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Ling Fung Cheung, G. Stephen Kocheril, Joseph Czekner, and Lai-Sheng Wang

AFFILIATIONS
Department of Chemistry, Brown University, 324 Brook Street, Providence, Rhode Island 02912, USA

Author to whom correspondence should be addressed: lai-sheng_wang@brown.edu

ABSTRACT

Boron can form strong bonds with transition metals in diatomic metal borides (MB), but the nature of the chemical bonding has not been well understood. Recently, a quadruple bond was discovered in RhB, consisting of two σ bonds formed between the Rh 4d and B 2s/2p orbitals and two π bonds between the Rh 4d_xz/4d_yz and the B 2p_y/2p_z orbitals. The bonding between the 5d transition metals and boron is expected to be even stronger. Here, we report an investigation on the electronic structure and chemical bonding of the 5d transition metal diatomic borides (IrB, PtB, and AuB) using high-resolution photoelectron imaging on the corresponding anions (MB⁻) and theoretical calculations. Vibrationally resolved photoelectron spectra are obtained for all three anions, and the electron affinities are measured for IrB, PtB, and AuB to be 1.995(1), 2.153(3), and 0.877(6) eV, respectively. It is found that the weakly anti-bonding 3σ molecular orbital (mainly of M 6s and B sp characters) is singly occupied in IrB (1Δ) and PtB (2Σ⁻), resulting in a bond order of three and half for these two diatomic borides. The 3σ orbital is doubly occupied in AuB (1Σ'), giving rise to a weak triple bond. Despite the lower bond order, the bonding in IrB and PtB is only slightly weaker than that in RhB due to the more favorable interactions between the M 5d orbitals and the B sp orbitals.

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I. INTRODUCTION

Transition metal borides (MB) have become an active area of investigation to search for ultrahard materials due to the strong covalent bonding between transition metals and boron. Particularly for 4d and 5d transition metals. The nature of the chemical bonding between a metal and boron plays a central role in determining the hardness of a given transition metal boride material among other factors. However, there have been limited previous experimental and theoretical investigations, and the nature of the chemical bonding has not been well understood even for the simplest diatomic transition-metal borides (MB). In a very recent study, we have found serendipitously that rhodium and boron can form a quadruple bond in the diatomic RhB (RhB⁻), the first experimentally confirmed quadruple bond in a diatomic species involving B.

The valence molecular orbital (MO) diagram for RhB, along with the orbital compositions, is reproduced in Fig. 1 for the convenience of discussion. The quadruple bond in RhB⁻ consists of two σ bonds formed between the Rh 4d_x and B 2s/2p orbitals and two π bonds between the Rh 4d_xz/4d_yz and the B 2p_y/2p_z orbitals. The 1σ MO was viewed as a B 2s lone pair previously, but it clearly has a significant contribution from the 4d_x orbital of Rh (Fig. 1). The covalent bonding nature of the 1σ MO was further confirmed by considering RhBH⁺, in which the 1σ orbital is “destroyed” by forming the B−H bond. It was shown that the Rh−B bond in RhBH⁺ is weakened and reduced to a triple bond [Rh⋯B−H]⁺. The quadruple bond in RhB⁻ is corroborated by the fact that its bond dissociation energy (D₀) is the largest (5.252 eV) among a series of late transition metal MB species reported recently, including 3d, 4d, and 5d transition metals. The bonding between the 5d transition metal and boron is expected to be stronger. Surprisingly, the D₀ of the isoelectronic IrB (4.928 eV) is lower than that of RhB, whereas that of PtB (5.235 eV) is the second largest among the late transition metal diatomic species.

To probe the electronic structure and elucidate the bonding in IrB and PtB, we have carried out a high resolution photoelectron
imaging study of their anions in conjunction with theoretical calculations. We have also investigated the AuB diatomic species for comparison. Spectroscopically, there was relatively little known about these species. Laser-induced fluorescence (LIF) spectroscopy was reported for IrB, and its ground state was deduced to be $^3\Delta_3$ with a vibrational frequency of 909.63 cm$^{-1}$ ($^{195}$Ir$^{11}$B) and 909.92 cm$^{-1}$ ($^{191}$Ir$^{11}$B). There was also one LIF spectroscopy study on PtB, which was found to have a $^2\Sigma^+$ ground state and a vibrational frequency of 903.60 cm$^{-1}$ (Pt$^{11}$B). There were no previous spectroscopy studies on AuB, except an early Knudsen cell experiment yielding a dissociation energy of 3.77 eV.

