

Spectral Signatures of Neutral Boron Oxide Clusters Containing Key Structural Units of the Vitreous State

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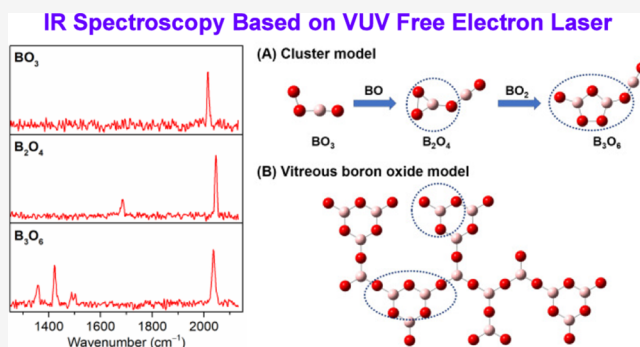
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ABSTRACT: Spectroscopic characterization of neutral boron oxide clusters is insightful for understanding the structures and properties of the bulk but has proven to be extremely challenging due to the difficulty in size selection. Here, we report a size-specific infrared spectroscopy study of a series of neutral boron oxide clusters using near-threshold photoionization with a tunable vacuum ultraviolet free electron laser. Quantum chemical calculations were carried out to understand the structures and bonding of the clusters and to help assign the experimental spectral features. The BO_3 , B_2O_4 , and B_3O_6 clusters focused in this study are found to have planar structures with BO , BO_3 , and B_2O_5 groups, which are key structural units in the two-dimensional network of the vitreous state. Chemical bonding analyses revealed structural stability arising from the synergy among the terminal $\text{B}\equiv\text{O}$ groups and $\text{B}-\text{O}$ σ bonds. This work provides spectral signatures for the key structural units of the bulk and paves the way for systematic studies on the stepwise formation and growth mechanisms of boron oxide materials.



1. INTRODUCTION

Boron oxide (B_2O_3) is widely used in many fields, such as glasses, optical materials, and highly energetic propellants.^{1–3} Bulk B_2O_3 exists in a vitreous state at ambient pressure and could crystallize under high pressure.¹ The vitreous B_2O_3 model was proposed to have a two-dimensional (2D) network of the boroxol $[\text{B}_3\text{O}_3\text{O}_3]$ groups connected by the BO_3 triangles, where O denotes the bridging oxygen atoms linking two structural units.^{4–7} It is generally accepted that the relative abundance ratio between BO_3 and $\text{B}_3\text{O}_3\text{O}_3$ structural units in glasses is roughly 1:1.⁶ Very recently, the $\text{B}_3\text{O}_3\text{O}_3$ structural units have been characterized in a 2D B_2O_3 crystalline polymorph on a Pt(111) substrate.⁸ However, the formation and growth mechanism of the 2D B_2O_3 network remains elusive. Spectroscopic studies of boron oxide clusters can provide important insights into structural evolution and chemical bonding that are relevant to the bulk.

Extensive efforts have been devoted to the spectroscopic investigation of ionic boron oxide clusters,^{9–20} for which size selection and detection are straightforward. Mass spectrometry combined with collision-induced dissociation displayed two series of boron oxide cluster cations with the formulas of $(\text{B}_2\text{O}_3)_n\text{BO}^+$ ($n = 0–6$) and $(\text{B}_2\text{O}_3)_n^+$ ($n = 0–5$), which were suggested to have the integral BO_3 triangles with branches terminated by BO groups.⁹ The combined studies of photoelectron spectroscopy (PES) and quantum chemical

calculations have provided significant information about the structures and bonding of boron oxide cluster anions.^{10–18} In particular, B_3O_2^- and B_4O_3^- were found to have a linear $\text{B}(\text{BO})_2^-$ and triangular $\text{B}(\text{BO})_3^-$ structure containing the key boronyl (BO) structural unit,¹⁰ which has stimulated the discovery of various boron boronyl complexes, boronyl boroxine, carbon boronyl clusters, and transition metal boronyl clusters.¹⁸ The diboronyl diborene $\text{B}_4\text{O}_2^{2-}$ has a highly stable global-minimum linear structure with a $\text{B}\equiv\text{B}$ triple bond ($[\text{O}\equiv\text{B}-\text{B}\equiv\text{B}-\text{B}\equiv\text{O}]^{2-}$), suggesting its viability as a building block in the condensed phase.¹²

