



# Cluster and periodic DFT calculations of adsorption and activation of CO<sub>2</sub> on the Cu(*hkl*) surfaces

Gui-Chang Wang <sup>a,\*</sup>, Ling Jiang <sup>a</sup>, Yoshitada Morikawa <sup>b</sup>, Junji Nakamura <sup>c</sup>,  
Zun-Sheng Cai <sup>a</sup>, Yin-Ming Pan <sup>a</sup>, Xue-Zhuang Zhao <sup>a</sup>

<sup>a</sup> Department of Chemistry, Nankai University, Weijin Road 94, Tianjin 300071, PR China

<sup>b</sup> Research Institute for Computational Sciences (RICS), and Research Consortium for Synthetic Nano-Function Materials Project (SNAF), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 2, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan

<sup>c</sup> Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan

Received 23 January 2004; accepted for publication 2 August 2004

Available online 19 August 2004

## Abstract

The adsorption behavior and thermal activation of carbon dioxide on the Cu(111), Cu(100), and Cu(110) surfaces have been investigated by means of density functional theory calculations and cluster models and periodic slabs. According to the cluster models, the optimized results indicate that the basis set of C and O atoms has a distinct effect on the adsorption energy, but an indistinct one on the equilibrium geometry. For the CO<sub>2</sub>/Cu(*hkl*) adsorption systems studied here, the final structure of adsorbed CO<sub>2</sub> is near linear and the preferred modes for the adsorption of CO<sub>2</sub> onto the Cu(111), Cu(100), and Cu(110) surfaces are the side-on adsorption at the cross bridge site with an adsorption energy of 13.06 kJ/mol, the side-on adsorption at the short bridge site (13.54 kJ/mol), and the end-on adsorption on the on-top site with C–O bonds located along the short bridge site (26.01 kJ/mol), respectively. However, the calculated adsorption energies from periodic slabs are lower as compared to the experimental data as well as the cluster model data, indicating that the periodic slab approach of generalized gradient approximation in the density function theory may be not suitable to obtain quantitative information on the interaction of CO<sub>2</sub> with Cu(*hkl*) surfaces.

© 2004 Elsevier B.V. All rights reserved.

**Keywords:** Carbon dioxide; Copper; Chemisorption; Single crystal surfaces; Density functional calculations; Clusters

## 1. Introduction

The surface chemistry of carbon dioxide has been a growing interest because of its abundance

\* Corresponding author. Tel.: +86 22 2350 4854/7956; fax: +86 22 2350 2458.

E-mail address: [wanguichang@nankai.edu.cn](mailto:wanguichang@nankai.edu.cn) (G.-C. Wang).

and extensive application as a cheap C1 feedstock [1]. Partly due to the oil crisis, there were considerable impetus for investigating the potential usefulness of carbon dioxide as a reactant in hydrocarbon synthesis. The interest in the copper–CO<sub>2</sub> system was partly stimulated by the implications of the discovery made by the catalysis study group in Imperial Chemical Industries that CO<sub>2</sub> is the main source of “carbon” in the synthesis of methanol using the H<sub>2</sub>–CO–CO<sub>2</sub> mixtures and their copper–zinc oxide catalyst [2]. There are several overviews of CO<sub>2</sub> interaction with metal complexes [3–7].

The interaction between CO<sub>2</sub> and copper surfaces has been studied by thermal desorption mass spectroscopy (TDS) [8], ultraviolet photoelectron spectroscopy (UPS) [9], X-ray photoelectron spectroscopy (XPS) [9,10], Auger electron spectroscopy (AES) [11], and ellipsometry [11]. Carbon dioxide is thought to be adsorbed on polycrystalline Cu both in physisorbed form with the adsorption energy ( $E_{\text{ads}}$ ) of 18.0 kJ/mol [8] and in an anionic (CO<sub>2</sub><sup>−</sup>) chemisorbed state ( $E_{\text{ads}} < 60.0$  kJ/mol [10]). Chorkendorff and coworkers [12], have reported the interaction of CO<sub>2</sub> with the Cu(100) surface based on TPD studies. They have also shown that methanol could be synthesized on Cu(100) forming a binary gas mixture of CO<sub>2</sub> (or CO) and H<sub>2</sub> [13,14] and that the reaction of adsorbed CO<sub>2</sub> with an H adatom is the rate-determining step for formate synthesis on the Cu(100) surface [15]. A first-principle density functional calculation of CO<sub>2</sub> adsorption on the (100) surface of Cu<sub>13</sub>(9,4,1) cluster model has been performed by Au and Chen [16], and revealed that the preferred adsorption mode is the side-on mode with near linear CO<sub>2</sub> lying at the short bridge site.

There are a few experiments performed with CO<sub>2</sub> on the Cu(110) surfaces. Rodriguez et al. [17] reported that CO<sub>2</sub> does not adsorb on Cu(110) under UHV conditions at 110 K. The dissociative sticking coefficient for CO<sub>2</sub> on Cu(110) has been measured by Nakamura et al. [18] in a temperature range of 400–600 K and found to be 10<sup>−11</sup> to 10<sup>−9</sup> with an activation energy of 67 kJ/mol. Campbell and Ernst [19] observed that the dissociation of CO<sub>2</sub> occurs with

a probability estimated to be about 10<sup>−9</sup> per collision at 573 K at a clean Cu(110) surface. Also, our recent energetic analysis [20] indicates that the most likely rate-determining step in the reverse water-gas shift (RWGS) reaction is the CO<sub>2</sub> dissociative adsorption, namely CO<sub>2,g</sub> → CO<sub>s</sub> + O<sub>s</sub>. In addition, there are some DFT studies of the interaction of CO<sub>2</sub> with various surfaces, such as Pd(111) [21], K/Pd(111) [22], and SnO<sub>2</sub>(110) [23], etc.

Frankly, the location of CO<sub>2</sub> at these crystal surfaces is a fundamental feature in the description of surface processes. Meanwhile, the adsorption and activation of CO<sub>2</sub> on metal surfaces can also be the very useful knowledge in understanding many electrochemically and heterogeneously catalyzed reactions [3–7,20,24]. However, no systematic work on the investigation of the adsorption and activation of CO<sub>2</sub> on the Cu(*hkl*) surfaces can be found in the literature to the best of our knowledge. In this article, the adsorption mode and binding characteristics of CO<sub>2</sub> on the Cu(111), Cu(100), and Cu(110) surfaces have been studied by means of density functional theory calculations. We address the relative strength of CO<sub>2</sub> adsorption on these Cu(*hkl*) surfaces, as well as the activation. We also try to probe into the adsorption characteristics of CO<sub>2</sub> on the well-defined single crystal copper surfaces.

## 2. Computational methods and models

The development of modern surface science provided the opportunity to investigate the interaction between catalysts and molecules or atoms in the atomic scale. However, quantum chemical computations of molecules containing transition metal atoms have proven to be more difficult than those for the first- and second-row atoms [25]. Recent advances in methodology based on the technologies of pseudopotential and plane wave basis sets and the high-speed computers have now made it possible to obtain quantitative information on the surface phenomena. In this work, cluster models of the surface and periodic slabs have been employed to simulate CO<sub>2</sub> adsorbed on the Cu(111), Cu(100) and Cu(110) surfaces.

