

Theoretical Study of the $\text{CH}_2 + \text{O}$ Photodissociation of Formaldehyde Adsorbed on the Ag(111) Surface

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Configuration interaction calculations of the ground and excited states of the H_2CO molecule adsorbed on the Ag(111) surface have been carried out to study the photoinduced dissociation process leading to polymerization of formaldehyde. The metal–adsorbate system has been described by the embedded cluster and multireference configuration interaction methods. The π^* electron-attachment H_2CO^- and $n-\pi^*$ internally excited H_2CO^* states have been considered as possible intermediates. The calculations have shown that H_2CO^* is only very weakly bound on Ag(111), and thus that the dissociation of adsorbed formaldehyde due to internal excitation is unlikely. By contrast, the H_2CO^- anion is strongly bound to Ag(111) and gains additional vibrational energy along the C–O stretch coordinate via Franck–Condon excitation from the neutral molecule. Computed energy variations of adsorbed H_2CO and H_2CO^- at different key geometries along the pathway for C–O bond cleavage make evident, however, that complete dissociation is very difficult to attain on the potential energy surface of either of these states. Instead, reneutralization of the vibrationally excited anion by electron transfer back to the substrate is the most promising means of breaking the C–O bond, with subsequent formation of the coadsorbed O and CH_2 fragments. Furthermore, it has been demonstrated that the most stable state for both dissociation fragments on Ag(111) is a closed-shell singlet, with binding energies relative to the gas-phase products of ~ 3.2 and ~ 1.3 eV for O and CH_2 , respectively. Further details of the reaction mechanism for the photoinduced C–O bond cleavage of H_2CO on the Ag(111) surface are also given.

I. Introduction

The photochemistry of adsorbates on metal surfaces has been actively investigated over the past few decades.^{1–7} These studies provide an excellent opportunity for exploring various non-thermal processes on the surface, including energy and charge transfer. In particular, photoexcited states can be intermediates for the subsequent decomposition² and desorption³ of molecular fragments, as well as for a variety of photochemical reactions on the surface.⁴

Two different mechanisms have usually been assumed to be responsible for the photoinduced formation of excited states of molecular adsorbates:⁵ direct excitation within the adsorbate and indirect excitation via substrate-mediated electron transfer (photoelectron attaches to the adsorbate and forms a negative ion state bound by an image charge to the surface). In both cases the resulting photoexcited state on the surface is usually significantly different from its gas-phase counterpart, even for

weakly bound systems, and a molecular approximation for the description of the adsorbate/surface states can be quite rough in this case. Therefore, knowledge of the potential energy surfaces (PESs) of these states is essential for gaining a proper understanding of the photochemical processes. Theoretical studies of the excited states on the metal surface that could be extremely helpful in this situation have only recently become available.^{6–8}

The object of the present study is the formaldehyde molecule adsorbed on the Ag(111) surface. Experimental investigations have shown that H_2CO is weakly bound to the silver surface (binding energy is about 0.27 eV), with only little perturbation of its vibrational and electronic properties relative to the gas-phase molecule.⁹ The H_2CO equilibrium geometry on the surface has been found in this study to be tilted by $\sim 60^\circ$ away from the surface normal, with an angle between the molecular plane and the tilt plane of 0° – 30° . Formaldehyde adsorbed on Ag(111) has been observed to polymerize upon UV irradiation with an energy threshold of $\sim 3.1 \pm 0.2$ eV.^{10,11} In the gas phase such polymerization can occur through the H_2CO photodissociation into H and HCO radicals with a reaction threshold of ~ 3.75 eV¹² and their subsequent combination with other H_2CO molecules.¹³ The observed threshold for the surface polymerization is, therefore, about 0.6 eV lower than the gas-phase value. The alternative molecular dissociation process, $\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}$, with a lower barrier of ~ 3.43 – 3.56 eV,¹⁴ does not

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induce polymerization in the gas phase. One should note that both gas-phase dissociation channels occur through $n-\pi^*$ excitation to the S_1 state with subsequent transition to the vibrationally excited S_0 state and fragmentation on the ground-state potential energy surface.¹² In the case of the physisorbed molecule, neither of these processes is likely because H₂CO vibrational excitation should easily induce desorption. Therefore, H₂CO adsorbed on Ag(111) must have a significantly different dissociation channel of much higher efficiency than is observed for the gas-phase system.

Several experimental investigations have been devoted to the characterization of the photoinduced polymerization mechanism of H₂CO adsorbed on Ag(111). In particular, the initial step for the formaldehyde polymerization on the surface has been assumed to be other than a thermal process,⁹ which means that either a direct photon or an indirect substrate-mediated electron excitation of the adsorbed formaldehyde produces an intermediate excited state that subsequently leads to dissociation. In both of these schemes, excited formaldehyde should dissociate into radical fragments which then react with neighboring molecules to form the polymer.

A possible substrate-mediated photodissociation mechanism has been examined by Fleck et al.¹¹ The authors have succeeded in inducing formaldehyde polymerization by means of irradiation of the adsorbed molecules by near-zero kinetic energy electrons. This work has indicated, therefore, that the intermediate state in the formaldehyde polymerization on Ag(111) is very probably a negative ion. This supports a substrate-mediated mechanism of dissociation in which the negative ion on the surface is formed as a result of photoinduced electron transfer from the surface. In addition, the energetic feasibility of the photoinduced formation of H₂CO⁻ on Ag(111) has been demonstrated in a companion study¹⁵ by employing a simple image-charge model: for an Ag–H₂CO⁻ surface distance estimated at 2–3 Å (which is customary for physisorbed molecules), the energy lowering of the H₂CO⁻ anion on the surface due to image-charge stabilization would be ~ 2.0 eV. This means that the energy of the H₂CO⁻ resonance state on the surface is about ~ 1.0 eV lower than the vacuum level (the electron affinity of formaldehyde in the gas phase used in the above calculations is -0.9 eV; the experimental value of ref 16 is -0.65 ± 0.05 eV). In this case, 3.3 eV photons that excite Ag electrons to 1.1 eV below the vacuum level (the work function of the Ag surface exposed to 2 langmuir H₂CO has been measured to be 4.4 eV¹⁷) are thought to lead to H₂CO⁻ formation on the surface. Moreover, large dissociation cross sections of H₂CO adsorbed on the Ag(111) surface compared to the gas-phase values observed in experiment,¹⁵ as well as a lower polymerization energy threshold, also indicate that direct excitation of formaldehyde is not a major polymerization channel.

Products of the photoinduced dissociation channel of the adsorbed formaldehyde have been studied in refs 15 and 18. The only adsorbed species formed due to the formaldehyde photodissociation (excitation by 4.32 eV photons has been employed) has been found to be the methylene radical, CH₂. This result naturally implies that either gas-phase or adsorbed oxygen should exist as well. Unfortunately, the unfavorable location of the oxygen spectrum has made it impossible to either confirm or rule out the presence of oxygen on the surface in this experiment. On the other hand, gas-phase oxygen has also not been observed at excitation energies of 3.49 and 4.66 eV,¹⁸ which makes the existence of some form of oxygen on the surface unavoidable. An energy analysis of the H₂CO⁻(ad) \rightarrow CH₂(ad) + O⁻(ad) process has been carried out in ref 15. The

authors have estimated O⁻ and CH₂ binding energies to the Ag(111) surface of ~ 7.0 and ~ 1.3 eV, respectively. By summation of the energy changes of all relevant processes, they have concluded that H₂CO⁻(ad) \rightarrow CH₂(ad) + O⁻(ad) is an exothermic reaction with an energy difference of -0.7 eV and have demonstrated, therefore, the feasibility of negative ion dissociation on the Ag surface. They have also noted in the same study that the fragmentation mechanism of the anion on the surface should be completely different from that in the gas phase since the lowest observed dissociation channel of gaseous H₂CO⁻ leads to H⁻ formation.

