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Ab initio study of neutral and ionized microclusters of MgO

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The equilibrium properties of small MgO clusters (MgO, Mg_2O, MgO_2, and Mg_2O_2) are calculated to obtain their dependence on computational constraints such as the basis set and level of computation. The results have led to the suggestion that the inclusion of the correlation correction at the second-order Moller-Plesset level is necessary for the atomization energy although the configuration parameters may be obtained at the Hartree-Fock level. Based on this suggestion, the calculated properties of the neutral and single-ionized MgO monomer are in excellent agreement with the experimental data and available values from very accurate calculations. For the triatomic clusters, Mg_2O is found to be more stable than MgO_2, whose geometrical structure is determined by the strong O-O interaction. The optimum configuration of Mg_2O_2 is a slightly distorted square with a D_{2h} symmetry. Upon ionization, these clusters undergo structural modifications, but these effects are softer than in alkali halide clusters due to the delocalized character of the hole. Our results show that the evaporization of a neutral oxygen atom provides the most favorable fragmentation channel for the neutral and single-ionized stoichiometric dimers.

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I. INTRODUCTION

Clusters have been interesting scientifically for some time as a way to study the progressive emergence of bulk crystalline properties from the atomic or molecule scale. Combined theoretical and experimental studies of such cluster progressions have a fascinating potential for basic science. A fundamental perception underlying the technological interest now being expressed in so-called cluster-assembled materials is that the size of the building block can potentially be varied over a much wider range than has been implied by molecular units on the one hand and ordinary "microscale" crystallites on the other. With this flexibility, one hopes to acquire control over a variety of electronic and structural properties which are, or may be shown to be, rather dramatically dependent on the size of the subunit.

Small clusters of MgO and CaO, containing up to 32 atoms, have been the subject of an experimental investigation that suggested structural dissimilarities between $(MgO)_n{}^+$ and $(CaO)_n{}^+$ clusters with $n<8$. The collision-induced fragmentation data indicated that $(MgO)_3$ subunits form the stable MgO clusters while for CaO clusters the basic unit is $(CaO)_2$ [1]. More recently, Ziemann and Castleman have studied stabilities and structures of stoichiometric and metal-rich MgO clusters of a broad size range using laser-ionization time-of-flight mass spectroscopy [2,3]. They have performed classical simulations based on the rigid and the polarization ion shell models to obtain qualitative information about primary fragmentation channels and cluster electronic properties of $(MgO)_n{}^+$, $(MgO)_nMg^+$ ($n<90$), and $(MgO)_nMg_2{}^+$ ($n=4-172$) clusters. Their results have led to a suggestion that MgO clusters may have some interesting electronic properties that warrant a detailed and systematic investigation based on first-principles methods.

The investigation based on first-principles methods requires a detailed study of a computational scheme which is accurate enough to deal with the interesting physical properties of the clusters that depend on variables such as the size, the charge, or the stoichiometric composition. Once the parameters of the quantum-mechanical procedure are defined, simulations can be carried out in a methodical way. Clusters containing a small number of atoms obviously provide a stepping stone for the evaluation of the parameters of the computational model.

Our work is focused on the equilibrium properties of monomer, triatomic, and dimer MgO clusters, including neutral and single-ionized species. The all-electron Hartree-Fock (HF) approach has been our reference framework in which correlation corrections and basis-set effects have been explored in detail. The most immediate goal is to define a reliable set of computational parameters for *ab initio* calculations on much larger clusters.

In addition we report an accurate description of the electronic structure of neutral and single-ionized MgO microclusters, containing up to four atoms. At this size range, one can exploit the information contained in the electronic wave functions of the optimum configurations to provide valuable information of central issues of the physics and chemistry of clusters. Our efforts have been directed to the analysis of the chemical bonding, the ionization-induced structural transitions, and the stability against fragmentation channels. A similar study has been performed by Galli, Andreoni, and Tosi on NaCl microclusters using the HF method in a pseudopotential approach [4]. Their calculations provide a reference point to show how the behavior of MgO clusters deviates from the standard ionic picture found in NaCl clusters.

The rest of the paper is organized in three sections. The computational analysis is presented in Sec. II; Sec. III contains the results and discussion of neutral and single-ionized microclusters; and in Sec. IV we summarize the main conclusions.

II. COMPUTATIONAL MODEL

All-electron HF calculations on neutral (in the singlet spin state) and single-ionized (in the doublet spin state) MgO clusters are performed using the GAUSSIAN90 program package [5]. In such calculations decisions involving the level of computation, the quality of a given basis set, and the procedure for configuration optimization are affected by the desired accuracy in the physical properties to be calculated, the available computational facility, and the cluster size. We have performed an extensive set of calculations on small aggregates of MgO containing two, three, and four atoms. Specifically, the effects of (i) basis set, (ii) correlation corrections, and (iii) geometric relaxations in neutral and ionized clusters have been explored in detail.

