Millimeter-wave spectroscopy of chromium monochloride (CrCl)

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The rotational spectrum of chromium monochloride in the ${}^6\Sigma^+$ ground electronic state has been observed with a source-modulated microwave spectrometer in the millimeter-wave region. The CrCl radical was produced in a free space absorption cell by a dc glow discharge in a mixture of AlCl_3 vapor and He using stainless steel electrodes. Chromium atom was supplied from the electrodes by the sputtering reaction. Observed spectral lines were analyzed by a least-squares fit and the molecular constants including the rotational and centrifugal distortion constants and the spin-spin and spin-rotation interaction constants were determined. The experimental rotational constants B_0 for ${}^{52}\text{Cr}{}^{35}\text{Cl}$ and ${}^{52}\text{Cr}{}^{37}\text{Cl}$ are 5 009.345 69(69) and 4 847.851 00(32) MHz, respectively, where the uncertainties attached to the last digit correspond to one standard deviation. © 1998 American Institute of Physics. [S0021-9606(98)00933-7]

I. INTRODUCTION

High-resolution spectroscopy has so far been applied to the study on many species containing typical elements only.^{1,2} In these chemical species orbital degeneracy in the electronic ground state is never higher than 2 (Π or E), and spin multiplicity is usually lower than quartet. Since a transition metal atom contains a number of unpaired d electrons, however, even for a simplest diatomic molecule the orbital degeneracy can be larger than 2 and the spin multiplicity higher than triplet. Such a species gives complex spectra and their analysis is accordingly difficult. Furthermore, since metal compounds, in general, are highly refractory, few methods are available to produce gaseous molecules efficiently for spectroscopic study at room temperature. These are some of the reasons why few species containing a transition metal atom have been studied with high-resolution spectroscopy.

Observation of the spectrum of such a molecule is useful not only to establish its existence in the gas phase and to obtain spectroscopic information. It also serves to check the accuracy of the molecular constants calculated with nonempirical molecular orbital methods and the reliability of the effective Hamiltonian used in the analysis.

A number of transition metal elements have relatively high cosmic abundance. Among hydrides of Fe, Cr, and the like, CrH was detected in relatively cool S -type stars and sunspots.^{3,4} Abundance of transition metal compounds (hydrides, oxides, halides, and so on) was calculated in a theoretical study based on chemical models of the reactions in stellar atmospheres.⁵ Such species, however, have rarely been observed in the interstellar and circumstellar spaces. Heavy metals are in general produced by nuclear reactions in the central region of a star. As a result of a supernova explosion or mass loss they are ejected toward the stellar atmosphere. Compounds including transition metal atoms could

thus exist in the interstellar space, connected with interstellar dust. However, unless much detailed high-resolution spectroscopic data are accumulated, we cannot identify them. In this sense the study on rotational spectra of transition metal compounds is urgently desired.

Among the compounds bearing chromium, chromium hydride, CrH ,⁶⁻¹¹ and chromium monoxide, CrO ,¹²⁻¹⁴ have extensively been investigated with various spectroscopic methods. Chromium monofluoride, CrF , has also been the subject of recent studies through electronic spectroscopy of the $A {}^6\Sigma^+ - X {}^6\Sigma^+$ and $B {}^6\Pi - X {}^6\Sigma^+$ band systems with the resolved rotational structure¹⁵⁻¹⁷ and through microwave spectroscopy.¹⁸ On the other hand, for CrCl Ermilov *et al.*¹⁹ approached the energy levels of the electronic states theoretically and indicated that the molecule has the electronic ground $X {}^6\Sigma^+$ state. Spectroscopically only low resolution emission spectra of electronic transitions were investigated.²⁰ Quite recently Bencheikh *et al.* reported on the analysis of the $A-X$ electronic transition with high-resolution near infrared spectroscopy.²¹

Species containing a transition metal atom such as chromium have hardly been studied with microwave spectroscopy.^{1,2} In the present study we have observed the rotational spectrum of the high-spin molecular species, CrCl, generated in a dc discharge plasma and have precisely determined its molecular constants, when no high-resolution works were available.²²

II. EXPERIMENT

The measurement was carried out using a 100 kHz source-modulated microwave spectrometer, which had been described in a previous paper.²³ Millimeter-wave radiation was generated by a tripler driven by klystrons. A liquid He cooled InSb detector was employed to detect microwave power. A free space absorption cell was a 2 m long, 10 cm diameter Pyrex tube, which contained a pair of cylindrical stainless-steel plates as electrodes for discharge. The cell was wound by a copper wire, through which dc current flowed to compensate the Earth's magnetic field.

