

## A laserinduced fluorescence study of bands of the red system of gaseous CoO: Evidence for a $4\Delta$ i ground state

A. G. Adam, Y. Azuma, Judith A. Barry, Gejian Huang, Michael P. J. Lyne, A. J. Merer, and J. O. Schröder

Citation: *The Journal of Chemical Physics* **86**, 5231 (1987); doi: 10.1063/1.452599

View online: <http://dx.doi.org/10.1063/1.452599>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/86/10?ver=pdfcov>

Published by the [AIP Publishing](#)

### Articles you may be interested in

Laserinduced Fluorescence Spectroscopy of CoS: Identification of a New Excited State Arising from the Ground State

*Chin. J. Chem. Phys.* **26**, 701 (2013); 10.1063/1674-0068/26/06/701-704

Hyperfine and spin-orbit structure of the  $4\Delta$  i ground state of CoO

*J. Chem. Phys.* **99**, 6336 (1993); 10.1063/1.465872

A laserinduced fluorescence study of the BiF  $AO^+ \rightarrow X^1 O^+$  system in the region 6550 to 7400 Å: Rotational analysis and evidence for an  $AO^+$  state potential maximum

*J. Chem. Phys.* **99**, 2365 (1993); 10.1063/1.465252

Conformational studies of xanthene by laserinduced fluorescence in a supersonic free jet: Inversion potentials in ground and excited singlet states

*J. Chem. Phys.* **98**, 836 (1993); 10.1063/1.464247

Laserinduced fluorescence of gaseous UF<sub>6</sub> in the A- $\tilde{X}$  band

*J. Chem. Phys.* **69**, 2181 (1978); 10.1063/1.436821



# A laser-induced fluorescence study of bands of the red system of gaseous CoO: Evidence for a ${}^4\Delta_1$ ground state

A. G. Adam, Y. Azuma, Judith A. Barry, Gejian Huang, Michael P. J. Lyne, A. J. Merer, and J. O. Schröder<sup>a)</sup>

*Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, B. C. V6T 1Y6, Canada*

(Received 24 November 1986; accepted 20 January 1987)

Three bands of the "red" system of gaseous CoO have been rotationally analyzed using laser-induced fluorescence techniques. The available evidence indicates that the lower levels are the  $\Omega = 7/2$  and  $5/2$  spin-orbit components of a  ${}^4\Delta_1$  electronic state, which is assigned as the ground state of the molecule. The cobalt nuclear hyperfine splittings are small in the ground state, which suggests that no unpaired electron in a  $\sigma$  molecular orbital derived from the Co  $4s$  atomic orbital is present, so that the electron configuration is presumably  $\sigma^2\delta^3\pi^2$ ; the ground state bond length ( $r_0$ ) is 1.631 Å. The upper electronic levels are heavily perturbed, both rotationally and vibrationally, and their hyperfine structures, though following case (a) behavior, are large and irregular. This work on CoO completes the determination of the ground state symmetries and bond lengths for the whole series of the  $3d$  transition metal monoxides; some comparisons for the members of the series are given.

## I. INTRODUCTION

With the recent determination of the ground state symmetry and bond length in gaseous nickel oxide, NiO, by Srdanov and Harris,<sup>1</sup> the only remaining  $3d$  transition metal monoxide for which no rotational analyses are available is cobalt oxide, CoO. However, cobalt oxide is not a complete spectroscopic blank because its ground state vibrational fundamental has been observed in an argon matrix by Green, Reedy, and Kay,<sup>2</sup> and a number of complex electronic bands in the red and near infrared have been reported by Malet and Rosen.<sup>3</sup>

In this paper we report analyses of three of the most prominent subbands of the red system of CoO, near 6400 Å, from laser-induced fluorescence spectra taken following the reaction of cobalt atoms with oxygen. The two strongest subbands are  $\Omega = 7/2-7/2$  transitions, where the lower state vibrational frequency,  $851.7\text{ cm}^{-1}$ , closely matches the matrix value for the ground state,  $846.4\text{ cm}^{-1}$ <sup>2</sup>; the third subband is an  $\Omega = 5/2-5/2$  transition. The conclusions are that the lower state of the red system is probably the ground state, and that it is  ${}^4\Delta_1$ , for which  $\Omega = 7/2$  is the lowest-energy spin-orbit component.

The upper state of the red system of CoO is very severely perturbed, both vibrationally and rotationally, in a manner reminiscent of the orange system of FeO.<sup>4</sup>

## II. EXPERIMENTAL

Gas phase CoO was prepared by the reaction of cobalt atoms with  $\text{O}_2$  in a Broida-type oven.<sup>5</sup> The temperature required for efficient evaporation of cobalt was well above the melting point of the metal ( $1495^\circ\text{C}$ ), and was high enough that extensive reaction occurred between the alumina crucible and the liquid metal. The principal reaction product was Thénard's Blue<sup>6</sup> (a beautiful purple-blue colored aluminate

of cobalt, first described in 1805) which unfortunately formed a scum on the liquid surface which seems to have limited the time for which we could operate the oven. Normally it was possible to run the oven only for about 2 h in each experiment. A further problem was the reaction between the cobalt vapor and the tungsten heating basket, where alloy formation weakened the tungsten to the extent that it usually broke after three firings of the oven, despite our efforts to keep the vapor away from the tungsten with thick claddings of zirconia felt.

No CoO chemiluminescence can be seen when cobalt reacts with  $\text{O}_2$  gas, though the presence of CoO is demonstrated by the observation of laser-induced fluorescence. This is exactly as in Srdanov and Harris' work on NiO,<sup>1</sup> where they showed that the thermodynamics of the reaction result only in the population of the ground state of the oxide. It was also found that  $\text{O}_2$  was a more efficient oxidant than  $\text{N}_2\text{O}$  for CoO production, which is the opposite of the way copper and manganese behave.

Laser excitation spectra in the ranges of the dyes DCM and rhodamine 6G were recorded using a Coherent Inc. model 599-21 dye laser pumped with about 3 W of 5145 Å argon laser light. Calibration was provided by the absorption spectrum of iodine,<sup>7</sup> together with 1.5 GHz interpolation markers from a Fabry-Perot étalon. The spectra were recorded using a PDP 11/23 computer to scan the laser and acquire the data; the line frequencies were determined by setting the cursor to the line centers on the computer's graphics terminal.

