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NMR of platinum catalysts. I. Line shapes

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The authors report spin-echo NMR studies of ^{195}Pt in small particles of Pt supported on alumina. For the samples studied, the fraction of Pt atoms on the surface (called the dispersion) ranged from 4% to 58%. The studies were at fields H_0 of 80 to 85 kG, frequency $\nu_0 = 74$ MHz, and at a temperature of 77 K. The lines are broad (3 – 5 kG), requiring special methods which permit substantial signal averaging ($\sim$50 000 echoes). In the low-dispersion (large-particle) samples, there is a strong absorption at the position of the ^{195}Pt NMR in bulk Pt metal ($H_0/\nu_0 = 1.138$ kG/MHz) which becomes progressively weaker as the particle size decreases. A peak which is near the ^{195}Pt resonance in typical diamagnetic compounds ($H_0/\nu_0 \simeq 1.09$ kG/MHz) is found in samples which are coated with adsorbed molecules. It disappears when the surface is cleaned. The authors show that this peak arises from the surface layer of Pt atoms, and that its position (H_0/ν_0) shows that coating the Pt atoms on the surface largely ties up the electron spins of the surface Pt atoms in bonds. The exact position of this peak depends on the chemical species which is adsorbed. The authors show that when Pt is cleaned, then exposed to air for long times, the surface peak reveals that the surface has reconstructed to form Pt(OH)$_6$.

I. INTRODUCTION

Heterogeneous catalysis is a field of great interest both because of its important technological applications and because it possesses deep questions of fundamental science.[1–3] In an effort to learn more about the microscopic details of heterogeneous catalysis and processes at surfaces in general, we have been applying NMR to the study of a typical catalyst, platinum metal.[4–8]

Heterogeneous catalysis is, of course, a surface phenomenon. The reaction takes place on the surface of the catalyst. To use NMR to study surfaces, we require many surface nuclei in the sample to give an observable signal. Consequently, we are forced to use large-surface-area samples, hence automatically small particles. Actually, this turns out to be quite convenient, since this is the kind of sample used by industry in catalytic processes.

Two types of NMR studies are conceivable: study of the nuclei of the catalyst itself and study of the nuclei of molecules adsorbed on the surface of the catalyst. We are carrying out both types of studies. Here we report on the former type: ^{195}Pt NMR. We divide the study into three topics, each in a separate paper: this paper and the two that follow (Refs. 9 and 10, hereafter referred to as papers II and III).

For studying the phenomena of adsorbed atoms, platinum has the advantage of being a well-known and well-characterized catalyst. For studying the NMR of the catalyst itself, platinum also possesses desirable properties: The ^{195}Pt nucleus has sufficient natural isotopic abundance (33.7%), a reasonably strong gyromagnetic ratio γ (9 MHz in 10 kG), and most importantly, a nuclear spin $I = \frac{1}{2}$, which eliminates the complexity of structure on the NMR line shape arising from electric quadrupole effects. (Nuclei with spin $\frac{1}{2}$ have zero electric quadrupole moment.) In addition, ^{195}Pt has one of the largest Knight shifts of any metal (−3.37%) and thus offers the possibility of resolving the NMR of surface layers of atoms in the bulk.

In this paper, we present NMR absorption line shapes for various samples of platinum catalysts. In these samples we vary the size of the Pt particles as well as the type of molecules adsorbed on the surfaces. From these line shapes, we demonstrate that (1) Pt particles even as large as 100 Å in diameter do not exhibit properties of bulk Pt, (2) Pt atoms on the surface of particles coated with adsorbed molecules give rise to a "surface peak" in the NMR absorption line shape, (3) these atoms are on "nonmetallic" nature, and (4) the position and shape of the surface peak vary with the type of adsorbed molecule and hence provide a "fingerprint" which can identify the adsorbed molecules. We also discuss some of the challenging technical problems which must be overcome to observe the ^{195}Pt resonance in small particles.

Yu, Gibson, Hunt, and Halperin have also studied NMR in small Pt particles.[11] They observed that portion of the line which occurs at the position of the NMR in bulk Pt and showed that there were changes associated with the small particle size. We compare our results with theirs in paper III. In the present paper, we discuss our samples in Sec. II, provide NMR background in Sec. III, describe our experimental techniques in Sec. IV, and present the results in Sec. V.

II. SAMPLES

Our samples consist of small particles of Pt metal supported on eta-alumina. The samples were prepared at Exxon Research Laboratories by a standard technique of impregnation[12]: The alumina is brought into contact with a solution of H_2PtCl_6. The solute deposits on the alumina, and the resulting material is dried and calcined at high temperatures. Then the platinum is reduced under hydrogen to form small metal crystallites dispersed on the surface of the alumina.

The sizes of the Pt particles in the resultant catalyst are usually characterized by a parameter called dispersion, which is the fraction of Pt atoms that are on the surface of the particles. Dispersion may be quantitatively determined, for example, by exposing the sample to hydrogen gas and measuring how much is adsorbed on the surface of the Pt particles.[12] (Hydrogen does not adsorb on alumina to any significant degree.)