The gas-phase products of photoinduced dissociation of formaldehyde adsorbed on Ag(111) have been studied in ref 18, but unfortunately at only two excitation wavelengths, 266 nm (4.66 eV) and 355 nm (3.49 eV). No gas-phase products have been detected at 3.49 eV except for the directly desorbed formaldehyde molecule, whereas at 4.66 eV both gas-phase CO formation and H₂CO desorption have been found. Hydrogen in an atomic or molecular form that might accompany gas-phase dissociation has not been observed, neither in the gas phase at 4.66 eV¹⁸ nor in the adsorbed form at 4.32 eV excitation.¹⁵ One should note that the hydrogen molecule is extremely weakly bound to Ag(111) (0.032 eV¹⁹) and, if it occurs, would be observed in the gas phase. Furthermore, despite the fact that atomic hydrogen can be bound quite strongly (the binding energy is about 2.5 eV²⁰), it usually recombines on the silver surface (at $T \sim 180$ K²¹) and desorbs as H₂. On the basis of the kinetic and rotational energies of the CO fragment, the authors of ref 18 have suggested two possible dissociation channels responsible for formation of CO in the gas phase: (a) via the polymerization and (b) by direct formaldehyde dissociation on the surface. However, the intermediate state of photodissociation and the fate of the H/H₂ fragments have not been identified in the above study. On the other hand, this investigation has indirectly confirmed that the lowest formaldehyde photoinduced polymerization channel on the surface occurs through C–O bond cleavage and the formation of adsorbed CH₂ and O fragments.

In the present study we consider the theoretical description of this photodissociation channel. The main questions to be considered are the following: why is the C–O bond cleavage so effective on the surface while the usual gas-phase channels are not, and what is the mechanism of the H₂CO photodissociation on the Ag surface? For this purpose the potential energies of adsorbed formaldehyde as well as its internally excited and electron-attachment states are calculated as functions of the distance from the cluster and several other geometric variables (orientation on the surface, C–O bond distance, and CH₂ fragment geometries), and the mechanism for photoinduced C–O bond cleavage in adsorbed formaldehyde is also analyzed. In addition, the electronic structure, binding energies, and geometric arrangement of the adsorbed photodissociation products, O and CH₂, are investigated.

II. Computational Methods

The silver–adsorbate system has been described using an embedded cluster method that allows us to carry out an accurate many-electron treatment of the adsorbate/surface portion of a system as well as to describe coupling in this region to the bulk lattice. Details of this method and reference to its previous applications to processes on metal surfaces involving ground and excited electronic states are reported in refs 6, 8, and 22.

There are 37 silver atoms in the surface layer and 27 each in both the middle and bottom layers of the Ag₉₁ cluster employed

in the present study. Up to five of the seven central silver atoms that are located on the surface layer nearest the adsorbed molecule have been described with a 28-electron Ag core and 4s, 4p, two 4d, 5s, and 5p atomic basis functions (AOs). All other silver atoms have either a 46-electron core plus a 5s function or a 47-electron core, depending on their remoteness from the central atom. Relativistic core potential functions are placed on all silver atoms, as described in ref 8. The hydrogen atoms are described by two s functions; carbon and oxygen have four s functions (10 primitive Gaussians), two p functions (five primitives), and one d function. An additional diffuse p function has been included in both the oxygen and carbon AO basis sets (with an exponent of 0.08 in each case) in order to afford a more accurate description of the formaldehyde anionic and internal $n-\pi^*$ excited states.

A localized molecular orbital (LMO) procedure²³ has been used to obtain pseudocanonical LMOs which are employed as basis in the multireference configuration interaction (MRD-CI) calculations²⁴ of the ground and excited states of the adsorbate-surface system. Two types of LMOs have been constructed: (a) those confined to the adsorption site, and (b) those representing the crystal environment. The electronic exchange interaction with reference atomic orbitals of the atoms of the adsorbate and the central Ag atoms with d functions has been employed as a criterion for defining the localization transformation, as has been proposed in refs 22 and 25. A partitioning procedure described in ref 23 has been employed to construct pseudocanonical orbitals on the basis of LMOs for use in the CI calculations. In particular, in the treatment with five Ag atoms having d functions (large cluster, 140 electrons in the Hartree-Fock self-consistent field (SCF)-MO treatment, 193 AOs), 70 doubly occupied LMOs have been divided into two partitions (56 and 14 MOs) characterized by the largest and smallest exchange integrals with the reference AOs, respectively. The 14 LMOs of the second partition have mostly 5s AO character from the silver atoms lying away from the central ring. All of the latter orbitals with the exception of the highest of them (HOMO) have been employed as a frozen core in the CI treatment. Similarly, two partitions of the virtual LMOs (24 and 99) have been constructed. Partitioning of the virtual MOs has been accomplished in such a way that the lowest unoccupied LMO (LUMO) has predominantly formaldehyde character (for example, the $\text{H}_2\text{CO } \pi^*$ orbital in the case of the equilibrium geometry of adsorbed formaldehyde). Then each set of LMOs has been used separately to diagonalize the Fock operator of self-consistent field theory.

The lowest four MOs of formaldehyde (occupied by the 1s and 2s electrons of O and C) and MOs of Ag(4s) and Ag(4p) character have also been placed in the frozen core in all CI calculations. The HOMO that is delocalized over the cluster has been included in the active space of the CI treatment in order to simulate electron excitation from orbitals lying near the Fermi level of the metal.

The resulting CI treatment includes 64 and 54 active electrons in the case of five and three Ag atoms with d functions, respectively. An energy threshold for the MRD-CI selection procedure of 0.1–0.5 $\mu\text{hartree}$ has been employed. The number of reference configurations has been varied from 1 (for some closed-shell states) up to ~ 20 (for open-shell states), so that their contribution (C*C) is at least 85% of the total weight of all configurations (symmetry-adapted functions, SAFs) included in the CI treatment. The number of generated SAFs and those selected in the MRD-CI procedure have been typically about 600 000 000 and 300 000, respectively (64 active electrons, T

$= 0.5 \mu\text{hartree}$). The resultant energies have been extrapolated to the full CI limit by employing the generalized Davidson correction.²⁶

Substrate-mediated electron attachment to the formaldehyde molecule has been described as an electron transfer from Ag_{91} to the lowest unoccupied MO having mostly H_2CO character (π^* at the equilibrium geometry of formaldehyde). This corresponds to the lowest charge-transfer state of the cluster-adsorbate system, $\text{Ag}_{91}^+-\text{H}_2\text{CO}^-$. Since the anion state of formaldehyde is metastable (electron affinity is -0.65 eV^{16}), inclusion of diffuse orbitals (in particular, those virtual MOs that belong primarily to the Ag_{91} system and are spread over the entire cluster) in its MO basis set causes the H_2CO^- diabatic state to be distributed over several CI roots. These states have mixed $\text{Ag}_{91}^+-\text{H}_2\text{CO}$ and $\text{Ag}_{91}^+-\text{H}_2\text{CO}^-$ character, and actually describe the continuous spectrum of the π^* electron auto-detachment states. This effect can also be observed in calculations of the H_2CO^- energy in the presence of the Ag_{91} AOs, but with zero charge on the Ag atoms (that is, something akin to basis set superposition error (BSSE) calculations²⁷): as the cluster-formaldehyde distance R decreases, H_2CO^- borrows diffuse silver MO character to simulate the continuous spectrum. To study formaldehyde anion dissociation on the Ag surface, however, one has to consider a diabatic π^* electron-attachment state of formaldehyde, that is, one that is not strongly mixed with Ag_{91} states. The BSSE calculations mentioned above have shown that such a diabatic state can be described quite accurately by employing the localization-partitioning procedure for the virtual MO space (to obtain a well-localized π^* , for example) and single-root CI calculations that maximize the contribution (at least 50% of the total value of C*C) of the configuration corresponding to electron transfer from the Ag_{91} HOMO to the π^* . The energy of the formaldehyde anion quasi-diabatic state in the presence of Ag AO basis functions at $R = 5a_0$ obtained in this way agrees very well with the computed energy of separated H_2CO^- in the same H, C, O basis (discrepancy is less than 0.15 eV). The above procedure has been applied for all energy calculations of adsorbed H_2CO^- reported in the present work.

The geometry of the adsorbed formaldehyde molecule on the Ag(111) cluster is shown in Figure 1. The following notation is used in the present work: R is the vertical distance between the Ag surface and the center of the C–O bond, and in calculations of the separately adsorbed O atom and CH_2 molecule, it is the vertical Ag surface–O or Ag surface–C distance, respectively; r_{CO} is the carbon–oxygen distance; ϑ is the tilting angle between the formaldehyde axis and the normal to the Ag surface; γ is the angle between the C–O axis and symmetry axis of the CH_2 fragment; φ is an angle between the molecular and tilt planes ($\varphi = 0$ has been used in all calculations).

