be due to the stabilizing effect of the hydrogen-bonding solvent.[22] The effect of solvent and substitution on the energy of this triplet biradical will be addressed in a subsequent paper. The second rate, $\tau = 85 \pm 10$ ns, corresponds to the cleavage of the 1,4-biradical and is in good agreement with the value obtained by Caldwell,[23] 93 ns, using nanosecond absorption spectroscopy. The enthalpy of reaction, $\Delta H_r$, for the photocleavage of valerophenone to acetophenone and propene is given by $\Delta H_r = E_{h\nu} (1 - \phi_1 - \phi_2)$. The experimental enthalpy of reaction, $18 \pm 6$ kcal/mol, approximates the value obtained from thermochemical calculations.[24,25]

## Conclusion

Pulsed time-resolved photoacoustic calorimetry can be used to obtain both kinetic and thermodynamic information. This tech-

nique has been applied to two simple chemical systems: the quenching of the $T_1$ state of benzophenone by DMH and the Norrish type II photocleavage of valerophenone. It remains to be seen what degree of complexity can be handled by this technique in a believable fashion. One of the major strong points of this method is that reactions having intermediates without chromophores can be studied, in terms of both kinetics and energetics. Ultimately, it is only the judicious interpretation of the kinetic and thermodynamic data that will demonstrate the future utility of this technique.

**Registry No.** Benzophenone, 119-61-9; 2,5-dimethylhexa-2,4-diene, 764-13-6; valerophenone, 1009-14-9.

(20) Although the formation of the 1,4-biradical from $T_1$ of valerophenone is actually longer,[18] 8 ns, than indicated, separating the $\tau_1$ into two sequential decays does not change the deconvolution results significantly. In fact, 8 ns is at the limit of the resolution of the transducer.

(21) Using $D(H–CH(OH)(C_6H_5)) = 81.2$ kcal/mol, $D(H–CH(CH_3)_2) = 97.9$ kcal/mol, and $D(H–H) = 104$ kcal/mol,[22] then the energy of the 1,4-biradical can be crudely estimated to be $\sim 75$ kcal/mol.

(22) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

(23) Caldwell, R. A.; Majima, T.; Pac, C. *J. Am. Chem. Soc.* **1982**, *104*, 629.

(24) Using $\Delta H_f^\circ$(acetophenone, l) = $-34.07$ kcal/mol, $\Delta H_f^\circ$(propene, g) = $+4.88$ kcal/mol, and assuming $\Delta H_f^\circ$(valerophenone, l) = $\Delta H_f^\circ$(isobutyl phenyl ketone, l) = $-52.63$ kcal/mol, then $\Delta H_r = 23.4$ kcal/mol.[26]

(25) It is assumed that the enol of acetophenone tautomerizes rapidly under the reaction conditions. The free energy differences between the enol and acetophenone is $\sim 5.5$ kcal/mol at 300 K.[27] The small energy release due to tautomerization would be difficult to detect with the present experimental design.

(26) See: Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970.

(27) Gero, A. *J. Org. Chem.* **1954**, *19*, 1960.

# Factors Determining CO Adsorption Sites on Pd and Pt (100) and (111) Surfaces: Theoretical Study

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**Abstract:** The atom superposition and electron delocalization molecular orbital theory and two-layer thick cluster models are used to predict the binding site preferences and bond lengths of CO on Pd(111) and -(100) and Pt(100) surfaces. Binding at 3-fold sites is predicted to be favored for Pd(111) and at 2-fold sites for Pd(100). These results are supported by the experimental literature. The difference between Pd and Pt vis-à-vis CO adsorption is shown to depend solely on the position of the metal valence bands: the Pd valence band lies about 1 eV higher in energy and the resulting enhancement of surface back-donation to the empty CO $\pi^*$ orbitals favors higher coordination sites than on the Pt surfaces. Metal orbital size and surface atom spacing differences are insufficient to alter the dominance of the band positions on these results. The dependence of CO adsorption on Pd and Pt valence band positions is used as a basis for extrapolating to the effects of electropositive and electronegative coadsorbates and electrochemical charging of CO covered surfaces in electrolytes.

