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Theoretical Investigation Of Coverage Effects Of CO Adsorption On Cu(100) Surface

M. Oluş ÖZBEK *1

Abstract

This work investigates the CO adsorption on the metallic Cu(100) surface using periodic DFT computations. CO adsorption was studied at varying coverages from 1/16 ML to 1/1 ML for a combination of adsorption positions (4-fold, bridge and top). The results showed that adsorption energies are coverage dependent, however, not enough to identify the adsorption site and coverage. However, C-O stretching frequencies are almost unique for studied coverage and adsorption positions. CO adsorption energy changes between -250 kJ/mol to +21 kJ/mol; similarly, the vibrations' range in the 1702 cm^{-1} to 2110 cm^{-1} interval, within the studied coverage and adsorption positions. Nevertheless, under the saturation coverage ($\theta_{CO} \approx 0.55$ML) the preferable adsorption site is the on-top position identified with a C-O stretching frequency around ~2100 cm^{-1} and with ~117 kJ/mol adsorption energy.

Keywords: DFT, Carbon monoxide, Copper, adsorption, vibration.

1. INTRODUCTION

The interactions of carbon monoxide (CO) with copper is of importance for heterogeneous catalysis. The non-dissociative adsorption of CO on copper based catalysis is the key point for several reactions where CO is converted to CO_2, H_2 and/or methanol (CH_3OH) [1, 2] . Owing to the industrial and financial aspects of these reactions CO+Cu systems have been of interest for decades. Especially low index surfaces (100), (110) and (111) of metallic copper, which are stable with low surface energies [3], as well as stepped surfaces [4, 5] and copper doped structures [6, 7] were commonly investigated for CO interactions. Among these, literature is especially rich for Cu(111) surface due to its higher stability [1, 8].

For the (100) surface, published literature dates back to early 1970's [9], however, not as rich. Since then, the authors inspected the different aspects of CO interactions including adsorption energy, geometry, electronic effects, and so on [1, 3-6, 9-25].

Older studies on the polycrystalline copper [26, 27] did not produce conclusive results and reported adsorption energies varying between 38 – 70 kJ/mol without relating to a definite coverage or adsorption position. Later studies (experimental and computational) showed that the

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CO prefers to adsorb on-top (1-fold, linear) positions [16, 21, 22] with a coverage dependent adsorption energy between ~40 kJ/mol to ~80 kJ/mol [9, 24, 25], ~0.57ML being the saturation coverage [5, 17, 23], after which CO-CO interactions became repulsive. Similarly, CO vibration bands measured in the 2100 cm^{-1} region were assigned to the on-top CO adsorption on Cu(100) terraces, here again, varying between 2064 cm^{-1} to 2120 cm^{-1} with coverage [2, 5, 10, 17-19, 24, 28-32].

Nonetheless, within our knowledge a complete set of adsorption related data for the Cu/Cu(100) system does not exist in the published literature. Although parts of the data set are available in different reports, comparing these different data sets is mostly unhealthy, and sometimes impossible because of the experimental studies conducted under different conditions and setups, or computational studies carried out using different settings, software and methodologies. Especially, data for the low coverage, beyond the saturation coverage, and most importantly site-specific data are not available. For this reason this work aims to supply a complete data set through uniform and standardized computations for better understanding and comparison of CO interactions with the metallic Cu(100) surface.

