The Adsorptions and Configurations of CO Molecules on W (110) and W (100) Surface: Molecular Orbital Theory

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The adsorption and configuration of CO molecules adsorbed on W (110) and W (100) surfaces have been calculated by the atomic superposition and electron delocalization molecular orbital (ASED-MO) method. Referred to as the ASED-MO method, it has been used in the present study to calculate the geometries, binding energies, vibrational frequencies, orbital energies, reduced overlap population (ROP), and charges. From these results adsorption properties of α-state and β-state were deduced. The calculated binding energies are in good agreement with the experimental result. On the W (110), the calculated average binding energies are 2.56 eV for the end-on configuration and 3.20 eV for the lying-down configuration. Calculated vibrational frequency is 1927 cm^{-1} at a 1-fold site and 1161 cm^{-1} at a long-bridge (2) site. These results are in reasonable agreement with experimental values. On the W(100) surface, calculated average binding energies of the end-on and the lying-down are 2.54 eV and 4.02 eV respectively. The differences for binding energy and configuration on the surfaces are explained on the basis of surface-atom coordination and atom-atom spacing. In the favored lying-down CO configuration on the W(110) and W(100) surfaces, 4σ and 1π donation interactions, coupled with the familiar 5σ donation to the surfaces and back-donations to the CO $2\pi^*$ orbital, are responsible for adsorption to the surface.

Key Words : Adsorption of carbon monoxide, Tungsten

Introduction

The Adsorption and configuration of carbon monoxide on the surface has been studied extensively with a wide variety of techniques.[1-10] The adsorption and configuration of CO molecules on transition-metal surfaces represent a large portion of the entire body of surface science studies and much of this effort has been motivated by COs role as a feedstock in the very technologically important catalytic process.[1]

The thermal desorption spectra of CO desorbed from the tungsten surface have shown two main desorption states; one of them, which is called α state (end-on configuration), appears about 400 K and the other, which is called β state (lying-down configuration), show two or three desorption peaks in the range of about 800 K to 1300 K. Propst and Piper[10] observed that the CO stretching vibration could not be seen in adsorbed CO on the W (100) surface at about 450 K, using high resolution electron energy loss spectroscopy (HREELS). They suggest that CO dissociation occurs upon chemisorptions on the tungsten surface. King[12] has reported that the adsorbed CO of β-state on W is dissociative adsorption. These studies have proved that desorption of β-state is due to recombination of $C_{(a)}$ and $O_{(a)}$, produced from dissociated CO by electron stimulated desorption (ESD), and the dissociative adsorption of β-state has been widely accepted in the system.[1,7,13] Shimizu[4] reports the dissociation of CO on W (110) oriented tips using an AP (Atom Probe). He suggests that CO molecules partially dissociate at high temperature.

Houston[6] observed a low CO stretching frequency in CO adsorbed on a W (110) surface at low coverage. He strongly suggests that the low frequency(C-O) for the CO/W (110) system corresponds to a tilted bonding configuration, based on the results of electron energy loss spectroscopy (EELS) intensity and work function measurement. The measurements[6] of EELS shows a CO stretching frequency at 2070 cm^{-1} and for the low coverage state intensity at 1360 cm^{-1}.

A fundamental aspect of adlayer structures and dynamics is the question of the dissociation of adsorbed carbon monoxide. Whether the adsorption of β-states of CO on tungsten surface is dissociative or non-dissociative has been the subject of argument. Madey[11] reports that the CO in β-state did not dissociate on W. This observation was based on the fact that the field emission was not revealed on the inherent dissociation of adsorbed CO and the thermal desorption spectra of this system did not show second-order kinetics.

Recently, Lee *et al.*[8,9] reported the adsorption of CO on W (111), using TDS (Thermal Desorption Spectroscopy), UPS (Ultraviolet Photoelectron Spectroscopy) and XPS (X-Ray Photoelectron Spectroscopy). They suggest the possibility of non-dissociated adsorption of β-state. Schroder *et al.*[3] report the adsorption and desorption of CO on W (110) surface, using sum frequency generation (SFG) and thermal desorption spectroscopy (TDS). They suggest CO dissociation is not predicted. Although a large number of studies has been

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reported on CO adsorption on tungsten surface, the number of studies on the W (110) surface and W (100) is quite limited. It is an interesting question as to whether the dissociative adsorption of β-states of CO on the tungsten is site dependent on surface. Understanding the adsorption and configuration of β-state, requires theoretical study. The present paper presents the results of a theoretical investigation into the adsorption and configuration of CO molecules over W (110) and W (100) surfaces. We have calculated binding energies, the charge transfer and vibrational stretching frequencies at each site on a surface.

