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# A Homonuclear Rotational Echo Double-Resonance Method for Measuring Site-Resolved Distance Distributions in I = $^1\!/_2$ Spin Pairs, Clusters, and Multispin Systems**

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The unique power and potential of high-resolution solid-state NMR spectroscopy to provide structure information at the atomic level for complex, disordered, and molecular solids have been amply demonstrated.[1,2] In particular, the analysis of internuclear dipole–dipole couplings can provide information about distances, bond connectivities, and spatial spin distributions.[3] For heteronuclear spin systems, one of the most powerful methods to accomplish this in a site-resolved fashion has been the rotational echo double-resonance (REDOR) technique,[4] where a difference signal is measured of signal amplitudes $S_0$ with the interaction absent (owing to magic-angle spinning, MAS) and reduced signal amplitudes $S'$ with the interaction recoupled (through application of inversion pulses during the rotor period). REDOR has been widely used for measuring internuclear distances and their distributions in biological systems and inorganic materials alike and has been adapted in many different versions and variants.[5–11] In contrast, an analogous homonuclear difference strategy of similar versatility has up to now not yet been realized for multispin systems. Although a large variety of homonuclear recoupling approaches have been published,[12–32] their calibration to yield information on dipolar couplings on the basis of simulations or model compound work has remained a difficult issue. While promising progress was recently reported using improved double-quantum excitation strategies,[14] important remaining issues include the limited efficiency of double-quantum coherence excitation, $T_2$ relaxation, and dipolar truncation effects.[33–35] The only homonuclear difference method known so far involves an excitation of zero-quantum coherences using the "transverse-echo simple excitation for the dephasing of rotational-echo amplitude (t-SEDRA)" method,[28] where the dephasing of transverse magnetization $I_{x1} + I_{x2}$ is compared with that under the influence of an effective Hamiltonian [Eq. (1)]. While transverse-echo SEDRA does succeed in eliminating the influence of $T_2$ relaxation upon the experimental data, applications to systems beyond isolated two-spin pairs have not been reported so far.

$$\bar{H} = \frac{\omega_0^{\text{eff}}}{2}[2I_{x1}I_{x2} + 2I_1 \cdot I_2] + \frac{J}{4}[2I_1 \cdot I_2 - 2I_{x1}I_{x2}] \tag{1}$$

Figure 1 introduces the concept of a homonuclear REDOR approach to be used for site-selective measurements of dipolar coupling strengths in multispin systems. Its higher efficiency stems from the difference approach, in which the amplitude of $I_z$, rather than the double-quantum transfer intensity, is being measured, both in the presence and in the absence of the dipolar coupling. Each part of the sequence contains two POST-C7[36] blocks for excitation and reconversion of the DQ coherences. In the $S'$ part, the two blocks are in phase, resulting in the re-introduction of the homonuclear dipole coupling into the MAS Hamiltonian. For a two-spin $-1/2$ system , the effective Hamiltonian is given by Equation (2).[36,37]

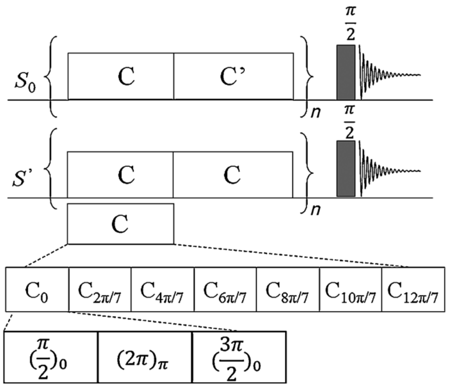

***Figure 1.*** Homonuclear REDOR pulse sequence, based on recoupling by POST-C7 blocks.

$$\bar{H}^0 = d^{jk}_{2221}T^{jk}_{22} + d^{jk}_{2-22-1}T^{jk}_{2-2} \tag{2a}$$

$$d^{jk}_{2221} = d^{jk}_{2-22-1}{}^{*} = \frac{343\left(i + e^{i\pi/14}\right)}{260\sqrt{2}} b_{jk} \exp[i(w_r t_0 - \gamma_{PR})] \sin 2\beta_{PR} \tag{2b}$$

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Here, $d^{jk}_{2221}$ and $d^{jk}_{2-22-1}$ are the orientation-dependent coefficients and $T^{jk}_{22}$ and $T^{jk}_{2-2}$ are the relevant double-quantum irreducible dipolar tensor operators; $b_{jk}$ represents the dipolar coupling constant between spins $j$ and $k$; $\gamma_{PR}$ and $\beta_{PR}$ are Euler angles relating the principal axis system of the dipolar coupling to the rotor fixed frame; $t_0$ is the time point at which the recoupling sequence is initiated.

