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# Deciphering the Structural Evolution and Electronic Properties of Magnesium Clusters: a New Aromatic Homonuclear Metal $Mg_{17}$ Cluster

Xin-Xin Xia,<sup>1,2</sup> Xiao-Yu Kuang,<sup>1,a)</sup> Cheng Lu,<sup>2,3,b)</sup> Yuan-Yuan Jin,<sup>1</sup>  
Xiao-Dong Xing,<sup>1</sup> Gabriel Merino,<sup>4</sup> and Andreas Hermann<sup>5,c)</sup>

<sup>1</sup>*Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065, China*

<sup>2</sup>*Department of Physics, Nanyang Normal University, Nanyang 473061, China*

<sup>3</sup>*Department of Physics and High Pressure Science and Engineering Center, University of Nevada, Las Vegas, Nevada 89154, United States*

<sup>4</sup>*Departamento de Física Aplicada, Centro de Investigación y de Estudios Avanzados, Unidad Mérida, Km 6 Antigua Carretera a Progreso, Apdo. Postal 73, Cordemex, 97310 Mérida, Yucatán, Mexico*

<sup>5</sup>*Centre for Science at Extreme Conditions and SUPA, School of Physics and Astronomy, The University of Edinburgh, Edinburgh EH9 3JZ, United Kingdom*

## ABSTRACT

The structures and electronic properties of low energy neutral and anionic  $Mg_n$  ( $n = 3-20$ ) clusters have been studied by utilizing a widely adopted CALYPSO structure searching method coupled with density functional theory calculations. A large number of low energy isomers are optimized at the B3PW91 functional with the 6-311+G(d) basis set. The optimized geometries clearly indicate that a structural transition from

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<sup>a)</sup> Electronic mail: [scu\\_kuang@163.com](mailto:scu_kuang@163.com) (Xiao-Yu Kuang).

<sup>b)</sup> Electronic mail: [cheng.lu@unlv.edu](mailto:cheng.lu@unlv.edu) (Cheng Lu).

<sup>c)</sup> Electronic mail: [a.hermann@ed.ac.uk](mailto:a.hermann@ed.ac.uk) (Andreas Hermann)

hollow three-dimensional configurations to filled-cage-like structures occurs at  $n = 16$  for both neutral and anionic clusters. Based on the anionic ground state structures, photoelectron spectra are simulated using time-dependent density functional theory (TD-DFT) and compared with experimental results. The good agreement validates that the current ground state structures, obtained from the symmetry-unconstrained searches, are true global minima. A detailed chemical bonding analysis distinctly indicates that the  $\text{Mg}_{17}$  cluster is the first neutral locally  $\pi$ -aromatic homonuclear all-metal cluster, which perfectly satisfies Hückel's well-known  $4N + 2$  rule.

## I. Introduction

Magnesium is an interesting metal that exhibits strong chemical activity. Its unique features have initiated extensive research in diverse fields such as superconductivity,<sup>1</sup> hydrogen storage,<sup>2,3</sup> nanomaterials,<sup>4,5</sup> even biomedicine.<sup>6,7</sup> Apart from their direct influence in these fields, magnesium clusters exhibit a number of unique phenomena and features. One of the most striking phenomena is the transition from weak van der Waals bonding to metallic bonding as the clusters grow in size. The critical size for nonmetallic to metallic behavior was experimentally established to be  $n = 18$  for anions,<sup>8</sup> and suggested to be  $n = 20$  for neutral clusters.<sup>9</sup> From a theoretical perspective, the precise size of the insulator-to-metal transition is yet to be determined.<sup>10-16</sup>

There has been a plethora of theoretical studies on the geometric structures and electronic properties of magnesium clusters.<sup>10-22</sup> Jellinek *et al.*<sup>11</sup> investigated neutral

and anionic magnesium clusters up to  $n = 22$  using gradient-corrected density functional theory, and found that the electron binding energies in the anionic clusters, derived from the gap between the two most external electrons, agree with electron photodetachment experiment data. Lyadin *et al.* investigated the structural evolution and electronic shells of neutral and cationic magnesium clusters using *ab initio* theoretical methods, where results showed that the metallic evolution is a slow and non-monotonous process.<sup>20</sup> Exhaustive structure optimization revealed the growth behaviors of larger neutral magnesium clusters and indicated that most of the ground state structures are non-symmetric in the size range of  $n > 20$ .<sup>22</sup> It is worth pointing out that the neutral ground state structures found in the different studies are not identical.<sup>11,20,22</sup> Thus, although structures of magnesium clusters have been extensively studied and specific structures have been described and analysed, the true ground state structures might still be debatable. Their electronic properties have been investigated by both experiment and theory, but these do not provide systematic information about their chemical bonding. It is therefore timely to (i) compare theoretical photoelectron spectra with the experimental PES data to verify the lowest-energy structures of Mg clusters; (ii) investigate the most probable fragmentation channels for magnesium clusters; and (iii) understand the chemical bonding of Mg clusters, which also serve to explain their stabilizing mechanisms.

To that end, we invoke the concept of aromaticity in our analyses. Aromaticity is traditionally confined to the realm of organic chemistry to describe cyclic, delocalized  $\pi$  bonding in planar and conjugate molecules possessing  $(4N + 2)$   $\pi$  electrons.<sup>23-29</sup>

