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Sn_{12}^{2-}: Stannaspherene

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During photoelectron spectroscopy (PES) experiments aimed at understanding the semiconductor-to-metal transition in tin clusters, the spectrum of Sn_{12}^- was observed to be remarkably simple and totally different from the corresponding Ge_{12}^- cluster, suggesting that Sn_{12}^- is a unique and highly symmetric cluster. Structural optimization starting from an icosahedral (I_h) cluster led to a slightly distorted cage with C_{5v} symmetry. However, adding an electron to Sn_{12}^- resulted in a stable closed-shell I_h−Sn_{12}^{2-} cluster, which was synthesized in the form of KSn_{12}^- ($K^+[Sn_{12}^{2-}]$) with a similar PES spectrum as Sn_{12}^-. The I_h−Sn_{12}^{2-} cage is shown to be bonded by four delocalized radial π bonds and nine delocalized on-sphere tangential σ bonds from the 5p orbitals of the Sn atoms, whereas the $5s^2$ electrons remain largely localized and nonbonding. The bonding pattern in Sn_{12}^{2-} is similar to the well-known $B_{12}H_{12}^{2-}$ cage, with the twelve $5s^2$ localized electron pairs replacing the twelve B−H bonds. The Sn_{12}^{2-} cage has a diameter of 6.1 Å and can host most transition metal atoms in the periodic table.

The PES apparatus, featuring a laser vaporization supersonic cluster beam source and a magnetic bottle electron analyzer, has been described in detail previously.[1] A disk of pure tin was used as the laser vaporization target with a helium carrier gas. Negatively charged tin clusters (Sn_x^-) were extracted from the cluster beam and were mass analyzed in a time-of-flight mass spectrometer. The cluster of interest was selected and then decelerated before being photodetached by a laser beam (193 nm from an excimer laser or 266 and 355 nm from a Nd:YAG laser). Photoelectrons were analyzed by the magnetic bottle time-of-flight analyzer and were calibrated by the known spectra of Cu^- and Au^-. The PES apparatus had an electron energy resolution of $\Delta E/E \sim 2.5\%$, that is, ~25 meV for 1 eV electrons.

Different from its lighter congeners, Si and Ge which are semiconductors, the normal allotrope of tin under ambient conditions (β-Sn) is a metal with a body-centered tetragonal lattice, but it also has a small band gap semiconducting phase (α-Sn) with a diamond lattice similar to Si and Ge that is stable at low temperatures.[2] Prior experimental[3−7] and theoretical[8−11] studies suggest that small tin clusters possess similar structures to those of Si and Ge. Small tin clusters were observed to exhibit melting temperatures exceeding that of the bulk,[4] consistent with the notion that small tin clusters have similar bonding configurations as those of the semiconductor Si and Ge clusters. Previous PES experiments[12−14] also suggested that the spectra of small Sn_x^- clusters are similar to those of the corresponding Ge_x^- clusters. However, these PES experiments were all done at low photon energies and under relatively low resolution.

In an effort to elucidate the semiconductor-to-metal transition as a function of size in tin clusters, we recently re-examined the PES of size-selected Sn_x^- clusters with high photon energies (up to 6.424 eV or 193 nm) and under well-controlled experimental conditions. In the size range of $x < 20$, we indeed observed that the PES spectra of Sn_x^- are similar to those of the corresponding Ge_x^-, with the exception of Sn_{12}^- (Figure S1). Whereas the spectrum of Ge_{12}^- is rather congested with numerous poorly resolved features, that of Sn_{12}^- is remarkably simple and well-structured (Figure 1a). Four bands were resolved in the binding energy range from 3 to 4 eV, followed by a large gap and two well-resolved bands around 5 eV. The lowest energy band yielded an adiabatic detachment energy, that is, the electron affinity of neutral Sn_{12}, to be 3.23 ± 0.05 eV and a vertical detachment energy (VDE) of 3.34 ± 0.03 eV. Although low-symmetry structures similar to Ge_{12} have been proposed for Sn_{12}, the relatively simple and characteristic PES spectrum of Sn_{12}^- immediately suggested that it should possess a high-symmetry structure different from that of Ge_{12}^-.

