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Electronic properties of CrF and CrCl in the $X {}^{6}\Sigma^{+}$ state: Observation of the halogen hyperfine structure by Fourier transform microwave spectroscopy

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The rotational spectra of the CrF and CrCl radicals in the $X^{6}\Sigma^{+}$ state were observed by employing a Fourier transform microwave spectrometer. The CrF and CrCl radicals were generated by the reaction of laser-ablated Cr with F₂ and Cl₂, respectively, diluted in Ar. A chromium rod made of chromium powder pasted with epoxy resin was ablated by a Nd:YAG laser. Rotational transitions were measured in the region between 8 and 26 GHz. Several hyperfine constants due to the halogen nuclei were determined by a least-squares analysis. The electronic properties of CrF and CrCl were derived from their hyperfine constants and were compared with those of other 3*d* transition metal monohalides: TiF, MnF, FeF, CoF, NiF, and FeCl. © 2004 American Institute of Physics. [DOI: 10.1063/1.1691021]

I. INTRODUCTION

Transition metal compounds often have high electronorbital and electron-spin angular momenta due to their *d*-electrons. The *d*-electrons cause a lot of low lying electronically excited states. Existence of such electronic states and their substates results in remarkably complex spectra to be observed by high resolution spectroscopic methods. It is quite complicated to analyze them and to understand the physical significance of spectroscopic constants. Since it is difficult to produce the transition metal compounds efficiently in the gas phase, high sensitivity spectrometers have been employed to study electronic spectra of such species. Moreover, most of the works carried out so far have been those of hydrides and oxides. Only a few works have been reported for other species like halides, nitrides, carbides, etc.

The diatomic transition metal halides MX (M = transition metal; X=F, Cl, Br, and I) are highly ionic species represented as M^+X^- . All unpaired electrons mainly exist on the metal atom because of the closed shell structure of the X^- ion. Thus their electronic states strongly reflect the character of the metallic ion, M^+ . It is interesting to compare electronic structures of MF, MCl, MBr, and MI, but there were only a limited number of works except for the ${}^{1}\Sigma^{+}$ species like CuX and AgX until several years ago.

Chromium monohalides (CrX) are the species that have scarcely been studied by any spectroscopic methods. Recently the electronic spectra of CrF and CrCl have been studied by a few groups. The first spectroscopic study on CrF was reported by Dubov *et al.*, who observed the $A^{6}\Sigma^{+}-X^{6}\Sigma^{+}$ transition with high resolution and carried out a rotational analysis.^{1,2} Devore *et al.*³ studied chemiluminescence of CrF and obtained low-resolution spectra of several electronic bands. Launila and his associates^{4,5} reported a high resolution Fourier transform spectrum of the A-Xband. Subsequently, they observed the $B^{6}\Pi - X^{6}\Sigma^{+}$ band as well as the $A^{6}\Sigma^{+} - X^{6}\Sigma^{+}$ band of CrF.⁶ Pure rotational transitions of CrF were observed by Okabayashi and Tanimoto⁷ in the discharge plasma of CF₄ diluted in He with chromium powder laid on an electrode plate.

For CrCl, the first reliable low-resolution electronic spectrum was observed by Rao and Rao.⁸ More lately, Oike *et al.* detected the pure rotational spectrum of CrCl in the discharge plasma of AlCl₃ diluted in He using stainless steel electrodes.^{9,10} Launila and his co-workers observed a high resolution Fourier transform spectrum of the $A \, {}^{6}\Sigma^{+} - X \, {}^{6}\Sigma^{+}$ and $B \, {}^{6}\Pi - X \, {}^{6}\Sigma^{+}$ bands of CrCl.^{11,12} Several theoretical calculations were also published for CrF and CrCl in the ground and low-lying electronic excited states.^{11–13}

Observation of the hyperfine structure is a powerful method to study the electronic property in the electronic state concerned,¹⁴ because the hyperfine interaction is quite sensitive to the environment where valence electrons move. Metal monohalides, however, are generally so ionic that their hyperfine splittings due to the halogen nuclei are often too small to be observed with a conventional millimeter-wave spectrometer. Indeed, the previous millimeter-wave studies on CrF and CrCl (Refs. 7, 9, 10) did not observe their hyperfine structures. In the present paper, we report results obtained by Fourier transform microwave (FTMW) spectroscopy, which is higher-resolution method than a conventional millimeter-wave spectroscopy, on the CrF and CrCl radicals generated by the laser-ablation technique. Their electronic properties have been determined from the hyperfine con-

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FIG. 1. Schematic diagrams of (a) a normal laser-ablation nozzle for CrCl generation and (b) a laser-ablation nozzle with pulsed discharge for CrF generation.

stants and discussed through a comparison with those of other metal monohalides.

