FEATURE ARTICLE

NMR of Electrocatalysts

Y. Y. Tong,[†] A. Wieckowski,* and E. Oldfield*

Department of Chemistry, University of Illinois at Urbana-Champaign, 600 South Mathews Avenue, Urbana, Illinois 61801

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It is now possible to investigate in detail metal/liquid interfaces by solid-state NMR under external potentiostatic control, in the presence of an electrolyte, by using the electrochemical NMR (EC NMR) technique. This permits the determination of the electronic properties of electrodes and of adsorbates as well as the study of the surface diffusion of adsorbates. The method also provides useful information on the dispersion of platinum fuel cell catalysts, on electrochemically generated sintering effects, and on the electronic effects caused by the presence of different surface adatoms. In general, EC NMR provides information on the following: (1) metal surface; (2) adsorbate structure/bonding details, such as 5σ and $2\pi^* E_f$ LDOS, metal-surface bonding to atoms in the adsorbate, and even bond lengths; (3) rates and activation energies for surface diffusion; and (4) electrode potential effects on the electronic properties of the electrochemical interface, as seen by both metal and ligand NMR. We review here, therefore, the current status of the EC NMR technique, together with its applications to investigating the metal/electrolyte interface.

I. Introduction

Access to atomic/molecular level information at surfaces or interfaces is essential in order to understand the critical roles they play in many areas of science and technology, especially in heterogeneous catalysis. Here, nanoparticles are of great interest because they have very high surface areas and therefore high specific activity. For example, a 2.5 nm particle has approximately half of its total number of atoms on the surface. Such surfaces are generally not amenable to investigation using electronic or ionic spectroscopies, and consequently, the recently developed technique of electrochemical NMR (EC NMR) spectroscopy is becoming a powerful technique with which to investigate such materials.^{1,2}

While NMR has a very low mass detection sensitivity, it is, nevertheless, an excellent method for investigating the surfaces and interfaces of the high-surface-area materials used in real-world applications and indeed has been used industrially to study systems such as clays, silicas and zeolites, beginning in the early 1950s.^{3,4} These early studies focused on adsorption and were followed by many more extensive investigations of both adsorption and diffusion in zeolites^{5,6} and by numerous studies of the effects of metals aimed at furthering our understanding of catalytic activity in heterogeneous systems.^{7–10} Technically, a typical high-field NMR instrument needs $\sim 10^{18} - 10^{19}$ NMR active atoms, for example, ¹⁹⁵Pt or ¹³C spins, to make a signal detectable within a reasonable time period (several hours). A 1

cm² sample of a single crystal metal surface contains only about 1015 atoms. So a surface area of at least 1 m² of NMR active atoms is needed to meet the sensitivity requirement, but this is really no impediment since high-surface-area materials are of practical importance and there are typically no sample availability limitations. NMR is also an ideal tool with which to investigate static, dynamic, and electronic structure at interfaces.^{11,12} Most catalyst materials are also "transparent" to NMR; that is to say, NMR can easily access buried surfaces/interfaces in most nanoscale catalysts-metal powders, oxide-supported metal catalysts, or carbon-supported catalysts, unlike optical and charged particle probe techniques. In addition, it is a nondestructive technique and can be applied under technically demanding environmental conditions close to real-world operating conditions; i.e., it permits detailed in situ investigations. As an example, it is possible to use EC NMR to investigate graphite-supported metal catalysts in an electrochemical environment under potential control.¹ Given adequate mass sensitivity then, NMR has an unique ability to provide a wealth of electronic and structural information at the atomic/molecular level, and in addition, NMR is well-known to permit access to motional information over a time span unattainable by any other spectroscopic technique. As a result, NMR of oxide-supported metal catalysts has played a key role in the development of many fundamental aspects of gas-phase heterogeneous catalysis at transition metal surfaces 12-16 and the techniques developed can now be adapted to the electrochemical environment.^{1,2,17,18} However, interfacing solid-state NMR with interfacial electrochemistry is a little more challenging than standard "gas-phase"

^{*} Corresponding authors.

[†] Present address: Department of Chemistry, Georgetown University, 37th & "O" Streets, Washington, DC 20057-1227.



Figure 1. ¹³C NMR spectra of CO adsorbed on a 10 nm Pt electrocatalyst, recorded at room temperature and at (A) 14.1 T with 1600 scans and (B) 8.5 T with 2000 scans. The S/N ratios are ca. 50:1 and 10:1, respectively.

techniques because of the basic incompatibility between NMR detection and the conduction requirements for electrode function. That is, the presence of conducting material in the NMR detection coil greatly degrades the so-called "quality factor" of the NMR probe, which substantially decreases sensitivity. Nevertheless, the advantages of interfacing in situ solid-state NMR with electrochemistry are many. For example: NMR gives a direct probe of the Fermi level local densities of states for both adsorbate and substrate; structure and bonding in an electrochemical environment can be investigated by using a variety of NMR interactions; surface dynamics can be readily probed; and, of course, the effects of potential control can be investigated in working electrochemical systems-even where the adsorbates (such as CN or NO on Pt) would be very difficult to handle in conventional gas phase or dry systems. Furthermore, by using high magnetic fields and high-surface-area electrode materials, the current state-of-the-art signal detection sensitivity is in fact quite reasonable and permits the routine acquisition of NMR spectra of surface species. As an example, we show in Figure 1 ¹³C NMR spectra of ¹³CO chemisorbed onto a 10 nm Pt sample having a CO coverage of about 0.8, recorded at room temperature and in (A) 14.1 and (B) 8.5 T magnetic fields. The numbers of scans were 1600 and 2000, and the S/N ratios (after using a 1 kHz line broadening) were 50:1 and 10:1, respectively, showing a significant S/N enhancement in the higher magnetic field. Sensitivity is also greatly enhanced at lower temperatures, where ¹³C NMR spectra can be recorded in as little as 10 min. For observing metal NMR signals, sensitivity is worse due to the extremely broad (MHz) line widths, the reasons for which we now describe.

II. Theoretical Principles

Metal NMR: the Knight Shift, the Korringa Relationship, and the Fermi Level Local Density of States. In electrochemistry, electrodes are of course an indispensable part of the electrical circuit, so the EC NMR of electrode surfaces has to deal with metallic systems. In NMR in general, a specific frequency shift with respect to a well-defined reference corresponds to a specific chemical environment (a structure).¹¹ In metal NMR, things are a little more complex in that the familiar "chemical" (or orbital) shift is usually overwhelmed by another interaction, due to the influence of conduction electrons.

The total NMR shift is determined by the Hamiltonian of the nuclear-electron hyperfine interaction, which can be written for a nuclear spin $I = \frac{1}{2}$ (as for ¹⁹⁵Pt, for example, or ¹³C in a "metallic" state) as

$$H = \gamma_{\rm n} \hbar \mathbf{I} \cdot \mu_{\rm B} \left\{ \frac{8\pi}{3} \mathbf{S}(\mathbf{r}) \cdot \delta(\mathbf{r}) - [\mathbf{S}/r^3 - 3\mathbf{r}(\mathbf{S} \cdot \mathbf{r})/r^5] - \mathbf{l}/r^3 \right\}$$
(1)

where $\mu_{\rm B}$ is the Bohr magneton and $\gamma_{\rm n}$ is the nuclear gyromagnetic ratio. I, S, and I are the nuclear spin, electron spin, and electron orbital moment operators, respectively. The symbol r is the radius vector of an electron with respect to the nucleus at the origin. The first term in the brace in eq 1 is the Fermi contact term, the second (square bracket) is the dipole term, and the third (l/r^3) is due to the orbital movement of surrounding electrons. In a magnetic field, the third term generates the orbital magnetism which is the origin of the familiar chemical shift $(\delta_{\rm CS})$, while the first term causes the electron spin magnetism which is the origin of the Knight shift (K). The orbital magnetism, or the chemical/orbital shift, exists in all sorts of materials, be they gaseous, liquid, or solid, and arises from the shielding of the external magnetic field at the nucleus by the otherwise quenched orbital angular momentum of the surrounding electrons. However, spin magnetism is primarily found in metallic or paramagnetic systems and is produced by the nonzero magnetic interactions between the nuclear and electron spins. The second (dipolar) term normally contributes to relaxation, but not to the shift, since the trace of the operator is zero.