Tables I and II show the dependence of the Mg-O separation and atomization energy for MgO microclusters on the basis set and level of computation. The atomization energy is defined as the energy necessary to dissociate the neutral (Mg_nO_m) or ionized ($Mg_nO_m{}^+$) clusters into neutral atoms (nMg + mO) or neutral atoms and a magnesium ion [Mg^+ + $(n-1)$Mg + mO], respectively. In these calculations the configuration of Mg_2O^+ is kept linear, whereas Mg_2O_2 and $Mg_2O_2{}^+$ have a square-shape configuration. For the expansion of the atomic orbitals of Mg and O we use the Gaussian basis sets 6-31G* (i.e., 6631/311/1 for Mg and 631/31/1 for O) and 6-311G* (i.e., 631111/42111/1 for Mg and 6311/311/1 for O) included in the package. The correlation corrections are introduced by means of second (MP2) or fourth-order (MP4) Moller-Plesset corrections to the HF energy.

We notice that the change in Mg-O separation in these clusters is less than 2% as we either use a better basis set (i.e., 6-311G*) or include the correlation correction at the MP2 level. At the HF level using the set 6-31G*, MgO is found to be unbound (Table I). When the MP2 correction is added to the HF energy, it becomes bound with the energy of 2.57 eV. The MP4 correction makes only a small change of the order of 0.2 eV. Similarly, the atomization energy of the ionized cluster Mg_2O^+ shows a significant change (3 eV) as we go from the HF to the HF + MP2 level and less than 0.4 eV after including MP4 corrections. For the basis set 6-311G*, the scenario remains the same in both cases. We therefore conclude that the inclusion of the correlation correction at the MP2 level is necessary for the atomization energy of MgO clusters, although the configuration parameters may be obtained at the HF level. Furthermore, the use of the extended basis set 6-311G* does not introduce significant changes either in the optimal cluster configuration or in the atomization energy.

TABLE I. Basis-set dependence of the Mg-O separation and the atomization energy for MgO and Mg_2O^+ clusters.

	Mg-O separation (Å)	Atomization energy (eV)		
Basis	HF	HF	MP2	MP4
	MgO			
6-31G*	1.739	1.52	−2.57	−2.79
6-311G*	1.751	1.57	−2.47	−2.73
	Mg_2O^+ (linear)			
6-31G*	1.734 1.825	3.51	−6.47	−6.08
6-311G*	1.737 1.825	3.49	−6.36	−6.01

TABLE II. Effect of the MP2 correction on the Mg-O separation in the neutral and ionized MgO and Mg_2O_2 clusters described with 6-31G* basis sets.

	Mg-O separation (Å)	
Cluster	HF	MP2
MgO	1.739	1.733
MgO^+	1.815	1.843
Mg_2O_2	1.836	1.881
$Mg_2O_2{}^+$	1.889	1.873

Important computational savings could be obtained if the optimum configurations found for the neutral clusters were also appropriate to describe the single-ionized clusters. This is the so-called *vertical* approximation, in contrast with the *adiabatic* approximation, where the geometrical configuration is allowed to relax. Comparison between these two types of calculations is shown in Table III. Here we report the HF + MP2 energies of single-ionized clusters computed in their optimized configurations (*adiabatic*) and in the configurations taken from the corresponding neutral species (*vertical*). In the vertical approximation, the total energy is underestimated by 0.12 eV (monomer), 0.38 eV (triatomic), and 0.86 eV (dimer) with respect to the corresponding adiabatic values. As we will see later, values of relevant physical properties such as atomization energies, ionization potentials, or fragmentation energies lie in the region of 2–10 eV. Hence, the use of vertical estimations affects these properties with variations between 1–10%.

In conclusion, the following procedure should provide an adequate quantitative description in extensive calcula-

TABLE III. Total energies at the HF + MP2 level of the single-ionized clusters with optimized configurations (adiabatic) and with the configurations of the corresponding neutral clusters (vertical).

	Total energy (hartree)	
Cluster	Adiabatic	Vertical
MgO^+	−274.3019	−274.2976
Mg_2O^+	−474.0893	−474.0752
$Mg_2O_2{}^+$	−549.1088	−549.0771

tions of neutral and ionized MgO clusters: (i) optimization of cluster geometry with HF calculations using the 6-31G* basis set; (ii) addition of the correlation correction at the MP2 level to the HF energy of optimized cluster configuration; and (iii) apply vertical approximation for ionized cluster calculations.

III. RESULTS AND DISCUSSION

A. Neutral clusters

The equilibrium geometries of MgO, Mg_2O, MgO_2, and Mg_2O_2 have been obtained using the abovementioned procedure. The most stable structures are shown in Fig. 1 along with their geometrical parameters. For triatomic clusters, namely, Mg_2O and MgO_2, we also consider linear and right-angle configurations, whereas for Mg_2O_2 we include the optimization keeping a square shape. Information concerning electronic states, Mulliken population analysis, and total energies is given in Table IV.