Theoretical Method

In the present study, we used the atom superposition and electron delocalization molecular orbital (ASED-MO) theory.[14-19] This technique has been used in previous studies of carbon monoxide adsorption on Pt ((100) and (111))[17] and carbon dioxide on surfaces (Fe (111), Pt (111)).[15] The parameters used in the present study are found in the literature of Anderson and coworker.[20,21] The ASED-MO theory is a semi-empirical approach for determining approximate molecular structures, force constants, bond strengths, electron spectra, and reaction energy surfaces and orbital starting with experimental atomic valence ionization potentials and the corresponding Slater orbital. This theory identifies two energy terms for the chemical bond formation. One is a pair-wise atom-atom repulsion energy called E_R. The other is attraction energy due to electron delocalization by the one-electron molecular orbital theory, E_{MO}, which is obtained by diagonalizing a Hamiltonian similar to the extended Hückel Hamiltonian:

$$E = E_R + E_{MO} \quad (1)$$

Figure 1 shows adsorption sites for CO molecules studied on a W (110) and W (100). Two metal atoms separated by 3.16 Å in a long bridge (1), by 4.48 Å in long bridge (2) on the W (110), and by 3.16 Å in di-σ bridge site on the W (100). The adsorption of 1-fold, 2-fold, 3-fold, and 4-fold denote end-on configurations, where CO is upright on the surface plane. In the remaining adsorption sites, di-σ brige, 4-fold (1), 4-fold (2), long-bridge (1), long-bridge (2), short-bridge, and μ/π, CO were adsorbed on the surface in lying-down configurations with both C and O end-forming bonds with W atoms of the surface.

For calculations on the metal surfaces we have modeled a metal cluster, as shown in Figure 2. Figure 2 shows cluster models of the W (110) surface and W (100). Clusters were bulk super imposable with a W-W nearest neighbor distance of 2.74 Å. Figure 2 (a, b) shows the top view and the side view of the W (110) with a three-layer-thick 27-atom cluster. Figure 2(c, d) shows the top view and the side view of W (100) surface with a three-layer 25 atom cluster.