On the other hand, a 90° phase shift inverts the sign of the effective Hamiltonian, resulting in Equation (3).

$$\begin{aligned}\bar{H}^{0'} &= R_z\left(\frac{\pi}{2}\right)\bar{H}^0 R_z^{-1}\left(\frac{\pi}{2}\right)\\ &= d^{jk}_{2221} R_z\left(\frac{\pi}{2}\right) T^{jk}_{22} R_z^{-1}\left(\frac{\pi}{2}\right) + d^{jk}_{2-22-1} R_z\left(\frac{\pi}{2}\right) T^{jk}_{2-2} R_z^{-1}\left(\frac{\pi}{2}\right)\\ &= -d^{jk}_{2221} T^{jk}_{22} - d^{jk}_{2-22-1} T^{jk}_{2-2}\end{aligned} \tag{3}$$

In the $S_0$ part of the homonuclear REDOR experiment presented here, the overall phase of the second block $C'$ is shifted by 90° relative to the $C$ block, thus cancelling the overall dipolar recoupling effect. In this case the intensity of the $S_0$ signal is affected by the same experimental imperfections and $T_2$-damping effects that are also present during the $S'$ part of the experiment, and are thus eliminated when the difference $S_o - S'$ is analyzed. Under the influence of the homonuclear dipolar coupling Hamiltonian, the magnetization evolves according to Equation (4a), where $NT_r$, the

$$\begin{aligned}&(I_{jz} + I_{kz})_{t=NT_r} \xrightarrow{\bar{H}^0} (I_{jz} + I_{kz})_{t=0} \cos(|d^{jk}_{2221}| NT_r) +\\ &\left[i\left(I_j^+ I_k^+ - I_j^- I_k^-\right)\cos\theta + \left(I_j^+ I_k^+ + I_j^- I_k^-\right)\sin\theta\right]\sin(|d^{jk}_{2221}| NT_r)\end{aligned} \tag{4a}$$

number of rotor cycles times the rotor period, defines the dipolar evolution time. The phase angle is given by Equation (4b).

$$\theta = \arg\left(\frac{343(i + e^{i\pi/14})}{260\sqrt{2}}\right) + w_r t_0 - \gamma_{PR} \tag{4b}$$

For the powder average, we obtain Equation (5).

$$S'_{(t=NT_r)} = \frac{1}{2}\int_0^{\pi} \cos(|d^{jk}_{2221}| NT_r) \sin\beta_{PR} d\beta_{PR} \tag{5}$$

Since the POST-C7 sequence is $\gamma$-encoded, only $\beta_{PR}$ is necessary for calculating the spatial average of dipolar effect.

Figure 2 (black symbols) shows the predicted dephasing for a two-spin system $I_j I_k$, in which $j$ represents the spin whose signal is being monitored. As in heteronuclear REDOR, the difference signal shows an initial build-up followed by an oscillatory part. In the limit of short evolution times where $\cos(|d^{jk}_{2221}| NT_r)$ can be approximated by $1 - {}^1\!/\!_2 (d^{jk}_{2221} NT_r)^2$ Equation (5) can be expressed as Equation (6) (see Section S-1 in the Supporting Information).

$$\frac{S_0 - S'}{S_0} = \frac{0.86\pi^2}{15} b^2_{jk} (NT_r)^2 \tag{6}$$

Thus, $b^2_{jk}$ can be evaluated by fitting the experimental $(S_0 - S')/S_0$ data with a simple parabola. Figure 2 further includes simulated homonuclear REDOR curves for $I_j(I_k)_n$ $(1 \leq n \leq 4)$ spin clusters using the SIMPSON software.[38] While both the initial dephasing as well as the oscillatory parts are highly sensitive to the order of the spin system, as expected, it is the initial dephasing part that lends itself to an easy generalization of Equation (6) to multispin systems: the term $b^2_{jk}$ simply needs to be replaced by $\sum_{j<k} b^2_{jk}$ summing over all the pairwise interactions encountered.