For our wavelength-resolved fluorescence experiments we used a microchannel-plate intensified array detector (PAR model 1461) mounted in the place of the exit slit of a 0.7 m spectrometer (Spex model 1702), and operated under control of the PDP 11/23 computer. In our previous work on FeO<sup>4</sup> we had had problems with the reproducibility of the scanning mechanism of the spectrometer, which meant that the combination differences in the wavelength-resolved flu-

<sup>a)</sup> Permanent address: Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, D-1000 Berlin 33, West Germany.

orescence spectra were only accurate to about  $\pm 2 \text{ cm}^{-1}$ . Since there are often 5–10 rotational lines in  $1 \text{ cm}^{-1}$  this is not enough to identify unambiguously the lines with the same upper level as the line being excited. Using the array detector we could switch off the spectrometer scanning mechanism, and calibrate the spectral “window” of the detector by setting the dye laser to three points across its wavelength range and recording spectra of the laser light scattered from a white card. The laser wavelength was given directly by a Burleigh model WA-20VIS wavemeter checked against the iodine atlas.<sup>7</sup> With this arrangement we could obtain calibration accuracy to about  $\pm 0.3 \text{ cm}^{-1}$  with a few seconds of integration time for the strong CoO lines. However, even with this sevenfold improvement in calibration accuracy there was still some ambiguity left in the identification of the lines of the wavelength-resolved patterns given by the weaker features because of the great density of lines in the CoO excitation spectrum.

### III. ROTATIONAL STRUCTURE OF THE 6338 Å BAND

The red system of CoO, as observed by laser excitation, is a long confused progression of very strongly red degraded bands, which we have investigated from 7000 to 5800 Å so far; it is probable that the system continues to both longer and shorter wavelengths. The principal vibrational intervals vary erratically from about 550 to about  $750 \text{ cm}^{-1}$ , and there are clearly bands from more than one electronic transition present. Some of the bands given as “strong” in the spectrum of an exploding wire<sup>2</sup> are not at all prominent in the laser excitation spectrum and vice versa. We list the wave numbers of the principal subband heads in Table I, and in Fig. 1 we show a portion of the excitation spectrum near 6400 Å, recorded with the intracavity assembly removed from the dye laser so as to give a linewidth of  $\sim 1 \text{ cm}^{-1}$ . Near 6400 Å there are four obvious subband heads with associated branch structure, while high resolution studies show that there is an irregular background of weak rotational lines throughout the region.

We chose the band at 6338 Å for our first studies since it lies near the maximum of the gain curve of the dye DCM, and it appears to have strong, mostly regular, branch structure. Its head is shown in Fig. 2. It is very clearly a parallel band, where the value of  $\Omega$  is quite high, as judged by the intensity of the first lines of the  $Q$  branch. Rotational analysis of the region in Fig. 2 was straightforward, though to be completely sure we carried out some wavelength-resolved

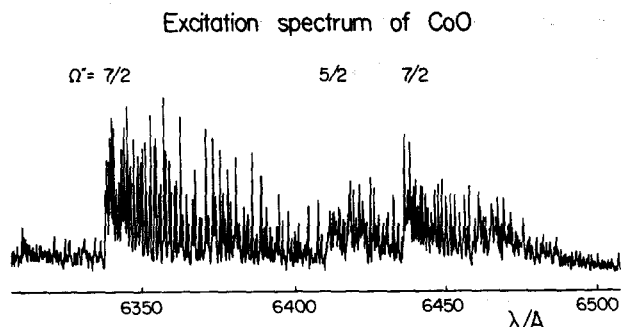


FIG. 1. Laser excitation spectrum of gas-phase CoO in the wavelength region 6310–6500 Å (CR 599 dye laser in broad-band operation).

fluorescence experiments to check which lines possessed common upper levels. The first lines of the  $R$  and  $P$  branches are hyperfine broadened and therefore not particularly prominent as a result of the parallel selection rules. The first line of the  $Q$  branch, though hyperfine-broadened also, is quite strong and unmistakable; its rotational assignment,  $Q(3.5)$ , shows unambiguously that the transition is an  $\Omega = 7/2-7/2$  subband.

As for the vibrational assignment, we can say nothing about the upper state vibrational quantum number until we have performed similar experiments using  ${}^{18}\text{O}_2$ , though  $v'$  is presumably at least 2 because the red system extends at least this far to longer wavelengths. Even with isotope data available the numbering may still be ambiguous because of the extensive large perturbations and the presence of apparently random “interloper” levels which are high vibrational levels of lower-lying electronic states obtaining oscillator strength by strong local interactions. The lower state is certainly the  $v'' = 0$  level of the  ${}^4\Delta_1$  state because laser excitation of lines of the 6338 Å band produces fluorescence about  $850 \text{ cm}^{-1}$  to the red of the exciting line, but nothing to the blue.

The cobalt hyperfine structure resulting from the  $I = 7/2$  spin of  ${}^{59}\text{Co}$  is responsible for the widening of the low  $J$  lines shown in Fig. 2. The hyperfine widths are seen to decrease with  $J$ , in the manner characteristic of case (a) coupling in both states. The  $P$  branch hyperfine widths are slightly larger than the  $R$  branch widths for lines with the

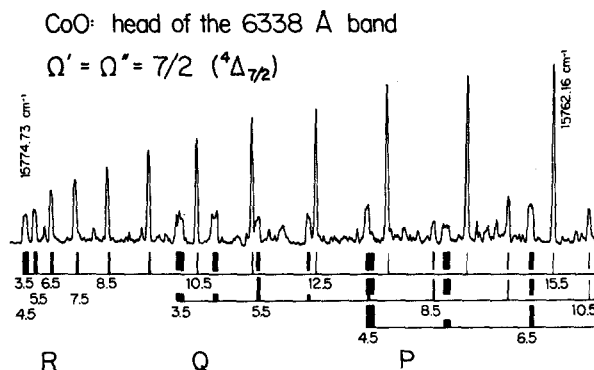


FIG. 2. Head of the 6338 Å subband ( $\Omega' = \Omega'' = 7/2$ ) in the excitation spectrum of CoO. The low  $J$  lines are hyperfine broadened. The signal-to-noise ratio is fairly high in this spectrum and all the weak lines in between the main lines are reproducible.

TABLE I. The most prominent bandheads of the red system of gaseous CoO, as observed by laser excitation.\* Values in  $\text{cm}^{-1}$ .

