}	9_{27}	2740.3633	5
6_{06}	5_{05}	2689.1643	-13	9_{46}	8_{45}	2740.9946	5
6_{16}	5_{15}	2689.1643	21[a]	8_{62}	7_{61}	2743.9734	1
5_{24}	4_{23}	2689.2356	-2	8_{44}	7_{43}	2746.3025	0
5_{14}	4_{13}	2689.9172	-1	12_{111}	11_{110}	2748.0024	1
4_{31}	3_{30}	2690.0786	3	12_{211}	11_{210}	2748.0024	1
4_{22}	3_{21}	2690.2546	-3	11_{39}	10_{38}	2748.1816	-7
5_{33}	4_{32}	2696.4285	-23[a]	9_{55}	8_{54}	2748.3435	-4
5_{42}	4_{41}	2697.7576	6	10_{37}	9_{36}	2749.0786	1
3_{21}	2_{02}	2697.9150	-5	9_{64}	8_{63}	2749.0864	0
7_{07}	6_{06}	2698.0210	-3	8_{53}	7_{52}	2749.4238	-6
7_{17}	6_{16}	2698.0210	3	9_{73}	8_{72}	2753.5591	1

maybe necessary to evaluate the Coriolis interaction between the $v_3 = 1$ and $v_2 = 2$ states more carefully. We will discuss this point briefly in the next section.

We eventually assigned 512 transitions to $H_2{}^{35}Cl^+$ (246 and 266 transitions to the ν_1 and ν_3 fundamental bands, respectively) and carried out a least-squares fit by including the pure rotational transition frequencies derived from the observed (*7*) after correction for the hyperfine splittings (*32*). The standard deviation of the fit was found to be 0.0005 cm^{-1}. Although the molecular constants in the ground state were already determined with reasonable accuracy from the analysis of the ν_2 fundamental band

TABLE V

Calculated Term Values of $H_2{}^{35}Cl^+$ (in cm^{-1})[a]

