Rotational and hyperfine analysis of the near infrared $^3\Phi_4 - X\,^3\Phi_4$ transitions of CoCl and CoI

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Electronic transitions of cobalt monochloride and cobalt monoiodide have been studied using laser vaporization–reaction free jet expansion and laser induced fluorescence spectroscopy in the near infrared region. The observed transitions have been identified as the $[10.3]\,^3\Phi_4 - X\,^3\Phi_4$ transition of CoCl and $[11.0]\,^3\Phi_4 - X\,^3\Phi_4$ transition of CoI. The magnetic hyperfine structure arising from the cobalt nucleus with $I = 7/2$ was resolved and analyzed. Accurate rotational and hyperfine parameters for the $[10.3]\,^3\Phi_4$ and $X\,^3\Phi_4$ states of CoCl and $[11.0]\,^3\Phi_4$ and $X\,^3\Phi_4$ states of CoI have been obtained. Comparison of Fermi contact parameters, b_F, for the upper states indicated that the observed $[10.3]\,^3\Phi_4 - X\,^3\Phi_4$ transition of CoCl and $[11.0]\,^3\Phi_4 - X\,^3\Phi_4$ transition of CoI have arisen from the promotion of an electron from the bonding σ orbital to a slightly antibonding σ orbital. Observed low-lying $^3\Phi$ states of the cobalt monohalides and hydride are also compared and discussed. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1589476]

I. INTRODUCTION

Interests in the structure of gaseous transition metal halide molecules are both in basic research[1] and practical application which include halogen metallurgy, chemical vapor transport, and deposition to the lamp industry.[2–4] Spectroscopic studies of transition metal diatomic halides have been an active area of research for many years.[5–8] The diatomic metal monohalides are simple model systems that can provide insight into the role of the d orbitals in chemical bonding.[5,9]

Amongst the cobalt monohalides, high resolution spectroscopic studies of CoF[10–13] and CoCl[14–17] have been performed in recent years. However, there has been no high resolution spectroscopic work on CoBr and CoI so far. In this paper, we report rotational and hyperfine analysis of the $^3\Phi_4 - ^3\Phi_4$ transition of CoCl and CoI in the near infrared region. Six and eight vibronic transition bands of CoCl and CoI, respectively, were recorded and analyzed. Accurate molecular parameters for both the upper and the ground $^3\Phi_4$ states have been determined by least squares fitting of line positions of observed bands simultaneously for each molecule, which yielded accurate molecular parameters for both the upper and lower $^3\Phi_4$ states. This work represents the first experimental investigation of the spectrum of CoI.

II. EXPERIMENT

CoCl and CoI molecules were produced in a supersonic free jet expansion in argon by the reaction of laser ablated cobalt atoms with phosphorous trichloride (PCl_3) and methyl iodide (CH_3I), respectively. The laser vaporization–reaction free jet expansion laser induced fluorescence spectrometer employed in this work had been described in earlier publications.[18,19] Only a brief description of the relevant ex-

perimental conditions will be given here. A laser pulse of 532 nm and 10 mJ from a Nd:YAG laser was focused onto the surface of a cobalt rod to produce cobalt metal vapor. A pulsed valve, synchronized with appropriate delay time, released gas mixtures of 1.8% of PCl_3 in argon to produce CoCl and 4.3% of CH_3I in argon to produce CoI. The Nd:YAG—pulsed valve system was operated at 10 Hz. The jet cooled CoCl and CoI molecules were excited by a c.w. Ti:sapphire ring laser pumped by an argon ion laser. Laser induced fluorescence signal was collected by a lens system and detected using a photomultiplier tube (PMT). The PMT output was fed into a boxcar integrator for averaging. A broadband scan between 750 and 900 nm was obtained initially, and the transition bands detected were eventually recorded under high resolution. The line width of the molecular transition was about 250 MHz and the line positions were measured with an absolute accuracy of about ± 0.002 cm^{-1}.
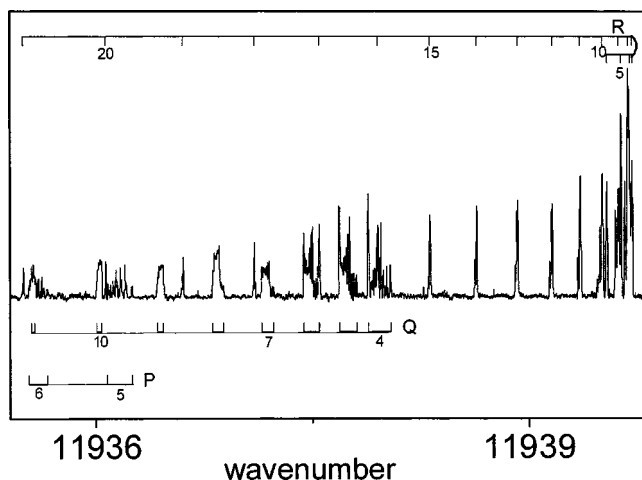
III. RESULTS AND DISCUSSION

