

On the Electronic Competition Effect upon CO Adsorption on Metals

H. A. C. M. HENDRICKX,¹ C. DES BOUVRIE, AND V. PONEC²

Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

Received October 3, 1985; revised July 24, 1987

IR spectra of CO adsorbed on Pd/SiO₂ have been monitored as a function of $\theta(\text{CO})$ and isotopic composition x , where $x = {}^{12}\text{CO}/({}^{12}\text{CO} + {}^{13}\text{CO})$. The results show that on rough curved surfaces of small particles of Pd there is no tendency to clustering of CO. Results do not support the idea of chemical (competition) effects. An alternative explanation of the large shifts ($\Delta\nu_{\text{max}}$) observed on flat single crystal planes is suggested: with increasing $\theta(\text{CO})$, CO molecules change their adsorption sites. The latter process is absent on small particles of Pd. © 1988 Academic Press, Inc.

INTRODUCTION

The first papers on the IR spectra of CO adsorbed on metals reported that the position of the absorption maximum ($\nu_{\text{max}}(\text{CO})$) shifted to higher wavenumbers when the surface coverage of CO increased (1). An explanation of this shift was also suggested: a resonance-like, repulsive interaction of CO dipoles was considered to lead to the increase of the frequency. (Only the symmetrical vibration of the dipole layer is observable; the anti-symmetrical vibration is IR-inactive). Several authors tested this hypothesis by using isotopic mixtures of ¹²CO and ¹³CO (1-4). They confirmed that a substantial part, if not all, of the total shift in ν_{max} is caused by variation of the coverage (θ) and that it can be explained in the manner just described.

Some problems remained to be solved. First of all, it was surprising that $\Delta\nu_{\text{max}}(\theta)$ [$\Delta\nu_{\text{max}}(\theta) = \nu_{\text{max}}(\theta = 1) - \nu_{\text{max}}(\theta = 0)$] was often found to be lower with powders than with single crystal planes. However, this was later identified as an artifact caused by clustering of CO on powders, an effect that also occurs on rough planes of single crystals (5-7). When care is taken to spread CO

well over the powder, for example, by increasing the temperature of the adsorbent, values of $\Delta\nu_{\text{max}}(\theta)$ can be obtained free of this artifact. Necessary measures in this respect were also taken when the data described below were obtained. Blyholder (8a) suggested, and many others followed him in his line of thinking, that $\nu_{\text{max}}(\text{CO})$ can also increase with increasing θ , because of a "chemical effect" that causes an excessive (some people even thought the entire observable) increase of $\nu_{\text{max}}(\theta)$. Naturally, attempts have been made to identify such a chemical effect ("chemical shift" in $\nu_{\text{max}}(\theta)$).

It has been suggested (9-11) that to this end the $\nu_{\text{max}}(\theta)$ should be determined and compared with the maximum possible effect of the dipole-dipole interaction as determined from the ¹²CO/¹³CO isotopic dilution experiments. The latter has been estimated to be always in the range of $\Delta\nu_{\text{max}}({}^{12}\text{CO}/{}^{13}\text{CO}) = 30$ to 40 cm^{-1} and to depend mainly on CO-CO distances. Everything in excess of this value, $\Delta\nu_{\text{excess}}$ [$\Delta\nu_{\text{excess}} = \Delta\nu_{\text{max}}(\theta) - \Delta\nu_{\text{max}}({}^{12}\text{CO}/{}^{13}\text{CO})$] should, according to these authors (9-11), be ascribed to the chemical (competition) effect. Values illustrating this point are shown in Table 1.

There are several speculative explanations for $\Delta\nu_{\text{excess}}$ in the literature. Blyholder (8a) suggested a "through-the-

¹ Present address: Unilever Research, Vlaardingen, The Netherlands.

² To whom correspondence should be addressed.

