Molecular Parameters of Chromium Hydride in its $X\,^6\Sigma^+$ State Determined by Far-Infrared Laser Magnetic Resonance Spectroscopy

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The far-infrared laser magnetic resonance spectrum of the CrH radical in the $v = 0$ level of its $X\,^6\Sigma^+$ state has been studied in detail. Signals associated with the five lowest rotational transitions have been detected. Nearly 500 resonances for ^{52}CrH have been assigned and used to determine molecular parameters which describe the rotational energy, the fine and proton hyperfine splittings, and the Zeeman effect. These parameters are well determined and their implications for the structure of CrH are discussed. A fourth-order correction to the spin–spin coupling has been identified for the first time. Precise zero-field rotational transition frequencies have been calculated which may allow the detection of the CrH radical in the interstellar medium. © 1991 Academic Press, Inc.

INTRODUCTION

The CrH molecule is a member of the first row transition metal hydrides. Both the physical and chemical properties of these compounds are complicated by the profusion of low-lying electronic states. The accurate description of those states is a particularly challenging problem for ab initio calculations (*1, 2*). The need for high quality spectroscopic data on these compounds to guide the calculations is therefore paramount.

Chromium hydride was first identified in 1937 by Gaydon and Pearse (*3*) through the observation, in emission from an arc source, of a complex band system in the ultraviolet at 368 nm. In later work using a high temperature furnace, Kleman and Liljeqvist (*4*) were able to detect two other band systems, one in the ultraviolet and the other in the near infrared. They performed a vibrational analysis of the infrared system. Kleman and Uhler (*5*) analyzed the rotational structure of the same system and showed that it arises from a $^6\Sigma$–$^6\Sigma$ transition. This work was supported and extended by O'Connor (*6, 7*) who photographed the infrared system in emission from a high current discharge tube. The ultraviolet transitions in CrH have been used to

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detect the molecule in stars (8) and sunspots (9). Smith (10) has also observed the ultraviolet systems of CrH in absorption in shock tube experiments. More recently, Van Zee *et al.* ($11, 12$) have studied CrH trapped in an argon matrix at 4 K by ESR. In this work, they confirmed that the lower $^6\Sigma$ state of the transitions analyzed by Kleman and co-workers ($4, 5$) is the ground state of the molecule and they also measured the fine structure and proton hyperfine splittings. Stevens Miller *et al.* (13) have recorded the photoelectron spectrum of the negative ion CrH$^-$ and identified transitions to the two lowest $^6\Sigma$ states of the neutral molecule.

In this paper we report the first observation of the rotational spectrum of CrH in its ground $^6\Sigma^+$ state, by the technique of far-infrared laser magnetic resonance (FIR LMR). As such, it forms part of a systematic study of the first row transition metal hydrides ($14, 15$) by the LMR technique. Transitions have been detected and analyzed for the first five rotational transitions. These assignments have been fitted to determine a much more reliable set of parameters for CrH in the $v = 0$ level of the $X^6\Sigma^+$ state. Although we have observed transitions for several naturally occurring isotopomers of CrH, we have chosen to analyze only the most abundant form, ^{52}CrH, in detail. After our work was completed, vibration–rotation transitions in CrH were detected by Lipus *et al.* (16), by the infrared LMR technique.

EXPERIMENTAL DETAILS

The pure rotational transitions of CrH were detected with the far-infrared laser magnetic resonance spectrometer at NIST, Boulder, which is described in detail elsewhere (17). The CrH was formed by flowing helium at 10.7 Pa (80 mT) over a few grams of Cr(CO)$_6$ crystals, and reacting the carbonyl with atomic hydrogen generated by a discharge in 200 Pa helium and 4 Pa wet hydrogen. Under these conditions the typical S/N ratio was 500:1 with a 1-sec time constant. Larger signals could be obtained with higher helium and hydrogen pressures, but the resultant broadening caused blending of the hydrogen hyperfine components and overlapping of lines. The magnetic field strength was measured by a rotating coil fluxmeter which was calibrated periodically against a proton NMR Gaussmeter. The uncertainty in the measurements is approximately 0.1 mT. This is due to the combined uncertainty of the rotating coil calibration and measurement, together with the uncertainty in determining the line position on the recordings.

There were 471 resonances from the lowest five rotational transitions of ^{52}CrH which were measured and fit (^{52}CrH has a natural abundance of 83.8%). In addition, resonances were detected from the $N = 6 \leftarrow 5$ transition on the 118.8-μm MeOH laser line and from the less abundant chromium isotopes. These were not measured precisely and so have not been included in the detailed analysis. Table I summarizes the observations. Figure 1 is a survey scan from 0 to 1 T for the 1100.8067 GHz laser line, in π polarization. Even under low resolution, the doubling due to the proton hyperfine splitting is observable on many of the resonances. Figure 2 is a higher-resolution scan of the 50–70 mT region of the spectrum in Fig. 1. The proton hyperfine structure of the lines is very clearly resolved. A close examination of the baseline just below the uppermost pair of lines in Fig. 2 shows four weak lines. These are probably due to the ^{53}CrH isotopomer. The ^{53}Cr (9.6% abundance) has a nuclear spin of 3/2

TABLE I

Summary of the Observations of Rotational Transitions in ^{52}CrH in Its $X^6\Sigma^+$ State, Studied by Far-Infrared Laser Magnetic Resonance

N'←N"	Laser Frequency (GHz)	Laser Wavelength (μm)	Laser Gas
1←0	403.7213	742.5728	HCOOH
	428.6285	699.4226	CH$_3$OH
2←1	729.9328	410.7124	CD$_3$OD
	764.6426	392.0687	CH$_3$OH
	765.8290	391.4614	^{13}CH$_2$F$_2$
3←2	1100.8067	272.3389	CH$_2$F$_2$
	1101.1594	272.2516	CH$_2$DOH
	1116.2455	268.5722	^{13}CH$_3$OH
4←3	1472.1993	203.6358	^{13}CH$_3$OH
5←4	1838.8393	163.0335	CH$_3$OH

which produces a four-fold hyperfine splitting of a similar magnitude to the proton splitting (*11, 12*).

ASSIGNMENT OF THE SPECTRA

The detailed measurements of the resonances associated with ^{52}CrH in the $v = 0$ level of the $X^6\Sigma^+$ state are given in Table II, along with the quantum number assignments.

The analysis was rather complicated for two reasons. First, the molecule is in a state of high multiplicity conforming to Hund's case (b) coupling scheme. Each rotational level with $N > 2$ splits into six closely spaced spin components. Figure 3 is a diagram which shows the positions of these components for the first four energy levels. The fine structure splitting has been exaggerated by a factor of 5 for clarity. Second, the Zeeman effects displayed by the molecule are highly nonlinear because the electron

FIG. 1. The LMR spectrum of chromium hydride (CrH $X^6\Sigma^+$) associated with the $N = 3 \leftarrow 2$ transition, recorded with the 1100.8067 GHz laser line of CH$_2$F$_2$ (272.3 μm) in π polarization. The scan is from 0–1 T with a time constant of 0.1 sec.
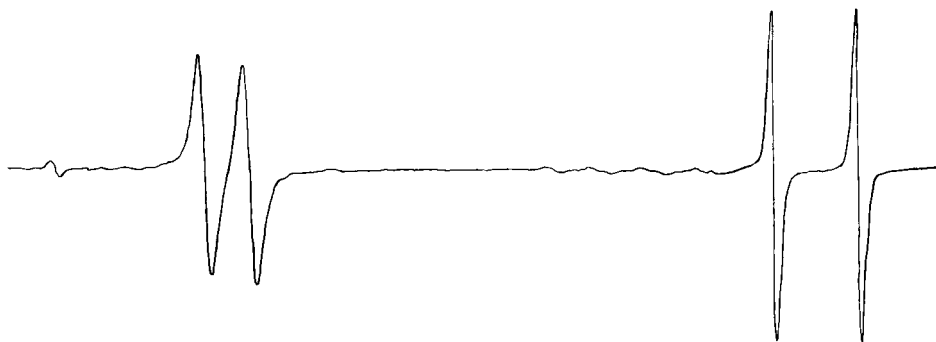
FIG. 2. The LMR spectrum of chromium hydride associated with the $N = 3 \leftarrow 2$ transition, recorded with the 1100.8067 GHz laser line of CH_2F_2 (272.3 μm) in π polarization. The scan is from 50–70 mT with a time constant of 0.3 sec.

spin is easily decoupled from the molecular framework by the magnetic field, a phenomenon which arises whenever the fine structure splittings are small (that is, comparable with the Zeeman energies). Above a certain flux density, at which the electron spin becomes fully decoupled, it is no longer possible to detect a signal by magnetic resonance techniques. The transitions are either tunable but too weak to be detected

FIG. 3. The lower rotational energy levels of CrH in the $X^6\Sigma^+$ state. The spin–rotation splittings are exaggerated by a factor of 5 for clarity.

or are intense but no longer tunable (18). For this reason, almost no transitions were observed above 1 T in the present work. The electron spin decoupling effects can be seen in Fig. 4, which shows the behavior of the individual M_F levels of the $N = 2$ rotational level of $^6\Sigma$ CrH as a function of applied magnetic field. The decoupling is marked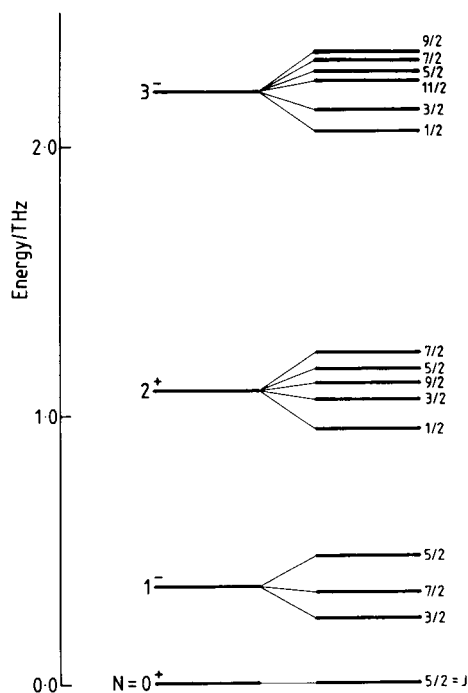 by a curvature in the levels starting at about 300 mT. In the high field limit, they behave as one of six possible M_S states ($M_S = \pm\frac{5}{2}, \pm\frac{3}{2}, \pm\frac{1}{2}$). The proton nuclear spin is similarly decoupled but at very much lower flux densities. The diagram also shows an avoided crossing between two $M_F = 0$ levels at about 470 mT. The avoided crossing is weak because it arises from nuclear spin hyperfine effects.

The assignments of the individual spectra were based on the experimental Zeeman patterns. These comprise the observed flux densities, the relative intensities, the line-widths (in mT), and the sign of the tuning rate, the last being determined from the shift in the resonance on altering the FIR laser frequency. These patterns were matched with the predictions of a computer program, which calculated the frequencies of individual M_J transitions as a function of applied magnetic field. We have used this procedure with success on many problems in the past, most recently for the FIR LMR spectrum of CH in its $^4\Sigma^-$ state (19). A typical output from the computer program is reproduced in Fig. 5 which shows the variation of individual $\Delta M = 0$ transitions
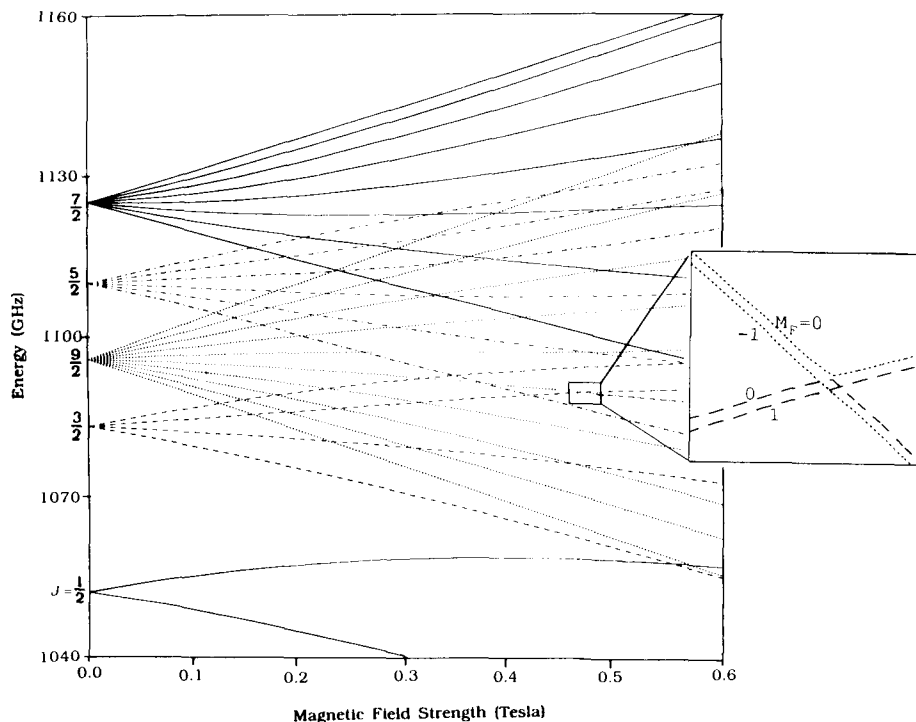

