SUPPLEMENTARY INFORMATION

A Photoelectron Spectroscopy and Quantum Chemical Study on Ternary Al-B-O Clusters: $Al_nBO_2^-$ and Al_nBO_2 (n = 2, 3)†

Ting Ou,[a] Yuan Feng,[b] Wen-Juan Tian,[a] Li-Juan Zhao,[b] Xiang-Yu Kong,[b]
Hong-Guang Xu,[b] Wei-Jun Zheng*[bc] and Hua-Jin Zhai*[a]

[a] *Nanocluster Laboratory, Institute of Molecular Science, Shanxi University, Taiyuan 030006, China*

[b] *Beijing National Laboratory for Molecular Sciences (BNLMS), State Key Laboratory of Molecular Reaction Dynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China*

[c] *University of Chinese Academy of Sciences, Beijing 100049, China*

*E-mail: zhengwj@iccas.ac.cn; hj.zhai@sxu.edu.cn

Figure S1. Alternative optimized isomeric structures of $Al_2BO_2^-$ anion cluster at the B3LYP/6-311+G(d) level. Relative energies (in kcal mol^{-1}) are indicated at the B3LYP and single-point CCSD(T) (in *italic*) levels. The B atom is shown in blue, Al in pink, and O in red.

Figure S2. Alternative optimized isomeric structures of Al_2BO_2 neutral cluster at the B3LYP/6-311+G(d) level. Relative energies (in kcal mol^{-1}) are indicated at the B3LYP and single-point CCSD(T) (in *italic*) levels. The B atom is shown in blue, Al in pink, and O in red.

Figure S3. Alternative optimized isomeric structures of $Al_3BO_2^-$ anion cluster at the B3LYP/6-311+G(d) level. Relative energies (in kcal mol^{-1}) are indicated at the

B3LYP and single-point CCSD(T) (in *italic*) levels. The B atom is shown in blue, Al in pink, and O in red.

Figure S4. Alternative optimized isomeric structures of Al_3BO_2 neutral cluster at the B3LYP/6-311+G(d) level. Relative energies (in kcal mol^{-1}) are indicated at the B3LYP and single-point CCSD(T) (in *italic*) levels. The B atom is shown in blue, Al in pink, and O in red.

Figure S5. Simulated photoelectron spectra of $Al_3BO_2^-$ cluster on the bases of isomers (b) **3b** (C_s, $^2A''$) and (c) **3c** (C_s, $^2A'$), as compared to experimental data at (a) 266 nm (4.661 eV). The simulations were done at the time-dependent B3LYP/6-311+G(d) (TD-B3LYP) level, by fitting calculated VDEs with unit-area Gaussian functions of 0.04 eV half-width.

Figure S6. Chemical bonding in $Al_2BO_2^-$ **2a** cluster. (a) AdNDP bonding pattern. Occupation numbers (ONs) are shown. (b) Canonical molecular orbitals (CMOs).

Figure S7. Chemical bonding in $Al_2BO_2^-$ **2b** cluster. (a) AdNDP bonding pattern. ONs are shown. (b) CMOs.

Figure S8. Chemical bonding in $Al_3BO_2^-$ **3a** cluster. (a) AdNDP bonding pattern; one extra electron is added in the analysis because the current version of AdNDP program applies for closed-shell species only. ONs are shown. (b) CMOs. SOMO stands for the singly occupied molecular orbital.

Figure S9. Chemical bonding in $Al_3BO_2^-$ **3d** cluster. (a) AdNDP bonding pattern; one extra electron is added in the analysis because the current version of AdNDP program applies for closed-shell species only. ONs are shown. (b) CMOs. SOMO stands for the singly occupied molecular orbital.

Figure S1. Alternative optimized isomeric structures of $Al_2BO_2^-$ anion cluster at the B3LYP/6-311+G(d) level. Relative energies (in kcal mol^{-1}) are indicated at the B3LYP and single-point CCSD(T) (in *italic*) levels. The B atom is shown in blue, Al in pink, and O in red.

