

## Comparative study of CO adsorption on flat, stepped, and kinked Au surfaces using density functional theory

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Our *ab initio* calculations of CO adsorption energies on low-Miller-index [(111) and (100)], stepped (211), and kinked (532) gold surfaces show a strong dependence on local coordination with a reduction in Au atom coordination leading to higher binding energies. We find trends in adsorption energies to be similar to those reported in experiments and calculations for other metal surfaces. The (532) surface provides insights into these trends because of the availability of a large number of kink sites which naturally have the lowest coordination (6). We also find that for all surfaces an increase in CO coverage triggers a decrease in the adsorption energy. Changes in the work function upon CO adsorption, as well as the frequencies of the CO vibrational modes, are calculated, and their coverage dependence is reported.

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### I. INTRODUCTION

Investigation of the adsorption of molecules on well-defined transition-metal surfaces has been of great academic as well as technological interest for the past few decades.<sup>1-3</sup> In this regard, there has been tremendous focus on CO adsorption because of its importance in many industrial processes and because of its relative simplicity.<sup>4-6</sup> Experimental and theoretical studies<sup>7,8</sup> of CO adsorption on a variety of transition-metal surfaces have thus contributed to laying a basic understanding of the initial steps in the oxidation process. The importance of identifications of “active sites” based on adsorption, desorption, and sticking coefficients has also been emphasized,<sup>1-3</sup> as real catalysts are known to consist of small metal clusters of various microfacets of different orientations containing defects such as steps and kinks.<sup>9</sup> In the special case of CO oxidation on nanometer-sized gold clusters on supported metal oxides, numerous studies have attempted to explain their unexpected catalytic activity. While nanoparticles may exhibit behavior which is unique to them, the presence of steps, kinks, corner sites, etc., on these particles does tempt the comparison with the behavior of single-crystal surfaces with similar local coordination. It has been reported that oxygen molecules dissociate more easily on step and kink sites and CO binds more strongly to such sites. Here the temperature programmed desorption (TPD) experiments of CO adsorption on low-coordinated sites on Au(211) and Au(332) (Refs. 10 and 11) provide insight into the role step and kink sites play in strengthening CO binding to the surface. Earlier calculations show that CO binding energy increases on Au(211) compared to Au(111).<sup>12,13</sup> Yim *et al.*<sup>11</sup> also showed an increase in CO binding energy on Au(332) with local coordination by artificially introducing defects on this surface. Hence, systematic information on the adsorption characteristics of CO on Au surfaces with varying number of step and kink sites can serve as a building block in advancing knowledge of the reactivity of metal particles.<sup>14</sup> To our knowledge, there are no published data or calculations for kinked gold surfaces, although such data are avail-

able for Cu.<sup>14</sup> Recent thermal-desorption spectroscopy (TDS) studies of CO on various surfaces of copper captured trends in the dependence of binding energies on coordination.<sup>14</sup> However, analysis based on coordination alone may not provide the full picture, as reported earlier.<sup>15</sup> We believe that a more in-depth understanding can be developed through systematic and detailed theoretical calculations using first-principles methods as in density functional theory (DFT). A number of such calculations have already been reported for various coverages of CO on low-Miller-index surfaces of transition metals,<sup>3,16</sup> but we were unable to find ones in which the coverage was the same as in experiments.

Renewed attention has been drawn to the chemisorption of CO on transition-metal surfaces since theoretical calculations show adsorption site preferences which are different from those experimentally observed.<sup>16-19</sup> These papers have discussed in detail the shortcomings of density functional theory in the treatment of the  $\pi$ - $d$  interaction. The goal of the present work is, however, to explore the role of coordination in the adsorption of CO on Au surfaces for given adsorption sites. We do so through a comparative study on the (111), (100), (211), and (532) surfaces of gold. After giving the computational details of our work in Sec. II, we shall first give a detailed analysis of the calculated adsorption energies based on coordination with comparison to other calculations and experiments. We then examine the implication of increasing CO coverage on these surfaces. The remainder of the paper is devoted to the characterization of these surfaces on the basis of electronic structure (work function and vibrational frequencies) and the changes in these quantities on the adsorption of CO. It is followed by our conclusions.