FIG. 4. The Zeeman effect for the $N = 2$ energy levels of CrH in the $X\,^6\Sigma^+$ state. The enlarged portion shows one of the many observed avoided crossings, and covers the range 460–480 mT and 1089.0–1089.5 GHz.
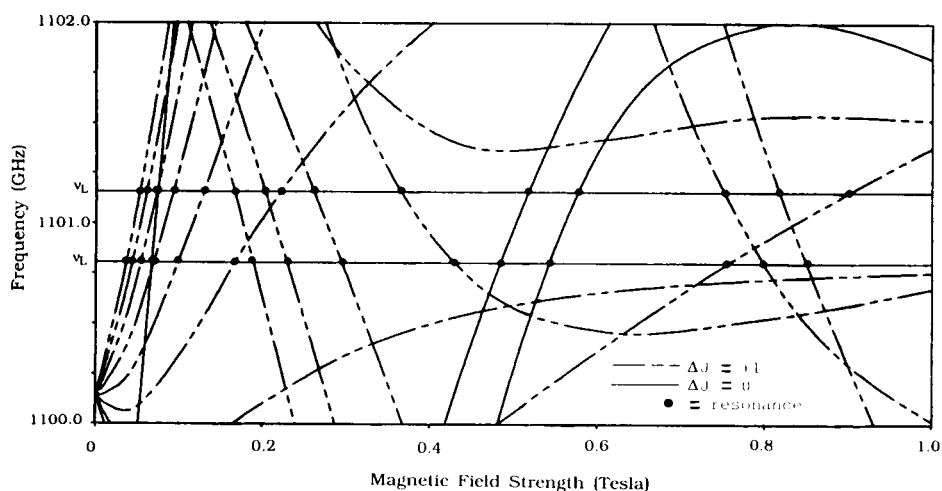
FIG. 5. The transition frequency versus magnetic field strength for the $N = 3 \leftarrow 2$ transition in CrH. The two solid horizontal lines indicate the laser frequencies, at 1100.8067 and 1101.1594 GHz. The circles indicate the resonances. The spectra observed with the lower-frequency laser line are shown in Figs. 1 and 2. Transition in π polarization.

for the $N = 3 \leftarrow 2$ transition. The hyperfine structure is not shown. The complicated, nonlinear behavior of these frequencies is immediately apparent. Horizontal lines corresponding to the frequencies of the 272.2- and 272.3-μm laser lines are also marked on the diagram. The spectra shown in Figs. 1 and 2 correspond to the lower of these two frequencies. Indeed, the assignment of these two spectra, recorded with laser lines separated by only 352.7 MHz, was the key which unlocked the analysis of the FIR spectrum. Corresponding resonances could be identified in the two spectra which enabled accurate measurements of the tuning rate to be made.

The initial predictions of the LMR spectra were made using the constants determined by O'Connor (6) and computing the eigenvalues of an effective Hamiltonian which included the electron spin Zeeman effect but ignored proton hyperfine structure. Initial assignments were made on the basis of these predictions. These in turn were fitted by a least-squares procedure to give improved values for the molecular parameters. Thus began an iterative process in which additional resonances were assigned followed by further refinement of the parameters and inclusion of higher-order terms. Further observations were made which were also added to the data set. All resonances were then remeasured under high resolution so that the proton hyperfine splitting could be resolved and fitted. These high-resolution scans covered 20 mT or less, as shown in Fig. 2.

The details of the complete assignments are given in Table II together with the experimental measurements. Because even in quite modest fields J ceases to be a good quantum number, we labeled the fine structure component by a running number which increases with energy (1 is the lowest level of a given M_J value, 2 is the next lowest, and so on) for a given value of N.

DETERMINATION OF MOLECULAR PARAMETERS

When the analysis was complete, the data were modeled by an effective Hamiltonian in order to determine values for the molecular parameters. The effective Hamiltonian employed for a molecule in a $^6\Sigma$ state is fairly standard. It has been described in detail in our paper on the $^4\Sigma$ state of CH ([19]). In order to fit the data within experimental error, we had to add two extra terms to this Hamiltonian. First, we included the fourth-order spin–orbit coupling term

$$\mathbf{H}_{so} = \tfrac{1}{12}\theta[35\,S_z^4 - 30\mathbf{S}^2 S_z^2 + 25S_z^2 - 6\mathbf{S}^2 + 3\mathbf{S}^4]$$ (1)

as described by Brown and Milton ([20]). The contribution which this term makes to the energy vanishes for states of quartet multiplicity or lower. Its effect has been identified so far in very few instances, for example, in the $X\,^5\Pi$ state of CrO ([21]). The calculations which we have carried out on CrH have been performed in a Hund's case (b) basis set. The matrix elements of the operator in Eq. (1) in this basis set are given by

$$\left\langle \Lambda'N'SJ'M_J' \,|\, \mathbf{H}_{so}^{(4)} \,|\, \Lambda NSJM_J \right\rangle$$

$$= \delta_{J'J}\delta_{M_J'M_J}\frac{\theta}{24}(-1)^{N+S+J}\begin{Bmatrix} J & S & N' \\ 4 & N & S \end{Bmatrix}(-1)^{N'-\Lambda'}\begin{pmatrix} N' & 4 & N \\ -\Lambda' & 0 & \Lambda \end{pmatrix}$$

$$\times [(2N'+1)(2N+1)]^{1/2}[(2S-3)(2S-2)\cdots(2S+4)(2S+5)]^{1/2}. \quad (2)$$

In Eq. 2, we have used standard spherical tensor notation ([22]). The second term which we have added to the effective Hamiltonian of Ref. ([19]) is the anisotropic correction to the electron spin Zeeman term ([23]),

$$\mathbf{H}_Z = g_l\mu_B(B_xS_x + B_yS_y),$$ (3)

where the x and y components of $\mathbf{B}$ and $\mathbf{S}$ are measured in the molecule-fixed axis system. Matrix elements of this operator in a Hund's case (b) basis set have been given elsewhere ([24]).

Using this Hamiltonian, we determined the molecular parameters for ^{52}CrH in the $v = 0$ level of the $X\,^6\Sigma^+$ state by a least-squares procedure. The basis set was truncated in the calculations at $\Delta N = \pm 4$ without loss in accuracy. Each experimental measurement was given the same weight (unity) in the fit. The residuals obtained are given in Table II, and the parameter values determined, together with their standard deviations, are given in Tables IIIa (in GHz) and IIIb (in cm^{-1}). The standard deviation of the fit, for a point of unit weight, is 1.8 MHz, which is close to the limit imposed by experimental error. Twelve parameter values are determined in the fit, including the fourth-order spin–orbit term θ and two proton hyperfine parameters b_F and c. These parameters are well determined by the data as can be judged by the relatively small values of the correlation coefficients κ_i which are also given in Table III. The sextic centrifugal distortion constant H had a small effect (~ 8 MHz) on the highest N transition included in the fit but was not well determined by the data. It was therefore constrained to the value computed from the formula ([25])

$$\mathbf{H}_0 \approx \mathbf{H}_e = \frac{2}{3}D_e\left\{12\left(\frac{B_e}{\omega_e}\right)^2 - \frac{\alpha_e}{\omega_e}\right\}.$$ (4)

TABLE II

Rotational Transitions in ^{52}CrH Measured by Far-Infrared Laser Magnetic Resonance

