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Photoelectron spectroscopic and computational study of $(M-CO_2)^-$ anions, $M = Cu, Ag, Au$

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In a combined photoelectron spectroscopic and computational study of $(M-CO_2)^-$, $M = Au, Ag, Cu$, anionic complexes, we show that $(Au-CO_2)^-$ forms both the chemisorbed and physisorbed isomers, $AuCO_2^-$ and $Au^-(CO_2)$, respectively; that $(Ag-CO_2)^-$ forms only the physisorbed isomer, $Ag^-(CO_2)$; and that $(Cu-CO_2)^-$ forms only the chemisorbed isomer, $CuCO_2^-$. The two chemisorbed complexes, $AuCO_2^-$ and $CuCO_2^-$, are covalently bound, formate-like anions, in which their CO_2 moieties are significantly reduced. These two species are examples of electron-induced CO_2 activation. The two physisorbed complexes, $Au^-(CO_2)$ and $Ag^-(CO_2)$, are electrostatically and thus weakly bound. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4935061>]

I. INTRODUCTION

Interest in carbon dioxide fixation derives both from environmental concerns and the prospect of converting CO_2 into fuels. Since the carbon in CO_2 is already in its highest oxidation state, any attempt to activate CO_2 must involve its reduction, and that implies adding negative charge to it. This, however, is challenging, because CO_2 must deform in order to accept an electron and the resulting bent CO_2^- anion is metastable, i.e., the electron affinity of CO_2 is -0.6 eV.¹⁻³ While some studies have dealt with free CO_2^- anions, most have focused on gas-phase, anionic complexes made up of CO_2 and various atoms and molecules.⁴⁻³³ Of particular interest are studies that found significant covalent character in the intermolecular bond between CO_2 and pyridine within the gas-phase $(pyridine-CO_2)^-$ anionic complex.^{6,7} The CO_2 moiety in that case exhibited a negative charge of -0.5 . Other (*N*-heterocyclic molecule- CO_2)⁻ anionic complexes were also found to be analogously bonded.^{8,9} In all these cases, the carbon dioxide moiety was found to be partially bent and to possess significant negative charge, i.e., to be partially reduced. At the macroscopic level, analogous reduction processes involving CO_2 and pyridine have been explored electrochemically.^{34,35}

More recently, Weber and co-workers have reported gas-phase, infrared photodissociation studies of transition metal- CO_2 anionic complexes, $[M(CO_2)_n]^-$, where $M = Cu, Ag, Au, Co,$ and Ni . Both electrostatically bound, atomic metal anion- CO_2 complexes (physisorption) and covalently bound anionic complexes (chemisorption) were found, where in the latter cases the CO_2 moieties were partially bent and had accepted some significant portion of the negative charge.²²⁻²⁹ The coinage metal- CO_2 anionic complexes, $(Au-CO_2)^-$, $(Ag-CO_2)^-$, and $(Cu-CO_2)^-$, are particularly interesting, since among those that are covalently bound, they are formate anion

analogs. In those cases, their s^1 coinage metal atoms substitute for the formate anion's hydrogen atom.

Here, we study the anionic complexes, $(Au-CO_2)^-$, $(Ag-CO_2)^-$, and $(Cu-CO_2)^-$, using anion photoelectron spectroscopy and theoretical calculations. Among these, we found differences in their physisorption and chemisorption behaviors. While $(Cu-CO_2)^-$ exhibited only chemisorption, and $(Ag-CO_2)^-$ showed only physisorption, $(Au-CO_2)^-$ displayed both chemisorption and physisorption isomers. These studies provide an additional context in which to view these fascinating species.

II. METHODS

A. Experimental

Anion photoelectron spectroscopy is conducted by crossing a mass-selected, negative ion beam with a fixed-energy photon beam and analyzing the energies of the resultant photodetached electrons. This technique is governed by the well-known energy-conserving relationship, $h\nu = EBE + EKE$, where $h\nu$, EBE , and EKE are the photon energy, electron binding energy (photodetachment transition energy), and the electron kinetic energy, respectively. Our photoelectron instrument, which has been described elsewhere,³⁶ consists of an ion source, a linear time-of-flight mass spectrometer, a mass gate, a momentum decelerator, a neodymium-doped, yttrium aluminum garnet (Nd:YAG) laser, operated in either the third harmonic (355 nm) or the fourth harmonic (266 nm) for photodetachment, and a magnetic bottle, electron energy analyzer with a resolution of 35 meV at $EKE = 1$ eV. The photoelectron spectra were calibrated against the well-known photoelectron spectrum of Cu^- .³⁷ The $(M-CO_2)^-$ ($M = Au, Ag, Cu$) anion complexes were generated in a laser vaporization ion source. It consisted of either a rotating, translating gold, silver, or copper rod, which was being ablated with second harmonic (532 nm) photon pulses from a Nd:YAG

