Adsorption of Ethylene on Neutral, Anionic, and Cationic Gold Clusters

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The adsorption of ethylene molecules on neutral, anionic, and cationic gold clusters consisting of up to 10 atoms has been investigated using density functional theory. It is demonstrated that C2H4 can be adsorbed on small gold clusters in two different configurations, corresponding to the π- and di-σ-bonded species. Adsorption in the π-bonded mode dominates over the di-σ mode for all considered cluster sizes n, with the exception of the neutral C2H4–Au5 system. A striking difference is found in the size dependence of the adsorption energy of C2H4 bonded to the neutral gold clusters in the π and di-σ configurations. The important role of the electronic shell effects in the di-σ mode of ethylene adsorption on neutral gold clusters is demonstrated. It is shown that the interaction of C2H4 with small gold clusters strongly depends on their charge. The typical shift in the vibrational frequencies of C2H4 adsorbed in the π and di-σ configurations gives a guidance to experimentally distinguish between the two modes of adsorption.

Introduction

The adsorption of unsaturated hydrocarbons on transition-metal surfaces has been studied extensively in order to understand the nature of hydrocarbon–metal interaction and chemical processes on solid surfaces; see, e.g., refs 1–6 and references therein. The most significant attention was paid to the investigation of ethylene adsorption7–17 because it is the simplest alkene containing an isolated carbon–carbon double bond. Hence, it can be treated as a prototype to study the interaction and reactivity of different alkenes on metal surfaces. Moreover, the ethylene epoxidation is one of the most important processes in the chemical industry because the product of such a reaction—ethylene oxide—is widely used in various applications; see, e.g., refs 1, 2, and 18–21 and references therein.

Ethylene can adsorb on metal surfaces in two different configurations.1,11,12,14 The first one is the π mode where one metal atom on the surface is involved in the adsorption of ethylene via a π bonding. The second one is the di-σ-bonded mode, where two metal atoms are involved in the adsorption via a σ bonding. It was found that the di-σ mode of adsorption is characterized by the increasingly important role of sp3 hybridization in ethylene, whereas sp2 hybridization (typical for free molecules) remains unchanged for π-bonded species.11,12,14

The bonding of ethylene with transition metals involves electron transfer from the filled bonding π orbital of the ethylene to the metal, alongside a back-donation from the d orbital of the transition metal to the empty π* antibonding orbital of ethylene, in accordance with the Dewar–Chatt–Duncanson model.22 Thus, the appearance of the sp3 character of hybridization in the di-σ-bonded ethylene can be explained by the increasing role of the electron back-donation from the metal to the π* antibonding orbital of ethylene. Hence, the di-σ-bonded ethylene is activated more strongly in comparison with the π-bonded one; thus, it can be more reactive.11,12 Therefore, an understanding of the specific mechanisms of ethylene adsorption on metal surfaces is important in order to gain a better insight of the catalytic processes and reactivity of adsorbed hydrocarbons.

Surprisingly, not many studies have been devoted to the investigation of ethylene adsorption on metal clusters and nanoparticles, despite the fact that chemical and physical properties of matter at nanoscale are very different from those of the corresponding bulk solids. These properties are often controlled by quantum size effects and significantly depend on the size and structure of atomic clusters.23

A remarkable example is gold. It is well-known that gold in its bulk form is a catalytically inactive and inert metal. However, gold at nanoscale manifests extraordinary catalytic activity that increases with a decrease in the cluster size of up to 1–5 nm.24–27 Moreover, recent studies demonstrate that catalytic activity of gold clusters adsorbed on an iron oxide support correlates with the presence of very small clusters of ∼10 atoms.28 It was also reported that gold clusters with the number of atoms n = 3–11 possess extraordinarily high electrocatalytic activity toward the O2 reduction reaction in acid solutions.29

The origin of such size-dependent catalytic activity of gold remains highly debated and has yet to be fully understood. A comprehensive survey of the field can be found in review papers and books; see, e.g., refs 23 and 30–34. It was demonstrated that the catalytic activity of gold clusters depends on the type of the support material, the presence of defects in the material (e.g., F-center defects), the environment, and doping or special additives; see, e.g., refs 25, 31, and 35–38 and references therein. However, experiments indicate that gold clusters deposited on an inert support can efficiently catalyze the process of styrene oxidation by dioxygen.27 Hence, the origin of catalytic activity derives from the cluster itself, and therefore, even free clusters can be effective catalysts.

