

## PHYSICAL SCIENCES

On the remarkable resistance to oxidation by the  $\text{Bi}_{18}^-$  clusterJun Ma<sup>1†</sup>, Teng-Teng Chen<sup>2,3,4\*†</sup>, Honglin Li<sup>5†</sup>, Dennis Bumüller<sup>6</sup>, Florian Weigend<sup>6</sup>, Tian Jian<sup>4</sup>, Manfred M. Kappes<sup>6,7</sup>, Detlef Schooss<sup>6\*</sup>, Wan-Lu Li<sup>5,8\*</sup>, Xiao-Peng Xing<sup>1\*</sup>, Lai-Sheng Wang<sup>4\*</sup>

The reactivity of  $\text{Bi}_n^-$  clusters ( $n = 2$  to 30) with  $\text{O}_2$  is found to display even-odd alternations. The open-shell even-sized  $\text{Bi}_n^-$  clusters are more reactive than the closed-shell odd-sized clusters, except  $\text{Bi}_{18}^-$ , which exhibits no observable reactivity toward  $\text{O}_2$ . We have investigated the structure and bonding of  $\text{Bi}_{18}^-$  to understand its remarkable resistance to oxidation. We find that the most stable structure of  $\text{Bi}_{18}^-$  consists of two  $\text{Bi}_8$  cages linked by a  $\text{Bi}_2$  dimer, where each atom is bonded to three neighboring atoms. Chemical bonding analyses reveal that each Bi uses its three  $6p$  electrons to form three covalent bonds with its neighbors, resulting in a  $\text{Bi}_{18}^-$  cluster without any dangling bonds. We find that the robust  $\text{Bi}_{18}$  framework along with the totally delocalized unpaired electron is responsible for the surprising inertness of  $\text{Bi}_{18}^-$  toward  $\text{O}_2$ . The  $\text{Bi}_{18}$  framework is similar to that in Hittorf's phosphorus, suggesting the possibility to create bismuth nanoclusters with interesting structures and properties.

## INTRODUCTION

Atomic clusters exhibit size-dependent chemical and physical properties. The high ratios of surface atoms and the presence of dangling bonds in general result in higher chemical reactivity for clusters than their bulk counterparts. However, certain clusters with special geometric and electronic structures can have enhanced chemical and thermodynamic stability, such as the fullerenes (1) or many metal clusters (2–5), which generally have high symmetries and large energy gaps between their highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals. Discovering clusters with enhanced chemical and thermodynamic stabilities remains one of the most important goals in cluster science ever since the discovery of the fullerenes (1).

Bismuth is the heaviest stable element and exhibits interesting electronic properties. Its low toxicity has earned it the reputation of being a “green metal” (6). Bismuth nanoparticles display quantum confinement effects, large magnetoresistance, and enhanced superconductivity (7–10). Supported bismuth nanoparticles can exhibit catalytic performance and enable ultralong-lifespan aqueous sodium storage (11). These interesting electronic properties have stimulated considerable interests in the syntheses of different bismuth nanostructures (12–15). For example, bismuth nanotubes have been synthesized (13, 14), and monolayer bismuthenes with unique electronic properties have been predicted (16, 17). Small bismuth clusters have also been studied (18–23). In particular, the electronic

structures of size-selected  $\text{Bi}_n^-$  clusters were studied by photoelectron (PE) spectroscopy (PES) (20–22), and the  $\text{Bi}_5^-$  cluster was shown to be a planar aromatic system similar to  $\text{C}_5\text{H}_5^-$  (21). The magnetic properties of gaseous  $\text{Bi}_n$  ( $n \leq 13$ ) clusters were examined using the Stern-Gerlach experiment (23), and an even-odd oscillation was observed: Even-sized clusters are closed-shell and diamagnetic, whereas the odd-sized clusters carry a single unpaired electron and are paramagnetic. The structures of bismuth clusters have been studied computationally (24–29), suggesting low-lying structures containing small units of  $\text{Bi}_4$ ,  $\text{Bi}_6$ , and  $\text{Bi}_8$ . Most of the bismuth atoms are found to be 3-coordinated, similar to the bonding pattern in bulk bismuth. The structures of  $\text{Bi}_n^+$  ( $n = 4$  to 14) have been probed by a combination of trapped ion electron diffraction (TIED) and ion mobility experiment (30), revealing that for  $n > 8$ , the clusters adopt prolate structures with coordination numbers of 3 and 4 and highly directional bonds. Despite the extensive studies on their electronic and atomic structures, the chemical reactivity of bismuth clusters has not been investigated and no chemically stable bismuth clusters have been discovered.

Here, we report a study of the chemical reactivity of  $\text{Bi}_n^-$  anionic clusters ( $n = 2$  to 30) with  $\text{O}_2$ . We observe an even-odd oscillation, where the open-shell even-sized  $\text{Bi}_n^-$  clusters are found to be substantially more reactive than the closed-shell odd-sized clusters, except  $\text{Bi}_{18}^-$ , which shows no detectable reactivity with  $\text{O}_2$ . This remarkable resistance to oxidation is elucidated on the bases of the unique structure and bonding of the  $\text{Bi}_{18}^-$  cluster from both the PES and TIED experiments. We find that the  $\text{Bi}_{18}^-$  cluster consists of two  $\text{Bi}_8$  cages linked by a  $\text{Bi}_2$  dimer, which can be viewed as a molecular analog of the Hittorf's phosphorous (31) with remarkable chemical and thermodynamic stabilities and suggests that Hittorf-like low-dimensional bismuth nanostructures may be possible.

## RESULTS

Chemical reactivity with  $\text{O}_2$ 

The reactivity of  $\text{Bi}_n^-$  ( $n = 2$  to 30) with  $\text{O}_2$  is studied on an instrument composed of a magnetron sputtering cluster source, a continuous flow reactor and a time-of-flight (TOF) mass spectrometer (see Materials and Methods) (32, 33). Figure 1 shows the relative

<sup>1</sup>Shanghai Key Lab of Chemical Assessment and Sustainability and Department of Chemistry, Tongji University, 1239 Siping Road, Shanghai 200092, China. <sup>2</sup>Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon 999077, Hong Kong (SAR), China. <sup>3</sup>HKUST Shenzhen-Hong Kong Collaborative Innovation Research Institute, Futian, Shenzhen 518045, China. <sup>4</sup>Department of Chemistry, Brown University, Providence, RI 02912, USA. <sup>5</sup>Aiiso Yufeng Li Family Department of Chemical and Nano Engineering, University of California San Diego, La Jolla, CA 92093, USA. <sup>6</sup>Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), 76131 Karlsruhe, Germany. <sup>7</sup>Institute of Physical Chemistry, Karlsruhe Institute of Technology (KIT), 76131 Karlsruhe, Germany. <sup>8</sup>Program of Materials Science and Engineering, University of California San Diego, La Jolla, CA 92093, USA.

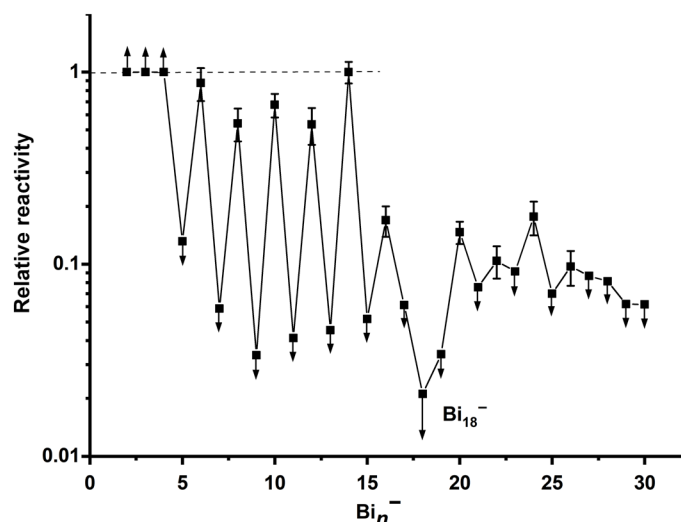
\*Corresponding author. Email: tengtengchen@ust.hk (T.-T.C.); detlef.schooss@kit.edu (D.S.); wal019@ucsd.edu (W.-L.L.); xingxp@tongji.edu.cn (X.-P.X.); lai-sheng\_wang@brown.edu (L.-S.W.)

