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# The pure rotational spectrum of $CoO(X^4\Delta_i)$ : Identifying the high-spin components

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#### Abstract

New measurements of the pure rotational spectrum of the CoO radical in its  $X^4\Delta_i$  state (v = 0 and v = 1) have been conducted using millimeter-wave direct absorption techniques. CoO was created by the reaction of cobalt vapor and N<sub>2</sub>O. Spectra arising from the  $\Omega = 3/2$  and 1/2 spin levels, both which exhibit  $\Lambda$ -doubling, have been recorded, as well as from the  $\Omega = 7/2$  and 5/2 ladders, which have been studied in the past. Rotational, fine structure,  $\Lambda$ -doubling and hyperfine parameters for the v = 0 and v = 1 states have been established from a global analysis of all four spin components. The data suggest a near-by  ${}^{4}\Sigma$  state. © 2005 Elsevier B.V. All rights reserved.

## 1. Introduction

Establishing the ground electronic states of molecules containing transition metals is useful in understanding their bonding characteristics [1]. Because of the presence of d electrons, many electron configurations are possible, which in turn generate a variety of electronic terms. Ab initio calculations are not necessarily conclusive in determining the electronic ground states of these species and experiments can be misleading. Cobalt oxide, CoO, is a good example.

Earlier work on CoO suggested a  ${}^{4}\Sigma^{-}$  ground electronic state (e.g. [2,3]), as was supported by several ab initio studies [4,5]. The first gas-phase high resolution investigation by Adam et al. in 1985 [6], identified  $\Omega = 5/2$  and 7/2 spin components in what was postulated to be a  ${}^{4}\Delta_{i}$  ground state. Subsequently, Clouthier et al. [7] conducted an analysis of the hyperfine structure of these two spin components using laser spectroscopy, and the  $A^{4}\Pi_{i}-X^{4}\Delta_{i}$  transition in the near-infrared was recorded by Ram et al. [8]. The latter work included rotational analyses of the 5/2–7/2 and 3/2–5/2 subbands, but the higher energy spin–orbit transitions could not be assigned. Recently, Barnes et al. [9] measured over 100 bands of CoO originating from the  $X^{4}\Delta_{7/2}$  spin component using beam techniques, while Namiki and Saito [10] recorded the first pure-rotational spectrum of CoO in its  $\Omega = 7/2$  and 5/2 sub-levels. Subsequent ab initio studies have suggested the ground state assignment as  ${}^{4}\Delta_{i}$  [11,12].

Here, new measurements of the pure rotational spectrum of CoO in its  $X^4\Delta_i$  state are presented. Transitions arising from all four spin components have been recorded for the v = 0 and v = 1 levels – the first complete rotational study of a molecule in a  $^4\Delta$  state. Improved spectroscopic constants have been derived for CoO and an interpretation of the  $\Lambda$ -doubling and hyperfine parameters is given.

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## 2. Experimental

The rotational spectrum of CoO was measured using the high temperature millimeter-wave spectrometer of the Ziurys group [13]. Briefly, the instrument is composed of a radiation source, a reaction chamber, and a detector. Phase-locked Gunn oscillators with Schottky diode multipliers provide frequency coverage over the range 65–650 GHz. The radiation is propagated quasi-optically through the reaction cell, which is a double-pass system, where it is subsequently detected by an InSb bolometer. The source is FM-modulated and signals are processed by a lock-in-amplifier at 2f.

CoO was created by the reaction of  $N_2O$  with cobalt vapor. The vapor was produced by heating solid cobalt in a Broida-type oven. Approximately 15–20 mTorr of  $N_2O$  was then added to the cell from beneath the oven. A dc discharge was not found necessary for the reaction.

Final frequency measurements were obtained by averaging 5 MHz scans, one in increasing and one in decreasing frequency. Averages of up to three scan pairs were required for the weaker features. Center frequencies were established by fitting each line to a Gaussian profile. Typical line-widths varied from 1000 kHz at 375 GHz to 1400 kHz at 525 GHz.

