A Density-Functional Study on the Interaction of C_2H Radical with Silver Clusters Ag^{n-} (n=1–4)

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Abstract

The interaction between C_2H radical and silver clusters Ag^{n-} (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-} (n=1-4) as an integrity in the most stable structures of C_2HAgn^{n-} (n=1-4). Detailed natural resonance theory (NRT) and natural bond order analyses show that the interaction between C_2H radical and Ag^{n-} (n=1-4) in the most stable structures of C_2HAgn^{n-} (n=1-4) are mainly ionic. Compared with that of C_2H radical and the Au^{n-} (n=1-4), the electronic component in C_2HAgn^{n-} (n=1-4) increased due to the strong relativistic effects of Au. The stretching vibrational frequencies of C=O and C–H in the ground states of C_2HAgn^{n-} (n=1-4) occur red shifts compared with those of the C_2H radical due to the interaction between the Ag^{n-} clusters and C_2H radical. The photoelectron spectra (PES) of the most stable structures of C_2HAgn^{n-} (n=1-4) have been simulated to facilitate their future experimental characterizations.

Keywords: DFT; C2H radical; Silver clusters; Interaction

Introduction

The past few years have witnessed increasing research activities in coin metal clusters [1-6] due 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 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 dihydroxydes (H_2O, H_2S, H_2Se) have been investigated using the DFT-B3LYP method [19], while the low-energy silver-cation-water clusters Ag_4(H_2O)_{n=4} 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_n 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 CP-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 linear 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-C_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-} clusters. In a very recent DFT study, our group investigated the interaction of C_2H radical with gold clusters Au^{n-} (n=1-4) [29]. Considering the similar 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_2HAgn^{n-} (n=1-4) complexes in hopes of understanding the interaction between Ag^{n-} (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-} (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 (α(f)=0.498, α(f)=1.464, and α(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 as the ∆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 CsC 2HAg- (n=1–4) anions and the ground-state structures of neutral CsC 2HAg (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 CsC 2HAg (n=1–4) clusters at B3LYP level are summarized in Table 3. Results and Discussion

Geometries

We start from C 2HAg and C 2HAg, the simplest clusters discussed in this work. As shown in Figure 1, the Ag-terminated C 2HAg- (Σg, 1A) is the ground state which lies 1.91, 2.00 and 1.98 eV lower than the Ag-inserted C 2HAg (Σg, 1A, 1B) at B3LYP, PBE1PBE and CCSD(T)//B3LYP levels, respectively. The C 2HAg (Σg, 1A) with C∞v symmetry proves to be similar with linear CoC 2H- [28] and C 2HAg- [29] in geometry in which the H atom in C 2H2 with an Ag atom and appears to be analogous in geometry to the linear CoC 2H and C 2HAg at the same level [28,29]. The ground state of C 2HAg- (1A) has a bond length of rAg-Ag = 2.13 Å, whereas the rAg-Ag = 2.02 Å in C 2HAg- (1N). The shorter rAg-Ag in C 2HAg- (1N) compared with that of C 2HAg (1A) indicates the extra electron of the anion is primarily localized among the C≡C system. The calculated natural atomic charges (q Ag= -0.23 and +0.66 |e|, and qC = -0.46 and -0.55|e| in C∞v C 2HAg- (1A) and C 2HAg (1N), respectively) confirm the conference. The WBIC-Ag=0.40 in C 2HAg- (1A) and WBIC-Ag=0.64 in C 2HAg (1N) (see Table 1) can also support the prediction. The next two isomers C 2HAg (1C) and C 2HAg (1D) is 6.40 and 8.54 eV higher than the ground state of C 2HAg- (1A) at CCSD (T)//B3LYP levels, respectively.

When C 2HAg radical interacts with Ag cluster, the C 2HAg (Σg, 1A) (depicted in Figure 2) is obtained which lies 2.21, 2.24 and 1.81 eV lower than the C 2HAg (Σg, 1A, 2B) at B3LYP, PBE1PBE and CCSD(T)//B3LYP levels, respectively. The perfectly linear structure contains a C≡C-Ag bond with rAg-C = 2.28 Å, and an Ag-Ag bond with rAg-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 Ag cluster [41,42] due to the interaction between C-H radical with Ag 2+ cluster. The Ag atoms connected to C of C 2H 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 two low-lying isomers with Y-shaped structure for Ag 2HAg-2B, CoC 2HAg-2B, CuC 2HAg-2B, and AuC 2HAg-2B [28,29].

