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Experimental and theoretical studies of neutral $Mg_mC_nH_x$ and $Be_mC_nH_x$ clusters

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Neutral $Mg_mC_nH_x$ and $Be_mC_nH_x$ clusters are investigated both experimentally and theoretically for the first time. Single photon ionization at 193 nm is used to detect neutral cluster distributions through time of flight mass spectrometry. $Mg_mC_nH_x$ and $Be_mC_nH_x$ clusters are generated through laser ablation of Mg or Be foil into CH_4/He expansion gas. A number of members of each cluster series are identified through isotopic substitution experiments employing $^{13}CH_4$ and CD_4 instead of CH_4 in the expansion gas. An oscillation of the vertical ionization energies (VIEs) of $Mg_mC_nH_x$ clusters is observed in the experiments. The VIEs of $Mg_mC_nH_x$ clusters are observed to vary as a function of the number of H atoms in the clusters. Density functional theory (DFT) and *ab initio* (MP2) calculations are carried out to explore the structures and ionization energies of $Mg_mC_nH_x$ clusters. Many $Be_mC_nH_x$ clusters are also generated and detected in the experiments. The structures and VIEs of $Be_mC_nH_x$ clusters are also studied by theoretical calculations. Calculational results provide a good and consistent explanation for the experimental observations, and are in general agreement with them for both series of clusters. © *2011 American Institute of Physics*. [doi:10.1063/1.3617571]

INTRODUCTION

Metal carbide and metal hydride clusters have been extensively investigated as new classes of materials for semiconductors, ceramics, catalysts, and particularly as hydrogen storage systems. Metal hydrides, such as $M_mAl_nH_x$ (M = Li, Na, Mg, B, Ti, Zr), have high hydrogen storage capacity (10.54 wt. % H for $LiAlH_4$, 7.41 wt. % H for $NaAlH_4$), low cost, and bulk availability.[1–3] Recently, we studied $Al_mC_nH_x$ clusters experimentally and theoretically for the first time.[4] $Al_mC_nH_x$ clusters can contain a high percentage of hydrogen by weight: 13.3 wt. % H for an $Al_2C_2H_{12}$ cluster, 10.25 wt. % H for an $Al_3C_2H_{12}$ cluster, and 12.8 wt. % H for an $Al_2C_4H_{15}$ cluster, suggesting that $Al_mC_nH_x$ clusters are potentially good hydrogen storage materials. The high temperature needed for hydrogen desorption (∼150 °C) is a major drawback for metal hydride materials, however. To solve this problem, carbon can be added as a dopant in hydrides to reduce the hydrogen desorption temperature.[5–7] Toe and co-workers[6] explored fast hydrogen desorption/adsorption on magnesium hydride-graphite nanocomposites, and concluded that graphite improves the desorption rate of MgH_2 by changing the reaction mechanism.

Group IIA metals have attracted considerable attention as potential low-weight hydrogen storage materials, particularly for beryllium-based and magnesium-based composites. Recently, Ding *et al.*[8] obtained low-resolution spectra of MgC_4H and MgC_6H using mass-selected resonance enhanced multiphoton ionization spectroscopy. Forthomme and co-workers[9] reported high resolution laser spectroscopy of MgC_4H. In their experiments, MgC_4H clusters are produced using an ablation source of magnesium and 10% acetylene seeded in helium. Boldyrev *et al.*[10] calculated geometries of small magnesium carbide clusters using B3LYP and MP2/6–31+G* levels of theory; however, no experimental or theoretical study of the $Mg_mC_nH_x$ cluster series has been reported.