We have been interested in the electronic structure and chemical bonding in size-selected boron and metal-doped boron clusters using photoelectron spectroscopy (PES) and computational chemistry. It has been shown that PES is a powerful experimental technique to probe the electronic structure and bonding of novel cluster species. Here, we report a high-resolution photoelectron (PE) imaging and theoretical study of IrB$^-$, PtB$^-$, and AuB$^-$. Vibrationally resolved PE spectra are obtained for all three anions, and the electron affinities are measured for IrB, PtB, and AuB to be 1.995(1), 2.153(3), and 0.877(6) eV, respectively, for the first time. In addition to the ground state ($^3\Delta_3$) of IrB, the $^3\Delta_2$ and $^1\Delta_2$ excited states are also observed, whereas only the ground electronic states are observed for PtB and AuB. Vibrational frequencies are obtained for the ground states of IrB ($^3\Delta_3$), PtB ($^2\Sigma^+$), and AuB ($^1\Sigma^+$): 925(8) cm$^{-1}$ for $^{195}$Ir$^{11}$B, 974(27) cm$^{-1}$ for $^{191}$Ir$^{11}$B, and 704(26) cm$^{-1}$ for Au$^{10}$B. It is found that the weakly antibonding 3$\sigma$ molecular orbital (mainly of M 6s and B sp characters) is singly occupied in IrB ($^3\Delta$) and PtB ($^2\Sigma^+$), resulting in a bond order of three and half for these two diatomic borides. The 3$\sigma$ orbital is doubly occupied in AuB ($^1\Sigma^+$), giving rise to a weak triple bond.

II. EXPERIMENTAL METHODS

The experiments were conducted using a high-resolution PE imaging apparatus, which has been described in detail previously. Briefly, the second harmonic of a Nd:YAG laser was focused onto a disk target pressed using a mixture of the metal (Ir, Pt, or Au), isotopically enriched $^{10}$B or $^{11}$B, and silver powders at room temperature. The silver powder was added as a binder and allowed robust targets to be produced by cold-press. The laser-induced plasma was cooled by a helium carrier gas seeded with 10% argon, initiating nucleation. The nascent clusters were entrained by the carrier gas and underwent a supersonic expansion, producing a cold cluster beam. Anionic clusters were extracted perpendicularly into a time-of-flight mass spectrometer. The MB$^-$ species of interest were mass selected before entering the interaction zone of the velocity-map imaging (VMI) analyzer. Diatomic anionic species were more challenging to produce in our cluster source, which favored the production of larger clusters. Significant anionic intensities for diatomic species were observed usually not under the best cooling conditions.

A second laser beam from a Nd:YAG laser or a Deyang Tech dye laser was used to photodetach electrons from the size-selected anions. Photoelectrons were focused onto a set of microchannel plates coupled with a phosphor screen and a charge-coupled-device camera. A typical experiment at a given photon energy required 152, 174301-2

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IV. EXPERIMENTAL RESULTS

A. IrB

The PE images and spectra for IrB\(^{-}\) are presented in Fig. 2 at six photon energies from 1.9662 eV [Fig. 2(a)] to 2.5188 eV [Fig. 2(f)]. Four main peaks were observed, and they are labeled X, A, a, and B. The sharp peak X in Fig. 2(b) defines the EA of IrB to be 1.995 ± 0.001 eV. The relative intensities and separations between these peaks suggest that they do not belong to a simple vibrational progression. Weak peaks due to vibrational hot bands were observed in the lower binding energy region below peak X, and they are labeled hb1, hb2, and hb3. A shoulder peak labeled x was observed on the lower binding energy side of peak A [Fig. 2(c)]. In addition, a weak peak was observed on the higher binding energy side of peaks X [Fig. 2(b)], A [Fig. 2(c)], and a [Fig. 2(d)], labeled hb4, hb5, and hb6, respectively. Finally, a weak peak b was observed at the high binding energy side [Fig. 2(f)] although this assignment was tentative because the signals were weak in the higher binding energy part of the spectrum. The binding energies of the observed peaks and their assignments are given in Table I and will be discussed in Sec. VI A. The PADs for peaks X, A, and B were examined, and the obtained \(\beta\) values at different electron kinetic energies are presented in Fig. 3.

B. PtB

Figure 4 displays the PE images and spectra of PtB\(^{-}\) at three photon energies from 2.1937 eV [Fig. 4(a)] to 2.4810 eV [Fig. 4(c)]. The most intense peak (X) denotes the 0–0 transition and defines the EA for PtB to be 2.153 ± 0.003 eV. A short vibrational
TABLE I. The experimental binding energies (BE) in eV and assignments of the observed peaks in the PE spectra of $^{193}$Ir$^{11}$B$^-$. The energy shifts (cm$^{-1}$) relative to peak X and their corresponding 0–0 transitions are also given. The calculated BE (eV) and vibrational frequencies (cm$^{-1}$) are also given for comparison.