In contrast with charged boron oxide clusters, investigation of neutral boron oxide clusters has proven to be extremely challenging due to the difficulty in size selection. Matrix-isolation infrared (IR) spectroscopy and electron-spin resonance have identified the BO , BO_2 , B_2O_2 , and B_2O_3 species.^{21–23} Despite the scarcity of experimental studies, many theoretical calculations have been devoted to neutral B_xO_y clusters.^{24–33} Here we report the first size-specific IR

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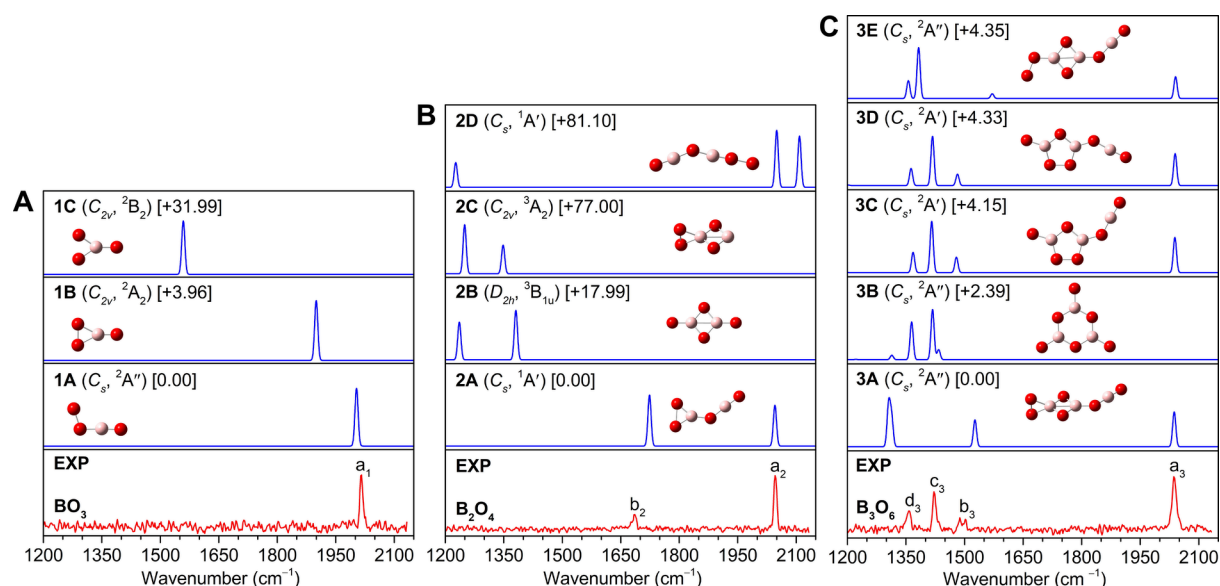


Figure 1. Comparison of experimental and theoretical IR spectra of neutral boron oxide clusters for (A) BO_3 , (B) B_2O_4 , and (C) B_3O_6 . The calculations were performed at the MN15L/cc-pVTZ level of theory, with the harmonic frequencies scaled by 0.961.³⁷ The symmetries and electronic states are indicated in the parentheses. The CCSD(T)/cc-pVTZ//MN15L/cc-pVTZ relative energies (in kcal/mol) are given in the brackets. The structures of the isomers are displayed in the inset (O – red; B – pink).