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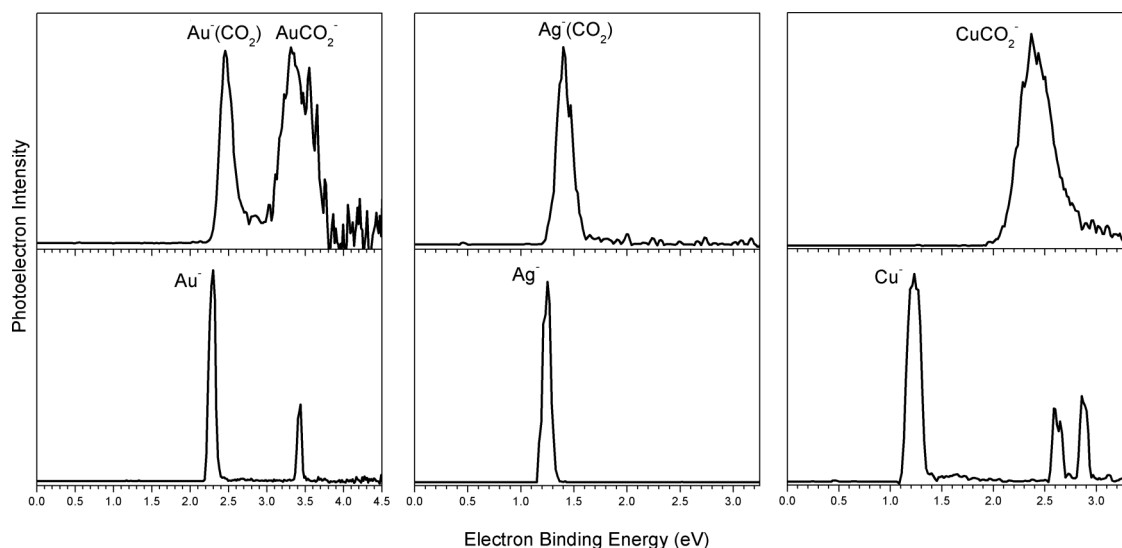


FIG. 1. Photoelectron spectra of $(\text{Au}-\text{CO}_2)^-$ and Au^- (266 nm), $(\text{Ag}-\text{CO}_2)^-$ and Ag^- (355 nm), and $(\text{Cu}-\text{CO}_2)^-$ and Cu^- (355 nm).

laser, while a 50%/50% He/ CO_2 gas mixture at 100 psi was being expanded from a pulsed valve over the rods.

B. Theoretical

The lowest energy structures of $(\text{M}-\text{CO}_2)^{-1/0}$ systems were obtained by density functional theory (DFT)-based electronic structure calculations with the Becke's three-parameter hybrid functional (B3LYP).³⁸⁻⁴⁰ The 6-311G+(3df) basis set⁴¹ was used for C and O, while the LANL2DZ⁴²⁻⁴⁴ and Stuttgart/Dresden (SDD)^{45,46} effective core potentials were used for Au, Ag, and Cu. All of the calculations were carried out using the Gaussian 09 software package.⁴⁷

The vertical detachment energy (VDE) is the energy difference between the ground state anion and its corresponding neutral at the geometry of the anion, i.e., these are vertical photodetachment transitions. The adiabatic detachment energy (ADE) is the energy difference between the lowest energy, relaxed geometry of the anionic cluster and the relaxed geometry of a structurally similar isomer (nearest minimum) of its neutral counterpart. The adiabatic electron affinity (EA) is the energy difference between the lowest energy, relaxed geometry of the anionic cluster and the relaxed geometry of the lowest energy isomer (the global minimum) of its neutral counterpart. When the nearest local minimum and the global minimum are one and the same, $\text{ADE} = \text{EA}$. The EBE value of the photoelectron spectral onset (threshold), E_T , can be compared with both the calculated ADE and EA values.

