<table>
<thead>
<tr>
<th><strong>Title</strong></th>
<th>Electronic transitions of cobalt monoboride</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Author(s)</strong></td>
<td>Ng, YW; Pang, HF; Cheung, ASC</td>
</tr>
<tr>
<td><strong>Citation</strong></td>
<td>Journal of Chemical Physics, 2011, v. 135 n. 20, article no. 204308</td>
</tr>
<tr>
<td><strong>Issued Date</strong></td>
<td>2011</td>
</tr>
<tr>
<td><strong>URL</strong></td>
<td><a href="http://hdl.handle.net/10722/148664">http://hdl.handle.net/10722/148664</a></td>
</tr>
<tr>
<td><strong>Rights</strong></td>
<td>Copyright 2011 American Institute of Physics. This article may be downloaded for personal use only. Any other use requires prior permission of the author and the American Institute of Physics. The following article appeared in Journal of Chemical Physics, 2011, v. 135 n. 20, article no. 204308 and may be found at <a href="http://jcp.aip.org/resource/1/jcpsa6/v135/i20/p204308_s1">http://jcp.aip.org/resource/1/jcpsa6/v135/i20/p204308_s1</a>; This work is licensed under a Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License.</td>
</tr>
</tbody>
</table>
Electronic transitions of cobalt monoboride
Y. W. Ng, H. F. Pang, and A. S.-C. Cheung

Citation: J. Chem. Phys. 135, 204308 (2011); doi: 10.1063/1.3663619
View online: http://dx.doi.org/10.1063/1.3663619
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v135/i20
Published by the American Institute of Physics.

Additional information on J. Chem. Phys.
Journal Homepage: http://jcp.aip.org/
Journal Information: http://jcp.aip.org/about/about_the_journal
Top downloads: http://jcp.aip.org/features/most_downloaded
Information for Authors: http://jcp.aip.org/authors

ADVERTISEMENT

Instruments for advanced science

Gas Analysis
- dynamic measurement of reaction gas streams
- catalysis and thermal analysis
- molecular beam analysis
- dissolved oxygen, protein
- fermentation, environmental studies

Surface Science
- STEM
- high voltage
- point detection in ion beam etch
- microanalytical imaging / surface imaging

Plasma Diagnostics
- plasma source characterization
- arc and discharge process monitoring
- analysis of neutral and radical species

Vacuum Analysis
- partial pressure measurement and control of pressure gases
- reaction diffusion process control
- vacuum diagnostics
- vacuum coating process monitoring

contact Hiden Analytical for further details
info@hideninc.com
www.HidenAnalytical.com

CLICK to view our product catalogue
Electronic transitions of cobalt monoboride

Y. W. Ng, H. F. Pang, and A. S.-C. Cheung

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong

(Received 21 August 2011; accepted 2 November 2011; published online 30 November 2011)

Electronic transition spectrum of cobalt monoboride (CoB) in the visible region between 495 and 560 nm has been observed and analyzed using laser-induced fluorescence spectroscopy. CoB molecule was produced by the reaction of laser-ablated cobalt atom and diborane (B₂H₆) seeded in argon. Fifteen vibrational bands with resolved rotational structure have been recorded, which included transitions of both Co¹⁰B and Co¹¹B isotopic species. Our analysis showed that the observed transition bands are ΔΩ = 0 transitions with Ω' = 2 and Ω'' = 3 lower states. Four transition systems have been assigned, namely, the [18.1]Π₁ – X³ Δ₂, the [18.3]Φ₁ – X³ Δ₃, the [18.6]X³ Δ₃, and the [19.0]2–X³ Δ₂ systems. The bond length, r₀, of the X³ Δ₃ state of CoB is determined to be 1.705 Å. The observed rotational lines showed unresolved hyperfine structure arising from the nuclei, which conforms to the Hund’s case (a) coupling scheme. This work represents the first experimental investigation of the CoB spectrum.


I. INTRODUCTION

Many transition metal (TM) borides are known catalysts for the hydrogenation of alkenes and alkynes, reduction of nitrogenous functional groups and deoxygenation reactions. Besides, metal borides are also refractory compounds process remarkable physical properties such as very high conductivity (TiB₂) (Ref. 2) and even superconductivity (MgB₂), and super hardness (ReB₂). Recently, boron nitride nanotubes could be synthesized from zirconium boride (ZrB₂) and even superhardness (ReB₂). A new boron compound of metal could be synthesized from zirconium boride (ZrB₂) in a nitrogen atmosphere using electric arc discharge. Despite the chemical and physical importance, very little is known about the chemical bonding of this class of boride compounds. Since diatomic TM boride is the simplest building block of the more complicated TM boride compounds, detail knowledge of the characteristic of chemical bonding and electronic structure of this simple system would be useful for understanding larger molecules and even their bulk properties.

