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## QUANTUM CHEMICAL TOPOLOGICAL STUDY OF INTERACTION OF CARBON MONOXIDE ON THE Pd (112) SURFACE

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*Dedicated to Dr Zahradník on the occasion of his 60th birthday.*

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Interaction of carbon monoxide with a stepped (112) Pd surface has been studied by a quantum chemical topological method. The adsorption of CO takes place preferentially in 5-fold hollow bound configurations i.e. on sites associated with steps. In all cases studied the bonding of CO molecule by carbon is energetically more favorable than that by oxygen. The dissociation of CO between neighbor 5-fold hollow positions can take place but is energetically less favorable than the nondissociative chemisorption on the same positions.

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In general, there are two distinct ways how to study diverse and complicated chemical problems theoretically. The first way is to study small and medium sized systems by very accurate non-empirical methods. The second way is to simplify theoretical methods as much as possible to obtain at least qualitative informations on large and complicated chemical systems. R. Zahradník was an outstanding pioneer in the latter field and brought many examples on the usefulness of very crude quantum chemical methods to solve rather complicated problems in the field of aromaticity, chemical reactivity and electron spectroscopy<sup>1</sup>. His work in this field was also extended to the study of metal surfaces<sup>2</sup>. His interest tempted one of us to prepare a set of quantum-chemical programs<sup>3</sup> which are based on the simplest assumption on topological properties of large molecular systems.

In this paper, the topological method is applied to an investigation of the adsorption of carbon monoxide on the (112) fcc Pd surface. This plane is the only low index plane which exhibits steps. It is well known experimentally that if the CO dissociation occurs it takes place particularly on step and kink sites. In addition the (112) plane consists of the two basic planes (100) and (111). This model is thus applicable, at least as the first approximation, for the study of the gas chemisorption on all three low index planes.

In our previous papers<sup>4,5</sup> we focused our attention to both dissociative and non-dissociative chemisorption of CO on nickel, copper and platinum fcc (112) surfaces. It appeared that the adsorption on the 5-fold hollow position is favorable on both Ni and Cu metals<sup>4</sup>, however, the dissociative adsorption is preferred only on the Ni surfaces. On the contrary, the adsorption on the top sites is favorable on Pt

metal<sup>5</sup> and both dissociative and non-dissociative adsorptions were found to play a role only on atop sites on a platinum surface.

With palladium the *n*-fold hollow sites were found to play a dominant role in adsorption on the low index planes (100), (110), (111), (210) in all experiments reported till now. At higher coverages the top positions were found, too, see e.g. refs<sup>6-23</sup>.

Theoretical papers dealing with the adsorption of CO on Pd are very scarce<sup>24-28</sup>. LCGTO-LSD model potential calculations have been performed for CO interacting with two, four and eight atom clusters of Pd, which modelled the low-index surface<sup>24</sup>. Scattered-wave- $X_\alpha$  molecular cluster calculations<sup>25</sup> were performed for the chemisorption of CO on Pd clusters and they were used for the interpretation of photoelectron spectra<sup>26</sup>. LCAO- $X_\alpha$  model potential calculations<sup>27</sup> suggested the localized character of CO chemisorption and the similarity among calculated energy levels for various surfaces of palladium.

### THEORETICAL

In this paper the same computational method has been used as in our previous work<sup>4</sup>. It is essentially a topological method based on the one-center Hamiltonian in which resonance integrals were calculated between all pairs of equivalent orbitals which belong to the nearest neighbor atoms. It has been found that such a trick is good enough to remove serious shortcomings of the Hückel method applied on all-electron systems<sup>29</sup>, which were questioned by Hoffmann<sup>30</sup>. Resonance integrals were calibrated on heats of formation of small molecules of the similar valence types rather than to atomic properties. In addition, orbital electronegativities (Table I) used as a basis for calculations of Coulomb integrals were empirically scaled to reproduce correctly charge distribution in small systems. The parametrization procedure was the same as in our previous paper<sup>4</sup>, in this particular case Pd<sub>2</sub>, Pd(CO)<sub>4</sub>, and PdO molecules were used for obtaining resonance integrals for Pd—Pd, Pd—C, and Pd—O bonds. The corresponding values of resonance integrals between equivalent orbitals, which lie on connections of nuclei, were 80, 103, and 45 kJ/mol for Pd—Pd,

