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Electronic structures of small sulfur clusters

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The electronic structures of small sulfur clusters, S_2–S_{12}, are calculated using the *ab initio* self-consistent discrete variational local-density-functional method, and the calculated ionization potential curve is in good agreement with that from experiment in the range from S_2 to S_8, and the calculated ionization potentials of clusters from S_9 to S_{12} are reliably predicted where measurements are lacking. We suggest that the different mixtures of atomic orbitals 3*s* and 3*p* on the highest occupied molecular orbitals for different clusters are related to the change of ionization potential with the cluster size. In addition, we point out that the two sulfur dimers in S_4 are bound by the van der Waals force.

I. INTRODUCTION

Since Berkowitz and Marquart studied sulfur clusters experimentally,[1] the stable geometric structures of small sulfur clusters, S_2–S_{12}, have been studied by experiments[2–5] and by theoretical calculations.[6–10] Although some experimental techniques such as x-ray structural analysis, vibrational spectroscopy, and so on, may provide some structural parameters such as bond length, bond angle, and dihedral angle, they cannot describe the structural model directly. In order to further determine the ground-state structures of the small sulfur clusters, several theoretical calculation methods, including both semiempirical calculations [modified neglect of differential overlap (MNDO) and complete neglect of differential overlay (CNDO)] and *ab initio* calculations [molecular dynamics (MD) (Ref. 9) and molecular orbital[10]] were employed among them Refs. 9 and 10, have systematically calculated the structures and stabilities of small sulfur clusters, respectively. In contrast to the structural parameters from experiment, the structural models of Ref. 10 are more reliable.

On the other hand, Berkowitz and Lifschitz[11] measured the changes of the ionization potentials (IP's) with the sulfur cluster size by using the technique of electron impact, and the obtained IP curve is zigzag. Although Vezin *et al.*[12] explained the IP curve of lithium clusters with the electronic shell model,[13] unfortunately, this model is only suitable to explain the "magic numbers" for monovalent metal clusters, and is inefficient for sulfur clusters. Also, it is very difficult to give an interpretation of the measured IP curves of sulfur clusters from experiment. We consider that *ab initio* calculation is an effective way to attack this problem; however, to date, no theoretical calculation explains the IP curve of sulfur clusters. In this paper, we employ the DV-LDF (discrete variational local-density functional) method, which will be briefly described in Sec. II, to study the electronic structures of small sulfur clusters. The calculated IP curve is in good agreement with the one from experiment, and the changes in the IP's with the cluster size is discussed.

II. METHOD

The DV-LDF method is a kind of molecular-orbital calculation method, and its theoretical foundation is LDF theory. The key points of this method are summarized as follows:

(a) The one-electron Hamiltonian underlying the DV-LDF method is

$$\hat{H}(\mathbf{r})=-\tfrac{1}{2}\nabla^2+V_c(\mathbf{r})+V_{\mathrm{xc}}(\mathbf{r}) , \tag{1}$$

where the Coulomb potential is

$$V_c(\mathbf{r})=-\sum_\nu \frac{Z_\nu}{|\mathbf{r}-R_\nu|}+\int\frac{\rho(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} \tag{2}$$

and the local exchange-correlation potential, $V_{\mathrm{xc}}(\mathbf{r})$ is taken to be of the Von Barth-Hedin form,[14] with the parameters taken from Moruzzi, Janak, and Williams,[15] $\mathbf{R}_\nu$ is the site vector of the νth nucleus in the cluster.

(b) The matrix elements of the Hamiltonian and overlap matrices are obtained by a weighted summation over a set of discrete sample points $\mathbf{r}_\mathbf{k}$,[16] i.e.,

$$H_{ij}=\langle\chi_i|\hat{H}|\chi_j\rangle=\sum_k\omega(\mathbf{r}_k)\chi_i^*(\mathbf{r}_\mathbf{k})\hat{H}(\mathbf{r}_\mathbf{k})\chi_j(\mathbf{r}_\mathbf{k}) , \tag{3}$$

$$S_{ij}=\langle\chi_i|\chi_j\rangle=\sum_k\omega(\mathbf{r}_\mathbf{k})\chi_i^*(\mathbf{r}_\mathbf{k})\chi_j(\mathbf{r}_\mathbf{k}) , \tag{4}$$

where $\omega(\mathbf{r}_\mathbf{k})$ are appropriate integration weights. We choose 900 sample points per atom for all atoms in our calculations.