TM borides are often used as catalysts, recently cobalt boride solid and CoB thin-film received special attention because of their ability to catalyze the production of hydrogen in the hydrolysis of sodium borohydride solution. Sodium borohydride shows superior qualities for providing a safe and practical way for hydrogen production, the use of CoB catalyst allows good control of the hydrogen production rate. As far as the study of TM monoboride molecules is concerned, Tzeli and Mavridis performed theoretical calculations on the 3d TM monoborides aiming at understanding their chemical bonding characteristics and also their ground state symmetry. CoB was predicted to have a X³ Δ₁ ground state and an equilibrium bond length, r₀ = 1.700 Å. Among all 3d TM monoborides only NiB (Ref. 9) has been studied experimentally, this work represents the first experimental work on the CoB molecule.

II. EXPERIMENTAL

In this paper, we report the analysis of electronic transitions of the CoB molecule recorded using the technique of laser vaporization/reaction free jet expansion and laser-induced fluorescence (LIF) spectroscopy in the visible region. Spectra of both Co¹⁰B and Co¹¹B isotopes were resolved and recorded. One of the aims in this work is to identify and characterize the ground state of CoB. Electronic configurations giving rise to the observed electronic states have also been examined using a molecular orbital energy level diagram.

Author to whom correspondence should be addressed. Electronic mail: hrsccsc@hku.hk. Tel.: (852) 2859 2155. Fax: (852) 2857 1586.
is probably due to unresolved hyperfine structure from the Co and B nuclei.

### III. RESULTS AND DISCUSSION

#### A. Low-resolution broadband spectrum

Low-resolution LIF spectrum of CoB in the visible region between 495 and 560 cm$^{-1}$ has been recorded. Figure 1 is a broadband low-resolution scan of the CoB spectrum, the bands identified are $\Delta \Omega = 0$ transitions with either $\Omega'' = 2$ or $\Omega'' = 3$ value. Spectra of both isotopes Co$^{10}$B and Co$^{11}$B have been observed. Fifteen vibrational bands were recorded and analyzed; their upper and lower state $\Omega$ values were characterized, and their band origin and rotational constant $B$ were obtained by least-squares fitting of the measured line positions. Further analysis was proven to be difficult, the usual regularities among vibrational bands are lacking and the grouping of these bands under an electronic transition system was not trivial. This situation is probably due to the fact that the electronic states are generally in case (c) coupling scheme and, therefore, electronic transition bands could only be characterized by individual $\Omega$ value. In addition, rotational transition lines are generally broadened by unresolved hyperfine structure from both the Co and B nuclei, and thus the measurement of line positions would be of lower accuracy. In the least-squares fit, the larger uncertainty in the measurement of line positions would eventually propagate to molecular parameters such as band origin and rotational constants. Furthermore, it is generally expected that the observation of isotopic molecules could readily help the assignment of vibrational quantum number, however, for Co$^{10}$B and Co$^{11}$B isotopes, the isotopic shift between them is relatively large and their transition bands are crowded, which made the association of isotopic transition bands difficult. Combining problems in case (c) coupling, larger uncertainties in rotational constants and also very minimum help from isotopic shifts, among the bands measured, we managed to identify four electronic transition systems, namely, the [18.1]$^3\Pi_2$–X$^3\Delta_2$, the [18.3]$^3\Phi_3$–X$^3\Delta_3$, the [18.6]$^3$–X$^3\Delta_3$, and the [19.0]$^2$–X$^3\Delta_2$ systems.