TABLE 1

IR Absorption of CO Adsorbed on Metals: Shift in the Absorption Maximum with Coverage [$\Delta\nu_{\max}(\theta)$] Compared with the Shift Expected for Dipole-Dipole Interaction [$\Delta\nu_{\max}^{(^{12}\text{CO}/^{13}\text{CO})}$] Determined from Isotopic Replacement

Metal	$\Delta\nu_{\max}(\theta)$ (cm^{-1})	$\Delta\nu_{\max}^{(^{12}\text{CO}/^{13}\text{CO})}$ (cm^{-1})	Ref.
Pd (100)			
90 K double coord.	69	36	13
200 K double coord.	58		13
200 K on top	7		13
Pd (111)			
200 K double coord.	65		13
200 K triple coord.	50		13
90 K on top	~5		13
Pt (111)			
On top	38	38	4, 6, 17
Pt on SiO ₂			
On top	32	40	18, 19
Ir film			
On top	80	50	15
Ir on SiO ₂	>27	52	16, 20
On top			

metal" effect: CO molecules have to compete for the metal d electrons and with an increasing $\theta(\text{CO})$ the back-donation of the d electrons into the antibonding $2\pi(\text{CO})$ orbitals becomes lower. Other authors (8b) suggested a "through-the-vacuum" effect: the 2π orbitals form a two-dimensional band, and speculated that the back-donation into a band, the centroid of which lies under the Fermie energy, is lower than that into the isolated 2π orbitals (the latter point is, or course, debatable).

We have decided to check the assumption that the $\Delta\nu_{\text{excess}}$ reflects the chemical competition effects (8a) experimentally, and the results are described below. It seems reasonable to expect that with small metal particles the chemical competition effect (or another similar one) should be more pronounced than with large particles or macroscopic monocrystals. This means that the $\Delta\nu_{\text{excess}}$ value should be largest with small particles if the authors of Refs. (8a, 9-11) were right. In the extreme case, $\Delta\nu_{\text{excess}}$ of small particles would be of the same magnitude as for monocrystals. It

would be so if the competition effect were size independent, which is not very probable.

Another point worthy of mention is that the theory of the chemical competition effect does not discriminate strongly between the "on top" and the "multiply bound" CO; both species should exhibit approximately the same effect. One might only expect $\Delta\nu_{\text{excess}}$ to be a little larger for the multiply bound CO than for the on-top CO because the former receives more electrons back-donated in its antibonding orbitals than the latter.

EXPERIMENTAL

Palladium catalysts, one with small and one with large particle size, have been prepared on a silica support (Aerosil 150). The preparation consisted of the following steps. First, the silica was suspended in water, the temperature was fixed at 350 K and the pH was fixed at about 8 to 9. Then an aqueous solution of $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$ was slowly added under continuous stirring. The concentration of Pd nitrate was such that at a complete adsorption (almost achieved) of Pd on silica the loading was 10% wt. Pd. The suspension was then filtered and dried overnight in air at 370 K. Under all circumstances the catalyst was kept free from chlorine. The reduction took place in a 25% hydrogen-75% nitrogen atmosphere at temperatures up to 600 K. For the large-particle catalyst the slow adsorption step was replaced by fast evaporation at 370 K. By electron microscopy the average particle sizes were determined to be 1.4 and 16.5 nm, respectively. The spectra of the adsorbed CO molecules were recorded in the transmission mode, using self-supporting pressed pellets. The pellets could be heated and cooled while in the beam; the reduction was also performed *in situ*. The spectrophotometer was a Perkin-Elmer 580B instrument connected to an Apple II+ microcomputer for data collection, storage,

TABLE 2
 $\Delta\nu_{\max}(\theta)$ and $\Delta\nu_{\max}({}^{12}\text{CO}/{}^{13}\text{CO})$ for Samples of Pd/SiO₂
 with Small (1.4 nm) and Large (16.5 nm)
 Metal Particle Sizes

Pd particle size: CO coordination type	$\Delta\nu_{\max}(\theta)$ (cm ⁻¹)	$\Delta\nu_{\max}({}^{12}\text{CO}/{}^{13}\text{CO})$ (cm ⁻¹)
1.4 nm		
On top	21	21
Double coord.	27	
16.5 nm		
On top	24	24
Double coord.	27	28

and evaluation. All spectra were converted to "change in extinction" versus frequency plots before being interpreted. The frequency versus coverage plots were calculated by integrating the CO peak at maximum coverage and assuming a linear relation between the coverage and the CO peak area. Among others, Ortega *et al.* (9, 13) have shown that this relation holds well in most cases.