It is possible to make Pt catalysts with essentially 100% dispersion, but these require a very small Pt loading (less than 1% Pt by weight). In order to have enough Pt in our samples to give us a sizable NMR signal, we made our first samples with 10% Pt by weight (90% alumina by weight). The resulting catalyst was found to have a dispersion of 46%. This means that 46% of the Pt atoms in the sample are surface atoms available for catalytic activity. We label this sample Pt-46-*R* (46 signifies the dispersion measured by hydrogen chemisorption, and *R* signifies "as received" from the preparation and characterization processes, i.e., untreated. This point will be discussed in more detail below.)

Two other samples were formed by heating portions of sample Pt-46 at high temperature, causing the Pt particles to coalesce and form larger particles. The dispersion was found to be 26% and 15% for these two samples, and we thus label them Pt-26-*R* and Pt-15-*R*, respectively.

To further characterize our samples, we took electron micrographs of these three samples using the HB-100 scanning transmission electron microscope (STEM). From these micrographs, we could determine the Pt particle-size distribution for each sample (Fig. 1). Theoretically, it is known[13] that particles which are formed by random coalescence should have a log-normal distribution in their diameters x:

$$N(x)=N_0\exp\left[-\frac{1}{2}\left[\frac{\ln(x/x_0)}{\ln\sigma}\right]^2\right]. \quad (1)$$

Note that this distribution as a function of $\ln x$ is Gaussian. The solid lines in Fig. 1 are best fits of Eq. (1) to the data. We were able to obtain a reasonable fit to samples Pt-15-*R* and Pt-26-*R* using the same value for $\sigma=1.61$ but were forced to use $\sigma=1.46$ for sample Pt-46-*R*. Perhaps the statistical behavior assumed for log-normal distributions is not valid for the very small particles which constitute sample Pt-46-*R*.

From measured size distributions, we are able to

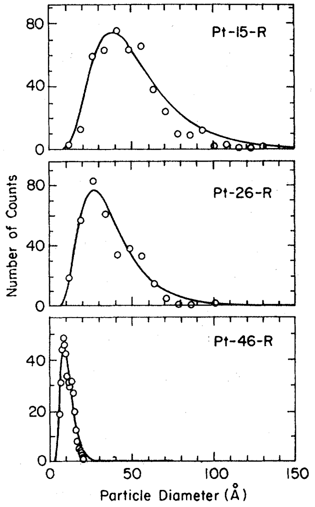


FIG. 1. Size distribution of Pt particles in samples Pt-15-*R*, Pt-26-*R*, and Pt-46-*R* obtained by electron microscopy. Solid curves are the best fit of a log-normal distribution to the data.

estimate the dispersion of these samples, thus providing us with an independent measurement of that quantity. First, we assume that the particles are Wulff crystals[14,15] (cubo-octahedron).[16] This may seem to be a gross simplification, especially for the smallest particles, but we have found that the results of this calculation are largely independent of the crystal shape used. For a Wulff crystal of diameter x, the number N_S of surface atoms and the number N_T of total atoms in the crystal are given by[16]

$$\begin{aligned} N_S(n) &= 30n^2-60n+32 , \\ N_T(n) &= 16n^3-33n^2+24n-6 , \qquad (2) \\ x(n) &= (n-1)x_w , \end{aligned}$$

where n is the number of atoms on an edge of the crystal, and $x_w = 7.8$ Å for Pt. The dispersion D is then given by

$$D = \frac{\sum_{n=2}^{\infty} N_w(n) N_s(n)}{\sum_{n=2}^{\infty} N_w(n) N_T(n)} , \qquad (3)$$

where $N_w(n)$ is the number of crystals of edge n in the sample, given approximately by

$$N_w(n) = \int_A^B N(x)dx , \qquad (4)$$

where

$$A = [x(n)+x(n-1)]/2$$

and

$$B[x(n)+x(n+1)]/2 .$$

Evaluating Eq. (3) with the use of x_0 and σ from the best fit to data, we obtain $D = 16\%$, 22%, and 61% for samples Pt-15-*R*, Pt-26-*R*, and Pt-46-*R*, respectively. These results are summarized in Table I. These values of dispersion agree reasonably well with those values obtained from hydrogen chemisorption, especially for samples Pt-15-*R* and Pt-26-*R*. The noticeably poorer agreement for sample Pt-46-*R* is probably due to the breakdown of the model for such small particles.

We later made three additional samples of yet different particle sizes (Table I). Using hydrogen chemisorption, we determined their dispersions to be 4%, 11%, and 58%, and we thus label them samples Pt-4-*R*, Pt-11-*R*, and Pt-58-*R*, respectively. We also obtained a sample of large, unsupported Pt particles (rods of 2-μm diameter) which, for our purposes, exhibits the properties of bulk Pt metal. We label this sample Pt-bulk.