### 3. Results and analysis

Using predictions for CoO based on Namiki and Saito [10], a search was conducted for the  $\Omega = 3/2$  and 1/2 spin-orbit components, which resulted in the observation of several sets of harmonically related octets (Co: I = 7/2). The first group consisted of two sets of octets, separated by ~5-10 MHz in frequency. These features were assigned to the  $\Omega = 3/2$  spin-component with  $\Lambda$ -doubling. In the second group, two distinct octets were also observed with a much larger separation of ~300 MHz. These lines were attributed to the  $\Lambda$ -doublets of the  $\Omega = 1/2$  sub-level. A further search of ~6B revealed no new spectral features, except for those arising from the first-vibrationally excited state (v = 1).

Five complete rotational transitions that included all four spin-orbit components were recorded for the v = 0state of CoO – a total of 213 new features. Three rotational transitions were measured for the v = 1 state; only one of these included all four spin levels. A subset of these data is presented in Table 1. The remainder can be found at http://www.chem.arizona.edu/faculty/ziur/ ziur-group.html.

A stick spectrum of the  $J = 15.5 \leftarrow 14.5$  rotational transition of CoO is presented in Fig. 1. The four spin-components of the ground state are shown with approximate experimental intensities, as well as the

v = 1 state, shifted ~4 GHz to lower frequency. In both vibrational states, the intensity of each spin-component diminishes with decreasing  $\Omega$  value, consistent with an inverted term.

In Fig. 2, laboratory spectra of the  $\Omega = 3/2$  and 1/2 spin-orbit components of the  $J = 12.5 \leftarrow 11.5$  transition of CoO (v = 0) are shown. The  $\Omega = 3/2$  data (a) consist of 16 resolved features. The larger splitting, indicated by the *F* quantum number, arises from the cobalt nuclear spin. Each hyperfine feature is further split by  $\sim 2$  MHz as a result of  $\Lambda$ -doubling. In the case of the  $\Omega = 1/2$  component (b), the doubling is much larger ( $\sim 300$  MHz) and necessitates a frequency break in the spectrum. The individual doublets, labeled by e and f, are in turn split into hyperfine octets.

The spectra of CoO were fit to the following effective Hamiltonian [14–16]:

$$H_{\rm eff} = H_{\rm rot} + H_{\rm so} + H_{\rm ss} + H_{\rm ld} + H_{\rm hf} + H_{\rm so}^{(3)} + H_{\rm eqQ}.$$
 (1)

This expression consists of rotational, spin–orbit, spin– spin,  $\Lambda$ -doubling, magnetic hyperfine, and quadrupole terms, as well as the third-order spin–orbit interaction. The v = 0 and v = 1 data sets were fit separately.

Unlike the past rotational analysis, A, the spin-orbit constant,  $\lambda$ , the spin-spin parameter, and  $\eta$ , the thirdorder spin-orbit correction, could all be fit independently. The value of A was found to be nearly identical to that derived from optical data (163 vs. 166 cm<sup>-1</sup>: [7]). In principle, four constants characterize A-doubling in <sup>4</sup> $\Delta$  states:  $\tilde{n}_{\Delta}$ ,  $\tilde{o}_{\Delta}$ ,  $\tilde{p}_{\Lambda}$ , and  $\tilde{q}_{\Lambda}$  [16]. In the case of CoO, however, this splitting is sufficiently small such that only  $\tilde{n}_{\Delta}$  and  $\tilde{o}_{\Delta}$  could be established. The parity assignment was arbitrarily set; switching the parity did not change the fit other than to reverse the signs of the  $\Lambda$ -doubling constants. For the hyperfine structure, the Frosch and Foley parameters a, b, and b + c were fit, as well as two centrifugal distortion corrections  $b_{\rm D}$  and  $(b+c)_{\rm D}$ . Both  $b_{\rm s}$ , the third-order spin-orbit distortion term to the Fermi contact interaction [17], and  $d_{\Delta}$ , used to account for differences in hf splittings between lambdadoublets, did not appear to influence the fit and hence were not used. It is interesting to note that  $b_s$  was no longer determinable using the full data set. The v = 1data were analyzed in an identical manner except Aand eqQ were held fixed to the values established from the v = 0 fit.

