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Dipolar Determinations in Solids by Relaxation-Assisted NMR Recoupling

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The determination of internuclear *I*−*S* distances and geometries in solids from dipolar coupling measurements constitutes one of the most important capabilities of NMR.[1] These determinations are usually complicated by the simultaneous presence of larger—but structurally uninteresting—interactions such as the anisotropic chemical shift. Dipolar contributions to a total powder NMR line shape can be successfully extracted using spin−echo double resonance (SEDOR),[2,3] a heteronuclear recoupling experiment which during recent years has been successfully extended to rotating solids.[4−6] In spite of their usefulness, the application of these techniques is challenged by the need of a third radio frequency (rf) channel for proton decoupling and by quadrupolar effects that can complicate the data evaluation. In the present paper, we discuss and demonstrate an alternative recoupling strategy that, by requiring irradiation on only one of the coupled species, is free from these technical and quantification demands.

The system to be considered here consists of an *I*−*S* spin pair, and the aim will be to retrieve their dipolar interactions by observation of the *S* spectrum. The Hamiltonian defining the signal can be expressed as[1]

$$H = \nu_S(\theta,\varphi)S_z + \nu_{IS}(\theta,\varphi)I_zS_z \qquad (1)$$

where ν_S represents the usually dominant local NMR interaction, ν_{IS} is the dipolar coupling frequency encoding the desired information, and both terms are assumed orientation dependent. The basic strategy by which SEDOR and its derived techniques effectively eliminate ν_S from eq 1 is illustrated in Figure 1A. It involves an initial excitation followed by an evolution period $\tau_1/2$, synchronous *I* and *S* π-pulses that reverse the S_z but leave unchanged the I_zS_z term, and a final $\tau_1/2$ period of free evolution. At the end of this period the initial and final contributions of ν_S will cancel while those of ν_{IS} will add up coherently, leading to a purely dipolar evolution.[2] A scenario in which a similar evolution can be recovered *without I* spin irradiation arises when the nuclear species to be recoupled possess different longitudinal relaxation times: $T_1^I < T_1^S$. The pulse sequence shown in Figure 1B[7] can then be used to encode the desired information. As for SEDOR this sequence begins with an initial free evolution period; this is followed by a storage delay in the order of T_1^I that results in the microscopic randomization of I_z while producing only a minor attenuation of S_z, and concluded by a reversal in the apparent sense of *S* precession. The stimulated echo that then forms succeeds in refocusing the ν_S but not the ν_{IS} interaction, leading to a net dipolar evolution by exclusive irradiation of the *S* spins. Since the pulse sequence involved in this experiment has apparent similarities to the one normally employed in 2D exchange NMR,[8,9] we refer to its use in structural determinations by the acronym DEAR (dipolar exchange-assisted recoupling).

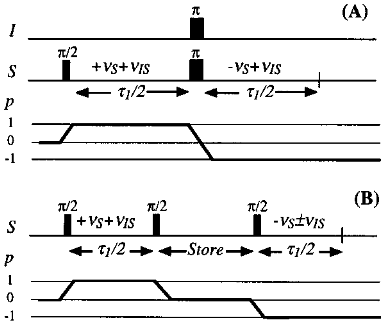

Figure 1. (A) Double resonance recoupling approach involving the inversion of I_z. (B) Single resonance approach exploiting the randomization of I_z by spin relaxation. Both experiments employ equal but counter-rotating periods of free *S* evolution ($p = 1 \rightarrow p = -1$), at the end of which local interactions are refocused.

