# The low-lying electronic states of CoF

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The emission spectrum of CoF has been investigated in the 820 nm–3.5 $\mu$m spectral region using a Fourier transform spectrometer. The bands were excited in a carbon tube furnace by the reaction of cobalt metal vapor and $CF_4$ at a temperature of about 2300 °C. The bands observed in the 3000–9000 $cm^{-1}$ region have been classified into three new transitions. The bands with 0-0 $R$-heads at 3458 $cm^{-1}$, 3759 $cm^{-1}$, and 4012 $cm^{-1}$ have been assigned as the $^3\Delta_1–^3\Phi_2$, $^3\Delta_2–^3\Phi_3$, and $^3\Delta_3–^3\Phi_4$ subbands of the $C\ ^3\Delta–X\ ^3\Phi_i$ electronic transition. To higher wave numbers, two bands with $R$-heads at 8396 $cm^{-1}$ and 8565 $cm^{-1}$ have been assigned as the $^3\Delta_2–^3\Phi_3$ and $^3\Delta_3–^3\Phi_4$ subbands of the $D\ ^3\Delta–X\ ^3\Phi_i$ transition. In addition, the bands with $R$-heads at 6339 $cm^{-1}$ and 6542 $cm^{-1}$ have been assigned as the 0-0 $^3\Phi_4–^3\Delta_3$ and $^3\Phi_3–^3\Delta_2$ subbands of the $G\ ^3\Phi–C\ ^3\Delta$ transition. The $G\ ^3\Phi–X\ ^3\Phi$ transition has been reported previously as the $[10.3]^3\Phi–X\ ^3\Phi$ transition. The rotational analysis of many bands of these transitions has been obtained and the molecular constants for the two new low-lying excited states have been extracted. Six new band involving the high vibrational levels of ground state (up to $v=6$) have been identified in the $^3\Phi_4–^3\Phi_4$ subband of the $G\ ^3\Phi–X\ ^3\Phi$ transition. The rotational analysis of these bands provides improved constants for the ground state. We have noticed, as have previous workers, the strong correspondence that exists between the states of transition metal monofluorides and monohydrides. In addition, all of the low-lying states of CoF and CoH are related to the low-lying terms of the $Co^+$ atom. We discuss these correlations between the energy levels of CoF, CoH, and $Co^+$. © *1996 American Institute of Physics.* [S0021-9606(96)01318-3]

## I. INTRODUCTION

In recent years progress has been made towards an understanding of the electronic structure of transition metal oxides[1] and hydrides.[2,3] The data for the corresponding halides are much more limited.[4,5] The main problem with studies of such molecules is the intrinsic complexity of the spectra. The transition metal atoms involved in the bonding have open $d$-shells which result in many low-lying electronic states with high multiplicities. Many of the spin components of different electronic states interact with each other and cause perturbations.

Metal fluorides are also potential stellar and interstellar molecules, although F has a relatively small cosmic abundance. Recently, AlF has been detected in the atmosphere of a carbon star[6,7] and HF was found in numerous red giant stars.[8] In these sources $^{19}F$ has an abundance more than 30 times higher than the normal solar abundance suggesting that $^{19}F$ nuclei are synthesized in the He-burning shells of old stars. Metal fluorides also have strong bonds, which favors their formation in stellar atmospheres.

Limited spectroscopic work is available on CoF. There are no published theoretical calculations available on the properties of CoF although some are in progress.[9] On the experimental side, Adam *et al.*[10] have reported a $^3\Phi–^3\Phi$ transition in the visible region by dye laser excitation spectroscopy and Ram *et al.*[11] have observed the $[10.3]^3\Phi–X\ ^3\Phi$ transition in the near infrared spectral region. The ground state of CoF is found to be an inverted $X\ ^3\Phi$ state with the $X\ ^3\Phi_4$ spin-component lying lowest in energy. The equilibrium rotational and vibrational constants were obtained for the individual spin-components from the analysis of several bands of the $[10.3]^3\Phi–X\ ^3\Phi$ transition in the 9000–12000 $cm^{-1}$ region.[11]

These assignments are consistent with expectations based on the available data for the isovalent CoH molecule.[12–18] The ground state of CoH is now well established as a $^3\Phi_i$ state and the electronic spectra of CoF are expected to be similar to those of CoH. For CoH, Freindorf *et al.*[16] have recently performed *ab initio* calculations which confirm the $^3\Phi_i$ assignment for the ground state of CoH and predict many low-lying excited electronic states below 2.0 eV. In this paper we have investigated the near infrared spectra of CoF in the 3000–9000 $cm^{-1}$ region. We have identified three new transitions which locate two new low-lying excited electronic states, $C\ ^3\Delta$ and $D\ ^3\Delta$ and we rename the $[10.3]^3\Phi$ state as the $G\ ^3\Phi$ state on the basis of the theoretical predictions for CoH. In addition to the analysis of new infrared electronic transitions of CoF, we discuss the correlation between the low-lying states of CoF, CoH, and $Co^+$.

## II. EXPERIMENT

The CoF molecules were excited in a carbon tube furnace operated with 100 Torr of He buffer gas and several

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Torr of $CF_4$ at 2300 °C. The emission from the furnace was observed with the 1 m Fourier transform spectrometer associated with the McMath–Pierce Solar Telescope of the National Solar Observatory at Kitt Peak. The spectrometer was operated with a $CaF_2$ beamsplitter, silicon filters, InSb detectors and three scans were coadded in 10 min of integration. The lower wave number limit was set by cold green glass (uranium) filters in front of the InSb detectors. The spectrometer resolution was 0.026 cm$^{-1}$.