To probe things in a little more detail, we need to briefly consider the classical theory of spin magnetism in nonmagnetic metals. This is the theory of Pauli paramagnetism,¹⁹ which explains the temperature-independent spin susceptibility. Its physical origin is that only electron spins at the Fermi energy can be polarized and thus create a nonzero spin density in an external magnetic field. Therefore, the Knight shift is metalspecific. In addition, the Korringa relationship,²⁰ which governs the nuclear spin-lattice relaxation in metals, is also metalspecific. The Korringa relationship²⁰ indicates that $1/T_1 \propto T$, where T_1 is the spin-lattice relaxation time and T is the absolute temperature of the sample. This unique temperature dependence is the NMR fingerprint of the metallic state. It results from the fact that only conduction electrons around the Fermi level can satisfy energy conservation for the electron-nuclear spin "flipflop" relaxation process, and the fraction of these electrons is proportional to $k_{\rm B}T$. The Knight shift and the Korringa relation therefore represent the two principal NMR probes of electronic structure in metals and of molecules bonded to the surfaces of metals.

The formal theory of metal NMR has been established within the framework of a generalized magnetic susceptibility.²¹ The complex generalized electron spin susceptibility is defined as

$$\chi(\mathbf{r},\mathbf{r}';\omega) = \chi'(\mathbf{r},\mathbf{r}';\omega) - i\chi''(\mathbf{r},\mathbf{r}';\omega)$$
(2)

It describes a magnetic response function of the metal at position \mathbf{r} to a time-varying magnetic field $\mathbf{H}(\mathbf{r}') \cos(\omega t)$ applied at position \mathbf{r}' , such that the spin magnetization $\mathbf{M}(\mathbf{r}; t)$ can be expressed as

$$\mathbf{M}(\mathbf{r};t) = \cos(\omega t) \int_{\text{sample}} \chi'(\mathbf{r},\mathbf{r}';\omega) \mathbf{H}(\mathbf{r}') \, \mathrm{d}\mathbf{r}' + \\ \sin(\omega t) \int_{\text{sample}} \chi''(\mathbf{r},\mathbf{r}';\omega) \mathbf{H}(\mathbf{r}') \, \mathrm{d}\mathbf{r}'$$
(3)

Formally, the static uniform susceptibility $\overline{\chi'}$, the Knight shift K, and the spin-lattice relaxation rate T_1^{-1} can all be expressed in terms of $\chi(\mathbf{r},\mathbf{r'};\omega)$ in the limit $\omega \rightarrow 0$:

$$\overline{\chi'} = V^{-1} \int_{\text{sample}} \int \chi'(\mathbf{r}, \mathbf{r}'; 0) \, \mathrm{d}\mathbf{r} \, \mathrm{d}\mathbf{r}' \tag{4}$$

$$K(\mathbf{R}) = \frac{2}{3} \int_{\text{sample}} \chi'(\mathbf{R}, \mathbf{r}'; 0) \, d\mathbf{r}' = \frac{2}{3} \int_{\text{sample}} \chi'(\rho = \mathbf{R} - \mathbf{R}_{\alpha}, \mathbf{r}'; 0) \, d\mathbf{r}'$$
(5)

$$T_1^{-1} = 2\mu_0 kT \left(\frac{2\gamma_e}{3}\right)^2 \frac{\chi''(\mathbf{R}, \mathbf{R}; \omega_{\rm S} - \omega_{\rm I})}{\omega_{\rm S} - \omega_{\rm I}} \tag{6}$$

where *V* is the sample volume, **R** is the position of the nucleus, \mathbf{R}_{α} is the Bravais lattice vector, γ_{e} is the electron gyromagnetic ratio, ω_{S} is the electronic, and ω_{I} is the nuclear Larmor frequency. If χ'' is temperature independent, then so is the product $T_{1}T$. In the Pauli approximation, eq 6 leads to the original Korringa relation²⁰ (for single band, s-type metals):

$$K^{2}T_{1}T = (\gamma_{e}/\gamma_{n})^{2}(h/4\pi k_{B}) = S$$
(7)

Here, $k_{\rm B}$ is the Boltzmann constant. Also, the ratio between the Knight shift and the static uniform susceptibility defines the hyperfine field, $\mathbf{H}_{\rm hf}(\rho)$:

$$K(\rho) = \frac{\Omega \chi'}{\mu_0 \mu_{\rm B}} \mathbf{H}_{\rm hf}(\rho) = \mu_{\rm B} \mathbf{H}_{\rm hf}(\rho) D(E_{\rm f};\rho)$$
(8)

where Ω is the atomic (Wigner-Seitz) volume, $\mu_{\rm B}$ is the Bohr magneton, and $D(E_{\rm f};\rho)$ is the Fermi level local density of states ($E_{\rm f}$ LDOS). In bulk metals having translational symmetry, the $D(E_{\rm f};\rho)$ is a constant over the whole space. These two equations, eqs 7 and 8, give the basis for the determination of $D(E_{\rm f};\rho)$ from NMR determinations of the Korringa relationship and the Knight shift.

For systems having more than one band which cuts the Fermi level, as with transition metals or chemisorbed CO, it is useful to break down the total E_f LDOS into two contributions of different symmetry. Under certain approximations, a general formalism can be established because any Bloch function can be expanded into a set of local Wannier functions and the latter can be approximated by local (l = s, p, d...) atomic orbitals.¹⁹ So the static uniform susceptibility, the Knight shift of the nuclear spin at the origin, and its relaxation rate can all be expressed as a sum of different *l,m*-like parts

$$\overline{\chi'} = \frac{\mu_0 {\mu_{\rm B}}^2}{\Omega} \sum_l \sum_{m=-l}^l \frac{D_{lm}(E_f)}{1 - \alpha_l} = \sum_{lm} \overline{\chi'_{lm}}(9)$$
(9)

$$K(\rho = 0) = \sum_{lm} \overline{\chi_{lm}}' \frac{\Omega \mathbf{H}_{hf,l}(0)}{\mu_0 \mu_{\rm B}} = \sum_{lm} K_{lm}(0)$$
(10)

$$S(T_1 T)^{-1} = \sum_{lm} k_l K_{lm}^2$$
(11)

Here, χ_{lm}' and K_{lm} are, respectively, the partial susceptibility and the Knight shift; $\alpha_l = I_l D_l(E_f)$ is the *l*-like Stoner enhancement factor with respect to its Pauli counterpart, where I_l is the *l*-like exchange integral; $\mathbf{H}_{hf,l}$ is the effective *l*-like hyperfine field, which can be nonzero (and negative) for $l \neq 0$, due to core-polarization; and k_l are the so-called "de-enhancement factors" for spin-lattice relaxation.

For transition metals, only contributions from s, p, d orbitals need to be considered, and generally, the s and p contributions are combined into one s-like term. Specifically, for ¹⁹⁵Pt NMR, one has²¹

$$K = K_{\rm s} + K_{\rm d} + K_{\rm orb} = \frac{\Omega}{\mu_0 \mu_{\rm B}} (\overline{\chi_{\rm s}'} \mathbf{H}_{\rm hf,s} + \overline{\chi_{\rm d}'} \mathbf{H}_{\rm hf,d} + \chi_{\rm orb} \mathbf{H}_{\rm hf,orb}) = \mu_{\rm B} D_{\rm s}(E_{\rm f}) \frac{\mathbf{H}_{\rm hf,s}}{1 - \alpha_{\rm s}} + \mu_{\rm B} D_{\rm d}(E_{\rm f}) \frac{\mathbf{H}_{\rm hf,d}}{1 - \alpha_{\rm d}} + \chi_{\rm orb} \frac{\mathbf{H}_{\rm hf,orb}}{\mu_{\rm B}}$$
(12)

$$S(T_{1}T)^{-1} = k(\alpha_{s})K_{s}^{2} + k(\alpha_{d})K_{d}^{2}R_{d} + (\mu_{B}D_{d}(E_{f})\mathbf{H}_{hf,orb})^{2}R_{orb}$$
(13)

$$k(\alpha) = (1 - \alpha)(1 + \alpha/4)$$
 (14)

In these equations, $\mathbf{H}_{hf,orb}$ is the orbital hyperfine field, which determines the familiar chemical shift; $D_s(E_f)$ and $D_d(E_f)$ are the separate s- and d-like densities of state at the Fermi level; the de-enhancement factor $k(\alpha)$ adopts a polynomial Shaw-Warren form for both s- and d-like contributions;²² and R_d and R_{orb} are the reduction factors due to orbital degeneracy at the Fermi level:^{22,23}

$$R_{\rm d} = \left[\frac{f^2}{3} + \frac{(1-f)^2}{2}\right]$$
 and $R_{\rm orb} = \frac{2f}{3}\left(2 - \frac{5f}{3}\right)$ (15)

where f = 0.7 is the relative weight of the t_{2g}- and e_g-type d-orbitals at the Fermi energy.

