

Perturbations in the pure rotational spectrum of CoCl (X 3 Φ i): A submillimeter study

M. A. Flory, D. T. Halfen, and L. M. Ziurys

Citation: The Journal of Chemical Physics **121**, 8385 (2004); doi: 10.1063/1.1795691 View online: http://dx.doi.org/10.1063/1.1795691 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/121/17?ver=pdfcov Published by the AIP Publishing

Articles you may be interested in

Rotational spectra of rare isotopic species of fluoroiodomethane: Determination of the equilibrium structure from rotational spectroscopy and quantum-chemical calculations J. Chem. Phys. **137**, 024310 (2012); 10.1063/1.4731284

Molecules in high spin states III: The millimeter/submillimeter-wave spectrum of the MnCl radical (X 7 Σ +) J. Chem. Phys. **122**, 054309 (2005); 10.1063/1.1824036

The pure rotational spectrum of TiF (X $4 \Phi r$):3d transition metal fluorides revisited J. Chem. Phys. **119**, 9496 (2003); 10.1063/1.1615753

Further studies of 3d transition metal cyanides: The pure rotational spectrum of NiCN (X 2 Δ i) J. Chem. Phys. **118**, 6370 (2003); 10.1063/1.1557471

The rotational spectrum of chloryl chloride, CICIO 2, in its ground vibrational state J. Chem. Phys. **110**, 11865 (1999); 10.1063/1.479179



Perturbations in the pure rotational spectrum of CoCl $(X^{3}\Phi_{i})$: A submillimeter study

M. A. Flory, D. T. Halfen, and L. M. Ziurys

Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, Arizona 85721

(Received 13 May 2004; accepted 29 July 2004)

The millimeter/submillimeter-wave spectrum of the CoCl radical $(X^{3}\Phi_{i})$ has been recorded using direct absorption techniques in the frequency range 340-510 GHz. This work is the first pure rotational study of this molecule. The radical was created by the reaction of Cl₂ with cobalt vapor. Rotational transitions arising from the Ω =4, 3, and 2 spin-orbit components of Co³⁵Cl have been measured, all of which exhibit hyperfine splittings due to the ⁵⁹Co nucleus (I=7/2). Transitions arising from the $Co^{37}Cl$ species were also recorded, as well as those originating in the v = 1, 2, 3, and 4 vibrational states of both isotopomers. The spin-orbit pattern exhibited by the molecule is unusual, with the $\Omega=3$ component significantly shifted relative to the other spin components. In addition, the regular octet hyperfine splittings become distorted above a certain J value for the $\Omega=3$ transitions only. These effects suggest that the molecule is highly perturbed in its ground state, most likely a result of second-order spin-orbit mixing with a nearby isoconfigurational ${}^{1}\Phi_{3}$ state. The complete data set for Co35Cl and Co37Cl were fit successfully with a case (a) Hamiltonian but required a large negative spin-spin constant of $\lambda = -7196$ GHz and higher order centrifugal distortion corrections to the rotational, spin-orbit, spin-spin, and hyperfine terms. The value of the spin-spin constant suggests that the $\Omega=3$ component is shifted to higher energy and lies near the $\Omega=2$ sublevel. The hyperfine parameters are consistent with a $\delta^3 \pi^3$ electron configuration and indicate that CoCl is more covalent than CoF. © 2004 American Institute of Physics. [DOI: 10.1063/1.1795691]

I. INTRODUCTION

Although cobalt has its origin in the helium shell burning in asymptotic giant branch stars and in explosive nucleosynthesis in supernovae,¹ it has many practical uses here on earth. For example, this element is employed as a catalyst in many industrial processes, such as hydroformylation,² and is used in olefin insertion reactions.³ Cobalt appears as the metal center in various biological molecules, including vitamin B₁₂, and in low symmetry sites in enzymes.⁴ It is used in metal alloys and in supramolecular chemistry in the construction of large metal complexes.⁵ Cobalt complexes have additionally served as dyes in ceramics and glass for thousands of years. Yet, despite the many applications of this element, the exact nature of how it bonds to even simple ligands is not well understood.⁶

The lack of understanding of the bonding in cobalt is illustrated by the history of a simple species, CoCl. Although cobalt (II) chloride is routinely used in general chemistry labs, until recently the electronic ground state of the monochloride CoCl was not known. Spectroscopic studies of this diatomic began as early as the 1930s, where various electronic bands were recorded in discharge experiments.^{7,8} However, the data were too complex to definitely assign an electronic ground state. As recently as 1997, theorists were still postulating what the term might be; using density functional theory methods, for example, Bridgeman concluded the ground state was ${}^{3}\Sigma^{-}$.⁹ However, in 2002, Adam *et al.*¹⁰ recorded two electronic systems of cobalt monochloride in

the range 415–725 nm using laser-ablation/molecular beam laser-induced fluorescence. They concluded both bands arose from a $X^{3}\Phi_{4}$ term. Consequently, in analogy to CoF (Ref. 11) and CoH,¹² these authors assigned the ground state of CoCl as $X^{3}\Phi_{i}$. Adam *et al.* also were able to resolve the cobalt hyperfine structure and determine the *h* parameter for several states. This work was followed by Fourier transform infrared spectroscopy of Hirao, Pinchemel, and Bernath in 2003,¹³ who recorded the same bands as Adam *et al.*, but also observed additional subbands; they were assigned to the $\Omega=3$ spin component of the ground state. In addition, the $[10.3]^{3}\Phi_{4}-X^{3}\Phi_{4}$ and $[11.0]^{3}\Phi_{4}-X^{3}\Phi_{4}$ electronic transitions were studied in the near infrared by Wong, Tam, and Cheung,¹⁴ who determined the *h* parameter in several vibronic levels.

Here we present the first investigation of the pure rotational spectrum of CoCl using millimeter/submillimeter direct absorption spectroscopy. Fifteen and twelve rotational transitions were recorded for Co³⁵Cl and Co³⁷Cl, respectively. All three spin components were clearly identified in the spectra, which repeated in both chlorine isotopomers and in several vibrational states, providing conclusive evidence that the electronic ground state is ${}^{3}\Phi_{i}$. In addition, cobalt hyperfine structure was resolved in all three sublevels. Both the fine and hyperfine structure showed evidence of perturbations from a nearby excited state. In this paper we present these results and their analysis. We also discuss the origin of perturbations and the nature of the bonding in CoCl.

