DOI: 10.1002/anie.201004617

Structural Diversity and Flexibility of MgO Gas-Phase Clusters**

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In memory of 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 a pressure of 227 GPa.[1,2] This indicates that MgO has an inherent structural stability, 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 indicate 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 $(MgO)_n$ clusters ($n \geq 15$) have also given 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 the most stable structures for a given value of n are cubelike, 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] So far, no systematic theoretical studies of the stoichiometric cationic clusters have been reported.

Herein 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 noncubic, but the neutral and charged ones also differ. 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 using density functional theory (DFT) have been performed on all the cluster sizes. Although several of the geometric structures reported here (but not all of them) have been found before with neutral[3,7,10–17] and anionic clusters[18] by different computational techniques, our calculations reveal unequivocally the global minima of all these configurations. Cationic clusters and their weakly bound complexes with Ar and O_2 have been investigated experimentally in a molecular beam. Changes in this cluster distribution induced by the interaction with tunable infrared radiation were used to obtain the cluster-size-specific IR-MPD spectra.[19]

Figure 1 shows the global minimum structures of neutral $(MgO)_n$ and cationic $(MgO)_n^+$ clusters with $n = 2$–7; for other low-energy isomers see Figures 1S and 2S in the Supporting Information. Figures 2 and 3 show a comparison between the experimental IR-MPD spectra and the calculated linear IR

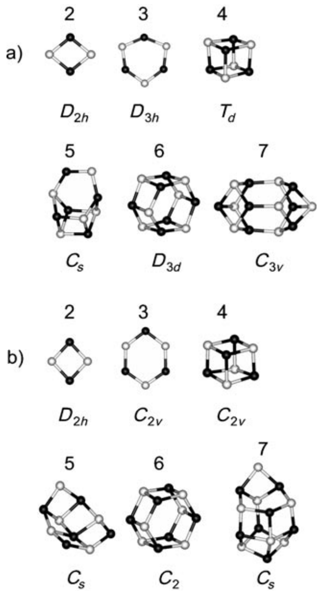

Figure 1. The most stable structures of a) neutral $(MgO)_n$ and b) cationic $(MgO)_n^+$ clusters with $n = 2$–7 (black: Mg, white: O).

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[**] We acknowledge financial support from the Deutsche Forschungsgemeinschaft (Cluster of Excellence UniCat and Sonderforschungsbereich 546) and the Fonds der Chemischen Industrie. K.K. thanks the International Max Planck Research School “Complex Surfaces in Materials Science” for a fellowship. We gratefully acknowledge the support of the Stichting voor Fundamenteel Onderzoek der Materie (FOM) for providing beam time on FELIX, and the FELIX staff for their skilful assistance, in particular Dr. B. Redlich and Dr. A. F. G. van der Meer.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201004617.

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 cagelike 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^{-1}. The $(MgO)_n^+$ clusters prefer more-open structures than the cubic ones. They usually have lower symmetry than their neutral counterparts because of the presence of an unpaired electron. It has also been found for vanadium oxide clusters that the addition or removal of an electron lowers the symmetry of the cluster anions or cations, respectively, compared to the neutral systems.[20]

The unpaired electron is delocalized over two oxygen atoms in the global minimum structures of $(MgO)_2^+$, $(MgO)_5^+$, and $(MgO)_7^+$. Removing an electron from the neutral clusters when $n = 3$, 4, and 6 results in a Jahn–Teller (JT) distortion that leads to the appearance of two or more nearly degenerate lowest energy states which differ in their spin localization. The information about spin localization is of particular interest for reactivity studies of gas-phase clusters.[21] The smallest ionic cluster $(MgO)_2^+$ shows a ring structure with D_{2h} symmetry, and the calculated IR spectrum is in excellent agreement with the experimental finding (for vibrational modes see Figure 3S in the 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^{-1}. A proper description of this cluster ion could only be achieved at the CCSD(T) level. Only for the lowest energy $^2B_1$ state, where the spin density is delocalized over two oxygen sites, does the calculated spectrum show satisfactory agreement with the IR-MPD spectrum (Figure 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^{-1}. Figure 2 shows that the combined calculated spectra for both isomers 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, the formation of peroxide from the O_2 complex can be ruled out, as the feature is reproduced in the IR spectrum of the Ar complex (see the Supporting Information). Other possible sources for this band could be the presence of isomers (such as $Mg_4O_2(O_2)^+$) or of a different species with the same mass/charge ratio. The excellent agreement between the calculated and experimental spectra of $(MgO)_5^+$ leaves no doubts about the structural assignment. The global minimum is an open sheetlike structure with C_s symmetry, with no resemblance to its neutral counterpart.