The potential energy surfaces along the M-C coordinate were computed by scanning the M-C bond length with a step width of 0.1 Å, while relaxing the rest of the cluster. Several different levels of theory, e.g., B3LYP/SDD, CCSD/SDD, and B3LYP/def2-TZVPP were used and compared to one another. In the cases of the first two examples, the 6-311G+(3df) basis set⁴¹ was used for C and O, while the SDD effective core potential was used for the noble metal atoms. However, in the case of B3LYP/def2-TZVPP, its basis set was applied to all the atoms. Natural population analysis (NPA), as implemented in the Gaussian 09 code, was also carried out to determine the

charge distributions in these clusters. NPA has been found to be satisfactory in predicting charge distributions.⁴⁸⁻⁵⁰

III. RESULTS

A. Experimental

The photoelectron spectra of $(\text{M}-\text{CO}_2)^-$ ($\text{M} = \text{Au}, \text{Ag}, \text{Cu}$) are shown in Figure 1. For comparison, the spectra of Au^- , Ag^- , and Cu^- are also presented below each respective spectrum. Consider the photoelectron spectrum of $(\text{Au}-\text{CO}_2)^-$. The lowest EBE peak is relatively narrow and is shifted to only slightly higher EBE compared to that of the lowest EBE peak in the photoelectron spectrum of Au^- . This gold-carbon dioxide anion peak is due to the anion-molecule complex, $\text{Au}^-(\text{CO}_2)$, where the interaction between Au^- and CO_2 is weak. $\text{Au}^-(\text{CO}_2)$ can be considered to be a solvated Au^- anion or alternatively an example of physisorption in the gas phase. In anion-molecule complexes such as these, the core anion, i.e., Au^- in this case, acts as the chromophore for photodetachment, and the resulting photoelectron spectrum looks like a slightly broadened version of the core anion's photoelectron spectrum, just shifted to slightly higher EBE.

The higher EBE feature in the photoelectron spectrum of $(\text{Au}-\text{CO}_2)^-$ is relatively broad, suggesting a significant structural difference between the anionic complex and its neutral counterpart. While this broad band overlaps with a sharp peak that is due to the solvation-induced shift of the higher EBE peak in the photoelectron spectrum of Au^- to slightly higher EBE, both the width and the center of the broad band are slightly lower in EBE than those of the higher EBE Au^- peak, showing that this band is not primarily due to the solvation of the higher EBE Au^- peak. Also, if this band had been due to the solvation of the lowest EBE peak in the Au^- spectrum, it would have involved a solvation shift (stabilization energy) of an eV or more, this being an unrealistically strong physisorption interaction between the Au^- atomic anion and a CO_2 molecule. Thus, the higher EBE feature in the photoelectron spectrum of $(\text{Au}-\text{CO}_2)^-$

is due to a strong, chemical bond-like interaction between the moieties; it is due to chemisorption. The photoelectron spectrum of $(\text{Au}-\text{CO}_2)^-$ provides evidence for the presence of two isomers, one physisorbed, $\text{Au}^-(\text{CO}_2)$ and the other chemisorbed, AuCO_2^- , both of which are labeled as such in Figure 1.

Next, consider the photoelectron spectrum of $(\text{Ag}-\text{CO}_2)^-$. Its single peak is shifted to only slightly higher EBE and is slightly broadened compared to the single narrow peak observed in the photoelectron spectrum of Ag^- . The amount of shift is comparable to that seen for $\text{Au}^-(\text{CO}_2)$, the lowest EBE peak in the spectrum of $(\text{Au}-\text{CO}_2)^-$. Thus, this silver-carbon dioxide anion peak is due to the anion-molecule complex, $\text{Ag}^-(\text{CO}_2)$. Since the interaction between Ag^- and CO_2 is weak, it can be viewed as a solvated anion and as another example of physisorption in the gas phase. Unlike the photoelectron spectrum of $(\text{Au}-\text{CO}_2)^-$, the photoelectron spectrum of $(\text{Ag}-\text{CO}_2)^-$ shows no evidence of a chemically bound (chemisorption) isomer. See Figure 1.