The spectral line positions were extracted from the observed spectra using a data reduction program called PC-DECOMP developed by Brault. The peak positions were determined by fitting a Voigt line shape function to each spectral feature.

The CoF spectra have been calibrated using HF impurity lines present in our spectra.[19] The strong CoF lines below 1 $\mu$m have been observed with a maximum signal to noise ratio of 14 and have a width of 0.035 cm$^{-1}$. This limits the precision of our measurements of the strong and unblended molecular transitions to ±0.001 cm$^{-1}$. For weaker bands the uncertainty of measurement is expected to increase to ±0.003 cm$^{-1}$ depending on signal to noise ratio, extent of blending and line broadening.

## III. OBSERVATIONS AND ANALYSIS

The observed spectra of CoF consist of many bands spread from 3000 to 12000 cm$^{-1}$. The bands observed in the 8700–12000 cm$^{-1}$ have been assigned previously to a $^3\Phi_i$–$X\,^3\Phi_i$ transition.[11] The present paper deals with the analysis of three new transitions located in the 3000–8700 cm$^{-1}$ region (Fig. 1). The group of bands located in the 3000–4600 cm$^{-1}$, 6200–6600 cm$^{-1}$, and 8300–8600 cm$^{-1}$ have been assigned as $C\,^3\Delta$–$X\,^3\Phi$, $G\,^3\Phi$–$C\,^3\Delta$, and $D\,^3\Delta$–$X\,^3\Phi$ transitions, respectively. In addition seven relatively weaker bands in the 8000–9000 cm$^{-1}$ region have been assigned to the $G\,^3\Phi_4$–$X\,^3\Phi_4$ subband. This extends the observation of this subband to include bands involving ground state vibrational levels up to $v=6$.

### A. $C\,^3\Delta$–$X\,^3\Phi$ transition

The bands in the 3000–4700 cm$^{-1}$ region have been classified into three subbands with the 0-0 $R$-heads at 3458 cm$^{-1}$, 3759 cm$^{-1}$, and 4012 cm$^{-1}$, assigned as $^3\Delta_1$–$^3\Phi_2$, $^3\Delta_2$–$^3\Phi_3$, $^3\Delta_3$–$^3\Phi_4$ subbands of a $^3\Delta$–$X\,^3\Phi$ transition. The branches in the different subbands were sorted using a color Loomis–Wood program running on a PC computer.

Since the bands of the $^3\Delta_1$–$^3\Phi_2$ subband are generally weaker in intensity than the other subbands, we have identified only the 0-0 band of this subband. A compressed portion of this subband is presented in Fig. 2. This band consists of two $P$, two $Q$, and two $R$ branches and the lower state combination differences from this subband match very well with the data obtained for the $X\,^3\Phi_2$ spin-component from the $G\,^3\Phi$–$X\,^3\Phi$ transition. The perturbation in the $X\,^3\Phi_2$ spin component, as previously observed during the analysis of the $G\,^3\Phi_2$–$X\,^3\Phi_2$ subband, has been confirmed from the analysis of the new subband. In addition perturbations have been
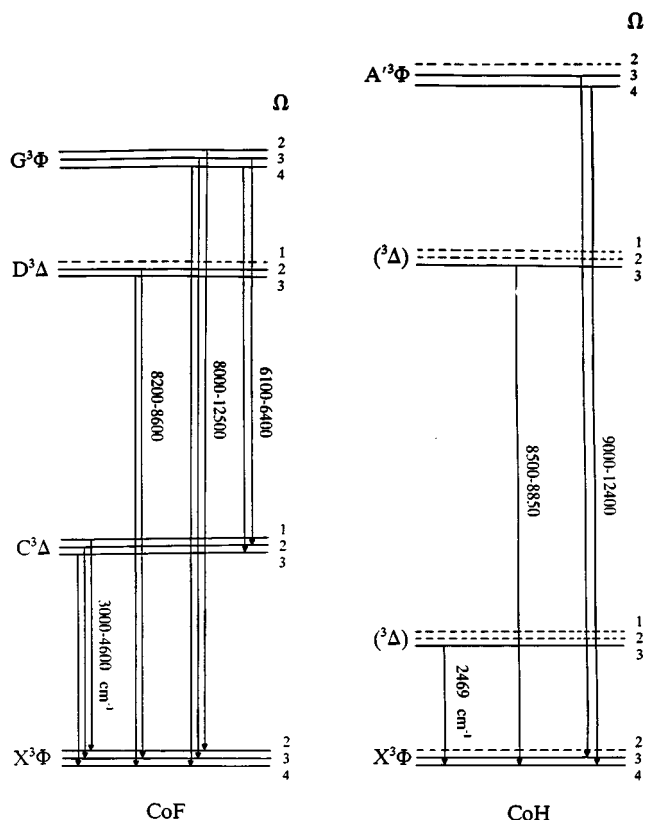


FIG. 1. A schematic energy level diagram of the low-lying electronic transitions of CoF and CoH.

identified in the $e$-parity levels at $J=19$ and $f$-parity levels at $J=19$ and 46 of the $C\,^3\Delta_1$ spin-component.