(Merino G. Sola M. Celebrating the 150th anniversary of the Kekulé benzene structure. *Phys. Chem. Chem. Phys.* 2016, 18, 11587-11588). Recently, this concept has been extended to inorganic molecules including organometallic compounds,<sup>30</sup> (Add the next reference Fernandez, I.; Frenking, G.; Merino, G. Aromaticity in Metallabenzenes and Related Compounds. *Chem. Soc. Rev.* 2015, 44, 6452-6463.) transition-metal systems<sup>31-34</sup> and, in particular, all-metal clusters.<sup>35-37</sup> The gallium-gallium bond is exemplary for our understanding of electronic structure and chemical bonding in organometallic chemistry, with the first example of metalloaromaticity.<sup>30</sup> Combined anion photoelectron spectroscopy and quantum chemical calculations on metal-boron clusters indicated that various planar  $M@B_n^-$  clusters feature planar aromatic boron rings, with delocalized  $\pi$ -electrons and the metal atom strongly covalently bound to the surrounding boron atoms.<sup>31,32</sup> (Add the next reference: Islas, R.; Heine, T.; Ito, K.; Schleyer, P. v. R.; Merino, G. Boron Rings Enclosing Planar Hypercoordinate Group 14 Elements. *J. Am. Chem. Soc.* 2007, 129, 14767-14774) A series of bimetallic metal anionic clusters with chemical composition  $MAl_4^-$  ( $M = Li, Na, \text{ or } Cu$ ) were synthesized and studied with photoelectron spectroscopy and *ab initio* calculations. This study showed that  $Al_4^{2-}$  maintains a square planar structure and aromaticity due to two delocalized  $\pi$  electrons present in all three  $MAl_4^-$  complexes.<sup>35</sup> Considering the concept of aromaticity, other small alkali metal and alkaline earth metal clusters were studied and for  $Li_2Mg_2$  it was shown that the cyclic  $\sigma$ -aromatic structures are more stable than the classical linear  $Li-Mg-Mg-Li$  structure.<sup>36</sup> These investigation extended the aromaticity concept to the

realm of all-metal species and highlighted its importance. Like aromaticity, which is then well-established in inorganic and all-metal systems, the concept of antiaromaticity (cyclic conjugated systems with  $4N$   $\pi$  electrons)<sup>38</sup> has recently been extended beyond organic molecules as well. The  $\text{Al}_4^{4-}$  anion in the  $\text{Li}_3\text{Al}_4^-$  mixed-metal cluster was shown to feature  $\pi$ -antiaromaticity (and  $\sigma$ -aromaticity).<sup>39</sup> (Islas, R.; Heine, T.; Merino, G. Structure and Electron Delocalization in  $\text{Al}_{42}$ - and  $\text{Al}_{44}$ -. *J. Chem. Theory Comp.* 2007, 3, 775-781.) In recent years, three-dimensional all-metal clusters, for instance the  $\text{Sb}_4$  unit in  $[\text{Ln}(\eta^4\text{-Sb}_4)_3]^{3-}$  ( $\text{Ln} = \text{La, Y, Ho, Er, Lu}$ )<sup>40</sup>, have been studied. Based on the results of chemical bonding analyses and Breslow's  $4N$  rule, the  $[\text{Ln}(\eta^4\text{-Sb}_4)_3]^{3-}$  ( $\text{Ln} = \text{La, Y, Ho, Er, Lu}$ ) compound was found to be the first locally  $\pi$ -antiaromatic all-metal system. Despite aromaticity and antiaromaticity having been observed in inorganic and all-metal systems, these concepts have been applied relatively little to homonuclear metal clusters. However, it is mandatory to do an exhaustive and comparative study in order to establish if an all-metal aromatic cluster can be classified as aromatic (ADD the next reference: Hoffmann R. The Many Guises of Aromaticity. *Am. Sci.* 2015, 103, 18) With this in mind, the exploration of the geometric structures, electronic properties and the nature of the chemical bonding in magnesium clusters, is an intriguing proposition.

In order to study systematically and in-depth the structural evolution and electronic properties of magnesium clusters, we have carried out comprehensive structure searches on neutral and anionic magnesium clusters in the size range from  $n = 3$  to 20, by combining a systematic exploration of the potential energy surface using

CALYPSO (Crystal structure AnaLYsis by Particle Swarm Optimization)<sup>41-44</sup> with density functional theory calculations. Subsequently, we reexamine the structure of particular neutral and anionic low-energy isomers of magnesium clusters with respect to those reported in previous experiments or theoretical calculations. We then study the stabilizing mechanism due to the electronic properties of specific neutral and anionic magnesium clusters and provide new insights for further theoretical and experimental explorations. The paper is organized as follows. The details of the computational method are presented in Sec. II. Then, our results and discussion are described in Sec. III. Finally, the main conclusions are summarized in Sec. IV.

## **II. Computational details**

The structures of low-lying isomers of neutral and anionic magnesium clusters were obtained using CALYPSO, which provides a local version of the particle swarm optimization (PSO) algorithm to explore the free-energy surfaces for any given (non-)periodic system. The algorithm can predict stable structures depending only on the chemical composition. It has successfully predicted structures for various systems ranging from clusters<sup>45</sup> to surface reconstructions<sup>43,46</sup> and crystal structures.<sup>42,44,47</sup> Here, structure predictions are performed for neutral and anionic magnesium clusters up to 20 atoms. Each generation contains 50 structures, 60% of which are generated by the PSO, while the others are new and will be generated randomly. We have followed 30 generations for each cluster to achieve convergence of the potential energy surface sampling. The searches generated 1000–1500 isomers for low energy

neutral and anionic magnesium clusters. Among those isomers, the fifteen energetically lowest-lying isomers are selected as candidates for the global minimum structure. Low energy structures within 3 eV of the global minimum structure are further optimized with subsequent frequency calculations. The calculations are performed using the all-electron density functional theory method with the B3PW91<sup>48-50</sup> generalized gradient approximation functional. The 6-311+G(d) basis set is selected for the confirmation of the lowest energy structures of magnesium clusters. The choice of B3PW91/6-311+G(d) level of theory set is based on a previous report.<sup>20</sup> The effect of spin multiplicity (up to septet and octet) is taken into account and no symmetry constraints are enforced in the geometric optimization procedure. All calculations are performed with the Gaussian09 program package.<sup>51</sup> The photoelectron spectra of the anionic magnesium clusters are simulated with the time-dependent density functional theory (TD-DFT) method. Chemical bonding analyses (B3PW91/6-311+G(d)) are conducted using the adaptive natural density partitioning (AdNDP)<sup>52</sup> method. The nucleus-independent chemical shift (NICS) and multicenter bond order are calculated by using the Multiwfn 3.3.8 program package.<sup>53</sup>

### **III. Results and discussions**

#### **A. Geometric structure**

We have performed a comprehensive structure search and all of the previously reported structures, including experimental and theoretical ones, are successfully reproduced in our search results. Based on those results, we optimize the candidates

of low-lying isomers and display the global minima structures of neutral and anionic magnesium clusters with up to 20 atoms in Figure 1. The vibrational frequencies are also calculated and listed in Table S1 (in the Supporting Information, SI) to assure true global minima for the ground state structures. Moreover, other typical low-energy isomers of all clusters, together with their corresponding symmetry, are displayed in Figure S1 (see SI).