III. Results and Analysis

A. Electronic States of H_2CO Adsorbed on the Ag(111) Surface. *1. Ground State of the $\text{Ag}_{91}-\text{H}_2\text{CO}$ System.* Molecular orbitals of the $\text{H}_2\text{CO}-\text{Ag}_{91}$ system at the equilibrium H_2CO geometry ($r_{\text{CO}} = 2.3a_0$) and at a vertical distance from the cluster of $R > 4a_0$ have almost pure H_2CO or Ag_{91} character, and the ground state of this system is unbound at the SCF level of treatment. Some binding between adsorbate and surface appears at the correlated CI level of treatment, which means that dynamic polarization or correlation effects play a major role in the interaction. This is consistent with the physisorbed character of the H_2CO adsorption on the Ag(111) surface that is observed

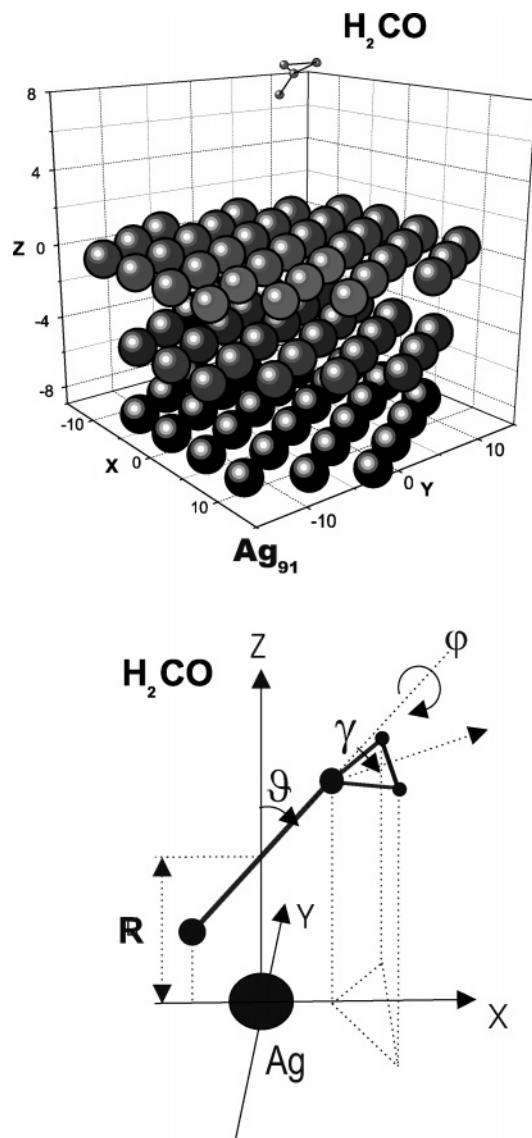


Figure 1. Ag₉₁ cluster (upper panel) and geometry of the formaldehyde molecule adsorbed on the Ag₉₁ cluster.

experimentally. Accurate calculations for such weak interactions are quite demanding since they require extremely large CI spaces.

Computed potential energy curves for the formaldehyde molecule as it approaches the surface at a hollow position are shown in Figure 2 as a function of the Ag–formaldehyde distance R . Experimental data for the formaldehyde geometry⁹ have been employed for these calculations: H₂CO is in its equilibrium geometry (planar molecule with $r_{CO} = 2.3a_0$), with a $\vartheta = 60^\circ$ tilting angle to the cluster normal. A hollow position has been chosen since it is usually preferable for most adsorbates on the Ag surface. The test calculations have not shown any notable variation of the H₂CO binding energy at different positions on the cluster, however.

The absolute energy minimum of the calculated H₂CO–Ag₉₁ ground-state PES (0.16 eV) is at $\vartheta = 90^\circ$, $R = 6.5a_0$ ($\vartheta = 30^\circ$, 60° , 90° , and 100° have been considered). The above value has been computed relative to the H₂CO–Ag₉₁ energy at $R = 18a_0$ and will be referred to below as a binding energy. No binding to the surface has been found at the formaldehyde tilting angles of $\vartheta = 30^\circ$ and 100° , whereas the difference in adsorption energies at $\vartheta = 90^\circ$ and 60° is less than 0.05 eV, that is, within the uncertainty of the calculations. Therefore, the Franck–

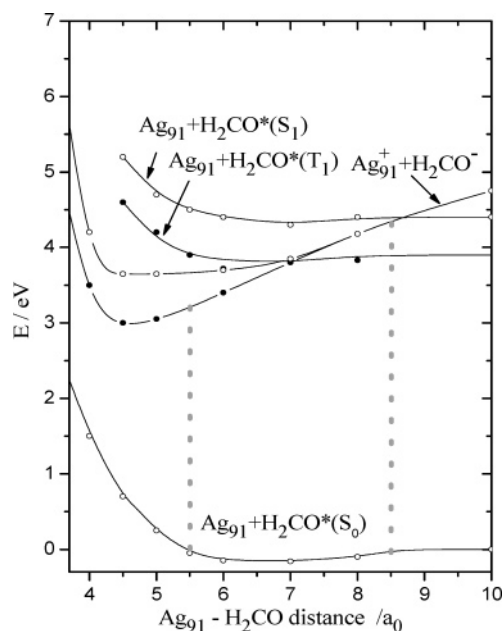


Figure 2. Computed potential energy curves of the H₂CO/Ag₉₁ system as a function of vertical distance R of the adsorbed molecule to the cluster (open and solid circles, singlet and triplet states, respectively). The H₂CO molecule has its gas-phase equilibrium geometry. Vertical dashed lines show the FC region.

Condon (FC) region for ϑ can be estimated as $\sim 50^\circ$ – 90° . These results are in a relatively good agreement with experimental observations: binding energy is 0.27 ± 0.02 eV and $\vartheta = 57^\circ \pm 6^\circ$.⁹ One can see from Figure 2 that the ground state has a quite wide FC region over the R coordinate (5.5 – $8.5a_0$), with an energy minimum at $R \sim 6.5a_0$. Since the molecule is tilted, the distance from the O atom to the surface is shorter ($\sim 5.9a_0$) than the equilibrium value of $R = 6.5a_0$, whereas the distance of the C atom to the surface is larger ($\sim 7.1a_0$). These values are quite typical for physisorbed systems.

2. Excited States. The initial photoinduced excitation of formaldehyde adsorbed on Ag(111) can be described as a Franck–Condon (or sudden) transition since this process is significantly faster than the nuclear relaxation in H₂CO (characteristic times are $\sim 10^{-16}$ s²⁸ and $\sim 10^{-14}$ s, respectively). Therefore, possible photoexcitation channels of the adsorbed formaldehyde must occur at the fixed equilibrium geometry of H₂CO. As has been mentioned above, Ag₉₁–H₂CO at its equilibrium geometry is a weakly bound system whose SCF orbitals have almost pure Ag or formaldehyde character. One can, therefore, clearly define the characteristic electronic configurations on the basis of the formaldehyde π^* MO population, namely the $n \rightarrow \pi^*$ internally excited and π^* electron-attachment (anionic) states. These electronic states are considered to be likely candidates for photoinduced direct and substrate-mediated population, respectively, followed by formaldehyde dissociation. It is important to recall, however, that these states are embedded in the set of the Ag₉₁ internally excited states, $Ag_{91}^* - H_2CO$. The latter, in fact, must represent the continuum lying directly above the Ag₉₁–H₂CO ground state. Since, on one hand, Ag₉₁ excited states are not the subject of the present study and, on the other hand, the dimensions of the secular equations increase rapidly with the number of roots considered explicitly, we have avoided including such states in the CI treatment.

Internal $n \rightarrow \pi^*$ excitation of formaldehyde does not notably change the shape of the cluster–molecule potential curve relative to that of the ground state (see Figure 2). The computed

energy of the $\text{Ag}_{91}\text{--H}_2\text{CO}^*$ triplet state (T_1) is 3.9 eV at large R and about 3.83 eV at $R = 7a_0$. Thus, the $\text{Ag}_{91}\text{--H}_2\text{CO}^*$ state is even slightly less bound than the ground state, with a difference in binding energy of only ~ 0.09 eV, which in turn is smaller than the uncertainty in the present calculations. The corresponding singlet state (S_1) is about 0.5 eV higher than the triplet. Calculation of the $n\text{--}\pi^*$ vertical excitation energies of isolated H_2CO employing the same AO basis set gives 3.67 and 4.11 eV for the triplet and singlet states, respectively (experimental values are $\sim 3.1\text{--}3.6$ and $3.5\text{--}4.2$ eV for the $^3\text{A}_2\text{--}^1\text{A}_1$ and $^1\text{A}_2\text{--}^1\text{A}_1$ transitions²⁹). Therefore, the computed $\text{Ag}_{91}\text{--H}_2\text{CO}^*$ excitation energies might be overestimated as much as ~ 0.6 eV because of both the basis set deficiencies and the limited CI dimensions.

