

Communications: Investigation of the superatomic character of Al_{13} via its interaction with sulfur atoms

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We investigated Al_nS^- ($n=3-15$) and Al_nS_2^- ($n=7-15$) clusters with mass spectrometry and photoelectron spectroscopy. We found that Al_{13} is relatively robust when it reacts with sulfur atoms, indicating that it has some superatomic character. However, Al_{13} cannot be simply considered as a superatom when it interacts with sulfur due to the following reasons: Al_{13} 's icosahedral structure has been distorted slightly by sulfur atoms; the vertical detachment energies and adiabatic detachment energies of Al_{13}S^- and $\text{Al}_{13}\text{S}_2^-$ clusters are not significantly different from those of their neighboring clusters; and the charge distributions in Al_{13}S^- and $\text{Al}_{13}\text{S}_2^-$ do not necessarily associate with superatomic behavior of Al_{13} . © 2010 American Institute of Physics. [doi:10.1063/1.3374431]

Al_{13} has a high electron affinity (3.57 eV),¹ very close to the electron affinity of chlorine atom (3.61 eV).² It has 39 valence electrons, only one electron short to jellium model shell closing, thus, its electronic structure can be considered as similar to those of halogen elements.³ In addition, its geometric structure has been found to be a highly symmetric, regular icosahedron, which is remarkably stable. Owing to its high electron affinity, special geometric and electronic structure, it has been suggested by theoreticians that Al_{13} can be viewed as a “superatom” or “superhalogen.”⁴ Many experiments have been carried out to investigate the superatom properties of Al_{13} . Thomas and co-workers^{5,6} conducted mass spectrometric and anion photoelectron spectroscopic studies on LiAl_n^- and KAl_n^- clusters. Their studies show that LiAl_{13} and KAl_{13} clusters might contain ionic bonding between the alkali cations and intact Al_{13}^- subunits. Bergeron *et al.*⁷ found that Al_{13}I^- is very stable and the extra electron charge in Al_{13}I^- is mostly localized at the Al_{13} unit. The same authors also found that the pronounced stability of $\text{Al}_{13}\text{I}_n^-$ clusters is associated with complementary pairs of iodine atoms occupying the on-top sites on the opposing Al atoms of the Al_{13} core.⁸ These experimental results have been considered as strong support to the theoretical prediction of superhalogen Al_{13} .

However, a recent paper by Han *et al.*⁹ argued that the extra electron charge is mostly localized on Al_n for all Al_nI^- and Al_nI_2^- clusters, therefore, they suggested that the electron charge localization in Al_{13}I^- and $\text{Al}_{13}\text{I}_2^-$ does not correlate with any superatomic behavior but has a simple electrostatic explanation. They also pointed out that the molecular orbital perturbation by two iodine atoms for Al_{15}^- is quite similar to that for Al_{13}^- , which means Al_{13} is not special when it interacts with iodine. Although it has been agreed by those authors that Al_{13} can be viewed as a superatom in the case of KAl_{13} , it is uncertain whether Al_{13} cluster can be considered as a superatom in general term.

We would like to propose that, in order to be considered as a *general* superatom, a cluster must be able to participate into chemical reactions as a whole unit and maintain its integrity before and after the reactions; further, it should be able to participate in many types of reactions and still maintain its integrity in those reactions. Based on that proposal, Al_{13} should be able to participate in many other reactions if it is, in general, a superatom. Hence, we decided to test the superatom properties of Al_{13} via its interaction with sulfur.

The experiments were conducted on a home-built apparatus consisting of a time-of-flight mass spectrometer and a magnetic-bottle photoelectron spectrometer, which has been described elsewhere.¹⁰ The Al_nS_m^- clusters anions were produced by laser vaporization of an Al/S mixture disk target, cooled with helium carrier gas, and mass-analyzed with the time-of-flight (TOF) mass spectrometer. Size-selected Al_nS_m^- clusters anions were photodetached with 266 nm photons. And the resultant electrons were energy-analyzed with the magnetic-bottle photoelectron spectrometer. The resolution of the magnetic-bottle photoelectron spectrometer was ~ 40 meV at electron kinetic energy of ~ 1 eV. The photoelectron spectra were calibrated with known spectra of Cu^- and Au^- .