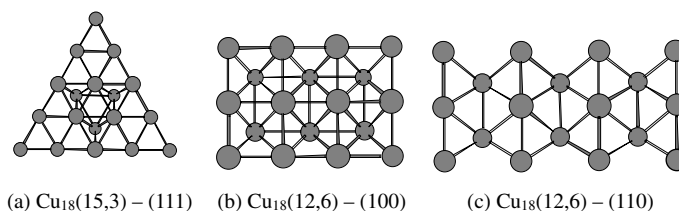


Fig. 1. The  $\text{Cu}_{18}(15,3)$  and  $\text{Cu}_{18}(12,6)$  cluster models represent the Cu(111), Cu(100), and Cu(110) surfaces, respectively.

The copper cluster models of  $\text{Cu}_{18}(15,3)$  (i.e. 15 atoms in the first and three atoms in the second layer), and  $\text{Cu}_{18}(12,6)$  (i.e. 12 atoms in the first, six atoms in the second layer) shown in Fig. 1 have been chosen to represent the Cu(111), Cu(100) and Cu(110) surfaces, respectively. The Cu(111), Cu(100) and Cu(110) surfaces are constructed using the bulk lattice constants of 3.615 Å [26]. The top views of these models at their initial configurations and the side views of the final optimized forms of models (a to r) for the  $\text{CO}_2$  adsorption are shown schematically in Fig. 2, where four adsorption modes (i.e. g, i, q, r) for bent  $\text{CO}_2$  molecule at the on-top sites have also been included. For the adsorption of  $\text{CO}_2$  on the Cu(100) surface, only two adsorption modes have been optimized, following the adsorption modes of inert  $\text{CO}_2$  on the Cu(100) surface has been studied by Au and Chen [16]. In the present calculations, the geometry of metal cluster was kept unchanged while the geometry of  $\text{CO}_2$  above the surface was fully optimized, due to the fact that there is indeed very little modification of the metal surface by the relatively weak adsorption of  $\text{CO}_2$  at low coverage [16]. For the initial linear  $\text{CO}_2$  structure, the C–O bond length was set at 1.160 Å. For initial bent  $\text{CO}_2$ , the C–O bond length was set at 1.240 Å while the O–C–O angle at 140.0°.

In the case of cluster models, the interaction of  $\text{CO}_2$  with the different adsorption sites on Cu(111), Cu(100) and Cu(110) surfaces has been studied by first-principle density functional calculations with the hybrid B3LYP exchange–correction functional [27,28] implemented in Gaussian 94 program package [29]. For Cu atoms, the relativistic effective core potentials (ECP) reported by Hay and Wadt [30] have been used to describe the 1s-2p core while the elec-

trons arising for the 3s, 3p, 3d, 4s, 4p shells are treated explicitly. It is customary to refer to these ECPs as LANL2. The standard double- $\zeta$  basis set, also reported by Hay and Wadt [30] and denoted as usual as LANL2DZ, is used to describe the electron density of the valence electrons of Cu, whereas the electron density of C and O atoms are respectively described with the standard STO-3G and 6-31G basis set. For comparison, six representative adsorption modes of  $\text{CO}_2$  on Cu(*hkl*) have also been optimized with 6-31G\*\* basis set in this work. The basis set superposition error (BSSE) has been considered and it is small (the results have not been reported here).

The natural bond orbital (NBO) procedure [31,32] provides an efficient method for obtaining bonds and lone pair electrons which compose an optimized Lewis structure of a molecule from modern ab initio wave functions. The set of orthonormal NBOs forms a compact and stable representation of the electron density in a molecule [33] and provides a convenient basis for investigating charge-transfer or hyperconjugative interactions in molecular systems [32]. Reed et al. [33] reported that the natural population analysis is an alternative to conventional Mulliken population analysis, and seems better to describe the charge distributions in compounds of high ionic character (i.e. those containing metal atoms), where Mulliken populations often contradicts seriously the density integration and the empirical measures of ionicity. In view of the discussion, the NBO method [34] is employed in the analysis of electron configuration and binding characteristics of the  $\text{CO}_2/\text{Cu}(\text{hkl})$  adsorption systems.

Comparative calculations based on a generalized gradient approximation in the density

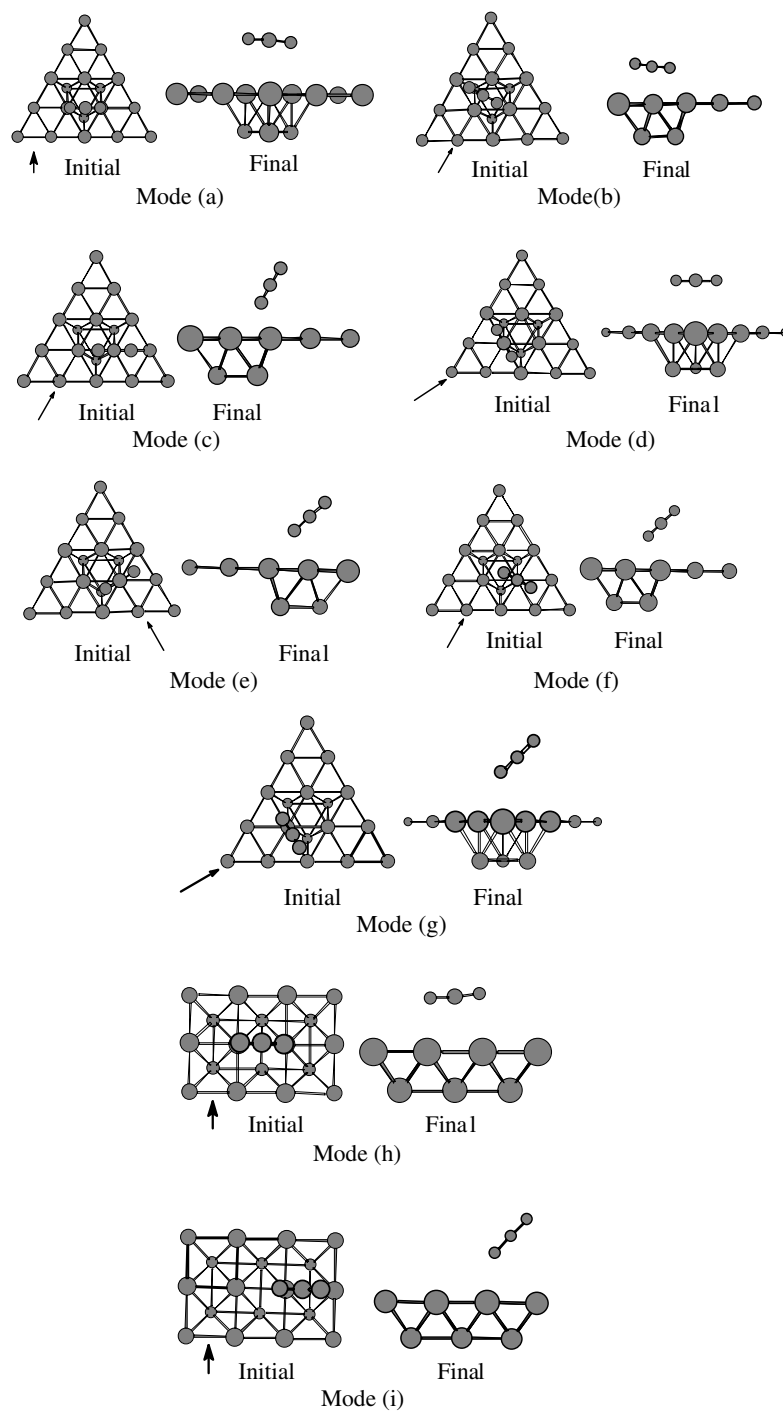


Fig. 2. Top views of the initial forms and side views of final optimized forms of different modes of  $\text{CO}_2$  adsorption at the B3LYP/LANL2DZ-6-31G level (the directions of side views are as indicated by arrows in the initial forms). In the view of final optimized form, the oxygen atom on the left of carbon atom is labeled as “left O” in text and tables.

