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# First-principles molecular dynamics study of CO adsorption on the Si(001) surface

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## Abstract

We present first-principles molecular dynamics calculations of CO adsorption on the Si(001) surface. We found two adsorption sites of CO on the Si(001) surface, on which the CO molecule adsorbs symmetrically and asymmetrically. The asymmetric structure is preferable: the calculated adsorption energies are 17.0 and 19.0 kcal/mol, respectively, on the symmetric and asymmetric sites. The electron density analysis shows that the main interaction between CO and the Si(001) surface is  $\sigma$ -donation on the asymmetric sites and  $\pi$ -back-donation on the symmetric sites. The calculated vibrational frequency of the CO stretch for the asymmetric site agrees well with the experimental HREELS spectra. The symmetric structure may also exist considering the small difference in the adsorption energy. © 1998 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Many studies concerned with Si surfaces have been done in order to develop promising semiconductor materials. We presented the first-principles molecular dynamics calculations for the acetylene/Si system [1]. Recently there are some reports that CO molecules adsorb on the Si(001) surface, though both the adsorption structure and the electronic structure are not clear [2–4].

Bu and Lin [2] studied the adsorption of CO on the Si(001) surface at 100 K by using high resolution

electron energy loss spectroscopy (HREELS), thermal desorption spectroscopy (TDS) and ultraviolet photoelectron spectroscopy (UPS). They found that the interaction between CO and the Si(001) surface is weak as revealed by the small red-shift of the CO stretching mode at  $2081\text{ cm}^{-1}$  from the free molecular mode at  $2145\text{ cm}^{-1}$  and by the small frequency of the Si–CO stretching mode at  $411\text{ cm}^{-1}$ . By these vibrational analyses, they concluded that the CO adsorbed on Si(001) has an end-on and upright position. They observed a TDS peak at 180 K. Young et al. [3] observed similar results.

Chamberlain et al. [4] found that CO adsorbs on the Si(001) surface especially for a high CO exposure of  $10^4\text{ L}$  ( $1\text{ L} = 10^6\text{ Torr}$ ) even at room

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temperature. The sticking probability is found to be small but not zero.

Recently, Kubo et al. [5] studied CO adsorption on the Si(001) surface by using HREELS and TDS. They confirmed the HREELS results reported by Bu and Lin [2] and Young et al. [3]. They also found CO species with the desorption temperature around 400 K, even for a low CO exposure of 0.5 L. They tentatively attributed these species to CO adsorbed in the defect site. The corresponding peak was not observed in the HREELS experiment as the amount of CO species was small. These CO species may be the same as those found by Chamberlain et al. [4].

Hu et al. [6] observed two CO stretching modes at 1701 and 2105  $\text{cm}^{-1}$  by the use of a molecular beam of CO in their HREELS experiments. The 1701  $\text{cm}^{-1}$  loss is not observed by thermal CO. To explain the experimental results, they performed first-principles quantum chemical calculations with a moderately large cluster model for the CO/Si system and reported that there are two stable sites on the Si(001) surface.

In the present study, we performed first-principles molecular dynamics [7] calculations with a repeated slab model for the CO/Si(001) system, to determine the stable adsorption sites, stable geometries and corresponding vibrational frequencies to analyze the electronic structures of the CO/Si(001) system.

## 2. Computational details

Our calculation is based on the generalized gradient approximation (GGA) in density functional theory (DFT) and Perdew and Wang's formula is used for the exchange-correlation energy and potential [8–12]. The GGA exchange-correlation potential is calculated using a method of White and Bird [13]. We have constructed the pseudopotential following Troullier and Martins' optimized norm-conserving pseudopotential scheme [14,15], except for the carbon  $p$  and oxygen  $p$  orbitals for which we have used the Vanderbilt's ultrasoft pseudopotential scheme [16]. We used a repeated slab geometry in which each slab consists of ten Si layers and the vacuum region with nine Si layers thickness. The lattice constant of the Si slabs used in our calculations is determined from the self-consistent GGA

calculations of bulk Si. The CO molecules are adsorbed on both surfaces of a slab and all atomic positions except for the two center-Si layers are relaxed. The cutoff energies for the wavefunction and charge density expansion are 25 and 196 Ry, respectively. Two inequivalent  $k$ -points in a  $1/4$  surface Brillouin zone are used for Brillouin zone sampling in the symmetric model. Four inequivalent  $k$ -points in a  $1/2$  surface Brillouin zone are used for the Brillouin zone sampling in the asymmetric model.

