ENHANCED INHOMOGENEOUS NUCLEAR SPIN ECHOES FOR DILUTE SPINS IN SOLIDS

A. PINES and T.W. SHATTUCK
Department of Chemistry, University of California, and Inorganic Materials Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720, USA

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We report the observation of enhanced and long-lived ^{13}C nuclear spin echoes in solids. These echoes can be used to determine limiting natural resolution and lineshapes due to the randomly distributed ^{13}C spins coupled via dipolar interactions, and to measure, directly, molecular diffusion in the solid state.

The method of nuclear spin echoes [1] has provided an extremely powerful tool for the direct study of diffusion in liquid-like systems. Unfortunately, this has not been applicable to solids, since in these systems the decay of spin coherence is normally dominated by strong dipolar interactions and is thus not easily reversible [2]. We wish to report the first observation of enhanced, long-lived ^{13}C nuclear spin echoes in solids. These experiments have allowed several novel features of high resolution solid state NMR to emerge, e.g., the feasibility of determining natural lineshapes and linewidths due to randomly distributed nuclei (in this case with internal dipolar coupling) and the direct measurement of atomic or molecular diffusion in the solid state. The latter extends to solids an approach reserved heretofore for liquids and recently extended to liquid crystals [3]. The details of these experiments will be presented elsewhere. In this communication, we describe briefly the approach employed and present some novel preliminary results.

NMR of rare nuclei, in natural isotopic abundance in solids, poses two challenging problems, namely low sensitivity and dipolar broading by abundant neighboring spins. We carry out the remainder of the discussion with the common example of ^{13}C (dilute) and ^{1}H (abundant). The problems can be overcome by cross-polarization between the ^{1}H and ^{13}C spin reservoirs and high power spin-decoupling [4]. Pulsed modulation of the ^{13}C rf output, on a time scale slow compared to the ^{1}H rf cycle time, can subsequently produce inhomogeneous nuclear spin echoes in the solid, provided the decoupled free induction decay is dominated by static magnetic field gradients over the $^{13}C-^{13}C$ dipolar coupling. This is certainly the case in all our current experiments.

Fig. 1 depicts schematically one of the rf modulation schemes employed in these studies. The first part of the experiment is a "single shot" total cross-polarization version of proton enhanced NMR [4–6]. There are various ways of achieving the cross-polarization, and the one used here is technically particularly convenient [6]; if P^0 is the power signal/noise obtained from the ^{13}C spins in a usual free induction decay, then by proper adjustment of the rf amplitude, the theoretical signal/noise obtainable after such a total cross-polarization is

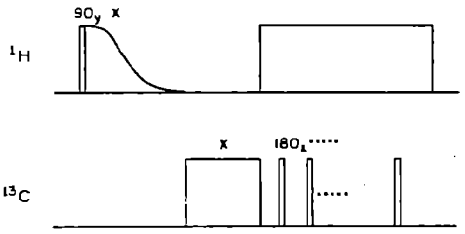

Fig. 1. Procedure employed for obtaining enhanced ^{13}C nuclear spin echoes, showing the rf modulation amplitudes and timing. Cross-polarization occurs from the demagnetized proton reservoir in the rotating frame. The large ^{13}C magnetization is then treated by a slow train of pulses during strong ^{1}H irradiation.

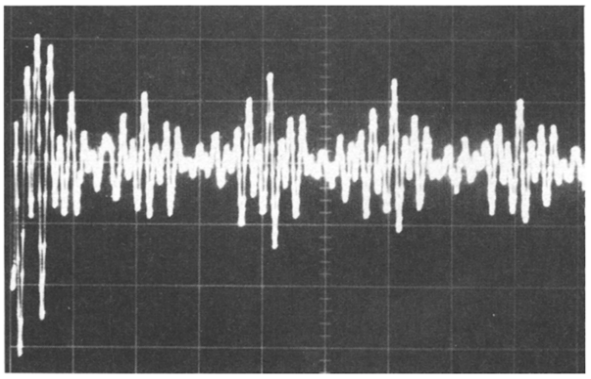

Fig. 2. Oscilloscope trace of ^{13}C detector output from sample of solid adamantane in response to sequence of fig. 1 with refocussing pulses (echoes) 20 msec apart. The oscilloscope scale is 10 msec/div.

given by P[†]:

$$P = \tfrac{1}{4}(\gamma_H/\gamma_C)^2(N_H/N_C)P^0, \qquad (1)$$

where γ and N are magnetogyric ratios and numbers of spins in the sample. This approach is quite powerful for the purposes of our present experiments; since large signals are observed in one shot [6, 8, 9] a substantial reduction in expenditure of rf energy is realized over multiple contacts with signal accumulation.