High resolution laser induced fluorescence spectra of CoCl and CoI between 750 and 900 nm have been recorded and analyzed. Six and eight transition bands belonging to CoCl and CoI were analyzed.
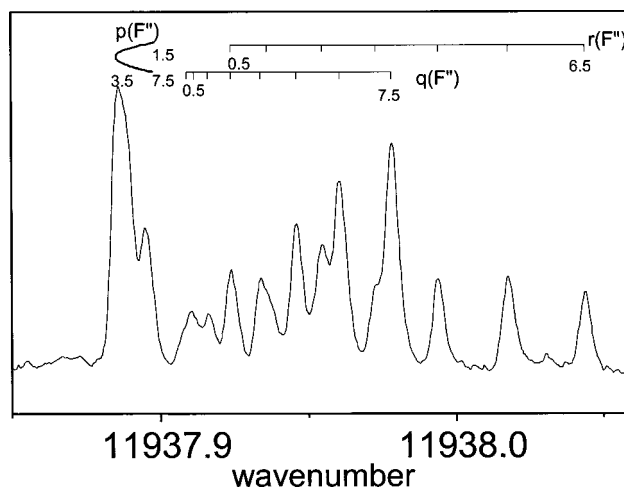
A. Spectrum of CoCl

Figure 1 shows the (4,0) band of the $[10.3]\,^3\Phi_4 - X\,^3\Phi_4$ transition. The first lines, $P(5)$, $Q(4)$, and $R(4)$ of the branches, are clearly resolved and assigned, which confirmed the transition observed belongs to a $\Omega' = \Omega'' = 4$ transition. With strong P and R branches, the transition has been assigned as a $^3\Phi_4 - X\,^3\Phi_4$ transition. The R branch appears to be slightly higher in intensity because hyperfine transitions are not resolved. Further evidence supporting our assignment is discussed in later section. It is easily noticed that in both the P and Q branches, the hyperfine widths decrease rapidly when J increases, which suggests that the angular momen-

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FIG. 1. (4,0) band of the [10.3] $^3\Phi_4 - X\,^3\Phi_4$ transition of CoCl.

FIG. 2. High resolution spectrum of the $Q(4)$ lines of the (4,0) band [10.3] $^3\Phi_4 - X\,^3\Phi_4$ transition of CoCl at 11 938 cm^{-1} showing resolved hyperfine components.

tum coupling of the $^3\Phi_4$ state is closed to Hund's coupling case (a_β). We have observed and analyzed six bands at the following positions 11 200, 11 571, 11 939, 12 305, 12 668, and 13 028 cm^{-1}. In addition, two much weaker bands at 12 274 and 12 631 cm^{-1} were also observed, unfortunately, due to low signal-to-noise ratio of the transition lines, a detailed analysis of rotational structure of these bands was not possible. Since chlorine has two isotopes: ^{35}Cl and ^{37}Cl, and the natural abundance of these isotopes are about 3:1, it is reasonable to explore the possibility that these two weaker bands belong to the Co^{37}Cl isotope. The shift in band heads between the 12 305 and 12 274 bands is 31 cm^{-1} and the 12 668 and 12 631 bands is 37 cm^{-1}, which agree well with the isotopic shift between the two isotopic species when the 12 305 and 12 668 cm^{-1} bands are assigned as the (5,0) and (6,0) bands of the Co^{35}Cl, respectively. Figure 2 shows the hyperfine transitions of the $Q(4)$ line. Hyperfine transition lines, caused by the cobalt nucleus with $I = 7/2$, satisfy selection rules $\Delta F = -1$, 0, and $+1$ are, respectively, labeled as $p(F'')$, $q(F'')$, and $r(F'')$. Due to the limitation of our wavelength coverage, the lowest vibrational level studied was with $v = 2$. A list of the wave numbers of the $(v, 0)$ bands with $v = 2$–7 of the $^3\Phi_4 - X\,^3\Phi_4$ transition of CoCl measured in this work is deposited to the EPAPS.[20]