It is well established by a variety of experimental techniques that carbon monoxide binds predominately to 1-fold sites (always standing vertically, carbon end down) on Pt(111)[1] and to 3-fold sites on Pd(111)[2] at low coverage. Further, an analogous tendency exists for the (100) surfaces where 1-fold and 2-fold coordinations are seen on Pt[3] but 2-fold alone is seen on Pd.[2,3d,4] The question

of why these differences exist naturally arises. An argument to explain this which considers the metal atom size was considered but found inadequate.[3c] One suggestive result lies in the work of Garfunkel et al.[1d] showing a shift of CO from 1-fold to 2-fold and possibly 3-fold sites on Pt(111) on increasing the coverage of coadsorbed potassium atoms. Ray and Anderson explained this result by using molecular orbital theory.[5] They predicted the shift of CO to higher coordinate sites to take place as a result of the destabilization (shifting up in energy) of the Pt valance band due to charge transfer from the coadsorbed potassium. This shift of the metal valence band closer in energy to the empty CO $\pi^*$ orbital energy levels leads to increased $\pi^*$ orbital mixing with and stabilization of Pt d band orbitals and decreased donation stabilization from the CO 5 $\sigma$ orbital which lies beneath the Pt valence band. As Ray and Anderson show, strong $\pi^*$ mixing favors high coordinate sites and strong 5 $\sigma$ mixing favors the 1-fold site on Pt(111), which explains the shift to high coordinate sites when CO and K are coadsorbed. The 4d ionization potential of the Pd atom is about 1 eV less than the 5d ionization potential of the

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(4) (a) R. L. Park and H. H. Madden, *Surf. Sci.*, **11**, 158 (1968). (b) H. Conrad, G. Ertl, J. Koch, and E. E. Latta, *Surf. Sci.*, **43**, 462 (1974). (c) R. J. Behm, K. Christmann, G. Ertl, M. A. Van Hove, P. A. Thiel, and W. H. Weinberg, *Surf. Sci.*, **88**, L59 (1979). (d) A. Ortega, F. M. Hoffmann, and A. M. Bradshaw, *Surf. Sci.*, **119**, 79 (1982). (e) A. Brown and J. C. Vickerman, Surf. Sci. *151*, 319 (1985).

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**Table I.** Atomic Parameters Used in the Calculations: Principal Quantum Numbers, $n$, Ionization Potentials, IP (eV), Orbital Exponents, $\zeta$ (au), and Respective Linear Coefficients, $C$, for Double-$\zeta$ d Orbitals[a]

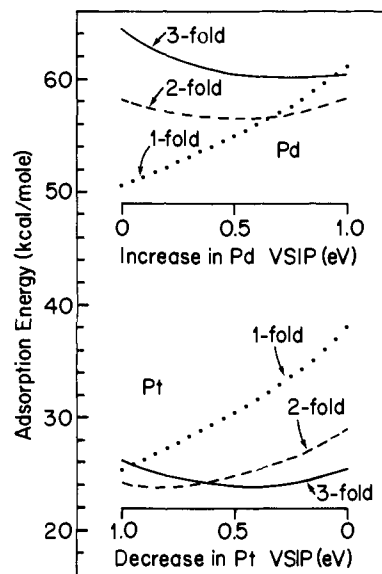| | s | | | p | | | d | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| atom | $n$ | IP | $\zeta$ | $n$ | IP | $\zeta$ | $n$ | IP | $\zeta_1$ | $C_1$ | $\zeta_2$ | $C_2$ |
| C | 2 | 18.5 | 1.658 | 2 | 9.76 | 1.618 | | | | | | |
| O | 2 | 26.98 | 2.146 | 2 | 12.12 | 2.127 | | | | | | |
| Pd | 5 | 9.25 | 2.19 | 5 | 5.84 | 1.89 | 4 | 10.06 | 5.983 | 0.5444 | 2.313 | 0.6591 |
| Pt | 6 | 10.5 | 2.55 | 6 | 6.46 | 2.25 | 5 | 11.1 | 6.013 | 0.6567 | 2.390 | 0.5715 |