2. COMPUTATIONAL DETAILS

The periodic DFT simulations were performed using the Quantum Espresso package [33]. Perdew–Burke–Ernzerhof (PBE) functional is used for the exchange-correlation energy. Norm conserving (NC) projector augmented wave (PAW) sets are used to describe the ionic core pseudopotential. Upon optimizing the Cu crystal structure, 5-layer p(1x1), p(2x2), p(3x3), p(3x1) and p(4x4) Cu(100) slabs were prepared with a minimum of 15 Å vacuum heights. During the simulations, the bottom 2 layers of the surface slabs were kept frozen while the top 3 layers and the interacting CO molecule(s) were relaxed. The Brillouin zone sampling was done with automatically generated Monkhorst–Pack k-points using 2x2x1, 3x3x1, 4x4x1, 3x8x1 and 8x8x1 meshes for p(4x4), p(3x3), p(2x2), p(3x1) and p(1x1) slabs, respectively. The gas phase CO molecule was modeled using a single gamma point, where the periodic molecules were separated with a minimum of 10 Å vacuum distances in all Cartesian Coordinates. The cut-off energies used in every simulation for the wavefunctions and the charge densities were 50 Ry and 350 Ry, respectively. All the results presented were obtained by relaxing the structures until the net force acting on the ions was Fnet < 0.001 Ry/Bohr. Necessary dipole corrections due to the asymmetric usage of slabs were included.

The adsorption energies of the CO molecules were calculated as the difference between the DFT energies of the products (CO adsorbed structure) and the sum of the reactants (clean Cu(100) surface + CO(g)).

$$\Delta E_{ads} = E_{CO/Cu(100)} - (E_{CO(g)} + E_{Cu(100)})$$

The work function (ϕ) is calculated as the difference between the Fermi energy (E_F) of the structure and the electrostatic potential (Ψ) of the vacuum.

$$\Phi = \Psi - E_F$$

The vibrational frequencies of adsorbed surface species were obtained by calculating the Hessian matrix. During the frequency computations symmetry was excluded explicitly. The frequencies of the surface ions were excluded basing on the frozen phonon approximation. The frequency plots were obtained using the vibrational band data and the corresponding intensities as produced by the software.

3. RESULTS AND DISCUSSION

The FCC Cu crystal structure was optimized with a lattice parameter of 3.643 Å, which is in good agreement (Δ=1.2%) with the experimentally reported value of 3.597 Å [34]. Figure 1 shows the top view of the Cu(100) slabs and the studied adsorption positions.

At this point it should be noted that the c(2x2) structure that was reported [10, 11, 17, 18, 21, 23] to form around 0.5 ML coverage with CO on-top positions was not modeled within this work in order not to break the continuity of the coverage dependent data; as well as not to limit the study to on-top sites.

Adsorption energies (E_{ads}), CO stretching frequencies (ν_{CO}), bond distances (|C-O| and |C-Cu|), work function (ϕ) and Bader-charge data (calculated but not included within) were produced for a wide range of coverage (θ_{CO}) and combinations of adsorption positions. When producing the complete set of data both homogenous and non-homogenous distributions (or combinations) of adsorption positions were studied. However, it was observed that the combination of different positions (such as 4-fold + 2-fold) did not have a major effect on the site-specific absorption data. For this reason, only the homogeneous combinations (such as 4-fold + 4-fold) of absorption positions were selected (Figure 2 and Table 1) and presented below.

Table 1 and Figure 3 show that the exothermicity of the CO adsorption decreases with the increasing coverage. The change is almost linear for the $\theta_{CO} > 0.2$ ML. Below this value a major difference was not observed between the adsorption energies of the 4-fold, bridge (2-fold) and the top (1-fold) positions. However, the differences become more pronounced at higher coverage. The most exothermic adsorptions belong to the on-top positions followed by the bridge and 4-fold positions, respectively. This finding is in line with the previous reports [16, 21, 22]. Although the trend and the preferred adsorption site agrees with the experimental data, previous studies reported E_{ads} changing between ~80 kJ/mol at low coverage (< 0.2 ML) to ~50 kJ/mol around saturation coverage (~0.55 ML) [5, 9, 17, 23-25, 35]. The computed value of 135 kJ/mol (for 0.22 ML) and ~90 kJ/mol (for 0.50 ML) appear to be overestimated. However, this kind of a mismatch is expected considering the temperature-pressure gap between the experiments and the DFT simulations (0 K, 0 bar). On the other hand, reported Cu-C and C-O bond lengths of 1.90 ± 0.1 Å and 1.15 ± 0.1 Å [11, 35, 36], are in perfect agreement with the produced data, especially with on-top adsorption at $\theta_{CO} = 0.50$ ML, where most of the previous experimental data is produced.

