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# Plane-wave pseudopotential density functional theory periodic slab calculations of CO adsorption on $Cu_2O(111)$ surface

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### Abstract

Plane-wave pseudopotential Density Functional Theory (DFT) periodic slab calculations have been performed to investigate carbon monoxide adsorption on the (111) surface of Cu<sub>2</sub>O. Negligible relaxation of this surface was found (surface energy =  $0.71 \text{ J m}^{-2}$ ), consistent with its non-polar nature. The on-top-Cu site of CO adsorption is favoured, with a binding energy of 1.50 eV. After adsorption, the Cu–C bond distance was found to be 1.82 Å and that of C–O was 1.15 Å. From the Density of States (DOS) plots, a distinct stabilization of both the Cu3d and CO  $5\sigma$  is observed with predominant back-bonding to CO  $2\pi^*$  from Cu. A red shift of  $-26 \text{ cm}^{-1}$  in the C–O stretch was found in good agreement with experimental results.

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*Keywords:* CO adsorption on  $Cu_2O(111)$ ; Density of state of  $Cu_2O(111)$ ; Adsorption energy of CO on  $Cu_2O(111)$ ; Infra-red band of CO on  $Cu_2O(111)$ ; Surface energy of  $Cu_2O(111)$ ;

# 1. Introduction

The copper oxide system has been studied extensively due to its widespread importance in catalysis, corrosion and high-performance materials. Cu/ZnO catalysts have been known for long years for their high performance in methanol synthesis [1,2] from syngas (CO, CO<sub>2</sub> and H<sub>2</sub>), for water gas shift reaction [3,4] and for methanol partial oxidation to formaldehyde [5,6]. For all these processes, the active species have been postulated to be Cu<sup>+</sup> ions [2]. It has also been shown that Cu<sub>2</sub>O is an effective photocatalyst for water splitting to H<sub>2</sub> and O<sub>2</sub> under visible light [7–9]. Information about the interaction and reaction of small molecules such as oxygen, carbon monoxide,

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water and methanol with Cu<sub>2</sub>O surfaces is important to understanding the mechanism of these catalytic processes.

The structure and electronic properties of  $Cu_2O(111)$  and  $Cu_2O(100)$  single crystals have been investigated in detail by Schulz and Cox [10–13] using low energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS), thermal desorption spectroscopy (TDS), and ultraviolet photoelectron spectroscopy (UPS). The adsorption of O<sub>2</sub> at room temperature was found to be molecular on stoichiometric (111) surfaces, but is dissociative on defected (111) surfaces that had been prepared by ion bombardment. The interaction of oxygen with the (100) surface was determined to be dissociative for several different surface preparation procedures.

The adsorption of carbon monoxide has been examined on the Cu<sub>2</sub>O(100) surface. At 120 K, carbon monoxide adsorbs molecularly, with the sticking coefficient independent of coverage up to 0.4 L exposure, suggesting the presence of a precursor state and a non-activated adsorption. The low-coverage adsorption energy was found to be 70 kJ/mol. There appears to be a fairly strong interaction between CO and the Cu3d orbitals, with some changes observed in the shape of the Cu3d features in the UPS valence band. A large decrease in the surface work function (-0.6 eV following a 1 L exposure increasing to -1.0 eV at saturation) was an indication of electron transfer from adsorbed carbon monoxide to the surface, predominantly sigma donation in nature.

Although some theoretical calculations have been performed on Cu<sub>2</sub>O, these were mainly concerned with band structures. The majority of surface calculations [14–16] were focused on the non-polar (111) or (110) surfaces where the Cu<sup>+</sup> ions sit between layers of oxygen ions (Fig. 1A). Bredow and Pacchioni [15] initiated a comparative study of both cluster and periodic slab calculations on the Cu<sub>2</sub>O(111) surface, using the CRYSTAL code [16]. The periodic slab used was 9 atomic layer in thickness and no lateral relaxation was allowed during geometry optimization. In this study, the authors concluded that a blue shift in the vibrational frequency of the adsorbed CO is expected, which was contradictory to experimental results [17]. The same authors followed up the work with another publication [18], well explaining the delicate relationship between the predicted vibrational frequency with the model employed for computation. Using a similar  $Cu_2O(111)$  cluster, Casarin et al. [19] have conducted a LDA DFT study of CO and NO adsorption on the (111) surface. They have found that X-down (where X = C, N) atop position is most favoured and the red shift in the vibrational frequency of the adsorbed CO is well reproduced. However, the binding energies are over-estimated due to the use of the LDA method.

