PHYSICAL REVIEW A, VOLUME 62, 053201

Small clusters of II-VI materials: Zn_iO_i, $i=1-9$

Jon M. Matxain, Joseph E. Fowler, and Jesus M. Ugalde
Kimika Fakultatea, Euskal Herriko Unibertsitatea, PK 1072, 20018 Donostia, Euskadi, Spain

(Received 12 January 2000; revised manuscript received 11 May 2000; published 18 October 2000)

Improvements in the characterization of II-VI compound-based solar cells, and the recent experimental characterization of small clusters and nanoparticles, make the study of small II-VI clusters very interesting. In this work, the ground states of small Zn_iO_i clusters are studied, where $i=1-9$. Ringlike structures have been found to be the global minima for clusters as large as $i=7$, and three-dimensional spheroid structures for larger ones, where $i=8$ and 9. This is due to the stability of obtuse O-Zn-O angles in the first case, and to the stability gained from higher coordination in the second case. Three-dimensional structures may be envisioned as being built from Zn_2O_2 and Zn_3O_3 rings, as was the case for ZnS three-dimensional global minima and other ZnO calculations. Calculated natural orbital charges become larger as the cluster size increases, showing a tendency toward bulk charges.

PACS number(s): 36.40.−c

I. INTRODUCTION

During the last decade interest in II-VI compounds has increased notably due to their paramount technological potential. Applications such as photovoltaic solar cells [1–10], optical sensitizers [11], photocatalysts [12,13], or quantum devices [14] have led to extensive investigations. To understand these phenomena it is essential to study the structure and electronic properties of these compounds, thereby providing more information for the optimization of these materials in order to enhance their applicability. Many theoretical studies have been reported concerning the electronic structure of these compound surface semiconductors. It was demonstrated that within the density-functional theory framework it is possible to reproduce the band energies and band gaps, along with the lattice constants, of the studied system. In order to do this, an approach based on self-interaction-corrected pseudopotentials was developed by Pollmann and co-workers [15–20], which is a valuble tool for studying quantitatively well-ordered, clean semiconductor surfaces.

Nevertheless, there are some properties related to these compounds that have been seen to be local phenomena—that is, when they occur, they occur at a certain point on the surface. One property of this type is adsorption. Thus it is important to study small clusters of these compounds, whose electronic and structural properties could give insight into understanding these local properties. In addition, the fact that cluster and nanoparticle characterization is becoming technologically possible is remarkable. This makes cluster science more interesting, since in addition to the capability of understanding some surface-related properties, the improvement of applications through the use of nanotechnology could be possible. Therefore, the literature in the field is growing rapidly. Many experimental [21–26] and theoretical [27–31] studies have been reported concerning clusters of various compositions, which have important and interesting applications.

Due to the interest in both II-VI compounds and clusters, it occurred to us that it would be interesting to perform a theoretical study of II-VI compound clusters, in this way fusing both fields. In this work we focus on zinc oxide clusters, Zn_iO_i, $i=1-9$. Previous molecular-dynamic calculations predicted that spheroid ZnO clusters are stable for $i \geqslant 11$, which may be related to fullerene-type structures [32]. These spheroid structures are built from hexagons and rombi—in other words, rings of Zn_2O_2 rombi, or Zn_3O_3 hexagons. In a previous work on zinc sulfide clusters we found similar building blocks used in order to form related spheroid structures [33].

II. METHOD

All geometries were fully optimized using the hybrid [34] Becke 3 Lee-Yang-Perdew (B3LYP) approximate gradient-corrected density-functional procedure [35–37]. Harmonic vibrational frequencies were determined by analytical differentiation of gradients.

The relativistic compact effective core potentials and shared-exponent basis set [38] of Stevens, Krauss, Basch, and Jasien (SKBJ) was used as the basic basis set in this study. *d* electrons of Zn were included in the valence, and an extra *d* function was added on both Zn ($\alpha=0.3264$) and O ($\alpha=0.85$) atoms, due to their importance in the formation of bonds. Note that pure angular momentum functions were used throughout this study. We denote the final basis set used as SKBJ(d).

Because there are so many possible structures for these clusters, several starting points for these complete B3LYP-SKBJ(d) optimizations were generated using a simulated annealing approach at the Stewart semiempirical model parameterization (PM3) [39] level of theory. Of course, additional starting points were derived from simple chemical intuition.

All the geometry optimizations and frequency calculations were carried out with the GAUSSIAN98 [40] package. For the PM3 simulated annealing technique the HYPERCHEM [41] program was used.

A. Basis set selection

In Sec. II it was mentioned that the basis set used during these calculations was SKBJ(d). Although a larger basis set is not expected to change the geometry of the obtained struc-

TABLE I. Relative energies (kJ/mol) between two minima of the same cluster size, calculated with the three described basis sets.

	SKBJ(d)	SKBJ(exp)	TZ2P
$\triangle E$ ($E_{GM^{(4)}}$-$E_{LM^{(4)}}$)	245.15	254.73	208.83
$\triangle E$ ($E_{GM^{(8)}}$-$E_{LM_1^{(8)}}$)	13.54	19.55	2.18
$\triangle E$ ($E_{GM^{(8)}}$-$E_{LM_2^{(8)}}$)	46.70	26.64	92.19

tures significantly, the relative energies between them may be affected. In order to check the reliability of our SKBJ(d) basis set, single-point energy calculations using larger basis sets were performed on several structures which will be detailed below. Two other basis sets were examined. The first was a simple expansion of the previously described SKBJ(d) basis.

Two s and p functions (with α=1.335122 and 1.120129), one d function (α=2.561376), and one f function (α =3.115413) were added in the Zn basis. The SKBJ(d) basis was expanded for O as well with the two new s and p functions having exponents α=1.206642 and 0.561051, and the f function an exponent of α=1.666029.

All of these added functions were energy optimized at the MP2 level of theory using the GAMESS [42] package. As the SKBJ(d) basis set only has one d function on O, it was decided that upon the addition of another function, the exponents of both should be energy optimized. The exponents for the two d functions in this expanded basis were 2.179302 and 0.628849. This expanded basis set will be referred to as SKBJ(exp). The second examined basis set was an all electron triple-ζ double polarization (TZ2P) basis ($14s11p6d2f/10s8p3d2f$) for Zn [43–45] and ($11s5p2d1f/4s3p2d1f$) for O [46,47]. The relative energies between two minima of each cluster size chosen is shown in Table I.