8385

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 130.18.123.11 On: Thu, 18 Dec 2014 01:13:07

II. EXPERIMENT

The spectrum of CoCl was recorded using one of the quasioptical millimeter/submillimeter direct absorption systems of the Ziurys' group. These instruments are described elsewhere.¹⁵ Briefly, millimeter-wave radiation originating at a Gunn oscillator/Schottky diode multiplier source is passed through a polarizing grid and a series of mirrors into a reaction chamber. This chamber is a double-pass system with a roof-top reflector at the far end. After its second pass through the cell, the radiation is directed back through the optics and is reflected by the grid into a He-cooled InSb detector. The source is modulated at a rate of 25 kHz and signals are recorded at 2f using a lock-in amplifier.

CoCl was produced by reacting cobalt vapor with pure Cl_2 . CCl_4 was originally used as the chlorine donator with some success, but switching to Cl₂ increased the signals fivefold. No dc discharge was necessary in either case. Cobalt vapor was obtained by melting chips of cobalt (Aldrich 99.5%) in a Broida-type oven through resistive heating. Because of cobalt's high melting point (\sim 1495 °C), the crucible was wrapped in zirconia insulation. Chlorine was added over the top of the crucible; between 0.5 and 1.0 mTorr of Cl₂ resulted in the best signal. Both chlorine isotopes were observed in their natural abundance of ³⁵Cl:³⁷Cl=3:1. No carrier gas such as argon was used, as it did not increase the signal-to-noise ratio. Use of a dc discharge increased the intensity of CoCl lines somewhat but also added additional noise, so in the end little net improvement was gained. The reaction mixture exhibited no obvious fluorescence.

Rotational constants from optical studies^{10,13} provided the basis for the initial measurements. After scanning through several transitions (~45 GHz) such that harmonic relationships and spectral patterns could be established, observed lines were identified. Transition frequencies were measured by averaging an even number of scans in both increasing and decreasing frequencies. These scans were typically 5 MHz in width, and two to four were necessary to obtain adequate signal to noise. Center frequencies were determined by fitting the observed lines to Gaussian profiles. The instrumental accuracy is $\approx \pm 50$ kHz. Typical linewidths were 1.0–1.5 MHz over the range 343–508 GHz.

III. RESULTS

It was clear from the beginning that CoCl was not a good Hund's case (a) species, and therefore did not have the regular intervals between the spin components exhibited by TiF (Ref. 16) or FeCl,¹⁷ for example. No obvious spin pattern was apparent in the spectra. Therefore, features were sought that repeated themselves in the ³⁷Cl isotopomer. This procedure enabled the vibrational progression in both isotopomers for the Ω =4 spin component to be located, v=1 through 4 for Co³⁵Cl and v=1 through 3 for Co³⁷Cl. The remaining sets of lines had to be due to the other Ω ladders and their respective vibrational satellite features. The second strongest of the remaining features, a likely candidate for the Ω =3 ladder, however, was shifted to lower frequency rela-



FIG. 1. A stick diagram illustrating the progression of the $J=43 \leftarrow 42$ rotational transition of $\operatorname{Co}^{35}\operatorname{Cl}(X \,{}^3\Phi_i)$, observed in the range 460.5–470 GHz (black lines), interspersed with its vibrational progression from the $J=44 \leftarrow 43$ transition (dashed lines) and lines originating from the $J=45 \leftarrow 44$ transition of $\operatorname{Co}^{37}\operatorname{Cl}$ (gray scale). Each line actually consists of an octet, but this detail is not shown. The unusual spin-orbit pattern of CoCl is evident, with the $\Omega=3$ component lying about 500 MHz lower in frequency relative to that of $\Omega=4$, while the $\Omega=2$ line is located ≈ 8 GHz to higher frequency. The vibrational pattern for the $\Omega=4$ ladder of $\operatorname{Co}^{35}\operatorname{Cl}$ is also easily identified, but the presence of the $\operatorname{Co}^{37}\operatorname{Cl}$ isotopomer, its vibrational satellite lines, and the vibrationally-excited states of the $\Omega=2$ and 3 components of $\operatorname{Co}^{37}\operatorname{Cl}$ complicate the spectrum.

tive to the $\Omega=4$ component, while the possible $\Omega=2$ line was located ~8 GHz higher. Both lines had counterparts in the ³⁷Cl isotopomer, as well as their own vibrational progression. After this tentative assignment was made, the Hirao, Pinchemel, and Bernath paper¹³ was published, which confirmed the $\Omega=3$ identification; the remaining sets of lines were assigned to the $\Omega=2$ component by process of elimination.

The spectral pattern is illustrated in Fig. 1, which is a stick figure ranging over 2B at the frequency of the J=43 \leftarrow 42 transition of Co³⁵Cl. The Ω =4 and 3 spin components are clustered at the left (lower frequency) and the $\Omega=2$ feature is at the far right (higher frequency), all indicated by solid black lines. The $\Omega=2$ and 3 components are considerably weaker in intensity. Vibrational satellite features due to $Co^{35}Cl$ are portrayed by dashed lines; the v = 1, 2, 3, and 4progression is clearly visible for the $\Omega=4$ component, and a few lines arising from the other spin levels are additionally present. The Co³⁷Cl lines for the v = 0 spin components are shown in gray scale; these appear at "odd" frequencies because they come from the $J=45\leftarrow44$ ($\Omega=4$ and 3) and J =44 \leftarrow 43 (Ω =2) transitions—a result of the isotopic shift. The remainder of the features arise from vibrationally excited states of the ³⁷Cl isotopomer. Not shown in this diagram are the hyperfine interactions, which split each depicted line into octets.

Representative data recorded for the main isotopomer of CoCl are shown in Fig. 2. Here a composite spectrum of the three spin components of the $J=35 \leftarrow 34$ transition has been created using two frequency breaks. The insert shows an enlarged version of the $\Omega=2$ data. The regular octet pattern, arising from the ⁵⁹Co spin of I=7/2, is apparent in each component. (Splittings due to the chlorine nuclear spin of I



FIG. 2. Spectra of the $J=35 \leftarrow 34$ rotational transition of $\operatorname{Co}^{35}\operatorname{Cl}(X^{3}\Phi_{i})$ showing all three spin-orbit components (v=0) on the same intensity scale. This spectrum is a composite of three separate frequency ranges that are actually widely spaced; hence, there are two breaks in the frequency scale (see Fig. 1). The octet hyperfine pattern arising from the cobalt nuclear spin of I=7/2 is clearly resolved in each sublevel. The $\Omega=3$ and 2 features are considerably weaker than those of $\Omega=4$, suggesting that they lie close in energy. However, these two components were still recorded with remarkable signal to noise, as the enlarged spectrum of the $\Omega=2$ octet demonstrates. These three data sets are 80 MHz wide and were acquired in single, 60 s scans.

