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The Tilting of CO Molecules Chemisorbed on a Pt(110) Surface: A Molecular-Orbital Study

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Abstract

The tilting of carbon monoxide molecules adsorbed on a Pt(110) surface has been modeled by using the extended Hückel molecular orbital (EHMO) method. Electronic properties, including total energies, were obtained for various adsorbate-substrate cluster systems in order to explore the qualitative features of this system. The tilting away from the surface normal is due to excessive close-packing of CO molecules along the atomic ridges of the Pt(110) surface. It is found energetically favorable for the tilting to alternate on either side of each ridge in a zig-zag fashion, as indicated by glide-plane symmetry in observed LEED patterns. A polar tilt angle of ~16° is found, in reasonable agreement with experimental values. This yields CO-CO distances which are similar to the smallest values found in organometallic clusters and small compared with values in CO and CO_2 crystals. An azimuthal twist in the direction of the ridges is found to be slightly unfavorable energetically with EHMO; although it is thought to have been observed in some experiments and not in others. The optimal polar tilt angle slightly changes with the size of the metal cluster. To obtain a tilted equilibrium direction one needs at least three CO molecules on neighboring Pt atoms, and 6 Pt atoms in two layers (directly beneath each other).

1. Introduction

The structural orientations of molecules chemisorbed on metal surfaces are expected to be closely related to reactivity. The properties of carbon monoxide on various Pt surfaces have been extensively studied with a variety of experimental [1-16] and theoretical [17-22] methods. There is an increasing number of experimental papers on orientation, and particularly on tilting, of CO chemisorbed on surfaces of platinum and other transition metals [2-4,14-16,23-34]. However, the general picture regarding why, when and how CO tilts is not clear at this moment. The simplest situation arises with fcc(110) substrates, where CO apparently adsorbs on the atomic ridges separated by troughs.

After CO adsorption, the fcc(110) substrates which have been investigated experimentally are believed to be non-reconstructed, i.e. they retain a structure close to the ideal bulk-like termination. On the basis of angle-resolved ultraviolet photoemission spectra (ARUPS), King and coworkers [2] concluded that in the Pt(110)-(2x1)-2CO structure the CO molecular axis is tilted 26±2° away from the surface normal; it would have an azimuth between the directions [$\bar{1}$12] and [$\bar{3}$34] (or other symmetry-equivalent directions), see Fig. 1. The (2x1) LEED pattern exhibits systematic spot extinctions that are explained by glide plane symmetry, the glide planes being parallel to the atomic ridges ([$\bar{1}$10] directions in Fig. 1). This requires CO molecules to alternately tilt to one and then the other side of an atomic ridge, in a zig-zag fashion, as shown in Fig. 1. If the molecules tilt in the [001] direction, a symmetry plane is maintained, leading to a p2mg structural symmetry. But

if the tilt occurs in another direction, only the glide plane is retained, yielding a plgl structural symmetry. The tilting is due to excessively close packing when CO molecules are adsorbed at neighboring sites along the atomic ridges. The close packing is relieved by alternating opposite tilts. The angle of tilt is therefore a sensitive measure of the CO-CO interactions. On Pt(110) the CO molecules are believed to be bonded to single Pt atoms of the ridges ("top-site" bonding) [22].

In more recent ARUPS studies, Rieger et al. [4] have found that on Pt(110) the CO molecules are tilted at about 20° off normal in the [001] directions of Pt(110), i.e. perpendicularly to the atomic ridges; this yields a p2mg symmetry equally compatible with observed LEED patterns. For CO on Ni(110), Lee and coworkers [23] found evidence for a coverage-dependent reversible tilting of the Ni-CO bond axis from normal to off-normal above a critical coverage of θ=0.66 CO/Ni monolayers; they used metastable quenching spectroscopy, thermal desorption spectroscopy and electron stimulated desorption ion angular distributions (ESDIAD). Riedl and Menzel [25] have observed with ESDIAD on the same system a CO tilting of about 17° (on top sites) and 19° (on bridge sites) with respect to the surface normal, strictly in the [001] azimuth, in excellent agreement with a very recent analysis of ARUPS data [28]. Other recent ESD experiments revealed a tilting angle of 18° for this phase [30]. This has been confirmed by Yates et al. [31] by ESDIAD. They have in particular found that at CO coverages below θ~0.75 CO/Ni a normal orientation of the CO bond exists and above this coverage CO molecules begin to be tilted ~19° away from the normal in the [001] direction.

No systematic theoretical work has been performed to date on this topic. We have set out to explore -by means of quantum chemical calculations- the conditions under which CO molecules tilt on fcc(110) surfaces. This system, CO/fcc(110), provides a very sensitive measure of CO-CO interactions in a close-packed configuration. It is characterized by repulsive CO-CO interactions, counterbalanced by restoring forces that tend to keep the CO molecules oriented perpendicularly to the surface.

2. Theoretical method, parameters and models

The QCPE version [35] of the EHMO method [35-38] has been used with slightly modified [39] parameters of Hoffmann [40,41] for Pt. For C and O the original parametrization of ICON8 [35] was retained. The simplest version of the EHMO method, as used here, employs charge-independent atomic ionization potentials, and so the net charge build-up on atoms is overestimated. However, the molecular orbitals and energies are of established usefulness. It is therefore expected that minor changes in atomic valence state ionization energies will not affect [42] the qualitative trends observed in our calculations for CO molecules on Pt(110) surfaces.

The bulk cubic Pt lattice parameter of 3.9239 Å (nearest-neighbor distance of 2.7746 Å) has been used [43] in all the calculations. Top-site positions have been assumed for the CO molecules, preferentially chemisorbed with a constant Pt-C bond length of 1.98 Å from the surface (carbon end down), with a frozen C-O distance of 1.15 Å; this choice is based on a structure determination by LEED of CO on

Pt(111) [34]. We found that the overall picture of the energetics of the CO chemisorption on the Pt(110) surface does not change appreciably with minor changes in the bond distances of Pt-C and C-O [44-47]. By repeating the calculations of the 8Pt + 3CO system, the 8Ni + 3CO system has also been studied with EHMO parameters for Ni [40,41], a lattice parameter of 3.5238 Å (nearest-neighbor distance of 2.4917 Å) [43] and r(Ni-C)= 1.75 Å and r(C-O)= 1.15 Å, appropriate for bridge sites.

A characteristic feature of a clean unreconstructed fcc(110) surface is its ridge-and-trough structure. Each ridge atom is bonded to two other ridge atoms in the topmost layer, to four trough atoms in the second metal layer and to one deeper atom in the third layer, totalling seven nearest neighbors. We have employed a 3-layer thick cluster consisting of 28 Pt atoms (see Fig. 2a) as a starting structure for most of our calculations. This cluster was represented by a top layer of 10 Pt atoms, a second layer of 12 Pt atoms and a third layer of 6 Pt atoms situated beneath the two off-center rows of the first layer Pt atoms (denoted by dashed circles in Figure 2a). The top-layer Pt atoms marked with a star in Fig. 2a are also those to which CO molecules are adsorbed. Starting from this structure we have gradually omitted parts of the 28-atom cluster to investigate which structural elements are most responsible for the results corresponding to the extended surface. Therefore, clusters consisting of 22, 20, 16, 12, 8, 6 and 3 Pt atoms with CO molecules, respectively, have also been studied (Table I, Structures 1-11), among others. In addition to the above structures we have also studied a different 28-atom Pt-cluster, employing 5 CO

molecules on a single center row of Pt atoms (Fig. 2b and Table I, Structures 12, 13): this provided a further check on the suitability of the cluster size. In all cases the top-layer metal atoms coincided with the xy-plane and the bond axes of Pt-C and C-O were always kept collinear, i.e. the Pt-C-O bond angle was kept at 180°.

As a start, the changes in the sums of one-electron energies have been calculated while gradually tilting all the CO molecules by the same polar angle at zero azimuth, i.e. while tilting toward the [001] direction. Two cases were distinguished: in the first case all the CO's are tilted in the +x direction and in the second case the tilts alternate in the +x and -x directions to yield a zig-zag (staggered) pattern. After finding an energy minimum at a certain polar angle, we also varied the azimuthal angle. Again, two cases were distinguished: first, a zig-zag herringbone arrangement was obtained by azimuthal rotations towards the +y direction (as shown in Fig. 1); second, CO pairing was obtained from the zig-zag arrangement by alternating azimuthal rotations towards +y and -y (this will be illustrated in Fig. 7).