The contour plots of the electronic density ρ of the optimized neutral clusters relative to the free atoms (Fig. 2) illustrate the electronic distribution in the bond formation. The solid and dashed lines represent zones of excess and deficiency of electronic density, respectively, showing a charge transfer from the magnesium to the oxygen in concordance with Mulliken population analysis. This effect is qualitatively similar for MgO, Mg_2O, and Mg_2O_2, and increases with the number of atoms. For MgO_2 the charge transfer from the magnesium is shared by the oxygen atoms forming the strong O-O bond. These maps show deviations from sphericity of the electronic clouds indicating the presence of polarization effects in the bonding. It is also remarkable that, except for the O-O interaction in MgO, the charge-density maps present zones of electronic deficiency along the bond lines. This result suggests the possibility of the simulation of these clusters by means of classical ionic models. From Mulliken population analysis, the more appropriate integer values of the charges on Mg and O in the stoichiometric clusters are 1 and -1, respectively. The use of these values has produced reasonable results in the work of Ziemann and Castleman [2,3].

TABLE IV. Symmetry, electronic states, atomic Mulliken charges (Q_{Mg}, Q_{O}) and total energies at the HF + MP2 level, in hartree, of MgO, Mg_2O, MgO_2, and Mg_2O_2 clusters.

Cluster	Symmetry	State	Q_{Mg}	Q_{O}	Energy
MgO (optimized)	$C_{\infty v}$	$^1\Sigma$	0.81	-0.81	-274.5921
Mg_2O (optimized)	C_{2v}	$^1A_1$	0.52	-1.04	-474.3191
Mg_2O (linear)	$D_{\infty h}$	$^1\Sigma$	0.54	-1.08	-474.3107
Mg_2O (right-angle)	C_{2v}	$^1A_1$	0.51	-1.02	-474.2990
MgO_2 (optimized)	C_{2v}	$^1A_1$	1.24	-0.62	-349.5475
MgO_2 (linear)	$D_{\infty h}$	$^1\Sigma$	1.06	-0.53	-349.4877
MgO_2 (right-angle)	C_{2v}	$^1A_1$	1.20	-0.60	-349.5278
Mg_2O_2 (optimized)	D_{2h}	$^1A_{1g}$	1.05	-1.05	-549.3735
Mg_2O_2 (square)	D_{2h}	$^1A_{1g}$	1.04	-1.04	-549.3585

For the MgO monomer, the calculated equilibrium distance $R=1.739$ Å, atomization energy $D=2.57$ eV, and vibrational frequency $\omega_e=767$ cm^{-1} are in excellent agreement with the corresponding experimental data: $R=1.749$ Å [6], $D=2.56\pm0.21$ eV [7], and $\omega_e=785$ cm^{-1} [6]. The reported values of D from Gaussian-1

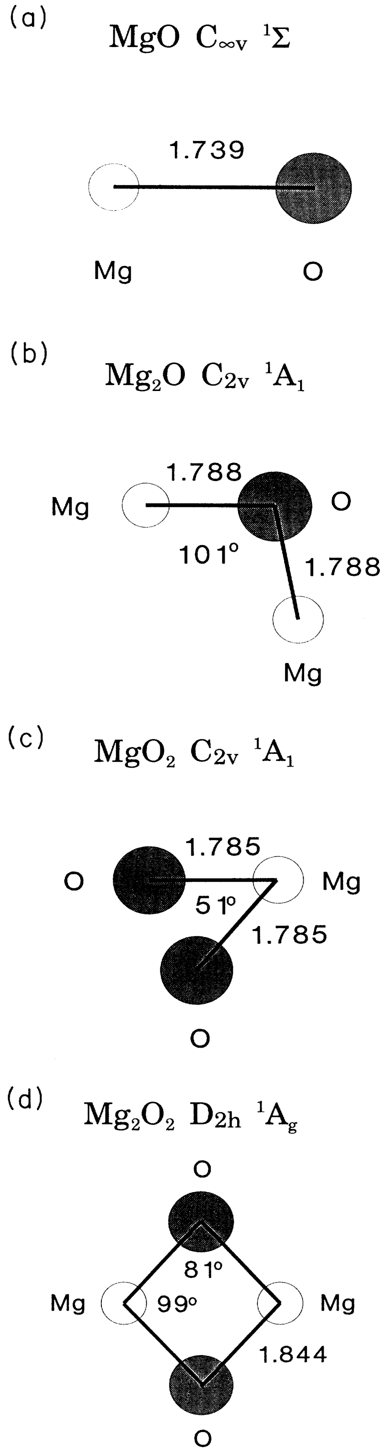

FIG. 1. Structures for (a) MgO, (b) Mg_2O, (c) MgO_2, and (d) Mg_2O_2.

theory [8], configuration interaction [9] (CI), and local-density [10,11] (LDA) calculations are 2.67, 2.61, and 3.27 eV, respectively, whereas the equilibrium distance obtained in the LDA calculation is 1.729 Å. The overall comparison with other theoretical work is satisfactory except the case of the LDA calculation, which tends to overestimate the atomization energy of MgO.