The structural assignment of the $(MgO)_6^+$ cluster ion is more challenging. The global optimizations yield three low-lying structures with similar energies (Figure 3 and Table 1, the zero-point energy correction (ZPVE) is negligible). In fact, different quantum chemical methods predict different energy orderings of the three structures. Figure 3 also shows 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 was performed at ambient temperature (ca. 30 °C), the population of high-lying isomers as well as an isomerization on the time scale of the experiment cannot be ruled out. The calculated and experimental spectra for the next larger cluster ion, $(MgO)_7^+$, again show good agreement. Except for a band at 780 cm^{-1}, all the features are reproduced in the calculated spectrum, which is an indication that the ground-state structure has been found. However, an addi-

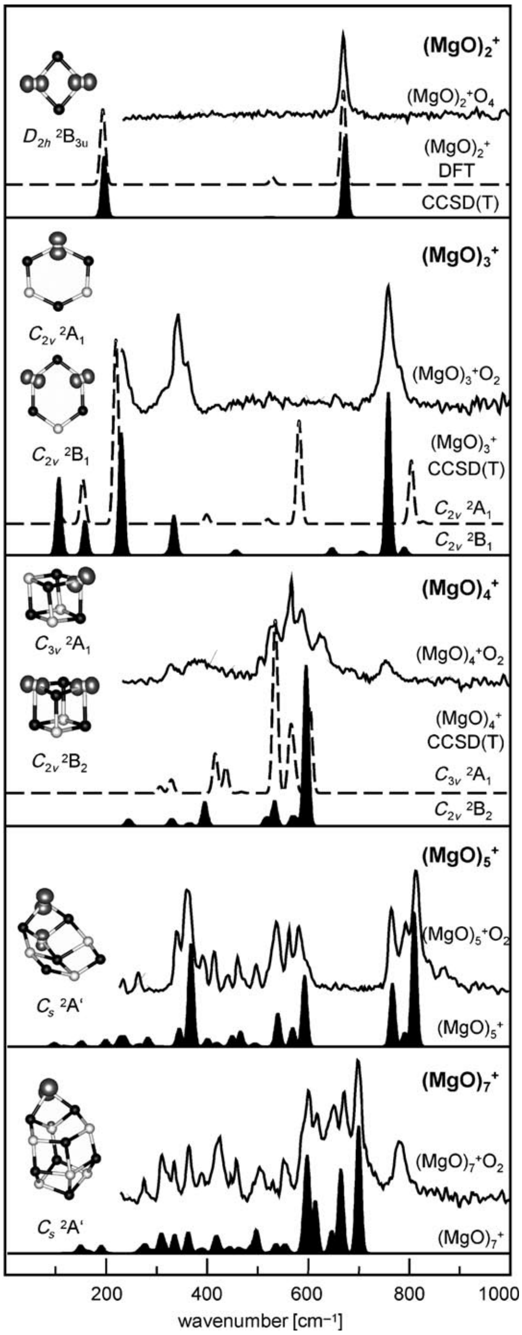

Figure 2. Comparison of the experimental IR-MPD and calculated linear IR absorption spectra for the most stable $(MgO)_n^+$ gas-phase clusters with $n = 2$–5 and 7 along with their geometrical structures. The calculated CCSD(T) and the DFT (B3LYP) spectra are shown for $n = 2$–4 and $n = 2$, 5, and 7,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

