$(\mathbf{MgO})_n^-$ ($n = 1$–5) Clusters: Multipole-Bound Anions and Photodetachment Spectroscopy

Maciej Gutowski*
Materials Resources, Pacific Northwest National Laboratory, Richland, Washington 99352

Piotr Skurski
Henry Eyring Center for Theoretical Chemistry, Department of Chemistry, University of Utah, Salt Lake City, Utah 84112
and Department of Chemistry, University of Gdansk, 80-952 Gdansk, Poland

Xi Li and Lai-Sheng Wang*
Department of Physics, Washington State University, 2710 University Drive, Richland, Washington 99352
and Environmental Molecular Sciences Laboratory, MS K8-88, Pacific Northwest National Laboratory, Richland, Washington 99352

(Received 7 July 2000)

Photoelectron spectra of $(\mathrm{MgO})_n^-$ ($n = 1-5$) reveal a surprising trend: The electron binding energy decreases from $n = 1$ to 4, and then increases from 4 to 5. *Ab initio* calculations suggest this pattern is related to the electrostatic interaction between the extra electron and the charge distribution of the neutral cluster. This interaction is significant in MgO^- and $(\mathrm{MgO})_5^-$, for which the lowest nonvanishing multipole moment (LNM) is a dipole; it is smaller for $(\mathrm{MgO})_2^-$ and $(\mathrm{MgO})_3^-$, for which a quadrupole is the LNM; and it is the smallest for $(\mathrm{MgO})_4^-$, for which an octopole is the LNM. The cubic $(\mathrm{MgO})_4^-$ is the first octopole-bound anion yet observed experimentally and characterized theoretically.

PACS numbers: 36.40.Wa, 33.60.–q

Extension of the concept of dipole-bound anions to higher multipoles has recently been attempted, and a few conflicting experimental [1–5] and theoretical [6–10] results were obtained. The results of Rydberg electron transfer experiments suggested that CS_2 [1], succinonitrile [3], and para-dinitrobenzene [5] support weakly bound, presumably quadrupole-bound, anions. Theoretical results, however, suggested that the excess electron in these systems could not be bound due to the electrostatic interaction with the charge distribution of the neutral molecule [9]. Additional experiments suggested quadrupole-bound anions in formamide clusters [4], but theoretical results are not yet available to verify these observations. Perhaps the most convincing evidence for a quadrupole-bound anion came from *ab initio* calculations on $(\mathrm{BeO})_2^-$ [9] and $(\mathrm{KCl})_2^-$ [10]. A rhombic D_{2h} structure is the global minimum for both systems and the charge distribution of the excess electron is localized in the neighborhood of the metal atoms. But experimental results are not yet available.

In this Letter, we present consistent experimental and theoretical results for the anions of $(\mathrm{MgO})_n$ ($n = 1-5$). Our photoelectron spectra reveal a surprising systematic decrease of electron binding energy from MgO^- to $(\mathrm{MgO})_4^-$, and then an increase from $(\mathrm{MgO})_4^-$ to $(\mathrm{MgO})_5^-$. A decomposition of *ab initio* calculated electron binding energies indicates that this unusual trend is related to the electrostatic interaction between the excess electron and the charge distribution of the neutral cluster. The tetramer is quite unique: The fundamental cube of the rocksalt structure is completed and the T_d symmetry dictates that the dipole and quadrupole moments vanish. Therefore, $(\mathrm{MgO})_4^-$ may be considered as an octopole-bound anion.

In Ref. [9], we discussed in detail criteria for identifying a multipole-bound anion. We started from a one-electron Schrödinger equation:

$$\left(-\frac{1}{2}\Delta + V_{\mathrm{elst}} + V_{\text{ooe-exch}}\right)\phi_{\mathrm{mbe}} = \varepsilon_{\mathrm{mbe}}\phi_{\mathrm{mbe}}, \quad (1)$$