RESULTS

The most essential data obtained are summarized in Table 2 and in Figs. 1 and 2.

As one can see in Table 2, the values obtained are considerably lower than those reported in Table 1. Figure 1 shows a comparison of the $\nu_{\max}(\theta)$ and $\nu_{\max}({}^{12}\text{CO}/{}^{13}\text{CO})$ plots. This comparison demonstrates, among other matters, that the data are free of troubles caused by clustering of CO.

It can be seen that there is no essential difference between the $\Delta\nu_{\max}$ to the left and right in Fig. 1.

DISCUSSION

The conclusions to be drawn from these results are clear. First, the experimental procedure applied does not lead to artifacts caused by clustering. Both functions, $\nu_{\max}(\theta)$ and $\nu_{\max}({}^{12}\text{CO}/{}^{13}\text{CO})$, are almost identical; an adsorption site covered by ¹³CO is with respect to the adsorbed ¹²CO molecules a "free" site, as far as the mutual interaction is concerned. This is true for both the CO molecules adsorbed with low coordination (on top) on a Pd atom and those that are multi-coordinated. The second conclusion concerns $\Delta\nu_{\max}$. The $\Delta\nu_{\max}(\theta)$ for the "on top" CO is estimated

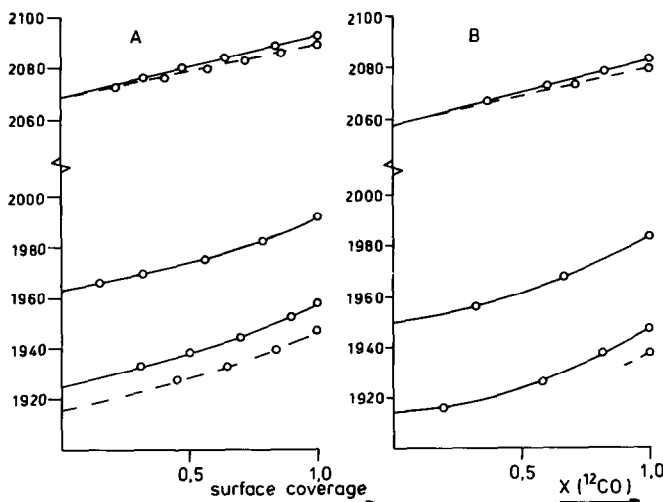


FIG. 1. CO adsorption on Pd/SiO₂ catalysts. (A) Frequency maximum of CO IR absorption (cm⁻¹) versus surface coverage; (B) frequency maximum (cm⁻¹) versus $x({}^{12}\text{CO})$; $x({}^{12}\text{CO}) = p({}^{12}\text{CO})/[p({}^{12}\text{CO}) + p({}^{13}\text{CO})]$. The solid lines refer to the 16.5-nm catalyst, the dashed lines to the 1.4-nm catalyst. The maximum CO pressure used was 1 Torr.