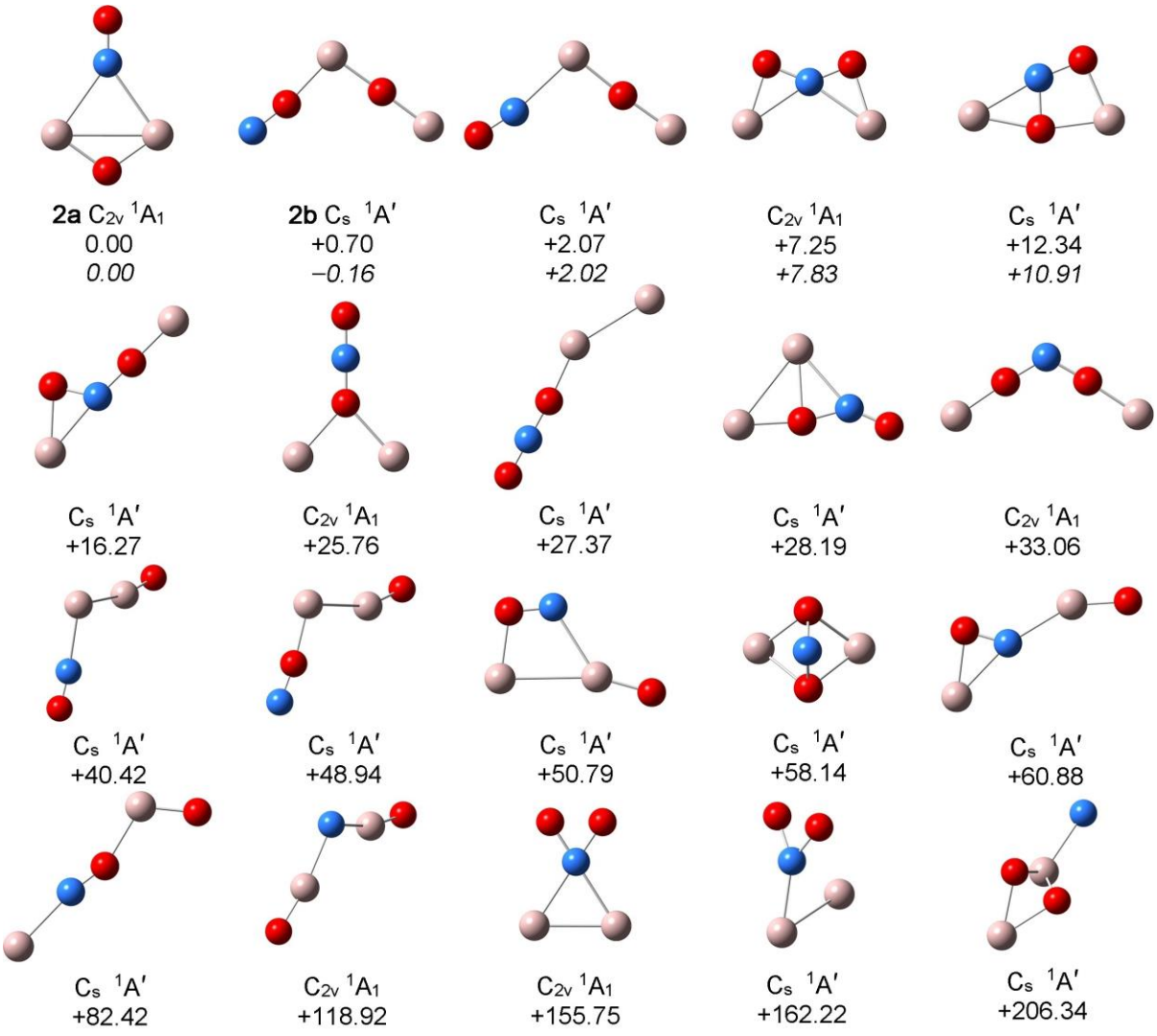

Figure S2. Alternative optimized isomeric structures of Al_2BO_2 neutral cluster at the B3LYP/6-311+G(d) level. Relative energies (in kcal mol^{-1}) are indicated at the B3LYP and single-point CCSD(T) (in *italic*) levels. The B atom is shown in blue, Al in pink, and O in red.