where orbital ϕ_{mbe} describes a multipole-bound electron with an electron binding energy $\varepsilon_{\mathrm{mbe}}$; V_{elst} represents the classical electrostatic potential from the exact charge distribution ρ of N, and the short-range occupied orbital exclusion effects (ooe) and exchange effects are included through the $V_{\text{ooe-exch}}$ operator. If Eq. (1) possesses a bound solution, then the resulting anionic state is due to the electrostatic interaction with the charge distribution of N [9] and the lowest nonvanishing 2^l-pole moment of ρ allows classifying the anion as 2^l-pole-bound. Since in practical calculations V_{elst} and $V_{\text{ooe-exch}}$ are not known, one approximates Eq. (1) at the Hartree-Fock (HF) self-consistent field (SCF) level, with ρ replaced by the HF density for N and $V_{\text{ooe-exch}}$ replaced by the HF exchange operators K. Hence, Eq. (1) becomes equivalent to the Koopmans' theorem (KT) description of the excess electron binding, with ε being the energy of the virtual orbital ϕ obtained in the HF calculation for N. The electron binding energy (BE) at the KT level of theory is given by $-\varepsilon$ and is labeled $\mathrm{BE}^{\mathrm{KT}}$. Orbital relaxation and electron correlation contributions, which are neglected when BE is calculated at the KT level, were taken into account by performing HF-SCF and coupled cluster calculations. The unrestricted scheme was used in the HF-SCF and second-order Møller-Plesset (MP2) calculations, and the restricted scheme in the coupled cluster calculations [11].

The HF-SCF polarization contribution to BE, denoted $\Delta\mathrm{BE}^{\mathrm{HF}}_{\mathrm{ind}}$, is defined as the difference between $\mathrm{BE}^{\mathrm{HF}}$ and $\mathrm{BE}^{\mathrm{KT}}$ [12], and the second-order dispersion interaction between the excess electron and the neutral molecule, $\Delta\mathrm{BE}^{\mathrm{MP2}}_{\mathrm{disp}}$, was extracted from the total correlation contribution to BE [12]:

$$\Delta\mathrm{BE}^{\mathrm{MP2}}_{\mathrm{disp}} = -\sum_{a\epsilon N}\sum_{r<s} \frac{|\langle \phi_a \phi_{\mathrm{mbe}} || \phi_r \phi_s \rangle|^2}{\varepsilon_a + \varepsilon_{\mathrm{mbe}} - \varepsilon_r - \varepsilon_s}, \quad (2)$$

where ϕ_a and ϕ_{mbe} are spin orbitals occupied in the UHF wave functions, ϕ_r and ϕ_s are unoccupied orbitals, and ε's are the corresponding orbitals energies. The remaining high-order correlation contribution to BE, denoted $\Delta\mathrm{BE}^{\mathrm{HO}}$, is defined as

$$\Delta\mathrm{BE}^{\mathrm{HO}} = \mathrm{BE}^{\mathrm{CC}} - \mathrm{BE}^{\mathrm{KT}} - \Delta\mathrm{BE}^{\mathrm{HF}}_{\mathrm{ind}} - \Delta\mathrm{BE}^{\mathrm{MP2}}_{\mathrm{disp}}, \quad (3)$$

where $\mathrm{BE}^{\mathrm{CC}}$ denotes the electron binding energy calculated at the coupled cluster level of theory. In the present study, single and double excitations were included in the coupled cluster treatment, and noniterative triples [13] were included for every cluster but the pentamer.

In our theoretical calculations, the diffuse character of the orbital describing the multipole-bound electron (see Fig. 1) necessitates the use of extra diffuse basis functions having low exponents [14]. We used aug-cc-pVDZ basis sets [15] supplemented with additional even-tempered three s, two p, and one d functions centered on every Mg atom. The geometric progression ratio for this extra set was equal to 3.5, and we started to build up the exponents α from the smallest s, p, and d exponents included in the aug-cc-pVDZ basis set designed for Mg. In addition, the Mg basis set was supplemented with one s ($\alpha = 3.422$), one p ($\alpha = 8.279$), and one d ($\alpha = 3.704$) basis function to recover the core-valence correlation effects. The lowest energy structures for the neutral and anions were characterized at the MP2 and density functional theory (B3LYP [16]) levels and harmonic frequencies were determined at the B3LYP level. The calculations were performed with the GAUSSIAN98 [17] and MOLPRO [18] programs, and the 3D plots of molecular orbitals were generated with the MOLDEN program [19].