In this work we employ periodic slab calculations using DFT GGA with the PWscf code [25] to investigate CO adsorption geometry, energy and changes in the density of state on  $Cu_2O(111)$ surface and compare our method to the above studies as well as to experimental works.

# 1.1. Methodology

All calculations have been performed within the density functional theory (DFT) using the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [20]. We have employed the pseudopotential method with ultrasoft pseudopotentials [21] and plane-wave basis sets up to a kinetic-energy cutoff of 50 Ry (200 Ry for the charge-density cutoff). The core radii (in a.u.) of the pseudopotentials used are: C2s (1.2, 1.6) 2p (1.3, 1.7) local-3d (1.7), O 2s (1.4, 1.6) 2p (1.4, 1.6), local-3d (1.4), Cu3d (1.8, 2.5) 4p (2.8) local-4s (2.8). The two values of the core radii indicate a channel that has been pseudized within the ultrasoft scheme. The first value will be the norm conserving core radius and the second is the ultrasoft one [22]. The use of ultrasoft pseudopotentials enables the plane-wave basis sets to be expanded to a much lower kinetic-energy cutoff of 50 Ry, as compared to the conventional norm-conserving type [23]. Brillouin zone integrations have been performed with the Marzari-Vanderbilt spreading technique [24], with a smearing parameter of 0.01 Ry to ease convergence due to surface states. All calculations have been performed using the PWscf 2.0.3 package [25].



Fig. 1. (A)  $Cu_2O(111)$  12 atomic-layered slab. The Cu and O atoms are coloured in orange (white) and red (black), respectively. (B) Unit surface area of the (1 × 1)  $Cu_2O(111)$  slab. The Cu and O atoms are coloured in orange (white) and red (black), respectively.

Surfaces are modelled using periodic supercells. 12 atomic layers were used in the calculations to represent a 2-dimensional (1 × 1) surface unit cell (a = b = 6.14 Å) with a 5 × 5 × 5 k-point grid (unless other wise specified). The slab has been fully relaxed until the forces experienced by the system were smaller than 10<sup>-3</sup> Ry/a.u. To study CO adsorption, a monolayer (corresponding to  $\theta = 1$ ) of CO was modelled at various geometries on both top-most and bottom-most sides of the slab, with the 6 outermost atomic layers relaxed. A vacuum layer of 15 Å was employed to prevent spurious interactions between image slabs. The various tests for convergence are summarized in Table 1.

The chemisorption energies  $E_{\text{chem}}$  are referred to the clean Cu<sub>2</sub>O(111) surface and the isolated adsorbate molecule:

$$E_{\rm chem} = 1/2[E_{\rm system} - (E_{\rm slab} + E_{\rm CO})] \tag{1}$$

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Surface energy convergence as a function of number of (i) atomic lavers (ii) **k**-points and (iii) vacuum thickness

No of atomic layers Surface energy (J m <sup>-2</sup> )	9 0.708	12 0.707	18 0.707
<b>k</b> -point scheme Surface energy (J m <sup>-2</sup> )	$\begin{array}{c} 3\times3\times3\\ 0.707 \end{array}$	$5 \times 5 \times 5 \\ 0.707$	$\begin{array}{c} 7\times7\times7\\ 0.707 \end{array}$
Vacuum thickness (Å) Surface energy (J m <sup><math>-2</math></sup> )	$\begin{array}{c} 3\times3\times3\\ 0.707 \end{array}$	$5 \times 5 \times 5 \\ 0.707$	$7 \times 7 \times 7$ $0.707$

where the total energy of the adsorbate–substrate system, of the clean stoichiometric surface, and of the free CO molecule in gas phase are represented by  $E_{\text{system}}$ ,  $E_{\text{slab}}$  and  $E_{\text{CO}}$  respectively. A factor of 1/2 was included to offset the use of the double-sided adsorption techniques. By this definition, stable adsorbates will have negative chemisorption energies.

The surface energy,  $E_{suf}$  of the clean Cu<sub>2</sub>O(111) was calculated using the following equation:

$$E_{\rm suf} = [E_{\rm slab} - N \times E_{\rm bulk}]/2A \tag{2}$$

where  $E_{\text{slab}}$  is the total energy of the (111) slab and  $E_{\text{bulk}}$  is the energy of the bulk per formula unit Cu<sub>2</sub>O. *N* is defined as the total number of formula units Cu<sub>2</sub>O in the slab and *A* is unit surface area (as shown in Fig. 1B), which is equal to  $3.268 \times 10^{-21} \text{ m}^2$ .