3. Results and discussion

We first examine the simpler CO adsorption geometries to obtain a feeling for the forces that affect the orientation of CO molecules on

fcc(110) surfaces. Consider the orientation of a single CO molecule adsorbed on a Pt(110) substrate. According to our calculations, a single CO molecule on an 8Pt cluster (which includes Pt atoms of the third layer but not of the second layer) is essentially indifferent to tilt, see Fig. 3. The total energy changes very little as a function of tilt angle. It turns out that the presence of third-layer atoms is quite important for the CO orientation. This is very clear in Fig. 4, where we omit third-layer atoms (but include second-layer atoms). The clusters in Fig. 4 contain zig-zag chains of CO molecules, which are seen to tilt to at least θ=40-50° in the [001] direction. Thus they will fall over until, beyond 50°, touching of the next Pt ridge starts. Figure 5 further confirms the influence of the third-layer Pt atoms. With parallel chains of CO molecules, the CO axes do not topple over in the presence of third-layer Pt atoms. In fact, with the simultaneous presence of both third-and second-layer Pt atoms, the molecules strongly prefer an upright orientation.

Summarizing so far, a cluster containing Pt atoms down to the third layer is necessary to provide a strong restoring force against CO tilting from the upright orientation. The various calculations show in addition that the lateral extent (parallel to the surface) of the cluster is otherwise relatively unimportant in this respect.

With the upright CO orientation and close packing along the ridges, there is considerable strain. The repulsive close-range forces between neighboring CO's can be relieved by the zig-zag staggering arrangement. Therefore, an energy minimum can be produced at a non-zero tilt angle where these repulsive forces balance the restoring forces. This is clearly apparent in Fig. 5. Figure 6 shows that the existence of the non-zero tilt and the value of the tilt angle are not much affected by the size of the metal cluster. For the largest Pt(110) clusters (Table I, Structures 1 and 12) the energy minimum can be located at 15-16° (see Fig. 5). This is somewhat smaller than the experimental values of ~20° [4] to ~26° [2]. Smaller clusters favor slightly reduced tilt angles, down to about 12°, see Fig. 6, while longer chains of CO molecules yield slightly increased tilt angles, near 17-18°, see Fig. 5. The latter effect is likely due to the larger numbers of CO-CO interactions per CO molecule, giving on the average more repulsion for the same amount of restoring force per molecule.

Near the optimum angle found above for the tilt in the [001] azimuth, ϕ=0°, the azimuth itself was varied next. No further energy lowering was found with non-zero azimuths. Examples of azimuthal dependence are shown in Fig. 7. This theoretical result supports the experimentally based conclusions of Rieger et al. [4] that on Pt(110) the CO molecules are tilted in the [001] direction of Pt(110), and not in a direction

between [$\bar{1}$12] and [$\bar{3}$34] as has been concluded by Hofmann et al. [2]. Our calculations on the 8Ni + 3CO system also show the same picture. However, the energy vs. tilt curve (Fig. 6) has a less steep descent in its initial part (at ~5°) and the minimum position is situated at a somewhat larger tilt angle (~18°) than in the comparable 8Pt + 3CO system (~13°). The experimental tilt angles are ~17° and ~19° for top and bridge sites, respectively [25]. Again we find no azimuthal rotation, in agreement with experiment [25]. For smaller clusters the location of the energy minimum seems to be associated with smaller angles. In the case of the 28Pt + 6CO system the energy difference between the energy minimum (CO's tilted by ~15°) and the non-tilted position is ~0.1 eV = 2.3 kcal/mol.

The diagrams displayed in Fig. 8 and 9 show the energy level correlations between the orbitals of a single Pt atom and one CO molecule, and the groups of levels belonging to the Pt cluster, as well as the separated group of three CO molecules at the same polar angles. From the molecular orbitals some obvious considerations concerning the probable connections between the tilting and the change in the electronic structure of CO molecules on Pt(110) surfaces can be made. The mixing of Pt and CO orbitals results in a rise of the Fermi level; however, the HOMO remains practically unchanged during tilting except at the largest angles when it moves upward. The position of the LUMO is nearly the same

for all angles. On tilting, gradual contractions appear in the energy bands related to the 3σ, 4σ and 1π orbitals of the separate CO cluster, leading in some cases to nearly degenerate levels. Comparing the diagrams in Figs. 8 and 9 for the 6Pt + 3CO and the separate 3CO systems, it can readily be seen that the most distinct change occurs in the location of the 4σ bands. There is a stabilization (lowering of the energy) of the 4σ levels in the 6Pt + 3CO system by ~0.4eV = 9 kcal/mole in comparison with the 3CO-cluster at the same polar angle. Besides strong mixing of the 5σ (CO) and 3d(Pt) orbitals, no other effect is apparent.

As one can see from the data in Table II, there are only small differences in the occupations of the 3σ molecular orbital, thus showing that this low-lying orbital is the least affected upon adsorption and tilting. However, appreciable differences occur in the 4σ and 1π and in particular the 5σ MO occupations between free and adsorbed CO molecules and on tilting. Upon adsorption, the overall occupation (added over C and O) of the 3σ MO increases slightly, while that of the 1π MO decreases slightly. By contrast, the occupations of the 4σ and 5σ MOs decrease markedly, by some 0.2 to 0.4 electrons, respectively, as if the adsorbed CO molecules were donating electrons from these orbitals relative to the nonadsorbed state. In addition, upon tilting noticeable trends occur in the occupation of the 4σ, 1π and 5σ orbitals: tilting increases the

overall occupations of the antibonding 5σ orbital and decreases those of the 4σ and 1π orbitals.

A comparison of Tables III and IV shows the great similarity in the most important electronic data and trends for the largest and smallest clusters: the 28Pt and 6Pt systems, where an energy minimum at non-zero tilt still exists. (Positive and negative values in bond populations mean attractive and repulsive interactions, respectively.) These results show how much we can reduce the metal-cluster size and still maintain nearly the same results. On tilting there are only small differences in the absolute values of electronic data (Tables III and IV), while the relative changes are quite large in, for instance, the Pt_2 - C_{31} interaction and in the next-neighbor C-C, C-O and O-O interactions which may contribute to the electronic explanation of tilting.

Table V lists electronic data for the 22Pt+6CO system which contains a large Pt cluster comparable in size to that contained in the largest system investigated, omitting the third-layer Pt atoms in the 28Pt+6CO system (cf. structures 1 and 2 in Table I). Comparing the corresponding data in Tables III and V, we can see that there appear marked changes on tilting mainly in the charges of the Pt atoms bearing the CO molecules. There is an opposite trend in the net charge on the Pt atoms in question when going from tilt angle 0° to 30° for these two systems. These

different electronic behaviors may be closely related to the opposite trends of the energy curves (see Figs. 4 and 5).

We may compare the effective CO radius implied by the CO tilt with radii found in other situations. At a 16° tilt in a zig-zag configuration on Pt(110), the distances we find between atoms in neighboring CO molecules are: d_{C-C} = 2.98 Å and d_{O-O} = 3.52 Å (the Pt-Pt distance along the ridge is 2.7746 Å and the Pt-C-O bond angles are still assumed to be 180°). Perhaps the carbon-carbon distance provides the best measure at the effective CO radius in this system: $\frac{1}{2}d_{C-C}$ = 1.49 Å. Note that the tilt angle is a sensitive measure of this radius: increasing the radius by 0.10 Å yields an additional tilt of 7°. A close analogue of this system is provided by CO adsorbed at ¾ monolayer coverage on Rh(111). This unusually high coverage for a surface forces some of the CO molecules into asymmetrical sites, but no tilt was detected by a LEED intensity analysis [33]. In that system, the smallest effective CO radii were found to be ~1.43 Å.

