NMR Study of the Chemisorption Bond of Carbon Monoxide on Platinum

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The authors report ^{13}C NMR studies of ^{13}CO adsorbed on small Pt particles and show that the data yield quantitative information about the CO-Pt bond. They find that the ^{13}C resonance position is shifted 200 ppm to higher frequency than in CO gas. They prove that the shift arises from polarization of the electron spins in the bond (a Knight shift) by showing that the spin-lattice relaxation obeys the Korringa law. Using ESR results from CO radicals, they deduce the local density of states of the CO 5σ orbital on the carbon atom at the Fermi energy. The NMR also reveals diffusion of CO on the Pt surface.

We report the use of NMR to study the bonding of a simple molecule, CO, to a metallic surface. Using spin-echoes, we observe the position and spin-lattice relaxation of the ^{13}C resonance of ^{13}CO adsorbed on small particles of Pt. Analysis of the NMR results yields quantitative information about the bonding of CO to Pt. We provide a direct demonstration of the mixing of the CO molecular orbitals with the Pt conduction-band states. We also observe the diffusion of the CO on the Pt surface.

Theories of the bonding of atoms or molecules to a metal postulate that in the bonding process the wave functions of the adsorbate mix with the conduction-band wave functions. A single sharp energy level of an isolated atom or molecule may then become smeared in energy, giving rise to a surface scattering resonance.[1] The associated local density of states on the adsorbate atom may be seen by photoemission. As a practical matter, photoemission reveals the adsorbate local density of states near its peak, but cannot follow it close to the Fermi energy. In our work, we find that the bonding imparts a "metallic" character to the Pt-CO bond, leading to a strong shift of the frequency of the ^{13}C NMR from that in CO gas. We show how measurement of the shift enables us to determine the local density of states on the carbon at the Fermi energy.

Our samples consist of small Pt particles supported on η alumina.[2] Their dispersions (fraction of Pt atoms on the surface) have been measured by hydrogen chemisorption[3]: they range from 4% to 76%, corresponding to particles 300 Å down to 10 Å in size. Our samples are cleaned at 300 °C by alternating flows of H_2 and O_2. After evacuation to 10^{-6} Torr, the system is cooled to room temperature and exposed to CO gas enriched to 90% in ^{13}C. CO is removed from the alumina base by pumping to 10^{-6} Torr and the sample is sealed. The coverages (number of chemisorbed CO molecules per surface Pt atom) range from 7.5% to 70% (saturation).

Figure 1 displays the ^{13}CO NMR resonance line of a 76%-dispersion sample with saturation coverage of CO. The area under the spin-echo is plotted versus the frequency shift, σ, relative to the standard reference compound tetramethyl-silane (TMS). Also indicated are the positions of a number of typical ^{13}C resonance lines in diamagnetic substances. As can be seen, the ^{13}CO resonance on Pt is shifted to a higher frequency than its resonance in the gas or in Pt carbonyl molecules by approximately 200 ppm, nearly as large a shift as the entire range of ^{13}C shifts in diamagnetic compounds (240 ppm), and about 160 ppm from the nearest ^{13}C resonance. The position and width of the
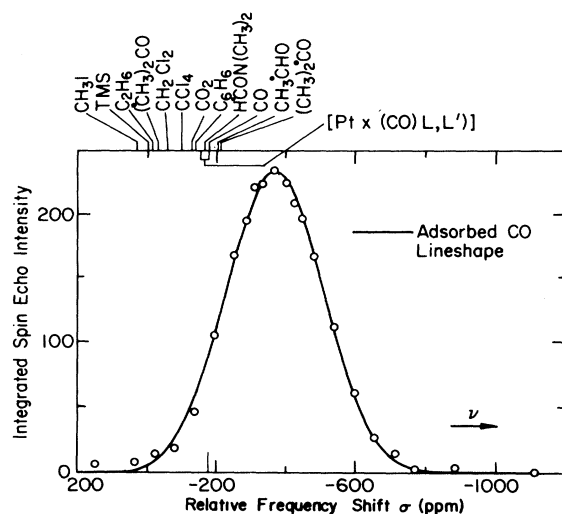