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The spectrum of the CrCl radical was incidentally observed,²² while we were searching for rotational transition lines of AlCl in the $a^3\Pi$ first excited electronic state by dc glow discharging in a mixture of AlCl₃ vapor and He gas. The experimental conditions on searching were 60 mTorr of the total pressure and 600 mA of the discharge current which was optimized for the search of the AlCl lines. In the region of 267–272 GHz, we found 6 paramagnetic lines of similar intensity separated by about 50 MHz. Each line did not show up any further splittings due to magnetic and chlorine nuclear quadrupole hyperfine interactions. It seemed that the frequency separation was not appropriate for AlCl in the excited triplet electronic state, where the separation would be dependent on the spin sublevels. The carrier was guessed through the following chemical evidence. When we used AlBr₃ instead of AlCl₃, these lines could not be observed. On the other hand, use of chlorine-containing volatile molecules, such as CCl₄ and SiCl₄, yielded the same six line spectrum, whose intensity was weaker than that with AlCl₃. This suggested that the six lines probably arose from a single species and that the plausibly new paramagnetic molecule contained a chlorine atom and an atom other than aluminum.

We then suspected that rather wide frequency separation resulted from fine structure in a high-spin species, which would be possible for a transition metal compound with several d electrons. The transition metal atom could only be supplied into the system through sputtering of stainless steel discharge electrodes, sole metal components in the cell. Stainless steel has nominal composition of Fe 70%, Cr 20%, and Ni 10%. So the metal atom having the ground or low-lying excited $^6\Sigma$ state was supposed to be either Cr or Fe. The plausible hyperfine interaction contribution decreases with increasing J and the splittings are not so large for high J transitions in the submillimeter-wave region. The Λ -doubling affects the pure rotational spectrum differently in each spin substate. Thus the observation of the rotational spectrum in various frequency regions yields a clue on the electronic state.

Experimental conditions were optimized for these lines: $P(\text{AlCl}_3)=5$ mTorr, $P(\text{He})=50$ mTorr, and discharge current of 700 mA. The cell was kept at 50 °C to prevent AlCl₃ from condensing on the cell wall. Higher temperature made the signal intensity stronger but caused the unstable discharge, apparently as gases adsorbed on the cell wall desorbed intermittently.

We observed a spectral pattern comprising equally intense 6 lines nearly every 10 GHz. Figure 1 shows a schematic pattern of the spectrum at eight different frequency regions. The frequency separations varied only slightly with rotational quantum numbers and were observed to be 30–80 MHz. This experimental finding of equal intensity and separation suggested the $^6\Sigma$ symmetry of the electronic state.

Inference of the electronic state gave no definite conclusion yet on what the molecular species was. To identify the molecule containing a chlorine atom we attempted to observe the rotational spectrum of a less abundant isotopic species (one-third of the parent species). For the two candidates of CrCl and FeCl we calculated the rotational constants and other spectroscopic constants of the chlorine isotopomer,

FIG. 1. A schematic spectral pattern of CrCl rotational transition shows that the separation between the component lines is nearly independent of rotational angular momentum. The splitting is thus due to fine structure interaction.

Cr³⁷Cl and Fe³⁷Cl, scaled from those of the ³⁵Cl species by the respective reduced masses.²⁴ We predicted the transition frequencies for the two molecules and were able to observe the $N=27-26$, $J=49/2-47/2$ transition in the region where the spectrum of the chromium species was expected to appear. Subsequent observation for other J transitions was critical for the determination of the carrier as CrCl in the $^6\Sigma^+$ electronic ground state. This assignment of CrCl in this system²² later stimulated the observation of the rotational spectrum of FeCl by Tanimoto *et al.*²⁵ and independently by Allen *et al.*²⁶

In the frequency region between 200 and 270 GHz, lines of the Cr³⁵Cl radical were observed and assigned to rotational transitions with $N=20-19$ to $27-26$. Figure 2 illustrates a typical transition line of Cr³⁵Cl near 230.2 GHz. It also shows that on application of a magnetic field of 50 G the CrCl line disappears by Zeeman effect. The remaining line on the low frequency side is due to Al³⁵Cl in a highly excited vibrational state of $v=11$, which lies at about 5600 cm⁻¹ in energy. For the Cr³⁷Cl species 21 lines were observed in the frequency region of 203 to 262 GHz. Tables I and II list the observed transition frequencies for the Cr³⁵Cl and Cr³⁷Cl species, respectively, along with their assignment.