All of the angles of adsorbed CO were optimized to the

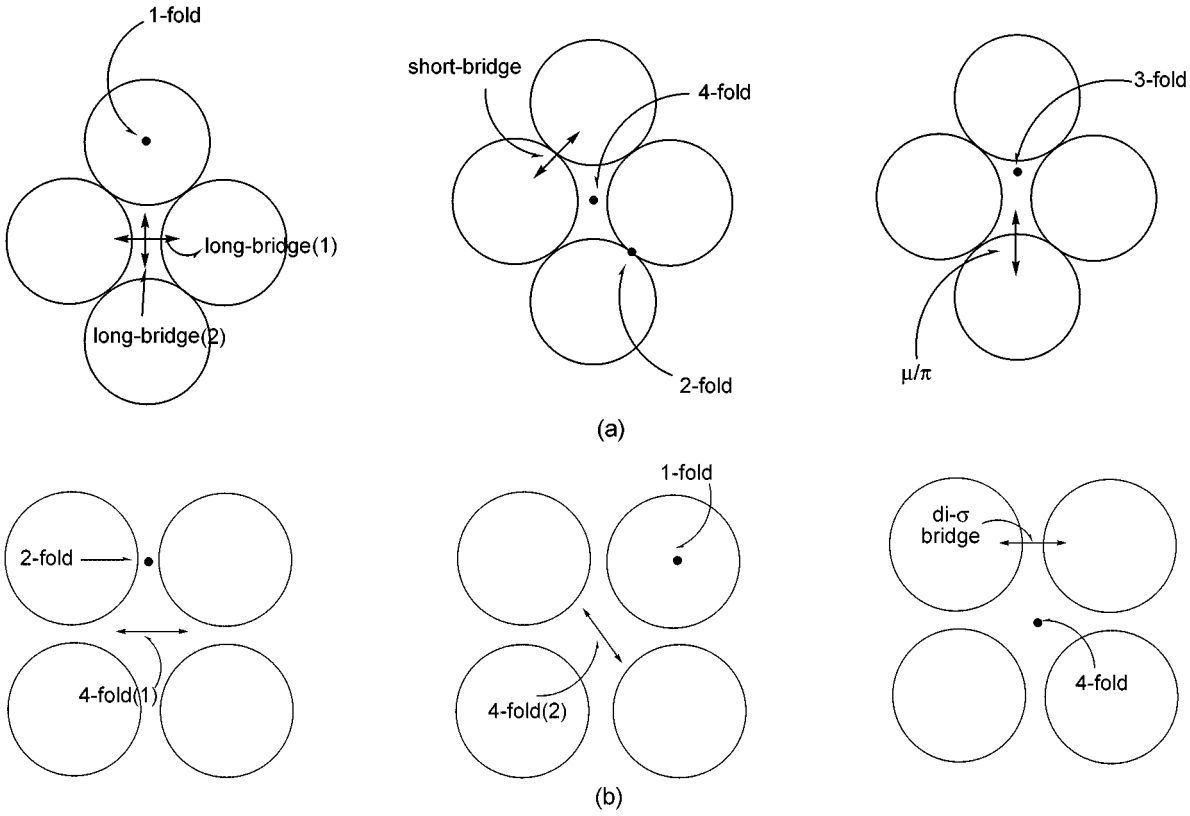

Figure 1. (a) Adsorption sites for CO molecule studied on the W (110) surface. Two metal atoms separated by 3.16 Å in the long bridge (1) and by 4.48Å in the long bridge (2). (b) Adsorption sites for CO molecule studied on the W (100) surface. Two metal atoms separated by 3.16 Å in the di-σ site.

nearest full degree and the distances to the nearest 0.01 angstrom. We did not considered the structural relaxation of the surface layer. We are interested in the question as to whether the adsorption to the β-states of CO on the model tungsten surface is site-dependent. Theory parameters are in Table 1.

Results and Discussion

We calculated binding energies for CO adsorbed on the W (110) and W (100) surface with respect to the increase in layer thickness as shown in Table 2. We found from the calculation that on proceding from two-layer to four-layer in layer thickness, CO binding energy increases slightly on average on the W(100). The binding energies of one-layer thickness have a large deviation from other layer thickness. Calculated binding energies of three-layer thickness are very close to the experimental value.[22] We found that a cluster model should be not less than two-layer thickness to examine the adsorption properties. However, we have chosen the three-layer thickness in this calculation because experimental value[22] on a W (110) and W (100) is 2.50-3.81 eV and 2.47-4.03 eV at 300-1000 K^o, respectively.

Table 3 shows calculated results of CO adsorption on W_{27} cluster model for the (110) surface. In end-on configuration, CO adsorbed molecules are carbon end down. C-O bond lengths are 1.16 Å, 1.18 Å, 1.19 Å and 1.19 Å, respectively. The binding energies are 2.66 eV, 2.48 eV, 2.59 eV, and 2.49 eV, respectively. The calculated structure details for CO molecule on the W (110) surface are shown in Figure 3(a, b). Adsorption of carbon monoxide is strongest at 1-fold in end-on configuration. In lying-down configuration, CO bond

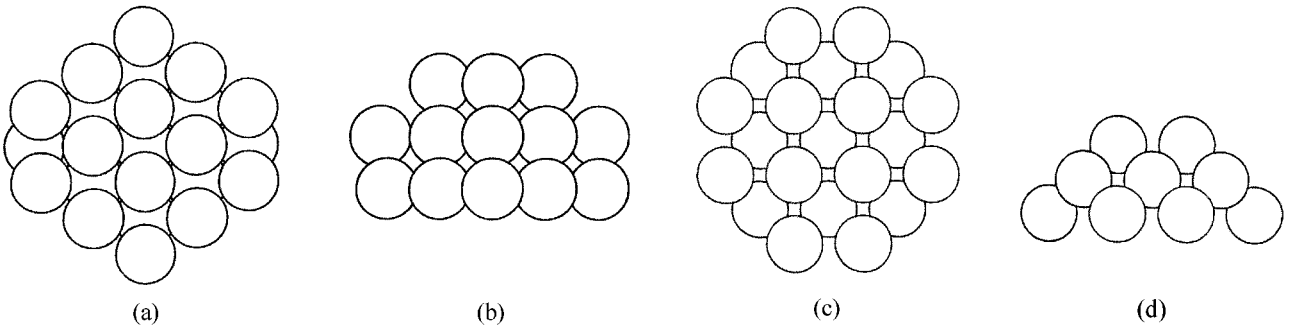

Figure 2. Cluster models of the W (110) and the W (100) surface with three-layer thickness. Clusters are bulk super imposable with a W-W nearest neighbor distance of 2.74 Å. (a) The top view of the W (110) with 27 atom cluster. (b) The side view of the W (110) clusters. (c) The top view of the W (100) with 25 atom cluster. (d) The side view of the W (100) clusters.