II. EXPERIMENT

The present experiment was carried out using a Fourier transform microwave spectrometer with a laser-ablation system at University of Tokyo.^{15,16} The CrCl radical was generated in an adiabatic expansion of laser-vaporized Cr with an Ar stream containing about 0.1% of Cl_2 with a conventional laser ablation nozzle source illustrated in Fig. 1(a). A chromium target rod was formed from chromium powder pasted with epoxy resin. As a power source of vaporization, the second harmonic (532 nm) of a Nd:YAG laser was employed with 40 mJ/pulse. Using this system, the CrCl signals were strong enough to be observed easily. A typical observed spectrum is illustrated in Fig. 2. When Cl_2 gas was replaced by CCl_4 vapor, the CrCl signal was also observed but was somewhat weaker. In total, 25 lines of CrCl were observed in the region between 9 and 20 GHz.



FIG. 2. Observed N=2-1, J=4.5-3.5 transition with the ³⁷Cl hyperfine structure of Cr³⁷Cl, which is generated by the reaction of laser-ablated Cr with 0.1% Cl₂ diluted in Ar without discharge. The spectrum is obtained after 240 shots of accumulation.



FIG. 3. Observed N=1-0, J=3.5-2.5, F=4-3 transition of CrF generated by the reaction of laser-ablated Cr with 0.1% F₂ and 2% He diluted in Ar (a) without discharge and (b) with discharge. Each spectrum is obtained after 200 shots of accumulation.

For the CrF generation, 0.1% F2 and 2% He diluted with Ar was used as a precursor of fluorine. However, the ablation system mentioned above did not give strong signal of CrF. When F_2 gas was replaced by CF_4 gas, the CrF signal was not observed at all. In order to improve the signal strength of CrF, we adopted another type of an ablation nozzle with simultaneous electrical discharge¹⁷ shown in Fig. 1(b). This combined production system provided about three times stronger signal of CrF than the conventional laser ablation system as shown in Fig. 3. The timing chart of the FTMW spectrometer is given in Fig. 4. The line strength of CrF is insensitive to the change in laser-shot timing with respect to the pulsed discharge. Using this system, CF₄ gas as well as F_2 gas gave the CrF signal, but the latter gave much stronger signal. In total, three lines of CrF were observed in the region between 22 and 26 GHz.



FIG. 4. Timing chart of the FTMW spectrometer with both laser ablation and electrical discharge.

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TABLE I. Molecular constants of CrF and CrCl in the $X {}^{6}\Sigma^{+}$ states.^a

	CrF	Cr ³⁵ Cl	Cr ³⁷ Cl	
B ₀	11369.61702(48)	5009.34629(76)	4847.85171(75)	MHz
D_0	15.06022(76)	3.52879(68)	3.30602(63)	kHz
H_0	-7.70^{b}	0.0^{b}	0.0^{b}	mHz
λ	16157.49(25)	7989.429(79)	7990.290(73)	MHz
λ_D	-15.500(44)	-13.270(50)	-12.776(57)	kHz
γ	408.557(10)	65.5799(44)	63.4714(45)	MHz
γ_D	-0.788(10)	-0.1296(33)	-0.1261(33)	kHz
γ_S	-8.06(72)	-4.06(70)	-4.85(82)	kHz
θ	-4.80(27)	-3.245(10)	-3.2528(97)	MHz
b_F	20.5(32)	-2.6710(52)	-2.2237(39)	MHz
с	-51.49(78)	-6.717(25)	-5.585(18)	MHz
eQq	•••	-17.401(28)	-13.748(20)	MHz

^aValues in parentheses are one standard deviation.

^bFixed in the analysis.