S#[a]	M_J	M_I''	Field (T)	o-c (MHz)	$\partial v/\partial B_0$ (MHz/mT)	S#	M_J	M_I''	Field	o-c	$\partial v/\partial B_0$
N = 1←0		**v = 403.7213 GHz**				4←2	$1\frac{1}{2}\leftarrow 2\frac{1}{2}$	$-\frac{1}{2}$	0.00452	-2.2	-38
3←1	$-1\frac{1}{2}\leftarrow -1\frac{1}{2}$	$-\frac{1}{2}$	0.60387	1.4	18	4←2	$1\frac{1}{2}\leftarrow 2\frac{1}{2}$	$\frac{1}{2}$	0.00473	-2.9	-36
3←1	$-1\frac{1}{2}\leftarrow -1\frac{1}{2}$	$\frac{1}{2}$	0.60582	1.7	18	5←3	$\frac{1}{2}\leftarrow 1\frac{1}{2}$	$-\frac{1}{2}$	0.00588	-1.8	-29
2←1	$-2\frac{1}{2}\leftarrow -2\frac{1}{2}$	$-\frac{1}{2}$	0.62426	1.3	15	5←3	$\frac{1}{2}\leftarrow 1\frac{1}{2}$	$\frac{1}{2}$	0.00609	-3.8	-27
2←1	$-2\frac{1}{2}\leftarrow -2\frac{1}{2}$	$\frac{1}{2}$	0.62701	0.7	15	5←3	$-\frac{1}{2}\leftarrow \frac{1}{2}$	$-\frac{1}{2}$	0.00834	-1.8	-20
3←1	$-1\frac{1}{2}\leftarrow -2\frac{1}{2}$	$-\frac{1}{2}$	0.20179	2.4	38	5←3	$-\frac{1}{2}\leftarrow \frac{1}{2}$	$\frac{1}{2}$	0.00876	-2.2	-19
3←1	$-1\frac{1}{2}\leftarrow -2\frac{1}{2}$	$\frac{1}{2}$	0.20352	1.9	38	4←3	$-1\frac{1}{2}\leftarrow -\frac{1}{2}$	$-\frac{1}{2}$	0.01454	-1.1	-11
3←1	$-\frac{1}{2}\leftarrow -1\frac{1}{2}$	$-\frac{1}{2}$	0.21537	-1.2	37	4←3	$-1\frac{1}{2}\leftarrow -\frac{1}{2}$	$\frac{1}{2}$	0.01544	-1.4	-11
3←1	$-\frac{1}{2}\leftarrow -1\frac{1}{2}$	$\frac{1}{2}$	0.21668	2.4	37	2←2	$3\frac{1}{2}\leftarrow 2\frac{1}{2}$	$\frac{1}{2}$	0.03825	-1.5	-4
3←1	$\frac{1}{2}\leftarrow -\frac{1}{2}$	$-\frac{1}{2}$	0.23558	4.0	34	2←2	$3\frac{1}{2}\leftarrow 2\frac{1}{2}$	$-\frac{1}{2}$	0.04076	-1.4	-4
3←1	$\frac{1}{2}\leftarrow -\frac{1}{2}$	$\frac{1}{2}$	0.23674	0.9	34	1←1	$2\frac{1}{2}\leftarrow 3\frac{1}{2}$	$-\frac{1}{2}$	0.15215	0.3	-35
3←1	$1\frac{1}{2}\leftarrow \frac{1}{2}$	b	0.26891	0.5	30	1←1	$2\frac{1}{2}\leftarrow 3\frac{1}{2}$	$\frac{1}{2}$	0.15341	1.2	-35
2←1	$2\frac{1}{2}\leftarrow 1\frac{1}{2}$	b	0.33373	1.8	23	2←1	$1\frac{1}{2}\leftarrow 2\frac{1}{2}$	$-\frac{1}{2}$	0.17526	0.7	-31
						2←1	$1\frac{1}{2}\leftarrow 2\frac{1}{2}$	$\frac{1}{2}$	0.17652	0.8	-31
N = 1←0		**v = 428.6285 GHz**				3←2	$\frac{1}{2}\leftarrow 1\frac{1}{2}$	$-\frac{1}{2}$	0.20637	0.0	-27
3←1	$-1\frac{1}{2}\leftarrow -2\frac{1}{2}$	$-\frac{1}{2}$	0.77442	3.8	48	3←2	$\frac{1}{2}\leftarrow 1\frac{1}{2}$	$\frac{1}{2}$	0.20768	0.7	-27
3←1	$-1\frac{1}{2}\leftarrow -2\frac{1}{2}$	$\frac{1}{2}$	0.77594	2.4	48	3←2	$-\frac{1}{2}\leftarrow \frac{1}{2}$	$-\frac{1}{2}$	0.25079	0.1	-23
3←1	$-\frac{1}{2}\leftarrow -1\frac{1}{2}$	$-\frac{1}{2}$	0.79126	5.2	48	3←2	$-\frac{1}{2}\leftarrow \frac{1}{2}$	$\frac{1}{2}$	0.25211	0.3	-23
3←1	$-\frac{1}{2}\leftarrow -1\frac{1}{2}$	$\frac{1}{2}$	0.79263	3.6	48	1←1	$\frac{1}{2}\leftarrow -\frac{1}{2}$	$-\frac{1}{2}$	0.29111	-5.0	25
3←1	$\frac{1}{2}\leftarrow -\frac{1}{2}$	$-\frac{1}{2}$	0.84123	0.3	46	1←1	$\frac{1}{2}\leftarrow -\frac{1}{2}$	$\frac{1}{2}$	0.29227	-4.7	25
3←1	$\frac{1}{2}\leftarrow -\frac{1}{2}$	$\frac{1}{2}$	0.84240	0.8	46	2←2	$-1\frac{1}{2}\leftarrow -\frac{1}{2}$	$-\frac{1}{2}$	0.31954	0.6	-19
3←1	$1\frac{1}{2}\leftarrow \frac{1}{2}$	$-\frac{1}{2}$	0.94754	-0.7	42	2←2	$-1\frac{1}{2}\leftarrow -\frac{1}{2}$	$\frac{1}{2}$	0.32090	0.9	-19
3←1	$1\frac{1}{2}\leftarrow \frac{1}{2}$	$\frac{1}{2}$	0.94850	0.1	42	4←3	$-1\frac{1}{2}\leftarrow -\frac{1}{2}$	b	0.33022	-1.2	5
2←1	$2\frac{1}{2}\leftarrow 1\frac{1}{2}$	b	1.34049	-1.2	26	2←1	$\frac{1}{2}\leftarrow 1\frac{1}{2}$	$-\frac{1}{2}$	0.37996	0.5	-34
						2←1	$\frac{1}{2}\leftarrow 1\frac{1}{2}$	$\frac{1}{2}$	0.38117	0.3	-34
N = 2←1		**v = 729.9328 GHz**				1←2	$-2\frac{1}{2}\leftarrow -1\frac{1}{2}$	$-\frac{1}{2}$	0.44167	0.5	-15
3←2	$2\frac{1}{2}\leftarrow 2\frac{1}{2}$	b	0.00838	-1.4	-20	1←2	$-2\frac{1}{2}\leftarrow -1\frac{1}{2}$	$\frac{1}{2}$	0.44304	1.0	-15
4←3	$1\frac{1}{2}\leftarrow 1\frac{1}{2}$	b	0.01471	-1.5	-11	3←2	$-1\frac{1}{2}\leftarrow -2\frac{1}{2}$	$-\frac{1}{2}$	0.46420	0.4	30
4←3	$1\frac{1}{2}\leftarrow 1\frac{1}{2}$	$-\frac{1}{2}$	0.24905	-0.2	8	3←2	$-1\frac{1}{2}\leftarrow -2\frac{1}{2}$	$\frac{1}{2}$	0.46515	0.0	30
4←3	$1\frac{1}{2}\leftarrow 1\frac{1}{2}$	$\frac{1}{2}$	0.25093	0.0	8	2←1	$-\frac{1}{2}\leftarrow \frac{1}{2}$	$-\frac{1}{2}$	0.49525	-0.3	-33
1←1	$3\frac{1}{2}\leftarrow 3\frac{1}{2}$	$-\frac{1}{2}$	0.28848	-0.7	-19	2←1	$-\frac{1}{2}\leftarrow \frac{1}{2}$	$\frac{1}{2}$	0.49615	-0.4	-33
1←1	$3\frac{1}{2}\leftarrow 3\frac{1}{2}$	$\frac{1}{2}$	0.28954	-0.7	-19	2←2	$-\frac{1}{2}\leftarrow -1\frac{1}{2}$	$-\frac{1}{2}$	0.55571	1.0	13
1←1	$2\frac{1}{2}\leftarrow 2\frac{1}{2}$	$-\frac{1}{2}$	0.36096	-1.8	-17	2←2	$-\frac{1}{2}\leftarrow -1\frac{1}{2}$	$\frac{1}{2}$	0.55740	0.4	13
1←1	$2\frac{1}{2}\leftarrow 2\frac{1}{2}$	$\frac{1}{2}$	0.36201	-1.7	-17	4←3	$-\frac{1}{2}\leftarrow -1\frac{1}{2}$	$-\frac{1}{2}$	0.57797	1.1	28
2←2	$1\frac{1}{2}\leftarrow 1\frac{1}{2}$	$-\frac{1}{2}$	0.46717	-0.2	-15	4←3	$-\frac{1}{2}\leftarrow -1\frac{1}{2}$	$\frac{1}{2}$	0.57909	1.5	28
2←2	$1\frac{1}{2}\leftarrow 1\frac{1}{2}$	$\frac{1}{2}$	0.46821	-0.6	-15	1←1	$-1\frac{1}{2}\leftarrow -\frac{1}{2}$	$-\frac{1}{2}$	0.61065	2.5	-29
1←1	$1\frac{1}{2}\leftarrow 1\frac{1}{2}$	$-\frac{1}{2}$	0.46968	0.8	-40	1←1	$-1\frac{1}{2}\leftarrow -\frac{1}{2}$	$\frac{1}{2}$	0.61123	2.2	-29
1←1	$1\frac{1}{2}\leftarrow 1\frac{1}{2}$	$\frac{1}{2}$	0.47159	1.0	-40	4←3	$\frac{1}{2}\leftarrow -\frac{1}{2}$	$-\frac{1}{2}$	0.71598	-1.3	29
2←2	$1\frac{1}{2}\leftarrow \frac{1}{2}$	$-\frac{1}{2}\leftarrow \frac{1}{2}$	0.88719	0.6	-13	4←3	$\frac{1}{2}\leftarrow -\frac{1}{2}$	$\frac{1}{2}$	0.71736	-1.8	29
2←1	$1\frac{1}{2}\leftarrow 1\frac{1}{2}$	$\frac{1}{2}$	0.88807	1.0	-13	5←3	$-\frac{1}{2}\leftarrow \frac{1}{2}$	$-\frac{1}{2}$	0.87051	0.0	3

[a] The label for the spin level, ordered by relative energy for a given N and M_J value.

[b] The proton hyperfine structure was not resolved for this resonance.

DISCUSSION

The parameters determined for ^{52}CrH in its $X^6\Sigma^+$ state are given in Table III, together with previous determinations of their values, where available (6, 11). Generally

TABLE II—Continued

S#[a]	M_J	M_I''	Field	o-c	$\partial v/\partial B_0$
5←3	$-\frac{1}{2}\leftarrow\frac{1}{2}$	$\frac{1}{2}$	0.87263	-0.2	3
1←2	$2\frac{1}{2}\leftarrow1\frac{1}{2}$	$-\frac{1}{2}$	1.02866	0.2	-28
1←2	$2\frac{1}{2}\leftarrow1\frac{1}{2}$	$\frac{1}{2}$	1.02960	-1.1	-28
1←1	$-3\frac{1}{2}\leftarrow-2\frac{1}{2}$	$-\frac{1}{2}$	1.08892	-0.1	-3
1←1	$-3\frac{1}{2}\leftarrow-2\frac{1}{2}$	$\frac{1}{2}$	1.09314	0.0	-3
3←1	$-\frac{1}{2}\leftarrow\frac{1}{2}$	b	1.16682	2.0	-12

N = 2←1   v = 764.6426 GHz

S#	M_J	M_I''	Field	o-c	$\partial v/\partial B_0$
2←1	$-3\frac{1}{2}\leftarrow-3\frac{1}{2}$	$-\frac{1}{2}$	0.04493	-0.2	13
2←1	$-3\frac{1}{2}\leftarrow-3\frac{1}{2}$	$\frac{1}{2}$	0.04817	0.2	13
3←1	$-2\frac{1}{2}\leftarrow-2\frac{1}{2}$	$-\frac{1}{2}$	0.05098	-0.6	14
3←1	$-2\frac{1}{2}\leftarrow-2\frac{1}{2}$	$\frac{1}{2}$	0.05342	-1.2	14
4←2	$-1\frac{1}{2}\leftarrow-1\frac{1}{2}$	$-\frac{1}{2}$	0.05937	-0.9	14
4←2	$-1\frac{1}{2}\leftarrow-1\frac{1}{2}$	$\frac{1}{2}$	0.06107	-1.0	14
4←2	$1\frac{1}{2}\leftarrow1\frac{1}{2}$	b	0.13247	-0.5	13
3←1	$2\frac{1}{2}\leftarrow2\frac{1}{2}$	$\frac{1}{2}$	0.25241	0.7	11
3←1	$2\frac{1}{2}\leftarrow2\frac{1}{2}$	$-\frac{1}{2}$	0.25372	-0.3	11
3←1	$1\frac{1}{2}\leftarrow1\frac{1}{2}$	$-\frac{1}{2}$	0.33685	2.8	-30
3←1	$1\frac{1}{2}\leftarrow1\frac{1}{2}$	$\frac{1}{2}$	0.33864	3.2	-30
3←1	$-2\frac{1}{2}\leftarrow-3\frac{1}{2}$	$-\frac{1}{2}$	0.01891	-1.9	30
4←1	$-1\frac{1}{2}\leftarrow-2\frac{1}{2}$	$\frac{1}{2}$	0.02279	-0.8	28
5←2	$-\frac{1}{2}\leftarrow-1\frac{1}{2}$	$-\frac{1}{2}$	0.02410	-0.8	26
5←2	$-\frac{1}{2}\leftarrow-1\frac{1}{2}$	$\frac{1}{2}$	0.02526	1.2	26
5←2	$\frac{1}{2}\leftarrow-\frac{1}{2}$	$-\frac{1}{2}$	0.02804	-0.7	23
5←2	$\frac{1}{2}\leftarrow-\frac{1}{2}$	$\frac{1}{2}$	0.02893	-0.9	23
4←2	$1\frac{1}{2}\leftarrow\frac{1}{2}$	b	0.03419	-1.6	20
3←2	$2\frac{1}{2}\leftarrow1\frac{1}{2}$	b	0.04413	-1.0	16
2←1	$3\frac{1}{2}\leftarrow2\frac{1}{2}$	$\frac{1}{2}$	0.06977	-0.6	9
2←1	$3\frac{1}{2}\leftarrow2\frac{1}{2}$	$-\frac{1}{2}$	0.07145	-0.4	9
4←1	$\frac{1}{2}\leftarrow1\frac{1}{2}$	$-\frac{1}{2}$	0.21939	2.9	-50
4←1	$\frac{1}{2}\leftarrow1\frac{1}{2}$	$\frac{1}{2}$	0.22077	1.8	-50
4←2	$-1\frac{1}{2}\leftarrow-\frac{1}{2}$	$-\frac{1}{2}$	0.26038	0.1	15
4←2	$-1\frac{1}{2}\leftarrow-\frac{1}{2}$	$\frac{1}{2}$	0.26149	0.1	15
5←2	$-\frac{1}{2}\leftarrow\frac{1}{2}$	$-\frac{1}{2}$	0.27447	0.2	17
5←2	$-\frac{1}{2}\leftarrow\frac{1}{2}$	$\frac{1}{2}$	0.27510	0.0	17
3←2	$-2\frac{1}{2}\leftarrow-1\frac{1}{2}$	$-\frac{1}{2}$	0.30662	0.0	12
3←2	$-2\frac{1}{2}\leftarrow-1\frac{1}{2}$	$\frac{1}{2}$	0.30837	0.3	12
5←2	$\frac{1}{2}\leftarrow1\frac{1}{2}$	b	0.33975	-0.1	17
2←1	$-\frac{1}{2}\leftarrow-1\frac{1}{2}$	$-\frac{1}{2}$	0.41932	5.1	43
2←1	$-\frac{1}{2}\leftarrow-1\frac{1}{2}$	$\frac{1}{2}$	0.42115	3.3	43
4←1	$-\frac{1}{2}\leftarrow\frac{1}{2}$	b	0.42914	1.7	-15
3←1	$-\frac{1}{2}\leftarrow-\frac{1}{2}$	$\frac{1}{2}\leftarrow-\frac{1}{2}$	0.49347	1.1	38

