

A Density-Functional Study on the Interaction of C_2H Radical with Silver Clusters $Ag_n^{0/-}$ ($n = 1 - 4$)

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Abstract

The interaction between C_2H radical and silver clusters $Ag_n^{0/-}$ ($n=1-4$) has been studied based on a systematic density functional theory (DFT) investigation. The DFT calculated results show that C_2H radical inclines to interact with silver clusters $Ag_n^{0/-}$ ($n=1-4$) as an integrity in the most stable structures of $C_2HAg_n^{0/-}$ ($n=1-4$) rather than being divided by Ag_n clusters. The $Ag_n^{0/-}$ ($n=1-4$) clusters remain their structural integrities as units in the ground states of $C_2HAg_n^{0/-}$ ($n=1-4$). Detailed natural resonance theory (NRT) and natural bond order analyses show that the interaction between the C_2H radical and the $Ag_n^{0/-}$ ($n=1-4$) in the most stable structures of $C_2HAg_n^{0/-}$ ($n=1-4$) are mainly ionic. Compared with that of C_2H radical and the $Au_n^{0/-}$ ($n=1-4$), the electronic component in $C_2HAg_n^{0/-}$ ($n=1-4$) increased due to the strong relativistic effects of Au. The stretching vibrational frequencies of $C\equiv C$ and $C-H$ in the ground states of $C_2HAg_n^{0/-}$ ($n=1-4$) occur red shifts compared with those of the C_2H radical due to the interaction between the $Ag_n^{0/-}$ clusters and C_2H radical. The photoelectron spectra (PES) of the most stable structures of $C_2HAg_n^{0/-}$ ($n=1-4$) have been simulated to facilitate their future experimental characterizations.

Keywords: DFT; C_2H radical; Silver clusters; Interaction

Introduction

The past few years have witnessed increasing research activities in coin metal clusters [1-6] due primarily to their important implications in electronics, telecommunications, aerospace, chemicals, and complicated physical and chemical properties. Many reactions using supported coin metals represented by Au nanoparticles as catalysts have been reported, including the combustion of hydrocarbons [7-10]. C_2H radical is one of the important reactive intermediates in hydrocarbon combustion processes [11-14]. So investigating the interaction of silver clusters with C_2H radical is valuable for understanding the remarkable catalytic effects discovered for silver nanoparticles [15-17].

In recent years, experimental and theoretical works have been conducted to study the interaction between metals and organic molecules because of its significant role for both heterogeneous and homogeneous catalytic systems. Mark B [18] reported the infrared molecular beam photo dissociation spectra of complexes formed from the reaction of silver clusters with methanol by pulsed laser vaporization from a target of the corresponding pure metal within a continuous-flow cluster source. Interactions of small neutral coinage metal clusters Ag_3 and Ag_4 with chalcogen dihydrides (H_2O , H_2S , H_2Se) have been investigated using the DFT-B3LYP method [19], while the low-energy silver-cation-water clusters $Ag_n(H_2O)_{n=1-6}$ have been investigated using the B3LYP and MP2 levels [20]. Jiang [21] investigated the reactions of laser-ablated silver atoms with carbon monoxide molecules in solid argon and neon using matrix-isolation IR spectroscopy, while CO adsorption on small neutral, anionic, and cationic silver clusters Ag_n has been studied with use of the PW91PW91 density functional theory (DFT) method [22]. The reactions of Ag_3 clusters with CH_3Br as well as the photo dissociation of the resulting complexes at 266 nm were studied in a radio frequency ion trap under multiple collision conditions [23]. The interaction between Fe and C_2H radical has been studied based on the PES analyses [24]. High-level *ab initio* calculations, using the CPD-G2 thaw and CP-G2 composite computational procedures (combined with spin projection techniques when appropriate), are used to explore the bonding between the metal mono cations Na^+ , Mg^+ , Al^+ , K^+ , and Ca^+ and the radicals C_2H [25]. Brugh [26] found that both the ground and the excited state of CrC_2H had liner structure and their

vibronic spectrum were complicated in the 11100-13300 cm^{-1} region. The first spectroscopic identification and characterization of YbC_2H has been reported by combining resonance-enhanced two photon ionization, laser-induced fluorescence and photoionization efficiency spectroscopy with density functional calculations [27]. Yuan [28] investigated the adsorption of C_2H radical on small cobalt clusters by mass spectrometry and PES of $Co_nC_2H^-$ ($n=1-5$) cluster anions.