We have identified three bands of the $^3\Delta_2$–$^3\Phi_3$ subband. The bands with $R$ heads at 3092, 3759, and 4366 cm$^{-1}$ have been assigned as 0-1, 0-0, and 1-0 bands. The rotational analysis of all of these bands has been performed. An expanded portion of the 0-0 band of this subband is presented in Fig. 3. Each band in this subband consists of two $R$, two $P$, and two $Q$ branches. The splitting of the branches in-
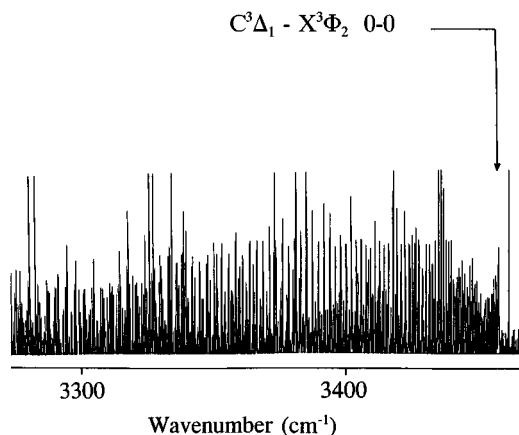


FIG. 2. A part of the compressed spectrum of the $^3\Delta_1$–$^3\Phi_2$ subband of the $C\,^3\Delta$–$X\,^3\Phi$ transition of CoF.
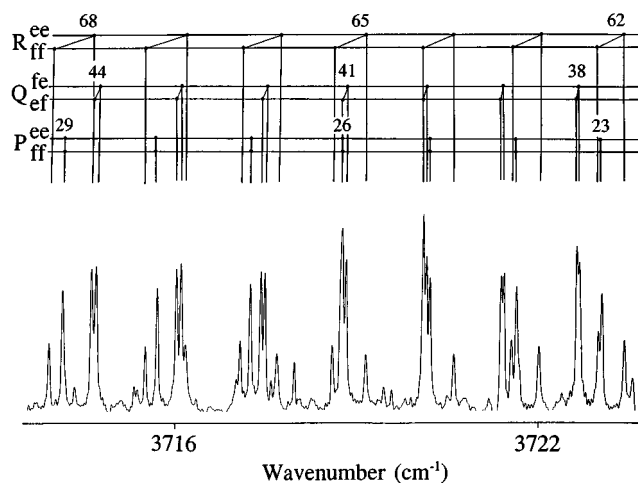
FIG. 3. An expanded portion of the $^3\Delta_2$–$^3\Phi_3$ subband of the $C\ ^3\Delta$–$X\ ^3\Phi$ transition of CoF.



FIG. 4. An expanded portion of the $^3\Delta_3$–$^3\Phi_4$ subband of the $C\ ^3\Delta$–$X\ ^3\Phi$ transition of CoF near the band origin.

creases rapidly at higher $J$ values. The rotational analysis indicates that the $\Omega$-doubling is mainly present in the excited $^3\Delta_2$ spin component. A local perturbation has been observed in the excited state $v=1$ vibrational level of this subband which affects only the $f$-parity levels at $J'=41$. Previously observed perturbation in the $v=1$ vibrational level of the $X\ ^3\Phi_3$ spin-component[11] has also been confirmed from the analysis of this subband.

To higher wave numbers, the band at 4012 cm$^{-1}$ has been identified as the 0-0 band of the $^3\Delta_3$–$^3\Phi_4$ subband of the $C\ ^3\Delta$–$X\ ^3\Phi$ transition. This band is the strongest band in this spectral region and likewise consists of two $P$, two $Q$, and two $R$ branches. The splitting in the branches also arises mainly from $\Omega$-doubling in the excited state. The other bands with $R$ heads at 3956, 4565, and 4628 cm$^{-1}$ have been assigned as the 1-1, 2-1, and 1-0 bands of this transition. An independent analysis of these bands provides ground state molecular constants very similar to the constants obtained in the previous analysis.[11] For example, the $\Delta G''(1/2)$ value of 672.700 07(65) determined in the present work is in excellent agreement with the value of 672.702 36(81) cm$^{-1}$ obtained in the previous work. Several perturbations have also been observed in the vibrational levels of the excited state. A part of the spectrum of the 0-0 band of this subband near the band origin is provided in Fig. 4.

## B. The $D\ ^3\Delta$–$X\ ^3\Phi$ system

Two bands observed in the 8100–8600 cm$^{-1}$ region have been assigned to a second new $^3\Delta$–$X\ ^3\Phi$ transition. The bands with the heads at 8396 and 8565 cm$^{-1}$ have been identified as the 0-0 bands of the $^3\Delta_2$–$^3\Phi_3$ and $^3\Delta_3$–$^3\Phi_4$ subbands of the $D\ ^3\Delta$–$X\ ^3\Phi$ transition. A portion of the compressed spectrum of these bands is provided in Fig. 5 where the $R$-heads of 0-0 bands of these subbands have been marked. The $^3\Delta_1$–$X\ ^3\Phi_2$ subband was not identified because of its weak intensity. Overlapping from several weaker bands present in the same spectral region also hinders the assignment of this subband. Each of these subbands consist of two
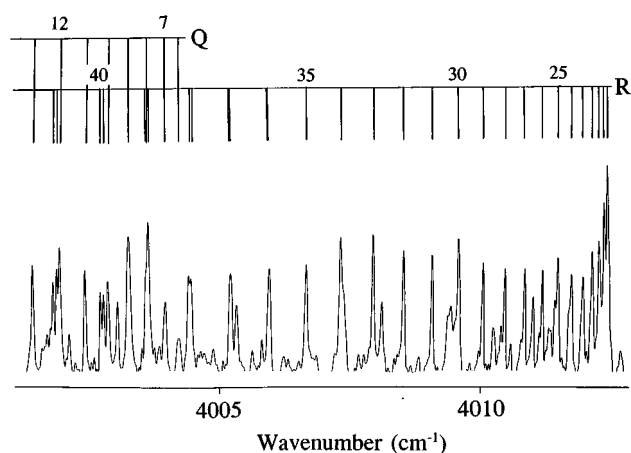
$P$, two $Q$, and two $R$ branches as expected for these transitions. Even though the first lines of the branches in these bands were not identified, the assignments could be made using lower state combination differences. The lower state constants from these subbands are very similar to the constants of the $X\ ^3\Phi_3$ and $X\ ^3\Phi_4$ spin components, confirming the lower state assignment. The analysis indicates that the splitting in the branches results from the $\Omega$-doubling in the excited state $^3\Delta_2$ and $^3\Delta_3$ spin components. A local perturbation has been observed in the excited state $v=0$ vibrational level of the $D\ ^3\Delta_3$ spin component. This perturbation affects only the $f$-parity levels at $J'=26$. The high $J$ lines ($J>80$) of this spin component are also affected by global interactions in the excited state.