(c) The calculation of Coulomb integrals is simplified by introducing the average self-consistent charge density ρ_{scc} approximation[17]

$$\rho(\mathbf{r})=\sum_{\nu,n,l}f_{nl}^\nu|R_{nl}(r_\nu)|^2 , \tag{5}$$

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where f_{nl}^{ν} is the Mulliken population for the nl atomic shell of atom ν, and $R_{nl}(\mathbf{r}_\nu)$ is the corresponding radial wave function, with $\mathbf{r}_\nu = \mathbf{r} - \mathbf{R}_\nu$.

Thus the one-electron state, the energy eigenvalue, and the bond order[18,19] which measures the strength of a covalent bonding are obtained through the charge self-consistent process.

In addition, we also perform the calculation of the transition state to obtain the first ionization potentials of a cluster.

In our calculations, the geometric structures are taken from Ref. 10, as shown in Fig. 1, and the numerical atomic orbitals $1s2s2p3s3p$ are chosen. In order to check the reliability of the set of atomic orbitals in our calculation, we calculated cluster S_5 with two sets of atomic orbitals which are $1s2s2p3s3p$ and $1s2s2p3s3p3d4s4p$, respectively. The calculated electronic configurations are $1s^2 2s^2 2p^6 3s^{1.89} 3p^{4.09}$ and $1s^2 2s^2 2p^6 3s^{1.84} 3p^{4.02} 3d^{0.09} 4s^{0.02} 4p^{0.02}$, and the energies of the HOMO's (highest occupied molecular orbitals) are -6.25 and -6.20 eV, respectively. Clearly, the difference either between the two electronic configurations or between the two energies of the HOMO's is very small, which indicates that it is reasonable for us to use the atomic orbitals $1s2s2p3s3p$ to perform calculations.

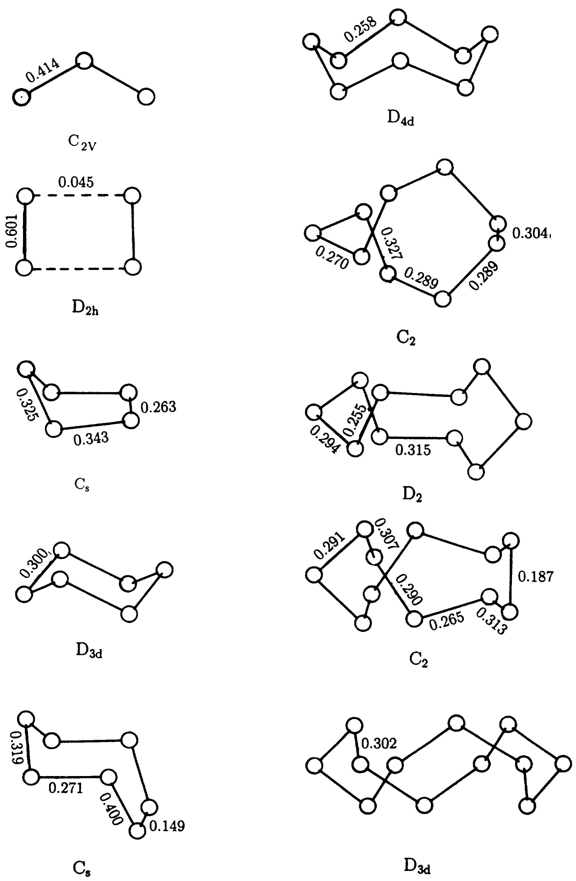

FIG. 1. The structures of small sulfur clusters, S_2–S_{12}. The labeled data are the calculated bond orders.