To the best of our knowledge, there have been no studies reported to date on the interaction between C_2H radical and $Ag_n^{0/-}$ clusters. In a very recent DFT study, our group investigated the interaction of C_2H radical with gold clusters $Au_n^{0/-}$ ($n=1-4$) [29]. Considering the same electron configuration between Au and Ag, which all have a closed d shell and a single s valence electron, it is natural to anticipate that silver clusters may have similar properties as gold clusters. In this work, we present an investigation on the structures and bonding characteristics of $C_2HAg_n^{0/-}$ ($n=1-4$) complexes in hopes of understanding the interaction between $Ag_n^{0/-}$ ($n=1-4$) clusters with C_2H radical. Detailed natural resonance theory (NRT) and IR spectra analyses are also used to show the interaction between $Ag_n^{0/-}$ ($n=1-4$) clusters and C_2H radical.

Theoretical Method

Structural optimizations and vibrational analyses were performed employing the B3LYP method [20,30]. For comparison, calculations were also carried out by the PBE1PBE with symmetry constraints [31,32]. The Stuttgart quasi-relativistic pseudo potential and the basis set augmented with two f-type polarization functions and one g-type

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polarization function (Stuttgart_rsc_1997_ecp+2f1g ($\alpha(f)=0.498$, $\alpha(f)=1.464$, and $\alpha(g)=1.218$) were employed for Ag and the 6-311+G(d, p) basis set implemented in Gaussian 03 was used for C and H [33,34]. Both the B3LYP and PBE1PBE produced similar ground-state structures and relative energies with slightly different bond parameters. Therefore, the following discussions were mainly focused on the B3LYP results. Further, relative energies for the isomers were refined using the coupled-cluster method with triple excitations (CCSD(T)) at the B3LYP structures [35,36]. Natural resonance theory (NRT) was used to calculate the bond orders and bond polarities. Adiabatic detachment energy (ADE) values were calculated as the energy difference between the anion and its neutral molecule at their ground-state structures, while vertical electron detachment energies (VDEs) of the anions were calculated from the Δ SCF energy difference between the neutral and anion ground states and the excitation energies of the neutral (triplet excited states only) calculated by time-dependent DFT (TDDFT) [37,38]. The simulated spectra were constructed by fitting the distribution of calculated VDE values with unit-area Gaussian functions of 0.04 eV at full width. The NBO 5.0 [39,40] program was used to calculate the bond orders and atomic charges.

The low-lying isomers of C₂HAg_n⁻ (n=1-4) anions and the ground-state structures of neutral C₂HAg_n (n=1-4) are depicted in Figure 1-5, respectively. Figure 6 shows the simulated photoelectron spectra. Natural atomic charges ($q/|e|$), Wiberg bond indexes calculated at the B3LYP level are listed in Table 1. Calculated NRT bond orders, covalent (CNRT) and ionic (INRT) of C(c)-Ag(c) in the ground states of C₂HAg_n^{0/-} (n=1-4) clusters at B3LYP level as well as ADE and VDE are tabulated in Table 2. C-C and C-H stretching vibration and C-H rocking vibration of the C₂H radical and the ground states of C₂HAg_n⁻ (n=1-4) clusters at B3LYP level are summarized in Table 3.

Results and Discussion

Geometries

We start from C₂HAg and C₂HAg₂, the simplest clusters discussed

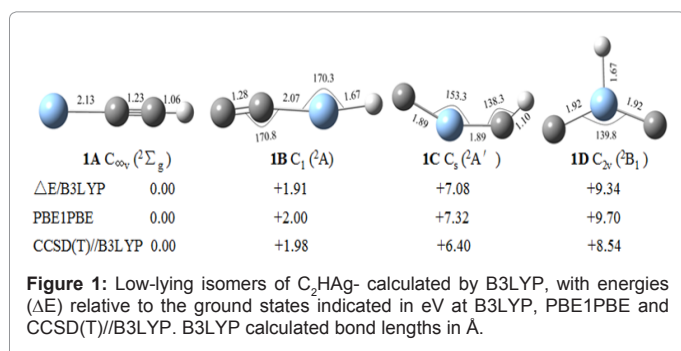


Figure 1: Low-lying isomers of C₂HAg- calculated by B3LYP, with energies (ΔE) relative to the ground states indicated in eV at B3LYP, PBE1PBE and CCSD(T)/B3LYP. B3LYP calculated bond lengths in Å.