All basis sets predict both the same global minima and the sequential positioning of the local minima. Nevertheless, for Zn_8O_8 the relative energies are quite small, and therefore we have decided to perform single-point calculations with both SKBJ(exp) and TZ2P for cases where the relative energies are smaller than 100 kJ/mol. In this way the validity of the SKBJ(d) relative energies is checked,

B. Reliability of B3LYP results

In order to check the feasibility of the B3LYP calculations, coupled cluster calculations [48,49] with single and double [50–53] substitutions and a correction term for the triple [54] substitution [CCSD(T)], were carried out for Zn_iO_i, $i=2$ and 3. For the smallest cluster, the TZ2P basis set was chosen, but the computational effort increased dramatically from $i=2$ to 3. Thus, only the relative energy corresponding to $i=2$ was calculated with this TZ2P basis set. Nevertheless we performed CCSD(T) calculations for $i=2$ and 3, with a smaller basis set, i.e., SKBJ(d). The obtained results for the relative energy of the first local minimum with respect to the ground state are shown in Table II. Note that for $i=2$, the CCSD(T)-TZ2P and CCSD(T)-SKBJ(d) relative energies are very similar: 188.06 and 183.04 kJ/mol, respectively. Note that part of the difference should be ascribed to relativistic effects that, although they are known [55] to be smaller for the first-row transition metals, are heaviest for Zn. This reinforces our statement of Sec. II A on the reliability of the SKBJ(d) basis set and validates the use of CCSD(T)-SKBJ(d) relative energies as reference values instead of the computationally more demanding CCSD(T)-TZ2P energies for further checks.

Both CCSD(T) and B3LYP predict the same sequence of global and local minima. The relative energies are found to be larger at the CCSD(T)-SKBJ(d) level of theory. For $i=2$ the difference between both methods is 62.87 kJ/mol, but it is lowered to 39.87 for $i=3$. These results illustrates the agreement between both methods and therefore B3LYP will be used hereafter.

III. RESULTS AND DISCUSSION

A. Structure of the calculated minima of Zn_iO_i clusters. $i=1-9$

In this section the calculated minima are presented. Although our interest is mainly centered on global minima, structures and properties of higher-lying local minima are presented as well.

The shown structures are labeled according to the following system: GM (global minimum) and LM (local minimum). The superscripts denote the number of ZnO units, and the subscripts the sequential positioning of the local minimum.

In order to make the presentation of the results easier to the reader, we have divided this section into small parts where structures of the same size are presented, starting from the smallest and moving on to the largest ones. In Table III geometrical values such as bondlengths and bond angles, point groups and electronic energies of all the calculated structures are given. These energies have been calculated with the SKBJ(d) basis set. It can be seen that for larger clusters, i.e., Zn_iO_i, $i\geqslant 6$, the relative energies are smaller than 100 kJ/mol, except for $LM_2^{(9)}$. Hence single-point calculations for these structures have been performed using the previously described SKBJ(exp) and TZ2P basis sets. The obtained results are shown in Table IV. SKBJ(exp) raises all relative energies except for $E_{GM^{(8)}}$-$E_{LM_2^{(8)}}$. TZ2P has exactly the opposite effect, and the effect is significantly larger. Note

TABLE II. CCSD(T) relative energies (kJ/mol) for Zn_iO_i, $i=2$ and 3.

	CCSD(T)-TZ2P	CCSD(T)-SKBJ(d)	B3LYP-SKBJ(d)
$\triangle E$ ($E_{GM^{(2)}}$-$E_{LM^{(2)}}$)	188.06	183.04	120.17
$\triangle E$ ($E_{GM^{(3)}}$-$E_{LM^{(3)}}$)	-	368.06	328.19

TABLE III. Zn-O bond lengths, O-Zn-O angles, symmetry groups and electronic energies of the calculated structures. For the local minima, energies relative to the corresponding global minimum in kJ/mol.

	R(Zn-O) Å	α(O-Zn-O)°	Point group	Elec. E. (hartree)
$GM^{(1)}$	1.713	–	$C_{\infty v}$	-241.987746
$GM^{(2)}$	1.892	103.7	D_{2h}	-484.121011
$LM^{(2)}$	1.976	106.2	C_{2v}	$+120.17$
$GM^{(3)}$	1.826	146.3	D_{3h}	-726.327972
$LM^{(3)}$	1.817–2.097	136.15	C_s	$+328.19$
$GM^{(4)}$	1.794	165.5	D_{4h}	-968.505017
$LM^{(4)}$	1.996	97	T_d	$+245.15$
$GM^{(5)}$	1.780	174.9	C_s	-1210.660351
$LM^{(5)}$	1.853–2.135	98.4–148.2	C_1	$+236.28$
$GM^{(6)}$	1.772	179.8	D_{6h}	-1452.805204
$LM_1^{(6)}$	1.907–2.102	134.0	D_{3d}	$+95.90$
$LM_2^{(6)}$	1.793–2.156	143.7–157.8	C_2	$+99.90$
$GM^{(7)}$	1.767	176.6	D_{7h}	-1694.944520
$LM_1^{(7)}$	1.766–1.882	143.6–172.6	C_s	$+43.91$
$LM_2^{(7)}$	1.783–2.180	92.93–165.2	C_s	$+74.86$
$GM^{(8)}$	1.86–2.185	92.6–152.5	D_{4d}	-1937.097872
$LM_1^{(8)}$	1.879–2.063	92.7–131.6	S_4	$+13.54$
$LM_2^{(8)}$	1.766	175.91	D_{4d}	$+46.70$
$GM^{(9)}$	1.89–1.99	93.1–130.7	C_{3h}	-2179.264012
$LM_1^{(9)}$	1.918–2.037	92.2–136.0	D_{3d}	$+29.79$
$LM_2^{(9)}$	1.766	175.1–177.7	C_1	$+127.91$

that all cases in which the TZ2P basis makes a large difference, comparison is being made between three-dimensional (3D) and ring structures. The TZ2P basis set stabilizes the 3D structures in every case. All basis sets predict both the same global minima and the sequential positioning of the local minima, except the case of $LM_1^{(6)}$ and $LM_2^{(6)}$, where SKBJ(d) and TZ2P predict the same sequential positioning, but SKBJ(exp) does not. Nevertheless the difference is very small, and all basis sets predict clearly the same global minimum. These results suggest that the SKBJ(d) energies given in Table III describe correctly the sequential positioning of the global and local minima, and that the calculated relative energies are correct. Therefore, throughout this paper results from Table III will be considered.

TABLE IV. Relative energies (kJ/mol) of the calculated structures of Zn_iO_i, $i=6-9$, using the SKBJ(d), SKBJ(exp), and TZ2P basis sets.