#### B. [18.1]$^3\Pi_2$–X$^3\Delta_2$ transition

The (0, 0) and (0, 1) bands of this system were recorded and analyzed. Each band shows resolved P, Q, and R branches. Line assignment was straightforward. The band head region of the (0, 0) band of this transition is shown in Figure 2. The observation of the P(3), Q(2), and R(2) first lines from their corresponding branches established the vibrational band is a $\Omega'' = 2$ and $\Omega'' = 3$ transition. The P and Q branches are stronger in intensity than the R branch, which is consistent with a transition with $\Delta \Lambda = -1$. Both the (0, 0) and (1, 0) bands are weak in intensity. It can be noticed easily in Figure 2 that there are unresolved structures in the low J lines and also the linewidth is wider than expected from the Doppler broadening, this is due to the hyperfine structure arising from the Co and B nuclei. The observed line positions of the vibrational bands were fit to the following expression:

$$\nu = \nu_0 + B''J''(J'' + 1) - D''[J''(J'' + 1)]^2$$

$$- (B'J'(J'+1) - D'[J'(J'+1)]^2),$$

where the ′ and ″ refer to the upper and lower states, respectively. The $\nu_0$ is the band origin, and $B$ and $D$ are rotational and centrifugal distortion constants, respectively. It is because only low J lines ($J < 12$) were measured, in our least-squares fit; the D constant for both the upper and lower states was set to zero. The least-squares fit of the transition lines in these bands were performed in two stages, first band by band and, subsequently, all bands were merged together in a single fit. Determined molecular constants for individual bands are given in Table I. The assignment of the upper and lower states will be discussed in Sec. III E. A list of the measured transition line positions of the observed [18.1]$^3\Pi_2$–X$^3\Delta_2$ system is available from the supplemental material. The $\Delta G_{1/2}$ measured for the X$^3\Delta_2$ is 734.68 cm$^{-1}$.

#### C. [18.3]$^3\Phi_3$–X$^3\Delta_3$ transition

As far as the intensity of vibrational bands is concerned, molecular transitions with $\Delta \Omega = 0$ and $\Omega'' = 3$ are generally stronger than those with $\Omega'' = 2$. We recorded the (3, 0),
The vibrational separations, $\Delta G_{1/2}$, $\Delta G_{3/2}$, and $\Delta G_{5/2}$ of the [18.3]$^3\Phi_3$ state are, respectively, 462.81, 446.08, and 424.56 cm$^{-1}$, and the equilibrium molecular constants determined are $T_e = 18012.6$, $\omega_c = 482.9$, and $\omega_eX_e = 9.5$ cm$^{-1}$. The $\Delta G_{1/2}$ for the $X^3\Delta_3$ was measured to be 731.66 cm$^{-1}$.

**D. [18.6]$^3\Delta_3$ and [19.0]$^2\Delta_2$ transitions**

It is well-known that information from isotopic molecules can be used to confirm the carrier of the spectrum. In this work, we recorded the (0, 0) band of the [18.6]$^3\Delta_3$ and [19.0]$^2\Delta_2$ transitions of both Co$^{10}$B and Co$^{11}$B isotopes. Molecular parameters of isotopic molecules are approximately related by different powers of the mass dependence $\rho = (\mu/\mu_i)$, where $\mu$ and $\mu_i$ are the reduced masses of Co$^{11}$B and one of the isotopes, respectively. Since Co$^{11}$B is the most abundant isotope, isotopic effects are calculated relative to it. The line list of the $\Delta\Omega = 0$ transitions with $\Omega' = 2$ and $\Omega'' = 3$ is available from the supplemental material. Table I also presents the observed molecular constants for both isotopic molecules; the values in parentheses are molecular constants calculated for the Co$^{10}$B isotope from those of Co$^{11}$B using the isotopic relationship. The agreement of these molecular constants is very good, which confirms the carrier of the spectrum is CoB undoubtedly. The sizeable difference between the band origins of the Co$^{10}$B and Co$^{11}$B isotopes reflects a large isotope effect of the vibrational constants for the electronic states. Since we measured only one vibrational band of these two electronic transitions and it is difficult to confirm the relative intensity of the branches; we just identify these bands using their $\Omega$ values, namely, the [19.0]$^2\Delta_2$ and the [18.6]$^3\Delta_3$ transitions. Figure 4 summarizes all transition bands observed in this work.

**E. Electronic configuration and the electronic states**

In order to better understand the electronic structure of CoB, we would like to examine molecules formed from Co and the $2p$ main group elements such as CoC to CoO. Using the molecular orbital (MO) energy level diagram discussed by Merer and co-workers for CoC and CoO, the MO energy levels formed are with 4$s$ and 3$d$ atomic orbitals (AOs) of the Co atom and the $2p$ AO of a main group element. Figure 5