TABLE I. Dispersion (in %) of Pt catalyst samples measured by three different methods: (1) hydrogen chemisorption, (2) electron microscopy, and (3) intensity of surface peak in NMR absorption line shape.

	Chemisorption	Microscopy	NMR
Pt-4-*R*	4		5
Pt-11-*R*	11		8
Pt-15-*R*	15	16	10
Pt-26-*R*	26	22	19
Pt-46-*R*	46	61	40
Pt-58-*R*	58		79

III. NMR BACKGROUND

A. Chemical shifts and Knight shifts

The NMR frequency ν_0 of a nuclear spin in a fixed external dc magnetic field H_0 varies between diamagnetic compounds, obeying a law for substance i,

$$2\pi\nu_0 = \gamma(1+K_i)H_0 , \qquad (5)$$

where $\gamma H_0/2\pi$ is the NMR frequency for a "bare" nucleus and K_i is called the "chemical shift." K_i has its origin in magnetic fields produced at the nucleus by currents induced in the surrounding electrons by application of H_0. It is associated with the electron orbital motion induced by H_0.

In metals, the conduction-electron spins are polarized by H_0, giving rise to an additional shift in ν_0 called the Knight shift. The Knight shift also obeys the relation given by Eq. (5). One may think of K_i in a metal to be the sum of chemical shift and Knight shift. Usually, for a given nuclear spin, Knight shifts are much greater in magnitude than chemical shifts. (For a more thorough discussion of

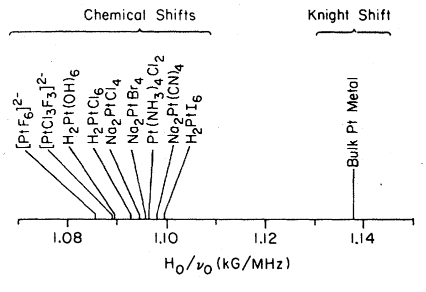


FIG. 2. Position of ^{195}Pt NMR resonances for various compounds. (See Ref. 18.)

chemical shifts and Knight shifts, see Ref. 17.)

Since one never studies bare nuclei, one never observes the situation $K_i = 0$. In practice, therefore, one chooses a compound as a standard reference ($K_i = 0$ for that compound by definition) and measures shifts of all other compounds with respect to the chosen reference. For platinum, H_2PtI_6 is the reference compound most commonly used in the current literature.[18] In Fig. 2, we show the position of the Pt NMR resonances for various compounds as well as bulk Pt metal. The compounds on the low-field side of the figure exhibit chemical shifts ($K_i < 1.0\%$ with respect to H_2PtI_6). Bulk Pt metal exhibits a large negative Knight shift ($K_i = -3.4\%$; see Ref. 18).

B. Line shapes for small particles

Consider a small particle of Pt atoms. We would expect the Pt nuclei in the particle's interior, far from any surface, to find themselves in an environment like that of bulk Pt metal. These nuclei should thus exhibit a Knight shift equal to that of bulk Pt metal.

On the other hand, Pt nuclei near the surface of the particle would certainly be in an environment different from that of bulk Pt metal and consequently exhibit different Knight shifts. In a large collection of particles of different sizes and shapes, there are many different kinds of sites for Pt nuclei near the surface. Since each different kind of site gives rise in general to a different Knight shift, we would find a distribution of Knight shifts among these nuclei in such a sample.

One can use a simple argument based on the tight-binding approximation to estimate the Knight shift of Pt atoms on a clean surface. In bulk metal there are matrix elements of the Hamiltonian which join the tight-binding wave functions of adjacent atoms. The size of these so-called "hopping" matrix elements determine the width of the energy bands. Matrix elements internal to a given atom determine the center of gravity of the band.

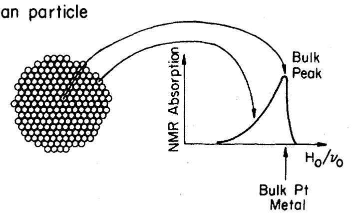
Surface atoms differ from bulk atoms in that they lack neighbors on one side, hence lack the corresponding hopping matrix elements. For example, if the surface is the $z = 0$ plane, the d functions $3z^2 - r^2$, xz, and yz, which have charge pointing along the z direction, will be strongly affected by the absence of a plane of atoms. The functions xy and $x^2 - y^2$ will be less strongly affected.

As a result, we expect that about $\frac{3}{5}$ of the total density of states of surface atoms will extend over a smaller spacing above and below the center of gravity of the band than for the bulk metal. Since the Pt band is nearly full, it will be only the remaining $\frac{2}{5}$ of the density of states which will intersect the Fermi energy and thus give rise to a Knight shift. This argument suggests that the Knight shift of atoms on a clean pt surface might be about $\frac{2}{5}$ of that in the bulk metal.