Table 1. Comparison of the Experimental Band Positions (cm^{-1}) of Neutral BO_3 , B_2O_4 , and B_3O_6 Clusters to the Theoretical Values of Isomers 1A, 2A, 3C, and 3D Calculated at the MN15L/cc-pVTZ Level of Theory^a

cluster	label	exptl.	calcd	assignment
BO_3	a_1	2016	Isomer 1A 2003 [260, ν_1 (a')]	B–O stretching mode of terminal BO
			Isomer 2A 2045 [579, ν_1 (a')]	B–O stretching mode of terminal BO
B_2O_4	a_2	2046	2045 [579, ν_1 (a')]	B–O stretching mode of terminal BO
	b_2	1687	1724 [724, ν_2 (a')]	Symmetric B–O stretching mode of the BO_3 unit
B_3O_6	a_3	2036	Isomer 3C 2039 [631, ν_1 (a')]	B–O stretching mode of terminal BO
			Isomer 3D 2039 [655, ν_1 (a')]	B–O stretching mode of terminal BO
			1479 [277, ν_2 (a')]	Symmetric B–O stretching mode of the BO_3 unit
			1482 [233, ν_2 (a')]	Symmetric B–O stretching mode of the BO_3 unit
B_3O_6	b_3	1502, 1489	1479 [277, ν_2 (a')]	Symmetric B–O stretching mode of the BO_3 unit
	c_3	1422	1416 [922, ν_3 (a')]	Antisymmetric B–O stretching mode of the BO_3 unit
	d_3	1358	1368 [363, ν_4 (a')]	Antisymmetric B–O stretching mode of the BO_3 unit

^aThe IR intensities (in km/mol) and modes (symmetries) are given in the brackets, and the harmonic frequencies are scaled by a factor of 0.961.³⁷

spectroscopic study of three neutral boron oxide clusters, BO_3 , B_2O_4 , and B_3O_6 , using near-threshold photoionization with a tunable vacuum ultraviolet free electron laser (VUV-FEL). These clusters are found to have planar structures containing the key structural units of BO, BO_3 , and B_2O_5 that are also found in the vitreous state.

2. RESULTS AND DISCUSSION

2.1. Spectral and Structural Assignment

The measurements of IR spectra of neutral boron oxide clusters (BO_3 , B_2O_4 , and B_3O_6) were carried out by using a VUV-FEL-based cluster spectroscopy apparatus (see [Supporting Information](#) for experimental details).³⁴ The boron oxide clusters were generated via laser vaporization of a ^{11}B -enriched target in a pulsed supersonic expansion of a $2\%\text{O}_2 + 5\%\text{Ar/He}$ mixture. Neutral boron oxide clusters were vibrationally excited with a tunable IR laser generated by the LaserVision system and subsequently photoionized after a ~ 50 ns delay by a VUV-FEL. The saturation of vibrational excitation and photoionization was prevented via careful study of IR and VUV-FEL power dependence. The IR spectra were recorded in

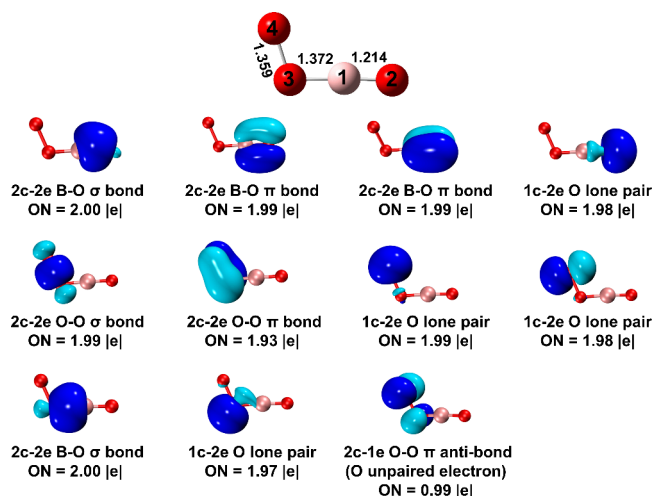


Figure 2. AdNDP bonding analysis for isomer 1A of BO_3 calculated at the PBE0/def2-SVP level of theory (O – red; B – pink). ON stands for the occupation number. The isovalue is set to 0.05. The bond distances (in Å) and atom labels are indicated.