†These authors contributed equally to this work.

reaction rates of  $\text{Bi}_n^-$  ( $n = 2$  to 30) with  $\text{O}_2$  by fitting the results obtained under different  $\text{O}_2$  flows (i.e., concentrations). The relative reaction rates are normalized to that of  $\text{Bi}_{14}^-$ . We find that the very small  $\text{Bi}_n^-$  clusters ( $n = 2$  to 4) reacted with  $\text{O}_2$  extremely fast and no bare  $\text{Bi}_n^-$  clusters can be detected after exposure to  $\text{O}_2$  even at low  $\text{O}_2$  flows (fig. S1). Hence, we can only estimate a lower limit of their relative reaction rates (represented by the  $\uparrow$  arrows in Fig. 1). For the very slow rates of some of the larger clusters, we can only estimate their higher limits (represented by the  $\downarrow$  arrows in Fig. 1) due to the very weak signals of the reaction products. Figure 1 reveals a clear even-odd oscillation of the reaction rates for  $n > 4$ , where the even-sized  $\text{Bi}_n^-$  clusters are much more reactive than their odd-sized neighbors. The only exception is  $\text{Bi}_{18}^-$ , which has even lower reactivity than all other odd-sized clusters. The reactivity of  $\text{Bi}_{18}^-$  with  $\text{O}_2$  is not measurable, as shown in the mass spectra in fig. S1. We do not observe any measurable oxidation products for  $\text{Bi}_{18}^-$  even when we increase the  $\text{O}_2$  flow to 10 standard cubic centimeter per minute, the highest possible on our instrument. This inertness of  $\text{Bi}_{18}^-$  toward  $\text{O}_2$  is remarkable, which must originate from its unique electronic and/or geometrical structure. To elucidate this extraordinary chemical stability of the  $\text{Bi}_{18}^-$  cluster, we have investigated its structure and electronic properties using PES and TIED together with theoretical calculations.

### Global minimum structure searches

We performed global minimum searches for the structure of  $\text{Bi}_{18}^-$  using a “supervised” basin hopping algorithm implemented in our in-house San Diego Global Minimum Search (SDGMS) package (34), alongside a particle-swarm optimization (PSO) algorithm implemented in CALYPSO (35), both in conjunction with density functional theory (DFT) calculations. Further details can be found in Materials and Methods. The three lowest-energy structures are depicted in Fig. 2A, with their Cartesian coordinates provided in table S1. The lowest energy structure I (Fig. 2B) can be topologically described as comprising of two  $\text{Bi}_8$  cages, connected by a  $\text{Bi}_2$  dimer highlighted in blue.

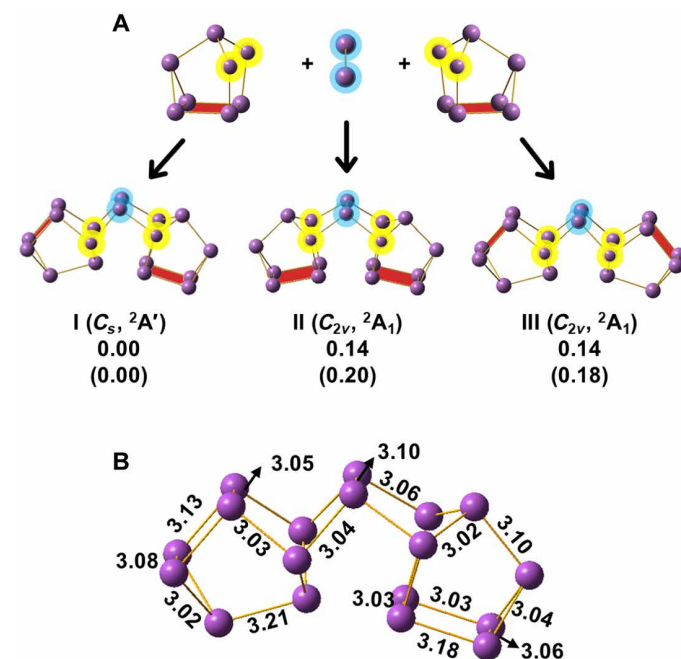


**Fig. 1. Relative reactivity of  $\text{Bi}_n^-$  ( $n = 2$ –30) with  $\text{O}_2$ .** All reaction rates are normalized to that of  $\text{Bi}_{14}^-$ . The  $\uparrow$  arrows represent lower limits because the reactions are too fast. The  $\downarrow$  arrows represent upper limits because the reactions are too slow. Note that the relative rate for  $\text{Bi}_{18}^-$  is negligible.

Each  $\text{Bi}_8$  cage includes a square  $\text{Bi}_4$  unit shaded in red, and a triangular pyramid  $\text{Bi}_4$  cap. In structure I ( $C_s$ ,  $^2A'$ ), the relative orientation of the two  $\text{Bi}_8$  units is inverted with respect to the connecting  $\text{Bi}_2$  dimer. All the Bi–Bi bond lengths range from 3.02 to 3.21 Å (Fig. 2B), consistent with Pyykkö’s single Bi–Bi bond distance (36). The other two low-lying isomers (II and III), both with  $C_{2v}$  symmetry, are structurally similar to the global minimum, except that in these isomers, the  $\text{Bi}_8$  units are symmetric relative to the connecting  $\text{Bi}_2$  dimer. Both are about 0.1 to 0.2 eV higher in energy than the global minimum, as calculated using the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof functional and triple- $\zeta$  basis set (PBE/TZP), as well as at the hybrid GGA PBE0/VTZ level. Thus, they are unlikely to have substantial populations under our experimental conditions. Structures I, II, and III can be regarded as stereoisomers, distinguished by different arrangements of the  $\text{Bi}_8$  cages.

