

## NMR investigation of the binding of CO on supported Pd clusters

Lino R. Becerra\* and Charles P. Slichter

*Department of Physics and Materials Research Laboratories, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801*

John H. Sinfelt

*Exxon Research and Engineering Company, Annandale, New Jersey 08801*

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The authors report an analysis of nuclear relaxation rates and Knight shifts of  $^{13}\text{C}$  molecules adsorbed on supported Pd clusters. They find that the relaxation rates for on-top (linear) and bridge-bonded CO are proportional to the temperature, an indication of the mixing of molecular orbitals with conduction-band levels. They establish that the relaxation rate of the bridge-bonded CO arises from the Fermi contact interaction. The relaxation rate for the linear-bonded CO is determined, in addition to the Fermi contact interaction, by the interaction of nuclear spins with electron spins in non- $s$  states and with the orbital moments of the electrons. These results indicate that at the Fermi surface bridge-bonded CO exhibits an antibonding combination of the  $5\sigma$  orbital of CO with the metal  $d$  band, while linear-bonded CO presents admixture also with the CO  $2\pi^*$  orbitals.

### I. INTRODUCTION

The adsorption of carbon monoxide on transition-metal surfaces has served as a model system for new experimental techniques and theoretical approaches in the study of surface processes. The mechanism of CO adsorption, however, is still under investigation and the nature of the CO-metal bond formed has been the subject of experimental<sup>1-4</sup> and theoretical<sup>5-10</sup> studies.

The main features of the bonding of CO to transition-metal surfaces were first described by Blyholder;<sup>11</sup> this simple picture considers that the CO orbitals involved in the bond are the highest-energy occupied molecular orbital (HOMO) and the lowest-energy unoccupied molecular orbital (LUMO). For CO, the HOMO corresponds to the  $5\sigma$  orbital and the LUMO is the  $2\pi$  orbital. These orbitals interact with  $d$  bands of the metal. The molecular  $5\sigma$  orbital transfers electron density to the metal  $d$  band while backdonation from the band partially fills the empty  $2\pi^*$  orbital in the molecule. The specific details of the bonding, e.g., the amount of donation and backdonation, their correlation to the strength of the bond, and participation of other orbitals, have been studied extensively with photoemission spectroscopy,<sup>12</sup> infrared spectroscopy,<sup>13</sup> and inverse photoemission<sup>14</sup> techniques and interpreted with several theoretical approaches.<sup>5-10</sup>

We have shown that NMR provides information about the bonding.<sup>16,17</sup> We found that NMR gives direct evidence of the mixing of the CO orbitals with metal orbitals at the Fermi surface through the study of the frequency shifts of the  $^{13}\text{C}$  resonance and the temperature dependence of the  $^{13}\text{C}$  spin-lattice relaxation time  $T_1$ . For nuclei in metals  $1/T_1$  is proportional to the temperature ( $T$ ),<sup>18</sup> demonstrating that as a result of the exclusion principle, only electrons near the Fermi surface are able to exchange energy with the nuclei. The number of such electrons is proportional to  $T$ .  $1/T_1$  for  $^{13}\text{C}$  adsorbed on transition-metal surfaces is proportional to the tem-

perature, a clear indication of the presence of conduction electrons on the molecule.<sup>16</sup> We also showed that the  $^{13}\text{C}$  resonance occurred at a higher frequency than the resonance in Pt or Pd carbonyls and demonstrated that this shift arose from the electron spin polarization residing on the  $^{13}\text{C}$  atom (i.e., a Knight shift).<sup>16,17</sup>

Single-crystal studies<sup>19</sup> show that on Pd(111) surfaces, at saturation coverage, CO bonds at bridge sites (attached to two surface atoms). Infrared studies<sup>2</sup> indicate that on very small clusters CO bonds primarily at linear sites. We found that the fraction of CO molecules bridge-bonded versus linear-bonded on Pd clusters varied with temperature and with cluster size (the bridge-bonding fraction increases if one increases either cluster size or temperature).<sup>20</sup>

In this paper we present an analysis of the NMR data for CO on Pd. The analysis enables us to characterize rather specifically the metal-CO orbitals involved in the bonding.