### II. COMPUTATIONAL DETAILS

*Ab initio* calculations performed in this study are based on the DFT (Refs. 20 and 21) in which the Kohn-Sham equations are solved within the pseudopotential approximation using plane-wave basis sets as formulated in the Vienna *ab initio* simulation package (VASP).<sup>22-24</sup> The electron-ion in-

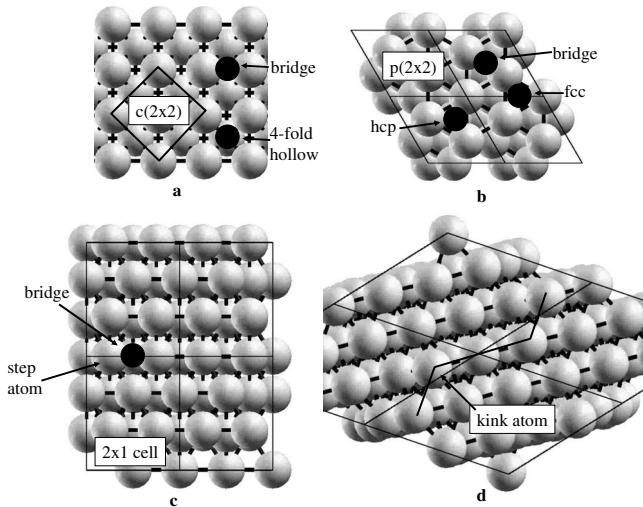


FIG. 1. Top views of (a) (100), (b) (111), (c) (211), and (d) (532) surfaces. Adsorption on different sites is shown. Gold atoms are represented by gray spheres and adsorption site of CO molecule is represented by solid black circles. Note that in unit cell of (532), eight atoms belong to eight different layers.

teraction for C, O, and Au is described by ultrasoft pseudo-potentials. A 450 eV plane-wave energy cutoff was used for all calculations which was found to be sufficient for similar systems.<sup>16,25</sup> In all calculations, the generalized gradient correction of Perdew and Wang<sup>26</sup> (PW91) was used which is found to give more accurate results than those based on the local-density approximation (LDA).<sup>3,27,28</sup> The bulk lattice constant was found to be 4.19 Å using a  $k$ -point mesh of  $10 \times 10 \times 10$  in reasonable agreement with experimental value of 4.08 Å.<sup>29</sup>

The slab supercell approach with in-plane periodic boundaries is employed to model the surface with the Brillouin-zone sampling based on the technique devised by Monkhorst and Pack.<sup>30</sup> Au(100) and Au(111) were modeled by a four-layer (16-atom) tetragonal and hexagonal supercells, respectively. These four layers are separated with 11 Å of vacuum. For Au(100), calculations were performed for a  $c(2 \times 2)$  overlayer corresponding to 0.5 ML coverage of CO, followed by calculations with full coverage. For Au(111), a  $p(2 \times 2)$  structure was used to represent coverage of 0.33 ML (one CO per unit cell). A coverage of 1 ML was obtained with three CO molecules per unit cell. CO molecules were adsorbed on several sites to find the preferred adsorption site in such a way that the CO molecule sits perpendicular to the surface with carbon atom binding to the surface, as reported in number of experiments.<sup>7,22,23</sup> A Monkhorst-Pack  $k$ -point mesh of  $4 \times 4 \times 1$  was used for the (100) surface and  $5 \times 5 \times 1$  was used for the (111) surface.

Au(211) is a surface with a monoatomic (100) step and a (111) three-atom wide terrace [see Fig. 1(c)]. It was modeled by an orthorhombic supercell of 17 layers separated with approximately 12 Å vacuum. For this surface, a  $(2 \times 1)$  unit cell was also modeled with 34 Au atoms (two-atom-long steps) with CO adsorbed on either the step edge or on the bridge (between two step edge atoms) sites. This supercell corresponds to 0.17 ML coverage on this surface as defined

in Ref. 31. To determine the coverage dependence of adsorption energies, calculations for 0.33 ML were also performed by incorporating an additional CO molecule to the same supercell. A Monkhorst-Pack  $k$ -point mesh of  $5 \times 4 \times 1$  was used for Au(211).

Finally, the kinked surface, Au(532) [see Fig. 1(d)], was modeled by a simple monoclinic supercell of five layers with each layer containing eight nonequivalent atoms. These five layers were separated by 12 Å of vacuum. A Monkhorst-Pack  $k$ -point mesh of  $3 \times 4 \times 1$  was used and CO was adsorbed on the kink site and three bridge sites between atoms 1 and 4. The top of the kink site was found to be the preferred one, which is also found to be the case in experimental observation on Cu(532).<sup>14</sup> Two different coverages for the (532) surface were modeled by adsorbing only one CO molecule on the kink site for the lower coverage and an additional CO molecule on a site next to the kinked site for the higher coverage.