The π^* electron-attachment state of the adsorbed formaldehyde molecule is described in the present calculations by the $\text{Ag}_{91}^+\text{--H}_2\text{CO}^-$ charge-transfer state. It is formed by excitation from one of the Ag_{91} levels near the Fermi level to the unoccupied π^* of H_2CO . The hole, therefore, is associated primarily with the HOMO of the SCF calculations. Singlet and triplet components of the $\text{Ag}_{91}^+\text{--H}_2\text{CO}^-$ state are shown in Figure 2. The energy of the singlet state rapidly increases at small R relative to its triplet counterpart due to the exchange interaction in the triplet state between the singly occupied metal hole and the π^* formaldehyde level. One should also note that additional metal–metal excitations can change the multiplicity of the system without energy change. Thus, the $\text{Ag}_{91}^+\text{--H}_2\text{CO}^-$ triplet state in the present calculations represents a low-energy threshold for electron transfer from the surface to the adsorbate. Its FC excitation spectrum is located in the energy range of 3.2–4.4 eV (see Figure 2). These values can be slightly overestimated, however, because of inaccuracies in the computed electron affinity of the formaldehyde anion and the Ag_{91} work function (their magnitudes are overestimated and underestimated, respectively, and the corresponding total value is about 0.6 eV higher in the calculations than is observed experimentally).

B. Electronic States of CH_2 and O Adsorbed on the $\text{Ag}(111)$ Surface. The electronic structure and binding energies of the O and CH_2 fragments on the Ag surface have been studied separately by employing a small Ag_{91} cluster (three Ag atoms with 4s/p/d functions placed near the adsorbate). This procedure considerably reduces the dimensions of the CI treatment and, therefore, the computational expenditure required to optimize the CH_2 geometry on the surface.

The energy variations of the oxygen singlet and triplet states with distance from the cluster are shown in Figure 3. The calculations have shown that, at small distances from the cluster, $R_{\text{Ag--O}} < 5a_0$, the (2p) AOs of oxygen and (5s) AOs of silver form a set of doubly occupied and virtual MOs of mixed character that are localized in the vicinity of adsorbate. The energetically highest MO among the mixed doubly occupied orbitals has $\text{O}(p_z)/\text{Ag}(5s)$ character. This MO also has an unbound counterpart in the set of virtual MOs, and it is energetically lowest among the mixed unoccupied orbitals. The oxygen atom, therefore, forms a valence bond with the metal surface. As a result of this characteristic of the metal–adsorbate system, the closed-shell state correlating with $\text{O}(^1\text{D})\text{--Ag}_{91}$ becomes energetically preferred at small cluster–oxygen distances over the two-open-shell triplet that correlates with the ground state of separated oxygen plus Ag_{91} cluster, $\text{O}(^3\text{P})\text{--Ag}_{91}$ (see Figure 3). Furthermore, at $R_{\text{Ag--O}} \sim 4a_0$ the latter triplet state undergoes a potential crossing with the charge-transfer state correlating with $\text{O}^-(^2\text{P}) + \text{Ag}_{91}^+$. Both states can be considered

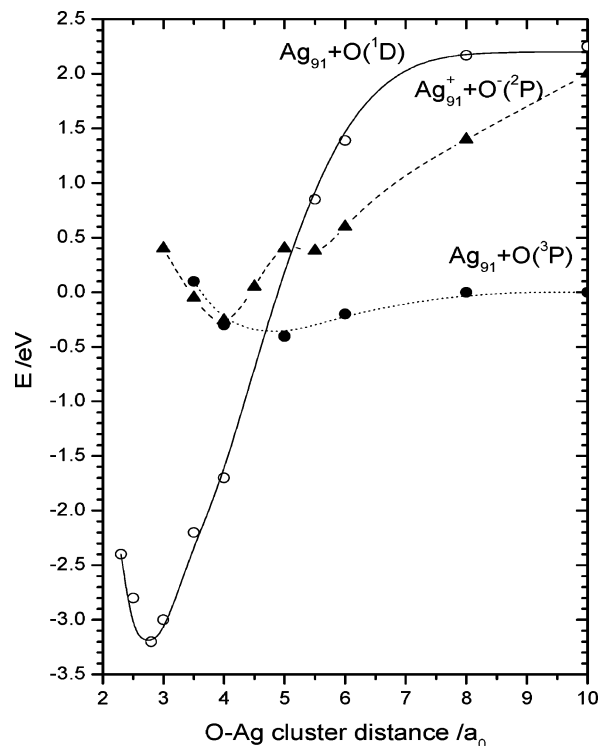


Figure 3. Computed potential energy curves for the O/ Ag_{91} system as a function of the distance from the oxygen atom to the cluster. (O approaches the cluster at the hollow position.) Solid and dotted lines are singlet and triplet states, respectively.

as diabatic components of the lowest triplet state, as they differ by only one open-shell MO at small $R_{\text{Ag--O}}$. Specifically, the $\text{O}^-(^2\text{P})\text{--Ag}_{91}^+$ system has two singly occupied MOs of $\text{Ag}(5s)/\text{O}(p_z)$ character, whereas $\text{O}(^3\text{P})\text{--Ag}_{91}$ occupies one $\text{Ag}(5s)/\text{O}(p_z)$ orbital and another of $\text{Ag}(5s)/\text{O}(p_{y/x})$ character (both MOs are localized in the vicinity of the adsorbate). At large distances from the cluster, $R > 5a_0$, the electronic structure of the charge-transfer state naturally changes: the additional electron is primarily localized in the $\text{O}(p_z)$ orbital, whereas the hole is described by the $\text{Ag}(5s)$ diffuse MO located near the Fermi level. Since the set of occupied diffuse $\text{Ag}(5s)$ MOs except for the highest one has been kept frozen in the calculations, the transition from $\text{Ag}(5s)/\text{O}(p_z)$ to $\text{Ag}(5s)$ character in the singly occupied MO does not occur smoothly, and this causes a slight curvature in the charge-transfer state's potential curve at $R_{\text{Ag--O}} \sim 5a_0$.

The computed binding energy of oxygen on the $\text{Ag}(111)$ surface (calculated as the minimum of the $\text{Ag}_{91}\text{--O}$ potential energy relative to the $\text{Ag}_{91}/\text{O}(^3\text{P})$ energy at $R_{\text{Ag--O}} = 18a_0$) is 3.25 eV at the hollow position of O on the $\text{Ag}(111)$ surface for an equilibrium distance of $R_{\text{Ag--O}} = 2.8a_0$. This result is in fairly good agreement with the experimental value of 3.47³⁰ or 3.52 eV³¹ for chemisorbed oxygen. The bridge and atop positions are less favorable (computed binding energies are 2.1 and 0.1 eV, respectively).

The energy of adsorbed CH_2 on the Ag surface has been computed at two tilting angles between the CH_2 symmetry axis and the normal to the surface, $\vartheta = 0^\circ$ and 60° , and with the hydrogen atoms always pointing away from the surface. The largest binding energy, 1.27 eV (relative to the energy of the $\text{CH}_2(^3\text{B}_1) + \text{Ag}_{91}$ system at a vertical distance from the C atom to the surface of $R_{\text{Ag--C}} = 18a_0$), has been obtained for the closed-shell singlet state for the vertical orientation of CH_2 ($\vartheta = 0^\circ$) and at a hollow site, with a C–H distance of 2.1–2.15 a_0 , H–C–H angle of $\sim 100\text{--}115^\circ$, and equilibrium distance

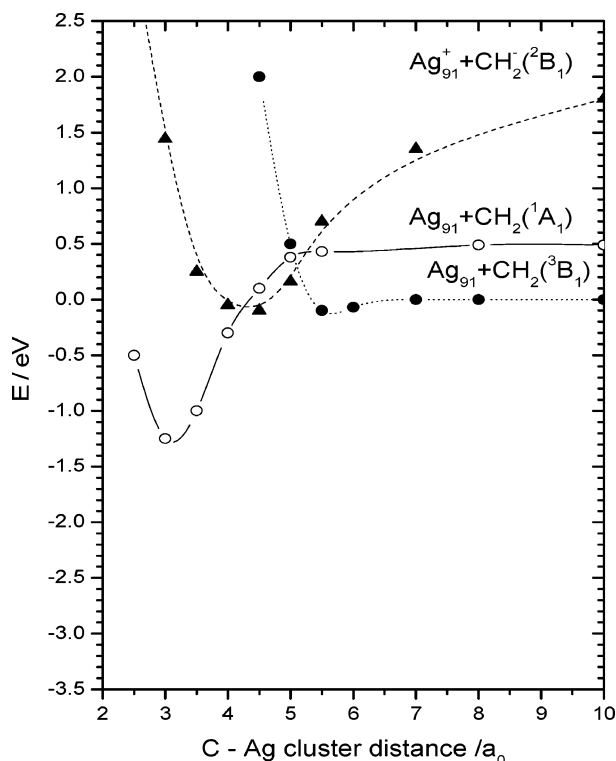


Figure 4. Computed potential energy curves of the CH₂/Ag₉₁ system as a function of the distance from the carbon atom to the cluster. [CH₂ approaches the cluster at the hollow position and its molecular symmetry axis is perpendicular to the surface; the inner geometry of CH₂ is optimized on the surface (see text).] Solid and dotted lines are singlet and triplet states, respectively.