It is important to note that several approximations have been made in order to derive eqs 12-14. First, it is assumed that the exchange integral I_l and the hyperfine field $\mathbf{H}_{hf,l}$ are properties of an atom in its atomic volume (the Wigner-Seitz cell) and to zero order, they do not change when the atomic volume is put into a different (chemical) environment, even in systems (such as surfaces and small particles) which lack translational symmetry. The changes in the NMR observables are assumed to be brought about only by changes in the $E_{\rm f}$ LDOS's. Second, it is assumed that the partition between the t_{2g} - and e_g -type d-orbitals at the Fermi energy, the f factor in eq 15, is also a constant. Third, there is still no reliable way to calculate the effective Stoner enhancement factors α_l and the exact form of the deenhancement factors k_l are also unknown. In practice, the hypothesis is made that k_l can take some form $k(\alpha)$ obtained from theoretical models developed for simple metals, i.e., $k_l =$ $k(\alpha_l)$. In eqs 12 and 13, the Shaw-Warren polynomial relation,²² eq 14, is adopted. This hypothesis is ad hoc and has little fundamental justification; however, the formalism leads to a good description of the data for bulk Pt as well as bulk Pd and has been used extensively for investigating both wet and dry small particle catalysts.

For chemisorbed CO, similar formalisms have been employed since metal–CO bonding produces 5σ and $2\pi^*$ bands in the CO molecules,²⁴ and this is, in a formal sense, the same as the two-band (d,s-like E_f LDOS) model for the metals. For ¹³C, we thus have

$$K = K_{5\sigma} + K_{2\pi^*} + K_{\text{orb}} = \mu_{\text{B}} D_{5\sigma}(E_{\text{f}}) \frac{\mathbf{H}_{\text{hf},5\sigma}}{1 - \alpha_{5\sigma}} + \mu_{\text{B}} D_{2\pi^*}(E_{\text{f}}) \frac{\mathbf{H}_{\text{hf},2\pi^*}}{1 - \alpha_{2\pi^*}} + K_{\text{orb}}$$
(16)

$$S(T_1T)^{-1} = k(\alpha_{5\sigma})K_{5\sigma}^{2} + k(\alpha_{2\pi^*})K_{2\pi^*}^{2}/2 + (13/5)[\mu_{\rm B}D_{2\pi^*}(E_{\ell})\mathbf{H}_{\rm hf orb}]^2 (17)$$

TABLE 1: Parameters Used for E_f LDOS Analysis

	<i>K</i> _{orb} (ppm)	$I_{s/5\sigma}$ (Ry) ^a	$I_{\mathrm{d}/2\pi^*}$ (Ry) ^a	$\mathbf{H}_{\mathrm{hf,s/5}\sigma}$ (kG)	$\begin{array}{c} \mathbf{H}_{\mathrm{hf},\mathrm{d}/2\pi^{*}} \\ \mathrm{(kG)} \end{array}$	H _{hf,orb} (kG)
¹⁹⁵ Pt ^b	2100	0.098	0.037	2700	-1180	1180
¹³ CO ^b	160	0.086	0.078	363	17	50

^{*a*} 1 Ry = 1 Rydberg = 13.6 eV. ^{*b*} For more details see ref 41 for Pt and ref 24 for CO.

Here again, $\alpha_l = I_l D_l(E_f)$ and the $k(\alpha_l)$ $(l = 5\sigma \text{ and } 2\pi^*)$ are from the Shaw-Warren relation, eq 14. In eqs 12, 13 and 16, 18, only the $D_l(E_f)$ are unknowns. The other hyperfine parameters are constants and are shown in Table 1. So by experimentally measuring *K* and $S(T_1T)^{-1}$ (for the metal or the ligand) and by solving two equations for two unknowns, 5σ and $2\pi^*$ $D(E_f)$ can be deduced for the ligand, as can the s- and d-like metal $D(E_f)$.

It is important to note that many metallic properties, such as the Knight shift and the Korringa relationship, are determined by the finite and quasicontinuous nature of the $E_{\rm f}$ LDOS. In more chemical terms, this means is that the HOMO–LUMO gap in metals is much smaller than the thermal energy $k_{\rm B}T$ and the value of the $E_{\rm f}$ LDOS reflects the frontier orbital contributions in a metallic system.²⁵ The $E_{\rm f}$ LDOS also represents an important metal surface attribute which can serve as a conceptual bridge between the delocalized band structure (physics) picture and the localized chemical bonding (chemical) picture of metal– adsorbate interactions. In particular, the local electronic information it carries is quite different from the overall density of states and appears to be more relevant to describing the catalytically active surface sites.

Diffusion: Strong versus Weak Collisions. In addition to determination of the chemical and/or Knight shift and the spinlattice relaxation times in the laboratory frame (T_1) , there is another important NMR observable: the spin-spin relaxation time (T_2) . While the chemical and/or Knight shift contains essentially static structural information, the temperature and/or magnetic field dependence of the relaxation times (both T_1 and T_2) are related to the dynamics of the observed nucleus. T_1 measures the rate at which the spin system returns to thermal equilibrium with its environment (the lattice) after a perturbation, while T_2 measures the rate of achieving a common spin temperature within the spin system. Both T_1 and T_2 provide important information on motions, which can cover the time scale from $\sim 10^{-9}$ to 10^2 s. Moreover, the temperaturedependence of these motions provides thermodynamic information in the form of activation energies for (ligand) motion on the catalyst surface, which in some cases may be related to catalytic activity.

The rationale behind using NMR to study surface diffusion is that the correlation time for diffusion, τ , can be related to the temperature dependence of the NMR relaxation rates observed for diffusing atoms or molecules.^{11,12} Under certain circumstances, such a relationship can be expressed analytically, permitting a quantitative analysis of the data in dynamic and thermodynamic terms.

When using the temperature dependence of the nuclear spinspin or nuclear spin-lattice relaxation rate to study molecular motion, as with the surface diffusion we are interested in, there exist so-called "strong" and "weak" collision limits. Different mathematical relationships are needed to describe these limits. Consider the nuclear spin-spin relaxation rate $(1/T_2)$ (as measured by a conventional Hahn-echo pulse sequence) and suppose that $\Delta \omega$ is the amplitude of the local field fluctuation responsible for relaxation. Also assume that τ is the correlation time for the motion, say a jump, which causes the local field to fluctuate. The strong collision limit is defined such that $\tau \gg 1/\Delta\omega$. At t = 0, that is, just after the first $\pi/2$ pulse which flips all nuclear spins into the *xy* plane, all spins are in-phase, and they retain their phase memory until $t = \tau$, when the collision changes the direction of the local field. Since τ is sufficiently long to dephase the spins, they lose all phase memory before the next collision. Therefore, $1/T_2 = 1/\tau$. In contrast, in the weak collision limit, $\tau \ll 1/\Delta\omega$. Since τ is relatively short, insufficient dephasing builds up between consecutive jumps. When the spin jumps randomly, many jumps are needed in order to accumulate sufficient dephasing, and one has $1/T_2 = (\Delta\omega)^2\tau$. We therefore have two limiting cases:

$$1/T_2 = 1/\tau$$
 for $\tau \gg 1/\Delta\omega$ (18)

and

$$1/T_2 = (\Delta \omega)^2 \tau$$
 for $\tau \ll 1/\Delta \omega$ (19)

Fortunately, the function

$$1/T_2 = (\Delta \omega)^2 \tau / (1 + (\Delta \omega)^2 \tau^2)$$
(20)

satisfies both limiting cases. In fact, eq 20 is similar to the typical spectral density function used for a randomly fluctuating local field at a frequency $\Delta \omega$, and as we show below, the use of these simple relations leads to information on both the rates of surface diffusion, and their associated energetics. Similar reasoning also applies to spin-lattice relaxation processes, however, the frequency defining the weak and strong collisions is now the nuclear Larmor frequency.