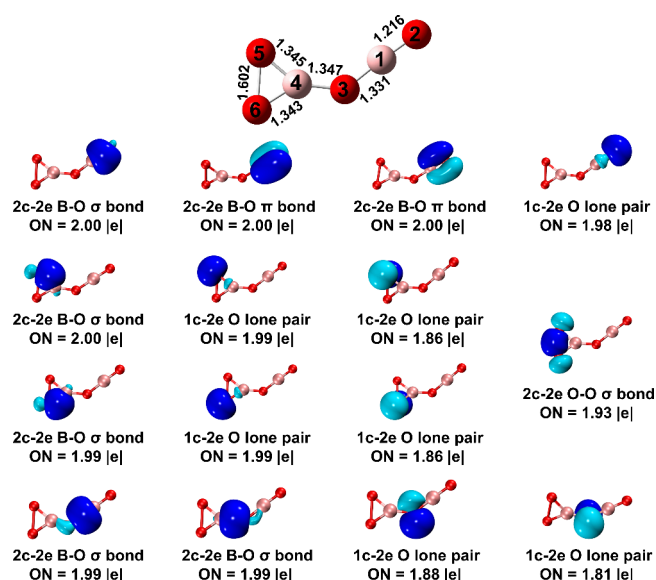


Figure 3. AdNDP bonding analysis for isomer 2A of B_2O_4 calculated at the PBE0/def2-SVP level of theory (O – red; B – pink). ON stands for the occupation number. The isovalue is set to 0.05. The bond distances (in Å) and atom labels are indicated.

the difference mode of operation (IR laser ON minus IR laser OFF) and were normalized with the IR power.

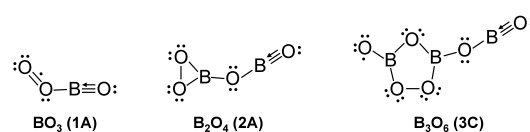
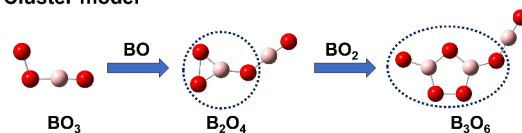


Figure 5. Lewis bonding structures of neutral BO_3 (isomer 1A), B_2O_4 (isomer 2A), and B_3O_6 (isomer 3C) clusters.

(A) Cluster model



(B) Vitreous boron oxide model

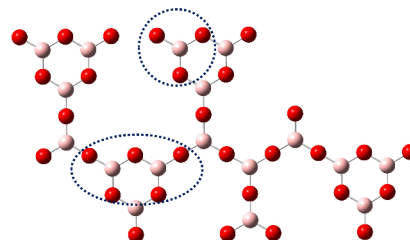


Figure 6. (A) Structural evolution of neutral BO_3 (isomer 1A), B_2O_4 (isomer 2A), and B_3O_6 (isomer 3C) clusters (O – red; B – pink). (B) Vitreous boron oxide model. The integral BO_3 and B_2O_5 units are circled with dash lines.