Currently, a large variety of catalytic reactions on gold clusters have been studied experimentally. This includes the processes of catalytic oxidation of carbon monoxide, as well as...
Adsorption in the C2H4, exhibits pronounced odd
on small gold clusters.44 The obtained theoretical data on
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Wang 91 correlation functional (B3PW91)46 is used. The choice
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Theoretical Methods
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the B3PW91 functional is consistent with our previous work on
cooperative adsorption and catalytic oxidation of ethylene
on small gold clusters.44 The obtained theoretical data on
dissociation energies and bonding in Au2 (1.904 eV, 2.546 Å)
and C2H4 (7.596 eV, 1.324 Å) are in a good agreement with
those of earlier experimental studies, Au2 (2.30 eV, 2.472 Å)47
and C2H4 (7.76 eV, 1.339 Å).48 The standard LANL2DZ basis
set of primitive Gaussians is used to expand the gold cluster
orbitals formed by the 5s²5p⁶5d¹⁰6s¹ outer electrons of Au (19
electrons per atom). The remaining 60 core electrons of the Au
atom are represented by the Hay–Wadt effective core potential
accounting for relativistic effects.49 For carbon and hydrogen,
the aug-cc-pVTZ basis set50 is employed. The single-point
counterpoise correction method has been used to calculate the
basis set superposition errors (BSSE). The zero-point energy
(ZPE) corrections have been analyzed. Calculations have been
carried out with the use of the Gaussian 03 code.51

The structural properties of neutral, anionic, and cationic gold
clusters have been the subject of numerous theoretical investiga-
tions; see, e.g., refs 30–32 for a review. In the present work,
the cluster geometries have been determined with the use of
the cluster fusion algorithm52 that belongs to the class of genetic
global optimization methods.53,54 We have successfully used a
similar approach to find the optimized geometries of various
types of atomic clusters.55–60 Additionally, the global reaction
route mapping (GRRM) technique within the scaled hypersphere
search (SHS) method has been used in order to find equilibrium
structures.55–57 The optimized structures of the gold clusters Au,n,
Auₙ⁻, and Auₙ⁺ (n = 1–10) obtained in the present work are
presented in the Supporting Information to this paper. These
structures are in good agreement with those reported in previous
theoretical studies; see, e.g., refs 32 and 61–64.

To obtain the most stable configuration of C2H4 adsorbed
on neutral, anionic, and cationic gold clusters, we have created a
large number of starting geometries by adding the C2H4
molecule in different positions (up to 30) on the surface of the
most stable cluster and up to eight isomer structures of the
corresponding Auₙ, Auₙ⁻, and Auₙ⁺ clusters. The starting
structures have been optimized further without any geometry
constraints.

Theoretical Results

Geometry Optimization for Ethylene Adsorbed on Neutral,
Cationic, and Anionic Gold Clusters. The results of the cluster
group geometry optimization for neutral C2H4–Auₙ, anionic
C2H4–Auₙ⁻, and cationic C2H4–Auₙ⁺ clusters within the size
range of n ≤ 10 are shown in Figures 1–3, respectively.

Gold clusters with adsorbed ethylene possess various isomer
forms whose number grows dramatically with cluster size.
Among the huge variety of different isomers, one can distinguish
two specific adsorption modes that correspond to the ω and di-σ

![Figure 1](image)

Figure 1. Optimized geometries of neutral C2H4–Auₙ clusters: (a) ω mode of adsorption and (b) di-σ mode of adsorption (in the case of a single Au atom, only one σ bond is formed). The C–C and C–Au
interatomic distances are given in angstroms.
configurations of the adsorbate. The appearance of two different modes of ethylene adsorption on small gold clusters is similar to that reported for ethylene adsorption on Au(100) and Au(111) surfaces. However, in the case of adsorption on the bulk, there are only two possible geometrical configurations of ethylene (we do not consider here $\mu$-bridging species because ethylene adsorption in such a configuration is not possible in the case of small clusters). Moreover, there are no structural changes of the bulk surface due to adsorption of ethylene. In the case of ethylene adsorption on small gold clusters, each of the $\pi$ and di-$\sigma$ configurations possesses a variety of structural isomers. These isomers correspond to the adsorption in nonequivalent positions on the surface of clusters. In Figures 1–3, we present the most stable structures of $\pi$- and di-$\sigma$-bonded ethylene adsorbed on small gold clusters. The C-C and C-Au interatomic distances are given in angstroms.