Wavelength group	5920 Å	6120 Å	6320 Å	6650 Å	6900 Å
Wave number and intensity	16 916 m 16 846 s	16 366 w 16 322 s 16 256 m 16 088 w	15 832 w 15 775 s 15 597 w 15 538 m	15 296 vw 15 228 w 15 036 m 15 004 s	14 705 w 14 477 m 14 469 s

\* The bandhead positions are taken from broad-band scans, and are probably accurate to  $\pm 3 \text{ cm}^{-1}$ ; s = strong, m = medium, w = weak.

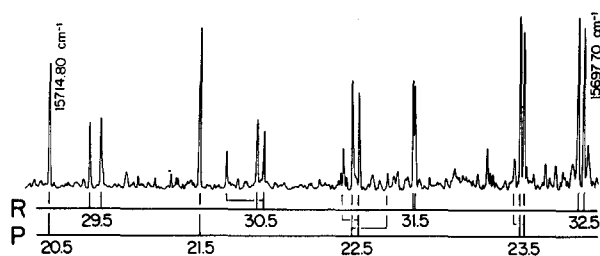


FIG. 3. Central portion of the 6338 Å band of CoO, showing the two principal upper state perturbations. This spectrum is a composite from several scans of the dye laser, so that the relative intensities of well-separated lines may not be accurate. The background of weak lines is reproducible, as in Fig. 2.

same  $J''$ , but about the same for lines with the same  $J'$ . This means that the hyperfine structure is wider in the upper state. Its sense can be deduced from the partly resolved hyperfine structure in the  $P(5.5)$  line, where higher dispersion spectra show clearly that the structure opens out on the high frequency side. Since the hyperfine energy in case ( $a_\beta$ ) coupling<sup>8</sup> goes as

$$E_{\text{hfs}} \approx \Omega[a\Lambda + (b+c)\Sigma](1/J) \times \frac{[F(F+1) - I(I+1) - J(J+1)]}{2(J+1)} \quad (1)$$

it is clear that the side of the rotational line the with more open hyperfine structure corresponds to the high values of  $F$ . The conclusion is that the value of  $\Omega[a\Lambda + (b+c)\Sigma]$  is positive in the upper state, such that the high  $F$  values give the high frequency hyperfine components. The implications of this will be discussed below.

As yet we have not performed experiments at sub-Doppler resolution to determine the hyperfine parameters; it is hoped that these can be carried out at a later date.

An interesting result of the hyperfine structure is that the  $Q$  branch lines, whose intensities should decrease as  $1/J$ , have essentially the same maximum fluorescence intensity over a considerable range of  $J$ , as can be seen in Fig. 2. This happens because the hyperfine structure collapses to give a sharper line with increasing  $J$ , and compensates for the decrease in the total intensity with  $J$ .

Returning to the rotational structure, the branches of Fig. 2 can be followed to higher  $J$  values, but beyond  $J' = 20.5$  they are split irregularly into two components,

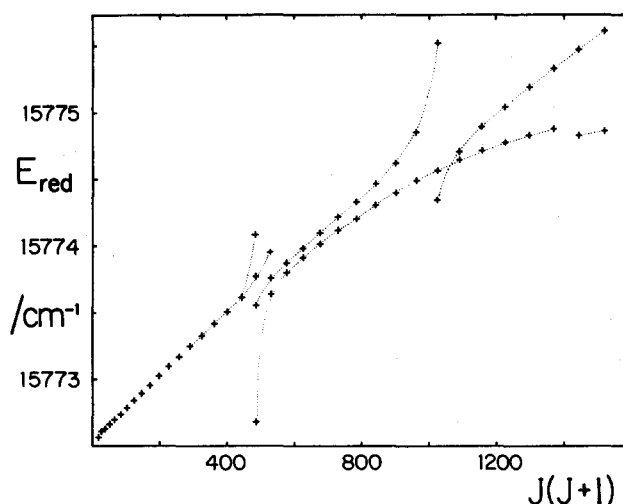


FIG. 4. Reduced upper state energy levels of the 6338 Å band of CoO ( $\Omega' = 7/2$ ), less a quantity  $0.405 J(J+1) - 6.4 \times 10^{-7} J^2(J+1)^2$ , plotted against  $J(J+1)$ .

with extra lines sometimes appearing. A portion of the center of the band showing the doubling and some of the extra lines is illustrated in Fig. 3. Combination differences prove that the doubling and the perturbations are in the upper state, and that there is no hint of any  $\Lambda$  doubling in the lower state. The upper state energy levels, with suitable scaling to magnify the details, are shown plotted against  $J(J+1)$  in Fig. 4. A very clear avoided crossing of one of the  $\Lambda$  components with an unseen orbitally nondegenerate state occurs near  $J = 30$ , and a smaller, but similar, avoided crossing occurs in the other  $\Lambda$  component near  $J = 36$ . The perturbation in the two  $\Lambda$  components near  $J = 22$  seems to be caused by a degenerate state with a small but nonzero  $\Omega$  doubling. Enough extra lines have been identified to give approximate rotational constants for the perturbing state:

$$T_0 = 15\,760.7 \text{ cm}^{-1}, B_{\text{eff}} = 0.432 \text{ cm}^{-1}.$$

It can be argued that all four perturbations might be caused by a single  $^4\Sigma$  state in case (a) coupling; in such a state<sup>9</sup> the  $^4\Sigma_{3/2}$  component has quite small  $\Omega$  doubling, but the two components of  $^4\Sigma_{1/2}$  have a large splitting between levels with the same  $J$  value so that they would cross the upper state of Fig. 4 at quite different places.

Least squares fits have been carried out to obtain the

TABLE II. Rotational constants for the analyzed bands of the red system of CoO.<sup>a</sup> Values in  $\text{cm}^{-1}$ .

Upper levels	$T_0$	$B$	$10^7 D$	$\sigma$
6338 Å, $\Omega = 7/2$	$15\,772.513 \pm 3$	$0.405\,31 \pm 9$	$6.4 \pm 19$	0.0038
6411 Å, $\Omega = 5/2$	$a + 15\,594.974 \pm 2$	$0.425\,0_3 \pm 24$	$27 \pm 7$	0.0049
6436 Å, $\Omega = 7/2$	$15\,535.77$	$0.422_4^b$	...	...
Lower levels ( $X^4\Delta_1$ )				
$\Omega = 5/2$	a	$0.502\,6_6 \pm 9$	$3.6 \pm 14$	0.0024
$\Omega = 7/2$	0	$0.500\,58 \pm 4$	$6.50 \pm 15$	0.0031

<sup>a</sup> Error limits are three standard deviations, in units of the last significant figure. The energy level expression was taken as  $E(J) = T_0 + BJ(J+1) - DJ^2(J+1)^2$ , i.e., omitting terms in  $\Omega^2$ ,  $a \approx 244 \text{ cm}^{-1}$ .