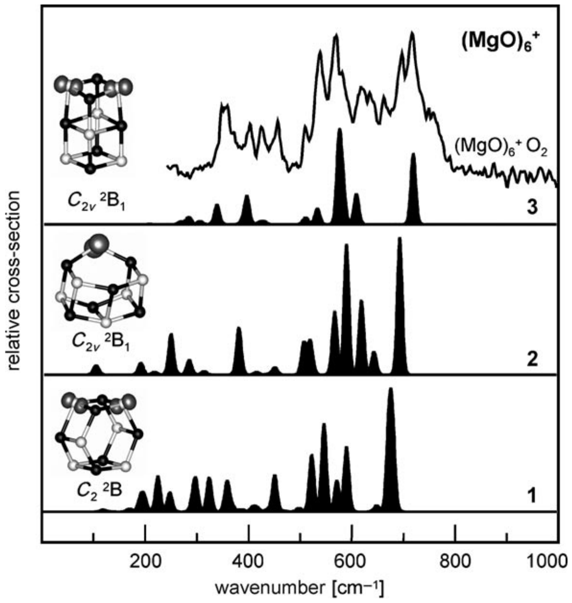

Figure 3. The IR-MPD spectrum of the (MgO)$_6^+$ cluster ion and the calculated linear IR absorption spectra for its three most stable structural isomers. The relative energies of the isomers are given in Table 1.

Table 1: Relative energies [kJ mol^{-1}] of isomers of the (MgO)$_6^+$ cluster ion (Figure 3) with different quantum chemical methods (TZVP basis set).

Method	1	2	3
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

tional isomer may be present in the experiment, see the above discussion for (MgO)$_4^+$.

In summary, geometric structures of neutral and cationic (MgO)$_n$ ($n = 2$–7) clusters have been predicted. These predictions have been verified in the case of the cationic species by comparison with the experimental gas-phase IR spectra. Small energy differences between low-energy isomers and close similarities between the calculated IR spectra prevent unequivocal structure assignment of the (MgO)$_4^+$ and (MgO)$_6^+$ cluster ions. Macroscopic MgO is a very rigid solid with only one known structure type. Our results demonstrate that, in contrast, small neutral and cationic gas-phase clusters of MgO display unusual structural diversity and flexibility, thus resembling alkali halide clusters.[22] Furthermore, the structures of cationic clusters may differ significantly from their neutral counterparts, even for such a prototype oxide as MgO. Thus, 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$_2$ were measured in the gas phase by using the Free Electron Laser for Infrared eXperiments (FELIX).[23] Magnesium oxide cluster cations were 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$_2$ was produced in the source at ambient temperature (30 °C), expanded into a vacuum to form a molecular beam, and then analyzed in a reflectron time of flight mass spectrometer. The molecular beam could be overlapped with counter-propagating IR light from FELIX. Depletion spectra were obtained by monitoring the relative intensity (with and without IR light) of the complexes as a function of the IR wavelength.[19] These spectra were converted into absorption spectra and normalized by the photon flux. Very similar IR spectra were measured for the weakly bound Ar and O$_2$ complexes. The O$_2$ complexes are shown as these species are more pronounced in the mass spectra and thus lead to a better signal-to-noise ratio in the spectra (see the Supporting Information).

All DFT calculations used the TURBOMOLE program package.[24] The global optimizations of cluster structures employed the B3-LYP hybrid exchange-correlation functional[25,26] and triple zeta valence plus polarization (TZVP) basis sets.[27–29] We applied our own implementation of the hybrid ab inito genetic algorithm (HAGA).[30] To speed up the DFT calculations we used 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 by 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] Single point calculations at the MP2 structures were carried out for $n = 6$. CCSD(T) structure optimizations and subsequent numerical frequency calculations were performed for $n = 2$–4.

Received: July 27, 2010
Revised: November 9, 2010
Published online: January 7, 2011

Keywords: gas-phase clusters · genetic algorithms · magnesium · photodissociation spectroscopy · structure elucidation

[1] A. B. Belonoshko, S. Arapan, R. Martonak, A. Rosengren, *Phys. Rev. B* **2010**, *81*, 054110.

[2] T. S. Duffy, R. J. Hemley, H.-K. Mao, *Phys. Rev. Lett.* **1995**, *74*, 1371 – 1374.

[3] P. J. Ziemann, A. W. Castleman, *Z. Phys. D* **1991**, *20*, 97 – 99; P. J. Ziemann, A. W. Castleman, *J. Chem. Phys.* **1991**, *94*, 718 – 728.