Unlike many other adsorption systems [37], for the CO/Cu(100) system, adsorption site cannot be identified based on the adsorption energy alone. However, CO stretching bands show clear differences with the adsorption sites.

Figure 4 and Figure 5 show that the CO vibrations have a strong position dependency that creates a major distinction to identify the adsorption site. The coverage dependent shifts of the vibrational bands do not affect the positional distinction. The means of simulated CO stretching bands appear at 1766 cm^{-1} for 4-fold, 1927 cm^{-1} for 2-fold and 2043 cm^{-1} for 1-fold adsorptions. Previous works on CO/Cu system(s) assign the bands measured around 2100 cm-1 to CO at on-top positions on Cu(100) terraces [2, 5, 10, 17-19, 24, 28-32]. These reported values vary between 2064 cm^{-1} to 2120 cm^{-1}, mainly with the CO dosing. The calculated vibrational data for 1-fold adsorption agrees quite well with these reports both with mean value and the range. Furthermore, the readily available data in this work relates the frequencies and its changes to the corresponding CO coverage. For the CO adsorption on the bridge sites IR bands between 1800 cm^{-1} and 1900 cm^{-1} were expected, but not observed in previous works [17]. Nonetheless, the frequency data corresponding to the CO adsorption on bridge positions agrees with this range, nonetheless, being wider.

When Figure 4 and Figure 5 are compared, it can be seen that the frequency is also coverage dependent. Figure 5 shows different intensities and bifurcated band. Both depend on the number of CO molecules adsorbed on the specific simulation. The non-interacting CO molecules produced similar bands that increase the intensities. However, the bifurcations may shed a light to a different phenomenon. Experimental works reported shoulders in the vibrational spectra that shift or diminish with the coverage [2, 5, 18, 21, 24, 32]. Two explanations given for this phenomenon are i) the dipole effects, and ii) adsorption of CO on different sites. The diversity of the data produced within this work may clarify this point. The intersecting regions in Figure 5 may appear to support the second idea, where the logical choice would be combination of on-top and bridge sites based on the adsorption energies. However, a deeper investigation shows that the matching frequencies of on-top and bridge positions belong to different surface coverages, which weakens the second idea. Furthermore, the simulations carried out using two different adsorption sites at various coverages (namely on-top and bridge sites) did not produce the shoulders as observed in previous works. On the other hand, Figure 5 shows that when more than one CO molecule exists on the surface the measured bands may bifurcate even for the same adsorption sites due to dipole interactions [24]. The simulations produced splits within the range of ~30 cm^{-1}, depending on the surface coverage. This agrees with the shoulders separated by ~10-20 cm^{-1} in the experimental works.

The calculated work function changes can be seen in Table 1 and Figure 6. The work function measurements are rather limited in the previous works [17, 23] and the reports vary. However, the common point is the increase in the work function with the coverage. Here again literature data is only available up to saturation coverage (~0.55 ML), without adsorption site distinctions. The work function increases for all the adsorption positions, which agrees with the previous reports, on-top adsorptions causing the highest changes.

4. CONCLUSION

CO interactions with the Cu(100) surface were investigated using periodic DFT computations. Adsorption energies, CO stretching frequencies, bond distances, work function and Bader-charge data were produced for a variety of CO coverage (0.0625 ML to 1.0 ML) and adsorption positions (4-fold, bridge and top) to fill in the gaps of missing data and uncertainties of the previous experimental works. The results showed that simultaneous existence of CO in two or more different adsorption sites did not have a major effect on the site-specific data. Although adsorption energies are coverage and site dependent, identification of adsorption position and coverage is not always possible basing on the adsorption energy alone. On the other hand, the CO stretching frequencies are almost unique for each coverage and adsorption site. The data produced for the on-top adsorption agrees well with the previous experimental works, in addition, introduces the possibility of adsorption in bridge positions at low coverages. The splitting of the stretching bands around 0.5 ML are caused by the dipole effects rather than the CO resting in two different sites.