J	K_a	K_c	v_1=1 state	v_3=1 state	Ground state
0	0	0	2643.2200(0.0000)	2630.1404(0.0000)	0.0000
1	0	1	2657.0588(0.0000)	2644.0259(0.0006)	14.0633
1	1	1	2659.1682(0.0006)	2646.0452(0.0000)	16.1918
1	1	0	2663.2788(0.0000)	2650.1792(0.0000)	20.3754
2	0	2	2682.0898(0.0005)	2669.0964(0.0012)	39.4935
2	1	2	2682.7002(0.0055)	2669.6819(0.0009)	40.1355
2	1	1	2695.0779(0.0022)	2682.0613(0.0013)	52.6720
2	2	1	2701.3740(0.0013)	2688.0879(0.0022)	59.0406
2	2	0	2703.9973(0.0004)	2690.8315(0.0042)	61.7210
3	0	3	2716.5662(0.0020)	2703.6321(0.0022)	74.5223
3	1	3	2716.6882(0.0030)	2703.7468(0.0020)	74.6551
3	1	2	2739.9905(0.0001)	2727.0703(0.0025)	98.3223
3	2	2	2742.7654(0.0154)	2729.7253(0.0015)	101.2236
3	2	1	2752.9644(0.2333)	2739.5005(0.0033)	111.0013
3	3	1	2764.9360(0.0025)	2750.9417(0.2333)	123.5558
3	3	0	2766.2620(0.0014)	2752.9397(0.0129)	124.9186
4	0	4	2760.5520(0.0037)	2747.7153(0.0037)	119.2117
4	1	4	2760.5730(0.0039)	2747.7346(0.0036)	119.2356
4	1	3	2794.9795(0.0013)	2782.1057(0.0031)	154.2059
4	2	3	2795.7837(0.0080)	2782.8635(0.0022)	155.0794
4	2	2	2816.2302(0.0138)	2803.3140(0.0052)	175.6799
4	3	2	2823.2561(0.0246)	2810.0286(0.0170)	183.0566
4	3	1	2829.6326(0.0583)	2816.9675(0.0087)	189.7080
4	4	1	2849.9919(0.0038)	2836.4797(0.0575)	209.8713
4	4	0	2850.5547(0.0031)	2836.9558(0.0197)	210.4532
5	0	5	2814.1934(0.0058)	2801.4868(0.0057)	173.7092
5	1	5	2814.1968(0.0059)	2801.4900(0.0057)	173.7133
5	1	4	2859.0464(0.0038)	2846.2446(0.0042)	219.3094
5	2	4	2859.2273(0.0058)	2846.4124(0.0038)	219.5150
5	2	3	2891.6013(0.0009)	2878.8552(0.0059)	252.3679
5	3	3	2894.4517(0.0205)	2881.5518(0.0043)	255.4578
5	3	2	2909.3562(0.4668)	2898.1077(0.0092)	271.8940
5	4	2	2924.4651(0.0314)	2912.6345(0.4717)	285.9036
5	4	1	2928.1550(0.0357)	2915.3667(0.0201)	289.7361
5	5	1	2956.5532(0.0054)	2942.5862(0.0324)	317.9978
5	5	0	2956.7683(0.0050)	2942.7817(0.0238)	318.2214
6	0	6	2877.5200(0.0085)	2864.9734(0.0084)	238.0453
6	1	6	2877.5205(0.0085)	2864.9739(0.0084)	238.0460
6	1	5	2932.5061(0.0062)	2919.8215(0.0060)	293.9495
6	2	5	2932.5430(0.0067)	2919.8550(0.0059)	293.9934
6	2	4	2976.1638(0.0031)	2963.4727(0.0060)	338.3337
6	3	4	2977.0020(0.0119)	2964.2529(0.0043)	339.2847
6	3	3	3006.0017(0.0304)	2993.2212(0.0111)	368.3665
6	4	3	3012.8970(0.0385)	2999.7666(0.0379)	375.9624
6	4	2	3024.0962(0.0965)	3012.1653(0.0164)	387.7200
6	5	2	3046.6145(0.0375)	3033.7915(0.1023)	409.9949
6	5	1	3048.4192(0.0369)	3035.4563(0.0352)	411.8745
6	6	1	3084.4922(0.0071)	3070.0325(0.0297)	447.8079
6	6	0	3084.5698(0.0069)	3070.1045(0.0270)	447.8889
7	0	7	2950.5293(0.0119)	2938.1709(0.0118)	312.2178
7	1	7	2950.5295(0.0119)	2938.1709(0.0118)	312.2180
7	1	6	3015.5510(0.0088)	3003.0188(0.0086)	378.3235
7	2	6	3015.5581(0.0089)	3003.0254(0.0086)	378.3325
7	2	5	3069.5923(0.0064)	3056.9861(0.0071)	433.2825
7	3	5	3069.7993(0.0093)	3057.1760(0.0064)	433.5295
7	3	4	3111.1079(0.0026)	3098.6001(0.0106)	475.4236
7	4	4	3113.8035(0.0265)	3101.1252(0.0077)	478.4834
7	4	3	3135.6404(0.4345)	3125.2217(0.0176)	502.2937
7	5	3	3151.4348(0.0553)	3140.4006(0.4463)	516.8547
7	5	2	3158.4683(0.0670)	3146.4827(0.0299)	524.1948