Finally, consider the photoelectron spectrum of $(\text{Cu}-\text{CO}_2)^-$. There is no similarity between the single broadened band in its photoelectron spectrum and the photoelectron spectrum of Cu^- . This band in the photoelectron spectrum of $(\text{Cu}-\text{CO}_2)^-$ is due to the chemically bound (chemisorption) isomer, CuCO_2^- . There is no evidence of a physisorbed/solvated anion $\text{Cu}^-(\text{CO}_2)$ isomer in the photoelectron spectrum of $(\text{Cu}-\text{CO}_2)^-$. See Figure 1.

Energetic parameters can also be determined from the spectra in Figure 1. The threshold energy (EBE) for each peak/band in the photoelectron spectra of $(\text{M}-\text{CO}_2)^-$ ($\text{M} = \text{Au}, \text{Ag}, \text{Cu}$) is denoted as E_T . If there is sufficient Franck-Condon overlap between the ground state of the anion and the ground state of the neutral and if there is no significant hot band signal, then E_T is an estimate of the value of ADE and perhaps of EA. However, if the structural difference is too great between the anion and the neutral, one will not be able to observe the origin transition, and the EBE of E_T will be significantly greater than

TABLE I. E_T , EA, and VDE values obtained from both experiment and theory.^a

Species	Expt. E_T	Theoretical EA	Expt. VDE	Theoretical VDE
$\text{Au}^-(\text{CO}_2)$	2.3	2.44/2.39	2.45	2.51/2.47
AuCO_2^-	3.0	2.51/2.41	3.31	3.28/3.18
$\text{Ag}^-(\text{CO}_2)$	1.25	1.38/1.53	1.40	1.42/1.57
CuCO_2^-	2.1	1.67/1.73	2.37	2.26/2.43

^aThe theoretical calculations of both EA and VDE values used the 6-311G+(3df) basis set for the C and O atoms and the LANL2DZ/SDD basis sets for the noble metal atoms at the B3LYP level of theory.

that of the true EA. The EBE of the intensity maximum for each peak is its VDE value. The E_T and VDE values of all four of the above species are listed in Table I and are compared there to our computed values of EA and VDE.

B. Theoretical

Four anionic species were observed experimentally in this work. The structures of both their anionic and their neutral forms were determined using the B3LYP/SDD computational method and are presented in Figure 2. There, the M-C bond length (Å), the C-O bond length (Å), and the O-C-O bond angle (in degrees) are shown for each case. For the physisorption species, $\text{Au}^-(\text{CO}_2)$ and $\text{Ag}^-(\text{CO}_2)$, their M-C bond lengths are both significantly longer than for typical chemical (single) bonds, indicating weak interactions between Au^-/Ag^- and CO_2 . Also, the C-O bond length is 1.16 Å, which is the same as in isolated CO_2 . The O-C-O moiety, however, is slightly bent, indicating that the metal atom does have some influence, albeit weak, on it.

For the chemisorption species, AuCO_2^- and CuCO_2^- , the M-C bond length is 2.30 Å and 2.04 Å, respectively, implying the formation of a single bond between M and C in both cases. A natural population analysis showed that in AuCO_2^- , the CO_2 moiety has a negative charge of $-0.45 e$, whereas