The smallest comparable CO-CO distances that we have found reported for organometallic complexes are as follows. In syn-1,6:8,13-biscarbonyl [14]annulene [48] two CO's are bridge-bonded across a 14-carbon ring with CO axes diverging by 21°: the C-C and O-O distances between the

carbonyls are 2.72 and 3.17 Å, respectively, giving an average of 2.96 Å and a radius of 1.48 Å. In the three molecules $[(CO)_4M\text{-}P(CH_3)_2]_2$, with M = V, Cr and Mn [49], there are pairs of nearly parallel carbonyls linearly bonded to two metal atoms, the metal-metal distances being 2.73, 2.90 and 3.67 Å, respectively: the C-C (O-O) distances in the three molecules are 3.18 (3.40) Å, 3.03 (3.22) Å and 3.54 (3.46) Å, respectively, giving averages of 3.29, 3.12 and 3.50 Å for the center-center separations. The corresponding radii are 1.65, 1.56 and 1.75 Å. Here the CO axes diverge from each other by 11.1°, 9.5° and -4.1°, respectively (the CO axes converge slightly for M = Mn).

Finally, we compare with three-dimensional molecular crystals [50] of CO and CO_2. No plane in these crystals yields a close-packed arrangement of molecules oriented perpendicularly to that plane, so that no direct comparison with our overlayer is possible. In the cubic α-CO crystal, with a CO bond length of 1.06 ± 0.01 Å, any C or O atom has near neighbors in other molecules at distances of 3.46 Å (C-O), 3.57 Å (C-C and O-O) and 3.69 Å (C-O) giving radii of 1.73, 1.78 and 1.85 Å, respectively. In the cubic CO_2 crystal, which has linear OCO molecules and a C-O bond length of about 1.07 Å, one finds interatomic distances between nearby molecules of 3.17 Å (C-O), 3.23 Å (O-O) and 3.98 Å (C-C), giving radii of 1.59, 1.62 and 1.99 Å.

From these various comparisons it appears that CO molecules are usually more tightly packed when held together in overlayers on metal surfaces than in clusters and in three-dimensional CO or CO_2 crystals.

4. Conclusions

Our molecular-orbital study of the adsorption system Pt(110)-(2x1)-2CO, and accessorily of Ni(110)-(2x1)-2CO, has substantially reproduced the CO tilting found experimentally. However, no azimuthal twist away from the [001] direction is found, in agreement with some experiments [4], but in disagreement with others [2], thus supporting the conclusions from the more recent experimental investigations.

In these systems (and very likely also for CO on Pd(110) [51,52]), the third-layer metal atoms located just underneath the top-layer ones are more important in orienting the CO molecules than the second-layer metal atoms. The equilibrium tilting angle is affected by the second-layer metal atoms and the presence of further metal atoms in the first and third layers, as well as by CO molecules on the nearest neighboring sites. The repulsions between the CO molecules on adjacent ridges (i.e. separated by the troughs) has very little effect on tilting and on the tilt angle.

The smallest cluster exhibiting the extended-surface properties is the 6Pt + 3CO system, consisting of one row of 3 Pt atoms in the top layer (bearing the 3CO molecules on 1-fold top sites) and one row of Pt atoms beneath the top layer.

The tilting of CO on 10-valence electron metal (110) faces may partly be due to the particular electronic structure having closed-shell configurations, and the particularity of fcc (110) faces for which rows of surface atoms are quite far from one another.

Despite the qualitative nature of EHMO calculations, we believe that the above-mentioned trends are reliable and can serve as a basis for more refined analyses.

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TABLE I

Substrate - Adsorbate Clusters Studied

No.of Structure	No.of Pt Atoms	No.of CO Molecules	Numberings of Pt Atoms[a,b]			Pt Atoms[a,b] to which CO Molecules are Bonded
			First Layer	Second Layer	Third Layer	
1	28[a]	6	1-10	11-22	23-28	2-4 ; 7-9
2	22[a]	6	1-10	11-22	-	2-4 ; 7-9
3	20[a]	6	1-10	15-18	23-28	2-4 ; 7-9
4	16[a]	6	1-10	-	23-28	2-4 ; 7-9
5	12[a]	3	1-5	15-18	23-25	2-4
6	8[a]	3	1-5	-	23-25	2-4
7	8[a]	2	1-5	-	23-25	2,4
8	8[a]	2	1-5	-	23-25	2,3
9	8[a]	1	1-5	-	23-25	3
10	6[a]	3	2-4	-	23-25	2,4
11	3[a]	3	2-4	-	-	2,4
12	28[b]	5	1-15	16-23	24-28	6-10
13	15[b]	5	1-15	-	-	

[a] cf. Fig. 2a

[b] cf. Fig. 2b

TABLE II

CO molecular orbital occupation[a)] before and after chemisorption in the 6Pt+3CO system (data taken from the reduced charge matrix normalized to two electrons regardless of occupation)

Tilt Angle θ	Species	MO	3σ		4σ		1π		5σ	
		Atom	C	O	C	O	C	O	C	O
0°	free CO		0.464	1.536	1.123	0.877	0.832	3.168	0.996	1.004
	adsd. CO		0.467	1.545	1.110	0.683	0.852	3.118	0.464	1.104
15°	free CO		0.464	1.536	1.122	0.878	0.836	3.164	1.002	0.998
	adsd. CO		0.467	1.544	1.109	0.683	0.856	3.113	0.468	1.105
30°	free CO		0.464	1.536	1.121	0.879	0.838	3.162	1.007	0.993
	adsd. CO		0.467	1.544	1.108	0.682	0.859	3.109	0.473	1.111

a) Values for 1π are doubled (doubly degenerate orbital)

TABLE III

Electronic data[c] for systems 28Pt + 6CO, 6CO and CO, with tilt angle variation ($0=0^{o},15^{o},30^{o}$): Net charge on individual atoms (top box) and bond population (bottom box)

Net Charge

Atoms (numbering[a] as in Fig. 2a)	28Pt-Cluster	28Pt+6CO			6CO			CO Molecule
		0°	15°	30°	0°	15°	30°	
$Pt_2(Pt_4),Pt_3$	-0.04,+0.09	0.58,0.56	0.62,0.53	0.62,0.53	-		-	-
$C_{29}(C_{33}),C_{31}$	-	+0.86	+0.86	+0.85	0.58,0.60	0.57,0.58	0.57,0.57	+0.57
$O_{30}(O_{34}),O_{32}$	-	-0.65	-0.65	-0.65	-0.58,-0.60	-0.57,-0.58	-0.57,-0.57	-0.57

Bond Population

Atom pairs(numbering[a] as in Fig. 2a)	28Pt-Cluster	28Pt+6CO			6CO			CO Molecule
		0	15°	30°	0°	15°	30°	
Pt_1-Pt_2	0.15	0.16	0.16	0.15	-	-	-	-
Pt_2-Pt_{23}	0.13	0.13	0.13	0.13	-	-	-	-
Pt_3-Pt_{24}	0.12	0.13	0.13	0.12	-	-	-	-
$Pt_{23}-Pt_{24}$	0.13	0.14	0.14	0.14	-	-	-	-
Pt_2-C_{29}	-	0.64	0.64	0.64	-	-	-	-
Pt_2-O_{30}	-	-0.03	-0.03	-0.03	-	-	-	-
Pt_2-C_{31}	-	-0.0001	+0.0013	+0.0036	-	-	-	-
Pt_2-O_{32}	-	+0.0003	+0.0003	+0.0002	-	-	-	-
$Pt_{23}-C_{29}$	-	-0.0007	-0.0008	-0.0009	-	-	-	-
$C_{(29)}-O_{(30)}$[b]	-	1.21	1.21	1.21	1.286	1.290	1.293	1.295
$C_{29}-C_{31}$	-	0.0168	0.0107	0.0026	0.0203	0.0126	0.0027	-
$C_{29}-O_{32}$	-	-0.0024	-0.0010	-0.0002	-0.0027	-0.0012	-0.0002	-

[a] Numberings of atoms are in subscript ($C_{29}O_{30}$ is on Pt_2, $C_{31}O_{32}$ on Pt_3, $C_{33}O_{34}$ on Pt_4, $C_{35}O_{36}$ on Pt_7, $C_{37}O_{38}$ on Pt_8, $C_{39}O_{40}$ on Pt_9)

[b] For all the directly bonded C-O molecules the same values apply.

[c] Values are given up to 4 decimals when the percentage in the changes of subsequent values is small.