For all surfaces, each atom was allowed to move in all three directions and the structures were relaxed until forces on each atom were converged to better than 0.01 eV/Å. The adsorption energies were calculated by subtracting the energies of a CO molecule in the gas phase and a clean Au surface from the total energy of CO/Au system,

$$E_{\text{ad}} = E_{\text{CO/Au}} - E_{\text{CO}} - E_{\text{clean}}. \quad (1)$$

Work functions were calculated by taking the difference of average vacuum potential and the Fermi energy for each surface. Finite-difference method was used to obtain vibrational properties of CO molecule in the gas phase and on the surfaces. CO internal stretching and CO-metal stretch frequencies were calculated in the direction perpendicular to the surface.

### III. RESULTS AND DISCUSSION

To understand trends in adsorption energies as a function of variation in the coordination of surface atoms, we present for completeness results for Au(111) and Au(100) which have already been explored both experimentally and theoretically.<sup>14,16,32–34</sup> We then include the results for the stepped surface Au(211) and the kinked surface Au(532).

#### A. Adsorption sites and bond length

A comparison of CO bond lengths and the surface-carbon distances on the surfaces of interest is presented in Table I. For cases in which CO is adsorbed on top of the metal atom, we note similarity in the CO bond length and surface-carbon distance. The C-O bond length is about 1.15 Å for adsorption on the five surfaces of interest here. Except for the case of Au(111), the CO molecule sits at about 2 Å on top of Au atoms, when at the bridge site; the Au-C bond is about 1.5 Å. These distances are very close to experimentally observed values and to the ones calculated by others.<sup>14,16,32–34</sup>

#### B. Adsorption energies and their coverage dependence

An atom on a (111) surface has the highest number of nearest neighbors (coordination 9) and in turn lowest adsorp-

TABLE I. Calculated structural properties of CO adsorbed on experimentally reported preferred adsorption sites on various Au surfaces. Here  $d_{C-O}$  is the CO bond length and  $d_{C-Au}$  is the CO-molecule distance from Au surfaces. All distances are in angstroms.

Surface	Au(111)	Au(100)	Au(211)	Au(532)
$d_{C-O}$	1.14	1.16	1.15	1.15
	1.15 <sup>a</sup>	1.17 <sup>a</sup>	1.17 <sup>a</sup>	
$d_{C-Au}$	2.22, 2.18 <sup>b</sup>	2.03	1.99	2.00
		1.50 <sup>a</sup>	1.46 <sup>a</sup>	

<sup>a</sup>Bridge site.

<sup>b</sup>References 12 and 13.

tion energy of all studied surfaces. For this particular surface, we have used a  $p(2 \times 2)$  cell which corresponds to 0.33 ML CO coverage on Au(111). The calculated adsorption energies are listed in Table II along with corresponding numbers of first- and second-nearest neighbors and the experimentally observed adsorption energies. We studied several possible adsorption sites (top, bridge, hcp hollow, and fcc hollow) and find only an energy difference of less than 0.01 eV between them. Our calculated value of 0.28 eV is lower than the experimentally observed value of 0.40 eV, but matches well with those obtained in other DFT calculations performed for 0.25 and 0.33 ML coverages with reported adsorption energies of 0.32 and 0.30 eV, respectively.<sup>12,16</sup> In general, we found a strong dependence of the adsorption energies on coverage, especially for Au(111), for which the adsorption energy dropped from 0.28 to 0.1 eV (corresponding to 0.33 and 1 ML, respectively). This also explains the small difference from other calculations which were performed for a smaller coverage and in turn larger adsorption energy.