<table>
<thead>
<tr>
<th>Band</th>
<th>BE</th>
<th>State</th>
<th>Energy shift relative to peak X</th>
<th>Energy shift relative to the 0–0 transitions</th>
<th>Assignment</th>
<th>BE (Theo.)</th>
<th>Freq. (Theo.)</th>
</tr>
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<tr>
<td>hb1</td>
<td>1.788</td>
<td>$^3\Delta_3$</td>
<td>$-1672(15)$</td>
<td>$-1672(15)$</td>
<td>$0^2$</td>
<td>1.920</td>
<td>882</td>
</tr>
<tr>
<td>hb2</td>
<td>1.891</td>
<td>$^3\Delta_3$</td>
<td>$-840(9)$</td>
<td>$-840(9)$</td>
<td>$0^2$</td>
<td>1.920</td>
<td>882</td>
</tr>
<tr>
<td>B</td>
<td>1.899</td>
<td>$^3\Delta_3$</td>
<td>$-778(9)$</td>
<td>$-778(9)$</td>
<td>$0^2$</td>
<td>1.920</td>
<td>882</td>
</tr>
<tr>
<td>X</td>
<td>1.995</td>
<td>$^3\Delta_3$</td>
<td>0</td>
<td>0</td>
<td>$0^0$</td>
<td>1.957</td>
<td>882</td>
</tr>
<tr>
<td>hb4</td>
<td>2.011</td>
<td>$^1\Delta$</td>
<td>$131(5)$</td>
<td>$-847(5)$</td>
<td>$1^1$</td>
<td>1.882</td>
<td>942</td>
</tr>
<tr>
<td>X</td>
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<td>$^3\Delta_3$</td>
<td>$925(8)$</td>
<td>$925(8)$</td>
<td>$1^1$</td>
<td>1.942</td>
<td>942</td>
</tr>
<tr>
<td>A</td>
<td>2.116</td>
<td>$^1\Delta$</td>
<td>$976(6)$</td>
<td>0</td>
<td>$0^0$</td>
<td>2.188/2.240</td>
<td>942</td>
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<tr>
<td>a</td>
<td>2.232</td>
<td>$^1\Delta$</td>
<td>$1908(9)$</td>
<td>$931(9)$</td>
<td>$1^1$</td>
<td>1.942</td>
<td>942</td>
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<tr>
<td>hb6</td>
<td>2.242</td>
<td>$^1\Delta$</td>
<td>$1996(9)$</td>
<td>$1013(9)$</td>
<td>$1^2$</td>
<td>2.382</td>
<td>942</td>
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<tr>
<td>B</td>
<td>2.355</td>
<td>$^3\Delta_2$</td>
<td>$2900(8)$</td>
<td>0</td>
<td>$0^0$</td>
<td>2.382</td>
<td>942</td>
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<tr>
<td>b</td>
<td>2.466</td>
<td>$^3\Delta_2$</td>
<td>$3795(45)$</td>
<td>$894(45)$</td>
<td>$1^1$</td>
<td>2.480</td>
<td>942</td>
</tr>
</tbody>
</table>

$^a$Calculated at the TD-B3LYP level using $^3\Delta_3$ state’s geometry, but the vibrational frequency of the $^1\Delta$ state could not be computed at the current level of theory.

$^b$Calculated at the MRCI+SO level, with all valence orbitals and electrons included in the active space.

progression (peaks a and b) was observed, as denoted by the vertical lines in Figs. 4(b) and 4(c), yielding a vibrational frequency for the ground state of $^{193}$Pt$^{10}$B to be 974 ± 27 cm$^{-1}$. The sharp peak near the threshold in Fig. 4(c) with a binding energy of 2.461(3) eV could not be assigned to a detachment transition from PtB$^-$, and it could be due to an impurity. A weak peak labeled hb1 was observed at the lower binding energy side of X, which should be due to a vibrational hot band of PtB$^-$. The $\beta$ values for the 0–0 transition obtained from the PADs at three electron kinetic energies are also displayed in Fig. 3. The binding energies of the observed vibrational peaks are given in Table II.

C. AuB$^-$

The AuB$^-$ anion was found to have a relatively low electron binding energy. Its PE image (Fig. 5) was measured at 1.4058 eV, which was already near the cutoff of our dye laser at the long wavelength side. In addition, the ion intensity of AuB$^-$ was relatively weak from our cluster source. Both the low detachment laser flux and the low ion intensity gave rise to a spectrum with relatively poor signal-to-noise ratios even with a long averaging time. The most intense peak (X) denotes the 0–0 transition and defines the...
EA of AuB to be $0.877 \pm 0.006$ eV. A short vibrational progression (peaks $a$ and $b$) was discernible, yielding a vibrational frequency for AuB to be $704 \pm 26$ cm$^{-1}$. The $\beta$ value obtained from the PAD of peak X is also shown in Fig. 3. The binding energies of the observed vibrational peaks are also given in Table II.