The experimental details are given in Sec. II. In Sec. III, the line-shape analysis and relaxation rate results are discussed. Finally, in Sec. IV, we present a summary of our findings.

### II. EXPERIMENT

Our samples contain small Pd clusters (diameters 10–200 Å) supported on silica. The Pd content is 5 wt %. The fraction of Pd atoms on the surface is called the dispersion and is measured by CO chemisorption. We have used samples with 12%, 22%, 33%, 46%, and 52% dispersions (labeled Pd12CO, Pd22CO, etc). From previous studies<sup>15</sup> we know the probability distribution of the cluster diameter as a function of dispersion; the average cluster diameters in our samples correspond to 104, 55, 35, 22, and 18 Å, respectively. The sample treatment has been described elsewhere.<sup>16</sup> Briefly, the metal surface is cleaned with alternate flows of  $\text{H}_2$  and  $\text{O}_2$  gases at 300°C. The sample is then cooled to room temperature

and exposed to  $^{13}\text{CO}$  (99%  $^{13}\text{CO}$ ) until saturation coverage is attained. Any weakly adsorbed CO is removed by pumping the sample to  $10^{-6}$  Torr. The sample is transferred under vacuum to an NMR sample tube, which is then flame sealed. Data are collected in a static field of 8.2 T (87.695 MHz resonance frequency for  $^{13}\text{C}$ ) with a home-made spectrometer. To measure relaxation times, we used the inversion-recovery technique. It consists of applying a  $180^\circ$  rf pulse to invert the magnetization, waiting a time  $T_d$  to allow relaxation towards equilibrium, and inspecting the magnetization with a  $90^\circ$ – $180^\circ$  spin-echo sequence. NMR absorption spectra as a function of  $T_d$  are generated by performing Fourier transforms of the second half of the spin echo.

### III. RESULTS

#### A. Line shapes

In Fig. 1 we depict the  $^{13}\text{C}$  NMR line shapes at 77 K for the different samples described above. Pd12CO and Pd33CO have similar line shapes. Pd52CO, however, displays significant intensity in the frequency range  $-200$  to  $+100$  ppm. It corresponds to a CO species on the clusters that exhibits a very short relaxation time ( $\sim 10$ – $20$  ms at 77 K). This signal disappears at temperatures above 200 K and is not observed in the large-cluster samples at any temperature. A full investigation of the nature of this species has not been done, however, its presence on small clusters and at low temperature suggests that it might correspond to CO attached to corners and edges. Upon raising the temperature, CO on edges and corners may migrate onto the cluster's facets acquiring the frequency shifts and relaxation rates observed for CO bonded on the facets. Hence, we can decompose the observed line shapes into a high- (HF) and a low- (LF) frequency component, the latter being present on small clusters at low temperatures. In Ref. 20, we showed how we could decompose the HF component by  $T_2$  experi-

ments into two lines representing linear- and bridge-bonded CO, respectively.

In this paper, we use the inversion-recovery technique, as described above, to measure the relaxation times of linear- and bridge-bonded CO as a function of temperature and cluster size. By taking the Fourier transform of the echo, we can determine the line-shape dependence on the delay time  $T_d$  and further decompose the HF component into linear- and bridge-bonded absorption lines. We compared the two schemes (using  $T_1$  and  $T_2$ ) and found that they are equivalent in decomposing the HF component.<sup>21</sup>

Since the spin-lattice relaxation times of the two sites are different, the magnetizations at the two sites recover from the inversion pulse at different rates. If all the linear sites have the same  $T_1$ , there will be a time when the magnetization at the linear site will be zero, with the result that the echo Fourier transform at that time will only reveal the line shape of the bridge-bonded CO.