From Figure 1, we can see that the neutral and corresponding anionic magnesium clusters have similar ground-state structures and follow the same structural evolution. For both neutrals and anions, only the  $\text{Mg}_3^{0/-}$  clusters are trigonal plane structures. For  $n \geq 4$ , the lowest energy structures of magnesium clusters form three-dimensional configurations. As the number of atoms increases, we find that eventually, for  $n \geq 16$ , one of the Mg atoms is fully encapsulated within the magnesium framework. So,  $n = 16$  is a structural transition point from hollow three-dimensional configurations to filled-cage-like structures. All of the lowest energy structures of neutral and anionic  $\text{Mg}_n$  ( $n = 3-20$ ) clusters, except for  $\text{Mg}_{14,16}$  and  $\text{Mg}_{12,14,20}^-$ , which are of  $C_1$  symmetry, possess relatively high point symmetry. Additionally, for  $n = 3-5, 9, 10, 13, 15, 19$ , the neutral and anionic clusters have the same geometries and point symmetries.

The optimized lowest energy structures found in our searches are largely in agreement with those discussed in earlier theoretical and experimental findings. However, we find a  $\text{Mg}_{13}$  cluster of  $C_s$  symmetry (Figure 1) to be the lowest energy structure in our study, while the  $\text{Mg}_{13}$  cluster with  $C_1$  symmetry (Figure S1), previously studied theoretically by Lyalin *et al.*<sup>20</sup>, is shown to be a transition state. For

Mg<sub>19</sub>, Lyalin *et al.*<sup>20</sup> claimed that global minimum structure has C<sub>2v</sub> symmetry whereas our result found it to be of C<sub>s</sub> symmetry, which is in agreement with the result reported by Heidari *et al.*<sup>22</sup> The structure of Mg<sub>20</sub> is in agreement with the result of Jellinek *et al.*,<sup>11</sup> and different from that reported by Lyalin *et al.*<sup>20</sup> The global minimum structure of Mg<sub>8</sub><sup>-</sup> is found here to be of C<sub>2</sub> symmetry, while the D<sub>4d</sub> symmetry structure proposed by Jellinek *et al.*<sup>11</sup> is not the lowest energy structure, as shown by the results of our harmonic vibration analysis. Note that the lowest energy Mg<sub>n</sub> (n = 3–20) clusters are found to prefer low spin state, except in the case of Mg<sub>18</sub><sup>0/-</sup> where the ground state are triplet and quartet, respectively. The spin states of all these lowest energy clusters are in good agreement with the results of Acioli *et al.*<sup>12</sup>

## **B. Electronic properties of anionic Mg<sub>n</sub><sup>-</sup> clusters with ground state structures**

In order to confirm the validity of the ground state structures (shown in Figure 1) of Mg<sub>n</sub><sup>-</sup> (n = 3–20) clusters, their photoelectron spectra were simulated using TD-DFT. The simulated spectra of the ground state structures are displayed in Figure 2, along with the available experimental spectra<sup>9</sup> for comparison. Simulated spectra of other low-energy isomers are shown in Figure S2 in the SI. The vertical detachment energy (VDE) was taken from the first peak position of the spectra and the adiabatic detachment energy (ADE) for the neutral clusters was measured by the corresponding intersection between the baseline and the rising edge of the first peak. Comparing the calculated and experimental numbers in Table 1, we can see that both the VDE and

the ADE values extracted from the simulated PES are in satisfactory agreement with the experimental data, supporting the reliability of our theoretical approach. The spectra themselves are in overall good agreement with experiment throughout, though spectral weight seems to be off in some cases (see  $\text{Mg}_{11,18,19}^-$ ). The photoelectron spectra for  $\text{Mg}_n^-$  with  $n = 3-13$  show only one major peak in the range of low binding energy ( $\leq 2.0$  eV), while several recognizable peaks are found in the binding energy range of 2.0–3.3 eV. Notice that for cluster sizes  $n = 16-19$ , the VDE's are larger than 2.0 eV, followed by a drop to 1.88 eV for  $n = 20$ . From the simulated PES, evidently the energy spacing between the first two main spectral features, which can be interpreted as the HOMO–LUMO gap for neutral magnesium clusters, has a local maximum (compared to their neighbors' gaps) for  $n = 4, 10$  and 20. This phenomenon is consistent with the neutral HOMO–LUMO gap analysis discussed below and offers a first hint towards stability of magic number clusters. Overall, the comparison of the experimental and simulated PES results lends support to the proposed ground state structures of magnesium clusters.

The experimental and theoretical values of ADE and VDE, listed in Table 1, have been plotted as function of cluster size in Figure 3 to explore more deeply their electronic properties. The theoretical values of ADE increase from 0.80 to 1.89 eV for  $n = 3-9$  (see Figure 3a). Afterward, the theoretical ADE reveals obvious odd–even oscillation from  $n = 13$  to 18. The theoretical ADEs successfully reproduce the overall experimental trend, and yield two striking minima at  $n = 10$  and 20, which are related to the shell model introduced by Thomas *et al.*<sup>9</sup> As shown in Figure 3b, the theoretical

values of the VDE keep increasing overall with increased numbers of Mg atoms, and two obvious minima appear again at  $n = 10$  and  $20$ . Again, the calculated VDEs are in good agreement with the experimental results, with only  $n = 6, 12, 18, 19$  deviating by more than  $0.1\text{eV}$ . Note that for most cluster sizes, the deviation between theoretical values of ADE and VDE is less than  $0.13\text{ eV}$ , with exceptions  $n = 6-8, 11,$  and  $18$ . This is in agreement with the observation that all clusters, except for  $\text{Mg}_{6-8,11,18}$ , basically retain the structural framework of the neutral ground state in the corresponding anionic cluster.