V. THEORETICAL RESULTS

A. IrB$^-$

The electron configuration for IrB$^-$ was found to be $1s^21\pi^22\sigma^21\delta^33\sigma^4$ with a $^2\Delta_{a\Sigma}$ ground state. The $^2\Sigma^+$ state with a $1\sigma^21\pi^22\sigma^21\delta^33\sigma^1$ electron configuration was calculated to be 0.237 eV higher in energy than the $^2\Delta$ state. This energy ordering is different from that of RhB$^-$, for which the $^2\Sigma^+$ state is the ground state.\cite{15} Detaching an electron from the $3\sigma$ orbital of the anion ground state yields either a $^3\Delta$ or $^1\Delta$ final state for IrB, while detaching an electron from the $1\pi$ orbital of the anion ground state gives the $^3\Sigma^-$ or the $^1\Pi$ excited state of IrB. Our calculated lowest energy state for IrB is the $^3\Delta$ state, consistent with the previous studies.\cite{13,15} The $^3\Delta$ state splits into three spin–orbit (SO) terms, $^3\Delta_3$, $^3\Delta_2$, and $^3\Delta_1$, but the splitting could not be computed at the level of theory used in the current work. Although it is not accessible from one-electron detachment, there is a $^3\Sigma^+$ excited state with an electron configuration of $1\sigma^21\pi^22\sigma^21\delta^33\sigma^2$, which corresponds to the ground state of RhB.\cite{15} Our calculations indicate that the $^3\Sigma^+$ and the $^1\Delta$ excited states are 0.176 eV and 0.231 eV higher in energy than the $^3\Delta$ ground state, respectively. The $^3\Sigma^+$ and the $^1\Pi$ excited states are computed to be 1.341 eV and 2.407 eV higher in energy than the ground state, respectively, and they are not accessible in the current experiment.

Our computed ADE to the $^3\Delta$ state is 1.957 eV (Table I), which is also the theoretical EA for IrB without considering the SO effects. The calculated bond length of IrB$^-$ is 1.808 Å, while that for neutral IrB is 1.763 Å for the $^3\Delta$ state and 1.722 Å for the $^1\Pi$ state, consistent with the antibonding characters of the $3\sigma$ orbital. The computed vibrational frequency is 882 cm$^{-1}$ for the $^2\Delta$ ground state of the $^{193}$Ir$^{10}$B$^-$ anion, 942 cm$^{-1}$ for the $^3\Delta$ ground state of neutral $^{193}$Ir$^{10}$B$^-$, and 994 cm$^{-1}$ for the $^1\Sigma^+$ excited state of neutral $^{193}$Ir$^{11}$B$^-$.

B. PtB$^-$

The PtB$^-$ anion has one more electron than IrB$^-$, and it is found to have a closed-shell electron configuration, $1\sigma^21\pi^22\sigma^21\delta^33\sigma^2$, with a $^1\Sigma^-$ ground state. Detaching an electron from the $3\sigma$ highest occupied molecular orbital (HOMO) gives rise to the $^3\Sigma^-$ ground state of neutral PtB. The calculated detachment energy or EA of PtB is 2.097 eV (Table II). Higher detachment channels were not computed because they were not accessible in the current experiment. The calculated bond lengths for the ground states of PtB$^-$ and PtB are 1.799 Å and 1.755 Å, respectively. The vibrational frequency for the $^{195}$Pt$^{10}$B$^-$ anion was calculated to be 913 cm$^{-1}$, while that for neutral $^{195}$Pt$^{10}$B was computed to be 984 cm$^{-1}$ (Table II).

C. AuB$^-$

The AuB$^-$ anion has one more electron than PtB$^-$, and it has an electron configuration of $1\sigma^21\pi^22\sigma^21\delta^33\sigma^22\pi^1$ with a $^2\Pi$ ground state. The computed bond length of AuB$^-$ is 2.097 Å for the $^1\Sigma^+$ state and 1.808 Å for the $^3\Delta$ state. Detaching an electron from the $3\sigma$ orbital gives rise to the $^3\Delta$ state, which is 1.957 eV higher in energy than the $^1\Sigma^+$ state (Table I).

The experimental binding energies (BE) in eV of the observed vibrational peaks in the PE spectra of $^{195}$Pt$^{10}$B$^-$ and Au$^{16}$B$^-$ are given for comparison. The calculated BE (eV) and vibrational frequencies (cm$^{-1}$) are also given. The calculated bond lengths for the ground states of PtB$^-$ and PtB are 1.799 Å and 1.755 Å, respectively. The vibrational frequency for the $^{195}$Pt$^{10}$B$^-$ anion was calculated to be 913 cm$^{-1}$, while that for neutral $^{195}$Pt$^{10}$B was computed to be 984 cm$^{-1}$ (Table II).

