

Electronic Supplementary Information

Observation of An Electron-Precise Metal Boryne Complex: $[\text{Bi}\equiv\text{BH}]^-$

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Table S1: The measured binding energies (BE) and assignments of the observed PES peaks of $\text{Bi}^{11}\text{BH}^-$. The energy shift (ΔE) relative to peak X, vibrational frequency of each electronic state and the β values are also given.

Peak	Assignment	BE (eV) ^a	ΔE (eV)	Frequency (cm^{-1}) ^a	β
X	$^2\Pi(3/2)$	1.988(1)	0		-0.8(2)
a	2_0^1	2.052(5)		540(40) ^b	0.1(1)
b	1_0^1	2.065(2)		613(8) ^c	-0.5(2)
c	2_0^2	2.122(2)			0.4(2)
d	1_0^2	2.140(2)			-0.5(2)
e	3_0^1	2.313(1)		2621(10)	-0.1(1)
A	$^2\Sigma^+(1/2)$	2.343(1)	0.355		0.6(2)
f	2_0^1	2.427(1)		675(8)	-0.2(2)
B	$^2\Pi(1/2)$	2.610(2)	0.622		-0.8(2)
g	1_0^1	2.681(6)		573(48)	-0.7(2)

^aThe numbers in the parentheses represent the uncertainty in the last digit.

^bThe bending frequency for Bi^{10}BH is measured to be 499(12) cm^{-1} .

^cThe Bi-B stretching frequency for Bi^{10}BH is measured to be 649(12) cm^{-1} .

Experimental methods. The experiments were performed using a high-resolution photoelectron imaging (PEI) apparatus newly equipped with a cryogenically-controlled 3D Paul trap.¹ The PEI system with the laser vaporization cluster source have been reported in detail previously.² Bismuth boride clusters were produced by laser vaporization of a disk target made by mixed powders of bismuth and boron and a He carrier gas. Both ¹¹B- and ¹⁰B-enriched boron targets were prepared and used in the current experiment. Clusters formed inside the nozzle were entrained by the carrier gas and underwent a supersonic expansion. After passing a skimmer, the cluster beams was sent directly into an in-line cryogenically-cooled 3D Paul trap, which was cooled by a two-stage closed-cycle helium refrigerator down to 4.2 K. The trapped anions were collisionally cooled by a mixed He/H₂ buffer gas (4:1 by volume) for 45 ms before being pulsed into the extraction region of a TOF mass spectrometer. The BiBH⁻ complex was produced by collisions between BiB⁻ produced from the laser vaporization source and H₂ in the buffer gas in the ion trap. The BiBH⁻ anion was intercepted by a detachment laser in the interaction zone of a velocity map imaging (VMI) system. Since BiBH⁻ and BiB⁻ have similar masses and cannot be selected by the mass gate, the mass selection was done by directly tuning the timing of the detachment laser to match with the ion arrival time in the interaction zone of the VMI lens system. Photodetachment was performed using a YAG-pumped dye laser, as well as the second (532 nm) and third harmonic (355 nm) output from a Nd:YAG laser. Photoelectrons were then focused onto a set of microchannel plates coupled with a phosphor screen and a charge-coupled-device camera. A typical experiment required about 100,000–300,000 laser shots to achieve reasonable signal-to-noise ratios. The VMI lens was calibrated using the PE images of Au⁻ and Bi⁻ at various photon energies. The PE images were analyzed by the maximum entropy method (MEVELER).³ The resolution of our VMI system was ~0.6 % for high kinetic energy electrons and as low as 1.2 cm⁻¹ for very slow electrons.²

Photoelectron angular distributions (PADs) were obtained from the PE images, which were characterized by the anisotropy parameter (β).⁴ The differential cross section of the photoelectrons can be expressed as

$$d\sigma / d\Omega = \sigma_{\text{Tot}}/4\pi [1 + \beta P_2(\cos\theta)] \quad (1)$$

where σ_{Tot} is the total cross section, P_2 is the second-order Legendre polynomial, and θ is the angle of the photoelectron relative to the laser polarization. Herein, the PADs can be described by

$$I(\theta) \sim [1 + \beta P_2(\cos\theta)], \quad (2)$$

where β has a value ranging from -1 to 2 .⁴ This model works well for single photon detachment transitions from randomly oriented molecules. Since photons carry one unit of angular momentum and angular momentum is conserved, the angular momentum change of the outgoing photoelectrons will be $l = \pm 1$, i.e., if an electron is detached from an s atomic orbital ($l = 0$), the outgoing photoelectron will have $l = 1$ (a p -wave) with $\beta = 2$. It is non-trivial to interpret the β value for ionization from a molecular orbital (MO) since MOs are linear combinations of atomic orbitals.⁵ Nevertheless, the β value is useful to qualitatively assess the symmetries of the molecular orbitals involved in the photodetachment process and is valuable for spectral assignment.