Beryllium is a member of Group IIA that has been most extensively explored using theoretical methods, but the least studied experimentally. Recently, some efforts have been concentrated on the studies of beryllium-doped carbon clusters. Chen *et al.* calculated linear structures for ground state beryllium–doped carbon clusters BeC_n^- (n = 1–8) at a B3LYP theoretical level with a 6–31+G* basis set.[11] Ghorri *et al.*[12] studied geometry and stability of Be_nC_m (n = 1–10) clusters using density functional theory (DFT) B3PW91/6–311+G* calculations. Naumkin[13] employed *ab initio* calculations to investigate Group IIA metal atoms (Be and Mg) attaching to unsaturated hydrocarbon molecules. Their calculations suggest that the metal can bind weakly to the hydrocarbon or attach to the C = C units. Thompson *et al.*[14] performed a matrix isolation study of Be reacting with C_2H_2 through a laser ablation approach: the major products were determined as the linear species BCCH and HBeCCH. Recently, Heaven *et al.*[15] reported spectroscopic studies of Be-containing species in the gas phase by using a variety of laser excitation techniques, providing insights concerning of the bonding and electronic structure of Be_2, BeO, BeOBe, Be_nO_m, BeOH, and BeC. To the best of our knowledge, $Be_mC_nH_x$ complexes have not been studied previously.

The purpose of the present work is to explore the new neutral $Mg_mC_nH_x$ and $Be_mC_nH_x$ clusters experimentally and theoretically. Neutral $Mg_mC_nH_x$ and $Be_mC_nH_x$ clusters are generated by laser ablation of Mg and Be metal targets into an expansion gas of mixed CH_4/ helium. A great number of neutral $Mg_mC_nH_x$ and $Be_mC_nH_x$ clusters are observed by single photon ionization (SPI) at 193 nm and time of flight

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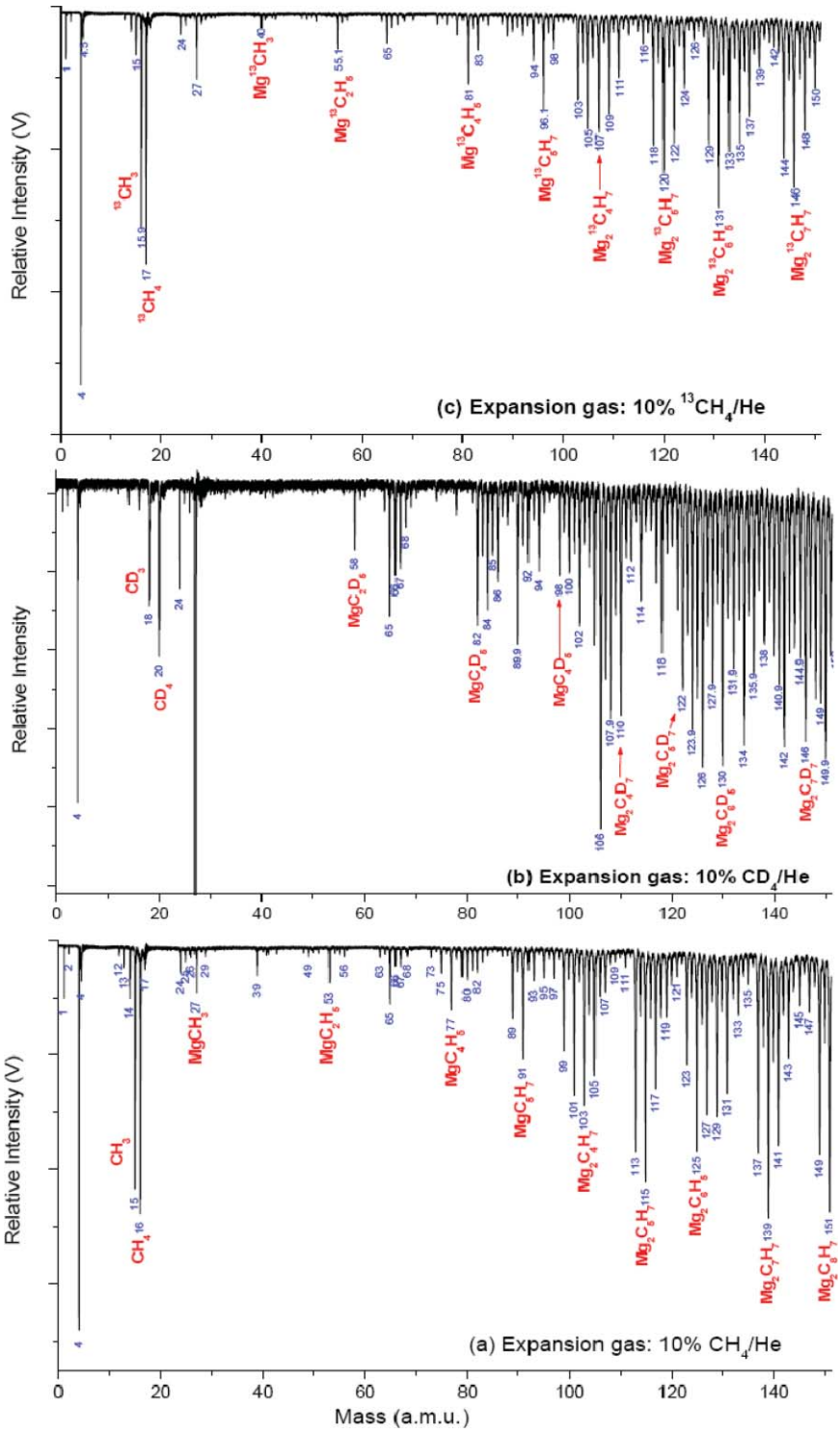

