Carbon-13 proton NMR cross-polarization times in solid adamantane*

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Recently, novel double-resonance techniques have been developed for high sensitivity and high resolution NMR of dilute spins in solids.[1-5] The basis of one set of these experiments is the transfer of nuclear magnetic polarization from one nuclear species (I), normally protons, to a dilute species (S) such as ^{13}C, under study, and the application of high power spin decoupling.[6-8] A prime candidate for application of the techniques is the determination of full ^{13}C chemical shielding tensors in organic single crystals.[9-11] An important consideration in the design and efficiency of such experiments is that of the dynamics of the polarization transfer from the I to the S systems since this ultimately determines the sensitivity enhancement, the time scale accessible, and thus the range of possible systems that can be studied. In this communication we present preliminary results on a study of cross-polarization dynamics by direct observation of the dilute nuclear spins, and an approach to "total cross-polarization".

To make the problem more concrete, Fig. 1 shows a schematic of the general approach. Two extreme cases may be considered: "multiple cross-polarization" and "total cross-polarization". In the first, a small amount of I polarization is transferred to the S spins and the cycle is repeated many times as indicated, with the S signal being accumulated. In the second, all or a substantial amount of the I polarization is transferred "in one shot"[4] and the experiment and observation of the S spins are performed once per I repolarization. It is not clear that the second approach is advantageous, since the dynamics of the cross-polarization may render the process slow and technically difficult. However, for experiments that require long observation times of the S spins, such as long-lived spin echoes or very high resolution spectroscopy, the multiple cross-polarization is clearly not possible, since it requires the expenditure of rf power and the maintenance of I spin order for unrealistically long times. Thus it is clear that a quantitative understanding of the process is a mandatory prerequisite for the development of these experiments.

The present experiments were performed on a small sample of solid polycrystalline adamantane. Cross-polarization occurs from a proton system demagnetized in the rotating frame.[12] This approach is selected since the analysis is simple and the technical requirements for total cross-polarization are not too stringent. The mechanism for the cross-polarization derives from fluctuations in the I–S magnetic dipolar coupling due to mutual spin flips amongst the I spins.[13] If the S field is turned on adiabatically in the cross-polarization step,

the maximal S polarization achievable is given by

$$M_S^{max} = (\gamma_I / \gamma_S)(N_I / N_S)^{1/2} M_S^{(0)} , \qquad (1)$$

where γ and N are magnetogyric ratios and numbers of spins, and $M_S^{(0)}$ is the normal S polarization when the S spin system is in equilibrium with the lattice. We found a maximal polarization of $X15$ due to the proton dipolar spin–lattice relaxation at 23 °C.

The cross-polarization times were obtained by observing the intensity of ^{13}C signals, for various ^{13}C irradiation times τ after adiabatic demagnetization of the proton system in the rotating frame. Both the magnitude of the polarization and the cross-polarization times depend on the magnitude of the ^{13}C rotating H_1 field and on frequency. The combined effects of loss of proton spin order in the demagnetized state due to dipolar spin–lattice relaxation and cross-polarization can be accounted for theoretically yielding cross-polarization times at various $^{13}C H_1$ fields. A plot of T_{IS}^{-1} vs H_1 is shown in Fig. 2 and is exponential over the whole range: $T_{IS}^{-1} \propto \exp(-\gamma H_1 \tau_c)$, in agreement with the $^{43}Ca-^{19}F$ work of McArthur et al.,[13] showing that the Lorentzian correlation function for the dipolar fluctuations is probably a common one.[14] The correlation time τ_c is ~140 μsec. Details will be published separately.

The magnitudes of the total cross-polarization times (~ secs) and the polarization achievable indicate that this
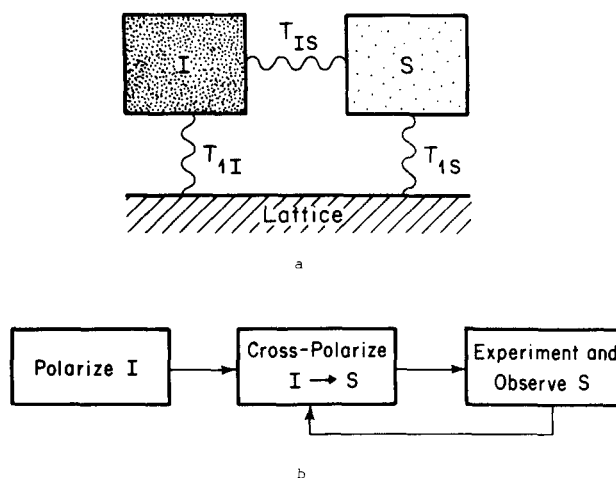

a

b

FIG. 1. General schematic of cross-polarization experiment. (a) shows the abundant I and dilute S nuclear species coupled to each other and to the lattice with characteristic times T_{IS} (cross-polarization times) and T_{1I}, T_{1S} (spin–lattice relaxation times). (b) shows the general approach.
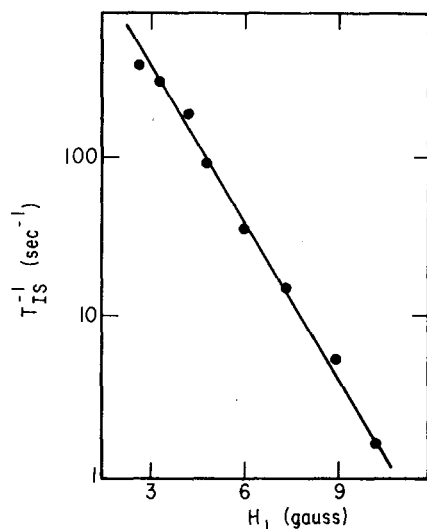
FIG. 2. Dependence of inverse cross-polarization time T_{IS}^{-1} on rotating ^{13}C H_1 field at resonance, in solid polycrystalline adamantane.

should be a powerful way of effecting sensitivity enhancement for NMR of dilute spins, and should permit serious savings in the expenditure of rf power. The experiments were performed on a homebuilt double-resonance spectrometer to be described in detail elsewhere. The proton frequency was 106 MHz and adiabatic demagnetization times from H_1 fields of several gauss ranged from

1–10 msec. We are grateful to Professor J. S. Waugh for valuable discussions and for communicating to us preliminary results of his recent work.

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