Figure 1 shows a comparison between the mass spectra of cluster anions generated by laser ablation of a pure aluminum target and an Al/S mixture target (Al/S atomic ratio 150:1). In the mass spectrum obtained with the pure aluminum target [Fig. 1(a)], the Al_{13}^- mass peak is significantly higher than its neighbors. Addition of sulfur into aluminum target changed the TOF mass spectrum dramatically. As we can see, in the mass spectrum [Fig. 1(b)] obtained with the Al/S mixture target, the Al_{13}^- mass peak does not show any special intensity although the percentage of sulfur in the sample is only about $\sim 0.66\%$. It is worth mentioning that the mass intensities of Al_{13}S^- and $\text{Al}_{13}\text{S}_2^-$ are not special, either.

Figure 2 presents the photoelectron spectra of Al_nS^- ($n=3-15$) and Al_nS_2^- ($n=7-15$) cluster anions with 266 nm photons. The vertical detachment energies (VDEs) and adiabatic detachment energies (ADEs) of Al_nS^- and Al_nS_2^- clus-

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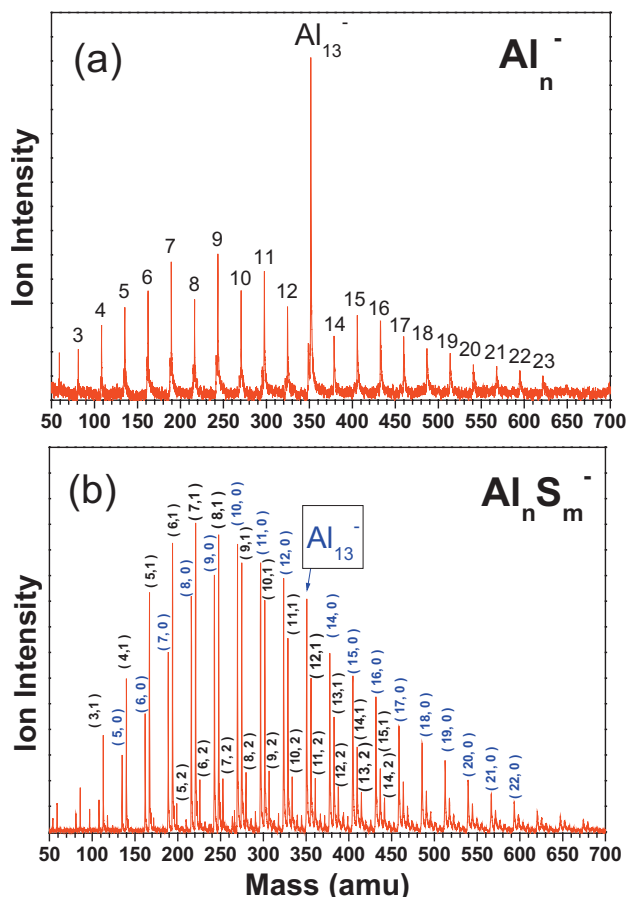


FIG. 1. Differences between the clusters obtained with a pure aluminum target and those with an Al/S mixed target. (a) Mass spectrum obtained with the pure aluminum target. (b) Mass spectrum obtained with the Al/S target (atomic ratio 150:1). The major peaks in (b) are labeled with notations of (n, m) where n denotes the number of Al atoms and m that of S atoms.

ter anions estimated from the photoelectron spectra are listed in Table S1.¹¹ Note the photoelectron spectra of small aluminum-sulfur clusters, such as $Al_n S^-$ ($n=1-9$) and $Al_n S_m^-$ ($n \leq 5, m \leq 3$), have also been reported by Nakajima *et al.*,^{12,13} our spectra are consistent with their work.

Figure 3 shows the variation in VDEs and ADEs with the number of aluminum atoms (n) in $Al_n S^-$ and $Al_n S_2^-$ clusters. We can observe an odd-even oscillation of VDEs and ADEs, that is, the $Al_n S^-$ and $Al_n S_2^-$ clusters with odd numbers of aluminum atoms have relatively higher VDEs and ADEs than their even-sized neighbors (except for $Al_3 S^-$). This probably can be explained with the number of valence electrons in the clusters. Since the total number of valence electrons is even for even-sized $Al_n S$ and $Al_n S_2$ neutral clusters, addition of an excess electron to the even-sized neutral clusters would result in one unpaired electron, while addition of the excess electron to the odd-sized neutral clusters would leave no unpaired electron. Therefore, the odd-sized cluster anions have relatively higher VDEs and ADEs than the even-sized cluster anions. In Fig. 3, the VDE of $Al_{11} S^-$ cluster is the highest. We note that the total number of valence electrons in $Al_{11} S^-$ including the negative charge is 40, which is jellium model close shell. It indicates that the electronic properties of $Al_n S$ clusters can still be explained with jellium model. We would also like to point out that the VDEs and

ADEs of $Al_{13} S_{1-2}^-$ fit the general trend for all $Al_n S_{1-2}^-$.