There is an important additional complication which should be mentioned. At a surface there is likely to be hybridization of Pt 6s or 6p states into the 5d wave functions. The 5d electrons produce the negative Knight shift of bulk Pt metal by core polarization of the inner s shells since d electrons by themselves produce no *net* shift in a powder sample. The 6s electrons should produce a positive Knight shift some 14.36 times larger, per unpaired electron-spin, than that of the 5d electrons.[19] In a given applied field, the number of unpaired spins is proportional to the density of states in energy. Ordinarily the 6s electrons are not important since the density of states of the 6s band is so much less than that of the 5d density of states. However, hybridization lets the 6s wave function partake of the high 5d density of states. Thus a hybridization of 5% 6s and 95% 5d would have a Knight shift only 23% of that for 100% 5d, the unhybridized case (assuming that the density of states is unchanged).

Atoms which are in interior layers near the surface would be expected to have Knight shifts between those of bulk Pt and those on the surface.

(a) Clean particle



(b) Coated particle

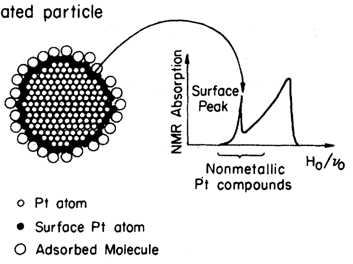


FIG. 3. General form of line shapes expected for a sample of small Pt particles which are (a) clean and (b) coated with adsorbed molecules.

Note, however, that if a surface atom has a well-defined site, as in a (111) plane, it should possess a unique Knight shift with a well-defined average value and a well-defined anisotropy. To the extent that proximity to corners or edges of the particle disturbs things, the surface resonance will be broadened. In order to see a well-defined resonance one would need a surface face sufficiently large for there to be many Pt atoms far from corners or edges. A resolved surface peak would result if the breadth of the surface peak were smaller than the difference in Knight shift between the surface layer and other layers. We believe this should happen with *clean* surfaces for particles which are larger than those on which we report.

For our particles we would expect the resulting NMR absorption line shape when the surface is clean to look like that shown in Fig. 3(a). The peak at the position of bulk Pt arises from Pt nuclei in the deep interior of the particles, whereas the broad smear at lower fields arises from Pt nuclei near the surface of the particles. The absorption at any given field H_0 is proportional to the number of Pt nuclei which exhibit the particular Knight shift corresponding to that field given by Eq. (5). Thus, the absorption line shape gives us the density function of Knight shifts in the sample.

Now consider Pt particles which are coated with adsorbed molecules. The Pt atoms on the surface of the particle are now chemically bonded to these molecules. In ordinary chemical bonds, the electron spins are completely tied up. If the conduction electrons of the surface atoms were likewise tied up in the bonds to the adsorbed atoms, the surface Pt atoms would actually become nonmetallic in nature. The nuclei of the surface atoms would experience zero Knight shift since their conduction electrons are all paired off in chemical bonds. We would expect these nuclei to give rise to a peak in the line shape somewhere near the position of the Pt resonance in nonmetallic compounds [Fig. 3(b)].

There are, of course, still many different kinds of sites, even for these surface nuclei. But if their spins are tied up in chemical bonds, they can only experience chemical, not Knight, shifts. The range of chemical shifts which surface Pt can exhibit in the different sites determines both the position and width of the peak. The fact that chemical shifts are much smaller than the Knight shift makes this peak narrow and thus easily resolvable from the rest of the line in contrast to the surface peak of a clean surface.

Thus, for a sample of Pt particles coated with adsorbed molecules, we should obtain a line shape with the following features: (1) a "bulk peak" due to nuclei in the deep interior of the larger particles, (2) a "surface peak" due to the nuclei of surface atoms which are bonded to the adsorbed molecules, and (3) a relatively structureless "smear" (between the two peaks) due to nuclei near the surface of the particles but not *on* the surface or, to be more precise, not chemically bonded to any adsorbed molecules.

IV. EXPERIMENTAL TECHNIQUES

A pulsed NMR spectrometer was used which operated at 74 MHz ($H_0 = 80-85$ kG for ^{195}Pt). Because of the large inhomogeneous broadening in our samples, we were unable to observe free induction decays. Thus we employed the well-known spin-echo technique that essentially removes the effect of inhomogeneous broadening by refocusing the nuclear magnetization into an echo.[17]

A spin echo consists of two back-to-back free induction decays. If all the nuclei in the NMR line could be excited, then the Fourier transform of the free induction decay would give us the line shape. The same should be true of the spin echo. Its Fourier transform would also give us the line shape. However, in our samples the line is so broad that only a small portion of the line can be excited at any one time. Thus, the Fourier transform only