FIG. 1. Mass spectra of $Mg_mC_nH_x$ clusters ionized by a 193 nm laser. Clusters are generated by laser ablation of pure Mg foil into a mixture of (a) 10% CH_4/He, (b) 10% CD_4/He, and (c) 10% $^{13}CH_4$/He expansion gases at 80 psi backing pressure.

mass spectrometry (TOFMS) detection. The structures, vertical ionization energies (VIEs), and adiabatic ionization energies (AIEs) of both sets of clusters are studied by DFT calculations at a B3LYP level, and *ab initio* calculations at the MP2 level with a 6–311+G* basis set, providing a good explanation for all experimental observations, and view of the structures of these metal carbon hydrides.

EXPERIMENTAL AND THEORETICAL METHODS

The experimental apparatus and laser sources have been described in previous publications from this laboratory,[16–18] and therefore only a brief description of the experimental scheme will be presented in this report. The neutral $Mg_mC_nH_x$ and $Be_mC_nH_x$ clusters are created in a laser ablation/expansion source through laser ablation (focused

532 nm laser, 10–20 mJ/pulse) of a target (Mg or Be foil) into a mixture of 10% hydrocarbon (CH_4) and helium used as the expansion gas. The ions created in the ablation source are removed by an electric field before the neutral clusters enter the ionization region. In order to distinguish different $Mg_mC_nH_x$ and $Be_mC_nH_x$ clusters with the same mass (isobars) in the mass spectra, methane-d_4 (99 at. % D, Aldrich) and methane-^{13}C (99 at. % ^{13}C, Aldrich) are also used as reactants instead of CH_4. The neutral clusters are ionized by an unfocused 193 nm laser and detected in a TOFMS. In order to avoid multiphoton ionization of neutral clusters, the 193 nm laser fluence is set to about 80 μJ/cm^2/pulse.

All the calculations reported in the present work are performed with the GAUSSIAN 03 program package.[19] The various possible lowest energy structures for small neutral $Mg_mC_nH_x$ and $Be_mC_nH_x$ clusters are calculated at the B3LYP/6–311+G* level of theory.[20,21] These structures are almost unchanged when they are refined using MP2 theory with the same basis set.[22] The ionization energies (VIEs and AIEs) for clusters are calculated at MP2 theory levels. The calculated structures for $Mg_mC_nH_x$ and $Be_mC_nH_x$ clusters presented in this report are obtained based on numerous attempts to find the lowest energy form for each cluster stoichiometry. For example, more than 30 different initial input structures of Mg_mC_n and Be_mC_n were attempted, and more than 100 structures are obtained for $Mg_mC_nH_x$ and $Be_mC_nH_x$ species. The chosen depicted isomeric structures are those for which the energy is the lowest and for which the ionizations energies are consistent with the experimental VIEs.