7	6	2	3189.8057(0.0442)	3176.6311(0.0711)	555.4465
7	6	1	3190.5869(0.0431)	3177.3767(0.0490)	556.2634
7	7	1	3233.5703(0.0091)	3218.5559(0.0315)	599.0652
7	7	0	3233.5974(0.0090)	3218.5813(0.0306)	599.0937
8	0	8	3033.2119(0.0160)	3021.0684(0.0160)	396.2163
8	1	8	3033.2122(0.0160)	3021.0684(0.0160)	396.2163
8	1	7	3108.2249(0.0121)	3095.8752(0.0119)	472.4778
8	2	7	3108.2263(0.0121)	3095.8765(0.0118)	472.4795
8	2	6	3172.3159(0.0094)	3159.8442(0.0092)	537.6602
8	3	6	3172.3635(0.0102)	3159.8872(0.0090)	537.7197
8	3	5	3224.8706(0.0056)	3212.4321(0.0099)	591.1021
8	4	5	3225.6904(0.0164)	3213.1882(0.0072)	592.0803
8	4	4	3263.3455(0.0446)	3250.7644(0.0186)	629.7263
8	5	4	3269.7534(0.0506)	3256.8025(0.0563)	637.2085
8	5	3	3286.5591(0.1347)	3275.5615(0.0266)	654.9121
8	6	3	3310.3367(0.0689)	3298.4360(0.1494)	678.4043
8	6	2	3314.1221(0.0688)	3302.0674(0.0501)	682.3562
8	7	2	3353.9873(0.0519)	3340.4949(0.0690)	722.2234
8	7	1	3354.3005(0.0512)	3340.7976(0.0605)	722.5520
8	8	1	3403.4756(0.0114)	3387.8601(0.0352)	771.4636
8	8	0	3403.4849(0.0113)	3387.8689(0.0349)	771.4734
9	0	9	3125.5557(0.0211)	3113.6511(0.0211)	490.0283
9	1	9	3125.5557(0.0211)	3113.6514(0.0211)	490.0283
9	1	8	3210.5288(0.0161)	3198.3882(0.0159)	576.4131
9	2	8	3210.5291(0.0161)	3198.3884(0.0159)	576.4136
9	2	7	3284.5337(0.0126)	3272.2339(0.0122)	651.6758
9	3	7	3284.5444(0.0128)	3272.2434(0.0121)	651.6899
9	3	6	3347.3733(0.0098)	3335.0332(0.0109)	715.6057
9	4	6	3347.5940(0.0136)	3335.2339(0.0096)	715.8831
9	4	5	3397.5498(0.0053)	3385.3503(0.0162)	766.5269
9	5	5	3400.0437(0.0331)	3387.6680(0.0118)	769.5142
9	5	4	3429.0740(0.4503)	3419.6523(0.0282)	801.0266
9	6	4	3445.1536(0.0765)	3435.1038(0.4693)	815.6875
9	6	3	3456.3230(0.0969)	3445.3447(0.0417)	827.3677
9	7	3	3489.7632(0.0815)	3477.6309(0.1113)	860.7996
9	7	2	3491.5537(0.0793)	3479.3892(0.0721)	862.6719
9	8	2	3538.9670(0.0611)	3525.1643(0.0744)	910.1501
9	8	1	3539.0869(0.0607)	3525.2805(0.0711)	910.2764
9	9	1	3593.8499(0.0139)	3577.6162(0.0403)	964.6567
9	9	0	3593.8530(0.0139)	3577.6191(0.0401)	964.6602
10	0	10	3227.5469(0.0274)	3215.9033(0.0274)	593.6392
10	1	10	3227.5469(0.0274)	3215.9033(0.0274)	593.6392
10	1	9	3322.4521(0.0211)	3310.5449(0.0209)	690.1182
10	2	9	3322.4521(0.0211)	3310.5449(0.0209)	690.1182
10	2	8	3406.2961(0.0164)	3394.1975(0.0161)	775.3838
10	3	8	3406.2986(0.0165)	3394.1997(0.0160)	775.3872
10	3	7	3479.0649(0.0133)	3466.8745(0.0132)	849.4202
10	4	7	3479.1216(0.0145)	3466.9253(0.0127)	849.4946
10	4	6	3540.1284(0.0089)	3528.0190(0.0146)	911.5320
10	5	6	3540.9231(0.0218)	3528.7468(0.0107)	912.5337
10	5	5	3587.0608(0.0577)	3574.7434(0.0275)	958.5574
10	6	5	3592.9055(0.0622)	3580.2158(0.0730)	965.8616
10	6	4	3615.7805(0.1714)	3605.8462(0.0391)	989.9910
10	7	4	3640.3101(0.0980)	3629.4883(0.1960)	1014.2039
10	7	3	3646.7466(0.0982)	3635.8020(0.0652)	1020.9214
10	8	3	3689.7307(0.0945)	3677.4609(0.1087)	1064.0872
10	8	2	3690.5046(0.0928)	3678.2278(0.0919)	1064.8977
10	9	2	3744.4492(0.0717)	3730.3691(0.0835)	1118.9546
10	9	1	3744.4939(0.0716)	3730.4124(0.0822)	1119.0015
10	10	1	3804.3091(0.0168)	3787.4829(0.0465)	1178.2808
10	10	0	3804.3103(0.0168)	3787.4839(0.0464)	1178.2817