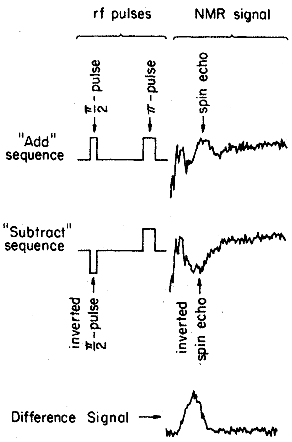


FIG. 4. Add-subtract spin-echo technique. Inverting the first rf pulse inverts the spin echo. By subtracting the inverted spin echo from the noninverted one, we effectively add spin echoes but subtract out the coherent noise due to the second rf pulse. The NMR signals shown were each obtained by signal averaging 20 000 times. The two rf pulses were separated by 50 μs.

gives us the line shape near the frequency of the applied rf pulses. Since the NMR signal is phase detected, this corresponds to the zero-frequency component of the Fourier transform, i.e., the area of the spin echo. By measuring the area of the spin echo at different values of H_0, holding ν_0 fixed, we can obtain the line shape, point by point.

The spin echoes from our samples are quite small and required extensive signal averaging. Each point on the line-shape plots was obtained by signal averaging a spin echo 50 000 times or more. With so much signal averaging, "coherent noise" is always a potential problem. This kind of noise arises from the transient electronic response of the NMR spectrometer to the rf pulses and may last long after the pulse is off and thus interfere with the observation of a spin echo. To eliminate the interference from coherent noise we used an "add-subtract" technique[20] (Fig. 4). This technique is based on the following principle: Inverting (180° phase shift) the first rf pulse of a spin-echo sequence inverts the spin echo, but, of course, does *not* invert the coherent noise, which arises principally from the second rf pulse. By subtracting the inverted spin echo from the noninverted spin echo, we effectively add the two spin echoes. On the other hand, the coherent noise due to the second pulse is subtracted out in this procedure. The adding and subtracting of the NMR signal is done digitally and on alternate pulse sequences to eliminate problems from small gain drifts.

V. RESULTS

A. Line shapes of untreated samples

Our initial line-shape measurements were done on untreated samples, i.e., samples which were opened to air after their initial preparation and characterization. The nature of the adsorbed molecules on these samples is discussed below. The line shapes from our six samples are shown in Fig. 5. As can be seen, the lines are very broad (3–5 kG at 74 MHz), extending the full range of Knight shifts from that of nonmetallic compounds to that of bulk Pt metal. All of the line shapes shown have been scaled to have the same area. As we move from samples of larger particles to those of progressively smaller particles, the intensity of the line shifts from the metallic end of the line shape (the high-field end) to the nonmetallic end (the low-field end). The two peaks discussed in Sec. III B can be clearly seen in some of the line shapes: a bulk peak at 1.138 kG/MHz and a peak at 1.089 kG/MHz, which, as we show below, is a surface peak.

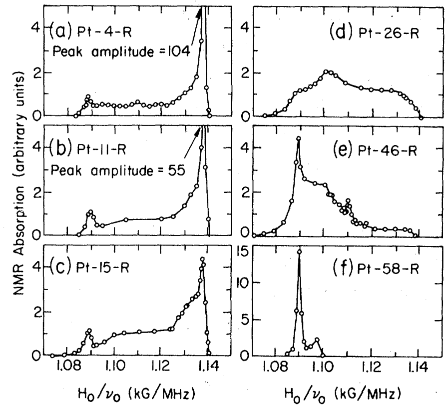


FIG. 5. NMR absorption line shapes for six samples at 77 K and $\nu_0 = 74$ MHz.

A small peak at 1.110 kG/MHz can be seen in some of the line shapes. This is a ^{207}Pb NMR signal due to lead[21] in the solder used in the construction of our NMR coil. It alone remains when the sample is removed from the coil.

1. Bulk peak

The bulk peak at 1.138 kG/MHz is very prominent in the line shapes of samples Pt-4-*R*, Pt-11-*R*, and Pt-15-*R* (Fig. 5) and occurs exactly at the position of the ^{195}Pt resonance in bulk Pt metal. This bulk peak arises from Pt nuclei in the larger particles where the environment is more like that of bulk Pt. Thus, the intensity of this peak progressively decreases for samples with smaller particles.

The bulk peaks are shown in more detail in Fig. 6, along with the line shape for sample Pt-bulk for comparison. As we can see, the bulk peaks in samples Pt-4-*R* and Pt-11-*R* [Figs. 6(b) and 6(c)] are very similar to that of Pt-bulk [Fig. 6(a)]. The nuclei giving rise to these peaks are in a very bulklike environment.

In contrast, the bulk peak in sample Pt-15-*R* [Fig. 6(d)] is much broader. The nuclei giving rise to this peak are *not* bulklike. They could very well be in regions of the particles where the Knight shift is spatially oscillating about its value in bulk Pt. This gives rise to Knight shifts both *above* as well as below the bulk value. Strong evidence for these oscillations is seen in the "slow beats" phenomenon which we discuss in paper III.