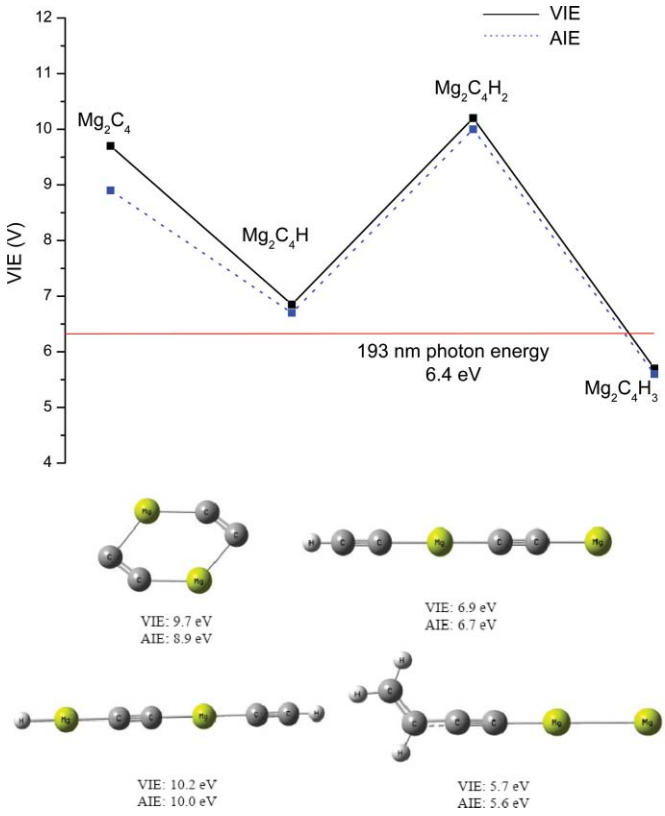

FIG. 2. The VIEs and AIEs of $Mg_2C_4H_{0,1,2,3}$ clusters plotted against the number of H atoms x in the clusters. The structures under the plot are the lowest energy structures of $Mg_2C_4H_{0,1,2,3}$ clusters optimized at the MP2/6–311+G* theory level. Values (in eV) below each geometry are VIEs and AIEs for the clusters calculated at the same theory level.

RESULTS AND DISCUSSION

$Mg_mC_nH_x$ clusters

Neutral $Mg_mC_nH_x$ clusters are created by ablation of Mg foil into a mixture of 10% CH_4/He expansion gas in our experiments. Under this condition, magnesium metal vapor created by laser ablation reacts with hydrocarbon compounds in the ablation source, and then $Mg_mC_nH_x$ clusters are formed during supersonic expansion and cooling processes. Figure 1(a) displays the distribution of neutral $Mg_mC_nH_x$ clusters ionized by SPI employing 193 nm light (unfocused, ~80 μJ/pulse). A great number of magnesium carbon hydride clusters are observed in the mass spectrum, for example, mass numbers 39 ($MgCH_3$), 53 (MgC_2H_5), 77 (MgC_4H_5), 91 (MgC_5H_7), 103 ($Mg_2C_4H_7$), 115 ($Mg_2C_5H_7$), 125 ($Mg_2C_6H_5$), 139 ($Mg_2C_7H_7$), 151 ($Mg_2C_8H_7$), 165 ($Mg_2C_9H_9$), and 175 ($Mg_2C_{10}H_7$) amu, etc. One notes that all signals identified for $Mg_mC_nH_x$ clusters in the 193 nm SPI experiments are odd mass numbers, indicating an oscillation of theVIEs of $Mg_mC_nH_x$ clusters. The detected $Mg_mC_nH_x$ clusters cannot all be uniquely distinguished and assigned in the present mass spectra (Fig. 1(a)) due to mass degeneracy (isobars) for some of clusters; for example, MgC_5H_7 and ($Mg_2C_3H_7$), have the same mass number (91 amu), $Mg_2C_4H_7$ and $Mg_3C_2H_7$ have the same mass number (103 amu), etc. In order to distinguish such clusters, isotopic CD_4/He and $^{13}CH_4$/He instead of $^{12}CH_4$/He mixtures are employed as the expansion gas to generate neutral $Mg_mC_nH_x$ clusters as displayed in Figs. 1(b) and 1(c). In the CD_4/He experiment (Fig. 1(b)), one identifies the peak at 82 amu (MgC_4D_5), which corresponds to the peak of mass number 77 amu (MgC_4H_5) in the $^{12}CH_4$/He experiment (Fig. 1(a)). In the $^{13}CH_4$/He experiment, this peak is assigned as the 81 amu ($Mg^{13}C_4H_5$) peak as shown in Fig. 1(c). A number of $Mg_mC_nH_x$ clusters observed in Fig. 1 are identified as $MgCH_3$, MgC_2H_5, MgC_4H_5, MgC_5H_7, $Mg_2C_4H_7$, $Mg_2C_5H_7$, $Mg_2C_6H_5$, $Mg_2C_8H_7$, $Mg_2C_9H_9$, and $Mg_2C_{10}H_7$, etc. One notes that many minor peaks are also observed in Fig. 1(a). They may be assigned to the isotopes ^{25}Mg (10%) and ^{26}Mg (11%). These isotopic signals with odd mass numbers may also overlap with some weak $Mg_mC_nH_x$ signals.