## 3. Results

### 3.1. Stable geometries

Considering experimental results [2,3,5], we assumed that the CO molecules are oriented almost vertical on the surface with carbon bonded to the first layer Si atoms. We performed geometry optimization for the four candidates of the adsorption sites as shown in Fig. 1 and found that there are two stable adsorption structures: an asymmetric structure optimized for the candidate in the (A) site and a symmetric structure optimized for the candidates in the (B) and (D) sites. We could not obtain a stable structure optimized for the candidate in the (C) site. We therefore describe in more detail the optimized adsorption models in the (A) and (D) sites, i.e. asymmetric and symmetric models, respectively.

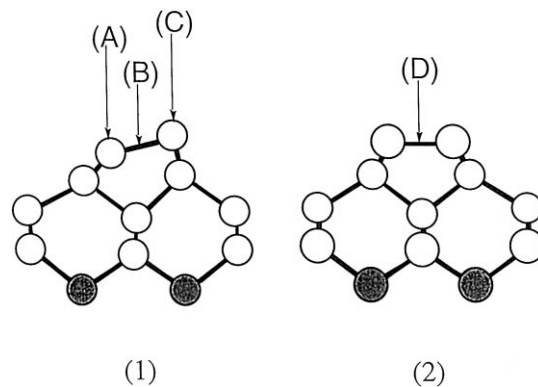


Fig. 1. Side views of the four candidates of adsorption sites on the Si(001) surface: (1) the asymmetric Si structure and (2) symmetric Si structure. Arrow shows the CO adsorption with C toward the Si surface. Open and solid circles indicate optimized and fixed Si atoms, respectively.