	SKBJ(d)	SKBJ(exp)	TZ2P
ΔE ($E_{GM^{(6)}}$-$E_{LM_1^{(6)}}$)	95.90	110.50	51.07
ΔE ($E_{GM^{(6)}}$-$E_{LM_2^{(6)}}$)	99.90	102.51	88.27
ΔE ($E_{GM^{(7)}}$-$E_{LM_1^{(7)}}$)	43.91	47.97	34.51
ΔE ($E_{GM^{(7)}}$-$E_{LM_2^{(7)}}$)	74.86	88.04	41.74
ΔE ($E_{GM^{(8)}}$-$E_{LM_1^{(8)}}$)	13.54	19.55	2.18
ΔE ($E_{GM^{(8)}}$-$E_{LM_2^{(8)}}$)	46.70	26.64	92.19
ΔE ($E_{GM^{(9)}}$-$E_{LM_1^{(9)}}$)	29.79	32.24	25.54

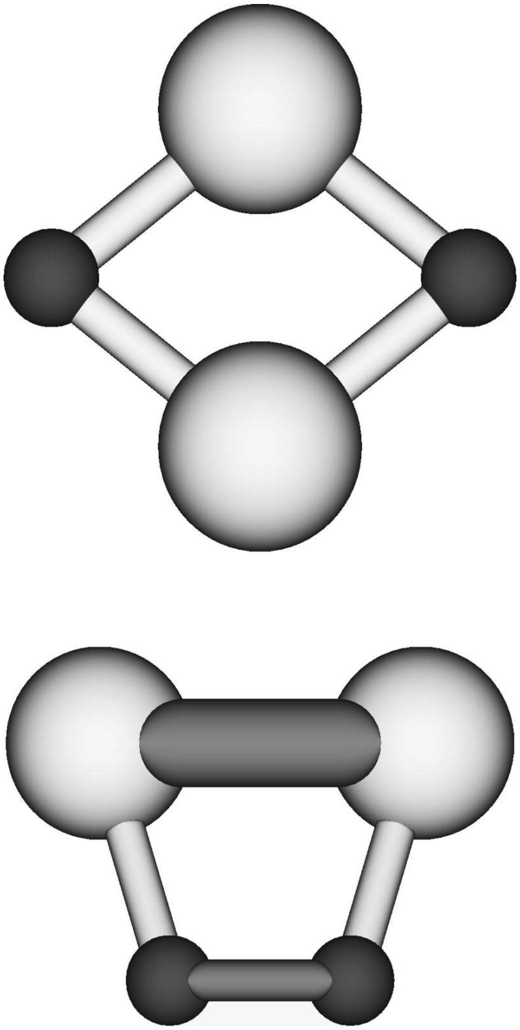

FIG. 1. Global minimum $GM^{(2)}$ and local minimum $LM^{(2)}$ of Zn_2O_2.

1. Zn_1O_1

Of course, a linear structure of $C_{\infty v}$ symmetry is found for ZnO. It is interesting to note the shortness of the bond length compared to the other larger structures, as can be appreciated in Table III. This length is lengthened to 1.893 Å in the triplet state, which is 22.22 kJ/mol more stable than the singlet reported in the table.

2. Zn_2O_2

$GM^{(2)}$, which belongs to the D_{2h} point group, and $LM^{(2)}$, of C_{2v} symmetry, are depicted in Fig. 1. Both structures are planar, and $LM^{(2)}$ lies 120 kJ/mol above the global minimum. The Zn-O bond length in both cases is longer than that of Zn_1O_1, but in the case of $LM^{(2)}$ these bonds are remarkably long, 1.976 Å compared to 1.892 Å of $GM^{(2)}$.

Zn_2S_2 structures are similar to these. In this case, the D_{2h} structure is the global minimum as well, and the relative energy between the minima is very similar: 117.10 kJ/mol for zinc sulfide and 120.17 for zinc oxide.

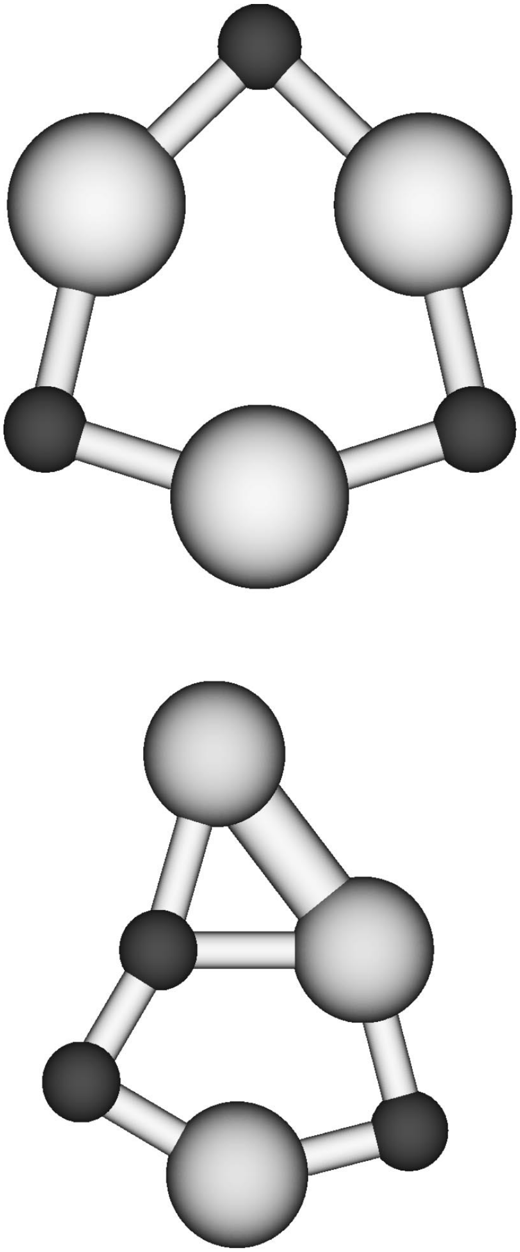

FIG. 2. Global minimum $GM^{(3)}$ and local minimum $LM^{(3)}$ of Zn_3O_3.

3. Zn_3O_3

In Fig. 2, $GM^{(3)}$ and $LM^{(3)}$ are depicted. The global minimum belongs to the D_{3h} point group, and the local minimum has only C_s symmetry. Both structures are planar, as was the case for Zn_2O_2, but the energy difference between them is much larger: 328.19 kJ/mol compared to 120.17 kJ/mol of the smaller one. The Zn-O bond length in $GM^{(3)}$ is 1.826 Å, shorter than that in $GM^{(2)}$ by 0.07 Å. The O-Zn-O angles are larger here, of course, due to geometrical reasons. Zn_3S_3 structures are similar to these, but it must be mentioned that the energy difference between the global and local minima is much larger in the case of zinc oxide (328.19 kJ/mol) than that for zinc sulfide (233.75 kJ/mol).