<sup>b</sup> As can be seen from Fig. 5, upper state constants are difficult to determine and a least squares fit has not been attempted.

TABLE III. Assigned lines to the 6338 Å band of CoO ( $\Omega' = \Omega'' = 7/2$ ), and lower state  $\Delta_2F''$ s, in  $\text{cm}^{-1}$ .

$J''$	$R$	$Q$	$P$	$\Delta_2F''$	$10^3(\text{O} - \text{C})$
3.5	15 774.7*	15 771.060			
4.5	15 774.7*	15 770.2*	15 766.64*		
5.5	15 774.509	15 769.2*	15 764.737		
6.5	15 774.110	15 768.002	15 762.704	14.015	1
7.5	15 773.526	15 766.64*	15 760.494	16.014	-2
8.5	15 772.760	15 765.024	15 758.096	18.011	-6
9.5	15 771.810	15 763.259	15 755.515	20.013	-5
10.5	15 770.668	15 761.291	15 752.747	22.015	-3
11.5	15 769.343	15 759.158	15 749.791	24.021	2
12.5	15 767.828	15 756.829	15 746.647	26.024	6
13.5	15 766.126	15 754.316	15 743.319	28.017	-1
14.5	15 764.236	15 751.615	15 739.811	30.019	2
15.5	15 762.159	15 748.715	15 736.107	32.018	2
16.5	15 759.892		15 732.219	34.011	-3
17.5	15 757.445		15 728.147	36.012	1
18.5	15 754.806		15 723.880	38.006	-2
19.5	15 751.994		15 719.439	40.005	1
20.5	15 749.350	15 747.947	15 714.801	42.000	0
	15 748.821	15 749.039			
21.5	15 745.600	15 745.906	15 709.994	43.995	0
		15 745.720			
22.5	15 742.273	15 742.345	15 705.347	45.987	-3
			15 704.829	15 705.045	
23.5	15 738.696	15 738.769	15 699.615	47.984	1
			15 699.735		
24.5	15 734.923	15 735.005	15 694.290	49.980	4
25.5	15 730.951	15 731.051	15 688.720	51.975	6
26.5	15 726.783	15 726.911	15 682.948	53.968	8
27.5	15 722.428	15 722.592	15 676.986	55.956	6
28.5	15 717.883	15 718.106	15 670.826	57.938	-2
29.5	15 713.130	15 713.500	15 664.491	59.929	0
30.5	15 709.131	15 708.185	15 657.951	61.908	-9
	15 707.960				
31.5	15 703.047	15 703.110	15 651.226	63.903	0
32.5	15 697.705	15 697.888	15 645.226	65.890	1
			15 644.057		
33.5	15 692.171	15 692.441	15 637.158	67.870	-4
34.5	15 686.424	15 686.786	15 629.837	69.861	3
35.5	15 680.487	15 680.945	15 622.311	71.836	-5
36.5	15 674.251	15 674.893	15 614.591	73.820	-2
37.5	15 667.933	15 668.678	15 606.670	75.787	-15 <sup>a</sup>
38.5	15 661.347	15 662.251	15 598.464	77.783	1
39.5	15 654.547	15 655.638	15 590.150	79.752	-8
40.5	15 647.498	15 648.844	15 581.594	81.738	2
41.5	15 640.453*	15 641.831	15 572.810	83.713	1
42.5		15 634.643	15 563.785	85.684	-2
43.5		15 627.272	15 554.769	87.641	-18 <sup>a</sup>
44.5		15 619.712		89.615	-15 <sup>a</sup>
45.5		15 611.954		91.591	-9 <sup>a</sup>
46.5		15 604.010		15 528.121	
47.5			15 518.405*		

<sup>a</sup>Not used in least squares fit; an asterisk indicates a blended line.

upper and lower state constants. For the lower state the  $\Delta_2F''$  combination differences have been fitted to the standard formula, while for the upper state we fitted the unperturbed levels from  $J = 5.5$  to 19.5. The results are given in Table II. Probably the most interesting feature of the rotational constants is that the upper state  $B$  value is smaller than the ground state value by nearly 20%, implying an increase of bond length on electronic excitation of about 10%. The rotational lines assigned in the 6338 Å band are listed in Table III, along with the averaged lower state  $\Delta_2F''$  combination differences and their residuals from the least squares fit.

#### IV. ROTATIONAL ANALYSIS OF OTHER NEARBY BANDS

Two other bands have been partially analyzed rotationally. These are another  $\Omega = 7/2-7/2$  band whose head lies at 6436 Å (see Fig. 1) and an  $\Omega = 5/2-5/2$  band at 6411 Å. As explained above these are not the only bands in this region, and a dense background of weaker lines still remains to be assigned.

The  $\Omega = 7/2-7/2$  band at 6436 Å has the same lower state combination differences as the 6338 Å band described in the previous section, to within our experimental error.

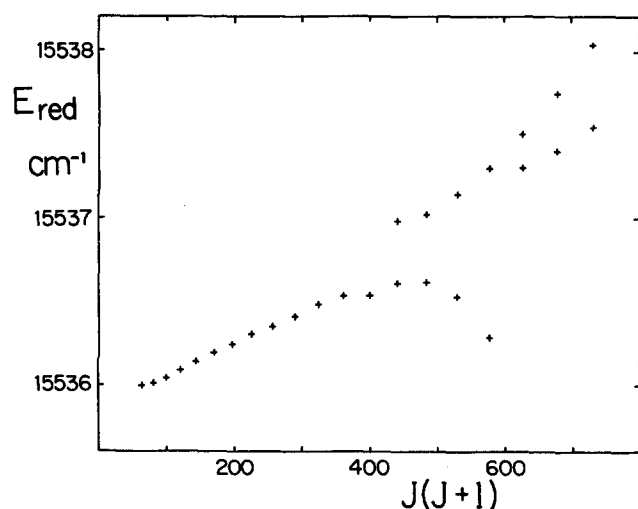


FIG. 5. Reduced upper state energy levels of the 6436 Å band of CoO ( $\Omega' = 7/2$ ) plotted against  $J(J+1)$ . A quantity  $0.42 J(J+1)$  has been subtracted to magnify the scale.