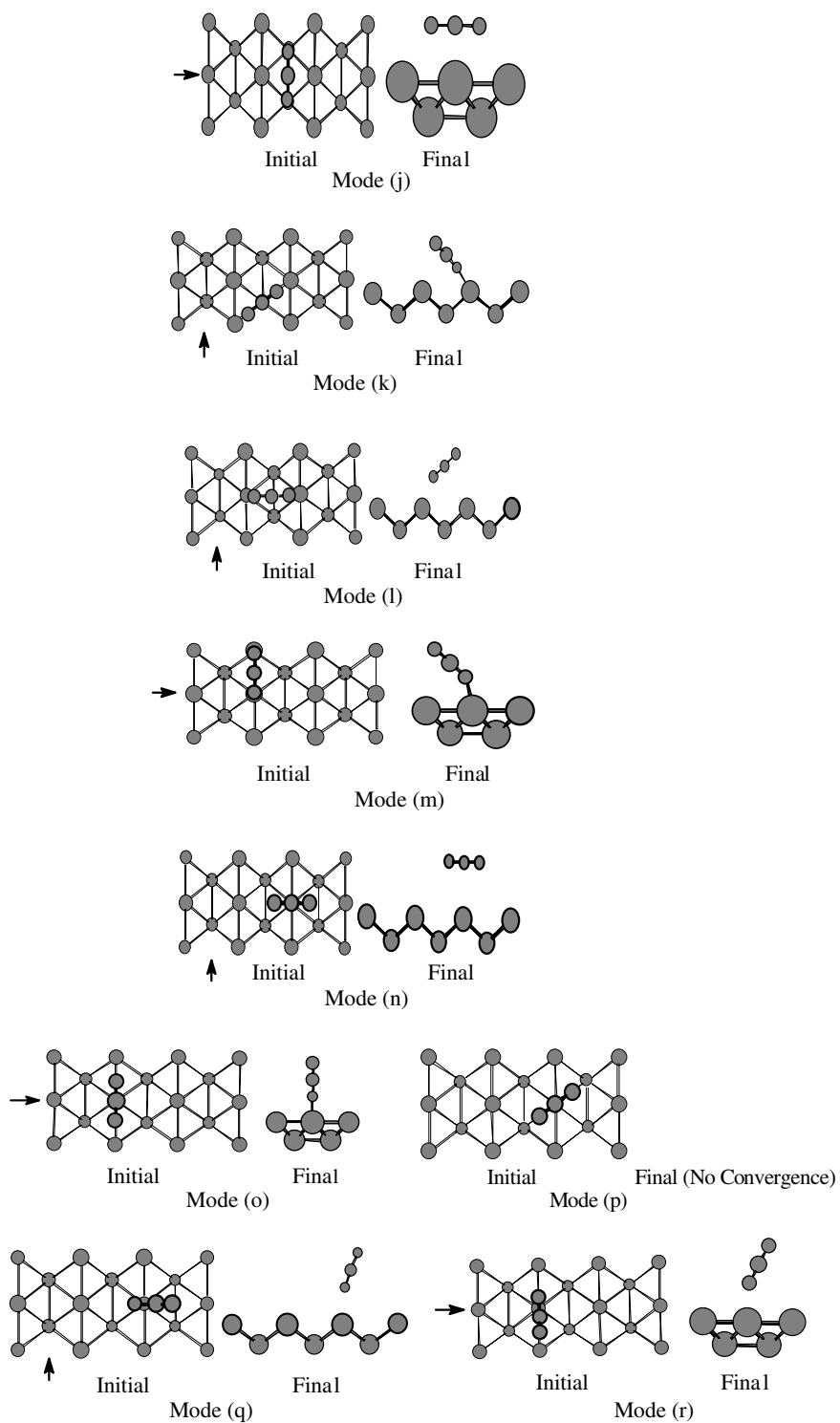


Fig. 2 (continued)

function theory with the slab model were carried out using a package “STATE” (Simulation Tool for Atom TEchnology) which has been successfully applied to adsorption problems in the case of semiconductor and metal surfaces [35–38]. We used the Perdew, Burke, and Ernzerhof exchange and correlation functional [39,40] as well as the Vanderbilt’s ultrasoft pseudopotentials [41]. The energy cutoffs of the plane wave basis sets are 25 Ry and 400 Ry for wave functions and charge density, respectively. In order to model the CO<sub>2</sub> coverage, the unit cell of 2 × 2 with four layers were used, and a vacuum region of 10 Å thickness in between two neighboring slabs. The surface Brillouin zone was sampled using a 4 × 4, 6 × 4, and 4 × 4 special *k*-point for the Cu(100), Cu(110) and Cu(111), respectively. For the structure optimization, the adsorbed CO<sub>2</sub> species and two top layers are allowed to relax. In addition, in order to get

more precision adsorption energy, we also used the larger unit cell, p(2 × 3) with six layers, in which the first three layers are allowed to be relaxed.

### 3. Results and discussion

Tables 1–4 list the adsorption energies and structural parameters of CO<sub>2</sub> adsorbed onto the Cu(111), Cu(100) and Cu(110) surfaces. The adsorption energy ( $E_{\text{ads}}$ ) is calculated according to the formula:

$$E_{\text{ads}} = E(\text{cluster}) + E(\text{CO}_2) - E(\text{cluster} + \text{CO}_2), \quad (1)$$

where  $E(\text{cluster})$ ,  $E(\text{CO}_2)$ , and  $E(\text{cluster} + \text{CO}_2)$  denote the calculated energy of a cluster without CO<sub>2</sub>, the free CO<sub>2</sub>, and a cluster with CO<sub>2</sub>, respectively. Similarly, one may calculate the adsorption energy of CO<sub>2</sub> adsorbed onto periodic slab. A pos-