[a] For sources see ref 5 and references therein.
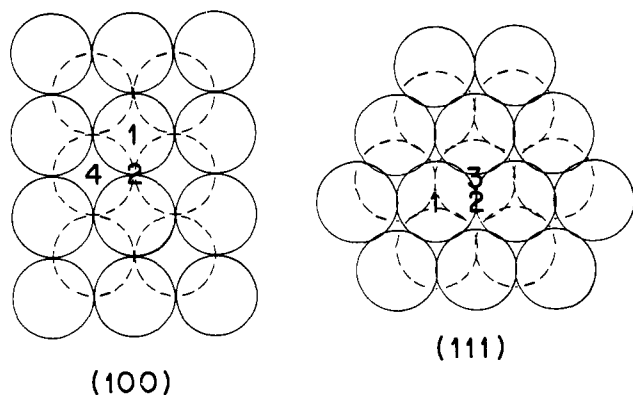


**Figure 1.** 18-atom cluster models of (100) Pd and Pt and 19-atom model of the Pd(111) surface. Clusters are bulk superimposable with Pd–Pd and Pt–Pt nearest neighbor distances of 2.74 and 2.77 Å, respectively. 14 unpaired electrons are assigned to the 18-atom clusters and 16 are assigned to the 19-atom cluster.

Pt atom, meaning the Pd 4d band is about 1 eV closer to the $\pi^*$ levels of CO than the Pt 5d band. Interestingly, in the Ray–Anderson study a $\sim$1 eV shift up to the Pt valence band was what caused CO to shift to the 3-fold site. With this background, the purpose of the present theoretical study is to calculate the binding sites of CO on the Pd(111) and Pd(100) surfaces and their dependence on the Pd valence band position. In addition, the binding of CO to Pt(100) is similarly investigated.

The same atom superposition and electron delocalization molecular orbital (ASED–MO) method used by Ray and Anderson in their study of CO on Pt(111) is used here. Atomic parameters are given in Table I. A discussion of the ASED–MO method is given in ref 5. The cluster models used are shown in Figure 1.

## CO Adsorption Sites on the Pd(111) Surface

The 3-fold site is predicted to be favored, as shown in Figure 2, followed by the 2-fold and then the 1-fold site. As expected from ultraviolet photoelectron spectroscopic (UPS) studies, the energy level structures are similar for the three sites (Figure 3) though stronger CO $\pi^*$ mixing with the filled Pd valence band orbitals is evident for the 3-fold site. However, as the Pd valence band is shifted down by increasing the s, p, and d atom valence state ionization potentials (VSIP) in 0.5-eV steps, the binding to the 1-fold site becomes favored when the shift is $\sim$1 eV (Figure 2). This shift places the Pd band on top of the Pt band, as shown in Figure 4. For comparison, the data from ref 6 are replotted in Figure 2, showing the preference for the 1-fold site on Pt(111) and the shift to the 3-fold site when the Pt VSIP are decreased 1 eV so that the Pt band overlaps the unshifted Pd band. Additional calculations for Pd were performed with the smaller 4d exponent decreased by 0.2 au, which results in C 2p–Pd 4d overlap integrals over a 1–3 Å range in internuclear distances being nearly identical with the C 2p–Pt 5d overlap integrals over this range. The qualitative results for CO on Pd(111) are the same, as shown in Table II. Therefore it is concluded that *the different CO binding site preferences on Pd(111) and Pt(111) are a result of*

(6) (a) H. Conrad, G. Ertl, and J. Kuppers, *Faraday Discuss. Chem. Soc.*, **58**, 116 (1974). (b) D. R. Lloyd, C. M. Quinn, and N. V. Richardson, *Solid State Commun.*, **20**, 409 (1976).



**Figure 2.** CO binding energies calculated as functions of VSIP for the (111) surfaces of Pd and Pt. Pt results are taken from ref 5 and are for a 10-atom cluster.
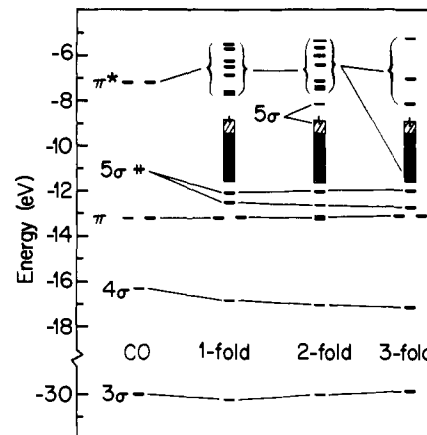