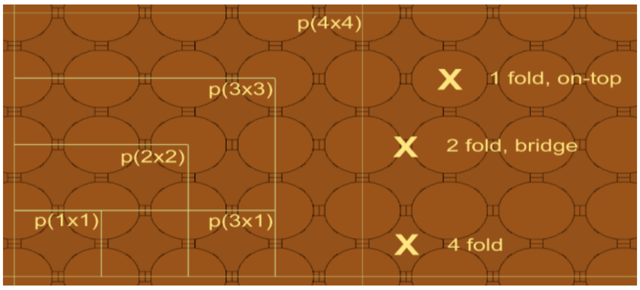

Figure 1 Top views of the a) p(1x1), p(2x2), p(3x3), p(3x1) and p(4x4) slabs, and b) CO adsorption positions. The darker shades represent the lower Cu layers. (Cu: orange)

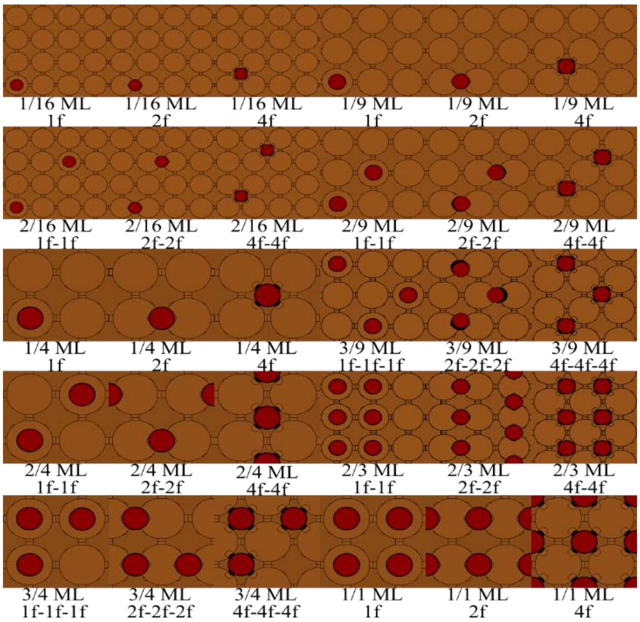

Figure 2 Top views of the CO adsorption geometries at given coverage and positions.

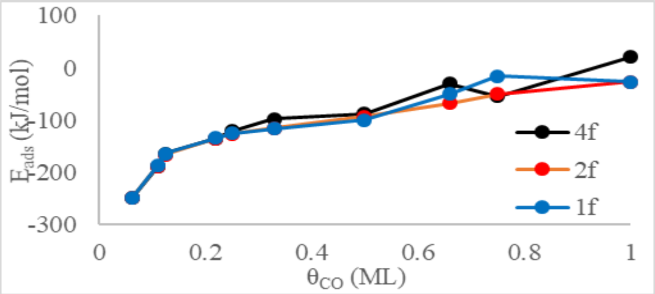

Figure 3 Adsorption energy of CO at varying coverage and adsorption positions.

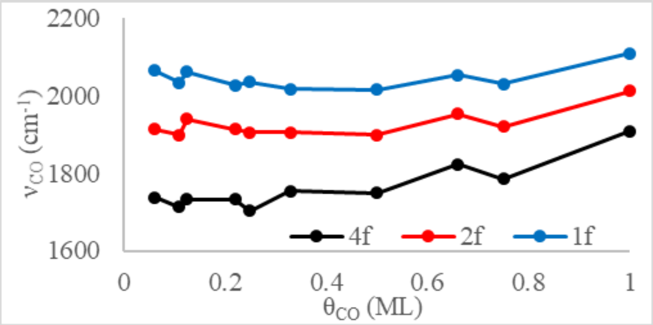

Figure 4 C-O stretching frequencies at given coverage and positions. Average value is plotted for the cases where more than one CO molecule is adsorbed.

