ENHANCED INHOMOGENEOUS NUCLEAR SPIN ECHOES FOR DILUTE SPINS IN SOLIDS

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Received 20 September 1973

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 line shapes 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 broadening 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 13C nuclear spin echoes, showing the rf modulation amplitudes and timing. Cross-polarization occurs from the demagnetized proton reservoir in the rotating frame. The large 13C magnetization is then treated by a slow train of pulses during strong 1H irradiation.](image-url)

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Fig. 2. Oscilloscope trace of $^{13}$C detector output from sample of solid adamantane in response to sequence of fig. 1 with re-
foocussing pulses (echoes) 20 msec apart. The oscilloscope scale
is 10 msec/div.
given by $P^\dagger$:

$$P = \frac{1}{4}(\gamma_1/\gamma_C)^2(N_1/N_C)P_0,$$

(1)

where $\gamma$ 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 sig-
nals are observed in one shot [6, 8, 9] a substantial re-
duction in expenditure of rf energy is realized over mul-
tiple contacts with signal accumulation.

In fig. 2 we show an example of the response of nat-
urally 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 tech-
nique 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 de-
cay ($T_2 > 200$ msec) demonstrating for the first time
the high resolution attainable in solids by combining
the effective removal of static magnetic field inhomog
enity 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 meas-
uring the irreversible loss of coherence with a spin echo
decay envelope in pulsed magnetic field gradients of
well-defined duration, magnitude and orientation [1]$^\star$, $^\star$.
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 in-
terpretable even when molecular reorientation is pre-
sent, and simply adaptable to studies of diffusion an-
isotropy. We believe that a particularly important ad-
ditional 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 ex-
perimental results obtained on our equipment, which
is being modified to produce oriented pulsed field gra-
dients and higher power rf output.

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

We gratefully acknowledge a grant from E.I. du Pont
de Nemours and Company for acquisition of a super-
conducting magnet, and support by the U.S. Atomic
Energy Commission through the Inorganic Materials
Research Division of the Lawrence Berkeley Laborato-
ry. We are grateful to E.L. Hahn for some valuable dis-
cussions, and to R. Milberg, J.J. Chang, E. Abramson,
D.D. Wilkinson and D.N. Shirley for their assistance
with the equipment and experiments.

$^\star$ The chemical shielding anisotropy will allow complete studies
to be carried out even in polycrystalline samples, by moni-
toring differential decay of the spectrum obtained by Fourier
transformation of the echoes.

$^\star\star$ 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 in-
duction decay, of course with reduced sensitivity.
References