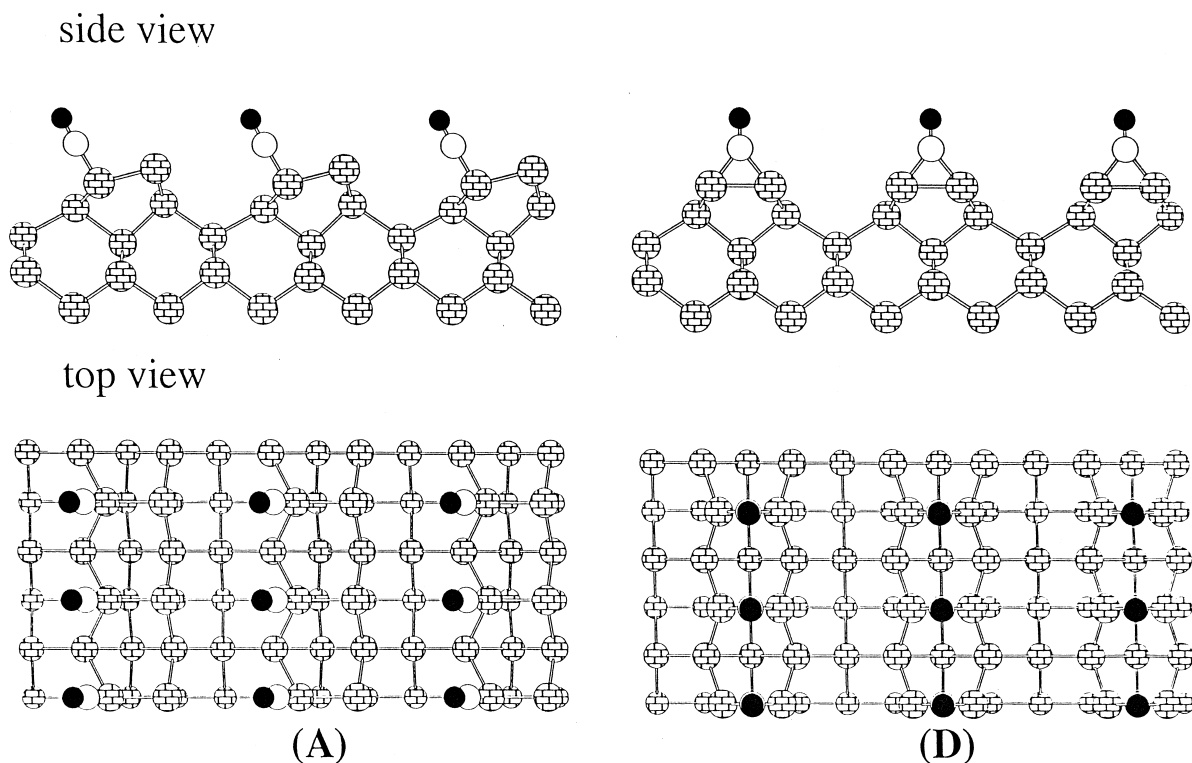


Fig. 2. Optimized structures of the Si(001) surface for (A) the asymmetric structure and (D) the symmetric structure. Open circles, hatched circles and solid circles indicate C, Si and O atoms, respectively.

The optimized structures for the asymmetric and symmetric models are shown in Fig. 2 and the geometrical parameters and the adsorption energies are indicated in Table 1. We found that in both models, the C, O and the first layer Si atoms lie on the same plane and that the Si dimer bond length (2.41 Å) is longer than that of the clean Si(001) surface (2.31 Å). In the symmetric model, the CO bond distance (1.22 Å) is significantly longer to that of the free CO molecule (1.17 Å), while that in the

Table 1  
Calculated structural parameters (Å) and the adsorption energy (kcal/mol) of CO adsorbed on the Si(001) surface

	Asymmetric model	Symmetric model	Free system
$R(\text{Si-Si})$	2.41	2.41	2.31
$R(\text{C-O})$	1.18	1.22	1.17
$R(\text{Si-C})$	1.83	1.96	
adsorption energy	19.0	17.0	

asymmetric model (1.18 Å) is essentially the same as that of free CO, suggesting that the CO bond is weakened more in the symmetric model than in the asymmetric model. This point is closely related with the adsorption mechanism of CO on a Si surface, i.e.  $\sigma$ -donation and  $\pi$ -back-donation mechanisms, as will be discussed later with the analyses of the electron density.

The asymmetric model is slightly more stable than the symmetric model. As shown in Table 1, the calculated adsorption energies in the symmetric and asymmetric models are 17.0 and 19.0 kcal/mol, respectively. Accordingly, the Si–C length is shorter in the asymmetric model. The calculated adsorption energies are larger than the experimental activation energy for desorption (about 11 kcal/mol) [2–5], though the relative stability is consistent with the result reported by Hu et al. [6]. Only from the above results, we can not conclude theoretically which model is preferable for the CO/Si(001) system.

Further analysis is necessary to compare with the experimentally observed quantities.

### 3.2. Vibrational frequencies

We have then performed the vibrational normal mode analyses of both models to obtain further information about the bonding nature. The result is shown in Table 2. The normal vibrational modes are calculated by diagonalizing the matrix of the mass-weighted Cartesian force constant, which was obtained by the numerical finite difference method. To estimate the error in our vibrational mode analyses, we have calculated the vibrational modes of free CO molecules and compared with the experimental results. The error in the normal modes of CO is about 3.0%. The C–O stretching frequency of the asym-

Table 2

Calculated and experimental vibrational frequencies for the CO stretching mode ( $\text{cm}^{-1}$ )

Calcd.		Exptl.	
asymmetric site	symmetric site	thermal CO	molecular beam
2142	1855	2081 <sup>a</sup>	1701 <sup>b</sup>
free CO		free CO	
2211		2145	

Refs. [2,3,5,6]. <sup>b</sup> Ref. [6].

metric model is calculated to be  $2142 \text{ cm}^{-1}$  which is in good agreement with the experimental value of  $2081 \text{ cm}^{-1}$  [2,3,5,6]. The corresponding value calculated for the symmetric model is  $1855 \text{ cm}^{-1}$ , which is much smaller than that of the asymmetric one.