Estimation of the Bi 6p contribution to the π orbital in BiBH using the measured spin-orbit splitting.⁶

The spin-orbit energy of a $2^{S+1}\Lambda_{\Omega}$ state is given by

$$E^{\text{SO}} = A\Lambda\Sigma$$

where $\Omega = \Lambda + \Sigma$. Thus, the spin-orbit energies of $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ are $A(1)(1/2) = 1/2 A$ and $A(1)(-1/2) = -1/2 A$, respectively.

The spin-orbit splitting is $E(^2\Pi_{1/2}) - E(^2\Pi_{3/2}) = -\frac{1}{2} A - \frac{1}{2} A = -A$. For a π^3 configuration,

$$A = -a_\pi$$

where a_π is the spin-orbit parameter for the π orbital. Thus, the spin-orbit splitting equals to a_π .

The π orbital that can be written as

$$|\pi\rangle = C_{\text{Bi}}|p\pi_{6p}\rangle + C_{\text{B}}|p\pi_{2p}\rangle$$

and

$$a_\pi = \langle \pi | H^{\text{SO}} | \pi \rangle = C_{\text{Bi}}^2 \zeta_{\text{Bi}}(6p) + C_{\text{B}}^2 \zeta_{\text{B}}(2p)$$

where $\zeta_{\text{Bi}}(6p)$ and $\zeta_{\text{B}}(2p)$ are the atomic spin-orbit parameters. In Table 5.6 of ref 6, we find that $\zeta_{\text{Bi}}(6p) = 10,100 \text{ cm}^{-1}$ and $\zeta_{\text{B}}(2p) = 10.7 \text{ cm}^{-1}$. Clearly, the contribution from boron is negligible and can be ignore. This gives

$$a_\pi = 10100 * C_{\text{Bi}}^2$$

Our measured splitting is $0.622 \text{ eV} = 5017 \text{ cm}^{-1}$. So $a_\pi = 10100 * C_{\text{Bi}}^2 = 5017$ or C_{Bi}^2 is about 0.5 or 50%.

The result of this spin-orbit analysis is that the π orbital of BiBH is composed of approximately 50% Bi $6p\pi$ character. The remaining character must be B $2p\pi$ character. We have calculated the atomic contribution to each MO. Bi $6p$ orbital contributes about 60% to the π bond, which qualitatively agrees with the estimation using the measured spin-orbit splitting in BiBH.

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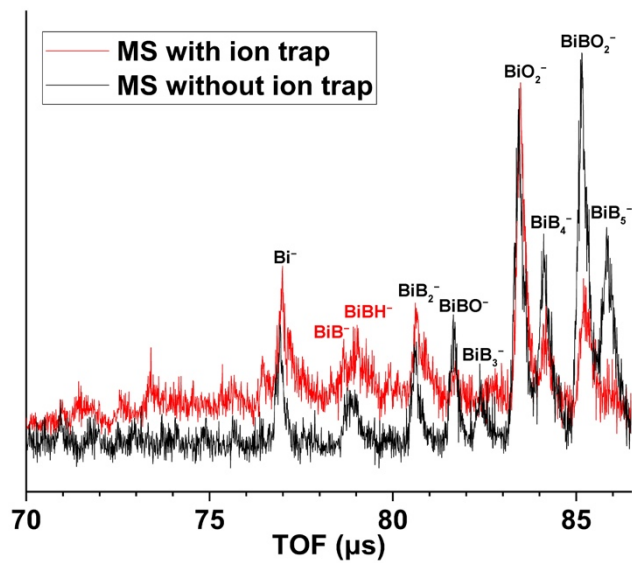


Figure S1. Mass spectrum of BiB_x^- clusters from laser vaporization of a $\text{Bi}/^{10}\text{B}$ target with and without ion trapping. The black curve is the mass spectrum taken without ion trapping; the red curve is the mass spectrum taken after ion trapping.

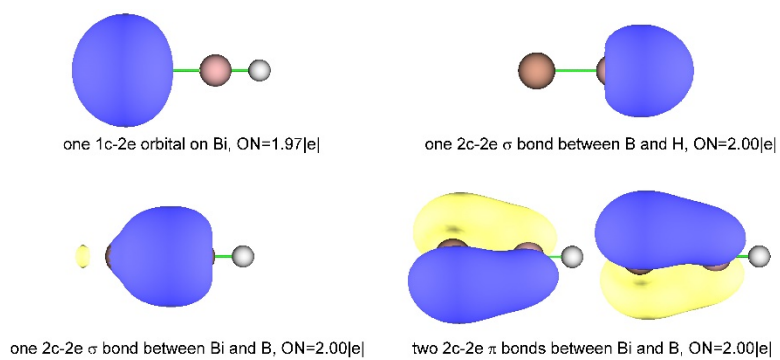


Figure S2. AdNDP analysis for the chemical bonding in BiBH^- .