## C. The $G\ ^3\Phi$–$C\ ^3\Delta$ system

In the 6100–6600 cm$^{-1}$ region, two bands with $R$-heads at 6339 and 6542 cm$^{-1}$ have been identified as the 0-0 bands of $^3\Phi_4$–$^3\Delta_3$ and $^3\Phi_3$–$^3\Delta_2$ subbands of the $G\ ^3\Phi$–$C\ ^3\Delta$ tran-


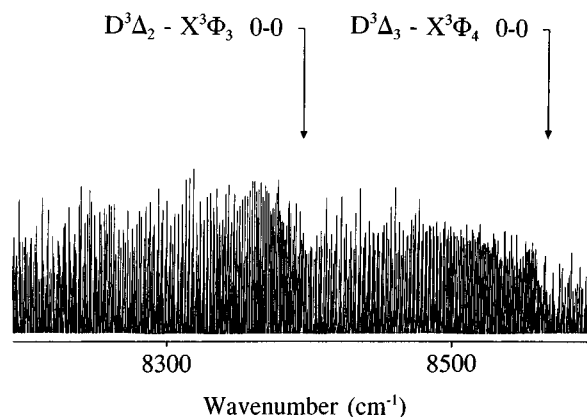
FIG. 5. A part of the compressed spectrum of the $D\ ^3\Delta$–$X\ ^3\Phi$ transition of CoF. The 0-0 bandheads of the two strong subbands have been marked.

TABLE I. Spectroscopic constants (in cm$^{-1}$) of the $X\ ^3\Phi$ state of CoF.[a]

| $v$ | $T_v$ | $B_v$ | $10^7 \times D_v$ | $10^{11} \times H_v$ | $10^{16} \times L_v$ | $10^8 \times q_{Dv}$ | $10^{12} \times q_{Hv}$ | $10^{16} \times q_{Lv}$ |
|---|---|---|---|---|---|---|---|---|
| | | | | $X\ ^3\Phi_4$ | | | | |
| 0 | 0.0 | 0.388 115 9(13) | 5.121 98(88) | −0.020 14(16) | ⋯ | ⋯ | ⋯ | ⋯ |
| 1 | 672.700 07(65) | 0.385 030 9(16) | 5.162 8(31) | 0.021 2(38) | −0.294(16) | ⋯ | ⋯ | ⋯ |
| 2 | 1 339.923 0(13) | 0.381 454 7(21) | 4.338 6(67) | −0.752(10) | 2.445(52) | ⋯ | ⋯ | ⋯ |
| 3 | 2 000.004 9(17) | 0.377 997 3(27) | 3.880(10) | −1.104(17) | 3.525(90) | ⋯ | ⋯ | ⋯ |
| 4 | 2 652.433 4(15) | 0.374 768 1(21) | 4.052 3(45) | −0.574 6(36) | ⋯ | ⋯ | ⋯ | ⋯ |
| 5 | 3 297.214 1(18) | 0.371 552 0(25) | 3.924 7(72) | −0.663 0(66) | ⋯ | ⋯ | ⋯ | ⋯ |
| 6 | 3 934.270 0(17) | 0.368 441 4(24) | 3.948 1(65) | −0.646 3(58) | ⋯ | ⋯ | ⋯ | ⋯ |
| | | | | $X\ ^3\Phi_3$ | | | | |
| 0 | $a$ | 0.388 229 4(28) | 5.271 3(67) | 0.112(10) | −0.838(53) | ⋯ | 0.632 8(47) | ⋯ |
| 1 | $a+668.795\ 94(87)$ | 0.385 023 3(33) | 5.522(11) | 0.473(17) | −3.504(87) | ⋯ | 0.312(16) | ⋯ |
| | | | | $X\ ^3\Phi_2$ | | | | |
| 0 | $b$ | 0.388 579 1(92) | 5.216(22) | −0.042(15) | ⋯ | 1.674(31) | −3.498(85) | 1.955(57) |
| 1 | $b+702.594\ 0(31)$ | 0.379 339(13) | −2.608(68) | −5.35(14) | ⋯ | −2.69(50) | 31.9(44) | −56.0(96) |

[a]The numbers in parentheses are one standard deviation in the last digit and letters $a$ and $b$ represent undetermined positions of the $v=0$ vibrational levels of the $X\ ^3\Phi_3$ and $X\ ^3\Phi_2$ spin-components, respectively.

sition. The $^3\Phi_2-^3\Delta_1$ subband could not be identified because of its weaker intensity and overlapping from the other bands present in the expected spectral region.

The $G\ ^3\Phi_4-C\ ^3\Delta_3$ subband has a band origin of 6 331.176 35(98) cm$^{-1}$ which is the difference of the band origins of the $G\ ^3\Phi_4-X\ ^3\Phi_4$ and $C\ ^3\Delta_3-X\ ^3\Phi_4$ subbands [6 331.173 06(81) cm$^{-1}$]. This subband is the stronger of the two subbands. This band also consists of $P$, $Q$, and $R$ branches each doubled because of larger $\Omega$-doubling in the $C\ ^3\Delta_3$ spin component. The next higher wave number band at 6542 cm$^{-1}$ has been identified as $G\ ^3\Phi_3-C\ ^3\Delta_2$ subband. Again the origin of this subband is approximately equal to the difference of the band origins of the $G\ ^3\Phi_3-X\ ^3\Phi_3$ and $C\ ^3\Delta-X\ ^3\Phi_4$ subbands. The rotational constants are also in excellent agreement with the constants of the $G\ ^3\Phi_3$ and the $C\ ^3\Delta_2$ spin components.