For the triatomic and dimer clusters the calculated results show that the optimized configurations do not represent a segment of MgO crystal. The Mg-O separation increases from the monomer (1.739 Å) to the dimer (1.844 Å) but it is still far from the bulk value (2.106 Å). The bond angle in Mg_2O and MgO_2 is 101° and 51°, respectively, indicating the strong bond between oxygen atoms in the latter [see Fig. 2(c)]. On the other hand, the O-Mg-O angle has increased to 99° in the Mg_2O_2 cluster from that of 51° in the MgO_2. This can be seen as a consequence of the larger negative charge on the oxygen in the case of the dimer compared with that in the triatomic.

The electronic structure of small clusters of MgO can also provide a good test bed to explore their stability in terms of the basic radial (two-body) and bending (three-body) interatomic forces. The magnitude of the atomiza-

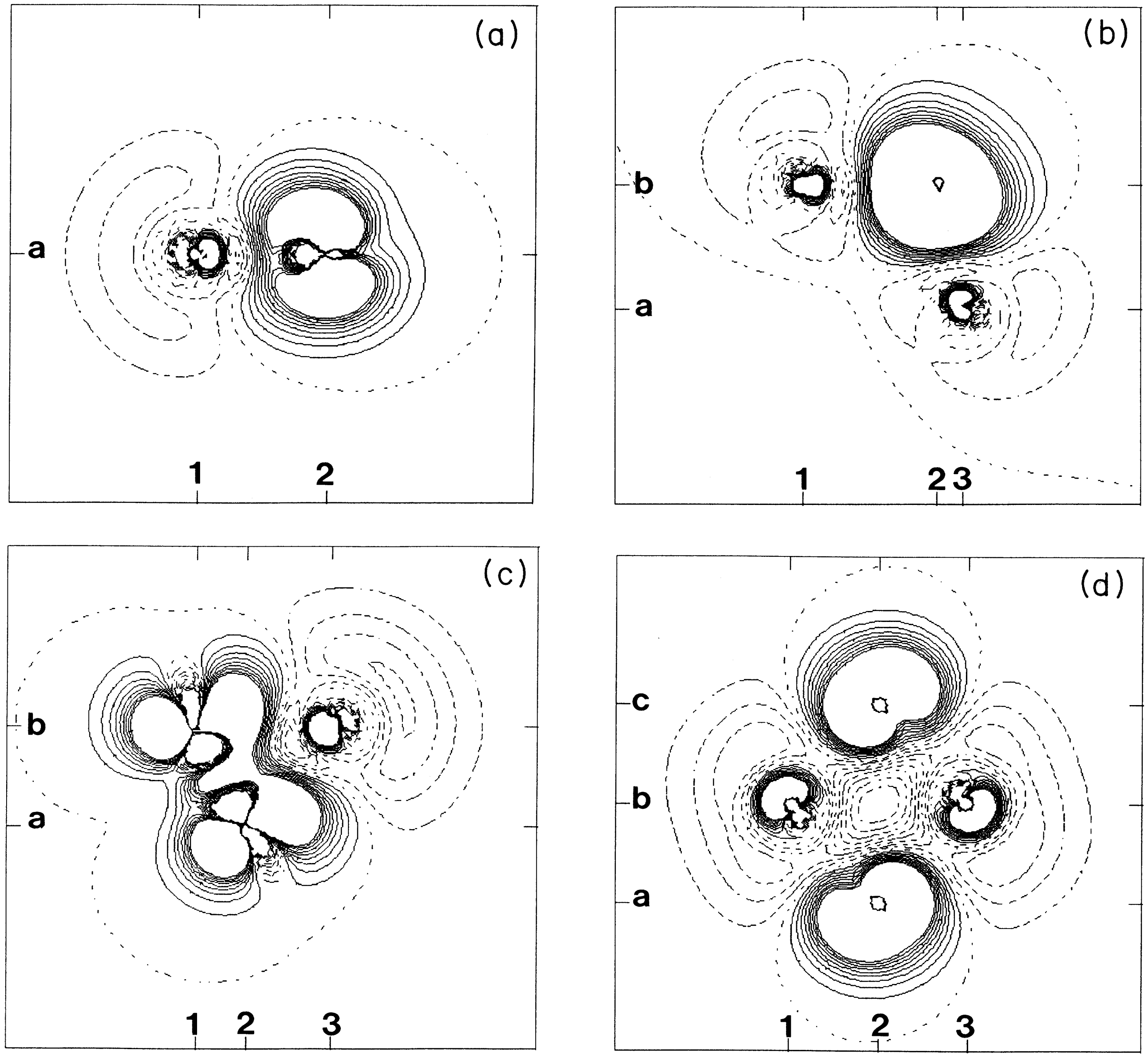

FIG. 2. Charge density of (a) MgO, (b) Mg_2O, (c) MgO_2, and (d) Mg_2O_2 relative to the free atoms. The positions of the atoms are (a) Mg (1-a), O (2-a); (b) Mg (1-b, 3-a), O (2-b); (c) Mg (3-b), O (1-b, 2-a); (d) Mg (1-b, 3-b), O (2-a, 2-c). The contour lines cover the range from 0 to 0.025 e/Å^3 with spacing of 0.0025 e/Å^3.

tion energy supplies such information. For example, the atomization energy of MgO, Mg_2O, and Mg_2O_2 clusters is 2.57, 5.55, and 10.30 eV, respectively. Thus the triatomic and dimer configurations can approximately be explained in terms of two-body Mg-O interactions since their atomization energy is, respectively, about two and four times the energy for the case of the monomer. Although three-body contributions provide the bending in the optimized configurations, they modify slightly the atomization energies. Nonclassical effects between alike atoms are almost negligible due to their weak interaction at large interatomic separation (>2.4 Å). The density maps shown in Fig. 2 confirm the dominant role of Mg-O bond in Mg_2O and Mg_2O_2 clusters.