Table 1. Atomic Parameters: Principal Quantum Number(n), Valence State Ionization Potential (IP), Orbital Exponents (ζ) and Respective Coefficient (C)

Atom	s			p			d					
	n	IP	ζ	n	IP	ζ	n	IP	ζ_1	C_1	ζ_2	C_2
C[a]	2	15.09	1.658	2	9.76	1.618						
O[a]	2	26.98	2.146	2	12.12	2.127						
W[b]	6	9.50	2.641	6	7.10	2.341	5	10.50	4.982	0.6940	2.068	0.5631

[a]Ref. 20, [b]Ref. 21

Table 2. Calculated Binding Energies (BE (eV)) for CO Adsorbed on the W (110) and W (100) Surface with respect to the increase in layer thickness

W(110)	End-on			Lying -Down					Expt[a]
	1-fold	2-fold	3-fold	4-fold	Short-bridge	Long-bridge (1)	Long-bridge (2)	π/μ	
One-layer	3.19	2.88	2.81	-	3.73	3.91	4.31	3.69	
Two-layer	2.59	2.37	2.38	2.50	2.86	3.00	3.67	2.59	
Three-layer	2.66	2.48	2.59	2.49	3.10	3.28	3.76	2.66	2.50-3.81
Four-layer	2.68	2.41	2.31	2.42	2.81	2.98	3.57	2.50	
W(100)	1-fold	2-fold	-	4-fold	di-σ bridge	4-fold(1)	4-fold(2)		Expt[a]
One-layer	3.38	3.25	-	2.77	5.19	6.00	5.69		
Two-layer	2.78	2.62	-	2.05	4.13	3.40	3.67		
Three-layer	2.92	2.67	-	2.05	4.36	3.69	4.00		2.47-4.03
Four-layer	2.91	2.79	-	2.23	4.44	4.17	4.32		

[a]Experimental value (eV): Ref. 22

Table 3. Calculated Results of CO Adsorbed on W_{27} cluster Model for the (110) Surface: Charge of Dissociated Carbon Monoxide; Q_c=0.00, Q_o=0.33; Dissociated Carbon and Oxygen are placed in 3-fold

Model	BE (eV)[a]	ROP[b]	R_{CO} (Å)[c]	h_C (Å)[c]	h_O (Å)[c]	ω_{CO} (cm^{-1})[d]	ω_{WC} (cm^{-1})	ω_{WO} (cm^{-1})	Q_C[e]	Q_O[e]
End-on										
1-fold	2.66	1.48	1.16	2.40	3.20	1927	752	658	0.77	-0.22
2-fold	2.48	1.40	1.18	1.67	2.85	1703	612	535	0.79	-0.32
3-fold	2.59	1.35	1.19	1.48	2.67	1602	557	487	0.77	-0.39
4-fold	2.49	1.34	1.19	1.49	2.68	1610	564	490	0.75	-0.42
Lying-down										
short-bridge	3.10	1.44	1.18	1.90	1.48	1729	886	776	0.63	0.53
long-brige (1)	3.28	1.36	1.20	1.75	1.35	1542	873	764	0.61	0.53
long-brige (2)	3.76	1.12	1.27	1.29	0.88	1161	746	652	0.59	0.61
μ/π	2.66	1.37	1.19	1.52	1.64	1605	831	727	0.70	0.33

[a]Experimental value (Ref. 22): 2.50-3.81 eV. [b]Reduced overlap population between C and O. [c]h (C) and h (O), the height of C and O of CO adsorbed surface respectively. [d]Experimental value (Ref. 3, 6): 1361 cm^{-1}-2100 cm^{-1}. [e]Q_c^c and Q_o^o are charge on C and O of CO adsorbed surface respectively.