III. EC NMR Methods

Two types of EC NMR experiment have been carried out: electrode potential dependent studies of an adsorbate (13CO, ¹³CN) at room temperature^{17,26,27} and temperature dependence studies of an adsorbate^{24,28} and of platinum electrocatalysts^{29,30} down to 10 K. For all of the EC NMR measurements, the electrode materials, either polycrystalline platinum black or carbon-supported commercial fuel cell grade platinum electrodes, were immersed in a supporting electrolyte, typically 0.5 M H₂SO₄. For temperature dependence studies, EC NMR samples were prepared in a conventional three electrode flow cell with oxygen-free N₂ or Ar as a protecting gas, then together with supporting electrolyte and under the protection of oxygenfree N₂ or Ar, were transferred into a pre-cleaned glass ampule and flame-sealed. The potential drift of a sample in a conventional three-electrode-cell, in an oxygen free environment, is only a few millivolts over 12 h. The same observation holds after transferring the electrode material from the NMR ampule back into the cell. These observations suggest that surface potentials do not change significantly once a sample is sealed (and do not change at all when the sample is frozen).

For room-temperature electrode-potential-dependence studies, we have incorporated an electrochemical cell inside an NMR probe.²⁶ This permits running NMR measurements while a (variable) external electrode potential is applied. Figure 2 shows a real probe as well as a schematic diagram of the setup. The working electrode material was loosely packed in the cell, which was placed inside an NMR coil and electrical connection to an external circuit (potentiostat) made by inserting a Pt wire into the sample. A very similar setup has also been developed by the Lausanne group.^{17,27} Our cell design permits both electrochemical sample preparation and characteriza-



Figure 2. Schematic diagram and picture of an EC NMR probe and its circuitry, showing the interface between NMR and electrochemistry.

tion (voltammetry) and NMR data acquisition under active potential control, avoiding sample transfer from the preparative electrochemical cell. A very important technical issue here is that while the potentiostat is on, there is considerable "noise" injected into the NMR probe, since the potentiostat leads act as excellent "antennas" right inside the NMR coil! This noise has to be removed by using extensive electronic filtering of the electrochemical leads entering the probe to eliminate external radio frequency pickup. The low-pass filter circuit elements $L_{counter}C_{counter}$, $L_{ref}C_{ref}$, and $L_{wk}C_{wk}$ in Figure 2 were designed for this purpose; plus, they serve a second purpose of acting as a high impedance to the rf pulses from the NMR spectrometer. These are typically ~1 kW and may be incompatible with long potentiostat life.

Another interesting type of EC NMR setup has been developed by the Berkeley group to investigate ¹³CO adsorption from the gas phase onto a carbon-supported platinum electrocatalyst.^{2,31} In their system, platinum electrocatalyst was pressed into a graphitized carbon cloth which was then cut into pieces and stacked into a cylindrical form which fits snugly into the cell's compartment. To reduce degradation in the quality factor of the NMR coil due to the presence of bulk electronic or ionic conductivity, the electrode layers were also alternately sandwiched with nonconductive fiberglass cloth. All the electrode layers were individually stitched with gold wire and were then connected to each other and to the external potentiostat. Cyclic voltammograms of high quality are obtained by using both types of EC NMR cell.

IV. Results

¹⁹⁵Pt NMR of Carbon-Supported Electrocatalysts: Layer Model, Dispersion, and a Potential-Scan-Generated Sintering Effect. ¹⁹⁵Pt NMR has been a tremendously successful probe of Pt metal surface properties. Work in this area began in the 1980s when Slichter, Sinfelt, and co-workers discovered several unique features of the ¹⁹⁵Pt NMR of oxide-supported small platinum particles.³² They found that the overall ¹⁹⁵Pt NMR line shape was extremely broad, extending downfield some 4 kG from the position of bulk platinum (1.138 G/kHz), and contained a feature on the low-field side (1.089 G/kHz) which arose from the oxidized Pt surface atoms. Later on, van der Klink and coworkers confirmed these observations, finding that the signal from clean-surface Pt atoms was centered at 1.100 G/kHz,33 a position clearly very different from the 1.138 G/kHz bulk position (the frequency difference is magnetic field dependent and is about 2.5 MHz in a field of 8.5 T). Interestingly, the clean metal surface atoms had close to a zero Knight shift. This observation can be explained, however, by the results of theoretical calculations on a five-layer Pt (001) cluster³⁴ carried out by Weinert and Freeman. Their results demonstrated that the surface shift must be due to a gradual drop in the d-like Fermi level local density of states on moving from the inside of the particle to the surface and that the cancellation between positive s-like and negative d-like electronic contributions to the Knight shift, eq 12, cause the overall Knight shift to be close to zero. It is this distinguishable surface signal which makes ¹⁹⁵Pt NMR unique in investigating the surface physics and chemistry of nanoscale platinum particles.

It is also of great interest that conductive carbon-supported nanoscale platinum electrodes retain quite closely the ¹⁹⁵Pt NMR spectral characteristics of isolated small platinum particles supported on oxides, ^{1,29,30,35} even in the presence an electrolyte, with the clean surface platinum atoms also resonating at 1.100 G/kHz. Typical features in the ¹⁹⁵Pt NMR spectra of a 2.5 nm carbon-supported commercial Pt electrocatalyst after different surface treatments are shown in Figure 3A-C. Figure 3A is the spectrum of an as-received sample, while Figure 3B shows a sample which has been electrochemically cleaned by holding the electrode potential within the electrochemical double-layer region with no potential cycling, until the reduction current could no longer be measured. Figure 3C shows the spectrum obtained after extensive potential cycling²⁹ where there are clearly discernible spectral differences from Figure 3B, as discussed below.

The ¹⁹⁵Pt NMR spectra of oxide-supported small Pt particles have been quantitatively deconvoluted previously into contributions from Pt atoms within different geometric layers, via the NMR layer model.³⁶ This model assumes that the nanoscale platinum particles can be represented by ideal cubooctahedral particles built up layer-by-layer from a central atom, that NMR



Figure 3. Typical point-by-point ¹⁹⁵Pt NMR spectra showing effects of electrochemical cleaning, sintering by potential cycling, and a layer-model analysis of the 2.5 nm sample: A, as-received catalyst; B, electrochemically cleaned in 0.5 M H₂SO₄ by holding electrode potential at 0.45 V vs the reversible hydrogen electrode; C, cleaned by extensive potential cycling; and D, layer-model deconvolution of spectrum B. The solid line in B is the result of the simulation.

signals from atoms within a given layer can be approximated by a Gaussian, and that the average Knight shift of the *n*th layer, K_n , which is the center of the corresponding Gaussian, "heals" back exponentially toward the bulk platinum position when moving inward. That is:

$$K_n = K_{\infty} + (K_0 - K_{\infty})\exp(-n/m)$$
 (21)

where *n* is the layer number, counting inward from the surface layer (where n = 0), *m* is the characteristic number (of layers) defining the "healing length" for the Knight shift, and K_0 and K_{∞} (= 3.34%) are the Knight shifts of the surface layer and the bulk, respectively. The relative contribution of each Gaussian is dictated by the fraction of the atoms within the corresponding layer, which can be determined from the size distribution of the sample. We have applied this model to deconvolute the clean surface spectrum (Figure 3B).³⁰ The results are shown in Figure 3D. The healing length, defined as m times the distance between two consecutive layers (0.229 nm for Pt), is 0.46 nm (\simeq 2 Pt layers) from the deconvolution shown in Figure 3D, which is to be compared with 0.35 nm, the value obtained in (gas-phase) oxide-supported Pt particles. In addition, the shape of a ¹⁹⁵Pt NMR spectrum conveys information on the size of the electrocatalyst. That is, the stronger the surface peak, the higher the dispersion, or the smaller the particle size.

The surfaces of as-received materials are covered by O and/ or OH species, as indicated by the peak at 1.098 G/kHz. Remarkably, these surfaces are effectively cleaned simply by holding the electrode potential within the electrochemical double-layer region. This mild surface reduction procedure is to be contrasted with the rigorous and often technically demanding methods employed at the solid/gas interface, which usually involve several cycles of high-temperature calcination and reduction, limiting the choice of catalyst support to, typically, nonconductive oxides such as alumina, titania, and silica.

