Letters to the Editor

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Communications

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Proton-Enhanced Nuclear Induction Spectroscopy. A Method for High Resolution NMR of Dilute Spins in Solids*

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We report preliminary results of a general technique for high resolution NMR of isotopically rare (^{13}C, ^{15}N, ^{2}H, etc.) or chemically dilute spins in solids. The method combines established ideas of double resonance[1,2] and spin decoupling[3] in a novel way. It exploits abundant spins I, of abundance N_I and magnetic moment $\gamma_I I\hbar$ (usually protons), present in the sample, as a reservoir of polarization for the rare spins S, to permit the accumulation of an adequately intense S-spin spectrum after a single polarization of the I spins to equilibrium. The general procedure is as follows: (1) Polarize I in high field. (2) Cool I to a low spin temperature in the rotating frame. (3) Establish I–S contact for a time τ. (4) Record the S free induction decay while decoupling I. Steps 3 and 4 are repeated $\sim N_I/N_S$ times during which the I polarization is depleted and the S signal accumulated. The spectrum is obtained by Fourier transformation. The repeated cross polarization (CP) of step 3 results in a gain in power sensitivity of $\mathcal{G}_{\mathrm{CP}}\sim(N_I/N_S)(\gamma_I/\gamma_S)^2$ over conventional Fourier transform spectroscopy. For $S={}^{13}$C and $I={}^1$H in typical organic compounds, $\mathcal{G}_{\mathrm{CP}}\approx 10^3$.

The expected gain has been verified in preliminary experiments using the natural abundance of ^{13}C in $\sim$50 mg of solid adamantane, $C_{10}H_{16}$ (Fig. 1). The spectrum of Fig. 1(c), recorded in 0.8 sec, is severely limited by the nonideal probe and receiver employed, and by magnetic inhomogeneity, but nonetheless demonstrates the power of the cross-polarization procedure. In natural abundance ^{13}C spectra we expect a residual S–S linewidth of the order of 5 Hz.[4]

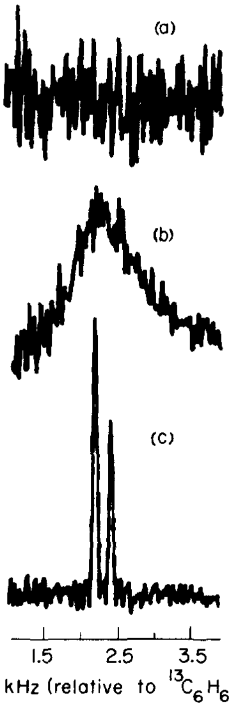

FIG. 1. Fourier transform NMR spectra of natural-abundance ^{13}C in polycrystalline adamantane at 24.46 MHz and room temperature. (a) Result of a single free induction decay. (b) Cross-polarization spectrum without decoupling (50 I–S contacts). (c) Cross-polarization spectrum with proton decoupling (14 contacts) obtained in 0.8 sec. Resolution (40 Hz) is determined by magnet inhomogeneity. The two lines are 87.5±1 ppm and 96.2±1 ppm upfield from a neat external reference of liquid $^{13}C_6H_6$ (proton decoupled).

Many versions of this method are clearly possible since the cooling, cross polarization, and decoupling can each be accomplished in several ways. In the present experiments the procedure, except for step 4, was the same as in the Lurie–Slichter[2] version of the Hartmann–Hahn[1] experiment. The steady spin-locking field acting on the I spins serves both for I–S contact (Step 3) and decoupling[3] (Step 4).

An important advantage of the present procedure over the indirect-detection methods[1,2] and their adaptations to higher resolution[5,6] is that the complete S-spin spectrum is obtained with adequate sensitivity in one shot, following a single polarization of the I spins, whereas the indirect methods employ repeated I repolarizations as the spectrum[1,2,5] or transient precession[6] is mapped out point by point. In typical solids having long T_{1I} and a rich S-spin spectrum the inherently high sensitivity of the indirect methods might be of little avail.[7]

If a single polarization is to be employed, it makes little difference how long it takes since it can be accomplished outside the spectrometer. Advantage can be taken of this fact by prepolarizing at very low temperature and high field, leading to a large further increase in sensitivity. Elementary calculations suggest that the cross-polarization method is capable of signal-to-noise ratios of $\sim$120 dB for ^{13}C in natural abundance in a 1 cm^3 sample. One can thus contemplate high resolution NMR of very rare spins and/or very small samples. Studies of chemical shift anisotropy of rare species (e.g., metals bound to proteins) or the dipolar structure of rare spin groups (e.g., ^{31}P in polyphosphate moieties) could be of value in structural studies.

By varying τ in step 2 above, one could study the dynamics of the cross-polarization process[8] for individual lines in the S-spin spectrum as an aid to spectral assignment and structure determination. This and other possibilities, as well as the analysis of various experimental procedures, will be discussed in detail elsewhere.

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[†] Hertz Foundation Predoctoral Fellow.

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[7] Certain of these methods could be improved. For example, the experiment of Ref. 6 would profit greatly from continuous observation of the locked I-spin signal, as it peters out, using the procedure specified by E. D. Ostroff and J. S. Waugh, Phys. Rev. Letters **16,** 1097 (1966).

[8] D. A. McArthur, E. L. Hahn, and R. Walstedt, Phys. Rev. **188,** 609 (1969).

Notes

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Thermodynamic Constants and Rate Constants of the Formation of the Pyrene Dimer Cation

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Although several papers[1–6] have been published concerning ESR and optical spectra of dimer cations of aromatic hydrocarbons, only a little is known about the dynamic properties[7–9] of the formation of dimer cations. We report here thermodynamic constants, ΔH and ΔS, and rate constants, k_f and k_b, of the reaction

$$\text{pyrene}^{+}+\text{pyrene}\underset{k_b}{\overset{k_f}{\rightleftarrows}}(\text{pyrene})_2{}^{+}.$$

The experimental apparatus and procedures for pulse radiolysis are described in the previous paper.[9] The temperature was controlled by a flow of cooled or heated nitrogen gas in a thermostatic box with a thin aluminum window to admit the electron beam and a quartz evacuated cell as a window for the analyzing light beam.

Our previous study[9] has shown that pyrene monomer cations are in equilibrium with pyrene dimer cations in irradiated oxygenated benzonitrile solutions of pyrene containing biphenyl in excess and that the relationship between the optical density and the concentration of pyrene is expressed by the equation

$$1/(D-D_a{}^0)=[1/l(\epsilon_m-\epsilon_a)C_0](1+K[\text{P}]),$$

where D is the observed optical density at the equilibrium state, $D_a{}^0$ is the optical density in the case that all the cation exists as the dimer cation, l is the optical