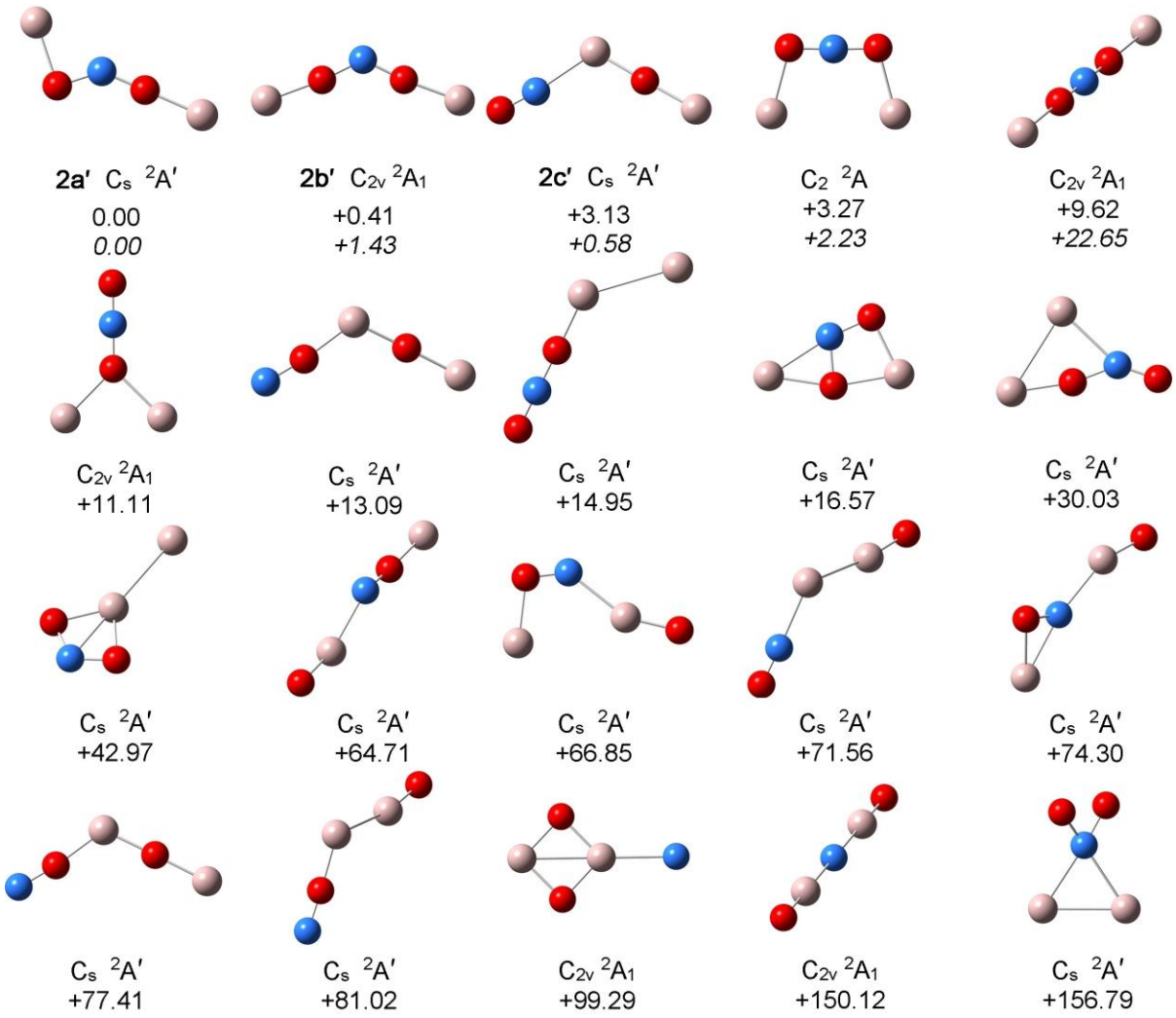

Figure S3. Alternative optimized isomeric structures of $Al_3BO_2^-$ anion cluster at the B3LYP/6-311+G(d) level. Relative energies (in kcal mol^{-1}) are indicated at the B3LYP and single-point CCSD(T) (in *italic*) levels. The B atom is shown in blue, Al in pink, and O in red.