FIG. 1. ^{13}CO line shape: Area under the ^{13}C spin-echo vs frequency shift (σ) relative to tetramethyl silane (TMS) for a 76%-dispersion sample with saturation coverage of CO. $\nu = (1 - \sigma)\nu_{TMS}$, where ν and ν_{TMS} are the ^{13}C NMR resonance frequency of CO and TMS, respectively. [Pt × (CO)L,L'] stands for Pt carbonyls in solution.

resonance is independent of dispersion for dispersions of 4%, 15%, 26%, and 76%, and independent of temperature from 77 to 415 K. The spread among the diamagnetic compounds is the so-called chemical shift which has its origin in orbital magnetization induced in the wave functions of the valence electrons of the different molecules.[4] The size of the shift of ^{13}CO on Pt is so far outside normal chemical shifts that it seems unlikely to be a chemical shift. We are thus led to postulate that it arises from a different mechanism, the polarization of electron spins—a Knight shift such as is found in metals.[4]

An isolated CO molecule has no unpaired electron spins, hence cannot give a Knight shift. However, as mentioned above, in the bonding of atoms or molecules to a surface the wave functions of the adsorbate mix with the conduction-band wave functions, so that a single sharp energy level of an isolated atom or molecule becomes smeared in energy. The associated local density of states on the carbon atom, $\rho_C(E)$, is nonzero for all values of E in the band, including for $E = E_F$. The resultant Knight shift, K, can then be shown to be

$$K = \tfrac{4}{3}(\gamma_e \hbar)^2 |\psi(\mathbf{R}_C)|^2 \rho_C(E_F), \tag{1}$$

where γ_e is the electron gyromagnetic ratio, $\hbar$ is Planck's constant divided by 2π, ψ is the wave function of the bonding orbital, $\mathbf{R}_C$ is the position of the carbon atom, and $\rho_C(E)$ is the density of states of the bonding orbital for a single spin orientation. Existence of a Knight shift thus provides both a demonstration of the mixing between the molecular and metallic wave functions, and a quantitative measure of the product $|\psi(\mathbf{R}_C)|^2 \rho_C(E_F)$.

It is therefore important to determine conclusively whether or not the displacement of the ^{13}CO resonance is a Knight shift. One can do this by NMR. In a metal, the coupling of the conduction-electron-spin magnetic moments to the nuclei not only displaces the NMR frequency (the Knight shift) but also produces a spin-lattice relaxation. One can test for the presence of such a shift by searching for the relaxation that must accompany it. The relationship between the spin-lattice relaxation time T_1 and the Knight shift K has been given by Korringa[5]:

$$T_1 T(K)^2 = (\hbar/4\pi k_B)(\gamma_e/\gamma_n)^2 B, \tag{2}$$

where T is the temperature, k_B is the Boltzmann constant, and γ_e and γ_n are gyromagnetic ratios of the electron and the nucleus, respectively. B is a constant close to unity. Taking $B = 1$, and expressing K in parts per million we get for ^{13}C, $T_1 T(K)^2 = 4.165 \times 10^6$ s K.

According to Eq. (2), T_1 must satisfy the following: (a) it must be independent of the applied field H_0 at which the resonance is observed; (b) it must be proportional to $1/T$; (c) it must yield for K a numerical

value corresponding reasonably well to the observed shifts.

The relaxation of the magnetization is observed by applying a train of spin-echo pulses. A steady-state echo signal is achieved which depends on how the time between the successive spin-echoes in the train compares with the spin-lattice relaxation time T_1. Figure 2 shows the steady-state echo height versus the time between successive echoes. A theoretical curve corresponding to relaxation characterized by a single exponential process with $T_1 = 150$ msec is shown in Fig. 2 as a solid black curve. The data at 77 K [Fig. 2(a)] do not correspond to a single exponential, indicating a distribution in relaxation rates. Nevertheless, the data at an applied field of 54 kG (solid crosses) superpose exactly on the data at 83 kG (open circles) showing that the relaxation rate is independent of H_0. The relaxation becomes exponential above 290 K [Fig. 2(b)]. We believe this change arises from the averaging out of the distribution of relaxation rates by diffusion of CO over the Pt surface. Diffusion is further confirmed by the observation of motional narrowing of our ^{13}C lines at higher temperatures. The diffusion rates required are consistent with the results of Gomer and Lewis obtained by field emission electron microscopy.[6] Since the relaxation above 290 K is characterized by a single relaxation time, T_1, we can compare its temperature dependence with the Korringa relation-
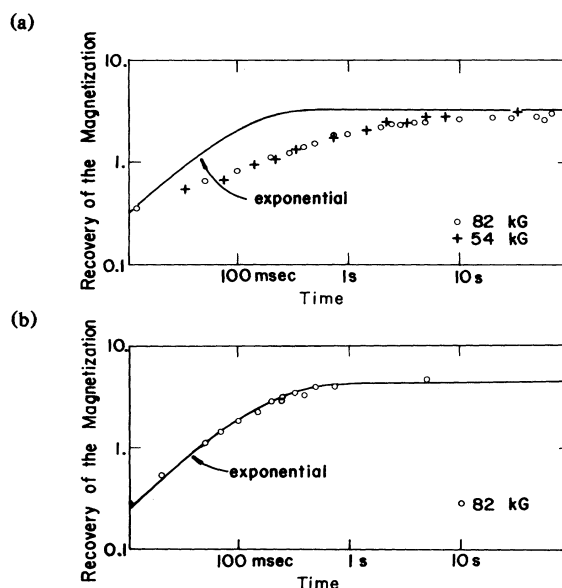

