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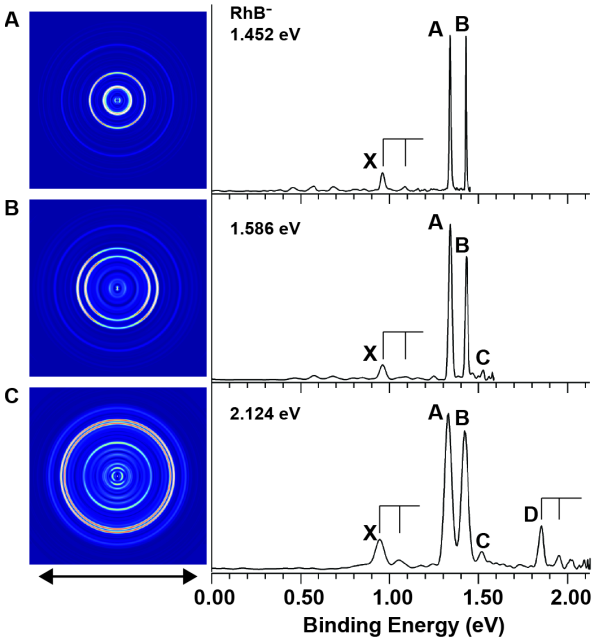
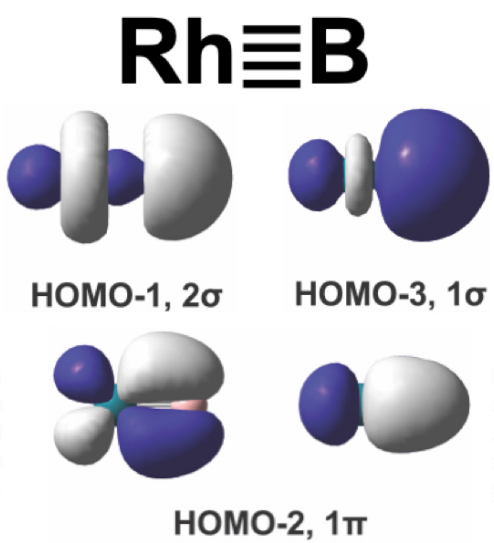
# Boron Makes Quadruple Bond with Rhodium




Photoelectron images and spectra of $RhB^-$ at three photon energies




The four bonding orbitals of RhB

Using photoelectron spectroscopy and computational chemistry, we studied the electronic structure and chemical bonding in $RhB_2O^-$ and $RhB^-$ and show that the boron atom engages in quadruple bonding with rhodium in $RhB(BO)^-$ and neutral RhB. The quadruple bonds consist of two $\pi$-bonds formed between the Rh $4d_{xy}/4d_{x^2-y^2}$ and B $2p_x/2p_y$ orbitals and two $\sigma$-bonds between the Rh $4d_{z^2}$ and B $2s/2p_z$ orbitals. To confirm the quadruple bond in RhB, we also investigated the linear Rh≡B-$H^+$ molecular ion and find a triple bond between Rh and B, which has a longer bond length, lower stretching frequency, and smaller bond dissociation energy in comparison with that of the Rh≡B quadruple bond in RhB.

Ever since Lewis' epochal work on the chemical bonds, the maximum bond order between two main-group atoms was known to be three. The maximum bond order between two metal atoms can be higher, known to be six between two group-VIB atoms ($Cr_2$, $Mo_2$, $W_2$) based on theoretical analyses. Recently the idea of quadruple bonding between two main-group atoms has been suggested in $C_2$ on the basis of high-level theoretical analyses. But this work ahs been controversial because this bond is weaker than the classical HC≡CH triple bond in terms of bond lengths and force constants. We provided both experimental and theoretical evidence that a quadruple bond exists in Rh≡B, and this result will change fundamentally how we understand and teach the concept of chemical bonding.

This work was done by four graduate students, partially supported by the NSF grant, one of the student (J. Czekner has received his PhD) and the leading author (Ling Fung Cheung) will receive his PhD in May 2020. The discovery was made serendipitously during our work on metal-doped boron clusters. The discovery was reported as a news story in the February 3, 2020 issue of the Chemical & Engineering News.

"Observation of Four-Fold Boron-Metal Bonds in $RhB(BO^-)$ and RhB" (L. F. Cheung, T. T. Chen, G. S. Kocheril, W. J. Chen, J. Czekner, and L. S. Wang), *J. Phys. Chem. Lett.* **11**, 659-663 (2020). DOI: 10.1021/acs.jpclett.9b03484.