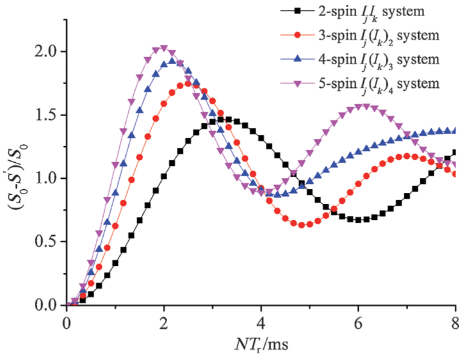

***Figure 2.*** Simulated homonuclear REDOR curves for $I_j(I_k)_n$ spin clusters $(1 \leq n \leq 4)$, assuming a tetrahedral geometry and a dipolar coupling constant $b_{jk} = 800$ Hz and a spinning rate of 12 kHz. The simulations neglect dipolar interactions among the $I_k$ spins.

The experimental values of $\sum_{j<k} b^2_{jk}$ thus determined from a parabolic analysis of REDOR curves by means of Equation (6) are directly proportional to the van Vleck dipolar second moment,[39] and can be compared with predicted values from structural models. Further simulations based on three-spin systems (see Figure S-2 in the Supporting Information) show that within this initial dephasing period, the REDOR curves are not influenced by the relative orientations of the dipolar vectors, making this approximate method particularly useful for multiple-spin systems with unknown spin geometries.

A further issue, not important in heteronuclear recoupling, but crucial in homonuclear recoupling, is the dipolar truncation phenomenon:[33–35] weaker couplings tend to get obscured by the presence of comparable or stronger ones, and homonuclear recoupling methods will thus underestimate $b_{jk}$ if spin $j$ is coupled to a spin $k$ that is strongly coupled to another spin $i$ such that $b_{ki} \geq b_{jk}$. Our simulations carried out on linear three-spin systems $I_j$-$I_k$-$I_i$ (see Figure S-3 in the Supporting Information) indicate that this problem is also minimized by the parabolic analysis at short dipolar evolution times. The data range of $\Delta S/S_0$ to which the analysis must be restricted in order to give a correct $b_{jk}$ measurement depends on the $b_{ki}/b_{jk}$ ratio. For example, if $b_{ki}/b_{jk} = 2$, the data range of $\Delta S/S_0$ for the dipolar analysis should not exceed 0.2, whereas significantly wider data ranges (up to $\Delta S/S_0 = 0.5$) can be used for the case $b_{ki}/b_{jk} \leq 1$. Consequently, homonuclear REDOR seems to be a promising alternative to the recent multiple-oscillating field techniques designed to overcome dipolar truncation.[35]

The performance of the homonuclear REDOR sequence was tested on eight crystalline inorganic phosphorus compounds with widely differing dipolar coupling strengths (Table 1). While most of them have singular phosphorus

*Table 1:* Isotropic $^{31}$P chemical shifts, CSA values, and experimental values of $\sum b_{jk}^2$ for the model compounds studied.

| Sample | $\delta_{iso}$, CSA [ppm] | $\sum b_{jk}^2$ [$\times 10^5$ Hz$^2$][a] |
|---|---|---|
| $Ag_7P_3S_{11}$ | 103.2, −15 | 1.11[b] (1.15) |
| | 101.4, −50 | 2.8 (2.79) |
| | 92.0, 40 | 3.0 (2.81) |
| $Na_4P_2O_7$ | 2.2, 88 | 8.6 (8.6, 8.5) |
| $BPO_4$ | −29.9, 19 | 6.9 (7.0) |
| $AlPO_4$ | −25.3, 18 | 4.7 (4.8) |
| $Li_3PO_4$ | 10.1, 25 | 4.8 (4.9) |
| $Al(PO_3)_3$ | −50.9, −119 | 20.6 (18.9) |
| GaP | −142.4, 0 | 16.3 (16.9) |
| $CdPS_3$ | 103.3, 26 | 34.3 (33.3) |