However, extensive potential cycling, which is still a widely used electrode-surface cleaning procedure, sinters the nanoscale electrocatalyst. Although the sample in Figure 3C started with the same as-received electrocatalyst as that shown in Figure 3B, the dispersion estimated from the corresponding ¹⁹⁵Pt NMR spectrum is only about 27%,³⁵ far lower than the 50% obtained



Figure 4. Superimposition of point-by-point, 8.47 T ¹⁹⁵Pt NMR spectra of 2.5 nm, carbon-supported Pt electrocatalysts without and with different chemisorbed ligands: Ru, CO, O, H, CN⁻, and S. The spectra were normalized by equalizing the amplitude at 1.131 G/kHz (indicated by the arrow). The invariance of signals beyond 1.131 G/kHz provides experimental confirmation of the Friedel-Heine invariance theorem in these systems. The surface peaks range over ~11000 ppm. (Reproduced with permission from ref 37. © American Chemical Society.)

from Figure 3B, a value of dispersion consistent with the results obtained by electrochemical measurements, X-ray diffraction, and transmission electron microscopy. This dispersion lowering provides clear evidence for sintering produced by potential cycling, an effect which needs to be borne in mind when analyzing the results of both ligand and metal electrochemical NMR experiments.

¹⁹⁵Pt Knight Shift as a Probe of Ligand Electronegativity. One virtue of ¹⁹⁵Pt NMR of nanoscale Pt particles is that Pt has a large Knight shift range (ca. 34 000 ppm). It is therefore sensitive to variations in local electronic environment, providing a powerful probe to investigate how adsorbates modify the chemical and physical properties of the metal surface. This question has naturally been one of the central themes of surface science and is of importance in relation to the ability to scientifically engineer metal surface properties for targeted applications. Combining ¹⁹⁵Pt NMR with interfacial electrochemistry offers an excellent way with which variations in the physical properties of metal surfaces caused by interfacial modifications can be followed. For example, the influence of a series of different ligands (H, O, S, CN-, CO, and Ru), electrochemically adsorbed onto carbon-supported nanoscale Pt particles, has been investigated by ¹⁹⁵Pt NMR, in an electrochemical environment.37

The starting electrode material used for these experiments was the same as described in the previous section. As shown there, the frequency difference between the resonance positions of surface and bulk platinum atoms at 8.5 T is about 2.5 MHz, large enough to provide a very convenient spectral visualization of how deep the influence of different adsorbates can go, as illustrated by the point-by-point ¹⁹⁵Pt NMR spectra (recorded at 80 K) of Pt with various adatoms presented in Figure 4. These spectra are normalized by equalizing their amplitudes at 1.131 G/kHz, indicated by the arrow. The interesting observation here is that the position of the high-field signal intensity (above 1.131 G/kHz), which is due to Pt atoms within the three innermost layers, is independent of adsorbate type. This independence provides direct experimental evidence for the validity of the



Figure 5. NMR layer-model simulations of the ¹⁹⁵Pt spectra shown in Figure 5. A, clean surface Pt; B, simulation of A; C, Pt with adsorbed Ru; D, Pt with adsorbed H; E, Pt with adsorbed CO; F, Pt with adsorbed cyanide; G, Pt with adsorbed S (from Na₂S solution); H, Pt with adsorbed O. The small dots are the variances between the experimental and fitted values. (Reproduced with permission from ref 37. \bigcirc American Chemical Society.)



Figure 6. Correlation between surface/subsurface frequency shifts (with respect to the Pt NMR reference H_2PtCl_6) and the Allred-Rochow electronegativity. The dashed horizontal line indicates the Knight shift of bulk platinum atoms. The solid straight lines are linear fits to the surface and subsurface shifts as a function of the electronegativity. Both have R^2 values of ca. 0.92. (Reproduced with permission from ref 37. \bigcirc American Chemical Society.)

Friedel-Heine invariance theorem,^{38,39} which states that the integral electronic properties at an atom, such as its local density of states (LDOS), are determined primarily by the surrounding medium, within a few electronic wavelengths. This is exactly what is observed: although the chemical identity of the adsorbates is quite varied, their influences, to a very good approximation, do not go beyond their next-nearest neighbors. That is, the high-field signals are invariant toward "boundary" changes.

In complete contrast to the Friedel-Heine invariance of the electronic properties observed for the innermost platinum atoms, the surface and subsurface NMR signals undergo major frequency shifts as different chemical species are adsorbed, as can be seen in Figure 4. The NMR layer model spectral deconvolution³⁶ technique was applied to each of these spectra in order to obtain the variations in the surface and subsurface Knight shifts. Due to Friedel-Heine invariance, the NMR parameters (peak position, width, relative intensity) for the three central layers were fixed to the clean-surface values, while the surface and subsurface peak positions were allowed to vary. For Pt/O, the position of the third layer was also varied, due to the long healing length in this system; plus, the surface peak areas were also varied in some simulations, due to saturation effects caused by longer T_1 values. The results of these simulations are shown in Figure 5, and the surface and subsurface peak shift values obtained are plotted in Figure 6 as a function of the Allred-Rochow electronegativity (defined as the electrostatic force exerted by the nucleus of the atom on its



Figure 7. Solid curve showing the relationship between the healing length and electronegativity as determined from eq 24. For comparison, we also show the three experimental points based on previous observations. See the text for details. (Reproduced with permission from ref 37. © American Chemical Society.)

valence electrons) of the bonded adsorbate atom. Remarkably, both the surface and subsurface peak positions map almost linearly the electronegativity of the adsorbate. The reason for this is as follows.

According to the layer model, eq 21, one has $K_1 = K_{\infty} + (K_0 - K_{\infty}) \exp(-1/m)$ (for the subsurface layer, n = 1). A simple mathematical conversion gives $m = 1/\ln[(K_0 - K_{\infty})/(K_1 - K_{\infty})]$. By replacing K_1 and K_0 by the correlation lines shown in Figure 6:

$$K_0 (\text{ppm}) = (-10.2 + 5.3\chi) \times 10^3$$
 (22)

$$K_1 (\text{ppm}) = (-21.5 + 5.8\chi) \times 10^3$$
 (23)

m (the healing length) can then be directly expressed as a function of the electronegativity χ :

$$m = 1/\ln[(23.2 + 5.3\chi)/(11.9 + 5.8\chi)]$$
(24)

In Figure 7, the healing length (= 0.229 *m*, where 0.229 nm is the layer thickness for Pt particles) is plotted as a function of the electronegativity (eq 24). This result shows that the larger the electronegativity of the adsorbate, the longer the healing length; that is, the deeper the influence of the adsorbate goes. It is also interesting to note that the value of the healing length *m* for hydrogen ($\chi = 2.2$) adsorption obtained via eq 24 is about 2.9, which is very close to the m = 2.6 value found by a detailed layer model analysis.³⁶ In addition, for the adsorption of the alkali metal elements ($\chi \sim 1$), eq 24 predicts $m \sim 2$, virtually the same *m* as that obtained for clean surface Pt particles in an

TABLE 2: Correlation between Clean Surface $E_{\rm f}$ LDOS and ¹³C Shifts of Chemisorbed CO³⁰

sample	clean surface $E_{\rm f}$ LDOS (Ry ⁻¹ atom ⁻¹)	total ¹³ C Shift of CO _{chemisorbed} (ppm w.r.t TMS)
PtCO ₇ (theory)	0	160
CO-Pt/oxides (dry)	14.8	330
CO-Pt/carbon (wet)	17.7	351
CO-Pt/carbon (wet)	18.6	383
PdCO ₇ (theory)	0	203
CO-Pd/oxides (dry)	24	500

electrochemical environment. One would therefore expect that alkali adsorption would not significantly change the ¹⁹⁵Pt NMR spectrum of small Pt particles after adsorption. This is exactly what has been observed experimentally (in a gas-phase system).⁴⁰ For comparison, these three experimentally estimated points are also shown in Figure 7.

The invariance of the frequency shifts of the more buried (deeper than the 3rd layer) Pt atoms to surface adsorbate electronegativity provides strong evidence demonstrating the applicability of Friedel-Heine invariance of the E_f LDOS in these nanoscale electrocatalyst systems. This is a rather interesting extension of the original Friedel-Heine invariance theorem to nanoscale systems and may have utility in describing the electronic surface structure of metal catalysts in different chemical environments. These results may also be expected to lead to useful general correlations between electronic properties and more conventional chemical descriptors (such as ligand electronegativity) which could be helpful in understanding the electronic structure of metal/adsorbate interfaces by providing guidelines for engineering new electrode surfaces.