We show such a sequence of echo transforms for various delay times in the inset in Fig. 2. By subtracting the bridge CO absorption line (scaled up to match the high-frequency side of the fully recovered line) from the recovered line, we can also deduce the line shape of linear-bonded  $^{13}\text{CO}$ . Such a decomposition is shown in Fig. 2.

The fact that the baseline has a wide flat region at the time the bridge-bonded CO line is partially recovered suggests that all the linear-bonded  $^{13}\text{CO}$ 's have very similar  $T_1$ 's (i.e., have zero crossings at the same time).

With the wide range of cluster sizes we have in our samples, we address the question of whether the frequency shift depends on cluster size. In Fig. 3 we depict the zero crossing line for three different samples with different cluster sizes; Pd46CO has clusters with diameters 10–30 Å, Pd33CO has 40–80 Å, and Pd12CO has 60–150 Å. This line arises from bridge-bonded CO. For the three samples, within signal to noise, the partially

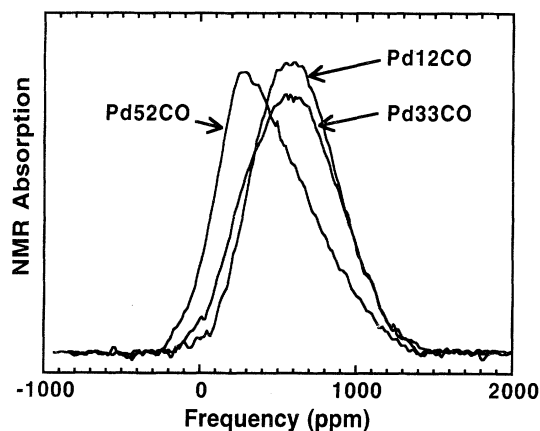


FIG. 1. NMR absorption spectra at 77 K for the different samples described in the text. [Spectra for Pd22CO and Pd46CO have not been included for clarity, 0 ppm refers to the  $^{13}\text{C}$  resonance of TMS (tetramethylsilane)].

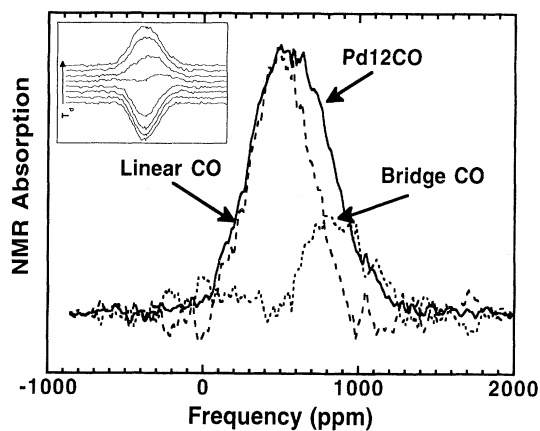


FIG. 2. NMR absorption spectrum of Pd12CO at 77 K. Inset: variation of the line shape as a function of the time  $T_d$  in an inversion recovery experiment. The linear and bridge assignments are described in the text.

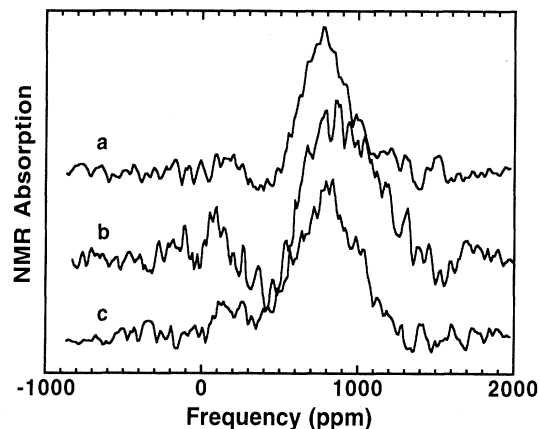


FIG. 3. Inversion recovery experiments for three samples with  $T_d$  chosen such that part of the lines are nulled: (a) Pd46CO at 270 K; (b) Pd33CO at 200 K; (c) Pd12CO at 100 K.

recovered line has the same frequency shift (800–900 ppm). Hence, we did not find evidence that cluster size has an effect on the shift of bridge-bonded CO. It seems then that even for the smallest clusters (Pd52CO) the local density of states of the conduction electrons on the surface does not change significantly to alter the shifts. If we were to make the clusters even smaller (i.e., transition-metal carbonyls), the shift (Knight shift) due to the conduction electrons would disappear since for these systems there is no conduction band developed.