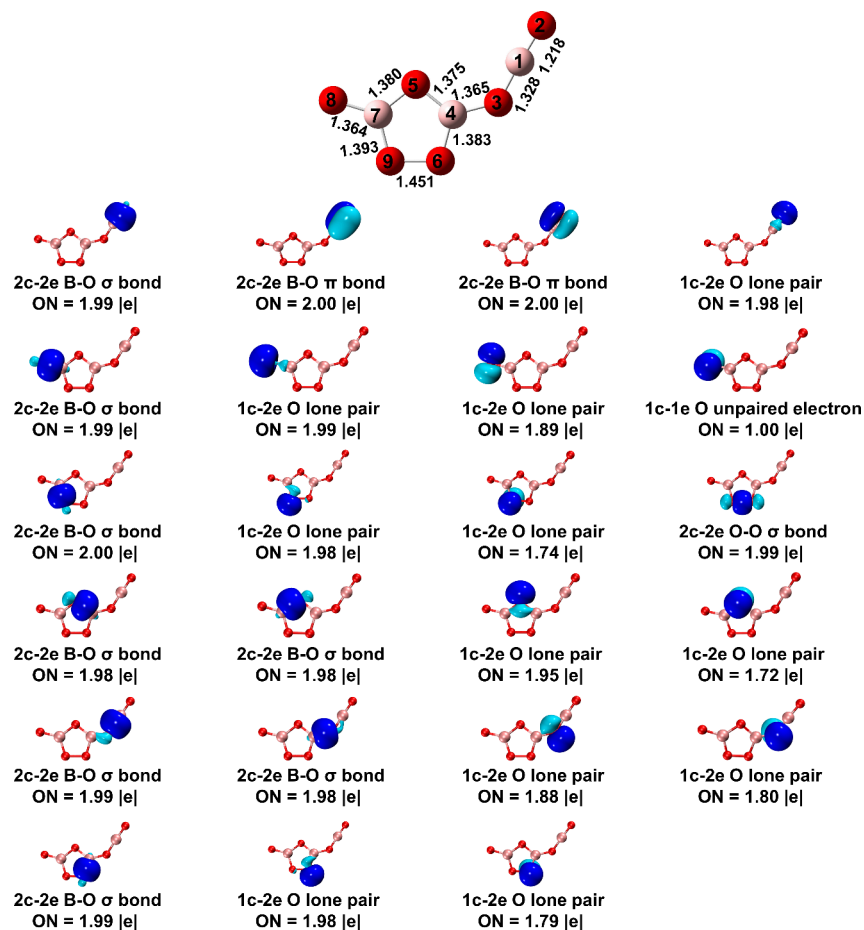


Figure 4. AdNDP bonding analysis for isomer 3C of B_3O_6 calculated at the PBE0/def2-SVP level of theory (O – red; B – pink). ON stands for the occupation number. The isovalue is set to 0.05. The bond distances (in Å) and atom labels are indicated.

For the BO_3 , B_2O_4 , and B_3O_6 clusters, global minimum-energy structure searches were performed by using the Molclus program.³⁵ Geometry optimizations and frequency calculations of the low-lying candidate structures were carried out at the MN15L/cc-pVTZ level of theory by using the Gaussian 16 package.³⁶ The possible electronic states of the BO_3 , B_2O_4 , and B_3O_6 clusters have been calculated. The electronic energies were further refined by single-point calculations at the CCSD(T)/cc-pVTZ level of theory by using the MN15L/cc-pVTZ optimized geometries. The isomers were sorted by the CCSD(T)/cc-pVTZ//MN15L/cc-pVTZ relative energies. The harmonic vibrational frequencies are scaled by a factor of 0.961.³⁷ The comparison of the experimental and theoretical IR spectra of BO_3 , B_2O_4 , and B_3O_6 is shown in Figure 1. The band positions and assignments are given in Table 1. The results of frequency calculations of identified isomers are detailed in Tables S2–S5, respectively. Mass spectra of boron oxide clusters and vibrational modes of identified isomers are shown in Figures S1 and S2, respectively.

The lowest-energy isomer of BO_3 (**1A**) is calculated to have a C_s structure ($^2\text{A}''$, Figure 1A) with an O_2 unit end-on-bonded to a BO unit. The **1A** structure with the $^4\text{A}''$ quartet state is 51.34 kcal/mol higher in energy than that with the $^2\text{A}''$ doublet state at the CCSD(T)/cc-pVTZ//MN15L/cc-pVTZ level of theory. The **1B** isomer ($^2\text{A}_2$) has a C_{2v} structure with a bridging O_2 , which lies 3.96 kcal/mol higher in energy than **1A**. The **1C** isomer ($^2\text{B}_2$) has a C_{2v} structure with three separate O atoms, which lies 31.99 kcal/mol above **1A**. In the simulated IR spectrum of isomer **1A** (Figure 1A), the B–O stretching mode of the terminal BO group is predicted to be 2003 cm^{-1} (ν_1 (a'), Table 1 and Figure S2), which is in excellent agreement with the experimental value of band a_1 (2016 cm^{-1}). In contrast, the B–O stretching mode of the terminal BO in isomers **1B** and **1C** is 1900 and 1559 cm^{-1} , respectively, which are totally different from the experimental observation. Thus, isomer **1A** is confirmed to be the global minimum of BO_3 , whereas the presence of isomers **1B** and **1C** can be ruled out.