¹³C Knight Shift of Adsorbed CO as a Molecular Probe of the Clean Surface Ef LDOS of Metals. The surface specificity of ¹⁹⁵Pt NMR is due to the fact that among the s-, d-, and orbital contributions to the total shift, eq 12, the variation in K_d dominates the change in K when the atomic volume containing the Pt nucleus of interest changes its geometric position relative to the surface.^{34,41} This is also the major reason for the success of the layer model³⁶ for ¹⁹⁵Pt NMR. However, not all transition metals possess such NMR surface specificity (actually, most of them do not). Fortunately however, because NMR has elemental specificity and is also nondestructive, it offers unique opportunities for investigating electrochemical problems from both sides of the electrochemical interface. Thus, the NMR of adsorbed (submonolayer) ligands, say, CO, CN, or NO, can also provide surface specific electronic structural information. This has been demonstrated by ¹³C NMR investigations of metal-CO interactions in a number of recent studies.30

To use ligand NMR to probe metal surface electronic properties, the first step is to establish the relationship between ligand NMR and metal surface properties. ¹³C and ¹⁹⁵Pt offer an ideal pair of NMR probes with which to investigate such a relationship. In particular, by carrying out detailed temperature-dependent T_1 relaxation measurements on a given Pt sample, a value for $S(T_1T)^{-1}$ can be obtained, and by using the two-band model, eqs 12 and 13, a pair of surface Pt s and d $D(E_f)$ s can be deduced. Similarly, $S(T_1T)^{-1}$ and K measurements of ¹³CO adsorbed onto the clean metal surfaces can give the corresponding ¹³C 5 σ and 2π * $D(E_f)$'s by solving eqs 15 and 16.

Now, it is clearly of fundamental interest to see if there exists any type of correlation between the clean surface $E_{\rm f}$ LDOS of the metal and the ¹³C Knight shift of the chemisorbed CO. The former is an important surface attribute defining the ability of



Figure 8. Correlation between the Fermi level total electronic densities of states at transition metal (Pt and Pd) surfaces (in Ry^{-1} atom⁻¹) and the corresponding ¹³C Knight shift of chemisorbed CO. (Reproduced with permission from ref 30. © American Chemical Society.)

the metal surface to donate (to act as a HOMO) as well as to accept (to act as a LUMO) electrons, while the latter measures, at least to a certain extent, the degree of metallization of chemisorbed CO (vide infra). We show in Table 2 a set of data for atop CO on Pt and Pd, shown graphically in Figure 8. The purely orbital contributions (chemical shifts) for atop CO on Pt and on Pd were calculated by using density functional theory (DFT) calculations on model COPt7 and COPd7 clusters in which CO sits atop the central metal atom, which is coordinated by the remaining six metal atoms.³⁰ For COPt₇, a value of 160 \pm 20 ppm from tetramethylsilane (TMS) was obtained for the orbital (chemical) shift, while for COPd₇, the value was 203 \pm 20 ppm. These calculated values are in good agreement with available experimental data on metal carbonyls while the standard deviations account for uncertainties due to use of different functionals and basis sets.³⁰ The clean surface $E_{\rm f}$ LDOS for Pd was estimated on the basis of the changes in magnetic susceptibility of small Pd particles with respect to their bulk value, by application of the exponential healing model.

As shown in Figure 8, the ¹³C NMR shift of CO responds linearly to the clean surface E_f LDOS before adsorption. The straight line is a linear fit to the data, giving a slope of 12 ppm Ry⁻¹ atom⁻¹. This linear relationship can be readily related to the frontier orbital interpretation of the Blyholder model.⁴² A higher clean surface E_f LDOS means more metal electrons and holes are available to engage in 5 σ -forward and $2\pi^*$ -backdonation. As the E_f LDOS increases, CO becomes more metallic, which results in a larger Knight shift. A correlation very similar in nature to this has also been found to exist in the gas phase, where the C–O vibrational stretch frequency (after chemisorption) was shown to correlate linearly with the clean Pt surface E_f LDOS before chemisorption.⁴³ The higher the surface E_f LDOS, the lower the C–O stretch frequency.

The linear relationship shown in Figure 8 is important for several reasons. First, it demonstrates the validity of the frontier orbital-interaction picture of metal surface chemistry, where the importance of the clean surface E_f LDOS is highlighted. Second, it puts ¹³C NMR spectroscopy of chemisorbed CO on a firmer footing, by probing the electronic properties of transition metal surfaces before CO chemisorption. Third, it implies that ligand NMR can indeed be used as a probe to investigate a variety of metal surfaces, be they poisoned or promoted by foreign adatoms, which may be of particular utility when the metal NMR does not possess surface specificity or has otherwise poor NMR characteristics (low- γ , quadrupolar).

Coupling EC NMR with in situ Infrared (IR) Spectroelectrochemistry. It may often be more informative to investigate a given system by using several different spectroscopic techniques. An example of this is the comparative study by EC



Figure 9. Typical ¹³C NMR spectrum and temperature-dependent T_1 data for an 8.8 nm Pt/C sample. The straight line through the origin is characteristic of the Korringa relationship, indicating the metallic state of adsorbed CO in this electrocatalyst system. (Adapted from ref 24.)

TABLE 3: 5σ and $2\pi^* D(E_t)$ s Deduced by the Two-Band Model from ¹³C NMR Data of CO Chemisorbed on Pt Electrocatalysts²⁴ and the Corresponding SNIFTIRS C–O Vibrational Stretching Frequencies⁴⁴

size (nm)	$5\sigma D(E_{\rm f})$ (Ry molecule) ⁻¹	$2\pi^* D(E_{\rm f})$ (Ry molecule) ⁻¹	IR frequency (cm) ⁻¹
8.8	0.6	6.4	2044
3.9	0.6	6.6	2043
3.2	0.6	6.5	2044
2.5	0.7	6.8	2038
2.0	0.6	7.3	2028

NMR and IR that was recently carried out on a series of carbonsupported Pt electrocatalysts.^{24,44}

It is now clear that CO acquires metallic properties upon adsorption onto transition metal surfaces, as indicated by the presence of a Knight shift and a Korringa relationship, measured via ¹³C NMR. Furthermore, by using the experimentally measured ¹³C Knight shift and the Korringa constant, a phenomenological two-band model permits a quantitative partitioning between the 5 σ and $2\pi^* D(E_f)$ at ¹³C to be obtained, providing insight into metal-CO bonding at the electronic structural level. These types of ¹³C NMR study have been carried out on ¹³CO chemisorbed (ex MeOH) onto a series of carbonsupported, fuel cell grade, commercial platinum electrocatalysts having different average particle size: 2.0, 2.5, 3.2, 3.9, and 8.8 nm, in which both metal and adsorbate $E_{\rm f}$ LDOS might be expected to vary with particle size. Shown in Figure 9 is a typical ¹³C NMR spectrum and temperature-dependent T_1 results for the 8.8 nm sample.²⁴ The straight line through the origin is characteristic of the Korringa relationship, indicating the presence of a metallic state for adsorbed CO in this electrocatalyst system.

Table 3 collects values of the 5σ and $2\pi^* D(E_f)$ deduced from the ¹³C NMR results, in addition to the corresponding infrared data⁴⁴ (vide infra). The results shown in Table 3 indicate that the major part of the total E_f LDOS at ¹³C is from the $2\pi^*$ like electrons, with the $2\pi^* D(E_f)$ being about 10 times larger than the $5\sigma D(E_f)$. These values are in good agreement with theoretical band structure calculations. The contribution to the spin-lattice relaxation rate $(1/T_1)$ is dominated by orbital and dipolar interactions, consistent with the dominance of π -like electrons at the Fermi level. Note that while the $5\sigma D(E_f)$ is almost constant, the $2\pi^* D(E_f)$ varies considerably from sample to sample. However, since NMR only reflects the electron density at one specific energy level, i.e., the Fermi level, it does



Figure 10. Correlations between ν_{CO} and 2 $\pi^* D(E_f)$. The straight line is the linear fit which gives a slope of $-19 \text{ cm}^{-1} \text{ Ry}^{-1}$ molecule⁻¹ and an intercept of 2167 cm⁻¹, with a $R^2 = 0.98$. (Part of the results shown in this figure have been published in refs 24 and 44.)

not provide complete information about the total electron densities for forward- and back-donation, which are the integrals of the LDOS from the bottom of the conduction band to the Fermi level. Nevertheless, as can be seen in Table 3, the variation in the total E_f LDOS between different samples appears to be mainly due to changes in the $2\pi^* D(E_f)$. This suggests that the changes in the chemical properties of adsorbed CO are primarily determined by variations in back-bonding. In particular, if the Fermi level cuts the tail of the $2\pi^*$ band as it rises, then the increase in the $2\pi^* D(E_f)$ would indicate an enhancement in back-donation, and a decrease in the corresponding vibrational C–O stretch frequency.