TABLE I  
Scaled orbital electronegativities for the elements under study in kJ/mol

Element	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>
Pd	-393	-195	-226	0
C	-1 473	-597	-108	0
O	-2 507	-991	-158	0

Pd—C, and Pd—O bonds, respectively. Similarly as in paper<sup>4</sup> the reduction of Pd—C and Pd—O bond energies in bridged and hollow positions due to larger bond lengths was obtained using the Morse function based on experimental data. The values of  $\beta$ -integrals between equivalent orbitals on neighbor atoms amount to 50 and Pd—O bonds. The identical parametrical procedure as that in ref.<sup>4</sup> gave us the possibility to compare directly results obtained in this paper with those presented in literature<sup>4</sup>.

Similarly as in that paper<sup>4</sup> the basic structural unit consisted of 27 atoms (cf. Fig. 1). All leftmost and foremost atoms were linked with corresponding rightmost and hindermost atoms to form a torus. This procedure was used to conserve periodic boundary conditions. By appropriate linking nine crystal planes were accounted for. Dissociated or nondissociated carbon monoxide was captured on atop centers and those multiple  $n$ -fold hollow sites which can be identified with directions of a crystal grow. The systems studied are depicted in Figs 2–4. There are three different on top positions on the surface and two subsurface planes and three different hollow positions: two-fold, three-fold, and five-fold hollow sites. The corresponding structures are denoted as I–IV in Fig. 2 as well as in subsequent tables. Orientations A and B (cf. Fig. 2) are those in which the C—O bond is perpendicular to a terrace or a step of the crystal. A total size of the system was 348 basis orbitals and a single calculation on the computer IBM 370 model 148 lasted about 35 min.

## RESULTS AND DISCUSSION

As has been said previously the torus represents an infinite crystal with nine elementary (112) planes. Due to the conservation of the translational symmetry, atoms

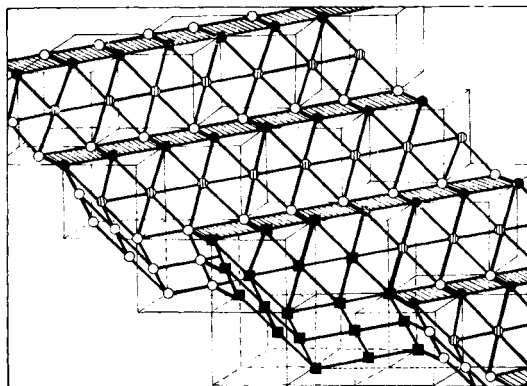


FIG. 1

The (12) plane of the Pd crystal. Atoms which constitute the basic structural unit are designed by full squares

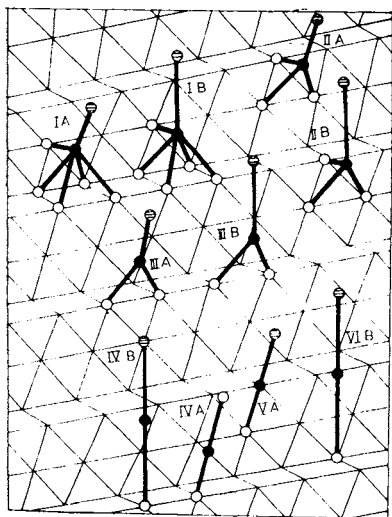


FIG. 2  
The list of linear CO captures studied in this paper

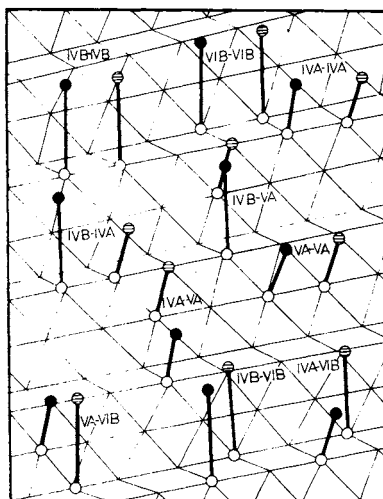


FIG. 3  
The list of dissociative CO captures between  $n$ -fold hollow centers studied in this paper