=3/2 were not resolved in the data—not surprising since cobalt has a nuclear moment about six times larger than that of Cl.¹⁸) As these data show, the overall splitting is smallest in the $\Omega=3$ lines and largest in the $\Omega=2$ hyperfine set. Also evident in this figure are the relative intensities of the three spin components, which are $\Omega = 4:3:2=25:2:1$. This ratio suggests a rotational temperature of $T_{\rm rot} \sim 270 - 430 \, {\rm K}$ based on the overall spin-orbit splitting of 6A or \sim 1440 K. The $\Omega=3$ and 2 components appear quite weak in comparison with the ground state $\Omega = 4$ lines; however, these data were actually recorded with high signal to noise with little scan averaging, as the insert for the $\Omega=2$ octet shows. Significant signal averaging was only necessary for highly-excited states, such as the v=1 level of the $\Omega=3$ component of $Co^{37}Cl.$ (The v = 0-1 spacing is 370 K.) The similar intensities of the $\Omega=2$ and 3 states suggests that they may be closer in energy than predicted by the spin-orbit splitting alone.

Selected transition frequencies for Co^{35}Cl in the v=0 state are presented in Table I. As the table shows, frequencies of the eight hyperfine components were typically measured per spin level per transition. Fifteen transitions were studied for the main CoCl isotopomer; several include all three spin components. In the case of Co^{37}Cl , twelve transitions were measured. The complete data set spans the range 343–507 GHz. The complete list of frequencies for both isotopomers is available electronically on EPAPS.¹⁹

In addition to the v = 0 lines, four transitions originating in each of the v = 1, 2, 3, and 4 levels of Co³⁵Cl ($\Omega = 4$ only) were recorded. Four to five transitions originating in each of the v = 1, 2, and 3 states of Co³⁷Cl ($\Omega = 4$ only) were mea-



FIG. 3. Spectra of the hyperfine octet recorded for the J=42—41 (left) and J=44—43 transitions of the $\Omega=3$ component of Co³⁵Cl (v=0). Unlike the octet in Fig. 2, these hyperfine patterns appear distorted. The J=42—41 features are broadened and appear to be additionally split, while the J=44—43 lines have evolved into nine components as opposed to eight. These nonets appeared in successive transitions to higher *J*. Each spectrum is 40 MHz wide and was acquired in a single 30 s scan.

sured as well. All lie in the range 373–493 GHz ($J \approx 34-47$). For each of the $\Omega=2$ and 3 spin components, four to five transitions were measured in the v = 1 level for both chlorine isotopomers, from 373 to 493 GHz ($J \approx 34-46$). In virtually every transition, frequencies for all eight hyperfine components were recorded, a total of 279 separate measurements. These data sets also are also available electronically on EPAPS.¹⁹

As may be evident from Table I many of the $\Omega=3$ frequencies were not measured, in particular for those above J> 38, although data has been recorded for the other two spin components in this range. These transitions were certainly located, but the hyperfine pattern exhibited unusual behavior that could not be satisfactorily analyzed. At the $J = 39 \leftarrow 38$ transition in the Ω =3 state of Co³⁵Cl, the individual lines of the hyperfine octet were found to broaden into multiple, unresolved features. By the $J = 44 \leftarrow 43$ transition, the lines become narrow again but there are nine such features, not eight. The extra lines likely arise from $\Delta F = \pm 2$ transitions, perhaps a result of mixing with a nearby vibrational state. These "nonets" remained in the $\Omega=3$ data up to the highest J level studied. A similar trend was observed in the $Co^{37}Cl$ isotopomer as well for the $\Omega=3$ levels. In contrast, the v =1 transitions for Ω =3 did not show any such perturbations. Wong, Tam, and Cheung also saw some perturbations in the cobalt hyperfine structure, but it was for the v = 7 level in the $[10.3]^3 \Phi_i$ excited state.¹⁴

Figure 3 shows examples of these perturbations for Co^{35}Cl . On the left, the $J=42\leftarrow41$ transition is displayed. The crisp octet pattern of Fig. 2 has clearly degenerated into broadened features for most of the hyperfine components. On the right, the $J=44\leftarrow43$ transition is shown. Here the lines have narrowed again, but there are nine components. These

TABLE I. Selected transition frequencies for $\text{Co}^{35}\text{Cl}(X^{3}\Phi_{i}:v=0)$ (in MHz).