Isomers	q _{C(c)}	q _{Ag(c)}	WBI _{C-C}	WBI _{C-Ag}	WBI _{C(c)}	WBI _{Ag(c)}
C _{ov} C ₂ HAg 1N	-0.55	+0.66	2.98	0.64	3.63	0.68
C _{ov} C ₂ HAg- 1A	-0.46	-0.23	2.95	0.40	3.37	0.45
C _s C ₂ HAg ₂ 2N	-0.48	+0.38	2.95	0.59	3.57	0.94
C _{ov} C ₂ HAg ₂ - 2A	-0.44	+0.22	2.94	0.50	3.53	1.27
C _{2v} C ₂ HAg ₃ 3N	-0.49	+0.21	2.94	0.59	3.62	1.37
C _{2v} C ₂ HAg ₃ - 3A	-0.43	+0.17	2.94	0.54	3.56	1.40
C _s C ₂ HAg ₄ 4N	-0.50	+0.21	2.83	0.41	3.55	1.39
C _s C ₂ HAg ₄ - 4A	-0.44	+0.23	2.94	0.53	3.57	1.36

Table 1: Calculated natural atomic charges($q/|e|$), Wiberg bond indexes(WBI), and total atomic bond orders of the ground states of C₂HAg_n^{0/-} (n=1-4) clusters at B3LYP Level. Ag(c) and C(c) represents atoms connected with C or Ag.

Isomers	NRT	CNRT	INRT	Covalent Percentage	ADE	VDE
C _{ov} C ₂ HAg 1N	1.00	0.36	0.64	0.36		
C _{ov} C ₂ HAg- 1A	0.52	0.17	0.35	0.33	1.21	1.29
C _s C ₂ HAg ₂ 2N	0.18	0.08	0.10	0.44		
C _{ov} C ₂ HAg ₂ - 2A	0.37	0.11	0.26	0.30	3.11	3.17
C _{2v} C ₂ HAg ₃ 3N	0.85	0.32	0.53	0.38		
C _{2v} C ₂ HAg ₃ - 3A	0.41	0.13	0.28	0.32	2.04	2.03
C _s C ₂ HAg ₄ 4N	0.40	0.05	0.35	0.13		
C _s C ₂ HAg ₄ - 4A	0.43	0.13	0.30	0.30	2.55	3.28

Table 2: Calculated NRT bond orders, covalent (CNRT) and ionic (INRT) of C(c)-Ag(c) in the ground states of C₂HAg_n^{0/-} (n=1-4) clusters at B3LYP level. Ag(c) and C(c) represents atoms connected with C or Ag. The ADE and VDE of the ions are also tabulated.

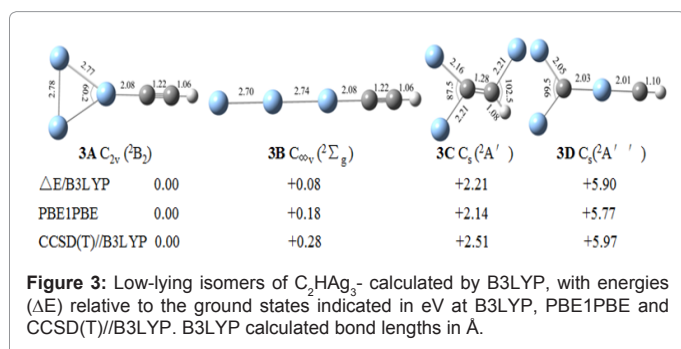
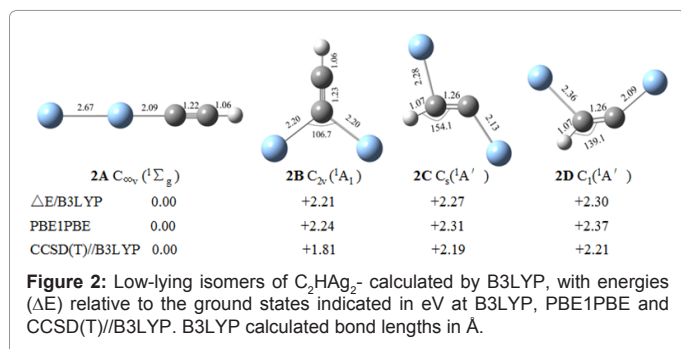
Isomers	C-H rocking vibration	C-C stretching vibration	C-H stretching vibration
C _{ov} C ₂ H	292.3	2082.9	3463.8
C _{ov} C ₂ HAg- 1A	612.4	1995.8	3433.2
C _{ov} C ₂ HAg ₂ - 2A	617.8	2013.2	3441.2
C _{2v} C ₂ HAg ₃ - 3A	621.5	2020.8	3444.5,
C _s C ₂ HAg ₄ - 4A	631.4	2026.6	3446.1