To confirm that linear-bonded CO does not have a cluster-size-dependent shift, we performed the following analysis. Given that the relative amount of each species (hence the NMR line) can be varied with temperature, we can find two samples of different dispersion that display the same line shape at different temperatures if there is no cluster dependence of the shifts. From our previous work<sup>20,22</sup> we found that Pd12CO at 100 K and Pd52CO at 300 K have the same amount of linear- and bridge-bonded CO. Figure 4 shows the superposition of both lines, indicating a good agreement with our model.

The observed frequency shift comes from two sources; chemical shifts (induced orbital magnetization of the valence electrons) and Knight shifts (interaction with the spins of the conduction electrons).<sup>23</sup> The chemical shifts can be determined from transition-metal carbonyls<sup>24</sup> if we assume they are the same on the metals. This is a reasonable and common assumption since bond distances and angles for a given type of bonding are similar in metal carbonyls and chemisorbed CO. The difference from the observed shift is then attributed to the Knight shift. Table I displays these shifts for linear- and bridge-bonded

TABLE I.  $^{13}\text{C}$ O shifts for linear- and bridge-bonded CO.

$^{13}\text{C}$ O shifts (ppm)	Linear	Bridge
Pd metal	$500 \pm 30$	$850 \pm 50$
Pd carbonyls <sup>24</sup>	210	230
Knight shift	290	620

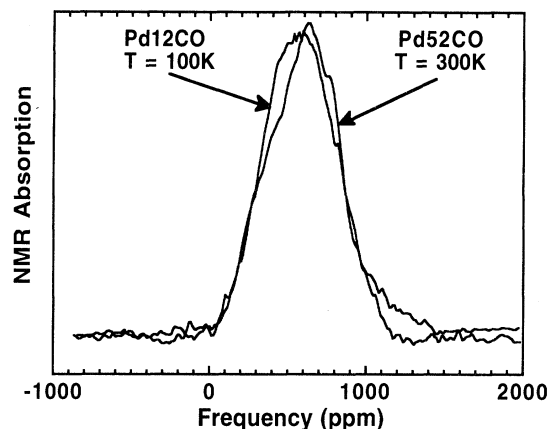


FIG. 4. For Pd12CO and Pd52CO their temperature was chosen so that their relative amounts of bridge- and linear-bonded CO are the same. There is no appreciable difference in their NMR absorption spectra although the samples have very different distribution of cluster sizes.

CO. Notice that the bridge site has a larger Knight shift than the linear one.

### B. Relaxation times

Using the inversion-recovery technique and the zero-crossing scheme to identify both species, we determined the relaxation times for both bonding sites as a function of temperature and cluster size. In Fig. 5 we depict the variation of  $1/T_1$  for linear- and bridge-bonded CO as a function of temperature for Pd52CO. Notice that for both bridge- and linear-bonded sites  $1/T_1$  is proportional

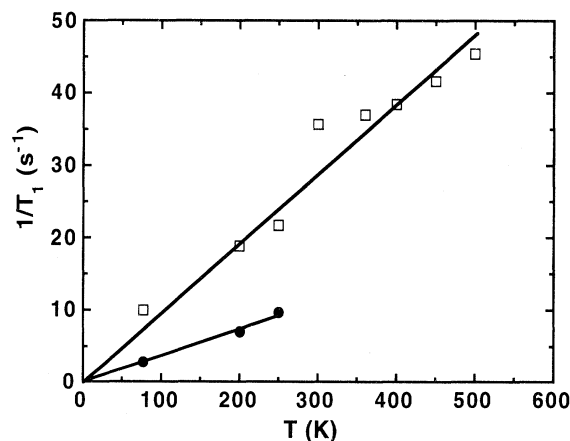


FIG. 5. Plot of  $1/T_1$  vs temperature for Pd52CO. The squares and the dots correspond to bridge- and linear-bonded CO, respectively (the linear-bonded CO signal is only observable below 250 K). The depicted lines are fits to the data giving  $T_1 T = 12$  and  $25$  K s for bridge and linear CO, respectively.