**Figure 3.** Energy levels for CO on Pd(111) with $\Delta$VISP = 0. Shaded Pd s–d band regions represent doubly occupied orbitals and cross-hatched regions singly occupied orbitals. Levels identified with CO have 0.1 or more electronic charge (Mulliken definition) on CO.
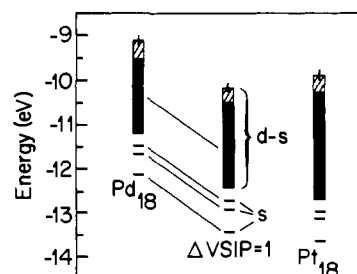


**Figure 4.** Pd band compared to Pd band with $\Delta$VSIP = 1 and Pt band with $\Delta$VSIP = 0.

**Table II.** Calculated CO Binding Energies, BE (eV), C Atom Heights above the Surface Plane, $h$ (Å), CO Internuclear Distances, $R$ (Å), and CO Charge, $q$, from a Mulliken Partitioning for Various Pd VSIP Shifts and Various Surface Sites, and Overlaps in Mulliken Definition (BE in Parentheses for Smaller Pd 4d Exponent Decreased by 0.200 au)

| CO on Pd(111), Pd(100), or Pt(100) | 1-fold | 2-fold | high coordinate |
|---|---|---|---|
| Pd(111) | | | |
| ΔVSIP of 0 | | | |
| BE | 2.19 (2.35) | 2.52 (2.59) | 2.79 (2.94) |
| $h$ | 1.88 | 1.45 | 1.31 |
| C–Pd overlap | 0.84 | 1.11 | 1.33 |
| $R$ | 1.18 | 1.23 | 1.27 |
| C–O overlap | 1.41 | 1.20 | 1.07 |
| $q$ | 0.07 | −0.46 | −0.75 |
| ΔVSIP of +1 | | | |
| BE | 2.65 (2.60) | 2.53 (2.28) | 2.62 (2.33) |
| $h$ | 1.92 | 1.52 | 1.39 |
| C–Pd overlap | 0.78 | 0.92 | 1.06 |
| R | 1.16 | 1.18 | 1.19 |
| C–O overlap | 1.50 | 1.41 | 1.36 |
| $q$ | 0.42 | 0.21 | 0.09 |
| Pd(100) | | | |
| ΔVSIP of 0 | | | |
| BE | 2.20 (2.43) | 2.60 (2.88) | 2.45 (2.35) |
| $h$ | 1.88 | 1.45 | 1.00 |
| C–Pd overlap | 0.83 | 1.11 | 1.26 |
| $R$ | 1.18 | 1.23 | 1.26 |
| C–O overlap | 1.41 | 1.21 | 1.13 |
| $q$ | 0.07 | −0.40 | −0.68 |
| ΔVSIP of +1 | | | |
| BE | 2.70 (2.73) | 2.77 (2.72) | 2.28 (2.91) |
| $h$ | 1.91 | 1.51 | 1.11 |
| C–Pd overlap | 0.78 | 0.94 | 1.00 |
| $R$ | 1.16 | 1.18 | 1.19 |
| C–O overlap | 1.50 | 1.41 | 1.37 |
| $q$ | 0.42 | 0.23 | 0.10 |
| Pt(100) | | | |
| ΔVSIP of 0 | | | |
| BE | 2.02 | 2.05 | 1.50 |
| $h$ | 2.03 | 1.64 | 1.25 |
| C–Pt overlap | 0.71 | 0.88 | 0.94 |
| $R$ | 1.16 | 1.18 | 1.19 |
| C–O overlap | 1.50 | 1.40 | 1.36 |
| $q$ | 0.44 | 0.27 | 0.10 |

*the different metal valence band positions.*

## CO Adsorption Sites on the Pt(100) and Pd(100) Surfaces

As shown in Table II the 1-fold and 2-fold sites are equally favored for CO adsorption on Pt(100), in agreement with experimental studies.[1a,3d]