### C. Relative stabilities and HOMO–LUMO gaps

The inherent stability of a given cluster might be determined by its binding energy ( $E_b$ ) per atom that, for neutral and anionic magnesium clusters, can be defined as:

$$E_b = \left[ (n-1)E(\text{Mg}) + E(\text{Mg}^Q) - E(\text{Mg}_n^Q) \right] / n, \quad Q = 0, -1, \quad (1)$$

where  $E$  is the total energy of the corresponding atom or cluster. The calculated results of  $E_b$  are summarized in Table 1 and are plotted as function of cluster size  $n$  in Figure 4a. For both the neutral and anionic magnesium clusters, the binding energies mostly increase with cluster size, and both curves show similar size dependence (see Figure 4b). Three weak local peaks of the binding energy occur at  $n = 4, 10$  and  $15$  for neutral clusters and  $n = 4, 9$  and  $15$  for anionic clusters, respectively. This indicates that  $\text{Mg}_{4,10,15}$  and  $\text{Mg}_{4,9,15}^-$  are more stable than their adjacent sized clusters. It is also

worth noticing that the  $E_b$  values of anionic  $\text{Mg}_n^-$  cluster are always higher than their neutral counterparts. This implies that the binding energy of an additional electron is larger in the clusters than in a single  $\text{Mg}^-$  anion.

The second-order difference of the energy ( $\Delta^2E$ ) is another important parameter that can reflect the relative stabilities of neutral and anionic clusters, and can be defined here as

$$\Delta^2E = E(\text{Mg}_{n-1}^Q) + E(\text{Mg}_{n+1}^Q) - 2E(\text{Mg}_n^Q), Q = 0, -1. \quad (2)$$

The  $\Delta^2E$  values for neutral and anionic  $\text{Mg}_n$  ( $n = 3-20$ ) clusters are listed in Table S2 and shown in Figure 4b. Figure 4b reveals for both neutral and anionic clusters irregularly oscillating behavior in the region of  $n = 3-9$  and odd-even oscillations for  $n = 12-18$ . Several pronounced peaks are found at  $n = 4, 7, 13, 15$  and  $17$ , signifying that the clusters  $\text{Mg}_4^{0/-}$ ,  $\text{Mg}_7^{0/-}$ ,  $\text{Mg}_{13}^{0/-}$ ,  $\text{Mg}_{15}^{0/-}$ , and  $\text{Mg}_{17}^{0/-}$  are more stable compared to their neighbors. Furthermore, the neutral  $\text{Mg}_{10}$  and anionic  $\text{Mg}_9^-$  clusters are relatively more stable due to their locally maximal  $\Delta^2E$  values.

The HOMO–LUMO gaps are calculated for the ground state  $\text{Mg}_n^Q$  ( $n = 3-20$ ,  $Q = 0, -1$ ) structures. The energy gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital is an indicator of relative stability.<sup>54</sup> The results for the clusters in their ground state structures are summarized in Table 1 and plotted in Figure 4c. By comparing the  $E_{gap}$  values of neutral and anionic magnesium clusters, it can be seen that the  $E_{gap}$  curve for neutral clusters shows a decreasing trend

with size, with significant fluctuations, while a much less pronounced trend is perceived for anionic clusters. In addition, the values for neutral clusters are always higher than for anionic clusters, indicating that neutral  $\text{Mg}_n$  clusters are relatively more stable than anionic clusters. Local maxima values of  $E_{gap}$  are found at  $n = 4, 7, 11, 13,$  and  $15$  for neutral and  $n = 10, 16,$  and  $18$  for anionic clusters, respectively. This suggests that these cluster sizes have a stronger stability than their size-adjacent clusters.

#### D. Fragmentation channels

Potential fragmentation paths can be studied from a thermodynamic viewpoint (not considering kinetic barriers) and the fragmentation energies  $E_f$  of the ground state magnesium clusters can be expressed as:

$$E_f = E(\text{Mg}_p) + E(\text{Mg}_{n-p}^Q) - E(\text{Mg}_n^Q), Q = 0, -1 \quad (3)$$

Generally speaking, if the fragmentation energy is negative for a particular fragmentation channel, the initial cluster is unstable and may dissociate spontaneously by releasing the amount of energy  $E_f$ . In this work, we have calculated all possible fragmentation channels for  $\text{Mg}_n^Q$  ( $n = 3-20, Q = 0, -1$ ) clusters and the respective values are positive in all cases, implying that the clusters are stable and must obtain energy to realize the fragmentations. The smaller the fragmentation energies of cluster are, the less stable the clusters will be. The easiest (least energy-costly) fragmentation channels and corresponding fragmentation energies ( $E_f$ ) for neutral and anionic

magnesium clusters are summarized in Table 2. From the table, it is evident that the  $\text{Mg}_n^0 \rightarrow \text{Mg} + \text{Mg}_{n-1}^0$  channel is the most popular route for all neutral and anionic magnesium clusters. For clarity, the fragmentation energies of this most probable fragmentation channel are displayed in Figure 4d as functions of cluster size  $n$ . We notice that, except for  $n = 8$ , the two curves of fragmentation energies show quantitatively very similar behavior across the cluster sizes  $n = 3$ –18. Several energy maxima found at  $n = 4, 9, 15$  and  $17$  suggest that initial clusters  $\text{Mg}_4^{0/-}$ ,  $\text{Mg}_9^{0/-}$ ,  $\text{Mg}_{15}^{0/-}$  and  $\text{Mg}_{17}^{0/-}$  are more stable than their neighbors and could be difficult to dissociate.

