Geometrical, energetic and electronic properties of Au_n–$(C_3H_6O)_m$ complexes ($n = 3, 5, m \leq n$): A density functional theory study*

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The interactions of acetone molecules with clusters of Au_3 and Au_5 are investigated by using a density functional theory (DFT) within a generalized gradient approximation (GGA). The geometries, adsorption energies and deformation electron density distributions are used to analyse these interactions. The present calculations show that more than one acetone molecule can be adsorbed onto small gold clusters, and this adsorption is different from that of single molecule absorption. The coordination number of the adsorption site on the gold cluster is the dominant factor responsible for the strength of the interactions. The effects of the Au–O bond lengths in the complexes on adsorption energies between Au clusters and acetone molecules are also examined.

Keywords: acetone molecule, gold cluster, complex, adsorption

PACC: 3640C, 3640B, 3120A

1. Introduction

The gold nanoparticles, being nontoxic and highly biocompatible, are attractive candidates for therapeutic drug delivery vehicles.[1] Several recent reports have focused on their applications in DNA sequencing and also as microscopy markers.[2] They can also be used as potential building blocks for functional nanostructured materials, electronic devices, and nanocatalysts.[3−5] There are several reactions that can occur on nanoparticles, such as catalysis, corrosion, coating, etc., and because these involve adsorption as the first step, the adsorption of small molecules onto nanoparticles has been quite thoroughly studied. Adsorptions of a range of organic molecules, including benzene thiol, thiolate,[6] methanol molecules,[7,8] acetone, diethyl ketone, acetaldehyde,[9] linear molecules of (poly) alkane,[10] planar molecules of thipphene or (poly) pheny thiol/thiolate to gold particles have been investigated.[11−15] In addition, a number of experimental and theoretical investigations have been carried out on adsorption of inorganic molecules such as carbon monoxide,[16] hydrogen,[17,18] oxygen,[19,20] among others.

In a recent experiment, Shankar *et al.*[21] have reported that gold nanoparticles synthesized in the presence of aldehydes/ketones can result in the formation of flat gold platelets with a fluid-like surface. Similar results were observed in the presence of acetone.[22] However, little is known about the strength and nature of the interaction between acetone and gold nanoparticles. Most recently, using a density functional theory (DFT) method within the local density approximation (LDA), Shafai *et al.*[9] have investigated the interaction of Au_n (n = 2, 3, 5, 7, 9, and 13) clusters and one acetone molecule. Their results showed that carbonyl oxygen is the preferred adsorption site of acetone molecule. They also found that the variation in the adsorption energies (AEs) closely follows the variation of the Au–O bond lengths as the size of gold cluster increases. Furthermore, an Au–H bond was observed in the study of the interaction of DNA bases with gold clusters.[23]

The complexes of metal clusters and several organic molecules are also interesting subjects. In a recent study by Hirabayashi *et al.*,[24] structures of nickel cluster ions adsorbed with methanol, Ni^{3+}–$(CH_3OH)_m$ (m = 1–3) and Ni^{4+}–$(CH_3OH)_m$ (m = 1–4), were studied using infrared photodissociation (IRPD) spectroscopy. The authors also performed the corresponding calculations by the density functional theory and showed that, for the Ni^{3+}–$(CH_3OH)_m$ (m = 1–3) complexes, the length of the Ni–O bond increases and the adsorption energy decreases as m

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increases. In addition, the spectra of OH stretching vibration for these three complexes have various degrees of red-shift beyond that of a free methanol molecule. Thus, the properties of the complexes containing one organic molecule may be different from those containing several molecules, which makes its necessity to investigate multi-molecule adsorptions.

As we know, there is no report on interactions of one gold cluster and several acetone molecules. Therefore, the present work strives to investigate this kind of interactions through calculating and analysing the geometrical, energetic and electronic properties of the complexes. Au_3 and Au_5 clusters are chosen as the adsorption hosts in the present investigations, because Au_3 is the simplest model holding the equivalent adsorption sites, while Au_5 cluster is different. It is expected that these investigations will provide a better understanding of the interactions among gold clusters and acetone molecules.

2. Computational details

All calculations in this study are performed by DFT code DMol^3 as implemented in the Materials Studio.[25−27] Double numerical quality basis sets with polarization functions (DNP) are used. The DNP basis sets are comparable to 6-31G** sets, and the numerical basis set is much more accurate than a Gaussian basis set of the same size. Here, P refers to include the polarizing functions. For H atoms, p-functions are included, while for C and O atoms, d-functions are used. For Au atom, f-functions are also included. Because it is a heavy element, relativistic effects become important in the core electrons. One method of incorporating these effects is to use the all electron relativistic option. As the name implies, the core electrons are still included in the calculation, but scalar relativistic effects are added in.[28,29] This is time-consuming but can yield a more accurate calculation results. Since the total electrons are odd, spin unrestricted calculations are used. The gradient corrected approach using the generalized approximation (GGA) is applied for exchange and correlation in the manner suggested by Perdew–Burke–Ernzerhof (PBE).[30,31] Delley[32] confirmed that the PBE functional with the efficient DNP numerical basis set gives enthalpies of formation for a large set of tested compounds and molecules from the NIST database closer to the experimental values than any other method available in DMol^3. The estimated error was found to be lower than that obtained with the hybrid B3LYP/6-31G** functional.

The convergence criteria applied during geometry optimization are 1.0×10^{-6} Ha for energy, 4.5×10^{-4} Ha/Å (1 Å = 0.1 nm) for force and 0.002 Å for displacement. The self-consistent-field convergence criterion is set so that the root-mean-square (rms) change in the electronic density is less than 1×10^{-5} electron/Å^3. In all calculations, an orbital cutoff of 4.0 Å is used.[26] We performed frequency analysis for each optimized structure to confirm it to be a minimum structure.