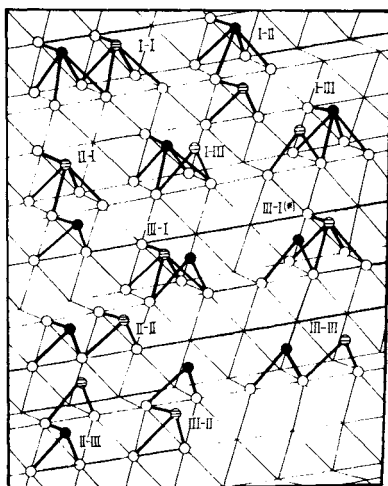


FIG. 4  
The list of dissociative CO captures between atop centers studied in this paper

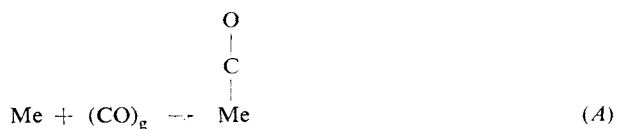
in respective planes are identical. Calculated charge densities and bond orders for Pd atoms on various planes are presented in Table II. It should be mentioned that bond orders are tabulated only for atoms lying on the same plane.

Unlike Ni, Cu (ref.<sup>4</sup>), and Pt (ref.<sup>5</sup>), the surface layer possesses no charge, the negative charge being concentrated in the bulk. The corresponding positive charge appears in the first subsurface level. The bond orders indicate the successive bond strength weakening in the direction toward the bulk. This behavior resembles that of the Ni, Cu, and Pt crystals with one exception. The unusually high bond order in the middle of the crystal indicates an enhanced stability of bulk phase of palladium.

Calculated band structures for surface (dotted and dashed curve) and total valence (full curve) electrons are presented in Fig. 5.

The curve presented is an envelope of Gaussian curves with the half-width of 15 kJ/mol their maximum being placed at energies of corresponding occupied MO's. It was assumed that the inclusion of 324 basis orbitals results in the problem large enough to provide the clustering of orbital energies in bands analogous to that in infinite ideal crystals.

An energy of associative chemisorption (energy gain) of the proces



and a total amount of charge on carbon monoxide are summarized in Table III.

From this table it is seen that the stability of the chemisorbed 5-fold hollow complex is higher than that of any atop complex and is much more higher than that of

TABLE II  
Charge densities  $q$  and bond orders  $p$  on the subsequent planes of the metal crystal

Plane	$q$	$p$
1	0.00	1.08
2	0.15	0.74
3	-0.02	0.68
4	-0.11	0.10
5	0.00	0.57
6	-0.11	0.10
7	-0.02	0.68
8	0.15	0.74
9	0.00	1.08

2- and 3-fold hollow complexes. The exceptionally high adsorption energy in the 5-fold positions appears to be remarkable and this suggests the preferential capture of the molecule on the ledge sites. On the contrary, the very low adsorption energy on edge positions should be pointed out. However, a remarkably high adsorption energy on atop positions suggests the preferential atop bonding on lower indexed crystal planes as (100) or (111). This is in a contradiction with the adsorption of CO on both Ni and Cu surfaces<sup>4</sup>. In all cases studied the capture of the CO molecule by oxygen is endoergic and it can thus hardly occur. The orientation of CO perpendicularly