The vibrational stretching frequency of CO (gas phase and adsorbed state) was calculated using the simple harmonic oscillator approximation method [26]. The optimized structure was first obtained and the length of the CO bond was then displaced, i.e. elongated and compressed along the CO bond length. The atomic position of C was kept fixed and only the O atom was moved to simulate the displacement. For each displacement, a singlepoint SCF calculation was conducted. The total SCF energy,  $E_{\rm SCF}$  derived from each displacement was then plotted against the displaced CO distance, R and fitted to a quadratic curve. The force constant, k, was extracted from the plot of  $E_{SCF}$ (J) versus R (m) by taking the 2nd derivative. The vibrational frequency of CO was then obtained from k and the reduced mass.

Considering the errors in the structural relaxation and the energy convergence with respect to the planewave cutoff energy and **k**-point mesh, an overall numerical accuracy for the chemisorption energies is about  $10^{-4}$  Ry.

# 2. Results and discussion

### 2.1. Geometric and electronic structure of bulk Cu<sub>2</sub>O

The methodology was validated by calculating the lattice constant and bulk modulus of Cu<sub>2</sub>O

Table 2				
Calculated	bulk	properties	of Cu	20

by fitting energy versus lattice constant data to the Murnaghan equation of state. The calculations were performed with a  $10 \times 10 \times 10$  Monkhorst-Pack k-point grid and a planewave kinetic cutoff energy of 50 Ry. The calculated properties of Cu<sub>2</sub>O are listed in Table 2, and compared with other theoretical studies [27,28] and experimental data [29–31]. A good agreement (both in theory and experiment) is noticed. The calculated total density of states (DOS) and atom-projected DOS (pDOS) for bulk Cu<sub>2</sub>O are presented in Fig. 2. There are 2 distinct bands in the valence region. The Cu band (predominantly Cu3d) occupies the region of 0 to -5 eV and the O band (predominantly O2p) occupies that of -5 to -7.5 eV. These structures are in accord with a number of published calculations [28,32] and experimental data [33,34].

### 2.2. Geometric structure of $Cu_2O(111)$ slab

Fig. 3A shows the stoichiometric  $Cu_2O(111)$ surface that is non-polar and consists of a 3-plane repeat unit with each copper layer sandwiched between 2 layers of oxygen anions. The  $Cu_2O(111)$ unit cell surface possesses hexagonal symmetry with 4 distinct atom-types— $Cu_{CUS}$ ,  $Cu_{CSA}$ ,  $O_{SUF}$ and  $O_{SUB}$ . The  $Cu_{CUS}$  is the surface copper that is coordinatively unsaturated. This atom-type acts as a Lewis acid site where most of the reaction is believed to take place.  $Cu_{CSA}$  is the coordinatively saturated copper atom which has the unique linear O–Cu–O bond symmetry.  $O_{SUF}$  is the outer-most surface oxygen which acts as a Lewis base site, and  $O_{SUB}$  is the subsurface oxygen that is 4-foldcoordinated.

The Cu<sub>2</sub>O(111) surface energy was calculated for slab thickness convergence with 9, 12 and 18 atomic layers, performed with a  $5 \times 5 \times 5$  Monkhorst-Pack **k**-point grid and a planewave kinetic

	Present work	Hartee–Fock [27]	FPLAPW [28]	Experimental [29-31]		
Lattice constant (Å)	4.34	4.28	4.30	4.27		
Cu–O (Å)	1.88	1.85	1.86	1.85		
Cu–Cu (Å)	3.07	3.03	3.04	3.01		
Bulk modulus (GPa)	104.23	93.00	108.00	112.00		



Fig. 2. Calculated density of states for bulk  $Cu_2O$ : (A) total density of states; (B) local density of states for Cu atoms; (C) local density of states for O atoms. Zero energy is the Fermi level.

cutoff energy of 50 Ry. The difference in energy is  $\sim 10^{-3}$  J m<sup>-2</sup>, well within the accuracy limit. To ensure the number of atomic layers used in the slab, **k**-point scheme and vacuum thickness chosen



Fig. 3. (A)  $Cu_2O(111)$  stoichiometric surface (details are found in text). (B) On-top-Cu configuration for CO adsorption on  $Cu_2O(111)$ . The Cu and O atoms are coloured in orange (white) and red (black), respectively.

are well-converged, a series of atomic layers, **k**-point and vacuum thickness convergence tests were carried out (and are reported in Table 1). Thus, the 12 atomic-layered supercell and the  $5 \times 5 \times 5$  Monkhorst-Pack **k**-point grid will be used for all adsorption studies at a cutoff energy of 50 Ry (as recommended in [21]).