1. Determination of spectroscopic parameters

The $^3\Phi_i$ state studied has three spin components, because of large spin–orbit interaction, only one substate, namely $\Omega'' = 4$, has been observed. For only one substate, the rotational energy levels could easily be represented using the following expression:

$$F(J) = T_o + BJ(J+1) - DJ^2(J+1)^2. \tag{1}$$

The hyperfine Hamiltonian can be represented by

$$\hat{H}_{hfs} = aI_z L_z + b\mathbf{I}\cdot\mathbf{S} + cI_z S_z, \tag{2}$$

where a, b, and c parameters are the same as defined by Frosch and Foley.[21] The three terms in the hyperfine Hamiltonian are respectively the nuclear spin–orbit, the Fermi contact and the dipolar electron spin and nuclear spin interactions. For a Φ state with large spin–orbit interaction, the angular momentum coupling case is appropriately described by the Hund's coupling case (a_β).[22] In such coupling case, the grand total quantum number F results from coupling the nuclear spin, I, with the angular momentum J, where $\mathbf{F} = \mathbf{I} + \mathbf{J}$. Matrix elements of a Φ state in Hund's coupling case (a_β) can be found in Azuma et al.[23] The matrix elements concerning the hyperfine Hamiltonian are:

$$\langle J\Omega IF|\hat{H}_{hfs}|J\Omega IF\rangle = \frac{\Omega\cdot h[F(F+1)-I(I+1)-J(J+1)]}{2J(J+1)}, \tag{3}$$

$$\langle J\Omega IF|\hat{H}_{hfs}|J-1,\Omega IF\rangle = \frac{h\sqrt{J^2-\Omega^2}\sqrt{(J+I+F+1)(F+J-I)(J+I-F)(F+I-J+1)}}{2J\sqrt{(2J+1)(2J-1)}}. \tag{4}$$

Since $h = a\Lambda + (b+c)\Sigma$, for the $^3\Phi_4$ substate (that is with $\Lambda = 3$ and $\Sigma = 1$) than $h = 3a + b + c$.

The observed line positions were fitted in two steps. Initially, information such as rotational constants and band origin of individual band were obtained in a band-by-band fit-

ting, and, eventually, a merged fit with all line positions measured was performed. A data set consisting of 785 hyperfine lines was simultaneously fit yielding a root-mean-squares (rms) error of 0.0012 cm^{-1}. Since only low J lines were observed in our experiment, the centrifugal distortion
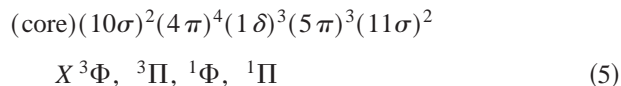
TABLE I. Molecular constants for the $[10.3]\,^3\Phi_4$ and $X\,^3\Phi_4$ states of CoCl (cm^{-1}).

State	v	T_v	B_v	h_v
$[10.3]\,^3\Phi_4$	7	13 026.7758(3)	0.158 355(6)	0.0528(2)
	6	12 666.6310(2)	0.157 404(7)	0.0538(2)
	5	12 303.8235(3)	0.157 655(6)	0.0546(2)
	4	11 938.3710(2)	0.158 210(7)	0.0549(2)
	3	11 570.2595(2)	0.158 888(7)	0.0551(2)
	2	11 199.4847(2)	0.159 652(7)	0.0551(2)
$X\,^3\Phi_4$	0	0	0.179 523(7)	0.0438(1)

constant D for the $X\,^3\Phi_4$ state was fixed at the value obtained using Fourier transform spectroscopy (FTS) by Hirao et al.[17] Molecular constants obtained for the observed vibronic levels are listed in Table I. The rotational constant of the $v=7$ level is unreasonably large, which indicates that the whole $v=7$ subband is subjected to a global perturbation. Detail of this perturbation is not known at the present moment, we could not pursue any further this perturbation. For obtaining equilibrium molecular constants, we did not include the molecular constants for the $v=7$ level. The results are presented in Table II. The experimentally determined rotational constants are effective parameters for the $\Omega=4$ sublevel of the $^3\Phi$ state and hence, the determined effective bond length for the $\Omega=4$ substates are $r_e=2.1746$ Å for the $[10.3]\,^3\Phi_4$ and $r_0=2.068$ Å for the $X\,^3\Phi_4$ states.