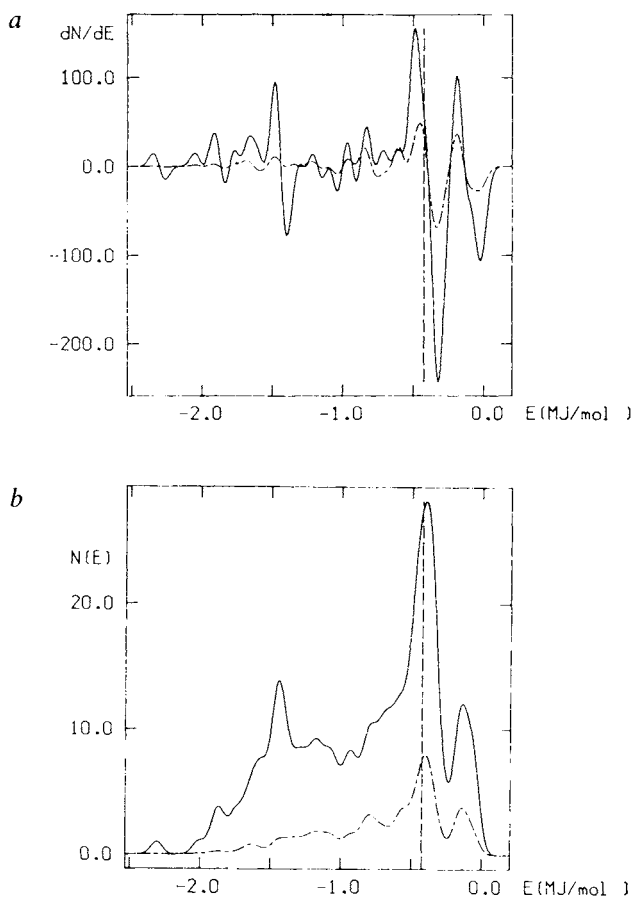


FIG. 5

The band structure of the surface (dotted and dashed curve) and all-valence (full curve) electrons calculated in this work for the (112) Pd surface. *a* Integral function, *b* derivative function

TABLE III

Adsorption energies  $E_{ad}$  in kJ/mol, total charges  $Q$  of adsorbed molecules and relative bond order changes  $-\Delta p$  on C—O bonds for all systems under study. The respective systems are displayed in Fig. 2

Systems	Caption of C			Caption of O		
	$E_{ad}$	$Q$	$-\Delta p$	$E_{ad}$	$Q$	$-\Delta p$
IA	197	-1.1922	1.4279	-17	-0.5692	0.6962
IB	161	-2.5856	1.7434	-17	-0.5694	0.6963
IIA	90	-0.8510	1.1569	-82	-0.2837	0.4526
IIB	89	-1.0050	1.1852	-78	-0.4258	0.5173
IIIA	12	-1.0886	0.9808	-114	-0.2015	0.3327
IIIB	14	-1.7241	0.9858	-112	-0.2424	0.3531
IVA	178	-0.5134	1.0720	-51	-0.6069	0.4493
IVB	139	-0.7068	1.1583	-70	-0.3623	0.5168
VA	180	-0.3795	0.9794	-48	-0.1211	0.4157
VB	138	-0.3784	0.9584	-68	-0.1469	0.5157

TABLE IV

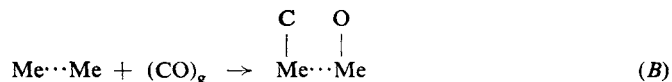
Chemisorption energies in kJ/mol and the sum of charges on chemisorbed atoms for dissociations displayed in Figs 3 and 4. The first index in those figures correspond to the position of the C caption and it is the row index in this table

System	Chemisorption energy				Charges			
	I	II	III		I	II	III	
I	30	-29	-70		-3.2916	-3.4926	-3.6528	
II	-127	-191	-232		-3.6460	-3.8250	-3.9670	
III	-229	-294	-327		-3.8633	-4.0253	-4.1650	
	IVA	IVB	VA	VB	IVA	IVB	VA	VB
IVA	-62	-412	-68	-87	-3.4348	-4.6333	-3.5310	-3.4993
IVB	-409	-132	-108	-395	-4.7810	-3.3565	-3.4536	-4.5122
VA	-124	-112	-51	-106	-3.3413	-3.3847	-3.8512	-3.4346
VB	-145	-146	-123	-108	-3.5283	-3.5283	-3.4514	-3.5017

to terrace plane (111) is more favorable than that perpendicular to the step (plane (100)).

With all systems a charge transfer from the metal to the CO molecule occurs in a course of the chemisorption. The strong charge transfer to the CO molecule suggests the predominant role of the back-donation mechanism. Such a transfer results in the fact that the CO molecule resembles alcoholate and the enhanced reactivity toward electrophilic agents can be anticipated in this case.

Energy of a dissociative chemisorption for the process



as well as sum of charges on C and O atoms are summarized in Table IV. It is seen that the dissociative chemisorption on the stepped surface (112) of palladium can occur only between multiple 5-fold hollow positions. However, the dissociative chemisorption is energetically much less favorable than the simple adsorption on the 5-fold hollow and on all top positions (cf. Table III). The energy of the linear capture on the 5-fold hollow position is about 170 kJ/mol higher and thus the nondissociative chemisorption should highly predominate.

