

## NMR OF ADSORBED MOLECULES AT LOW TEMPERATURES

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### Introduction

Nuclear spin lattice relaxation in insulating solids becomes very inefficient at low temperatures.  $T_1$  for one sample of lightly doped  $\text{CaF}_2$  at 10 mK has been reported to be several months.(1) Thus the high sensitivities expected to accompany the large equilibrium polarizations at low temperatures are generally impossible to obtain. However a remarkable exception occurs for nuclear spins at the surface of a solid which is covered by a film of  $^3\text{He}$ . Friedman, Millet and Richardson (FMR) discovered (2), in the case of solid tetrafluoroethylene, that there is efficient joint relaxation among  $^3\text{He}$  and  $^{19}\text{F}$  Zeeman energy and phonons. The details of the mechanism are not fully agreed upon, but clearly involve random modulation of  $^3\text{He}$ - $^3\text{He}$  and  $^3\text{He}$ - $^{19}\text{F}$  dipole-dipole interaction caused by quantum mechanical exchange within the  $^3\text{He}$  surface film.(3) The effect has been studied in many systems. The effective relaxation time of the surface spins depends on their gyromagnetic ratio and is very sensitive to their proximity to the  $^3\text{He}$  spins at the surface: it ranges from tens of seconds to a few hours in typical cases.(4).

The polarization of surface spins I through this FMR effect can of course spread to interior spins of the same species through spin diffusion induced by the I-I dipole-dipole interaction.(5) However this process is slow at best: the diffusion constant D for  $^{19}\text{F}$  in  $\text{CaF}_2$  is of the order of  $10^{-12} \text{ cm}^2 \text{ sec}^{-1}$ . When the spins are widely separated, for example because of low isotopic abundance, D is very much smaller. Moreover the presence of nuclear spins of another species X induces a "diffusion barrier" because the local fields they produce detune the Larmor resonances of neighboring I spins from one another.(6) The result is that in very many cases only the spins in one or two surface layers ever become polarized in practice. (It is still advantageous to use finely divided powder samples, but only to increase the fraction of their spins which are at the surface and therefore contribute to the NMR signal.)

The situation being what it is, NMR at very low temperatures would seem uniquely suited to the study of atomic and molecular species at solid surfaces. The electronic structures of surface states are often profoundly different from those associated with the bulk or the gaseous state: this circumstance is responsible, for example, for most of the features of heterogeneous chemical catalysis. NMR, well established as a spectroscopy which is diagnostic of changes in local electronic structure, can be extremely useful in the study of such systems. This observation is quite obvious: indeed, a large literature on NMR studies of surfaces exists. However one might expect such studies to benefit by

making use of the enormous gains in sensitivity which accompany spin systems polarized at millikelvin temperatures.

### Inhomogeneous Broadening

We have found, initially to our surprise, that nearly all samples studied at millikelvin temperatures display variable but typically large (several or many KHz) amounts of inhomogeneous line broadening, although the natural widths (as defined, for example, by echo decay envelopes) may be only a few Hz. It is now believed that this broadening has its origin in trace (ppm) quantities of paramagnetic impurities. These impurities, completely polarized at low temperatures, produce inhomogeneous Weiss fields in a sample composed of irregularly sized and shaped powder particles. At higher temperatures these fields are averaged by rapid electronic relaxation. A description of these effects will be presented elsewhere.

### Experimental

We use a commercially available dilution refrigerator (Oxford Instrument Co.) which allows previously prepared and sealed samples to be broken and lowered from a room temperature vacuum lock into a reservoir of pure liquid  $^3\text{He}$ . The liquid is cooled by thermal contact, through silver sinters, with the  $^3\text{He}$ - $^4\text{He}$  mixture in the mixing chamber. Below these chambers lies an RF plate, thermally anchored to the 1.2K stage of the refrigerator. This plate supports the tunable capacitors of the double resonance probe and the sample coil which surrounds the Kel-F sample cup in a saddle configuration. The capacitors can be adjusted from outside the cryostat by means of gears and drive rods, to tune and match the RF coil at either of two adjustable frequencies.

The temperature is monitored and regulated by means of a carbon resistor mounted on the mixing chamber. The resistor is calibrated against the nuclear magnetic susceptibility of protons adsorbed on the surface of silica powder, which follows Curie's law. The uncertainties in temperature were about 20%. However the temperature is apparently not an important variable in the experiments, since the relaxation time is found to be essentially temperature independent in the region from 10 mK to 800 mK.

The NMR signals were recorded by pulse techniques. No signal averaging was employed. Experiments were carried out in a field 3.39 Tesla over the temperature range 20-200 mK. Relaxation times were

measured by saturation - recovery, monitoring the recovering magnetization by small (<10 degree) tip pulses.

The rhodium and platinum catalysts were prepared by reducing aqueous solutions of the metal salts in the presence of finely divided (70 A.U.) silica, followed by replacement of hydrogen by  $^{13}\text{C}$ -labelled CO or doubly labelled ethylene. The stannic oxide catalyst sample was provided by J. Fraissard.

#### $^{13}\text{CO}$ on Rh:SiO<sub>2</sub>

Fig. 1 shows an example in which the inhomogeneous broadening mentioned above is relatively slight. The line shape is characteristic of an axially symmetric chemical shielding anisotropy of ca. 360 ppm. That value is the same, within experimental error, as previously reported(7) for pure solid CO. Thus we are led to the somewhat surprising conclusion that the electronic structure of CO is not greatly affected by bonding to a Rh surface.