III. ANALYSIS

The measured transition frequencies were analyzed by a least-squares method. Since the CrCl radical in its $X^6\Sigma^+$ ground state has five unpaired electrons, the analysis was

FIG. 2. A typical transition line of Cr^{35}Cl near 230.2 GHz. On application of a magnetic field the CrCl line disappears by the Zeeman effect. The remaining line on the low frequency side is due to diamagnetic aluminum monochloride in a vibrationally excited state of $v=11$ in the electronic ground state.

carried out using the Hamiltonian of Hund's case (a) or (b) with the inclusion of the spin-rotation and spin-spin interactions:

$$H = H_R + H_{SR} + H_{SS}, \quad (1)$$

where H_R , H_{SR} , and H_{SS} are Hamiltonians for the rotation, spin-rotation, and spin-spin interactions, respectively. The explicit forms of the various terms are as follows:

$$H_R = B\mathbf{N}^2 - D\mathbf{N}^4, \quad (2)$$

$$H_{SR} = \gamma(\mathbf{N} \cdot \mathbf{S}) + \gamma_D(\mathbf{N} \cdot \mathbf{S})\mathbf{N}^2 + \gamma_H(\mathbf{N} \cdot \mathbf{S})\mathbf{N}^4, \quad (3)$$

and

$$H_{SS} = \frac{2}{3}\lambda(3S_z - \mathbf{S}^2) + \frac{2}{3}\lambda_D(3S_z - \mathbf{S}^2)\mathbf{N}^2. \quad (4)$$

The matrix elements of the Hamiltonian in a case (a) basis set were given by Ram *et al.*¹¹ and used in our case (a) treatment. The higher-order term in the spin-orbit interaction $H_{SO}^{(4)}$ was also included in the analysis:⁹

$$H_{SO}^{(4)} = \frac{1}{12}\theta[35S_z^2 - 30\mathbf{S}^2S_z^2 + 25S_z^2 - 6\mathbf{S}^2 + 3\mathbf{S}^4]. \quad (5)$$

The molecular constants determined are given in Table III. Calculated frequencies are listed in Tables I and II. The standard deviations of the fit are 39 and 41 kHz for Cr^{35}Cl and Cr^{37}Cl , respectively.

On the other hand, the more appropriate basis set for molecules in a Σ state will be a Hund's case (b) basis set. In a Σ state, electron spins do not couple to the molecular axis, but to the axis of rotation through a weak magnetic field generated by the end-over-end rotation of the molecule. We also calculated the matrix elements in a case (b) representation. The matrix elements of the spin-rotation interaction for a ${}^6\Sigma$ state in this basis are

$$\begin{aligned} \langle N' SJ' | H_{SR} | NSJ \rangle = & \frac{1}{2}[\gamma + \gamma_D N(N+1)] \\ & \times [J(J+1) - N(N+1) \\ & - S(S+1)] \delta_{N'N} \delta_{J'J}, \end{aligned} \quad (6)$$

where $\delta_{N'N}$ is Kronecker's delta and those of the spin-spin interaction are