III. ANALYSIS

The observed transition frequencies were analyzed by a least-squares analysis for Σ states using a case $(b)_{\beta J}$ coupling scheme.¹⁴ The Hamiltonian employed is

$$H_{\rm eff} = H_{\rm rot} + H_{\rm ss} + H_{\rm sr} + H_{\rm hf}, \tag{1}$$

where $H_{\rm rot}$ represents the rotational energy including the centrifugal distortion, H_{ss} the spin-spin interaction, H_{sr} the spin-rotation interaction, and $H_{\rm hf}$ the hyperfine interaction. In order to fit the data within experimental error, two extra higher order terms which do not appear in the electronic states of triplet or lower multiplicity were needed: the third order spin-rotation coupling term γ_S and the fourth order spin-orbit coupling term θ .^{18,19} As in Ref. 19, the basis set was truncated in the calculations at $\Delta N = \pm 4$ without loss in accuracy. Other matrix elements including the hyperfine interactions were cited from Ref. 14. The molecular constants were determined by a least squares calculation. In order to determine the molecular constants accurately, the least squares calculation was simultaneously carried out for the combined millimeter-wave^{7,9,10} and the present FTMW data. The FTMW data were subjected to the analysis with 100 times larger weights than the millimeter-wave data. The standard deviation of the fit was about 20 kHz for each species. The molecular constants determined are listed in Table I. The observed microwave frequencies and the residuals of the fit are summarized in Table II for CrF and Table III for CrCl. The residuals for CrF in Table II are zero for all the FTMW measurements, because two independent hyperfine parameters b_F and c were determined from three transition frequencies observed. However, even if the experimental errors were taken into account, the molecular constants determined by the least squares fit were affected only within their stan-

TABLE II. Observed transition frequencies of CrF in MHz.

N'-N"	J'-J''	F'-F''	Obs. Freq.	O-C ^a
1-0	3.5-2.5	3.0-2.0	22471.6995	0.000
1 - 0	3.5-2.5	4.0-3.0	22473.7032	0.000
2-1	0.5 - 1.5	1.0 - 2.0	25745.3591	0.000

^aObserved minus calculated frequency.

TABLE III. Observed transition frequencies of CrCl in MHz.

			Cr ³⁵ Cl		Cr ³⁷ Cl		
N'-N''	J'-J''	F'-F''	Obs. Freq.	O-C ^a	Obs. Freq.	O-C ^a	
1-0	3.5-2.5	2.0-1.0	9776.6689	0.0051	9516.5201	0.0016	
1 - 0	3.5-2.5	3.0-2.0	9776.2031	0.0004	9516.1605	0.0038	
1 - 0	3.5-2.5	3.0-3.0			9520.0175	-0.0035	
1 - 0	3.5-2.5	4.0-3.0	9776.8345	0.0011	9516.6666	0.0007	
1 - 0	3.5-2.5	5.0 - 4.0	9777.8688	-0.0065	9517.4953	-0.0012	
2 - 1	0.5 - 1.5	1.0 - 1.0	11079.4766	0.0018	10544.8231	-0.0036	
2 - 1	0.5 - 1.5	1.0 - 2.0	11085.0263	0.0023	10549.3519	0.0031	
2 - 1	0.5 - 1.5	2.0 - 2.0	11078.5297	-0.0007	10543.9359	-0.0002	
2 - 1	0.5 - 1.5	2.0 - 3.0	11081.1719	-0.0034	10546.1688	0.0006	
2 - 1	4.5-3.5	3.0-2.0	19931.1515	-0.0079	19323.7664	-0.0009	
2 - 1	4.5-3.5	4.0-3.0	19930.9807	0.0085	19323.6201	-0.0016	
2 - 1	4.5-3.5	5.0 - 4.0	19931.4387	-0.0036	19324.0005	0.0019	
2 - 1	4.5-3.5	6.0 - 5.0	19932.0832	0.0030	19324.5066	-0.0014	

^aObserved minus Calculated frequency.

dard errors. This was because the hyperfine constants were indirectly restricted by the millimeter-wave data through the simultaneous least squares determination of the hyperfine and other constants.