[4] W. A. Saunders, *Phys. Rev. B* **1988**, *37*, 6583 – 6586; W. A. Saunders, *Z. Phys. D* **1989**, *12*, 601 – 603.

[5] D. van Heijnsbergen, G. von Helden, G. Meijer, M. A. Duncan, *J. Chem. Phys.* **2002**, *116*, 2400 – 2406.

[6] A. I. Boldyrev, J. Simons, *J. Phys. Chem.* **1996**, *100*, 8023 – 8030.

[7] S. Moukouri, C. Noguera, *Z. Phys. D* **1992**, *24*, 71 – 79; S. Moukouri, C. Noguera, *Z. Phys. D* **1993**, *27*, 79 – 88.

[8] J. M. Recio, A. Ayuela, R. Pandey, A. B. Kunz, *Z. Phys. D* **1993**, *26*, Suppl. 1, 237 – 239.

[9] A. I. Boldyrev, J. Simons, P. von R. Schleyer, *Chem. Phys. Lett.* **1995**, *233*, 266 – 272.

[10] J. M. Recio, A. Ayuela, R. Pandey, A. B. Kunz, *J. Chem. Phys.* **1993**, *98*, 4783 – 4792.

[11] E. de La Puente, A. Aguado, A. Ayuela, J. M. Lopez, *Phys. Rev. B* **1997**, *56*, 7607 – 7614.

[12] M. J. Malliavin, C. Courday, *J. Chem. Phys.* **1997**, *106*, 2323 – 2330.

[13] X. Lü, X. Xu, N. Wang, Q. Zhang, *Int. J. Quantum Chem.* **1999**, *73*, 377–386.

[14] F. Bawa, I. Panas, *Phys. Chem. Chem. Phys.* **2001**, *3*, 3042–3047.

[15] M. Srnec, R. Zahradnik, *Eur. J. Inorg. Chem.* **2007**, 1529–1543.

[16] C. Roberts, R. L. Johnston, *Phys. Chem. Chem. Phys.* **2001**, *3*, 5024–5034.

[17] R. Dong, X. Chen, X. Wang, W. Lu, *J. Chem. Phys.* **2008**, *129*, 044705.

[18] G. D. Geske, A. I. Boldyrev, X. Li, L. S. Wang, *J. Chem. Phys.* **2000**, *113*, 5130–5133.

[19] Details on the experimental methods can be found in A. Fielicke, G. von Helden, G. Meijer, *Eur. Phys. J. D* **2005**, *34*, 83–88.

[20] a) K. R. Asmis, G. Santambrogio, M. Brümmer, J. Sauer, *Angew. Chem.* **2005**, *117*, 3182–3185; *Angew. Chem. Int. Ed.* **2005**, *44*, 3122–3125; b) H. J. Zhai, J. Dobler, J. Sauer, L. S. Wang, *J. Am. Chem. Soc.* **2007**, *129*, 13270–13276; c) G. Santambrogio, M. Brümmer, L. Wöste, J. Döbler, M. Sierka, J. Sauer, G. Meijer, K. Asmis, *Phys. Chem. Chem. Phys.* **2008**, *10*, 3992–4005.

[21] K. Kwapien, M. Sierka, J. Döbler, J. Sauer, *ChemCatChem* **2010**, *2*, 819–826.

[22] T. P. Martin, *Phys. Rep.* **1983**, *95*, 167–170; N. G. Phillips, C. W. S. Conover, L. A. Bloomfield, *J. Chem. Phys.* **1991**, *94*, 4980–4987.

[23] D. Oepts, A. F. G. van der Meer, P. W. van Amersfoort, *Infrared Phys. Technol.* **1995**, *36*, 297–308.

[24] TURBOMOLE 5.10, developed by the University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, 2007–2008; http://www.turbomole.com.

[25] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.

[26] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.

[27] A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829–5835.

[28] K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theor. Chem. Acc.* **1997**, *97*, 119–124.

[29] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

[30] M. Sierka, *Prog. Surf. Sci.* **2010**, *85*, 398–434.

[31] M. Sierka, A. Hogekamp, R. Ahlrichs, *J. Chem. Phys.* **2003**, *118*, 9136–9148.

[32] MOLPRO, version 2008.1, a package of ab initio programs, H.-J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, M. Schütz et al., see http://www.molpro.net.