Surface relaxations were found to be minimal and the changes are summarized in Table 3. The  $Cu_{CSA}-O_{SUF}$  bond length shrinks slightly from 1.881 to 1.860 Å, while the O- $Cu_{CUS}$  length increases to 1.909 Å. To determine the effect of relaxation on tri-layer (TL) spacing (see Fig. 3A), each TL is defined as one neutral layer consisting of one plane of Cu cations sandwiched between two planes of oxygen anions. After relaxation, the TL distance decreased from 3.071 Å to

	Before relaxation	After relaxation	% Change
O-Cu <sub>CUS</sub> (Å)	1.8809	1.9088	1.5
Cu <sub>CUS</sub> –Cu <sub>CUS</sub> (Å)	1.8809	1.8597	-1.1
Cu <sub>CU</sub> –OS <sub>UB</sub> (Å)	1.8809	1.9093	1.5
Tri-layer (Å)	3.0715	3.0527	-0.6

3.053 Å. This has caused a more compact surface where the oxygen anions sink in and the copper cations become more exposed. The negligible relaxation is in accordance to the non-polar character of the surface.

# 2.3. Electronic structure of $Cu_2O(111)$ slab

The calculated total DOS of the 12 atomic-layered slab is compared with the bulk total DOS in Fig. 4. A notable difference between the two DOS plots is the existence of the emerging states at +1 eV and -3.6 eV (compare Fig. 4 to Fig. 2A). To better understand the nature of these surface states, the local DOS of the Cu<sub>2</sub>O(111) slab is calculated and shown in Fig. 5. From the local DOS plots, the surface state band just above the Fermi level is predominantly the empty Cu4s state (Fig. 5B). The contributions from the Cu3d and O2p are minimal. In the energy range of 0 to -4 eV, the local DOS of the Cu3d and O2p have overlapping peak areas, hence substantial hybridization between the Cu3d and O2p is expected



Fig. 4. Total density of states for the Cu<sub>2</sub>O slab (with surface state indicated). Zero energy is the Fermi level.



Fig. 5. (A) Local DOS of  $Cu_{CUS}$  3d. (B) Local DOS of  $Cu_{CUS}$  4s. (C) Local DOS of  $O_{SUF}$  2p. (The bulk local DOS is represented by the dashed lines and that of the slab is represented by the solid lines.) Zero energy is the Fermi level.

and therefore, results in the surface states at  $\sim -3.6 \text{ eV}$  (Fig. 5C).

Table 3 Interatomic distances: Cu<sub>2</sub>O(111) surface relaxation

# 2.4. CO adsorption studies on $Cu_2O(111)$ surface: on-top-Cu configuration

Calculations for the gas-phase CO molecule have been carried out using the same supercell approach used for the slab studies. As it is generally found in DFT calculations, structural properties are relatively well described. The CO molecule was placed in the middle of a  $8 \times 8 \times 8$  (in Å) supercell. The C–O distance was found equal to 1.1401 Å, very close to the experimental value of 1.13 Å.

Before presenting the results of CO adsorption on the  $Cu_2O(111)$  surface it is worth discussing the previous three computational studies that have been conducted. Bredow and Pacchioni [15] first investigated the interaction of CO with the  $Cu_2O(111)$  surface of a  $Cu_{28}O_{14}$  cluster. The authors have employed the Hartree-Fock (HF), configuration interaction (CI) and post-HF density-functional (DF) methods using embedded cluster and periodic slab models for the  $Cu_2O(111)$ surface. They have found the following. A Cu<sub>CUS</sub>–C distance of 2.01 Å, a C–O bond length shortening of 0.01 Å, a blue shift of the stretching frequency of the coordinated CO by  $80 \text{ cm}^{-1}$  and a binding energy of 0.86 eV. Casarin and Vittadini [19] studied the chemisorption of CO and NO on  $Cu_2O(111)$  using the DMOL code, with the local density approximation (LDA) within the DFT framework. The authors found that a Cu<sub>CUS</sub>-C distance of 1.77 Å, a C-O bond lengthing of 0.01 Å upon adsorption, a red shift of the stretching frequency of the coordinated CO by  $39 \text{ cm}^{-1}$ and binding energy of 2.08 eV. With the exception of the overestimation of the binding energy their results were in good agreement with experiments, typically reproducing the red shift observed by Zecchina and co-workers [12]. Using the GAUSS-IAN94 package, Pacchioni et al. [13] revisited their previous investigation of CO adsorption on  $Cu_2O(111)$  and concluded that a shift in CO vibrational frequency of the order of  $\pm 10 \text{ cm}^{-1}$  $(\pm 0.001 \text{ eV})$  may be difficult to predict theoretically. This shift arises from two phenomena: the wall effect (Pauli repulsion) and the back-donation of electrons from the surface to the adsorbate, which critically depend on the method and model chosen for the calculations.