3. Results and discussions

To test the reliability of our present calculations, benchmark calculations are carried out for the dimer of Au_2 and the results are compared with the experimental data in the literature. The calculated bond length and binding energy (BE) are 2.486 Å and 1.18 eV/atom, which are in good agreement with of 2.4715 Å and 1.15 eV/atom determined experimentally.[33] Besides, we performed additional calculations on acetone molecule. The calculated bond lengths of the acetone molecule are C–C = 1.514 Å, C–O = 1.224 Å, and C–H = 1.094 Å, which are again in good agreement with the experimental values[34] of 1.507 Å, 1.222 Å and 1.085 Å, respectively. Because this study involves the electrons transferred away from the adsorption sites on Au clusters, the adiabatic ionization energies (IP) of them have been estimated. The calculated IPs of Au_3 and Au_5 are 7.04 eV and 7.40 eV, while the experimental values are 7.27 eV and 7.61 eV[35] respectively. Obviously, the present calculations at the GGA PBE/DNP level can provide a reasonable result, therefore this theoretical level is used in all the following calculations.

Before we study the structural properties of the complexes formed between gold clusters and acetone molecules, the structural properties of the pure gold clusters Au_3 and Au_5 have been recalculated, because their energetic, geometrical and electrical properties will be used in later investigations. Some authors reported that the global minimum of Au_3 is a C_{2v} geometry with an angle around 137°, which is in agreement with the results of Li *et al.* (DFT–LDA in VASP)[36] and those of Fernández *et al.* (DFT–GGA in code SIESTA).[37] In this article, equilateral triangle is chosen because it has three equivalent adsorption sites although its energy is slightly higher than that of the C_{2v} geometry. Our Au–Au bond length of

2.618 Å agrees well with Shafai *et al.*'s 2.60 Å (DFT–LDA in VASP)[9] and Li *et al.*'s 2.61 Å (DFT–LDA in VASP).[35] It is shorter by about 0.1 Å than that of Bravo-Pérez *et al.* (RECP).[38] We also calculated the bond length of the dimer Au_2 using effective core potential (RECP) and all electron relativistic calculations, respectively, in order to estimate the effect of RECP. The calculated results are 2.543 Å and 2.486 Å. Compared with the experimental value 2.4715 Å, we can find that the RECP gives a larger value. Planar Au_5 cluster has C_{2v} symmetry and consists of three edge-sharing triangles, with an average Au–Au bond distance of 2.63 Å, which is the same as the result of Shafai *et al.*[9] and agrees with others'.[36] The ground state geometries of Au_3^-, Au_3^+, Au_5^- and Au_5^+ have also been investigated. The geometry of Au_3^- is linear chain ($D_{\infty h}$) with average bond length 2.537 Å while Au_3^+ is equilateral triangle structure with bond length 2.594 Å. The geometries of Au_5^- and Au_5^+ have the same symmetry as that of Au_5, and average bond lengths change a little. These results are in agreement with those of Fernández *et al.*[37]

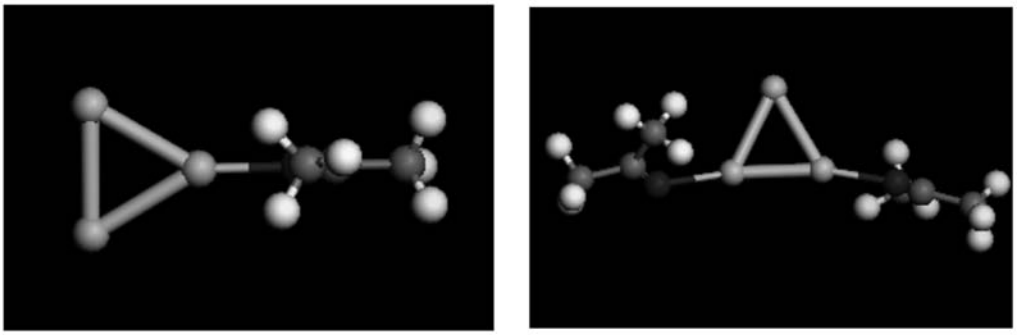
Shafai *et al.*[9] have investigated the interaction between Au_n ($n = 3$, 5, 7, 9, and 13) clusters and single acetone molecule. In their study only one adsorption site is considered although different sites with different coordination numbers exist when $n \geq 3$. They pointed out that the largest BE is obtained when gold atom or dimer interacts with carbonyl oxygen of acetone molecule. We have attempted to optimize for other adsorption sites, such as bridge and hollow sites; however, these other two geometries also ultimately transform into on-top site geometries. Moreover, the present investigations are concerned with the influences of both the coordination number and the number of the adsorbed acetone molecules on the adsorptions rather than the global minima of the complexes. Therefore, the geometries with carbonyl oxygen on the top site of Au clusters are mainly considered in the present calculations although there may be other lower energy configurations.

The three vertexes of the equilateral triangle Au_3 cluster are equivalent, while in a planar Au_5 cluster, its five vertexes can be divided into three types: 2 two-coordinate (2C) sites (c, e), 2 three-coordinate (3C) sites (a, b), and 1 four-coordinate (4C) site (d) (Fig. 1(ix)). Hereafter, the letters (a, b, c, d, e) are used to indicate these adsorption sites on an Au_5 cluster. Moreover, there are some equivalent complexes in multi-molecule adsorptions of the gold clusters. For example, the complex consisting of Au_5 and three acetone molecules at (a, c, d) adsorption sites [Au_5–$(C_3H_6O)_3$ (acd)] has the same configuration as Au_5–$(C_3H_6O)_3$ (bed) complex. In this work, the number of acetone molecules absorbed on Au_3 cluster is from one to three and on Au_5 is from one to five, respectively. Therefore, 22 different Au_3–$(C_3H_6O)_m$ and Au_5–$(C_3H_6O)_m$ complexes in total have been studied after excluding the equivalent complexes, including 3 configurations for the Au_3 cluster, and 19 for the Au_5 cluster.