TABLE IV

Electronic data[a] for systems 6Pt + 3CO, 3CO and CO, with tilt angle variation ($\theta=0^{o},15^{o},30^{o}$): Net charge on individual atoms (top box) and bond population (bottom box)

Net Charge

Atoms (numbering[b] as in Fig. 1a)	6Pt Cluster	6Pt+3CO			3CO			CO Molecule
		0°	15°	30°	0°	15°	30°	
$Pt_2(Pt_4),Pt_3$	+0.02,-0.03	0.12,0.35	0.13,0.36	0.16,0.41	-	-	-	-
$C_{29}(C_{33}),C_{31}$	-	+0.88	+0.88	+0.87	0.58,0.60	0.57,0.58	0.57,0.57	+0.57
$O_{30}(O_{34}),O_{32}$	-	-0.65	-0.65	-0.64	-0.58,-0.60	-0.57,-0.58	-0.57,-0.57	-0.57

Bond Population

Atom pairs (numbering[b] as in Fig. 1a)	6Pt Cluster	6Pt+3CO			3CO			CO Molecule
		0°	15°	30°	0°	15°	30°	
Pt_1-Pt_2	0.20	0.19	0.19	0.19	-	-	-	-
Pt_2-Pt_{23}	0.20	0.16	0.16	0.16	-	-	-	-
Pt_3-Pt_{24}	0.26	0.23	0.23	0.22	-	-	-	-
$Pt_{23}-Pt_{24}$	0.20	0.23	0.23	0.23	-	-	-	-
Pt_2-C_{29}	-	0.64	0.64	0.64	-	-	-	-
Pt_2-O_{30}	-	-0.03	-0.03	-0.03	-	-	-	-
Pt_2-C_{31}	-	-0.0006	+0.0008	+0.0034	-	-	-	-
Pt_2-O_{32}	-	+0.0003	+0.0003	+0.0003	-	-	-	-
$Pt_{23}-C_{29}$	-	-0.0006	-0.0007	-0.0006	-	-	-	-
$C_{(29)}-O^{d}_{(30)}$	-	1.22	1.22	1.22	1.286	1.290	1.294	1.295
$C_{29}-C_{31}$	-	0.0154	0.0099	0.0025	0.0203	0.0126	0.0027	-
$C_{29}-O_{32}$	-	-0.0022	-0.0009	-0.0002	-0.0027	-0.0012	-0.0002	-

[a] Values are given up to 4 decimals when the percentage in the changes of subsequent values is small.

[b] Numberings of atoms are in subscript. (See footnote "a" of Table III for CO positions.)

[c] The numberings of 28Pt+6CO are used for the corresponding atoms of the 6Pt+3CO system for easy comparison to data in Table III.

[d] For all the directly bonded C-O molecules the same values apply.

TABLE V

Electronic data[a] for systems 22Pt + 6CO, 6CO and CO, with tilt angle variation ($0=0^{o},15^{o},30^{o}$): Net charge on individual atoms (top box) and bond population (bottom box)

Net Charge

Atoms (numbering[b] as in Fig. 1a)	22Pt Cluster	22Pt+6CO			6CO			CO Molecule
		0°	15°	30°	0°	15°	30°	
$Pt_2(Pt_4),Pt_3$	0.20,0.24	0.63,0.39	0.59,0.49	0.59,0.52	-	-	-	-
$C_{29}(C_{33}),C_{31}$	-	+0.90	+0.90	+0.89	0.58,0.60	0.57,0.58	0.57,0.57	+0.57
$O_{30}(O_{34}),O_{32}$	-	-0.64	-0.64	-0.64	-0.58,-0.60	-0.57,-0.58	-0.57,-0.57	-0.57

Bond Population

Atom pairs (numbering[b] as in Fig. 1a)	22Pt Cluster	22Pt+6CO			6CO			CO Molecule
		0°	15°	30°	0°	15°	30°	
Pt_1-Pt_2	0.15	0.16	0.16	0.17				
Pt_2-Pt_{23}	-	-	-	-	-	-	-	-
Pt_3-Pt_{24}	-	-	-	-	-	-	-	-
$Pt_{23}-Pt_{24}$	-	-	-	-	-	-	-	-
Pt_2-C_{29}	-	0.64	0.64	0.64	-	-	-	-
Pt_2-O_{30}	-	-0.03	-0.03	-0.03	-	-	-	-
Pt_2-C_{31}	-	-0.0005	+0.0015	+0.0022	-	-	-	-
Pt_2-O_{32}	-	-0.0003	-0.0003	-0.0002	-	-	-	-
$Pt_{23}-C_{29}$	-	-	-	-	-	-	-	-
$C_{(29)}-O_{(30)}$[d]	-	1.21	1.21	1.22	1.286	1.290	1.293	1.295
$C_{29}-C_{31}$	-	0.0176	0.0099	0.0024	0.0203	0.0126	0.0027	-
$C_{29}-O_{32}$	-	-0.0025	-0.0011	-0.0002	-0.0027	-0.0012	-0.0002	-

[a] Values are given up to 4 decimals when the percentage in the changes of subsequent values is small.

[b] Numberings of atoms are in subscript. (See footnote "a" of Table III for CO positions.)

[c] The numberings of 28Pt+6CO are used for the corresponding atoms of the 6Pt+3CO system for easy comparison to data in Table III.

[d] For all the directly bonded C-O molecules the same values apply.

Figure Captions

Fig. 1 Geometry for CO on fcc(110), showing angles of tilt θ and azimuth ϕ for CO rotation, and (2x1) unit cell.

Fig. 2 Geometry of (a) cluster 28Pt+6CO, and (b) cluster 28Pt+5CO, in top view. Numbering identifies individual Pt atoms. Stars mark CO adsorption sites (top sites). Dashed circles and numbers correspond to third layer metal atoms.

Fig. 3 Total energy of cluster 8Pt+1CO, as a function of CO tilt θ.

Fig. 4 As Fig. 3 for 3Pt+3CO, 15Pt+5CO and 22Pt+6CO, with zig-zag tilting.

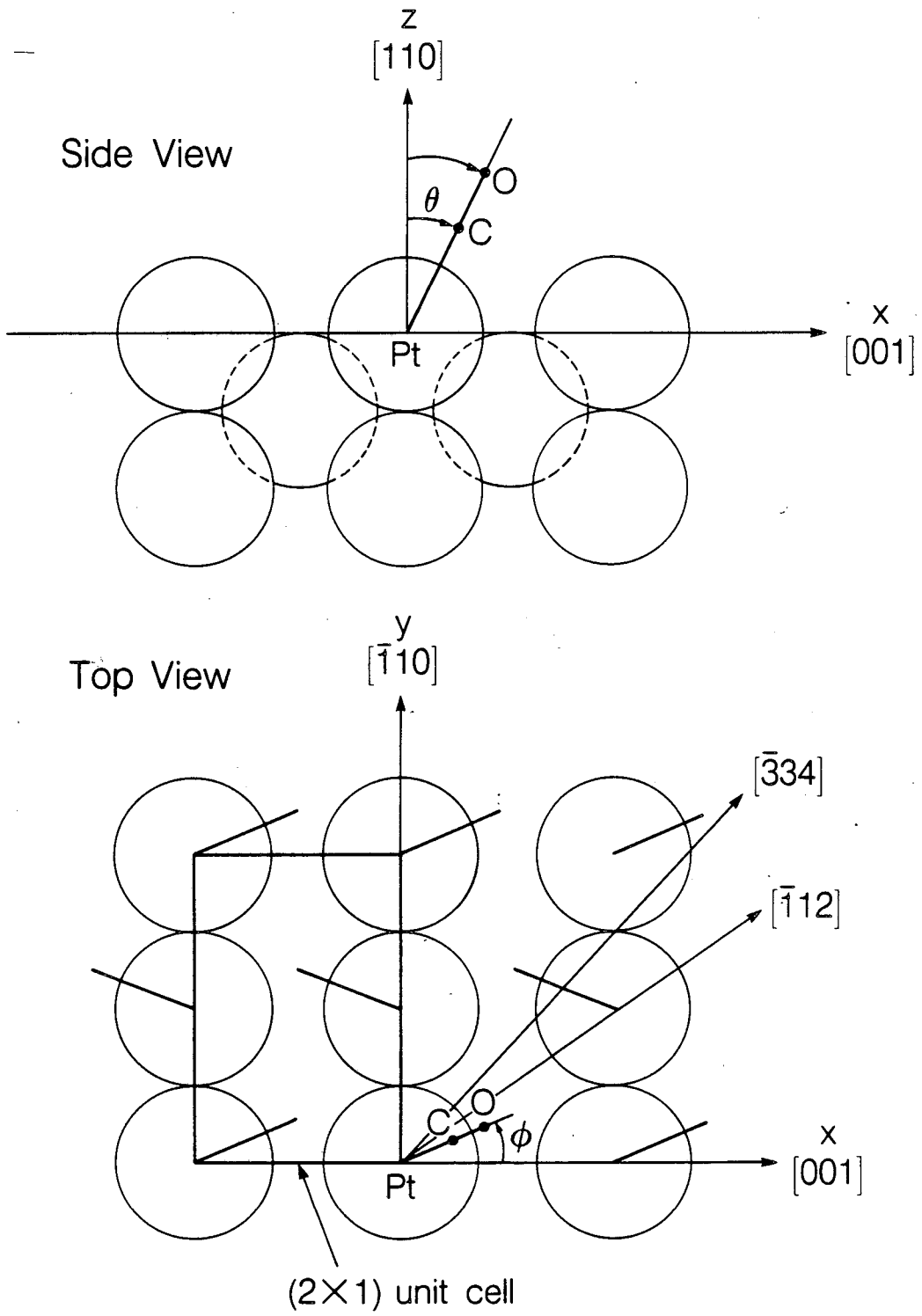
Fig. 5 As Fig. 3 for (a) 28Pt+6CO and (b) 28Pt+5CO, with both parallel tilts, giving a (1x1) unit cell, and zig-zag tilts, giving a (2x1) unit cell.