![Figure 3: The (2, 0) band of the [18.3]$^3\Phi_3$ transition of CoB.](image)
represents qualitatively the relative energy order of the MOs formed from the Co and B atoms. The lower energy 8σ and 3π MOs and the higher energy 10σ and 4π MOs are formed from the main group 2p AO and Co 3dσ, 3dπ and 4pσ and 4pπ AOs. The 9σ MO is essentially the Co 4s AO. The 1δ MO is the Co 3dδ AO, because there is no other σ symmetry orbital around. The ground state CoC (Ref. 15) and CoN (Ref. 16) are

\[
\text{CoC}(X^2\Sigma^+) : (8\sigma)^2(3\pi)^4(1\delta)^4(9\sigma)^1 \rightarrow 2\Sigma^+, \quad (2)
\]

\[
\text{CoN}(X^1\Sigma^+) : (8\sigma)^2(3\pi)^4(1\delta)^4(9\sigma)^2 \rightarrow 1\Sigma^+. \quad (3)
\]

The Aufbau principle works very well in atoms, it is also possible to follow this thinking in adding electrons to the MOs in diatomic molecules. From Figure 5, we noticed that the energy of the 9σ and 1δ MOs are quite close; there could easily be two possible arrangements for the ground electron configuration for CoB so that adding one more electron could arrive at the configuration of CoC, they are either

\[
(8\sigma)^2(3\pi)^4(1\delta)^4 \rightarrow 1\Sigma^+, \quad (4)
\]

or

\[
(8\sigma)^2(3\pi)^4(1\delta)^3(9\sigma)^1 \rightarrow a^1\Delta \text{ and } X^3\Delta_i. \quad (5)
\]

From the first lines of rotational branches, we concluded that the lower state has Ω = 3 and Ω = 2 spin components. Close examination of configurations of Eqs. (4) and (5) indicates that only the \(3\Delta_i\) electronic state in Eq. (5) has Ω = 3 and 2 components, therefore, the ground state of CoB is reasonable to be of the electronic configuration in Eq. (5). Since the number of electrons in the δ MO is more than half-filled, the \(3\Delta_i\) state arises from configuration of Eq. (5) is an inverted \(3\Delta_i\) state. For a \(3\Delta_i\) state, the Ω = 3 component is the lowest in energy, and the Ω = 1 component is of the highest energy. Our observation of the lower state with Ω = 2 and 3 fits well with the \(3\Delta_i\) state to be the ground state. Another two pieces of information from our experimental work also indicate that the ground \(3\Delta_i\) state is an inverted state. First, the Ω = 2 transitions are generally weaker in intensity than the Ω = 3 transitions, which is consistent with the situation that the Ω = 2 component is of lower population and is higher in energy than the Ω = 3 component. Second, the effective \(B_{\text{eff}}\) value of an electronic state is given by the following expression:

\[
B_{\text{eff}} = B_v(1+\Sigma\Lambda/\Lambda A), \quad (6)
\]

where \(B_v\) is the rotational constant for the ν vibrational level and A is the spin-orbit constant for the electronic state, and Σ and Λ are quantum number of the projection of the spin and orbital angular momentum operators along the \(z\)-axis. Since the \(B_{\text{eff}}\) value of the Ω = 2 (with Σ = 0) component is larger than the Ω = 3 (Σ = 1) component, which implies that the spin-orbit constant, \(A\), has a negative value. As far as the ground state electronic configuration of CoC is concerned, it has one more valence electron than CoB and that extra electron goes to the 1δ MO, which gives rise to the ground electronic configuration in Eq. (2).

Tzeli and Mavridis8 performed multireference configuration interaction calculations on the 3d transition metal monoborides employing a correlation consistent basis set of quintuple cardinality (5Z), and predicted the ground state to be \(1\Delta_i\) for CoB. Their calculated equilibrium bond length, \(r_e = 1.700\ \text{Å}\), is in good agreement with our determined value \(r_e = 1.705\ \text{Å}\) for the \(X^3\Delta_i\) state. Their calculated \(\omega_e = 708\ \text{cm}^{-1}\) compares reasonably well with our measured vibrational separation \(\Delta G_{12} = 731.7\ \text{cm}^{-1}\). In this work, we only observed parallel transitions and have no information on the spin-orbit components. It is possible to get some estimate of the magnitude of the spin-orbit parameter for the \(X^3\Delta_i\) state from the atomic value of the cobalt atom, the 1δ orbital is essentially the Co 3dδ AO, and Lefebvre-Brion and Field17 tabulated a value of \(\zeta = 530\ \text{cm}^{-1}\) for Co atom. As a comparison, the spin-orbit constant, \(A\), for the ground \(X^3\Delta_i\) state of CoO (Ref. 18) with an electronic configuration of \((8\sigma)^2(3\pi)^4(1\delta)^3(4\pi)^2\) was determined to be \(-332.4\ \text{cm}^{-1}\). Since the first-order energy expression for calculating spin-orbit components is \(\Lambda\Lambda\Sigma\), the separation between spin-orbit components is quite probable to be in hundreds of wavenumbers. Further work would be necessary to obtain the spin-orbit separations of the \(X^3\Delta_i\) state.