S#	M_J	M_I''	Field	o-c	$\partial v/\partial B_0$
2←1	$\frac{1}{2}\leftarrow-\frac{1}{2}$	$\frac{1}{2}$	0.49520	2.4	38
4←1	$1\frac{1}{2}\leftarrow2\frac{1}{2}$	$\frac{1}{2}$	0.54049	2.5	15
4←1	$1\frac{1}{2}\leftarrow2\frac{1}{2}$	$-\frac{1}{2}$	0.54118	1.1	15
2←2	$2\frac{1}{2}\leftarrow\frac{1}{2}$	$-\frac{1}{2}\leftarrow\frac{1}{2}$	0.62652	1.6	-10
2←1	$2\frac{1}{2}\leftarrow1\frac{1}{2}$	$\frac{1}{2}$	0.63012	1.6	-10
2←1	$2\frac{1}{2}\leftarrow1\frac{1}{2}$	$\frac{1}{2}$	0.86156	1.9	10
2←2	$2\frac{1}{2}\leftarrow\frac{1}{2}$	$-\frac{1}{2}\leftarrow\frac{1}{2}$	0.86246	2.2	10

N = 2←1   v = 765.8290 GHz

S#	M_J	M_I''	Field	o-c	$\partial v/\partial B_0$
3←1	$-2\frac{1}{2}\leftarrow-2\frac{1}{2}$	$-\frac{1}{2}$	0.12188	-3.6	20
3←1	$-2\frac{1}{2}\leftarrow-2\frac{1}{2}$	$\frac{1}{2}$	0.12388	-3.1	20
4←2	$-1\frac{1}{2}\leftarrow-1\frac{1}{2}$	$-\frac{1}{2}$	0.12388	-4.6	22
4←2	$-1\frac{1}{2}\leftarrow-1\frac{1}{2}$	$\frac{1}{2}$	0.12530	-3.0	22
4←2	$1\frac{1}{2}\leftarrow1\frac{1}{2}$	b	0.20171	-2.4	21
3←1	$1\frac{1}{2}\leftarrow1\frac{1}{2}$	$-\frac{1}{2}$	0.29806	-2.5	-32
3←1	$1\frac{1}{2}\leftarrow1\frac{1}{2}$	$\frac{1}{2}$	0.29985	-1.9	-32
3←1	$2\frac{1}{2}\leftarrow2\frac{1}{2}$	$\frac{1}{2}$	0.34222	-3.0	15
3←1	$2\frac{1}{2}\leftarrow2\frac{1}{2}$	$-\frac{1}{2}$	0.34296	-3.2	15
3←1	$-2\frac{1}{2}\leftarrow-3\frac{1}{2}$	$-\frac{1}{2}$	0.05597	-2.9	34
3←1	$-2\frac{1}{2}\leftarrow-3\frac{1}{2}$	$\frac{1}{2}$	0.05794	-4.4	34
4←1	$-1\frac{1}{2}\leftarrow-2\frac{1}{2}$	$-\frac{1}{2}$	0.05934	-4.0	34
4←1	$-1\frac{1}{2}\leftarrow-2\frac{1}{2}$	$\frac{1}{2}$	0.06092	-3.1	34
5←2	$-\frac{1}{2}\leftarrow-1\frac{1}{2}$	$-\frac{1}{2}$	0.06424	-2.6	33
5←2	$-\frac{1}{2}\leftarrow-1\frac{1}{2}$	$\frac{1}{2}$	0.06556	-2.6	33
5←2	$\frac{1}{2}\leftarrow-\frac{1}{2}$	$-\frac{1}{2}$	0.07166	-2.0	31
5←2	$\frac{1}{2}\leftarrow-\frac{1}{2}$	$\frac{1}{2}$	0.07277	-4.3	31
4←2	$1\frac{1}{2}\leftarrow\frac{1}{2}$	$-\frac{1}{2}$	0.08382	-5.1	28
4←2	$1\frac{1}{2}\leftarrow\frac{1}{2}$	$\frac{1}{2}$	0.08456	-5.7	27
3←2	$2\frac{1}{2}\leftarrow1\frac{1}{2}$	b	0.10709	-2.9	22
2←1	$3\frac{1}{2}\leftarrow2\frac{1}{2}$	$\frac{1}{2}$	0.18481	-3.6	12
2←1	$3\frac{1}{2}\leftarrow2\frac{1}{2}$	$-\frac{1}{2}$	0.18597	-4.3	12
4←1	$\frac{1}{2}\leftarrow1\frac{1}{2}$	$-\frac{1}{2}$	0.19604	1.4	-51
4←1	$\frac{1}{2}\leftarrow1\frac{1}{2}$	$\frac{1}{2}$	0.19746	1.8	-51
4←2	$-1\frac{1}{2}\leftarrow-\frac{1}{2}$	$-\frac{1}{2}$	0.33101	-3.4	19
4←2	$-1\frac{1}{2}\leftarrow-\frac{1}{2}$	$\frac{1}{2}$	0.33206	-2.9	19
5←2	$-\frac{1}{2}\leftarrow\frac{1}{2}$	b	0.33827	4.7	20
4←1	$-\frac{1}{2}\leftarrow\frac{1}{2}$	$-\frac{1}{2}$	0.36080	0.0	-20
4←1	$-\frac{1}{2}\leftarrow\frac{1}{2}$	$\frac{1}{2}$	0.36143	-0.9	-20
3←2	$-2\frac{1}{2}\leftarrow-1\frac{1}{2}$	$-\frac{1}{2}$	0.39575	-3.0	15
3←2	$-2\frac{1}{2}\leftarrow-1\frac{1}{2}$	$\frac{1}{2}$	0.39728	-3.1	15
5←2	$\frac{1}{2}\leftarrow1\frac{1}{2}$	b	0.40412	-2.1	20
2←1	$-\frac{1}{2}\leftarrow-1\frac{1}{2}$	$-\frac{1}{2}$	0.44727	-2.0	42

speaking, the agreement is good although the parameters are much more precisely determined in the present work. We discuss each of them briefly in turn.

The rotational constant B_0 and the centrifugal distortion constant D_0 are now very accurately determined. Using the value for α_e of 5.42594(90) GHz, determined from the recent study of the infrared spectrum of CrH (19), the value for the equilibrium

TABLE II—*Continued*

S#[a]	M_J	M_I''	Field	o-c	$\partial\nu/\partial B_0$
2←1	$-\frac{1}{2}\leftarrow -1\frac{1}{2}$	$\frac{1}{2}$	0.44907	-1.9	42
3←1	$-\frac{1}{2}\leftarrow -\frac{1}{2}$	$\frac{1}{2}\leftarrow -\frac{1}{2}$	0.52638	-1.5	34
2←1	$\frac{1}{2}\leftarrow -\frac{1}{2}$	$\frac{1}{2}$	0.52823	-2.1	34
2←2	$2\frac{1}{2}\leftarrow \frac{1}{2}$	$-\frac{1}{2}\leftarrow \frac{1}{2}$	0.53365	-2.3	-15
2←1	$2\frac{1}{2}\leftarrow 1\frac{1}{2}$	$\frac{1}{2}$	0.53654	-2.3	-15
4←2	$\frac{1}{2}\leftarrow -\frac{1}{2}$	$-\frac{1}{2}$	$0\frac{1}{2}$ 6571	-1.0	45
4←2	$\frac{1}{2}\leftarrow -\frac{1}{2}$	$\frac{1}{2}$	0.56693	-1.1	45
4←2	$-\frac{1}{2}\leftarrow -1\frac{1}{2}$	$-\frac{1}{2}$	0.56893	-0.6	41
4←2	$-\frac{1}{2}\leftarrow -1\frac{1}{2}$	$\frac{1}{2}$	0.57030	0.4	41

$N = 3\leftarrow 2$ $\nu = 1100.8067$ GHz

S#[a]	M_J	M_I''	Field	o-c	$\partial\nu/\partial B_0$
3←2	$-3\frac{1}{2}\leftarrow -3\frac{1}{2}$	$-\frac{1}{2}$	0.03634	-0.6	21
3←2	$-3\frac{1}{2}\leftarrow -3\frac{1}{2}$	$\frac{1}{2}$	0.03718	-0.6	21
4←3	$-2\frac{1}{2}\leftarrow -2\frac{1}{2}$	$-\frac{1}{2}$	0.04366	-0.6	19
4←3	$-2\frac{1}{2}\leftarrow -2\frac{1}{2}$	$\frac{1}{2}$	0.04450	-0.1	19
5←4	$-1\frac{1}{2}\leftarrow -1\frac{1}{2}$	$-\frac{1}{2}$	0.05408	1.4	17
5←4	$-1\frac{1}{2}\leftarrow -1\frac{1}{2}$	$\frac{1}{2}$	0.05503	0.5	17
1←1	$-\frac{1}{2}\leftarrow -\frac{1}{2}$	$-\frac{1}{2}$	0.06605	-3.8	48
1←1	$-\frac{1}{2}\leftarrow -\frac{1}{2}$	$\frac{1}{2}$	0.06781	-3.3	48
6←5	$-\frac{1}{2}\leftarrow -\frac{1}{2}$	$-\frac{1}{2}$	0.07058	-0.1	14
6←5	$-\frac{1}{2}\leftarrow -\frac{1}{2}$	$\frac{1}{2}$	0.07153	-0.3	14
6←5	$\frac{1}{2}\leftarrow \frac{1}{2}$	$-\frac{1}{2}$	0.09977	0.0	11
6←5	$\frac{1}{2}\leftarrow \frac{1}{2}$	$\frac{1}{2}$	0.10077	-0.4	11
5←4	$1\frac{1}{2}\leftarrow 1\frac{1}{2}$	$-\frac{1}{2}$	0.16844	0.3	7
5←4	$1\frac{1}{2}\leftarrow 1\frac{1}{2}$	$\frac{1}{2}$	0.16944	0.3	7
1←1	$4\frac{1}{2}\leftarrow 4\frac{1}{2}$	$-\frac{1}{2}$	0.18812	2.5	-16
1←1	$4\frac{1}{2}\leftarrow 4\frac{1}{2}$	$\frac{1}{2}$	0.18923	1.5	-16
1←1	$3\frac{1}{2}\leftarrow 3\frac{1}{2}$	$-\frac{1}{2}$	0.22863	0.0	-14
1←1	$3\frac{1}{2}\leftarrow 3\frac{1}{2}$	$\frac{1}{2}$	0.22979	0.0	-14
2←1	$2\frac{1}{2}\leftarrow 2\frac{1}{2}$	$-\frac{1}{2}$	0.29376	1.3	-11
2←1	$2\frac{1}{2}\leftarrow 2\frac{1}{2}$	$\frac{1}{2}$	0.29487	0.7	-11
3←2	$2\frac{1}{2}\leftarrow 2\frac{1}{2}$	$\frac{1}{2}$	0.42566	0.2	-4
3←2	$2\frac{1}{2}\leftarrow 2\frac{1}{2}$	$-\frac{1}{2}$	0.42725	0.4	-4
1←1	$-1\frac{1}{2}\leftarrow -1\frac{1}{2}$	$-\frac{1}{2}$	0.48368	-1.4	11
1←1	$-1\frac{1}{2}\leftarrow -1\frac{1}{2}$	$\frac{1}{2}$	0.48537	-1.4	11
2←2	$-\frac{1}{2}\leftarrow -\frac{1}{2}$	$-\frac{1}{2}$	0.54025	-2.0	11
2←2	$\frac{1}{2}\leftarrow -\frac{1}{2}$	$-\frac{1}{2}\leftarrow \frac{1}{2}$	0.54194	-2.0	11
3←2	$3\frac{1}{2}\leftarrow 3\frac{1}{2}$	b	0.76037	0.9	3
3←3	$\frac{1}{2}\leftarrow -\frac{1}{2}$	$-\frac{1}{2}\leftarrow \frac{1}{2}$	0.79854	0.5	-6
3←2	$\frac{1}{2}\leftarrow \frac{1}{2}$	$\frac{1}{2}$	0.79960	0.8	-6
2←1	$1\frac{1}{2}\leftarrow 1\frac{1}{2}$	$\frac{1}{2}$	0.84414	-0.5	-11
2←1	$1\frac{1}{2}\leftarrow 1\frac{1}{2}$	$-\frac{1}{2}$	0.84488	0.3	-11