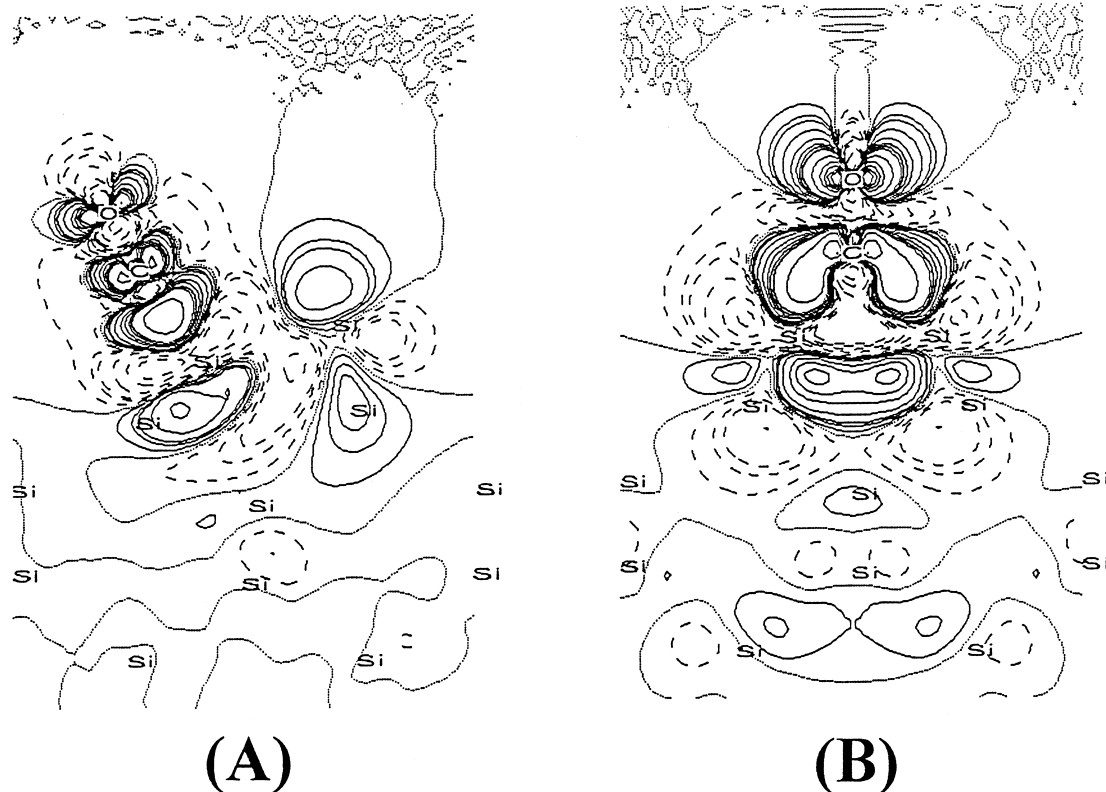


Fig. 3. The difference electron densities of the CO/Si(001) surface for (A) the asymmetric model and for (B) the symmetric model. The cut planes of (A) and (B) are perpendicular to the surface and contain the C, O and first layer Si atoms. Solid curves correspond to charge densities of 0.0003, 0.0007, 0.001, 0.002, 0.004, 0.006, 0.008, 0.01, 0.02, 0.04, 0.06, 0.08 and 0.1. Dotted curves correspond to charge densities of  $-0.0003$ ,  $-0.0007$ ,  $-0.001$ ,  $-0.002$ ,  $-0.004$ ,  $-0.006$ ,  $-0.008$ ,  $-0.01$ ,  $-0.02$ ,  $-0.04$ ,  $-0.06$ ,  $-0.08$  and  $-0.1$ .