In pondering the possible high-symmetry structures for Sn_{12}^-, we started from the highest symmetry possible for a twelve-atom cluster, the icosahedral cage (for computational details, see Supporting Information). However, the Jahn−Teller effect led to a slightly lower symmetry C_{5v} ($^2A_1$) species (Figure 2a), which is only slightly distorted from the I_h structure, mainly by the depression of one apex atom. The computed first VDE (3.27 eV) of the C_{5v} Sn_{12}^- is in excellent agreement with the experimental value of 3.34 eV. By adding one electron to Sn_{12}^-, we found that the resulting Sn_{12}^{2-} species is a highly stable I_h cage with a closed electron shell (Figure 2b and Figure S2).[15] Several other low-symmetry structures, including those suggested for Ge_{12}, have also been calculated for Sn_{12}^{2-}, but they are all much higher in energy (Figure S2). We were able to make Sn_{12}^{2-} in the form of KSn_{12}^- ($K^+[Sn_{12}^{2-}]$) experimentally by laser vaporization of a tin target containing ~15% K. The photoelectron spectrum of KSn_{12}^- (Figure 1b) is very similar to that of Sn_{12}^-, suggesting that the Sn_{12}^{2-} motif is not distorted greatly due to the presence of K^+. The ADE and VDE for the ground-state transition were measured as 2.99 ± 0.05 and 3.08 ± 0.03 eV, respectively, for KSn_{12}^-. Our calculations showed that the K^+ counterion is outside the Sn_{12}^{2-} cage with a C_{3v} ($^1A_1$) symmetry (Figure 2c). Indeed, only relatively small structural perturbations were observed in the Sn_{12}^{2-} cage as a result of the K^+ coordination. The isomer with K^+ inside the Sn_{12}^{2-} cage is much higher in energy by 3.1 eV because of the large size of the K^+ ion, which expands the cage diameter from 6.07 Å (Figure 2b) to ~6.45 Å. We also calculated K coordinated to the two low-lying isomers of Sn_{12}^-. We found they are both higher in energy and yield VDEs smaller than the experiment (Table S1). Only the

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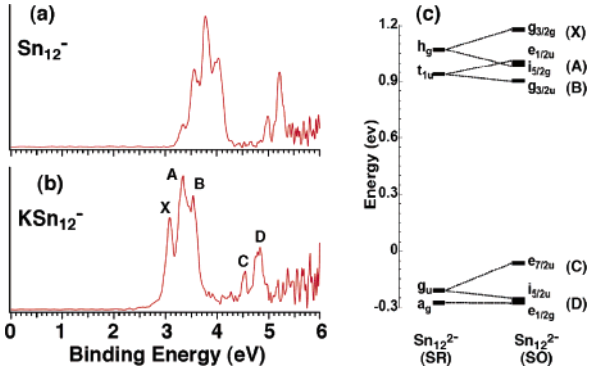

Figure 1. Photoelectron spectra of (a) Sn_{12}^- and (b) KSn_{12}^- at 193 nm. (c) Scalar relativistic (SR) energy levels of the 5p-based valence molecular orbitals of the I_h Sn_{12}^{2-} and the correlation to the spin−orbit (SO) coupled levels of I_h* Sn_{12}^{2-}, where the asterisk indicates the double-group symmetry. See Supporting Information for computational details.

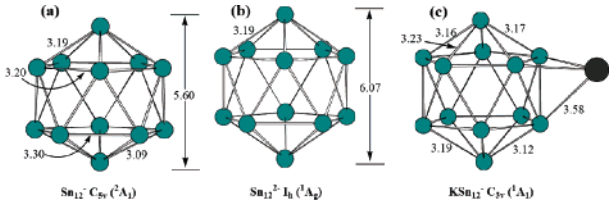

Figure 2. Optimized structures: (a) Sn_{12}^-; (b) Sn_{12}^{2-}; (c) KSn_{12}^-. The bond distances and cage diameters are in Å. See Supporting Information for computational details.