### E. Chemical bonding analysis

From a comprehensive analysis of the electronic properties of the magnesium clusters, it is clear that the neutral  $\text{Mg}_{17}$  cluster is relatively stable, which caught our interest. The neutral cluster  $\text{Mg}_{17}$ , a filled-cage-like structure, has  $D_{4d}$  symmetry, four peripheral  $\text{Mg}_4$  fragments and one central Mg atom. To gain insight into its bonding properties, we analysed the molecular orbitals (MO) of the neutral square  $\text{Mg}_4$  unit (Figure S3a), which, as isolated  $\text{Mg}_4$  cluster, is a metastable species. The highest occupied MO (HOMO) of  $\text{Mg}_4$  (Figure S3b) is a completely delocalized  $\pi$  orbital. There are also four lone-pair MOs and two pairs of  $\sigma$  electrons can be shared by four Mg–Mg bonds, resulting in a  $\sigma$  bond order of 0.5. Both the  $\pi$  bonding patterns and the lone-pair MOs of  $\text{Mg}_4$  are analogous to the previously discovered aromatic  $\text{Al}_4^{2-}$ .<sup>35</sup> In principle the system satisfied the Hückel rule for a  $\pi$ -aromatic system. To provide

further evidence for a possible aromatic character, we calculated its nucleus-independent chemical shift (NICS)<sup>55,56</sup> and multicenter bond order<sup>57</sup> (see Table S3). NICS(0)<sub>zz</sub>, NICS(0.5)<sub>zz</sub> and NICS(1)<sub>zz</sub> are -37.1, -36.6, and -34.0 ppm, respectively. NICS<sub>zz</sub> is identical to the z-component of the induced magnetic field (Merino, G.; Heine, T.; Seifert, G. The Induced Magnetic Field in Cyclic Molecules. *Chem. Eur. J.* 2004, 10, 4367-4371 AND Heine, T. Islas, R.; Merino, G.  $\sigma$  and  $\pi$  Contributions to the Induced Magnetic: Indicators for the Mobility of Electrons in Molecules. *J. Comput. Chem.* 2007, 28, 302-309 AND 58. Islas, R.; Heine, T.; Merino, G. The Induced Magnetic Field. *Acc. Chem. Res.* 2012, 45, 215-228). All of the large negative NICS indices suggested that Mg<sub>4</sub> cluster can be classified as aromatic. In addition, the total value of multicenter bond order is 0.0322, thus reconfirming the aromatic character of the Mg<sub>4</sub> cluster.

The ground state structure of neutral Mg<sub>17</sub> found here contains two square Mg<sub>4</sub> frameworks. In order to improve our understanding of the bonding in the Mg<sub>17</sub> cluster, we performed chemical bonding analyses using the AdNDP method. The detailed results are displayed in Figure 5. The 34 valence electrons in neutral Mg<sub>17</sub> cluster can be divided into two sets. The first set consists of delocalized  $\sigma$ -bond elements, while the other set is composed of delocalized  $\pi$ -bond elements. In the first set, the AdNDP analysis revealed eight 4c-2e  $\sigma$ -bonds with ON = 1.81 |e|, which are responsible for the bonding within the eight peripheral cyclo-Mg<sub>4</sub> units, and eight 4c-2e  $\sigma$ -bonds with ON = 1.71 |e|, which are likely due to the bonding between the central Mg with peripheral Mg<sub>3</sub> units. The second set includes two 8c-2e  $\pi$ -bonds, which are best

described as two completely delocalized  $\pi$  bonds with 4 electrons in total and embody the strong bond among eight peripheral Mg atoms, and one 9c–2e  $\pi$ -bond with an occupation number (ON) of 1.77 |e|, which has an interesting sandwich shape and creates strains in the interior between the central Mg atom and the two apical  $\text{Mg}_4$  units. The 9c–2e  $\pi$  bonds on two  $\text{Mg}_4$  units are quite similar to the 4c–2e bonds in the neutral square planar  $\text{Mg}_4$  cluster (Figure S3c), which in turn are similar to the  $\text{Sb}_4$  fragments of 5c–2e  $\pi$ -bonds in  $[\text{Ln}(\eta^4\text{-Sb}_4)_3]^{3-}$  complex<sup>40</sup>, rendering it locally  $\pi$ -aromatic according to Hückel’s  $4N + 2$  rule. Why should such peculiar  $\text{Mg}_4$  fragments occur in the  $\text{Mg}_{17}$  cluster? They are stabilised in  $\text{Mg}_{17}$  due to the strong interactions between the  $\text{Mg}_4$  units and the central Mg atom and more importantly due to the presence of local aromaticity. Therefore, the neutral  $\text{Mg}_{17}$  cluster can be considered to be  $\pi$ -aromatic.

Moreover,  $\text{Mg}_{17}$  cluster is a 34 electron system, which possesses a closed electronic shell according to the jellium superatom model.[cite: JPCC 113, 2664 (2009)] For a detailed illustration of the electronic structure of the  $\text{Mg}_{17}$  cluster, we plotted its molecular orbitals (Figure S4). Combining the multicentre bonding and molecular orbitals analyses on the  $\pi$ -aromatic  $\text{Mg}_{17}$  cluster indicates that the electronic configuration of  $\text{Mg}_{17}$  can be labeled as  $1\text{S}^21\text{P}^61\text{D}^42\text{S}^21\text{D}^61\text{F}^{14}$ .