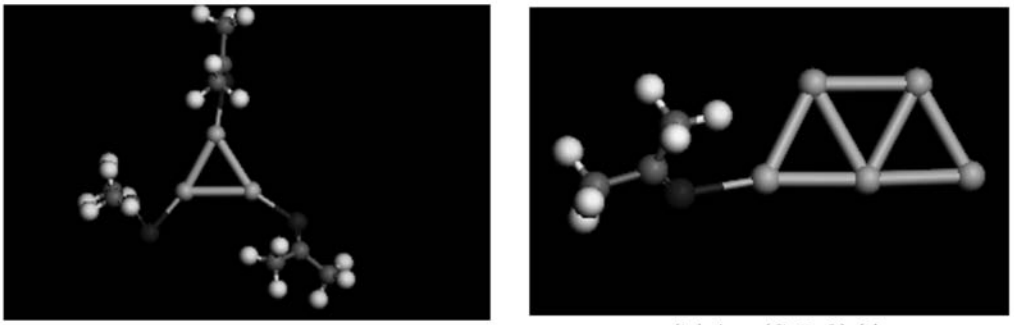
3.1. Structural properties of Au_3–$(C_3H_6O)_m$ ($m = 1$–3) complexes

The BEs, C=O bond lengths, Au–O bond lengths, Au–H distances, average Au–Au bond lengths and C–C–C bond angles of acetones in the complexes are given in Table 1.

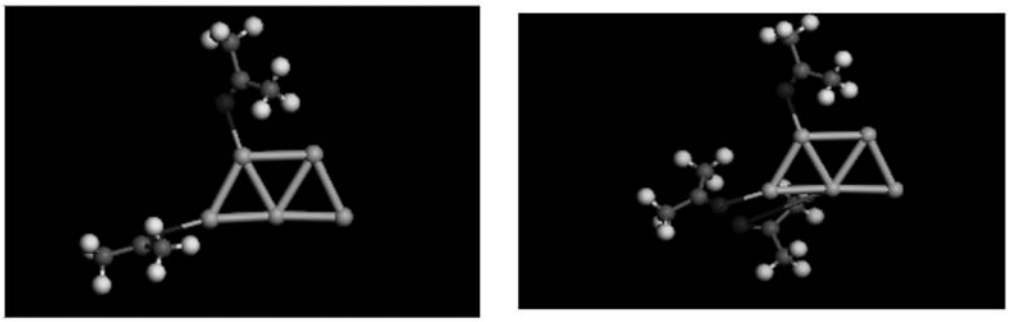
For Au_3–$(C_3H_6O)_m$ ($m = 1$–3) complexes, it can be seen from Figs. 1(i)–1(iii) that the bonds between carbonyl oxygen and gold atom (Au–O bond) are all within the plane of the Au_3 cluster regardless of whether 1, 2, or 3 acetone molecules are adsorbed on Au_3. From Table 1, we can see that upon adsorption, the C=O bond length increases from 1.224 to 1.328 Å for the Au_3–$(C_3H_6O)_m$ ($m = 1$–3) complexes as m increases. The increase of C=O bond lengths in acetone molecule indicates that some charge transfer between Au atom and O atom occurs.[9] Besides that, upon adsorption, the C–C–C bond angles of acetones increase from 116° to 120° for the Au_3–$(C_3H_6O)_m$ ($m = 1$, 2). While in Au_3–$(C_3H_6O)_3$ complex, one of the C–C–C bond angles remains 116° but the other two change to 120°. The interactions between Au atom of adsorption site and hydrogen atom are also examined. The average Au–H distance decreases from 2.947 Å to 2.850 Å, while the average Au–Au bond length shortens form 2.607 Å to 2.572 Å as m increases from one to three. When one acetone molecule is adsorbed, the longest Au–Au bond of Au_3 cluster is the opposite edge of the adsorption site and the other two adjacent bonds are nearly equivalent. When two acetone molecules are adsorbed, the bond between two adsorption sites of Au_3 cluster is the shortest. When three acetone molecules are adsorbed, the average Au–Au bond length is shortened once more. These facts indicate that the adsorptions strengthen the interactions among Au atoms, which results in the shortening of the bond lengths.



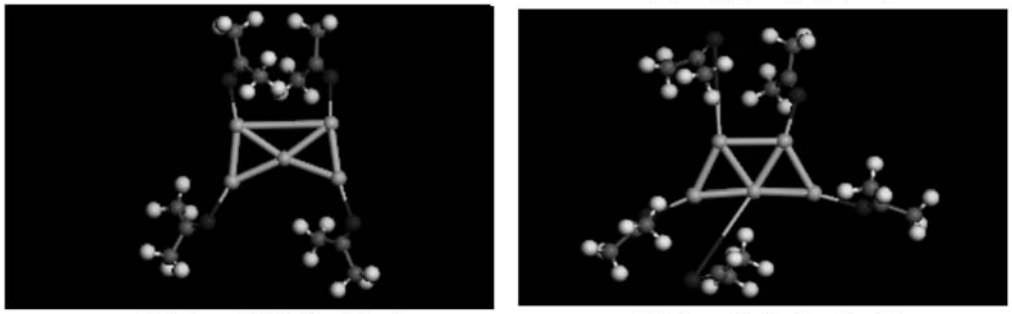
(i) Au_3–(C_3H_6O) (ii) Au_3–$(C_3H_6O)_2$