We investigated the structures of $Al_n S^-$ and $Al_n S_2^-$ ($n=12, 13$) clusters with density functional calculations using the GAUSSIAN 03 program package¹⁴ at B3LYP/6-31G (d) level. The geometries of the low-lying isomers obtained by theoretical calculations are shown in Fig. 4. No symmetry constraint was imposed during the geometry optimizations. The vibrational frequencies were calculated to confirm that the structures are real minima. The total energies of all optimized structures were refined using single-point B3LYP/6-311+G* calculations. The calculated relative energies, VDEs, and ADEs of these isomers are summarized in Table I.

The low-energy isomers of $Al_{12} S^-$ all have S atom occupying an exterior site rather than interior site. We have tried to put the S atom at the center of aluminum cage, such as $I_h \cdot S @ Al_{12}$ structure, as initial structures for geometric optimization, but found the cluster is relatively unstable when the S atom occupies the interior site. The calculated VDE and ADE of isomer 1A are in agreement with the experimental values. The theoretical VDEs of isomer 1B and 1C are close to the experimental data, but their relative energy are higher than isomer 1A and their ADEs are much lower than the experimental values. Thus, the existence of isomer 1B and 1C in our experiments can be excluded. Thus, isomer 1A might be the most possible isomer detected in our experiments. The structure of Al_{12} unit in isomer 1A is very different from the structures of bare Al_{12} or Al_{12}^- .¹⁵⁻¹⁷ For the $Al_{12} S_2^-$ cluster, the sulfur atoms also prefer to occupy the exterior sites. The theoretical VDE (3.06 eV) and ADE (2.52 eV) of isomer 2A of $Al_{12} S_2^-$ are consistent with the experimental value. The Al_{12} unit in $Al_{12} S_2^-$ cluster is distorted significantly by addition of the sulfur atoms.

For $Al_{13} S^-$ cluster, the isomers 3A and 3B are nearly degenerated in energy. Isomer 3A has C_{2v} symmetry with the S atom occupying a bridge site. And isomer 3B has C_{3v} symmetry with the S atom bonded to three Al atoms equally. The theoretical ADEs of isomer 3A and 3B are calculated to be 2.85 eV, very close to the experimental value (3.00 eV). The theoretical VDE of isomer 3B agrees with the experiment better than that of isomer 3A. The theoretical VDE of isomer 3C is also close to the experimental value. However, its theoretical ADE is far off. Consequently, we suggest that isomer 3B probably is what is observed in the experiments. It is quite clear that the S atom in $Al_{13} S^-$ cluster also prefer to occupy the exterior site. In contrast to the large distortion of Al_{12} 's structure by sulfur atom, addition of sulfur atom to Al_{13} causes very little deformation in the structure of Al_{13} unit. For the low-lying isomers of $Al_{13} S_2^-$, the S atoms also stay outside of the Al_{13} unit. The VDEs of isomers 4A, 4B and 4C are all consistent with the experimental VDE of $Al_{13} S_2^-$. The ADEs of isomers 4B and 4C are 2.37 and 2.05 eV, respectively. These values are far away from the experimental ADE (3.11 eV). The ADE of isomer 4A is about 0.55 eV lower than the experiment value, which can be considered as a reasonable agreement at this level of theory. Compared to the structure of $Al_{13} S^-$, the Al_{13} unit in $Al_{13} S_2^-$ is more distorted than that in $Al_{13} S^-$, but the distortion is not so radical as that in $Al_{12} S_2^-$. This indicates that Al_{13} is more