In order to assign the upper state of our observed transitions, we assume single configuration can be used to describe the electronic states involved; we consider the promotion of an electron from either \(1\sigma\) or \(9\sigma\) MO in electronic configuration (5) to higher energy MO. If an electron was taken from the 1δ MO, the electronic configurations of the upper state

---

**FIG. 4.** Observed vibrational transitions of CoB.

**FIG. 5.** Molecular orbital energy level diagram of CoB.
would be $\delta^2\sigma^1\pi^1$ and also $\delta^2\sigma^1\pi^1$, in any case the spin multiplicities would be quintet, triplet, and singlet states, and the quintet states would be of lower energy. Since the ground state is basically a triplet state, for $\Delta S = 0$ transition, a triplet excited state is preferred. For promoting an electron from the $9\sigma$ to $4\pi$ MO, the following electronic configuration is obtained:

$$(8\sigma)^2(3\pi)^4(1\delta)^3(4\pi)^1 \rightarrow 1\Pi, 3\Pi, 1\Phi, \text{and } 3\Phi.$$  \hspace{1cm} \hspace{1cm} (7)$$

The electronic configuration in Eq. (7) gives rise to four excited states of which the $3\Pi_1$ and $3\Pi_1'$ have spin-orbit components with $\Omega = 2$ and $\Omega = 3$, respectively. For assigning the upper state, besides the $\Delta S = 0$ selection rule, we also based on the observed intensity pattern to establish $\Delta \Lambda$ values. The assignment of the [18.1]$^3\Pi_2$ state fits the $\Delta \Lambda = -1$ and [18.3]$^3\Pi_3$ state fits the $\Delta \Lambda = +1$ pattern. We, therefore, assigned the observed transitions as [18.1]$^3\Pi_2$–$X^3\Delta_2$ and [18.3]$^3\Pi_3$–$X^3\Delta_3$ systems.

In summary, we report the first observation of electronic transition spectrum of CoB. Four transition systems have been observed and analyzed. The bond length, $r_0$, of the ground $X^3\Delta_3$ state has been determined to be 1.705 Å. The large hyperfine width observed in the spectral lines provides good support to having an unpaired electron in the $9\sigma$ ($4\pi\sigma$) orbital in the ground state.

**ACKNOWLEDGMENTS**

The work described here was supported by a grant from the Research Grants Council of the Hong Kong Special Administrative Region, China (Project No. HKU 701008).

**TABLE II. Comparison of molecular properties of the Group VIII A monoborides.**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>CoB</th>
<th>RhB$^a$</th>
<th>IrB$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground state</td>
<td>$^3\Delta_3$</td>
<td>$^1\Sigma^+$</td>
<td>$^3\Delta_3$</td>
</tr>
<tr>
<td>Electronic configuration$^c$</td>
<td>$\delta^3\sigma^1$</td>
<td>$\delta^4$</td>
<td>$\delta^3\sigma^1$</td>
</tr>
<tr>
<td>Bond length, $r_0$ (Å)</td>
<td>1.705</td>
<td>1.614</td>
<td>1.767</td>
</tr>
<tr>
<td>$\Delta G_{1/2}$ (cm$^{-1}$)</td>
<td>731.7</td>
<td>$\sim$920</td>
<td>909.6</td>
</tr>
<tr>
<td>Ground electronic configuration of metal atom</td>
<td>$4\sigma^2 3d^7$</td>
<td>$5\sigma^1 6d^6$</td>
<td>$6\sigma^2 5d^5$</td>
</tr>
</tbody>
</table>

$^a$Reference 19.
$^b$Reference 20.
$^c$Electronic configuration giving rise to the ground state.

12. See supplementary material at http://dx.doi.org/10.1063/1.3663619 for the observed line positions of the [18.1]$^3\Pi_2$–$X^3\Delta_2$, [18.3]$^3\Phi_3$–$X^3\Delta_3$, [18.6]$^3\Lambda_1$, [19.0]$^2\Sigma^+$–$X^3\Delta_2$ transition.