![Photoelectron image and spectrum of AuB$^-$ at 1.4058 eV. The double arrow below the images indicates the laser polarization. The vertical lines represent vibrational structures.](image-url)
state. The additional electron occupies the antibonding $2\pi$ LUMO of the neutral AuB. Detachment of the electron from the $2\pi$ orbital in AuB$^-$ yields the $2\Sigma$ ground state of AuB. The EA of AuB was computed to be 0.764 eV (Table II). The bond lengths for the anion and neutral were calculated to be 1.949 Å and 1.906 Å, respectively. The vibrational frequency was computed to be 614 cm$^{-1}$ for the Au$^{10}$B$^-$ anion and 710 cm$^{-1}$ for neutral Au$^{10}$B (Table II).

VI. SPECTRAL ASSIGNMENTS AND COMPARISON BETWEEN EXPERIMENT AND THEORY

A. IrB$^-$

The electronic structure of IrB is complicated because of the SO-splitting in its open-shell ground state ($^3\Delta_{21}$) and the fact that the $^3\Delta$ excited state is close in energy to the triplet ground state. Vibrational hot bands added further spectral congestions, resulting in the somewhat complicated PE spectra shown in Fig. 2. The observed detachment transitions are represented in the energy level diagram in Fig. 6, and the detailed assignments and comparison with theory are given in Table I.

Peak X represents the 0–0 transition to the $^3\Delta_3$ ground state. The EA for IrB (1.995 eV) determined from peak X agrees well with the calculated value (1.957 eV, Table I). Peak A is assigned to the transition to the $^3\Delta$ excited state of IrB. The calculated binding energy (2.188 eV) for the $^3\Delta$ state is in good accord with the experimental data (2.116 eV, Table I). This assignment yields an excitation energy of 976 cm$^{-1}$ for the $^3\Delta$ state relative to the $^3\Delta_3$ ground state, compared to our computed excitation energy of 1863 cm$^{-1}$ (0.231 eV) at the TD-B3LYP level and 2283 cm$^{-1}$ (0.283 eV) at the MRCI level (Table I). In a previous LIF study, a band system to the $^3\Delta$ state was observed, but its energy relative to the ground state was not observed and a computed value of 1500 cm$^{-1}$ was given instead. These relatively large discrepancies between the theoretical values and the experimental data are likely due to strong electron correlation effects in this system. Peak B is assigned to the transition to the $^3\Delta_3$ state. Its separation from peak X is 2900 cm$^{-1}$, slightly smaller than the computed value at the MRCI level (3428 cm$^{-1}$, Table I). The $\beta$ values for the X, A, and B peaks display similar trends as a function of electron kinetic energies (Fig. 3), in agreement with the fact that all three states are produced from electron detachment from the same MO. Apparently, the $^3\Delta_3$ state is too high in energy and not accessible in the current experiment. The remaining peaks are due to vibrational excitations and hot band transitions (Fig. 6).

A short vibrational progression was observed for each of the three final electronic states, as indicated by the vertical lines in Fig. 2(c) for the $^3\Delta_3$ state, Fig. 2(d) for the $^3\Delta$ state, and Fig. 2(f) for the $^3\Delta_2$ state. Because all three electronic states are originated from electron detachment from the slightly antibonding $3\sigma$ orbital, the measured vibrational frequencies for these states are similar and close to the computed frequency of 942 cm$^{-1}$ (Table I). Our measured vibrational frequency (925 cm$^{-1}$) for the $^3\Delta_2$ state of Ir$^{187}$Ir$^{11}$B is consistent with the previously reported value (909 cm$^{-1}$), considering the relatively large error bar in the current measurement. Several hot band transitions were observed, involving $v = 1$ and 2 of the anion and different final neutral states, as shown schematically in Fig. 6. The hot band transitions yielded an average experimental vibrational frequency for the anion as 844 cm$^{-1}$, in good agreement with the computed frequency of 882 cm$^{-1}$ (Table I). The smaller anion vibrational frequency in comparison with that of the neutral ground state is consistent with the antibonding nature of the $3\sigma$ orbital.