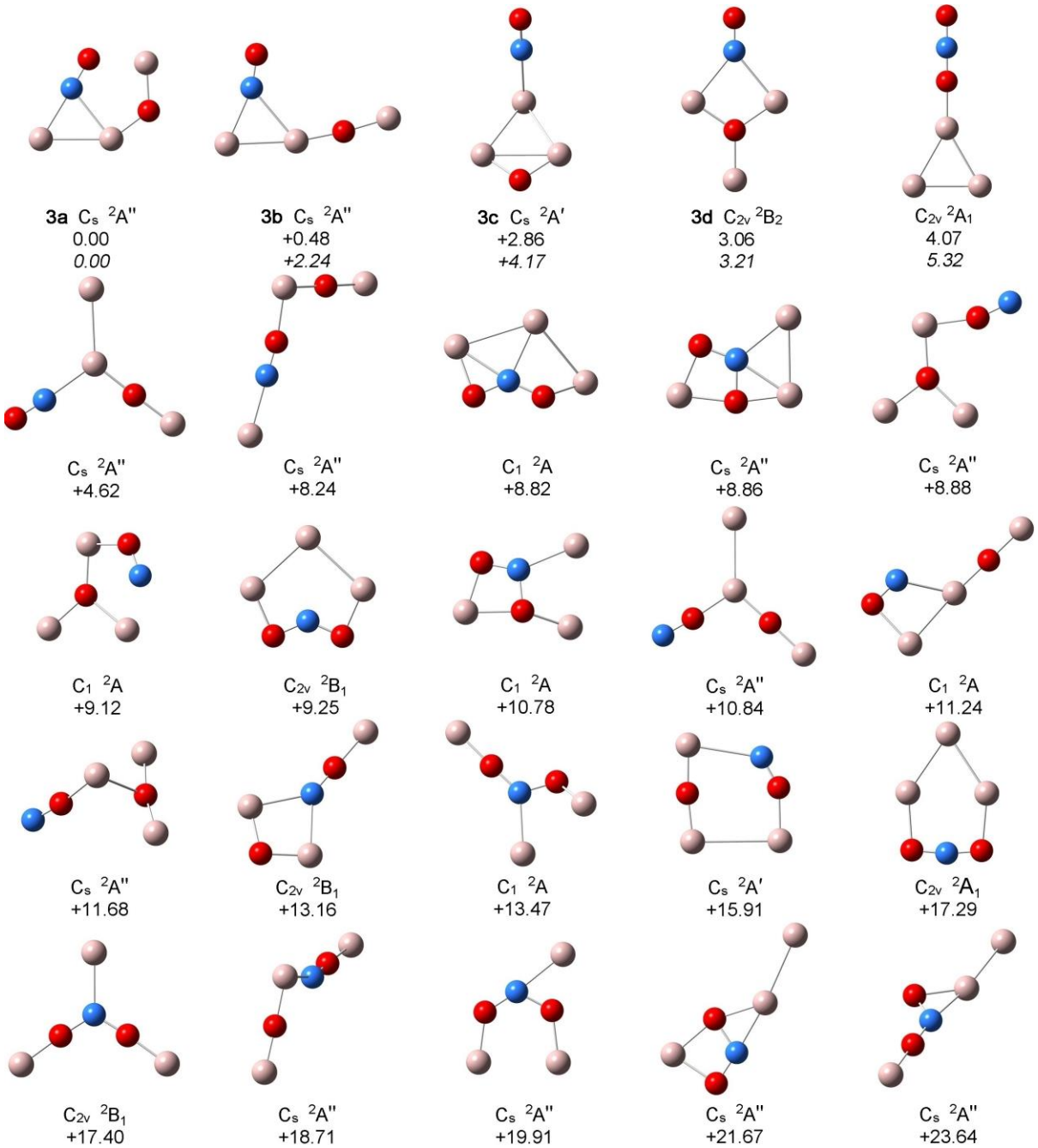

Figure S4. Alternative optimized isomeric structures of Al_3BO_2 neutral cluster at the B3LYP/6-311+G(d) level. Relative energies (in kcal mol^{-1}) are indicated at the B3LYP and single-point CCSD(T) (in *italic*) levels. The B atom is shown in blue, Al in pink, and O in red.