### D. Additional bands in the $G\ ^3\Phi_4-X\ ^3\Phi_4$ subband

In a previous paper we have reported an analysis of the $G\ ^3\Phi-X\ ^3\Phi$ transition located near 1 $\mu$m. The bands due to three subbands, $^3\Phi_4-^3\Phi_4$, $^3\Phi_3-^3\Phi_3$, and $^3\Phi_2-^2\Phi_2$, have been observed. We analyzed the rotational structure of several bands of these subbands and obtained the principal mo-

lecular constants for the individual spin components. From this analysis we concluded that the ground state of this molecule is a $^3\Phi_i$ state. For the $G\ ^3\Phi_4-X\ ^3\Phi_4$ subband we obtained a high resolution rotational analysis of 12 bands involving the ground state vibrational levels $v=0$, 1, and 2 and the excited state vibrational levels $v=0$–5.

During the course of the analysis of the $D\ ^3\Delta-X\ ^3\Phi$ transition we identified several very weak bands which were later identified as belonging to the $G\ ^3\Phi_4-X\ ^3\Phi_4$ subband on the basis of a rotational analysis. These bands involve higher vibrational levels of the ground state $X\ ^3\Phi_4$ spin component.

Six new bands with origins at 8111, 8183, 8259, 8336, 8828, and 8911 cm$^{-1}$ have been identified as 3-6, 2-5, 1-4, 0-3, 2-4, and 1-3 bands, respectively. Each of these bands have a single $R$ and a single $P$ branch and no $\Omega$-doubling is resolved. The excited state combination differences from these bands match very well with the values obtained from the previous analysis. The molecular constants for different vibrational levels were obtained from the combined fit of the present data and the previous data for the $G\ ^3\Phi_4-X\ ^3\Phi_4$ reported earlier.[11] The line positions of all of the new bands are available from PAPS[20] or by request from the authors.

TABLE II. Spectroscopic constants (in cm$^{-1}$) of the $C\ ^3\Delta$ state of CoF.[a]

| $v$ | $T_v$ | $B_v$ | $10^7 \times D_v$ | $10^{11} \times H_v$ | $10^{15} \times L_v$ | $10^5 \times q_v$ | $10^8 \times q_{Dv}$ | $10^{12} \times q_{Hv}$ | $10^{16} \times q_{Lv}$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | | $C\ ^3\Delta_3$ | | | | | |
| 0 | 4 005.021 79(67) | 0.368 314 1(20) | 4.487 8(88) | −1.189(15) | 0.471 7(78) | 5.10(18) | −6.50(14) | 13.82(27) | −6.92(15) |
| 1 | 4 621.427 7(10) | 0.365 606 5(47) | 4.614(59) | −1.39(28) | 11.93(43) | ⋯ | 1.97(22) | −28.1(18) | 24.8(37) |
| 2 | 5 230.439 7(16) | 0.363 927 8(67) | 9.695(87) | 13.41(44) | −18.38(74) | ⋯ | 0.87(37) | −6.9(35) | −0.882(84) |
| | | | | $C\ ^3\Delta_2$ | | | | | |
| 0 | $a+3\ 751.556\ 98(77)$ | 0.369 515 6(34) | 5.319(16) | −0.238(40) | 0.830(36) | ⋯ | 2.655(57) | −5.11(29) | 16.26(36) |
| 1 | $a+4\ 359.355\ 43(87)$ | 0.366 645 4(30) | 5.418 2(69) | 0.034 1(56) | ⋯ | ⋯ | 0.147(22) | 0.296(39) | ⋯ |
| | | | | $C\ ^3\Delta_1$ | | | | | |
| 0 | $b+3\ 450.029\ 4(30)$ | 0.369 804 1(99) | 5.467(25) | −0.111(21) | 0.052 9(61) | ⋯ | −3.903(36) | 5.727(97) | −2.805(64) |

[a]Numbers in parentheses are one standard deviation in the last digit.

TABLE III. Spectroscopic constants (in cm$^{-1}$) of the $D\ ^3\Delta$ state of CoF.[a]

| $v$ | $T_v$ | $B_v$ | $10^7 \times D_v$ | $10^{12} \times H_v$ | $10^4 \times q_v$ | $10^8 \times q_{Dv}$ | $10^{12} \times q_{Hv}$ | $10^{16} \times q_{Lv}$ |
|---|---|---|---|---|---|---|---|---|
| | | | | $D\ ^3\Delta_3$ | | | | |
| 0 | 8 559.099 9(14) | 0.366 546 9(17) | 4.847 5(24) | −0.081(14) | −4.404(23) | −2.511(94) | 1.06(12) | −0.313(54) |
| | | | | $D\ ^3\Delta_2$ | | | | |
| 0 | $a$+8 389.368 81(77) | 0.365 926 3(25) | 4.902 8(32) | ⋯ | ⋯ | −1.448(17) | 0.513(32) | ⋯ |

[a]Numbers in parentheses are one standard deviation in the last digit.