[a] Numbers in parentheses are theoretical $\sum b_{jk}^2$ values calculated from the crystal structures over a range of three times the closest P–P distance. Deviation ±10%. [b] $\Delta S/S_0 < 0.2$, no correction applied.[40]

sites, for $Ag_7P_3S_{11}$, site-selective homonuclear dipole coupling strengths are available from resolved resonances. Figure 3 compares the experimental results for these compounds with simulated curves based on simplified two- or three-spin clusters and with the parabolae predicted by Equation (6) from the crystallographic $\sum_{j<k} b_{jk}^2$ values. Clearly homonuclear REDOR can sensitively differentiate phosphorus atoms in various bonding situations. In $Ag_7P_3S_{11}$ the isolated $PS_4^{3-}$ unit shows much slower dephasing than the dimeric $P_2S_7^{4-}$ group. Further, the dimeric $P_2S_7^{4-}$ groups in $Ag_7P_3S_{11}$, the dimeric $P_2O_7^{4-}$ groups in $Na_4P_2O_7$, and the trimeric repeat units (two P-O-P linkages) in $Al(PO_3)_3$ can be clearly differentiated by the differences in dipolar coupling strengths. As Figure 3 illustrates, Equation (6) predicts the initial data range of homonuclear REDOR curves very well. By fitting parabolae to simulated curves for two-, three-, four-, and five-spin systems within $0 \leq \Delta S/S_0 \leq 0.5$, we find that this approximation will lead to a systematic underestimation by 10% when applied to experimental data. When this correction is taken into account, the experimental values of $\sum_{j<k} b_{jk}^2$ deduced from these curves show excellent agreement with the values calculated from the respective crystal structures (Table 1). In contrast, the simplified spin-cluster models (with the exception of $CdPS_3$, where the two-spin interaction is completely dominant) systematically underestimate the coupling because they do not include longer-range interactions. All of these results confirm that dipolar truncation effects do not interfere with the analysis of homonuclear REDOR curves at short evolution times. For compounds with strong dipolar coupling, several spinning speeds will be required to generate enough data points within the $\Delta S/S_0 < 0.5$ range.

Detailed consideration of chemical shift anisotropy effects (see Figure S-5) reveal that experimental fitting results can be easily corrected for if the CSA is known independently from separate experimental data. These corrections will be important for compounds with larger CSAs and for REDOR studies at higher magnetic field strengths.

Figure 4 shows an initial application to a number of phosphate-based glasses. The data obtained for a binary sodium phosphate glass of composition $0.57\,Na_2O$–$0.43\,P_2O_5$ clearly reveals the ability of homonuclear REDOR of differentiating between the different types of $Q^{(n)}$ species on the basis of their different numbers of P-O-P linkages. From the curvatures we measure $\sum_{j<k} b_{jk}^2$ values of 16.1 and $8.5 \times 10^5$ Hz$^2$ for $Q^{(2)}$ and $Q^{(1)}$ species, respectively, in close agreement with expected values from the model compounds.