Therefore, there is another  $\Omega = 7/2$  upper level some  $237 \text{ cm}^{-1}$  below the first one. Now the prominent groups of subbands in the red system of CoO are separated by about  $600 \text{ cm}^{-1}$ , so that the second  $\Omega = 7/2$  upper level cannot belong to the same electronic state. In addition the hyperfine patterns of the low  $J$  lines in the 6436 Å band are much wider than those of the 6338 Å band, also indicating that a different excited electronic state is involved. The comparatively high intensity of the 6436 Å band suggests that it could belong to another overlapping  $^4\Delta$ - $^4\Delta$  electronic transition, but in view of our experience with  $\text{FeO}^4$ , where the strong interactions between the  $^5\Delta$  upper state of the orange system and the high vibrational levels of lower electronic states produce some surprisingly intense interloper bands (e.g.,  $\lambda = 5820 \text{ Å}$ ), we must defer a definite decision until we have examined much more of the spectrum at high resolution.

We have assigned the 6436 Å band up to  $J' = 26.5$  so far. Like the 6338 Å band it shows  $\Lambda$  doubling in the upper state beginning at about  $J = 20$ , and a similar density of rotational perturbations. The upper state levels are plotted against  $J(J+1)$  in Fig. 5, following the format of Fig. 4. An approximate upper state  $B$  value is included in Table II.

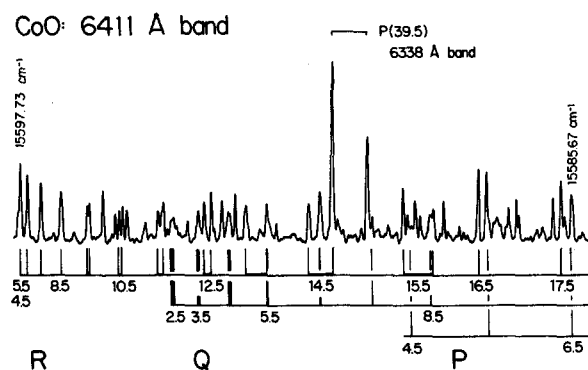


FIG. 6. Laser excitation spectrum of the head of the 6411 Å band of CoO ( $\Omega' = \Omega'' = 5/2$ ). Lines with no assignments marked belong to other bands.

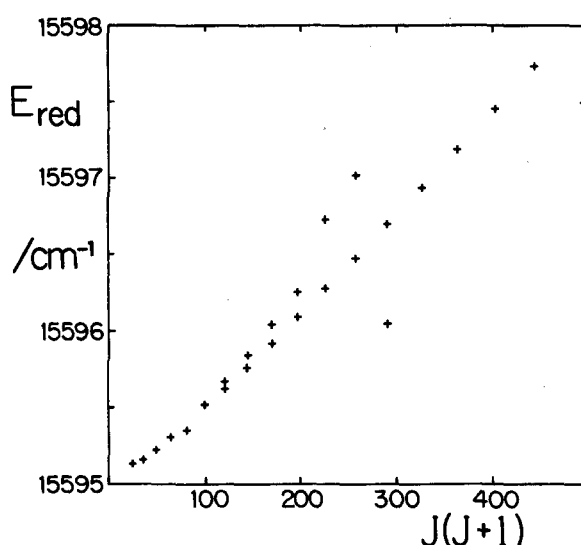


FIG. 7. Reduced upper state energy levels of the 6411 Å band of CoO ( $\Omega' = \Omega'' = 5/2$ ) plotted against  $J(J+1)$ . A quantity  $0.42 J(J+1)$  has been subtracted to magnify the scale.

The  $\Omega = 5/2$ - $5/2$  band at 6411 Å is quite weak compared to the two  $\Omega'' = 7/2$  bands, and because of extensive perturbations in the upper state we have not been able to follow it beyond  $J' = 20.5$ . The region around the head of the band is illustrated in Fig. 6, and the upper state energy levels are plotted against  $J(J+1)$  in Fig. 7. The  $\Lambda$  doubling in the upper state is much larger than in the  $\Omega = 7/2$  subbands, and is already apparent at Doppler-limited resolution at about  $J = 10$ . The importance of this subband is that it provides the rotational constant  $B_\Omega$  for another component of the  $^4\Delta_i$  ground state, such that the true  $B$  value for the ground state (and hence the bond length) can be obtained.

Unfortunately it has not been possible to obtain  $B''_{5/2}$  with the same accuracy as  $B''_{7/2}$ . The reason is that we cannot follow the structure to as high a  $J$  value as in the  $\Omega = 7/2$ - $7/2$  band at 6338 Å, which means that the data set is more limited. One of the  $\Lambda$  components disappears at  $J' = 16.5$ , and the higher  $J$  combination differences, which come from the other  $\Lambda$  component, give a  $D''$  value which is only 60% of that expected. Rather frustratingly, this other component disappears as well at  $J' = 20.5$ , and as yet we have been unable to follow this band to higher  $J$ . Bands where upper state perturbations of this type occur are common in the FeO spectrum<sup>4</sup>; often the branch structure will fade out and then reappear shifted some  $10$ - $20 \text{ cm}^{-1}$ , so that analysis is quite impossible without very extensive wavelength-resolved fluorescence studies. The greater experimental difficulties in preparing CoO have made such studies impractical so far.

As for the unusual  $D$  value it may indicate that there is  $\Lambda$  doubling in the  $\Omega = 5/2$  component of the ground state. Obviously  $\Lambda$  doubling shifts in one  $\Lambda$  component can be forced to fit the simple  $\Delta_2 F$  expression in  $B$  and  $D$  over a limited range of  $J$ , and will give an anomalous  $D$  value. Further work is needed to clarify this point.

The assigned lines of the 6411 and 6436 Å bands are listed in Table IV, and the upper state constants for the 6411 Å band are given in Table II; they were determined from a

TABLE IV. Rotational lines assigned in the 6411 and 6436 Å bands of CoO. Values in  $\text{cm}^{-1}$ .