From the size distribution of particles in sample Pt-15-*R* (Fig. 1), we see that the largest particles

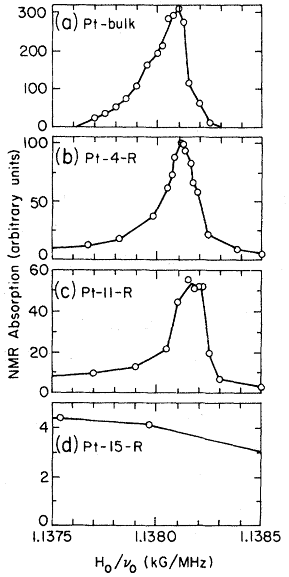


FIG. 6. Bulk peaks from Fig. 5 in more detail. For comparison, the line shape of sample Pt-bulk is also shown.

which contribute significantly to the total NMR absorption are about 100 Å in diameter. The fact that we do not see any truly bulklike peak in this sample indicates that even these particles are not bulklike in nature.

We have not yet been able to propose a model that can account for both the large difference between the bulk peaks of samples Pt-15-*R* and Pt-11-*R* and the comparatively *small* difference between those of samples Pt-11-*R* and Pt-4-*R*. Perhaps electron micrographs of samples Pt-4-*R* and Pt-11-*R* would shed some light on this problem.

2. *Surface peak*

A peak at 1.089 kG/MHz is evident in all the line shapes (Fig. 5). This peak occurs near the position of ^{195}Pt resonance in nonmetallic compounds and grows progressively smaller in samples with larger particles. These facts suggest that the peak may be a surface peak as described in Sec. III B. In fact, if this model is correct, the area of these peaks relative to the total area of the line should be equal to the dispersion, i.e., the number of surface Pt atoms (whose nuclei give rise to the surface peak) relative to the total number of Pt atoms in the sample. Such a measurement provides a test of the assumption that the peak arises from surface atoms, and also another independent measurement of the dispersion. With the use of the peaks as drawn in Fig. 7 (in samples Pt-26-*R* and Pt-46-*R*, where only the low-field side of the surface peak is well resolved from the line, the high-field side of the peak was drawn by assuming the peaks to be symmetric about 1.089 kG/MHz), we obtained dispersions as shown in the figure, in fair agreement with values obtained by hydrogen chemisorption for the same samples (see Table I). The agreement clearly confirms the hypothesis that the peak arises from surface Pt atoms.

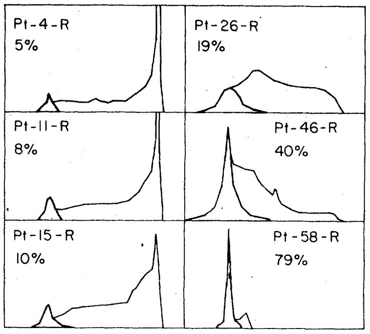


FIG. 7. Dispersion obtained from area of surface peak relative to total area of the line.

As remarked earlier, the samples designated by *R* have a cover layer of molecules, which we identify later in this paper. The position of the resonance shows that *R* virtually eliminates the ^{195}Pt Knight shift, evidently by tying up the Pt electron spins. Relaxation data further support this reasoning. The ^{195}Pt spin lattice relaxation time at the surface peak is very long, as is discussed in paper II.

B. Treated samples

If the peak at 1.089 kG/HMz is due to surface Pt atoms, it ought to be sensitive to what kinds of molecules are adsorbed on the surface of the Pt particles. Since sample Pt-46-*R* has a prominent and resolved surface peak, we carried out several chemical treatments on this sample, varying the type of adsorbed molecule.

1. *Cleaned*

We "cleaned" sample Pt-46-*R* by heating it to 300 °C (well below the temperature at which the Pt particles coalesce) and treating it with hydrogen and oxygen as shown in Table II. This procedure removes adsorbed molecules from the surface of the Pt particles. The sample was removed from the

TABLE II. Procedure for cleaning a sample by alternately flowing gas over it and pumping on it, as shown. Temperature of sample is maintained at about 300 °C.

Time duration	Procedure
18 h	Evacuate
10 min	Flow H_2 at 1 atm
5 min	Vacuum pump
10 min	Flow O_2 at 1 atm
5 min	Vacuum pump
10 min	Flow H_2 at 1 atm
5 min	Vacuum pump
10 min	Flow O_2 at 1 atm
5 min	Vacuum pump
10 min	Flow H_2 at 1 atm
5 min – 1h	Vacuum pump

oven and sealed under vacuum in a glass ampoule while still warm. We label this sample Pt-46-clean.

The Pt line shape of this sample is shown in Fig. 8(b). As we compare this with the original sample Pt-46-*R* [Fig. 8(a)], we see two major differences: (1) The peak at 1.089 kG/MHz is gone, and (2) the intensity of the high-field shoulder between 1.12 and 1.14 kG/MHz is significantly larger. This result is consistent with the model of a clean surface presented in Sec. III B: The surface Pt atoms now see themselves in a metallic environment, causing the peak at 1.089 kG/MHz to disappear and the intensity of the metallic end of the line shape to increase.