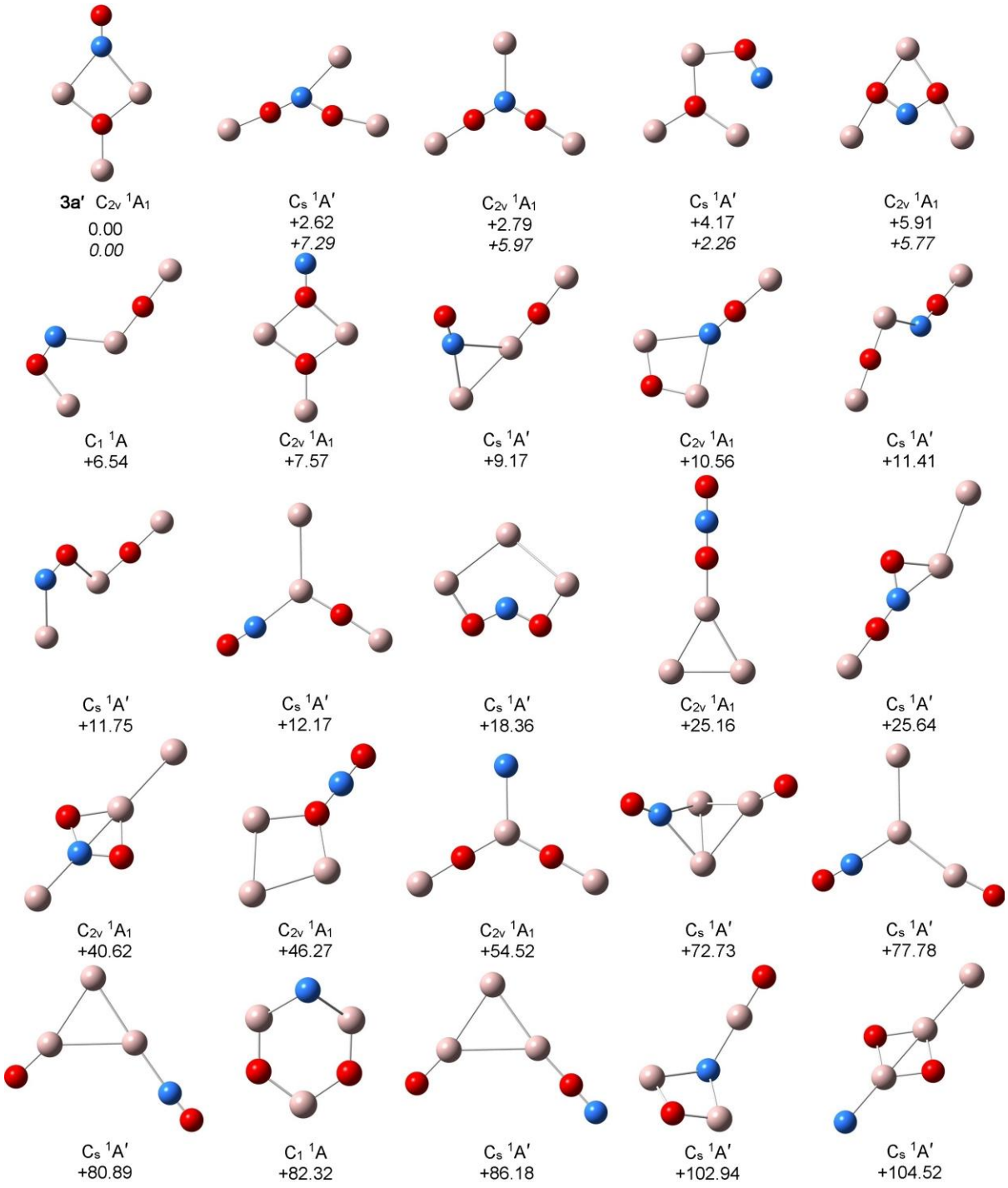

Figure S5. Simulated photoelectron spectra of $Al_3BO_2^-$ cluster on the bases of isomers (b) **3b** (C_s, $^2A''$) and (c) **3c** (C_s, $^2A'$), as compared to experimental data at (a) 266 nm (4.661 eV). The simulations were done at the time-dependent B3LYP/6-311+G(d) (TD-B3LYP) level, by fitting calculated VDEs with unit-area Gaussian functions of 0.04 eV half-width.