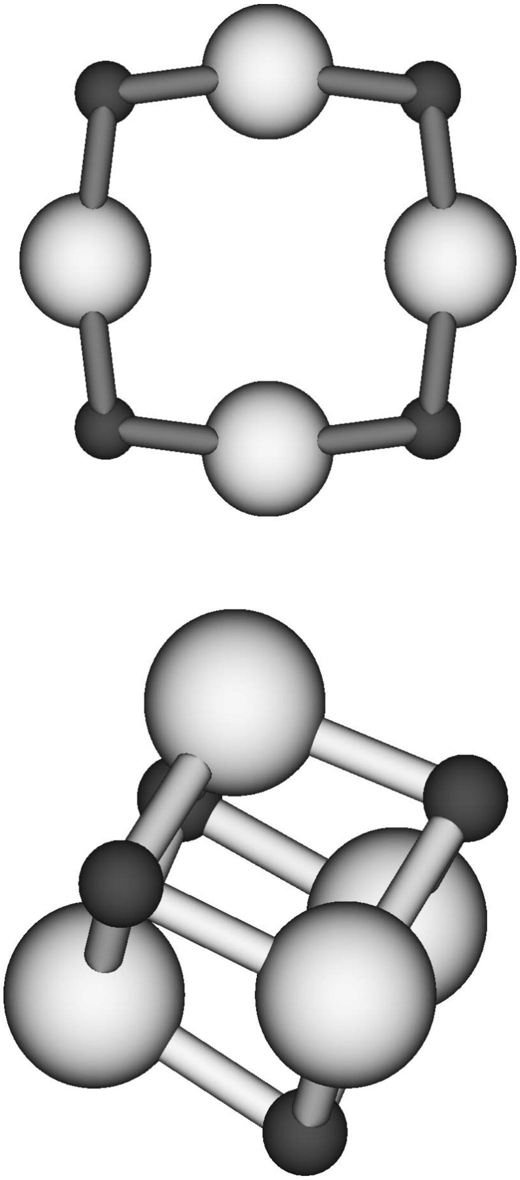

FIG. 3. Global minimum $GM^{(4)}$ and local minimum $LM^{(4)}$ of Zn_4O_4.

4. Zn_4O_4

In Fig. 3, $GM^{(4)}$, of D_{4h} symmetry and $LM^{(4)}$, of T_d symmetry, are given. It may be observed that the global minimum is a planar ring, like Zn_2O_2 and Zn_3O_3, but the characterized local minimum is the first three-dimensional structure. It is constructed from six Zn_2O_2 units, forming a sort of deformed cube. It lies 245.15 kJ/mol higher in energy than the global minimum. The planar global minimum has Zn-O bonds that are shorter than those found in $GM^{(3)}$ and, again, O-Zn-O angles which are larger. The Zn-O bond lengths in $LM^{(4)}$, on the other hand, are almost 0.2 Å larger than those in $GM^{(4)}$. This, of course, is a result of both the higher coordination number and the strained O-Zn-O bond angles (97°). In addition to this, O-Zn-O angles tend to linearity in the ring structures, and in $GM^{(4)}$ are already 165.5°).

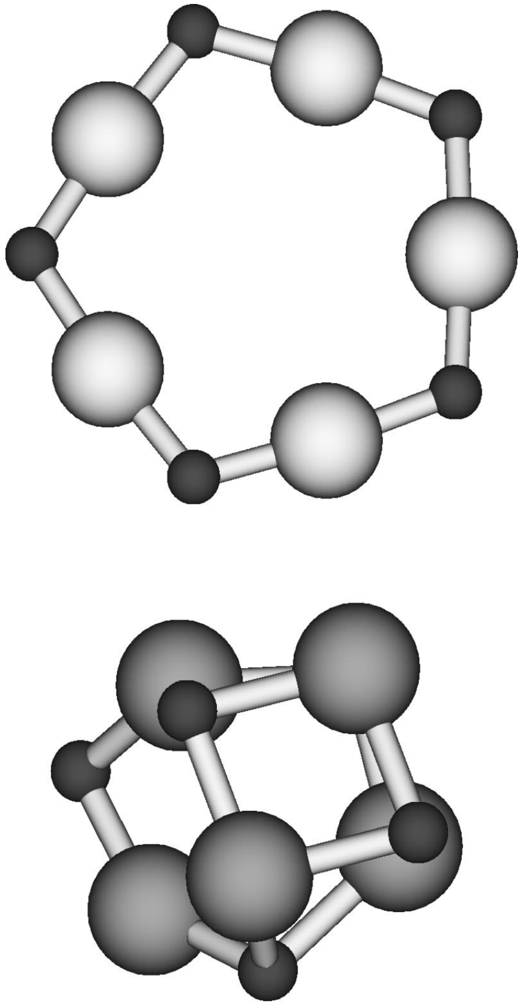

FIG. 4. Global minimum $\mathrm{GM}^{(5)}$ and local minimum $\mathrm{LM}^{(5)}$ of Zn_5O_5.

Characterized Zn_4S_4 structures are similar to these. However, again the energy difference between global and local minima is much larger in the case of Zn_4O_4: 245.15 kJ/mol compared to 117.27 kJ/mol for Zn_4S_4.

5. Zn_5O_5

The calculated $\mathrm{GM}^{(5)}$ of D_{5h} symmetry and $\mathrm{LM}^{(5)}$ of C_1 symmetry are shown in Fig. 4. As was the case for Zn_4O_4, a planar ring structure is found to be the global minimum, and a three-dimensional structure to be the local minimum. This $\mathrm{LM}^{(5)}$ has two different building blocks: four Zn_2O_2 units and two Zn_3O_3 units. The relative energy between these two structures is less than that found between the two Zn_4O_4 structures by only 9 kJ/mol, being 236.28 kJ/mol. In the planar ring the Zn-O bond lengths are 1.780 Å, similar to those of Zn_4O_4, and the O-Zn-O bond angles are very close to linearity: 174.9°.

Similar structures, with a smaller energy difference, were found for Zn_5S_5. The ring structure of Zn_5S_5 broke planarity somewhat, and was only 68.19 kJ/mol more stable than the three-dimensional local minimum.

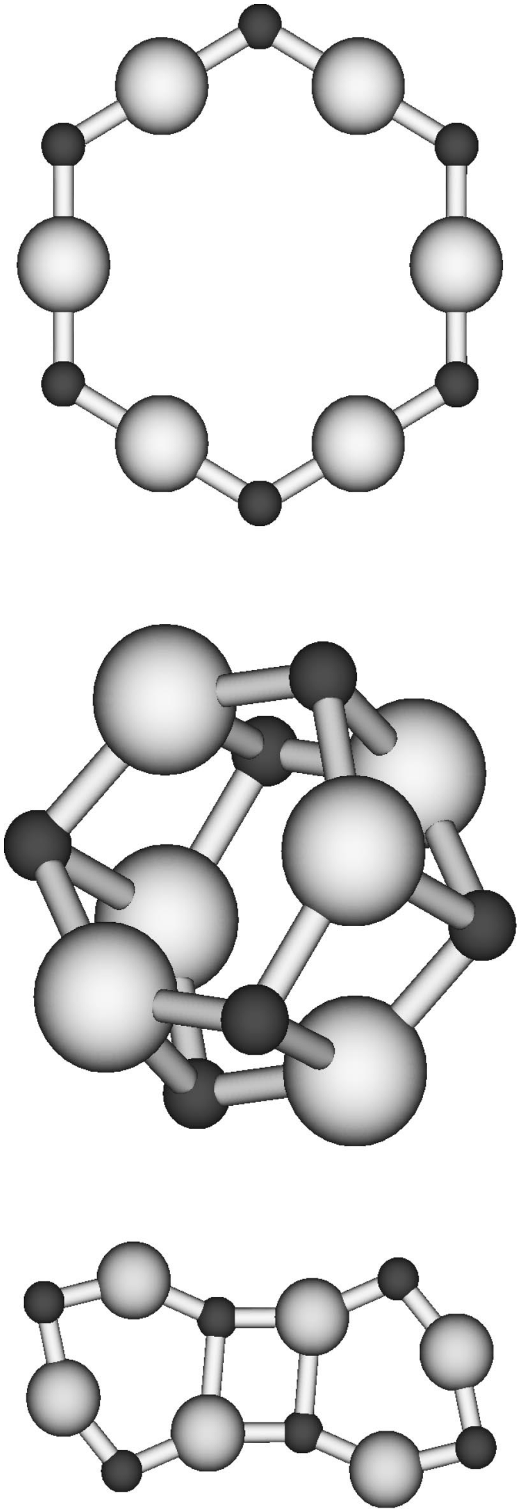

FIG. 5. Global minimum $\mathrm{GM}^{(6)}$ and two local minima $\mathrm{LM}_1^{(6)}$ and $\mathrm{LM}_2^{(6)}$ of Zn_6O_6.