B. PtB$^-$

The calculated ADE for PtB$^-$ is 2.097 eV, which agrees well with the experimental value (2.153 eV), as shown in Table II. The observed vibrational progression yielded a vibrational frequency of 974 cm$^{-1}$ for the ground state of the $^{195}$Pt$^{10}$B isotopomer probed experimentally, in excellent agreement with the calculated frequency of 984 cm$^{-1}$ (Table II). The previous LIF experiment yielded a vibrational frequency of 903.6 cm$^{-1}$ for the $^{195}$Pt$^{11}$B isotopomer, in line with the expected isotope shift. Peak $h$/$h_1$ represents the transition from the first vibrational excited state of the anion to the neutral ground state, yielding an experimental frequency of 829 cm$^{-1}$ for the $^{195}$Pt$^{10}$B$^-$ anion, compared with the calculated vibrational frequency of 913 cm$^{-1}$ (Table II). The increase in the vibrational frequency upon photodetachment is consistent with the antibonding nature of the $3\sigma$ HOMO in PtB$^-$. The $\beta$ values for the X peak of PtB$^-$ are similar to those of the detachment features of IrB$^-$ (Fig. 3), confirming the fact that electron detachment takes place from the same orbital in the two systems.

C. AuB$^-$

The experimental ADE of 0.877 eV for AuB$^-$ is relatively low, in agreement with the computed value of 0.764 eV (Table II). The observed vibrational progression yielded a frequency of 704 cm$^{-1}$, agreeing well with the calculated frequency of 710 cm$^{-1}$. The poor signal-to-noise ratios of the PE spectrum prevented us from resolving any hot band transitions to yield an experimental vibrational frequency for the anion. The computed frequency of 614 cm$^{-1}$
for Au$^{10}\text{B}^-$ is significantly smaller than that for neutral Au$^{10}\text{B}$, consistent with the strong antibonding nature of the $2\pi$ LUMO of AuB.

### D. The bond dissociation energies of the MB$^-$ anions

In Table III, the experimental bond dissociation energies of the three MB molecules are compared with the calculated results. In the cases of IrB and AuB, the calculated $D_0$ values are in good agreement with the previous experimental data. However, the current level of theory seemed to have overestimated the $D_0$ value for PtB.

More interestingly, we can now obtain the experimental bond dissociation energies for IrB$^-$, PtB$^-$, and AuB$^-$ using our measured $\text{EA}$ values and the known $\text{EA}$s for the atoms and the $D_0$ of the neutral MB species. Because there are two possible dissociation limits, MB$^+$→ M$^+$ + B or M + B$^-$, two possible $D_0$(MB$^-$) values can be obtained using the following relationships:

$$D_0(\text{M}^+\text{B}^-) = \text{EA(}\text{MB}) + D_0(\text{MB}) - \text{EA(M)}$$

and

$$D_0(\text{M}^-\text{B}^-) = \text{EA(}\text{MB}) + D_0(\text{MB}) - \text{EA(B)}.$$  

The results are given in Table IV, in comparison with our calculated values. The theoretical data are in good agreement with the experimentally deduced values. Again we found that the $D_0$ values for the PtB$^-$ anions are slightly overestimated, similar to the case for the PtB neutral (Table III). It is interesting to note that the $D_0$(MB$^-$) values are all larger than the respective $D_0$(MB) values (Table III) because the $\text{EAs}$ of the atoms are all smaller than the $\text{EAs}$ of the MB molecules.

### VII. DISCUSSION: THE CHEMICAL BONDING IN DIATOMIC METAL BORIDES

The calculated bond lengths for the three MB diatomic boride molecules are remarkably short and are all shorter than the respective triple bond lengths based on Pytkko’s self-consistent triple-bond covalent radii, as shown in Table III. The calculated bond length for IrB (1.763 Å) agrees well with the experimental value (1.765 Å), whereas the experimental bond length of PtB (1.741 Å) is slightly shorter than the calculated value (1.755 Å). There is no experimental measurement for the bond length of AuB, but the calculated value should be reliable. The valence MO diagrams and occupancies of the three MB species are shown in Fig. 7, which is similar to that of RhB (Fig. 1). The 1σ MO is a bonding orbital between the M 5d$_\text{φ}$ and the B 2s atomic orbitals with small contributions from the B 2p$_\text{x}$ orbital (Table V). The 1τ MOs are bonding orbitals between the M 5d$_\text{ς}$ and the B 2p$_\text{σ}$ atomic orbitals. The 2σ MO is a bonding orbital between the M 5d$_\text{φ}$ and the B sp hybridized orbitals. The 16 MOs are of pure M 5d characters, while the 3σ MO is a weak antibonding orbital mainly between the M 6s and the B sp hybridized orbitals. While the major contribution to the 3σ MO is the M 6s orbital, there is a significant contribution from the M 6p$_\text{φ}$ orbital (Table V), which is out of phase with the B sp orbital for the weak antibonding interaction. Not shown is the 2π antibonding orbital, which is occupied by the extra electron in AuB$^-$ (Sec. V C). The detailed orbital compositions based on the closed shell species [IrB (1Σ$^+$), PtB$^-$ (1Σ$^-$), and AuB (1Σ$^+$)] are given in Table V.