For the oxygen-excess triatomic cluster MgO_2 the atomization energy is 4.62 eV in the optimized configuration and 2.99 eV in the linear configuration. This strong variance of the atomization energy with the cluster configuration suggests that the O-O interaction controls the stability in this case. In the optimized configuration, the O-O interaction is attractive, as shown in Fig. 2(c). It is remarkable that the O-O distance in MgO_2 is only 0.3 Å greater than that in the O_2 molecule.

In the triatomic clusters, the Mg-excess cluster is found to be more stable than the O-excess cluster against the dissociation into atoms. This contradicts the results of the calculations based on the LDA approximation [10], which predict the higher stability of the O-excess cluster. For the triatomic and dimer clusters we have also studied the following fragmentations involving combinations of monoatomic, diatomic, and triatomic products:

$$\text{(A)}\quad Mg_2O \rightarrow MgO + Mg\ ,\quad E_A = 2.97\ \text{eV}$$

$$\text{(B)}\quad MgO_2 \rightarrow Mg + O_2\ ,\quad E_B = -0.54\ \text{eV}$$

$$\text{(C)}\quad MgO_2 \rightarrow MgO + O\ ,\quad E_C = 2.05\ \text{eV}$$

$$\text{(D)}\quad Mg_2O_2 \rightarrow Mg_2O + O\ ,\quad E_D = 4.75\ \text{eV}$$

$$\text{(E)}\quad Mg_2O_2 \rightarrow MgO_2 + Mg\ ,\quad E_E = 5.67\ \text{eV}$$

$$\text{(F)}\quad Mg_2O_2 \rightarrow 2MgO\ ,\quad E_F = 5.15\ \text{eV}$$

where E's stand for the dissociation energy. It is to be noted here that the geometrical configuration of reactants and products has been full optimized, and their total energies calculated at the HF + MP2 level. Accordingly, we have found that MgO_2 is unstable and converts to Mg and O_2 in concordance with the lack of oxygen-rich clusters in mass spectra from gas aggregation [2,3] and sputtering [1] experiments, and collision-induced-fragmentation data [1]. The Mg-excess triatomic is stable by almost 3 eV to the most favorable fragmentation path. For the dimer we have found that the loss of an oxygen atom is preferable than the loss of a MgO monomer by only 0.40 eV. Both reactions are competitive and this result could be inverted as we increase the cluster size. Finally, notice that the evaporation of a MgO molecule is energetically more favorable by only a single step (F) than by the combination of two steps [(E) and (C) or (D) and (A)].

In the HF calculations of NaCl clusters [4], Galli, Andreoni, and Tosi have reported that the most stable fragmentation products of Na_2Cl and Na_2Cl_2 are NaCl + Na and 2(NaCl) with dissociation energies of 0.74 and 2.14 eV, respectively. In comparison, the dissociation energies of the corresponding MgO clusters are found to be 2.97 and 5.15 eV, respectively. Since the structural configurations are very similar in both cases, we believe that the higher stability of the NaCl monomer (4.20 eV) compared to the MgO monomer (2.56 eV) provides the lower dissociation energy for metal-excess and dimer clusters of NaCl.

B. Single-charged clusters

Computations on MgO^+, Mg_2O^+, and $Mg_2O_2{}^+$ have been carried out optimizing geometrical parameters at the HF level and including MP2 correlation corrections for the total energy of the optimized configurations (i.e., adiabatic approximation). In addition, we have performed HF + MP2 calculations on the same ionized species using the corresponding optimized configurations of the neutral clusters (i.e., vertical approximation). Both sets of calculations provide information about the electronic relocalization and the geometrical relaxation due to the ionization and also enable us to check the validity of the vertical approximation.

In Fig. 3 we plot the optimized structures for the single-charged clusters. There are structural distortions upon the ionization process: the monomer becomes 4% larger, the Mg-excess triatomic undergoes a transition from C_{2v} to $C_{\infty v}$, and the Mg-O bond increases 2% in the dimer retaining the D_{2h} symmetry. In NaCl microclusters Galli, Andreoni, and Tosi [4] have found an ionization-induced structural transition for the dimer. The optimized configuration of $Na_2Cl_2{}^+$ consists of a chlorine atom weakly attached to the center of a linear Na-Cl-Na chain. This C_{2v} configuration presents an optimized ${}^2A_1$ state for $Mg_2O_2{}^+$ with a total energy 2.79 eV higher than the one obtained with a D_{2h} symmetry. The reason for this different behavior in this case, we believe, is due to a greater preference of the hole to localize on one center in NaCl clusters, in contrast to a more delocalized scenario in MgO clusters (see Fig. 4). This is a clear illustration of the different ionicities of NaCl and MgO at the microcluster scale.