6. Zn_6O_6

The calculated structures $\mathrm{GM}^{(6)}$, $\mathrm{LM}_1^{(6)}$, and $\mathrm{LM}_2^{(6)}$ are represented in Fig. 5. $\mathrm{GM}^{(6)}$ belongs to the D_{6h} point group, $\mathrm{LM}_1^{(6)}$ to the D_{3d} point group, and $\mathrm{LM}_2^{(6)}$ to the C_2 point group. $\mathrm{LM}_1^{(6)}$ is built of two ‘‘parallel’’ Zn_3O_3 units joined together by six Zn_2O_2 units. The same building blocks are found in the two other cases. $LM_2^{(6)}$ is a planar structure with two Zn_3O_3 rings linked together by a Zn_2O_2 ring. As in smaller cases of planar rings, in $GM^{(6)}$ one may appreciate the tendency to form linear O-Zn-O bond angles and short bond lengths. Thus we find angles of 179.8° and bonds of 1.772 Å, similar to the previous cases. In the three-dimensional structure we find larger bond lengths, in a wide range from 1.907 to 2.102 Å, and bond angles of 134.0°. It should be pointed out that the relative energy between $GM^{(6)}$ and $LM_1^{(6)}$ is drastically reduced compared to those seen for the isomers of Zn_4O_4 and Zn_5O_5. For Zn_6O_6, the relative energy between planar and three-dimensional structures is 95.90 kJ/mol. We see that there is a tendency to form more stable three-dimensional structures as the cluster size increases.

Related clusters were characterized for Zn_6S_6 (though no analog of $LM_2^{(6)}$ was found). For smaller clusters we have seen that the planar ringlike structures were more stable for zinc oxide. Here that trend continues, and while this ring is the global minimum for the zinc-oxide cluster it is not so for zinc sulfide, where the D_{3d} structure is the global minimum. This stability of planar zinc-oxide structures may explain the relative stability of $LM_2^{(6)}$, while a related structure was not observed for Zn_6S_6.

7. Zn_7O_7

The global minimum of D_{7h} symmetry $GM^{(7)}$ and the calculated local minima are depicted in Fig. 6. $LM_1^{(7)}$ and $LM_2^{(7)}$ belong to the C_s point group. It is interesting to point out that two planar structures are again found to be the most stable ones. $GM^{(7)}$ is a one-ring structure and $LM_1^{(7)}$ a three-ring structure. $LM_1^{(7)}$ lies 43.91 kJ/mol above the global minimum. In both cases the bond lengths are very similar, but the bond angles differ considerably for geometrical reasons. $LM_2^{(7)}$ is the lowest-lying three-dimensional structure, and can be seen as a structure of two joined ring structures: a Zn_3O_3 ring and a bent Zn_4O_4 ring. Half of the Zn_4O_4 ring is linked to the Zn_3O_3 ring, in this way forming new Zn_2O_2 rings as in $GM^{(6)}$, and a second bent Zn_4O_4 ring. This structure lies 74.86 kJ/mol above the global minimum. This difference is less than in smaller clusters, and therefore one would expect that in larger clusters the three-dimensional structures will become the global minima. A structure related to $LM_2^{(7)}$ was found to be the global minimum for Zn_7S_7, the ring structure lying 107.52 kJ/mol higher in energy.

8. Zn_8O_8

As mentioned above, the main difference at first sight between $GM^{(8)}$ and the previously seen global minima is that $GM^{(8)}$ is nonplanar. There has been a transition from a situation in which planar ring structures were favored, to a situation where three-dimensional structures are favored. Examining the trend in relative energies between the ring and three-dimensional structures for $i=4$–8, we find that the ring structure was more stable for $i=4$ by 245.15 kJ/mol. That difference was reduced to 236.28 kJ/mol for $i=5$, but it is still large. For $i=6$, the three-dimensional structure is closer to the ring, 95.9 kJ/mol higher in energy, and this difference is reduced to 43.91 kJ/mol for $i=7$. Finally, the three-dimensional $GM^{(8)}$ is more stable than the ring by 46.7 kJ/mol, and $GM^{(9)}$ more stable by 127.91 kJ/mol. It is clear

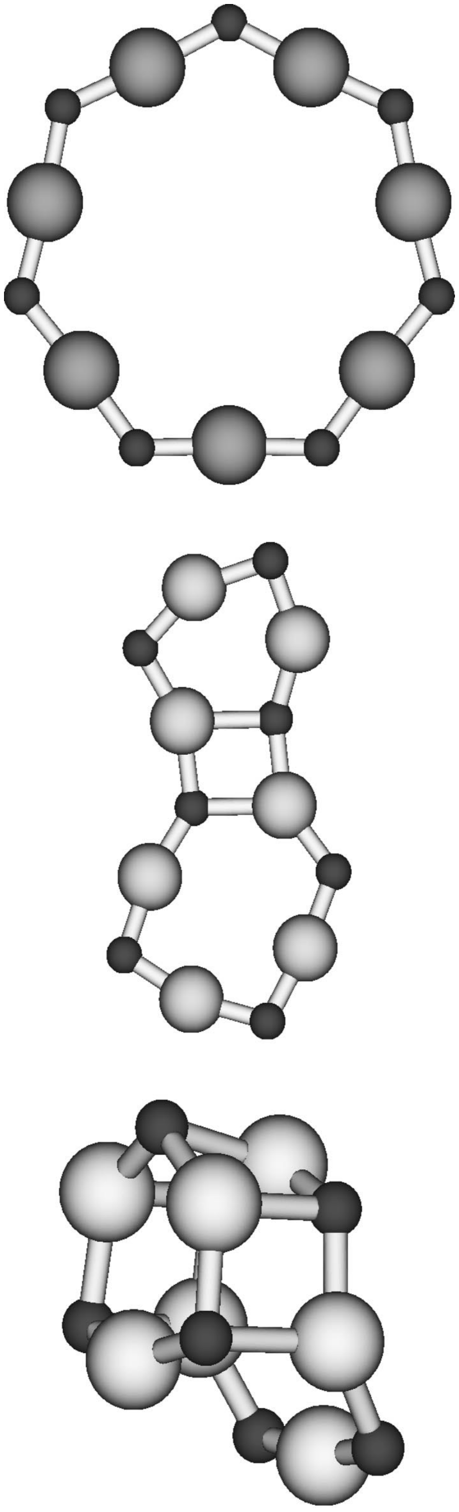

FIG. 6. Global minimum $GM^{(7)}$ and two local minima $LM_1^{(7)}$ and $LM_2^{(7)}$ of Zn_7O_7.