2. Interpretation of hyperfine parameters

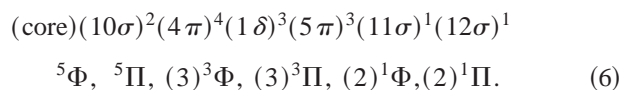As indicated by Bernath and co-workers in CoF[11,12] and CoCl,[17] and Adam et al. in CoF[10,13] and CoCl,[16] the electronic states and electronic spectra of cobalt monohalides and cobalt hydride[24,25] are very similar. The $[20.7]\,^3\Phi_4 - X\,^3\Phi_4$ and $[21.3]\,^3\Phi_4 - X\,^3\Phi_4$ transitions of CoCl were suggested by Adam et al.[16] using laser induced fluorescence spectroscopy that these transitions arise from the promotion of an electron from the $11\sigma\rightarrow 12\sigma$ molecular orbital. However, recent FTS work of Hirao et al.[17] indicated that the upper state of the $[21.3]$ transition is probably $^3\Delta_i$ state but the $^3\Phi_i$ assignment of Adam et al.[16] could not be definitely ruled out. The electronic configurations suggested by Adam et al.[16] for the lower and upper states are as follows:

$$(core)(10\sigma)^2(4\pi)^4(1\delta)^3(5\pi)^3(11\sigma)^2$$

$$X\,^3\Phi,\ ^3\Pi,\ ^1\Phi,\ ^1\Pi \qquad (5)$$

and

TABLE II. Equilibrium molecular constants for the $[10.3]\,^3\Phi_4$ state of CoCl and $[11.0]\,^3\Phi_4$ state of CoI (cm^{-1}).

Parameter	$[10.3]\,^3\Phi_4$ of CoCl	$[11.0]\,^3\Phi_4$ of CoI
T_e	10 260.905(46)	11 059.763(3)
ω_e	378.764(31)	226.075(3)
$\omega_e x_e$	1.334(7)	0.7218(9)
$\omega_e y_e$	0.004(3)	$-0.002\,05(8)$
B_e	0.162 43	0.065 465
α_e	0.0013	0.000 277
r_e (Å)	2.1746	2.5295

$$(core)(10\sigma)^2(4\pi)^4(1\delta)^3(5\pi)^3(11\sigma)^1(12\sigma)^1$$

$$^5\Phi,\ ^5\Pi,\ (3)^3\Phi,\ (3)^3\Pi,\ (2)^1\Phi,(2)^1\Pi. \qquad (6)$$

It is generally agreed that the $^3\Phi$ state arises from electronic configuration (5) is the ground state. The $[20.7]\,^3\Phi$ state arises from the promotion of one electron from $11\sigma\rightarrow 12\sigma$ orbital as indicated in electronic configuration (6).[17] Such situation is similar to the transition in CoH with the promotion of an electron from $7\sigma\rightarrow 8\sigma$ molecular orbital as observed by Barnes et al.[24] Magnetic hyperfine structure gives useful information about the bonding in the molecule because hyperfine parameters are related to expectation values of the coordinates of electron near the spinning nucleus.[26] Hyperfine parameters can be expressed as averages over electronic coordinates and are listed as follows (in cm^{-1} unit):

$$a=\left(\frac{\mu_o}{4\pi hc}\right)gg_N\mu_B\mu_N\sum_i\ \langle r_i^{-3}\rangle, \qquad (7)$$

$$b_F=\left(\frac{\mu_o}{4\pi hc}\right)\frac{8\pi}{3}gg_N\mu_B\mu_N\left(\frac{1}{2S}\right)\sum_i\ \langle\psi_i^2(0)\rangle, \qquad (8)$$
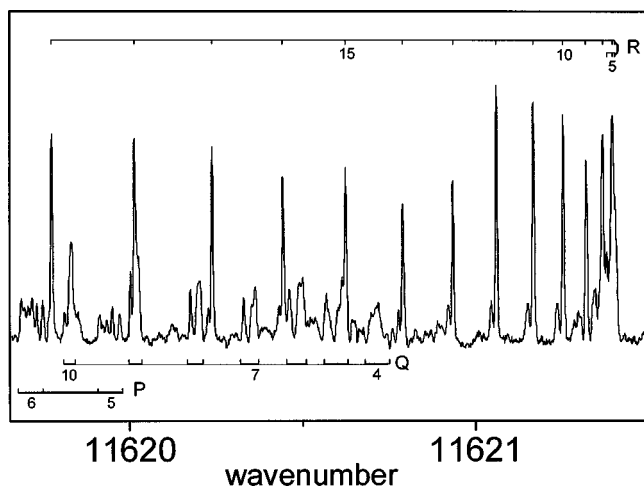
$$c=\left(\frac{\mu_o}{4\pi hc}\right)\frac{3}{2}gg_N\mu_B\mu_N\left(\frac{1}{2S}\right)\sum_i\ \langle 3\cos^2\vartheta_i-1\rangle\langle r_i^{-3}\rangle, \qquad (9)$$