We found that the lowest-energy isomer (**2A**) for B_2O_4 has a zigzag planar structure with a $^1\text{A}'$ electronic state (Figure 1B), which is consistent with a previous calculation.²⁷ The **2A** structure with the $^3\text{A}''$ open-shell triplet state is 16.01 kcal/mol higher in energy than that with the $^1\text{A}'$ close-shell singlet state. The highly symmetric rhombus **2B** isomer ($^3\text{B}_{1u}$, D_{2h}) lies 17.99 kcal/mol above **2A**. The C_{2v} **2C** isomer has a rhombus B_2O_2 core with a side-on-bonded O_2 and a $^3\text{A}_2$ electronic state, which lies 77.00 kcal/mol above **2A**. The OBOBO bend structure (isomer **2D**) with a $^1\text{A}'$ electronic state is predicted to be 81.10 kcal/mol higher in energy than **2A**. The simulated IR spectrum of isomer **2A** agrees best with the experiment. The B–O stretching mode of the terminal BO and symmetric B–O stretching mode of the BO_3 unit in **2A** is calculated to be 2045 and 1724 cm^{-1} (Table 1), respectively, which agree well with the experimental values of band a_2 (2046 cm^{-1}) and band b_2 (1687 cm^{-1}). Note that the computed intensity of the 1724 cm^{-1} peak is higher than that of the 2045 cm^{-1} peak, while the opposite trend is observed in the experimental spectrum. This might be due to the fact that the experimental intensity of vibrational peak depends not only on the IR absorption cross section but also on the VUV absorption cross section, the efficiency of intramolecular vibrational relaxation, etc.³⁸ The simulated IR spectra of isomers **2B–2D** are completely different from the experiment.

The largest cluster studied here is B_3O_6 . Our calculations indicate that the lowest-energy isomer (**3A**, $^2\text{A}''$) has a rhombus B_2O_4 core with a side-on-bonded O_2 and a terminal OBO unit (Figure 1C). The **3B** isomer (C_s , $^2\text{A}''$) has a hexagonal ring structure and it lies 2.39 kcal/mol above **3A**. The **3B** structure with the $^4\text{A}''$ quartet state lies higher in energy by 0.76 kcal/mol than that with the $^2\text{A}''$ doublet state. The **3C** isomer (C_s , $^2\text{A}'$) has a five-membered ring containing an O_2 unit with an elongated O–O bond ($1.451\text{ \AA}$), which lies 4.15 kcal/mol above **3A**. The **3C** structure with the $^4\text{A}''$ quartet state is 39.08 kcal/mol higher in energy than that with the $^2\text{A}'$ doublet state. Isomer **3D** (C_s , $^2\text{A}'$) can be considered to be a different conformation of **3C**, with a different orientation of the terminal OBO unit. The **3E** isomer (C_s , $^2\text{A}''$) also has a rhombus B_2O_4 core with an end-on-bonded O_2 and a terminal OBO unit, which lies 4.35 kcal/mol above **2A**. The simulated IR spectra of isomers **3C** and **3D** are very similar to each other because of their structural similarity and they both agree well with the experiment. The simulated IR spectral patterns of isomers **3A** and **3E** are clearly different from the experiment, despite the fact that the computed frequency for their B–O stretching mode agrees with the a_3 band observed experimentally. Isomer **3B** can be safely ruled out because of the lack of the high frequencies mode near the observed a_3 band.