[a] The values in the parentheses denote the mixing ratio of the perturbing state.

(*6*) and the millimeter-wave spectra (*7*), we treated them as adjustable parameters, expecting that an improvement in the determination might be possible, because our data are more extensive. Table I lists the molecular constants of $H_2{}^{35}Cl^+$ determined from the least-squares analysis. The spectroscopic parameters in the ground state are in very good agreement with those from the ν_2 fundamental band (*6*) and the millimeter-wave transitions (*7*) but they are determined more accurately here. The millimeter-wave lines helped reduce the standard errors of $\tilde{B}_0$ and $\tilde{C}_0$ by a factor of about five. Also Φ_{KJ}, which was fixed to the corresponding value for H_2S in Ref. (*6*), is determined

TABLE VI

Calculated Term Values of $H_2{}^{37}Cl^+$ (in cm^{-1})[a]

J	K_a	K_c	$v_1=1$ state	$v_3=1$ state	Ground state
0	0	0	2641.4932(0.0000)	2628.1064(0.0000)	0.0000
1	0	1	2655.3264(0.0000)	2641.9861(0.0005)	14.0569
1	1	1	2657.4011(0.0005)	2643.9729(0.0000)	16.1521
1	1	0	2661.5193(0.0000)	2648.1130(0.0000)	20.3422
2	0	2	2680.3223(0.0004)	2667.0237(0.0010)	39.4523
2	1	2	2680.9114(0.0058)	2667.5918(0.0007)	40.0764
2	1	1	2693.3142(0.0021)	2679.9897(0.0013)	52.6325
2	2	1	2699.5076(0.0013)	2685.9194(0.0021)	58.9015
2	2	0	2702.1543(0.0004)	2688.6873(0.0047)	61.6038
3	0	3	2714.7454(0.0017)	2701.5105(0.0018)	74.4292
3	1	3	2714.8611(0.0027)	2701.6201(0.0017)	74.5567
3	1	2	2738.1848(0.0001)	2724.9561(0.0022)	98.2386
3	2	2	2740.8718(0.0164)	2727.5386(0.0015)	101.0653
3	2	1	2751.0520(0.1647)	2737.3679(0.0033)	110.8974
3	3	1	2762.9116(0.0024)	2748.7085(0.1647)	123.2593
3	3	0	2764.2627(0.0014)	2750.6526(0.0142)	124.6462
4	0	4	2758.6687(0.0031)	2745.5366(0.0030)	119.0578
4	1	4	2758.6885(0.0033)	2745.5549(0.0030)	119.0804
4	1	3	2793.0837(0.0012)	2779.9055(0.0027)	154.0334
4	2	3	2793.8486(0.0078)	2780.6316(0.0020)	154.8731
4	2	2	2814.3760(0.0125)	2801.1523(0.0049)	175.5464
4	3	2	2821.2100(0.0261)	2807.7048(0.0156)	182.7522
4	3	1	2827.6460(0.0695)	2814.7246(0.0089)	189.4856
4	4	1	2847.7456(0.0037)	2833.9939(0.0687)	209.3554
4	4	0	2848.3254(0.0030)	2834.4575(0.0215)	209.9538
5	0	5	2812.2366(0.0048)	2799.2410(0.0047)	173.4832
5	1	5	2812.2397(0.0049)	2799.2439(0.0047)	173.4871
5	1	4	2857.0503(0.0033)	2843.9507(0.0035)	219.0382
5	2	4	2857.2195(0.0052)	2844.1089(0.0032)	219.2335
5	2	3	2889.6482(0.0010)	2876.5918(0.0053)	252.1308
5	3	3	2892.3699(0.0206)	2879.1831(0.0043)	255.1110
5	3	2	2910.4314(0.4398)	2895.8706(0.0091)	271.6802
5	4	2	2922.2114(0.0330)	2907.1123(0.4447)	285.3982
5	4	1	2925.9839(0.0389)	2912.9414(0.0207)	289.3147
5	5	1	2954.0212(0.0053)	2939.8159(0.0357)	317.2012
5	5	0	2954.2454(0.0049)	2940.0129(0.0256)	317.4336
6	0	6	2875.4768(0.0070)	2862.6489(0.0069)	237.7350
6	1	6	2875.4773(0.0070)	2862.6494(0.0069)	237.7357
6	1	5	2930.4060(0.0052)	2917.4307(0.0051)	293.5757
6	2	5	2930.4397(0.0057)	2917.4617(0.0049)	293.6167
6	2	4	2974.0620(0.0028)	2961.0679(0.0052)	337.9504
6	3	4	2974.8474(0.0112)	2961.8054(0.0040)	338.8557
6	3	3	3003.9868(0.0265)	2990.9050(0.0105)	368.0737
6	4	3	3010.6194(0.0392)	2997.2358(0.0339)	375.4319
6	4	2	3021.9531(0.1103)	3009.7981(0.0164)	387.3662
6	5	2	3044.0918(0.0391)	3031.1006(0.1161)	409.2271
6	5	1	3045.9602(0.0390)	3032.7720(0.0366)	411.1692
6	6	1	3081.6155(0.0071)	3066.9395(0.0319)	446.6733
6	6	0	3081.6973(0.0069)	3067.0132(0.0288)	446.7585
7	0	7	2948.3867(0.0098)	2935.7566(0.0097)	311.8103
7	1	7	2948.3867(0.0098)	2935.7566(0.0097)	311.8105
7	1	6	3013.3372(0.0074)	3000.5222(0.0071)	377.8376