lengths are 1.18 Å, 1.20 Å, 1.27 Å, and 1.19 Å, respectively. Each height (h_o), in which is W-O distance, is 1.48 Å, 1.35 Å, 0.88 Å, and 1.64 Å, respectively. The binding energies are 3.10 eV, 3.28 eV, 3.76 eV, and 2.66eV, respectively. From the calculated binding energies in Table 3, the CO molecule in the long-bridge (2) is the most stable. These results of binding energies qualitatively agree with the thermal desorption spectra of Lee *et al.*[9] which show three high-temperature β-states and a low-temperature α-state. The reduced overlap populations (ROP) of CO bonds have been used successfully on this system as an indication of the strength of a given bond and vibrational frequencies. The ROPs of CO bonds in lying-down configuration, which is relative to the ROP of the free CO bond (1.48 *via* the calculation used in this work), were less than those of end-on configuration. They are dependent the height (hc (Å), ho (Å)) from the surface, as shown in Table 3. We discuss on the vibrational analysis method in a previous study.[17(a)] Calculated vibrational frequencies are in reasonable agreement with experimental values.[3,6] In particular, the large decrease of ROP in the long-bridge (2), which was the most stable, is remarkable. This means that the CO vibrational frequency becomes lower, and the breakage of the CO bond is feasible in the long bridge (2). Calculated energy level positions for CO free, 1-fold, and long bridge (2) are shown in Figure 4(a). Hatched band regions indicate a singly occupied orbital. In the process of adsorption, the main role of the s-d band is withdrawing or donating to the CO molecule as a reservoir of electrons. The differences between CO free state and CO adsorption are negligible on 4σ and 1π orbital, but 5σ and 2π orbital shifts are responsible for the decreased adsorption energy. These observation suggest that the 5σ and 2π orbitals play an important role in CO adsorption on the surface. The 5σ orbital of the CO molecule is primarily responsible for the chemical bond formation to the substrate, and the donation of the 5σ electrons to the metal is simultaneously accompanied by back-donation of metal electrons in the 2π orbital of adsorbed CO. Comparing the 1-fold of end-on configuration and the long bridge (2) of the lying-down, the 2π state interacts strongly with the s-d band in both configurations and electrons are back donated from metals. The main difference in the electronic structure arises in the 5σ, 4σ, and 1π state of adsorbed CO. The 5σ orbital state of the lying-down configuration is more strongly mixed with metals than that of the end-on configuration. 4σ and 1π donation interactions in the lying-down configuration coupled with the familiar 5σ donation to the surfaces.

Table 4 shows the calculated results of CO adsorbed on W_{25} cluster model for the (100) surface. The calculated bond distance of the gas-phase free CO molecule is 1.18 Å, which is about 4% longer than the experimental value.[23] On the 1-fold, 2-fold, 4-fold, di-s bridge, 4-fold (1), and 4-fold (2), we carried out full optimization for carbon monoxide, in which there was varied C-O bond length. The W-C distances are called height (h_c). To examine a tilted configuration on the surface, the WCO angles were optimized to the nearest full degree. In end-on configuration, the C-O bond lengths were 1.17 Å on the 1-fold and 2-fold and 1.20 Å on the 4-fold. Comparing the adsorbed CO molecules with the gas-phase free, we found the CO molecule distances changed little. The heights (h_c) were 2.03 Å, 1.50Å, 0.79 Å, respectively. In end-on configuration, the binding energies were 2.92 eV, 2.67 eV, and 2.05 eV, respectively. The adsorption of carbon monoxide was also strongest at the 1-fold, and likewise the W (110) surface in end-on configuration. In lying-down configuration, the C-O bond lengths were 1.19 Å, 1.32 Å, and 1.22 Å, respectively. This is significantly longer than the free gas phase. Heights (h_o) was 1.35 Å, 0.43 Å, and 0.76 Å, respectively. The binding energies were 4.36 eV, 3.69 eV, and 4.00 eV, respectively. The calculated structure details for CO molecule on the W (100) surface are shown in Figure 3(c, d). Adsorption on the di-s bridge site, on which the distance of two W atoms is 3.16 Å apart, is 0.36 eV more stable than on the 4-fold (2), on which the distance of two W atoms is 4.48 Å apart. The order of stability for adsorbed CO is di-s bridge > 4-fold (2) > 4-fold (1). The corresponding vibrational stretching frequencies are 1643 cm^{-1}, 1410 cm^{-1} and 893 cm^{-1}. These results of binding energies are in reasonable agreement with a study of Lee,[26] in which he suggests that three high temperatures are b-states and a low temperature is a-state. ROPs of bonds in end-on configu-