IV. RESULTS AND DISCUSSION

Hyperfine splittings arising from the nuclear spin of fluorine and chlorine were observed for CrF and CrCl, respectively. The hyperfine parameters of Frosch and Foley,²⁰ a, b_F and c, are represented as

$$a = 2\,\mu_B g_N \mu_N \frac{1}{\Lambda} \sum_i l_{iz} \left\langle \frac{1}{r_i^3} \right\rangle_o, \qquad (2)$$

$$b_F = \frac{8\pi}{3} g_s \mu_B g_N \mu_N \frac{1}{n} \sum_i \langle |\Psi(0)_i|^2 \rangle_s, \qquad (3)$$

and

$$c = \frac{3}{2} g_s \mu_B g_N \mu_N \frac{1}{n} \sum_i \left\langle \frac{3 \cos^2 \theta_i - 1}{r_i^3} \right\rangle_s, \tag{4}$$

where *n* refers to the number of unpaired electrons. In the present study, however, the Frosch and Foley *a* hyperfine parameter was not determined because the *a* constant is meaningless in the Σ electronic state without an electronic orbital angular momentum.

The electron configuration of CrF is supposed to be $(\operatorname{core})(9\sigma)^1(1\delta)^2(4\pi)^2$, and the unpaired electrons belong to the 9σ , 1δ , and 4π orbitals. The 1δ orbital is essentially the $3d(\operatorname{Cr})$ orbital. The 4π orbital is mainly constructed from the $3d(\operatorname{Cr})$ orbital but includes small amounts of the $4p(\operatorname{Cr})$ and $2p(\operatorname{F})$ orbitals. The 9σ and 10σ orbitals mainly consist of the $4s(\operatorname{Cr})$ and $3d(\operatorname{Cr})$ orbitals, respectively, but includes small amounts of the $2s(\operatorname{F})$ and $2p(\operatorname{F})$ orbitals. Thus, the hyperfine constant b_F is associated with the $2s(\operatorname{F})$ orbital included in the 9σ orbital. Similarly, the parameter *c* represents the contribution of the $2p(\operatorname{F})$ orbitals to the 9σ and 4π orbitals.

The $b_F(F)$ and c(F) constants of CrF are related to the atomic constants A(F) = 52870 and P(F) = 4400 MHz, re-

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spectively, listed in Ref. 21. These hyperfine parameters are thus simplified to the following approximate equations:

$$b_{F}(\mathbf{F}) = \frac{8\pi}{3} g_{s} \mu_{B} g_{N} \mu_{N} \frac{1}{5} [\langle |\Psi(0)|^{2} \rangle_{9\sigma} + 2 \langle [\Psi(0)]^{2} \rangle_{4\pi} + 2 \langle |\Psi(0)|^{2} \rangle_{1\delta}] = \frac{8\pi}{3} g_{s} \mu_{B} g_{N} \mu_{N} \frac{1}{5} [c_{9\sigma}^{F(2s)} \langle |\Psi(0)|^{2} \rangle_{2s\sigma(\mathbf{F})}] \simeq \left[\frac{c_{9\sigma}^{F(2a)}}{5} \right] A(\mathbf{F}),$$
(5)

and

$$c(\mathbf{F}) = \frac{3}{2} g_s \mu_B g_N \mu_N \frac{1}{5} \left[\left\langle \frac{3\cos^2 \theta - 1}{r^3} \right\rangle_{9\sigma} + 2 \left\langle \frac{3\cos^2 \theta - 1}{r^3} \right\rangle_{1\delta} + 2 \left\langle \frac{3\cos^2 \theta - 1}{r^3} \right\rangle_{4\pi} \right]$$
$$= \frac{3}{10} g_s \mu_B g_N \mu_N \left[c_{9\sigma}^{F(2p)} \left\langle \frac{3\cos^2 \theta - 1}{r^3} \right\rangle_{2p\sigma(\mathbf{F})} + 2 c_{4\pi}^{F(2p)} \left\langle \frac{3\cos^2 \theta - 1}{r^3} \right\rangle_{2p\pi(\mathbf{F})} \right]$$
$$= \frac{6}{25} \left[c_{9\sigma}^{F(2p)} - c_{4\pi}^{F(2p)} \right] P(\mathbf{F}), \tag{6}$$