$J' \leftarrow J''$	$F' \leftarrow F''$	Ω	ν	$ u_{\rm obs-calc} $	$J' \leftarrow J''$	$F' \leftarrow F''$	Ω	ν	$\nu_{\rm obs-calc}$
32 ← 31	28.5←27.5	3	343 577.266	0.798	39 <i>←</i> 38	35.5←34.5	4	418 949.486	0.432
	29.5←28.5		343 573.101	0.799		36.5←35.5		418 946.485	0.395
	30.5←29.5		343 568.622	0.748		37.5←36.5		418 943.351	0.399
	31.5←30.5		343 563 901	0.714		38.5←37.5		418 940 039	0.399
	$32.5 \leftarrow 31.5$		343 558 348	0.104		39.5 ← 38.5		418 936 591	0.437
	$32.5 \leftarrow 31.5$ $33.5 \leftarrow 32.5$		343 553 534	0.487		$40.5 \leftarrow 39.5$		418 932 956	0.460
	34 5-33 5		343 547 873	0.407		40.5 40.5		418 929 154	0.487
	35.5, 34.5		343 541 013	0.007		42.5 41.5		418 025 100	0.531
	55.5~54.5		545 541.915	0.007		$42.3 \leftarrow 41.3$	2	416 925.199	0.551
36 ← 35	32.5←31.5	4	386 846.516	0.057		265. 255	2	426 261 052	0.851
	33.5←32.5		386 843.072	0.048		$30.3 \leftarrow 33.3$		420 201.933	0.370
	34.5←33.5					$37.3 \leftarrow 30.3$		420 257.470	0.055
	35 5 ← 34 5					38.5←37.5		426 253.059	-0.126
	$36.5 \leftarrow 35.5$		386 831 518	0.132		39.5←38.5		426 248.671	-0.165
	30.5< 35.5 37.5 <u>←</u> 36.5		386 827 245	0.132		40.5←39.5		426 244.357	-0.033
	37.5 - 30.5		296 927 772	0.178		41.5←40.5		426 240.113	0.267
	$30.5 \leftarrow 37.5$		300 022.773	0.243		42.5←41.5		426 235.905	0.697
	$39.5 \leftarrow 30.5$	2	296 260 742	0.321	40 . 20	265, 255	4	120 612 727	0.124
	$32.5 \leftarrow 31.5$	3	380 309.743	-0.694	$40 \leftarrow 39$	$30.3 \leftarrow 35.5$	4	429 643.737	0.124
	33.5←32.5 24.5 - 22.5		380 300.488	-0.491		37.5←36.5		429 640.871	0.085
	34.5←33.5		386 362.939	-0.399		38.5←37.5		429 637.847	0.050
	35.5←34.5		386 359.259	-0.258		39.5←38.5		429 634.695	0.049
	36.5←35.5		386 355.318	-0.198		40.5←39.5		429 631.415	0.080
	37.5←36.5		386 351.238	-0.100		41.5←40.5		429 627.971	0.106
	38.5←37.5		386 346.885	-0.099		42.5←41.5		429 624.387	0.152
	39.5←38.5		386 342.280	-0.177		43.5←42.5		429 620.603	0.155
	32.5←31.5	2	393 809.112	0.150		36.5←35.5	2	437 069.490	0.600
	33.5←32.5		393 804.384	-0.253		37.5←36.5		437 065.025	0.102
	34.5←33.5		393 799.670	-0.512		38.5←37.5		437 060.638	-0.224
	35.5←34.5		393 794.953	-0.645		39.5←38.5		437 056.365	-0.341
	36.5←35.5		393 790.238	-0.650		40.5←39.5		437 052.057	-0.401
	37.5←36.5		393 785.701	-0.353		41.5←40.5		437 047.781	-0.338
	38.5←37.5		393 781.104	0.005		42.5←41.5		437 043.646	-0.045
	39.5←38.5		393 776.625	0.602		43.5←42.5		437 039.585	0.411
37 <i>←</i> 36	33.5←32.5	4	397 550.793	0.564	$45 \leftarrow 44$	41.5←40.5	4	483 060.020	0.525
	34.5←33.5		397 547.501	0.538		42.5←41.5		483 057.630	0.401
	35.5←34.5		397 544.039	0.548		43.5←42.5		483 055.209	0.360
	36.5←35.5		397 540.364	0.548		44.5←43.5		483 052.618	0.262
	37.5←36.5		397 536.535	0.598		45.5←44.5		483 050.037	0.286
	38.5←37.5		397 532.509	0.652		46.5←45.5		483 047.371	0.338
	39.5←38.5		397 528.265	0.689		47.5←46.5		483 044.533	0.329
	40.5←39.5		397 523.860	0.763		48.5←47.5		483 041.608	0.344
	33.5←32.5	3	397 060.610	0.546		41.5←40.5	2	490 959,967	0.485
	34.5←33.5		397 057 088	0.334		42.5←41.5		490 956 020	0.192
	35 5 ← 34 5		397 053 684	0.409		43 5←42 5		490 952 087	-0.020
	36.5←35.5		397 050 157	0.527		44 5-43 5		490 947 968	-0.351
	37.5←36.5		397 046 484	0.527		$45.5 \leftarrow 44.5$		490 944 403	-0.063
	38.5, 37.5		307 040.404	0.884		46.5 45.5		400 040 582	0.005
	30.5 - 37.5		207 022 591	0.864		40.5 45.5		490 940.382	0.035
	39.3←30.3 40.5, 20.5		207 024 260	0.808		47.5~40.5		490 930.904	0.340
	$40.3 \leftarrow 39.3$	2	397 034.209	0.830		46.3←47.3		490 955.555	0.850
	$33.3 \leftarrow 32.5$	2	404 030.294	0.889	$47 \leftarrow 46$	44.5←43.5	4	504 397.066	-0.292
	34.3←33.3 25.5 - 24.5		404 031.336	0.376		45.5←44.5	•	504 394 712	-0.460
	55.5←34.5		404 626.970	0.134		46 5←45 5		504 392 419	-0.467
	36.5←35.5		404 622.277	-0.097		$47.5 \leftarrow 46.5$		504 389 987	-0.514
	37.5←36.5		404 617.726	-0.069		48 5 47 5		504 387 516	-0.503
	38.5←37.5		404 613.186	0.084		49 5 48 5		504 384 800	-0.530
	39.5←38.5		404 608.812	0.516		47.3←40.3 50.5 / 10.5		504 202 221	_0.539
	40.5←39.5		404 604.263	0.883		50.5←49.5		504 382.221	-0.559

anomalous splittings cannot be due to the chlorine nucleus, as the expected pattern would be quartets of octets. Also, the chlorine hyperfine interactions would be expected to play a role at lower, not higher, *J*. Hyperfine interactions arising from fluorine have been resolved in CoF,²⁰ producing doublets of octets [I(F) = 1/2], but not the unusual pattern observed here. (The fluorine magnetic moment is about a factor of 3 larger than that of chlorine.¹⁸)

IV. ANALYSIS

The observed rotational transitions were analyzed using an effective ${}^{3}\Phi_{i}$ Hamiltonian of the form

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

This Hamiltonian describes molecular frame rotation (\mathbf{H}_{rot}), spin-orbit coupling (\mathbf{H}_{so}), spin-spin coupling (\mathbf{H}_{ss}), and the magnetic hyperfine interactions (\mathbf{H}_{hf}), including their centrifugal distortion corrections. The coupling scheme employed in this analysis is Hund's case (a_{β}). Therefore, $\mathbf{J}=\mathbf{L}+\mathbf{S}$ and $\mathbf{F}=\mathbf{J}+\mathbf{I}$. This scheme is appropriate because the spin splittings are far larger than the hyperfine interactions.