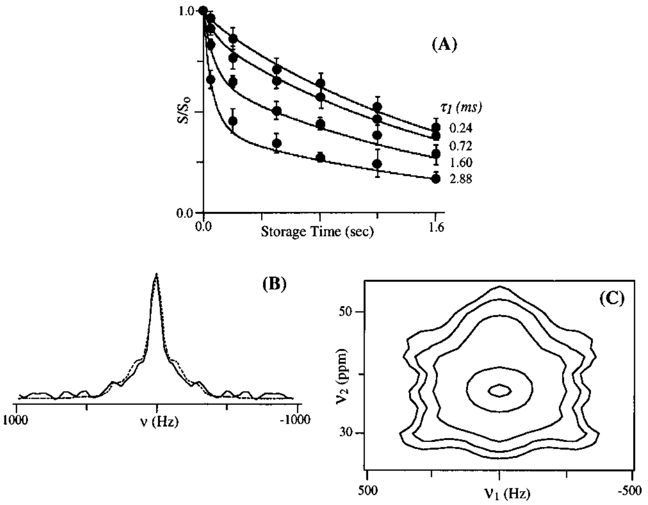

Figure 2. Results afforded by the sequence in Figure 1B for $^{13}C_\alpha$−^{14}N spin pairs in natural abundance alanine. (A) ^{13}C signal attenuation observed as a function of dephasing and storage times. Curves correspond to the simultaneous best fit of all data according to an exchange model (eq 2) that assumes $T_1^{^{13}C_\alpha} = 1.8 \pm 0.6$ s, $T_1^{^{14}N} = 0.09 \pm 0.06$ s, $r_{C-N} = 1.50 \pm 0.36$ Å (lit. 1.487 Å[14]). (B) ^{13}C−^{14}N dipolar NMR spectrum (−) obtained upon synchronously stepping the initial and final evolution periods by 166 μs dwells (48 τ_1 points) and using a 300 ms storage time. The best fit simulation (- - -) only needs to consider the ^{13}C−^{14}N internuclear distance. (C) 2D ^{13}C−^{14}N separated-local-field spectrum correlating the internuclear coupling (ν_1) with the sum of dipolar and shielding anisotropies (ν_2). All data were collected on a home-built double-tuned 7.1 T NMR spectrometer while rapidly (≥7 kHz) spinning the sample perpendicular to B_o (i.e., with all anisotropies scaled by $-^1/_2$).

Once a purely dipolar evolution is encoded, different protocols can be followed to retrieve the desired structural information. Experiments can be carried out on either static or rotating samples, provided that in the latter case anisotropies are at least partially reintroduced using rotor-synchronized rf irradiation[10] or off-magic-angle spinning.[11] Figure 2 illustrates three DEAR alternatives that were explored for an *I*−*S* system where *I* =

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^{14}N, a quadrupolar nucleus. Part A shows a relatively general approach, whereby S signals are monitored as a function of different evolution and storage times. The quantitative interpretation of these data can be undertaken with the aid of an exchange matrix $\boldsymbol{K}$, describing the changes introduced by spin relaxation on the various components $S(m_I)$ of classical magnetization vectors associated to different I eigenstates.[12,13] Assuming isolated $I-S$ spin pairs, dominant Zeeman interactions and negligible multiple-quantum relaxation, the only non-zero elements in this $(2I + 1)(2I + 1)$ matrix are

$$\boldsymbol{K}_{i,i+1} = \boldsymbol{K}_{i+1,i} = -1/T_1^{\mathrm{I}} \qquad \text{(2a)}$$

$$\boldsymbol{K}_{i,i} = -[1/T_1^{\mathrm{S}} + \sum_{i\neq j} \boldsymbol{K}_{i,j}] \qquad \text{(2b)}$$

Diagonalization of $\boldsymbol{K}$ allows one to obtain the general time dependence of the S signal,[13] whose renormalization leads to dipolar dephasing curves depending exclusively on the relaxation times of both nuclei and on their internuclear distance (Figure 2A). Alternatively, purely dipolar $I-S$ powder spectra can be obtained by performing a pointwise digitization of the stimulated echoes arising for storage intervals exceeding T_1^{I} (Figure 2B); notice that a similar $^{13}C-^{14}N$ coupling trace could only have been retrieved using SEDOR-derived methods if perfect π-pulses were applied on the ^{14}N transitions. DEAR can also be implemented in a full two-dimensional fashion by taking the initial and final precession periods as t_1 and t_2 variables of a 2D NMR experiment. When carried out in the long storage time regime (complete I_z randomization), this experiment yields a relaxation-independent distribution correlating the anisotropic S chemical shift with its heteronuclear I coupling (Figure 2C).[15]