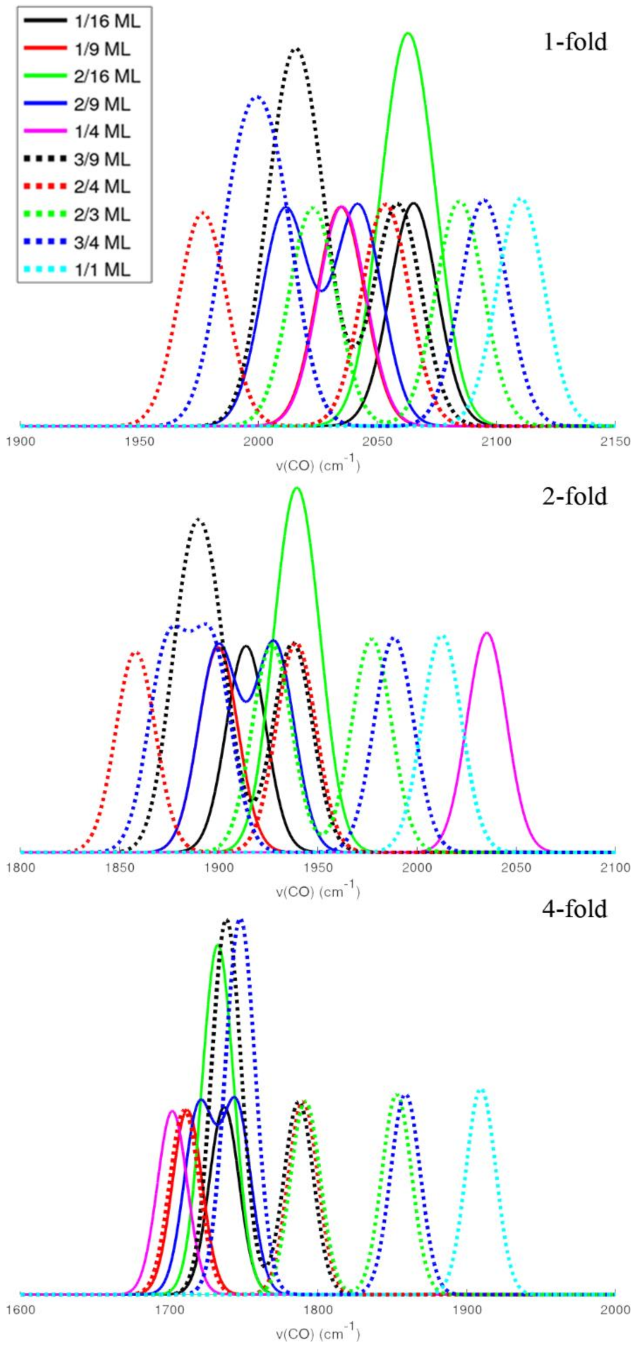

Figure 5 simulated vibrational spectrum of the CO adsorbed on Cu(110) surface at various coverage and adsorption positions.

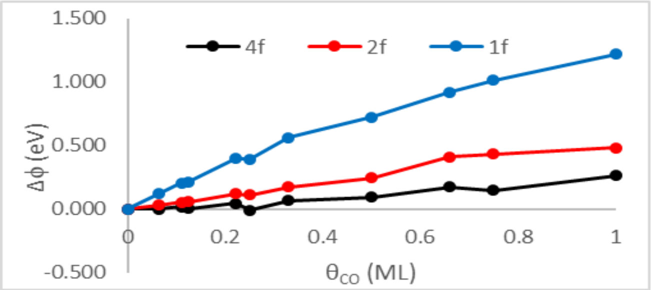

Figure 6 Changes in the work function for CO adsorption on Cu(100) at various coverage and adsorption positions.