Thus, isomers **3C** or **3D** should be responsible for the observed spectrum of B_3O_6 . The barrier of the **3D** $\rightarrow$ **3C** isomerization is calculated to be 2.0 kcal/mol at the CCSD(T)/cc-pVTZ//MN15L/cc-pVTZ level (Figure S3). Such a low barrier might be readily overcome under our source conditions so that the interconversion between isomers **3D** and **3C** is feasible, indicating the possible coexistence of both conformers. Furthermore, the symmetric B–O stretching mode of the BO_3 unit in isomers **3C** and **3D** is calculated to 1479 and 1482 cm^{-1} , respectively, consistent with the small splitting of experimental band b_3 (1502 and 1489 cm^{-1} , Figure 1C and Table 1). Since **3C** and **3D** are conformers linked by wide-amplitude motion and separated only by a small barrier, they cannot be distinguished experimentally and it is likely that both contribute to the experimental spectrum. As given in Table S1, the relative Gibbs free energies of isomers **3A–3E** as a function of temperature reveal that isomer **3C** is the most stable from 0 to 298.15 K at the MN15L level of theory, supporting the above structural assignment. These results also imply that the CCSD(T) single-point calculation is reliable for assessing the relative energies of small clusters and may not be necessarily accurate for the larger clusters, such as B_3O_6 .

2.2. Chemical Bonding Features

To elucidate the stability of the observed boron oxide clusters, we performed chemical bonding analyses for the identified structures (isomers **1A**, **2A**, **3C**, and **3D**) by using the adaptive natural density partitioning (AdNDP) method³⁹ with the Multiwfn software.⁴⁰ The AdNDP bonding analyses for the representative B_2O_4 (isomer **2A**) have been performed by using different theoretical methods and the results are compared in Table S6. It is found that the AdNDP bonding analysis results are sensitive to the basis set and the AdNDP bonding analysis at the PBE0/def2-SVP level of theory yields more reasonable chemical bonding picture. Thus, these results are used for the present discussion.

As illustrated in Figure 2, the terminal BO group in BO_3 (isomer **1A**) involves one two-center two-electron ($2c\text{-}2e$) B–

O σ bond, two 2c-2e B–O π bonds, and one 1c-2e O lone pair, featuring a B $\equiv$ O triple bond. For the 2c-2e B–O σ bond, the contribution mainly arises from the interactions between B(1) (22.29%: 2s (10.18%), 2p (11.86%)) and O(2) (77.71%: 2s (35.53%), 2p (41.97%)) (Table S7). The interactions between B(1) and O(2) contribute to two different B–O π bonds (see Figure 2 and Table S7). The end-on-bonded O₂ consists of one 2c-2e O–O σ bond, one 2c-2e O–O π bonds, and two 1c-2e O lone pairs. The unpaired electron of the O(3) atom occupies the empty antibonding orbital, forming the 2c-1e O–O π antibond.

For isomer 2A of B₂O₄, the bonding features of the terminal B(1)O(2) group are similar to those in isomer 1A, which is consistent with the similar bond distances (Figures 2 and 3). As given in Figure 3, the bond distances of B(4)–O(5) (1.345 Å) and B(4)–O(6) (1.343 Å) are longer than that of B(1)–O(2) (1.216 Å), which supports the trend of vibrational frequencies (Table 1 and Figure S2). Indeed, two 2c-2e B–O σ bonds, four 1c-2e O lone pairs, and one sharing 2c-2e O–O σ bond are engaged in these two B(4)O(5) and B(4)O(6) groups, indicative of different bonding features from the terminal B(1)O(2) group. Two 2c-2e B–O σ bonds and two 1c-2e O lone pairs are involved in the B(1)O(3) and B(4)O(3) groups. The 1c-2e O(3) lone pair with occupation number of 1.81 lel essentially corresponds to the out-of-plane p_z orbital.