The density maps of Fig. 4 show the electronic charge of the neutral clusters relative to the ionized species at the same configuration. The solid lines indicate zones of loss of electronic density, due either to the ionization or the electronic relocalization, whereas the dashed lines indicate the electronic gain due to the electronic relocalization. In all cases, we observe that the ionization is accompanied by a change in the symmetry of the oxygen $2p$ orbitals involved in the bonding. This change modifies the symmetry of the electronic state of the monomer ($\Sigma \rightarrow \Pi$) and the dimer ($A_g \rightarrow B_{2u}$). On the other hand, the electron hole is spread out over the MgO molecule and is more localized over each center in the triatomic and dimer clusters. Above all, the important point to notice is the presence of both magnesium and oxygen contributions to the hole. The numerical values, from Mulliken population analysis in the unrelaxed configurations of the ionized clusters, show similar Mg-O "compositions" of the hole distribution (76–24 % in the monomer and 44–56 % in the dimer) to the values in the corresponding relaxed configurations (71–29 % and 48–52 %). These results illustrate a small variation in the electronic structure due to the vertical approximation.

For the diatomic MgO^+ the equilibrium distance is 1.815 Å with a vibrational frequency of 756 cm^{-1} and an atomization energy of 1.88 eV. Schamps and Lefebvre-Brion [12] report values of 1.811 Å, 809 cm^{-1}, and 1.73 eV from accurate *ab initio* calculations based on Nesbet's linear-combination-of-atomic-orbitals–self-consistent-field method. The most recent experimental value of the atomization energy is 2.3±0.13 eV [7].

The ionized metal-rich triatomic Mg_2O^+ presents an optimized configuration with a linear disposition of the nuclei [Fig. 3(b)], the equilibrium distances being 1.73 and 1.85 Å and the atomization energy being 6.50 eV. Mg_2O^+ is well described either in terms of a Mg^+ cation attached to the neutral MgO molecule or by means of a Mg atom attached to the ionized monomer. These pictures give support to the suggested configurations for Ca_2O^+ and Sr_2O^+ based on photodissociation spectra [13]. Polarization effects cause the higher atomization energy (6.50 eV) of the triatomic as compared with the sum of MgO and MgO^+ values (4.44 eV). In the ionized dimer the Mg-O-Mg angle becomes the one larger than 90° and the configuration is now more similar to a square. The atomization energy of this species is the same one calculated for the neutral dimer (10.30 eV).

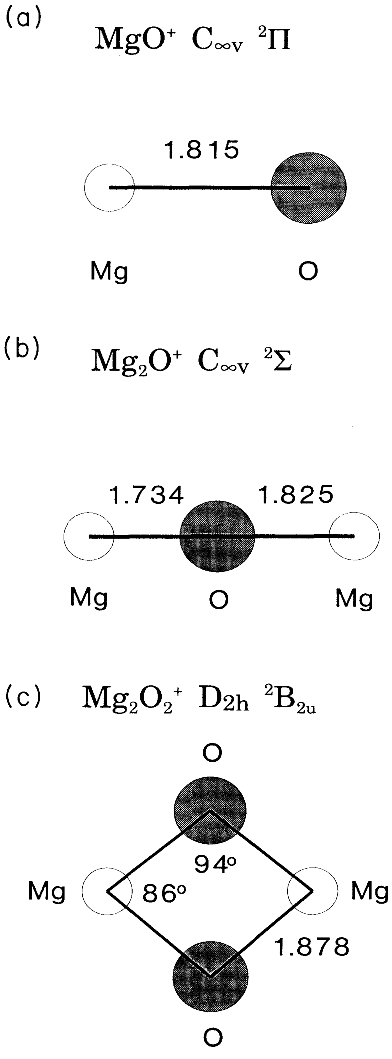

FIG. 3. Structures for (a) MgO^+, (b) Mg_2O^+, and (c) $Mg_2O_2^+$.

The calculated ionization potentials for the monomer, triatomic, and dimer clusters are 7.90, 5.80, and 7.20 eV, respectively. The experimental ionization potential for the monomer is 7.90±0.01 eV [7]. The corresponding vertical values are 8.01, 6.16, and 8.06 eV, showing differences to the adiabatic values less than 1 eV, as pointed out in Sec. II. These differences are mainly due to the structural relaxations upon ionization. We have found that even in the case of configurational symmetry breaking ($Mg_2O \rightarrow Mg_2O^+$) the electronic structures of the vertical and adiabatic configurations present a great similarity. In NaCl calculations, the differences between vertical and adiabatic values are larger than twice the values obtained here, in concordance with the stronger effect of the ionization on NaCl clusters.