### Photoelectron spectroscopy

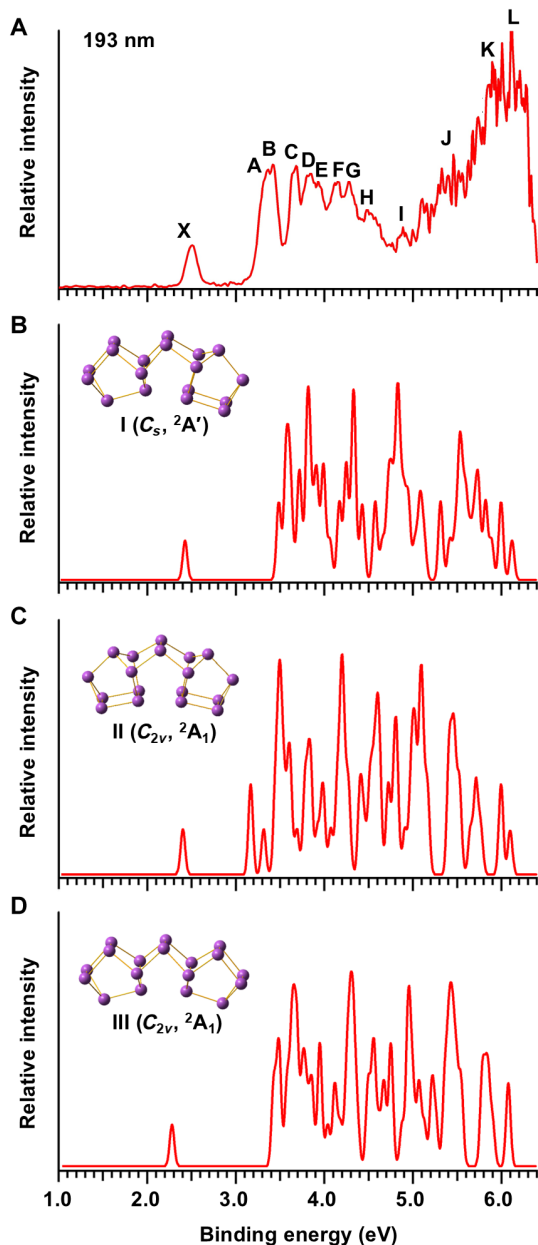
The electronic structure of  $\text{Bi}_{18}^-$  is probed by PES using a magnetic-bottle TOF apparatus (see Materials and Methods) (37). Figure 3A shows the spectrum of  $\text{Bi}_{18}^-$  at 193 nm (6.424 eV), displaying well-resolved spectral features in the low binding energy side. The observed PES features are labeled with letters (X and A to H). The higher binding energy side is more congested: the labels I to L are only for the sake of discussion. A sharp ground-state peak (X) is observed, which is from detachment transition from the ground state of  $\text{Bi}_{18}^-$  to that of  $\text{Bi}_{18}$ , whereas peaks A to L all represent detachment transitions to excited electronic states of neutral  $\text{Bi}_{18}$ . The first vertical detachment energy (VDE) is measured from the maximum of peak X to be 2.50 eV and the first adiabatic detachment



energy (ADE) is measured from the onset of peak X to be 2.40 eV, which also represents the electron affinity of neutral  $\text{Bi}_{18}$ . The experimental VDEs of all the observed PES features are given in table S2. The sharp peak X indicates that there is little structural change between  $\text{Bi}_{18}^-$  and neutral  $\text{Bi}_{18}$ . The large energy gap (0.86 eV) between peaks X and A suggests that neutral  $\text{Bi}_{18}$  is closed-shell with a large HOMO-LUMO gap.

The simulated spectra of isomers I to III, obtained by using the  $\Delta\text{SCF-TDDFT}$  (self-consistent field-time-dependent density functional theory) method (see Materials and Methods), are compared

with the experimental spectrum in Fig. 3. The first VDEs and ADEs of all the three isomers are computed at PBE/TZP (table S3). The theoretical first VDEs of isomers I and II agree well with the experimental data, but that of isomer III shows a larger deviation. Among isomers I and II, the overall pattern of the simulated spectrum for isomer I agrees better with the experiment. In particular, the HOMO-LUMO gap of isomer I is in excellent agreement with the experimental observation, providing considerable credence for isomer I as the global minimum of  $\text{Bi}_{18}^-$ . We also optimized the neutral structure corresponding to isomer I and found that the neutral  $\text{Bi}_{18}$  structure is nearly identical to the anion, consistent with the sharp ground state peak observed in the PE spectrum.



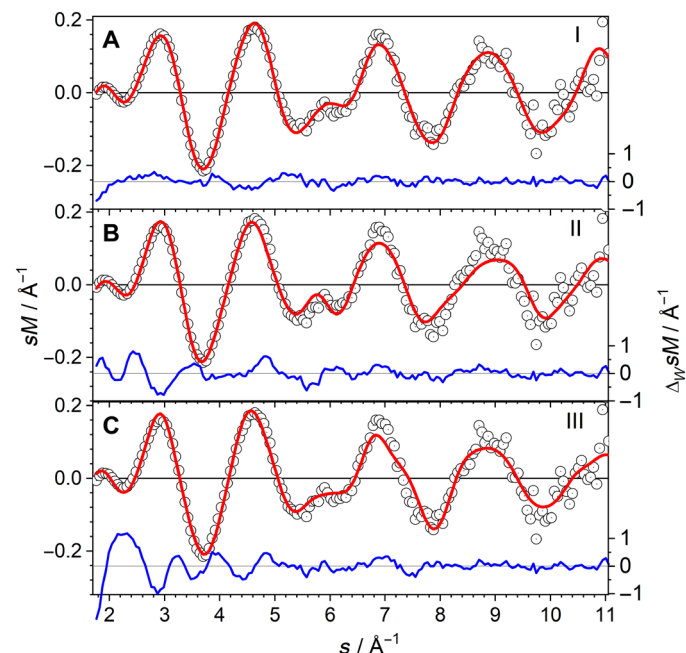
**Fig. 3. Photoelectron spectroscopy.** (A) The PE spectrum of  $\text{Bi}_{18}^-$  at 193 nm (6.424 eV). (B to D) The simulated spectra from the global minimum I and the two low-lying isomers (II and III) of  $\text{Bi}_{18}^-$ . The simulations were done at the TD-PBE/TZP level of theory (see Materials and Methods).

### Trapped ion electron diffraction

The structure of  $\text{Bi}_{18}^-$  is further validated using the TIED technique (38, 39) (see Materials and Methods) by comparing the experimental scattering function to simulated scattering functions based on the three low-lying structures I to III, as shown in Fig. 4. The simulated scattering functions of structures I to III lead to profile factors of 6.1, 10.0, and 15.0%, respectively. The profile factor  $R_w$  is a quantitative measure of the agreement between the simulated and experimental molecular scattering functions. It is the lowest for structure I among the considered structures, thereby confirming that structure I is the experimentally probed structure and corroborating the global minimum structure obtained from the comparison between PES and the computed structures above.

### Chemical bonding analysis of $\text{Bi}_{18}^-$

The bonding in the global minimum of  $\text{Bi}_{18}^-$  is analyzed using the adaptive natural density partitioning (AdNDP) approach (40), as shown in Fig. 5A. We found a  $6s^2$  lone pair for each Bi atom. The



**Fig. 4. Trapped ion electron diffraction.** (A to C) Comparison of the experimental (circles) and simulated (red) molecular scattering functions for the global minimum I and the low-lying isomers II and III of  $\text{Bi}_{18}^-$ . The blue line in each panel shows the weighted residuals.

occupation number of the lone pairs ( $ON = 1.97$  to  $1.99$  |e|) is close to the ideal value of  $2.0$  |e|, suggesting very little  $s$ - $p$  hybridization similar to other Bi-containing clusters (41, 42). This is due to the relativistic effects that stabilize the  $6s$  electron and destabilize the  $6p$  electrons (43, 44). Each Bi atom uses its three  $6p$  electrons to form three covalent bonds, yielding a total of 27 classical two-center two-electron ( $2c$ - $2e$ ) Bi—Bi  $\sigma$  bonds. In addition, we found an  $18c$ - $1e$  bond, which is completely delocalized over the  $Bi_{18}$  framework. The AdNDP analyses reveal a near perfect bonding situation in  $Bi_{18}^-$  without any dangling bond. The ideal bond angles should be  $90^\circ$  for bonding by the  $6p$  orbitals. In fact, many bond angles in the  $Bi_{18}^-$  global minimum are around  $90^\circ$  (fig. S2A). The unpaired electron in  $Bi_{18}^-$  occupies the LUMO of neutral  $Bi_{18}$  [singly occupied molecular orbital (SOMO) in Fig. 5B]. Consistent with the AdNDP analyses, both the SOMO and the spin density (Fig. 5C) show that the unpaired electron is completely delocalized over the whole  $Bi_{18}$  framework.