Fig. 6 As Fig. 3 for 8Ni+3CO, 20Pt+6CO, 16Pt+6CO, 12Pt+3CO, 8Pt+3CO and 6Pt+3CO, with zig-zag tilts in all instances.

Fig. 7 Total energy of cluster 28Pt+5CO as a function of azimuth ϕ, for two different fixed tilt angles (θ=10° and 18.5°) and for two twist arrangements: twists (a) and (b) respect the glide-plane symmetry, while twists (c) and (d) do not.

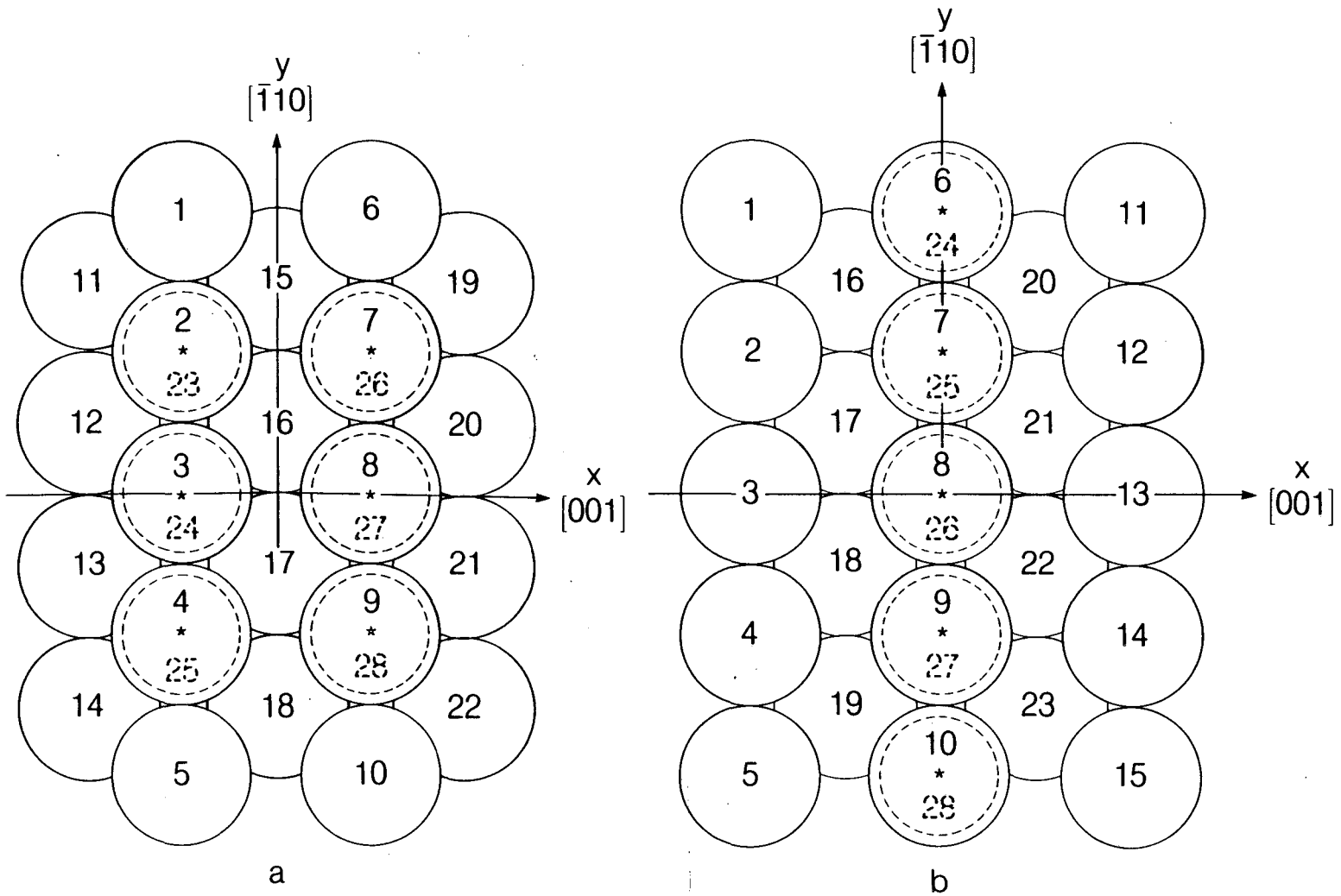
Fig. 8 Electronic structure of cluster 6Pt+3CO, compared to that of its constituents Pt, 6Pt, 3CO and CO. The (zig-zag) tilt angle θ is varied in the full cluster. Cross-hatched bands are filled with electrons up to the HOMO=highest occupied molecular orbital; LUMO=lowest unoccupied molecular orbital.

Fig. 9 Electronic structure of the 3CO cluster of Fig. 9, as a function of (zig-zag) tilt angle θ, compared to that of a single CO molecule.