S#	M_J	M_I''	Field	o-c	$\partial\nu/\partial B_0$
4←2	$-2\frac{1}{2}\leftarrow -3\frac{1}{2}$	$-\frac{1}{2}$	0.02123	-1.1	33
4←2	$-2\frac{1}{2}\leftarrow -3\frac{1}{2}$	$\frac{1}{2}$	0.02229	-0.6	33
5←3	$-1\frac{1}{2}\leftarrow -2\frac{1}{2}$	$-\frac{1}{2}$	0.02445	-0.6	29
5←3	$-1\frac{1}{2}\leftarrow -2\frac{1}{2}$	$\frac{1}{2}$	0.02551	-0.8	29
6←4	$-\frac{1}{2}\leftarrow -1\frac{1}{2}$	$-\frac{1}{2}$	0.02883	0.4	26
6←4	$-\frac{1}{2}\leftarrow -1\frac{1}{2}$	$\frac{1}{2}$	0.02989	0.3	26
6←5	$\frac{1}{2}\leftarrow -\frac{1}{2}$	$-\frac{1}{2}$	0.03533	-0.4	22
6←5	$\frac{1}{2}\leftarrow -\frac{1}{2}$	$\frac{1}{2}$	0.03638	0.2	22
5←5	$1\frac{1}{2}\leftarrow \frac{1}{2}$	$-\frac{1}{2}$	0.04588	-0.6	17
5←5	$1\frac{1}{2}\leftarrow \frac{1}{2}$	$\frac{1}{2}$	0.04699	-0.3	18
4←4	$2\frac{1}{2}\leftarrow 1\frac{1}{2}$	$-\frac{1}{2}$	0.06673	-0.1	13
4←4	$2\frac{1}{2}\leftarrow 1\frac{1}{2}$	$\frac{1}{2}$	0.06800	-0.5	13
2←1	$2\frac{1}{2}\leftarrow 3\frac{1}{2}$	$-\frac{1}{2}$	0.11083	0.9	-25
2←1	$2\frac{1}{2}\leftarrow 3\frac{1}{2}$	$\frac{1}{2}$	0.11214	0.9	-25
3←1	$1\frac{1}{2}\leftarrow 2\frac{1}{2}$	$-\frac{1}{2}$	0.12620	1.2	-22
3←1	$1\frac{1}{2}\leftarrow 2\frac{1}{2}$	$\frac{1}{2}$	0.12751	0.5	-22
3←3	$3\frac{1}{2}\leftarrow 2\frac{1}{2}$	$-\frac{1}{2}$	0.13775	0.1	6
3←3	$3\frac{1}{2}\leftarrow 2\frac{1}{2}$	$\frac{1}{2}$	0.13938	0.1	6
4←2	$\frac{1}{2}\leftarrow 1\frac{1}{2}$	$-\frac{1}{2}$	0.14682	0.3	-19
4←2	$\frac{1}{2}\leftarrow 1\frac{1}{2}$	$\frac{1}{2}$	0.14825	1.2	-19
4←3	$-\frac{1}{2}\leftarrow \frac{1}{2}$	$-\frac{1}{2}$	0.17715	0.7	-15
4←2	$1\frac{1}{2}\leftarrow 2\frac{1}{2}$	$-\frac{1}{2}$	0.20473	0.7	-25
4←2	$1\frac{1}{2}\leftarrow 2\frac{1}{2}$	$\frac{1}{2}$	0.20516	1.2	-25
2←1	$-\frac{1}{2}\leftarrow -1\frac{1}{2}$	$-\frac{1}{2}$	0.21950	-0.4	58
2←1	$\frac{1}{2}\leftarrow -1\frac{1}{2}$	$\frac{1}{2}$	0.22081	0.2	58
3←3	$-1\frac{1}{2}\leftarrow -\frac{1}{2}$	$-\frac{1}{2}$	0.23496	1.4	-7
3←3	$-\frac{1}{2}\leftarrow -\frac{1}{2}$	$\frac{1}{2}$	0.23644	1.5	-7
5←3	$\frac{1}{2}\leftarrow 1\frac{1}{2}$	$-\frac{1}{2}$	0.27932	0.2	-13
5←3	$\frac{1}{2}\leftarrow 1\frac{1}{2}$	$\frac{1}{2}$	0.27980	0.1	-13
2←2	$-2\frac{1}{2}\leftarrow -1\frac{1}{2}$	$-\frac{1}{2}$	0.34164	1.6	-4
2←2	$-1\frac{1}{2}\leftarrow -1\frac{1}{2}$	$-\frac{1}{2}\leftarrow \frac{1}{2}$	0.34312	1.9	-4
3←3	$-1\frac{1}{2}\leftarrow -\frac{1}{2}$	$-\frac{1}{2}$	0.35575	2.2	5
3←3	$-\frac{1}{2}\leftarrow -\frac{1}{2}$	$-\frac{1}{2}\leftarrow \frac{1}{2}$	0.35775	2.3	5
3←2	$-1\frac{1}{2}\leftarrow -2\frac{1}{2}$	$-\frac{1}{2}$	0.40197	2.0	40
3←2	$-\frac{1}{2}\leftarrow -2\frac{1}{2}$	$-\frac{1}{2}\leftarrow \frac{1}{2}$	0.40303	-0.1	40
4←3	$-\frac{1}{2}\leftarrow \frac{1}{2}$	$-\frac{1}{2}$	0.41748	0.5	12
4←3	$-\frac{1}{2}\leftarrow \frac{1}{2}$	$\frac{1}{2}$	0.41869	0.8	12
4←3	$-\frac{1}{2}\leftarrow -1\frac{1}{2}$	$-\frac{1}{2}$	0.47328	-2.0	38
4←3	$-\frac{1}{2}\leftarrow -1\frac{1}{2}$	$\frac{1}{2}$	0.47444	-0.3	38
1←1	$-3\frac{1}{2}\leftarrow -2\frac{1}{2}$	$-\frac{1}{2}$	0.47802	0.9	-4
1←1	$-2\frac{1}{2}\leftarrow -2\frac{1}{2}$	$-\frac{1}{2}\leftarrow \frac{1}{2}$	0.48075	1.0	-4
3←3	$-\frac{1}{2}\leftarrow -\frac{1}{2}$	$-\frac{1}{2}\leftarrow \frac{1}{2}$	0.49360	1.2	-36

rotational constant B_e is calculated to be 186.53808 GHz. This corresponds to an equilibrium bond length of 0.16554092(20) nm. The best ab initio calculation so far (*2*) gives a value of 0.1688 nm.

Five spin–spin coupling and spin–rotation parameters have been determined in our work. The major parameter is the spin–spin coupling constant λ which is determined

TABLE II—*Continued*

S#[a]	M_J	M_I''	Field	o-c	$\partial v/\partial B_0$
3←2	$-\frac{1}{2} \leftarrow \frac{1}{2}$	$\frac{1}{2}$	0.49475	0.5	-36
3←1	$\frac{1}{2} \leftarrow 1\frac{1}{2}$	b	0.55159	-0.2	-26
2←2	$-2\frac{1}{2} \leftarrow -1\frac{1}{2}$	b	0.63107	2.1	2
5←4	$-\frac{1}{2} \leftarrow -1\frac{1}{2}$	$-\frac{1}{2}$	0.79431	1.0	26
5←4	$-\frac{1}{2} \leftarrow -1\frac{1}{2}$	$\frac{1}{2}$	0.79589	-0.7	26

N = 3←2   v = 1101.1594 GHz

S#[a]	M_J	M_I''	Field	o-c	$\partial v/\partial B_0$
3←2	$-3\frac{1}{2} \leftarrow -3\frac{1}{2}$	$-\frac{1}{2}$	0.05265	-1.3	23
3←2	$-3\frac{1}{2} \leftarrow -3\frac{1}{2}$	$\frac{1}{2}$	0.05349	-1.5	23
4←3	$-2\frac{1}{2} \leftarrow -2\frac{1}{2}$	$-\frac{1}{2}$	0.06131	-1.3	21
4←3	$-2\frac{1}{2} \leftarrow -2\frac{1}{2}$	$\frac{1}{2}$	0.06221	-2.0	21
6←5	$-\frac{1}{2} \leftarrow -\frac{1}{2}$	$-\frac{1}{2}$	0.09354	-0.4	16
6←5	$-\frac{1}{2} \leftarrow -\frac{1}{2}$	$\frac{1}{2}$	0.09448	-0.7	16
6←5	$\frac{1}{2} \leftarrow \frac{1}{2}$	$-\frac{1}{2}$	0.12967	-0.2	12
6←5	$\frac{1}{2} \leftarrow \frac{1}{2}$	$\frac{1}{2}$	0.13062	-0.3	12
1←1	$4\frac{1}{2} \leftarrow 4\frac{1}{2}$	$-\frac{1}{2}$	0.16502	-0.4	-15
1←1	$4\frac{1}{2} \leftarrow 4\frac{1}{2}$	$\frac{1}{2}$	0.16617	-0.7	-15
1←1	$3\frac{1}{2} \leftarrow 3\frac{1}{2}$	$-\frac{1}{2}$	0.20225	0.6	-13
1←1	$3\frac{1}{2} \leftarrow 3\frac{1}{2}$	$\frac{1}{2}$	0.20340	0.4	-13
5←4	$1\frac{1}{2} \leftarrow 1\frac{1}{2}$	$-\frac{1}{2}$	0.22283	-0.2	6
5←4	$1\frac{1}{2} \leftarrow 1\frac{1}{2}$	$\frac{1}{2}$	0.22382	-0.4	6
2←1	$2\frac{1}{2} \leftarrow 2\frac{1}{2}$	$-\frac{1}{2}$	0.26068	0.7	-11
2←1	$2\frac{1}{2} \leftarrow 2\frac{1}{2}$	$\frac{1}{2}$	0.26184	0.7	-11
3←2	$2\frac{1}{2} \leftarrow 2\frac{1}{2}$	b	0.36284	-1.0	-7
1←1	$-1\frac{1}{2} \leftarrow -1\frac{1}{2}$	$-\frac{1}{2}$	0.51714	-1.9	10
1←1	$-1\frac{1}{2} \leftarrow -1\frac{1}{2}$	$\frac{1}{2}$	0.51886	-1.9	10
2←2	$-\frac{1}{2} \leftarrow -\frac{1}{2}$	$-\frac{1}{2}$	0.57605	-2.3	9
2←2	$\frac{1}{2} \leftarrow -\frac{1}{2}$	$-\frac{1}{2} \leftarrow \frac{1}{2}$	0.57784	-2.5	9
3←3	$\frac{1}{2} \leftarrow -\frac{1}{2}$	$-\frac{1}{2} \leftarrow \frac{1}{2}$	0.74770	0.4	-8
3←2	$\frac{1}{2} \leftarrow \frac{1}{2}$	$\frac{1}{2}$	0.74874	0.5	-8
2←1	$1\frac{1}{2} \leftarrow 1\frac{1}{2}$	$\frac{1}{2}$	0.81303	-0.7	-12
2←1	$1\frac{1}{2} \leftarrow 1\frac{1}{2}$	$-\frac{1}{2}$	0.81371	0.4	-12
3←2	$3\frac{1}{2} \leftarrow 3\frac{1}{2}$	b	0.90370	0.1	2
4←2	$-2\frac{1}{2} \leftarrow -3\frac{1}{2}$	$-\frac{1}{2}$	0.03157	-0.5	35
4←2	$-2\frac{1}{2} \leftarrow -3\frac{1}{2}$	$\frac{1}{2}$	0.03258	-0.5	36
5←3	$-1\frac{1}{2} \leftarrow -2\frac{1}{2}$	$-\frac{1}{2}$	0.03596	-0.9	32
5←3	$-1\frac{1}{2} \leftarrow -2\frac{1}{2}$	$\frac{1}{2}$	0.03702	-2.6	32
6←4	$-\frac{1}{2} \leftarrow -1\frac{1}{2}$	$-\frac{1}{2}$	0.04195	-1.2	28
6←4	$-\frac{1}{2} \leftarrow -1\frac{1}{2}$	$\frac{1}{2}$	0.04295	-0.8	28
6←5	$\frac{1}{2} \leftarrow -\frac{1}{2}$	$-\frac{1}{2}$	0.05071	-1.4	24
6←5	$\frac{1}{2} \leftarrow -\frac{1}{2}$	$\frac{1}{2}$	0.05172	-0.7	24
5←5	$1\frac{1}{2} \leftarrow \frac{1}{2}$	$-\frac{1}{2}$	0.06506	-2.2	19