Table 3: C-H rocking vibration, C-C and C-H stretching vibration (cm⁻¹) of the ground states of C₂HAg_n⁻ (n=1-4) clusters at B3LYP level.

in this work. As shown in Figure 1, the Ag-terminated C₂HAg⁻ (²Σ_g⁻, 1A) is the ground state which lies 1.91, 2.00 and 1.98 eV lower than the Ag-inserted C₁C₂HAg⁻ (²A, 1B) at B3LYP, PBE1PBE and CCSD(T)//B3LYP levels, respectively. The C₂HAg⁻ (²Σ_g⁻, 1A) with C_{ov} symmetry proves to be similar with linear CoC₂H⁻ [28] and C₂Hau⁻ [29] in geometry in which C₂H as a unit combines with Co or Au by its terminal C atom. Interestingly, the ground states of neutral C₂HAg (¹Σ_g⁺, 1N) possesses the similar linear structure which can be obtained by replacing one of the H atom in C₂H₂ with an Ag atom and appears to be analogous in geometry to the linear CoC₂H and C₂Hau at the same level [28,29]. The ground state of C₂HAg⁻ (1A) has a bond length of r_{C-Ag}=2.13 Å, whereas the r_{C-Ag} is 2.02 Å in C₂HAg (1N). The shorter r_{C-Ag} in C₂HAg (1N) compared with that of C₂HAg⁻ (1A) indicates the extra electron of the anion is primarily localized among the C≡C-Ag conjugate system. The calculated natural atomic charges ($q_{Ag(c)} = -0.23$ and $+0.66 |e|$, and $q_{C(c)} = -0.46$ and $-0.55 |e|$ in C_{ov}C₂HAg⁻ (1A) and C₂HAg (1N), respectively) confirm the conference. The WBIC-Ag=0.40 in C₂HAg⁻ (1A) and WBI_{C-Ag}=0.64 in C₂HAg (1N) (see Table 1) can also support the prediction. The next two isomers C₂HAg⁻ (1C) and C₂HAg⁻ (1D) is 6.40 and 8.54 eV higher than the ground state of C₂HAg⁻ (1A) at CCSD (T)//B3LYP levels, respectively.