Table 1
Adsorption energy (E_{ads}, kJ/mol), C-O stretching frequency (ν_{CO}, cm^{-1}), C-O and C-Cu bonds distances (Å), and change in work function ($\Delta\phi$, eV) for the studied coverage (θ_{CO}, ML) and positions.

θ_{CO}	Site	E_{ads}	ν_{CO}	|C-O|	|C-Cu|	$\Delta\phi$
1/16	4 fold	-249	1737	1.197	2.141	0.000
(0.0625)	2 fold	-250	1914	1.170	1.983	0.029
	1 fold	-249	2064	1.154	1.847	0.121
1/9	4 fold	-190	1712	1.198	2.138	0.015
(0.1111)	2 fold	-189	1899	1.170	1.980	0.053
	1 fold	-187	2034	1.154	1.842	0.204
2/16	4 fold	-164	1729	1.197	2.144	0.003
(0.1250)			1736	1.197	2.138	
	2 fold	-166	1934	1.170	1.981	0.059
			1945	1.170	1.981	
	1 fold	-165	2057	1.154	1.842	0.212
			2067	1.154	1.844	
2/9	4 fold	-135	1720	1.195	2.127	0.044
(0.2222)			1745	1.195	2.166	
	2 fold	-135	1899	1.169	1.985	0.120
			1928	1.169	1.982	
	1 fold	-134	2011	1.154	1.840	0.396
			2042	1.154	1.840	
1/4	4 fold	-121	1702	1.195	2.138	-0.012
(0.2500)	2 fold	-127	1905	1.169	1.981	0.111
	1 fold	-125	2035	1.154	1.841	0.394
3/9	4 fold	-97	1738	1.190	2.138	0.069
(0.3333)			1739	1.192	2.162	
			1787	1.190	2.138	
	2 fold	-115	1883	1.170	1.991	0.172
			1896	1.170	1.991	
			1938	1.167	2.008	
	1 fold	-116	2010	1.155	1.841	0.563
			2021	1.155	1.838	
			2059	1.155	1.838	
2/4	4 fold	-87	1710	1.188	2.174	0.094
(0.5000)			1789	1.188	2.179	
	2 fold	-93	1858	1.168	1.992	0.244
			1939	1.168	1.992	
	1 fold	-100	1976	1.155	1.840	0.722
			2054	1.155	1.840	
2/3	4 fold	-15	1792	1.179	2.144	0.174
(0.6666)			1853	1.181	2.183	
	2 fold	-68	1928	1.166	1.986	0.409
			1979	1.165	1.980	
	1 fold	-50	2023	1.153	1.851	0.919
			2084	1.153	1.851	
3/4	4 fold	-16	1747	1.180	2.197	0.148
(0.750)			1748	1.179	2.183	
			1859	1.180	2.202	
	2 fold	-51	1874	1.164	1.982	0.432
			1896	1.167	1.994	
			1988	1.164	1.982	
	1 fold	-55	1992	1.153	1.851	1.014
			2006	1.154	1.851	
			2094	1.153	1.851	
1/1	4 fold	21	1909	1.174	2.207	0.264
(1.0000)	2 fold	-26	2012	1.163	1.981	0.479
	1 fold	-27	2110	1.152	1.857	1.218

a) Average Eads is reported when more than one CO molecules are adsorbed. b) Average bond lengths are reported for 2-fold and 4-fold positions. c) The X and Y positions of these geometries were kept frozen to prevent shifting into other positions.

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The Declaration of Conflict of Interest/ Common Interest

No conflict of interest or common interest has been declared by the authors.

Authors' Contribution

The author solemly performed the computations and wrote the manuscript.

The Declaration of Ethics Committee Approval

The author declare that this document does not require an ethics committee approval or any special permission.

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