$$b=b_F-\tfrac{1}{3}c. \qquad (10)$$

A common method of obtaining estimates of the hyperfine parameters is to use a free atom comparison method to compare the determined parameters with ab initio results for atom.[27] The a and c parameters were calculated using the above expressions and the values of $\langle r_i^{-3}\rangle$,[28] and $\langle 3\cos^2\theta_i-1\rangle$.[29,30] For the $X\,^3\Phi$ state, we obtained $a=0.020\,71\ cm^{-1}$ and $c=-0.015\,22\ cm^{-1}$ from such calculations. Experimentally, $h=3a+b+c$ was determined to be $0.04380\ cm^{-1}$, which gives an estimate of the b_F parameter to be $-0.008\,18\ cm^{-1}$. This value is quite small, which is consistent with the electronic configuration of no unpaired electron occupying any of the $s\sigma$ orbital. Such a small value of b_F for the $X\,^3\Phi_4$ state was also obtained by Adam et al.[16] For the upper state $[10.3]\,^3\Phi$, the value of a and c should be similar to that of the $X\,^3\Phi_4$ state, so that estimated value of the b_F parameter for the upper state is $0.003\,12\ cm^{-1}$.

Electronic configuration (6) gives rise to three excited $^3\Phi$ states. It is not possible to calculate a b_F value for the particular near infrared state studied, since these three $^3\Phi$ states cannot be treated separately. However, one can estimate the range within which the b_F values lie. The b_F values calculated can then be compared to experimentally determined b_F values. The Slater determinant electronic wave functions for the three $^3\Phi$ states can be written.[24]

$$|^3\Phi;\delta^3\pi^3(^3\Phi)\times\sigma\sigma(^1\Sigma^+)\rangle$$

$$=\frac{1}{\sqrt{2}}|(\delta^{2+}\pi^+\sigma\bar\sigma)-(\delta^{2+}\pi^+\bar\sigma\sigma)\rangle, \qquad (11)$$

FIG. 3. (2,0) band of the [11.0] $^3\Phi_4$–$X\,^3\Phi_4$ transition of CoI.

FIG. 4. High resolution spectrum of the (2,0) band of the [11.0] $^3\Phi_4$–$X\,^3\Phi_4$ transition of CoI at 11 619 cm^{-1} showing partially resolved hyperfine components.

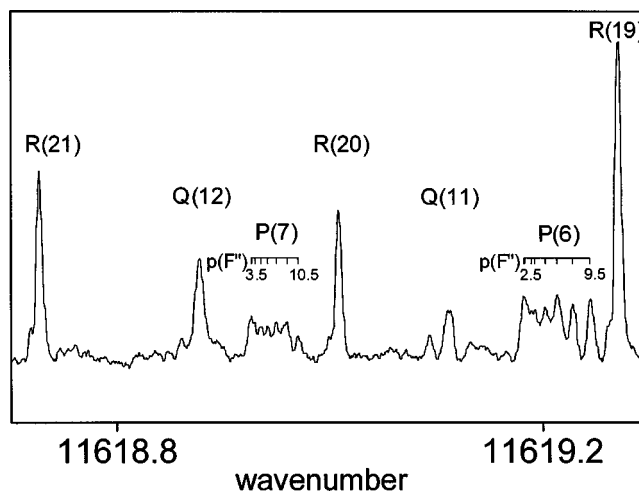$$\big|\,^3\Phi;\delta^3\pi^3(^1\Phi)\times\sigma\sigma(^3\Sigma^+)\big\rangle$$

$$=\frac{1}{\sqrt{6}}\big|-2(\delta^{2+}\bar{\pi}^+\sigma\sigma)+(\delta^{2+}\pi^+\sigma\bar{\sigma})+(\delta^{2+}\pi^+\bar{\sigma}\sigma)\big\rangle,$$

$$\text{(12)}$$

$$\big|\,^3\Phi;\delta^3\pi^3(^3\Phi)\times\sigma\sigma(^3\Sigma^+)\big\rangle$$

$$=\frac{1}{\sqrt{12}}\big|-3(\bar{\delta}^{2+}\pi\sigma\sigma)+(\delta^{2+}\pi^+\sigma\bar{\sigma})$$

$$+(\delta^{2+}\pi^+\bar{\sigma}\sigma)+(\delta^{2+}\bar{\pi}^+\sigma\sigma)\big\rangle.\qquad\text{(13)}$$