The results of these analyses are given in Table 2. For the v = 0 data, one set of constants was established by fitting the data obtained in this work only, and another set was determined from a combined fit with the spectra of Namiki and Saito [10]. Also given in the table are the previous constants from Namiki and Saito, which included spectra from the  $\Omega = 7/2$  and 5/2 ladders only. The constants are in reasonable agreement, given the difference in data sets.

Table 1 Selected transition frequencies of  $\text{CoO}(X^4\Delta_i)^a$ 

$J + 1 \leftarrow J$	$F+1 \leftarrow F$	$\Omega = 3.5$		$\Omega = 2.5$		Par	$\Omega = 1.5$		$\Omega = 0.5$	
		v <sub>obs</sub>	$v_{o-c}$	v <sub>obs</sub>	$v_{o-c}$		v <sub>obs</sub>	$v_{o-c}$	v <sub>obs</sub>	$v_{o-c}$
$v = 0$ $12.5 \leftarrow 11.5$	0	255120 055	0.010	25/025 200	0.010		250020 550	0.164	250046 400	0.150
	$9 \leftarrow 8$	3/5120.0/5	0.218	376835.209	-0.018	e	3/8030.7/9	-0.164	379046.408	-0.156
	10 0	275100 020	0 155	27(925.0(9	0.004	I	3/8032.965	-0.101	3/9350.9/3	-0.100
	$10 \leftarrow 9$	3/5108.829	0.155	3/6825.068	0.004	e	378023.640	-0.052	3/9044.509	-0.054
	11 10	275004 522	0 100	27(911.0(5	0.049	I	3/8025.913	0.096	3/9348.961	-0.141
	$11 \leftrightarrow 10$	373094.323	0.108	3/0811.905	0.048	e f	378014.229	0.011	3/9041.910	0.13/
	12 11	275077 141	0.056	276705 822	0.022	1	378010.482	0.156	379340.332	-0.010
	$12 \leftarrow 11$	5/50//.141	0.050	570795.825	0.055	e f	378002.000	0.074	379038.394	0.134
	13 / 12	375056 700	0.014	376776 701 <sup>b</sup>	0.015	1	377088 606	0.221	379034 047	-0.030
	$13 \leftarrow 12$	575050.700	0.014	570770.701	0.015	f	377990 900	0.052	379338 567	_0.073
	14 ← 13	375033 238	0.020	376754 580	-0.023	e	377972 570	0.006	379029 154	0.017
	14 \ 15	575055.250	0.020	570754.500	0.025	f	377974 756	0.000	379333 623	0.001
	15 ← 14	375006 634	-0.043	376729 525	-0.015	e	377954 242	-0.058	379023 414	0.001
	15 11	575000.051	0.015	510125.525	0.015	f	377956 457	0.024	379328.014	0.021
	16 <i>←</i> 15	374977 042	-0.018	376701 433	-0.059	e	377933 770	-0.021	379017 108	-0.030
	10 10	<i>5713771</i> 012	01010	0,0,01100	01000	f	377936.015	0.021	379321.724	0.068
16.5 ← 15.5	$13 \leftarrow 12$	494945.902	-0.139	497207.128	-0.049	f	498800.214	-0.153		
						e	498796.030 <sup>c</sup>	-0.645		
	$14 \leftarrow 13$	494937.861	-0.110	497200.108	-0.034	f	498796.030 <sup>c</sup>	0.420		
						e	498791.953	0.037		
	$15 \leftarrow 14$	494928.492	-0.091	497191.866	0.031	f	498789.743	-0.173		
						e	498786.169	-0.051		
	$16 \leftarrow 15$	494917.800	-0.071	497182.256	0.006	f	498783.305	0.022	500511.008	0.424
						e	498779.629	-0.044	500208.043	0.440
	$17 \leftarrow 16$	494905.802	-0.025	497171.403	0.024	f	498775.798	0.092	500509.012	0.098
						e	498772.001	-0.005	500206.033	0.104
	$18 \leftarrow 17$	494892.468	0.025	497159.306	0.091	f	498767.240	0.060	500506.897	-0.041
						e	498763.464	-0.013	500203.910	-0.048
	$19 \leftarrow 18$	494877.816	0.106	497145.832	0.085	f	498757.754	0.057	500504.586	-0.067
						e	498754.022	0.031	500201.556	-0.136
	$20 \leftarrow 19$	494861.829	0.214	497131.084	0.121	f	498747.278	0.029	500502.049	-0.006
						e	498743.570	0.029		
v = 1										
15.5 ← 14.5	$12 \leftarrow 11$	461320.356	0.156	463424.609	-0.007	t	464898.770	0.028		
	10 10	461211 702	0.144	462417.050	0.000	e	464895.528	0.041		
	$13 \leftarrow 12$	461311./02	0.144	463417.050	0.099	Ι	464893.226	-0.241		
	14 12	461201 204	0.011	462407 790	0.020	e	464890.124	-0.086		
	$14 \leftarrow 15$	401301.304	-0.011	403407.780	0.039	1	404887.213	0.139		
	15 / 14	461280 402	0.064	462207.000	0.025	e f	404883./3/	-0.038		
	15 ← 14	401269.402	-0.004	403397.009	0.025	1	404879.477	-0.025		
	16 15	461275 075	0.021	162281 626	0.026	e f	404870.130	-0.085	466407 155	0.060
	$10 \leftarrow 15$	401275.975	-0.051	405564.050	-0.050	I P	464867 605	0.050	466180 333	-0.009
	17 ← 16	461260 893	-0.033	463370 844	0.045	f	464861 052	0.000	466494 805	0.145
	1/ 10	101200.075	0.055	+05570.0 <b>-</b> +	0.045	e	464857 603	-0.101	466177 832	0.092
	18 ← 17	461244 219	0.002	463355 181	-0.173	f	464849 980	-0.001	466491 755	_0 192
	10 17		0.002		5.175	e	464846.797	0.085	466174.849	-0.089
	19 ← 18	461225.920	0.052	463338.340	0.014	f	464837.812	-0.021	466488.979	0.226
	-					е	464834.548	-0.014	466171.639	-0.148