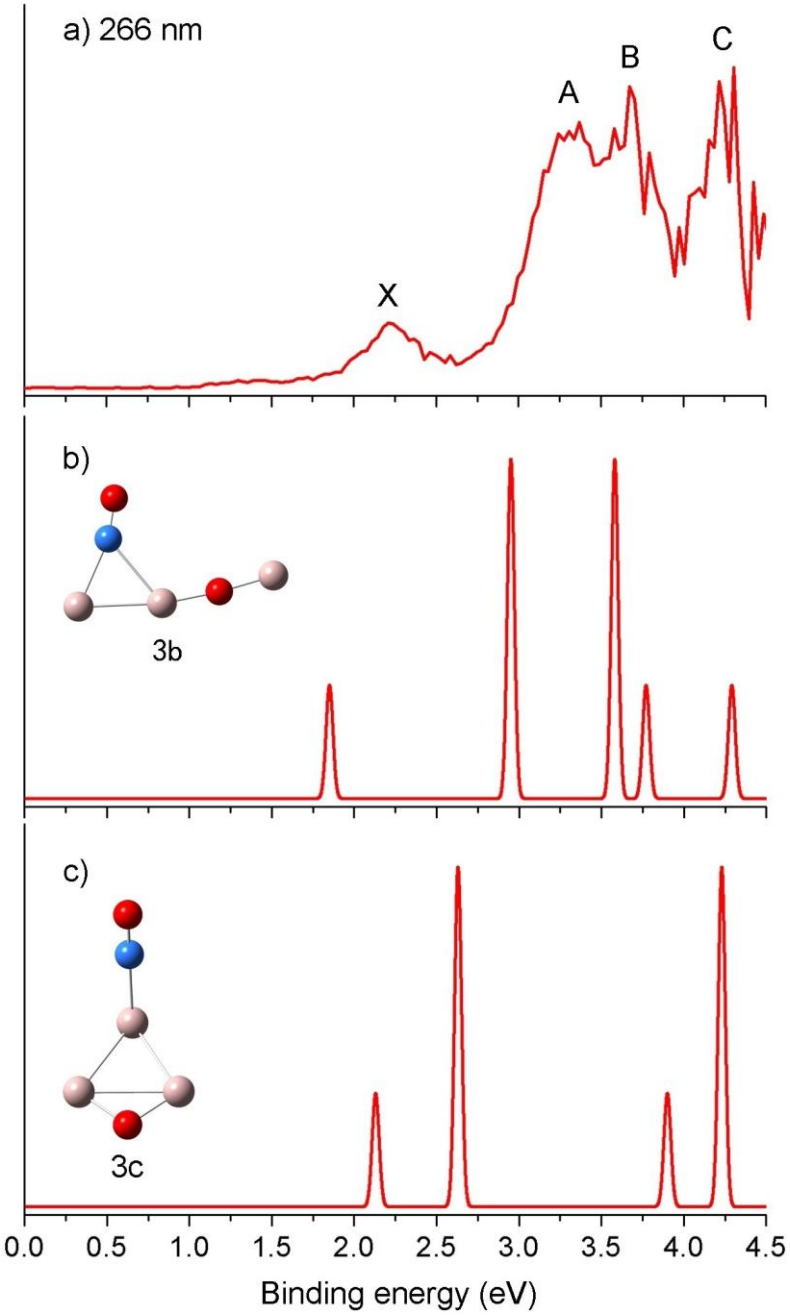

Figure S6. Chemical bonding in $Al_2BO_2^-$ **2a** cluster. (a) AdNDP bonding pattern. Occupation numbers (ONs) are shown. (b) Canonical molecular orbitals (CMOs).