The interaction of gold clusters with ethylene results in an electron donation from the C2H4 to the gold cluster alongside a back-donation from the cluster to the adsorbate, in accordance with the Dewar– Chatt–Duncanson model. The rearrangement of the electronic structure and electron transfers upon adsorption lead to a dramatic change in cluster geometry. The interplay of electronic and geometry shell effects also influences the cluster structure. Free neutral gold clusters possess planar, two-dimensional (2D) structures when the cluster size is up to 13 Au atoms. In the Supporting Information, we present the most stable structures obtained for Au$_n$, Au$_n^+$, and Au$_n^-$ clusters ($n = 1$–$10$) within the B3PW91/LANL2DZ DFT method. Figure 1 demonstrates that the adsorption of C2H4 in the $\pi$ configuration leads to a prevalence of three-dimensional (3D) structures of gold clusters for $n \geq 9$; the structures of small Au$_3$ and Au$_4$ clusters transform to those that are energetically favorable for free cations, Au$_3^+$ and Au$_4^+$, respectively. For $n < 9$, ethylene favorably adsorbs at the cluster edge where the carbon–carbon bond lies in the plane of the cluster, with the exception of the C2H4–Au$_6$ system, where the carbon–carbon bond is located perpendicular to the cluster plane (see Figure 1).

The adsorption of C2H4 in the di-$\sigma$ configuration results in a considerable rearrangement in the structure of neutral gold clusters. Thus, the geometry of Au$_3$ and Au$_6^-Au_{10}^-$ clusters changes upon C2H4 adsorption. It is known that gold clusters possess a large number of energetically close-lying structural isomers. Interaction with the adsorbate can easily alter their energy order. It is important to note that interaction with the adsorbate can be responsible for structural rearrangements even for the relatively large clusters. Thus, recent DFT calculations demonstrate that the morphology of the Au$_{79}$ nanoparticle can be transformed by interactions with a CO atmosphere.

It is not surprising that the structures of positively and negatively charged ionic gold clusters change upon ethylene adsorption. Figure 2 demonstrates that, although anionic gold clusters Au$_n^-$ with $n = 1$–$10$ remain planar upon ethylene adsorption (for both the $\pi$ and the di-$\sigma$ adsorption configurations), they manifest considerable structural rearrangements. Thus, gold cluster anions alter their structure upon ethylene adsorption in the $\pi$ configuration for $n = 4$, 7, 8, and 10. In the case of the di-$\sigma$ mode of ethylene adsorption, structural rearrangements occur for gold cluster anions with $n = 3$–8. A carbon–carbon bond of the adsorbed ethylene lies in a cluster plane for all structures presented in Figure 2.

Figure 3 shows that, in the case of ethylene adsorption on gold cluster cations, Au$_n^+$, the resulting cluster systems...
C$_2$H$_4$—Au$^+$ exhibit 3D structures for $n = 5–10$, in the case of the $\pi$ mode of ethylene adsorption, and $n = 8$ and 10, in the case of the di-$\sigma$ mode. In both cases of the $\pi$ and di-$\sigma$ modes of ethylene adsorption, the structural rearrangements in gold cluster cations occur for $n \geq 5$.

Such a severe change in the morphology of gold clusters due to the interaction with ethylene makes the procedure of structural optimization rather complicated. To get energetically favorable structures of C$_2$H$_4$—Au$_n$, C$_2$H$_4$—Au$^{-}$, and C$_2$H$_4$—Au$_n^+$ clusters, it is necessary to consider the adsorption of ethylene not only on the most stable structures of the corresponding Au$_n$, Au$^{-}$, and Au$_n^+$ clusters but also on a large number of their energetically less favorable isomer states. In the present work, we have taken into account up to eight isomer structures of the host gold clusters. This insures that we do not miss energetically favorable structures with considerable change in cluster geometry due to C$_2$H$_4$ adsorption.

Energetics of Ethylene Adsorption on Neutral, Anionic, and Cationic Gold Clusters. We first study the energetics of C$_2$H$_4$ adsorption on neutral gold clusters Au$_n$ with $1 \leq n \leq 10$. The spin states of the optimized C$_2$H$_4$—Au$_n$ structures are doublet and singlet for odd and even $n$, respectively. The adsorption energy is defined as

$$E_{\text{ads}} = E_{\text{tot}}(\text{Au}_n) + E_{\text{tot}}(\text{C}_2\text{H}_4) - E_{\text{tot}}(\text{Au}_n - \text{C}_2\text{H}_4),$$

(1)

where $E_{\text{tot}}(\text{M})$ denotes the total energy of the most stable structure of the molecule (cluster) “M”.

Table 1 reports the molecular adsorption energies, $E^\text{ads}$, and $E^\text{ads, ZPE}$, calculated for C$_2$H$_4$ adsorbed on the neutral Au$_n$ clusters as the $\pi$ and di-$\sigma$ species, respectively. The adsorption energies modified with corrections for zero-point vibrational energy ($E^\text{ads, ZPE}$) and basis set superposition errors ($E^\text{ads, BSSE}$) are also listed in Table 1.