<sup>a</sup> In MHz; residuals from combined fit.

<sup>b</sup> From [10].

<sup>c</sup> Unresolved lines, not included in the least squares fit.

### 4. Discussion

Because all four  $\Omega$  ladders have been measured in both the v = 0 and v = 1 levels, equilibrium constants can be obtained for CoO. These parameters are listed in Table 2. The bond distance  $r_e$  was calculated to be 1.627862(1) Å. This value varies slightly from that of Ram et al. [8], who found  $r_e = 1.628626(32)$  Å. Our bond length agrees well with the equilibrium value derived from computational methods. Dolg et al. [11],



Fig. 1. A stick figure of the  $J = 15.5 \leftarrow 14.5$  rotational transition of CoO(X<sup>4</sup> $\Delta_i$ ), showing line positions and approximate relative intensities of the four spin components in the v = 0 and v = 1 states. The pattern is fairly regular, with  $\Lambda$ -doubling present in the  $\Omega = 3/2$  and 1/2 sublevels.

for example, calculated  $r_e = 1.637$  and 1.623 Å for CI(SD) and CI(SD) + Q levels of theory, respectively. In contrast, a shorter bond length of 1.599 Å was obtained for the proposed  ${}^{4}\Sigma^{-}$  state. Bauschlicher and Maitre [12] determined  $r_e = 1.6208$  Å using CASSCF methods.