## CONCLUSIONS

The calculation indicates that the adsorption of CO takes place preferentially in a linearly bound configuration at sites associated with the steps on the 5-fold hollow positions and on atop positions with almost the same energy. Palladium resembles thus both nickel and platinum in this respect the binding energy being as low as that in platinum unlike Ni. The attachment of oxygen is endoergic and thus improbable. The dissociation of CO between 5-fold hollow positions is exoergic but energetically much less favorable than the simple adsorption of any site of the crystal and also much less favorable than that on either Ni or Pt.

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## REFERENCES

1. Zahradník R., Pancíř J.: *HMO Energy Characteristics*. Plenum Publ. Corp., New York 1970.
2. Pancíř J., Zahradník R.: *J. Mol. Struct., Theochem* **94**, 25 (1983).
3. Pancíř J.: *Collect. Czech. Chem. Commun.* **45**, 2453 (1980); **45**, 2463 (1980).
4. Pancíř J., Haslingerová I., Nachtigall P.: *Surface Sci.* **181**, 413 (1987).
5. Pancíř J., Haslingerová I., Nachtigall P.: *Chem. Phys.*, in press.
6. Bradshaw A. M., Hoffmann F. M.: *Surface Sci.* **72**, 513 (1978).
7. Bradshaw A. M., Hoffmann F. M.: *Surface Sci.* **52**, 449 (1975).



8. Hoffmann F. M., Bradshaw A. M. in: *Proc. 7th Int. Vacuum Congr. and 3rd Int. Conf. on Solid Surfaces, Vienna 1977*; p. 1167.
9. Tracy J. C., Palmberg P. W.: *J. Chem. Phys.* **51**, 4852 (1969).
10. Park R. L., Madden H. H., jr: *Surface Sci.* **11**, 188 (1968).
11. Conrad H., Ertl G., Koch J., Latta E. E.: *Surface Sci.* **43**, 462 (1974).
12. Bader S. D., Blakely J. M., Brodsky M. B., Friddle R. J., Panosh R. L.: *Surface Sci.* **74**, 405 (1978).
13. Ertl G., Kuppers J.: *Low Energy Electrons and Surface Chemistry*, p. 227. Verlag Chemie, Weinheim 1974.
14. Unwin R., Bradshaw A. M.: *Chem. Phys. Lett.* **58**, 58 (1978).
15. Grunze M.: *Chem. Phys. Lett.* **58**, 409 (1978).
16. Conrad H., Ertl G., Kuppers J., Wang S. W., Gerard K., Haberland H.: *Phys. Rev. Lett.* **42**, 1082 (1979).
17. Madey T. E., Yates J. T., jr, Bradshaw A. M., Hoffmann F. M.: *Surface Sci.* **89**, 370 (1979).
18. Sheppard N., Nguyen T. T. in: *Advances in Infrared and Raman Spectroscopy*, Vol. 5 (R. J. Clarke and R. E. Hester, Eds). Heyden 1978.
19. Soma-Noto Y., Sachtler W. M. H.: *J. Catal.* **32**, 315 (1974).
20. Brown A., Vickerman J. C.: *Surface Sci.* **151**, 319 (1985).
21. Bradshaw A. M., Ortega A., Hoffmann F. M.: *Surface Sci.* **119**, 79 (1982).
22. Ertl G., Ran P.: *Surface Sci.* **15**, 443 (1969).
23. Ertl G., Conrad H., Koch J., Latta E. E.: *Surface Sci.* **43**, 462 (1974).
24. Andzelm J., Salahub D. R.: *Int. J. Quantum Chem.* **29**, 1091 (1986).
25. Rosén A., Grundevik P., Morovic T.: *Surface Sci.* **95**, 477 (1980).
26. Lloyd D. R., Quinn C. M., Richardson N. V.: *Surface Sci.* **63**, 174 (1977); **63**, 574 (1977).
27. Katsuki S., Taketa H.: *Solid State Commun.* **39**, 711 (1981).
28. Pacchioni G., Kouřtecký J., Fantucci P.: *Chem. Phys. Lett.* **92**, 486 (1982).
29. Del Re G.: *Electronic Aspects of Biochemistry*, pp. 221–235. Academic Press, New York 1964; *J. Am. Chem. Soc.* **1958**, 4031.
30. Hoffmann R., Lipscomb W. N.: *J. Chem. Phys.* **36**, 2179 (1962).

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