The next surface in this hierarchy is Au(100), on which atoms have eight nearest neighbors. Unlike the (111) surface, only a few calculations and experiments have been performed on this surface.<sup>33,37,38</sup> We have studied a  $c(2 \times 2)$  coverage, which corresponds to a 0.5 ML CO coverage on Au(100). Of the three possible adsorption sites for this surface, we found the bridge site to be slightly energetically preferable over the top site with an energy difference of 0.04 eV. We obtained an adsorption energy of 0.38 eV for Au(100), which is larger than that on the more coordinated

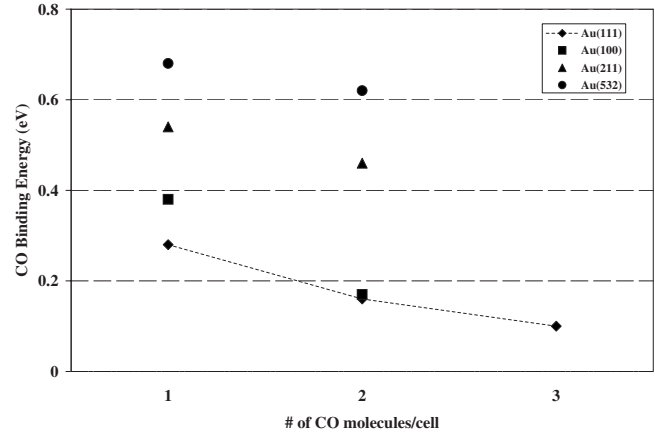


FIG. 2. CO binding energy as a function of CO coverage.

but less corrugated (111). This value is again lower compared to the experimental value of 0.601 eV obtained using electron-energy-loss spectroscopy (EELS).<sup>39</sup> Although no other calculations are available for this coverage, a much smaller adsorption energy was reported for 1 ML coverage, in agreement with our high-coverage calculations which show a strong drop in adsorption energy with increasing coverage.

The step atoms on Au(211) have coordination 7, and hence are next in order in this series. We have used a  $(2 \times 1)$  cell for (211), corresponding to about 0.17 ML CO coverage. The CO molecule is adsorbed on the top and bridge sites of the step edge of (211), as shown in Fig. 1(c) with adsorption energy of 0.54 eV. There are no experimental results available for this particular surface but TPD study on another stepped surface, Au(332), showed 0.57 eV for the adsorption energy, which is reasonably close to our calculated value.<sup>10</sup>

On Au(532) surface CO was adsorbed on the Au atom at the kink site. The adsorption energy for this case was found to be 0.68 eV, which is the same as for the previous surface with coordination 7. Such similarities in adsorption energies for the (211) and (532) surfaces have also been seen experimentally for Cu using TDS. Figure 2 shows the trends in adsorption energies versus CO coverage on the presently

TABLE II. Calculated adsorption energies of CO on various Au surfaces for the on-top site (unless otherwise stated).

Surface		Au(111)	Au(100)	Au(211)	Au(532)
$N_{NN}$		9	8	7	6
$E_{ad}$ (eV)	1 CO/cell	0.28	0.38 (0.46 <sup>a</sup> )	0.54 (0.65 <sup>a</sup> )	0.68
	2 CO/cell	0.16	0.17	0.46	0.62
	3 CO/cell	0.1			
$E_{ad}$ , expt. (eV)		0.4 <sup>b</sup>	0.6 <sup>b</sup>	0.52 <sup>c</sup>	

<sup>a</sup>Bridge site.

<sup>b</sup>Reference 35.

<sup>c</sup>Reference 36.

TABLE III. Calculated CO frequencies:  $\nu_{\text{C-O}}$  represents the molecular stretching mode and  $\nu_{\text{S-CO}}$  is the molecule-surface stretch mode.  $\text{CO}_{\text{mol}}=2132 \text{ cm}^{-1}$ .

Surface	Au(111)	Au(100)	Au(211)	Au(532)
$\nu_{\text{C-O}} \text{ (cm}^{-1}\text{)}$	2046	2040	2034	2035
	2004 <sup>a</sup>	2019 <sup>a</sup>	2012 <sup>a</sup>	2034 <sup>a</sup>
		1902 <sup>b</sup>		
$\nu_{\text{S-CO}} \text{ (cm}^{-1}\text{)}$	255	278	288	314

<sup>a</sup>Higher CO coverage.

<sup>b</sup>Bridge site.

studied gold surfaces. Note that for each case CO binding energy decreases with increasing CO coverage.