To fit the data, the spin-orbit constant A was initially set (165 cm^{ce1}) to the value for CoF (-233 cm⁻¹).²¹ It was later determined that this value did not provide a good fit, so A was varied until an optimal value was obtained. In the final fit, it was then fixed to this value (166 cm⁻¹). Higher order corrections to the spin-orbit and spin-spin constants were found to be necessary for a satisfactory analysis (A_H , A_L , and λ_H). The hyperfine splittings were fit to the *a*, *b*, and (b+c) parameters only, as no improvement was obtained by using eQq. An additional term was also added to the hyperfine Hamiltonian exclusively for the $\Omega=3$ levels of the form

$$h_{3D} = 3[F(F+1) - J(J+1) - I(I+1)]/2.$$
(2)

This term was originally created for the analysis of the ${}^{3}\Phi_{3}$ sublevel of CoH.²²

The data for both chlorine isotopomers and their v=1 states were fit in an identical manner. For Co³⁷Cl, however, the range of *J* was smaller and hence the higher order centrifugal distortion corrections were not needed. The resulting spectroscopic parameters from these global fits are provided in Table II. Also given are the B_e and α_e constants derived from the v=0 and v=1 data only for both species. For comparison, the constants for Co³⁵Cl (v=0 and v=1) derived from the infrared measurements of Hirao, Pinchemel, and Bernath¹³ are listed as well. These constants were established from the $\Omega=4$ and 3 components only, however, so there is some (expected) disagreement between the two parameter sets. The rms of the fits for Co³⁵Cl are 434 (v=0) and 373 kHz (v=1), and 212 (v=0) and 277 kHz (v=1) for the chlorine-37 isotopomer.

V. DISCUSSION

This study has resulted in the identification of the third spin component (Ω =2) for CoCl, which confirms the ${}^{3}\Phi_{i}$ ground state assignment for CoCl. The lack of λ doubling in any Ω ladder, which might have been present in a Π or Δ state, is additional evidence for the Φ term. Also of note is the large shift of the Ω =3 spin component relative to the Ω =4 and 2 sublevels, which manifests itself in a large (negative) value of λ . Furthermore, the hyperfine structure of this sublevel appears perturbed. Both effects, which will be discussed in the following sections, probably arise from interactions with an isoconfigurational excited ${}^{1}\Phi$ state, which has a single spin ladder with Ω =3. Evidence of similar perturbations occur in the $X {}^{3}\Delta_{i}$ state of FeC, where the Ω =2 sublevel is shifted relative to the case (a) spin-orbit pattern.²³ An excited ${}^{1}\Delta_{2}$ state is thought to be the perturber in this case. FeC has a large value of λ (1 285 GHz), except it is positive, and the shift is in the opposite direction in frequency.

A. Fine structure splittings

The spin-orbit and spin-spin interactions compete in a ${}^{3}\Phi$ state to establish the fine structure pattern. When the spin-orbit constant A is larger than λ , the pattern is fairly regular for a "good case (a)" molecule. Examples are TiF in its $X^{4}\Phi_{r}$ state, where A = 1000 GHz and $\lambda = 4$ GHz (Ref. 16) and FeCl $(X^{6}\Delta_{i})$, for which A = -2274 GHz and $\lambda = 16.4$ GHz.¹⁷ In the case of FeC ($X^{3}\Delta_{i}$), where some evidence of perturbations is observed, $A \approx \lambda$.²³ For CoCl, however, λ is greater than A (-7196 GHz versus -5000 GHz). The large value of λ is needed to compensate for the large frequency shift of the $\Omega=3$ spin component, which may be perturbed by a ${}^{1}\Phi_{3}$ term. Second-order spin-orbit interactions connect the ${}^{1}\Phi_{3}$ and ${}^{3}\Phi_{3}$ states via the $\hat{\mathbf{l}}_{i}\cdot\hat{\mathbf{s}}_{i}$ operator. Although the $^{1}\Phi$ state has not yet been observed in the spectrum of CoCl, theoretical calculations predict such a term 2000 cm⁻¹ higher in energy for CoH, which has an identical electron configuration.¹² For CoCl, a substantially heavier molecule, a lower energy would be expected for this state.

It is possible to estimate the energy separation between the ${}^{3}\Phi_{3}$ and ${}^{1}\Phi_{3}$ states, ΔE , by "undiagonalizing" the spinorbit energy matrix, as described in Refs. 24 and 25. The off-diagonal matrix element for this interaction is $\langle {}^{3}\Phi_{3}|\hat{\mathbf{H}}_{so}|{}^{1}\Phi_{3}\rangle$, where $\hat{\mathbf{H}}_{so} = \sum_{i} a_{i}\hat{\mathbf{i}}_{i}\cdot\hat{\mathbf{s}}_{i}$. Assuming that both these states arise from a single $\delta^{3}\pi^{3}$ electron configuration, then

$$\left\langle {}^{3}\boldsymbol{\Phi}_{3} \left| \sum_{i} a_{i} \hat{l}_{i} \cdot \hat{s}_{i} \right| {}^{1}\boldsymbol{\Phi}_{3} \right\rangle = a_{\delta} - \frac{a_{\pi}}{2}, \tag{3}$$

while the diagonal elements are

$$\left\langle {}^{3}\Phi_{4} \middle| \sum_{i} a_{i}\hat{l}_{i} \cdot \hat{s}_{i} \middle| {}^{3}\Phi_{4} \right\rangle = -\left\langle {}^{3}\Phi_{2} \middle| \sum_{i} a_{i}\hat{l}_{i} \cdot \hat{s}_{i} \middle| {}^{3}\Phi_{2} \right\rangle$$
$$= a_{\delta} + \frac{a_{\pi}}{2}.$$
(4)

Considering 2λ as the displacement due to the perturbation, the difference in energy between the ${}^{1}\Phi_{3}$ and ${}^{3}\Phi_{3}$ states can be expressed as

$$\Delta E = \frac{1}{2\lambda} \left[\left(a_{\delta} - \frac{a_{\pi}}{2} \right)^2 + 4\lambda^2 \right].$$
(5)

Here it is assumed that the effective λ is λ^{so} .