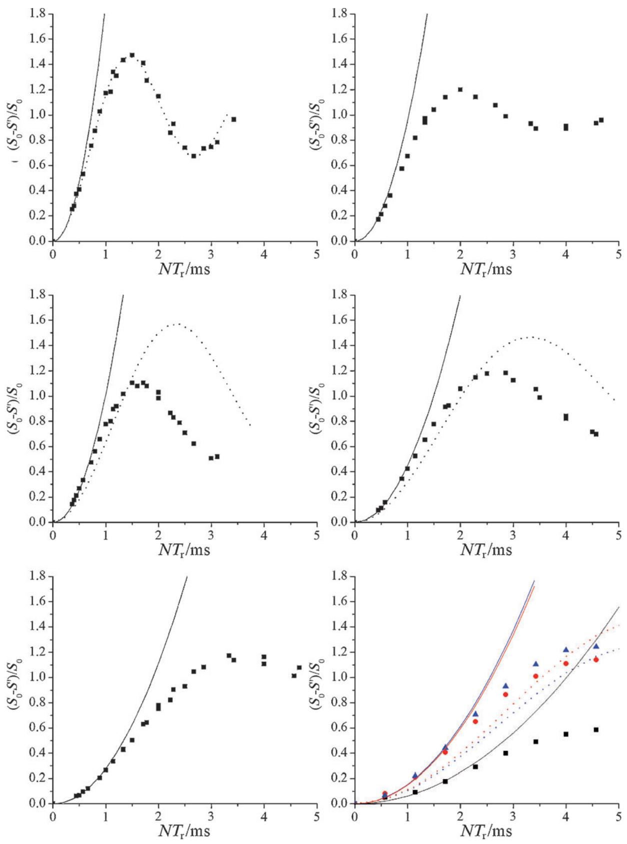

*Figure 3.* Homonuclear $^{31}$P REDOR decay curves, simplified spin-cluster simulations (dotted curves), and predicted parabolae (solid curves) based on Equation (6) using $\sum_{j<k} b_{jk}^2$ from the crystal structures. Top: $CdPS_3$ (left) and GaP (right); middle: $Al(PO_3)_3$ (left) and $Na_4P_2O_7$ (right); bottom: $Li_3PO_4$ (left) and $Ag_7P_3S_{11}$ (right). Squares, solid circles, and triangle symbols represent data for $PS_4^{3-}$ groups and the two crystallographically nonequivalent P atoms of the $P_2S_7^{4-}$ group, respectively; for the latter, dotted curves show spin-pair simulations.

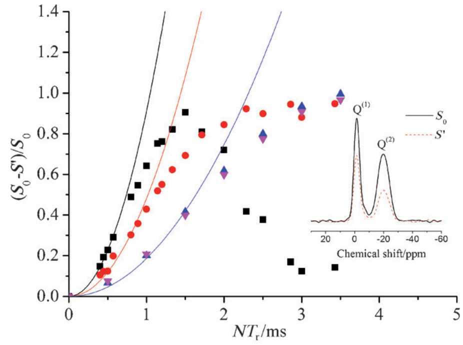

*Figure 4.* Homonuclear REDOR results on phosphate materials; squares and circles: data for $Q^{(2)}$ and $Q^{(1)}$ units in $0.57\,Na_2O$–$0.43\,P_2O_5$ glass. Inset: spectra for measurement of $S_0$ and $S'$ at $NT_r = 0.89$ ms.) Triangles: $Q^{(0)}$ units in gel-prepared $AlPO_4$; inverted triangles: $Q^{(0)}$ units in $0.5\,AlPO_4$–$0.5\,SiO_2$ glass. Solid curves represent parabolic fits, resulting in the $\sum_{j<k} b_{jk}^2$ values stated in the text.

In addition, data are shown for a mesoporous sol–gel glass of composition 0.5 $AlPO_4$–0.5 $SiO_2$. This material had been previously conjectured, but never proven, to be phase separated on the nanoscale.[41] The identical $\sum_{j<k} b_{jk}^2$ values of $3.3\times10^5$ $Hz^2$ measured for this material and for pure glassy $AlPO_4$ provides strong evidence for this assertion. These results suggest that homonuclear REDOR may be a suitable probe for detecting and quantifying the extent of nanoscale segregation and phase-separation processes in glasses, glass-ceramics, and nanocomposite materials.

In summary we report a new solid-state NMR recoupling technique to measure site-resolved homonuclear dipolar interactions in spin pairs and clusters. It combines efficiency, facile data analysis, and easy extension to multiple-spin systems covering a wide range of dipolar coupling strengths. The method is not affected by dipolar truncation and allows CSA effects to be accounted for by simple calibration. These advantages will facilitate novel structural research elucidating short-, medium-range, and nanoscale ordering phenomena in disordered solid materials. While the present contribution focuses on $^{31}$P NMR studies of inorganic materials, the method can be applied analogously to other spin-1/2 nuclei that are either abundant ($^{19}$F, $^{1}$H) or can be prepared with isotopic enrichment ($^{13}$C, $^{15}$N), making this method also applicable to biological solids. Detailed structural applications to a wide variety of technological and biological materials are currently in progress.

## Experimental Section

$Na_4P_2O_7$, $BPO_4$, $AlPO_4$, $Li_3PO_4$, GaP, and $Al(PO_3)_3$ were obtained commercially (Sigma–Aldrich, 98–99 %). Other materials were prepared following standard literature procedures (see the Supporting Information). Measurements were carried out on a BRUKER Avance DSX 300 spectrometer, at MAS speeds of 7.0–11.0 kHz, under steady-state conditions (with presaturation combs). One pulse block spans two rotor periods. Implicit in the C7 scheme, the $^{31}$P nutation frequency is seven times higher than the spinning rate.

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[40] In this compound dipolar truncation effects are important for the isolated $PS_4^{3-}$ groups, whose spins are coupled to those of the $P_2S_7^{4-}$ units, requiring the more limited fitting range $\Delta S/S_0 < 0.2$.

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