It is worthwhile to note that the ionization energies represent around twice the fragmentation energies required to dissociate the neutral clusters through the most likely channels. This result indicates the preference for fragmentation processes with respect to the ionization in the neutral clusters.

Finally, we discuss the fragmentation channels explored in the ionized clusters, along with the dissociation energies from the adiabatic (E_{ad_l}) and the vertical (E_{ver_l}) calculations:

$$\text{(A)}\quad Mg_2O^+ \rightarrow MgO^+ + Mg\ ,\quad E_{\mathrm{ad}_A} = 4.62\ \text{eV}\ ,$$
$$E_{\mathrm{ver}_A} = 4.35\ \text{eV}$$
$$\text{(B)}\quad Mg_2O^+ \rightarrow MgO + Mg^+\ ,\quad E_{\mathrm{ad}_B} = 3.93\ \text{eV}\ ,$$
$$E_{\mathrm{ver}_B} = 3.55\ \text{eV}$$
$$\text{(C)}\quad Mg_2O_2{}^+ \rightarrow Mg_2O^+ + O\ ,\quad E_{\mathrm{ad}_C} = 3.80\ \text{eV}\ ,$$
$$E_{\mathrm{ver}_C} = 3.32\ \text{eV}$$
$$\text{(D)}\quad Mg_2O_2{}^+ \rightarrow MgO_2 + Mg^+\ ,\quad E_{\mathrm{ad}_D} = 5.67\ \text{eV}\ ,$$
$$E_{\mathrm{ver}_D} = 4.81\ \text{eV}$$
$$\text{(E)}\quad Mg_2O_2{}^+ \rightarrow MgO + MgO^+\ ,\quad E_{\mathrm{ad}_E} = 5.85\ \text{eV}\ ,$$
$$E_{\mathrm{ver}_E} = 5.10\ \text{eV}\ .$$

It is to be noted here the equivalent picture provided by vertical and adiabatic calculations, with quantitative discrepancies less than 0.5 eV for the lowest energetic paths. In the following, we will refer to the values from adiabatic calculations. For the Mg-rich triatomic cluster the loss of the cation Mg^+ is more favorable than the loss of the Mg atom by 0.69 eV, being the lowest dissociation energy greater than the one involved in the fragmentation of the neutral cluster. The lowest dissociation energy for ${NaCl_2}^+$ is 2.13 eV according to the HF calculations [4], involving the metallic cation as a fragment. As for the neutral Na-excess cluster, the higher stability of the NaCl monomer with respect to MgO explains the difference in the dissociation energy.

Our value of 3.93 eV for Mg_2O^+ is somewhat higher than that expected from Ziemann and Castleman (2.3 eV) in their tentative explanation of metal-excess mass spectra data [2], but is fully consistent with the series of atomic *s*-*p* transitions proposed by Saunders to explain photodissociation spectra of SrO and CaO clusters [13]. The photodissociation bands for Sr_2O^+ (2.0 eV) and Ca_2O^+ (2.15 eV) lie within the limits of the *s*-*p* transitions [14] obtained in Sr and Sr^+ (1.775–2.941 eV) and Ca and Ca^+ (1.88–3.12 eV), respectively. If the same behavior is expected for nonstoichiometric MgO clusters, the dissocia-