$R_{\text{Ag-C}} = 3a_0$. The binding energies at the bridge and atop positions on the cluster are smaller, ~ 1.0 and ~ 0.75 eV, respectively.

The electronic structure of the Ag₉₁-CH₂ system is very similar to that of Ag₉₁-O. At small Ag₉₁-C vertical distances, $R_{\text{Ag-C}} < 5a_0$, the C(p) AOs are mixed with Ag(5s). Specifically, the C(p_z) AO gradually takes on Ag(s) character (z is the CH₂ symmetry axis and is perpendicular to the surface, and x is the H-H axis). Only the C(p_x) AO is not mixed with Ag orbitals since it is localized in the C-H bond. The C(p_y) component is the least involved in the internal methylene bonding and, therefore, the most mixed with Ag₉₁ AOs. Its unbound counterpart, C(p_y)/Ag(5s), has the lowest energy among the virtual MOs with carbon character. At small $R_{\text{Ag-C}}$, therefore, the singlet closed-shell Ag₉₁-CH₂ state becomes the ground state (Figure 4), similar to what has been observed in the case of adsorbed oxygen. In contrast to the oxygen atom, however, which is bound to the surface mainly through its p_z orbital, CH₂ is bound through the p_y MO and thus with significantly less overlap with the Ag₉₁. The charge distribution of the adsorbed CH₂ is characterized by some change in its equilibrium geometry on the surface, namely in an increase in C-H bond length and a decrease in H-C-H angle. The geometry of adsorbed methylene is therefore very close to that in gas-phase CH₂(¹A₁) or CH₂(²B₁). The equilibrium C-H stretch and bond angle values for the CH₂ fragment on the Ag surface in isolated formaldehyde as well as in its gaseous neutral and anionic states are summarized in Table 1. The triplet state of the adsorbed CH₂ molecule correlates with CH₂(³B₁) at large distances from the cluster, whereas at small $R_{\text{Ag-C}}$, the two open shells have localized C(p_y)/Ag(s) character and the corresponding diabatic state converges to Ag₉₁⁺-CH₂⁻ at large $R_{\text{Ag-C}}$ (see dashed lines in Figure 4).

TABLE 1: Equilibrium Geometry of the Methylene Group in Various Systems

	C-H/ a_0	H-C-H angle/deg
H ₂ CO [ref 32]	2.083	121.1
CH ₂ (³ B ₁) [ref 33]	2.03	134
CH ₂ (¹ A ₁) [ref 33]	2.097	102
CH ₂ (² B ₁) [ref 34]	2.15	100.4
CH ₂ ^{ads} [present calc]	2.1–2.15	100–115

C. Photoinduced C-O Bond Cleavage in H₂CO Adsorbed on the Ag(111) Surface. Photodissociation of gaseous formaldehyde occurs due to UV excitation to H₂CO*(S₁) and luminescence or internal conversion back to the vibrationally excited ground state, H₂CO(S₀), with subsequent C-H bond cleavage.¹³ The experimental studies of refs 9–11 and 15 emphasize that this dissociation channel of formaldehyde is not at all probable on the surface, and the present calculations support this conclusion. In particular, the calculations have shown that H₂CO* is physisorbed on the Ag surface and therefore its direct dissociation is as unlikely as it is in the gas phase. The H₂CO(S₁) state lifetime of $\sim 10^{-7}$ – 10^{-9} s³⁵ is significantly longer than typical times for adsorbate quenching on the surface by degenerate electron transitions in the metal ($\sim 10^{-13}$ – 10^{-15} s⁵). Therefore, the gas-phase dissociation channel is ineffective on the metal surface as well.

The H₂CO π^* electron-attachment state is obviously a more appropriate candidate for the dissociation process on the surface. The formaldehyde anion is strongly bound to the surface with a larger equilibrium r_{CO} value than the ground state. It therefore gains kinetic energy on the excited PES after it is formed on the surface. Taking into account the fact that the lifetime of the excited state of adsorbates on the metal surfaces (usually estimated as 10^{-15} – 10^{-13} s⁵) is comparable to the characteristic time of nuclear motion in H₂CO ($\sim 10^{-14}$ s), one may suppose that nuclear relaxation occurs directly on the PES of adsorbed H₂CO*, with C-O bond stretching as the most effective and fast relaxation path. The computed data discussed above in section III.B make evident, however, that the energetically optimal state for the final coadsorbed fragments produced by formaldehyde C-O bond cleavage on the Ag surface is a closed-shell singlet. This state obviously must correlate with the ground state of the H₂CO-Ag₉₁ system at the formaldehyde equilibrium geometry. Therefore, reneutralization of the electron-attachment state by electron transfer back to the substrate must occur somewhere along the dissociation path. Insight into the mechanism of adsorbed formaldehyde photodissociation will be obtained below by considering key points on the C-O bond-breaking path for both the electron-attachment and neutral H₂CO state PESs.

1. Intermediate Geometries of Adsorbed H₂CO on the C-O Bond Cleavage Pathway. To explore formaldehyde dissociation, we have analyzed several intermediate structures on the pathway from the bound H₂CO molecule to its fragments, O and CH₂.

First, the internal adsorbate geometry and orientation relative to the cluster must change significantly with C-O bond stretching. Two limiting cases based on the energy optimization data for H₂CO (see section III.A) and its fragments on the surface (see section III.B) have been considered: (a) One limiting case is the “formaldehyde” geometry in which the molecule is planar and the geometric parameters of the CH₂ fragment are frozen as in gas-phase H₂CO, but the r_{CO} coordinate is varied with $\vartheta = 60^\circ$ at all R and r_{CO} values. (b) The other case is the “fragment” geometry in which the molecule is no longer planar and the geometry of CH₂ and its orientation relative to the surface are fixed as optimized separately on the

small Ag₉₁ cluster (see section III.B and Table 1) and r_{CO} and ϑ are varied. In the latter case distances from the surface to the oxygen and carbon atoms are optimized independently at each r_{CO} and the resultant ϑ value is kept fixed over R (as in case a, R is the vertical distance from the Ag surface to the C–O bond midpoint). Obviously, these two models optimally describe only the initial and final points of the reaction path and can be quite rough approximations at intermediate points. For reasons that will be discussed below, the point of maximum deviation from both models corresponds to C–O coordinate stretch in the interval of $r_{\text{CO}} = 3.5\text{--}5a_0$. Therefore, we have chosen one point in this range, namely at $r_{\text{CO}} \sim 4.4a_0$, to compute the potential energy of the H₂CO–Ag₉₁ system in both limiting geometries. At $r_{\text{CO}} < 4.4a_0$ the “formaldehyde” geometry, and at $r_{\text{CO}} > 4.4a_0$ the “fragment” geometry, has been employed in the calculations. Of course, such a simplified description of the geometric variations does not provide an optimal energy pathway for the overall dissociation process, and one can expect that the energy actually required may be somewhat lower than calculated as a result.