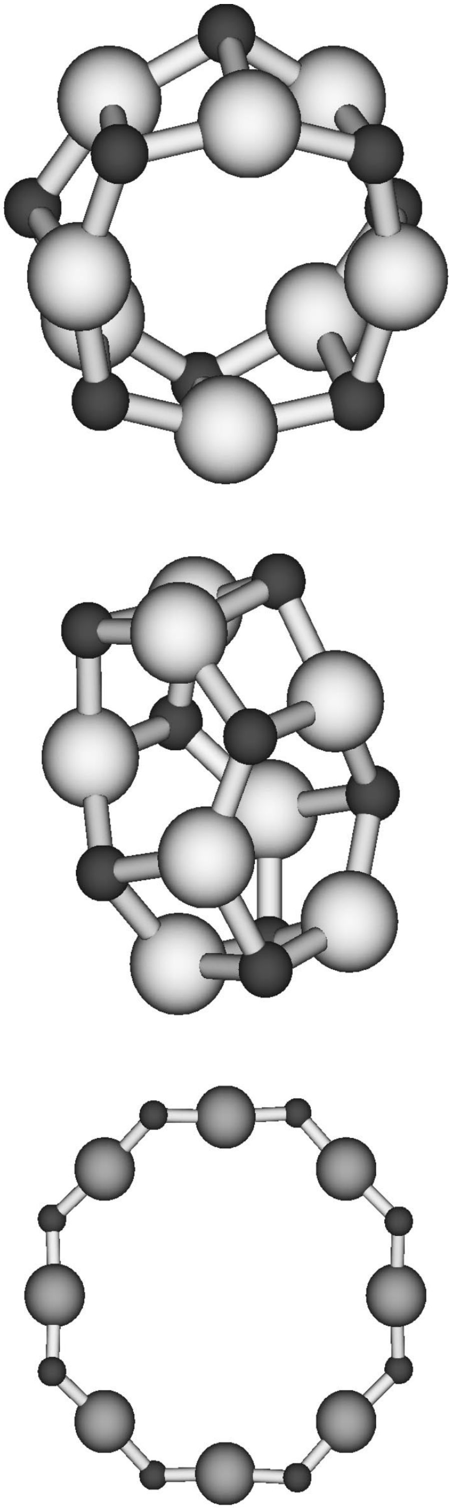

FIG. 7. Global minimum $\mathrm{GM}^{(8)}$ and two local minima $\mathrm{LM}_1^{(8)}$ and $\mathrm{LM}_2^{(8)}$ of $\mathrm{Zn}_8\mathrm{O}_8$.

that as the size of the cluster increases, the 3D structures become more stable than the rings.

In Fig. 7 the calculated structures are shown. $\mathrm{GM}^{(8)}$ has D_{4d} symmetry, $\mathrm{LM}_1^{(8)}$ has S_4 symmetry, and $\mathrm{LM}_2^{(8)}$ has D_{4d} symmetry as well. Therefore, these three calculated structures are very symmetric. $\mathrm{GM}^{(8)}$ may be viewed as being built of two ''parallel'' $\mathrm{Zn}_4\mathrm{O}_4$ rings linked together by $\mathrm{Zn}_2\mathrm{O}_2$ rings. $\mathrm{LM}_1^{(8)}$ is also a three-dimensional structure built of $\mathrm{Zn}_2\mathrm{O}_2$ and $\mathrm{Zn}_3\mathrm{O}_3$ rings. It may be viewed as a four-faced polyhedron, where each face is built of a $\mathrm{Zn}_2\mathrm{O}_2$ and $\mathrm{Zn}_3\mathrm{O}_3$ ring, which are rotated in order to build the next face. This structure has $\mathrm{Zn}_2\mathrm{O}_2$ rings at the top and bottom. In total, six rombi and four hexagons are found in this structure. $\mathrm{GM}^{(8)}$ and $\mathrm{LM}_1^{(8)}$ are energetically very close, they are separated by only 13.54 kJ/mol. The bond lengths and bond angles are similar to other three-dimensional structures, as may be observed in Table III. No completely planar ring is found; $\mathrm{LM}_2^{(8)}$ has all zincs in the same plane, but the oxygen atoms alternate up and down along the ring. In this way the bond angles are close to linearity, 175.9 in this case. In a completely planar ring these angles could not be so obtuse and yet have a structure that maintains favorable angles about the oxygen atoms, which would make the molecule less stable. Nevertheless, this ring structure is only 43.70 kJ/mol above the global minimum in energy. For $\mathrm{Zn}_8\mathrm{S}_8$ similar structures were found, but the S_4 structure was the global minimum, and was 166.33 kJ/mol more stable than the ring structure.

9. Zn_9O_9

In Fig. 8 the calculated structures $\mathrm{GM}^{(9)}$, $\mathrm{LM}_1^{(9)}$, and $\mathrm{LM}_2^{(9)}$ are depicted. $\mathrm{GM}^{(9)}$ is a three-dimensional spheroid structure composed of $\mathrm{Zn}_2\mathrm{O}_2$ and $\mathrm{Zn}_3\mathrm{O}_3$ rings. These $\mathrm{Zn}_3\mathrm{O}_3$ blocks may be envisioned as caps of a polyhedron joined by a ring formed of $\mathrm{Zn}_2\mathrm{O}_2$ and $\mathrm{Zn}_3\mathrm{O}_3$ units. The ring is formed by alternating one $\mathrm{Zn}_3\mathrm{O}_3$ unit and two joined $\mathrm{Zn}_2\mathrm{O}_2$ units. There are six rombi and five hexagons in this structure, which has C_{3h} symmetry. $\mathrm{LM}_1^{(9)}$ is formed of three stacked $\mathrm{Zn}_3\mathrm{O}_3$ rings, linked together by $\mathrm{Zn}_2\mathrm{O}_2$ units. It may be constructed by adding an extra $\mathrm{Zn}_3\mathrm{O}_3$ ring to $\mathrm{LM}_1^{(6)}$. This structure lies 29.79 kJ/mol above the global minimum. As in the previous case, the ring structure is no longer planar, with the oxygen atoms above and below the plane formed the Zn atoms. This structure is labeled $\mathrm{LM}_2^{(9)}$, and belongs to the C_s point group. This structure is predicted to be 127.91 kJ/mol less stable than $\mathrm{GM}^{(9)}$.

B. Natural orbital charges

At this point we analyze the natural orbital charges, obtained by natural bonding analysis [56] at the B3LYP-SKBJ(d) level of theory, which are given in Table V. The cationic nature of zinc and the anionic nature of oxygen can be observed in all the structures. The atomic charges are larger as the cluster size increases, and a trend toward charge separation of the bulk ($|1.91e|$) is clearly observed.