The values of b_F for the three wave functions can be obtained by calculating eigenvalues of the one-electron Fermi contact operators for the two σ orbitals. This calculation was performed to CoH.[24] With the assumption that the dominant contribution to the hyperfine parameter was from the Co atom, the estimated b_F values for CoCl would be similar to that of CoH. With atomic beam data[31] for Co atom and using the three wave functions (11)–(13), b_F values of 0.0965, 0.0603, and 0 cm^{-1} are obtained.[24] The b_F value of the [20.7] $^3\Phi_4$ state of CoCl was measured to be 0.063 cm^{-1}, which agrees well with the medium size value calculated. As for the [21.3] transition, if the upper state is $^3\Phi_i$ state, its b_F value fits well with the largest value calculated. If the upper state of the [21.3] transition is $^3\Delta_i$ state, the large b_F value suggests that the $^3\Delta_i$ should arise from an electronic configuration with an unpaired electron in an $s\sigma$ orbital. Although the electronic configuration proposed by Hirao et al.[17] for the $^3\Delta_i$ state has an unpaired electron in the 12σ orbital which has considerable $s\sigma$ character, such configuration involves moving the two electrons from the 11σ orbital to the 5π and the 12σ orbitals. It is expected that such two-electron jump transition should be extremely weak, however, it is puzzling that the [21.3] transition is of considerable intensity.[17] In our work, the [10.3] $^3\Phi_4$ states with a very small b_F value of $-0.003\,12$, which fits into the pattern and agrees well with the smallest b_F value predicted. We could conclude that the [10.3] $^3\Phi_4$–$X\,^3\Phi_4$ transition of

CoCl also arises from the $11\sigma\rightarrow12\sigma$ transition and the [10.3] $^3\Phi_4$ state is another $^3\Phi_4$ state arisen from the electronic configuration (6).

B. Spectrum of CoI

A total of eight vibronic transition bands have been observed and analyzed. Each band consists of P, Q, and R branches. The first line of each branch was unambiguously assigned which confirms the transition with $\Omega'=\Omega''=4$. Figure 3 shows the band head region at 11 621 cm^{-1} and a portion of the Q branch. The R branch appears to be stronger because of the overlapping of unresolved hyperfine components. Since ^{60}Co^{127}I is the only detectable isotope, we could not use the usual isotopic shift method to assign vibrational numbering of the transition bands observed. We searched the spectral region from 750 to 900 nm and could not find any other transition band below 11 172 cm^{-1}. Therefore, it would be reasonable to assign the 11 172 cm^{-1} band to be the (0,0) band of the [11.0] $^3\Phi_4$–$X\,^3\Phi_4$ transition. Figure 4 shows a portion of the spectrum at higher resolution. The magnetic hyperfine transitions of the P branch at 11 619 cm^{-1} are relatively resolved. The Fermi contact interaction of both $^3\Phi_4$ states of CoI are small, only the stronger $\Delta F=\Delta J$ transitions in these bands were assigned. The line positions of the eight observed bands of the [11.0] $^3\Phi_4$–$X\,^3\Phi_4$ transition have been also tabulated and deposited into the EPAPS.[20]

1. Determination of spectroscopic parameters

Similar to the CoCl molecule, the observed line positions for $v=0$–7 level of the [11.0] $^3\Phi_4$–$X\,^3\Phi_4$ transition of CoI were merged in a grand least squares fit using expressions given in (1)–(4). The centrifugal distortion constants, D, for the both $^3\Phi_4$ states were fixed at values given by the Kratzer relation. A total of 610 hyperfine lines were used and yielded a rms error of 0.0016 cm^{-1}. The results of the least squares fit are tabulated in Table III and the equilibrium molecular constants also were included in Table II. The deter-

TABLE III. Molecular constants for the [11.0] $^3\Phi_4$ and $X\,^3\Phi_4$ states of CoI (cm^{-1}).