7	2	6	3013.3437(0.0075)	3000.5283(0.0071)	377.8459
7	2	5	3067.3437(0.0057)	3054.4434(0.0061)	432.7546
7	3	5	3067.5344(0.0083)	3054.6201(0.0055)	432.9873
7	3	4	3108.9304(0.0027)	3096.1113(0.0096)	474.9563
7	4	4	3111.4675(0.0258)	3098.5078(0.0077)	477.8794
7	4	3	3137.9597(0.4825)	3122.8303(0.0172)	501.9207
7	5	3	3148.9062(0.0568)	3133.2351(0.4942)	516.0874
7	5	2	3156.1150(0.0720)	3143.9033(0.0301)	523.6099
7	6	2	3186.9514(0.0458)	3173.6089(0.0764)	554.3560
7	6	1	3187.7703(0.0449)	3174.3706(0.0511)	555.2092
7	7	1	3230.2993(0.0092)	3215.0972(0.0334)	597.5435
7	7	0	3230.3281(0.0091)	3215.1233(0.0323)	597.5737
8	0	8	3030.9563(0.0132)	3018.5525(0.0131)	395.6992
8	1	8	3030.9563(0.0132)	3018.5525(0.0131)	395.6992
8	1	7	3105.8848(0.0100)	3093.2622(0.0098)	471.8687
8	2	7	3105.8860(0.0101)	3093.2632(0.0098)	471.8704
8	2	6	3169.9209(0.0081)	3157.1633(0.0078)	536.9875
8	3	6	3169.9641(0.0088)	3157.2029(0.0076)	537.0432
8	3	5	3222.4890(0.0053)	3209.7483(0.0087)	590.4336
8	4	5	3223.2454(0.0153)	3210.4534(0.0067)	591.3562
8	4	4	3261.0952(0.0381)	3248.2231(0.0175)	629.2048
8	5	4	3267.1870(0.0504)	3254.0073(0.0496)	636.3904
8	5	3	3284.2261(0.1511)	3273.0344(0.0264)	654.3940
8	6	3	3307.4980(0.0710)	3295.4956(0.1659)	677.3396
8	6	2	3311.4299(0.0720)	3299.1826(0.0509)	681.4370
8	7	2	3350.7473(0.0536)	3337.1106(0.0725)	720.7551
8	7	1	3351.0791(0.0530)	3337.4231(0.0629)	721.1021
8	8	1	3399.7761(0.0114)	3384.0002(0.0370)	769.5156
8	8	0	3399.7861(0.0114)	3384.0093(0.0366)	769.5261
9	0	9	3123.1733(0.0174)	3111.0239(0.0173)	489.3887
9	1	9	3123.1733(0.0174)	3111.0239(0.0173)	489.3887
9	1	8	3208.0483(0.0133)	3195.6472(0.0131)	575.6687
9	2	8	3208.0486(0.0133)	3195.6475(0.0131)	575.6692
9	2	7	3281.9834(0.0107)	3269.4072(0.0103)	650.8513
9	3	7	3281.9929(0.0109)	3269.4160(0.0102)	650.8643
9	3	6	3344.7988(0.0088)	3332.1665(0.0095)	714.7476
9	4	6	3344.9988(0.0122)	3332.3503(0.0085)	715.0061
9	4	5	3395.0764(0.0055)	3382.5637(0.0147)	765.7595
9	5	5	3397.3889(0.0316)	3384.7344(0.0116)	768.5864
9	5	4	3432.3928(0.4671)	3417.0500(0.0274)	800.4419
9	6	4	3442.3008(0.0773)	3426.4260(0.4860)	814.6045
9	6	3	3453.7698(0.1033)	3442.5869(0.0416)	826.6018
9	7	3	3486.5562(0.0838)	3474.3142(0.1182)	859.3770
9	7	2	3488.4395(0.0819)	3476.1255(0.0738)	861.3413
9	8	2	3535.3010(0.0629)	3521.3811(0.0775)	908.2598
9	8	1	3535.4292(0.0625)	3521.5020(0.0737)	908.3940
9	9	1	3589.7109(0.0140)	3573.3325(0.0420)	962.2573
9	9	0	3589.7144(0.0140)	3573.3357(0.0419)	962.2610
10	0	10	3225.0242(0.0225)	3213.1553(0.0225)	592.8640
10	1	10	3225.0242(0.0225)	3213.1553(0.0225)	592.8640
10	1	9	3319.8164(0.0174)	3307.6648(0.0172)	689.2263
10	2	9	3319.8164(0.0174)	3307.6650(0.0172)	689.2266
10	2	8	3403.5767(0.0138)	3391.2141(0.0134)	774.3965
10	3	8	3403.5789(0.0138)	3391.2161(0.0134)	774.3997
10	3	7	3476.2998(0.0116)	3463.8262(0.0113)	848.3750
10	4	7	3476.3501(0.0127)	3463.8718(0.0109)	848.4438
10	4	6	3537.3987(0.0085)	3524.9839(0.0130)	910.5115
10	5	6	3538.1199(0.0201)	3525.6523(0.0100)	911.4470
10	5	5	3584.5039(0.0487)	3571.9082(0.0258)	957.7456
10	6	5	3589.9929(0.0608)	3577.0957(0.0635)	964.6975
10	6	4	3613.2175(0.1903)	3603.1194(0.0386)	989.2776
10	7	4	3637.1133(0.0999)	3626.2458(0.2151)	1012.7969
10	7	3	3643.8142(0.1021)	3632.6990(0.0656)	1019.7832
10	8	3	3686.1060(0.0970)	3673.7434(0.1132)	1062.2529
10	8	2	3686.9292(0.0954)	3674.5415(0.0942)	1063.1128
10	9	2	3740.3401(0.0736)	3726.1604(0.0863)	1116.6111
10	9	1	3740.3882(0.0734)	3726.2056(0.0849)	1116.6619
10	10	1	3799.7524(0.0169)	3782.7700(0.0483)	1175.4231
10	10	0	3799.7537(0.0169)	3782.7710(0.0483)	1175.4243