to  $T$ , characteristic of nuclear relaxation rates determined by the interaction with conduction electrons, also, bridge-bonded CO has consistently larger values of  $1/T_1T$  (about a factor of 2 larger) than the linear CO. Table II presents the variation with cluster size of  $1/T_1T$  for linear- and bridge-bonded CO. Within experimental error, there is no significant dependence of the relaxation rates with cluster size

The experimental relaxation rate  $1/T_{1\text{exp}}$  is a sum of several individual contributions.<sup>18</sup> One of them arises from the Fermi contact term, which also gives rise to the Knight shift  $K$ . We denote its relaxation rates as  $1/T_{1K}$ . The other contributions come from the electron spin-nuclear spin dipolar interaction (relaxation rate  $1/T_{1d}$  sometimes termed the dipolar rate) and the electron orbit-nuclear spin interaction (relaxation rate  $1/T_{1L}$  sometimes termed the orbital rate). The latter two interactions can cause NMR line broadening, since they produce resonance frequency shifts that depend on the orientation of the static magnetic field relative to the CO bonds. The dipolar interaction does not shift the center of gravity of the NMR line while the orbital one produces shifts (chemical shift) similar to those observed in palladium carbonyls.<sup>18</sup> The experimental relaxation time,  $T_{1\text{exp}}$ , then is given by

$$\frac{1}{T_{1\text{exp}}} = \frac{1}{T_{1K}} + \frac{1}{T_{1d}} + \frac{1}{T_{1L}}. \quad (1)$$

For the Fermi contact interaction, there is a relation between the Knight shift and the relaxation time  $T_{1K}$  (Korringa law):<sup>18</sup>

$$T_1TK^2 = \frac{\hbar}{4\pi k_B} \left[ \frac{\gamma_e}{\gamma_n} \right]^2 B, \quad (2)$$

where  $\gamma_e, \gamma_n$  are the electronic and nuclear gyromagnetic ratios respectively,  $k_B$  and  $\hbar$  are Boltzmann's and Planck's constants, and  $B$  is a correction for many-body effects and is usually approximately 1. For our purposes, in order to avoid adding too many unknown parameters, we set  $B=1$ .

For the case of <sup>13</sup>C Eq. (2) becomes

$$T_{1K}TK^2 = 4.16 \times 10^6 \text{ K s}. \quad (3)$$

Assuming that the Korringa law holds for the contact interaction [Eq. (3)], we can use it together with the measured Knight shifts from Table I to determine  $T_{1K}$ . The contribution of the other two interactions can then be determined by subtracting the Korringa term from the experimental one. Table III shows these results for Pd52CO.

For bridge-bonded CO, the main mechanism for relax-

TABLE II. Variation with cluster size of  $1/T_1T$  for linear- and bridge-bonded CO.

$1/T_1T$ (K s) <sup>-1</sup>	Pd52CO	Pd12CO
Linear	0.038±0.002	0.0322±0.007
Bridge	0.093±0.007	0.080±0.007

TABLE III. Results for Pd52CO after subtraction of the Korringa term from the experimental data.

$1/T_1T$ (K s) <sup>-1</sup>	Linear	Bridge
$1/T_{1\text{exp}}T$	0.038	0.093
$1/T_{1K}T^a$	0.020	0.092
$1/T_{1d}T + 1/T_{1L}T$	0.018	0.001

<sup>a</sup>From Eq. (3) and Table I.

ation is the Fermi contact term, while for linear-bonded CO the combined dipolar and orbital interactions are as important as the contact term. This result agrees with the observed shifts: bridge-bonded CO has a large Knight shift whereas linear-bonded CO has a small one.

