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# Structural Diversity and Flexibility of MgO Gas-Phase Clusters

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*In memoriam Hans Georg von Schnering*

Magnesium oxide, MgO, is a prototype material of (simple) metal oxides. The NaCl-type structure of bulk MgO is the only phase observed in experiments up to the pressure of 227 GPa.[1,2] This indicates an inherent structural stability of MgO which can be expected to persist when passing from the bulk solid to molecular clusters. Indeed, mass spectra of $(MgO)_n^+$ and $(MgO)_nMg^+$ cluster ions along with calculations using rigid ion and polarizable ion shell model potentials indicated compact cubic structures similar to fragments of the MgO crystal lattice[3] with the most abundant clusters based on a $(MgO)_3$ subunit.[4] The spectra and cluster compositions observed in IR resonance-enhanced multiphoton ionization experiments on large neutral $(MgO)_n$ ($n \geq 15$) clusters also gave indications for cubic structures.[5] Up to now, computational studies have almost exclusively investigated neutral MgO clusters, without direct comparison to experiment,[3,6-8,10-17] despite the fact that most experiments were performed on cationic clusters. The main conclusion from these studies has been that for a given value of $n$ the most stable structures are cube-like, except for $(MgO)_{3n}$ clusters for which rings and stacks of rings are preferred. The geometric structures of the cationic MgO clusters have been assumed to be the same as for neutral ones (vertical ionization approximation)[8] except for small hypermagnesium ions,[9] and no systematic theoretical studies of the stoichiometric cationic clusters have been reported so far.

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the authors.

In this study we demonstrate that, in contrast to the bulk material, neutral and cationic gas-phase clusters of MgO display unusual structural diversity and flexibility. Not only are the structures of the clusters in most cases non-cubic, but they also differ between neutral and charged ones. The atomic structures of cationic stoichiometric $(MgO)_n^+$ ($n$ = 2-7) clusters were determined by combining quantum chemical calculations with infrared multiple photon dissociation (IR-MPD) experiments. In particular, global structure optimizations have been performed for all the cluster sizes using density functional theory (DFT). Although several of the geometric structures reported here (but not all of them) have been found before for neutral[3,7,10-17] and anionic clusters[18] by different computational techniques, our calculations unequivocally reveal the global minima among all these configurations. In the experiment, cationic clusters and their weakly bound complexes with Ar and $O_2$ are investigated in a molecular beam. Changes in this cluster distribution induced by the interaction with tunable infrared radiation are used to obtain the cluster-size specific IR-MPD spectra.[19]

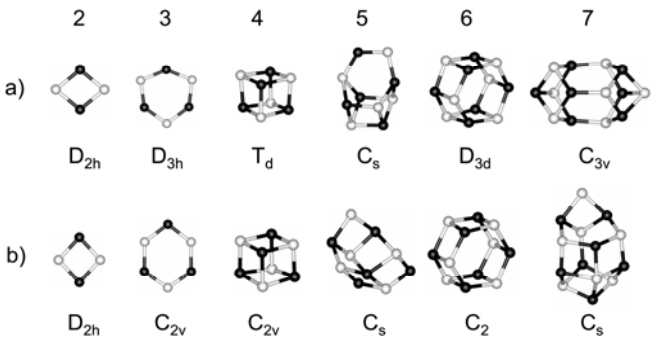


***Figure 1.*** The most stable structures of a) neutral $(MgO)_n$ and b) cationic $(MgO)_n^+$ clusters with $n$ = 2-7 (black: Mg, white: O).

Figure 1 presents the global minimum structures of neutral $(MgO)_n$ and cationic $(MgO)_n^+$ clusters with $n$ = 2-7; for other low energy isomers see Figs 1S and 2S in the electronic supporting information. Figures 2 and 3 show a comparison between the experimental IR-MPD spectra and the calculated linear IR absorption spectra for the $(MgO)_n^+$ gas-phase clusters. Except for $n$ = 2 and 4 the most stable isomers of neutral $(MgO)_n$ clusters form cage-like structures instead of pieces of the MgO crystal lattice. In general, the global minima of neutral clusters are energetically well separated from the next lowest energy structures by at least 30 kJ/mol. The cationic $(MgO)_n^+$ clusters prefer more open structures over the cubic ones. They usually have lower symmetry than their neutral counterparts because of the presence of an unpaired electron. For vanadium oxide clusters, it has also been found that addition or removal of an electron lowers the symmetry of the cluster anions or cations, respectively, compared to the neutral systems.[20]