## IV. Conclusions

In summary, we have studied the structural evolution and electronic properties of neutral and anionic Mg clusters having up to 20 atoms using the unbiased CALYPSO

structure searching method combined with density functional theory calculations. The ground state structures of both neutral and corresponding anionic Mg clusters have similar geometric structures and show the same structural evolution with increasing atom number. The simulated photoelectron spectra are in excellent agreement with experimental measurements. On the basis of fragmentation energy calculations, we identified that the  $\text{Mg}_n^{\text{O}} \rightarrow \text{Mg}_{n-1}^{\text{O}} + \text{Mg}$  channel is the route favored by all the neutral and anion  $\text{Mg}_n$  clusters ( $n = 3-20$ ), but is endothermic in all cases. A detailed chemical bonding analysis reveals that the neutral  $\text{Mg}_{17}$  cluster is the first locally  $\pi$ -aromatic cluster among medium-sized homonuclear metal clusters. To some extent, we expect that this result may provide a new twist on the concept of aromaticity and stimulate theoretical analyses of the chemical bonding in other known or as yet unknown homonuclear metal clusters.

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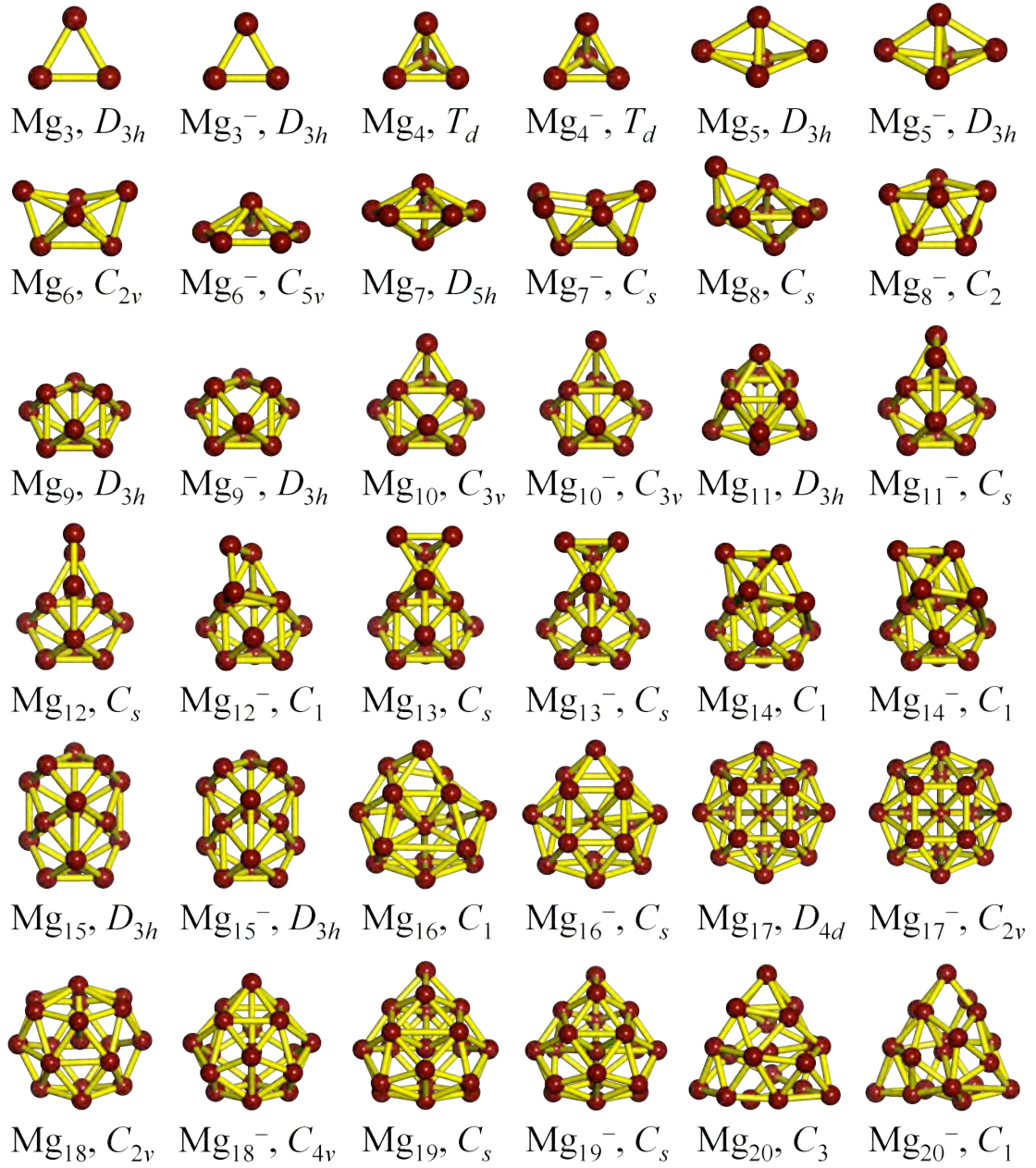


Figure 1. The lowest energy structures of  $Mg_n^Q$  ( $n = 3-20$ ,  $Q = 0, -1$ ) clusters.

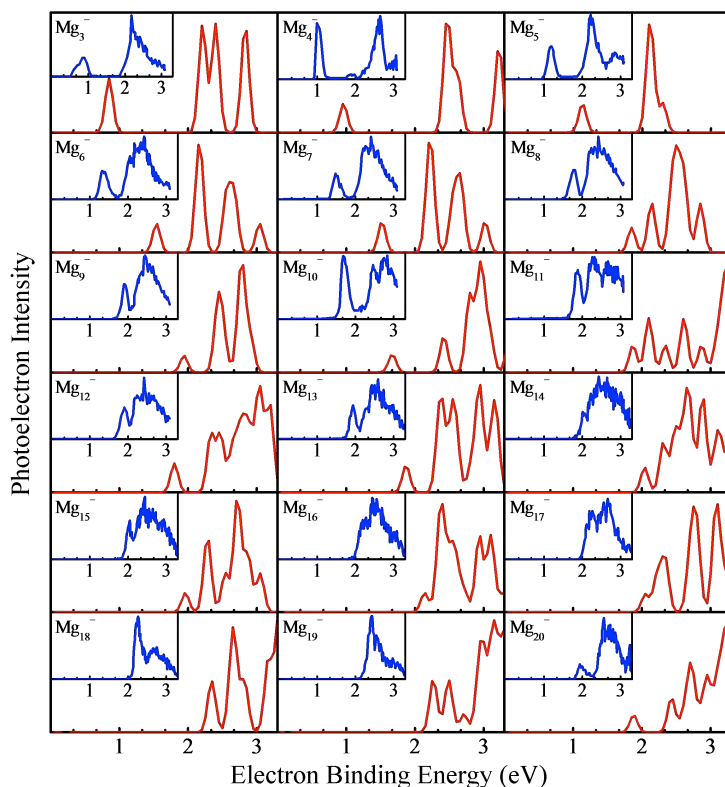


Figure 2. Comparison of the simulated photoelectron spectra (outer) with the experimental PES (inset) from reference 9 of lowest energy  $\text{Mg}_n^-$  ( $n = 3-20$ ) clusters.