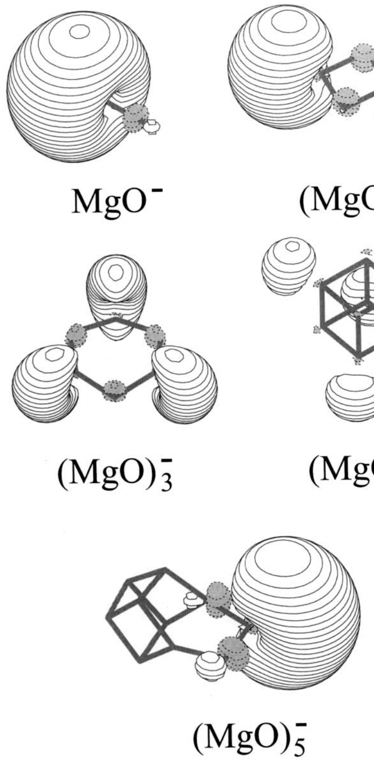

FIG. 1. Structures of the minimum energy $(\mathrm{MgO})_n^-$ ($n = 1-5$) clusters. The highest occupied molecular orbitals, where the extra electron resides, are also plotted with a 0.02 contour spacing.

The experimental apparatus used in this work has been described elsewhere [20]. A pure Mg disk target was laser vaporized with a He carrier gas pulse containing 0.05% O_2. The oxide clusters, formed by reactions of O_2 and Mg in the laser vaporization plasma, were entrained in the carrier gas and underwent a supersonic expansion. Negative clusters were extracted from the cluster beam and sent into a time-of-flight mass analyzer. Clusters of interest were mass selected and decelerated before being intercepted by a detachment laser beam in the interaction zone of a magnetic-bottle time-of-flight photoelectron analyzer. For the current experiment, the second harmonic of a Nd:YAG laser (532 nm, 2.331 eV) was used for the detachment. The electron kinetic energy resolution of the apparatus was better than 30 meV for 1 eV electrons.

The photoelectron spectra of $(\mathrm{MgO})_n^-$ ($n = 1-5$) are shown in Fig. 2. These spectra represent photodetachment transitions from the ground state of each anion to the ground and excited states of the neutral. Three vibrationally resolved states were observed for MgO^-. The transition to the ground state ($^1\sum^+$) showed a short vibrational progression with an adiabatic detachment energy (ADE) of 1.622 eV. The spectra of $(\mathrm{MgO})_2^-$ and $(\mathrm{MgO})_3^-$ each revealed a broad band with successively lower electron binding energies. The spectral widths indicate that there should be some geometry changes between the anion and the neutral ground state. The ground-state transition of $(\mathrm{MgO})_4^-$ is similar to that of $(\mathrm{MgO})_3^-$, and both have very similar electron binding energies. The spectrum of $(\mathrm{MgO})_5^-$ was observed to have a higher electron binding energy with a broad ground-state band. The observed ADEs and vertical detachment energies (VDEs) for $(\mathrm{MgO})_n^-$ ($n = 1-5$) are summarized in Table I.

The most surprising observation is the decrease of ADEs from MgO^- to $(\mathrm{MgO})_4^-$. A decrease of electron binding energy with increasing cluster size is highly unusual. This must be due to a unique molecular interaction between the extra electron and the neutral clusters. As shown in our theoretical study, this surprising trend from the monomer to the tetramer is due to the diminishing electrostatic interactions between the excess electron and the neutral cluster.

Although there have been numerous previous theoretical studies on MgO clusters [21], there are no studies

TABLE I. The observed adiabatic (ADE) and vertical (VDE) electron binding energies for $(MgO)_n^-$ ($n = 1-5$),[a] and the theoretical coupled cluster results for VDE (THEO) in eV.