In the mass spectra of Fig. 1, only $Mg_mC_nH_x$ clusters with odd mass numbers are observed in 193 nm SPI experiments, indicating a special relationship between the cluster structures and their ionization energies, which are systematically change with the number of H atoms in the clusters. In our previous study of neutral $Al_mC_nH_x$ clusters,[4] the same behavior is observed: only clusters with odd mass number are detected in the mass spectrum generated by 193 nm SPI. Theoretical calculation demonstrates that the VIEs of $Al_mC_nH_x$ clusters vary as a function of the number of H atoms in the clusters. In order to explore the experimental results in the present study, theoretical calculations are also preformed to investigate the structures and VIEs of $Mg_2C_4H_x$ clusters at the MP2/6–311+G* theory level. First, we perform an exhaustive

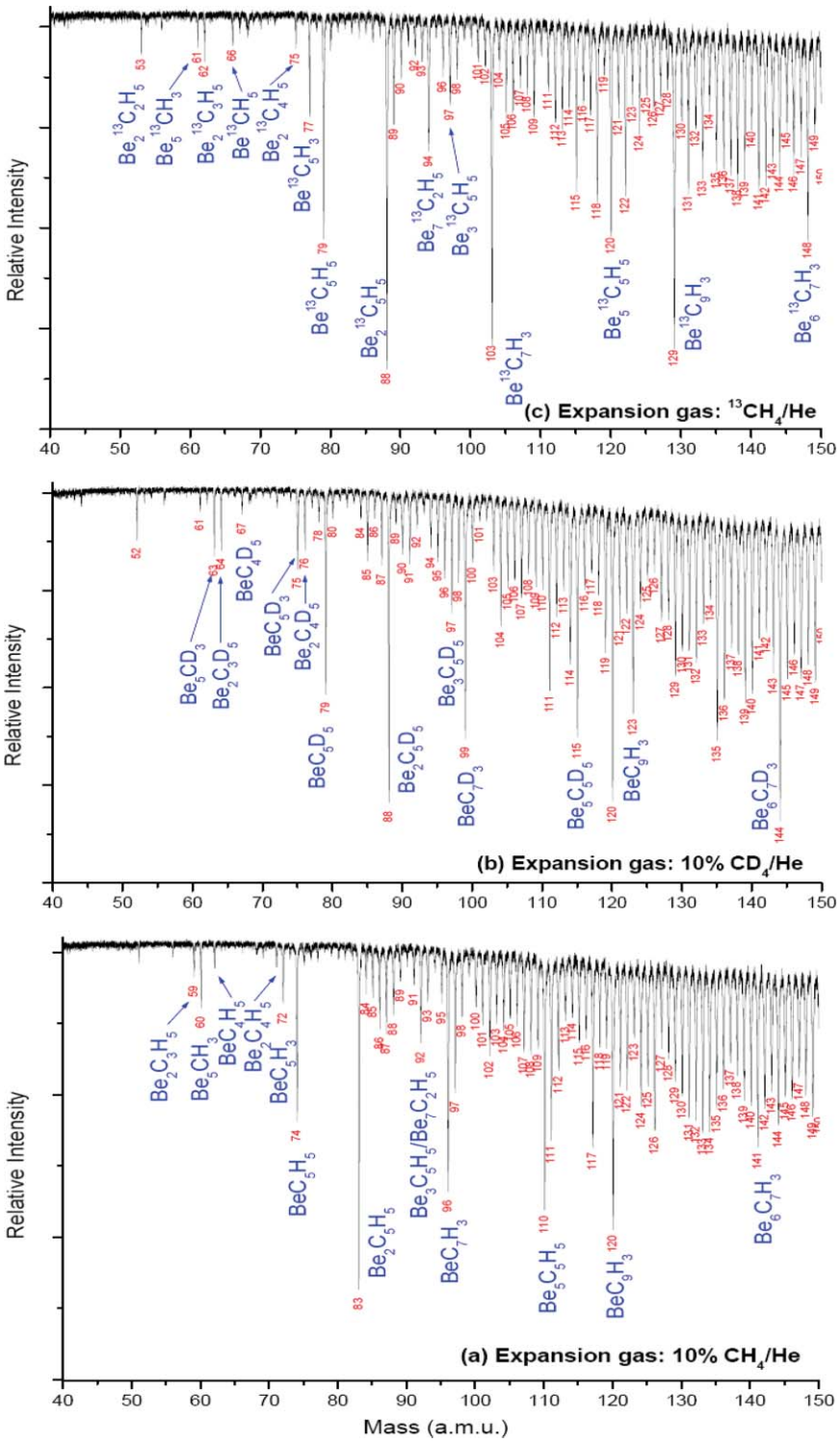

FIG. 3. Mass spectra of $Be_mC_nH_x$ clusters ionized by a 193 nm laser. Clusters are generated by laser ablation of pure Be foil into a mixture of (a) 10% CH_4/He, (b) 10% CD_4/He, and (c) 10% $^{13}CH_4$/He expansion gases at 80 psi backing pressure.

search for the initial geometries of Mg_2C_4, and then try to find lowest energy structures of $Mg_2C_4H_{1-3}$ on the basis of consideration of all the Mg_2C_4 isomers. As shown in Fig. 2, a C_{2h} ring structure is obtained as the global minimum energy of Mg_2C_4: this structure is in good agreement with the reports of Boldyrev *et al.