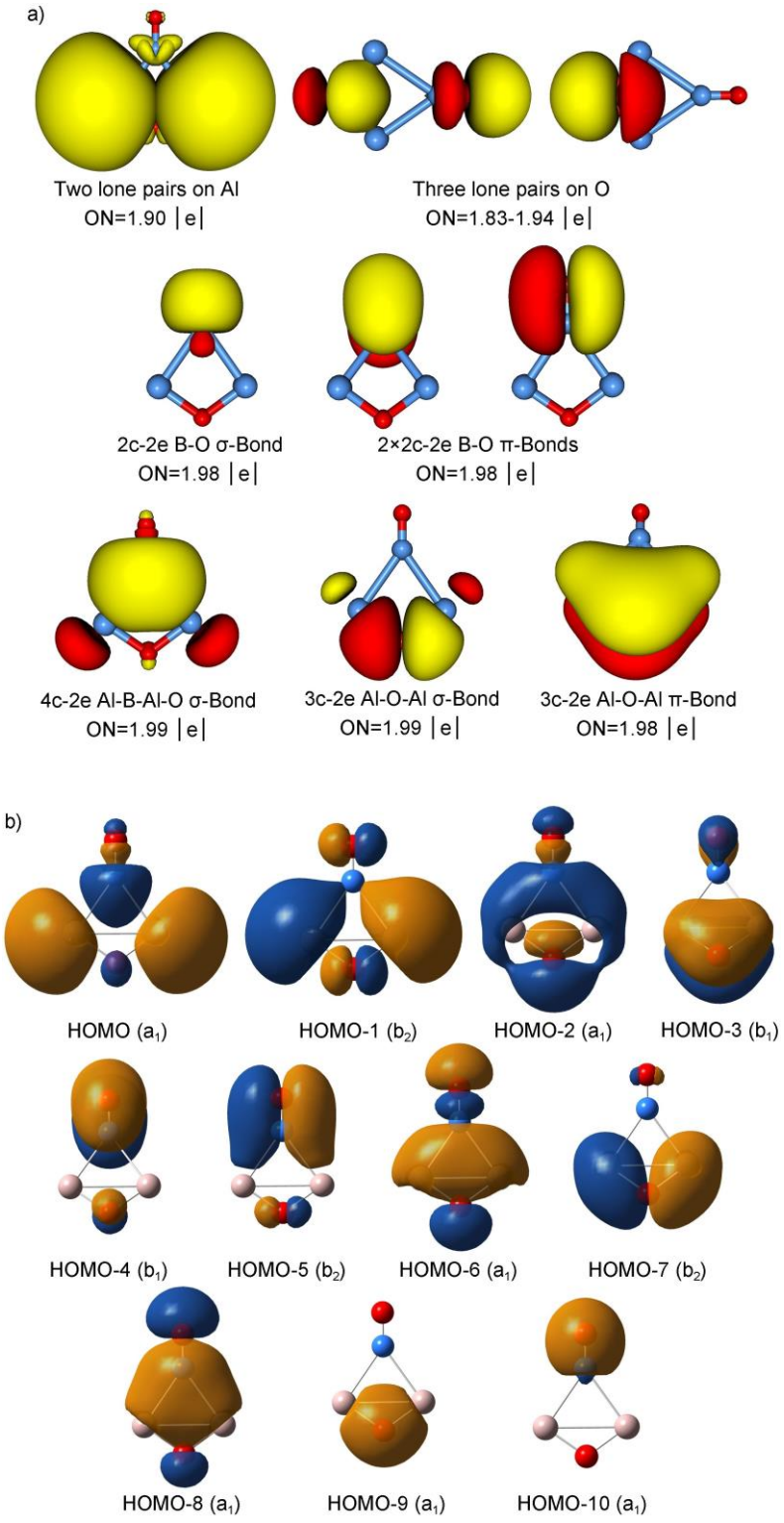

Figure S7. Chemical bonding in $Al_2BO_2^-$ **2b** cluster. (a) AdNDP bonding pattern. ONs are shown. (b) CMOs.