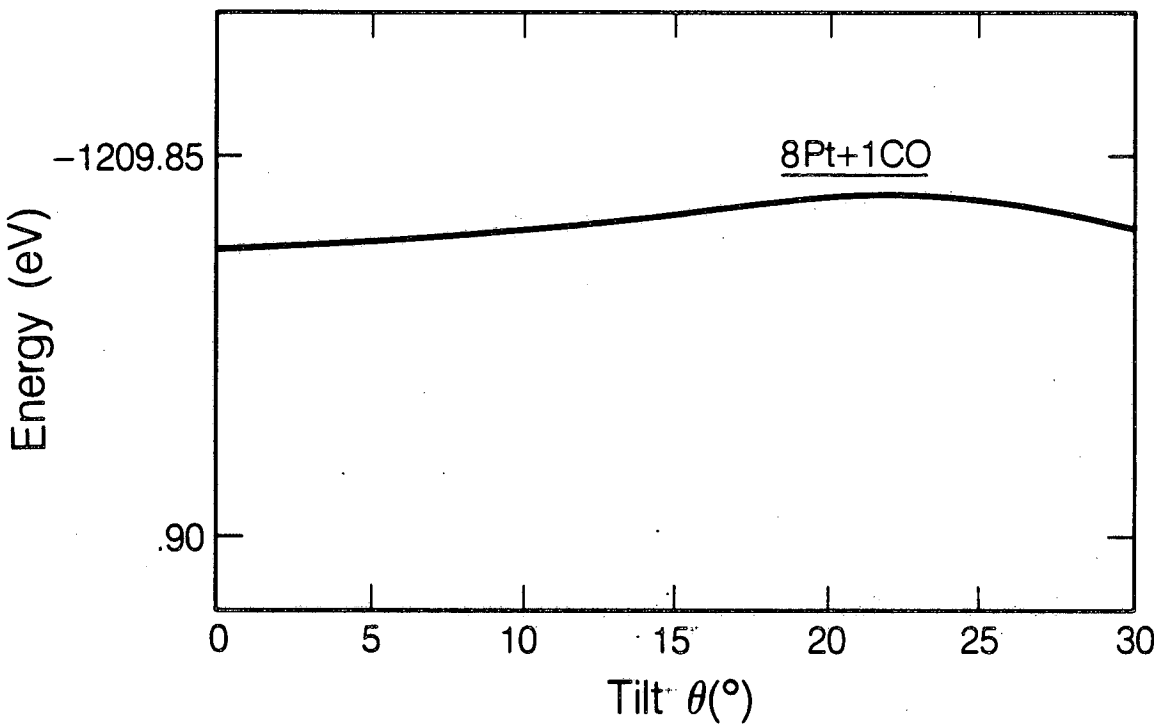
XBL 863-9147

Fig. 1



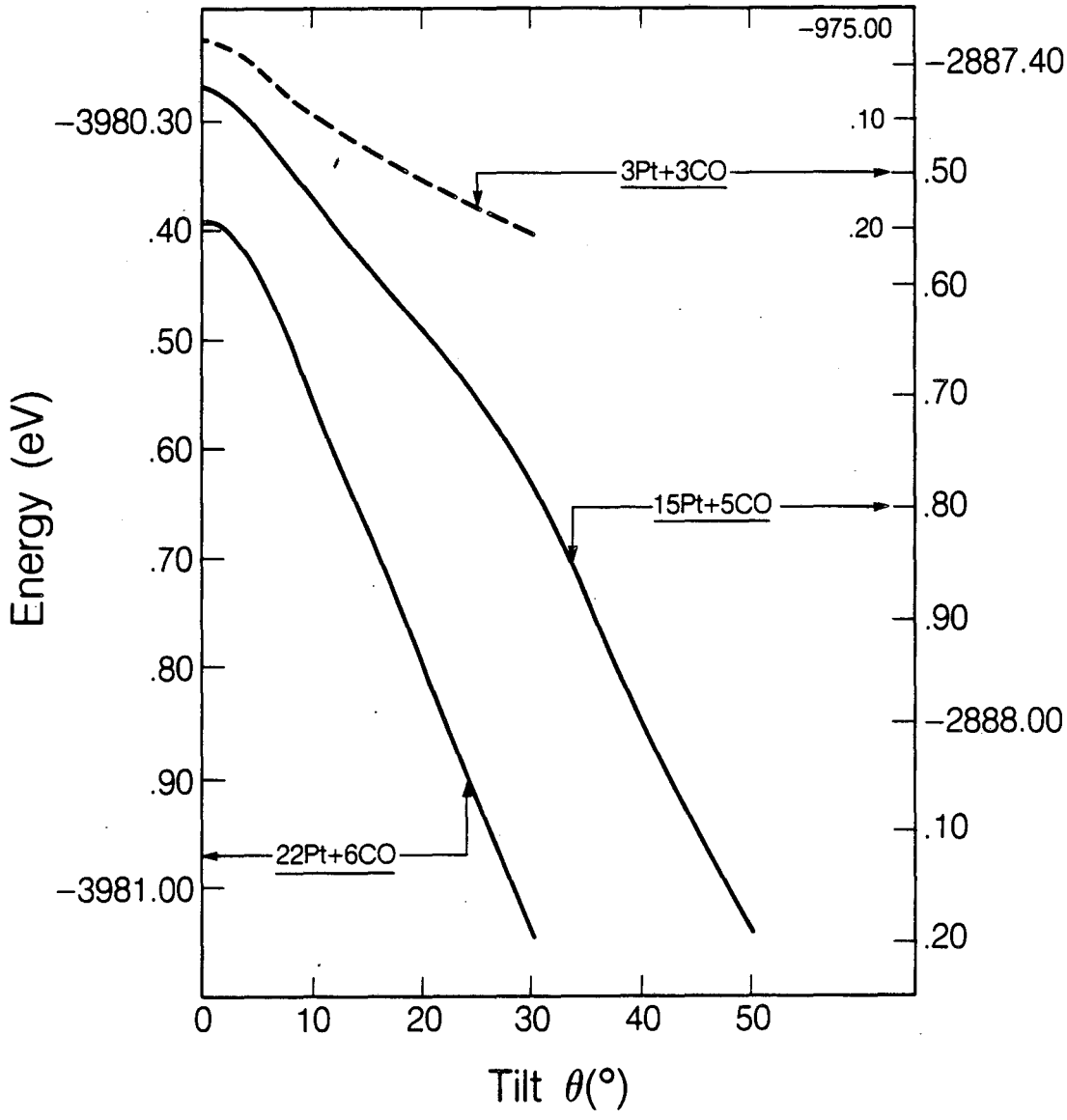
XBL 863-9148

Fig. 2



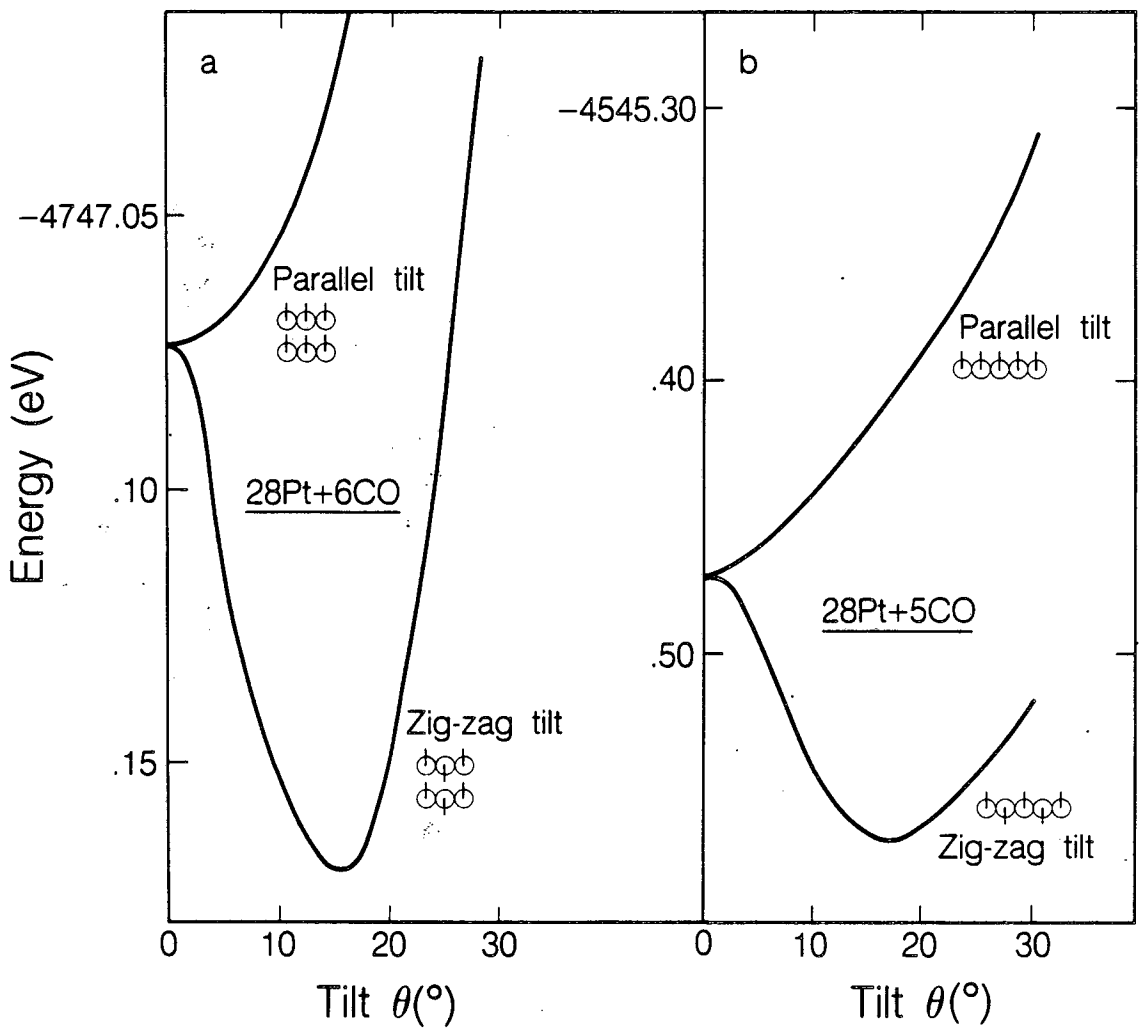
XBL 863-9149