In the absence of the satellite branches or transitions with $\Delta\Sigma \neq 0$, we were unable to determine a single set of molecular constants by fitting the observed wave numbers to a Hund's case (a) Hamiltonian. Therefore we decided to obtain an independent fit of each subband by fitting the observed line positions to the following Hund's case (c) expression:

$$F_v(J) = T_v + B_v J(J+1) - D_v[J(J+1)]^2 + H_v[J(J+1)]^3$$
$$+ L_v[J(J+1)]^4 \pm 1/2\{qJ(J+1)$$
$$+ q_D[J(J+1)]^2 + q_H[J(J+1)]^3$$
$$+ q_L[J(J+1)]^4\}. \tag{1}$$

In the final fit the lines of the different subbands were weighted depending on the signal to noise ratio and the extent of blending and perturbations. All connected subbands and vibrational levels were fitted together. The perturbed transitions were not directly included in the fit but the corresponding combination differences for the unperturbed levels were included. The molecular constants for the $X\ ^3\Phi$, $C\ ^3\Delta$, $D\ ^3\Delta$, and $G\ ^3\Phi$ states are provided in Tables I, II, III, and IV.

The $e/f$ parity assignment has been made arbitrarily. There are both local and global perturbations in the rotational energy levels and the $\Omega$-doubling constants are effective values that empirically account for some of the energy level splittings. In particular, the $\Omega$-doubling constants in $C\ ^3\Delta_3$ and $D\ ^3\Delta_3$ spin components reflect strong interactions with other states.

## IV. DISCUSSION

So far two $^3\Phi - X\ ^3\Phi$ electronic transitions of CoF have been observed, one near 600 nm by Adam et al.[10] and the other near 1 $\mu$m by the authors.[11] In addition to the $G\ ^3\Phi_i - X\ ^3\Phi_i$ transition we have observed numerous bands from 3000 to 9000 cm$^{-1}$ as discussed in this paper. There are no theoretical calculations available but the isovalent CoH molecule provides a guide for the assignment of these new transitions.

A $^3\Phi_i - X\ ^3\Phi_i$ transition of CoH has recently been observed by Barnes et al.[17] as well as by the authors near 1.2 $\mu$m.[18] Unfortunately, no electronic transitions of CoH have been reported below 1 $\mu$m, though some complex spectra have been observed recently and are being analyzed.[21] Recently Freindorf et al.[16] have published a very helpful ab initio calculation of the spectroscopic properties of low-lying excited electronic states of CoH. This calculation predicts many low-lying singlet, triplet, and quintet states giving rise to numerous red and infrared transitions. Two groups of triplet states each composed of $^3\Phi$, $^3\Delta$, $^3\Pi$, and $^3\Sigma^-$ states have been predicted below 1.7 eV. The first group correlates with the ground state dissociation limit Co[$^4F(d^7s^2)$]+H[$^2S$]

TABLE IV. Spectroscopic constants (in cm$^{-1}$) of the $G\ ^3\Phi$ state of CoF.[a]

| $v$ | $T_v$ | $B_v$ | $10^7 \times D_v$ | $10^{12} \times H_v$ | $10^{15} \times L_v$ | $10^8 \times q_{Dv}$ | $10^{12} \times q_{Hv}$ | $10^{16} \times q_{Lv}$ |
|---|---|---|---|---|---|---|---|---|
| | | | | $G\ ^3\Phi_4$ | | | | |
| 0 | 10 336.194 85(45) | 0.351 670 4(13) | 5.177 39(86) | ⋯ | ⋯ | ⋯ | ⋯ | ⋯ |
| 1 | 10 911.125 91(60) | 0.349 002 7(14) | 5.142 90(87) | ⋯ | ⋯ | ⋯ | ⋯ | ⋯ |
| 2 | 11 480.671 82(53) | 0.346 359 6(13) | 5.109 02(85) | ⋯ | ⋯ | ⋯ | ⋯ | ⋯ |
| 3 | 12 044.879 08(60) | 0.343 739 1(14) | 5.074 32(87) | ⋯ | ⋯ | ⋯ | ⋯ | ⋯ |
| 4 | 12 603.788 00(97) | 0.341 145 6(16) | 5.048 5(21) | 0.045(11) | ⋯ | ⋯ | ⋯ | ⋯ |
| 5 | 13 157.445 7(16) | 0.338 576 0(21) | 5.030 3(42) | 0.157(28) | ⋯ | ⋯ | ⋯ | ⋯ |
| | | | | $G\ ^3\Phi_3$ | | | | |
| 0 | $a$+10 285.418 01(68) | 0.352 665 5(30) | 5.263 1(83) | 1.17(13) | −0.067 7(65) | 0.533(24) | −1.756(69) | 1.188(42) |
| 1 | $a$+10 862.959 9(11) | 0.350 127 3(56) | 4.532(56) | −23.3(23) | 11.78(30) | −1.35(22) | 15.0(16) | −35.9(27) |
| 2 | $a$+11 435.282 6(18) | 0.347 902 8(83) | 5.23(10) | 211.3(47) | −31.41(71) | ⋯ | ⋯ | ⋯ |
| | | | | $G\ ^3\Phi_2$ | | | | |
| 0 | $b$+10 157.285 6(15) | 0.353 148(11) | 5.211(76) | ⋯ | ⋯ | ⋯ | −8.67(44) | 24.2(13) |
| 1 | $b$+10 734.595 3(22) | 0.350 178(15) | 4.70(20) | −221(11) | 31.1(19) | ⋯ | −16.7(21) | 54.2(80) |

[a]Numbers in parentheses are one standard deviation in the last digit.

while the second group dissociates to the first excited atomic limit $Co[^4F(d^8s^1)] + H[^2S]$ at about 4000 cm$^{-1}$ higher in energy.[22] The ground state of CoH is of $^3\Phi$ symmetry and is derived from the electronic configuration $6\sigma^2 7\sigma^2 d\pi^3 d\delta^3$. According to this calculation the excited states in order of increasing energy are of $^3\Sigma^-$, $^3\Pi$, and $^3\Delta$ symmetry. The $1\,^3\Delta$ state is predicted to lie 3700 cm$^{-1}$ above the $X\,^3\Phi$ state for CoH. The observed position of the $C\,^3\Delta - X\,^3\Phi$ transition of CoF is in excellent agreement with this prediction. Allowed transitions from the $2\,^3\Delta$ and $2\,^3\Phi$ states of the second group of triplet states to the ground $X\,^3\Phi$ state are expected to be present at 10 600 and 13 100 cm$^{-1}$, respectively. The 8400 cm$^{-1}$ and 10 300 cm$^{-1}$ transitions of CoF are most probably the isovalent transitions.