It has been shown that the ZPE and BSSE corrections can slightly modify the adsorption energy of O$_2$ on small binary alloy clusters of gold. In the case of the adsorption of C$_2$H$_4$ on gold clusters, the above corrections, in principle, can affect differently the $\pi$ and di-$\sigma$ configurations. Therefore, to clarify this effect, we have employed the ZPE and BSSE corrections in the adsorption energy of C$_2$H$_4$ on Au$_n$. We found that the ZPE correction systematically reduces adsorption energy of ethylene on gold clusters by 0.06–0.08 eV, irrespective of adsorbate configuration. The BSSE corrections reduce the ethylene adsorption energy by 0.14–0.17 eV. Although the ZPE and BSSE corrections slightly modify absolute values of the adsorption energy of C$_2$H$_4$ bonded to neutral gold clusters, they do not change the general behavior of $E^\text{ads}$ and $E^\text{ads, ZPE}$ as a function of cluster size. A similar conclusion on the role of BSSE corrections in the adsorption of ethylene and formaldehyde on small gold clusters has been made in ref 45. Therefore, all results reported below are presented without ZPE and BSSE corrections.

Figure 4 shows the evolution of the molecular adsorption energy, $E_{\text{ads}}$, calculated for the most bound $\pi$ and di-$\sigma$ configurations of adsorbed C$_2$H$_4$ as a function of cluster size $n$.

In our previous work, we have studied the adsorption of ethylene on small neutral gold clusters in the $\pi$-bonded configuration. Here, we demonstrate that C$_2$H$_4$ can be adsorbed on small gold clusters in two different configurations, corresponding to the $\pi$- and di-$\sigma$-bonded species. Figure 4 shows that the $\pi$-bonded mode of C$_2$H$_4$ adsorption is energetically favorable in the considered range of cluster sizes $n$, with the exception of a single Au atom that interacts with one carbon atom in C$_2$H$_4$, forming a $\sigma$ bond, and the Au$_5$ cluster, where the di-$\sigma$-bonded configuration of C$_2$H$_4$—Au$_5$ is 0.05 eV more bounded compared with the $\pi$-bonded one. A similar behavior of $E^\text{ads}$ and $E^\text{ads, ZPE}$ as a function of cluster size has been reported recently for small gold clusters consisting up to 5 atoms.

It is seen from Figure 4 that the adsorption energy of the $\pi$-bonded C$_2$H$_4$ on Au$_n$ clusters exhibits a maximum at $n = 3$ and 4, followed by a fast drop with a minimum at $n = 6$. For $6 \leq n \leq 10$, the adsorption energy of $\pi$-bonded C$_2$H$_4$ shows a weak oscillatory behavior as a function of $n$.

The $n$ evolution of the adsorption energy calculated for the di-$\sigma$-bonded C$_2$H$_4$ is considerably different from that of the $\pi$-bonded C$_2$H$_4$. Figure 4 demonstrates that the adsorption energy of the di-$\sigma$-bonded C$_2$H$_4$ has an odd—even oscillatory behavior with a local maxima for odd numbers of Au atoms at $n = 3, 5, 7,$ and $9$. For clusters with an even number of $n$, the adsorption energy $E_{\text{ads}}$ of the di-$\sigma$-bonded C$_2$H$_4$ is small. Hence, C$_2$H$_4$ readily adsorbs in the di-$\sigma$ configuration—but only for neutral gold clusters with an odd number of Au atoms.

It is interesting to note that, in the case of C$_2$H$_4$ adsorption on a Au(111) surface, the di-$\sigma$ mode ($E^\text{ads}_{d\sigma} = 0.6502$ eV) is energetically more favorable in comparison with the $\pi$ mode ($E^\text{ads}_{\pi} = 0.1545$ eV). A similar effect is observed for C$_2$H$_4$ adsorbed on a Au(100) surface where theoretical values of $E^\text{ads}_{d\sigma} = 0.7790$ eV and $E^\text{ads}_{\pi} = 0.2456$ eV have been reported. It is known that the type of C$_2$H$_4$ bonding depends upon the surface structure. It has been found that the $\pi$-bonded mode dominates in the adsorption of low-coordinated atoms and step
The total charge transfer to the adsorbed C\textsubscript{2}H\textsubscript{4} depends on the balance between the donation and back-donation processes. Figure 6 demonstrates that, in the case of the \( \pi \) mode of adsorption, the total charge transfer \( \Delta q^{C_{2}H_{4}} \) is relatively small and evolves with \( n \) similar to \( r_{c-C} \). For the di-\( \sigma \) mode of adsorption, the back-donation from the gold to the \( \pi^{*} \) antibonding orbital of ethylene dominates over electron transfer from C\textsubscript{2}H\textsubscript{4} to the cluster. The total charge transfer to C\textsubscript{2}H\textsubscript{4} adsorbed in a di-\( \sigma \) configuration is large and varies in the range of 0.29–0.43 au for \( n = 2–9 \). It is seen from Figure 6 that \( \Delta q^{C_{2}H_{4}} \) calculated for the di-\( \sigma \)-bonded C\textsubscript{2}H\textsubscript{4} exhibits pronounced odd–even oscillations as a function of cluster size \( n \), with the exception of \( n = 1 \). Note that, for \( n = 1 \), the charge transfer \( \Delta q^{C_{2}H_{4}} \) is small because, in this case, only one Au–C \( \sigma \) bond is formed. Similar odd–even oscillations have been found in the \( n \) dependence of the adsorption energy of O\textsubscript{2} on Au\textsubscript{6} clusters; see, e.g., refs 23, 61, and 70 and references therein. However, the adsorption energy of CO does not present any odd–even effects.\textsuperscript{70}