For isomer 3C of B₃O₆, the bonding features of the terminal B(1)O(2) group are again analogous to those in isomers 1A and 2A. As shown in Figure 4 and Table S9, the unpaired electron is located in the O(8) atom. Conventional 2c-2e B–O σ bonds and 1c-2e O lone pairs are observed in the other BO groups. The bonding features of isomer 3D (Figure S4) are similar to those of 3C because of structural similarity.

With the help of the AdNDP analyses, we can describe the bonding features of these clusters heuristically using the Lewis bonding structures, as shown Figure 5. Note that the terminal B $\equiv$ O triple bond involves a donor–acceptor bond from O $\rightarrow$ B.

2.3. Structural Features

The structural evolution of the BO₃, B₂O₄, and B₃O₆ clusters is schematically depicted in Figure 6A. The most stable structure of BO₃ (isomer 1A) can be viewed as O₂ being end-on-bonded to a BO unit. The addition of BO to BO₃ leads to B₂O₄, which incorporates a BO₃ triangle (circled with dash in Figure 6A) and a terminal BO unit. The addition of BO₂ to B₂O₄ produces B₃O₆, which features a B₂O₅ unit (circled with dash in Figure 6A) and a terminal BO unit. All the BO₃, B₂O₄, and B₃O₆ clusters exhibit planar structures. The average B–O distance of the BO₃ unit in B₂O₄ and the B₂O₅ unit in B₃O₆ is 1.341 Å (Figure 3) and 1.377 Å (Figure 4), respectively, which are very close to that of vitreous boron oxide (1.372 Å). These similarities suggest that the B₂O₄ and B₃O₆ clusters already exhibit bulklike structural properties of the vitrified state. Indeed, the BO₃ and B₂O₅ groups are key structural units in the vitreous model proposed from experimental and theoretical studies (Figure 6B).^{1,4–7,9} This finding is supported by the recent characterization of the boroxol [B₃O₃Ø₃] groups in two-dimensional boron oxide crystal on a Pt(111) substrate.⁸ The interconnection of the BO₃ and B₃O₃Ø₃ groups affords a unique mechanical softness, as demonstrated in the fabricated 2D boron that extends over highly ordered surface areas with negligible defect density.⁸ These results should have important

implications for transferring the 2D film to other substrates for potential applications.

3. CONCLUSION

We report the size-specific infrared spectra of a series of neutral boron oxide clusters via near-threshold photoionization with a tunable vacuum ultraviolet free electron laser. Quantum chemical calculations have been performed to identify the structures and to understand the experimental spectra. The agreement between experimental and theoretical results allows for structural characterization of the BO₃, B₂O₄, and B₃O₆ clusters. These clusters are found to have planar structures with BO, BO₃, and B₂O₅ groups, which are key structural units in the two-dimensional network of vitreous boron oxides. Chemical bonding analyses revealed structural stability arising from the synergy among the terminal B $\equiv$ O groups and B–O σ bonds. The present systems serve as models for spectroscopic determination of key structural units of bulk boron oxides and paves the way for size-dependent studies of larger systems to understand the stepwise formation and growth mechanisms of two-dimensional boron oxide network.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.6c04122>.

Detailed experimental and theoretical methods; time-of-flight mass spectrum (Figure S1); vibrational modes of isomers 1A, 2A, 3C, and 3D (Figure S2); potential energy profiles of the 3D $\rightarrow$ 3C isomerization (Figure S3); AdNDP bonding analysis for isomer 3D (Figure S4); Gibbs free energies of isomers 3A–3E (Table S1); normal mode (symmetry), degeneracy, harmonic vibrational frequencies, and IR intensities of isomers 1A, 2A, 3C, and 3D (Tables S2–S5); comparison of AdNDP bonding analysis results for the terminal BO group in isomer 2A of B₂O₄ calculated by different theoretical methods (Table S6); AdNDP bonding analysis for isomers 1A, 2A, and 3C (Tables S7–S9); and Cartesian coordinates (PDF)

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Notes

The authors declare no competing financial interest.

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