Figure 3 presents another recoupling application to $^{13}C-^{19}F$ pairs, a case which fulfills the $T_1^{\mathrm{I}} < T_1^{\mathrm{S}}$ condition by virtue of the larger magnetogyric ratio of the ^{19}F. The decay curves observed for the various ^{13}C sites as a function of storage delay (Figure 3B) unambiguously map their distances with respect to the abundant ^{19}F within the monomer. An exact quantitative analysis of these data requires ancillary studies concerning the potential presence of molecular motions and the effects arising due to ^{19}F in neighboring monomer units. These additional investigations, which would also be necessary if SEDOR-derived methods were used, exceed the scope of the present paper and were consequently not attempted. Still it is worth noting that in cases such as this one, where only spin-$^1/_2$ nuclei are involved, the possibility of unambiguously determining the T_1 values of the coupled species leaves the internuclear distances being sought as sole variables governing the decay of the DEAR dephasing curves.

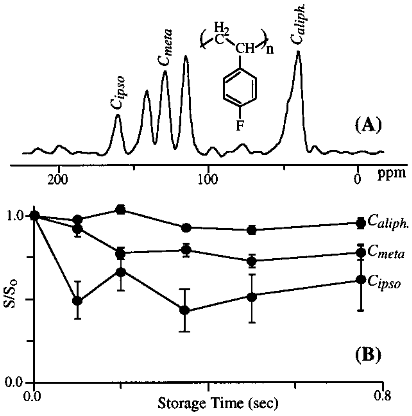

Figure 3. ^{13}C DEAR decay curves observed for aliphatic and aromatic sites in poly(p-fluorostyrene) due to their coupling to the ^{19}F. (A) 7.1 T CPMAS NMR spectrum of a sample synthesized by suspension polymerization in deareated water.[16] ^{13}C T_1 times measured for this solid ranged between 3.9 ± 0.4 and 9.0 ± 1.1 s, $T_1^{^{19}F}$ was 0.56 ± 0.06 s. (B) Dephasing observed for the indicated sites as a function of storage times. Anisotropies were introduced by sample spinning at 90°; high-resolution was subsequently achieved by changing the spinning angle to 54.7°.

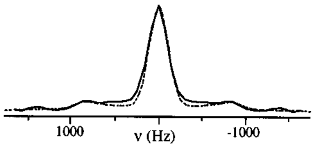

Figure 4. Carbonyl dipolar spectrum arising from 10% ^{13}C-enriched dilabeled zinc acetate. Experimental data (—) were acquired using the pulse sequence in Figure 1B ($\Delta\tau_1/2$ = 200 μs, 48 τ_1 points) and a storage time slightly shorter than the $T_1^{^{13}CH_3}$ (5 vs 7 s). The simulated line shape (- - -) assumed a $^{13}C-^{13}C$ distance of 1.55 Å;[18] other experimental parameters are as in Figure 2.

We conclude by illustrating an alternative recoupling application, this time to the analysis of homonuclear systems. The case under consideration involves isotopically enriched ^{13}C pairs where one of the coupled spins belongs to a methyl group. The rapid motion undergone by these moieties around their C_3 symmetry axes endows them with an efficient longitudinal relaxation mechanism, and leads to $T_1^{\mathrm{CH_3}}$ times that are usually an order of magnitude shorter than those of other carbon nuclei.[17] This in turn makes them suitable I spin candidates for DEAR distance determinations. Figure 4 illustrates these considerations with the carbonyl dipolar spectrum resulting upon applying the sequence in Figure 1B to a sample of $Zn(^{13}CH_3\text{-}^{13}CO_2)_2$ diluted in a nonenriched background. As happened when quadrupolar nuclei were involved, the dipolar patterns obtained in this manner can be quantified without considering local shielding interactions or the exact role played by the rf.

The aforementioned data illustrate some of the possibilities that stimulated echo sequences in combination with spin relaxation open for the determination of $I-S$ dipolar couplings. Even though when spin-$^1/_2$ are involved the maximum theoretical DEAR dephasing is only 50% of that provided by SEDOR, both methods become comparable when dealing with quadrupolar nuclei. Thus, we trust that technical simplicity and ease of quantification will help incorporate relaxation-driven recoupling strategies into the arsenal of NMR structure determination methods.

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