Table 1

Structural parameters and adsorption energies for the adsorption of CO<sub>2</sub> onto the Cu(*hkl*) surfaces at the B3LYP/LANL2DZ-STO-3G level<sup>a</sup>

| Cu(111) surface | Cu–C distance (Å)       | C–O distance |               | O–C–O angle (°) | Adsorption energy (kJ/mol) |
|-----------------|-------------------------|--------------|---------------|-----------------|----------------------------|
|                 |                         | Left O–C (Å) | Right C–O (Å) |                 |                            |
| Mode (a)        | 3.650                   | 1.227        | 1.229         | 179.21          | 1.02                       |
| Mode (b)        | 3.475                   | 1.226        | 1.231         | 179.48          | 4.53 (–2.78)               |
| Mode (c)        | 3.745                   | 1.231        | 1.226         | 179.94          | 2.94                       |
| Mode (d)        | 3.770                   | 1.228        | 1.228         | 179.58          | 1.38                       |
| Mode (e)        | 3.739                   | 1.231        | 1.226         | 179.73          | 3.18                       |
| Mode (f)        | 3.740                   | 1.231        | 1.226         | 179.75          | 2.67                       |
| Mode (g)        | 3.636                   | 1.230        | 1.227         | 178.90          | 2.23                       |
| Cu(100) surface |                         |              |               |                 |                            |
| Mode (h)        | 3.105                   | 1.229        | 1.229         | 176.55          | 11.78 (7.02)               |
| Mode (i)        | 3.920                   | 1.232        | 1.226         | 179.78          | 2.33                       |
| Cu(110) surface |                         |              |               |                 |                            |
| Mode (j)        | 3.619                   | 1.228        | 1.228         | 179.23          | 9.92                       |
| Mode (k)        | 3.009                   | 1.225        | 1.233         | 179.25          | 12.27                      |
| Mode (l)        | 2.680                   | 1.231        | 1.231         | 178.05          | 20.04                      |
| Mode (m)        | 3.135                   | 1.223        | 1.234         | 177.99          | 18.27                      |
| Mode (n)        | 3.300                   | 1.229        | 1.229         | 179.46          | 13.29                      |
| Mode (o)        | 3.467                   | 1.232        | 1.223         | 177.87          | 22.80 (18.24)              |
| Mode (p)        | No geometry convergence |              |               |                 |                            |
| Mode (q)        | 3.357                   | 1.235        | 1.224         | 178.30          | 22.08                      |
| Mode (r)        | 3.379                   | 1.234        | 1.223         | 178.09          | 22.73                      |

Note: the data in parentheses are including the zero energy correction and thermal energy correction at room temperature.

<sup>a</sup> The Cu–C distance represents the distance from C atom to the nearest-neighbor Cu atom.

Table 2

Structural parameters and adsorption energies for the adsorption of CO<sub>2</sub> onto the Cu(*hkl*) surfaces at the B3LYP/LANL2DZ-6-31G level

| Cu(111) surface | Cu–C distance (Å)       | C–O distance |               | O–C–O angle (°) | Adsorption energy (kJ/mol) |
|-----------------|-------------------------|--------------|---------------|-----------------|----------------------------|
|                 |                         | Left O–C (Å) | Right C–O (Å) |                 |                            |
| Mode (a)        | 3.108                   | 1.187        | 1.188         | 179.97          | 18.19                      |
| Mode (b)        | 3.100                   | 1.187        | 1.189         | 179.98          | 19.33 (13.06)              |
| Mode (c)        | 3.597                   | 1.191        | 1.185         | 179.40          | 15.49                      |
| Mode (d)        | 3.167                   | 1.188        | 1.188         | 179.38          | 15.59                      |
| Mode (e)        | 3.517                   | 1.190        | 1.185         | 179.35          | 14.72                      |
| Mode (f)        | 3.471                   | 1.191        | 1.185         | 179.53          | 15.47                      |
| Mode (g)        | 3.531                   | 1.191        | 1.185         | 179.38          | 14.84                      |
| Cu(100) surface |                         |              |               |                 |                            |
| Mode (h)        | 2.989                   | 1.188        | 1.188         | 178.93          | 22.06 (13.54)              |
| Mode (i)        | 3.612                   | 1.193        | 1.185         | 179.10          | 20.18                      |
| Cu(110) surface |                         |              |               |                 |                            |
| Mode (j)        | 3.104                   | 1.188        | 1.188         | 179.07          | 12.69                      |
| Mode (k)        | 3.060                   | 1.184        | 1.193         | 179.18          | 25.77                      |
| Mode (l)        | 2.911                   | 1.193        | 1.183         | 179.46          | 31.75                      |
| Mode (m)        | 3.170                   | 1.182        | 1.195         | 179.17          | 28.72                      |
| Mode (n)        | 2.981                   | 1.189        | 1.189         | 178.55          | 20.91                      |
| Mode (o)        | 3.476                   | 1.192        | 1.182         | 179.98          | 32.28 (26.01)              |
| Mode (p)        | No geometry convergence |              |               |                 |                            |
| Mode (q)        | 3.424                   | 1.191        | 1.183         | 179.97          | 23.86                      |
| Mode (r)        | 3.411                   | 1.194        | 1.181         | 179.01          | 29.62                      |

Note: the data in parentheses are including the zero energy correction and thermal energy correction at room temperature.

Table 3

Structural parameters and adsorption energies for the adsorption of CO<sub>2</sub> onto the Cu(*hkl*) surfaces at the B3LYP/LANL2DZ-6-31G\*\* level

| Mode     | Cu–C distance (Å) | C–O distance |               | O–C–O angle (°) | Adsorption energy (kJ/mol) |
|----------|-------------------|--------------|---------------|-----------------|----------------------------|
|          |                   | Left O–C (Å) | Right C–O (Å) |                 |                            |
| Mode (a) | 3.301             | 1.169        | 1.170         | 179.68          | 16.05                      |
| Mode (b) | 3.345             | 1.170        | 1.171         | 180.00          | 15.30 (6.27)               |
| Mode (h) | 3.226             | 1.169        | 1.169         | 179.55          | 18.34 (6.87)               |
| Mode (i) | 3.692             | 1.173        | 1.166         | 179.68          | 15.00                      |
| Mode (l) | 3.467             | 1.174        | 1.165         | 180.00          | 23.71                      |
| Mode (o) | 3.601             | 1.173        | 1.164         | 179.68          | 29.46 (27.95)              |

Note: the data in parentheses are including the zero energy correction and thermal energy correction at room temperature.

itive value of  $E_{\text{ads}}$  implies that the adsorption of CO<sub>2</sub> from gas-phase is thermodynamically favorable.

### 3.1. Effect of basis set of C and O atoms

In the following discussion, we use the adsorption energies not including the zero point energy and thermal chemical correction.

In the case of cluster models, we begin our studies of the CO<sub>2</sub>/Cu(*hkl*) adsorption systems by examining the effect of basis set of C and O atoms. The adsorption energy can be considered as a kind of quantitative criterion to appraise which kind of basis set is more fit for the system studied here. The data reported in Tables 1 and 2 reveal that the adsorption energy of CO<sub>2</sub> on a given adsorption mode calculated from the STO-3G basis set

Table 4

Structural parameters and adsorption energies for the adsorption of CO<sub>2</sub> onto the periodic slabs

| Mode     | Cu–C distance (Å) | C–O distance |               | O–C–O angle (°) | Adsorption energy (kJ/mol) |
|----------|-------------------|--------------|---------------|-----------------|----------------------------|
|          |                   | Left O–C (Å) | Right C–O (Å) |                 |                            |
| Mode (a) | 3.480             | 1.190        | 1.180         | 180.00          | –5.02                      |
| Mode (b) | 3.430             | 1.190        | 1.180         | 179.50          | –3.06                      |
| Mode (h) | 3.370             | 1.190        | 1.190         | 179.20          | –6.31 (–0.23)              |
| Mode (m) | 3.690             | 1.190        | 1.180         | 179.80          | –2.67                      |
| Mode (n) | 4.320             | 1.180        | 1.180         | 180.00          | –3.69                      |
| Mode (o) | 4.710             | 1.190        | 1.200         | 179.00          | –2.22                      |