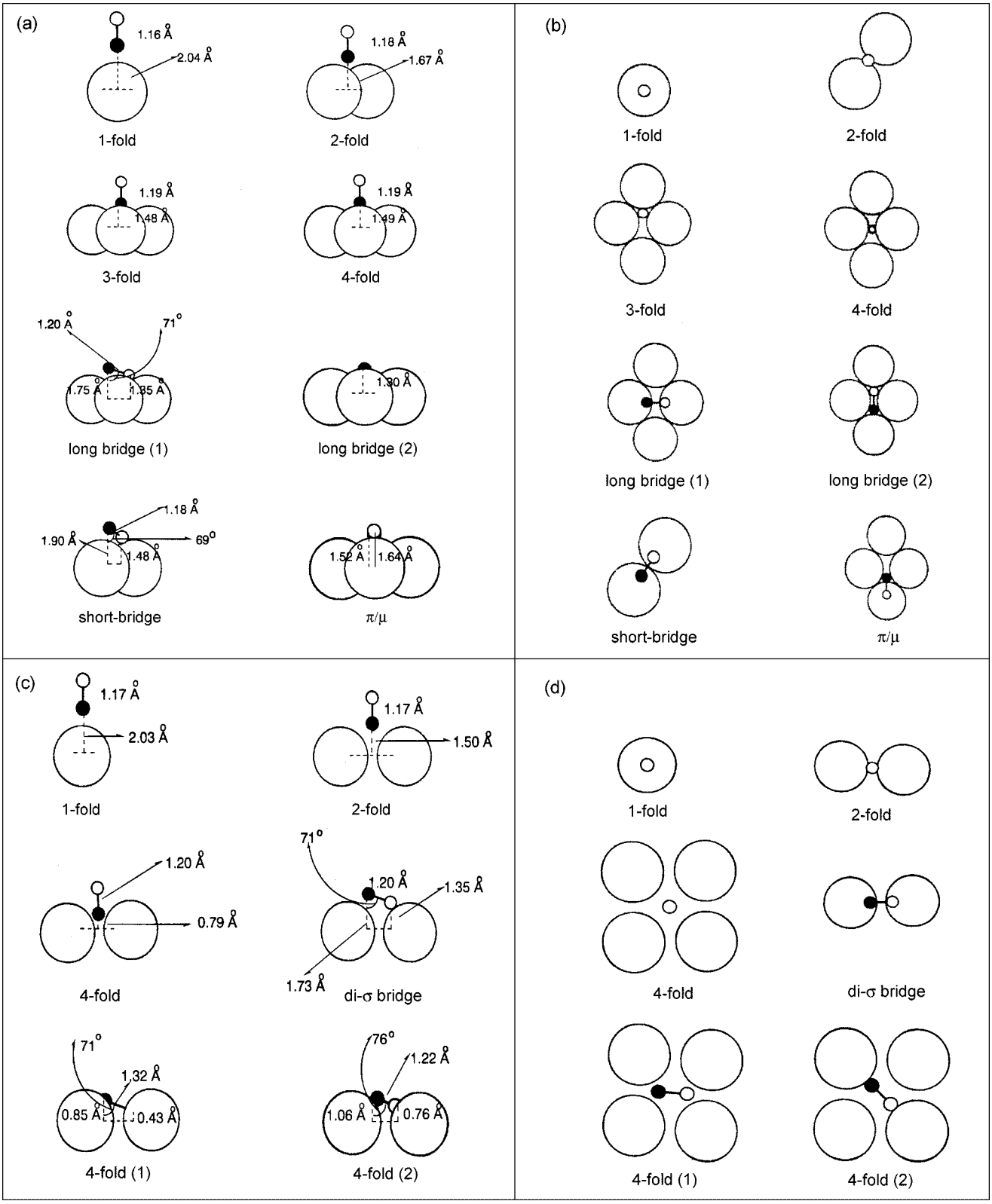

Figure 3. Structure details for CO molecules on the surface and side views to rotate 90 degree from x-axis. (a) Side views for the structure details on the W (110). (b) Top views for the structure details on the W (110). (c) Side views for the structure details on the W (100). (d) Top views for the structure details on the W (100). Large circles indicate tungsten atom, black circles indicate carbon atom, and small circles indicate oxygen.

rations are larger than those of the lying-down configurations. In particular, ROP of the 4-fold (1) site in the lying-down is remarkably small and the vibrational frequency, $W_{CO}(cm^{-1})$, is 893 cm^{-1}. This may imply a decrease that the