The δ orbitals in CoCl must be centered on the cobalt atom, as chlorine has no *d* orbitals. Hence, to a reasonable approximation, $2a_{\delta} = \zeta_{Co} = -536 \text{ cm}^{-1}.^{24,25}$ Because a_{δ} $+a_{\pi}/2 = 3A$, it follows that $a_{\pi}/2 = -232 \text{ cm}^{-1}$. The energy separation between the ${}^{1}\Phi_{3}$ and ${}^{3}\Phi_{3}$ states is then estimated to be $\Delta E \approx -480 \text{ cm}^{-1}$. This calculation implies that the ${}^{1}\Phi$ state lies within the ground state spin-orbit manifold. Because of the very large value of λ , a close-lying perturbing state is probably expected. Furthermore, the negative value

TABLE II.	Spectroscopic	constants for	$\operatorname{CoCl}(X^{3}\Phi_{i})$	in MHz. ^a
-----------	---------------	---------------	--------------------------------------	----------------------

		v = 0		v = 1			
	Submillimeter Co ³⁵ Cl	Submillimeter Co ³⁷ Cl	Optical CoCl ^{c,d}	Submillimeter Co ³⁵ Cl	Submillimeter Co ³⁷ Cl	Optical CoCl ^c	
B	5422.94(85)	5232.870(21)	5375.79(72)	5391.41(47)	5207.61(41)	5346.22(75)	
D	0.010 73(88)	0.005 407 9(67)	0.003 783(51)	0.007 88(38)	0.007 15(30)	0.003 847(54)	
$H(10^{6})$	1.89(36)			0.50(11)	0.407(82)		
$L(10^{17})$	3.56(73)						
Α	-5000000^{b}	-4.020000	-6985000	$-5\ 000\ 000^{b}$	$-5\ 000\ 000^{b}$	-6955080(120)	
A_D	-3.68(13)	-3.413(64)	3.27(21)	-9.390(46)	-8.047(81)	-3.63(22)	
A_{H}^{D}	0.000 766(25)	0.000 673(11)		0.000 656 0(42)	0.000 574 2(27)		
$A_{L}(10^{13})$	1.89(38)			0.102(37)	0.066(25)		
λ	-7 195 700(3300)	-5 791 400(1900)		-6 985 300(2300)	-7 009 700(5000)		
λ_D	-34.25(63)	-30.19(32)		-6.47(15)	-8.14(33)		
λ_{H}^{D}	-0.00013(10)	-0.000158(42)					
a	512(45)	530(41)		569(56)	636(72)		
b	135(10)	148.6(7.5)		256(40)	219(40)		
(b+c)	-170(140)	-220(120)		-310(180)	-530(220)		
h_{3D}	-0.88(20)	-0.76(15)		-0.63(23)	-0.40(25)		
$h_{\Omega=4}$	1339.2(3.2)		1318(16)				
rms	0.434	0.212		0.373	0.277		
B _e	5438.7	5245.5					
α_e	31.5	25.3					

^aNumbers in parentheses are errors to three standard deviations for the last significant figure.

^bHeld fixed to value established from initial fitting (see text).

^cFrom Hirao, Pinchemel, and Bernath¹³ based on Ω =4 and 3 data only.

^dFrom Adam *et al.*,¹⁰ based on Ω =4 data only.

of the effective λ parameter suggests that the $\Omega=3$ substate is shifted to higher energy in this case. Hence, the proposed ${}^{1}\Phi$ state lies lower in energy relative to the $\Omega=3$ substate. In Fig. 4, this energy ordering is shown. Note that the $\Omega=3$ sublevel is shifted closer to the $\Omega=2$ substate in energy. Without this perturbation, it would lie at 3*A* in energy, or near 500 cm⁻¹. This proposed shift is supported by the similar intensities of spectra originating from these two levels.

Another possible perturber is a ${}^{3}\Delta_{3}$ state. The study of Hirao, Pinchemel, and Bernath¹³ suggests that there is a ${}^{3}\Delta_{i}$ state in CoCl lying about ~20 000 cm⁻¹ above ground state. Because it is inverted, the $\Omega=3$ level would lie lowest in energy. This ${}^{3}\Delta_{i}$ state would therefore interact significantly with the ${}^{3}\Phi_{3}$ sublevel, although the $\Omega=2$ level would additionally be affected.

B. Hyperfine splitting

As discussed, a series of rotational levels in the $\Omega=3$ ladder displays highly irregular hyperfine patterns from probable mixing with a vibrational state. Evidence for secondorder spin-orbit perturbations is also found in what appears to be the more regular hyperfine interactions. The hyperfine splitting per Ω is described by the equation

$$h_{\Omega} = a\Lambda + (b+c)\Sigma, \tag{6}$$

where h_{Ω} is the hyperfine parameter for each sublevel. Because Σ varies from 1, 0 to -1 for $\Omega=4$, 3, and 2, the overall hyperfine splittings should uniformly increase or decrease with Ω value; this pattern does not occur for CoCl. Furthermore, $h_{\Omega=3}$ should be the average of $h_{\Omega=4}$ and $h_{\Omega=2}$. However, the average for the $\Omega=4$ and 2 ladders is 2513 MHz, which is significantly different from that of $\Omega=3$, which has $h_{\Omega=3}$ = 1755 MHz. Moreover, the global fit required the inclusion of a h_{3D} centrifugal distortion correction for the $\Omega=3$ hyperfine interactions. This term likely accounts for more than centrifugal distortion because $h_{3D}/h_{\Omega=3}$ >D/B. As discussed by Azuma *et al.*,²⁴ the Fermi contact and spin



FIG. 4. A qualitative energy level diagram showing the relative positions of the three spin components arising from the ground state, $X^{3}\Phi_{i}$, indicated by Ω . Also depicted are the first three excited vibrational levels of the $\Omega=4$ substate, shown in gray scale. A low-lying excited electronic ${}^{1}\Phi_{3}$ state, located at $E \approx 400-500 \text{ cm}^{-1}$, may be responsible for perturbing the $\Omega=3$ sublevel of the $X^{3}\Phi_{i}$ state and shifting it to higher energy.

dipolar hyperfine interactions have cross terms with the spinorbit matrix elements that involve both the ${}^{3}\Phi$ and ${}^{1}\Phi$ states.

