Crossover between ionic/covalent and pure ionic bonding in magnesium oxide clusters

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An empirical potential with fluctuating charges is proposed for modelling (MgO)n clusters in both the molecular (small n) and bulk (n → ∞) regimes. Vectorial polarization forces are explicitly taken into account in the self-consistent determination of the charges. Our model predicts cuboid cluster structures, in agreement with previous experimental and theoretical results. The effective charge transferred between magnesium and oxygen smoothly increases from 1 to 2, with an estimated crossover size above 300 MgO molecules.

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Crystalline magnesium oxide is a purely ionic compound in which the Mg2+ and O2− ions carry a charge Z around ±2. In gas phase, the oxide anion O2− is unstable and spontaneously decays into O− + e due to the strong electron-electron repulsion. As a result, the effective atomic charge in the MgO molecule is much smaller than 2: independent ab initio calculations by Ziemann and Castelmann and by Recio et al. found Z ~ 0.8. In the intermediate sizes regime, (MgO)n clusters are thus expected to show intriguing properties due to a partially covalent character of the chemical bonding. Beyond condensed matter or molecular physics, these clusters received some special attention in the astrophysics community, where they have been involved in the nucleation process of dust in circumstellar shells around M-stars.

Despite the vast amount of experimental and theoretical investigations on neutral or charged clusters, the way and the rate at which chemical bonding evolves from ionic/covalent at small sizes toward purely ionic in the bulk remains essentially unexplored. Because the electrostatic field created by the ions does not vanish in finite systems, the highly polarizable oxide anion has a rather floppy and deformable outer electron cloud, which could be responsible for a partial screening of the repulsion between cations. However, the situation is complicated by the possible coordination-dependence of the charge transferred locally.

Theoretical studies of (MgO)n clusters can be effectively separated into two groups. Ab initio or density-functional theory (DFT) based calculations have been performed on specific geometries, in a rather limited size range. These works predict that small clusters exhibit cuboid-like shapes similar to NaCl rocksalt clusters. The apparent coordination transfer, as estimated from Mulliken populations, is indeed size- and coordination-dependent, and lies between 1 and 1.5 for 2 ≤ n ≤ 13. More empirical methods have also been used to predict optimal structures. Ziemann and Castelmann and, more recently, Roberts and Johnston have used the rigid ion model (Born-Mayer + Coulomb interactions) potential with two possible values of the charge transferred. When a charge Z = 1 is taken, cuboids are preferentially found as the stable geometries. For Z = 2, as in the bulk, small clusters show instead hollow, fullerene-like structures. The effects of polarization have been studied by Köhler and coworkers using the polarizable ion model due to Rüttner. Wilson investigated MgO “nanotubes” made of hexagonal (MgO) rings stacked. For this he developed a more sophisticated compressible-ion model with explicit coordination-dependent polarizabilities.

None of these empirical potentials account for the different charges transferred in MgO clusters. Only in Ref. the authors explicitly employed a size-dependent value of the charge Z, using an arbitrary law Z(n) = (2ζn + 1)/(ζn + 1). ζ was taken such that the crossover between ionic/covalent and purely ionic, for which Z equals 1.5, occurs approximately at n* = 20. However, the low energy structures found by Köhler and coworkers significantly deviate from regular cuboids or stacked hexagons in this size range. An improved treatment of electrostatics and charge transfer is provided by fluctuating charges (fluc-q) potentials based on the principle of electronegativity equalization. Such potentials have been used in simulations of water and molten salts, and have recently proven valuable in describing the heterogeneous bonding in coated fullerenes and nanotubes. They have been extended to include dipolar terms and the corresponding polarization. In MgO clusters atomic polarization cannot be neglected, and we provide here a self-consistent treatment of these effects. Briefly, the system is made of N magnesium cations and M oxygen anions, each carrying a charge qi and located at the position vector ri. The total potential energy of the system is written as V = Vrep + VQ. The repulsion interaction Vrep is taken in the usual Born-Mayer format as a function of the distance r_{ij} between ions i and j:

\[ V_{\text{rep}}(\{r_i\}) = \sum_{i<j} D \exp(-\beta r_{ij}), \]  