[a] The values in the parentheses denote the mixing ratio of the perturbing state.

fairly well. In the excited vibrational states, all the centrifugal distortion constants up to the sextic constants were treated as adjustable parameters and are determined reasonably well. The sign of the Coriolis coupling constant h'_{13} was chosen to be positive. The sign of h_{13} was then found to be negative, when the phase of the matrix element was chosen as

$$\langle v_1 = 1, J, k | iJ_c | v_3 = 1, J, k \pm 1 \rangle = \pm(1/2)\sqrt{J(J+1) - k(k \pm 1)}.$$

The assignment of $H_2{}^{37}Cl^+$ was easily made after removing the assigned lines of the

TABLE VII

Rotational and Centrifugal Distortion Constants of $H_2{}^{35}Cl^+$ (in cm^{-1})

	(000)	(100)	(001)	(010)	Equilibrium
A	11.25339	11.08123	11.02606	11.70296	11.22835
B	9.12371	8.97939	9.01413	9.31603	9.15450
C	4.94149	4.86130	4.88189	4.87263	5.04582
$\tau_{aaaa} \times 10$	-0.10717	-0.10510	-0.10534	-0.13790	
$\tau_{bbbb} \times 10^2$	-0.50809	-0.50150	-0.51308	-0.58983	
$\tau_{cccc} \times 10^3$	-0.27452	-0.28304	-0.25656	-0.27048	
$\tau_{aabb} \times 10^2$	0.49564	0.47566	0.51239	0.61662	
$\tau_{bbcc} \times 10^3$	-0.53366	-0.55339	-0.49932	-0.54327	
$\tau_{aacc} \times 10^3$	-0.61297	-0.62904	-0.56276	-0.70441	
$\tau_{abab} \times 10^2$	-0.11236	-0.10562	-0.12388	-0.13086	
I^A (amuÅ^2)	1.498004	1.521278	1.528890	1.440459	1.501345
I^B (amuÅ^2)	1.847674	1.877369	1.870134	1.809529	1.841458
I^C (amuÅ^2)	3.411447	3.467718	3.453098	3.459657	3.340910
Δ (amuÅ^2)	0.065769	0.069071	0.054074	0.209669	-0.001893
α^A		0.17216	0.22733	-0.44957	
α^B		0.14432	0.10958	-0.19232	
α^C		0.08019	0.05960	0.06886	

^{35}Cl species, because its energy level structure is very similar to that of $H_2{}^{35}Cl^+$. A least-squares fit was performed with 382 assigned lines (190 and 192 transitions to the ν_1 and ν_3 bands, respectively). The standard deviation of the fit was found to be 0.0005 cm^{-1}. The molecular constants of $H_2{}^{37}Cl^+$ obtained from the least-squares fit are listed in Table II. All the centrifugal distortion constants up to the sixth order were treated as adjustable parameters and are determined reasonably well.