Note: the data in parentheses corresponding to the large unit system calculation result.

is lower than that from the 6-31G basis set. For instance, the largest adsorption energy for CO<sub>2</sub> adsorbed on the Cu(111) surface (namely, the adsorption mode (b)) is 4.53 kJ/mol based on the B3LYP/LANL2DZ-STO-3G calculation and by using the comparative basis set of 6-31G, a satisfying adsorption energy of 19.33 kJ/mol is obtained. Because the experimental adsorption energy for CO<sub>2</sub> onto Cu(111) surface given by Hadden et al. is 4–5 kcal/mol (16.73–20.91 kJ/mol) [42], the calculated adsorption energy from the STO-3G basis set for C and O atoms is underestimated. This may be due to the shortcoming of the STO-3G basis set, which would induce inadequate description of the Cu–CO<sub>2</sub> binding. Also, it can be found from Tables 2 and 3 that the adsorption energy of CO<sub>2</sub> on a given adsorption mode calculated from the 6-31G\*\* basis set is lower than that from the 6-31G basis set. To validate this observation, comparative calculations have been continuously performed on the CO<sub>2</sub>/Cu(100) and CO<sub>2</sub>/Cu(110) cluster model systems with three kinds of basis set (i.e. STO-3G, 6-31G, and 6-31G\*\*).

According to the CO<sub>2</sub>/Cu(100) and CO<sub>2</sub>/Cu(110) cluster model systems, results similar to those obtained for Cu(111) can be seen from Tables 1–3. The interaction of carbon dioxide with Cu(100) surface has been investigated by TPD and the adsorption energy has been measured to 25–30 kJ/mol in the coverage range 0.05–0.40 ML [12]. From Table 2 it is easy to find that the calculated results agree well with the experiments. For the CO<sub>2</sub>/Cu(110) adsorption system, we cannot compare directly our calculated adsorption energies with the experimental results for the lacking

of the latter, but it would be expected that the adsorption energies of CO<sub>2</sub> on this open plane with its more coordinatively unsaturated Cu atoms will be higher than those of CO<sub>2</sub> adsorbed on either the Cu(100) or the closely packed Cu(111) surface. Among other studies, the highest adsorption energy of CO<sub>2</sub>, computed by Au and Chen [16] with the Slater DFT code on a Cu<sub>14</sub>(9,4,1) cluster which is taken as a cluster model of the Cu(100) surface, was 26.31 kJ/mol, which is also in good agreement with the experimental value 25–30 kJ/mol [12].

### 3.2. Preferred mode and adsorption energy

To find the preferred mode for CO<sub>2</sub> reacting on copper surface, we firstly examine its adsorption behavior on the Cu(111) surface. From Table 2 and Fig. 2, one can see that the CO<sub>2</sub> molecule remains nearly linear with the O–C–O angle of  $\approx 179.50^\circ$  in the final optimized form. For the adsorptions of CO<sub>2</sub> on the on-top sites, namely modes (c–g), the difference in adsorption energy between them is mild ( $\approx 15$  kJ/mol). In the final optimized forms of modes (c–g), the molecular axis of CO<sub>2</sub> is tilted from the surface normal by  $\approx 45.00^\circ$  with the exception of mode (d) (the molecular axis is nearly parallel to the surface). The side-on adsorption of linear CO<sub>2</sub> along bridge and cross bridge site (modes (a) and (b)) give the final optimized forms of near linear CO<sub>2</sub> structures but with the adsorption energies of 18.19 and 19.33 kJ/mol, respectively. Also, the molecular axis of CO<sub>2</sub> in those two modes is nearly parallel to the surface. Among the CO<sub>2</sub> adsorptions on the Cu(111) sur-

face, mode (b) has the highest adsorption energy (19.33 kJ/mol), indicating that the preferred mode for CO<sub>2</sub> adsorbed on the Cu(111) surface is the side-on adsorption of linear CO<sub>2</sub> at the cross bridge site (namely mode (b)).

For the adsorption of CO<sub>2</sub> on the Cu(100) surface, the data reported in Table 2 reveal that the preferred adsorption mode, namely mode (h), is the side-on adsorption of linear CO<sub>2</sub> at the short bridge site with an adsorption energy of 22.06 kJ/mol. In mode (i), the final optimized forms of CO<sub>2</sub> from the initial bent structure is tilted from the surface normal by 43.17° with an adsorption energy of 20.18 kJ/mol. It is in good agreement with the TPD studies [12] and cluster DFT calculations [16] of CO<sub>2</sub> adsorbed on the Cu(100) surface.

In the case of Cu(110) surface, the adsorption mode (p) of linear CO<sub>2</sub> on the on-top site with O atoms located above the hollow site exhibits no geometry convergence. Hence, we turn our attention to other possible adsorption modes. It is easy to find from Table 2 that the adsorption energies of CO<sub>2</sub> on the Cu(110) surface for different modes are in the order of (o) > (l) > (r) > (m) > (k) > (q) > (n) > (j). The preferred mode is the end-on adsorption of linear CO<sub>2</sub> on the on-top site with C–O bonds located along the short bridge site (cf. mode (o), shown in Fig. 2) with an adsorption energy of 32.28 kJ/mol, closely followed by mode (l) with an adsorption energy of 31.75 kJ/mol. The least stable mode is the mode (j), the side-on adsorption of linear CO<sub>2</sub> molecule at the cross long-bridge site, with an adsorption energy of 12.69 kJ/mol. Interestingly, there are three final optimized forms (i.e. mode (k), (m), and (o)) which are different from other side-on adsorption modes. One of the O atoms of CO<sub>2</sub> is bonded with Cu atom at the on-top site, while the other C–O bond is tilted upward in these three modes, especially in mode (o), the molecular axis of CO<sub>2</sub> is nearly perpendicular to the surface. Thus, these three modes would be classified as the stilted end-on adsorption of near linear CO<sub>2</sub> molecules.

For CO<sub>2</sub> adsorbed onto the periodic slabs, it can be seen from Table 4 that the equilibrium structures are similar to those calculated from cluster models, whereas the adsorption energies are

very small (smaller than zero) even though the large unit cell was used (i.e. p(2 × 3)-6 layers with three layer relaxed). This means that the DFT-GGA is not able to describe the dispersion (i.e. van der Waals) interactions that are known to be the driving force for the physisorption [43,44]. The reason might be due to the fact that the long-range exchange and the vdW correction interaction are not included in the pure exchange–correction function [45]. Furthermore, since the interaction of CO<sub>2</sub> with copper surfaces is so weak (i.e. physisorption), it is reasonable to suggest that this kind of interaction may be a local interaction (not like the strong interaction such as atom adsorption on metals and it is more dependent on the cluster size effect). So, we expected that the cluster model might be more suitable to simulate the local interaction, whereas the slab model might be more fit to the case of strong bonding adsorption state. Since the electronic structure of substrate in the slab model is more delocalised as compared to the cluster model, we predict that the interaction between copper substrate with CO<sub>2</sub> in the slab model is not so strong as the cluster model [46].