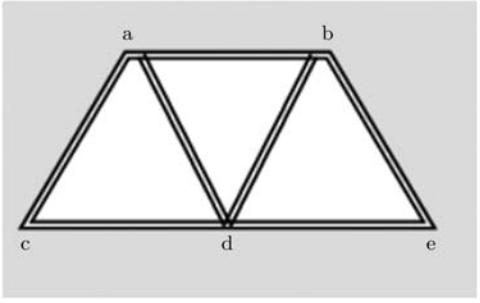
(iii) Au_3–$(C_3H_6O)_3$ (iv) Au_5–(C_3H_6O) (c)



(v) Au_5–$(C_3H_6O)_2$ (ac) (vi) Au_5–$(C_3H_6O)_3$ (acd)



(vii) Au_5–$(C_3H_6O)_4$ (abce) (viii) Au_5–$(C_3H_6O)_5$ (abcde)



(ix)

Fig. 1. Eight structures of Au_n–$(C_3H_6O)_m$ complexes obtained from *ab initio* calculation ($n = 1$–3, $m = 1$–5). The Au atoms and C atoms are shown in gray, H atoms in white, and O atoms in black respectively.

3.2. Structural properties of Au_5–$(C_3H_6O)_m$ (m = 1–5) complexes

Table 1 also contains the calculation results of all Au_5–$(C_3H_6O)_m$ (m = 1–5) complexes. In these complexes, the C=O bond lengths lengthen, most C–C–C bond angles increase, and average Au–Au bond lengths do not show a significant change except for Au_5–$(C_3H_6O)_4$ (abce) complex.

In the case where Au_5 adsorbs one acetone molecule, three different Au_5–(C_3H_6O) complexes have been studied and their different adsorption sites are represented as (a), (c) and (d) respectively. Au_5–(C_3H_6O) (c) (Fig. 1(iv)) has the largest BE while Au_5–(C_3H_6O) (d) has the smallest one, due to different coordination numbers of these sites, i.e. site (c), site (a), site (d) are 2C site, 3C site and 4C site, respectively. Correspondingly, the average Au–Au bond length of the structure of Au_5–(C_3H_6O) (d) is the longest and that of the Au_5–(C_3H_6O) (c) is the shortest in these three cases, which shows that the shorter the average Au–Au bond length is, the stronger the BE is. These facts imply that the most active sites on planar Au_5 cluster are sites (c, e), which are the lowest-coordinate Au atoms of Au_5. This conclusion is in agreement with the previous experimental and theoretical observation of multiple CO adsorptions on small Au cluster anions.[17]

Six Au_5–$(C_3H_6O)_2$ complexes are considered, with adsorption sites (ab), (ac) (Fig. 1(v)), (ad), (ce), (ae) and (cd), respectively. The BEs of these six Au_5–$(C_3H_6O)_2$ complexes range from 98.08 eV to 98.45 eV. It is interesting to note that all Au–O bonds lie within the planar Au_5 cluster's plane for Au_5–$(C_3H_6O)_m$ (m = 1 or 2) complexes.

Six stable Au_5–$(C_3H_6O)_3$ complexes have been considered in this study. Their adsorption sites are (abc), (abd), (bcd), (ace), (acd) (Fig. 1(vi)), and (cde), respectively. The structure of Au_5–$(C_3H_6O)_3$ (ace) has the largest BE while the structure of Au_5–$(C_3H_6O)_3$ (abd) has the smallest one, due to different adsorption sites' coordination numbers of the gold cluster, namely, site (c) and site (e) are the most active adsorption sites and site (d) is the most inactive site. Unlike the cases of Au_5–$(C_3H_6O)_m$ (m = 1 or 2) complexes, on site (d), all the Au–O bonds of Au_5–$(C_3H_6O)_3$ (bcd), Au_5–$(C_3H_6O)_3$ (cde) and Au_5–$(C_3H_6O)_3$ (acd) (Fig. 1(vi)) are out of Au_5 clusters' plane, and the Au–O bond lengths are more than 5.0 Å, indicating that there is no actual interaction between Au and O atoms. Meanwhile in these three Au_5–$(C_3H_6O)_3$ complexes, the C–C–C bond angles of the acetone are about 116° on site (d), indicating that three acetone molecules have no obvious change. However, a large rotation of an acetone molecule makes one of its hydrogen atoms closer to site (d) with Au–H distance about 2.8 Å. This rotation also keeps the acetone molecule close to the Au_5 cluster and results in stronger interaction between hydrogen atom and Au atom. Similarly, Au_5–$(C_3H_6O)_4$ (abce) (Fig. 1(vii)) has the largest BE, while Au_5–$(C_3H_6O)_4$ (abde) has the smallest in the three Au_5–$(C_3H_6O)_4$ complexes. The Au–O bonds of Au_5–$(C_3H_6O)_4$ (bcde) and Au_5–$(C_3H_6O)_4$ (abde) are out of the plane of Au_5 cluster on site (d). It is worth while mentioning that all four Au–O bonds of the Au_5–$(C_3H_6O)_4$ (abce) lie within the plane of Au_5 cluster. These Au–O bonds changed the geometry of the host Au_5 cluster, while the geometries of the host Au_5 in other complexes do not display a significant change. Since the case of Au_5–$(C_3H_6O)_5$ (abcde) (Fig. 1(viii)) is similar to that of Au_5–$(C_3H_6O)_4$ (abde), we will not discuss the former in detail.

