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Two-stage feature of Hartmann-Hahn cross relaxation in magic-angle sample spinning

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In magic-angle sample-spinning experiments the Hartmann-Hahn cross relaxation between protonated ^{13}C and protons usually proceeds in two stages, except in fast internal rotating $^{13}CH_3$. The protonated ^{13}C magnetization of powder samples changes very rapidly during the first tens of microseconds due to the fast energy exchange between each protonated ^{13}C and its directly bonded ^1H spins; then it approaches at a much slower rate to a quasiequilibrium value via the energy exchange between these $^{13}CH_n$ subsystems and the remaining ^1H spins. This fact means that the whole ^1H spin system is not in a quasiequilibrium state and is not describable by a single spin temperature at least during the first stage of the cross relaxation. The two-stage feature has been obviously revealed by the depolarization experiment for ^{13}C magnetization. The expression for protonated ^{13}C magnetization as a function of depolarization time has been deduced, which reaches agreement with the experiments semiquantitatively. The depolarization experiment offers a reliable approach to distinguishing between ^{13}CH and $^{13}CH_2$ signals in organic solids.

It is generally accepted that the time dependence of Hartmann-Hahn cross relaxation[1] between rare and abundant spins in NMR may be described by a single exponential function.[2,3] The theory most commonly put forward[4-6] describes the spin system as separate I- and S-spin reservoirs which are free to exchange energy in arbitrarily small units, and assigns a temperature to each of the two spin reservoirs so that the cross-relaxation process is describable by a change of spin temperature.

However, non-single-exponential phenomena have also been noted and analyzed. Hahn and his co-workers[1,7,8] have pointed out in their detailed analyses on cross relaxation that the exponential decay law is not valid for a short period of time at the beginning, when the relaxation is diffusion limited. Later Müller, Kumar, Baumann, and Ernst[3] observed strong transient oscillations in the polarized ^{13}C magnetization as a function of the cross-polarization time in a static ferrocine single crystal. The model adopted to explain the transient oscillation is essentially a modification of that proposed by Slusher and Hahn.[7] It is assumed that the dipolar interactions of the isolated S spin with the I spins are neglected except for the coupling to the directly bonded I spin in the SI group.

It is our intention in this paper to report that in cross-polarization magic-angle sample-spinning (CP-MASS)[1,9-11] experiments protonated ^{13}C magnetization of powder samples usually undergoes a two-stage change during the cross polarization except in fast internal rotating $^{13}CH_3$: it changes very rapidly during the first tens of μsec, then approaches at a much slower rate to a quasiequilibrium value exponentially. This two-stage feature is very common, not being restricted to those samples with fast internal molecular motion like ferrocine.

This two-stage feature was first observed in a selective polarization inversion experiment.[12] However, it is more advisable to reveal the feature with the depolarization method, where, instead of the polarized S magnetization in the standard CP-MASS experiment, the depolarized S magnetization is monitored. The pulse sequence utilized is shown in Fig. 1, which is a simple modification of the standard CP pulse sequence. Two additional intervals t_i and t_{c2} are inserted between the usual polarization time t_{c1} and detection time t_d. Both irradiations H_{1I} and H_{1S} are turned on during t_{c2} as they are during t_{c1}, while only the irradiation H_{1S} is turned on during t_i. As usual, during t_{c1}, I magnetization is locked along H_{1I}, while a polarized S magnetization is created along H_{1S}. During t_i (which is about 1 msec in our experiment) however, the I magnetization will gradually disappear due to spin-spin relaxation, while S magnetization is still locked along H_{1S} with only a little loss in intensity. During t_{c2}, when H_{1I} is turned on again, the polarization transfer happens again after an interruption during t_i, but in the reversed direction with respect to that during t_{c1}, that is, the S magnetization is now depolarized. The time dependence of the S magnetization as a function of depolarization time t_{c2} is recorded and analyzed.