Consider now the character of the two CO orbitals said to be important in bonding, the  $5\sigma$  and the  $2\pi^*$ . The  $5\sigma$  orbital may be thought of roughly as an  $sp$  hybrid on carbon, directed away from the oxygen atom. Because it has substantial  $s$  character, it can give rise to a Knight shift. The  $2\pi^*$  is made up of an antibonding combination of  $p$  orbitals on the carbon and the oxygen. The  $2\pi^*$  orbital therefore does not contain any  $s$  character and cannot therefore give a net Knight shift. (Of course, the  $2\pi^*$  might give a small Knight shift from core polarization effects,<sup>18</sup> but these would be negative shifts, the opposite of what we see.)

The large Knight shift of the bridge-bonded site must therefore arise from the  $5\sigma$  orbital. But, to produce relaxation and a Knight shift this orbital must be at the Fermi surface. Table III also shows that for linear-bonded CO, the  $s$  character of the bonding can only account for half the observed relaxation rate. Therefore there must also be some  $2\pi^*$  orbital at the Fermi surface to provide the dipolar and orbital interactions responsible for the  $T_1$  of linear-bonded sites.

We therefore conclude that for bridge-bonded CO, there is a strong admixture of  $5\sigma$  orbital into metal wave functions at the Fermi surface, and that for linear-bonded CO there is  $5\sigma$  and  $2\pi^*$  orbital admixture in metal wave functions at the Fermi surface.

The idea that there is strong admixture of  $5\sigma$  with the metal  $d$  electrons at the Fermi energy is at first sight surprising since the canonical pictures of density of states of adsorbed CO on metals show the  $5\sigma$  orbital below the bottom of the  $d$  bands. How can we say that there is  $5\sigma$  at the Fermi surface? In Ref. 5 Hoffman gives a clear exposition of various conceptual approaches to thinking about the chemisorption bond. This same article contains the key to understanding this paradox.

Consider the  $5\sigma$  orbital of a CO before bonding, and the metal  $d$  orbital to which it will eventually bond. The  $5\sigma$  and  $d$  can form a bonding combination at a lower energy, and an antibonding one at a higher energy. It is this bonding combination that lies below the  $d$  band. Our experiment therefore shows that the antibonding combination must be close to the Fermi energy, giving the <sup>13</sup>C its Knight shift.

This result has actually been predicted in part in an in-

teresting calculation by Andzelm and Salahub.<sup>8</sup> They did calculations for clusters of Pd atoms with a single CO molecule bridge-bonded. In Fig. 2 of their paper, they show the CO energy levels for clusters of Pd atoms. They indeed find the  $d$ - $5\sigma$  antibonding orbital to be very close to the Fermi energy.

Calculations for linear-bonded CO on Pd clusters have been reported,<sup>25</sup> and compared to bridge-bonded CO. It has been found that linear-bonded CO experience smaller donation and backdonation effects. Hence the conduction electron density on the molecule is reduced compared to bridge-bonded CO and might result in smaller NMR absorption shifts and relaxation rates.

#### IV. CONCLUSIONS

We have determined that on Pd bridge-bonded CO has a  $5\sigma$  character that dominates the line shift and determines the relaxation rate. Since the  $5\sigma$  bonding level lies

well below the Fermi level, the  $5\sigma$ - $d$  antibonding level must lie close to the Fermi level. For linear-bonded CO, the smaller Knight shift shows that there is not much  $5\sigma$  state at the Fermi surface, but the strong conduction electron contribution to the  $^{13}\text{C}$  spin-lattice relaxation rates shows that the  $2\pi^*$  state must have a significant component near the Fermi level. Also, we have found that linear-bonded CO have a weaker interaction with the conduction electrons than bridge-bonded CO in agreement with other experiments and calculations.

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\*Present address: MIT National Magnet Laboratory, NW14/5122, 170 Albany St., Cambridge, MA 02139.

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