Table 1. Total binding energies (BE), C=O, Au–O, Au–H, average Au–Au bond lengths, total energies and the C–C–C bond angles. The number (1, 2, 3) denotes the value of one of the several equivalent adsorption sites for Au_3 and the letter (a, b, c, d, e) after the data for Au_5 denotes the value of different adsorption sites.

system	BE/eV	bond length/Å			average Au–Au/Å	C–C–C/(°)
		C=O	Au–O	Au–H		
C_3H_6O	43.99	1.224	–	–	–	116.4
Au_3–(C_3H_6O)	48.89	1.261	2.066	2.947	2.607	120.5
Au_3–$(C_3H_6O)_2$	93.42	1.256(1)	2.129(1)	2.924(1)	2.605	120.2(1)
		1.257(2)	2.116(2)	2.842(2)		120.2(2)
Au_3–$(C_3H_6O)_3$	137.79	1.268(1)	2.092(1)	2.911(1)	2.572	120.8(1)
		1.328(2)	2.116(2)	3.081(2)		120.0(2)
		1.261(3)	2.138(3)	2.786(3)		116.0(3)
Au_5–(C_3H_6O) (a)	54.00	1.250	2.153	2.902	2.632	120.1
Au_5–(C_3H_6O) (c)	54.05	1.246	2.184	2.698	2.631	119.0

Table 1 *continued*

system	BE/eV	bond length/Å			average Au–Au/Å	C–C–C/(°)
		C=O	Au–O	Au–H		
Au_5–(C_3H_6O) (d)	53.75	1.242	2.300	2.872	2.640	120.0
Au_5–(C_3H_6O)$_2$ (ab)	98.28	1.251 a	2.193 a	2.869 a	2.641	120.0 a
		1.249 b	2.149 b	2.954 b		120.0 b
Au_5–(C_3H_6O)$_2$ (ae)	98.37	1.248 a	2.184 a	2.957 a	2.633	119.9 a
		1.250 e	2.173 e	2.907 e		119.6 e
Au_5–(C_3H_6O)$_2$ (ad)	98.18	1.251 a	2.162 a	2.930 a	2.642	119.9 a
		1.242 d	2.289 d	2.944 d		119.6 d
Au_5–(C_3H_6O)$_2$ (ac)	98.45	1.256 a	2.142 a	2.981 a	2.637	120.0 a
		1.248 c	2.180 c	2.674 c		118.9 c
Au_5–(C_3H_6O)$_2$ (ce)	98.35	1.244 c	2.241 c	2.740 c	2.631	118.7 c
		1.243 e	2.241 e	2.665 e		118.6 e
Au_5–(C_3H_6O)$_2$ (cd)	98.08	1.246 c	2.212 c	2.825 c	2.638	118.8 c
		1.236 d	2.480 d	2.636 d		118.5 d
Au_5–(C_3H_6O)$_3$ (abc)	142.55	1.256 a	2.135 a	2.933 a	2.643	120.2 a
		1.247 b	2.241 b	2.858 b		119.2 b
		1.251 c	2.194 c	2.668 c		119.3 c
Au_5–(C_3H_6O)$_3$ (abd)	142.43	1.251 a	2.153 a	2.855 a	2.646	119.5 a
		1.249 b	2.200 b	2.956 b		120.1 b
		1.243 d	2.266 d	3.051 d		119.6 d
Au_5–(C_3H_6O)$_3$ (acd)	142.68	1.256 a	2.144 a	2.979 a	2.638	120.0 a
		1.250 c	2.159 c	2.771 c		119.1 c
		1.232 d	5.161 d	2.882 d		116.5 d
Au_5–(C_3H_6O)$_3$ (ace)	142.69	1.260 a	2.140 a	3.061 a	2.645	120.0 a
		1.248 c	2.207 c	2.719 c		119.3 c
		1.249 e	2.220 e	2.687 e		119.0 e
Au_5–(C_3H_6O)$_3$ (bcd)	142.61	1.251 c	2.164 c	2.792 c	2.634	119.2 c
		1.250 b	2.181 b	2.977 b		119.8 b
		1.232 d	5.209 d	2.868 d		116.4 d
Au_5–(C_3H_6O)$_3$ (cde)	142.59	1.244 c	2.245 c	2.824 c	2.632	118.8 c
		1.232 d	5.135 d	2.814 d		116.6 b
		1.248 e	2.204 e	2.838 e		118.7 e
Au_5–(C_3H_6O)$_4$ (bedc)	186.91	1.256 b	2.157 b	2.998 b	2.637	119.9 b
		1.246 e	2.219 e	2.732 e		118.7 e
		1.233 d	5.145 d	2.814 d		116.1 d
		1.250 c	2.199 c	2.797 c		119.0 c
Au_5–(C_3H_6O)$_4$ (abde)	186.60	1.229 a	4.336 a	2.338 a	2.637	116.8 a
		1.254 b	2.142 b	3.037 b		119.9 b
		1.227 d	5.532 d	2.715 d		116.3 d
		1.248 e	2.173 e	2.737 e		119.2 e
Au_5–(C_3H_6O)$_4$ (abce)	187.11	1.269 a	2.114 a	2.993 a	2.833	120.3 a
		1.273 b	2.096 b	2.743 b		120.5 b
		1.264 c	2.121 c	2.971 c		120.2 c
		1.267 e	2.117 e	2.986 e		119.5 e
Au_5–(C_3H_6O)$_5$ (abcde)	231.08	1.233 a	4.762 a	2.154 a	2.638	116.3 a
		1.253 b	2.156 b	3.010 b		119.5 b
		1.250 c	2.192 c	2.882 c		119.0 c
		1.232 d	5.090 d	2.743 d		116.3 d
		1.247 e	2.212 e	2.716 e		119.0 e