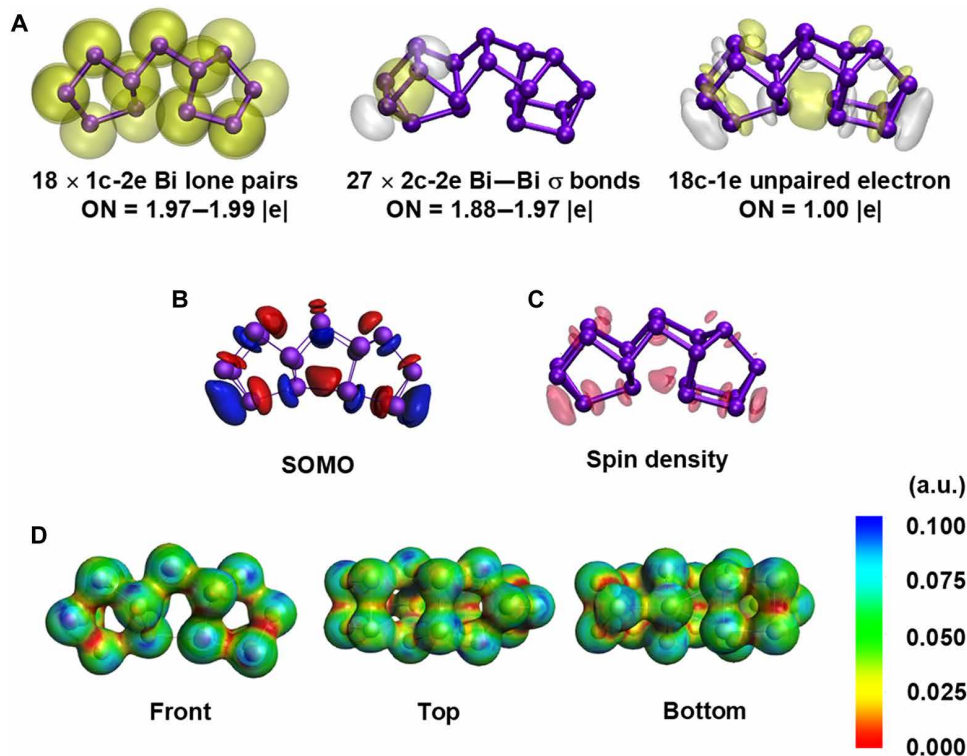
Structures **I**, **II**, and **III** are stereoisomers and the only difference between them are the orientation of the two  $Bi_8$  units relative to the  $Bi_2$  bridge (Fig. 2A). The different orientation of the  $Bi_8$  units results in slightly different bond angles at the  $Bi_2$  bridge,  $94^\circ$  for **I**,  $104^\circ$  for **II**, and  $89^\circ$  for **III** (fig. S2). While the ideal bond angle for Bi without  $s$ - $p$  hybridization is  $90^\circ$ , small participation of the  $6s$  orbital in the bonding would lead to a bond angle somewhat above  $90^\circ$ . Thus, the  $94^\circ$  bond angle in structure **I** is probably optimal in this sense, underlying its slightly higher stability.

### Understanding the inertness of $Bi_{18}^-$ toward $O_2$

One-electron transfer was observed to be the key for the reactions of  $Ag_n^-$  and  $Au_n^-$  clusters with  $O_2$ , where a strong even-odd effect was

observed (32, 45). The even-sized clusters with an unpaired electron and lower electron binding energies were readily reactive with  $O_2$  to form  $M_n(O_2^-)$  charge-transfer complexes (46–49), whereas the closed-shell odd-sized clusters with high electron binding energies are not reactive toward  $O_2$ . Except for the highly reactive small  $Bi_n^-$  ( $n = 2$  to 4) clusters and  $Bi_{18}^-$ , a similar even-odd effect is observed for the reactivity of the  $Bi_n^-$  clusters with  $O_2$  (Fig. 1). However, there are two notable differences between the  $O_2$  reactivity of the  $Bi_n^-$  clusters and that of the coinage metal clusters. First, the odd-sized  $Bi_n^-$  clusters do exhibit reactivity, albeit much weaker than the even-sized clusters. Second, many  $Bi_n^-$  clusters can react with more than one  $O_2$  molecule (fig. S1), suggesting that the reaction of the  $Bi_n^-$  clusters with  $O_2$  is more complicated, not simply a one-electron transfer process. This is because Bi can form stable oxides, in contrast to Ag and Au, which are resistant to oxide formation.

The question is, why is the open-shell  $Bi_{18}^-$  cluster so inert toward  $O_2$ ? The answer lies in the unique structure and bonding of this highly stable cluster. Even though the binding energy of the unpaired electron in  $Bi_{18}^-$  is relatively low, its totally delocalized nature (Fig. 5, B to D) is not favorable for one-electron transfer. Second, there is no dangling bond or unsaturated surface site on  $Bi_{18}^-$  for binding with  $O_2$  or forming Bi—O bonds. Each Bi atom in  $Bi_{18}^-$  is covalently satisfied. Figure 6 shows the SOMO and spin density of  $Au_6^-$  and  $Au_{20}^-$ , two prototypical reactive gold clusters with  $O_2$ . Even though the unpaired electron in the gold clusters is also delocalized, there is more electron density in the apex sites (2, 50), which are coordinatively unsaturated and provide the reactive sites for  $O_2$  (46–49). The TIED results on small  $Bi_n^+$  clusters ( $n < 15$ ) showed that all the global minima of these clusters contain 2- or

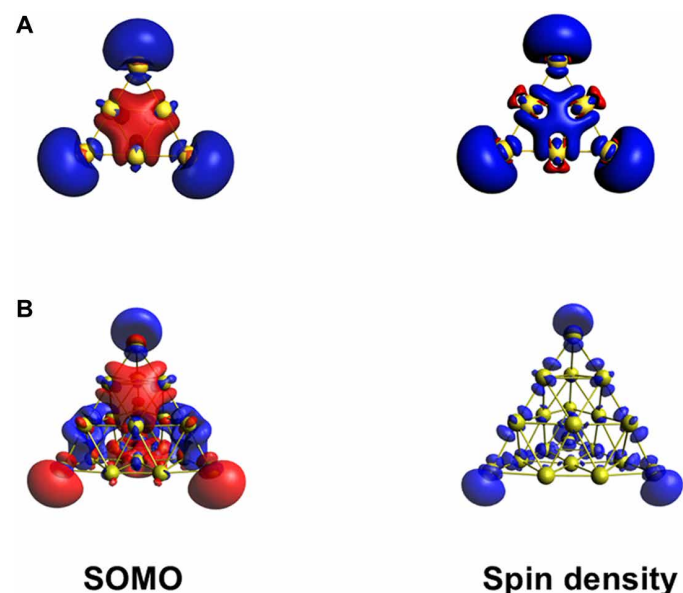


**Fig. 5. Bonding analyses.** (A) AdNDP bonding analyses for the global minimum structure **I** of  $Bi_{18}^-$ , showing 18  $6s$  lone pairs and 27 Bi—Bi  $\sigma$  bonds, along with one delocalized  $18c$ - $1e$  bond. (B) The singly occupied molecular orbital (SOMO) of  $Bi_{18}^-$  (isovalue = 0.02 a.u.). (C) The spin density in the  $Bi_{18}^-$  cluster. (D) Electrostatic potential isovalue contour surfaces from different viewpoints (unit, a.u.).



4-coordination sites (30). It is expected that all the  $\text{Bi}_n^-$  clusters, other than  $\text{Bi}_{18}^-$ , should also contain undercoordinated Bi sites, which can be the active sites for  $\text{O}_2$  reaction.