In the present work upon adsorption on the  $Cu_2O(111)$  surface the C–O bond length has increased to 1.15 Å. The equilibrium distance between the CO molecule and  $Cu_{CUS}$  was measured to be 1.82 Å. The computed binding energy of the on-top-Cu configuration (as shown in Fig. 3B) was found to be -1.50 eV.

### 2.5. Electronic structural changes upon adsorption

The local DOS of the Cu 3d and Cu 4s are illustrated in Fig. 6. From Fig. 6A, an overall stabilization of the Cu<sub>CUS</sub> 3d orbital can be seen. It has moved to a lower energy by  $\sim 1.5$  eV. The 5 $\sigma$  orbital of CO is also strongly stabilized by  $\sim 3$  eV upon



Fig. 6. Changes observed in the density-of-states for the on-top-Cu configuration: (A) local DOS of  $Cu_{CUS}$ 3d; (B) local DOS of  $Cu_{CUS}$ 4s. The dashed-line and solid-line represent the local DOS of the orbital before CO adsorption, and that after CO adsorption, respectively. The dotted-line shows the DOS of CO upon adsorption. Zero energy is the Fermi level.

adsorption, becoming almost degenerate with the  $1\pi$  orbital. As observed in CO adsorption with other transition metal oxides (TMO) with partially or fully filled d orbitals, two dominant mechanisms contribute to the coordination: CO  $\rightarrow$  TMO  $\sigma$  donation and TMO  $\rightarrow$  CO  $\pi$  back donation.

In Fig. 6A, a peak of low intensity (contribution from the CO molecule) can be seen at -3.2 eV. This is assigned to the  $\pi$  back donation of Cu3d  $\rightarrow$  CO. The participation of Cu<sub>CUS</sub>4s in CO adsorption can be seen from Fig. 6B. Before adsorption, the band seen at +1 eV is due to the largely unpopulated Cu4s. However, upon adsorption of CO, the sharp band is delocalized, overlapping substantially with the bands due to adsorbed CO.

A Löwdin Charge Population (LCP) analysis was computed and the results are summarized in Table 4. This LCP analysis was performed by using a projection of the plane wave states onto a localised basis set by the technique described by Sanchez-Portal and Artacho [35]. A population analysis of these projected states can then be used to determine quantities such as atomic charges and electron populations. It is widely accepted that the absolute magnitude of the atomic charges have little physical meaning, as they display an extreme sensitivity to the atomic basis set with which they are calculated. However, consideration of their relative values, in contrast to their absolute magnitudes, can yield useful information. From Table 4, an opposite behaviour of the  $\sigma$  (predominantly from carbon 2s) and  $\pi$  (predominantly from carbon 2p) orbitals can be seen in the CO molecule. The charge population of C2p increases from 2.19 to 2.52 and that of C2s decreases from 1.64 to 1.39. This change is coupled to the changes in charge population of Cu<sub>CUS</sub>. This is an indication that the magnitude of CO  $5\sigma$  donation is smaller than that of the  $\pi$  back donation. This behaviour of Cu<sup>+</sup> is again illustrated in a recent work by Walter et al. [36], investigating CO adsorption on zirconia-supported copper. The copper atom on the zirconia-support is coordinated in a similar fashion to that in  $Cu_2O(111)$  surface. The dominant loss of charge due to adsorption occurs in the regions directly above and below the copper atom, corresponding to a depopulation of a  $d_{z^2}$ -like orbital. The binding energy of CO in this work by Walter et al. was found to be -1.34 eV which is in good agreement with our calculation. In addition to the electrostatic contribution in to the bonding, the reduction of charge in the  $d_{z^2}$  orbital of Cu is evident. Many studies have shown that upon adsorption of CO on copper surfaces, there is a repulsive interaction between the  $5\sigma$  lone pair state and copper electron density. This reduction of electron density on Cu diminishes the degree of repulsion that occurs upon CO adsorption.

