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Communication

A frequency-selective REDOR experiment for an SI_2 spin system

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ABSTRACT

A frequency-selective REDOR experiment is described for SI_2 spin systems. The experiment causes the net dipolar dephasing of the S spin to evolve only under the influence of one of the I spins. The experiment is based on a single pair of appropriately phased 90° I-spin pulses, and the I spin causing the S-spin dipolar dephasing is determined by the relative phases between the two 90° pulses. The experiment is demonstrated on a sample of $^{15}N_2$-L-asparagine.

1. Introduction

Rotational-echo, double-resonance (REDOR) is a useful high-resolution, magic-angle spinning NMR experiment for measuring heteronuclear dipolar interactions in solids [1,2] The experiment is especially well suited for isolated SI spin pairs, where the possibility of measuring internuclear distances accurately is readily realized. REDOR has been successfully applied to more complex spin systems involving SI_n spin system [3–6], but the data analysis is usually more complicated and model dependent [7]. Several modifications of REDOR have been developed to simplify SI_n and S_mI_n spin systems, including frequency-selective dipolar recoupling (FDR) [8,9], θ-REDOR [10], MSREDOR [11], frequency-selective REDOR (FSR) [12,13] and DANTE-based frequency-selective REDOR (dbFSR) [14,15].

In this communication we introduce a REDOR experiment designed to cause the S spin of the SI_2 spin system to evolve only under the influence of one of the I spins. The resulting dipolar evolution is identical to that of an isolated SI spin pair. The experiment makes use of a single pair of 90° pulses inserted at the midpoint of the dipolar evolution period of the REDOR experiment. The relative phasing between the two 90° pulses determines which I spin causes the net dipolar evolution of the S spin. The experiment requires an isotropic chemical shift difference between the two I spins and the I–I homonuclear dipolar interaction be relatively weak.

2. Discussion

An example of the modified ^{13}C–^{15}N REDOR (S is ^{13}C and I is ^{15}N) pulse sequence is shown in Fig. 1. The net dipolar evolution period is eight rotor cycles for the illustrated sequence. The proton channel is not shown, but protons are used to enhance the ^{13}C magnetization via cross-polarization (CP) and are decoupled thereafter by a strong rf decoupling field. All ^{13}C pulses, aside from the CP contact, are rotor-synchronized 180° pulses. The pulse sequence is made of two traditional REDOR pulse trains separated by a single ^{13}C Hahn-echo 180° pulse [16] having the same phase as the CP pulse. Rotor cycles 1–4 and 9–12 make the two REDOR pulse trains with ^{13}C 180° pulses at integer multiples of the rotor period, T_r, and ^{15}N 180° pulses at half-integer multiples of T_r [17,18]. The pair of ^{15}N 90° pulses centered about the middle of the experiment provides a way to control which of two chemically distinct ^{15}N spins causes net ^{13}C dipolar dephasing. Inspection of the sequence shows that the absence of the two ^{15}N 90° pulses results in no net dipolar evolution of the ^{13}C magnetization, because the Hahn-echo pulse refocuses the two identical REDOR parts of the experiment. Of course, omitting all ^{15}N pulses also results in no net ^{13}C dipolar evolution.

The net dipolar evolution of a ^{13}C spin coupled to two ^{15}N spins is strongly determined by the time, τ, between the two ^{15}N 90° pulses, the respective phases between the two 90° pulses and the position of the ^{15}N carrier frequency relative to the two ^{15}N resonances. These issues will be illustrated using $^{15}N_2$-L-asparagine, where 1141 Hz separates the two ^{15}N isotropic chemical shifts on our spectrometer. One of the ^{15}N resonances is set to exact resonance, so the other ^{15}N resonance is 1141 Hz off-resonance. The experiment can be explained by simply considering the toggling of the ^{15}N spin states. Recall that the purpose of the REDOR ^{15}N 180° pulses is to toggle the ^{15}N spin states $I_z \leftrightarrow -I_z$ synchronously with the sample rotation to generate a non-zero average dipolar interaction that causes net dipolar dephasing of the ^{13}C transverse magnetization. Now consider the effect of the 90° pulse pair $90°_x$–τ–$90°_x$. The effect of the first $90°_x$ pulse is to transform $I_z \rightarrow I_y$ for both ^{15}N spin systems. The time τ is chosen so that the transverse