3.3. Energetic properties of Au_3–(C_3H_6O)$_m$ (m = 1–3) and Au_5–(C_3H_6O)$_m$ (m = 1–5) complexes

The adsorption energy (AE) of various adsorption cases was checked to display the character of the energetically interaction among acetone molecules and gold clusters. The AE between one acetone molecule and gold cluster can be determined by the expression

$$E_{\rm b} = E_{{\rm Au}_n-({\rm C_3H_6O})} - \left(E_{{\rm Au}_n} + E_{({\rm C_3H_6O})}\right), \quad (1)$$

where $E_{\rm b}$ stands for the AE between one acetone molecule and gold cluster, $E_{{\rm Au}_n}$ is the total energy of the gold cluster, and $E_{({\rm C_3H_6O})}$ is the total energy of acetone molecule. We also calculated $E_{{\rm b}(N)}$ (N is the number of acetone molecules adsorbed on gold

cluster) which denotes the AE between one acetone molecule and the Au_n–$(C_3H_6O)_{N-1}$ complex, because the present investigation systems have several molecules adsorbed. The calculation formula is as follows:

$$E_{b(N)} = E_{Au_n-(C_3H_6O)_N} - \big(E_{Au_n-(C_3H_6O)_{N-1}} + E_{(C_3H_6O)}\big), \quad (2)$$

where $E_{Au_n-(C_3H_6O)_N}$ is the total energy of the Au_n–$(C_3H_6O)_N$ complex, and the zero-point vibrational energies of each radical are included in the calculations. All the calculated AEs for Au_3–$(C_3H_6O)_m$ are collected in Table 2. From the table, one can find that the AEs decrease from 1.169 eV to 0.734 eV when the numbers of the adsorbed acetone molecules increase from 1 to 3, and correspondingly, the Au–O bonds increase from 2.092 Å to 2.138 Å. This is due to the fact that the variation in the AE follows the variation in Au–O bond length. The condition agrees with the case that one acetone is adsorbed on different gold clusters, where the AEs change along with Au–O bond lengths as the gold atoms increase (the shorter the Au–O bond is, the larger the AE is).[9]

Table 2. Adsorption energies between acetone and Au_3, Au_3–(C_3H_6O), and Au_3–$(C_3H_6O)_2$ complex (units in eV).

Au_3	1 C_3H_6O	2 C_3H_6O	3 C_3H_6O
adsorption energy	1.169	0.923	0.734

Table 3 displays the AEs of different Au_5 adsorption sites. When one acetone is adsorbed, the AE of Au_5–(C_3H_6O) (c) (0.877 eV) is the largest and that of the Au_5–(C_3H_6O) (d) (0.563 eV) is the smallest. Therefore, site (c) is the most favoured adsorption site, which is in agreement with the conclusion from coordination number. It is also noted that the site with the shortest Au–O bond length on the Au_5–(C_3H_6O) complex is site (a), but not site (c), which is due to the interaction between hydrogen and gold atom. The Au–H distance of Au_5–(C_3H_6O) (c) complex is 2.698 Å, which is much shorter than 2.902 Å and 2.872 Å of the other two complexes. The shorter Au–H distance results in stronger interaction between Au and H atoms, and weaker the interaction between Au and O atoms. It at last causes the increasing of the Au–O bond. Because of the influence of the interaction of Au and H atoms, the AEs do not show obvious relationship with their corresponding Au–O bond lengths when one acetone molecule is adsorbed onto different sites with different coordination numbers of Au_5. When two acetone molecules are adsorbed at the same time, we first considered the case that the two adsorption sites have same coordination number within a certain Au_5–$(C_3H_6O)_2$ complex. In Au_5–$(C_3H_6O)_2$ (ab) and Au_5–$(C_3H_6O)_2$ (ce) complexes, the AEs at site (a) and site (b) are both 0.648 eV, while at site (c) and site (e) they are both 0.663 eV. Besides, the AEs at sites (c) and (e), where coordination numbers are smaller, are larger than those at sites (a) and (b) where coordination numbers are larger. In a certain Au_5–$(C_3H_6O)_2$ complex, if two adsorption sites have different coordination numbers, the site with smaller coordination number has larger AE. For example, in Au_5–$(C_3H_6O)_2$ (ac) complex, the AE of 2C site (c) (0.850 eV) is larger than that of 3C site (a) (0.815 eV). In the case where Au_5 adsorbs several acetone molecules, the AEs of different adsorptive sites do not display obvious relationship with the corresponding Au–O bond lengths or adsorptive site's coordination numbers. This is due to the existence of the interactions between Au and H, between Au and O atoms, and among acetone molecules themselves. In fact, the coordination numbers continue to affect the AEs, but the interactions among acetone molecules themselves become increasingly stronger as the number of acetone molecules increases, which will affect the AE of each site. Combining the bond lengths in Table 1 and AE in Table 3, we also find that the Au–O bonds of sites (d) are about 5.0 Å and the corresponding Au–H bonds are 2.0–3.0 Å when the absorbed acetone molecules are over 2, which imply that the adsorption still exists between the Au_5 cluster and the acetone molecule at site (d) but the Au–O bond is replaced by Au–H bond. The adsorption energy at this site is determined by the Au–H interaction but not the Au–O interaction. Therefore, generally speaking, in a certain Au_5–$(C_3H_6O)_m$ (m = 2–5) complex, the AE of site (d) is often the smallest among all AEs of different sites regardless of the number of acetone molecules adsorbed by gold clusters, because site (d) is a 4C site which is large enough to counteract the effect of the interaction among acetone molecules themselves.