We should point out that the above calculation results are corresponding to the energy of electrons at the temperature of absolute zero, and the experimental TPD temperature is much higher than zero, and the corrections of zero point energy (ZPE) and the thermal chemical energy are required. Thus, we have also investigated the effect of zero point energy and thermal chemical correction (at room temperature, i.e. 298 K) to the CO<sub>2</sub> adsorption energy for the cluster model, and the calculated results are listed in Tables 1–3 (see the data in parentheses). It can be seen that the contribution to the CO<sub>2</sub> adsorption energy is almost the same for the Cu(111), Cu(100) and Cu(110) surfaces, i.e., the adsorption energy decreased by ≈1.60 kcal/mol after the zero point energy and thermal chemical corrections. Using the 6-31G basis set, the CO<sub>2</sub> adsorption energies of Cu(111), Cu(100) and Cu(110) were calculated to be 13.03 kJ/mol, 13.54 kJ/mol and 26.01 kJ/mol, respectively.

In a word, the final structure of adsorbed CO<sub>2</sub> is near linear and the preferred modes for the

adsorption of CO<sub>2</sub> onto the Cu(111), Cu(100), and Cu(110) surfaces are mode (b), (h), and (o) (shown in Fig. 2), respectively. Meanwhile, a close scrutiny of the data given in Table 2 permits us to draw a conclusion that the adsorption energy of CO<sub>2</sub> is larger on the Cu(110) surface than on Cu(100) and Cu(111), giving the following order for the CO<sub>2</sub>–Cu(*hkl*) binding strengths, Cu(110) > Cu(100) > Cu(111).

### 3.3. Electron configuration and binding characteristics of CO<sub>2</sub> with the Cu(*hkl*) surfaces

In this section, we will have a closer look at the electron configuration and the binding characteristics of CO<sub>2</sub> on the Cu(*hkl*) surfaces. At the B3LYP/LANL2DZ-6-31G level, the NBO analysis has been done under the optimized geometries of the Cu(*hkl*)–CO<sub>2</sub> complexes. For selected two modes with a relatively higher adsorption energy from each copper single crystal surface, only the representative results of the natural electron configura-

tion are given for the CO<sub>2</sub>/Cu(*hkl*) systems in Table 5. To address the binding characteristics, we report the results from NBO analysis for the C–O bond with the largest occupancy in Table 6.

Based on the present DFT calculation at the B3LYP/6-31G level, the natural electron configuration for C and O atoms in free CO<sub>2</sub> molecule is [core] 2s(0.69) 2p(2.33) 3p(0.03) and [core] 2s(1.75) 2p(4.72) (tabulated in Table 5), respectively. Among the selected adsorption modes, the extended 3s and 3p orbitals of C atom in modes (a, b, h, l) are similar variation, whereas there is no extended 3s orbital of C atom in modes (i, o). For instance, the electrons in the 3s orbital of C atom are all 0.01e corresponding to modes (a, b, h, l). For the left O atom, the natural electron configuration in modes (a, b, h) is the same with the decrease of 2s orbital electron by 0.01e after optimization, while for modes (i, l, o) the extended 3s and 3p orbitals of O atom in modes (i, l, o) are similar variation (see Table 5). There is no extended orbital of the right O atom for all selected

Table 5

The representatively natural electron configuration of CO<sub>2</sub> from first-principle density functional calculations at the B3LYP/LANL2DZ-6-31G level

| Mode                   | Atom     | Natural charge                    | Natural electron configuration             | Natural charge of CO <sub>2</sub> |
|------------------------|----------|-----------------------------------|--------------------------------------------|-----------------------------------|
| CO <sub>2</sub> (free) | C        | 0.95312                           | [core] 2s(0.69) 2p(2.33) 3p(0.03)          | 0.00000                           |
| O                      | –0.47656 | [core] 2s(1.75) 2p(4.72)          |                                            |                                   |
| O                      | –0.47656 | [core] 2s(1.75) 2p(4.72)          |                                            |                                   |
| Mode (a)               | C        | 0.93518                           | [core] 2s(0.69) 2p(2.33) 3s(0.01) 3p(0.04) | –0.01239                          |
| O(left)                | –0.46963 | [core] 2s(1.74) 2p(4.72)          |                                            |                                   |
| O(right)               | –0.47794 | [core] 2s(1.74) 2p(4.73)          |                                            |                                   |
| Mode (b)               | C        | 0.93567                           | [core] 2s(0.69) 2p(2.33) 3s(0.01) 3p(0.04) | –0.01366                          |
| O(left)                | –0.46840 | [core] 2s(1.74) 2p(4.72)          |                                            |                                   |
| O(right)               | –0.48093 | [core] 2s(1.75) 2p(4.73)          |                                            |                                   |
| Mode (h)               | C        | 0.94209                           | [core] 2s(0.69) 2p(2.32) 3s(0.01) 3p(0.04) | –0.00622                          |
| O(left)                | –0.47384 | [core] 2s(1.74) 2p(4.72)          |                                            |                                   |
| O(right)               | –0.47447 | [core] 2s(1.74) 2p(4.72)          |                                            |                                   |
| Mode(i)                | C        | 0.96441                           | [core] 2s(0.69) 2p(2.31) 3p(0.03)          | –0.00604                          |
| O(left)                | –0.52078 | [core] 2s(1.75) 2p(4.76) 3p(0.01) |                                            |                                   |
| O(right)               | –0.44967 | [core] 2s(1.74) 2p(4.70)          |                                            |                                   |
| Mode (l)               | C        | 0.96944                           | [core] 2s(0.69) 2p(2.31) 3s(0.01) 3p(0.03) | –0.00743                          |
| O(left)                | –0.53918 | [core] 2s(1.74) 2p(4.79) 3p(0.01) |                                            |                                   |
| O(right)               | –0.43769 | [core] 2s(1.74) 2p(4.69)          |                                            |                                   |
| Mode (o)               | C        | 0.99240                           | [core] 2s(0.68) 2p(2.30) 3p(0.03)          | –0.00761                          |
| O(left)                | –0.55312 | [core] 2s(1.73) 2p(4.81) 3p(0.01) |                                            |                                   |
| O(right)               | –0.43689 | [core] 2s(1.75) 2p(4.69)          |                                            |                                   |

Table 6

The representatively NBO analysis results for the C–O bond with the largest occupancy computed for CO<sub>2</sub>/Cu(*hkl*) systems at the B3LYP/LANL2DZ-6-31G level<sup>a</sup>

|                        | Occupancy | C (%)                             |       |       | O (%)                             |       |       |
|------------------------|-----------|-----------------------------------|-------|-------|-----------------------------------|-------|-------|
|                        |           | 100 C <sub>A</sub>   <sup>2</sup> | 2s    | 2p    | 100 C <sub>A</sub>   <sup>2</sup> | 2s    | 2p    |
| CO <sub>2</sub> (free) | 1.99937   | 35.26                             | 50.00 | 50.00 | 64.74                             | 33.42 | 66.58 |
| Mode (a)               | 1.99914   | 35.22                             | 50.03 | 49.97 | 64.78                             | 33.59 | 66.41 |
| Mode (b)               | 1.99919   | 35.20                             | 50.08 | 49.92 | 64.80                             | 33.50 | 66.50 |
| Mode (h)               | 1.99905   | 35.15                             | 50.00 | 50.00 | 64.85                             | 33.68 | 66.32 |
| Mode (I)               | 1.99920   | 34.92                             | 50.20 | 49.80 | 65.08                             | 33.06 | 66.94 |
| Mode (l)               | 1.99903   | 34.59                             | 50.04 | 49.96 | 65.41                             | 33.94 | 66.06 |
| Mode (o)               | 1.99905   | 34.29                             | 49.96 | 50.04 | 65.71                             | 34.45 | 65.55 |

<sup>a</sup> C<sub>A</sub> is the polarization coefficient.

modes, probably due to the difference in the final optimized form. Meanwhile, the natural charge of oxygen atom of CO<sub>2</sub> nearer to the copper surface is more than that of O atom apart from the surface. In addition, one can observe that the amount of electron in C and O atoms change indistinctly after CO<sub>2</sub> adsorbed onto the Cu(*hkl*) surfaces.