We performed calculations for  $\text{O}_2$  binding on the global minimum structure **I** in various configurations, as shown in Fig. 7A. The results reveal that all adsorption energies are very small, demonstrating the weak binding ability of  $\text{Bi}_{18}^-$  with the  $\text{O}_2$  molecule. Furthermore, we have conducted ab initio molecular dynamics (AIMD) simulations at room temperature on the strongest adsorption site (Fig. 7B). We find that the  $\text{O}_2$  molecule is completely released from the  $\text{Bi}_{18}^-$  cluster after only 128 fs, indicating that this is not even a weak physical adsorption and demonstrating the unprecedented resistance to  $\text{O}_2$  oxidation by  $\text{Bi}_{18}^-$ .



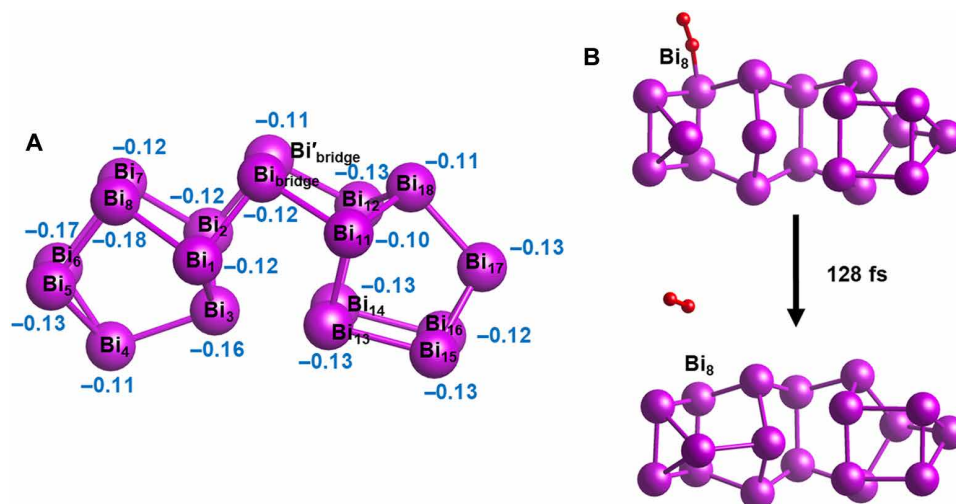
**Fig. 6. Comparison of SOMO and spin density.** The SOMO and spin density of (A)  $\text{Au}_6^-$  and (B)  $\text{Au}_{20}^-$ . The isovalue = 0.03 a.u.

### The $\text{Bi}_{18}$ cluster is a molecular bismuth analog of Hittorf's phosphorus

The neutral  $\text{Bi}_{18}$  cluster is a highly stable covalent molecular cluster with a large HOMO-LUMO gap (0.86 eV). Its structure is similar to that found in Hittorf's phosphorus (or violet phosphorus), consisting of similar  $\text{P}_8$  units linked by  $\text{P}_2$  units (31, 51). Bulk bismuths or two-dimensional bismuthenes adopt rhombohedral structures, which consist of puckered layered structures containing 3-coordinated atoms (16). All group V elements have such rhombohedral structures, but phosphorus has many more structural allotropes than its heavier congeners. In addition to the white, red, and black (rhombohedral) phosphorous, there also exists the Hittorf's phosphorous (31, 51), which are polymeric forms  $\text{P}_8$  or  $\text{P}_9$  cages linked by  $\text{P}_2$  or  $\text{P}_4$  units. The  $\text{Bi}_8$  unit in the  $\text{Bi}_{18}$  cluster is similar to the  $\text{P}_8$  units in Hittorf's phosphorous. However, there are no similar bulk bismuth allotropes like the Hittorf's phosphorous. The present work shows that the Bi atoms in small clusters can exhibit strong covalent bonding, giving rise to stable molecular units analogous to its lighter congeners. The structure of  $\text{Bi}_{18}$  suggests that extended structures consisting of the  $\text{Bi}_8$  motif linked by a  $\text{Bi}_2$  unit may be possible, giving rise to Bi nanostructures analogous to Hittorf's phosphorous. On the basis of the remarkable resistance to oxidation by the  $\text{Bi}_{18}^-$  cluster, the putative Bi nanostructure should be highly stable both chemically and thermodynamically.

### DISCUSSION

We report the discovery of a remarkably stable  $\text{Bi}_{18}^-$  cluster that is resistant to oxidation. Despite the presence of an unpaired electron, the unique structure and bonding characteristics of  $\text{Bi}_{18}^-$  result in its inertness toward  $\text{O}_2$ . The global minimum of the  $\text{Bi}_{18}^-$  cluster, along with its two next lowest-lying isomers, consists of two  $\text{Bi}_8$  cages linked by a  $\text{Bi}_2$  dimer with varying arrangements of the  $\text{Bi}_8$  cages, similar to that in the Hittorf's phosphorous. Each Bi atom forms three covalent bonds, leading to a highly stable structure with no dangling bonds. Theoretical calculations confirmed the weak binding affinity of  $\text{Bi}_{18}^-$  for  $\text{O}_2$  molecules, with complete desorption



**Fig. 7. Interaction of  $\text{O}_2$  with  $\text{Bi}_{18}^-$ .** (A) Adsorption energies (eV) of  $\text{O}_2$  on different sites of  $\text{Bi}_{18}^-$  at the PBE-D3/TZV2P level. (B) AIMD simulation of the adsorbed  $\text{O}_2$  undergoing desorption after 128 fs.

occurring at room temperature. The high chemical stability of the  $\text{Bi}_{18}^-$  cluster suggests the potential for creating Bi nanostructures analogous to Hittorf's phosphorus, which may exhibit interesting electronic properties. Recent research on bismuth-based metal clusters (52, 53) suggests promising prospects for synthesizing stable  $\text{Bi}_{18}$ -containing nanoclusters.

## MATERIALS AND METHODS

### Reactions of $\text{Bi}_n^-$ with $\text{O}_2$

The reactivity of  $\text{Bi}_n^-$  ( $n = 2$  to 30) with  $\text{O}_2$  was studied on an instrument composed of a magnetron sputtering cluster source, a continuous flow reactor and a TOF mass spectrometer (32, 33). In brief, clusters were generated in the source chamber and entered the flow reactor together with the helium buffer gas. The nascent clusters were thermalized to the temperature of the reactor maintained at 120 K and then reacted with  $\text{O}_2$ , which was introduced downstream. After passing through a skimmer at the end of the flow reactor, the oxidized products and the unreacted clusters were analyzed by the TOF mass spectrometer. The intensities of individual  $\text{Bi}_n^-$  clusters with  $\text{O}_2$  flow ( $I$ ) and without  $\text{O}_2$  ( $I_0$ ) were measured at various  $\text{O}_2$  flow rates. The relative reaction rates were obtained by linearly fitting  $\ln(I/I_0)$  versus the  $\text{O}_2$  flow rate.

### Photoelectron spectroscopy

The PE spectrum of  $\text{Bi}_{18}^-$  was obtained using a magnetic-bottle TOF PE spectrometer coupled with a laser vaporization supersonic cluster source, details of which have been described previously (37). In brief, bismuth clusters were produced by laser vaporization of a Bi disk target followed by supersonic expansion with a helium carrier gas seeded with 5% argon. Negatively charged clusters were analyzed by a TOF mass spectrometer perpendicular to the cluster beam. The  $\text{Bi}_{18}^-$  cluster of current interest was mass selected and decelerated before being photodetached by the 193-nm (6.424 eV) radiation from an ArF excimer laser. The resolution of the apparatus was around 2.5%, that is, about 25 meV for 1-eV electrons.