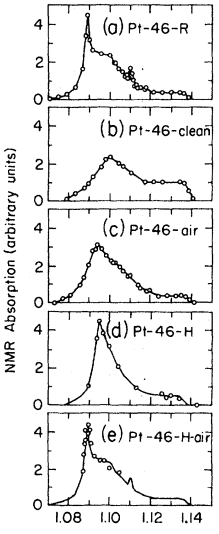


FIG. 8. NMR absorption line shapes for treated samples: (a) Pt-46-*R*, untreated [same as Fig. 5(c)], (b) Pt-46-clean, adsorbed molecules cleaned from surface of Pt particles, (c) Pt-46-air, exposed sample Pt-46-clean to air, (d) Pt-46-H, exposed sample Pt-46-H to air for several weeks.

2. Expose to air

In order to introduce adsorbed molecules onto the surface of the Pt particles without any further heat treatments, we simply broke open the glass ampoule containing sample Pt-46-clean and exposed it to air. This probably had the effect of coating the samples with adsorbed oxygen. We label this sample Pt-46-air.

The line shape of this sample is shown in Fig. 8(c). We observe that (1) a surface peak has reappeared, but now at a different position (1.095 kG/MHz) and somewhat broader than in the original sample PT-46-*R* and (2) the intensity of the high-field shoulder (between 1.12 and 1.14 kG/MHz) has been reduced to the original intensity in the untreated sample Pt-46-*R*. The peak in T_1 is also found to have moved to this new position (1.095 kG/MHz).

Since the surface peak arises from chemical shifts of the surface Pt bonded to adsorbed molecules, we expect that the position and width of this peak will depend on the nature of the adsorbed molecule. Comparison of the line shape of the original sample Pt-46-*R* and sample Pt-46-air clearly indicates that adsorbed molecules in these two samples are different.

3. Exposed to hydrogen

We treated sample Pt-46-*R* again. We first "cleaned" it (as described in Sec. IV B 1) and then exposed it to hydrogen at about 0.5 atm and then cooled it to room temperature under positive hydrogen pressure. Finally we pumped off the excess hydrogen and sealed the sample in a glass ampoule

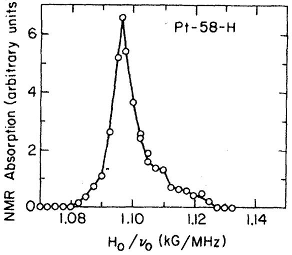


FIG. 9. NMR absorption line shape for sample Pt-58-H, prepared by cleaning sample Pt-58-*R* and then exposing it to hydrogen.

under vacuum. This treatment should have the effect of coating the Pt particles with adsorbed hydrogen at nearly 100% coverage. We label this sample Pt-46-H.

The line shape for this sample is shown in Fig. 8(d). A surface peak is present at 1.095 kG/MHz which is approximately at the same position as the peak in sample Pt-46-air but the peak is somewhat narrower. Also, the low intensity shoulder at high field is identical to that of samples Pt-46-*R* and Pt-46-air. It appears that this shoulder is signature of coated Pt particles.

We also treated sample Pt-58-*R* the same way as sample Pt-46-H, i.e., we cleaned it and exposed it to hydrogen. We label this sample Pt-58-H. Its line shape (Fig. 9) also showed a prominent surface peak at 1.096 kG/MHz, which is approximately at the same position at the surface peak in sample Pt-46-H.

4. Forming the R peak

Although exposure to hydrogen or to air did not reproduce the *R* peak, we have subsequently succeeded in reproducing it. We first reproduced it accidentally in a manner which led us to make an identification of the peak by a line of reasoning that we later found to be incorrect. We inadvertently cracked the vial containing sample Pt-46-H, exposing it to air. Several months later on examining the resonance (of what we now called Pt-46-H-air), we found the signal shown in Fig. 8(e). [We only took data near the surface peak where the difference in line shapes are most prominent. The line drawn is the line shape of sample Pt-46-*R* in Fig. 8(a).] Clearly we had reproduced the *R* resonance. We guessed that OH must somehow be involved.

We are currently studying the circumstances for formation of the *R* peak and plan to report on those results elsewhere. The circumstances cited above, however, led us to measure the position of the ^{195}Pt resonance in $H_2Pt(OH)_6$. In this compound, each Pt atom is bonded to six OH groups. If OH groups were responsible for the very paramagnetic position of the surface peak, then this effect ought to show up in $H_2Pt(OH)_6$ also, resulting in a very paramagnetic chemical shift of the Pt resonance. We measured the position of the Pt line in this compound and found it to be at 1.0895 kG/MHz, exactly at the *same* position as the surface peak. [This corresponds to a chemical shift 0.093% with respect to H_2PtI_6. To our knowledge, only $(PtF_6)^{2-}$ and $(PtCl_3F_3)^{2-}$ have more paramagnetic chemical shifts.]