The appearance of the odd–even oscillations in \( E_{ads} \) and \( \Delta q^{C_{2}H_{4}} \) for the di-\( \sigma \) mode of adsorption is a result of the electronic shell effects\textsuperscript{3,2,7,2} in the gold clusters and can be described within the jellium model. Despite its simplicity, the jellium model can explain, at least on the qualitative level, many physical properties and chemical reactivity of metal clusters.\textsuperscript{3,2,7,2}

Indeed, each Au atom has one 6s electron that delocalizes in the whole volume of the cluster. The delocalized electrons are moving in the field of a uniform positive charge background, which binds the valence electron cloud. The gold clusters with an even number of atoms (valence electrons) have a closed electronic shell structure. Hence, these clusters are more stable and less reactive in comparison with open shell clusters possessing an odd number of atoms (valence electrons).

The prevalence of the electron transfer from the cluster to the adsorbate (back-donation process) is responsible for the promotion of the di-\( \sigma \) mode of C\textsubscript{2}H\textsubscript{4} adsorption. Indeed, the di-\( \sigma \) mode of C\textsubscript{2}H\textsubscript{4} adsorption on small gold clusters with an odd number of atoms leads to the transfer of an unpaired electron from the gold cluster to the ethylene antibonding \( \pi^{*} \) orbital, causing the weakening of the C–C bond. The neutral gold clusters with an even number of valence electrons possess a closed electronic shell structure; hence, electron transfer to the adsorbate and formation of the di-\( \sigma \)-bonded species is suppressed.

Figure 7 demonstrates the evolution of molecular adsorption energy, \( E_{ads} \), and C–C bond distances, \( r_{C-C} \), as a function of cluster size \( n \) for C\textsubscript{2}H\textsubscript{4} adsorbed on the anionic Au\textsubscript{n}\textsuperscript{−} (left column) and cationic Au\textsubscript{n}\textsuperscript{+} (right column) clusters with \( 1 \leq n \leq 10 \).

The adsorption energy of C\textsubscript{2}H\textsubscript{4} on a gold cluster depends on the balance between donation and back-donations processes; hence, it can be manipulated by the cluster charge. It is seen from Figure 7a,b that excess of the negative or the positive charges on gold clusters strongly influences the molecular adsorption. Thus, the interaction of C\textsubscript{2}H\textsubscript{4} with the negatively charged gold clusters Au\textsubscript{n}\textsuperscript{−} becomes weaker if compared with the neutrals, whereas excess of the positive charge results in strengthening of the C\textsubscript{2}H\textsubscript{4} and Au\textsubscript{n}\textsuperscript{+} bond.

Figure 7a demonstrates that the \( \pi \) mode of C\textsubscript{2}H\textsubscript{4} adsorption is not stable for Au\textsuperscript{−} and Au\textsubscript{+}. The adsorption energy of the \( \pi \)-bonded C\textsubscript{2}H\textsubscript{4} on the gold cluster anions Au\textsubscript{n}\textsuperscript{−} is 0.17 eV, in the case of a trimer Au\textsubscript{3}\textsuperscript{−}, and this increases with an increase

\( \sigma \)-bonded ethylene is activated strongly in comparison with the \( \pi \)-bonded one; thus, it can be more reactive in catalytic processes.
in the cluster size: up to 0.82 eV at \( n = 7 \) and dropping to 0.54 eV at \( n = 8 \), while slowly increasing with an increase in the cluster size up to \( n = 10 \).