### Trapped ion electron diffraction

The structure of  $\text{Bi}_{18}^-$  was determined experimentally by comparing scattering functions from the Karlsruhe TIED apparatus and simulated scattering functions based on candidate structures from DFT calculations. Details of the TIED experiment and the data analysis have been described elsewhere (38, 39) and only a brief description of the experimental procedure is given here. About  $10^5$  to  $10^6$   $\text{Bi}_{18}^-$  clusters, generated from a magnetron sputtering source (54), were stored in a radio-frequency quadrupole ion trap and thermalized through collisions with a He buffer gas to a temperature of  $95 \pm 5$  K. The ion cloud was irradiated by an electron beam (40 keV, ca. 2 to 3  $\mu\text{A}$ ) from a long focal length electron gun. Diffracted electrons from the clusters were detected by a phosphor screen assembly and integrated on an external charge-coupled device camera. A reference picture was accumulated by repeating the sequence without cluster ions in the trap. After typically accumulating several hundred such electron scattering exposures, the background-corrected diffraction pictures were radially averaged, yielding the total scattering  $I^{\text{tot}}$  as a function of the scattering angle  $\theta$  represented by the electron momentum transfer  $s = (4\pi/\lambda)\sin(\theta/2)$  as function of the electron wavelength  $\lambda$ . Considering the atomic scattering intensity  $I^{\text{at}}$  and an additional a priori unknown and unspecific flat background

$I^{\text{back}}$ , the experimental reduced molecular scattering function is calculated as

$$sM^{\text{expt}} = s(I^{\text{tot}} - I^{\text{at}} - I^{\text{back}}) / I^{\text{at}}$$

The theoretical reduced molecular scattering function is approximated by

$$sM^{\text{theo}} = S_c \sum_i^N \sum_{j \neq i}^N \exp\left(-\frac{l_{ij}^2}{2} s^2\right) |f_i(s)| |f_j(s)| \cos(\eta_i - \eta_j) \frac{\sin(s k_s r_{ij})}{k_s r_{ij}}$$

where  $N$  is the number of atoms in the cluster,  $S_c$  and  $k_s$  are scaling factors for the amplitudes and distances,  $f_i$  and  $\eta_i$  are partial wave elastic scattering amplitude and phase, and  $r_{ij}$  the distance between two atoms in the cluster.  $l_{ij}^2$  are mean squared vibrational amplitudes (55) and account for thermal vibrations. Here, a single (averaged) value has been used.

The comparison of experimental data and the theoretical function was accomplished by a  $\chi^2$  fit minimizing the weighted differences by variation of  $S_c$ ,  $k_s$ ,  $l_{ij}$ , and parameters of the background polynomial  $I^{\text{back}}$ . Before the fit,  $sM^{\text{theo}}$  is convoluted by a Gaussian ( $\sigma = 0.14 \text{ \AA}^{-1}$ ) to simulate experimental broadening effects, such as finite electron beam and cluster ion cloud size. Beam attenuation by scattering at the finite trap opening is taken into account by weighting  $sM^{\text{theo}}$  with an error function centered at the maximum theoretical scattering angle corresponding to  $s = 14 \text{ \AA}^{-1}$ . The level of agreement between experiment and model structure is then determined by a weighted profile factor (38), which is given by

$$R_w = \sqrt{\sum_i w_i (sM_i^{\text{theo}} - sM_i^{\text{expt}})^2 / \sum_i w_i (sM_i^{\text{expt}})^2}$$

The sums go over all experimental and corresponding theory data points. The weighting factors  $w_i$  are calculated from the error propagated SD of the experimental data.

### Theoretical methods

A global minimum search was conducted to determine the most stable structures of the anion  $\text{Bi}_{18}^-$  and the neutral  $\text{Bi}_{18}$  using both a "supervised" Basin Hopping algorithm implemented in SDGMS (34) and the PSO algorithm in CALYPSO (35). DFT calculations were performed with SDGMS using the ADF 2024.1 program system (56). The generalized gradient approximation (GGA) PBE functional (57) was used with a Slater double- $\zeta$  basis set with one polarization function (DZP) (58). The frozen-core approximation was applied to the inner shells [ $1s^2-4d^{10}$ ] for bismuth in the all-electron ADF calculations. Relativistic effects were taken into consideration by the zeroth-order regular approximation (59). After obtaining the lowest lying isomers, larger triple- $\zeta$  basis sets (TZP) and hybrid PBE0 functional (60) were used to more accurately determine the relative energies. To eliminate prediction bias, we used a different prediction method PSO for neutral species, using the projector augmented wave method (61) as implemented in the periodic VASP code (62) in conjunction with CALYPSO.

PE spectra of the predicted global minimum structure and the other two  $C_{2v}$  stereoisomers were simulated using  $\Delta\text{SCF-TDDFT}$  method (2) along with the PBE functional. The first VDE (VDE1) was computed as the energy difference between the anionic ground state and the corresponding neutral state at the anion's geometry. The ADE was calculated as the energy difference between the anionic

and neutral species at their respective optimized geometries. To simulate the PE spectra, each VDE was fitted with a Gaussian function of 0.06 eV width. The relative intensities in the simulated PE spectra were empirically determined, with a value of one for singlet states and two for triplet states.

Chemical bonding analyses were performed using molecular orbital theory at the PBE/TZP level and the AdNDP method (40), which involves diagonalizing the first-order reduced density matrix to optimally converge the electron density description. During the search for multicenter two-electron ( $nc$ -2e) bonds, the density matrix is iteratively depleted of density corresponding to the appropriate bonding elements, generating 1c-2e, 2c-2e, and  $nc$ -2e bonds. These calculations were carried out using the Gaussian 09 package (63). Fully relativistic energy-consistent pseudopotentials (ECP-60MDF) (64) and the cc-pVTZ (VTZ) (65) basis set were used for bismuth (Bi).

The reactivity of  $\text{Bi}_{18}^-$  with  $\text{O}_2$  was examined by calculating the adsorption energy of  $\text{O}_2$  on different sites of  $\text{Bi}_{18}^-$  using the PBE functional corrected by D3 van der Waals dispersion (66), combined with TZV2P MOLOPT basis sets optimized for multigrid integration (67), as implemented in the CP2K package (68). Norm-conserving pseudopotentials (69) were used to describe the interactions between the frozen cores and the valence shell electrons. The cutoff value was set to 450 rydbergs, and the number of grids was set to 5. The simulation box size was  $30 \text{ \AA} \times 30 \text{ \AA} \times 30 \text{ \AA}$ . During geometry optimizations, the convergence criteria were set to  $3 \times 10^{-3}$  bohr for atomic displacements and  $4.5 \times 10^{-4}$  hartree/bohr for forces. The ab initio molecular dynamics simulations were performed in the canonical (NVT) ensemble at 300 K using the Nose-Hoover thermostat algorithm (70) with a time step of 1 fs.