*[10] For the lowest energy structure of Mg_2C_4H, the H atom bonds to a C atom at one end of a linear structure of C–C–Mg–C–C–Mg, and for the lowest energy structure of $Mg_2C_4H_2$, the two H atoms bond to Mg and C at two ends of the same Mg_2C_4 structure. The lowest energy structure of $Mg_2C_4H_3$ is found to be planar, in which two H atoms bond to one end C atom while another one bonds to a neighbor C atom of C–C–C–C–Mg–Mg as shown in Fig. 2.

The VIEs and AIEs for the lowest energy structures of $Mg_2C_4H_{0-3}$ clusters are calculated at the MP2/6–311+G* level of theory. Based on such calculations, VIEs for

$Mg_2C_4H_x$ clusters are Mg_2C_4 (9.7 eV), $Mg_2C_4H_1$ (6.85 eV), $Mg_2C_4H_2$ (10.2 eV), and $Mg_2C_4H_3$ (5.7 eV), respectively. In Fig. 2, the VIEs of neutral $Mg_2C_4H_{0-3}$ clusters are plotted against the number of H atoms in the clusters. An oscillation of the VIEs of $Mg_2C_4H_{0-3}$ clusters with the number of H atoms is observed because adding H atoms to the clusters changes the electronic configuration of the clusters from open shell (x = odd) to closed shell (x = even). The calculational results are in very good agreement with the experimental observations that all signals identified for $Mg_mC_nH_x$ clusters in the 193 nm SPI are found for odd mass numbers (Fig. 1(a)): for example, $Mg_2C_4H_1$ (97 amu), $Mg_2C_4H_3$ (99 amu), $Mg_2C_4H_5$ (101 amu), $Mg_2C_4H_7$ (103 amu), $Mg_2C_4H_7$ (105 amu), etc. This agreement indicates that the calculated geometric structures of the clusters are believable and likely correct. A similar tendency is also found for AIEs of $Mg_2C_4H_{0-3}$ clusters as shown in Fig. 2.