Figure 7b shows that the size dependence of \( E_{ads} \) for \( \pi \)-bonded \( \text{C}_2\text{H}_4 \) on the gold clusters cations \( \text{Au}_n^+ \) is very different from that of \( \text{Au}_n^- \). Thus, \( \text{C}_2\text{H}_4 \) readily adsorbs on the cationic monomer \( \text{Au}^+ \) and dimer \( \text{Au}_2^+ \) with an adsorption energy of 2.95 and 3.58 eV, respectively. Further increase in cluster size results in the sharp decrease in \( E_{ads} \) up to 2.06 eV for \( n = 3 \), followed by its slow decrease for \( 3 \leq n \leq 6 \). At \( n = 7 \), the adsorption energy \( E_{ads} \) exhibits a maximum, followed by the second sharp decrease at \( n = 8 \) and 9.

For any \( n \) in the range of \( 1 \leq n \leq 10 \), the adsorption energy of the \( \pi \)-bonded \( \text{C}_2\text{H}_4 \) on cationic, \( E_{ads}^\pi(\text{Au}_n^+) \), neutral, \( E_{ads}^\pi(\text{Au}_n) \), and anionic, \( E_{ads}^\pi(\text{Au}_n^-) \), gold clusters satisfies the relation: \( E_{ads}^\pi(\text{Au}_n^-) > E_{ads}^\pi(\text{Au}_n) > E_{ads}^\pi(\text{Au}_n^+) \).

Indeed, the excess of the positive charge on the cluster favors the process of electron transfer from the \( \text{C}_2\text{H}_4 \) to the gold cluster, which stabilizes the \( \pi \) mode of adsorption and strengthens the \( \text{Au}^-\text{C} \) bond. A similar effect has been found for the adsorption of \( \text{CO} \) on small anionic and cationic gold clusters.\(^{75,76} \) It was found that the adsorption energy of \( \text{CO} \) is larger in the case of a cluster of cations and smaller in the case of anions. With the increasing cluster size, the differences in adsorption energies for different charge states become smaller.\(^{76} \)

It is important to mention that strengthening the \( \text{Au}^-\text{C} \) bond for \( \text{C}_2\text{H}_4 \) adsorbed on the gold clusters with an excess of the positive charge is responsible for a cooperative effect in the simultaneous adsorption of \( \text{C}_2\text{H}_4 \) and \( \text{O}_2 \) on neutral gold clusters.\(^{44} \) Indeed, the adsorption of \( \text{O}_2 \) on \( \text{Au}_n^- \) results in an electron transfer from the gold cluster to the antibonding \( 2\pi^* \) orbital of \( \text{O}_2 \). In this case, \( \text{C}_2\text{H}_4 \) effectively adsorbs on the positively charged gold cluster. A similar effect has also been predicted for the adsorption of propene on \( \text{O}_2^-\text{Au}_n^- \) clusters.\(^{41} \) It was supposed that the binding of propene to \( \text{O}_2^-\text{Au}_n^- \) should be stronger than the binding to the \( \text{Au}_n^- \) due to the effective charge transfer from the gold cluster to the oxygen molecule.\(^{41} \)

The excess of the positive or the negative charge on gold clusters results in a considerable change in the adsorption energy of the \( \text{di-}\sigma \)-bonded \( \text{C}_2\text{H}_4 \). As has been discussed above, the adsorption energy of the \( \text{di-}\sigma \)-bonded \( \text{C}_2\text{H}_4 \) on small neutral gold clusters exhibits odd—even oscillations as a function of the cluster size. These oscillations appear as a result of the electronic shell effects in gold clusters: \( \text{Au}_n \) with an odd \( n \) have one unoccupied electron that can easily transfer to the empty \( \pi^* \) antibonding orbital of \( \text{C}_2\text{H}_4 \). Such an electron transfer favors the \( \text{di-}\sigma \) configuration of the adsorbed \( \text{C}_2\text{H}_4 \).

Figure 7a demonstrates that there is no odd—even oscillation in the adsorption energy of the \( \text{di-}\sigma \)-bonded \( \text{C}_2\text{H}_4 \) on the anionic \( \text{Au}_{10}^- \) clusters. In that case, the cluster always possesses a weakly bounded electron that can transfer to the adsorbate.

In the case of the cationic \( \text{Au}_{n+}^+ \) clusters, the electron back-donation process to \( \text{C}_2\text{H}_4 \) is suppressed for any \( n \). Figure 7b shows that \( E_{ads} \) calculated for the \( \text{di-}\sigma \)-bonded \( \text{C}_2\text{H}_4 \) on \( \text{Au}_{n+}^- \) exhibits two profound minima at \( n = 3 \) and 9. In accordance with the spherical jellium model, \( \text{Au}_3^+ \) and \( \text{Au}_9^+ \) clusters possess a closed shell electronic structure with two and eight valence electrons, respectively. Hence, \( \text{Au}_3^+ \) and \( \text{Au}_9^+ \) are chemically inactive, in particular, in the processes where electron transfer from the cluster to the adsorbate is responsible for formation of the chemical bond.