Second, the optimum location of the CH₂ and O fragments on the cluster is naturally changed as C–O stretch proceeds. Two key points have been taken into consideration in choosing the lowest energy site: (a) over the entire reaction pathway both carbon and oxygen should be away from the atop position, as that is least favorable for each of the fragments; (b) one can expect that the energy difference between hollow and bridge positions increases with r_{CO} since the binding of both fragments to the surface becomes stronger as dissociation proceeds (H₂CO is physisorbed, whereas CH₂ and O are chemisorbed on Ag₉₁). Thus, we have chosen to keep the O atom close to the hollow position over the whole dissociation path, whereas the CH₂ location has been varied between bridge and hollow positions. Projections on the Ag cluster of O and CH₂ at several intermediate points on the C–O stretch pathway are illustrated in Figure 5. The shaded circles indicate the Ag atoms with the set of 4s/p/d basis functions. It can be seen that their positions have been changed in Figure 5f in order to keep the H₂CO molecule surrounded by the Ag atoms with the d AOs. However, the total energy of the system does not depend on which five (contiguous) Ag atoms are chosen, and the energy values obtained for both cluster types can be compared directly.

The resulting computed energy curves of the H₂CO–Ag₉₁ system in its ground and charge-transfer states are given in Figures 6 and 7 as a function of the R and r_{CO} distances. The calculated energies of the H₂CO–Ag₉₁ system at $R = 18a_0$ and for isolated H₂CO (in both cases H₂CO is in its equilibrium geometry, $r_{\text{CO}} = 2.3a_0$) have been used as the zero-energy reference for the adsorbed H₂CO and gas-phase H₂CO energy diagrams, respectively. To have a clearer comparison between the energy variations of adsorbed and gaseous formaldehyde, we have assumed the same geometry in both cases at each r_{CO} value.

2. C–O Bond Cleavage of Neutral Formaldehyde in the Gas Phase and on the Surface. To understand the nature of the C–O bond cleavage in adsorbed formaldehyde, it is helpful to first consider this process in the gas phase. The C–O bond stretching in gaseous formaldehyde is accompanied by a change in electronic structure from closed shell at the equilibrium point to a four-open-shell singlet state at the dissociation limit corresponding to the O(³P) + CH₂(³B₁) fragments. At intermediate points a configuration with two open shells may also make an important contribution. For example, up to $r_{\text{CO}} \sim 3.0a_0$ the leading configuration is a closed shell, but at $r_{\text{CO}} \sim 3.5a_0$ a

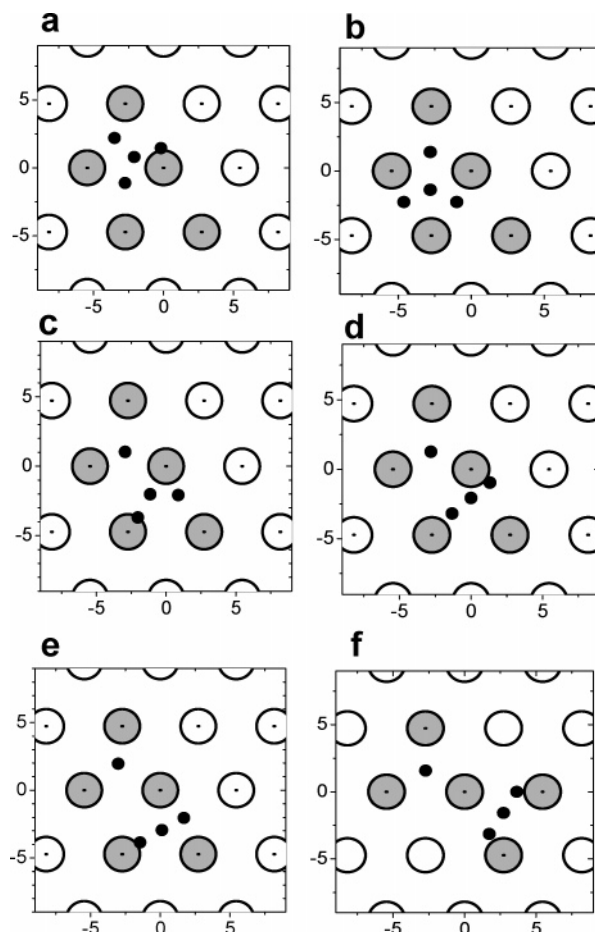


Figure 5. Projections of positions of the formaldehyde molecule and its fragments, O and CH₂, on the Ag₉₁ cluster at different r_{CO} values: (a) $r_{\text{CO}} = 2.3a_0$ ($\vartheta = 60^\circ$); (b) $r_{\text{CO}} = 3.0a_0$ ($\vartheta = 60^\circ$); (c) $r_{\text{CO}} = 3.5a_0$ ($\vartheta = 60^\circ$); (d) $r_{\text{CO}} = 4.4a_0$ ($\vartheta = 87.4^\circ$); (e) $r_{\text{CO}} = 5.3a_0$ ($\vartheta = 87.8^\circ$); (f) $r_{\text{CO}} = 6.3a_0$ ($\vartheta = 88.2^\circ$). The shaded Ag atoms have 4s/p/d AO basis functions.

two-open-shell electronic configuration makes a 25% contribution to the H₂CO ground state, whereas at $r_{\text{CO}} = 4.4a_0$ the leading configuration becomes a four-open-shell one ($\sim 40\%$). At $r_{\text{CO}} > 5a_0$ dissociation of H₂CO has occurred almost completely and the CH₂ fragment must be in the equilibrium methylene geometry, CH₂(³B₁). It is clear, therefore, that up to $r_{\text{CO}} \sim 3.0a_0$ formaldehyde remains physisorbed on the Ag surface (see Figure 6a) since the internal C–O binding is so strong that the H₂CO and Ag₉₁ MOs are not significantly mixed. As r_{CO} continues to increase, however, the internal binding of H₂CO is weakened (contribution of the open-shell electronic configurations becomes significant in the ground state of isolated formaldehyde) and the attraction to the surface of the molecular fragments, CH₂ and O, becomes correspondingly stronger. Specifically, already at $r_{\text{CO}} = 3.2a_0$ and $R < 5a_0$, the MOs of H₂CO are notably mixed with Ag₉₁(5s) MOs and this leads to chemisorption of H₂CO on the surface with a binding energy of ~ 0.5 eV (see Figure 6). As a result, the ground state of adsorbed formaldehyde is always closed shell, similar to that for adsorbed oxygen and methylene, and upon separation from the Ag surface it correlates with the two- or four-open-shell ground state of the partially or completely dissociated gaseous formaldehyde.

As can be seen from the previous discussion, the major change in the formaldehyde electronic structure from molecule to gaseous fragments occurs in the range of $r_{\text{CO}} \sim 3.5\text{--}5a_0$ and this range, therefore, can be considered as intermediate between

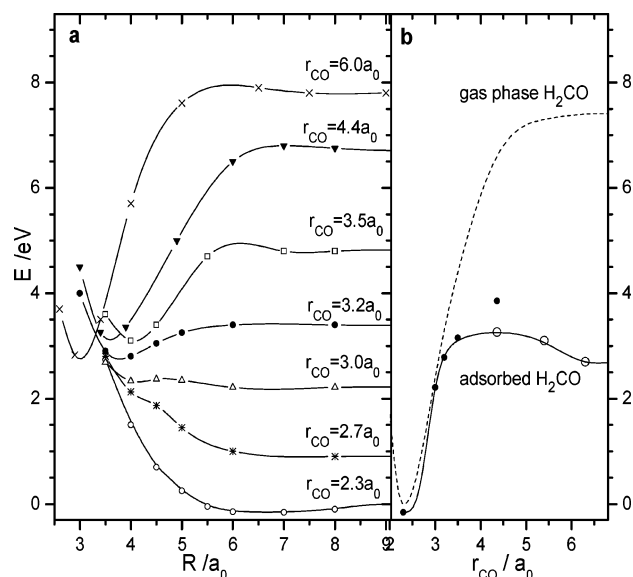


Figure 6. Left panel: computed potential energy curves of the H₂CO–Ag₉₁ system at different r_{CO} values as functions of R . H₂CO is in the “formaldehyde” geometry at $r_{\text{CO}} = 2.3, 3.0, 3.2$, and $3.5a_0$, and in the “fragment” geometry at $r_{\text{CO}} = 4.4$ and $6.3a_0$ (see text). Right panel: potential energy curves of H₂CO as a function of CO distance in the gas phase (dotted curve) and adsorbed on the surface at the equilibrium geometry with respect to R (“formaldehyde” and “fragment” equilibrium geometry are shown by solid and open circles, respectively).

the “formaldehyde” and “fragment” geometries. We have chosen $r_{\text{CO}} = 4.4a_0$ as a key structure since at this C–O separation the contribution of the closed-shell electronic configuration to the ground state in isolated H₂CO is already negligible in comparison with its two- and four-open-shell counterparts, but the carbon and oxygen AOs are still notably mixed in the corresponding MOs. The computed equilibrium energies of the adsorbed molecule at both the “formaldehyde” and “fragment” geometries are shown in the potential diagram given in Figure 6b. The energy of the H₂C–O stretched molecule at the “fragment” geometry is about 0.6 eV lower on the surface, despite the fact that in the gas phase the “formaldehyde” geometry is preferred by an energy difference of ~ 0.5 eV. One should note that in the gas phase the weight of the four-open-shell configuration in the H₂C–O ground state increases from $\sim 46\%$ to 62% as the geometry is changed from planar “formaldehyde” to that of the bent “fragment”. These data therefore make evident that each of the fragments forms its own bond with the surface, which significantly facilitates C–O bond cleavage in adsorbed formaldehyde.