Figure 2 illustrates two well-known important points. Comparing Na_2PtCl_4 and Na_2PtBr_4 we see that for the same coordination the resonance frequency shifts when the chemical species of the ligand is changed. Comparing the compound H_2PtCl_6 and $Pt(NH_3)_4Cl_2$ we see this point again. Comparing the compound H_2PtCl_6 in which Pt has six Cl neighbors with Na_2PtCl_4 which Pt has four Cl neighbors, we see that changing the coordination for a given species of ligand also changes the ^{195}Pt chemical shift. Since $H_2Pt(OH)_6$ has such a large paramagnetic chemical shift, substitution of other ligands for OH should produce big effects.

We therefore conclude that since the position of the *R* surface peak coincides exactly with the ^{195}Pt absorption in $H_2Pt(OH)_6$, the surface Pt must have sixfold coordination to OH's. This conclusion requires that there be a source of hydrogen atoms sufficient to provide six hydrogen atoms per surface Pt. It also requires that the surface reconstruct. Sinfelt, Via, and Lytle have informed us that their extended x-ray absorption fine-structure studies of very high dispersion Pt samples which had been exposed to air show that following such treatment there are no Pt—Pt bonds, a result consistent with the idea of some form of reconstruction.

VI. OTHER WORK

Yu *et al.*[11] also studied small Pt particles with the use of NMR. Their samples consisted of *unsupported* Pt particles. They observed a narrow peak at the position of bulk Pt, very much like our samples Pt-4-*R* and Pt-11-*R*. None of their samples exhibit the features we observed in our higher dispersion samples. For example, in sample Pt-15-*R*, we observe the "slow beats" phenomenon in the spin echoes (see paper III). Under the same conditions, Yu *et al.* did not observe this phenomenon in their samples but instead observed spin diffusion, which indicates a much smaller inhomogeneous broadening. We conclude that the Pt particles in their samples are at least larger than those in our sample Pt-15-*R*.

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

[2] J. J. McCarroll, Surf. Sci. 53, 297 (1975).

[3] G. A. Somorjai, Surf. Sci. 89, 496 (1979).

[4] H. E. Rhodes, C. P. Slichter, and J. H. Sinfelt, Bull. Am. Phys. Soc. 25, 272 (1980).

[5] H. T. Stokes and C. P. Slichter, Bull. Am. Phys. Soc. 25, 273 (1980).

[6] H. E. Rhodes, Ph.D. Thesis, University of Illinois, 1981 (unpublished).

[7] H. T. Stokes, H. E. Rhodes, P.-K. Wang, C. P. Slichter, and J. H. Sinfelt, in *Nuclear and Electron Resonance Spectroscopies Applied to Materials Science,* edited by E. M. Kaufmann and G. K. Shenoy (North-Holland, New York, 1981), pp. 253–258.

[8] C. P. Slichter, Bull. Magn. Reson. 2, 73 (1980); C. P. Slichter, Surf. Sci. 106, 382 (1981).

[9] H. E. Rhodes, P.-K. Wang, C. D. Makowka, S. L. Rudaz, H. T. Stokes, C. P. Slichter, and J. H. Sinfelt, proceding paper, Phys. Rev. B 26, 3569 (1982).

[10] H. T. Stokes, H. E. Rhodes, P.-K. Wang, C. P. Slichter and J. H. Sinfelt, following paper, Phys. Rev. B 26, 3575 (1982).

[11] I. Yu, A. A. V. Gibson, E. R. Hunt, and W. P. Halperin, Phys. Rev. Lett. 44, 348 (1980).

[12] J. H. Sinfelt, Ann. Rev. Mater. Sci. 2, 641 (1972).

[13] C. G. Granqvist and R. A. Buhrman, J. Appl. Phys. 47, 2200 (1976).

[14] S. Ino, J. Phys. Soc. Jpn. 27, 941 (1969).

[15] C. Solliard, Surf. Sci. 106, 58 (1981).

[16] R. VanHardevelt and F. Hartog, Surf. Sci. 15, 189 (1969).

[17] C. P. Slichter, *Principles of Magnetic Resonance,* 2nd ed. (Springer, New York, 1980).

[18] G. C. Carter, L. G. Bennett, and D. J. Kahan, in *Progress in Material Science,* edited by B. Chalmers, J. W. Christian, and T. B. Massalski (Pergamon, New York, 1977), Vol. 20, Part I, pp. 295–302. Also, R. Garth Kidd and J. Goodfellow, in *NMR and the Periodic Table,* edited by Robin K. Harris and Brian E. Mann (Academic, New York; 1978), p. 251.

[19] A. M. Clogston, V. Jaccarino, and Y. Yafet, Phys. Rev. 134, A650 (1964).

[20] This technique was inspired by a similar technique of D. M. Follstaedt and D. C. Barham, Sandia Laboratories, Albuquerque, NM, internal Report No. SAND77-0147 (unpublished).

[21] R. J. Snodgrass and L. H. Bennett, Phys. Rev. 134, A1294 (1964).