As is well known, high speed spinning at magic angle causes a chemical shift powder pattern to become a single narrow line or a centerband flanked by sideband.[13,14] The intensity of the single line or the centerband is now taken

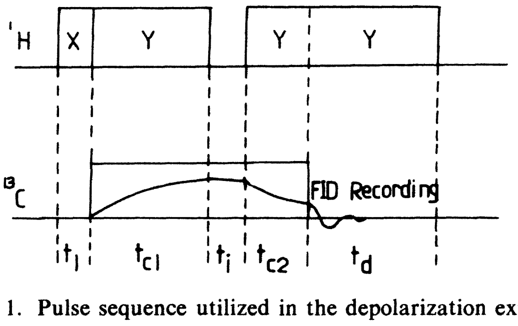

FIG. 1. Pulse sequence utilized in the depolarization experiment, where t_{c1} is the polarization time for S spins, t_i is the dephase time for I spins, and t_{c2} is the depolarization time for S spins. The development of the S magnetization is schematized by a solid line.

as the measure of the S magnetization.

Figure 2 shows the time dependence of intensity of ^{13}COOH and ^{13}CH$_2$ signals in a powder sample glycine, keeping t_{c1} at 5 msec and t_i at 1 msec. While the ^{13}COOH signal decreases single exponentially, the ^{13}CH$_2$ obviously decays in two stages with a turning point at $t_{c2} \approx 40$ μsec. Figure 3 shows the similar situation of ^{13}CH signal in a powder sample terephthatic acid with a turning point at $t_{c2} \approx 80$ μsec. The data shown have been obtained on the Bruker MSL-300 spectrometer with a spinning rate of 4 kHz.

The two-stage feature can be explained with the following model, which is essentially the same as that proposed by Müller *et al.*:[3] each isolated S spin and its directly bonded I spins make up a quasi-isolate SI_n subsystem, which is in thermal contact with a reservoir made up of remaining I spins. The energy exchange in each SI_n subsystem is very fast due to the strong direct dipolar interaction and determines the rapid change of S magnetization in the first stage of cross polarization. The much slower one between these subsystems and the remaining I spins via spin diffusion determines the second stage.

The two-stage feature signifies that the cross relaxation between protonated ^{13}C and protons belongs to the diffusion bottleneck limit,[1] so that the proton spin system is not always describable by a single temperature, at least so during the first stage.

In addition, it is also noted that the turning point of ^{13}C signal in ^{13}CH$_n$ group is just at about $(n+1)^{-1}$ of its initial value. This fact is by no means occasional and can be well understood if it is taken into account that the ratio of heat capacities[8,15] of the ^{13}C and ^{1}H in the subsystems ^{13}CH$_n$ is just n^{-1} under the Hartmann-Hahn matching condition.[1] Besides, this fact offers a reliable approach to distinguishing between ^{13}CH and ^{13}CH$_2$ signals in organic solids, because the relative intensity at the turning point is independent of the relaxation rate to a certain extent.

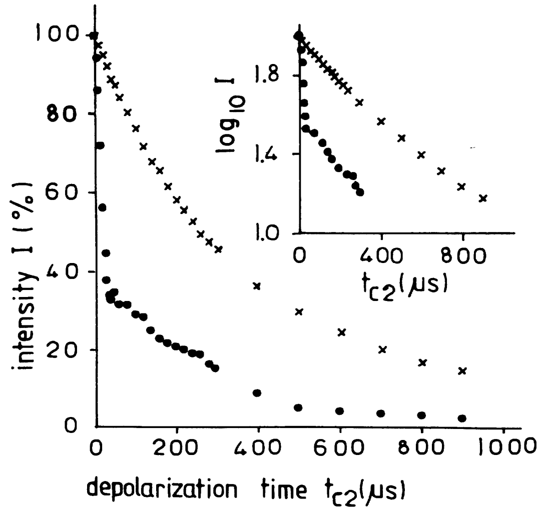

FIG. 2. The time dependence of intensity of ^{13}C signals on t_{c2} in a powder sample glycine in the depolarization experiment, keeping t_{c1} at 5 msec and t_i at 1 msec. × stands for ^{13}COOH signal, and ● stands for ^{13}CH$_2$ signal.

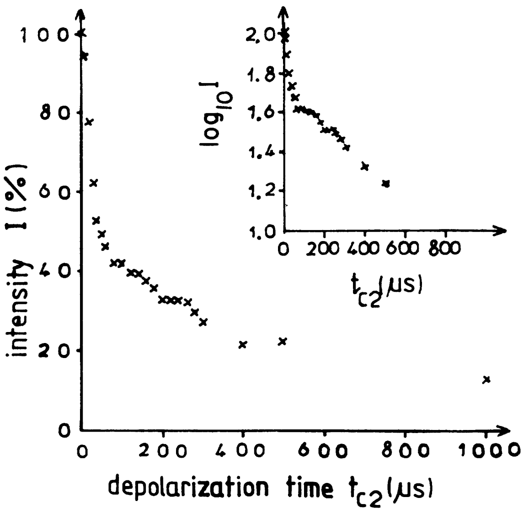

FIG. 3. The time dependence of ^{13}CH signal on t_{c2} in a powder sample terephthalic acid in the depolarization experiment, keeping t_{c1} at 5 msec and t_i at 1 msec.