The hyperfine parameters can also be used to establish bonding characteristics of CoCl. For example, the *a* parameter, which has a value of 512 MHz, results from the I·L interaction. Because the two unpaired electrons in CoCl are predicted to be in π and δ orbitals, they both contribute to this term, and can account for its relatively large value. For comparison, a(Co) = 604 MHz in CoF (Ref. 20) and a(Co)= 621 MHz in CoH.²² Because *a* is inversely proportional to the average distance, cubed, of the unpaired electrons from the nucleus with the spin, or $\langle 1/r^3 \rangle$, a smaller value of this parameter implies that the unpaired electrons are located further from the nucleus. In fact, $\langle 1/r^3 \rangle = 2.7 \times 10^{31} \text{ m}^{-3}$ for CoCl, while this quantity is $3.3 \times 10^{31} \text{ m}^{-3}$ in CoH (Ref. 22) and $3.2 \times 10^{31} \text{ m}^{-3}$ in CoF.²¹ The same quantity for the cobalt atom is $4.4 \times 10^{31} \text{ m}^{-3}$.²² Thus, the unpaired electrons are located in more diffuse orbitals in CoCl than the other species; the larger size of the electronegative chorine atom relative to hydrogen and fluorine may be pushing the cobalt electron density further from the Co nucleus.

The Fermi contact term b_F primarily arises from electrons in σ orbitals which, assuming a single electron configuration, do not exist for CoCl. A nonzero value for b_F can arise from spin polarization, but then it is usually negative.²⁶ Because (b+c) is not well defined in CoCl, in turn neither is b_F . The value determined here for b_F is 33 ± 48 MHz—which within the errors could be negative.

The dipolar constant *c* is calculated to be -305 ± 140 MHz—roughly comparable to the *c* parameters for CoF (-196 MHz) and CoH (-456 MHz).^{20,22} This constant depends on the expectation value of the operator $\Sigma_i (3 \cos^2 \theta_i - 1)/r_i^3$, where *i* is the summation over the unpaired electrons. From *c*, the angular factor $\langle 3 \cos^2 \theta - 1 \rangle$ can be calculated for CoCl, using $\langle 1/r^3 \rangle$ derived from *a*; its value is -0.3901. For pure d_{π} and d_{δ} orbitals, these angular factors are +2/7 and -4/7, respectively,²⁷ which add to -0.286. Hence, the sign of *c* appears to be correct. The slightly larger angular value may result from polarization of the π and δ orbitals by the nearby chlorine atom.

The hyperfine constants can be used as well to calculate the percent contribution of the two atoms in CoCl to the molecular orbitals of the unpaired electrons. The valence electron configuration of CoCl is $(11\sigma)^2(1\delta)^3(5\pi)^3$.¹⁰ The δ orbital must exclusively be created from cobalt 3*d* orbitals, but the 5π orbital could also arise in part from Cl 3*p*. Because both π and δ electrons contribute to the *a* and *c*, these parameters can be expressed as²⁸

$$a(\mathrm{Co}) = 2\mu_{B}g_{N}\mu_{N}\frac{1}{3}[2\langle 1/r^{3}\rangle_{1\delta} + \langle 1/r^{3}\rangle_{5\pi}],$$

$$c(\mathrm{Co}) = \frac{3}{2}g_{s}\mu_{B}g_{N}\mu_{N}\frac{1}{2}\left[\left\langle\frac{3\cos^{2}\theta - 1}{r^{3}}\right\rangle_{1\delta} + \left\langle\frac{3\cos^{2}\theta - 1}{r^{3}}\right\rangle_{5\pi}\right].$$
(7)

If only cobalt contributed to *a* and *c*, then the expectation values of $\langle 1/r^3 \rangle$ and $\langle 3 \cos^2 \theta - 1 \rangle$ could be replaced by those

of atomic cobalt. However, if chlorine does contribute to the 5π orbital, then the participation of cobalt is a factor less than one. If cobalt's contribution is expressed as the coefficient $c_{5\pi}^{Co}$, then the above equations can be recast as²⁰

$$a(\text{Co}) \approx \left[\frac{2 + c_{5\pi}^{\text{Co}}}{3}\right] a_{3d}^{01},$$

$$c(\text{Co}) \approx \left[-\frac{3(2 - c_{5\pi}^{\text{Co}})}{14}\right] a_{3d}^{12},$$
(8)

where $a_{3d}^{\kappa k}$ is the hyperfine parameter for atomic cobalt. For $a_{3d}^{01} = 617.9$ MHz and $a_{3d}^{12} = 857.1$ MHz, ²⁰ $c_{5\pi}^{Co}$ is estimated to be 0.486 and 0.339, from the *a* and *c* parameters, respectively. In contrast, $c_{4\pi}^{Co}$ for CoF was found to be 0.934. Obviously these calculations are only estimates, but they do suggest that CoCl has more covalent character to its bonding than CoF. Based on electronegativity arguments, such a result might be expected, although previous studies have indicated that CoCl is as ionic as its fluorine analog.^{10,13}

C. Bonding trends in 3d transition metal chlorides

Trends within the 3*d* transition metal oxides and sulfides have been discussed in depth by various authors.^{29–31} The so-called "double-hump" structure in bond length is apparent in both these species, namely, there is an increase in the bond distance occurring from vanadium to manganese, a decrease at iron, and then a second increase towards copper. The increase from vanadium to manganese is due to the addition of electrons to antibonding orbitals. The highest σ^* orbital does not receive an electron until manganese. After this, bond lengths decrease due to core contraction of the metal as no new antibonding orbitals are being filled; the trend repeats in the second half of the third row.

A somewhat different trend is found in the 3*d* halides. As discussed by Sheridan, McLamarrah, and Ziurys,¹⁶ the fluorides exhibit a noticeable increase in bond length at MnF, but only a minor one from cobalt to copper. In addition, another large increase in bond distance appears at titanium. This trend is shown in Fig. 5. The difference in bond length trends between the oxides/sulfides versus the fluorides arises from the presence of an extra electron in the latter species, as well as the difference in the energies of the F and O atomic orbitals. As a result, the orbital energies vary, and the electron configurations differ significantly from the oxides to the fluorides (see Ref. 17).