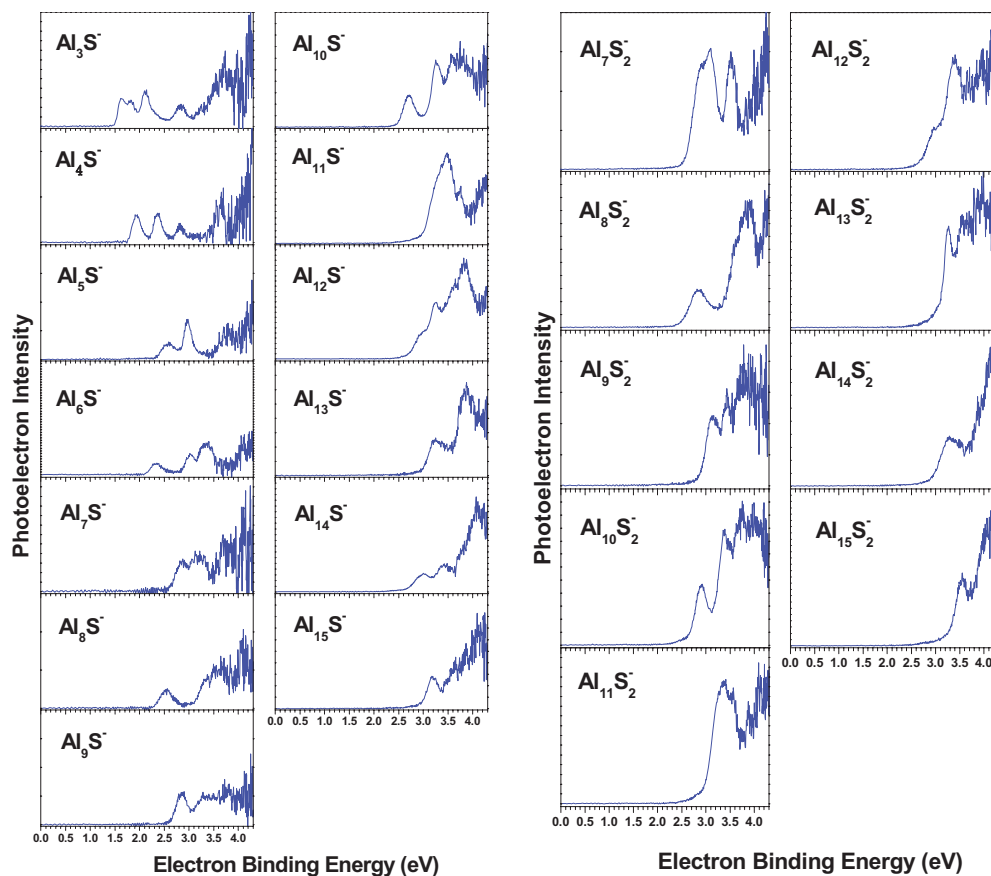


FIG. 2. Photoelectron spectra of Al_nS^- ($n=3-15$) and Al_nS_2^- ($n=7-15$) cluster anions measured with 266 nm photons.

stable than Al_{12} when it interacts with a sulfur atom. That is consistent with the characteristics of a superatom.

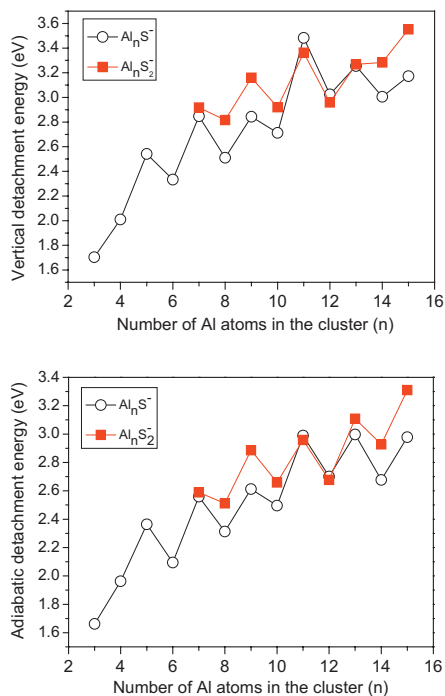
One major reason for Al_{13} to be considered as superatom (superhalogen) is its high electron affinity. Since the electron affinity of Al_{13} is much higher than that of sulfur atom (2.08 eV), we would expect most of the negative charge in Al_{13}S^- cluster to be localized on Al_{13} . We investigated the charge distributions of Al_{12}S^- and Al_{13}S^- , and found that the excess electron is mainly localized on the Al_n core, with about $0.65e$

on Al_{12} and approximately from $0.60e$ to $0.65e$ on Al_{13} . Al_{13} is not very different from Al_{12} in this case. These results support the suggestion of Han and Jung⁹ that the localization of charge does not necessarily correlate with any superatomic behavior but has a simple electrostatic explanation. Analysis of charge distributions in $\text{Al}_{12}\text{S}_2^-$ and $\text{Al}_{13}\text{S}_2^-$ shows that the charges on Al_{12} and Al_{13} are $0.28e$ and $0.22e$, respectively, which is not consistent with any superatomic property.