III. RESULTS AND DISCUSSION

Figure 2 displays the calculated IP's of small sulfur clusters from S_2 to S_{12}, and the experimental IP's which are available[11] for clusters from S_2 to S_8. The two IP curves exhibit the same trends; moreover, the calculated IP's of S_7 and S_8 are exactly accordant with the ones from experiment, respectively, indicating that not only that the geometrical structures of Ref. 10 are reasonable but also that our calculated IP's are reliable. So, though no experimental IP's can be used for comparison from S_9 to S_{12}, our calculated IP's may properly predict the trend of IP's in this range of the cluster size. We hope there will be experimental IP's to test this prediction. On the other hand, after carefully analyzing the trend of the calculated IP cure, we find that the trend of IP's from S_2 to S_6 is similar to that from S_7 to S_{11}; the IP's of the latter are smaller than the ones of the former in toto, that is, a periodicity is shown in our calculated IP curve of sulfur clusters. This kind of periodicity is also found in the experimental IP curve of Se clusters,[20] where the IP curve from Se_2 to Se_{35} is given. However, comparison the geometric structures of the corresponding clusters such as S_2 to S_7, S_3 to S_8, S_4 to S_9, S_5 to S_{10}, and S_6 to S_{11}, seem not to be a direct way to explain for this periodicity efficiently. Since the electronic shell model also seems unsuitable to explain the periodicity it is necessary that other points of view be used to study this periodicity in detail.

The calculated electronegativity and the energy gap between HOMO and LUMO (lowest unoccupied molecular orbital) for each cluster are listed in Table I. Here the electronegativity of a cluster is defined as the negative value of the HOMO energy.[21] From Table I, the variational tendency of the electronegativities with cluster size is the same as that of the calculated IP's. As is known, electronegativity is a measure of the ability that some electronic charges of a cluster are changed, in other words, the larger the value of the electronegativity of a cluster, the harder it is for a cluster to lose its electronic charges. Therefore it requires more energy to ionize one

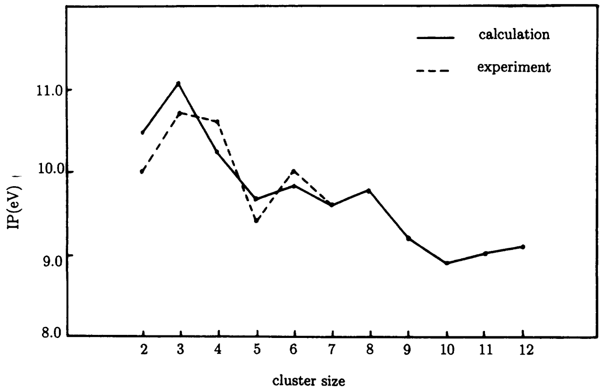

FIG. 2. Ionization potentials of S_n as a function of cluster size. Comparison between the calculated IP's (for $n = 2$–12) and the experimental IP's (for $n = 2$–8).

TABLE I. The electronegativities and the HOMO-LUMO gaps for sulfur clusters. EN denotes electronegativity.

	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}	S_{11}	S_{12}
EN	5.96	7.19	6.49	6.20	6.80	6.64	7.15	6.57	6.50	6.67	6.86
gap (eV)	5.06	1.55	1.44	3.13	3.79	3.62	4.09	3.63	3.57	3.54	3.87

TABLE II. Mulliken populations of HOMO's and the average valence electronic configurations for clusters.