where $c_{9\sigma}^{\rm F(2s)}$ shows $2s({\rm F})$ character in the 9σ orbital. The coefficients $c_{4\pi}^{\rm F(2p)}$ and $c_{9\sigma}^{\rm F(2p)}$ represent the contributions of the 2p(F) orbitals to the 4π and 9σ orbitals, respectively. The angular factor $\langle 3 \cos^2 \theta - 1 \rangle_{2p\pi}$ and $\langle 3 \cos^2 \theta - 1 \rangle_{2p\sigma}$ are taken to be -2/5 and 4/5, respectively.²¹ In order to reproduce the observed value $b_F(F) = 20.5$ MHz, we obtained $c_{9\sigma}^{F(2s)} = 0.19\%$. Similarly, the $c_{4\pi}^{F(2p)} - c_{9\sigma}^{F(2p)}$ value was derived to be 4.9% from c(F) = -51.49 MHz. These values are consistent with the conjecture that the 4π and 9σ orbitals are predominantly formed from the Cr atomic orbitals. This means that the fluorine atom exists almost as a closed shell F⁻ ion and is hardly associated with unpaired electrons.

Recently, there are several reports on hyperfine interactions for the fourth-row metal monofluoride radicals bearing unpaired electrons. Hyperfine analysis similar to that performed in the preceding paragraph was also carried out for several monofluorides to estimate the contributions of fluorine atomic orbitals to the relevant molecular orbitals. The results are summarized in Table IV. It is interesting that the $c_{4\pi}^{F(2p)}$ value of an early 3*d* transition metal monofluoride TiF $[(\operatorname{core})(9\sigma)^1(1\delta)^1(4\pi)^1]$ is very close to those of late 3d transition metal fluorides CoF $[(core)(9\sigma)^2(1\delta)^3(4\pi)^3]$ and NiF [(core)(9σ)²(1δ)⁴(4π)³]. The 4π orbitals of these three species are mainly composed of the $3d\pi(M)$ orbitals of the metals and partially of the $2p\pi(F)$ orbital of fluorine. This hybrid scheme also applies to the other fluorides (CrF, MnF, and FeF) in Table IV. Thus, their $c_{4\pi}^{F(2p)}$ values may reasonably be estimated to be about 5%.

The $c_{9\sigma}^{F(2s)}$ values of CaF [(core)(9 σ)¹], TiF, and CrF have similar values of about 0.2%. Since the 9σ orbitals of

TABLE IV. Contributions of the 2p and 2s orbitals of fluorine to the 4π , 9σ , and 10σ orbitals of the fourth-row metal monofluorides in %.²

		$c_{4\pi}^{\mathrm{F}(2p)}$	$c_{9\sigma}^{\mathrm{F}(2p)}$	$c_{10\sigma}^{\mathrm{F}(2p)}$	$c_{9\sigma}^{\mathrm{F}(2s)}$	$c_{10\sigma}^{\mathrm{F}(2s)}$	Ref.
CaF	$^{2}\Sigma^{+}$		0.80	•••	0.23		22
TiF	$^{4}\Phi$	4.6(1)	0.7(8)	•••	0.23(8)		23
CrF	${}^{6}\Sigma^{+}$	[5.6] ^b	[0.7] ^b	•••	0.19(9)		This work
MnF	$^{7}\Sigma^{+}$	[5] ^c	[1] ^c	[7] ^c	$[0.2]^{d}$	$[0.6]^{d}$	24
FeF	$^{6}\Delta$	[5] ^e	[1] ^e	[9] ^e	$[0.2]^{f}$	$[0.7]^{f}$	25
CoF	${}^{3}\Phi_{4}$	6.6	•••	•••		•••	26
NiF	$^{2}\Pi_{3/2}$	4.5(3)	•••	•••	•••		27

^aNumbers in parentheses in the table and footnotes b-f represent three standard deviations. Errors for CaF and CoF are small enough.

^bAssumed value to reproduce $c_{4\pi}^{F(2p)} - c_{9\sigma}^{F(2p)} = 4.9(2)$. See text. ^cAssumed value to reproduce $c_{4\pi}^{F(2p)} - c_{9\sigma}^{F(2p)} + c_{10\sigma}^{F(2p)} = 2.7(assumed)$. ^dAssumed value to reproduce $c_{9\sigma}^{F(2s)} + c_{10\sigma}^{F(2s)} = 0.79$. ^eAssumed value to reproduce $-c_{9\sigma}^{F(2p)} + c_{10\sigma}^{F(2p)} + c_{10\sigma}^{F(2p)} = 4.9(3)$.