$$\begin{aligned} \langle N' SJ' | H_{SS} | NSJ \rangle = & -\frac{2\sqrt{30}}{2}\lambda_{\text{eff}}(-1)^{S+N+J} \begin{Bmatrix} J & N & S \\ 2 & S & N \end{Bmatrix} \begin{Bmatrix} 1 & 1 & 2 \\ S & S & S \end{Bmatrix} S(S+1)(2S+1) \sqrt{\frac{N(N+1)(2N+1)}{(2N-1)(2N+3)}} \delta_{N',N} \\ & - 2\sqrt{5}\lambda_{\text{eff}}(-1)^{S+N+J} \begin{Bmatrix} J & N+2 & S \\ 2 & S & N \end{Bmatrix} \begin{Bmatrix} 1 & 1 & 2 \\ S & S & S \end{Bmatrix} S(S+1)(2S+1) \sqrt{\frac{(N+1)(2N+1)}{(2N+3)}} \delta_{N',N+2} \\ & - 2\sqrt{5}\lambda_{\text{eff}}(-1)^{S+N+J} \begin{Bmatrix} J & N-2 & S \\ 2 & S & N \end{Bmatrix} \begin{Bmatrix} 1 & 1 & 2 \\ S & S & S \end{Bmatrix} S(S+1)(2S+1) \sqrt{\frac{N(N-1)}{(2N-1)}} \delta_{N',N-2}. \end{aligned} \quad (7)$$

The term H_{SS} possesses off-diagonal elements with respect to S_z . The term in the curly brackets in this expression represents a 6- j symbol. The coefficient λ_{eff} is not a constant in the individual matrix elements but includes a term dependent on N , since the molecule suffers from the perturbation due to the centrifugal distortion. This was treated by Mizushima and Hill²⁷ for the analysis of the O_2 microwave spectrum. The general expression for λ_{eff} is as follows:

$$\lambda_{\text{eff}} = \lambda + \lambda_D \mathbf{N}^2. \quad (8)$$

The matrix elements of the spin-spin coupling constant λ_{eff} are thus seen to be

$$\lambda_{\text{eff}} \equiv \lambda + N(N+1)\lambda_D \quad (9)$$

for the $\langle N|N \rangle$ elements, and

$$\lambda_{\text{eff}} \equiv \lambda + (N^2 + N + 1)\lambda_D \quad (10)$$

for the $\langle N-1|N+1 \rangle$ elements.

The matrix elements of the spin-orbit interaction $H_{SO}^{(4)}$ were given by the equation:

TABLE I. Observed transitions of $^{52}\text{Cr}^{35}\text{Cl}$ in case (a) and (b).

N'	J'	—	N''	J''	Obs. Freq. /MHz	Calc. Freq.(a) /MHz	o-c ^a (a) /kHz	Calc. Freq.(b) /MHz	o-c ^a (b) /kHz
20	35/2		19	33/2	200127.714	200127.773	−59	200127.735	−21
20	37/2		19	35/2	200205.627	200205.617	10	200205.666	−39
20	39/2		19	37/2	200240.420	200240.442	−22	200240.451	−31
20	41/2		19	39/2	200274.359	200274.423	−64	200274.389	−30
20	43/2		19	41/2	200328.678	200328.697	−19	200328.683	−5
20	45/2		19	43/2	200411.925	200411.909	16	200411.947	−22
21	37/2		20	35/2	210125.605	210125.619	−14	210125.589	16
21	39/2		20	37/2	210202.170	210202.127	43	210202.158	12
21	41/2		20	39/2	210240.094	210240.123	−29	210240.122	−28
21	43/2		20	41/2	210276.969	210276.968	1	210276.947	22
21	45/2		20	43/2	210332.150	210332.126	24	210332.123	27
21	47/2		20	45/2	210414.047	210414.015	32	210414.039	8
22	39/2		21	37/2	220122.150	220122.186	−36	220122.166	−16
22	41/2		21	39/2	220197.496	220197.498	−2	220197.516	−20
22	43/2		21	41/2	220238.171	220238.166	5	220238.155	16
22	45/2		21	43/2	220277.481	220277.493	−12	220277.483	−2
22	47/2		21	45/2	220333.426	220333.455	−29	220333.461	−35
22	49/2		21	47/2	220414.201	220414.206	−5	220414.217	−16
23	41/2		22	39/2	230117.280	230117.289	−9	230117.283	−3
23	43/2		22	41/2	230191.606	230191.530	76	230191.537	69
23	45/2		22	43/2	230234.510	230234.465	45	230234.446	64
23	47/2		22	45/2	230275.954	230275.956	−2	230275.957	−3
23	49/2		22	47/2	230332.657	230332.651	6	230332.665	−8
23	51/2		22	49/2	230412.466	230412.420	46	230412.416	50
24	43/2		23	41/2	240110.816	240110.769	47	240110.777	39
24	45/2		23	43/2	240184.025	240184.043	−18	240184.042	−17
24	47/2		23	45/2	240228.912	240228.916	−4	240228.890	22
24	49/2		23	47/2	240272.355	240272.305	50	240272.317	38
24	51/2		23	49/2	240329.683	240329.670	13	240329.692	−9
24	53/2		23	51/2	240408.553	240408.586	−33	240408.567	−14
25	45/2		24	43/2	250102.523	250102.482	41	250102.507	16
25	47/2		24	45/2	250174.899	250174.881	18	250174.874	25
25	49/2		24	47/2	250221.402	250221.422	−20	250221.390	12
25	51/2		24	49/2	250266.552	250266.483	69	250266.505	47
25	53/2		24	51/2	250324.483	250324.461	22	250324.490	−7
25	55/2		24	53/2	250402.618	250402.635	−17	250402.599	19
26	47/2		25	45/2	260092.320	260092.297	23	260092.342	−22
26	49/2		25	47/2	260163.819	260163.901	−82	260163.890	−71
26	51/2		25	49/2	260211.829	260211.886	−57	260211.848	−19
26	53/2		25	51/2	260258.425	260258.426	−1	260258.459	−34
26	55/2		25	53/2	260316.963	260316.967	−4	260317.001	−38
26	57/2		25	55/2	260394.441	260394.493	−52	260394.439	2
27	49/2		26	47/2	270079.954	270080.095	−141 ^b	270080.159	−205 ^b
27	51/2		26	49/2	270150.719	270150.972	−253 ^b	270150.958	−239 ^b
27	53/2		26	51/2	270200.110	270200.213	−103 ^b	270200.169	−59 ^b
27	55/2		26	53/2	270247.931	270248.068	−137 ^b	270248.110	−179 ^b
27	57/2		26	55/2	270307.047	270307.126	−79 ^b	270307.166	−119 ^b
27	59/2		26	57/2	270383.795	270384.083	−288 ^b	270384.011	−216 ^b