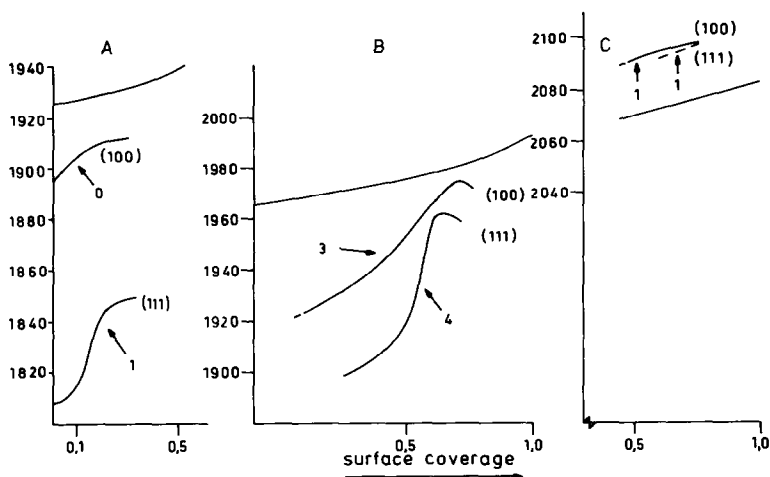


FIG. 2. Frequency maximum (cm^{-1}) versus surface coverage for CO adsorption on Pd. (A) Triple and quadruple coordinated CO; (B) double coordinated CO; (C) Single coordinated, on top, CO. For other symbols, see text.

to be 21 to 24 cm^{-1} , and $\Delta\nu_{\text{max}}(^{12}\text{CO}/^{13}\text{CO})$ about 22 to 25 cm^{-1} . For the double coordinated CO values are found of approximately 28 cm^{-1} , for the "triple" coordinated CO 33 cm^{-1} is found. Both these last values were obtained by monitoring either the $\nu(\theta)$ or the $\nu(^{12}\text{CO}/^{13}\text{CO})$. The changes in frequency are obviously very similar with the 16.5- and 1.4-nm catalysts. The values leave no room for speculation on a possible competition effect leading to an appreciable $\Delta\nu_{\text{excess}}$. The results therefore support the objections previously raised against Blyholder's (and other similar) ideas (4, 21). Nevertheless, the situation deserves some comment. First, it should be noticed that our results do not differ essentially from those of other authors who worked with Pd powders. Eischens *et al.* (1) reported spectra that lead to a $\Delta\nu_{\text{max}}(\theta)$ of about 34 cm^{-1} . The $\Delta\nu_{\text{max}}(^{12}\text{CO}/^{13}\text{CO})$ amounts to 33 cm^{-1} , as measured here. The latter is a typical value for Pd, monocrystals as well as powders, and a similar value has also been found by other authors, e.g., by Ortega *et al.* (37 cm^{-1}) for double-bonded CO on Pd(100) (9). On other metals similar values were found (29 cm^{-1} for CO "on top" of Pt (12); 45 cm^{-1} for CO on Ir and 35 cm^{-1} for Ni (14).

However, the $\Delta\nu_{\text{max}}(\theta)$ is usually found to be considerably larger than here, when adsorption of multicoordinated CO is followed on flat surfaces. This can be derived from the schematic reproduction of various literature data summarized in Fig. 2.

The lines in Fig. 2 with the crystallographic orientation of the surface indicated have been obtained by various other authors (9, 11, 13) on different crystal planes. The three lines without any indication have been obtained from the present work. The numbers at the arrows indicate the number of ordered LEED patterns observed in that specific interval of θ . For example, CO on Pd(111) between $\theta = 0.35$ and $\theta = 0.70$ exhibits four different sharp LEED patterns (13). As stated before, it seems very unlikely that the "competition" effects are less pronounced on the small particles than on the bulk (monocrystalline) metals. In contrast, however, it is reasonable to expect that the free movement and compression of the adsorbed CO layer as a whole on the flat surfaces, which can lead to changes in the LEED patterns, is restricted on (small) particles with many rough microplanes. A lateral movement of a CO layer on a metal substrate with varying θ has been observed by Ortega *et al.* (9, 13)

for Pd(100) and by Hoffmann and Ortega for Pd(111) (1, 3, 11). For example, at a relative low coverage an ordered structure is formed on the Pd(111); with the double-bonded CO there is a $c(4 \times 2)$ structure near $\theta = 0.5$ and then, as the coverage θ increases, each newly adsorbing CO molecule makes the whole layer more compressed and rotated a little further. It is reasonable to expect that upon this process the distance between a CO molecule and the adsorption site (and/or metal surface) changes a little. This change can bring about a change in the overlap of the anti-bonding CO orbitals and the metal orbitals, resulting in a decrease in the back-donation and thus leading to a higher IR absorption frequency. As can be seen in Fig. 2, the compression stage, between $\theta = 0.5$ and $\theta = 0.6$, coincides with the steepest frequency change with the coverage θ . Therefore, we suggest that the large $\Delta\nu_{\text{excess}}$ (observed with single crystal planes) is due to the changes in the CO adsorption geometry (i.e., the changing overlap of CO and metal orbitals) and a varying direct donation and back-donation, not to the "competition for back-donating electrons."