^fAssumed value to reproduce $c_{9a}^{F(2s)} + c_{10a}^{F(2s)} = 0.87(3)$.

these three species are primarily constructed from the 4s(M)orbital, it is appropriate to assume that CaF, TiF, and CrF have similar $c_{9\sigma}^{F(2s)}$ values. Under this assumption, CaF, TiF, and CrF have possibly similar $c_{9\sigma}^{F(2p)}$ values. Indeed, the coefficient for CaF, 0.80%, is very close to that of TiF, 0.7(8)%, even though the experimental error of the latter is large. If the $c_{9\sigma}^{\mathrm{F}(2p)}$ value of CrF is assumed to be 0.7%, the $c_{4\pi}^{\mathrm{F}(2p)}$ value is obtained to be 5.6%, which is a reasonable value in comparison with those of other metal monofluorides (about 5%).

For MnF $[(\operatorname{core})(9\sigma)^{1}(1\delta)^{2}(4\pi)^{2}(10\sigma)^{1}]$ and FeF $[(\operatorname{core})(9\sigma)^{1}(1\delta)^{3}(4\pi)^{2}(10\sigma)^{1}]$, there is a more serious problem in the analysis of the hyperfine interaction. In an early 3d transition metal fluoride like TiF, the 9σ and 10σ orbitals have dominant contributions of the 4s(M) and $3d\sigma(M)$ orbitals, respectively. However, in a late 3d transition metal monofluoride like NiF, the 4s(M) and $3d\sigma(M)$ orbitals strongly mix to form the hybrid 9σ and 10σ orbitals. For MnF and FeF, the 9σ orbitals are still mainly constructed from the 4s(M) orbitals, but include certain amounts of the $3d\sigma(M)$ orbitals. It is very difficult to separate out the contribution of the hybridization to the observed hyperfine constants. Since the $c_{9\sigma}^{\mathrm{F}(2p)}$ and $c_{10\sigma}^{\mathrm{F}(2p)}$ values of MnF and FeF depend strongly on the hybridization, we cannot estimate the $c_{9\sigma}^{F(2p)}$ and $c_{10\sigma}^{F(2p)}$ values separately. In the present analysis we thus assume that the $c_{9\sigma}^{F(2p)}$ values of MnF and FeF have slightly larger value (1%) than those of early 3d transition metal fluorides, although the uncertainties attached are large. Under this assumption, the $c_{10\sigma}^{F(2p)}$ values of MnF and FeF are estimated to be 7% and 9%, respectively. These values are much larger than the $c_{9\sigma}^{F(2p)}$ values (about 1%). This means that the $2p\sigma(F)$ orbital interacts more strongly with the $3d\sigma(M)$ orbital than with the 4s(M) orbital. This finding probably reflects that the $3d\sigma(M)$ orbital extends more widely along the molecular axis than the 4s(M) orbital.

A similar analysis was carried out for $c_{9\sigma}^{\hat{F}(2s)}$ and $c_{10\sigma}^{F(2s)}$ If $c_{9\sigma}^{F(2s)}$ of MnF and FeF are similar to those of early 3dtransition metal monofluorides (0.2%), the $c_{10\sigma}^{F(2s)}$ values are obtained to be 0.6% and 0.7% for MnF and FeF, respectively. These values are apparently larger than the assumed $c_{9\sigma}^{F(2s)}$

TABLE V. Contributions of the 3p and 3s orbitals of chlorine to the 5π , 11σ , and 12σ orbitals of the fourth-row metal monochlorides in %.^a

		$c_{5\pi}^{\operatorname{Cl}(3p)}$	$c_{11\sigma}^{{\rm Cl}(3p)}$	$c_{12\sigma}^{{\rm Cl}(3p)}$	$c_{11\sigma}^{{\rm Cl}(3s)}$	$c_{12\sigma}^{{\rm Cl}(3s)}$	Ref.
CaCl	$^{2}\Sigma^{+}$		2.4		0.41	•••	30
CrCl	${}^{6}\Sigma^{+}$	[8] ^b	[2] ^b	•••	-0.23 ^c	•••	This work
FeCl	$^{6}\Delta$	[8] ^d	[2] ^d	[11] ^d	[0.4] ^e	[0.4] ^e	32

^aValues in parentheses in footnotes b-e represent three standard deviations. Errors for CaCl values are small enough.