The total electrostatic energy VQ is expressed as

\[ V_{\text{Q}}(\{r_i\}) = \sum_i \left[ \varepsilon_i q_i + \frac{1}{2} r_{ii} q_i^2 - \frac{1}{2} \alpha_i E_i^2 \right] + \sum_{i<j} J_{ij}(r_{ij}) q_i q_j + \lambda \left( Q - \sum_i q_i \right). \]
\[ J_{ij}(r) = \left[ r^2 + (U_{ij}^0)^{-2} \exp(-\gamma_{ij}r^2) \right]^{-1/2}. \]

\[ \alpha_i = \alpha_M \text{ or } \alpha_O \text{ are the atomic polarizabilities, and } E_i \]

\[ E_i = \sum_{j \neq i} q_j \vec{J}_{ij} \]

Finally, the last term in Eq. \((2)\) includes a Lagrange multiplier \(\lambda\), which accounts for the conservation of the total charge \(Q\) of the system. Given an instantaneous set of positions \(\{\vec{r}_i\}\), the charges \(\{q_i\}\) are found by minimizing Eq. \((2)\) above. Thanks to the linear dependence of the electric fields \(E_i\)'s on the charges, the expression of \(V_Q\) is quadratic in the \(q_i\)'s, and its minimization can be done readily using linear algebra. The charges are solution of \(Q\) is expressed as

\[ C_{ij} = J_{ij} - \sum_k \alpha_k \left( \frac{\partial J_{ki}}{\partial \vec{r}_{ki}} \cdot \frac{\partial J_{kj}}{\partial \vec{r}_{kj}} \right), \]

with \(J_{ii} = U_{ii}^0\). The polarizability of the cluster can be calculated by imposing external electric fields and by computing the variations of the electric dipole. The previous expressions need to be modified accordingly to incorporate this effect. This model has 11 independent parameters, including \(D, \beta\), the \(\alpha_i\)'s, the \(U_{ij}^0\)'s and \(\gamma_{ij}\)'s. Only the difference in electronegativities \(\Delta \varepsilon = \varepsilon_M - \varepsilon_O\) is physically relevant. In order to make the model transferable from the molecular range up to the bulk, some constraints must be imposed on these parameters. In the MgO diatomics, the equilibrium distance, charge transferred and electric dipole are known (see for instance Ref. \(10\) and references therein). For this molecule, one must minimize the energy function \(V\) with respect to the Mg–O distance \(r\). After some calculation we find \(V_{MgO}(r) = D e^{-\beta r} + V_{MgO}^Q(r)\) with the electrostatic term:

\[ V_{MgO}^Q(r) = \frac{(\Delta \varepsilon)^2}{2(\alpha_M + \alpha_O)[J_{MgO}^r(r)]^2 + 2J_{MgO}(r) - U_{MgMg}^0 - U_{OO}^0}, \]

were we have employed the notation \(J_{MgO}^r = dJ_{MgO}/dr\).

In the (B1) crystal, the charge transferred \(Z\) and lattice constant \(a\) are chosen as reference data. Using the assumption \(J_{MgO}(a) \sim 1/a\), one finds the binding energy per ion:

\[ \frac{V_{\text{bulk}}(a)}{N} = 6De^{-\beta a} + \frac{V_{Q}^{\text{bulk}}(a)}{N}, \]

\[ \frac{V_{\text{bulk}}^Q(a)}{N} = \frac{(\Delta \varepsilon)^2}{M/a - U_{MgMg}^0 - U_{OO}^0}, \]