C_{3v} KSn_{12}^- (Figure 2c) yields a calculated VDE (3.0 eV) in good agreement with the experiment (3.08 ± 0.03 eV), lending considerable credence to the stability of the Sn_{12}^{2-} cage.

To help understand the chemical bonding in the I_h−Sn_{12}^{2-} cage, we analyzed its valence molecular orbitals. Sn has a valence electron configuration of $5s^25p^2$. We found that because of the large energy separation between the 5s and 5p shells there is little s−p hybridization in Sn_{12}^{2-}. The $5s^2$ electron pair is largely localized on each Sn atom, leaving only the two 5p electrons responsible for bonding on the Sn_{12}^{2-} cage. Figure 1c shows the valence molecular orbital diagram at the scalar relativistic (SR) and spin−orbit (SO) coupled levels. It is shown that the MO levels of Sn_{12}^{2-} with the SO effect are in excellent agreement with the PES spectral pattern of $K^+[Sn_{12}^{2-}]$; the observed spectral features (X, A, B, C, D) are labeled in Figure 1c next to the SO levels.

Among the thirteen valence orbitals, four are delocalized radial π-bonding orbitals (a_g and t_{1u}) formed from the radial p_z atomic orbitals. The remaining nine orbitals (g_u and h_g) are delocalized in-sphere σ-bonding orbitals from the tangential p_x and p_y atomic orbitals (Figure S3a). The bonding pattern in Sn_{12}^{2-} is remarkably similar to that in the famous $B_{12}H_{12}^{2-}$ molecule (Figure S3b), which was first predicted to be a stable molecule by molecular orbital theory[16] and subsequently synthesized.[17] The B_{12} cage in $B_{12}H_{12}^{2-}$ is also bonded similarly by four delocalized radial π-bonding orbitals and nine in-sphere delocalized σ orbitals with 12 localized B−H bonds, which are equivalent to the $5s^2$ electrons in the Sn_{12}^{2-} cage. Because of the delocalized π bonding in Sn_{12}^{2-} and its spherical symmetry, a name, stannaspherene, is suggested for this highly stable and symmetric cluster. In fact, our calculations suggest that the bare Sn_{12}^{2-} dianion is electronically stable with a 0.2 eV electron binding energy, more stable than C_{60}^{2-} or C_{70}^{2-}.[18]

Small polyhedral Sn clusters are known in inorganic complexes and the Zintl phases.[19,20] However, the I_h−Sn_{12}^{2-} empty cage has not been known before. The high stability of this cluster suggests that it may be synthesized in the solid state using suitable ligands or counterions. More excitingly, the Sn_{12}^{2-} cage has a diameter of ~6.1 Å, only slightly smaller than that of C_{60}, and can host an atom inside much like the endohedral fullerenes. Indeed, theoretical calculations have shown that $Cd@Sn_{12}$ is a stable I_h cage[21], and several endohedral Pb_{12} clusters, such as $Al@Pb_{12}^+$ and $Pt@Pb_{12}^{2-}$, have been synthesized.[22−24] A recent report revealed stable Cu−Sn cluster compositions from high-temperature annealing and suggested core−shell-type structures.[25] The stability of the stannaspherene and its large internal volume suggest that Sn_{12}^{2-} may trap many different types of atoms to form endohedral stannaspherenes.

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Supporting Information Available: Theoretical details, the comparison of the photoelectron spectra of Sn_x^- and Ge_x^- ($x = 11-13$), alternative structures for Sn_{12}^{2-}, and the comparison of the molecular orbital contours of Sn_{12}^{2-} and $B_{12}H_{12}^{2-}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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