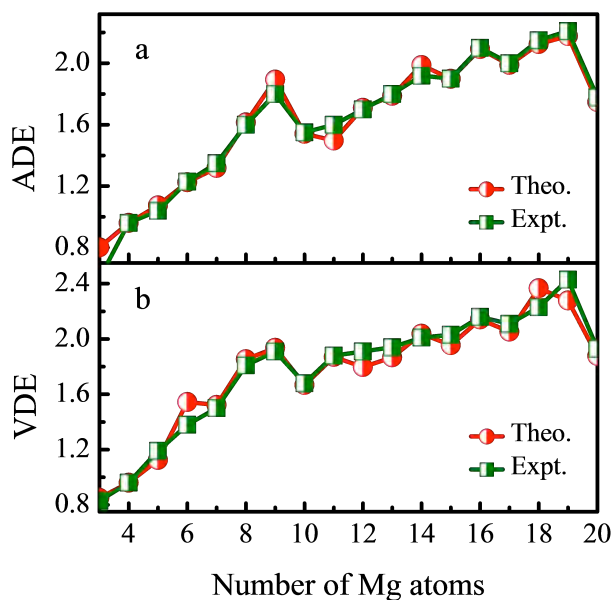


Figure 3. Adiabatic detachment energies (ADEs) and vertical detachment energies (VDEs) of  $\text{Mg}_n^-$  ( $n = 3-20$ ) clusters: red circles, theory; green squares, experiment.

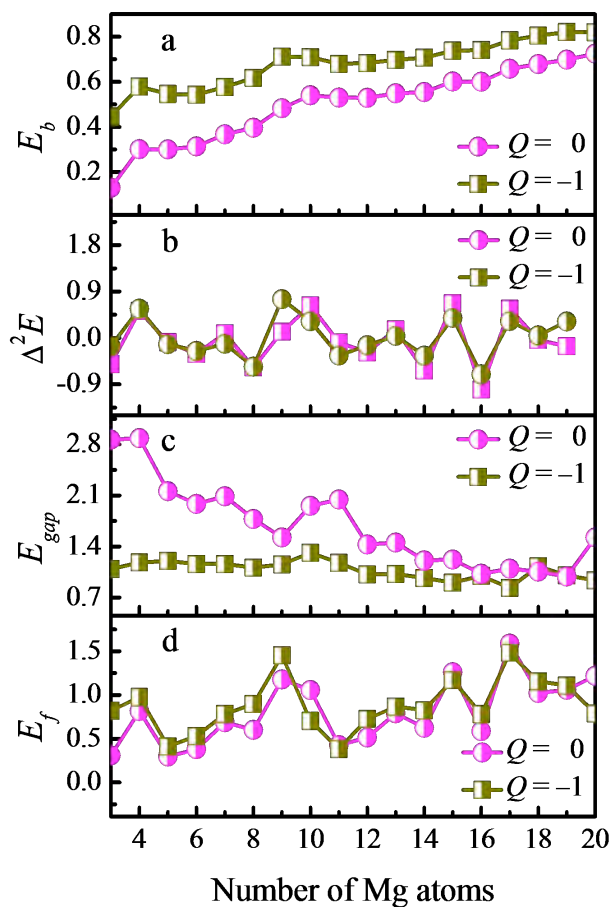


Figure 4. The averaged binding energies  $E_b$  (a), second-order energy differences  $\Delta^2 E$  (b), HOMO-LUMO energy gaps  $E_{gap}$  (c) and fragmentation energies of the most probable fragmentation channels (d) for lowest energy  $Mg_n^Q$  ( $n = 3-20$ ,  $Q = 0, -1$ ) clusters as functions of cluster size  $n$ .

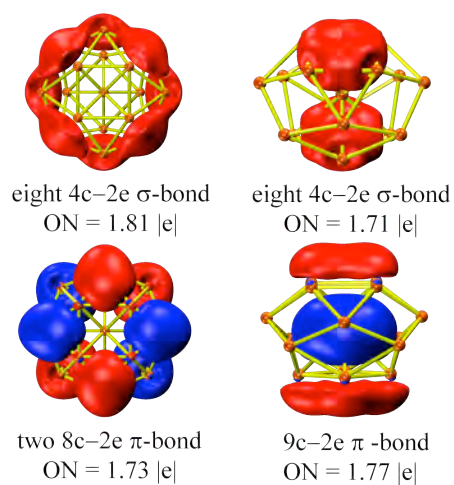


Figure 5. Chemical bonding analyses of neutral  $Mg_{17}$  cluster using the AdNDP

method. ON stands for occupation number.

Table 1. The calculated binding energies ( $E_b$ ) and HOMO–LUMO energy gaps  $E_{gap}$  of the lowest-energy  $\text{Mg}_n^Q$  ( $n = 3\text{--}20$ ,  $Q = 0, -1$ ) clusters. And the data of theoretical and experimental vertical detachment energies (VDEs) and adiabatic detachment energies (ADEs) for the lowest-energy  $\text{Mg}_n^-$  ( $n = 3\text{--}20$ ) clusters. All of energies are shown in the unit of eV.