$J$	6411 Å ( $\Omega' = \Omega'' = 5/2$ )			6436 Å ( $\Omega' = \Omega'' = 7/2$ ) <sup>a</sup>		
	$R$	$Q$	$P$	$R$	$P$	
2.5	15 597.270*	15 594.293				
3.5	15 597.577*	15 593.751				
4.5	15 597.730*	15 593.067	15 589.2*			
5.5	15 597.730*	15 592.23*	15 587.557			
6.5	15 597.577*	15 591.183	15 585.670			
7.5	15 597.270*	15 590.039*	15 583.654	15 537.998	15 524.45	
8.5	15 596.818	15 588.739	15 581.492	15 537.505	15 522.347	
9.5	15 596.194	15 596.240	15 579.076	15 536.866	15 519.996	
10.5	15 595.432	15 595.512	15 576.718	15 536.061	15 517.490	
11.5	15 594.523	15 594.647	15 574.076* 15 574.125	15 535.096	15 514.839	
12.5	15 593.461	15 593.618	15 571.307 15 571.389	15 533.976	15 512.039	
13.5	15 592.254	15 592.708	15 568.389 15 568.512	15 532.692	15 509.082	
14.5	15 590.896	15 591.441	15 565.323 15 565.493	15 531.241	15 505.950	
15.5	15 589.390	15 588.739	15 562.106 15 562.559	15 529.644	15 502.682	
16.5	15 587.729		15 558.734 15 559.270	15 527.897	15 499.226	
17.5	15 585.919		15 555.222 15 554.561	15 525.955	15 495.625	
18.5	15 583.958		15 551.558	15 523.820	15 491.877	
19.5	15 581.845		15 547.736	15 521.589 15 521.967	15 487.959	
20.5			15 543.770	15 519.128 15 519.536	15 483.815	
21.5			15 539.646	15 516.412 15 517.029	15 479.586	15 479.959
22.5				15 513.383 15 514.393	15 475.130	15 475.539
23.5				15 511.448 15 511.650	15 470.420	15 471.035
24.5				15 508.438 15 508.784	15 465.395	15 466.408
25.5					15 461.468	15 461.670
26.5					15 456.463	15 456.809
27.5					15 451.345	15 451.840

<sup>a</sup> Low  $J$  lines are severely hyperfine broadened. An asterisk indicates a blended line.

least squares fit to the upper levels  $J' = 5.5$ – $7.5$  and  $9.5$ – $16.5$  of the less perturbed  $\Lambda$  component.

## V. DISCUSSION

The rotational analyses reported here show that the most intense bands of the red system of CoO in laser excitation have  $\Omega'' = 7/2$ , and that the next most intense bands have  $\Omega'' = 5/2$ . This is consistent with the lower state being  $^4\Delta_i$ , where the lowest-energy spin-orbit component is  $\Omega = 7/2$ , followed by  $\Omega = 5/2$ . A very similar situation was found in the orange system of FeO,<sup>4</sup> where the bands with  $\Omega'' = 4$  coming from the lowest spin-orbit component of the  $^5\Delta_i$  ground state completely dominated the excitation spectrum.

The next question is whether the  $^4\Delta_i$  lower state of the CoO red system is the real ground state or a low-lying metastable excited state. There are two alternative possibilities for the ground state: one is  $\sigma\pi^2\delta^4\ ^4\Sigma^-$ , which was hypothesized by Krauss and Stevens,<sup>10</sup> extrapolating from their CAS-MCSCF calculations on FeO, while the other is  $\sigma^2\pi^2\delta^3\ ^4\Delta_i$ . It seems certain that these two states must lie fairly close in energy because this is what is found for the corresponding states throughout the transition metal oxide series, but as yet we cannot decide unambiguously between them. The clearest evidence would be if the red system were to be observed in the absorption spectrum of CoO isolated in a low-temperature matrix, because absorption from a state other than the ground state has never been found in low-temperature matrix work. Nevertheless the evidence favoring the  $^4\Delta_i$  state as

the ground state is fairly strong, as we now summarize.

(i) Wavelength-resolved laser-induced fluorescence experiments where we excited the  $Q(3.5)$  line of the  $\Omega'' = 7/2$  band at 6338 Å give the vibrational interval  $\Delta G''_{1/2} = 851.7 \pm 0.3\text{ cm}^{-1}$ . This value must be compared to Green, Reedy, and Kay's value<sup>2</sup> of  $846.4\text{ cm}^{-1}$  from their low-temperature matrix IR spectrum. The small gas-to-matrix shift of  $5.3\text{ cm}^{-1}$  that this implies seems very reasonable. On the other hand, we have to note that the corresponding gas-to-matrix shift in FeO is  $-2.0\text{ cm}^{-1}$ , that is, in the opposite sense.<sup>2,11</sup> Also it is known that the states of TiO corresponding to the  $\sigma\pi^2\delta^4\ ^4\Sigma^-$  and  $\sigma^2\pi^2\delta^3\ ^4\Delta_i$  states of CoO, namely  $\sigma\delta\ a\ ^1\Delta$  and  $\sigma^2\ b\ ^1\Sigma^+$ , have vibrational frequencies that are within  $5\text{ cm}^{-1}$  of each other.<sup>12</sup> Naively, it would be expected that the gas-to-matrix shifts in FeO and CoO should be virtually identical, so that an element of doubt creeps in, but the bonding properties of the  $\sigma$  and  $\delta$  orbitals change considerably across the  $3d$  transition series as the  $3d$  orbital shrinks in size with increasing atomic number, so that direct comparison between TiO and CoO may be misleading.

(ii) Van Zee *et al.* reported<sup>13</sup> that no low-temperature ESR spectrum has been observed for CoO under conditions where CoO was thought to be present, despite considerable effort. In their experiments ESR spectra are observed for molecules with  $\Sigma$  electronic ground states, but *not* orbitally degenerate ground states. The single exception to this statement is when the ground state is an odd-multiplicity case (a) state where the  $\Omega = 0$  component lies some way below the others and is the only one populated in the low-temperature



matrix: an example is NiO, where the ground state is  $^3\Sigma^-(0^+)$ , and no ESR spectrum is observed. Molecules in  $\Sigma$  states with even spin multiplicity show ESR spectra whatever the spin coupling. A good example is NbO, where an ESR spectrum is seen<sup>14</sup> even though the  $^4\Sigma_{3/2}$  component of the ground state lies  $62\text{ cm}^{-1}$  above the  $^4\Sigma_{1/2}$  component.<sup>15</sup> The negative result<sup>13</sup> of Van Zee *et al.* therefore argues against  $^4\Sigma^-$  as the ground state of CoO though, naturally, it is only prudent to treat a negative result with caution.