^aObserved minus calculated transition frequencies. b^bRough measurement. Not included in the least-squares analysis.

$$\begin{aligned}
\langle N' \Lambda' S J' | H_{\text{SO}}^{(4)} | N \Lambda S J \rangle = & \frac{\theta}{24} (-1)^{N+S+J} \begin{Bmatrix} J & S & N' \\ 4 & N & S \end{Bmatrix} (-1)^{N'-\Lambda'} \begin{pmatrix} N' & 4 & N \\ -\Lambda & 0 & \Lambda \end{pmatrix} \sqrt{(2N'+1)(2N+1)} \\
& \times \sqrt{(2S-3)(2S-2)(2S-1)2S(2S+1)(2S+2)(2S+3)(2S+4)(2S+5)} \delta_{J',J}. \quad (11)
\end{aligned}$$

TABLE II. Observed transitions of $^{52}\text{Cr}^{37}\text{Cl}$.

N'	J'	—	N''	J''	Obs. Freq. /MHz	Calc. Freq.(a) /MHz	$o-c^a$ (a) /kHz	Calc. Freq.(b) /MHz	$o-c^a$ (b) /kHz
21	43/2		20	41/2	203503.423	203503.457	−34	203503.425	−2
21	45/2		20	43/2	203558.246	203558.271	−25	203558.257	−11
21	47/2		20	45/2	203636.106	203636.081	25	203636.116	−10
22	39/2		21	37/2	213028.106	213028.131	−25	213028.098	8
22	41/2		21	39/2	213099.728	213099.693	35	213099.735	−7
22	43/2		21	41/2	213141.251	213141.272	−21	213141.266	−15
22	45/2		21	43/2	213182.050	213182.044	6	213182.029	21
22	47/2		21	45/2	213237.523	213237.522	1	213237.523	0
22	49/2		21	47/2	213314.376	213314.359	17	213314.378	−2
23	41/2		22	39/2	222701.856	222701.892	−36	222701.871	−15
23	43/2		22	41/2	222772.565	222772.530	35	222772.555	10
23	45/2		22	43/2	222816.084	222816.088	4	222816.071	13
23	47/2		22	45/2	222858.705	222858.711	−6	222858.711	−6
23	49/2		22	47/2	222914.825	222914.797	28	222914.809	16
23	51/2		22	49/2	222990.804	222990.793	11	222990.795	9
27	49/2		26	47/2	261380.333	261380.280	53	261380.329	4
27	51/2		26	49/2	261447.980	261447.999	−19	261447.980	0
27	53/2		26	51/2	261496.991	261497.038	−47	261496.985	6
27	55/2		26	53/2	261545.128	261545.094	34	261545.146	−18
27	57/2		26	55/2	261603.191	261603.145	46	261603.193	−2
27	59/2		26	57/2	261676.669	261676.745	−76	261676.666	3

^aObserved minus calculated transition frequencies.