with \(M\) the Madelung constant. For a set of parameters, the total energies corresponding to the diatomics and to crystal must be minimized with respect to \(r\) or \(a\), respectively. This is done numerically using the Ohno form of the Coulomb integral, Eq. \((1)\) above. The full parameterization of the model can then be achieved by minimization of an error function \(\chi^2\), to reproduce some dimer and crystal properties. The following values have been adopted: \(D = 6656\ \text{eV}, \beta = 4.89\ \text{Å}^{-1}, U_{MgMg}^0 = 0.46, U_{OO}^0 = 1.13, U_{MgO}^0 = 0.85, \gamma_{MgMg} = 0.35\ \text{Å}^{-2}, \gamma_{OO} = 0.49\ \text{Å}^{-2}, \gamma_{MgO} = 0.36\ \text{Å}^{-2}, \Delta \varepsilon = 0.935, \alpha_M = 0.18\ \text{Å}^3, \) and \(\alpha_O = 0.46\ \text{Å}^3\).

**FIG. 1:** Lowest energy structures of \((\text{MgO})_n\) clusters from Monte Carlo minimization using the self-consistent polarizable fluc-\(q\) model.
This set predicts the charge transfer to be 0.92 in the MgO molecule, and 1.92 in the crystal. The equilibrium distance is 1.86 Å in the molecule and the crystal lattice constant is 1.78 Å. These data correspond to respective errors of 6% and 16% when compared with the experimentally measured values. The binding energies cannot be compared with reference values, because the present model includes extra self-energy $U^{\text{eff}}$ terms.

The lowest energy structures of $(\text{MgO})_n$ clusters have been searched using the basin-hopping or Monte Carlo minimization algorithm. For each size in the range $2 \leq n \leq 30$, 5000 Monte Carlo steps were performed starting from a random guess geometry. We also locally optimized databases of structures found by global optimization of the rigid ion model with fixed charges $\pm 1$ and $\pm 2$. In many cases, the global minimum was found to lie within the database obtained with $Z = \pm 1$.

The structures of the global minima are represented in Fig. 1. Beyond $n = 3$, they are based on small $(\text{MgO})_4$ cubic units. The cuboid picture found in the present Communication is essentially similar to the results of Roberts and Johnston, obtained with a genetic algorithm, except for the slight distortions due here to polarization. We do not find evidences for hollow or “spiky” geometries. Stacking of $(\text{MgO})_3$ hexagonal units leads to isomers slightly less stable than cuboids at the same size. This partly explains why the global minima at $n = 14$ and $n = 22$ differ from the results of Roberts and Johnston. Actually the fact that hexagonal rings are less favored in the present model is not in strong contradiction with experimental results, for two reasons. Firstly, experiments have been performed by mass spectrometry on charged species, which may well exhibit different structures than neutrals. Secondly, most magic numbers peaks interpreted as the signature of hexagonal stacks are indeed compatible with cuboid like geometries.

The variations with size of the binding energy of the lowest energy structures found with the present polarizable fluc-q model are depicted in Fig. 2. The binding energy $E$ shows a global increase, which can be fitted approximately in a liquid drop fashion as $E(n) = -15.13n + 1.83n^{2/3} + 0.89n^{1/3} + 1.45$. The values of the latter parameters are slightly changed if we include larger cubic clusters such as $(\text{MgO})_{108}$. By construction, the crystal binding energy found from this expression is close to the numerical minimization of Eq. 1.

As can be noted in Fig. 2, there are some deviations from the smooth behavior of the fitted energy. To see them more clearly, the second energy difference $\Delta_2 E(n) = 2E(n) - E(n + 1) - E(n - 1)$ has been represented in the inset of this figure. This quantity is usually convenient to find the special stabilities of some sizes. The most stable clusters appear here at $n = 2, 4, 6, 9, 12, 18, \text{ and } 24$. The sizes $n = 15, 21, \text{ and } 27$ can be added as relatively stable. All these clusters are perfect cuboids. The magic character of the $n = 15$ cluster is less marked, due to the fact that $(\text{MgO})_{16}$ is also a cuboid.