As for the bond length in the  $^4\Delta_i$  state, this can be determined from the formula<sup>16</sup>

$$B_{\text{eff},\Sigma} = B(1 + 2B\Sigma/A\Lambda) \quad (2)$$

which is derived by applying second-order perturbation theory to the matrix elements of the spin-uncoupling operator,  $-2B\mathbf{J}\cdot\mathbf{S}$ . Taking  $B_{\Omega=7/2} = 0.50058\text{ cm}^{-1}$  and  $B_{\Omega=5/2} = 0.50266\text{ cm}^{-1}$ , we find

$$B_0 = 0.5037_0; \quad A\Lambda \simeq -244\text{ cm}^{-1} \quad (3)$$

which gives

$$r_0(X^4\Delta_i) = 1.631\text{ \AA}. \quad (4)$$

The bond length is not particularly sensitive to the value of the spin-orbit coupling parameter  $A\Lambda$ , so that Eq. (4) should be correct to  $0.001\text{ \AA}$ . On the other hand, the value of  $A\Lambda$  is probably only accurate to  $\pm 10\%$ , judging from our experience with FeO, because Eq. (2) neglects the centrifugal distortion terms  $A_D$  and  $\lambda_D$ , which can have a sizable effect. The upper state bond lengths are about  $1.80\text{ \AA}$ , which represent a lengthening of  $10\%$  compared to the ground state; however such a change is not out of line with the changes observed in  $\text{FeO}^4$  and  $\text{MnO}$ .<sup>17</sup>

We turn now to the electron configurations of the states of CoO which, for lack of an alternative, we shall discuss in the single configuration approximation. As yet there have been no detailed *ab initio* calculations of the electronic structure of CoO, or the energies of its electronic states, but the experimental evidence comes from the spin-orbit coupling constants and, in particular, the hyperfine structure. It is well known that if an unpaired electron is present in a molecular orbital derived from the  $4s$  atomic orbital of the metal there will be a large positive Fermi contact interaction ( $H_{\text{Fermi contact}} = b\mathbf{I}\cdot\mathbf{S}$ ) caused by the penetration of the  $s$  electron into the spinning nucleus. The evidence given in

Sec. III is that the ground state hyperfine structure is quite small, but that the upper  $^4\Delta$  state has a fairly large hyperfine splitting in the sense corresponding to a positive Fermi contact parameter. The spin-orbit coupling constant for the ground state shows clearly that there is a "hole" in the  $3d\delta$  orbital, and the same is probably true for the upper state since the band structure falls into groups indicating that the spin-orbit components of a vibrational band lie close together, or in other words that  $(A\Lambda)' \simeq (A\Lambda)''$ . Therefore it is logical to assign the electron configurations as

$$\sigma\pi^2\delta^3\sigma^* (^4\Delta \text{ upper state}) \leftarrow \sigma^2\pi^2\delta^3 (^4\Delta \text{ ground state}) \quad (5)$$

which are equivalent to those of the orange system of FeO. In this description the  $\sigma$  molecular orbital is derived principally from the Co  $4s$  atomic orbital while the others are derived mainly from Co ( $3d$ ).

It is then not surprising that the upper state of the CoO red system is heavily perturbed. The configuration  $\sigma\pi^2\delta^3\sigma^*$  proposed for the upper state produces 19 electronic states, with multiplicities up to sextet and orbital angular momenta up to  $\Lambda = 4$ , many of which will interact strongly with each other. In addition there will be interactions with the even larger number of states derived from the configuration  $\pi^3\sigma^2\pi^2\delta^3\sigma^*$ , which is equivalent to that of the  $1\text{ }\mu\text{m}$  bands of FeO. In this configuration an electron has been promoted from the next  $\pi$  orbital down, which is essentially the  $2p\pi$  molecular orbital of the oxygen atom (and which is filled in the ground state) to the metal  $3d\sigma$  orbital ( $\sigma^*$ ); the promotion can be thought of as a charge-transfer transition. So far the evidence indicates that the CoO spectrum is very similar to the FeO spectrum both in the density and nature of the observed perturbations. The only perturbing state about which we can say anything definite appears to be a  $^4\Sigma$  state which must interact with the  $^4\Delta$  upper state by second order spin-orbit coupling.

Since this analysis of bands of the CoO spectrum completes the determination of the ground state bond lengths and symmetries for the  $3d$  transition metal monoxides, it is appropriate to tabulate their principal molecular constants for comparison purposes. This has been done in Table V. It is not the aim of this paper to attempt detailed correlations of the bond lengths and frequencies with the electronic structure, but it is hoped that this table will stimulate further *ab*

TABLE V. Ground states of the monoxides of the  $3d$  transition metals.<sup>a</sup>

Ground state	$\Delta G_{1/2}/\text{cm}^{-1}$	$B_0/\text{cm}^{-1}$	$r_0/\text{\AA}$	$A\Lambda$ or $\lambda/\text{cm}^{-1}$	Electron configuration	Ref.
<sup>45</sup> ScO $^2\Sigma^+$	964.65	0.513 43	1.668	...	$\sigma$	19
<sup>48</sup> TiO $^3\Delta_i$	1000.02	0.533 84	1.623	101.30	$\sigma\delta$	20
<sup>51</sup> VO $^4\Sigma^-$	1001.81	0.546 38	1.592	2.03	$\sigma\delta^2$	21, 22
<sup>52</sup> CrO $^3\Pi_r$	884.98	0.524 43	1.621	63.22	$\sigma\delta^2\pi$	23
<sup>55</sup> MnO $^6\Sigma^+$	832.41	0.501 22	1.648	(1.13)	$\sigma\delta^2\pi^2$	17
<sup>56</sup> FeO $^5\Delta_i$	871.15	0.516 81	1.619	-189.89	$\sigma\delta^3\pi^2$	12
<sup>59</sup> CoO $^4\Delta_i$	851.7	0.503 7 <sub>0</sub>	1.631	(-240)	$\sigma^2\delta^3\pi^2$	this work
<sup>58</sup> NiO $^3\Sigma^-$	828.5	0.505 <sub>8</sub>	1.631	(18)	$\sigma^2\delta^4\pi^2$	1
<sup>63</sup> CuO $^2\Pi_i$	629.39	0.442 08	1.729	-277.04	$\sigma^2\delta^4\pi^3$	24, 25

<sup>a</sup>The spin-orbit coupling constants given are  $A\Lambda$  for degenerate electronic states and  $\lambda$  [the coefficient of  $2(3S_z^2 - S^2)/3$  in the spin Hamiltonian] for  $\Sigma$  electronic states. Values in parentheses are still preliminary.