Figure 7c,d demonstrates the \( n \) evolution of the \( \text{C}^-\text{C} \) bond distance, \( r_{C-C} \), in \( \text{C}_2\text{H}_4 \) adsorbed on \( \text{Au}_{n+}^- \) and \( \text{Au}_{n+}^+ \) clusters, respectively. The \( \text{C}^-\text{C} \) bond in the \( \pi \)-bonded \( \text{C}_2\text{H}_4 \) on the anionic and the cationic clusters is enlarged up to 1.36–1.40
The anharmonic corrections can be taken into account, for example, by the vibrational self-consistent field method based on the quartic force field. However, such a consideration goes far beyond the scope of the present paper. To distinguish between $\pi$ and $\sigma$ modes of C$_2$H$_4$ adsorption, one should calculate the shift in the C–C stretching frequencies of the adsorbed C$_2$H$_4$ with respect to the free molecule. In that case, the anharmonic corrections to the vibrational energy levels can be partly canceled. Therefore, in this paper, we perform an analysis of the vibrational spectra of the adsorbed C$_2$H$_4$ in the harmonic approximation.

Following ref 11, we have selected two vibrational modes: $v_6$ and $v_8$, corresponding to the direct C–C and the in-plane CH$_2$ scissoring modes of vibrations, respectively. Information on the shift of the vibrational frequencies of C$_2$H$_4$ upon its adsorption can be obtained from infrared or Raman spectroscopy. Figure 8 presents the frequency dependence of the Raman scattering activity calculated for a C$_2$H$_4$ molecule adsorbed in the $\pi$ (Figure 8a) and $\sigma$ (Figure 8b) configurations on the neutral Au$_n$ clusters with $n = 1$–10. The stretching modes corresponding to the $v_6$ and $v_8$ vibrations in C$_2$H$_4$ are marked by the vertical arrows. It is seen from Figure 8a that the spectral dependences of the Raman scattering activity calculated for the $\pi$-bonded ethylene on Au$_n$ clusters are similar for all the cluster sizes $n$ considered. The first maximum at 960 cm$^{-1}$ corresponds to the symmetric and asymmetric swinging of H atoms in the direction perpendicular to the plane of C$_2$H$_4$—similar to the $v_2$ and $v_3$ vibrational modes in free C$_2$H$_4$. These vibrations remain unchanged in the $\pi$-bonded C$_2$H$_4$. Two intensive maxima at 1280 and 1560 cm$^{-1}$ correspond to the $v_6$ and $v_8$ vibrational modes in C$_2$H$_4$. These lines are red shifted in comparison with the free C$_2$H$_4$.

Solid lines in Figure 9 demonstrate shifts $\Delta \nu_6^\pi$ and $\Delta \nu_8^\pi$ in harmonic frequencies $v_6$ and $v_8$ due to the $\pi$ mode of C$_2$H$_4$ adsorption on small neutral gold clusters. For the $\pi$-bonded C$_2$H$_4$, the scissoring mode $v_6$ is shifted by 30–40 cm$^{-1}$ toward low frequencies if compared with the $v_6$ mode. Both the $\Delta \nu_6$ and the $\Delta \nu_8$ shifts vary in the range of 58–142 cm$^{-1}$ and exhibit a similar dependence on the cluster size with local minima at $n = 6$ and 8. The relatively small frequency shifts, $\Delta \nu_6$ and $\Delta \nu_8$, correspond to the values of the $\pi\sigma$ parameter typical for the $\pi$-bonded C$_2$H$_4$.

Figure 8 demonstrates that the spectral behavior of the Raman scattering activity calculated for the $\sigma$-bonded C$_2$H$_4$ is different from that obtained for the $\pi$-bonded C$_2$H$_4$. Thus, for cluster sizes $n = 2, 4, 5, 7,$ and 9, a broad band appears in the frequency region of 900–1300 cm$^{-1}$. This band results from the strong mixing of the C–C stretching mode $v_6$ of the hydrogen swinging ($v_2$ and $v_3$) and twisting ($v_4$) modes. The coupling of the $v_2, v_3, v_4$, and $v_6$ vibrational modes occurs as a result of considerable deformations in C$_2$H$_4$. These deformations include the bending of H atoms with respect to the plane of a free C$_2$H$_4$ due to the sp$^3$ hybridization in di-$\sigma$-bonded C$_2$H$_4$, as well as the twisting of CH$_2$ groups with respect to each other along the C–C bond. Such twisting is especially noticeable for C$_2$H$_4$–Au$_n$ and C$_2$H$_4$–Au$_{1-n}$ clusters. The strong coupling between different vibrational modes makes identification of $v_6$ and $v_8$ vibrations rather difficult: the mixed modes form new levels, neither of which represents the true $v_6$ and $v_8$ states.