![Binding Energy vs. Size](image)

**FIG. 2:** Binding energy of $(\text{MgO})_n$ clusters in the range $1 \leq n \leq 30$. The horizontal dashed line marks the asymptotic bulk limit. The open circles correspond to the structures of Fig. 1, the solid line is a fit of the form $E(n)/n = a + bn^{-1/3} + cn^{-2/3} + dn^{-1}$, with parameters given in the text. Inset: second energy difference $\Delta_2 E(n) = 2E(n) - E(n + 1) - E(n - 1)$ versus $n$.

We turn now to the problem of charge transfer, and more generally to the ionic or covalent nature of the chemical bonding in MgO clusters. In Fig. 3 we have represented the average charge $\langle q \rangle$ carried by the ions in the cluster, regardless of their position inside the cluster or coordination number. This quantity is defined as the mean value over all magnesium ions, which is the exact opposite of the mean value over all oxygen ions. This definition is somewhat loose and arbitrary, because all ions do not play the same role in the cluster due to the large surface/volume ratio. From Fig. 3 we see that charge transfer is strongly size-dependent in the present fluctuating charges model, and that the convergence toward the bulk limit is much slower than assumed by Köhler and coworkers. In fact, knowing that the average charge effectively reaches about 2 electrons at large $n$ allows us to fit the variations of $\langle q \rangle$ with $n$ as $\langle q \rangle(n) \approx 2 - a'n^{-1/3} - b'n^{-2/3} - c'n^{-1}$. The effective crossover size between mixed ionic/covalent bonding and pure ionic bonding can then be estimated as $n^*$ such that $\langle q \rangle(n^*) \sim 3/2$. To get more realistic values for $n^*$, we have included the data corresponding to larger cubic clusters, namely $(\text{MgO})_{32}$ and especially the $6 \times 6 \times 6$ cluster $(\text{MgO})_{108}$. Because the size range covered remains relatively small, the value for the latter cluster was given a weight of 10 in the fitting process, with respect to smaller sizes. Using this procedure, we find the crossover size to be located at $n^* \sim 300 \pm 100$ depending on the presence of the large cluster in the fit. Including the value for $(\text{MgO})_{108}$ results in an increase of $n^*$, and including the data for larger clusters should further shift the crossover size toward several hundreds or thousands MgO molecules.
Within the present empirical model, electrostatic properties are naturally coordination dependent. In the inset of Fig. 3, the modulus of the charge transferred is plotted for each ion in the (MgO)$_{108}$ nanocrystal versus its coordination number. Several features are of interest. First, the magnitude of the charge transferred increases with coordination, as expected from the decreasing intensity of the electric field. This is in agreement with the electronic structure calculations performed by Recio et al. by Veliah et al., and more recently by Coudray et al. Second, the charge carried by magnesium ions is more sensitive to coordination than the charge carried by oxygen ions. This is also in agreement with the findings of Veliah et al. The above results confirm that conventional potentials with fixed charges are not fully appropriate to describe MgO clusters. This had been addressed by Wilson who considered phenomenological coordination-dependent polarizabilities within the compressible-ion model. Coordination-dependent charges are a natural outcome of the present potential, allowing to study MgO clusters in a wide range of condensed phases. While the present potential is able to treat large clusters beyond the possibilities of first principles-based computations, the needed inversion of a square matrix can be a limiting factor. Fortunately, extended Lagrangian techniques can reduce the computational cost significantly, making the polarizable fluctuating model valuable in thermodynamical context.

To conclude, we proposed an empirical model to describe ionic/covalent bonding in MgO clusters. This model is based on fluctuating charges and incorporates atomic polarization in a self-consistent way. By fitting it on both molecular and bulk properties we found that small clusters preferentially exhibit cubic geometries, showing magic numbers in good agreement with experiments. The average charge carried by magnesium or oxygen atoms smoothly increases, and the crossover between ionic/covalent and pure ionic bonding was estimated to be above 300 molecules. The model correctly predicts that the charge transferred depends on coordination.

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