We see another support for our idea in the study by Campuzano and Greenler (14) of CO on Ni(111). Figure 4 of their paper is a frequency versus coverage plot in which several distinct areas can be found. In the intervals from $\theta = 0.1$ to $\theta = 0.2$ and from $\theta = 0.25$ to 0.6 , the frequency shift can be explained fully by the CO-CO interactions. In the interval from $\theta = 0.2$ to $\theta = 0.25$ a sharp change in $\nu_{\text{max}}(\text{CO})$ occurs. This is because the mode in which CO is adsorbed changes. In contrast to what is observed on Pd, on Ni the CO molecule in threefold or twofold coordinations is not slowly pushed through a range of slightly different configurations, but once the surface is covered to about 20%, the adsorption mode flips over abruptly from a triple to a double coordination. Similar effects have been described by other authors (10, 22).

It is sometimes far from easy to distinguish between CO slowly being pushed through different adsorption positions and CO going more abruptly from one coordination site to another. This can be observed if one inspects more closely the results for CO adsorbed on Pd(111) at $\theta < 0.33$. Between $\theta = 0$ and $\theta = 0.1$, the frequency changes only marginally. Between $\theta = 0.1$ and $\theta = 0.2$ it changes by about 30 cm^{-1} . Finally, between $\theta = 0.2$ and $\theta = 0.33$ it no longer changes much. The whole frequency change is about 41 cm^{-1} . Although such a change, in theory, can be still explained in terms of CO-CO interactions, it is very hard to imagine that in this particular case this is the right explanation because at low coverages the CO molecules are too far from each other to interact so strongly by dipole-dipole interactions or by (see Ref. (22)) interaction between the 2π orbitals of CO. Presumably, in this region of θ , about 10 to 15 cm^{-1} at maximum can be ascribed to the CO-CO (dipolar) interactions. That leaves the additional 25 to 30 cm^{-1} to be explained. Two possible explanations are conceivable:

(1) CO is adsorbed at random on the surface, up to $\theta = 0.1$. Then, as the coverage increases, the adsorbate transforms from the random distribution into $(\sqrt{3} \times \sqrt{3})$ -R30° structure, which transformation causes the frequency change of 25 to 30 cm^{-1} by changes in the metal-CO bond.

(2) CO is adsorbed initially (for whatever reason) on the tetrahedral coordination sites (up to $\theta = 0.1$) and then, at $\theta = 0.1$, CO begins to be adsorbed at the octahedral sites. This change from tetrahedral to octahedral sites then causes the 25 to 30 cm^{-1} jump.

From the IR and LEED data alone it is difficult to determine which explanation is correct. However, bearing in mind that the difference between the tetrahedral and the octahedral adsorption site might be well about 25 cm^{-1} (23) and the fact that the IR absorption bands at $\theta = 0.15$ and $\theta = 0.23$

(10) show a shoulder on the low-frequency side, this makes us believe that the second explanation might be preferred.

The reader will have noticed that our suggestion is to relate the $\Delta\nu_{\text{excess}}$ to the changes in the metal-CO bonding caused by changes in the CO positions. However, according to some authors (8b), we should have looked for changes in the metal-CO bonding caused by the formation of a two-dimensional $2\pi(\text{CO})$ band and by the changes therein upon increasing $\theta(\text{CO})$ coverage. We have not done this, for several reasons. First, we are not convinced that the variations in the surface $2\pi(\text{CO})$ band are of the size which would explain the data. Second, more importantly, even if the model (8b) worked well for Cu (with $2\pi(\text{CO})$ band filled to less than one half) it is not transferable to Pd: it would require a $2\pi(\text{CO})$ band filled to more than one-half (i.e., without additional assumptions, more than two electrons in the 2π (antibonding) orbital of CO). Third, the results in Fig. 1 and similar results concerning other metals (see e.g. Ref. 20) show that the rather long-range dipole-dipole interactions are approximately the same (i.e., ν varies with θ in a similar way) for flat and curved surfaces. Why would then the relatively short-range interactions upon the formation of a $2\pi(\text{CO})$ band be so different on the two surfaces just mentioned, causing a much higher $\Delta\nu_{\text{excess}}$ on the flat surfaces? Finally, the largest changes of ν with θ on flat ideal surfaces are found at the very low coverages, where the formation of a band can hardly be of importance.