For C 2HAg- clusters, as shown in Figure 3, C 2HAg- anion possesses a ground state of C 2HAg- (B 3, 3A), which lies 0.28, 2.51 and 5.97 eV lower

<table>
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<th>Isomers</th>
<th>NRT</th>
<th>CNRT</th>
<th>INRT</th>
<th>Covalent Percentage</th>
<th>ADE</th>
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<td>0.53</td>
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Table 1: Calculated natural atomic charges(q/|e|), wiberg bond indexes(WBIC) and total atomic bond orders of the ground states of CsC 2HAg (n=1–4) clusters at B3LYP Level. Ag(c) and C(c) represents atoms connected with C or Ag.
than C∞v (2∑g, 3B). The C2H unit exists as an integrity with the Ag4 cluster still inclined to maintain their integrities as structural units in the most stable structures of C2HAgn- (n=1-4) [29], the C-C bond (1.20 Å) and shorter than that in C2H radical (1.33 Å) of ethene. The calculated Wiberg’s bond index, WBI C-C larger than 2.83 (listed in Table 1) can 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 C2HAgn- (n=1-4) increased due to the strong relativistic effects of Ag.

Clearly, combined with the reported results on Agn interacting with CO [21,22], CD3OH [18], OH2, SH2, SeH2 [19], Agn 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 Agnω- (n=1-4) as integrities in the most stable structures of C2HAgnω- (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 C2HAgnω- (n=1-4) have the covalent component under 45 % (0.33 and 0.36 in C2HAgn- (n=1-4) as integrities) and C-H bond stretching vibrations of C2HAgnω- (n=1-4) occur with an increase in n.

The interaction of Agnω- (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 bond stretching vibrations of C2HAgnω- (n=1-4) occurred red shifts compared to that of C2H radical, similar to the situation in C2HAgω- (n=1-4) clusters as integrities and Agnω- (n=1-4) clusters. The calculated Wiberg’s bond index, WBI C-C larger than 2.83 (listed in Table 1) can 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 C2HAgnω- (n=1-4) have the covalent component under 45 % (0.33 and 0.36 in C2HAgn- (n=1-4) as integrities) and C-H bond stretching vibrations of C2HAgnω- (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 C$_2$H radical. These calculated values may help identify C$_2$HAgn-$_{(n=1-4)}$ systems in future IR measurements.

Electron detachment energies

As listed in Table 2, for C$_2$HAgn-$_{(n=1-4)}$, the calculated ADEs and VDEs at B3LYP level are between 1.21 and 3.28 eV. The electronic binding energies of C$_2$HAgn-$_{(n=1-4)}$ 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 at B3LYP level are between 0.13, and 0.30, respectively. To facilitate future experiments, the PES spectra of the ground structure of C$_2$HAgn-$_{(n=1-4)}$ 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 C$_2$HAgn-$_{(n=1-4)}$ ground states demonstrated in Figure 6. Among these anionic clusters, C$_2$V$_2$C$_2$HAg$_4$ and C$_2$V$_1$C$_2$HAg$_4$ 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$_2$V$_1$C$_2$HAg$_4$ and C$_2$V$_2$C$_2$HAg$_4$ possess an exceptionally wide X-A energy gaps which are 2.46 and 1.91 eV, respectively. These calculated values may help identify C$_2$HAgn-$_{(n=1-4)}$ systems in future PES measurements.

Conclusion

The interaction of C$_2$H radical with small Ag$_n$$_{(n=1-4)}$ clusters using DFT calculations was investigated based on the study of the geometrical and electronic properties of C$_2$HAgn-$_{(n=1-4)}$ isomers. The C$_2$H radical prefer to interact with the Ag$_n$$_{(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 C$_2$H 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 C$_2$HAgn-$_{(n=1-4)}$ occur smaller red shifts compared to C$_2$H radical. To facilitate the future experiment, the PES of stable structures were simulated. The current study provides further insight into the interaction between C$_2$H radicals and silver clusters, which may lead to understanding the remarkable catalytic effects discovered for silver nanoparticles.

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References