#### A. IrB

Unlike the isoelectronic and quadruply bonded Rh$\equiv\text{B}$ (1Σ$^+$), IrB has a triplet ground state (1Δ) with the promotion of a 16 electron to the 3σ antibonding orbital (Fig. 7(a)), which weakens the quadruple bond. This difference in their electronic structure is due to the relativistic effects, as also reflected in the different atomic configurations of Rh and Ir: The Rh atom has a [Kr]4d$^5$5s$^1$ ground state configuration, while Ir has a [Xe]4f$^{14}$5d$^5$6s$^1$ configuration. The strong relativistic effects tend to stabilize the 6s orbital more than the 5d orbitals in Ir, hence also stabilizing the 3σ MO in IrB relative to that in RhB. The EA of IrB (1.995 eV) is much higher than that of RhB (0.961 eV), consistent with the stabilization of the 3σ MO in IrB. We computed the differences in orbital energies between the 3σ SOMO and the 16 HOMO for the 1Σ$^-$ state in Rh$\equiv\text{B}$ and Ir$\equiv\text{B}^-$. The SOMO–HOMO gap in Rh$\equiv\text{B}$ is 2.107 eV, while that in IrB is only 0.454 eV. This explains why in neutral IrB the 1Δ state is lower in energy than the 1Σ$^-$ state due to the small 16 to 3σ promotion energy.

Although not accessible from one-electron detachment from the 1Au$^2$ ground state of the anion, the 1Σ$^-$ state of IrB is calculated to be only 0.176 eV higher in energy than the 1Δ ground state. The 1Σ$^-$ excited state of IrB, in which the 16 HOMO is fully occupied like in Rh$\equiv\text{B}$, is calculated to have an extremely short bond length.

### Table III

<table>
<thead>
<tr>
<th>Species</th>
<th>$r_0$ (Å)</th>
<th>$r_{\text{MB}}$ (Å)</th>
<th>$D_0$ (Expt.)</th>
<th>$D_0$ (Theo.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IrB</td>
<td>1.763</td>
<td>1.775</td>
<td>4.928</td>
<td>5.085</td>
</tr>
<tr>
<td>PtB</td>
<td>1.80</td>
<td>1.83</td>
<td>5.235</td>
<td>5.668</td>
</tr>
<tr>
<td>AuB</td>
<td>1.906</td>
<td>1.96</td>
<td>3.812</td>
<td>3.734</td>
</tr>
</tbody>
</table>

*a* Experimental bond length 1.7675 Å from Ref. 13.

*b* Experimental bond length 1.741 Å from Ref. 30.

*c* From Ref. 50.

*d* From Ref. 25.

*e* From Ref. 6.

### Table IV

<table>
<thead>
<tr>
<th>Species</th>
<th>$D_0$(M$^-$B$^-$) (Expt.)</th>
<th>$D_0$(M$^-$B$^-$) (Theo.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir</td>
<td>5.359</td>
<td>5.759</td>
</tr>
<tr>
<td>Pt</td>
<td>5.539</td>
<td>5.698</td>
</tr>
<tr>
<td>Au</td>
<td>6.643</td>
<td>7.108</td>
</tr>
</tbody>
</table>

*e* The electron affinities for the atoms are from Ref. 62.
(1.722 Å) and a very high vibrational frequency (994 cm⁻¹), consistent with its true quadruple bond nature. Hence, the bond order of the 3Δ ground state of IrB can be considered to be three and half, consistent with the slightly smaller \(D_0\) value of IrB relative to that of the quadruply bonded Rh\(\equiv\)B. The bond order of IrB agrees well with the fact that its bond length is shorter than the triple bond length (Table III). It is interesting to note that the \(\sigma\) orbital compositions in IrB (Table V) are identical to those in RhB (Fig. 1), whereas the two \(\sigma\) orbitals in IrB are slightly more covalent than those in RhB. It is clear that the 1\(\sigma\) MO is a strong bonding orbital, not a B 2s lone pair, as generally assumed previously.

### B. PtB

The PtB molecule has one more electron than IrB with a configuration of 1\(\sigma^2\)1\(\pi^2\)2\(\sigma^2\)18\text{3zs}\text{3sz}\text{3zp} [Fig. 7(b)]. Because the 1\(\sigma\) MO is nonbonding, the bond order of PtB is the same as that of IrB. However, the \(D_0\) value of PtB (5.235 eV) is substantially larger than that of IrB (4.928 eV) and is close to that of the quadruply bonded Rh\(\equiv\)B (5.252 eV). The stronger bond in PtB is also reflected by its short bond length (Table III) and large vibrational frequency: 974 cm⁻¹ for PtB (1.722 Å) and a very high vibrational frequency (994 cm⁻¹) for IrB (1.931 Å). The increased EA of PtB (2.153 eV) relative to that of IrB (1.995 eV) is consistent with the increased stability of the 6s orbital in Pt compared to that in Ir.