C. Cohesive energy

The cohesive energy per zinc oxide unit is calculated as $E_f=(iE_{Zn}+iE_O-E_{Zn_iO_i})/i$, where i is the number of ZnO units. The cohesive energy may be plotted versus the inverse of the cubic root of i, and then a line can be fit to the ob-

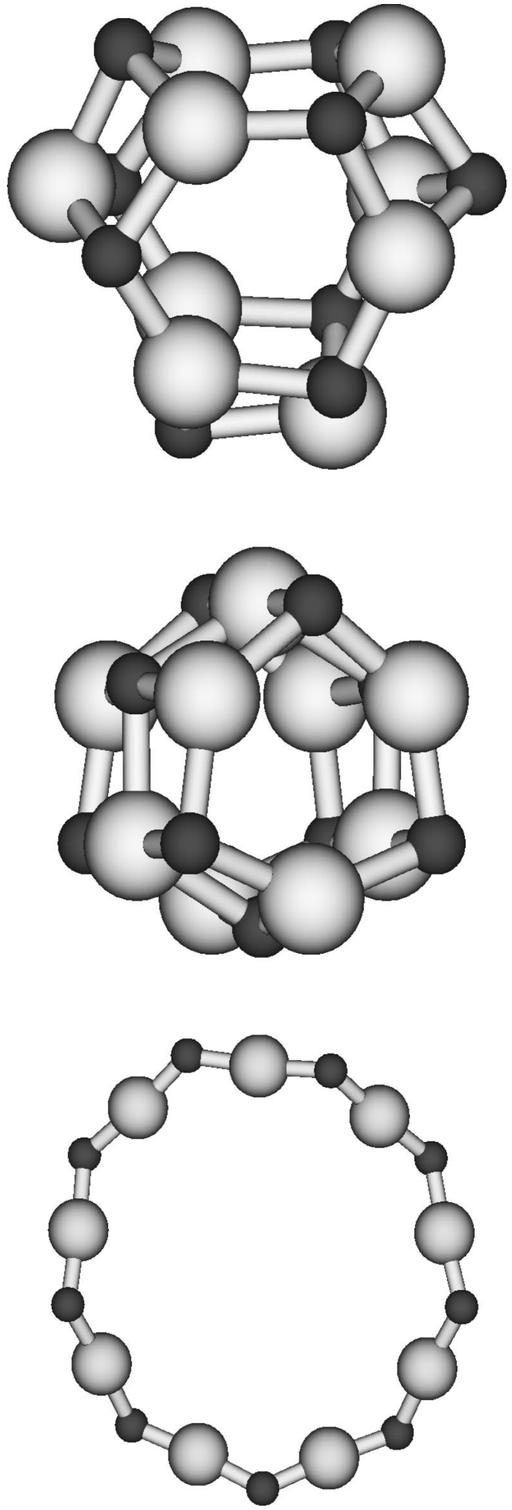

FIG. 8. Global minimum $GM^{(9)}$ and two local minima $LM_1^{(9)}$ and $LM_2^{(9)}$ of Zn_9O_9.

TABLE V. Natural orbital charges (*e*) of the shown global minima.

	Zn	O
$GM^{(1)}$	0.973	−0.973
$GM^{(2)}$	1.335	−1.335
$GM^{(3)}$	1.412	−1.412
$GM^{(4)}$	1.432	−1.432
$GM^{(5)}$	1.451	−1.451
$GM^{(6)}$	1.465	−1.465
$GM^{(7)}$	1.477	−1.477
$GM^{(8)}$	1.532	−1.532
$GM^{(9)}$	1.559	−1.559

tained points. Extrapolating this to $i^{-1/3}=0$, that is, to $i=\infty$, or the bulk, a theoretical value which can be compared to the experimental one may be obtained.

In Ref. [33] the same approach was used for Zn_iS_i. The representative points were seen to be those corresponding to three-dimensional structures. In the case of Zn_iO_i only two points belong to three-dimensional structures: those corresponding to $GM^{(8)}$ and $GM^{(9)}$. Therefore, in order to obtain a meaningful extrapolation the cohesive energy of larger three-dimensional clusters should be taken into account, and for this purpose further calculations must be made.

The cohesive energies of the calculated global minima are given in Table VI.

IV. CONCLUSIONS

It has been seen that planar ring structures are the global minima for Zn_iO_i, $i=1$–7, and three-dimensional structures are the global minima for $i=8$ and 9. These three-dimensional global minima, along with the other calculated three-dimensional local minima, may be viewed as being built of Zn_2O_2 rombi and Zn_3O_3 hexagons (and an occasional Zn_4O_4 unit), as they were for zinc sulfide. However, for zinc sulfide ring structures are the global minima for $i=1$–5, and three-dimensional structures are the global minima for $i=6$–9. This different behavior is mainly attributable to two factors. The rigidity of angles about the oxygen atom (as opposed to sulfur's more flexible bonding) plays a part, but the major difference is that sulfur atoms benefit much more from additional valence than do oxygen atoms. Clusters containing oxygen atoms are not highly stabilized by the additional bonds found in the three-dimensional structures, making ring structures the global minima for clusters with $i<8$.

TABLE VI. Cohesive energy E_f (kJ/mol) of characterized global minima.

	E_f (kJ/mol)
$GM^{(1)}$	84.06
$GM^{(2)}$	275.09
$GM^{(3)}$	403.26
$GM^{(4)}$	447.72
$GM^{(5)}$	462.92
$GM^{(6)}$	468.55
$GM^{(7)}$	470.47
$GM^{(8)}$	476.52
$GM^{(9)}$	484.95

In Ref. [33] the authors predicted stable spheroid structures for Zn_iO_i, $i>11$. We have seen, however, that these spheroid structures are stable for smaller cases, such as $i=8$ and 9. Therefore, the onset of the stability for spheroid structures is $i=8$, according to our calculations.

In summary, there are two main factors determining whether a ring or three-dimensional structure will be the global minimum for the small zinc-oxide clusters: the stability of very obtuse O-Zn-O bond angles, and the stability gained from higher coordination. For Zn_iO_i, $i=1-7$, the first term outweighs the second, and ring structures are predicted to be the global minima. For $i=8$ and greater, however, the size of the cluster allows for both obtuse O-Zn-O bond angles and higher coordination in the three-dimensional spheroid structures, making these the most stable. These three-dimensional clusters can be envisioned as being built of smaller building blocks, basically Zn_2O_2 and Zn_3O_3 rings.

ACKNOWLEDGMENTS

This research was funded by Euskal Herriko Unibertsitatea Grant UPV 203.215-G50/98. J.E.F. would like to thank Eusko Jaurlaritza (the Basque Government) for funding.