	MgO^-	$(MgO)_2^-$	$(MgO)_3^-$	$(MgO)_4^-$	$(MgO)_5^-$
ADE	1.622(10)	1.11(8)	0.72(6)	0.70(6)	0.98(6)
VDE	1.622(10)	1.25(5)	0.79(3)	0.80(5)	1.18(5)
THEO	1.590	1.194	0.766	0.762	1.290

[a] Numbers in parentheses represent uncertainties in the last digit.

on the negatively charged MgO clusters considered here. As shown in Fig. 1, we found that the dimer (D_{2h}) and the trimer (D_{3h}) are cyclic planar, and the tetramer (T_d) and the pentamer (C_s) are three-dimensional [22]. The geometrical relaxation from the neutral to anionic lowest-energy structure was found to be significant for the monomer and the pentamer as the B3LYP bond distances increase by as much as 0.06 and 0.04 Å, respectively. For the other clusters, the bond distances were modified by less than 0.02 Å. We found that the excess electron in the anions is described by a fully symmetric orbital, and the density is localized primarily in the vicinity of the positively charged Mg atoms, as shown in Fig. 1. The mean square radial extent for each orbital is 41, 48, 106, 157, and 80 a.u. for $n = 1-5$, respectively. The excess electron is localized outside the cluster to minimize repulsion with the negatively charged oxygen atoms. For $(MgO)_5^-$, the excess electron is localized primarily on the MgO moiety outside the distorted $(MgO)_4$ cube.

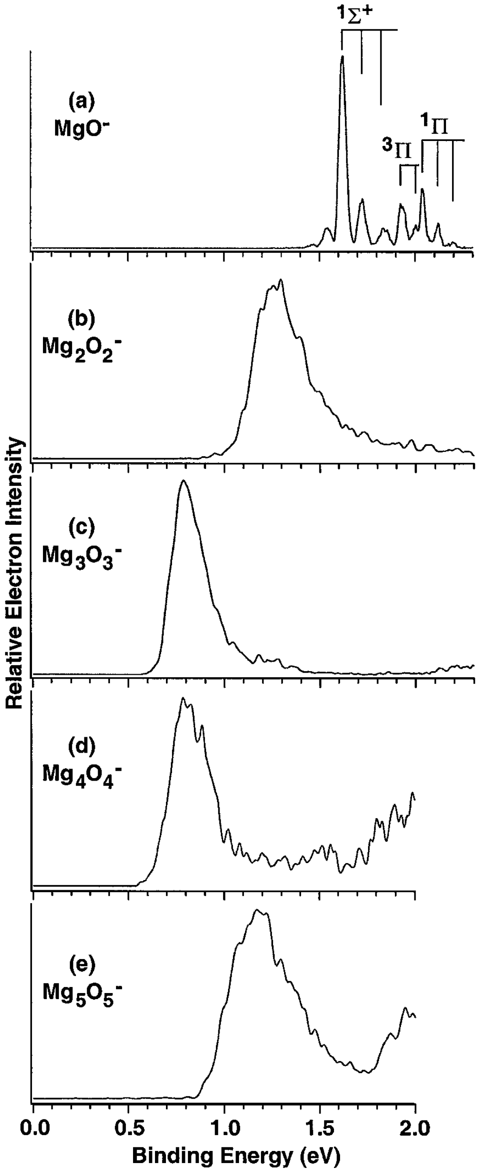

FIG. 2. Photoelectron spectra of $(MgO)_n^-$ ($n = 1-5$) at 532 nm (2.331 eV). Transitions to the ground state ($^1\Sigma^+$) and the first two excited states ($^3\Pi, ^1\Pi$) of MgO are indicated.

The lowest nonvanishing multipole moment of neutral $(MgO)_n$ is dipole, quadrupole, quadrupole, octopole, and again dipole for $n = 1-5$, respectively, as dictated by the structure of these clusters. The BE^{KT}, ΔBE_{ind}^{HF}, ΔBE_{disp}^{MP2}, and ΔBE^{HO} components of BE^{CC} calculated at the optimal anionic MP2 geometries are depicted in Fig. 3. For every cluster, the excess electron is bound at the KT level of theory. Importantly, the dependence on the cluster size is very similar for BE^{CC} and BE^{KT} (Fig. 3), suggesting that the electrostatic interaction between the excess electron and the charge distribution of the neutral clusters is primarily responsible for the observed trend in the ADEs and VDEs. The KT binding energy is very significant and amounts to 1.30 and 0.83 eV for the monomer and the pentamer, for which the MP2 dipole moments are 9.94 and 6.95 D, respectively. The dipole moment disappears for the dimer, trimer, and tetramer. The electrostatic potential decays faster than $1/r^2$ for large separations from the neutral, and the KT binding energies are smaller for these systems than for the monomer or pentamer. For the dimer, the KT binding energy is still significant (0.56 eV) due to a large quadrupole moment of the neutral. In fact, the eigenvalues of the quadrupole tensor, defined as in Eq. (2) of Ref. [9], are $Q_1^{MP2} = 71.26$, $Q_2^{MP2} = -2.02$, and $Q_1^{MP2} = -69.24$ D Å.