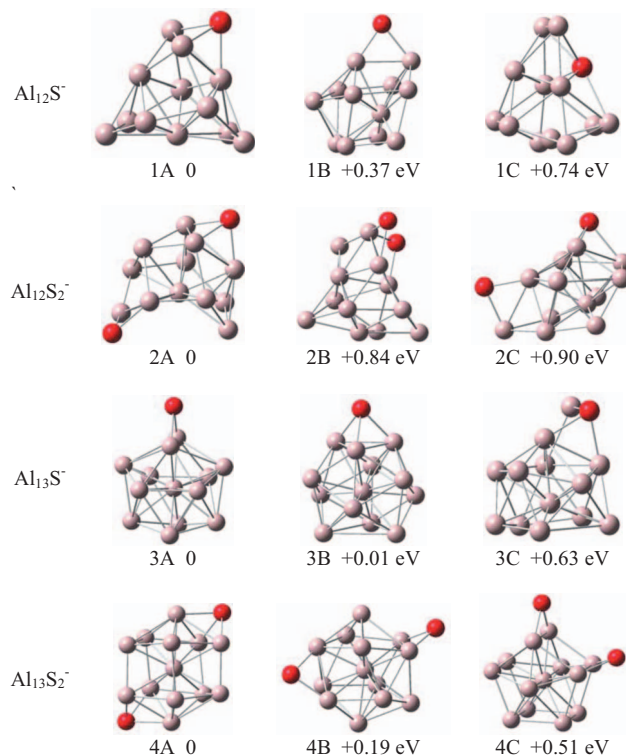
TABLE I. The calculated relative energies, VDEs, and ADEs of the low energy isomers of $\text{Al}_{12,13}\text{S}_{1,2}^-$ clusters as well as the comparison between the experimental and theoretical results.

Cluster	Symmetry	Multiplicity	ΔE (eV)	VDE (eV)		ADE (eV)	
				Theo.	Expt. ^a	Theo.	Expt. ^a
Al_{12}S^- (1A)	C_1	2	0	2.93	3.02	2.65	2.70
	C_1	2	0.37	2.97		2.28	
	C_1	2	0.74	2.89		1.92	
$\text{Al}_{12}\text{S}_2^-$ (2A)	C_1	2	0	3.06	2.96	2.52	2.68
	C_1	4	0.84	2.54		1.68	
	C_1	4	0.90	2.48		1.61	
Al_{13}S^- (3A)	C_{2v}	1	0	2.88		2.85	
	C_{3v}	1	0.01	3.07	3.25	2.85	3.00
	C_1	1	0.63	2.98		2.22	
$\text{Al}_{13}\text{S}_2^-$ (4A)	C_2	1	0	2.94	3.27	2.56	3.11
	C_2	1	0.19	3.12		2.37	
	C_{2v}	3	0.51	3.29		2.05	

^aEstimated experiment uncertainties: ± 0.08 eV.

FIG. 3. VDEs and ADEs of $Al_n S_m^-$ cluster anions.

To summarize, our results show that Al_{13} is quite robust when it reacts with sulfur atoms. Addition of sulfur atoms to Al_{13} causes only slightly deformation in Al_{13} 's icosahedral structure. That is somewhat consistent with the superatomic behavior. Nevertheless, the structures of Al_{13} unit in $Al_{13}S^-$ and $Al_{13}S_2^-$ are still different from those of bare Al_{13} or Al_{13}^- even if the distortion is small. That is not completely in agreement with the superatomic behavior. Other observations do not support the superatomic behavior of Al_{13} . First, our mass spectral results show that the mass distributions of Al_{13}^- and $Al_{13}S^-$ generated by an Al/S sample does not support the superatomic character of Al_{13} . Second, the VDEs of $Al_{13}S^-$ and $Al_{13}S_2^-$ are not significantly different from those of their neighbors. Third, the charge distributions in $Al_{13}S^-$ and $Al_{13}S_2^-$ do not necessarily associate with superatomic behavior. Burgert *et al.*¹⁸ found that the isolated Al_{13}^- clusters react with HCl only if additional energy is supplied, indicating that Al_{13}^- is quite stable at low kinetic energy. However, the aluminum atoms can be ruptured away from Al_{13}^- clusters as soon as the reaction is initiated, which means Al_{13} cannot keep its integrity upon reaction with HCl. It was found two decades ago that Al_{13}^- is quite inert when it reacts with O_2 .¹⁹ Recently, Burgert *et al.* showed that the reaction rate of Al_{13}^- increased significantly when singlet oxygen was used instead of triplet oxygen.²⁰ And the theoretical calculations of Yuan *et al.*²¹ suggest that the reaction between Al_{13}^- and O_2 is exothermic and the inertness of Al_{13}^- is mainly due to the presence of a reaction barrier (2.9–5.8 kcal/mol). These findings are in agreement with our study. Overall, we would like to suggest that Al_{13} has some superatomic character and behavior, but it cannot be simply considered as a superatom in general term.