The computed energies of adsorbed H₂CO on its dissociation path are shown in Figure 6b. According to these data, complete dissociation of neutral formaldehyde requires ~ 3.25 eV excitation energy on the C–O stretch coordinate. There is a barrier of ~ 0.5 eV (with the potential maximum at $r_{\text{CO}} \sim 4.4a_0$) above the total energy of the dissociation products on the surface. One can expect, however, that the actual barrier should be lower if the internal geometry of the dissociated molecule and its position on the surface would be completely optimized. At the same time, it is clear that, even at an excitation energy greater than 3.25 eV, the adsorbed formaldehyde molecule cannot effectively dissociate on the neutral PES since it is only weakly bound to the Ag surface up to $r_{\text{CO}} \sim 3.2a_0$, and thus vibrational excitation would quickly lead to its desorption from the surface. This conclusion agrees with the fact that thermally induced polymerization has not been observed experimentally.⁹

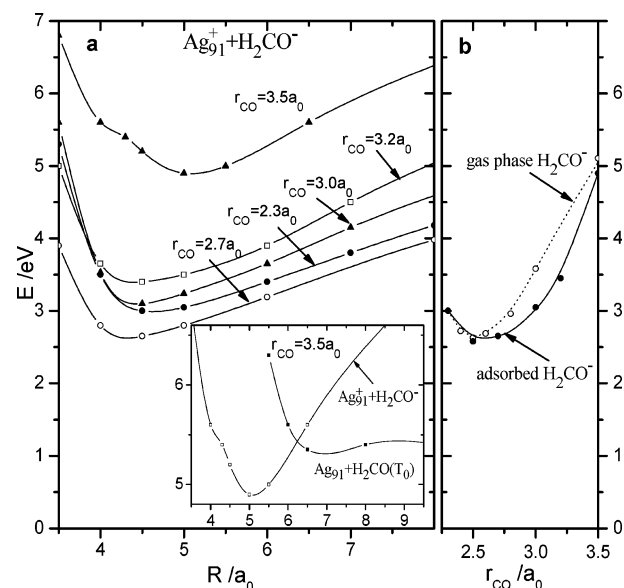


Figure 7. Left panel: computed potential energy curves of the Ag₉₁⁺–H₂CO[−] system at different r_{CO} values as functions of R . H₂CO[−] is in the “formaldehyde” equilibrium geometry for all points. Right panel: potential energy curves of H₂CO[−] as a function of CO distance in the gas phase (dotted curve) and adsorbed on the cluster at the optimal distance from the Ag cluster. The scale of energy variation of gaseous H₂CO[−] has been shifted to match the energy at $r_{\text{CO}} = 2.3a_0$ to the corresponding value of adsorbed H₂CO[−].

3. C–O Bond Cleavage of the π^* Electron-Attachment State of Adsorbed H₂CO. Since the molecular orbitals of the Ag cluster and formaldehyde are quite well separated at $r_{\text{CO}} < 3.2a_0$ (see section III.A), the formaldehyde anion at its nearly equilibrium geometry is bound to the surface by a pure Coulombic attraction. The corresponding substrate-mediated π^* electron-attachment state can be described in terms of an electron transfer from the highest diffuse Ag₉₁ MO (that is close to the Fermi level) to the π^* localized on H₂CO. The resulting two-open-shell state therefore possesses pure charge-transfer character, Ag₉₁⁺–H₂CO[−]. The energy variation of the triplet charge-transfer state over the R and r_{CO} coordinates is shown in parts a and b, respectively, of Figure 7.

One should emphasize that the charge-transfer state described above has a quasi-adiabatic character since its potential curve can be crossed by that of the internal formaldehyde (H₂CO*–Ag₉₁) and Ag₉₁ (H₂CO–Ag₉₁^{*}) excited states (see Figure 2 and inset of Figure 7a). The latter actually form a continuum above the H₂CO–Ag₉₁ ground state and describe a possible quenching of the electron-attachment state on the surface. However, such states obviously do not have an effect on the dissociation mechanism since they do not affect the formaldehyde electronic structure. We also do not consider the H₂CO*–Ag₉₁ diabatic component because it has weakly bound character and is not involved in the dissociation on the surface either.

Increasing the C–O bond distance above $r_{\text{CO}} \sim 3.2a_0$ leads to a notable mixing of H₂CO and Ag₉₁ MOs at small R and, as a result, to essential changes in the electronic structure of the electron-attachment state. Specifically, the two-open-shell electronic configuration corresponding to the electron transfer from the doubly occupied mixed Ag/H₂CO MO localized near the adsorbate–cluster bond to its virtual counterpart becomes lower in energy. Therefore, at small R and large r_{CO} the Ag₉₁⁺–H₂CO[−] charge-transfer state is predominantly valence in character and this electronic structure change can result in a complicated shape for the adiabatic potential curve, as for example in the case of $r_{\text{CO}} = 3.5a_0$ (see inset of Figure 7a).

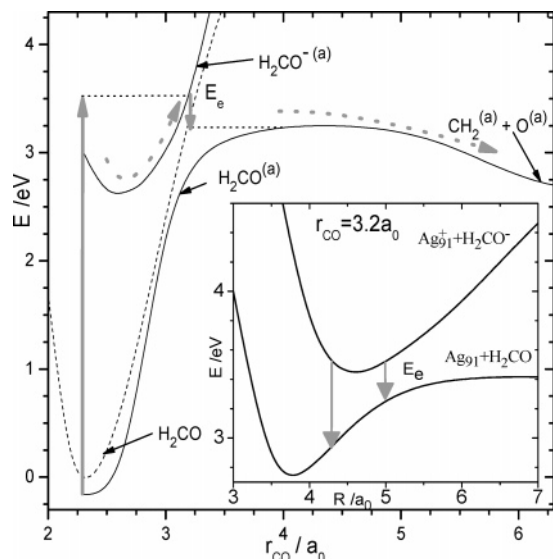


Figure 8. Reaction pathway of C–O bond cleavage in adsorbed formaldehyde. Excitation brings the adsorbed H_2CO to the π^* electron-attachment state, $\text{H}_2\text{CO}^-(a)$. The subsequent reneutralization of $\text{H}_2\text{CO}^-(a)$ [the transition is shown in energy diagrams for the r_{CO} and R (inset) coordinates] leads to formation of vibrationally excited $\text{H}_2\text{CO}(a)$ that can then dissociate and form the coadsorbed O and CH_2 fragments (E_e is detachment electron energy).

It can be seen from Figure 7 that the formaldehyde anion formed via a Franck–Condon transition (at $r_{\text{CO}} \sim 2.3a_0$, $R \sim 5.5\text{--}8.5a_0$) acquires vibrational energy on the excited PES and that its nuclear motion is directed toward larger r_{CO} and smaller R values that must facilitate dissociation. However, as the r_{CO} distance subsequently increases, the energy of the electron-attachment state on the surface rises rapidly and direct dissociation on the $\text{Ag}_{91}^+-\text{H}_2\text{CO}^-$ PES becomes impossible (see Figure 7b). One thus has to conclude that the electron-attachment state must undergo deexcitation (or reneutralization) back to the ground state in order to achieve complete dissociation.

IV. Discussion: Pathway of Photoinduced Dissociation of Adsorbed H_2CO

To define the possible dissociation path of the formaldehyde molecule on the surface, it is helpful to summarize the data discussed above.