*initio* studies on these very difficult systems. Of special interest for *ab initio* work will be the spin-orbit coupling constants and the hyperfine parameters, both of which are very sensitive tests of *ab initio* wave functions, and which have been mostly neglected so far. In particular the Fermi contact hyperfine parameter is an important quantity since it carries information about what happens to the metal 4s electrons when the molecule is formed. In Table V we list the first order spin-orbit coupling constants,  $A\Lambda$ , for the degenerate electronic states, and the second order spin-orbit constants,  $\lambda$ , for the  $\Sigma$  electronic states. In passing we note that the value of  $A\Lambda$  for the  $X^4\Delta_i$  state of  $\text{FeO}^-$  ( $A\Lambda = -230 \text{ cm}^{-1}$ ) has also been measured,<sup>18</sup> and is very close to what we find for the ground state of CoO.

The hyperfine parameters are not listed in Table V, but they are now known accurately for  $\text{ScO}$ ,<sup>26</sup>  $\text{VO}$ ,<sup>21</sup>  $\text{MnO}$ ,<sup>27</sup> and  $\text{CuO}$ ,<sup>28</sup> either from solid state ESR or from gas phase optical and microwave studies. We have not yet measured the hyperfine parameters for  $\text{CoO}$ ,  $X^4\Delta_i$  but, as described above, it is clear that the hyperfine widths in the ground state are small; this is consistent with the proposed electron configuration  $\sigma^2\pi^2\delta^3$ .

To summarize, this work represents the first rotational analysis of bands of CoO. The results give the bond length and electron configuration of the ground state, and complete the series of determinations of the ground states of the 3d transition metal monoxides.

## ACKNOWLEDGMENTS

A. J. M. and A. G. A. thank the Natural Sciences and Engineering Research Council of Canada for financial support, and acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. J. O. S. thanks the Deutsche Forschungsgemeinschaft for a postdoctoral fellowship which enabled him to spend part of 1986 at the University of British Columbia. We also thank Dr. Ulf Sassenberg (University of Stockholm, Sweden) for his assistance in the early stages of the work.

- <sup>1</sup>V. I. Srdanov and D. O. Harris, *J. Chem. Phys.* (submitted).
- <sup>2</sup>D. W. Green, G. T. Reedy, and J. G. Kay, *J. Mol. Spectrosc.* **78**, 257 (1979).
- <sup>3</sup>L. Malet and B. Rosen, *Bull. Soc. R. Sci. Liège* **14**, 382 (1945); B. Rosen, *Nature* **156**, 570 (1945).
- <sup>4</sup>A. S.-C. Cheung, A. M. Lyyra, A. J. Merer, and A. W. Taylor, *J. Mol. Spectrosc.* **102**, 224 (1983).
- <sup>5</sup>J. B. West, R. S. Bradford, J. D. Eversole, and C. W. Jones, *Rev. Sci. Instrum.* **46**, 164 (1975).
- <sup>6</sup>L. J. Thénard, *J. Mines* **15**, 128 (1805).
- <sup>7</sup>S. Gerstenkorn and P. Luc, *Atlas du Spectre d'Absorption de la Molécule d'Iode* (CNRS, Paris, France, 1978); S. Gerstenkorn and P. Luc, *Rev. Phys. Appl.* **14**, 791 (1979).
- <sup>8</sup>C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill, New York, 1955).
- <sup>9</sup>I. Kopp and J. T. Hougen, *Can. J. Phys.* **45**, 2581 (1967).
- <sup>10</sup>M. Krauss and W. J. Stevens, *J. Chem. Phys.* **82**, 5584 (1985).
- <sup>11</sup>A. W. Taylor, A. S.-C. Cheung, and A. J. Merer, *J. Mol. Spectrosc.* **113**, 487 (1985).
- <sup>12</sup>K.-P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).
- <sup>13</sup>R. J. Van Zee, C. M. Brown, K. J. Zeringue, and W. Weltner, *Acc. Chem. Res.* **13**, 237 (1980).
- <sup>14</sup>J. M. Brom, C. H. Durham, and W. Weltner, *J. Chem. Phys.* **61**, 970 (1974).
- <sup>15</sup>A. J. Merer, U. Sassenberg, J. L. Féménias, and G. Cheval, *J. Chem. Phys.* **86**, 1219 (1987).
- <sup>16</sup>G. Herzberg, *Spectra of Diatomic Molecules*, 2nd ed. (Van Nostrand, Princeton, 1950).
- <sup>17</sup>R. M. Gordon and A. J. Merer, *Can. J. Phys.* **58**, 642 (1980).
- <sup>18</sup>T. Andersen, K. R. Lykke, D. M. Neumark, and W. C. Lineberger, in *Electronic and Atomic Collisions*, edited by D. C. Lorents, W. E. Meyerhof, and J. R. Peterson (Elsevier, Amsterdam, 1986), p. 791.
- <sup>19</sup>R. Stringat, Ch. Athénour, and J.-L. Féménias, *Can. J. Phys.* **50**, 395 (1972).
- <sup>20</sup>W. H. Hocking, M. C. L. Gerry, and A. J. Merer, *Can. J. Phys.* **57**, 54 (1979).
- <sup>21</sup>A. S.-C. Cheung, R. C. Hansen, and A. J. Merer, *J. Mol. Spectrosc.* **91**, 165 (1982).
- <sup>22</sup>A. S.-C. Cheung, A. W. Taylor, and A. J. Merer, *J. Mol. Spectrosc.* **92**, 391 (1982).
- <sup>23</sup>A. S.-C. Cheung, W. Zyrnicki, and A. J. Merer, *J. Mol. Spectrosc.* **104**, 315 (1984).
- <sup>24</sup>O. Appelblad and A. Lagerqvist, *Phys. Scr.* **10**, 307 (1974).
- <sup>25</sup>O. Appelblad and L. Klynning, USIP Report 81-02, University of Stockholm (1981).
- <sup>26</sup>W. Weltner, D. McLeod, and P. H. Kasai, *J. Chem. Phys.* **46**, 3172 (1967).
- <sup>27</sup>C. A. Baumann, R. J. Van Zee, and W. Weltner, *J. Phys. Chem.* **86**, 5084 (1982).
- <sup>28</sup>M. C. L. Gerry, A. J. Merer, U. Sassenberg, and T. C. Steimle, *J. Chem. Phys.* (in press).