Neutral $Be_mC_nH_x$ clusters

Neutral $Be_mC_nH_x$ clusters are generated in the ablation/expansion source in our experiments through laser ablation of Be target into 10% CH_4/He expansion gas. Figure 3(a) displays the distribution of neutral $Be_mC_nH_x$ clusters ionized by SPI employing 193 nm light. A great number of the $Be_mC_nH_x$ clusters is identified in the mass spectrum; for example, $Be_2C_3H_5$, Be_5CH_3, BeC_4H_5, $Be_2C_4H_5$, BeC_5H_3, BeC_5H_5, $Be_2C_5H_5$, $Be_3C_5H_5/Be_7C_2H_5$, BeC_7H_3, $Be_5C_5H_5$, and BeC_9H_3, etc. All these clusters can be distinguished through isotopic experiments, in which isotopic CD_4/He and $^{13}CH_4$/He instead of $^{12}CH_4$/He mixtures are employed as the expansion gas. For example, the peak of 83 amu ($Be_2C_5H_5$) in Fig. 3(a) corresponds to the peak of mass number 88 amu ($Be_2C_5D_5$) in Fig. 3(b), and to the peak of mass number 88 amu ($Be_2{}^{13}C_5H_5$) in Fig. 3(c). In the experiments, the signals with both odd (59, 83, 117, 141 amu, etc.) and even mass numbers (74, 96, 110, 120 amu, etc.) are observed in the mass spectrum. This is different from the observation of $Mg_mC_nH_x$ (and $Al_mC_nH_x$) clusters (Fig. 1(a)) under the same experimental conditions: only species with odd mass numbers are observed for these latter two clusters. One notices that a significant signal for the $Be_2C_5H_5$ cluster is detected, while no signals from the $Be_2C_5H_{1-4}$ clusters are detected.

In the present study, we explore the structures, VIEs, and AIEs of $Be_2C_5H_{0-5}$ clusters through theoretical calculations at MP2/6–311+G theory levels. The most stable structure of Be_2C_5 is a 7-membered planar ring as displayed in Fig. 4: this structure is in agreement with that reported by Ghouri.[12] The structures of $Be_2C_5H_{1-4}$ clusters shown in Fig. 4 are formed by adding H atoms on the most stable structure of Be_2C_5. We have tried to find all the isomers of $Be_2C_5H_{1-5}$ on the basis of all the Be_2C_5 isomers that we can generate; the lowest energy isomers of $Be_2C_5H_{1-4}$ are shown in Fig. 4. The present study is not aimed at an exhaustive search for all the various possible isomers of $Be_mC_nH_x$ clusters. The VIEs and AIEs for the $Be_2C_5H_{0-4}$ clusters are also calculated at the MP2/6–311+G* level of theory; for example, Be_2C_5 (9.7 eV), $Be_2C_5H_1$ (8.4 eV), $Be_2C_5H_2$ (9.3 eV), $Be_2C_5H_3$ (6.5 eV), $Be_2C_5H_4$ (8.7 eV), and $Be_2C_5H_5$ (5.4 eV). In Fig. 4, VIEs of neutral $Be_2C_5H_{0-5}$ clusters are plotted against the number of H atoms in the clusters. Note that the VIEs of $Be_2C_5H_{0-5}$ clusters vary as a function of the number of H atoms in the clusters. VIE of $Be_2C_5H_5$ (5.4 eV) is lower than 6.4 eV of single photon energy of 193 nm radiation. In the experiments, one notices that a significant signal of $Be_2C_5H_5$ cluster is detected, and also that signals of $Be_2C_5H_{1-4}$ clusters are not detected by 193 nm SPI. Therefore, the calculational results of neutral $Be_2C_5H_{0-5}$ clusters are in very good agreement with the experimental observations. A similar tendency is also found for AIEs of the $Be_2C_5H_{0-5}$ as shown in Fig. 4.