We calculated energy levels by diagonalizing the Hamiltonian matrix and determined the molecular constants by a least-squares fit to the observed transition frequencies. The calculated frequencies from the case (b) analysis are included in Tables I and II. The standard deviations of the fit are 32 and 13 kHz for Cr^{35}Cl and Cr^{37}Cl , respectively. The molecular constants in the case (b) are given in the fourth and fifth columns of Table III.

IV. RESULTS AND DISCUSSION

We have observed the rotational spectrum for both chlorine isotopic species of the high-spin radical CrCl and determined its precise molecular constants. The ground-state rotational constant B_0 agrees with the near-infrared value²¹ within their 3 σ , when their B_e value is converted into B_0 using the vibration-rotation interaction constant α . The rotational constants B_0 give the interatomic distances of $r_0 = 2.197\,140\,3\,(9)\,\text{\AA}$ and $2.197\,084\,6\,(9)\,\text{\AA}$ for Cr^{35}Cl and Cr^{37}Cl , respectively. This bond length is slightly shorter than the Cr–Cl distance of monomeric chromium dichloride ($2.207\,(10)\,\text{\AA}$) determined by Hargittai *et al.* with electron diffraction in vapor phase.²⁸ The Cr–Cl distance for CrCl_2

in a nitrogen matrix, on the other hand, was determined with x-ray absorption fine structure (XAFS) spectroscopy to be $2.257\,(2)\,\text{\AA}$,²⁹ substantially longer than the gas phase value. The corresponding interatomic distance in the crystalline compound CrCl_3 is $2.340\text{--}2.347\,\text{\AA}$ for the monoclinic crystal structure at room temperature.³⁰ It seems that addition of a chlorine atom to the chromium atom causes the elongation of the metal-halide bond length. The r_0 bond length of CrCl is about $0.02\,\text{\AA}$ longer than that of FeCl ($r_0 = 2.176\,987(1)\,\text{\AA}$).

When the present ground state rotational constant is combined with the vibration-rotation interaction constant α ($29.13\,\text{MHz}$) reported by Bencheikh *et al.*,²¹ the equilibrium interatomic distance is determined to be $2.193\,952\,(2)\,\text{\AA}$.

The equilibrium bond length can also be estimated from the isotopically invariant Dunham constant U_{01} . This constant is estimated from the rotational constants for two isotopic species under the assumption that the anharmonicity in the potential function contributes negligibly to the lower order Dunham constants. This procedure yields the equilibrium bond length of $2.193\,78\,(1)\,\text{\AA}$. This distance is about $0.000\,18\,\text{\AA}$ shorter than the value derived above. Thus the

TABLE III. Molecular constants of the CrCl radical.

	Hund's Case (a)		Hund's Case (b)	
	$^{52}\text{Cr}^{35}\text{Cl}$	$^{52}\text{Cr}^{37}\text{Cl}$	$^{52}\text{Cr}^{35}\text{Cl}$	$^{52}\text{Cr}^{37}\text{Cl}$
B_0/MHz	5009.34695(81)	4847.8524(10)	5009.34569(69)	4847.85100(32)
D_0/kHz	3.52892(72)	3.30613(83)	3.52846(60)	3.30573(26)
γ/MHz	65.534(22)	63.462(31)	65.646(26)	63.607(13)
γ_D/kHz	−0.0839(87)	−0.105(11)	−0.151(12)	−0.1849(57)
λ/MHz	7992.5(27)	7997.1(39)	7981.0(25)	7981.5(14)
λ_D/kHz	−13.214(54)	−12.752(78)	−13.249(45)	−12.746(24)
θ/MHz	−2.11(82)	−2.7(12)	−3.24(63)	−3.86(34)

effect of anharmonicity on the equilibrium distance was of the order of 0.000 2 Å in this molecule. This procedure can be used to estimate approximate r_e from the data for two isotopomers, when the constant α is not available.