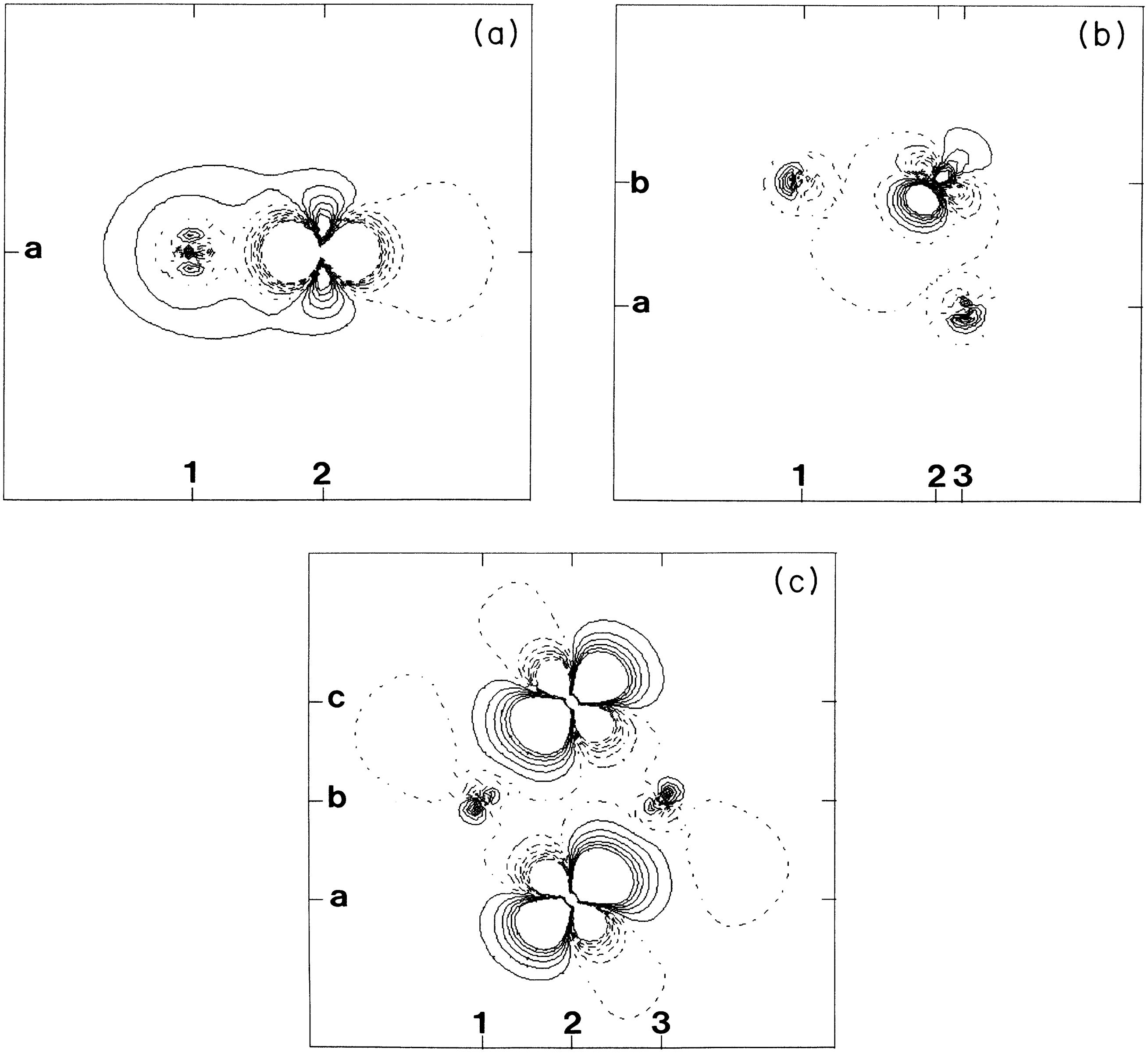

FIG. 4. Charge density of (a) MgO, (b) Mg_2O, and (c) Mg_2O_2 relative to the ionized clusters at the same configuration. The positions of the atoms are (a) Mg (1-a), O (2-a); (b) Mg (1-b, 3-a), O (2-b); (c) Mg (1-b, 3-b), O (2-a, 2-c). The contour lines cover the range from 0 to 0.025 e/Å^3 with spacing of 0.004 e/Å^3.

tion energy should lie between the *s*-*p* electronic transition energy for Mg (2.70 eV) and Mg^+ (4.40 eV). That is the case for our vertical (3.55 eV) and adiabatic (3.93 eV) predictions for Mg_2O^+.

As in the case with the neutral dimer, in $Mg_2O_2{}^+$ the evaporization of an oxygen atom is again the most favorable channel of fragmentation, whose dissociation energy lies about 1.5 eV below other possible dissociation paths. Experimentally, direct information of fragment products [1] indicates that the loss of a neutral O atom is the most probable channel for $Mg_5O_5{}^+$. We notice here that $Na_2Cl_2{}^+$ is also reported [4] to follow the same fragmentation path (i.e., evaporization of a Cl atom) with dissociation energy of about 0.05 eV (0.07 eV is the experimental value [15]). This small value is suggested to be due to the high instability of the C_{2v} configuration of $Na_2Cl_2{}^+$ cluster.

IV. CONCLUSIONS

The effect of computational constraints on the cluster configuration and atomization energy for small MgO clusters have been explored as a prelude to the calculations on larger MgO clusters [16]. The calculated results show that an adequate description of the cluster geometry can be obtained at the HF level. However, the addition of the MP2 correction is necessary for the atomization energy. For the case of ionized clusters, the adiabatic calculations have been found to provide small corrections (< 10%) to the corresponding vertical energies. The nature of bonding and dissociation paths has been predicted by both types of calculations (vertical and adiabatic) in a very similar way.

The ionization process is not found to produce significant distortions in the structural configurations of MgO neutral clusters. This is in contrast to the case of NaCl microclusters, where a relatively stronger effect of ionization is predicted. Our results demonstrate that this difference is mainly due to the character of the hole that is predicted to be delocalized in MgO clusters.

The fragmentation products of MgO dimers show that the evaporization of a single O atom is the most favorable dissociation path. The calculated dissociation energies are found to be greater than those of NaCl microclusters. The large atomization energy of the NaCl monomer and the high instability of the triangular $Na_2Cl_2{}^+$ have been proposed to explain this difference. Finally, the ionization energy of the neutral clusters is predicted to be about twice the dissociation energies of both neutral and ionized MgO microclusters.

Note added in proof. Moukouri and Noguera [Z. Phys. D **24**, 71 (1992)] have recently reported a self-consistent tight binding calculation on MgO clusters. For $(MgO)_2$ cluster, the parallelogram is found to be the ground-state configuration. The Mg-O separation is reported to be 1.77 Å in MgO and 1.73 Å in $(MgO)_2$ cluster.

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