The 2-fold site for CO on Pd(100) is clearly predicted to be favored, in agreement with experiment, as shown in Figure 5. The energy level structure is very similar to that for CO on the Pd(111) surface (Figure 3) except there is some $\pi^*$ mixing in the filled metal band for the 2-fold site and considerable mixing for the 4-fold site. When the Pd VSIP are increased 1 eV, so that the Pd band overlaps the Pt band, the 1-fold site is becoming competitive with the 2-fold site. As for the (111) surfaces, it may be concluded that *the band position determines the stable binding sites for CO on the (100) surfaces of Pd and Pt.*

## Other Properties

Our calculations successfully produce the trends in binding energies, though they overestimate them as a whole. Initial binding of CO to Pt(111) is estimated experimentally to be about 33 kcal/mol[7] and about 34 kcal/mol on Pd(111) and 36.5 kcal/mol on Pd(100).[4b] Trends in CO charges (Table II) are also correct in that the work function decreases for CO on Pt(111)[7,8] and increases for CO on the Pd(111) and Pd(100) surfaces.[4b] It may be seen that with a Pt VSIP increase of 1 eV, CO charges on various surface sites are very close to the Pt surface values, again
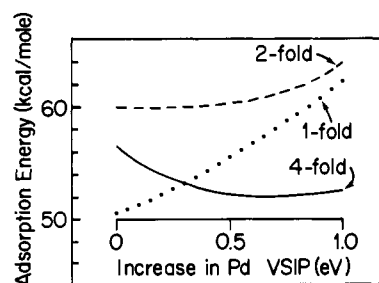
(7) G. Ertl, M. Neumann, and K. M. Streit, *Surf. Sci.*, **64**, 393 (1977).
(8) K. Horn and J. Pritchard, *J. Phys.* **38**, C4-164 (1977).



**Figure 5.** CO binding energies calculated as functions of VSIP for the Pd(100) surface.

indicating the dependence of $5\sigma$ donation to the surface and surface back-donation to $\pi^*$ orbitals on the metal band position. It is furthermore evident that in higher coordinate sites further charge is transformed to the CO $\pi^*$ orbitals, resulting in greater CO bond elongation at these sites. This elongation is greater when the metal band lies higher, also reflecting more back-bonding to the $\pi^*$ orbitals. The C–Pd distance is smaller when the band is higher, showing its dependence on CO p–metal $d\pi$ bonding in the form of $\pi^*$ mixing with surface orbitals. The CO and MC overlap populations given in Table II show the expected variations with CO bond length and height.

The predicted bond lengths in Table II are be accurate within several 0.01 Å. A low energy electron diffraction (LEED) study by Behm et al.[4c] shows that on the (100) surface the Pd–C distance is 1.93 Å (± 0.07) and the CO distance is 1.15 Å (± 0.1). Our respective calculated values of 1.99 and 1.21 Å agree well. A

near-edge X-ray absorption fine-structure study by Stohr et al.[9] of CO adsorbed on Pt(111) which is cathodically charged by coadsorbed sodium yielded a CO bond length of 1.27 ± 0.06 Å with CO adsorbed possibly in the 3-fold site. Anderson and Ray[5] predicted 1.27 Å for this bond when the Pt valence bond is cathodically shifted by 1.5 eV, a shift which clearly favors adsorption on the 3-fold site. As may be seen in Table II, for CO adsorption on the 3-fold site of Pd(111), the CO bond length is also 1.27 Å. Van Hove et al.[10] have found through LEED measurements that when benzene and CO are coadsorbed on Rh(111) both occupy 3-fold sites. The 3-fold site preference in this case is attributed to steric constraints with perhaps some encouragement from the weak donating ability of benzene, which will help favor high-coordinate sites for CO. The Rh 4d ionization potential is the same as Pt 5d, so the bands overlap, and since Rh has only one less electron than Pt, the adsorption bond should be similar. The predicted bond length for CO on the 3-fold site of uncharged Pt(111) is 1.19 Å, and on the 1.0 eV cathodically shifted surface it is 1.25 Å.[5] These values bracket 1.21 Å determined by Van Hove et al. for the Rh(111) surface.[10]

## Conclusions

It is evident from this study that the metal band positions determine the binding sites of CO on (111) and (100) surfaces of Pd and Pt. The higher-lying Pd band allows greater backbonding to CO $\pi^*$ orbitals, which favors adsorption at the high-coordinate 3-fold site on the (111) surface compared to 1-fold bonding to the Pt(111) surface. This also causes the preference for the 2-fold site on Pd(100) while on Pt(100) the 2-fold and 1-fold sites are equally attractive to CO. The new ordering of site preference on the (100) surfaces is a structure effect.