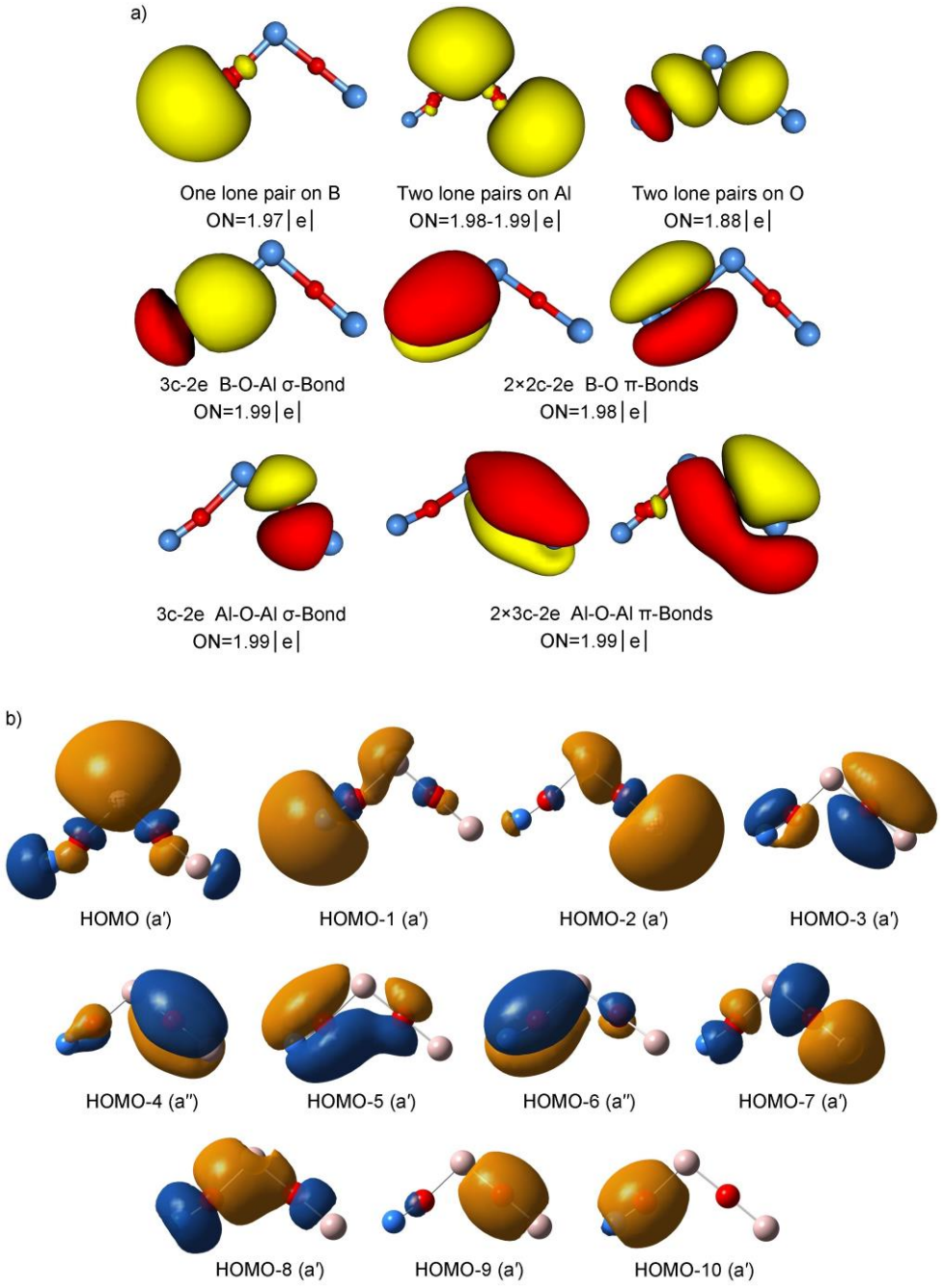

Figure S8. Chemical bonding in $Al_3BO_2^-$ **3a** cluster. (a) AdNDP bonding pattern; one extra electron is added in the analysis because the current version of AdNDP program applies for closed-shell species only. ONs are shown. (b) CMOs. SOMO stands for the singly occupied molecular orbital.

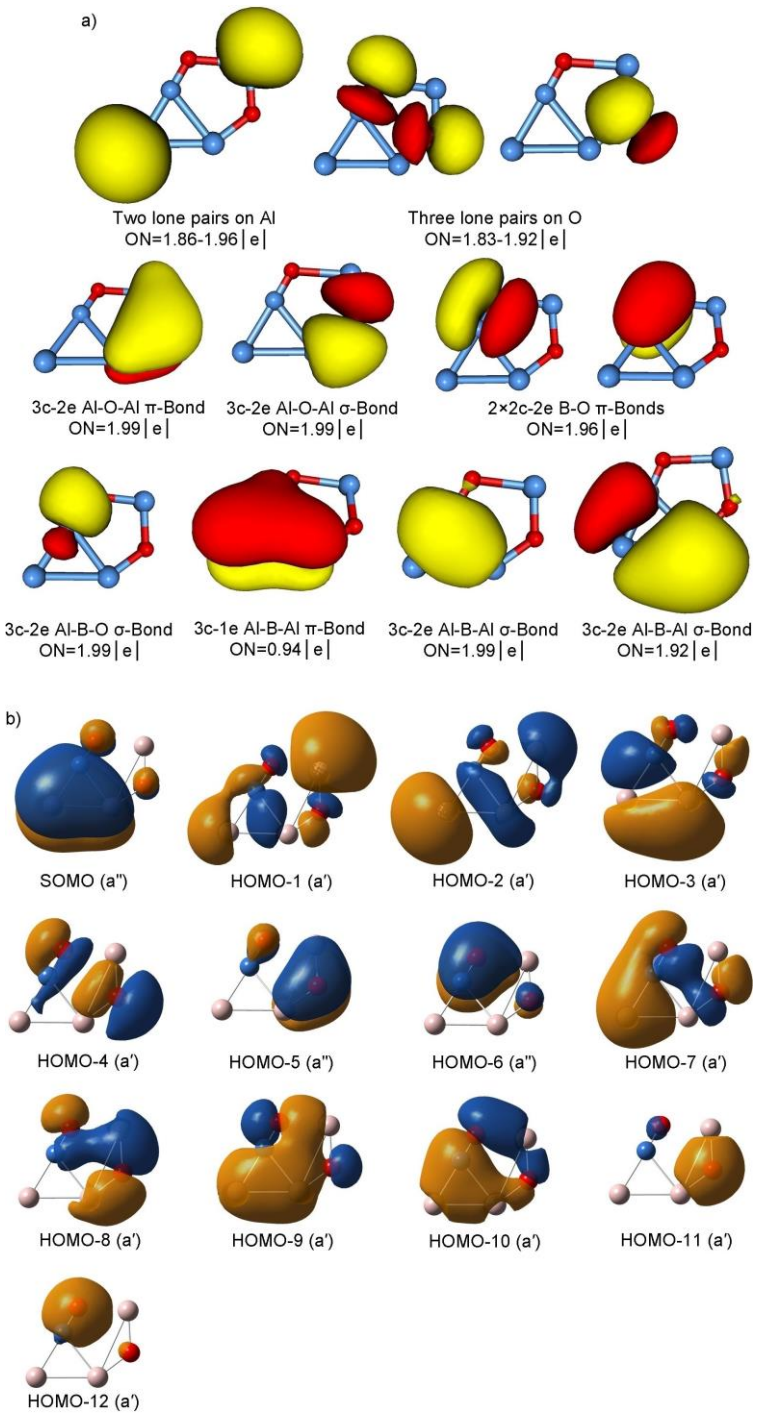

Figure S9. Chemical bonding in $Al_3BO_2^-$ **3d** cluster. (a) AdNDP bonding pattern; one extra electron is added in the analysis because the current version of AdNDP program applies for closed-shell species only. ONs are shown. (b) CMOs. SOMO stands for the singly occupied molecular orbital.