For $(MgO)_3$, the eigenvalues of the quadrupole tensor 4.16, −2.08, −2.08 D Å are much smaller than those for the dimer. We expect that this quadrupole moment is not sufficient to bind an electron, and the binding results from multipoles higher than the quadrupole. In fact, only two nonzero Cartesian components of the third-order tensor are significant: $\langle xxy \rangle = -\langle yyy \rangle = 64.70$ D Å^2 and the value of BE^{KT} is 0.10 eV. For $(MgO)_4$, the lowest nonvanishing multipole moment is octopole and the only nonzero Cartesian component of the third-order tensor, $\langle xyz \rangle$, is as large as -59.21 D Å^2. The value of BE^{KT} is only 0.06 eV. Therefore, we conclude that $(MgO)_4^-$ may be considered as an octopole-bound anion.

The polarization of the neutral cluster by the excess electron, measured by ΔBE_{ind}^{HF}, is important for the monomer and the pentamer only (Fig. 3). The dispersion term ΔBE_{disp}^{MP2} slowly decreases as the size of the cluster increases, and its relative contribution to BE^{CC} is as large as 52% and 42% for the trimer and the tetramer, respectively. The high-order correlation term, ΔBE^{HO}, is very large and destabilizing for the monomer. This is apparently related to a serious overestimation of the dipole moment of MgO at the SCF level of theory. The $\Delta\text{BE}^{\text{HO}}$ term is small for the dimer and it contributes 30% and 46% to BE^{CC} for the trimer and the tetramer, respectively. The values of BE calculated at the coupled cluster level of theory are in excellent agreement with the experimental values of VDE (Table I and Fig. 3).

In summary, the photoelectron spectra of $(\text{MgO})_n^-$ ($n = 1-5$) display an unusual decrease of electron binding energy from $n = 1$ to 4 and a subsequent increase from 4 to 5. We found this pattern was due to a component of the electron binding energy that describes the electrostatic interaction between the excess electron and the charge distribution of the neutral cluster. This charge distribution produces a dipolar ($1/r^2$) long-range potential for the dimer and the pentamer, quadrupolar ($1/r^3$) potential for the dimer and the trimer, and octopolar ($1/r^4$) for the tetramer. These MgO clusters appear to provide interesting systems for the investigation of multipole binding of an excess electron. The cubic $(\text{MgO})_4$ anion is the first octopole-bound anion yet studied.

This research (M. G. and L. S. W.) was supported by the U.S. DOE, Office of Basic Energy Sciences, Chemical Sciences Division. L. S. W. also acknowledges partial support by the Alfred P. Sloan Foundation. P. S. and M. G. were supported partially by NSF, the Polish State Committee for Scientific Research (KBN), and computer time from the Center for High Performance Computing at the University of Utah. The experiment was performed at EMSL, a national scientific user facility sponsored by DOE's Office of Biological and Environmental Research and located at PNNL, which is operated by Battelle Memorial Institute.