^bAssumed value to reproduce $c_{5\pi}^{\text{Cl}(3p)} - c_{11\sigma}^{\text{Cl}(3p)} = 6.4(1)$. See text.

^cNegative $c_{11\sigma}^{\text{Cl}(3s)}$ value is an effective one affected by the spin-polarization. ^dAssumed value to reproduce $-c_{5\pi}^{\text{Cl}(3p)} + c_{11\sigma}^{\text{Cl}(3p)} + c_{12\sigma}^{\text{Cl}(3p)} = 4.6(44)$. ^eAssumed value to reproduce $c_{11\sigma}^{\text{Cl}(3s)} + c_{12\sigma}^{\text{Cl}(3s)} = 0.78(42)$.

values. Probably, this is also explained by the extended nature of the $3d\sigma(M)$ orbital along the molecular axis as mentioned above.

For CrCl [(core)(11 σ)¹(1 δ)²(5 π)²], a similar analysis was carried out to obtain $c_{11\sigma}^{\text{Cl}(3s)} = -0.23\%$ and $c_{5\pi}^{\text{Cl}(3p)} - c_{11\sigma}^{\text{Cl}(3p)} = 6.4(3)\%$ from the observed $b_F(\text{Cl})$ and c(Cl)values and the atomic chlorine constants of $A(^{35}Cl) = 5723$ and $P(^{35}Cl) = 439.0 \text{ MHz.}^{21}$ It is impossible to explain the negative $c_{11\sigma}^{Cl(3s)}$ value using Eq. (3). Such anomaly is often accounted for by the contribution of the spin polarization.²⁸ Table V summarizes the contributions of various chlorine atomic orbitals in the fourth-row metal monochlorides. Since studies on such metal monochlorides are limited, it is very difficult to discuss their electronic properties systematically. However, by the analogy with metal monofluorides, it is likely that the $c_{11\sigma}^{\text{Cl}(3s)}$ value of CaCl [(core)(11 σ)¹] can be used in the analysis of CrCl. Under this assumption, the $c_{5\pi}^{\text{Cl}(3p)}$ value of CrCl is estimated to be about 8%. Similarly, the electronic properties of FeCl [(core) $(11\sigma)^{1}(1\delta)^{3}(5\pi)^{2}(12\sigma)^{1}$] assumed to reproduce hyperfine parameters are shown in Table V, but they suffer from considerable uncertainties originating from the poor experimental accuracy. Even if such uncertainties are considered, each parameter in Table V is systematically larger than the corresponding value of the metal monofluoride in Table IV. This probably reflects the fact that metal monochlorides are less ionic and more covalent than the corresponding monofluorides, contrary to the qualitative comparison between FeF and FeCl in Ref. 32.

The electric quadrupole coupling constant eQq of Cr³⁵Cl is obtained to be -17.4 MHz. The $eQq(^{35}Cl)$ values of the fourth-row elements published previously are summarized in Fig. 5. The eQq value is known to be a good measure of the ionic character of a chemical bond.³⁶ The KCl molecule is so ionic that its eQq(Cl) constant is close to zero. On the other hand, BrCl is an almost purely covalent molecule and its eQq(Cl) value is close to the atomic value, -109.74 MHz.³⁶ The 3d transition metal monochlorides (ScCl \sim CuCl) are grouped into ionic species on the basis of their small eQq(Cl) values. Their absolute values seem to increase monotonically along with the atomic number of metals, although FeCl has a slightly different eQq(Cl) value. This perhaps suggests that the covalent character of the 3d transition metal monochlorides changes correspondingly along with increasing atomic number of the metals. Since the eQq



FIG. 5. The $eQq(^{35}Cl)$ values of the fourth-row element monochlorides in MHz. The values are cited from Refs. 29–35. Experimental errors of the species except for FeCl are small enough.

constant is a molecular property and affected by the distributions of core- as well as valence-electrons, it is difficult to discuss the constants more quantitatively without the help of a high-level *ab initio* calculation when the orbital polarization is striking. The understanding of these hyperfine constants including eQq(Cl) should be a good subject of current theoretical calculations.

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