---

[1] A. Kampmann and D. Lincot, J. Electroanal. Chem. **418**, 73 (1996).
[2] Y.Y. Loginov, K. Durose, H.M. Al-Allak, S.A. Galloway, S. Oktik, A.W. Brinkman, H. Richter, and D. Bonnet, J. Cryst. Growth **161**, 159 (1996).
[3] A. Niemegeers and M. Burgelman, J. Appl. Phys. **81**, 2881 (1997).
[4] K. Li, A.T.S. Wee, J. Lin, K.L. Tan, L. Zhou, S.F.Y. Li, Z.C. Feng, H.C. Chou, S. Kamra, and A. Rohatgi, J. Mater. Sci.: Mater. Electron. **8**, 125 (1997).
[5] K. Omura, A. Hanahusa, T. Arita, H. Higuchi, T. Aramoto, T. Nishio, S. Sibutani, S. Kumazawa, M. Murozono, Y. Yabuuchi, and H. Takakura (unpublished).
[6] C. Ferekides and J. Britt, Sol. Energy Mater. Sol. Cells **35**, 255 (1994).
[7] H.C. Chou, A. Rohatgi, N.M. Jokerst, S. Kamra, S.R. Stock, S.L. Lowrie, R.K. Ahrenkiel, and D.H. Levi, Mater. Chem. Phys. **43**, 178 (1996).
[8] S. Naseem, D. Nazir, R. Mumtaz, and K. Hussain, J. Mater. Sci. Technol. **12**, 89 (1996).
[9] J. Touukova, D. Kindl, and J. Tousek, Thin Solid Films **293**, 272 (1997).
[10] T.L. Chu and S.S. Chu, Solid-State Electron. **38**, 533 (1995).
[11] P.J. Sebastian and M. Ocampo, Sol. Energy Mater. Sol. Cells **44**, 1 (1996).
[12] A.J. Hoffman, G. Mills, H. Yee, and M.R. Hoffmann, J. Phys. Chem. **96**, 5546 (1992).
[13] S. Kuwabata, K. Nishida, R. Tsuda, H. Inoue, and H. Yoneyama, J. Electrochem. Soc. **141**, 1498 (1994).
[14] E. Corcoran, Sci. Am. **263**, 74 (1990).
[15] P. Schroer, P. Kruger, and J. Pollmann, Phys. Rev. B **47**, 6971 (1993).
[16] P. Schroer, P. Kruger, and J. Pollmann, Phys. Rev. B **48**, 18 264 (1993).
[17] P. Schroer, P. Kruger, and J. Pollmann, Phys. Rev. B **49**, 17 092 (1994).
[18] D. Vogel, P. Kruger, and J. Pollmann, Phys. Rev. B **52**, 14 316 (1995).
[19] J. Pollmann, P. Kruger, M. Rohlfing, M. Sabisch, and D. Vogel, Appl. Surf. Sci. **104/105**, 1 (1996).
[20] D. Vogel, P. Kruger, and J. Pollmann, Phys. Rev. B **54**, 5495 (1996).
[21] A. Ecker, E. Weckert, and H. Schnockel, Nature (London) **387**, 379 (1997).
[22] R. Rousseau, G. Dietrich, S. Kruckeberg, K. Lutzenkirchen, D. Marx, L. Schweikhard, and C. Walther, Chem. Phys. Lett. **295**, 41 (1998).
[23] J. Cizeron and M.P. Pileni, J. Phys. Chem. B **101**, 8887 (1997).
[24] V.S. Gurin, J. Phys. Chem. **100**, 869 (1996).
[25] B. Guo, K. Kerns, and A. Castleman, Science **255**, 1411 (1992).
[26] B. Guo, S. Wei, J. Purnell, S. Buzza, and A. Castleman, Science **256**, 515 (1992).
[27] J.E. Fowler and J.M. Ugalde, Phys. Rev. A **58**, 383 (1998).
[28] A. Tomasulo and M.V. Ramakrishna, Chem. Phys. **210**, 55 (1996).
[29] P. Fuentealba and O. Reyes, J. Phys. Chem. A **103**, 1376 (1999).
[30] M. Haser, U. Schneider, and R. Ahlrichs, J. Am. Chem. Soc. **114**, 9551 (1992).
[31] L. Lou, T. Guo, P. Nordlander, and R.E. Smalley, J. Chem. Phys. **99**, 5301 (1993).
[32] E.C. Behrman, R.K. Foehrweiser, J.R. Myers, B.R. French, and M.E. Zandler, Phys. Rev. A **49**, R1543 (1994).
[33] J.M. Matxain, J.E. Fowler, and J.M. Ugalde, Phys. Rev. A **61**, 053201 (2000).
[34] A.D. Becke, J. Chem. Phys. **98**, 5648 (1993).
[35] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
[36] C. Lee, W. Yang, and R.G. Parr, Phys. Rev. B **37**, 785 (1988).
[37] A.D. Becke, Phys. Rev. A **38**, 3098 (1988).
[38] W.J. Stevens, M. Krauss, H. Basch, and P.G. Jasien, Can. J. Chem. **70**, 612 (1992).
[39] J.J.P. Stewart, J. Comput. Chem. **12**, 320 (1991).
[40] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, B. J. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ciolowski, J. V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martins, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, and J. A. Pople,

GAUSSIAN 98 (Revision A5), Gaussian, Inc., Pittsburgh, PA, 1998.

[41] HyperChem^{TM}, Release 4.5 for Windows, Molecular Modeling System, Copyright 1994, 1995 Hypercube, Inc.

[42] GAMESS, M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S.J. Su, T.L. Windus, M. Dupuis, and J.A. Montgomery, J. Comput. Chem. **14**, 1347 (1993).

[43] A.J.H. Wachters, J. Chem. Phys. **52**, 1033 (1970).

[44] P.J. Hay, J. Chem. Phys. **66**, 4377 (1977).

[45] D.M. Hood, R.M. Pitzer, and H.F. Schaefer, J. Chem. Phys. **71**, 705 (1979).

[46] A D. McLean and G.S. Chandler, J. Chem. Phys. **72**, 5639 (1980).

[47] R. Krishnan, J.S. Binkley, R. Seeger, and J.A. Pople, J. Chem. Phys. **72**, 650 (1980).

[48] J.A. Pople, R. Krishnan, H.B. Schlegel, and J.S. Binkley, Int. J. Quantum Chem. **14**, 545 (1978).

[49] R.J. Bartlett and G.D. Purvis, Int. J. Quantum Chem. **14**, 516 (1978).

[50] J. Cizek, Adv. Chem. Phys. **14**, 35 (1969).

[51] G.D. Purvis and R.J. Bartlett, J. Chem. Phys. **76**, 1910 (1982).

[52] G.E. Scuseria, C.L. Janssen, and H.F. Schaefer III, J. Chem. Phys. **89**, 7382 (1988).

[53] G.E. Scuseria and H.F. Schaefer III, J. Chem. Phys. **90**, 3700 (1989).

[54] J.A. Pople, M. Head-Gordon, K. Raghavachari, and G.W. Trucks, Chem. Phys. Lett. **164**, 185 (1989).

[55] P.E.M. Siegbahn, Adv. Chem. Phys. **43**, 333 (1996).

[56] A.E. Reed, L.A. Curtiss, and F. Weinhold, Chem. Rev. **88**, 899 (1988).