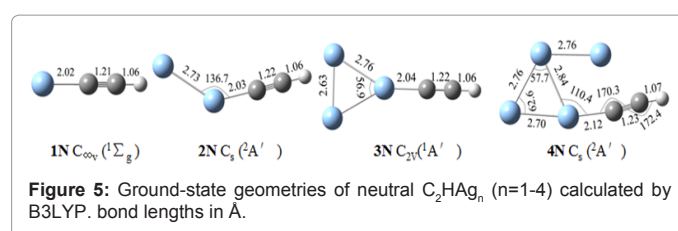
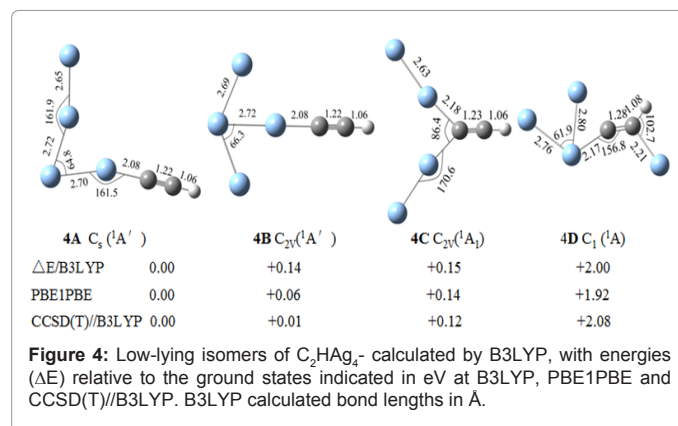
When C₂H radical interacts with Ag₂ cluster, the C_{ov} (¹Σ_g⁺, 2A) (depicted in Figure 2) is obtained which lies 2.21, 2.24 and 1.81 eV lower than C_{2v} (¹A₁, 2B) at B3LYP, PBE1PBE and CCSD (T)//B3LYP levels, respectively. The perfectly linear structure contains a C≡C triple bond with r_{C=C} = 1.22 Å, C-Ag σ-bond with r_{C-Ag} = 2.09 Å, and an Ag-Ag bond with r_{Ag-Ag} = 2.67 Å. Our calculated Ag-Ag bond lengths in 2A and 2N are longer than the experimental value 2.53 Å and 2.61 Å in single Ag₂ cluster [41,42] due to the interaction between C₂H radical with Ag₂^{0/-} cluster. The Ag atoms connected to C of C₂H radical in 2A and 2N carry the net atomic charges of +0.22 and +0.38 |e|, respectively. It is interesting to notice that our calculation produces nearly the same second low-lying isomers with Y-shaped structure for Ag₂C₂H- 2B, Co₂C₂H- and Au₂C₂H- [28,29].

For C₂HAg₃⁻ clusters, as shown in Figure 3, C₂HAg₃⁻ anion possesses a ground state of C_{2v} (²B₂, 3A), which lies 0.28, 2.51 and 5.97 eV lower



than C_{∞v}(²Σ_g⁻, 3B), C_s(²A', 3C) and C_s(²A'', 3D) at CCSD(T)//B3LYP level, respectively. It is interesting that the ground state of C_{2v}C₂HAg₃⁻ (²B₂, 3A), as well as C_{2v}C₂HAg₃(¹A', 3N) possesses a perfect triangular Ag₃ unit similar to that of the ground state Ag₃ clusters [43]. Distinctive similarities were also observed in the ground states of C_{2v}C₂HAg₃ and C_{2v}C₂HAg₃⁻ [29]. The Ag-Ag bond length in C₂HAg₃⁻ (1A) is 2.77 or 2.78 Å, which is shorter than that in D_{3h}Ag₃²⁺ (2.88 Å) [44] but longer than that in C_{2v}Ag₃ (2.67 Å) and D_{3h}Ag₃⁻ (2.69 Å) [42]. Similar to Au₃ triangular [29], Ag₃ triangular unit can serve as substituent to replace one H atom in C₂H₂ to form the head-on coordinated C₂HAg₃- 3A and C₂HAg₃ 3N. Apparently, the C₂H unit exists as an integrity with the C≡C triple bond length of 1.22 Å and r_{C-H}=1.06 Å in the ground state of C₂HAg₃- 3A, C₂HAg₃ 3N, and the second low-lying isomer C_{∞v}(²Σ_g⁻, 3B). The third isomer C_s(²A', 3C) appears to be similar to acetylene in geometry, while the C-C bond length is 1.28 Å, longer than the C≡C triple bond of acetylene (1.20 Å) and shorter than the C=C bond (1.33 Å) of ethene. The Ag atoms connected to C of C₂H radical in 3A and 3N carry the net atomic charges of +0.17, and +0.21 [e], respectively.