$n$	$\text{Mg}_n$		$\text{Mg}_n^-$		VDE		ADE	
	$E_b$	$E_{gap}$	$E_b$	$E_{gap}$	Theo.	Expt. <sup>a</sup>	Theo.	Expt. <sup>a</sup>
3	0.13	2.86	0.45	1.09	0.85	0.83	0.80	0.60
4	0.30	2.89	0.58	1.18	0.96	0.96	0.96	0.96
5	0.30	2.16	0.55	1.20	1.13	1.19	1.07	1.04
6	0.31	1.98	0.54	1.16	1.54	1.38	1.23	1.23
7	0.37	2.09	0.58	1.16	1.52	1.50	1.32	1.35
8	0.40	1.78	0.62	1.11	1.85	1.81	1.61	1.60
9	0.48	1.53	0.71	1.15	1.94	1.91	1.89	1.80
10	0.54	1.96	0.71	1.31	1.67	1.68	1.54	1.55
11	0.53	2.04	0.68	1.17	1.87	1.88	1.50	1.60
12	0.53	1.43	0.68	1.02	1.80	1.91	1.71	1.70
13	0.55	1.45	0.70	1.02	1.87	1.94	1.79	1.80
14	0.55	1.21	0.71	0.97	2.04	2.01	1.99	1.92
15	0.60	1.22	0.74	0.90	1.96	2.03	1.90	1.90
16	0.60	1.03	0.74	1.00	2.14	2.16	2.09	2.10
17	0.66	1.10	0.78	0.83	2.05	2.11	1.99	2.00
18	0.68	1.06	0.81	1.13	2.37	2.23	2.12	2.15
19	0.70	0.99	0.82	1.00	2.28	2.43	2.18	2.21
20	0.72	1.52	0.82	0.94	1.88	1.93	1.75	1.78

<sup>a</sup>Reference 9

Table 2. The easiest fragmentation channels and corresponding fragmentation energies ( $E_f$ ) for  $\text{Mg}_n^Q$  ( $n = 3-20$ ,  $Q = 0, -1$ ) clusters.

Cluster	$\text{Mg}_p + \text{Mg}_{n-p}$	$E_f(\text{eV})$	Cluster	$\text{Mg}_p + \text{Mg}_{n-p}^-$	$E_f(\text{eV})$
Mg <sub>3</sub>	Mg + Mg <sub>2</sub>	0.31	Mg <sub>3</sub> <sup>-</sup>	Mg + Mg <sub>2</sub> <sup>-</sup>	0.82
Mg <sub>4</sub>	Mg + Mg <sub>3</sub>	0.82	Mg <sub>4</sub> <sup>-</sup>	Mg + Mg <sub>3</sub> <sup>-</sup>	0.98
Mg <sub>5</sub>	Mg + Mg <sub>4</sub>	0.30	Mg <sub>5</sub> <sup>-</sup>	Mg + Mg <sub>4</sub> <sup>-</sup>	0.41
Mg <sub>6</sub>	Mg + Mg <sub>5</sub>	0.38	Mg <sub>6</sub> <sup>-</sup>	Mg + Mg <sub>5</sub> <sup>-</sup>	0.53
Mg <sub>7</sub>	Mg + Mg <sub>6</sub>	0.69	Mg <sub>7</sub> <sup>-</sup>	Mg + Mg <sub>6</sub> <sup>-</sup>	0.78
Mg <sub>8</sub>	Mg + Mg <sub>7</sub>	0.60	Mg <sub>8</sub> <sup>-</sup>	Mg + Mg <sub>7</sub> <sup>-</sup>	0.90
Mg <sub>9</sub>	Mg + Mg <sub>8</sub>	1.18	Mg <sub>9</sub> <sup>-</sup>	Mg + Mg <sub>8</sub> <sup>-</sup>	1.46
Mg <sub>10</sub>	Mg + Mg <sub>9</sub>	1.06	Mg <sub>10</sub> <sup>-</sup>	Mg + Mg <sub>9</sub> <sup>-</sup>	0.70
Mg <sub>11</sub>	Mg + Mg <sub>10</sub>	0.43	Mg <sub>11</sub> <sup>-</sup>	Mg + Mg <sub>10</sub> <sup>-</sup>	0.38
Mg <sub>12</sub>	Mg + Mg <sub>11</sub>	0.51	Mg <sub>12</sub> <sup>-</sup>	Mg + Mg <sub>11</sub> <sup>-</sup>	0.73
Mg <sub>13</sub>	Mg + Mg <sub>12</sub>	0.79	Mg <sub>13</sub> <sup>-</sup>	Mg + Mg <sub>12</sub> <sup>-</sup>	0.87
Mg <sub>14</sub>	Mg + Mg <sub>13</sub>	0.63	Mg <sub>14</sub> <sup>-</sup>	Mg + Mg <sub>13</sub> <sup>-</sup>	0.83
Mg <sub>15</sub>	Mg + Mg <sub>14</sub>	1.26	Mg <sub>15</sub> <sup>-</sup>	Mg + Mg <sub>14</sub> <sup>-</sup>	1.17
Mg <sub>16</sub>	Mg + Mg <sub>15</sub>	0.59	Mg <sub>16</sub> <sup>-</sup>	Mg + Mg <sub>15</sub> <sup>-</sup>	0.78
Mg <sub>17</sub>	Mg + Mg <sub>16</sub>	1.59	Mg <sub>17</sub> <sup>-</sup>	Mg + Mg <sub>16</sub> <sup>-</sup>	1.48
Mg <sub>18</sub>	Mg + Mg <sub>17</sub>	1.02	Mg <sub>18</sub> <sup>-</sup>	Mg + Mg <sub>17</sub> <sup>-</sup>	1.16
Mg <sub>19</sub>	Mg + Mg <sub>18</sub>	1.06	Mg <sub>19</sub> <sup>-</sup>	Mg + Mg <sub>18</sub> <sup>-</sup>	1.11
Mg <sub>20</sub>	Mg + Mg <sub>19</sub>	1.22	Mg <sub>20</sub> <sup>-</sup>	Mg + Mg <sub>19</sub> <sup>-</sup>	0.79