So far we have not been able to identify electronic transitions with $\Delta\Sigma \neq 0$ so that the relative position of the individual spin components is unknown, although work is in progress at University of New Brunswick[23] to measure these intervals. There are a few bands left unassigned because of their very weak intensity and heavy overlapping from stronger bands. Some of these bands may also be due to transitions involving quintet electronic states as predicted by Freindorf et al.[16]

The ground state constants do not vary in a regular manner. If the rotational constants and vibrational intervals of the $X\,^3\Phi_4$ spin component are fitted using the customary expressions the values $B_e = 0.389\,824(95)$ cm$^{-1}$, $\alpha_e = 0.003\,317(29)$ cm$^{-1}$, $\omega_e = 677.59(37)$ cm$^{-1}$, $\omega_e x_e = 2.16(20)$ cm$^{-1}$, and $\omega_e y_e = -0.161(28)$ cm$^{-1}$ are obtained. Although these constants are not well determined, no attempt was made to add additional constants because of the irregular vibrational dependence. This irregular behavior is probably caused by global interactions of these levels with nearby states. The observed local perturbations in various spin components could not be characterized in this work because of a lack of data. These perturbations provide a signature of several unobserved excited states consistent with the predictions of Freindorf et al.[16]

As noted by us and other workers,[24] there is remarkable correspondence between the electronic states of transition metal monohydrides and monohalides (particularly monofluorides). In the specific case of CoH and CoF, the known low-lying states are shown in Fig. 1. The CoH states in Fig. 1 are from the papers on the $A'\,^3\Phi - X\,^3\Phi$ transition[17,18] and our unpublished work.[21] While it is not certain that the $\Omega = 3$ CoH spin-components at 2469 cm$^{-1}$ and 8830 cm$^{-1}$ originate from $^3\Delta$ states, the ab initio calculations and the correspondence with CoF (Fig. 1) strongly suggest it.

The CoH calculations of Freindorf et al.[16] seem to be very reliable and the correspondence with CoF is excellent. This suggests that the ordering of all of the low-lying states of CoF can be obtained from the CoH calculation.[16] The low-lying states of CoH are indicated in Fig. 6, along with the customary spectroscopic letter labels. Of course, some of the details in Fig. 6 may be wrong for both CoH and CoF but the overall picture is probably correct.

The strong correspondence (Fig. 1) between M–F and M–H states is surprising at first sight because the $M^+F^-$
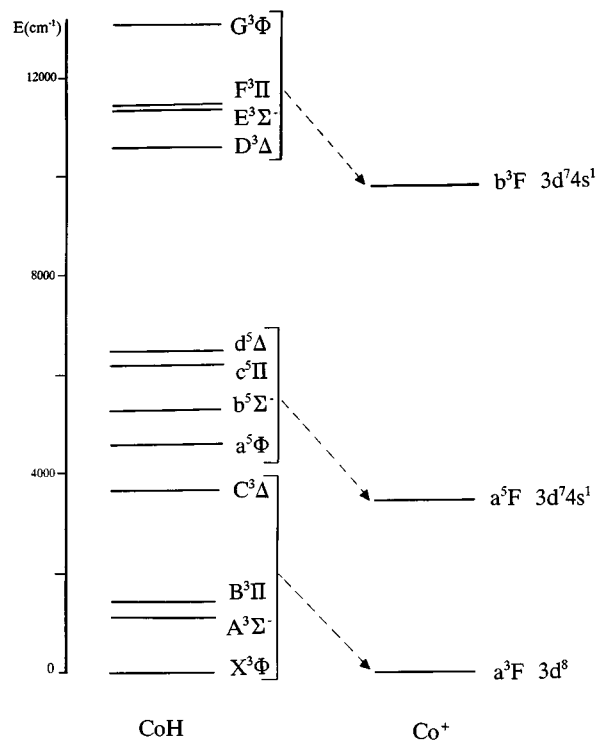


FIG. 6. Correspondence between the electronic states of CoH and atomic energy levels of Co$^+$. The CoH energy levels are from the ab initio calculations of Freindorf et al. (Ref. 16).

bond is expected to be much more ionic than the M–H bond. In both cases, however, the single bond forms by loss or pairing of an $s$ electron from the metal to leave a metal $d^n s^1$ or $d^{n+1}$ configuration. Qualitatively the diatomic electronic states then arise from the effects of the F$^-$ or H$^-$ ligand on the M$^+$ $d^n s^1$ and $d^{n+1}$ configurations. This simple picture is the most successful scheme for rationalizing the low-lying states of the MF and MH molecules. Barnes et al.,[17] for example, have used this model for CoH. The customary qualitative molecular orbital model is not very successful for transition metal-containing diatomics because there are large number of low-lying diatomic configurations that are very similar in energy.