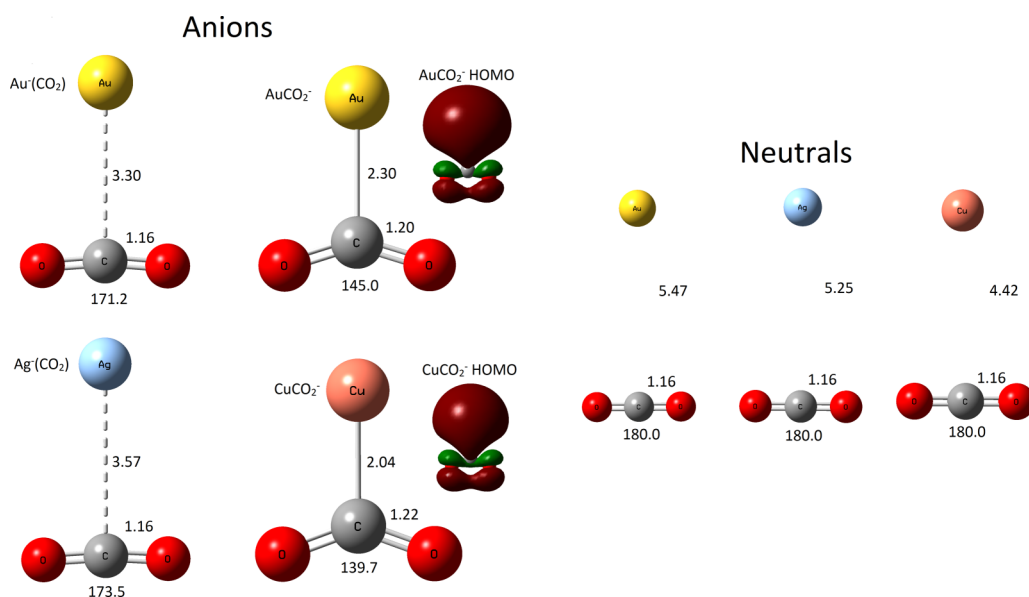


FIG. 2. Calculated structures of $\text{Au}^-(\text{CO}_2)$, AuCO_2^- , $\text{Ag}^-(\text{CO}_2)$, CuCO_2^- , AuCO_2 , AgCO_2 , and CuCO_2 . HOMOs of AuCO_2^- and CuCO_2^- are also presented.

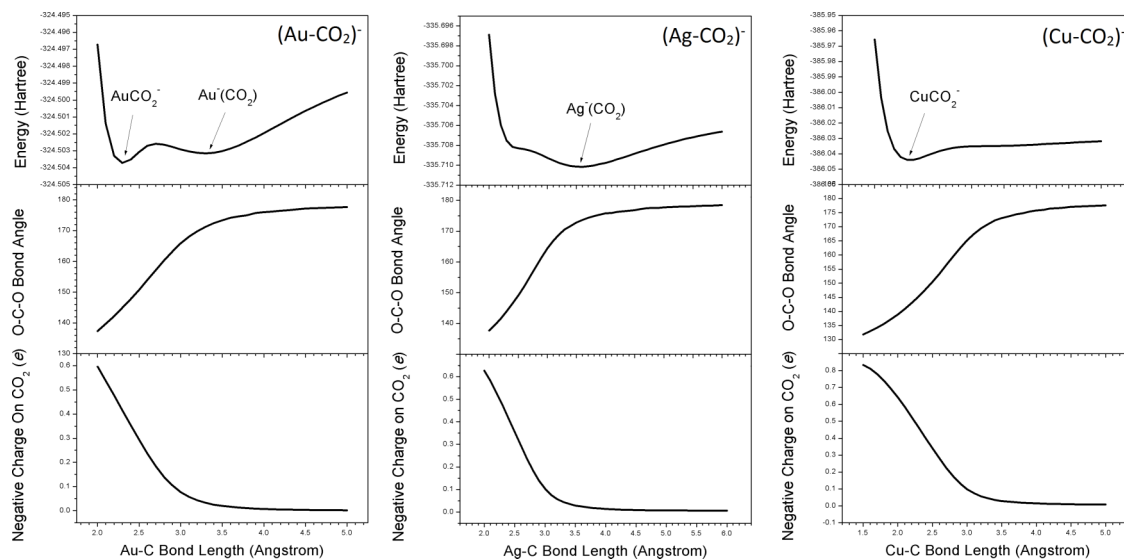


FIG. 3. The curves of potential energy (Hartree), O–C–O bond angle ($^{\circ}$), and negative charge on CO_2 (e) versus the M–C bond length (\AA) obtained from B3LYP/SDD level of theory.

in CuCO_2^- , its charge is $-0.64 e$. Therefore, the CO_2 moiety has been significantly reduced in both these complexes. The CO_2 moiety in CuCO_2^- has been activated more than it has been in AuCO_2^- , this being consistent with their relative M–C bond lengths. It is also consistent with the difference in their C–O bond lengths, i.e., in CuCO_2^- , the C–O bond (1.22 \AA) is longer than that in AuCO_2^- (1.20 \AA), both being longer than the C–O bond length in isolated CO_2 (1.16 \AA). This implies that the more negative charge is on the CO_2 moiety, the more the C–O bond is weakened. The difference in negative charges is also consistent with the O–C–O bond angles. This angle is bent more in CuCO_2^- (139.7°) than in AuCO_2^- (145.0°), and in CuCO_2^- , it is close to that of the isolated CO_2^- anion (134°). The difference in the amount of negative charge on the CO_2 moiety in CuCO_2^- versus in AuCO_2^- is likely due to the electronegativity difference between the metal atoms, i.e., $\text{Au} > \text{Cu}$. Since, like the hydrogen atom, gold and copper atoms each have only one valence electron, both AuCO_2^- and CuCO_2^- are isostructural and isoelectronic to the formate anion; they are metalloformates.²² The highest occupied molecular orbitals (HOMOs) of AuCO_2^- and CuCO_2^- accommodate the excess electron, and these are also shown in Figure 2. Note the charge transfer from the metal atoms to the CO_2 moieties.