The fundamental vibrational frequency ω_e is related to the equilibrium rotational constant B_e and the centrifugal distortion constant D_e through the relation²⁴ $\omega_e = 2\sqrt{B_e^3/D_e}$. This relation is approximately valid, even when the equilibrium constants are replaced by the effective constants in the ground state; thus the vibrational frequencies ω_e for Cr³⁵Cl and Cr³⁷Cl are estimated to be 398.2 and 391.7 cm⁻¹, respectively. The former is favorably compared with the frequency 396.662 cm⁻¹ from the electronic spectroscopy.²¹

The spin-rotation interaction constant γ determined in the present study is considerably smaller than that for the CrF radical. The ratio γ/B for the CrCl radical is about 40% of that for CrF. The spin-rotation interaction arises from the microscopic electron spin-nuclear rotation interaction $\gamma^{(1)}$ and from second-order interactions with other electronic states $\gamma^{(2)}$.^{31,32} In heavy molecules the second-order contribution is dominant. A few electronic states have been assessed experimentally by electronic spectroscopy and theoretically by density functional theory (DFT) and ligand field theory (LFT) treatments.²¹ The electronic energy level scheme of CrCl and CrF resembles each other and the lowest excited state is in both molecules the $B^6\Pi$ state, which lies slightly below the $A^6\Sigma^+$ state, the upper state of the electronic transition analyzed experimentally. If the single perturber approximation is valid and the interacting state is the lowest $^6\Pi$ state, the difference in γ/B for both molecules amounts to about 10%. This suggests that the γ constant results from the interaction with various higher energy states in addition to the experimentally known lower states.

The observed spin-spin interaction constant of CrCl (7 981.0 MHz) is about half the value for CrF (16 162.4 MHz).¹⁸ The spin-spin interaction also results from a direct first-order interaction and second-order spin-orbit interactions. The second-order contribution from the spin-orbit interaction will be dominant in heavy molecules like CrCl. Experimentally or theoretically assessed electronic excited $^4\Sigma^+$ states^{19,21,33} do not interact with the ground state by the spin-orbit interaction because of the $\pm$ reflection symmetry selection rule. The interaction with the nearest $B^6\Pi$ state cannot explain the difference in λ for both molecules, since the transition energies to this excited state from the ground state do not differ significantly. The experimentally unknown $^4\Sigma^-$ state may be important for this interaction.

All observed lines are single with no magnetic and nuclear quadrupole hyperfine splitting observed. Since the CrCl species has a highly ionic character, represented as Cr⁺Cl⁻, as exemplified by the molecular orbital calculation,²¹ the five unpaired electrons probably reside mainly near the chromium nucleus and one electron is transferred to the chlorine atom. Consequently the chlorine nucleus was approximately surrounded by the spherical distributions of the electrons and hence the quadrupole hyperfine interaction becomes small. Magnetic hyperfine interaction depends on the distance between the unpaired electron and the nucleus with a nuclear spin. In the ionic structure suggested above

the relevant distance is rather large and also the magnetic hyperfine structure is small. This is consistent with the appearance of the spectral lines as a single line in the observed frequency regions.

In the present study the least-squares analysis was made in two ways, in terms of the case (a) and (b) basis sets. Initial analysis was made using the wave functions in Hund's case (a). This analysis showed that addition of observed transitions in the higher frequency region into the analysis affected the lower-order molecular constants as well as higher order centrifugal distortion corrections, although the residuals remained in the same order of magnitude. We thus calculated the rotational energy in the case (b) basis. In this case the anomalous behavior in the least-squares analysis was not detected. The resulting residuals were slightly smaller as compared with the case (a) basis calculations when the same order of the centrifugal corrections were included.

As described in the Experiment we used AlCl₃ to observe the rotational spectrum of CrCl. The cell temperature was maintained at about 50 °C. Replacement of AlCl₃ with more volatile compounds required the cell cooled to temperatures below the melting point of the compounds. This may mean that some precursor molecules formed on the surface are involved in the formation of transition metal compounds.

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