CONCLUSIONS

We do not find any support for the idea of chemical (competition) effects. However, data in the literature offer an alternative explanation in terms of changes in the adsorption sites occurring with increasing $\theta(\text{CO})$ on flat metal surfaces, but this effect is absent on curved rough surfaces of small metal particles.

ACKNOWLEDGMENTS

The authors wish to thank Inf. G. H. Renes for taking the electron micrographs, Mr. W. C. Bauer for designing our new IR transmission cell, and Mr. J. Jansen for skillfully building this cell. Financial support by ZWO/SON (The Netherlands) and NATO Scientific Committee are gratefully acknowledged.

REFERENCES

1. Eischens, R. P., Francis, S. A., and Pliskin, W. A., *J. Phys. Chem.* **60**, 194 (1956).
2. Hammaker, R. M., Francis, S. A., and Eischens, R. P., *Spectrochim. Acta* **21**, 1295 (1965).
3. Stoop, F., Toolenaar, F. J. C. M., and Ponec, V., *J. Catal.* **73**, 50 (1982).
4. Crossley, A., and King, D. A., *Surf. Sci.* **58**, 379 (1976).
5. Crossley, A., and King, D. A., *Surf. Sci.* **95**, 131 (1980).
6. Shigeishi, R. A., and King, D. A., *Surf. Sci.* **58**, 379 (1976).
7. Hollins, P., *Surf. Sci.* **107**, 75 (1981).
8. (a) Blyholder, G., *J. Phys. Chem.* **68**, 2772 (1964); (b) Chesters, M. A., Pritchard, J., and Sims, M. L., in "Adsorption-Desorption Phenomena" (F. Ricca, Ed.), p. 277. Academic Press, New York, 1972; Woodruff, D. P., Hayden, B. E., Prince, K., and Bradshaw, A. M., *Surf. Sci.* **123**, 397 (1982).
9. Ortega, A., Hoffmann, F. M., and Bradshaw, A. M., *Surf. Sci.* **119**, 79 (1982).
10. Gelin, P., and Yates, J. T., *Surf. Sci.* **136**, L1 (1984).
11. Hoffmann, F. M., and Ortega, A., *Prepr. Conf. Vibrations in Adsorbed Layers, Jülich, West Germany*, (1978).
12. Primet, M., *J. Catal.* **88**, 273 (1984).
13. Ortega, A., Ph.D. Thesis, Free University, Berlin, 1980.
14. Campuzano, J. C., and Greenler, R. G., *Surf. Sci.* **83**, 301 (1979).
15. Reinalda, D., and Ponec, V., *Surf. Sci.* **91**, 113 (1979).
16. Reinalda, D., Ph.D. Thesis, Leiden University, The Netherlands, 1979.
17. Crossley, A., and King, D. A., *Surf. Sci.* **68**, 528 (1977).
18. Toolenaar, F. J. C. M., Poort, v. d. G. J., Stoop, F., and Ponec, V., *J. Chim. Phys.* **78**, 927 (1981).
19. Heyne, H., and Tompkins, F. C., *Trans. Faraday Soc.* **63**, 1274 (1967).
20. Toolenaar, F. J. C. M., Bastein, A. G. T. M., and Ponec, V., *J. Catal.* **82**, 35 (1983).
21. King, D. A., *J. Electron Spectrosc.* **29**, 11 (1983).
22. Hayden, B. E., *Surf. Sci.* **131**, 419 (1983).
23. Doyen, G., and Ertl, G., *Surf. Sci.* **43**, 197 (1974).