In all three neutral $\text{M}(\text{CO}_2)$ species, the metal atom is far away from CO_2 . Also, both the O–C–O bond angle and the C–O bond length are the same in these neutral species as in an isolated CO_2 molecule. Together, these structural parameters show that there is very little interaction between M and CO_2 . Also, notice that the structures of the physisorbed anionic complexes, $\text{Au}^-(\text{CO}_2)$ and $\text{Ag}^-(\text{CO}_2)$, are similar to those of the neutral species. The structures of the chemisorbed species, AuCO_2^- and CuCO_2^- , on the other hand, are quite different from those of the neutral species.

The calculated EA and VDE values obtained from B3LYP/SDD and B3LYP/LANL2DZ computational methods are listed in Table I. These two methods gave similar results. The theoretical EA and VDE values for the physisorption

species, $\text{Au}^-(\text{CO}_2)$ and $\text{Ag}^-(\text{CO}_2)$, are in very good agreement with the experimental E_T and VDE results. Thus, the observed E_T values are also EA values in those cases. While the theoretical VDE values for the chemisorption species, AuCO_2^- and CuCO_2^- , are in very good agreement with the experimental VDE values, the theoretical EA values for these species are smaller than the spectral E_T values; see Table I. This is likely due to structural differences between AuCO_2^- and CuCO_2^- and their neutral counterparts, these leading in turn to less Franck-Condon overlap during photodetachment.

Figure 3 plots the potential energy (Hartrees), the O–C–O bond angle ($^{\circ}$), and the negative charge on the CO_2 moiety (e) for all three $(\text{M}-\text{CO}_2)^-$ systems as a function of the M–C bond length with the remainder of the complex relaxed. All of these computations were performed at the B3LYP/SDD level of theory. Along the potential energy surface of $(\text{Au}-\text{CO}_2)^-$, there are two wells, these corresponding to AuCO_2^- and $\text{Au}^-(\text{CO}_2)$, the chemisorbed and physisorbed isomers, respectively. Note that their energies are very similar to each other, with a calculated barrier of only $0.03 eV$. This very low barrier is probably why they co-exist in our experiment. Along the potential energy surfaces of $(\text{Ag}-\text{CO}_2)^-$ and $(\text{Cu}-\text{CO}_2)^-$, there is only one well in each, these corresponding to physisorbed $\text{Ag}^-(\text{CO}_2)$ and to chemisorbed CuCO_2^- . The feature at $\sim 2.4 \text{ \AA}$ on the potential energy surface of $(\text{Ag}-\text{CO}_2)^-$ is an inflection point and not a well. In all three $(\text{M}-\text{CO}_2)^-$ systems, the O–C–O bond angle exhibits an asymptote that leads to 180° , while the negative charge on the CO_2 moiety has an asymptote that trends to zero.

IV. DISCUSSION

There are a couple of differences between our findings (ultraviolet photoelectron spectroscopy and theory) and those of Weber and coworkers (infrared photodissociation spectroscopy and theory).^{24,26} In the photoelectron spectrum of $(\text{Ag}-\text{CO}_2)^-$, evidence for only the physisorbed $\text{Ag}^-(\text{CO}_2)$ isomer was seen. In the infrared photodissociation work,²⁶ the