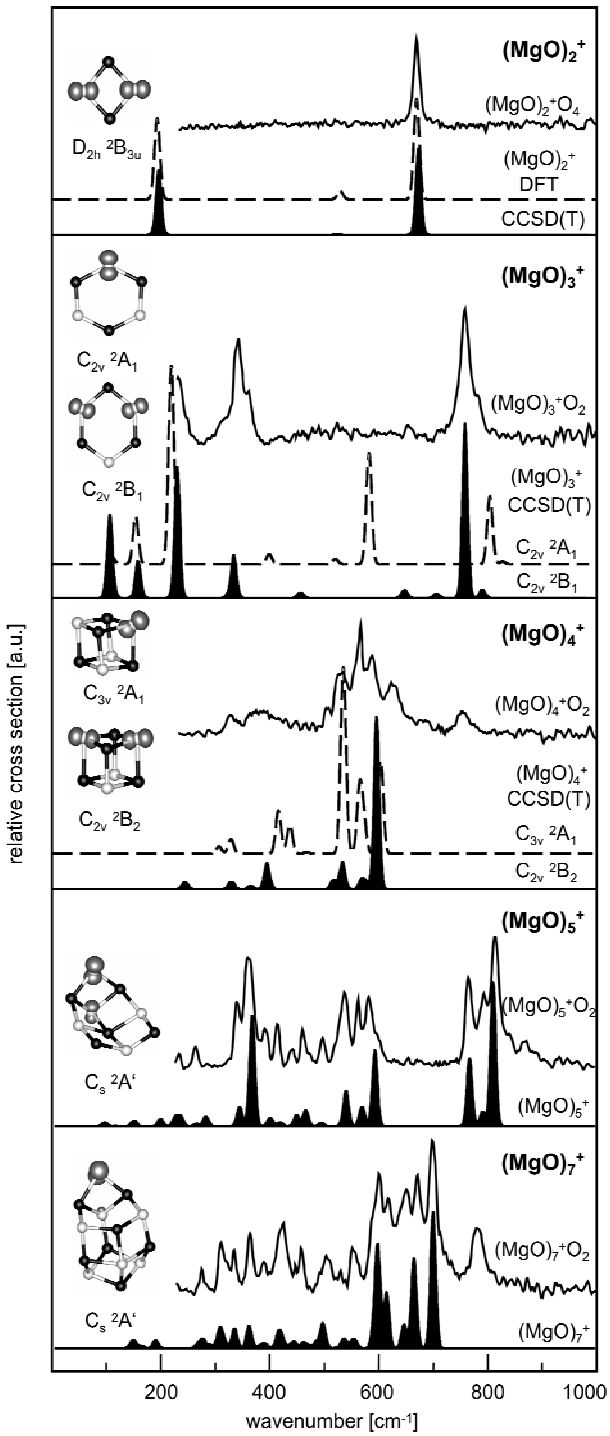


***Figure 2.*** Comparison of the experimental IR-MPD and calculated linear IR absorption spectra for the most stable $(MgO)_n^+$ gas-phase clusters with $n$ = 2-5 and 7 along with their geometrical structures. For $n$ = 2-4 the calculated CCSD(T) and for $n$ = 2, 5, 7 the DFT (B3LYP) spectra are shown. The calculated spectra are convoluted with Gaussian functions. (Mg: black, O: white, isosurface of spin density: red).