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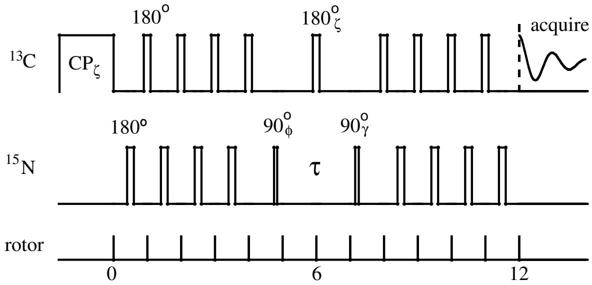

Fig. 1. The selective REDOR pulse sequence based on a single pair of 90° pulses is shown. Net dipolar dephasing of the ^{13}C magnetization is caused by the on-resonance ^{15}N spin system if the phases ϕ and γ of the two 90° pulses are the same. Net dipolar dephasing of the ^{13}C magnetization is caused by the off-resonance ^{15}N spin system if the phases ϕ and γ of the two 90° pulses are shifted by 180°. Except where indicated all pulses are 180°. The ^{13}C Hahn-echo pulse located at the midpoint of the experiment and is shown with the same phase ζ as the cross-polarization pulse.

off-resonance ^{15}N magnetization precesses 180° relative to the on-resonance ^{15}N magnetization. Hence, just prior to the start of the second $90°_x$ pulse the on-resonance ^{15}N spin system is still I_y but the off-resonance ^{15}N spin system is $-I_y$. Application of the second $90°_x$ pulse causes $I_y \rightarrow -I_z$ for the on-resonance ^{15}N spin system and $-I_y \rightarrow I_z$ for the off-resonance ^{15}N spin system. The net effect, then, of the $90°_x$–τ– $90°_x$ is to toggle the on-resonance ^{15}N spin system from $I_z \leftrightarrow -I_z$ while the off-resonance ^{15}N spin system experiences no net change in I_z. As a result, only the on-resonance ^{15}N spin system will cause net dipolar dephasing of the ^{13}C magnetization. A nice feature of the experiment is that the off-resonance ^{15}N spin system can be chosen to cause the net ^{13}C dipolar dephasing by simply changing the phase of the second pulse from $x \rightarrow \bar{x}$.

REDOR is performed as a difference experiment. A ^{13}C control signal, S, is acquired by omitting all ^{15}N rf pulses. A dipolar dephased ^{13}C signal, S_r, is obtained by application of the ^{15}N pulse train. The normalized difference signal is $\Delta S/S = 1 - S_r/S$. Experiments were performed on a home-built triple-channel spectrometer operating at a ^1H frequency of 151.39 MHz. ^{13}C and ^{15}N 180° pulse lengths were 10 μs and 10.8 μs, respectively. The REDOR pulse trains used *xy*-4 or *xy*-8 phasing [19,20]. The proton decoupling rf field strength was 115 kHz. The sample was spun at 4344 Hz stabilized to ±0.2 Hz by a custom sample spinning rate controller [21]. The time between midpoints of the two 90° pulses is determined by the difference in isotropic chemical shifts, $\Delta\nu$, of the two ^{15}N resonances, which is 1141 Hz, and set to produce a 180° precession of the off-resonance ^{15}N transverse magnetization. This time is given by $1/2\Delta\nu$ and is 438 μs. For the results presented below, the ^{15}N carrier frequency was set to the ^{15}N resonance of the $N^{\delta2}$ nitrogen.