Sn	Mulliken population	Electronic configurations
S_2	100%3p	$3s^{1.98}3p^{4.02}$
S_3	13%3s +86%3p	$3s^{1.92}3p^{4.08}$
S_4	100%3p	$3s^{1.97}3p^{4.03}$
S_5	1.5%3s +88%3p	$3s^{1.90}3p^{4.10}$
S_6	8.6%3s +91%3p	$3s^{1.88}3p^{4.12}$
S_7	1.5%3s +94%3p	$3s^{1.87}3p^{4.13}$
S_8	14%3s +86%3p	$3s^{1.86}3p^{4.14}$
S_9	3%3s +96%3p	$3s^{1.87}3p^{4.13}$
S_{10}	1.5%3s+97%3p	$3s^{1.88}3p^{4.12}$
S_{11}	2%3s +94%3p	$3s^{1.86}3p^{4.14}$
S_{12}	4%3s +86%3p	$3s^{1.87}3p^{4.13}$

valence electron valence electron in the case of a larger value of electronegativity. For this reason, there is the same tendency between the electronegativities and the IP's for the clusters. However, the changes of the gaps with the cluster size are only in rough agreement with those of IP's. In addition, it is noted that the gaps are larger than 3.10 eV for clusters from S_5 to S_{12}, and are small for clusters S_3 and S_4; that is, there is a large gap for a ring sulfur clusters, and a small gap for an open sulfur cluster except for S_2, which indicates that the ring sulfur clusters are more stable than the open sulfur clusters. Furthermore, among all of the sulfur clusters concerned, the gap for the S_8 is the largest; therefore, it is more stable than the other clusters, which is compatible with the results from both experiment and total-energy calculation.

Table II lists the Mulliken populations of HOMO's for the sulfur clusters. The main components of a HOMO for a sulfur cluster are the valence orbitals 3p of sulfur atoms. Furthermore, it is found that for any three-neighbor clusters, if the 3s component on the HOMO of the second cluster is greater than the ones of the other two, the IP of this cluster is also larger than the ones of the other two clusters, displaying a peak in Fig. 2. Thus any peak in the IP curve is related to a local maximum of the 3s-3p hybridization in the local range corresponding to three-neighbor clusters. It is not difficult for us to understand this phenomenon; in fact, on the one hand, the ionization potential of a cluster reflects the ability that one electron on a HOMO is ionized; on the other hand, the energy of the 3s orbital is lower than that of the 3p orbital, so the electron on a HOMO which characterizes the features of 3s and 3p is not easily ionized, corresponding to a higher IP. For these reasons, we conclude that the variant 3s-3p hybridization of HOMO's for different sulfur clusters are associated with the wavy IP curve of these clusters.

Table II also lists the average valence-electron distributions of a sulfur atom in clusters. The electronic configuration of S_4 is very close to that of S_2, which implies that the interaction between the sulfur dimers in S_4 is very weak, i.e., the two sulfur dimers are bound by the van der Waals force. Moreover, the electronic configuration of S_2 is very close to that of an isolated atom, $3s^2 3p^4$. However the electronic configurations of the other clusters, S_3 and S_5–S_{12}, show that more than 0.1 electrons are transferred from the 3s orbital to the 3p orbital. Thus, in summary, there is noticeable 3s-3p hybridization in most sulfur clusters studied here except for S_2 and S_4 consistent with the result of Mulliken populations of HOMO's.

In addition, a calculation of related bond orders between sulfur atoms in a cluster have also been performed, as displayed in Fig. 1. It can be seen that the interaction between the two dimers in S_4 is indeed very weak, and in the cases of S_7 or S_{11} there is a weak S-S bond, which can be broken down more easily.

IV. CONCLUSIONS

In summary, after carrying out calculations of electronic structures of small sulfur clusters by using the DV-LDF method, we have obtained ionization potentials of the sulfur clusters from S_2 to S_{12}, and the calculated IP's are in good agreement with those from experiment in the range S_2–S_8. Also, the IP's for clusters S_8–S_{12} have been predicted. The calculated IP curve shows a periodicity that is somewhat similar to the periodicity in the experimental IP curve of Se clusters, and the periodicity should be studied further. After an analysis of the electronic structures, we suggest that the different 3s-3p hybridizations for different clusters are associated with the wavy IP curve. In addition, we point out that the two sulfur dimers in S_4 are bound by van der Waals force.

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