In the global minimum structures of $(MgO)_2^+$, $(MgO)_5^+$ and $(MgO)_7^+$ the unpaired electron is delocalized over two oxygen atoms. For $n$ = 3, 4 and 6 removing an electron from the neutral clusters results in a Jahn-Teller (JT) distortion leading to the appearance of two or more nearly degenerate lowest energy states which differ by spin localization. The information about spin localization is of particular interest for reactivity studies of gas-phase clusters.[21] The smallest $(MgO)_2^+$ ionic cluster shows a ring structure with $D_{2h}$ symmetry and the calculated IR spectrum is in excellent agreement with experiment (for vibrational modes see Fig. 3S in supporting information). For $(MgO)_3^+$ the JT distortion leads to a $C_{2v}$ symmetric structure with $^2B_1$ and $^2A_1$ states separated by less than 2 kJ/mol. A proper description of this cluster ion could only be achieved at the CCSD(T) level. Only for the lowest energy $^2B_1$ state with the spin density delocalized over two oxygen sites the calculated spectrum shows satisfactory agreement with the IR-MPD spectrum (Fig. 2). For $n$ = 4 the JT distortion leads to $C_{2v}$ and $C_{3v}$ symmetric structures with the lowest $^2B_2$ ($C_{2v}$) and $^2A_1$ ($C_{3v}$) electronic states separated only by 2.2 kJ/mol. Figure 2 shows that for both isomers the calculated spectra would reproduce the experimental one, except for the weak band at about 750 $cm^{-1}$. A band at such a frequency could be due to a peroxide species. However, formation of peroxide from the $O_2$ messenger can be ruled out as the feature is reproduced in the IR spectrum obtained for the Ar complex (see electronic supporting information). Possible other sources for this band could be the presence of isomers (like $Mg_4O_2(O_2)^+$) or of a different species with the same mass/charge ratio. For $(MgO)_5^+$ the excellent agreement between calculated and experimental spectra leaves no doubts about the structural assignment. The global minimum is an open sheet-like structure with $C_s$ symmetry with no resemblance to its neutral counterpart.

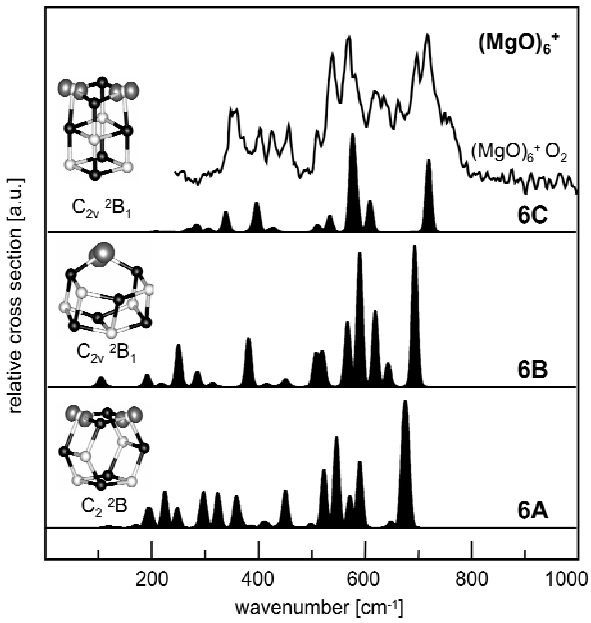


***Figure 3.*** The IR-MPD spectrum of the $(MgO)_6^+$ cluster ion and the calculated linear IR absorption spectra for its three most stable structural isomers (shown as insets). The relative energies of the isomers are given in Table 1.

For the $(MgO)_6^+$ cluster ion the structural assignment is more challenging. The global optimizations yield three low lying structures with similar energies (Fig. 3 and Table 1, note that the zero-point energy correction (ZPVE) is negligible). In fact, different quantum chemical methods predict different energy orderings of the three structures. Figure 3 shows also that the calculated spectra for all three isomers reproduce some features of the experimental spectrum. This may indicate that the IR-MPD spectrum for the $(MgO)_6^+$ cluster ion reflects the presence of a mixture of all three isomers. As the experiment has been performed at ambient temperature (~30 °C), the population of high lying isomers, as well as an isomerisation on the time scale of the experiment cannot be

ruled out. For the next larger cluster ion, $(MgO)_7^+$, the calculated and experimental spectra again show good agreement. Except for a band at 780 $cm^{-1}$ all features are reproduced in the calculated spectrum, which is an indication that the ground state structure has been found, but an additional isomer may be present in the experiment, see the discussion for $(MgO)_4^+$ above.