### C. Vibrational properties and work function

The vibrational frequency of a CO molecule in the gas phase was calculated by fully relaxing a single molecule in a large supercell with the size of approximately  $6 \times 6 \times 22 \text{ \AA}^3$ . The frequency of the stretching mode was calculated to be  $2132 \text{ cm}^{-1}$ . This can be compared with the very accurate experimentally measured vibrational frequency of an isolated CO molecule of  $2079 \text{ cm}^{-1}$  using EELS and  $2080 \text{ cm}^{-1}$  using infrared (IR) spectroscopy.<sup>40,41</sup> For CO-covered Au surfaces, we have calculated two modes: the surface-molecule ( $\nu_{\text{Au-CO}}$ ) and the molecule stretching frequencies ( $\nu_{\text{CO}}$ ). We find a small drop in the vibrational frequency compared to that for the free CO as a result of the bonding of CO with the Au surface atoms. The calculated frequencies for all surfaces are summarized in Table III. As shown in Fig. 3, the CO stretching frequency decreases as CO binding energy increases since the stronger CO bond does not allow the molecule to vibrate faster although the differences are not substantially large.

We find a small increase in the surface-CO frequency ( $\nu_{\text{Au-CO}}$ ) which we correlate to the decrease in coordination of the substrate surface. The stronger effect can be seen on the bridge site, for which the CO stretching frequency drops drastically to  $1902 \text{ cm}^{-1}$ , correlating with an increase in co-

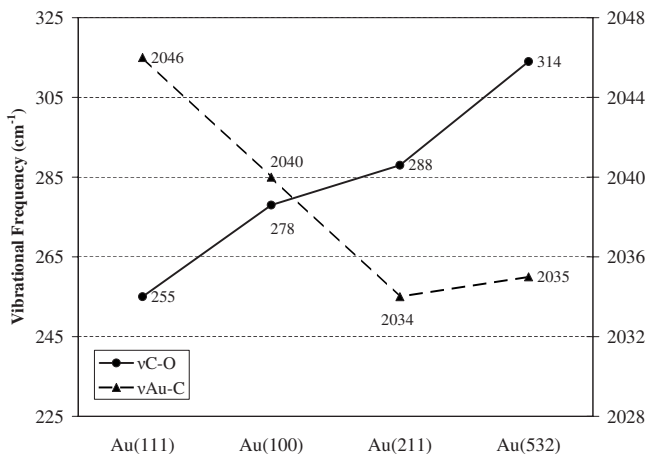


FIG. 3. C-O and Au-CO vibrational frequencies.

TABLE IV. Calculated work functions for clean and CO-adsorbed Au surfaces along with available experimental values (Refs. 42–44).

	Au(111)	Au(100)	Au(211)	Au(532)
Clean	5.11	5.14	5.09	5.03
CO/Au	4.55	4.51	4.71	4.67
Clean <sup>expt</sup>	$5.26 \pm 0.04$	$5.22 \pm 0.04$		

ordination. In Table III, we have also reported vibrational frequencies for the higher CO coverages considered in this work. We found a significant decrease in vibrational frequencies with increase in CO coverage for close-packed surfaces for which we could achieve high coverage. The change was not significant for the kinked surface when doubling the coverage. This can be correlated with the change in the binding energy with increasing coverage as reported in Table II, where the most significant drop in the binding energy occurs for the (100) and (111) surfaces. Note that in the present study, one CO molecule represented 0.33, 0.5, and 0.17 ML coverages on Au(111), Au(100), and Au(211), respectively. Doubling the coverage increased dramatically the effective concentration of CO for (111) and (100) surfaces but not as much for (211) and (532) surfaces. As the interaction between CO molecules grows stronger with concentration, the binding energy to the metal surface gets weaker, triggering a softening of the CO-metal vibrational mode.

We have extracted the work function for all the surfaces mentioned above with and without CO molecules and our results are summarized in Table IV along with the available experimental values for clean surfaces. Our calculated work functions are smaller than the experimental values.<sup>42,43,45</sup> We show a systematic decrease in the work function for the clean surfaces with decrease in the coordination of surface atoms. A similar behavior has been seen in experimental studies for (111), (100), and (110) surfaces<sup>42,43,45</sup> and theoretical studies on other metal surfaces.<sup>42,43,45</sup>

### D. Local electronic structure

Previous investigations pointed to substantial coordination-dependent alteration of the substrate electronic structure upon CO adsorption.<sup>30,35</sup> To probe this further we have chosen to examine the changes in the local electronic densities of states (LDOSs) of the Au surface atoms when CO is adsorbed on the top and the bridge sites on a step edge or on a kink site. In Figs. 4(a) and 4(b) we show the LDOSs for an Au atom at the step edge [Fig. 4(a)] and at the kinked site [Fig. 4(b)] along with that of the oxygen and carbon atoms. For the case of CO/Au(211), we note a strong shift (as much as 2 eV) in the *d* band toward stronger binding, along with a substantial narrowing of the *d* band when the CO is adsorbed at atop site, reflecting the strong coupling between the electronic structures of CO on one hand and the gold step atom on the other. The shift as well as the narrowing is also noticeable for the case of CO adsorption at the bridge site but is