In fig. 2 we show an example of the response of naturally abundant ^{13}C nuclei in a polycrystalline sample of adamantane ($C_{10}H_{16}$) to this type of excitation with an externally imposed magnetic field gradient. Echoes are indeed observed and the oscilloscope trace depicts the type of signal/noise observable by this technique even in small samples ($\approx$ 50 mg) with detector bandwidths of $\approx$ 10 kHz. A train of echoes with closely spaced pulses exhibits a prolonged exponential decay[‡] ($T_2 > 200$ msec) demonstrating for the first time the high resolution attainable in solids by combining the effective removal of static magnetic field inhomogeneity with the sensitivity and resolution enhancement.

Of considerable interest to us is the possibility which our technique introduces, of measuring directly rapid diffusion in the solid state. This is accomplished by measuring the irreversible loss of coherence with a spin echo decay envelope in pulsed magnetic field gradients of well-defined duration, magnitude and orientation [1]*, **. Preliminary high temperature experiments on adamantane, an excellent prototype "plastic solid", and other materials, are under way in our laboratory and should provide a direct check of previous studies employing proton spin relaxation in the demagnetized state and plastic flow measurements [11]. Our approach offers the promise of being generally applicable, directly interpretable even when molecular reorientation is present, and simply adaptable to studies of diffusion anisotropy. We believe that a particularly important additional application of this approach will be to trapped and adsorbed species in solids and to dynamical studies of anisotropic diffusion in partially oriented biological systems. Details will shortly be presented of full experimental results obtained on our equipment, which is being modified to produce oriented pulsed field gradients and higher power rf output.

The experiments were performed on a homebuilt double-resonance spectrometer operating at 106 MHz for ^1H.

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† This is 1/4 the power signal/noise available following a maximum efficiency transfer. Such an adiabatic cross-polarization can be achieved by multiple adiabatic cross-over or by adiabatic remagnetization of the ^{13}C reservoir [7].

‡ In agreement with early predictions of Anderson and of Kittel and Abrahams concerning lineshapes for randomly distributed spins [10].

* The chemical shielding anisotropy will allow complete studies to be carried out even in polycrystalline samples, by monitoring differential decay of the spectrum obtained by Fourier transformation of the echoes.

** In cases where the diffusion shortens the proton spin–lattice relaxation times making the cross-polarization ineffective, echoes are still observed following a normal pulsed free induction decay, of course with reduced sensitivity.

References

[1] E.L. Hahn, Phys. Rev. 80 (1950) 580;
H.Y. Carr and E.M. Purcell, Phys. Rev. 88 (1952) 415.
[2] W.-K. Rhim, A. Pines and J.S. Waugh, Phys. Rev. Letters 25 (1970) 218; Phys. Rev. B3 (1971) 684.
[3] R. Blinc, J. Pirs and I. Zupancic, Phys. Rev. Letters 30 (1973) 546.
[4] A. Pines, M.G. Gibby and J.S. Waugh, J. Chem. Phys. 59 (1973) 569.
[5] D.A. McArthur, E.L. Hahn and R.E. Walstedt, Phys. Rev. 188 (1969) 609.
[6] A. Pines, Proceedings of the First Specialized Colloque Ampere, Krakow, Poland (August, 1973).
[7] A. Pines, in preparation.
[8] J.S. Waugh, private communication.
[9] M. Goldman, Proceedings of the First Specialized Colloque Ampere, Krakow, Poland (August, 1973);
A. Abragam, Proceedings of the Autumn meeting of the British Radio Spectroscopy Group, Sussex, England (September, 1973).
[10] C. Kittel and E. Abrahams, Phys. Rev. 90 (1953) 238.
[11] H.A. Resing, N.T. Corke and J.N. Sherwood, Phys. Rev. Letters 20 (1968) 1227.