We list the observed transition wavenumbers with the assignments in Tables III and IV. Also, the term values for the ground, $v_1 = 1$, and $v_3 = 1$ states calculated with the best fit molecular constants are listed in Tables V and VI.

DISCUSSIONS

Botschwina (*18*) estimated the vibrational frequency for the $2\nu_2$ band to be 2352 cm^{-1}. The effect of the Coriolis interaction between the $v_2 = 2$ and $v_3 = 1$ states can be treated as a second-order perturbation. Since the Coriolis interaction operator is expressed as $H_C^{223} = h_{223} i J_y$, the $\tilde{C}$ rotational constant for the $v_3 = 1$ state should contain the second-order contribution of the amount of $|h_{223}|^2/\Delta E(v_3 = 1 - v_2 = 2)$.

TABLE VIII

Rotational and Centrifugal Distortion Constants of $H_2{}^{37}Cl^+$ (in cm^{-1})

	(000)	(100)	(001)	(010)	Equilibrium
A	11.22012	11.04807	10.99404	11.66706	11.19572
B	9.12378	8.97997	9.01407	9.31580	9.15453
C	4.93501	4.85504	4.87542	4.86623	5.03918
$\tau_{aaaa} \times 10$	-0.10611	-0.10524	-0.10419	-0.13717	
$\tau_{bbbb} \times 10^2$	-0.51006	-0.50164	-0.51538	-0.59071	
$\tau_{cccc} \times 10^3$	-0.27424	-0.27972	-0.26484	-0.27928	
$\tau_{aabb} \times 10^2$	0.49386	0.47913	0.50297	0.60587	
$\tau_{bbcc} \times 10^3$	-0.53579	-0.53998	-0.51743	-0.55651	
$\tau_{aacc} \times 10^3$	-0.60841	-0.63225	-0.57810	-0.73385	
$\tau_{abab} \times 10^2$	-0.11131	-0.10554	-0.11545	-0.10800	
I^A (amuÅ^2)	1.502446	1.525844	1.533343	1.444891	1.505721
I^B (amuÅ^2)	1.847659	1.877248	1.870146	1.809573	1.841452
I^C (amuÅ^2)	3.415926	3.472188	3.457677	3.464208	3.345312
Δ (amuÅ^2)	0.065821	0.069097	0.054187	0.209744	-0.001861
α^A		0.17205	0.22608	-0.44694	
α^B		0.14381	0.10971	-0.19202	
α^C		0.07997	0.05959	0.06878	

If we take the Coriolis coupling parameter for H_2S obtained by Lechuga-Fossat *et al.* (*33*) as an estimate for H_2Cl^+, the contribution to the $\tilde{C}$ rotational constant is estimated to be 1×10^{-4} cm^{-1}, which is about the same magnitude of the standard error of the parameters.

From the fitted parameters, the rotational constants A, B, and C were derived after correcting the centrifugal distortion contributions (*28, 34*) with the aid of the planarity relations (*28*). In Tables VII and VIII, these constants are listed together with the derived τ constants and the inertial defects. The observed inertial defect in the $v_1 = 1$ state is larger than that in the ground state. If ω_1 is larger than ω_3 as calculated by Botschwina (*18*), Δ_{100} should be smaller than Δ_{000}. In this context, it is interesting to note that ω_1 is smaller than ω_3 in the calculation by DeFrees and McLean (*17*) while they predicted correctly that ν_1 is larger than ν_3. In H_2S, the inertial defect in the $v_1 = 1$ state is larger than that in the ground state as expected, since ω_1 is smaller than ω_3.