FIG. 4. Structures and relative energies of the low-lying isomers of $Al_{12}S^-$, $Al_{12}S_2^-$, $Al_{13}S^-$, and $Al_{13}S_2^-$. The relative energies to the most stable isomers are shown. The sulfur atoms are shown in red.

- X. Li and L.-S. Wang, *Phys. Rev. B* **65**, 153404 (2002).
- U. Berzins, M. Gustafsson, D. Hanstorp, A. Klinkmüller, U. Ljungblad, and A. M. Mätensson-Pendrill, *Phys. Rev. A* **51**, 231 (1995).
- X. Li, H. B. Wu, X. B. Wang, and L. S. Wang, *Phys. Rev. Lett.* **81**, 1909 (1998).
- S. N. Khanna and P. Jena, *Phys. Rev. B* **51**, 13705 (1995).
- O. C. Thomas, W. J. Zheng, T. P. Lippa, S. J. Xu, S. A. Lyapustina, and K. H. Bowen, *J. Chem. Phys.* **114**, 9895 (2001).
- W. J. Zheng, O. C. Thomas, T. P. Lippa, S. J. Xu, and K. H. Bowen, *J. Chem. Phys.* **124**, 144304 (2006).
- D. E. Bergeron, A. W. Castleman, T. Morisato, and S. N. Khanna, *Science* **304**, 84 (2004).
- D. E. Bergeron, P. J. Roach, A. W. Castleman, N. Jones, and S. N. Khanna, *Science* **307**, 231 (2005).
- Y. K. Han and J. Jung, *J. Am. Chem. Soc.* **130**, 2 (2008).
- H.-G. Xu, Z.-G. Zhang, Y. Feng, J. Yuan, Y. Zhao, and W. Zheng, *Chem. Phys. Lett.* **487**, 204 (2010).
- See supplementary material at <http://dx.doi.org/10.1063/1.3374431> for the experimental VDEs and ADEs of $Al_n S_{1,2}^-$ clusters.
- A. Nakajima, T. Taguwa, K. Nakao, K. Hoshino, S. Iwata, and K. Kaya, *J. Chem. Phys.* **102**, 660 (1995).
- A. Nakajima, N. Zhang, H. Kawamata, T. Hayase, K. Nakao, and K. Kaya, *Chem. Phys. Lett.* **241**, 295 (1995).
- M. J. Frisch, G. W. Trucks, and H. B. Schlegel *et al.*, GAUSSIAN 03, Revision B.04, Gaussian, Inc., Pittsburgh, PA, 2003.
- B. K. Rao and P. Jena, *J. Chem. Phys.* **111**, 1890 (1999).
- Z. H. Li, A. W. Jasper, and D. G. Truhlar, *J. Am. Chem. Soc.* **129**, 14899 (2007).
- R. Fournier, *J. Chem. Theory Comput.* **3**, 921 (2007).
- R. Burgert, S. T. Stokes, K. H. Bowen, and H. Schnockel, *J. Am. Chem. Soc.* **128**, 7904 (2006).
- R. E. Leuchtner, A. C. Harms, and J. A. W. Castleman, *J. Chem. Phys.* **91**, 2753 (1989).
- R. Burgert, H. Schnockel, A. Grubisic, X. Li, S. T. Stokes, K. H. Bowen, G. F. Gantefor, B. Kiran, and P. Jena, *Science* **319**, 438 (2008).
- Q. H. Yuan, J. B. Li, X. L. Fan, W. M. Lau, and Z.-F. Liu, *Chem. Phys. Lett.* **489**, 16 (2010).