The bond lengths of the chlorides are also plotted in Fig. 5. At first glance, the chlorides and fluorides exhibit a similar trend, as might be expected from their identical electron configurations. The bond distances of the chlorides are naturally longer than the fluorides by about 0.4 Å due to the difference in atomic or ionic radii (0.35 or 0.45 Å).³² However, the bond distances shorten slightly at CrCl and CuCl, while they increase in the fluoride species. The decrease in bond distance from MnCl to CoCl is more dramatic than in the fluorides, as well. These variations may result from the fact that



FIG. 5. A graph showing the periodic trend in bond lengths for the 3d transition metal chlorides vs the fluorides. The two series show very similar characteristics. Slight deviations occur at Cr and Cu, however, where the bond lengths decrease in the chlorides but increase in the fluorides. These differences suggest subtle variations in bonding between the two sets of halides.

the chlorine bonds from 3p orbitals, which are considerably closer in energy to the 3d/4s transition metal orbitals than the 2p of the F atom. Greater molecular orbital overlap in the chlorides produces these subtle bonding differences.

VI. CONCLUSIONS

Although the three spin-orbit components have been identified in CoCl in its $X^{3}\Phi_{i}$ state, the irregular pattern, coupled with unusual hyperfine splittings, suggests that the ground state is perturbed by a close-lying excited state or states. Because the Ω =3 sublevels appear to exhibit the most irregularity, the perturbing state may be the isoconfigurational ${}^{1}\Phi_{3}$ term. These states can interact via second-order spin-orbit coupling, which enters in as an off-diagonal term in both the spin and hyperfine Hamiltonians. Interpretation of the hyperfine parameters suggests that the bonding in CoCl is more covalent than in CoF. An examination of the bond distances of the 3*d* chlorides versus the fluorides shows that these species are similar, although subtle differences in their bonding appear to be present.

ACKNOWLEDGMENTS

This research was supported by NSF Grant No. CHE-98-17707. The authors would like to thank Dr. J. M. Brown for the use of his Hamiltonian fitting program and Dr. Phillip M. Sheridan for his comments.

- ¹D. Arnett, *Supernovae and Nucleosynthesis* (Princeton University Press, Princeton, NJ, 1996).
- ²D. Shriver and P. Atkins, *Inorganic Chemistry*, 3rd ed. (Freeman, New York, 1999).
- ³N. Koga and K. Morokuma, Chem. Rev. (Washington, D.C.) **91**, 823 (1991).
- ⁴J. E. Huheey, E. A. Keiter, and R. L. Keiter, *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed. (Harper Collins, New York, 1993).
- ⁵J. C. Noveron, M. S. Lah, R. E. Del Sesto, A. M. Arif, J. S. Miller, and P. J. Stang, J. Am. Chem. Soc. **124**, 6613 (2002).
- ⁶R. S. Ram, P. F. Bernath, and S. P. Davis, J. Chem. Phys. **104**, 6949 (1996).
- ⁷P. Mesnage, C. R. Acad. Bulg. Sci. **201**, 389 (1935).
- ⁸K. R. More, Phys. Rev. **54**, 122 (1938).
- ⁹A. J. Bridgeman, J. Chem. Soc. Dalton Trans. **1997**, 4765.
- ¹⁰A. G. Adam, J. R. D. Peers, Y. Teng, and C. Linton, J. Mol. Spectrosc. 212, 111 (2002).
- ¹¹A. G. Adam, L. P. Fraser, W. D. Hamilton, and M. C. Steeves, Chem. Phys. Lett. **230**, 82 (1994).
- ¹² M. Freindorf, C. M. Marian, and B. A. Hess, J. Chem. Phys. **99**, 1215 (1993).
- ¹³T. Hirao, B. Pinchemel, and P. F. Bernath, J. Mol. Spectrosc. **219**, 119 (2003).
- ¹⁴A. L. Wong, W. S. Tam, and A. S.-C. Cheung, J. Chem. Phys. **119**, 3234 (2003).
- ¹⁵L. M. Ziurys, W. L. Barclay, Jr., M. A. Anderson, D. A. Fletcher, and J. W. Lamb, Rev. Sci. Instrum. 65, 1517 (1994).
- ¹⁶P. M. Sheridan, S. K. McLamarrah, and L. M. Ziurys, J. Chem. Phys. **119**, 9496 (2003).
- ¹⁷ M. D. Allen, B. Z. Li, and L. M. Ziurys, Chem. Phys. Lett. **270**, 517 (1997).
- ¹⁸C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (Dover, New York, 1975).
- ¹⁹See EPAPS Document No. E-JCPSA6-121-021439 for a complete list of transitions arising from both Co³⁵Cl and Co³⁷Cl. A direct link to this document may be found in the online article's HTML reference section. The document may also be reached via the EPAPS homepage (http:// www.aip.org/pubservs/epaps.html) or from ftp.aip.org in the directory /epaps/. See the EPAPS homepage for more information.
- ²⁰T. Okabayashi and M. Tanimoto, J. Mol. Spectrosc. **221**, 149 (2003).
- ²¹A. G. Adam and W. D. Hamilton, J. Mol. Spectrosc. 206, 139 (2001).
- ²²S. P. Beaton, K. M. Evenson, and J. M. Brown, J. Mol. Spectrosc. 164, 395 (1994).
- ²³ P. M. Sheridan, L. M. Ziurys, and T. Hirano, Astrophys. J. **593**, L141 (2003).
- ²⁴ Y. Azuma, J. A. Barry, M. P. J. Lyne, A. J. Merer, J. O. Schröder, and J.-L. Féménias, J. Chem. Phys. **91**, 1 (1989).
- ²⁵ W. J. Balfour, A. J. Merer, H. Niki, B. Simard, and P. A. Hackett, J. Chem. Phys. **99**, 3288 (1993).
- ²⁶A. Carrington and A. D. McLachlan, *Introduction to Magnetic Resonance* (Harper and Row, New York, 1967).
- ²⁷ D. J. Clouthier, G. Huang, A. J. Merer, and E. J. Friedman-Hill, J. Chem. Phys. **99**, 6336 (1993).
- ²⁸J. M. Brown and A. Carrington, *Rotational Spectroscopy of Diatomic Molecules* (Cambridge University Press, Cambridge, 2003).
- ²⁹ A. J. Merer, Annu. Rev. Phys. Chem. **40**, 407 (1989).
- ³⁰A. J. Bridgeman and J. Rothery, J. Chem. Soc. Dalton Trans. 2000, 211.
- ³¹I. Kretzschmar, D. Schröder, H. Schwartz, and P. B. Armentrout, Advances in Metal and Semiconductor Clusters (Elsevier, New York, 2001).
- ³²G. Bodner and H. Pardue, *Chemistry: An Experimental Science* (Wiley, New York, 1995).