Table 3. Adsorption energies of different adsorption sites in a certain Au_5–$(C_3H_6O)_m$ complex. The letters (a, b, c, d, e) denote different adsorption sites (units in eV).

system	a	b	c	d	e
Au_5–(C_3H_6O) (a)	0.841	–	–	–	–
Au_5–(C_3H_6O) (c)	–	–	0.877	–	–
Au_5–(C_3H_6O) (d)	–	–	–	0.563	–
Au_5–$(C_3H_6O)_2$ (ab)	0.648	0.648	–	–	–
Au_5–$(C_3H_6O)_2$ (ae)	0.704	–	–	–	0.739
Au_5–$(C_3H_6O)_2$ (ad)	0.802	–	–	0.523	–
Au_5–$(C_3H_6O)_2$ (ac)	0.815	–	0.850	–	–
Au_5–$(C_3H_6O)_2$ (ce)	–	–	0.663	–	0.663
Au_5–$(C_3H_6O)_2$ (cd)	–	–	0.723	0.409	–
Au_5–$(C_3H_6O)_3$ (abc)	0.611	0.499	0.702	–	–
Au_5–$(C_3H_6O)_3$ (abd)	0.635	0.635	–	0.511	–
Au_5–$(C_3H_6O)_3$ (acd)	0.682	–	0.851	0.524	–
Au_5–$(C_3H_6O)_3$ (ace)	0.762	–	0.715	–	0.604
Au_5–$(C_3H_6O)_3$ (bcd)	–	0.856	0.777	0.561	–
Au_5–$(C_3H_6O)_3$ (cde)	–	–	0.882	0.633	0.882
Au_5–$(C_3H_6O)_4$ (bcde)	–	0.690	0.641	0.561	0.716
Au_5–$(C_3H_6O)_4$ (abde)	0.329	0.403	–	0.354	0.545
Au_5–$(C_3H_6O)_4$ (abce)	0.773	0.773	0.878	–	0.878
Au_5–$(C_3H_6O)_5$ (abcde)	0.550	0.550	0.863	0.339	0.863

It is very interesting that, for the Au_5–$(C_3H_6O)_4$ (abce) complex, the geometry of the Au_5 host is changed significantly, and all AEs become larger than those of other Au_5–$(C_3H_6O)_4$ complexes. Only in this case, the geometry of the host Au cluster is changed obviously, which is caused by the symmetry distribution of the four acetone molecules. For Au_5–$(C_3H_6O)_5$ complexes, the AEs of sites (a) and (b) are 0.550 eV, while those of sites (c) and (e) are 0.863 eV. And at site (d), the AE is only 0.339 eV.

3.4. Electronic properties of complexes for Au_3–$(C_3H_6O)_m$ (m = 1–3) and Au_5–$(C_3H_6O)_m$ (m = 1–5)

The distributions of deformation electron density (DED) have been examined in order to further understand the interaction in Au_n–$(C_3H_6O)_m$ complexes. The DED is the difference between the molecular and the unrelaxed atomic charge densities, which can be calculated as follows:

$$\rho_{\rm d}(r) = \rho(r) - \sum_{\alpha} \rho_{\alpha}(r - R_{\alpha}), \qquad (3)$$

where $\rho(r)$ is the molecular charge density and $\rho_{\alpha}(r - R_{\alpha})$ is the density of the free atom α located at coordinates R_{α}.[39] Regions of positive DED indicate the formation of bonds, while negative regions indicate the electron loss. In Fig. 2, –0.03 electrons/Å^3 scale is used in these pictures to display the DED of Au clusters and acetone molecules. Figures 2(i) and 2(ii) show that for both the Au_3–(C_3H_6O) and Au_5–(C_3H_6O) complexes, the DED on acetone molecules are stronger than those on Au_3 or Au_5 cluster, although there are DEDs on Au atoms to form the Au–Au bonds.

The DED of Au_3 cluster in Fig. 2(iii) shows that the DEDs on three vertexes of the triangle are equivalent, which agrees with the conclusion from coordination number. The positive DED of Au_5 cluster is shown in Fig. 2(iv). From the figure, we can find that the DEDs of vertexs (a) and (b) are equivalent, and those of vertexs (c) and (e) are equivalent, too. Besides, it also shows that the DED of vertex (d) is slightly smaller than those of the other vertexes. This order agrees with that of the AEs of three different types of adsorption sites when one acetone molecule is adsorbed on Au_5, i.e. the larger the DED is, the higher the AE is. This fact can be accounted for the different coordination numbers of different adsorption sites on Au_5 cluster. In Au_3–$(C_3H_6O)_m$ (m = 1, 2) complex, the DEDs of the adsorption sites are larger than the other bare vertexe(s) in that the DED will become larger after acetone molecule is adsorbed on it.