Given the proved fact that C₂H radical inclines to interact with silver clusters Ag_n^{0/-} (n=1-3) as an integrity and Ag_n^{0/-} (n=1-3) clusters remain their structural integrities as units in the most stable structures of C₂HAg_n^{0/-} (n=1-3), we design a series of isomers. The four low-lying isomers are listed in Figure 4. Isomer 4A with C₂H attaching directly to one Ag atom of a distorted tetrahedral Ag₄ cluster is the ground state, which lies 0.01 and 0.12 eV lower in energy than isomer 4B and 4C at CCSD(T)//B3LYP level, respectively. 4A and 4B can be considered to be essentially degenerate in energy and may coexist in experiments. It is interesting that the Ag₂ units attaching to C atom exists in the third lowest-lying structure 4C. For C₂HAg₄⁻, isomer 4N possesses a planar diamond Ag₄ unit similar to Ag₄ neutral cluster [43]. The C-C bond length of isomer 4N is 1.23 Å, longer than that of the C≡C bond (1.20 Å) and shorter than the C=C bond (1.33 Å) of ethene. The calculated WBI_{C-C}=2.83 well supports the bonding pattern. Both C₂H radical and Ag₄ cluster still incline to maintain their integrities as structural units when C₂H radical interacts with Ag₄ cluster.



Clearly, combined with the reported results on Ag_n interacting with CO [21,22], CD₃OH [18], OH₂, SH₂, SeH₂ [19], Ag_n clusters incline to maintain as integrities in the ground states. Simultaneously, C₂H radical prefer to maintain its integrity when C₂H radical interacts with Fe, Cr, Yb, Co and Au [25,26,27-29].

Bonding characteristics

Based upon analyses above, we can easily conclude that C₂H radical inclines to interact with silver clusters Ag_n^{0/-} (n=1-4) as integrities in the most stable structures of C₂HAg_n^{0/-} (n=1-4). The calculated wiberg's bond index, WBI_{C-C} larger than 2.83 (listed in Table 1) can also support the bonding pattern. Further, NRT analyses give some deep understanding of the bonding characteristics in these systems. As shown in Table 2, The C(c)-Ag(c) (Ag(c) and C(c) represents atoms connected with C or Ag) bonds in the ground states of C₂HAg_n^{0/-} (n=1-4) have the covalent component under 45 % (0.33 and 0.36 in C₂HAg⁻ anion (1A) and C₂HAg (1N) , 0.30 and 0.44 in C₂HAg₂⁻ 2A and C₂HAg₂ 2N, 0.32 and 0.38 in C₂HAg₃⁻ 3A and C₂HAg₃ 3N, 0.30 and 0.13 in C₂HAg₄⁻ 4A and C₂HAg₄ 4N). So the interactions between Ag_n^{0/-} (n=1-4) clusters and C₂H radical in the ground states isomers are mainly ionic. Compared with that of C₂HAg_n^{0/-} (n=1-4) [29], the electronic component in C₂HAg_n^{0/-} (n=1-4) increased due to the strong relativistic effects of Au.

The interaction of Ag_n^{0/-} (n=1-4) clusters with C₂H radical brings about IR spectral changes of the C₂H moiety. Table 3 lists C-H rocking vibration, C-C and C-H stretching vibration of the ground states of C₂HAg_n^{0/-} (n=1-4) clusters at B3LYP level. Distinctly, both C≡C and C-H bond stretching vibrations of C₂HAg_n^{0/-} (n=1-4) occur red shifts compared to that of C₂H radical, similar to the situation in C₂HAg_n^{0/-} (n=1-4) series. Furthermore, as a result of the increasing d→π* interaction of the occupied Ag 4d orbital to the empty anti-bonding π* of C₂H radical, smaller red shift in the C≡C and C-H bond stretching bands of C₂HAg_n^{0/-} (n=1-4) occur with an increase in n. However, with the increasing in the number of Ag atoms, the blue-shifts of C-H rocking vibration become increasingly obvious due to the

increasing interaction between the Ag_n⁻ clusters and C₂H radical. These calculated values may help identify C₂HAg_n⁻ (n=1-4) systems in future IR measurements.