Our calculations also provide predictions of CO bond length and binding site charges when the Pd and Pt surfaces are charged by coadsorbed species or electrochemically. In either case electronic charge is added to or subtracted from the surface metal atoms. The addition of electrons to the surface corresponds to cathodic charging and will shift the band up and decrease the work function. Removal of electrons corresponds to anodic charging and a shift down of the band with increased workfunction. In the electrochemical case only a fraction of the change in applied potential appears as a change in the effective potential between the metal and the adsorbate.[11,12] This fraction is believed to be >0.8. This shift in metal valence ionization potentials on charging an electrode surface has been seen in photoemission into electrolyte studies.[13] Thus the band shift is nearly proportional to changes in applied potential and such shifts are the basis for modeling the effects of changes in applied potential with the ASED–MO theory. In an ab initio approach to this problem electrons could be added to or subtracted from a cluster model or the bulk band, resulting in these band shifts. Thus in an ASED–MO or ab initio study adsorbate bonding will be influenced by the varying electron-donating or -accepting capability of the metal surface due to charging. The electric field does not enter into the hamiltonian for the system but can be derived from the resulting charge density distribution. The electric field has been used in an ad hoc Stark effect formation to estimate variations in adsorbate vibrational frequencies with field,[14] but such an approach does not yield

information about charge transfer to or from the adsorbate, adsorbate polarization, or the potential dependence of adsorbate binding site preferences and vibrational frequencies of the adsorbate against the metal surface. The ASED–MO band-shifting technique gives this information as well as the potential dependence of adsorbate frequencies. From the results of the calculations in this paper, anodic charging, or the adsorption of electronegative atoms such as oxygen or halogens to Pd(111) and Pd(100) surfaces, will tend to favor 1-fold CO bonding and shorter CO bonds, meaning higher CO vibrational frequencies. Cathodic charging, or the adsorption of electropositive atoms such as the alkali metals, will maintain 3-fold site bonding on Pd(111) and may make 4-fold sites competitive with the 2-fold sites on the (100) surface. The past work of Ray and Anderson shows the shift of CO from 1-fold to 3-fold sites and decreasing CO vibrational frequencies on Pt(111) due to negative surface charging by coadsorbed K atoms;[5] they have also shown that anodic charging of a Pt electrode in an aqueous electrolyte (CO displaces weakly held $H_2O$) favors 1-fold bonding and increasing CO vibrational frequencies,[15] in qualitative agreement with experimental work of Russell et al.[16] For the Pt(100) surface it may be deduced from the results of the present paper that cathodic charging will cause the 2-fold site and perhaps, with sufficient charging, the 4-fold site to be favored for CO. Anodic charging may lead to preference for 1-fold coordination. High coordination and cathodic charging will decrease the CO vibrational frequency.

It should be remarked that these trends do not hold up across the transition-metal series. For metals to the left of Pd and Pt the d band occupation decreases. This can allow stable bonding of CO parallel to the surfaces because of the possibility of a net donation bonding from the filled $\pi$ orbitals to the surface valence bands. For Ru(001) the antibonding counterparts to the $\pi$-donation orbitals are half-filled so CO bonds upright on a 1-fold site but with cathodic charging it lies down in a $\mu/\pi$ site, according to a recent ASED–MO study.[17] This is seen according to an experimental high resolution electron energy loss spectroscopy (HREELS) study by Hoffmann and de Paola for clean Ru(001) and the 0.1 monolayer K doped surface.[18] In the case of Cr(110) the antibonding counterparts to the $\pi$-donation bonds are empty, so ASED–MO calculations predict parallel CO bonding.[19] This has been determined to be the case by Shinn and Madey in a study using HREELS and other experimental techniques.[20] Theory and experiment agree that parallel bonded CO on these surfaces is highly activated with a large bond stretch, a greatly decreased vibrational frequency, a greatly reduced dissociation barrier, and a high dissociative chemisorption energy. In contrast, upright bonded CO on the Pd and Pt surfaces desorbs readily.

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