## 2.6. Vibrational analysis

The donation (CO-5 $\sigma$ ) and back donation (metal-3d) of electrons in the case of CO adsorption on transition metal surfaces affects its infrared frequency [37]. Due to the antibonding nature of the  $2\pi^*$  orbital, this predominant back-donation consequently results in a red shift of the CO stretching frequency relative to its gas phase value of 2143 cm<sup>-1</sup>. On the other hand a shift to higher

Table 4

Löwdin Charge Population (LCP) results for Cu<sub>2</sub>O(111) surface before and after CO adsorption: on-top-Cu configuration

	Before adsorption		Total	After adsorption			Total	
	s orbital	p orbitals	d orbitals		s orbital	p orbitals	d orbitals	
Cu <sub>CUS</sub>	0.63	0.00	9.87	10.49	0.69	0.00	9.68	10.37
Cu <sub>CSA</sub>	0.73	0.00	9.67	10.40	0.73	0.00	9.69	10.41
O <sub>SUF</sub>	1.81	5.14	0.00	6.97	1.81	5.16	0.00	6.96
O <sub>SUB</sub>	1.77	5.19	0.00	6.96	1.77	5.20	0.00	6.97
С	1.64	2.19	0.00	3.83	1.39	2.52	0.00	3.91
0	1.60	4.39	0.00	6.00	1.60	4.38	0.00	5.98

Bold represents an increase in electronic population.

Italic represents an decrease in electronic population.

-	-					
Method	Binding energy (eV)	Cu <sub>CUS</sub> –C (Å)	C–O (Å)	$v_{\rm gas\ phase}\ ({\rm cm}^{-1})$	$v_{adsorbed} (cm^{-1})$	$\Delta v \ (\mathrm{cm}^{-1})$
А	1.36	1.82	1.15	2051	2028	-23
В	2.08	1.77	1.14	2169	2130	-39
С	-	_	_	2143	2127	-16
This work	1.50	1.82	1.15	2082	2056	-26

Table 5 Comparison of structural and energetic data for CO adsorption on  $Cu_2O(111)$ 

A: Cu<sub>28</sub>O<sub>14</sub> cluster (without point charge)-B3LYP GGA; Ref. [15].

B: Cu<sub>22</sub>O<sub>20</sub> cluster (with pseudohydrogen)—LDA; Ref. [19].

C: Experimental (FTIR); Cu<sub>2</sub>O powder; Ref. [17].

wavenumbers (blue shift) is seen on some oxides such as MgO,  $Cr_2O_3$ , and  $Al_2O_3$  by IR [38]. Detailed computational analyses have been conducted in order to understand the frequency shifts of CO [39,40]. The blue shift has been attributed to the wall effect as well as to a field-dipole interaction.

In this work, the CO molecule was perturbed along the z-direction of the supercell, keeping the Cu<sub>2</sub>O(111) surface slab fixed. Various minute displacements of the O atom from the C atom were done in progressive steps and an SCF calculation was carried out at each step. Using the method mentioned in the methodology section, the vibrational frequency of CO was calculated within the simple harmonic oscillator approximation. Our calculated vibrational frequency of both the gasphase CO and adsorbed CO on Cu<sub>2</sub>O(111) surface is 2082 cm<sup>-1</sup> and 2056 cm<sup>-1</sup> respectively. Hence a red-shift of -26 cm<sup>-1</sup> is observed upon the adsorption of CO on the Cu<sub>2</sub>O(111) surface.

# 3. Conclusions

Table 5 summaries the results, in comparison with other works. The periodic plane wave DFT approach used in this work provides an accurate way of describing CO adsorption on Cu<sub>2</sub>O(111) surface. With respect to previous studies the present work is similar to that of the cluster results (without point charge) by Bredow and Pacchioni [15]. Although the cluster model of Casarin et al. [19] has overestimated the binding energy, because of the use of the LDA method, it has provided the closest values to experimental results for the C–Cu distance. The strong  $\pi$  back-donation is demonstrated by the overall decrease in electronic charge on  $Cu_{CUS}$  in the LCP analysis (Table 4) and a redshift in the vibrational frequency of CO by  $-26 \text{ cm}^{-1}$ . This suggests that for partially covalent compounds, like  $Cu_2O$ , DFT periodic slab models "paint" a realistic and adequate picture describing solid-gas interactions.

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