FIG. 2. ^{13}CO signal strength vs time between pulses for 76%-dispersion sample with saturation coverage of CO. (a) Signal at 77 K at static fields of 54 kG (pluses) and 82 kG (circles). The solid curve represents exponential recovery with a single relaxation time of 150 ms. (b) Signal at 321 K and 82 kG demonstrating that at this temperature the recovery is exponential (single relaxation time).

ship. In Fig. 3 we plot $1/T_1$ versus temperature. The product $T_1 T$ is indeed a constant, in agreement with the Korringa relationship. We find $T_1 T = 46$ s K.

The fact that there is a distribution of relaxation times implies that there is a distribution of Knight shifts: $\langle K^2 \rangle = \langle K \rangle^2 + \langle \Delta K^2 \rangle$ where $\langle K \rangle$ is the first moment of the distribution, and $\langle \Delta K^2 \rangle$ the second moment relative to the average shift (a line-broadening contribution). Taking $B = 1$, we get $\langle K^2 \rangle^{1/2} = 300$ ppm. For reasonable estimates of $\langle \Delta K^2 \rangle$ from the spread in relaxation rates, one obtains $\langle K \rangle$ of the order 100 to 200 ppm, agreeing with the experimentally observed displacement (200 ppm from Pt carbonyl molecules). Spin-lattice relaxation of ^{13}CO thus satisfies all three conditions required by the Korringa relationship and gives strong confirmation that the displacement is indeed a Knight shift. We therefore demonstrate the mixing of the CO orbitals with the conduction band. The fact that the shift is independent of dispersion from 4% to 76% suggests that the Pt wave functions of importance in the bond at E_F are insensitive to the interior regions of the metal, in agreement with the earlier finding that the position of the NMR of the surface layer of Pt atoms is also independent of dispersion.[2]

As shown in Eq. (1), the measured Knight shift yields the product $|\psi(\mathbf{R}_C)|^2 \rho_C(E_F)$, and hence gives information about the bond. Two orbitals of the CO molecule are of prime importance in discussing binding, the so-called 5σ orbit (the highest-energy orbit occupied in the free molecule) and the $2\pi^*$ orbit (the lowest-lying empty orbit in the free molecules).[7] The values of $|\psi(\mathbf{R}_C)|^2$ for the 5σ and $2\pi^*$ orbits may be estimated from the hyperfine splitting of the electron spin resonance lines of CO radicals arising from the coupling between the ^{13}C nuclei and the electron spin.[8] The isotropic hyperfine coupling gives a magnetic field splitting, ΔH, of the ESR line of

$$\Delta H = \tfrac{8}{3} \pi \gamma_n \hbar |\psi(\mathbf{R}_C)|^2. \tag{3}$$
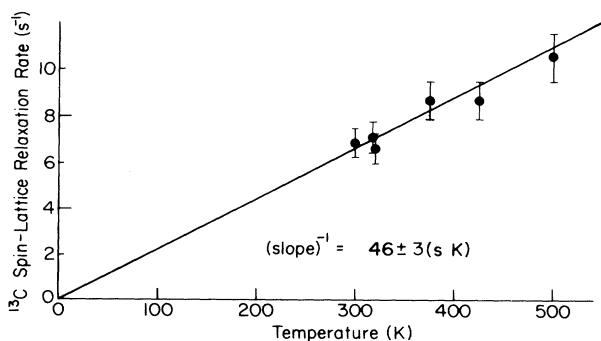

FIG. 3. Spin-lattice relaxation rate, $1/T_1$, vs temperature, T, demonstrating that $T_1 T = \text{const}$ $(46 \pm 3$ s K$)$ in agreement with the Korringa relation.