In situ subtractively normalized interfacial Fourier transform infrared reflectance spectroelectrochemistry (SNIFTIRS) studies confirm this prediction.⁴⁴ They also yield a linear correlation between ν_{CO} and the $2\pi^* D(E_f)$, Table 3, with a slope of -19 (± 2) cm⁻¹ Ry⁻¹ molecule⁻¹ and an intercept of 2167 \pm 20 cm⁻¹, as shown in Figure 10. Since the SNIFTIRS method tends to overestimate the IR frequency, particularly when CO has a sub-saturation coverage, the latter value appears to be quite close to the value expected for free CO, $\nu = 2143$ cm⁻¹. On the basis of these results, the following overall physical picture of carbon monoxide adsorbed onto a platinum electrode can be proposed: Since the 5σ orbital of CO is essentially nonbonding, with the lone pair concentrated on carbon and the $2\pi^*$ orbital is a much less polarized antibonding orbital, the change in CO stretch frequency is mainly governed by changes in $2\pi^*$ backdonation: the higher the back-donation, the lower the CO stretch frequency.

The above example demonstrates the complementary nature of in situ infrared spectroscopy and EC NMR, in providing insights into the details of surface chemistry of electrochemisorbed CO on platinum. While infrared (IR)-a major research technique of the interfacial electrochemical communityprovides important qualitative information regarding the bond strengths of adsorbed CO, it offers somewhat less insight into the electronic relocations which occur within the bond, the electron distribution as a function of sample composition and morphological detail. For instance, how the bond changes as a function of particle size is difficult to learn using infrared alone. However, a ¹³C NMR analysis of the 5 σ and $2\pi^* E_f$ LDOS at the carbon atom offers a quantitative description of metal-CO bonding in terms of changes in the $E_{\rm f}$ LDOS. The joint IR/ NMR approach provides new information on the electronic structure of the metal/solution interface which is relevant to the characterization of industrial fuel cell catalysts, as well as other

Figure 11. Temperature dependence of spin–spin relaxation rates of chemisorbed 13 CN (panel A) and 13 CO (panel B) on 10 nm Pt electrocatalyst surfaces. The solid lines are the fits to eq 25, and the numbers are the corresponding results of the fits. (Adapted from refs 26 and 28.)

interfacial electrochemical systems of practical importance, by combining bond strength (IR) and quantitative $E_{\rm f}$ LDOS NMR results.

Surface Diffusion. A unique feature of NMR in general is its ability to access diffusional information on nuclear-spinbearing atoms and molecules, which would otherwise be rather difficult to obtain. In our studies, we have been interested in the surface diffusion of chemisorbed ligands, such as CO and CN, which are amenable to ¹³C NMR analysis.

The temperature dependence of $1/T_2$ for ¹³CN and for ¹³CO on polycrystalline platinum black at saturation coverage are shown in Figure 11.^{26,28} For CO or CN adsorbed onto small platinum particles, $1/T_2$ can be expressed as

$$1/T_2 = 1/T_2^{\text{RL}} + 1/T_2^{\text{Pt}} + 1/T_2^{\text{dip}} + 1/T_2^{\text{diff}} = 1/T_2^{\text{RL}} + aT + (\Delta \omega)^2 \tau / (1 + (\Delta \omega)^2 \tau^2) + 1/(N\tau)$$
(25)

where $1/T_2^{\text{RL}}$ is the temperature independent "rigid lattice" contribution, and $1/T_2^{\text{Pt}} (= aT)$, where *a* is a constant and *T* the absolute temperature) accounts for the effects of platinum spins. $1/T_2^{\text{dip}} = (\Delta \omega)^2 \tau / (1 + (\Delta \omega)^2 \tau^2)$ arises from dipolar interactions between neighboring carbon-13 spins, where $\Delta \omega$ is the dipolar field in Hz and $\tau = \tau_0 \exp(E/k_BT)$, with τ_0 a preexponential factor, chosen to be 10^{-13} s, and *E* is the activation energy for surface diffusion); $1/T_2^{\text{diff}} (= 1/N\tau)$, where *N* is the number of jumps needed to dephase the carbon spins) comes from the field difference (positive or negative) between adjacent adsorption sites, due to the presence of a significant magnetic field inhomogeneity on the particle surface.

The solid lines in Figure 11 are the fits to eq 25 with $1/T_2^{\text{RL}}$, a, $\Delta\omega$, E, and N as fitting parameters. The results of the fits (in which $1/T_2^{\text{RL}}$ are 293 and 930 s⁻¹ for CO and CN, respectively) are also shown in Figure 11. Clearly, this simple model describes the experimental data very well, for both ¹³CO and ¹³CN. It is interesting to note that the activation energy found for CO (7.8 kcal/mol) is close to that found for CO on "dry" alumina-supported Pt clusters, as well as that found in single-crystal studies. The results of the fits also indicate that the activation energy for surface diffusion is higher for CN than for CO, while the difference in the constant *a* suggests, paradoxically, that

Figure 12. Temperature dependence of spin–lattice relaxation rates for chemisorbed $CH_3^{13}CN$ and $^{13}CH_3CN$. The clear absence of a Korringa relationship for $^{13}CH_3CN$ (solid circles) indicates that the carbon atom in the methyl group does not acquire significant metallic character. (Adapted from ref 45.)

Figure 13. Potential dependence of ${}^{13}C$ shifts for ${}^{13}CO$ (circles) and ${}^{13}CN$ (squares) chemisorbed on a 10 nm Pt electrocatalyst. (Adapted from ref 1.)

platinum has more of an electronic influence on the ¹³C spinspin relaxation of CO than on that of CN. The latter may, however, be related to the fact that the J-coupling is mediated by orbital electrons between ¹³C and ¹⁹⁵Pt and is expected to be primarily influenced via σ -bonding rather than through π -bonding, for $|\psi|^2 = 0$ at C for the $2\pi^*$ orbital. If the ¹⁹⁵Pt-¹³C dipolar interaction were the only mechanism for $1/T_2^{\text{Pt}}$, the ratio in *a* values would yield $r_{\text{Pt-CN}}/r_{\text{Pt-CO}}$ equal to 1.9, which is unrealistic. Thus, while the activation energy values may indicate an overall stronger metal surface bonding for Pt-CN than for Pt-CO, the *a* values suggest that σ -bonding is stronger in the latter case. Finally, $\Delta \omega$ for the ¹³C-¹³C dipolar interaction is essentially identical in each of the systems investigated, consistent with a similar adsorbate coverage for both samples.

Isotopic Labeling for Site Selectivity. Specific isotopic labeling is a useful, structurally specific NMR technique when the natural abundance of the nucleus of interest is too low to be detected under normal conditions, such as with ¹³C, ¹⁵N, and ¹⁷O. As an example, we consider here the bonding of a larger species, acetonitrile (CH₃CN), bonded to Pt in an electrochemical environment.⁴⁵ ¹³C 1/*T*₁ versus *T* data for CH₃¹³CN and ¹³CH₃CN adsorbed onto platinum are shown in Figure 12. A linear 1/*T*₁ versus *T* plot, reflecting Korringa behavior with *T*₁*T* = 170 s K, is only obtained with the CH₃¹³CN adsorbate. This indicates that at least the carbon of the CN group is directly attached to platinum, and that the ¹³C has acquired metallic character. Note that the value of *T*₁*T* = 170 s K for CH₃¹³CN is quite close to that of ¹³CN (135 s K). The *T*₁*T* product for the ¹⁵N system at room temperature is 224 s K, showing that

Figure 14. NO stripping CVs for NO on (A) Pt black and (B) carbon-supported 2.5 nm Pt. A saturated NO adlayer was generated by immersing the pre-cleaned Pt electrode materials in an acidic solution of Na¹⁵NO₂ for ca. 1 h.