Fig. 3



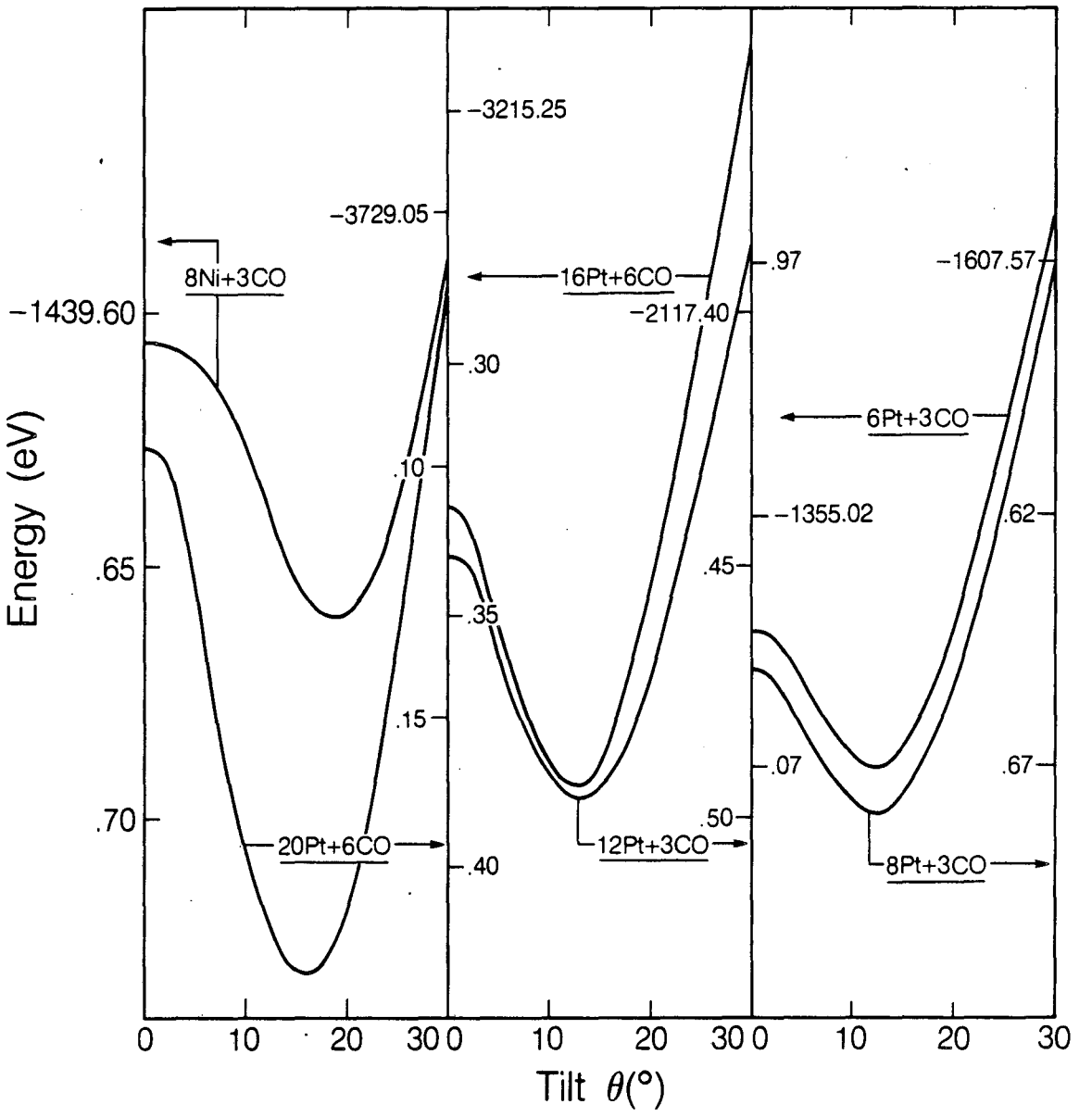
XBL 863-9145

Fig. 4



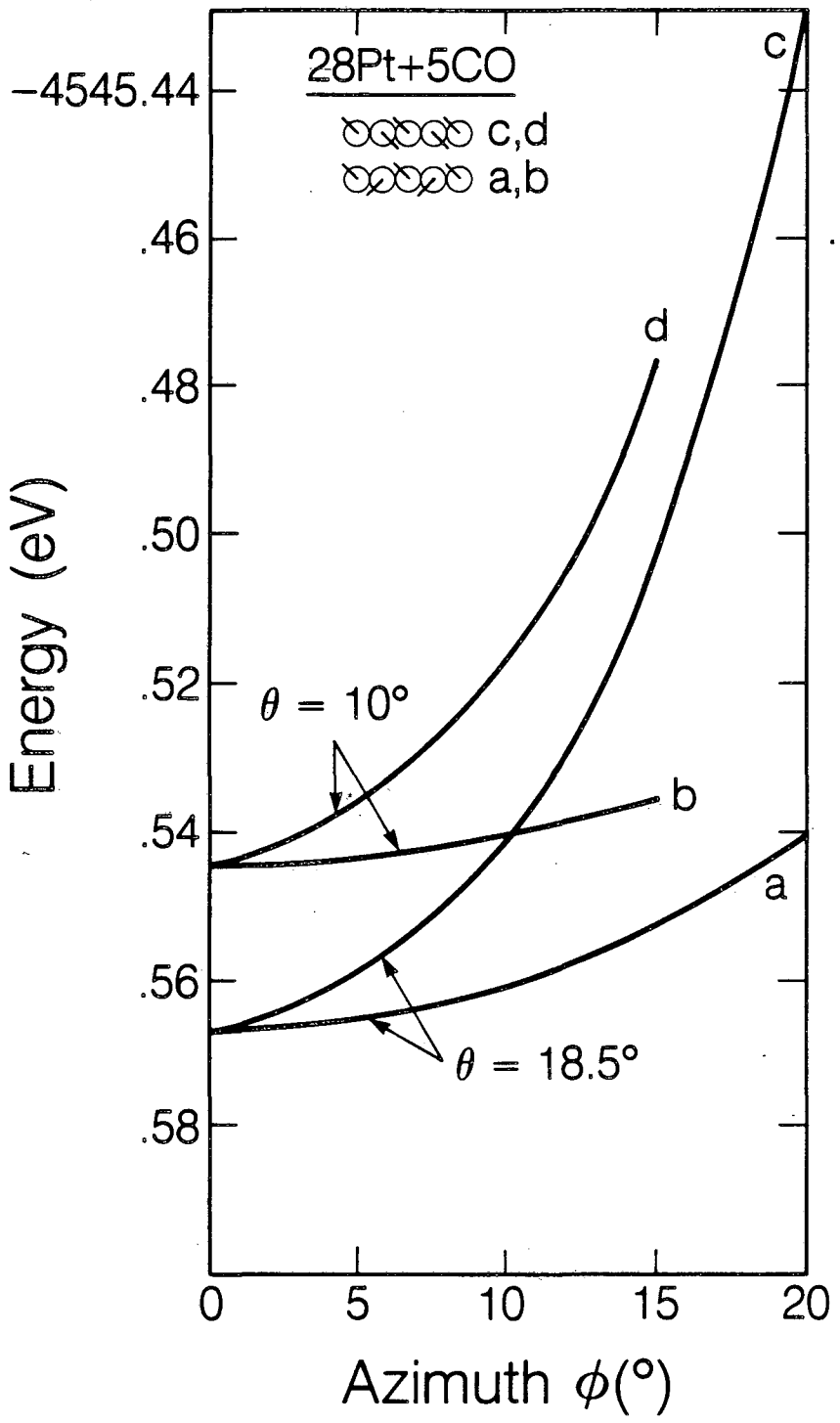
XBL 863-9142

Fig. 5



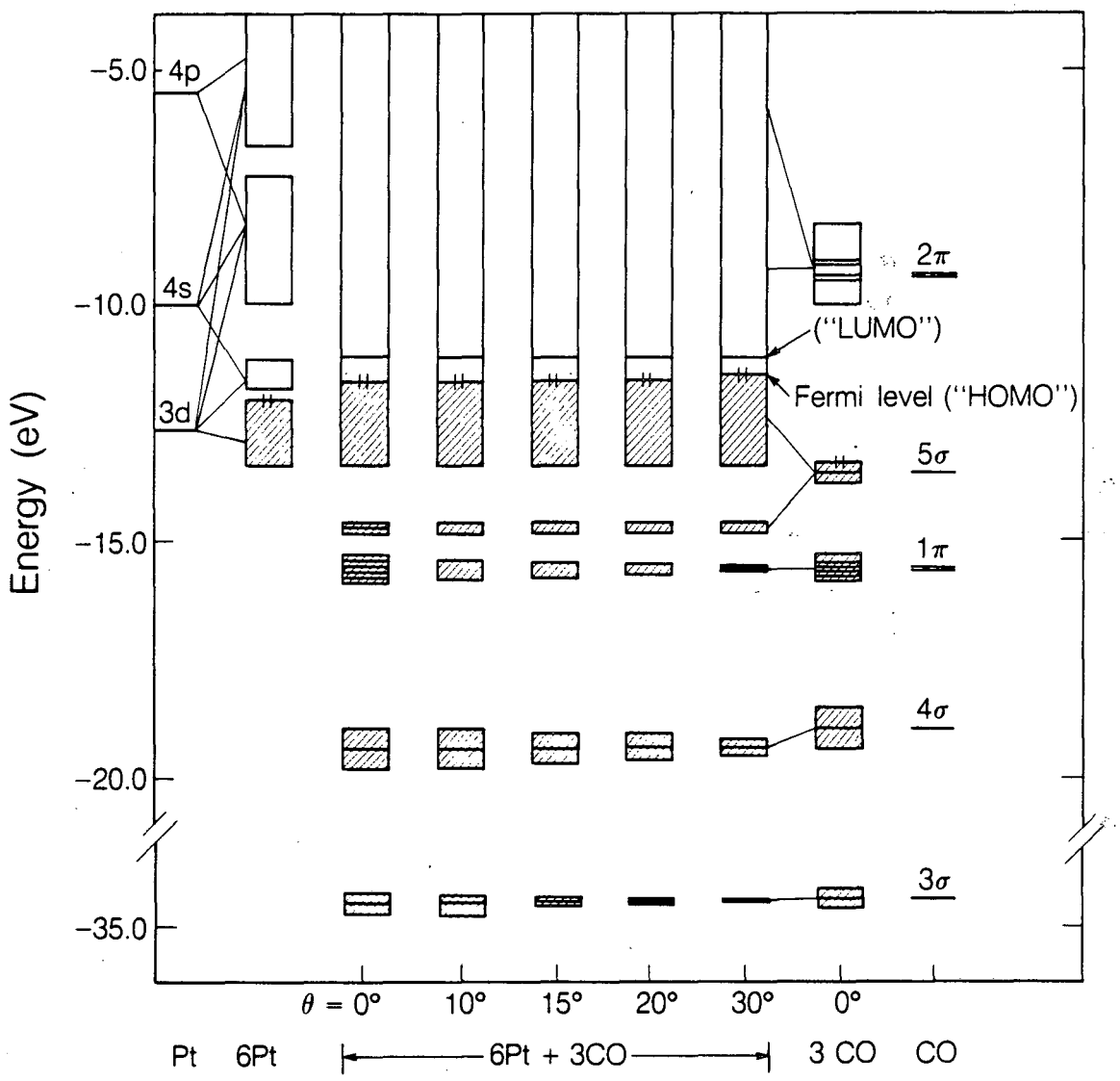