State	v	T_v	B_v	h_v
[11.0] $^3\Phi_4$	7	12 713.8556(3)	0.063 378(3)	0.0468(7)
	6	12 498.1909(3)	0.063 663(3)	0.0470(8)
	5	12 280.9974(3)	0.063 945(3)	0.0453(7)
	4	12 062.2949(3)	0.064 224(3)	0.0471(8)
	3	11 842.0921(3)	0.064 505(3)	0.0469(7)
	2	11 620.4061(3)	0.064 779(3)	0.0476(7)
	1	11 397.245(3)	0.065 046(3)	0.0476(7)
	0	11 172.6177(3)	0.065 320(3)	0.0476(7)
$X\,^3\Phi_4$	0	0	0.074 587(3)	0.0429(7)

mined rotational constants are effective parameters for the $\Omega=4$ sublevel and hence, the effective bond length of the $\Omega=4$ substate are $r_e=2.5295$ Å for the [11.0] $^3\Phi_4$ and $r_0=2.3698$ Å for the $X\,^3\Phi_4$ state of CoI. This is the first time that molecular constants for CoI have been reported.

2. Interpretation of hyperfine parameters

Using expressions (7)–(10), we could estimate the hyperfine parameters of CoI. Since such values are coming from the *ab initio* results for Co atom, the a and c parameters would be similar to those used for CoCl, that is $a=0.020\,71$ and $c=-0.015\,22\,\mathrm{cm}^{-1}$. The b_F values obtained from using the experimentally determined h in Table III are $-0.009\,08$ and $-0.004\,38$ for the [11.0] $^3\Phi_4$ and the $X\,^3\Phi_4$ states. The molecular orbital energy levels formed from the Co atom's $3d$ and $4s$ atomic orbitals and the iodine $5p$ orbitals are very similar to those in CoCl. The electronic configuration of the valence orbitals of CoI are $\delta^3\pi^3\sigma^2$ and $\delta^3\pi^3\sigma^1\sigma^1$, which are similar to those configurations in (5) and (6) giving rise to the ground and low-lying electronic states, respectively. Amongst the three $^3\Phi$ states expected to arise from the $\delta^3\pi^3\sigma^1\sigma^1$ configuration, the [11.0] $^3\Phi$ state is the only one studied so far. The earlier discussions concerning the three different sizes of the hyperfine b_F parameters of

the CoCl molecule should also be valid for CoI. For a small value of the $b_F=-0.009\,08\,\mathrm{cm}^{-1}$ obtained for the [11.0] $^3\Phi$ state, it would be consistent to assign the [11.0] $^3\Phi-X\,^3\Phi$ transition as arising from a $\sigma\to\sigma$ transition.

C. Discussion

It is interesting to study and compare the known $^3\Phi$ states of the cobalt hydride and monohalides. Table IV listed the molecular constants for the low-lying $^3\Phi$ states determined so far. It is well known that there is a strong correspondence between the electronic states of the Co–F and Co–H, even though the $\mathrm{Co^+F^-}$ bond is much more ionic than Co–H bond.[12] In both cases, the single bond forms by loss or pairing of an s electron from the metal to leave $d^n\,s^1$ or d^{n+1} configuration. Using molecular orbitals (MO), we could also describe the ionic nature of the cobalt monohalides. There are nine valence electrons in the $4s$ and $3d$ orbitals of the cobalt atom and five valence electrons in the p orbitals of the halogen. The lowest σ and π MOs are essentially formed from the p atomic orbitals of the halogen atom, the filling up of these orbitals requires a transfer of electron from the Co atom to the π MO. Such move of electron from the Co atom to the halogen atom forms the expected $\mathrm{Co^+X^-}$ ionic compound. The upper states involved the promotion of an electron from a closed σ bonding orbital to the slightly antibonding σ orbital, it is expected that the bond length of the upper states would be longer than the $X\,^3\Phi$ state as shown in Table IV. In addition, it is commonly known that the electronegativities of constituent atoms in a molecule play a very important role in determining the bond type. In the case of cobalt monohalides, the electronegativities of F, Cl, and I, are, respectively, 4, 3.1, and 2.6 and for Co is 1.8. It is reasonable that cobalt monohalides are ionic compounds and the ionicity decreases from F to I. Our experiments showed that the $^3\Phi$ electronic states studied in the near infrared region for CoCl and CoI are quite similar to that of the CoF, it is reasonable to expect CoBr have similar electronic state in this energy region. We searched for the near infrared

TABLE IV. Molecular constants for the low-lying $^3\Phi$ states of cobalt monohalides and hydride (cm^{-1}).