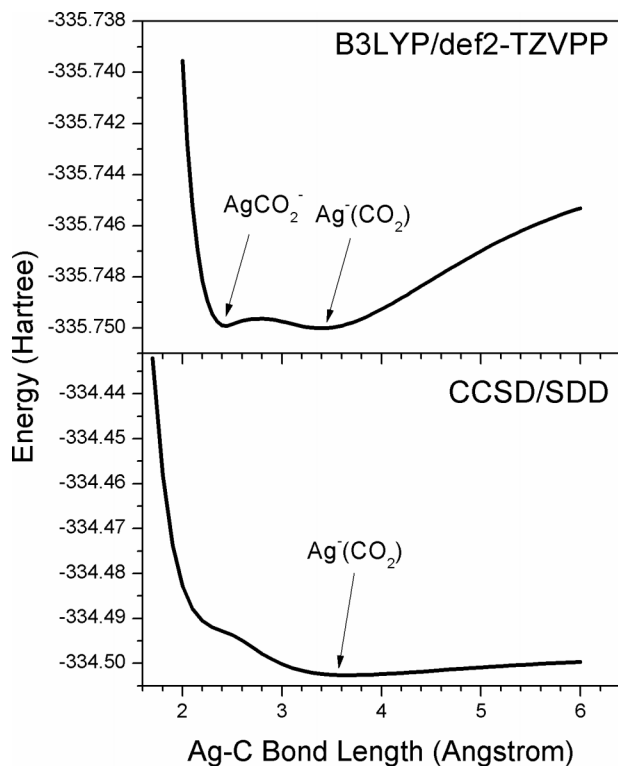


FIG. 4. The potential energy surfaces of $(\text{Ag}-\text{CO}_2)^-$ obtained from B3LYP/def2-TZVPP and CCSD/SDD levels of theory.

authors did not study the $(\text{Ag}-\text{CO}_2)^-$ cluster experimentally. Nevertheless, calculations at the B3LYP/def2-TZVPP level of theory in that study predicted the viability of the chemisorbed AgCO_2^- isomer. As noted above, our calculations at the B3LYP/SDD level of theory found only the physisorbed $\text{Ag}^-(\text{CO}_2)$ isomer. To further investigate this situation, we conducted calculations at both the B3LYP/def2-TZVPP and the CCSD/SDD levels of theory. The results are shown in Figure 4. Using B3LYP/def2-TZVPP, we saw two potential wells, i.e., one for AgCO_2^- and the other for $\text{Ag}^-(\text{CO}_2)$, but AgCO_2^- is higher in energy. At the CCSD/SDD level of theory, however, we observed only one well, and it corresponds to physisorbed $\text{Ag}^-(\text{CO}_2)$. Thus, CCSD/SDD and B3LYP/SDD gave the same qualitative result. To summarize, both the anion photoelectron spectrum of $(\text{Ag}-\text{CO}_2)^-$ and these two levels of theory imply that physisorbed $\text{Ag}^-(\text{CO}_2)$ is the only isomer of $(\text{Ag}-\text{CO}_2)^-$ that is stable.

In the case of $(\text{Au}-\text{CO}_2)^-$, calculations both by Weber *et al.* and by us found nearly iso-energetic chemisorbed and physisorbed isomers. Yet, while the photoelectron spectrum of $(\text{Au}-\text{CO}_2)^-$ showed strong evidence for both physisorbed and chemisorbed isomers, only the chemisorbed AuCO_2^- isomer was observed in the IR photodissociation work.²⁴ Different source conditions likely account for these differing observations. This is in fact the only case where a direct comparison can be made between the current work and Weber's work.²⁴ In the case of CuCO_2^- , there is no disagreement between the current experiments and Weber's theoretical findings.²⁸

Interestingly, there are partial parallels between the physisorbed and chemisorbed isomers of $(\text{M}-\text{CO}_2)^-$ and those of $(\text{M}-\text{O}_2)^-$, $\text{M} = \text{Au}, \text{Ag}, \text{Cu}$. For gold and copper, both

chemisorbed, MO_2^- and physisorbed, $\text{M}^-(\text{O}_2)$ isomers are known to coexist.^{51,52} In the case of silver, on the other hand, only physisorbed $\text{Ag}^-(\text{O}_2)$ is known, it having been reported in neon matrices⁵³ and in RF-octopole ion trap reactions⁵⁴ as well as having been revealed through calculations.⁵⁵ No chemisorbed AgO_2^- has been reported. As in $(\text{M}-\text{CO}_2)^-$ complexes, silver stands apart in $(\text{M}-\text{O}_2)^-$ complexes as well.

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