Electron detachment energies

As listed in Table 2, for C₂HAg_n⁻ (n=1-4), the calculated ADEs and VDEs at B3LYP level are between 1.21 and 3.28 eV. The electronic binding energies of C₂HAg_n⁻ (n=1-4) well fall within the energy range of conventional excitation lasers used in PES measurements (266 nm, 4.661 eV) [45-48]. We notice that the difference between ADE and VDE of C₂HAg_n⁻ is the largest (0.73 eV). This reflects the different covalent components between anionic and neutral species. It can be confirmed from the calculated NRT results that the covalent percentage of C₂HAg₄⁻ 4N and C₂HAg₄⁻ 4A is 0.13, and 0.30, respectively. To facilitate future experiments, the PES spectra of the ground structure of C₂HAg_n⁻ (n=1-4) were simulated based on the time-dependent density functional theory (TDDFT) calculations. Several important features are observed from the comparison of the simulated PES of the C₂HAg_n⁻ (n=1-4) ground states demonstrated in Figure 6. Among these anionic clusters, C_{ov} C₂HAg₂⁻ and C_s C₂HAg₄⁻ have the highest first VDE values of 3.17 and 3.28 eV, with small X-A energy gaps of 0.46 and 0.69 eV, respectively. However, C_{ov} C₂HAg₃⁻ and C_v C₂HAg₃⁻ possess an exceptionally wide X-A energy gaps which are 2.46 and 1.91 eV, respectively. These calculated values may help identify C₂HAg_n⁻ (n=1-4) systems in future PES measurements.

Conclusion

The interaction of C₂H radical with small Ag_n⁻ (n=1-4) clusters using DFT calculations was investigated based on the study of the geometrical and electronic properties of C₂HAg_n⁻ (n=1-4) isomers. The C₂H radical prefer to interact with the Ag_n⁻ (n=1-4) clusters

through its terminal C atom. The terminal C atom inclines to connect with one or two silver atoms of the silver clusters. The NBO and NRT analyses indicate that the interaction between C₂H radical and Ag_n⁻ (n=1-4) clusters is mainly ionic. Just the interaction, the C≡C and C-H stretching bands of the global minima C₂HAg_n⁻ (n=1-4) occur smaller red shifts compared to C₂H radical. To facilitate the future experiment, the PES of stable structures were simulated. The current study provides further insight into the interaction between C₂H radicals and silver clusters, which may lead to understanding the remarkable catalytic effects discovered for silver nanoparticles.

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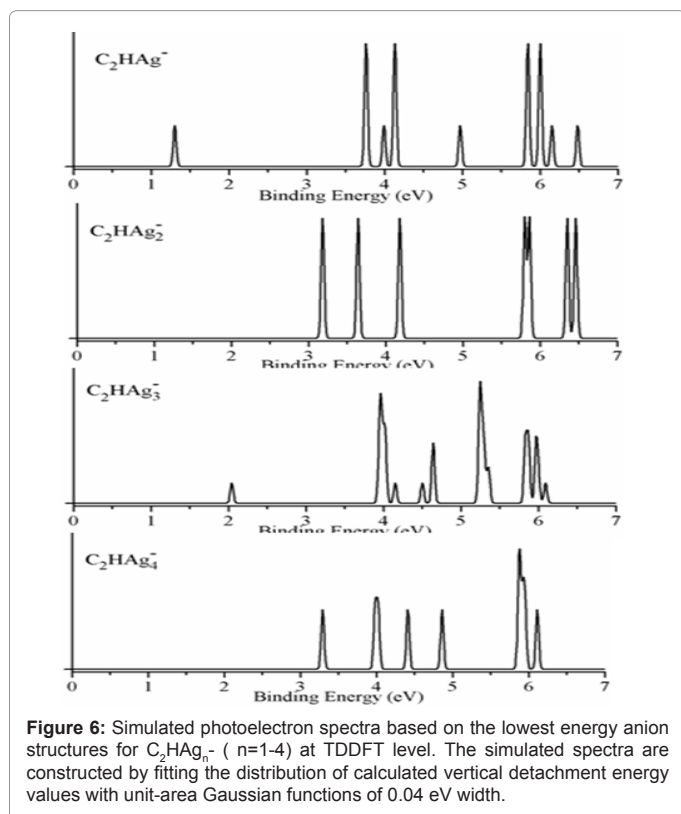


Figure 6: Simulated photoelectron spectra based on the lowest energy anion structures for C₂HAg_n⁻ (n=1-4) at TDDFT level. The simulated spectra are constructed by fitting the distribution of calculated vertical detachment energy values with unit-area Gaussian functions of 0.04 eV width.

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