Results are shown in Fig. 2 for the ^{13}C resonance of the C^{β} carbon of $^{15}N_2$-L-asparagine. X-ray diffraction work shows the C^{β} carbon of asparagine is 2.422 Å from the $N^{\delta2}$ nitrogen and 2.483 Å from the N′ nitrogen [22]. The diamonds show the data obtained with the ^{15}N carrier frequency set to the ^{15}N resonance of the $N^{\delta2}$ nitrogen and both 90° pulses having the same phase. Hence, the diamonds represent dephasing of the ^{13}C magnetization caused by the ^{15}N spins at the $N^{\delta2}$ position. A fit of the data (using the standard REDOR universal dephasing curve for an isolated spin pair) gives a dipolar coupling of 208 Hz, which corresponds to a C^{β}–$N^{\delta2}$ distance of 2.45 Å. The solid circles are data obtained under the same condition except the phase of the second 90° pulse is shifted by 180° relative to the phase of the first 90° pulse. Consequently, the solid circles represent dephasing of the ^{13}C magnetization by the ^{15}N spins of the N′ nitrogen. The fit to the solid circles provides a dipolar coupling of 194 Hz, which gives a C^{β}–N′ distance of 2.50 Å. Both REDOR determined distances are in excellent agreement with the respective distances determined by X-ray diffraction experiments. For comparison, a standard REDOR experiment that couples the ^{13}C spins of the C^{β} carbon simultaneously to both ^{15}N spins of asparagine was also performed, and that data is shown as the open circles. A three-spin simulation using the two REDOR-determined dipolar couplings (208 and 194 Hz) and an N′–C^{β}–$N^{\delta2}$ angle [22] of 123° describes the data very well. Clearly the three-spin REDOR results are very different from both of the selective frequency REDOR data sets.

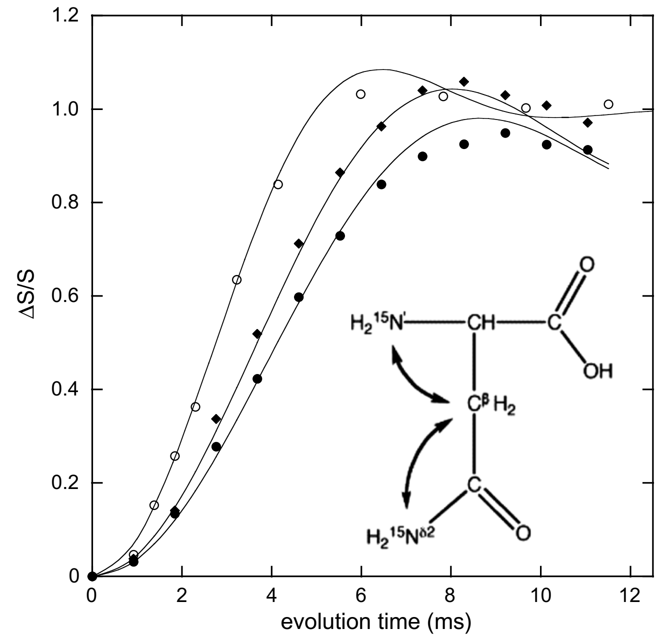

Fig. 2. Data sets for the frequency-selective REDOR experiment and the standard REDOR experiment are shown. The solid lines are simulations of the respective data sets. Asparagine is shown for reference.

3. Conclusions

We have shown that the addition of a pair of suitably phased 90° pulses to the REDOR experiment causes an SI_2 spin system to evolve as an SI spin system. The relative phases of the two 90° pulses determines which I spin is responsible for the net dipolar dephasing of the observed S spin. The experiment is easy to implement because it uses ordinary pulses and should be applicable to any spin-1/2 system. The experiment can be easily extended to SI_3 systems, requiring only an additional scaling factor to the observed $\Delta S/S$ values. For S spins coupled to three or more I spins, frequency-selective REDOR experiments based on DANTE and gaussian pulses are more appropriate.

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