The above vibrational analysis strongly supports that the asymmetric CO model is preferable on the Si(001) surface. However, since the asymmetric CO is stable only by 2 kcal/mol(calculated value) relative to the symmetric one, the symmetric CO structure may appear on Si(001): actually the C–O stretching frequency calculated ( $1855\text{ cm}^{-1}$ ) is close to the peak at  $1701\text{ cm}^{-1}$  observed by the molecular beam technique [6].

### 3.3. Electron densities

We analyze the electronic structure of the CO/Si(001) system using the difference of electron density defined as follows,

$$\rho^{\text{diff}}(\mathbf{r}) = \sum_{i,k} w_k \rho_{i,k}^{\text{TOTAL}}(\mathbf{r}) - w_k \rho_{i,k}^{\text{CO}}(\mathbf{r}) - w_k \rho_{i,k}^{\text{Si}}(\mathbf{r}), \quad (1)$$

where  $i$  is the band index,  $\mathbf{k}$  the  $k$ -point vector in the Brillouin zone,  $w_k$  the weight of the  $k$ -point sampling and  $\rho_{i,k}^{\text{TOTAL}}(\mathbf{r})$ ,  $\rho_{i,k}^{\text{Si}}(\mathbf{r})$  and  $\rho_{i,k}^{\text{CO}}(\mathbf{r})$  represent, respectively, the charge densities of the Si surface with CO, the Si surface and CO, in the state  $\{i, \mathbf{k}\}$ . In Fig. 3, the difference electron densities for (A) the asymmetric model and (B) the symmetric model on

the cut planes perpendicular to the surface are shown. In the asymmetric model, the density decreases from the CO  $\sigma$ -orbital and increases in the Si dangling bond region. This means that the main interaction is  $\sigma$ -donation. However, in the symmetric model, the density increases in the CO  $\pi^*$ -orbital and decreases from the Si dangling bond region. This means that the main interaction is  $\pi$ -back-donation. This interaction explains why the CO distance is longer in the symmetric model than that in the asymmetric one. Of course, we can observe both  $\sigma$ -donation and  $\pi$ -back-donation character to different extents in both the asymmetric and symmetric interactions.

Next, in order to analyze the adsorption mechanism, we use the partial electron densities of the Si surface (without CO) defined by

$$\rho^{\text{LUMO}}(\mathbf{r}) = \sum_{i,k}^{\epsilon_{\text{LUMO}} \leq \epsilon_{i,k} \leq \epsilon_{\text{LUMO}} + 1\text{ eV}} w_k \rho_{i,k}(\mathbf{r}), \quad (2)$$

$$\rho^{\text{HOMO}}(\mathbf{r}) = \sum_{i,k}^{\epsilon_{\text{HOMO}} - 1\text{ eV} \leq \epsilon_{i,k} \leq \epsilon_{\text{HOMO}}} w_k \rho_{i,k}(\mathbf{r}), \quad (3)$$

where  $\epsilon_{\text{LUMO}}$  and  $\epsilon_{\text{HOMO}}$  are, respectively, the lowest unoccupied and the highest occupied levels of the