Figure 15. ¹⁹⁵Pt and ¹⁵N NMR results for NO on Pt: (A) 80 K point-by-point ¹⁹⁵Pt NMR spectra of carbon-supported 2.5 nm NO covered (open squares) and clean surface (solid circles) Pt samples. The presence of NO on Pt surfaces modifies the surface and subsurface electronic properties. The modified surface peak position K_0 follows the correlation shown in Figure 6, i.e., eq 22. (B) Room-temperature ¹⁵N NMR spectrum of NO asdsorbed onto Pt black. The peak positions and line widths are ca. 275 and 800 ppm, respectively, and T_1 was estimated to be ca. 2s.

the spin-lattice relaxation of ¹⁵N in chemisorbed CH₃C¹⁵N is much more efficient than in chemisorbed C¹⁵N, where T_1T varied in the range ~3000-4000 s K. Indeed, after taking into account the $\gamma_{13C}/\gamma_{15N} \sim 2.5$ factor in eq 7, the relaxation of ¹⁵N appears even more efficient than that of the "metallic" ¹³C in CH₃¹³CN. This suggests that both C and N in the CN group are directly attached to the platinum surface, forming a parallel or side-on orientation with respect to the Pt-Pt surface bonds. The clear absence of a Korringa relationship for ¹³CH₃CN (solid circles) suggests that the carbon atom in the methyl group does not acquire significant metallic character. This implies that neither C-C bonding nor antibonding orbitals are involved with bonding to the platinum surface, while both ¹³C and ¹⁵N atoms in the CN group are strongly involved, in contrast to the situation with CN itself, where cyanide has a C-down, on-top bonding.

Potential-Dependent EC NMR. One major motivation in developing EC NMR was to combine the ability of interfacial electrochemistry to control surface potential, with the analytical ability of NMR, for investigation of fundamental issues related to interfacial electrochemical processes. For example, understanding the nature of electric field (electrode potential) effects on the electronic structure at the solid/liquid interface is still a central theme in electrocatalysis and in the theory of the electrical double layer.46 To illustrate some such effects via NMR, we show in Figure 13 the electrode-potential-induced ¹³C line shifts for CO (circles)¹⁷ and CN (squares)²⁶ on polycrystalline Pt. These results were obtained under active external potentiostatic control. Apparently, for both adsorbates, there is a linear relation between the electrode potential and the line shift: the more negative the potential, the larger the frequency shift. ¹³C therefore becomes more deshielded as the potential goes more negative, and the slope is about -71 ppm/V for ¹³CO and -50 ppm/V for ¹³CN. For CO on Pd, the slope was found to be even larger: about -136 ppm/V.¹⁷

A similar response in C–O vibrational frequency, ν_{CO} , to variations in the electrode potential, has been reported.⁴⁷ There, ν_{CO} decreased when the electrode potential became more cathodic. However, the origin of this so-called vibrational Stark

effect has been controversial for some time, since a clear picture of how the short-range (electronic) bonding and the longerrange (electrostatic) field effects at surfaces are controlled by varying either the electrode or the surface potential, has not been available.

EC NMR provides an additional technique with which to begin to probe these questions since the response of ¹³C NMR to the electrode potential has been found to be due essentially to the Knight shift.¹⁷ The ¹³C NMR chemical shift response of CO to electric fields (in biomolecules) has been found to be much smaller than the values estimated at the electrochemical interface.¹⁷ In addition, for CO on Pd, a corresponding change in the nuclear spin-lattice relaxation rate as a function of applied field has also been observed,¹⁷ indicating the electronic nature of the change in the NMR shift. The magnitude of the cleansurface $E_{\rm f}$ LDOS of the adsorbant is therefore responsible for the extent of the Knight shift, as well as the vibrational stretch frequency of chemisorbed CO.^{30,43} That is to say, the higher the clean surface $E_{\rm f}$ LDOS, the larger (lower) the ¹³C Knight shift³⁰ (C-O stretch frequency⁴³) of CO will be after chemisorption. Both relationships are linear, with slopes of about 12 and $-4 \text{ cm}^{-1} \text{ Ry}^{-1}$ atom⁻¹, respectively, giving a ratio of -3ppm/cm⁻¹. This is to be compared with the ratio of -2.8 ppm/ cm^{-1} obtained independently from the slopes (-71 and 25 cm^{-1} / V, respectively) of δ (¹³C) and ν_{CO} versus electrode potential relationships for CO on Pt black. These variations in v_{CO} can also be directly correlated with changes in $2\pi^*$ back-donation: The higher the back-donation, the lower the CO stretch frequency. When taken together, all these observations suggest that the potential dependence of both the ¹³C NMR shift and the vibrational stretch frequency of adsorbed CO are primarily electronic in nature and originate from changes in the $E_{\rm f}$ LDOS at the metal surface and at the adsorbate, induced by electrode polarization.

NO Chemisorbed on Pt Electrodes. The adsorption of NO onto transition metal surfaces is of great scientific and technological interest in gas-phase catalysis, such as the catalytic reduction of NO_x species to N_2 and O_2 taking place in a three-

way automobile emission catalyst.⁴⁸ More fundamentally, the dissociation energy of NO is about one-half that of CO, and its adsorption behavior, e.g., the degree of dissociation, coverage, and bonding geometry (atop, bridge, and 3-fold hollow sites), is quite different from that of CO. Consequently, it is an attractive second species with which to probe metal–ligand interactions at catalyst surfaces.

Saturated NO adlayers on Pt electrodes can be readily generated by immersing pre-cleaned electrode materials into an acidic solution of sodium nitrite, which offers an exceptionally simple (as well a relatively inexpensive) route to the production of chemisorbed ¹⁵NO (from Na¹⁵NO₂). By using electrochemical stripping, the coverage of NO can also be varied. In Figure 14, we show the NO stripping CVs for a Pt black (A) and a 2.5 nm carbon-supported Pt (B) sample. For NMR measurements, samples were then transferred into pre-cleaned glass ampules (without NO stripping) and flame-sealed immediately after transfer. We show in Figure 15 preliminary ¹⁹⁵Pt and ¹⁵N NMR spectra of NO on Pt. Figure 15A is the first point-by-point ¹⁹⁵Pt NMR spectrum of 2.5 nm carbon-supported Pt particles with (open squares) and without (solid circles) NO. The low-field peak (around 1.100 G/kHz) comes from the Pt surface atoms. Moving inward from the particle surface, the ¹⁹⁵Pt NMR signal shifts upfield, eventually "healing back" to the Pt bulk value at 1.138 G/kHz. Again, the presence of NO on Pt surfaces modifies the surface and subsurface electronic properties. It is also interesting to note that the signal far downfield (below 1.08 G/kHz) may indicate that a small portion of adsorbed NOs retain (at least partially) their spin density. Figure 15B is the first roomtemperature ¹⁵N NMR spectrum of NO adsorbed onto Pt black. The peak position and line width are ca. 275 and 800 ppm, respectively, and T_1 was found to be ca. 2s, which gives a value of $T_1T \sim 600$ s K. Notice that T_1T is about 3000 to 4000 s K for the nonbonding N in adsorbed CN and 225 s K for the bonding N in CH₃CN. Therefore, a value of 600 s K indicates that for adsorbed NO, N is most likely bonded to the platinum surface.

The molecular orbitals of NO are very similar to those of CO, except that NO has an unpaired electron in its $2\pi^*$ orbital. Fundamentally therefore, NO–metal bonding does not differ qualitativly from metal–CO bonding. Thus, these preliminary results show that it should now be possible to carry out detailed EC NMR investigations of NO–Pt systems. Since detailed UHV and IR spectroelectrochemistry (vibrational Stark effect) studies of NO adsorption have already been reported,^{49,50} a comparison between the IR and NMR (E_f LDOS) information should prove to be very interesting when viewed in light of the results on CO obtained recently.

V. Conclusions

EC NMR has made considerable progress during the past few years. It is now possible to investigate in detail metal/liquid interfaces under potential control to deduce electronic properties of electrodes (platinum) and of adsorbates (CO, CN, or NO) and to study the surface diffusion of adsorbates. The method can also provide information on the dispersion of commercial carbon-supported platinum fuel cell electrocatalysts and on electrochemically generated sintering effects. Such progress has opened up many new research opportunities since we are now in the position to harness the wealth of electronic (E_f LDOS) as well as dynamic and thermodynamic information which can be obtained from NMR experiments. As such, it is to be expected that EC NMR will continue to thrive and may eventually become a major characterization technique in the field of interfacial electrochemistry. Acknowledgment. This work was supported by the United States National Science Foundation (Grant CTS 97-26419), by an equipment grant from the United States Defense Advanced Research Projects Agency (grant DAAH 04-95-1-0581), and by the U.S. Department of Energy under grant DEFG02-96ER45439.

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