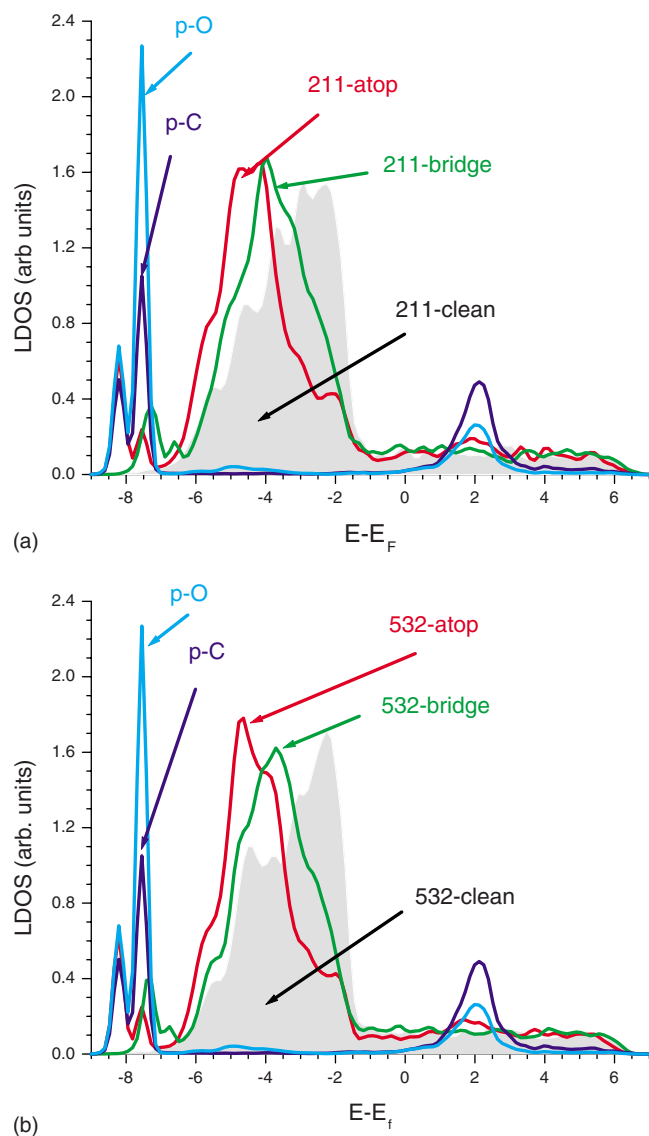


FIG. 4. (Color online) (a) Local densities of states for Au, O, and C atoms for the cases of CO on Au(211). (b) Same as (a) but for the cases of CO on Au(532).

not as dramatic as for the case of atop adsorption. Another feature worth mentioning is the *sp-d* hybridization at about 8.5 eV binding energy which is present in the atop adsorption case and absent in the bridge case. However, a weaker hybridization is noticed for both cases at about 7.5 eV below the Fermi level. Similar features are observed for the case of CO/Au(532), where the kink atoms experience the same changes in the electronic structure as the step atom for the same adsorption, pointing to the fact that alterations in the electronic structure resulting from a reduction in the coordination are not linear and saturate for low coordination. (Here a kink atom has a coordination 6, while a step atom has a coordination 7.)

#### IV. CONCLUSIONS

In this paper, we have presented results of theoretical investigations of CO adsorption on two low-Miller-index surfaces and a stepped and a kinked gold surface. The CO molecules were adsorbed on several sites on these surfaces to determine the preferred adsorption sites and to explain trends in adsorption energies resulting from differences in local geometrical and electronic structure. For all cases, we found that the CO adsorption energy depends strongly on coverage and drops with increase in coverage. We also find the adsorption energy to increase with decrease in local coordination of surface atoms for low-Miller-index surfaces and to saturate for the low-coordinated (stepped and kinked) surfaces, which are the most favorable surfaces for CO adsorption. A very small drop in the vibrational frequency of the free CO molecule was noted when it was adsorbed on the metal surface but differences within the set of surfaces was found to be negligible for on-top adsorption, but significant for other sites. Work function of adsorbate-covered surfaces was found to decrease in all cases as compared to the clean surfaces.

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