S#	M_J	M_I''	Field	o-c	$\partial v/\partial B_0$
5←5	$1\frac{1}{2} \leftarrow \frac{1}{2}$	$\frac{1}{2}$	0.06611	-1.7	19
4←4	$2\frac{1}{2} \leftarrow 1\frac{1}{2}$	$-\frac{1}{2}$	0.09385	-1.6	13
4←4	$2\frac{1}{2} \leftarrow 1\frac{1}{2}$	$\frac{1}{2}$	0.09506	-2.2	13
2←1	$2\frac{1}{2} \leftarrow 3\frac{1}{2}$	$-\frac{1}{2}$	0.09680	1.4	-25
2←1	$2\frac{1}{2} \leftarrow 3\frac{1}{2}$	$\frac{1}{2}$	0.09812	1.7	-25
3←1	$1\frac{1}{2} \leftarrow 2\frac{1}{2}$	$-\frac{1}{2}$	0.11020	0.0	-22
3←1	$1\frac{1}{2} \leftarrow 2\frac{1}{2}$	$\frac{1}{2}$	0.11157	0.7	-22
4←2	$\frac{1}{2} \leftarrow 1\frac{1}{2}$	$-\frac{1}{2}$	0.12824	1.2	-19
4←2	$\frac{1}{2} \leftarrow 1\frac{1}{2}$	$\frac{1}{2}$	0.12962	1.1	-19
4←3	$-\frac{1}{2} \leftarrow \frac{1}{2}$	$-\frac{1}{2}$	0.15379	-0.2	-15
4←3	$-\frac{1}{2} \leftarrow \frac{1}{2}$	$\frac{1}{2}$	0.15527	0.4	-15
3←3	$-1\frac{1}{2} \leftarrow -\frac{1}{2}$	$-\frac{1}{2}$	0.19529	1.1	-11
3←3	$-\frac{1}{2} \leftarrow -\frac{1}{2}$	$\frac{1}{2}$	0.19677	0.7	-11
3←3	$3\frac{1}{2} \leftarrow 2\frac{1}{2}$	$-\frac{1}{2}$	0.20587	-0.8	5
3←3	$3\frac{1}{2} \leftarrow 2\frac{1}{2}$	$\frac{1}{2}$	0.20762	-1.3	5
2←1	$-\frac{1}{2} \leftarrow -1\frac{1}{2}$	$-\frac{1}{2}$	0.22559	-3.7	59
2←1	$\frac{1}{2} \leftarrow -1\frac{1}{2}$	$-\frac{1}{2} \leftarrow \frac{1}{2}$	0.22691	-3.5	59
3←3	$-3\frac{1}{2} \leftarrow -2\frac{1}{2}$	b	0.24191	-0.2	5
5←3	$\frac{1}{2} \leftarrow 1\frac{1}{2}$	$-\frac{1}{2}$	0.25475	-0.3	-15
5←3	$\frac{1}{2} \leftarrow 1\frac{1}{2}$	$\frac{1}{2}$	0.25528	-0.4	-15
2←2	$-2\frac{1}{2} \leftarrow -1\frac{1}{2}$	$-\frac{1}{2}$	0.26994	0.9	-6
2←2	$-1\frac{1}{2} \leftarrow -1\frac{1}{2}$	$\frac{1}{2}$	0.27152	1.0	-6
2←2	$-4\frac{1}{2} \leftarrow -3\frac{1}{2}$	b	0.34260	-0.7	3
3←2	$-2\frac{1}{2} \leftarrow -3\frac{1}{2}$	$-\frac{1}{2}$	0.37389	2.2	24
3←2	$-2\frac{1}{2} \leftarrow -3\frac{1}{2}$	$\frac{1}{2}$	0.37532	1.5	24
1←1	$-3\frac{1}{2} \leftarrow -2\frac{1}{2}$	$-\frac{1}{2}$	0.39791	0.8	-5
1←1	$-2\frac{1}{2} \leftarrow -2\frac{1}{2}$	$-\frac{1}{2} \leftarrow \frac{1}{2}$	0.40012	0.8	-5
3←2	$-1\frac{1}{2} \leftarrow -2\frac{1}{2}$	$-\frac{1}{2}$	0.41089	0.2	40
3←2	$-\frac{1}{2} \leftarrow -2\frac{1}{2}$	$-\frac{1}{2} \leftarrow \frac{1}{2}$	0.41185	2.4	40
3←3	$-1\frac{1}{2} \leftarrow -\frac{1}{2}$	$-\frac{1}{2}$	0.41857	1.2	6
3←3	$-\frac{1}{2} \leftarrow -\frac{1}{2}$	$-\frac{1}{2} \leftarrow \frac{1}{2}$	0.42031	1.3	7
4←3	$-\frac{1}{2} \leftarrow \frac{1}{2}$	$-\frac{1}{2}$	0.44621	0.4	13
4←3	$-\frac{1}{2} \leftarrow \frac{1}{2}$	$\frac{1}{2}$	0.44753	-0.3	13
5←4	$-\frac{1}{2} \leftarrow \frac{1}{2}$	b	0.52420	0.0	-2
2←3	$1\frac{1}{2} \leftarrow \frac{1}{2}$	$-\frac{1}{2}$	0.54695	1.5	-17
2←3	$1\frac{1}{2} \leftarrow \frac{1}{2}$	$\frac{1}{2}$	0.54885	1.5	-17
4←3	$-1\frac{1}{2} \leftarrow -2\frac{1}{2}$	$-\frac{1}{2}$	0.58223	0.5	23
4←3	$-1\frac{1}{2} \leftarrow -2\frac{1}{2}$	$\frac{1}{2}$	0.58365	0.8	23
2←2	$-2\frac{1}{2} \leftarrow -1\frac{1}{2}$	b	0.77531	1.7	3
5←4	$-\frac{1}{2} \leftarrow -1\frac{1}{2}$	$-\frac{1}{2}$	0.80756	1.3	27
5←4	$-\frac{1}{2} \leftarrow -1\frac{1}{2}$	$\frac{1}{2}$	0.80914	-0.4	27
1←1	$-4\frac{1}{2} \leftarrow -3\frac{1}{2}$	$-\frac{1}{2}$	0.88509	0.3	-2

to be 6.980191(51) GHz. This was only poorly determined previously as 8.1 ± 2.1 GHz by O'Connor in his work on the A–X band system (*6, 7*). Because CrH conforms to a Hund's case (b) coupling scheme in the $X^6\Sigma^+$ state, the effect of λ is greatest on the lowest rotational energy levels. These levels were not well identified in the optical spectrum of O'Connor, but they are just the levels involved in the FIR LMR spectrum.

TABLE II—*Continued*

S#[a]	M_J	M_I''	Field	o-c	$\partial v/\partial B_0$
1←1	$-4\frac{1}{2} \leftarrow -3\frac{1}{2}$	$\frac{1}{2}$	0.88935	0.5	-2

N = 3←2   v = 1116.2455 GHz

S#	M_J	M_I''	Field	o-c	$\partial v/\partial B_0$
2←1	$-1\frac{1}{2} \leftarrow -1\frac{1}{2}$	$-\frac{1}{2}$	0.01094	3.4	24
2←1	$-1\frac{1}{2} \leftarrow -1\frac{1}{2}$	$\frac{1}{2}$	0.01221	2.8	23
2←1	$3\frac{1}{2} \leftarrow 3\frac{1}{2}$	$-\frac{1}{2}$	0.28669	2.4	-25
2←1	$3\frac{1}{2} \leftarrow 3\frac{1}{2}$	$\frac{1}{2}$	0.28927	3.0	-24
3←2	$-2\frac{1}{2} \leftarrow -2\frac{1}{2}$	$-\frac{1}{2}$	0.46289	1.2	28
3←2	$-2\frac{1}{2} \leftarrow -2\frac{1}{2}$	$\frac{1}{2}$	0.46384	1.6	28
4←3	$-1\frac{1}{2} \leftarrow -1\frac{1}{2}$	$-\frac{1}{2}$	0.56073	0.8	28
4←3	$-1\frac{1}{2} \leftarrow -1\frac{1}{2}$	$\frac{1}{2}$	0.56184	0.2	28
4←3	$-\frac{1}{2} \leftarrow -\frac{1}{2}$	$-\frac{1}{2}$	0.66167	0.4	38
4←2	$-\frac{1}{2} \leftarrow \frac{1}{2}$	$\frac{1}{2} \leftarrow -\frac{1}{2}$	0.66299	-0.3	38
5←4	$-\frac{1}{2} \leftarrow -\frac{1}{2}$	$-\frac{1}{2}$	0.71892	0.0	27
5←4	$-\frac{1}{2} \leftarrow -\frac{1}{2}$	$\frac{1}{2}$	0.72013	-0.1	27
2←1	$-2\frac{1}{2} \leftarrow -2\frac{1}{2}$	$-\frac{1}{2}$	0.91540	2.9	24
2←1	$-1\frac{1}{2} \leftarrow -2\frac{1}{2}$	$-\frac{1}{2} \leftarrow \frac{1}{2}$	0.91640	3.7	24
6←3	$-\frac{1}{2} \leftarrow -1\frac{1}{2}$	$-\frac{1}{2}$	0.07424	0.4	50
6←3	$-\frac{1}{2} \leftarrow -1\frac{1}{2}$	$\frac{1}{2}$	0.07508	-0.4	50
6←4	$\frac{1}{2} \leftarrow -\frac{1}{2}$	$-\frac{1}{2}$	0.08509	0.9	46
6←4	$\frac{1}{2} \leftarrow -\frac{1}{2}$	$\frac{1}{2}$	0.08603	-0.2	46
5←4	$1\frac{1}{2} \leftarrow \frac{1}{2}$	$-\frac{1}{2}$	0.10209	-0.4	40
5←4	$1\frac{1}{2} \leftarrow \frac{1}{2}$	$\frac{1}{2}$	0.10309	1.0	40
4←3	$2\frac{1}{2} \leftarrow 1\frac{1}{2}$	$-\frac{1}{2}$	0.13183	-1.2	33
4←3	$2\frac{1}{2} \leftarrow 1\frac{1}{2}$	$\frac{1}{2}$	0.13304	-0.6	33
3←2	$-3\frac{1}{2} \leftarrow -2\frac{1}{2}$	$-\frac{1}{2}$	0.14949	-1.6	30
3←2	$-3\frac{1}{2} \leftarrow -2\frac{1}{2}$	$\frac{1}{2}$	0.14991	-1.0	30
4←3	$-2\frac{1}{2} \leftarrow -1\frac{1}{2}$	$-\frac{1}{2}$	0.15281	-2.5	32
4←3	$-2\frac{1}{2} \leftarrow -1\frac{1}{2}$	$\frac{1}{2}$	0.15339	-1.1	32
4←1	$1\frac{1}{2} \leftarrow 2\frac{1}{2}$	$-\frac{1}{2}$	0.25277	2.5	-19
4←1	$1\frac{1}{2} \leftarrow 2\frac{1}{2}$	$\frac{1}{2}$	0.25504	3.4	-18
5←3	$-\frac{1}{2} \leftarrow -1\frac{1}{2}$	$-\frac{1}{2}$	0.36872	1.2	39
5←3	$-\frac{1}{2} \leftarrow -1\frac{1}{2}$	$\frac{1}{2}$	0.36972	0.3	39
2←1	$-\frac{1}{2} \leftarrow -1\frac{1}{2}$	$-\frac{1}{2}$	0.49851	-1.5	46
2←1	$\frac{1}{2} \leftarrow -1\frac{1}{2}$	$\frac{1}{2}$	0.49983	-0.1	46
4←3	$\frac{1}{2} \leftarrow -\frac{1}{2}$	$-\frac{1}{2}$	0.58343	1.2	33
4←2	$\frac{1}{2} \leftarrow \frac{1}{2}$	$\frac{1}{2} \leftarrow -\frac{1}{2}$	0.58449	0.4	33
6←5	$\frac{1}{2} \leftarrow -\frac{1}{2}$	$-\frac{1}{2}$	0.60830	2.0	26
6←5	$\frac{1}{2} \leftarrow -\frac{1}{2}$	$\frac{1}{2}$	0.60920	2.0	26
2←1	$-2\frac{1}{2} \leftarrow -3\frac{1}{2}$	$-\frac{1}{2}$	0.61537	3.6	22
2←1	$-1\frac{1}{2} \leftarrow -3\frac{1}{2}$	$-\frac{1}{2} \leftarrow \frac{1}{2}$	0.61727	3.7	22
4←1	$1\frac{1}{2} \leftarrow 2\frac{1}{2}$	$\frac{1}{2}$	0.68599	2.0	13

S#	M_J	M_I''	Field	o-c	$\partial v/\partial B_0$
4←1	$1\frac{1}{2} \leftarrow 2\frac{1}{2}$	$-\frac{1}{2}$	0.68657	1.6	13
3←2	$-1\frac{1}{2} \leftarrow -2\frac{1}{2}$	$-\frac{1}{2}$	0.83439	0.0	32
3←2	$-1\frac{1}{2} \leftarrow -2\frac{1}{2}$	$\frac{1}{2}$	0.83561	0.7	32
2←1	$-2\frac{1}{2} \leftarrow -2\frac{1}{2}$	$\frac{1}{2} \leftarrow -\frac{1}{2}$	0.90735	-0.6	20
2←1	$-1\frac{1}{2} \leftarrow -2\frac{1}{2}$	$\frac{1}{2}$	0.90867	0.5	20
1←1	$-2\frac{1}{2} \leftarrow -4\frac{1}{2}$	$-\frac{1}{2} \leftarrow \frac{1}{2}$	0.91414	1.1	5