	CoF		CoCl		CoI		CoH
$X\,^3\Phi$	$B_e=0.389\,82$[b] $r_e(\text{Å})=1.7349$ $\omega_e=677.59$ $A^a=-232.873$	$X\,^3\Phi$	$B_e=0.179\,317\,2$[d] $r_e(\text{Å})=2.0696$ $\Delta G_{1/2}=430.418$	$X\,^3\Phi_4$	$B_0=0.074\,587$ $r_0(\text{Å})=2.3698$	$X\,^3\Phi_4$	$B_e=7.255\,382$[f] $r_e(\text{Å})=1.5313$ $\Delta G_{1/2}=1858.793$
$[10.3]^3\Phi$	$B_e=0.354\,022$[b] $r_e(\text{Å})=1.8231$ $\omega_e=580.35$	$[10.3]^3\Phi_4$	$B_e=0.162\,43$ $r_e(\text{Å})=2.1746$ $\omega_e=378.76$	$[11.0]^3\Phi_4$	$B_e=0.065\,465$ $r_e(\text{Å})=2.5295$ $\omega_e=226.07$	$A'\,^3\Phi_4$	$B_0=6.375\,41$[f] $r_0(\text{Å})=1.6335$
$[18.8]^3\Phi$	$B_e=0.3781$[c] $r_e(\text{Å})=1.762$ $\omega_e=673.3$ $A=-195.507$	$[20.4]^3\Phi$	$B_0=0.168\,617\,4$[d] $r_0(\text{Å})=2.1343$ $A=-131.2941$ $\omega_e=403.57$[e]				
$[19.2]^3\Phi$	$B_e=0.3785$[c] $r_e(\text{Å})=1.761$ $\omega_e=580.35$	$[21.0]^{3\Delta}$ $(^3\Phi)$	$B_0=0.170\,845\,6$[d] $r_0(\text{Å})=2.1203$ $A=-207.5324$ $\omega_e=393.73$[e]				

[a]Spin–orbit interaction parameter.
[b]Molecular constants for this state were taken from Ref. 12.
[c]Molecular constants for this state were taken from Ref. 13.

[d]Molecular constants for this state were taken from Ref. 17.
[e]Molecular constants for this state were taken from Ref. 16.
[f]Molecular constants for this state were taken from Ref. 25.

laser induced fluorescence spectrum of CoBr using the same apparatus by reacting CH_3Br or CH_3CH_2Br with laser ablated Co atom. A weak transition has been detected in the near infrared region; however, it was so weak that no further analysis was possible. We have good reason to believe that this weak transition detected would be the $^3\Phi_4$–$^3\Phi_4$ transition similar to those studied in this work. The weakness of this band may be due to insufficient CoBr molecule production from the reactions used and also the presence of two bromine isotopes with about the same abundance causing further weakening of transition intensity.

The measurement of spin–orbit separations of transition metal monohalide and hydride molecules is usually difficult. The main reason is that electronic states with $\Lambda \neq 0$ always obey Hund's case (a) coupling so the strong branches arise from transition between these states are always with $\Delta\Sigma = 0$ and the satellite branches are extremely weak. Furthermore, the spin–orbit separation of these molecules is usually quite large. The common method of using laser ablation–supersonic expansion for producing molecules for spectroscopic studies is slightly disadvantaged because molecules produced this way are relatively cold. With a large spin–orbit separation, the next spin level is high in energy and could not be appreciably populated. Despite of the difficulty, there have been some recent progress in measuring the spin-orbit separation of these molecules: The spin–orbit splitting of the $\Omega = 4$ to $\Omega = 3$ of the $X\,^3\Phi$ of CoH was measured to be 728 cm^{-1}.[32] Adam *et al.*[13] analyzed a weak transition of CoF near 513 nm with $\Delta\Sigma = \Delta\Omega = -1$ established the spin–orbit interaction parameter for $X\,^3\Phi$ and the $[18.8]\,^3\Phi$ states. Recently, Hirao *et al.*[17] obtained the spin–orbit constant for the $[20.4]\,^3\Phi$ and $[21.0]\,^3\Delta\,(^3\Phi)$ states of CoCl. For CoI, only the lowest spin component $\Omega = 4$ has been studied, experimental work using wavelength resolved fluorescence spectroscopy would be useful for measuring the spin–orbit separation of CoI as in the case of the CoH and CoF molecules. In addition, in order to properly understand the effect of the halogen ions in these diatomic compounds, detailed theoretical calculations would be necessary.

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