The appearance of the sp$^3$ hybridization character in di-$\sigma$-bonded C$_2$H$_4$ results in a considerable red shift in the stretching frequencies. Such shifts, $\Delta \nu_6^{\sigma - \sigma}$ and $\Delta \nu_8^{\sigma - \sigma}$, in harmonic frequencies $v_6$ and $v_8$ are shown by the dashed lines in Figure 9.

It is seen that the $\Delta \nu_6^{\sigma - \sigma}$ shift is considerably larger than the $\Delta \nu_8^{\sigma - \sigma}$, which can be explained by the strong coupling between the $v_2, v_3, v_4$, and $v_6$ vibrational levels. The $\Delta \nu_6^{\sigma - \sigma}$ and $\Delta \nu_8^{\sigma - \sigma}$ frequency shifts vary in the range of 200–370 cm$^{-1}$ for $n = 2$–10. These values correspond to the $\pi\sigma$ parameter typical for the $\sigma$-bonded C$_2$H$_4$. Thus, the analysis of the vibrational modes of C$_2$H$_4$ adsorbed on gold clusters allows one to identify the specific modes of C$_2$H$_4$ adsorption and the rate of rehybridization upon adsorption.

**Conclusions**

In summary, we have demonstrated that C$_2$H$_4$ can be adsorbed on small gold clusters in two different configurations, corresponding to the $\pi$- and $\sigma$-bonded species. Adsorption in the $\pi$-bonded mode dominates over the $\sigma$-mode over all considered cluster sizes $n$, with the exception of the neutral...
We found a striking difference in the size dependence of the adsorption energy of C2H4 bonded to neutral gold clusters in the \( \pi \) and di-\( \sigma \) configurations. The adsorption energy, calculated for the di-\( \sigma \)-bonded C2H4, exhibits pronounced odd–even oscillations, showing the importance of the electronic shell effects in the di-\( \sigma \) mode of ethylene adsorption on gold clusters. The different rates of hybridization in the \( \pi \)- and di-\( \sigma \)-bonded C2H4 can be responsible for the different rates of catalytic activation and, hence, different reactivities of adsorbed C2H4.

We have also demonstrated that the interaction of C2H4 with small gold clusters strongly depends on the cluster charge. Hence, ethylene adsorption and reactivity can be manipulated by the cluster charge. The strengthening of the ethylene–cluster interaction for gold clusters with an excess of the positive charge is responsible for the cooperative effect in the simultaneous adsorption of C2H4 and O2 on neutral gold clusters. This effect can play an important role in the mechanism of catalytic oxidation of alkenes by dioxygen on the surface of gold clusters.

Finally, we have shown that the analysis of the vibrational modes of C2H4 adsorbed on gold clusters allows one to identify the specific modes of C2H4 adsorption, the rate of rehybridization upon adsorption, and thus the C2H4 reactivity.

In the present work, we have considered the adsorption of ethylene molecules onto small gold clusters consisting of up to 10 atoms. Many interesting problems beyond the scope of the present work arise when considering multiple molecular adsorptions on gold nanoparticles with larger sizes up to 1–5 nm, where the strong dependence of the catalytic activity of gold nanoparticles has been observed experimentally. In particular, multiple molecular adsorptions on the surface of gold nanopar-

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**Figure 8.** Raman scattering activity of the neutral C2H4–Au\(_n\) clusters: (a) \( \pi \)-bonded C2H4 and (b) di-\( \sigma \)-bonded C2H4. Gaussian broadening of half-width 45 cm\(^{-1}\) has been used. The stretching modes corresponding to the \( \nu_6 \) and \( \nu_8 \) vibrations in C2H4 are marked by the vertical arrows. Note that, in the case of a single Au atom, only one \( \sigma \) bond is formed.
particles can result in a considerable change in cluster morphology, even for relatively large cluster sizes.

Another important direction for future development is to investigate the effect of alloying on the adsorption and catalytic activation of alkenes on gold clusters. The doping of a gold cluster with an atomic impurity can result in considerable changes in the geometrical and electronic structure of the cluster, thereby modifying and controlling the catalytic activity. Understanding how to enhance and control chemical reactions on a cluster surface is, therefore, a vital task for nanocatalysis.

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Supporting Information Available: Figure of the optimized structures of the most stable neutral, anionic, and cationic gold clusters calculated within the size range of $1 \leq n \leq 10$ in the B3PW91/LanL2DZ approximation. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes


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