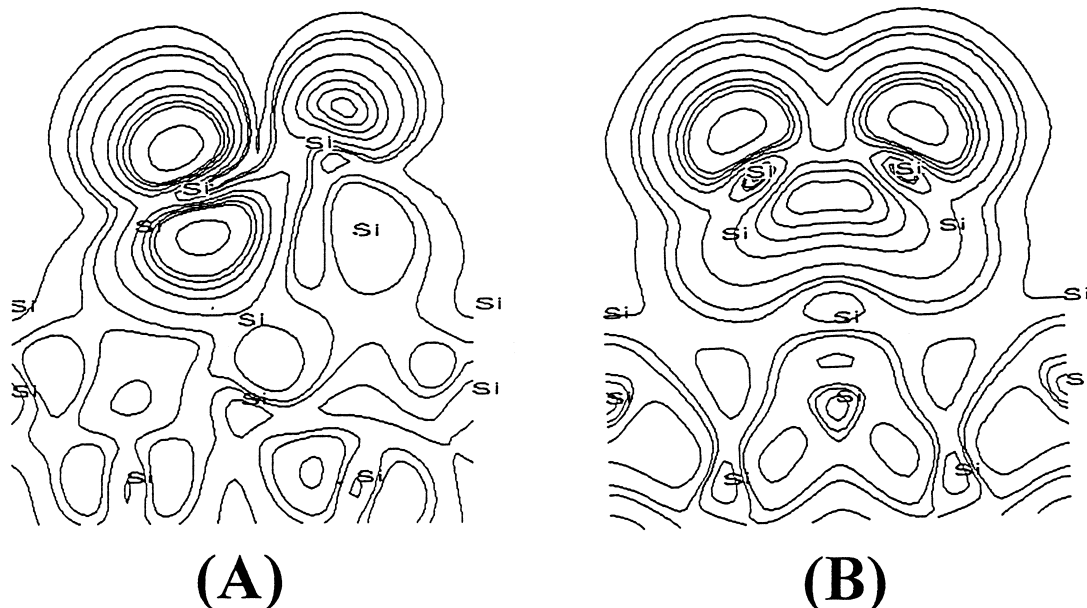


Fig. 4. The partial electron densities of the Si(001) surface for (A)  $\rho^{\text{LUMO}}(\mathbf{r})$  and for (B)  $\rho^{\text{HOMO}}(\mathbf{r})$ . The cut planes of (A) and (B) are perpendicular to the surface and contain the first-layer Si atoms. Solid curves correspond to charge densities of 0.0003, 0.0007, 0.001, 0.002, 0.004, 0.006, 0.008, 0.01, 0.02, 0.04, 0.06, 0.08 and 0.1.

system. In the asymmetric model, the CO adsorption reaction path is mainly controlled by the unoccupied partial electron density defined by Eq. (2) of the Si clean surface, since the  $\sigma$ -donation from CO to the Si clean surface is dominant. However, in the symmetric model, the CO adsorption is mainly controlled by the occupied partial electron density given by Eq. (3), since  $\pi$ -back-donation from the Si surface to CO occurs. Thus, in Fig. 4,  $\rho^{\text{LUMO}}$  is shown for (A) and  $\rho^{\text{HOMO}}$  for (B) in the planes perpendicular to the surface. In Fig. 4 (A) the density accumulates on the first layer Si atoms more on the lower Si atom than on the upper Si, in agreement with the calculated result that the  $\sigma$ -donation adsorption occurs at the lower Si site. This analysis shows that the surface reconstruction occurs due to the  $\sigma$ -donation from CO to the surface. While, Fig. 4 (B) for the symmetric model shows that the  $\pi$  back-donation interaction occurs near the center of the Si–Si bond in the first Si layer.

We have assumed so far that the CO molecule is adsorbed on the Si atoms of the first layer of the  $(2 \times 1)$  unit cell. We check the unit-cell dependence by calculating both models in the  $(2 \times 2)$  unit cell. The  $(2 \times 2)$  unit cell consists of optimized model  $(2 \times 1)$  and optimized Si clean surface  $(2 \times 1)$  unit cells. The adsorption energies of the asymmetric and symmetric models are calculated to be 18.5 and 16.2 kcal/mol, respectively, which are almost identical with those 19.0 and 17.0 kcal/mol of the  $(2 \times 1)$  unit cell, respectively. This result shows that the effect of neighboring cells is not so significant.

#### 4. Conclusion

The following points are clarified by performing the first-principles molecular dynamics calculations of the CO-adsorbed Si(001) surface. We found two adsorption structures: the asymmetric structure with CO adsorbed on one of the first layer Si atoms (lower one) and the symmetric structure with CO adsorbed between the first layer Si atoms. The calcu-

lated adsorption energy of the asymmetric CO structure is 19 kcal/mol and the CO stretching frequency calculated for the asymmetric structure agrees well with the experimental data. The electron density analyses show that the asymmetric form is preferable for the  $\sigma$ -donation from CO to the Si surface. However, the symmetric structure may appear on the Si(001) surface considering the small difference in the adsorption energy. The calculated adsorption energy is 17 kcal/mol and the main interaction is  $\pi$ -back-donation interaction.

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