### C. AuB

The AuB molecule has a closed-shell electronic structure with the antibonding 3\(\sigma\) orbital fully occupied [Fig. 7(c)]. The fully occupied 3\(\sigma\) antibonding orbital significantly weakens the bond in AuB, yielding an overall bond order of three. The bond dissociation energy of AuB (3.773 eV), measured from a previous Knudsen cell experiment,1 is smaller than that of PtB, but it is still quite substantial, in accord with the multiple bonding nature in AuB. In fact, our calculated AuB bond length (1.906 Å) is shorter than the triple bond length estimated from Pyykko’s self-consistent covalent radii for the AuB triple bond (1.96 Å), as shown in Table III. A previous calculation gave a \(D_0\) value of 3.52 eV and a bond length of 1.931 Å for AuB, mainly due to the strong relativistic effects of Au. The previous calculation showed that the relativistic effects increased the \(D_0\) of AuB from 1.26 eV (non-relativistic) to 3.52 eV and reduced its bond length from 2.256 Å to 1.931 Å. In the current study, we experimentally measured the vibrational frequency for Au\(\equiv\)B as

![Fig. 7. Schematics of the MO diagrams for the transition metal MB diatomics (left) and the MO occupations for (a) IrB, (b) PtB, and (c) AuB.](image)

### Table V: Valence Orbital Compositions for the Closed Shell IrB (3Σ\(^-\)), PtB\(^-\) (1Σ\(^+\)), and AuB (1Σ\(^+\)).

<table>
<thead>
<tr>
<th></th>
<th>3(\sigma)</th>
<th>1(\delta)</th>
<th>2(\sigma)</th>
<th>1(\pi)</th>
<th>1(\sigma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IrB</td>
<td>66%6s + 8%6p(_x)+13%2p(_x)+3%2s</td>
<td>100%5d(_x)+5d(_y)+5d(_z)</td>
<td>45%5d(_x)+39%2s + 12%2p(_y) + 16%2p(_z) + 50%2s + 4%2p(_x) + 37%5d(_x)+5%6s + 38%5d(_x)+2+8%6s + 45%2s + 4%2p(_x)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PtB(^-)</td>
<td>54%6s + 6%6p(_x)+24%2p(_x)+11%2s</td>
<td>100%5d(_x)+5d(_y)+5d(_z)</td>
<td>47%5d(_x)+2+10%6s + 31%2s + 10%2p(_z) + 11%2p(_y) + 38%5d(_x)+2+8%6s + 45%2s + 4%2p(_x)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AuB</td>
<td>49%6s + 2%6p(_x)+19%2p(_x)+29%2s</td>
<td>100%5d(_x)+5d(_y)+5d(_z)</td>
<td>48%5d(_x)+2+15%6s + 34%2s + 1%2p(_x) + 39%2s + 5%2p(_x)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


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observed for IrB (X species were measured for the first time. Three electronic states were
AuB. Vibrationally resolved photoelectron spectra were obtained for
VIII. CONCLUSION
We have used high resolution photoelectron imaging and theoretical
calculations to examine the nature of the chemical bonding in
three late 5d transition metal diatomic boride species, IrB, PtB, and
AuB. Vibrationally resolved photoelectron spectra were obtained for
the corresponding anions, and the electron affinities of the three
species were measured for the first time. Three electronic states were
observed for IrB (X 2Σ ̃, 1Σ ̃, and 3Σ ̃), whereas only the ground state
was observed for PtB (X 2Σ ̃) and AuB (X 1Σ ̃). Theoretical results
show that IrB, PtB, and AuB all have multiple bonding characters.
In the ground states of IrB and PtB, the antibonding 3σ orbitals
are singly occupied, resulting in an overall bond order between a
triple bond and a quadruple bond. The antibonding 3σ orbital is fully
occupied in AuB, giving rise to a weak triple bond. The current study
provides new insight into the nature of the strong bonding interac-
tions in diatomic species between the late 5d transition metals and
boron.

ACKNOWLEDGMENTS
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(Grant No. CHE-1763880). We would like to thank one of
the reviewers who made the suggestion to deduce the bond dissociation
energies for the anions.

DATA AVAILABILITY
The data that support the findings of this study are available
from the corresponding author upon reasonable request.

REFERENCES
S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, Revision C.1 (Gaussian, Inc., Wallingford, CT, 2009).