From Table 5 one can also find that the calculated charge of CO<sub>2</sub> is so small and nearly equals to zero, which means that the CO<sub>2</sub><sup>δ−</sup> species is difficult to be produced during the processes of CO<sub>2</sub> adsorption on clean copper surfaces. In fact, the experimental result of UPS showed that the CO<sub>2</sub><sup>δ−</sup> species has been observed at the CO<sub>2</sub>/K/Cu system while only physisorbed state, CO<sub>2</sub> (phys.), was observed on the CO<sub>2</sub>/Cu system due to weak interaction between CO<sub>2</sub> and clean copper surfaces [47]. In general, the lower the work function of the substrate, the stronger the interaction between CO<sub>2</sub> and substrate, and the easier the formation of the CO<sub>2</sub><sup>δ−</sup> species [7,47]. Thus, for the cases with low work function, for examples, in the Fe(100) surface [48], or the defected Cu surface [10], or the pre-adsorbed system like CO<sub>2</sub>/K/Cu(100) [47], which have been confirmed the formation of CO<sub>2</sub><sup>δ−</sup> species. For the formation of CO<sub>2</sub><sup>δ−</sup> species on the various cases, we will give a systemic investigation in a separate paper later.

From Table 6, it is easy to find that the occupancy of C–O bond slightly decreases after CO<sub>2</sub> adsorbed onto the Cu(*hkl*) surfaces. For example, the occupancy of C–O bond in the free CO<sub>2</sub> molecule (1.99937) drops to 1.99905 in mode (o). Sim-

ilar findings hold true for the change of the 100|C<sub>A</sub>|<sup>2</sup> (C<sub>A</sub> is the polarization coefficient) of C atom in the C–O bond. For the free CO<sub>2</sub> molecule, the 100|C<sub>A</sub>|<sup>2</sup> of C atom in the C–O bond is 35.26% with the contributions of C (2s) (50.00%) and C (2p) (50.00%) and the contribution to the C–O bond from O (2s) and O (2p) is 33.42% and 66.58%, respectively. In the mode (o) with the highest adsorption energy, the 100|C<sub>A</sub>|<sup>2</sup> of C atom (34.29) is smaller than that of C atom in free CO<sub>2</sub> molecule, and the contribution to the C–O bond from C (2s) and C (2p) is no longer equal because of adsorption behavior.

### 3.4. Activation of CO<sub>2</sub> on the Cu(*hkl*) surfaces

In general, a major objective in studying CO<sub>2</sub>–surface interactions is investigating the activation because of its implications for many chemical processes. A comprehensive overview of CO<sub>2</sub> activation by metal complexes has been given by Behr [3]. Overviews of CO<sub>2</sub> activation in biologically relevant processes as well as in heterogeneous catalysis, in electrochemistry and other fields have been reported [4,5]. Recently, Solymosi [6] and Freund and Rorbert [7] have provided comprehensive reviews of CO<sub>2</sub> interaction with clean and modified single crystal metal surfaces and of related works on real catalyst surfaces. In this section, we will make an attempt to investigate the activation of CO<sub>2</sub> on the Cu(111), Cu(100), and Cu(110) surfaces. Electron density from Bonding Mulliken population analysis between C and O atoms at

Table 7

Electron density from Bonding Mulliken population analysis between C and O atoms at the B3LYP/LANL2DZ-6-31G level

|                        | Left O–C | Right C–O |
|------------------------|----------|-----------|
| CO <sub>2</sub> (free) | 0.465353 | 0.465353  |
| Mode (a)               | 0.432538 | 0.426999  |
| Mode (b)               | 0.444095 | 0.427075  |
| Mode (h)               | 0.417777 | 0.417441  |
| Mode (i)               | 0.418299 | 0.458075  |
| Mode (l)               | 0.407081 | 0.450471  |
| Mode (o)               | 0.434244 | 0.418905  |

the B3LYP/LANL2DZ-6-31G level are reported in Table 7.

The results shown in Table 7 indicate that all the C–O electron densities decrease after CO<sub>2</sub> adsorbed onto the Cu(*hkl*) surfaces, suggesting that the C–O bonds in CO<sub>2</sub> molecule gain somewhat activation during the interaction of CO<sub>2</sub> with the copper single crystal surfaces. For instance, the electron densities for left O–C and right C–O in final optimized form of mode (o) (0.434244 and 0.418905, respectively) are smaller than those for the free CO<sub>2</sub> molecule (0.465353). The elongated C–O distances (listed in Table 2) also confirm the activation of C–O bonds in adsorbed CO<sub>2</sub> relative to free CO<sub>2</sub> molecule (1.160 Å) [26]. Furthermore, non-dissociative adsorption of CO<sub>2</sub> molecule on the Cu(*hkl*) surfaces can be inferred from those findings. The activation can be also demonstrated by the above-mentioned analysis for slightly decrease of the occupancy of C–O bond. This kind of weakly adsorbed behavior of CO<sub>2</sub> agrees well with the experiments [3–7,17,18,45]. A close scrutiny of the data given in Tables 2–7 permits us to draw a conclusion that the degree of activation of CO<sub>2</sub> adsorbed on the Cu(*hkl*) surfaces is in the order of Cu(110) > Cu(100) > Cu(111).

#### 4. Conclusions

In the present work, the interaction of CO<sub>2</sub> with the Cu(*hkl*) surfaces has been investigated by means of quantum chemical DFT calculations and cluster models and periodic slabs. The calculated adsorption energies from periodic slabs are

lower as compared to the experimental data as well as the cluster model data, indicating that the periodic slab approach of generalized gradient approximation in the density function theory is not suitable to obtain quantitative information on the CO<sub>2</sub>/Cu(*hkl*) adsorption systems studied here. Through examining the effect of basis set of C and O atoms, it is reasonable to conclude that the results calculated from the 6-31G basis set are more reliable than those from the STO-3G and 6-31G\*\* basis set. Optimized results show that the final structure of adsorbed CO<sub>2</sub> is near linear and the preferred modes for the adsorption of CO<sub>2</sub> are the side-on adsorption at the cross bridge site (namely mode (b)), the side-on adsorption at the short bridge site (mode (h)), and the end-on adsorption on the on-top site with C–O bonds located along the short bridge site (mode (o)) on the Cu(111), Cu(100), and Cu(110) surfaces, respectively.