N = 4←3   v = 1472.1993 GHz

S#	M_J	M_I''	Field	o-c	$\partial v/\partial B_0$
2←1	$2\frac{1}{2} \leftarrow 2\frac{1}{2}$	b	0.05877	0.4	-11
3←2	$1\frac{1}{2} \leftarrow 1\frac{1}{2}$	b	0.08781	1.5	-8
2←1	$1\frac{1}{2} \leftarrow 1\frac{1}{2}$	b	0.12456	1.3	-3
2←2	$\frac{1}{2} \leftarrow -\frac{1}{2}$	$-\frac{1}{2} \leftarrow \frac{1}{2}$	0.13683	1.8	-6
2←2	$\frac{1}{2} \leftarrow \frac{1}{2}$	$\frac{1}{2}$	0.13783	1.6	-6
2←2	$-\frac{1}{2} \leftarrow -\frac{1}{2}$	$-\frac{1}{2}$	0.18442	1.6	-11
2←2	$-\frac{1}{2} \leftarrow \frac{1}{2}$	$\frac{1}{2} \leftarrow -\frac{1}{2}$	0.18647	2.5	-11
1←1	$-5\frac{1}{2} \leftarrow -5\frac{1}{2}$	$-\frac{1}{2}$	0.20100	-0.2	8
1←1	$-5\frac{1}{2} \leftarrow -5\frac{1}{2}$	$\frac{1}{2}$	0.20279	0.1	8
4←3	$-3\frac{1}{2} \leftarrow -3\frac{1}{2}$	$-\frac{1}{2}$	0.21382	0.8	24
4←3	$-3\frac{1}{2} \leftarrow -3\frac{1}{2}$	$\frac{1}{2}$	0.21486	0.8	24
3←2	$-3\frac{1}{2} \leftarrow -3\frac{1}{2}$	$-\frac{1}{2}$	0.23184	-0.4	18
3←2	$-3\frac{1}{2} \leftarrow -3\frac{1}{2}$	$\frac{1}{2}$	0.23263	-0.5	18
1←1	$-4\frac{1}{2} \leftarrow -4\frac{1}{2}$	$-\frac{1}{2}$	0.26536	0.7	5
1←1	$-4\frac{1}{2} \leftarrow -4\frac{1}{2}$	$\frac{1}{2}$	0.26725	1.3	5
5←4	$-1\frac{1}{2} \leftarrow -1\frac{1}{2}$	$-\frac{1}{2}$	0.35292	-0.3	14
5←4	$-1\frac{1}{2} \leftarrow -1\frac{1}{2}$	$\frac{1}{2}$	0.35382	-0.7	14
1←1	$\frac{1}{2} \leftarrow \frac{1}{2}$	$-\frac{1}{2}$	0.36197	-1.4	9
1←1	$\frac{1}{2} \leftarrow \frac{1}{2}$	$\frac{1}{2}$	0.36467	-1.2	9
6←5	$-1\frac{1}{2} \leftarrow -1\frac{1}{2}$	$-\frac{1}{2}$	0.37712	0.9	12
6←5	$-1\frac{1}{2} \leftarrow -1\frac{1}{2}$	$\frac{1}{2}$	0.37807	0.6	12
6←6	$-\frac{1}{2} \leftarrow -\frac{1}{2}$	b	0.61908	0.6	6
2←1	$4\frac{1}{2} \leftarrow 4\frac{1}{2}$	$-\frac{1}{2}$	0.76594	0.6	-9
2←1	$4\frac{1}{2} \leftarrow 4\frac{1}{2}$	$\frac{1}{2}$	0.76994	0.6	-9
3←1	$1\frac{1}{2} \leftarrow 2\frac{1}{2}$	b	0.04397	1.4	-15
1←1	$2\frac{1}{2} \leftarrow 1\frac{1}{2}$	$-\frac{1}{2}$	0.05861	1.9	-12
3←2	$\frac{1}{2} \leftarrow 1\frac{1}{2}$	b	0.05940	1.4	-11
1←1	$2\frac{1}{2} \leftarrow 1\frac{1}{2}$	$\frac{1}{2}$	0.06013	1.3	-12
2←2	$1\frac{1}{2} \leftarrow \frac{1}{2}$	$-\frac{1}{2}$	0.07545	2.9	-11
2←2	$1\frac{1}{2} \leftarrow \frac{1}{2}$	$\frac{1}{2}$	0.07803	2.8	-11
1←1	$3\frac{1}{2} \leftarrow 2\frac{1}{2}$	$-\frac{1}{2}$	0.08466	1.8	-8
1←1	$3\frac{1}{2} \leftarrow 2\frac{1}{2}$	$\frac{1}{2}$	0.08587	2.6	-8
1←1	$-4\frac{1}{2} \leftarrow -5\frac{1}{2}$	$-\frac{1}{2}$	0.09143	0.8	19
1←1	$-4\frac{1}{2} \leftarrow -5\frac{1}{2}$	$\frac{1}{2}$	0.09319	2.0	19

Consequently, the parameter is now very well characterized. Van Zee *et al.* also deduced a value for λ of 4962 ± 75 MHz (0.1655 ± 0.0025 cm^{-1}) from the ESR spectrum of matrix-isolated CrH (*11, 12*). The large difference from our value is a measure of matrix-dependent effects which occur in the determination of spin splittings from ESR spectra for molecules in Σ states (see, e.g., Ref. (*26*)). The fine structure splittings are

TABLE II—*Continued*

S#[a]	M_J	M_I''	Field	o-c	$\partial v/\partial B_0$
1←1	$-3\frac{1}{2} \leftarrow -4\frac{1}{2}$	$-\frac{1}{2}$	0.10098	0.8	17
1←1	$-3\frac{1}{2} \leftarrow -4\frac{1}{2}$	$\frac{1}{2}$	0.10277	0.9	17
1←1	$-\frac{1}{2} \leftarrow \frac{1}{2}$	$-\frac{1}{2}$	0.10325	-0.1	38
1←1	$-\frac{1}{2} \leftarrow \frac{1}{2}$	$\frac{1}{2}$	0.10530	-1.0	38
2←1	$-2\frac{1}{2} \leftarrow -3\frac{1}{2}$	$-\frac{1}{2}$	0.11293	0.2	15
2←1	$-2\frac{1}{2} \leftarrow -3\frac{1}{2}$	$\frac{1}{2}$	0.11472	0.2	15
2←2	$\frac{1}{2} \leftarrow -\frac{1}{2}$	$-\frac{1}{2}$	0.11972	1.8	-12
2←2	$\frac{1}{2} \leftarrow \frac{1}{2}$	$\frac{1}{2} \leftarrow -\frac{1}{2}$	0.12241	2.5	-12
4←3	$-\frac{1}{2} \leftarrow -1\frac{1}{2}$	$-\frac{1}{2}$	0.12320	2.4	20
3←3	$\frac{1}{2} \leftarrow -1\frac{1}{2}$	$-\frac{1}{2} \leftarrow \frac{1}{2}$	0.12472	1.7	20
3←2	$-2\frac{1}{2} \leftarrow -2\frac{1}{2}$	$\frac{1}{2} \leftarrow -\frac{1}{2}$	0.12899	-0.3	13
3←2	$-1\frac{1}{2} \leftarrow -2\frac{1}{2}$	$\frac{1}{2}$	0.13067	1.5	13
2←2	$2\frac{1}{2} \leftarrow 1\frac{1}{2}$	$-\frac{1}{2}$	0.14188	1.3	-6
2←2	$2\frac{1}{2} \leftarrow 1\frac{1}{2}$	$\frac{1}{2}$	0.14346	0.7	-6
4←2	$-2\frac{1}{2} \leftarrow -3\frac{1}{2}$	$-\frac{1}{2}$	0.15084	-0.6	21
4←2	$-2\frac{1}{2} \leftarrow -3\frac{1}{2}$	$\frac{1}{2}$	0.15168	-1.4	21
1←1	$-1\frac{1}{2} \leftarrow -\frac{1}{2}$	$-\frac{1}{2}$	0.15336	-3.2	32
1←1	$-1\frac{1}{2} \leftarrow -\frac{1}{2}$	$\frac{1}{2}$	0.15520	-3.3	32
5←3	$-1\frac{1}{2} \leftarrow -2\frac{1}{2}$	$-\frac{1}{2}$	0.17199	0.4	20
5←3	$-1\frac{1}{2} \leftarrow -2\frac{1}{2}$	$\frac{1}{2}$	0.17283	0.5	20
6←5	$-\frac{1}{2} \leftarrow -1\frac{1}{2}$	$-\frac{1}{2}$	0.20152	-0.5	22
6←5	$-\frac{1}{2} \leftarrow -1\frac{1}{2}$	$\frac{1}{2}$	0.20252	-1.0	22
4←4	$1\frac{1}{2} \leftarrow \frac{1}{2}$	$-\frac{1}{2}$	0.20447	0.2	9
4←4	$1\frac{1}{2} \leftarrow \frac{1}{2}$	$\frac{1}{2}$	0.20610	0.0	9
5←4	$-\frac{1}{2} \leftarrow -1\frac{1}{2}$	$-\frac{1}{2}$	0.20668	-1.2	18
5←4	$-\frac{1}{2} \leftarrow -1\frac{1}{2}$	$\frac{1}{2}$	0.20758	-2.1	18
3←4	$1\frac{1}{2} \leftarrow -\frac{1}{2}$	$-\frac{1}{2} \leftarrow \frac{1}{2}$	0.24932	0.9	-6
3←3	$1\frac{1}{2} \leftarrow \frac{1}{2}$	$\frac{1}{2}$	0.25158	0.7	-6
3←3	$2\frac{1}{2} \leftarrow 1\frac{1}{2}$	$\frac{1}{2}$	0.27295	1.3	5
4←3	$-1\frac{1}{2} \leftarrow -1\frac{1}{2}$	$\frac{1}{2} \leftarrow -\frac{1}{2}$	0.29985	0.2	-10
3←3	$-\frac{1}{2} \leftarrow -\frac{1}{2}$	$\frac{1}{2} \leftarrow -\frac{1}{2}$	0.30075	-0.2	-10

N = 5←4   v = 1838.8393 GHz

S#[a]	M_J	M_I''	Field	o-c	$\partial v/\partial B_0$
4←3	$-4\frac{1}{2} \leftarrow -4\frac{1}{2}$	$-\frac{1}{2}$	0.28611	1.8	22
4←3	$-4\frac{1}{2} \leftarrow -4\frac{1}{2}$	$\frac{1}{2}$	0.28715	2.5	22
3←2	$-3\frac{1}{2} \leftarrow -3\frac{1}{2}$	$-\frac{1}{2}$	0.33357	-0.3	17
3←2	$-2\frac{1}{2} \leftarrow -3\frac{1}{2}$	$-\frac{1}{2} \leftarrow \frac{1}{2}$	0.33454	-0.3	17
4←3	$\frac{1}{2} \leftarrow \frac{1}{2}$	$-\frac{1}{2}$	0.33835	-7.4	23
4←3	$\frac{1}{2} \leftarrow \frac{1}{2}$	$\frac{1}{2}$	0.33956	-14.1	23
3←2	$-4\frac{1}{2} \leftarrow -4\frac{1}{2}$	$-\frac{1}{2}$	0.35606	0.8	26
3←2	$-4\frac{1}{2} \leftarrow -4\frac{1}{2}$	$\frac{1}{2}$	0.35706	2.0	26
5←4	$-3\frac{1}{2} \leftarrow -3\frac{1}{2}$	$-\frac{1}{2}$	0.38328	0.1	16