The  $\Lambda$ -doubling constant  $\tilde{n}_{\Delta}$  is in the diagonal matrix element for the  $\Omega = 1/2$  sub-level, while  $\tilde{o}_{\Delta}$  is off diagonal for the  $\langle 3/2 | \hat{H}_{LD} | 1/2 \rangle$  element [16]. In contrast, the  $\tilde{p}_{\Delta}$  term is in the diagonal element for the  $\Omega = 3/2$  spin component. Based on the values of  $\tilde{n}_{\Delta}$  and  $\tilde{o}_{\Delta}$ , however,  $\tilde{p}_{\Delta}$  is estimated to be <0.001 MHz, and hence could not be confidently fit. (The error on  $\tilde{o}_{\Delta}$  is 0.0082 MHz.) Consequently, it is odd that Ram et al. [8] were able to establish  $\tilde{q}_{\Delta} = q_{\Delta} = 0.0181$  MHz and  $\tilde{p}_{\Delta} = p_{\Delta} + 4q_{\Delta}$ = 3.646 MHz especially since they only analyzed  $\Omega = 5/2$  and 7/2 data of the ground state.

Both excited  ${}^{4}\Pi$  and  ${}^{4}\Sigma$  states contribute to the  $\Lambda$ -doubling in a  ${}^{4}\Delta$  state. Assuming the  $\Lambda^{4}\Pi$  state is the main  $\Pi$  contributor in CoO, the energy of the principal perturbing  ${}^{4}\Sigma$  state can be estimated from the  $\Lambda$ -doubling constants using the expressions [16],

$$\tilde{n}_{\Delta} \cong \frac{-24\sqrt{5}a^3B}{(E_{\Delta} - E_{\Pi})^2 (E_{\Delta} - E_{\Sigma})},\tag{2}$$

$$\tilde{o}_{\Delta} \cong \frac{-72a^2 B^2}{\left(E_{\Delta} - E_{\Pi}\right)^2 \left(E_{\Delta} - E_{\Sigma}\right)}.$$
(3)

Here, *a* is the spin-orbit constant associated with the one electron operator  $\sum_i a_i \hat{l}_i \hat{s}_i$ , and *B* is the rotational constant. Equating the denominators of these expressions and using the values of  $\tilde{n}_{\Delta}$  and  $\tilde{o}_{\Delta}$  determined here yields a  $\approx -226 \text{ cm}^{-1}$ . This agrees well with the spin-orbit constants established for the X<sup>4</sup> $\Delta$  state



Fig. 2. Spectra recorded for  $\text{CoO}(X^4\Delta_i)$  in its  $\Omega = 3/2$  and 1/2 spin ladders. In (a) ( $\Omega = 3/2$ ), the eight hyperfine components arising from the cobalt nuclear spin, labeled by quantum number *F*, are split again into doublets indicated by e and f, as a result of  $\Lambda$ -doubling. In (b) ( $\Omega = 1/2$  data), the  $\Lambda$ -doubling is much larger such that two distinct sets of octets are present, separated by over 300 MHz. (a) is a single, 120-MHz wide scan of about 1 min in duration, while (b) is a composite of two such scans, with a frequency break of ~150 MHz.

 $(-163 \text{ cm}^{-1})$  and A<sup>4</sup>II states  $(-152 \text{ cm}^{-1})$  in CoO. None of these values agree with the Co<sup>+</sup> spin–orbit constant of  $-536 \text{ cm}^{-1}$  [18], suggesting that cobalt oxide is not entirely represented by a Co<sup>+</sup>O<sup>-</sup> configuration.

Using  $a \approx 163 \text{ cm}^{-1}$ , and assuming  $E_{\Pi} - E_{\Delta} = E(A^4\Pi) \approx 5500 \text{ cm}^{-1}$  [8], the  $\Lambda$ -doubling constants imply that a  ${}^{4}\Sigma^{-}$  state lies  $\sim 2200-3100 \text{ cm}^{-1}$  above ground state. This energy is remarkably close to a low-lying state at 3038 cm<sup>-1</sup> identified by Barnes et al. [9]. These authors postulate that this state is the B<sup>4</sup>\Sigma<sup>-</sup> term arising from a  $\sigma^{1}\delta^{4}\pi^{2}$  electron configuration. In order for it to contribute to  $\Lambda$ -doubling, however, the state must have a different electron configuration to connect with the  $\sigma^{2}\delta^{2}\pi^{3}$  A<sup>4</sup> $\Pi$  state. An alternative is a  $\sigma^{1}\delta^{2}\pi^{4}$  configuration.