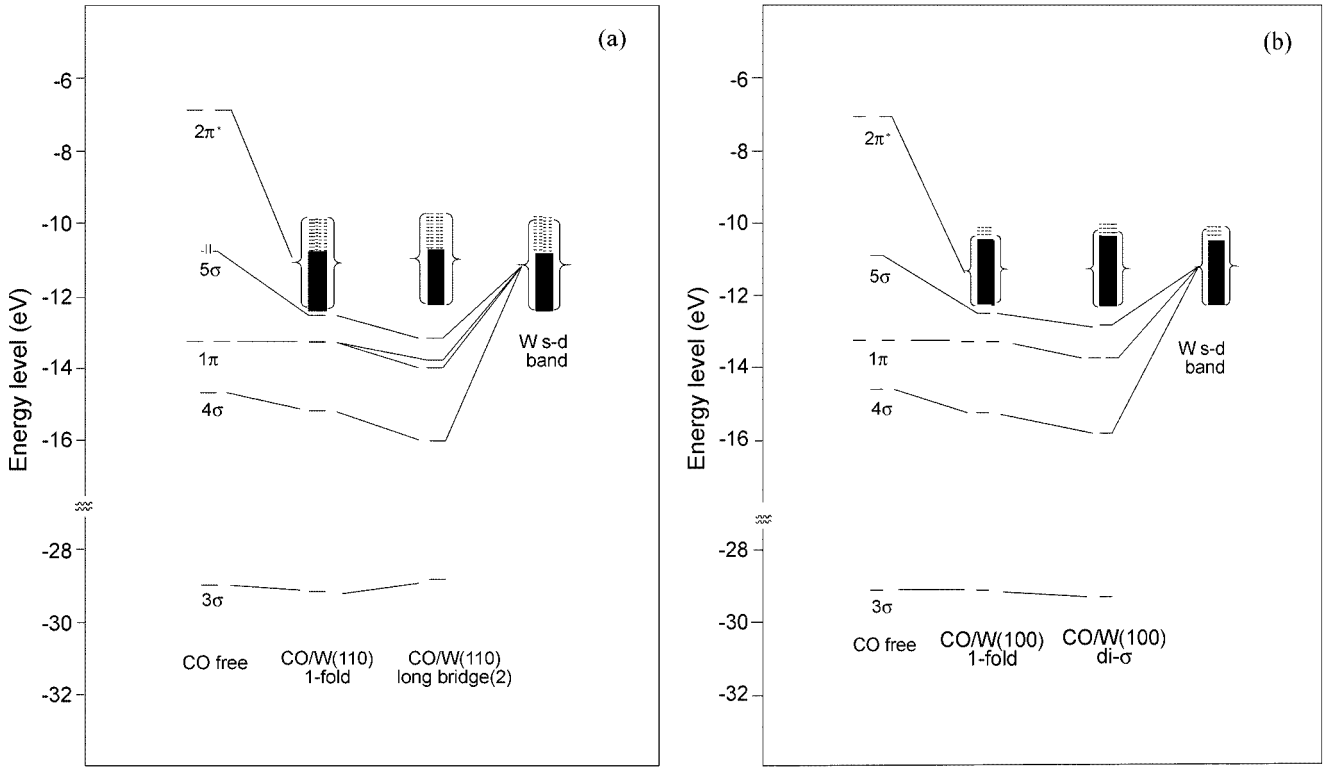

Figure 4. (a) Energy level correlation diagram for CO adsorbed on the 1-fold site in end-on configuration and on the long-bridge (2) in lying-down on W (110). (b) Energy level correlation diagram for CO adsorbed on the 1-fold site in end-on configuration and on the di-σ bridge in lying-down on W (100). Hatched regions half-filled.

Table 4. Calculated Results of CO Adsorbed on W_{25} cluster Model for the (100) Surface: Charge of Dissociated Carbon Monoxide; Q_c=0.15, Q_o=0.15; Dissociated Carbon is placed in 4-fold site and Oxygen is placed in 2-fold

Model	BE (eV)[a]	ROP[b]	R_{CO} (Å)	h_C (Å)[c]	h_O (Å)[c]	ω_{CO} (cm^{-1})	ω_{WC} (cm^{-1})	ω_{WO} (cm^{-1})	Q_C[d]	Q_O[d]
End-on										
1-fold	2.92	1.46	1.17	2.03	3.20	1839	763	667	0.76	-0.24
2-fold	2.67	1.44	1.17	1.50	2.67	1686	542	474	0.76	-0.22
4-fold	2.05	1.31	1.20	0.79	1.99	1435	322	282	0.78	-0.48
Lying-down										
di-σ bridge	4.36	1.39	1.19	1.73	1.35	1643	946	827	0.68	0.52
4-fold (1)	3.69	0.95	1.32	0.85	0.43	893	566	494	0.37	0.44
4-fold (2)	4.00	1.27	1.22	1.06	0.76	1410	498	436	0.56	0.50

[a]Experimental value (Ref. 22): 2.47-4.03 eV. [b]Reduced overlap population between C and O. [c]h(C) and h(O), the height of C and O respectively. [d]Q_c^c and Q_o^o are charge on C and O respectively.

bond strength of the CO bond in the 4-fold (1), and the breakage of the CO bond is feasible as is the long bridge (2).