According to the present calculations, the formaldehyde π^* electron-attachment state formed by electron transfer from the surface has additional vibrational energy in the C–O bond after excitation. Formaldehyde anion is strongly bound, and despite high vibrational excitation, its ultimate fate is reneutralization by electron transfer back to the substrate, which leads to formation of the formaldehyde ground state on the surface. Electron detachment must occur suddenly (without change of nuclear positions) and the final energy of adsorbed H_2CO (as well as the energy of the outgoing electron) obviously depends on the relative position of the charge-transfer and ground states. Subsequent C–O bond breaking can occur only if the energy accumulated by adsorbed H_2CO in its ground state after anion reneutralization is enough to overcome the dissociation barrier.

Let us consider this process relative to the r_{CO} coordinate. Computed potential energy curves along the r_{CO} coordinate from the ground and electron-attachment states of formaldehyde on the Ag_{91} surface are given in Figure 8 (the curves present corresponding equilibrium energies at optimized R for each r_{CO}). Initial excitation is shown by the vertical arrow from the ground to the anion state. Since adsorbed H_2CO^- possesses high

vibrational excitation accumulated primarily in the C–O stretch coordinate, the density of its vibrational wave function can be approximately described as concentrated mainly in the zero kinetic energy region of the PES. Therefore, electron detachment must occur most effectively at the classical turning point, in particular, at the largest r_{CO} value for the one-dimensional description presented in Figure 8. This transition is shown in the diagram by the vertical arrow from the anion to the ground state of adsorbed formaldehyde. The same transition is also shown in the inset of Figure 8 for the potential energy variation with respect to the R coordinate. Since the molecular kinetic energy is near zero at the transition point, the energy of the final state must be above the barrier in order to have dissociation.

For example, if the excitation energy of the adsorbed formaldehyde anion is about 3.6 eV (relative to the ground state of the equilibrium $\text{Ag}_{91}-\text{H}_2\text{CO}$ at $R \sim 6.2a_0$), the maximal C–O bond stretching that can be accessed on the $\text{Ag}_{91}^+-\text{H}_2\text{CO}^-$ surface is $r_{\text{CO}} \sim 3.2a_0$. In this case transition to the ground state occurs most probably at $r_{\text{CO}} \sim 3.2a_0$ and $R = 4.3a_0$ or $R = 5a_0$ (see Figure 8, inset), with an energy of the outgoing electron of ~ 0.6 or ~ 0.25 eV, respectively. At $r_{\text{CO}} \sim 3.2a_0$, $R = 5a_0$, the energy of ground-state formaldehyde (~ 3.3 eV) is above the barrier on the C–O cleavage path, and thus dissociation on the ground PES may occur in this case. One should note that the process described above is the fastest dissociation channel for formaldehyde since the adsorbed molecule needs only half a vibrational period to pass the whole way from the initially excited electron-attachment state to the fragments on the surface. The prompt C–O bond breaking is also a more effective channel with significantly larger cross section in comparison with the H/HCO dissociation (that occurs due to the weak coupling between the S_1 and S_0 or T_0 surfaces in the gas phase) as has been noted in ref 15.

The dissociation threshold energy in the present calculations can be estimated as ~ 3.6 eV, which corresponds to a maximal C–O bond stretching of $\sim 3.2a_0$ in the anion state. This is the minimum r_{CO} for which (a) the ground-state PES becomes strongly bound to the Ag cluster, and (b) the energy of the ground state formed via a FC transition ($R \sim 5a_0$) is above the dissociation barrier. The next point included in the present calculations is for $r_{\text{CO}} = 3.0a_0$, which corresponds to an excitation energy below the dissociation barrier. This system therefore needs additional kinetic energy accumulated in the anion state at the transition point, which is unlikely.

One should, of course, take into consideration the uncertainty of the present calculations, which can lead to overestimation of the electron-attachment state energy as well as the height of the dissociation barrier, as has been discussed above in sections III.A.1 and III.B.2. This uncertainty does not, however, affect the general dissociation mechanism, which can be briefly described as adsorbed formaldehyde dissociation facilitated by an intermediate excited state. The role of the intermediate state is to accumulate vibrational energy primarily in the C–O stretch coordinate, which allows formaldehyde to overcome the dissociation barrier on the ground-state PES. The latter is significantly lowered by the surface due to the strong binding of the CH_2 and O fragments with $\text{Ag}(111)$. It is clear, therefore, that an internally excited formaldehyde state [that is physisorbed on $\text{Ag}(111)$] cannot serve as such an intermediate since it does not gain enough vibrational energy upon excitation.

Finally, one should also consider alternative energy relaxation processes of the excited formaldehyde anion that may occur on the Ag surface. First, the dissociation processes discussed above must compete with formaldehyde desorption from the surface

following its reneutralization, which must also occur at an excitation energy below the C–O bond cleavage threshold. Such desorption is usually described by the Antoniewicz model³⁶ and is accompanied by high average kinetic energy of the desorbed molecules, as has been experimentally observed and analyzed for formaldehyde adsorbed on Ag(111) in ref 18. Furthermore, the C–O bond cleavage mechanism described above implies prompt dissociation, i.e., without vibrational energy redistribution over the internal formaldehyde coordinates during the lifetime of the formaldehyde anion on the surface. If the latter process occurs, however, other dissociation channels involving C–H bond breaking following the anion reneutralization must be considered, for example, the threshold energy for the HCO + H dissociation channel on the gas-phase formaldehyde S₀ surface is ~3.75 eV.¹² If one also takes into account the strong binding of the H atom and probably also the HCO radical with the Ag(111) surface (experimental value for H is ~2.5 eV²⁰), it can be supposed that the corresponding barrier is even lower on the Ag surface. One should stress, however, that such a HCO + H or CO + 2H dissociation mechanism on the Ag(111) surface supposes that (a) there is a vibrational energy redistribution on the anion PES from the C–O to the C–H bond (which implies a longer lifetime for the anion state than is the case for C–O bond cleavage, as well as a significant excess of the vibrational energy above the C–H bond cleavage threshold), and (b) the dissociation fragments should be strongly bound to the surface [from this point of view CO/H₂ dissociation is rather unlikely since both fragments are weakly bound to Ag(111)]. These characteristics of the dissociation process are in general agreement with the experimental observations such as the high-energy threshold for the photoinduced formation of CO from adsorbed H₂CO and the absence of H₂ in the reaction products. On the other hand, it is clear that this mechanism for the C–H bond cleavage is oversimplified and its confirmation requires additional theoretical (or experimental) study.

V. Summary

The embedded cluster method combined with the MRD-CI procedure has been employed for the study of the photoinduced dissociation of a formaldehyde molecule adsorbed on the Ag(111) cluster that leads to the surface polymerization of H₂CO.

The computed PES of the adsorbed formaldehyde indicates that the molecule at its equilibrium geometry is tilted by an angle of ~30°–90° relative to the normal to the surface. Its binding energy to the Ag(111) surface is ~0.16 eV, which is in good agreement with the experimental data, and its equilibrium distance from the surface is ~6.5a₀. Adsorbed formaldehyde dissociation through C–O bond cleavage has a barrier on the reaction pathway of ~3.25 eV.

The n–π* excited state of formaldehyde is even less bound to the Ag surface than the ground state, and dissociation of adsorbed H₂CO* is unlikely either directly on the excited PES or after deexcitation to the ground state.

By contrast, the electron-attachment state is strongly bound to Ag(111) with a notably larger equilibrium C–O distance, r_{CO} ~ 2.5a₀, and a smaller equilibrium distance from the surface, R ~ 4a₀, than for neutral H₂CO. Although the formaldehyde anion cannot dissociate directly, it gains an excess of vibrational energy under excitation that is concentrated primarily in the C–O bond. Renutralization of the anion via an FC transition can lead to formation of the vibrationally excited ground state with energy above the dissociation barrier, and that makes subsequent C–O bond cleavage possible. Alternatively, the

molecule can desorb after the reneutralization, which can also occur at excitation energies below H₂CO dissociation threshold.

The estimated energy threshold of this dissociation process is about 3.6 eV. This value is slightly higher than the experimentally observed polymerization threshold of 3.1 ± 0.2 eV. The discrepancy may be caused by overestimation of the computed energy of the electron-attachment state as well as by using geometries for the intermediate formaldehyde state that have not been fully optimized in the present theoretical treatment.

It has been demonstrated that the lowest state of the O + CH₂ fragments on the Ag(111) surface is a closed-shell singlet. The optimized equilibrium geometry of the methylene radical adsorbed on Ag(111) has r_{C–H} ~ 2.12a₀ and an H–C–H angle of ~110°. The maximal binding energy in each case (3.2 and 1.2 eV for O and CH₂, respectively) has been found to occur for the hollow position.

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