The Co$^+$ atom has a ground state $a\,^3F$ term from the $3d^8$ configuration[22] which gives rise to the $X\,^3\Phi$, $A\,^3\Sigma^-$, $B\,^3\Pi$, and $C\,^3\Delta$ states in CoH (Fig. 6) in the 0–3700 cm$^{-1}$ range.[16] The first excited Co$^+$ term, $a\,^5F$, results in the $a\,^5\Phi$, $b\,^5\Sigma^-$, $C\,^5\Pi$, and $d\,^5\Delta$ states between 4600 and 6500 cm$^{-1}$. Finally, the $b\,^3F$ term from the $4d^7 4s^1$ configuration gives the $D\,^3\Delta$, $E\,^3\Sigma^-$, $F\,^3\Pi$, and $G\,^3\Phi$ CoH states from 10 600 cm$^{-1}$ to 13 100 cm$^{-1}$. The atomic terms in Fig. 6 are the weighted $(2J+1)$ average of the atomic energy levels.[22] Notice that both the $X$, $A$, $B$, and $C$ states and the $a$, $b$, $c$, and $d$ states follow the order $\Phi$, $\Sigma^-$, $\Pi$, and $\Delta$ and that the $D$ to $G$ states have the opposite energy order. This ordering of the states which arise from a particular Co$^+$ atomic term is difficult to predict without a high quality ab initio calculation. However, given a particular order, such as $\Phi$, $\Sigma^-$, $\Pi$, and $\Delta$, the pattern repeats itself. Other transition metal hydrides and

fluorides such as FeH (Ref. 25) and FeF (Ref. 21) seem to have low-lying states which follow analogous patterns.

## V. CONCLUSION

The near infrared spectrum of CoF has been observed using the 1 m Fourier transform spectrometer of the National Solar Observatory. The molecules were made in a carbon tube furnace at a temperature of about 2300 °C from the reaction of Co metal vapor and $CF_4$. The bands observed in the 3000–9000 cm$^{-1}$ spectral regions have been classified into three new electronic transitions $C\ ^3\Delta - X\ ^3\Phi$, $D\ ^3\Delta - X\ ^3\Phi$, and $G\ ^3\Phi - C\ ^3\Delta$. In addition, six new bands involving ground state vibrational levels up to $v=6$ have been identified for the $G\ ^3\Phi_4 - X\ ^3\Phi_4$ subband. The ground state vibrational intervals and rotational constants do not vary with $v$ in a normal fashion indicating the presence of global interactions with nearby states. The strong correlation between the low-lying states of CoF, CoH, and Co$^+$ is noted.

## ACKNOWLEDGMENTS

[1] A. J. Merer, Annu. Rev. Phys. Chem. **40**, 407 (1989).

[2] C. J. Cheetham and R. F. Barrow, Adv. High Temp. Chem. **1**, 7 (1967).

[3] P. B. Armentrout and J. L. Beauchamp, Acc. Chem. Res. **22**, 315 (1989).

[4] B. Rosen, *Spectroscopic Data Relative to Diatomic Molecules* (Pergamon, Oxford, 1970).

[5] W. E. Jones and G. Krishnamurthy, J. Phys. B **13**, 3375 (1982).

[6] A. J. Cernicharo and M. Guélin, Astron. Astrophys. **183**, L10 (1987).

[7] L. M. Ziurys, A. J. Apponi, and T. G. Phillips, Astrophys. J. **433**, 729 (1994).

[8] A. Jorissen, V. V. Smith, and D. L. Lambert, Astron. Astrophys. **261**, 164 (1992).

[9] S. Mattar (private communication).

[10] A. G. Adam, L. P. Fraser, W. D. Hamilton, and M. C. Steeves, Chem. Phys. Lett. **230**, 82 (1994).

[11] R. S. Ram, P. F. Bernath, and S. P. Davis, J. Mol. Spectrosc. **173**, 158 (1995).

[12] L. Klynning and M. Kronekvist, Phys. Scr. **24**, 21 (1981).

[13] T. D. Varberg, E. J. Hill, and R. W. Field, J. Mol. Spectrosc. **138**, 630 (1989).

[14] K. Lipus, T. Nelis, E. Bachem, and W. Urban, Mol. Phys. **68**, 1171 (1989).

[15] S. P. Beaton, K. M. Evenson, T. Nelis, and J. M. Brown, J. Mol. Spectrosc. **164**, 395 (1994).

[16] M. Freindorf, C. M. Marian, and B. A. Hess, J. Chem. Phys. **99**, 1215 (1993).

[17] M. Barnes, A. J. Merer, and G. F. Metha, J. Mol. Spectrosc. **164**, 395 (1995); (private communication).

[18] R. S. Ram, P. F. Bernath, and S. P. Davis, J. Mol. Spectrosc. **175**, 1 (1996).

[19] R. B. LeBlanc, J. B. White, and P. F. Bernath, J. Mol. Spectrosc. **164**, 574 (1994).

[20] See AIP document No. PAPS JCPSA-104-6949-71 for 71 pages of data tables. Order by PAPS number and journal reference from American Institute of Physics Auxiliary Publication Service, Carolyn Gehlbach, 500 Sunnyside Boulevard, Woodbury, New York 11797-2999. The price is $1.50 for each microfiche (98 pages) or $5.00 for photocopies of up to 30 pages and $0.15 for each additional page over 30 pages. Airmail additional. Make checks payable to the American Institute of Physics.

[21] R. S. Ram, P. F. Bernath, and S. P. Davis, J. Mol. Spectrosc. (submitted).

[22] C. E. Moore, *Atomic Energy Levels* (National Bureau of Standards, Gaithersburg, 1952), Vol. II.

[23] A. G. Adam (private communication).

[24] For example, A. J. Merer (private communication).

[25] S. R. Langhoff and C. W. Bauschlicher, J. Mol. Spectrosc. **141**, 243 (1990).