## Supplementary Materials

This PDF file includes:

Figs. S1 and S2

Tables S1 to S3

## REFERENCES AND NOTES

- H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, *C<sub>60</sub>: Buckminsterfullerene*. *Nature* **318**, 162–163 (1985).
- J. Li, X. Li, H. J. Zhai, L. S. Wang,  $\text{Au}_{20}$ : A tetrahedral cluster. *Science* **299**, 864–867 (2003).
- D. E. Bergeron, P. J. Roach, A. W. Castleman, N. O. Jones, S. N. Khanna, Al cluster superatoms as halogens in polyhalides and as alkaline earths in iodide salts. *Science* **307**, 231–235 (2005).
- L. F. Cui, L. S. Wang, Stable icosahedral hollow cage clusters: Stannaspherenes ( $\text{Sn}_{12}^{2-}$ ) and plumbaspherenes ( $\text{Pb}_{12}^{2-}$ ). *Int. Rev. Phys. Chem.* **27**, 139–166 (2008).
- Y. Jia, C.-Q. Xu, C. Cui, L. Geng, H. Zhang, Y.-Y. Zhang, S. Lin, J. Yao, Z. Luo, J. Li, Rh<sub>19</sub>—: A high-spin super-octahedron cluster. *Sci. Adv.* **9**, eadi0214 (2023).
- R. Mohan, Grenn bismuth. *Nat. Chem.* **2**, 336 (2010).
- B. Weitzel, H. Micklitz, Superconductivity in granular systems built from well-defined rhombohedral Bi-clusters: Evidence for Bi-surface superconductivity. *Phys. Rev. Lett.* **66**, 385–388 (1991).
- Y. W. Wang, J. S. Kim, G. H. Kim, K. S. Kim, Quantum size effects in the volume plasmon excitation of bismuth nanoparticles investigated by electron energy loss spectroscopy. *Appl. Phys. Lett.* **88**, 143106 (2006).
- F. Y. Yang, K. Liu, K. Hong, D. H. Reich, P. C. Seanson, C. L. Chien, Large magnetoresistance of electrodeposited single-crystal bismuth thin films. *Science* **284**, 1335–1337 (1999).
- J. Heremans, C. M. Thrush, Y. M. Lin, S. Cronin, Z. Zhang, M. S. Dresselhaus, J. F. Mansfield, Bismuth nanowire arrays: Synthesis and galvanomagnetic properties. *Phys. Rev. B* **61**, 2921–2930 (2000).
- H. Zhu, F. Wang, L. Peng, T. Qin, F. Kang, C. Yang, Inlaying bismuth nanoparticles on graphene nanosheets by chemical bond for ultralong-lifespan aqueous sodium storage. *Angew. Chem. Int. Ed.* **62**, e202212439 (2023).
- T. Som, A. Simo, R. Fenger, G. V. Troppe, R. Bansen, N. Pfänder, F. Emmerling, J. Rappich, T. Boeck, K. Rademann, Bismuth hexagons: Facile mass synthesis, stability and applications. *ChemPhysChem* **13**, 2162–2169 (2012).
- Y. Li, J. Wang, Z. Deng, Y. Wu, X. Sun, D. Yu, P. Yang, Bismuth nanotubes: A rational low-temperature synthetic route. *J. Am. Chem. Soc.* **123**, 9904–9905 (2001).
- R. Boldt, M. Kaiser, D. Köhler, F. Krumeich, M. Ruck, High-yield synthesis and structure of double-walled bismuth-nanotubes. *Nano Lett.* **10**, 208–210 (2010).
- F. Pan, B. Peerless, S. Dehnen, Bismuth-based metal clusters—From molecular aesthetics to contemporary materials science. *Acc. Chem. Res.* **56**, 1018–1030 (2023).
- M. Pumera, Z. Sofer, 2D monoelemental arsenene, antimonene, and bismuthene: Beyond black phosphorus. *Adv. Mater.* **29**, 1605299 (2017).
- R.-W. Zhang, C.-W. Zhang, W.-X. Ji, S.-S. Yan, Y.-G. Yao, First-principles prediction on bismuthylene monolayer as a promising quantum spin hall insulator. *Nanoscale* **9**, 8207–8212 (2017).
- R. E. Walstedt, R. F. Bell, Ionization and fragmentation of Bi microclusters by electron impact. *Phys. Rev. A* **33**, 2830–2832 (1986).
- M. E. Geusic, R. R. Freeman, M. A. Duncan, Neutral and ionic clusters of antimony and bismuth: A comparison of magic numbers. *J. Chem. Phys.* **89**, 223–229 (1988).
- M. L. Polak, J. Ho, G. Gerber, W. C. Lineberger, Photoelectron spectroscopy of negatively charged bismuth clusters:  $\text{Bi}_2^-$ ,  $\text{Bi}_3^-$ , and  $\text{Bi}_4^-$ . *J. Chem. Phys.* **95**, 3053–3063 (1991).
- H. J. Zhai, L. S. Wang, A. E. Kuznetsov, A. I. Boldyrev, Probing the electronic structure and aromaticity of pentapnictogen cluster anions  $\text{Pn}_5^-$  ( $\text{Pn} = \text{P, As, Sb, and Bi}$ ) using photoelectron spectroscopy and ab initio calculations. *J. Phys. Chem. A* **106**, 5600–5606 (2002).
- M. Gausa, R. Kaschner, G. Seifert, J. H. Faehrmann, H. O. Lutz, K. H. Meiwes-Broer, Photoelectron investigations and density functional calculations of anionic  $\text{Sb}_n^-$  and  $\text{Bi}_n^-$  clusters. *J. Chem. Phys.* **104**, 9719–9728 (1996).
- S. Yin, X. Xu, R. Moro, W. A. de Heer, Measurement of magnetic moments of free  $\text{Bi}_n \text{Mn}_m$  clusters. *Phys. Rev. B* **72**, 174410 (2005).
- L. Gao, P. Li, H. Lu, S. F. Li, Z. X. Guo, Size- and charge-dependent geometric and electronic structures of  $\text{Bi}_n$  ( $\text{Bi}_n^-$ ) clusters ( $n = 2$ –13) by first-principles simulations. *J. Chem. Phys.* **128**, 194304 (2008).
- J. M. Jia, G. B. Chen, D. N. Shi, B. L. Wang, Structural and electronic properties of  $\text{Bi}_n$  ( $n = 2$ –14) clusters from density-functional calculations. *Eur. Phys. J. D* **47**, 359–365 (2008).
- H. K. Yuan, H. Chen, A. L. Kuang, Y. Miao, Z. H. Xiong, Density-functional study of small neutral and cationic bismuth clusters  $\text{Bi}_n$  and  $\text{Bi}_n^+$  ( $n = 2$ –24). *J. Chem. Phys.* **128**, 094305 (2008).
- A. D. Zdetsis, Theoretical predictions of a new family of stable bismuth and other group 15 fullerenes. *J. Phys. Chem. C* **114**, 10775–10781 (2010).
- A. J. Karttunen, M. Linnolahti, T. A. Pakkanen, Structural and electronic trends among group 15 polyhedral fullerenes. *Theor. Chem. Acc.* **129**, 413–422 (2011).
- J. Akola, N. Atodiresel, J. Kalikka, J. Larrucea, R. O. Jones, Structure and dynamics in liquid bismuth and  $\text{Bi}_n^+$  clusters: A density functional study. *J. Chem. Phys.* **141**, 194503 (2014).
- R. Kelting, A. Baldes, U. Schwarz, T. Rapps, D. Schooss, P. Weis, C. Neiss, F. Weigend, M. M. Kappes, Structures of small bismuth cluster cations. *J. Chem. Phys.* **136**, 154309 (2012).
- M. Ruck, D. Hoppe, B. Wahl, P. Simon, Y. Wang, G. Seifert, Fibrous red phosphorus. *Angew. Chem. Int. Ed.* **44**, 7616–7619 (2005).
- J. Ma, X. Cao, X. Xing, X. Wang, J. H. Parks, Adsorption of  $\text{O}_2$  on anionic silver clusters: Spins and electron binding energies dominate in the range up to nano sizes. *Phys. Chem. Chem. Phys.* **18**, 743–748 (2016).
- J. Ma, X. Cao, H. Liu, B. Yin, X. Xing, The adsorption and activation of NO on silver clusters with sizes up to one nanometer: Interactions dominated by electron transfer from silver to NO. *Phys. Chem. Chem. Phys.* **18**, 12819–12827 (2016).
- J. Burkhardt, T. T. Chen, W. J. Chen, D. F. Yuan, W. L. Li, L. S. Wang, Probing the structures and lanthanum-lanthanum bonding in  $\text{La}_2\text{Bi}_n^-$  ( $n = 4$ –6) clusters. *Inorg. Chem.* **63**, 17215–17224 (2024).
- Y. Wang, J. Lv, L. Zhu, Y. Ma, CALYPSO: A method for crystal structure prediction. *Comput. Phys. Commun.* **183**, 2063–2070 (2012).
- P. Pyykkö, Additive covalent radii for single-, double-, and triple-bonded molecules and tetrahedrally bonded crystals: A summary. *J. Phys. Chem. A* **119**, 2326–2337 (2015).
- L. S. Wang, Photoelectron spectroscopy of size-selected boron clusters: From planar structures to borophenes and borospherenes. *Int. Rev. Phys. Chem.* **35**, 69–142 (2016).
- D. Schooss, M. N. Blom, J. H. Parks, B. von Issendorff, H. Haberland, M. M. Kappes, The structures of  $\text{Ag}_{35}^+$  and  $\text{Ag}_{35}^-$ : Trapped ion electron diffraction and density functional theory. *Nano Lett.* **5**, 1972–1977 (2005).
- D. Schooss, M. M. Kappes, Trapped ion electron diffraction of metal cluster ions, in *Encyclopedia of Interfacial Chemistry*, K. Wandelt, Ed. (Elsevier, 2018), pp. 567–579.
- D. Y. Zubarev, A. I. Boldyrev, Developing paradigms of chemical bonding: Adaptive natural density partitioning. *Phys. Chem. Chem. Phys.* **10**, 5207–5217 (2008).
- T. Jian, L. F. Cheung, T. T. Chen, L. S. Wang, Bismuth-boron multiple bonding in  $\text{BiB}_2\text{O}^-$  and  $\text{Bi}_2\text{B}^-$ . *Angew. Chem. Int. Ed.* **56**, 9551–9555 (2017).