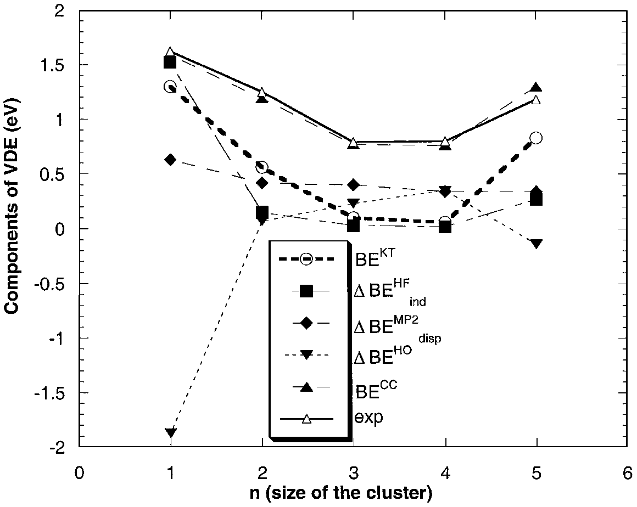

FIG. 3. The BE^{KT}, $\Delta\text{BE}_{\text{ind}}^{\text{HF}}$, $\Delta\text{BE}_{\text{disp}}^{\text{MP2}}$, and $\Delta\text{BE}^{\text{HO}}$ components of BE^{CC} calculated at the optimal anionic MP2 geometries and compared to the experimental VDE for $(\text{MgO})_n^-$ clusters.

---

*Corresponding authors: maciej.gutowski@pnl.gov or ls.wang@pnl.gov

[1] R. N. Compton, F. B. Dunning, and P. Nordlander, Chem. Phys. Lett. **253**, 8 (1996).

[2] C. Desfrancois, H. Abdoul-Carime, and J. P. Schermann, Int. J. Mod. Phys. B **10**, 1339 (1996).

[3] H. Abdoul-Carime and C. Desfrancois, Eur. Phys. J. D **2**, 149 (1998).

[4] C. Desfrancois *et al.,* Chem. Phys. **239**, 475 (1998).

[5] C. Desfrancois *et al.,* J. Chem. Phys. **111**, 4569 (1999).

[6] K. D. Jordan and J. F. Liebman, Chem. Phys. Lett. **62**, 143 (1979).

[7] J. Simons and K. D. Jordan, Chem. Rev. **87**, 535 (1987).

[8] G. L. Gutsev, R. J. Bartlett, and R. N. Compton, J. Chem. Phys. **108**, 6756 (1998).

[9] M. Gutowski and P. Skurski, Chem. Phys. Lett. **303**, 65 (1999).

[10] G. L. Gutsev, P. Jena, and R. J. Bartlett, J. Chem. Phys. **111**, 504 (1999).

[11] P. J. Knowles, C. Hampel, and H.-J. Werner, J. Chem. Phys. **99**, 5219 (1993).

[12] M. Gutowski and P. Skurski, J. Phys. Chem. B **101**, 9143 (1997).

[13] J. D. Watts, J. Gauss, and R. J. Bartlett, J. Chem. Phys. **98**, 8718 (1993).

[14] M. Gutowski, K. D. Jordan, and P. Skurski, J. Phys. Chem. A **102**, 2624 (1998).

[15] R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, J. Chem. Phys. **96**, 6796 (1992).

[16] P. J. Stephens *et al.,* J. Phys. Chem. **98**, 11 623 (1994).

[17] M. J. Frisch *et al.,* GAUSSIAN98, Revision A.7, Gaussian, Inc., Pittsburgh, PA, 1998.

[18] MOLPRO is a package of *ab initio* programs written by H.-J. Werner and P. J. Knowles.

[19] G. Schaftenaar and J. H. Noordik, J. Comput.-Aided Mol. Design **14**, 123 (2000).

[20] L. S. Wang, H. S. Cheng, and J. Fan, J. Chem. Phys. **102**, 9480 (1995).

[21] J. M. Recio *et al.,* J. Chem. Phys. **98**, 4783 (1993); A. I. Boldyrev and J. Simons, J. Phys. Chem. **100**, 8023 (1996); M.-J. Malliavin and C. Coudray, J. Chem. Phys. **106**, 2323 (1997); E. de la Puente *et al.,* Phys. Rev. B **56**, 7607 (1997); P. V. Sushko, A. L. Shluger, and C. R. A. Catlow, Surf. Sci. **450**, 153 (2000).

[22] Other structures were considered, but were all found to be higher in energy. For example, a cyclic D_{4h}, a C_{2v}, and a solvated electron structure were examined for $(\text{MgO})_4^-$, but were found to be higher in energy by at least 10 kcal/mol at the B3LYP level of theory.