The results from NBO analysis indicate that CO<sub>2</sub> forms essentially a covalent bond for all modes. It has been observed that the adsorption energies ( $E_{\text{ads}}$ ) for carbon dioxide are in the order of Cu(110) > Cu(100) > Cu(111). Similar finding holds true for the trend in the degree of CO<sub>2</sub> activation, suggesting that the reactivity for CO<sub>2</sub> dissociation on the Cu(*hkl*) surfaces might follow the order of Cu(110) > Cu(100) > Cu(111). Our present cluster DFT calculations are in accord with the experimental reports. Additionally, we plan to deconvolve rigorous and detailed DFT calculations of the decomposition pathway of molecules (i.e. H<sub>2</sub>O, CO<sub>2</sub>, HCOO, etc.) on transition metal surfaces to gain an insight into relevant heterogeneously catalyzed reactions in the future.

#### Acknowledgment

This work was supported by the National Natural Science Foundation of China (Grants no. 20273034), the C1 Chemistry & Technology (Taiyuan University of Technology) of China and the State Key Laboratory of Coal Conversion of China. This work was also supported by Nankai University ISC.

## References

- [1] K. Weissmehl, H.-J. Arpe, Industrielle Organische Chemie, Verlag Chemie, Weinheim, 1976.
- [2] G.C. Chinchin, M.S. Spencer, K.C. Waugh, D.A. Whan, J. Chem. Soc. Faraday Trans. 1 83 (1987) 2193.
- [3] A. Behr, Carbon Dioxide Activation by Metal Complexes, Verlag Chemie, Weinheim, 1988.
- [4] J. Paul, C.-M. Pradier, in: M.D. Hazch, N.K. Boardman (Eds.), The Biochemistry of Plants, vol. 10, Academic Press, New York, 1987, p. 132.
- [5] W.A. Ayers (Ed.), Catalytic Activation of Carbon Dioxide, ACS Symp. Ser. 363, Am. Chem. Soc., Washington, 1988.
- [6] F. Solymosi, J. Mol. Catal. 65 (1991) 337.
- [7] H.-J. Freund, M.W. Roberts, Surf. Sci. Rep. 25 (1996) 225.
- [8] R.A. Chadden, H.D. Vandervell, K.C. Waugh, G. Webb, Catal. Lett. 1 (1988) 27.
- [9] P.R. Norton, R.L. Tapping, Chem. Phys. Lett. 38 (1976) 207.
- [10] R.G. Copperthwaite, P.R. Davies, M.A. Morris, M.W. Roberts, R.A. Ryder, Catal. Lett. 1 (1988) 11.
- [11] F.H.P.M. Habraken, E. Kieffer, G.A. Bootsma, Surf. Sci. 83 (1979) 45.
- [12] P.B. Rasmussen, P.A. Taylor, I. Chorkendorff, Surf. Sci. 269/270 (1992) 352.
- [13] P.B. Rasmussen, P.M. Holmblad, T. Askgaard, C.V. Ovesen, P. Stolze, N.K. Norskov, I. Chorkendorff, Catal. Lett. 26 (1994) 373.
- [14] J. Nerlov, S. Sckerl, J. Wambach, I. Chorkendorff, Appl. Catal. A 191 (2000) 97.
- [15] P.A. Taylor, P.B. Rasmussen, C.V. Ovesen, I. Chorkendorff, Surf. Sci. 261 (1992) 191.
- [16] C.T. Au, M.D. Chen, Chem. Phys. Lett. 278 (1997) 238.
- [17] J.A. Rodriguez, W.D. Clendening, C.T. Campbell, J. Phys. Chem. 93 (1989) 5238.
- [18] J. Nakamura, J.A. Rodriguez, C.T. Campbell, J. Phys. (Condens. Matter) 1 (1989) 149.
- [19] C.T. Campbell, K.-H. Ernst, in: D.J. Dwyer, F.M. Hoffmann (Eds.), Surface Science of Catalysis, ACS Symp. 482, 1992, p. 130.
- [20] G.C. Wang, L. Jiang, X.Y. Pang, Z.S. Cai, Y.M. Pan, X.Z. Zhao, Y. Morikawa, J. Nakamura, Surf. Sci. 543 (2003) 118.
- [21] M.P. Habas, F. Mele, M. Sodupe, F. Illas, Surf. Sci. 431 (1999) 208.
- [22] J.M. Ricart, M.P. Habas, A. Clotet, D. Curulla, F. Illas, Surf. Sci. 460 (2000) 170.
- [23] M. Melle-Franco, G. Pacchioni, A.V. Chadwick, Surf. Sci. 478 (2001) 25.
- [24] J.R.B. Gomes, J.A.N.F. Gomes, Surf. Sci. 471 (2001) 59.
- [25] R.A. van Santen, M. Neurock, Catal. Rev. Sci. Eng. 37 (1995) 557.
- [26] D.R. Lide, CRC Handbook of Chemistry and Physics, 79th ed., CRC Press, Boca Raton, FL, 1998.
- [27] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
- [28] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
- [29] M.J. Frisch et al., Gaussian 94, Revision E.3, Inc., Pittsburgh, PA, 1995.
- [30] P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 299.
- [31] J.P. Foster, F. Weinhold, J. Am. Chem. Soc. 102 (1980) 7211.
- [32] A.E. Reed, F. Weinhold, J. Chem. Phys. 78 (1983) 4066.
- [33] A.E. Reed, R.B. Weistock, F. Weinhold, J. Chem. Phys. 83 (1985) 735.
- [34] E.D. Glendening, A.E. Reed, J.E. Carpenter, F. Weinhold, NBO Version 3.1.
- [35] T. Hayashi, Y. Morikawa, H. Nozoye, J. Chem. Phys. 114 (2001) 7615.
- [36] Y. Morikawa, K. Iwata, K. Terakura, Appl. Surf. Sci. 169/170 (2001) 11.
- [37] Y. Morikawa, K. Iwata, J. Nakamura, T. Fujitani, K. Terakura, Chem. Phys. Lett. 304 (1999) 91.
- [38] S. Smsuda, R. Szuki, M. Aoki, Y. Morikawa, R. Kishi, M. Kawai, J. Chem. Phys. 114 (2001) 8546.
- [39] P. Hohenberg, W. Hohn, Phys. Rev. B 136 (1964) 864; W. Kohn, L.J. Sham, Phys. Rev. A 140 (1965) 1133.
- [40] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
- [41] D. Vanderbilt, Phys. Rev. B 41 (1990) 7892.
- [42] R.A. Hadden, H.D. Vandervell, K.C. Waugh, G. Webb, in: M.J. Philips, M. Ternan (Eds.), Proc. 9th Int. Cong. on Catalysis, vol. 4, The Chemical Institute of Canada, Ottawa, 1988, p. 1835.
- [43] G. Henkelman, H. Johsson, Phys. Rev. Lett. 86 (2001) 664.
- [44] A. Kokalj, A. Dal Corso, S. de Gironcoli, S. Baroni, Surf. Sci. 507–510 (2002) 62.
- [45] M. Kamiya, T. Tusneda, K. Hirao, J. Chem. Phys. 117 (2002) 6010.
- [46] E.M. King, S.J. Clark, C.F. Verdozzi, C.G. Ackland, J. Phys. Chem. B 105 (2001) 641.
- [47] J. Krause, D. Borgmann, G. Wedler, Surf. Sci. 347 (1996) 1.
- [48] H.-J. Freund, H. Behner, B. Bartos, G. Wedler, H. Kuhlenbeck, M. Neumann, Surf. Sci. 180 (1987) 550.