The inertial defect at equilibrium should contain only the electronic contribution. It is estimated to be 0.0001 amu Å^2 by using the rotational g factors obtained for H_2S

TABLE IX

Rotational and Centrifugal Distortion Constants of $H_2{}^{32}S$ (in cm^{-1})

	(000)	(100)	(001)	(010)	(020)	Equilibrium
A	10.360736	10.201121	10.142957	10.722718	11.114901	10.368442
B	9.016244	8.892537	8.937375	9.222203	9.443464	9.014553
C	4.731854	4.661994	4.677492	4.670098	4.609337	4.824843
$\tau_{aaaa} \times 10$	-0.08302	-0.08193	-0.08033	-0.10297	-0.12837	
$\tau_{bbbb} \times 10^2$	-0.49745	-0.49012	-0.50432	-0.58061	-0.67542	
$\tau_{cccc} \times 10^3$	-0.24626	-0.24113	-0.23908	-0.24544	-0.24193	
$\tau_{aabb} \times 10^2$	0.42822	0.42347	0.43116	0.52066	0.63541	
$\tau_{bbcc} \times 10^3$	-0.47605	-0.46176	-0.46355	-0.50015	-0.51498	
$\tau_{aacc} \times 10^3$	-0.55274	-0.54759	-0.52786	-0.61870	-0.69458	
$\tau_{abab} \times 10^2$	-0.09818	-0.09733	-0.10137	-0.11023	-0.13013	
I^A (amuÅ^2)	1.627069	1.652527	1.662004	1.572142	1.516669	1.625859
I^B (amuÅ^2)	1.869695	1.895705	1.886195	1.827940	1.785111	1.870046
I^C (amuÅ^2)	3.562585	3.615970	3.603989	3.609695	3.657279	3.493923
Δ (amuÅ^2)	0.065821	0.067737	0.055791	0.209614	0.355499	-0.001982
α^A		0.159615	0.217779	-0.361982	-0.392183[a]	
α^B		0.123707	0.078869	-0.205959	-0.221261[a]	
α^C		0.069860	0.054362	0.061756	0.060761[a]	

[a] The value is the differences between the values for the (010) and (020) states.

(*35, 36*). However, the derived values for both the ^{35}Cl and the ^{37}Cl species are negative and much larger than the estimated value, as shown in Tables VII and VIII. A question arises here. Is this large negative value specific to ions? To answer this question, we reexamined the inertial defect of H_2S by using the molecular constants from recent papers (*33, 37, 38*). The values are listed in Table IX. It was found that the inertial defect at the equilibrium was similarly large and negative for both H_2S and H_2Cl^+. We conclude that these larger inertial defects may arise from neglecting the higher-order vibration–rotation terms (γ, etc.) rather than an abnormal electronic contribution. Support for this conclusion may be obtained by examining the rotational constants in the $v_2 = 1$ state and in the $v_2 = 2$ state of H_2S. The γ constants are calculated to be $\gamma_{22}^{A} = 0.0151$, $\gamma_{22}^{B} = 0.0765$, and $\gamma_{22}^{C} = 0.0005$ cm^{-1}, which are of the right order of magnitude to explain the inertial defect.

The equilibrium molecular structure was therefore determined by taking an average of the three structures obtained from the three possible combinations of the equilibrium rotational constants to be $r_e = 1.30412(17)$ Å and θ_e(H–Cl–H) = 94.243(27)° for $H_2{}^{35}Cl^+$ and $r_e = 1.30411(17)$ Å and θ_e(H–Cl–H) = 94.244(26)° for $H_2{}^{37}Cl^+$. The molecular structures obtained for the two isotopic species agree very well. They also agree very well with the ab initio values, $r_e = 1.303$ Å and θ_e(H–Cl–H) = 94.244°, obtained by Botschwina (*18*). The τ constants derived for H_2Cl^+ may be compared with those for H_2S (*39, 40*).

The structure of H_2Cl^+ is compared to that of the isoelectronic molecule H_2S r_e(H–S) = 1.33588(18) Å and θ_e(H–S–H) = 92.258(27)°.[3] The bondlength in H_2Cl^+ is shorter by 0.03 Å, and the angle is larger by about 2°. This seems to be brought about by the additional positive charge. A similar shortening in the bondlength and a slight widening in the bond angle were observed for SH_3^+ compared with PH_3 (*41*).

The ν_1 vibrational frequency is higher than the ν_3 frequency in H_2Cl^+, in contrast to H_2S. The interchange in the frequencies was also observed for a pair of isoelectronic molecules, H_2O (*42*) with H_2F^+ (*43*). This interchange has been correctly predicted by a recent ab initio calculation by Botschwina (*18*). The intensity of the ν_3 band was found experimentally to be stronger than that of the ν_1 band by a factor of about 2.

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[3] These structural parameters were calculated from the equilibrium rotational constants listed in Table IX. Reference (*39*) gave $r_e = 1.3356$ Å and $\theta_e = 92.12°$.

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