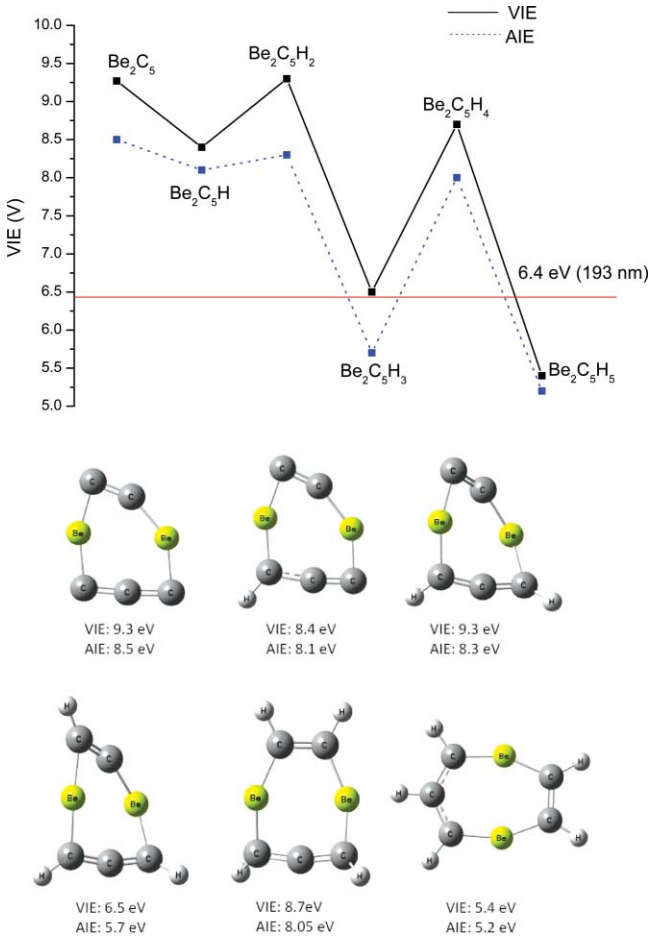

FIG. 4. The VIEs and AIEs of $Be_2C_5H_{0,\,1,\,2,\,3,\,4,\,5}$ clusters plotted against the number of H atoms x in the clusters. The structures under the plot are the lowest energy structures of $Be_2C_5H_{0,\,1,\,2,\,3,\,4,\,5}$ clusters optimized at the MP2/6–311+G* theory level. Values (in eV) below each geometry are VIEs and AIEs for the clusters calculated at the same theory level.

CONCLUSIONS

Neutral $Mg_mC_nH_x$ and $Be_mC_nH_x$ clusters are studied for the first time by experimental and theoretical methods. Many $Mg_mC_nH_x$ clusters are generated through laser ablation and supersonic expansion cooling. Only some of the neutral $Mg_mC_nH_x$ clusters with odd mass numbers (i.e., an odd number of electrons) are detected by SPI at 193 nm. On the basis of our calculations, VIEs and AIEs of $Mg_mC_nH_x$ clusters vary systematically with the number of H atoms, because adding

H atoms to the clusters changes the electronic configuration of the clusters from open shell (x = odd) to closed shell (x = even). Theoretical calculations are in agreement with the major experimental observations. A great many $Be_mC_nH_x$ clusters are also generated and detected in our experiments. Some of them can be identified through isotopic experiments. Cluster structures, VIEs, and AIEs are calculated by DFT and *ab initio* methods: both linear and ring structures are obtained for small clusters and many low energy isomers can be generated for both cluster species. Some cluster stoichiometries can be positively identified through ^{13}C and D isotope substitution experiments. Experiments are presently underway to expand this cluster series to other Group IIA metals and to $Li_mC_nH_x$ species. We are also presently exploring processes for the reversible removal of hydrogen from the general $M_mC_nH_x$ cluster series (e.g., $M_mC_nH_x \rightarrow M_mC_n + x/2\ H_2$), and for the reversible attachment of hydrogen to the general M_mC_n cluster series (e.g., $M_mC_n + x/2\ H_2 \rightarrow M_mC_nH_x$).

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