The energy level correlation diagram for CO adsorbed on the W_{25} cluster model of the (100) surface is shown in Figure 4(b). CO bonding to the surface is predominantly a results of 5σ stabilization due to mixing with the tungsten orbital having s and d character, and back-donation to the $2\pi^*$ orbital from the tungsten d orbital. 4σ and 1π donation interactions are in lying-down configuration coupled with the familiar 5σ donation to the surfaces. Then the lying-

Table 5. Orbital Energies (eV) of adsorbed carbon monoxide and dissociated atom on W (100) and W (110) Surface

	W (100) Surface				W (110) Surface			
Orbital	4-fold(1)	di-σ bridging	4-fold (2)	Dissociated[a] Atom	short -bridge	μ/π	long -bridge (2)	Dissociated[a] Atom
5σ	13.28	12.77	13.15	13.40	12.61	12.66	13.10	13.54
1π	13.88	13.76	13.71	13.78	13.81	13.77	13.81	13.90
4σ	16.18	15.99	16.02	16.33	15.90	15.69	16.11	16.49

[a]Dissociated atom: Dissociated Oxygen and Carbon

down CO configuration also favored adsorption on the W (100) surfaces, likewise for the W (110). This discussion is reasonable agreement with study of Anderson.[20]

We discussed the properties of the β-state in next. We can see that the ROP of the 4-fold (1) is the smallest among lying-down configurations, as shown in Table 4. On the W (110) surface, the ROP of the long-bridge (2) is the smallest among lying-down configurations, as shown in Table 3. Table 5 shows the orbital energies of adsorbed carbon monoxide and dissociated carbon atom and oxygen on W (110) and W (100) surface. On the W (100) surface, the orbital energies of 4-fold (1) are close to those of the dissociated atom. The orbital energies of long bridge (2) are the closest to the dissociated structure among the orbital energies on the W (110). These results means that the orbital energy level is related to the ROP and could establish the experiment of Houston[6] that the precursor state to the dissociation for adsorbed CO molecule on W (110) surface is the lying-down (tilted) configuration.

The vibrational frequency (Wc-o (cm^{-1})), on which the 4-fold (1) is 893 cm^{-1}, is the smallest value among lying-down configurations. It is indicates a relation with the ROP of the CO molecule. However, the charges of C and O in adsorbed carbon monoxide are very different from those of the dissociated carbon monoxide, as shown in Table 4. The calculated vibrational frequency (Wc-o (cm^{-1})) of the long-bridge (2) is 1161 cm^{-1}, it is the smallest value among lying-down configurations on the W (110) surface. This value is in reasonable agreement with the experimental value of Houston, which is 1360 cm^{-1}. It can also be described as evidence of adsorbed CO. This frequency is also related with ROP, and the charges of the long-bridge (2) are very different from those of the dissociated atoms, as shown in Table 3. These charges of C and O atoms are different from the charge of lying-down configurations. Thus, the CO molecule binds weakly to the surface. This model could explain the experiment of Schoder,[3] where it is claimed that β-state configuration of CO is non-dissociated. However, it is an irony that the CO molecule structure of lying-down configurations facilitated the dissociation of the CO molecule electronically, but the CO molecule was not an C atom and an O atom geometrically. It is still unclear whether the β-states of CO on the surface are adsorbed non-dissociatively. There is a limitation on the present calculation. To examine the CO dissociation mechanism, more extensive theoretical calculations have to be performed to investigate such transition states as well as reaction paths between α-state and β-states, the structural relaxation of the surface, and together with the layer role of cluster.

Conclusions

In the present study we arrived at the following results by using the ASED-MO theory.

1. The differences in binding energy and configuration on the surface are explained on the basis of surface-atom coordination and atom-atom spacing.

2. Binding energies of the W (100) surface are stronger than that of the W (110) surface.

3. In the favored lying-down CO configuration, 4σ and 1π donation interactions coupled with the familiar 5σ donation to the surfaces, and back-donations to the CO $2\pi^*$ orbital are responsible for adsorption to the surface.

4. The W (110) cluster model could give an explanation for the experimental results of Schorder and Houston, where it is claimed that the β-state configuration of CO is non-dissociative.

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