42. S. Pande, T. Jian, N. S. Khetrapal, L. S. Wang, X. C. Zeng, Structural evolution of gold-doped bismuth clusters  $\text{AuBi}_n^-$  ( $n = 4-8$ ). *J. Phys. Chem. C* **122**, 6947–6954 (2018).
43. P. Pykkö, Relativistic effects in structural chemistry. *Chem. Rev.* **88**, 563–594 (1988).
44. Y. L. Wang, H. S. Hu, W. L. Li, F. Wei, J. Li, Relativistic effects break periodicity in group 6 diatomic molecules. *J. Am. Chem. Soc.* **138**, 1126–1129 (2016).
45. B. E. Salisbury, W. T. Wallace, R. L. Whetten, Low-temperature activation of molecular oxygen by gold clusters: A stoichiometric process correlated to electron affinity. *Chem. Phys.* **262**, 131–141 (2000).
46. D. Stolic, M. Fischer, G. Gantefor, Y. D. Kim, Q. Sun, P. Jena, Direct observation of key reaction intermediates on gold clusters. *J. Am. Chem. Soc.* **125**, 2848–2849 (2003).
47. R. Pal, L. M. Wang, Y. Pei, L. S. Wang, X. C. Zeng, Unraveling the mechanisms of  $\text{O}_2$  activation by size-selected gold clusters: Transition from superoxo to peroxo chemisorption. *J. Am. Chem. Soc.* **134**, 9438–9445 (2012).
48. A. P. Woodham, G. Meijer, A. Fielicke, Activation of molecular oxygen by anionic gold clusters. *Angew. Chem. Int. Ed.* **51**, 4444–4447 (2012).
49. N. S. Khetrapal, D. Deibert, R. Pal, L. F. Cheung, L. S. Wang, X. C. Zeng, How  $\text{O}_2$ -binding affects structural evolution of medium even-sized gold clusters  $\text{Au}_n^-$  ( $n = 20-34$ ). *J. Phys. Chem. Lett.* **12**, 3560–3570 (2021).
50. H. J. Zhai, B. Kiran, B. Dai, J. Li, L. S. Wang, Unique CO chemisorption properties of gold hexamer:  $\text{Au}_6(\text{CO})_n^-$  ( $n = 0-3$ ). *J. Am. Chem. Soc.* **127**, 12098–12106 (2005).
51. G. Schusteritsch, M. Uhrin, C. J. Pickard, Single-layered Hittorf's phosphorus: A wide-bandgap high mobility 2D materials. *Nano Lett.* **16**, 2975–2980 (2016).
52. F. Pan, B. Peerless, S. Dehnen, Bismuth-based metal clusters—From molecular aesthetics to contemporary materials science. *Acc. Chem. Res.* **56**, 1018–1030 (2023).
53. C. C. Shu, D. W. Szczepaniak, A. Munoz-Castro, M. Sola, Z. M. Sun,  $[\text{K}_2(\text{Bi}@\text{Pd}_{12}@\text{Bi}_{20})]^{4-}$ : An endohedral inorganic fullerene with spherical aromaticity. *J. Am. Chem. Soc.* **146**, 14166–14173 (2024).
54. H. Haberland, M. Mall, M. Moseler, Y. Qiang, T. Reiners, Y. Thurner, Filling of micron-sized contact holes with copper by energetic cluster impact. *J. Vac. Sci. Technol. A* **12**, 2925–2930 (1994).
55. *CRC Handbook of Chemistry and Physics* (CRC Press, Boca Raton, FL, ed. 66, 1986), pp. B-203–219.
56. ADF, 2024.1, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands; <http://www.scm.com>.
57. J. P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**, 3865–3868 (1996).
58. E. van Lenthe, E. J. Baerends, Optimized Slater-type basis sets for the elements 1–118. *J. Comput. Chem.* **24**, 1142–1156 (2003).
59. E. van Lenthe, E. J. Baerends, J. G. Snijders, Relativistic regular two-component Hamiltonians. *J. Chem. Phys.* **99**, 4597–4610 (1993).
60. C. Adamo, V. Barone, Toward reliable density functional methods without adjustable parameters: The PBE0 model. *J. Chem. Phys.* **110**, 6158–6170 (1999).
61. P. E. Blöchl, Projector augmented-wave method. *Phys. Rev. B* **50**, 17953–17979 (1994).
62. G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **6**, 15–50 (1996).
63. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09 Revision C.01* (Gaussian Inc., 2009).
64. B. Metz, H. Stoll, M. Dolg, Small-core multiconfiguration-Dirac–Hartree–Fock-adjusted pseudopotentials for post- $d$  main group elements: Application to PbH and PbO. *J. Chem. Phys.* **113**, 2563–2569 (2000).
65. K. A. Peterson, D. Figgen, E. Goll, H. Stoll, M. Dolg, Systematically convergent basis sets with relativistic pseudopotentials. II. Small-core pseudopotentials and correlation consistent basis sets for the post- $d$  group 16–18 elements. *J. Chem. Phys.* **119**, 11113–11123 (2003).
66. S. Grimme, J. Antony, S. Ehrlich, H. Krieg, A consistent and accurate *ab initio* parametrization of density functional dispersion correction (DFT-D) for the 94 elements H–Pu. *J. Chem. Phys.* **132**, 154104 (2010).
67. J. VandeVondele, J. Hutter, Gaussian basis sets for accurate calculations on molecular systems in gas and condensed phases. *J. Chem. Phys.* **127**, 114105 (2007).
68. J. Hutter, M. Iannuzzi, F. Schiffmann, J. VandeVondele, cp2k: Atomistic simulations of condensed matter systems. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **4**, 15–25 (2014).
69. S. Goedecker, M. Teter, J. Hutter, Separable dual-space Gaussian pseudopotentials. *Phys. Rev. B* **54**, 1703–1710 (1996).
70. S. Nosé, A unified formulation of the constant temperature molecular dynamics methods. *J. Chem. Phys.* **81**, 511–519 (1984).

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