XBL 863-9151

Fig. 6



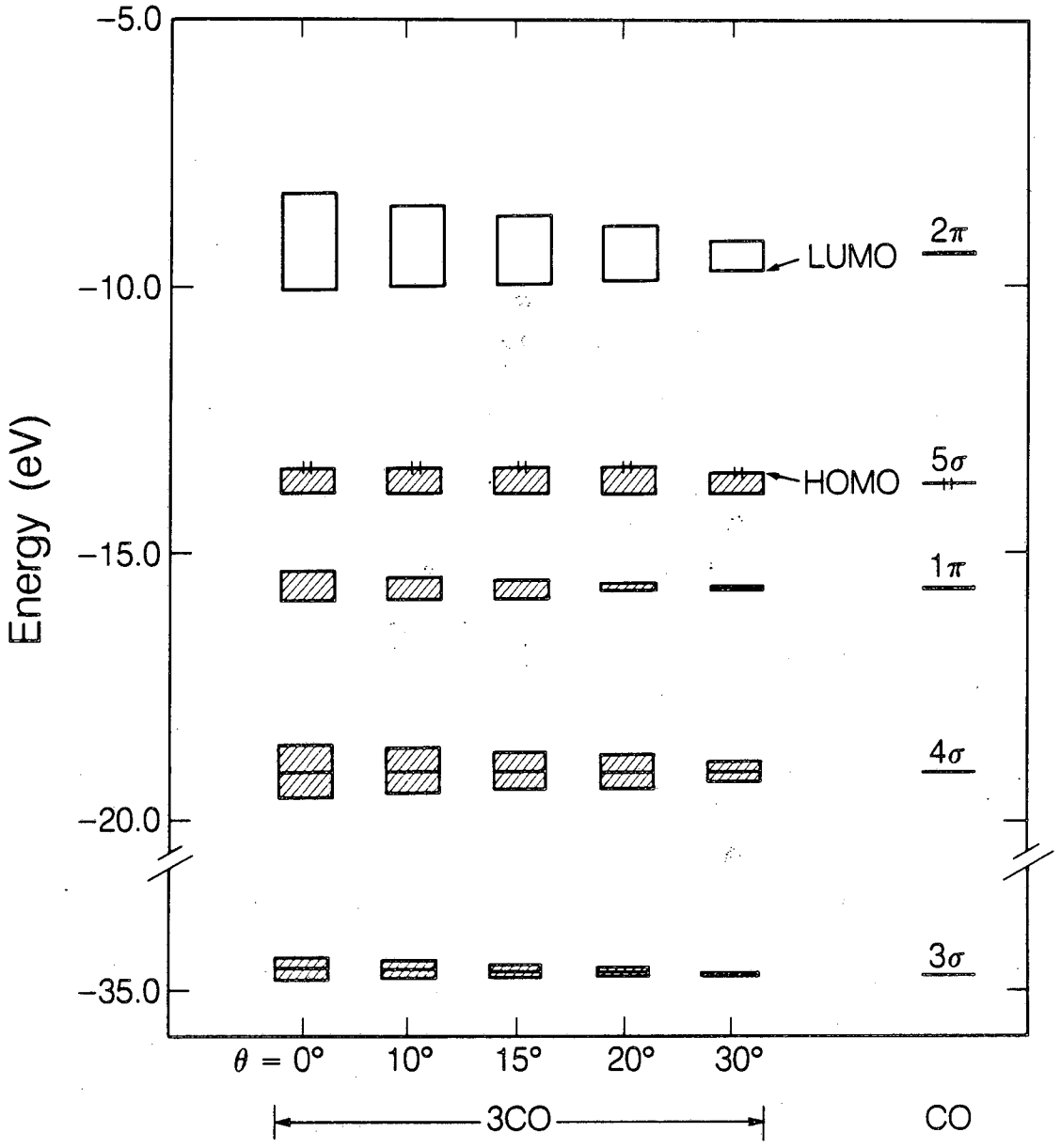
XBL 863-9143

Fig. 7



XBL 863-9146

Fig. 8



XBL 863-9144

Fig. 9

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