It is worthwhile here to emphasize that the depolarization experiment is superior to the standard CP-MASS in revealing the details of cross relaxation process. With the latter it is difficult to know the real maximum polarized S signal and the exact time dependence of S signal to be determined by cross polarization alone, because the creation of S polarization depends not only on the cross-relaxation process itself, but also on some other factors, such as $T_{1\rho}$ of I spin, and Hartmann-Hahn matching condition. In the depolarization scheme, however, the finite initial S magnetization at the beginning of t_{c2} will certainly reach zero at last and the turning point occurs during the first tens of μsec. Therefore, the depolarization experiment adequately exposes the two-stage feature, and exactly reveals the relative intensity of S signal at turning point.

The quantitative expression for ^{13}C magnetization in high-speed spinning powder samples as a function of depolarization time can be deduced, starting from the formula for static single crystal obtained by Müller *et al.*:[3]

$$M_{sx}=M_{\infty}\left(1-\tfrac{1}{2}e^{-Rt}-\tfrac{1}{2}e^{-3Rt/2}\cos\tfrac{1}{2}bt\right) , \qquad (1)$$

where M_{sx} is the polarized ^{13}C magnetization for ^{13}CH group, b is dipolar coupling between ^{13}C and its directly bonded proton, R is the spin diffusion rate among protons, and t is the polarization time.

It is easy to obtain an expression for depolarized ^{13}C magnetization under the otherwise same condition:

$$M_{sx}=M_0\left(\tfrac{1}{2}e^{-Rt}+\tfrac{1}{2}e^{-3Rt/2}\cos\tfrac{1}{2}bt\right) . \qquad (2)$$

For a static powder sample, we will get a broadened powder pattern due to the anisotropic chemical shift. Each spot in the line corresponds to certain molecular orientations and may oscillate with a characterized frequency as the function of depolarization time because of the orientation dependence of b.

As the sample turns, the contributions from all the magnetically equivalent ^{13}C spins in the molecules with different orientations will be added to form a single narrow line or a center band flanked by side bands. The oscillations with different frequencies destructively interfere with each other, resulting in a rapid exponential decay of the ^{13}C magnetization. The time dependence of the dipolar coupling due to the sample spinning will also have an effect on the behavior of the ^{13}C magnetization, but it can be neglected to a first approximation, because the decay occurs during tens of μsec which is only tens of a percent of the rotational period of the sample. The expression for ^{13}C magnetization can thus be obtained from Eq. (2), after summing over all orientations of the crystallines. Instead of $\cos\frac{1}{2}bt$ in Eq. (2), one gets $\sum_i(I_i\cos\frac{1}{2}b_i t)/(\sum_i I_i)$, which can be approximated to $\exp(-t^2/2T_2^2)$,[16] where

$$(1/T_2^2)=\sum_i I_i(\tfrac{1}{2}b_i)^2\Big/\left(\sum_i I_i\right) .$$

After the replacement, the depolarized ^{13}C magnetization in the ^{13}CH group in a high-speed spinning powder sample at magic angle will be obtained:

$$M_{sx}=M_{s0}(\tfrac{1}{2}e^{-Rt}+\tfrac{1}{2}e^{-3Rt/2}e^{-t^2/2T_2^2}) , \qquad (3)$$

where the second term represents the initial rapid drop. Roughly speaking, ^{13}C in $^{13}CH_2$ turns out to be

$$M_{sx}=M_{s0}(\tfrac{1}{3}e^{-Rt}+\tfrac{2}{3}e^{-3Rt/2}e^{-t^2/2T_2^2}) . \qquad (4)$$

Equations (3) and (4) predict not only the basic two-stage feature of protonated ^{13}C signals, but also the correct turning point of them in the depolarization experiment, reaching agreement with the experiments semiquantitatively.

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