S#	M_J	M_I''	Field	o-c	$\partial v/\partial B_0$
5←4	$-3\frac{1}{2} \leftarrow -3\frac{1}{2}$	$\frac{1}{2}$	0.38428	0.4	16
4←3	$-3\frac{1}{2} \leftarrow -3\frac{1}{2}$	$-\frac{1}{2}$	0.40316	0.2	21
4←3	$-3\frac{1}{2} \leftarrow -3\frac{1}{2}$	$\frac{1}{2}$	0.40422	0.2	21
4←3	$-2\frac{1}{2} \leftarrow -2\frac{1}{2}$	$-\frac{1}{2}$	0.47318	-0.5	17
4←3	$-2\frac{1}{2} \leftarrow -1\frac{1}{2}$	$\frac{1}{2} \leftarrow -\frac{1}{2}$	0.47423	-0.2	17
2←1	$5\frac{1}{2} \leftarrow 5\frac{1}{2}$	$-\frac{1}{2}$	0.48214	1.3	-18
1←1	$-6\frac{1}{2} \leftarrow -6\frac{1}{2}$	$-\frac{1}{2}$	0.48350	1.1	4
2←1	$5\frac{1}{2} \leftarrow 5\frac{1}{2}$	$\frac{1}{2}$	0.48487	0.5	-18
1←1	$-6\frac{1}{2} \leftarrow -6\frac{1}{2}$	$\frac{1}{2}$	0.48656	0.5	4
5←4	$-2\frac{1}{2} \leftarrow -2\frac{1}{2}$	$-\frac{1}{2}$	0.52435	-1.6	14
5←4	$-2\frac{1}{2} \leftarrow -2\frac{1}{2}$	$\frac{1}{2}$	0.52529	-0.7	14
6←5	$-2\frac{1}{2} \leftarrow -2\frac{1}{2}$	$-\frac{1}{2}$	0.53616	-1.2	11
6←5	$-2\frac{1}{2} \leftarrow -2\frac{1}{2}$	$\frac{1}{2}$	0.53706	-0.9	11
3←2	$-3\frac{1}{2} \leftarrow -2\frac{1}{2}$	$\frac{1}{2} \leftarrow -\frac{1}{2}$	0.55089	-1.6	31
3←2	$-2\frac{1}{2} \leftarrow -2\frac{1}{2}$	$\frac{1}{2}$	0.55222	-0.8	31
2←1	$-3\frac{1}{2} \leftarrow -3\frac{1}{2}$	$-\frac{1}{2}$	0.57231	1.5	18
2←1	$-3\frac{1}{2} \leftarrow -3\frac{1}{2}$	$\frac{1}{2}$	0.57368	0.2	18
6←6	$-1\frac{1}{2} \leftarrow -1\frac{1}{2}$	b	0.89223	0.3	5
1←1	$-\frac{1}{2} \leftarrow \frac{1}{2}$	$-\frac{1}{2}$	0.30961	-1.1	20
1←1	$-\frac{1}{2} \leftarrow \frac{1}{2}$	$\frac{1}{2}$	0.31173	-0.7	20
5←4	$-1\frac{1}{2} \leftarrow -2\frac{1}{2}$	$-\frac{1}{2}$	0.33454	-0.6	19
5←4	$-1\frac{1}{2} \leftarrow -2\frac{1}{2}$	$\frac{1}{2}$	0.33549	-1.0	19
3←2	$-1\frac{1}{2} \leftarrow -2\frac{1}{2}$	$-\frac{1}{2}$	0.33827	-0.4	7
3←2	$-1\frac{1}{2} \leftarrow -2\frac{1}{2}$	$\frac{1}{2}$	0.34043	0.1	7
1←1	$-1\frac{1}{2} \leftarrow -\frac{1}{2}$	$-\frac{1}{2}$	0.36737	0.2	18
1←1	$-1\frac{1}{2} \leftarrow -\frac{1}{2}$	$\frac{1}{2}$	0.36938	-0.6	18
6←6	$-\frac{1}{2} \leftarrow -1\frac{1}{2}$	$-\frac{1}{2}$	0.37829	1.5	13
6←6	$-\frac{1}{2} \leftarrow -1\frac{1}{2}$	$\frac{1}{2}$	0.37940	-1.6	13
1←1	$-2\frac{1}{2} \leftarrow -1\frac{1}{2}$	$-\frac{1}{2}$	0.44012	-0.9	17
1←1	$-2\frac{1}{2} \leftarrow -1\frac{1}{2}$	$\frac{1}{2}$	0.44186	-0.6	17
1←1	$-3\frac{1}{2} \leftarrow -2\frac{1}{2}$	b	0.48851	1.3	3
6←6	$1\frac{1}{2} \leftarrow \frac{1}{2}$	b	1.15523	-0.5	2

so precisely defined in our work that we have also been able to determine a value for the fourth-order spin–spin splitting term θ. The effects of this term are to modify the spin splittings slightly from the spin–spin and spin–rotational formulas. This is one of the first clear-cut identifications of such effects. The magnitude of the parameter is in accord with the expectation from the paper by Brown and Milton (20) who show

TABLE IIIa

The Parameters (in GHz) for ^{52}CrH in the $v = 0$ Level of the $X^6\Sigma^+$ Ground State as Determined in the Least-Squares Fit of FIR LMR Data (the g-Factors Are Dimensionless; the Numbers in Parentheses Indicate the Standard Deviation in the Last Digits)

Parameter	Value determined	κ_i[a]	Previous value
B_0	183.825 110 (33)	5.7	183.80[b]
D_0	0.010 4781 (10)	5.2	0.0104 (3)[b]
H_0	4.76 x 10^{-7} (FIXED)		
γ	1.508 931 (53)	2.4	1.5 (3)[b]
γ_D	1.035 (24) x 10^{-4}	1.9	
λ	6.980 191 (51)	1.8	8.1 (2.7)[b]
λ_D	2.947 (64) x 10^{-4}	1.6	
θ	-2.317 (31) x 10^{-3}	1.1	
b_F	-0.034 80 (20)	1.0	±0.049 (5)[c]
c	0.041 81 (64)	1.0	
g_S	2.001 663 (39)	5.4	2.0017 (50)[c]
g_r	-1.280 (21) x 10^{-3}	1.5	
g_l	-4.201 (50) x 10^{-3}	5.0	

[a] Correlation coefficient $\kappa_i = (\chi^{-1})_{ii}$, where χ is the matrix of correlation coefficients.
[b] Value from O'Connor (6).
[c] Value from Van Zee et al. (11).

that $|\theta| \approx \zeta^4/\Delta E^3$, where ζ is the spin–orbit coupling parameter and ΔE is the energy separation of the admixed electronic states from the ground $^6\Sigma^+$ state. Taking ζ to be 230 cm^{-1} (27, 28) and ΔE to be about 30 000 cm^{-1}, the approximate excitation energy of the lowest $^6\Pi$ state (5), we obtain $|\theta| \approx 3.1 \times 10^{-3}$ GHz.

The two parameters b_F and c which describe the proton magnetic hyperfine interaction are both determined. This is the first such determination for a transition metal hydride. However, it should be emphasized that the *sign* of these parameters is not

TABLE IIIb

The Parameters (in cm^{-1}) for ^{52}CrH in the $v = 0$ Level of the $X^6\Sigma^+$ Ground State as Determined in the Least-Squares Fit of FIR LMR Data (the Numbers in Parentheses Indicate the Standard Deviation in the Last Digits; the Values for the Dimensionless g-Factors Are Given in Table IIIa)

Parameter	Value (cm^{-1})	κ_i[a]
B_0	6.131 745 6 (11)	5.7
D_0	3.495 1 (34) x 10^{-4}	5.2
H_0	1.59 x 10^{-8} (FIXED)	
γ	5.033 23 (18) x 10^{-2}	2.4
γ_D	3.451 (81) x 10^{-6}	1.9
λ	2.328 341 (17) x 10^{-1}	1.8
λ_D	9.831 (21) x 10^{-6}	1.6
θ	-7.73 (10) x 10^{-5}	1.1
b_F	-1.160 7 (67) x 10^{-3}	1.0
c	1.395 (21) x 10^{-3}	1.0

Note. Conversion from GHz (Table IIIa) to cm^{-1} based upon $c = 2.99792458 \times 10^8$ m/sec.
[a] Correlation coefficient $\kappa_i = (\chi^{-1})_{ii}$, where χ is the matrix of correlation coefficients.

determinable from our observations. The ab initio calculations show that the open shell electrons in CrH are almost completely localized on the Cr atom (I, 2). In these circumstances, the Fermi contact interaction is expected to arise by spin polarization (29) and the parameter b_F to be negative. Specifically, the four unpaired electrons in the $3d\delta$ and $3d\pi$ orbitals each make negative contributions to b_F whereas the fifth electron in the $3d\sigma$ orbital probably makes a positive contribution. If these contributions are similar in magnitude, then the combined effect produces a negative Fermi contact parameter. We have assumed this to be the case in making the assignments given in Table II. The magnitude of the isotropic hyperfine coupling constant has also been determined from the ESR spectrum (II) as 1.6 ± 0.2 mT (or 45 ± 6 MHz), later revised to 0.8 mT, or 22 MHz ($I2$). Our value of $-34.8(7)$ MHz differs significantly from these estimates but must be regarded as the more reliable in view of the higher quality of our data. The dipolar hyperfine parameter c gives information on the unpaired electron density in the neighborhood of the proton:

$$c/\mathrm{MHz} = \frac{10^{-6}}{h} \sum_i \frac{3g_i\mu_B g_N \mu_N \mu_0}{8\pi} \left\langle \hat{\Phi}_i^s \frac{3\cos^2\theta_i - 1}{r^3} \right\rangle_s \tag{5}$$

using standard notation (30). The net effect of the five unpaired electrons in $3d$ orbitals is to produce a spherically symmetric charge distribution centered on the chromium atom. The dipolar parameter c can therefore be estimated by assuming that the open shell electrons in CrH are located on the molecular axis at a distance r_0 from the proton. In this case, ($3\cos^2\theta - 1$) = 2 and c is calculated to be 51.2 MHz, in reasonably good agreement with the experimental value, 41.8 MHz. In particular, the fact that the parameter is calculated to be positive lends support to our contention that b_F is negative. More detailed work on the hyperfine parameters of CrH is clearly needed.

The Zeeman effect for CrH in its $X\,^6\Sigma^+$ state is well described by the three parameters listed in Table III, g_S, g_r, and g_l. The electron spin g-factor g_S is determined to be $2.001663(39)$, in good agreement with the value of $2.0017(29)$ from ESR and slightly less than the free spin g-value as would be expected for a small relativistic correction (29). The value determined for the anisotropic correction to the electron spin g-factor, g_l, is $-0.4201(50) \times 10^{-2}$, in excellent agreement with that expected from Curl's relationship (31), $g_l = -\gamma/2B = -0.4104 \times 10^{-2}$. The ability to model the Zeeman effect in CrH accurately and with g-factors of normal magnitude is in marked contrast to our experience with FeH, CoH, and NiH in their ground states ($^4\Delta$, $^3\Phi$, and $^2\Delta$, respectively); for example, for NiH, $g_S = 1.84$ ($I5$). The implication is that the ground $^6\Sigma^+$ state of CrH is not seriously perturbed by other low-lying states. Indeed, it is quite probable that there are very few such low-lying states, which is not the case for the other molecules. A qualitative extension of the ab initio calculations for CrH (I, 2) suggests that these conclusions are valid but further theoretical work is needed to confirm them.

Chromium hydride exists in stellar atmospheres (8, 9) and may also be present in the cold interstellar medium in sufficient concentration to allow its detection by FIR astronomy. To guide the searches for these transitions, we have calculated the zero-field frequencies of the first few rotational transitions in the ground state, based on

TABLE IV

The Predicted Zero-Field Transition Frequencies (in GHz) with $\Delta J = \pm 1$ or 0 and $\Delta F = \Delta J$,
between the Lowest Three Rotational Levels in ^{52}CrH

N'←N"	J'←J"	F'←F"	ν (GHz)	line strength[a]
1←0	3/2←5/2	3←2	337.260	1.6
		2←1	337.267	1.0
	7/2←5/2	4←3	362.618	3.0
		3←2	362.628	2.3
	5/2←5/2	2←2	396.541	1.5
		3←3	396.590	2.1
2←1	1/2←3/2	0←1	718.610	0.4
		1←2	718.623	1.0
	3/2←3/2	1←1	744.761	0.7
		2←2	744.833	1.2
	5/2←3/2	2←1	776.030	0.5
		3←2	776.104	0.8
	9/2←7/2	5←4	734.948	4.4
		4←3	734.951	3.5
	5/2←7/2	2←3	750.669	0.1
		3←4	750.746	0.2
	7/2←7/2	3←3	764.024	0.9
		4←4	764.073	1.2
	3/2←5/2	1←2	685.487	0.4
		2←3	685.504	0.6
	5/2←5/2	2←2	716.756	1.2
		3←3	716.775	1.7
	7/2←5/2	4←3	730.101	2.3
		3←2	730.110	1.7

Note. The prediction is based on the constants given in Table IIIa. The estimated uncertainty in the predictions is 0.003 GHz. The linestrength of each transition, uncorrected for any population factors, is also given.

[a] Linestrength defined in Ref. (*32*).

the molecular parameters determined in this work. The results are given in Table IV. The calculated linestrengths, defined for example in Ref. (*32*), are also given.

RECEIVED: May 3, 1991

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