***Table 1.*** Relative energies [kJ/mol] of $(MgO)_6^+$ cluster ion isomers (*c.f.* Fig. 3) with different quantum chemical methods (TZVP basis set).

| Method | **6A** | **6B** | **6C** |
|---|---|---|---|
| B3LYP | 0.0 | 25.1 | 11.8 |
| ZPVE (B3LYP) | 0.0 | -0.2 | 1.3 |
| MP2 | 9.2 | 0.0 | 8.2 |
| CCSD(T) | 1.8 | 3.3 | 0.0 |

In summary, geometric structures of neutral and cationic $(MgO)_n$ ($n$ = 2-7) clusters have been predicted. In case of the cationic species these predictions have been verified by comparison with the experimental gas-phase IR spectra. Only for $(MgO)_4^+$ and $(MgO)_6^+$ cluster ions small energy differences between low energy isomers and close similarities of calculated IR spectra prevent unequivocal structure assignment. The bulk MgO is a very rigid solid with only one structure type known. Our results demonstrate that, in contrast, small neutral and cationic gas-phase clusters of MgO display unusual structural diversity and flexibility, thereby resembling alkali halide clusters.**[22]** Furthermore, even for such a prototype oxide as MgO the structures of cationic clusters may differ significantly from their neutral counterparts. Therefore, the vertical ionization approximation does not seem to be generally applicable to metal oxide clusters.

## *Experimental Section*

IR-MPD spectra of the complexes of $(MgO)_n^+$ with Ar and $O_2$ are measured in the gas phase using the Free Electron Laser for Infrared eXperiments (FELIX).[23] Magnesium oxide cluster cations are generated by pulsed laser vaporization from an isotopically enriched $^{26}Mg$ rod (purity >98%) in a mixture of 1 % oxygen and 5 % argon in helium. A distribution of pure cationic clusters as well as their complexes with Ar and $O_2$ is produced in the source at ambient temperature (30 °C), expands into vacuum to form a molecular beam and is then analyzed in a reflectron time of flight mass spectrometer. The molecular beam can be overlapped with counter-propagating IR light from FELIX. Depletion spectra are obtained by monitoring the relative intensity (with and without IR light) of the complexes as a function of the IR wavelength.[19] These are converted to absorption spectra and normalized by the photon fluence. For the weakly bound Ar and $O_2$ complexes very similar IR spectra are measured. The $O_2$ complexes are shown as these species are more pronounced in the mass spectrum, leading to a better signal-to-noise ratio in the spectra (see electronic supporting information).

All DFT calculations used the TURBOMOLE program package.[24] The global optimizations of cluster structures employ the B3-LYP hybrid exchange-correlation functional[25,26] and triple zeta valence plus polarization (TZVP) basis sets.[27-29] We apply our own implementation of the hybrid ab inito genetic algorithm (HAGA).[30] To speedup DFT calculations we use the multipole accelerated resolution of identity (MARI-J) method[31] along with the TZVP auxiliary basis sets.[28] All minima were verified by vibrational analysis as well as testing the stability of their wave functions. MP2 and CCSD(T) calculations were performed for $(MgO)_n^+$, $n$ = 2-4 and 6 with the same TZVP basis set as the B3LYP calculations. Initially MP2 optimizations with TURBOMOLE were performed, followed by CCSD(T) calculations with MOLPRO.[32] For $n$ = 6 single point calculations at the MP2 structures were carried out. For $n$ = 2-4 CCSD(T) structure optimizations and subsequent numerical frequency calculations were performed.

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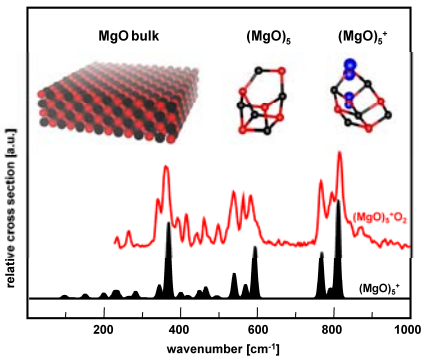


There is only one structure type known for bulk MgO. In contrast, quantum chemical calculations combined with infrared multiple photon dissociation experiments demonstrate that neutral and cationic gas phase clusters of MgO display unusual structural diversity and flexibility.