Vedrine and Naccache have observed the ^{13}C hyperfine splitting of CO^+ corresponding to an unpaired electron in the 5σ orbital.[9] They find $\Delta H = 277$ G. Lunsford and Jayne have observed an ESR which is evidently a CO^- radical, and which gives for the $2\pi^*$ orbital a ΔH of 13 G.[10] Combining Eqs. (1) and (3), we deduce that for a Knight shift of 200 ppm, $\rho_C(E_F) = 0.048$ state/eV if the Knight shift arises from the 5σ state, or 1.0 state/eV if it arises from a $2\pi^*$ state.

To select between these two possibilities, we need to review what is known about the two states. Photoemission from the 5σ orbit of CO adsorbed on Pt surfaces has been seen to have its peak about 9 eV below the Fermi level, but the tails of the 5σ photoemission cannot be followed all the way to the Fermi energy since they are obscured by much larger changes in the Pt contribution to photoemission produced by adsorption of the CO.[11] However, were the 5σ density of states uniform from the observed peak to E_F, the corresponding $\rho_C(E_F)$ would be 0.11 state/eV. Thus a measured value of 0.04 state/eV is not unreasonable.

In principle, the $2\pi^*$ level can be seen by inverse photoemission. To explain a $\rho_C(E_F)$ of 1.0 state/eV would require an inverse photopeak 1 eV or less in width located at the Fermi energy. Though the experiment has not been done for CO on Pt, it has been completed for CO adsorbed on Ni(111) surfaces and Pd(100) surfaces.[12] The $2\pi^*$ level lies several electronvolts above E_F and is several electronvolts wide, thus having a $\rho_C(E_F)$ much less than 1.0 state/eV. It seems highly unlikely that the $2\pi^*$ state of CO on Pt can account for such a $\rho_C(E_F)$.

We conclude that the Knight shift probably arises from the 5σ level so that our experiment gives the local density of states, $\rho_C(E_F)$, for the 5σ orbital. The result complements the photoemission data which reveal the form of $\rho_C(E)$ far from E_F.

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[1]An excellent review of the theory of bonding to surfaces which also includes a good list of basic references is J. Robert Schrieffer and Paul Soven, Phys. Today **28**, 24 (1975).

[2]A description of studies of the ^{195}Pt resonance for the Pt-CO system, together with references to our other work on Pt, can be found in C. D. Makowka, C. P. Slichter, and J. H.

Sinfelt, Phys. Rev. Lett. **49**, 379 (1982).

[3]J. H. Sinfelt, Prog. Solid State Chem. **10**, 55 (1975).

[4]Charles P. Slichter, *Principles of Magnetic Resonance* (Springer-Verlag, New York, 1980), 2nd ed., corrected second printing, Chap. 4.

[5]J. Korringa, Physica (Utrecht) **16**, 601 (1950).

[6]R. Lewis and R. Gomer, Nuovo Cimento 5, Suppl. 2, 506 (1967).

[7]G. Blyholder, J. Phys. Chem. **68**, 2772 (1964). Also see *The Nature of the Surface Chemical Bond,* edited by T. N. Rhodin and G. Ertl (North-Holland Amsterdam, 1979).

[8]Charles P. Slichter, *The Nature of the Surface Chemical Bond,* edited by T. N. Rhodin and G. Ertl (North-Holland, Amsterdam, 1979), p. 308.

[9]J. C. Vedrine and C. Naccache, Chem. Phys. Lett. **18**, 190 (1973).

[10]J. H. Lunsford and J. P. Jayne, J. Chem. Phys. **44**, 1492 (1966).

[11]J. N. Miller, D. T. Ling, P. M. Stefan, D. L. Weissman, M. L. Shek, I. Lindau, and W. E. Spicer, Phys. Rev. B **24**, 1917 (1981).

[12]F. J. Himpsel and T. H. Fauster, Phys. Rev. Lett. **49**, 1583 (1982); J. Rogozik, J. Kuppers, and V. Dose, to be published.