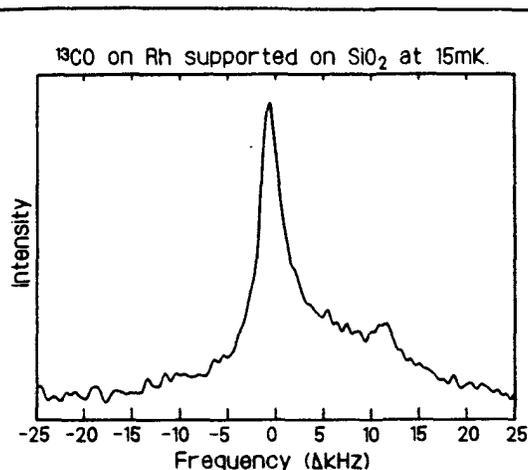


Figure 1.  $^{13}\text{C}$  powder pattern (single shot) of CO on Rh:SiO<sub>2</sub>.

#### $^{13}\text{CO}$ on SnO<sub>2</sub>(8)

The situation here is quite different. A large degree of inhomogeneous broadening is present, but not enough to obscure the fact that no shielding anisotropy of any magnitude approaching that in free CO is present. The results are consistent with a bridged carbonate-like structure for the adsorbed CO, consistent with earlier conjectures(9) on the mechanism of action of metal oxide oxidation catalysts.

#### $^{13}\text{C}_2\text{H}_4$ on Pt:SiO<sub>2</sub>

This sample shows such a large degree of inhomogeneous broadening that no structural information is available from the spectrum. However the spin lattice relaxation (Fig. 2) gives evidence of the presence of two distinct carbon species of equal populations, the one with the longer relaxation time being structurally located somewhat further from the geometrical surfa-

ce(4). Moreover the center of gravity of the spectrum shifts progressively during recovery from saturation, suggesting that the species with different relaxation times have distinct chemical shifts. It is tempting to associate these species with the two carbons of the original  $\text{C}_2\text{H}_4$  molecule, which is imagined to retain its integrity and is bonded to the Pt surface through one end. Indeed such structures have been clearly identified by Wang, Slichter and Sinfelt(10) in samples prepared by somewhat similar methods. However it is difficult to believe that two  $^{13}\text{C}$  spins separated by the length of a chemical bond would not indulge in mutual spin flips and recover with a common relaxation time over the time scale of Fig. 2. Thus we must conclude that in the present sample the ethylene has been dissociated in the course of adsorption, the two carbons ending up in separated sites with different chemical structures. This series of catalysts, whose properties are known to be sensitive to the details of preparation, is still under active study in our laboratory.

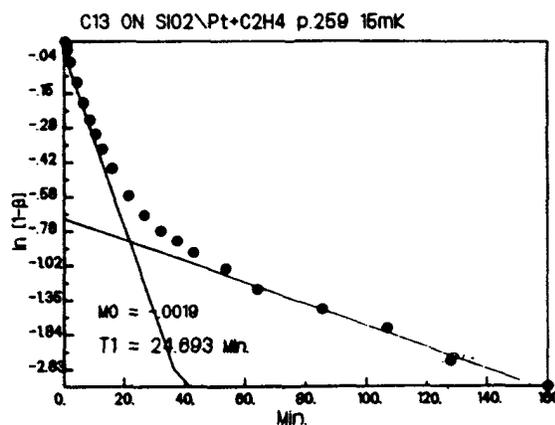


Figure 2. Recovery of  $^{13}\text{C}$  magnetization after saturation in a sample of doubly labelled  $\text{C}_2\text{H}_4$  adsorbed on Pt on a SiO<sub>2</sub> support. The T1 value shown in the figure refers to the shorter of the two relaxation times into which the recovery curve has been decomposed. Note that the populations of the two independently relaxing species are equal.

#### Conclusion

The high sensitivity expected by working at millikelvin temperatures and making use of the FMR relaxation mechanism is fully realized. Spectra of sub-monolayer coverages of adsorbates on substrates of quite moderate specific area are routinely obtained. However a by product of the low temperatures is that small quantities of paramagnetic impurities become fully spin polarized, so that (even if their T<sub>1</sub>'s remain short) they produce a spectrum of internal shift fields in a typical powder sample which may obscure the fine structure arising from chemical shifts. In typical catalyst preparations containing transition metals it is hard to see how trace quantities of such impurities can be regularly avoided. While there is some structure specificity in the spin lattice relaxation(4), it may turn

out that NMR is better suited to the study of these materials at temperatures high enough (perhaps 4K and higher) to ensure averaging of the local paramagnetic fields by electronic relaxation.

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#### References

1. P. L. Kuhns, P. C. Hammel, O. Gonen and J. S. Waugh, *Phys. Rev. B* **35**, 4591 (1987).
2. L. Friedman, P. Millet and R. C. Richardson, *Phys. Rev. Lett.* **47**, 1078 (1981).
3. A. Schuhl, F. B. Rasmussen and M. Chapellier, *J. Low Temp. Phys.* **57**, 483 (1984).
4. O. Gonen, P. Kuhns, C. Zuo and J. Waugh, *J. Magn. Res.* **81**, 491 (1989).
5. N. Bloembergen, *Physica* **15**, 386 (1949).
6. O. Gonen and J. S. Waugh, *Physica A* **156**, 219 (1989).
7. A. A. Gibson, T. A. Scott and E. Fukushima, *J. Magn. Res.* **27**, 29 (1977).
8. O. Gonen, P. L. Kuhns, J. S. Waugh and J. Fraissard, *J. Phys. Chem.* **93**, 503 (1989).
9. P. G. Harrison and G. W. Thornton, *Chem. Soc. Faraday Trans. 1*, **71**, 461 (1975).
10. P. K. Wang, C. P. Slichter and J. H. Sinfelt, *Phys. Rev. Lett.* **53**, 82, (1984).