Table 2 Spectroscopic parameters for  $\text{CoO}(X^4\Delta_i)^a$ 

Parameter	This work $(v = 0)$	Combined fit $(v = 0)$	This work $(v = 1)$	Previous work $(v = 0; \Omega = 7/2 \text{ and } 5/2)^{b}$
В	15096.3673(38)	15096.3664(29)	14976.798(10)	15096.8969 (14)
D	0.0209598(68)	0.0209573(59)	0.021051(18)	0.0209695(36)
A	-4881000(78000)	-4884000(62000)	$-4884000^{\circ}$	$-4982900^{\circ}$
$A_{\rm D}$	-4.13(37)	-4.14(29)	-4.1825(12)	-4.73853(43)
λ	199800(6000)	200000(4700)	201963(67)	219400 <sup>c</sup>
η	48700(1400)	48800(1100)	49799(33)	35624°
$\tilde{n}_{\Delta}$	-51.103(16)	-51.103(17)	-53.370(36)	
$\tilde{o}_{\Delta}$	0.1524(82)	0.1527(76)	0.1506(63)	
a	685.7(2.1)	685.9(1.2)	686.4(6.3)	649.1(1.3)
b	-292(12)	-297(10)	-314(34)	
С				-135.9(2.2)
(b+c)	-323.9(3.0)	-328.9(1.5)	-327(10)	-274.2(2.3)
$b_{\mathbf{D}}$	-0.0770(98)	-0.0751(74)	-0.078(25)	
$(b+c)_{\rm D}$	0.200(14)	0.1802(89)	0.217(39)	
bs				-9.41(45)
eqQ	-60(18)	-52.4(7.4)	$-52.4^{\circ}$	-37.9(1.5)
rms	0.095	0.104	0.096	0.021
Be	15156.151(10)			
α <sub>e</sub>	119.569(10)			
r <sub>e</sub>	1.627862(1) Å			

<sup>a</sup> In MHz; errors are  $3\sigma$  and apply to the last quoted decimal places.

<sup>b</sup> From [10].

<sup>c</sup> Held fixed.

The proposed electron configuration for CoO in its ground state is  $9\sigma^2 \ 1\delta^3 \ 4\pi^2$ . The *a* hyperfine constant, therefore, must originate solely from the single unpaired  $\delta$  electron. Because this orbital arises exclusively from the cobalt atom, the *a* parameter should reflect the atomic hyperfine constant of  $a_{3d(Co)}^{01} = 617.9$  MHz [19]; a = 685.7 (2.1) MHz for CoO, which is in relatively good agreement.

Both  $\pi$  and the  $\delta$  electrons contribute to the *c* hyperfine constant. Because *c* is directly proportional to  $\langle 3\cos^2\theta_i - 1/r_i^3 \rangle$ , angular factors play a major role in determining its value. For the  $3d\pi$  and  $3d\delta$  orbitals,  $\langle 3\cos^2\theta_i - 1 \rangle = 2/7$  and -4/7, respectively [7], and thus they should effectively cancel each other. The *c* constant should therefore be small; we measure c = -32 (12) MHz.

The Fermi contact term is  $b_{\rm F} = -303$  (12) MHz. No s electrons are present in unfilled  $\sigma$  orbitals in CoO, and therefore spin polarization must be responsible for this interaction. Usually spin polarization results in a small, negative value of  $b_{\rm F}$  [20]; while the term established here is negative, it is not particularly small. However, three unpaired electrons are available in CoO to exchange with the  $\sigma$  bonding electrons. As demonstrated in other molecules, multiple unpaired electrons can make a significant contribution to spin polarization. In CrH, for example, there is one unpaired electron in a  $\sigma$  orbital. Its positive contribution to  $b_{\rm F}$  is negated by the effects of spin polarization due to four unpaired  $\pi$  and  $\delta$  electrons [21]. The net result is a negative value of  $b_{\rm F}$ . The large negative value of  $b_{\rm F}$  in CoO probably results from the same phenomenon.

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