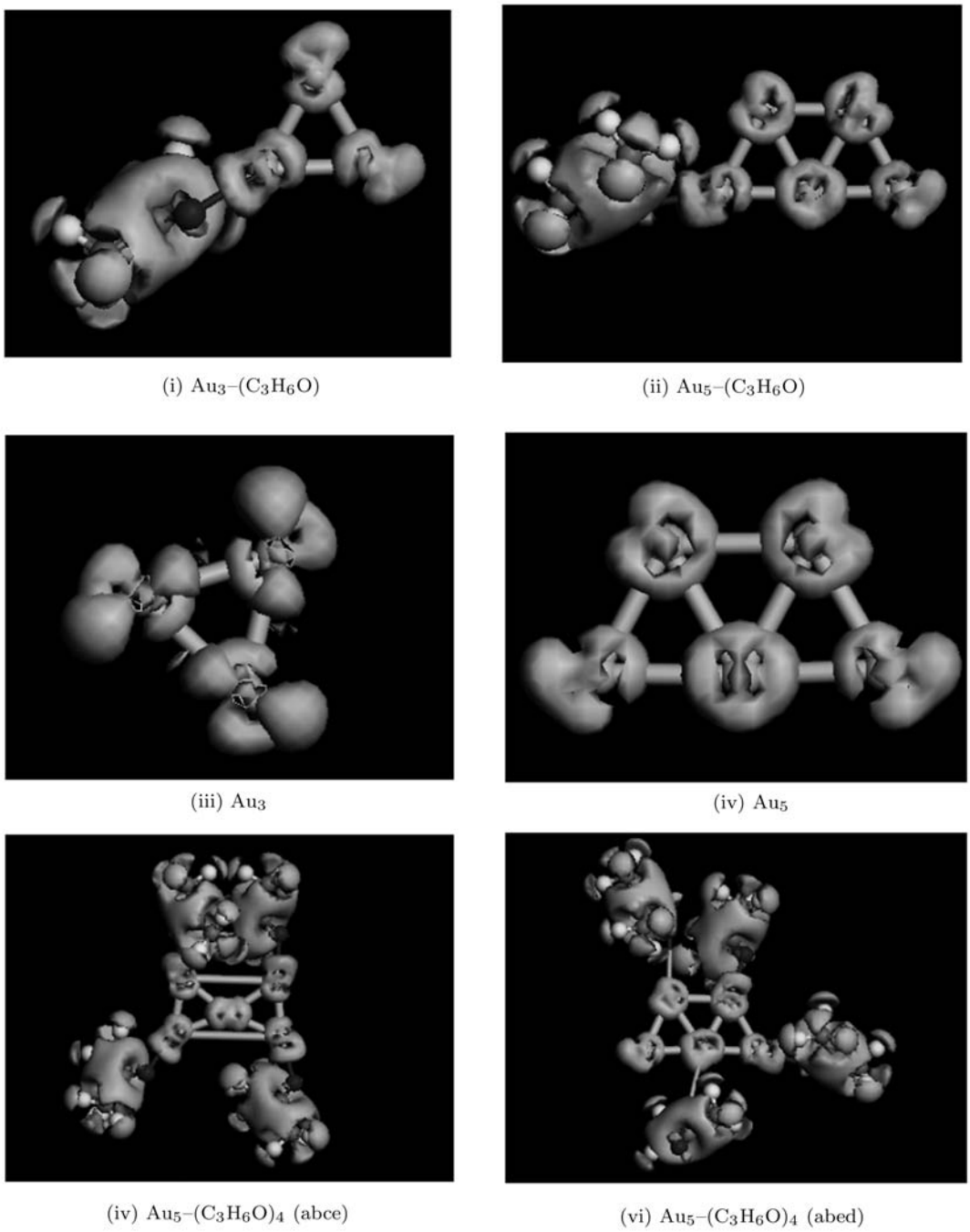


Fig. 2. Deformation electron density surface of Au_n–$(C_3H_6O)_m$ complexes and Au_3, Au_5 clusters at –0.03 electrons/Å^3.

When two or three acetone molecules are adsorbed, the results are similar to the case of adsorbing one. When four acetone molecules are adsorbed, the Au_5–$(C_3H_6O)_4$ (abce) complex (Fig. 2(v)) is different from other configurations because the geometry of Au_5 cluster nearly changed into a rectangle. Since four vertexes of a rectangle are equivalent, their DEDs are nearly equal and all larger than other Au_5–$(C_3H_6O)_4$ complexes, which is similar to those of two opposite Au_3–$(C_3H_6O)_2$ with a mutual vertex. This fact can be understood as that the interactions of symmetry four acetone molecules and Au_5 exceed the interactions among the Au atoms in Au_5 cluster, which results in the rectangle geometry of Au_5 cluster to balance the interactions. For the Au_5–$(C_3H_6O)_4$ (abed) complex (Fig. 2(vi)), although equivalent sites (a) and (b) both adsorb one acetone molecule, the DED of site (a) becomes a little bit smaller than that of site (b).

Correspondingly, the Au–O bond of site (a) becomes longer than site (b) and the AE of site (a) is smaller than site (b). On the whole, the views displayed by the DEDs are in agreement with those displayed by the AE and geometrical properties.

4. Conclusions

In this paper, density functional theory is applied to investigate the geometries, energetic and electronic properties of acetone molecules adsorbed on small gold clusters. The results indicate that small gold clusters can adsorb more than one acetone molecule. One atom of the gold clusters can only adsorb one acetone molecule directly. The geometries of the host gold clusters change slightly except for Au_5–$(C_3H_6O)_4$ (abce) complex. For Au_3–$(C_3H_6O)_m$ ($m = 1$–3) complex, the AEs decrease as m increases. For Au_5 clusters, the energetically preferred adsorption site turns out to be the lowest-coordinate gold atom. When one acetone is adsorbed, the sequence of the preferred adsorptive site is site (c), site (a), site (d). It is found that the AEs are affected by both coordination numbers and interactions among acetone molecules themselves. Because of all the effects from interactions of Au–O and Au–H as well as those among acetone molecules themselves, the AEs of different adsorptive sites do not always vary along with the change of Au–O bond lengths. This result is different from the case that one acetone is adsorbed on different gold clusters, where the AE closely follows the variation in the Au–O bond length as the size of gold cluster increases.[9] In a word, the cases including several acetone molecules adsorbed onto gold clusters are obviously different from those including only one acetone molecule. This study has provided a more complete understanding of the interaction between gold clusters and acetone molecules.

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