

A Comparison between REDOR and θ -REDOR for Measuring ^{13}C - ^2D Dipolar Interactions in Solids

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^{13}C -observe REDOR and θ -REDOR experiments for recovering the ^{13}C - ^2D dipolar interaction during MAS NMR are compared. It is found that limited ^2D RF power may severely compromise the performance of the REDOR experiment whereas the θ -REDOR experiment can be designed to work well. Results are presented for an isolated ^{13}C - ^2D spin pair with a large deuterium quadrupolar coupling constant and for a ^{13}C coupled to three methyl deuterons undergoing fast methyl group rotation. © 1999 Academic Press

Key Words: REDOR; θ -REDOR; deuterium; MAS.

INTRODUCTION

Recoupling dipolar interactions between rare-spin nuclei while magic angle spinning has received considerable attention (1). A measurement of the dipolar coupling between two nuclei provides the internuclear distance and, hence, useful structural information. Frequently, the solid-state NMR dipolar recoupling experiments are performed on samples that have been isotopically labeled at specific chemical sites. Many experiments have been performed with ^{13}C - ^{13}C (2–13) and ^{13}C - ^{15}N (14–17) spin pairs, and other spin pairs (18–29) have received some attention. Recoupling the ^{13}C - ^2D dipolar interaction is of interest because of the extensive use of deuterium labeling. However, there are only a few cases where the ^{13}C - ^2D dipolar coupling has been measured by MAS NMR, and this has been done through rotational-echo, double-resonance NMR (REDOR).

^{13}C -observe REDOR experiments monitor the dipolar dephasing of the ^{13}C spins caused by the restored heteronuclear dipolar interaction. Conventional REDOR experiments rely on π pulses applied to the ^{13}C and the ^2D radiofrequency (RF) channels. An ideal ^2D π pulse causes spins in the $m = -1$ and $m = 1$ spin states to interchange while those spins initially in the $m = 0$ spin state undergo no net change in their magnetic quantum number. All deuterium spins must make two single-quantum transitions during the π pulse. However, for finite RF pulse power each of the two transitions may be inefficient, especially if the deuterium quadrupolar coupling constant is large, and the fraction of deuterium spins making the desired transitions may be less than ideal. Thus, a ^{13}C - ^2D REDOR experiment may not perform as well as desired. Recently, a

variant of the REDOR experiment, called θ -REDOR, that makes use of a pulse differing from a π pulse was described (30). A comparison between ^{13}C -observe REDOR and θ -REDOR experiments is presented here for the ^{13}C - ^2D spin pair, and it will be shown that it is not always best to use π pulses in recoupling the ^{13}C - ^2D dipolar interaction. Two important cases will be examined: a single ^{13}C - ^2D spin pair with a large deuterium quadrupolar coupling constant and a ^{13}C coupled simultaneously to three methyl deuterons which have small deuterium quadrupolar coupling constants due to fast rotation of the methyl group.

EXPERIMENTAL AND SAMPLE DESCRIPTIONS

^{13}C - ^2D dipolar interactions were studied for ^{13}C - and ^2D -labeled alanine and zinc acetate dihydrate samples. Figure 1 shows the sites of ^{13}C and ^2D labeling for the two molecules. These labeled molecules were recrystallized with their respective natural-abundance counterparts. The alanine sample was prepared by recrystallizing 20.6 mg of [$3 - ^{13}\text{C}$, $1 - ^2\text{D}$]DL-alanine (99 at.% ^{13}C ; 98 at.% ^2D) and 406.8 mg natural-abundance DL-alanine from water. The zinc acetate dihydrate sample was prepared by recrystallizing 20.6 mg [$1 - ^{13}\text{C}$, $^2\text{D}_3$]zinc acetate dihydrate (99 at.% ^{13}C ; 99 at.% ^2D) with 401.1 mg natural-abundance zinc acetate dihydrate from water. The isotopically enriched and the natural-abundance materials were obtained from Isotec, Inc., and Aldrich, respectively.

The quadrupolar coupling constant, QCC, is equal to 167 kHz for the methine deuteron of alanine (21). The separation between the ^{13}C and ^2D labels in alanine is 2.17 Å, and this distance corresponds to a dipolar coupling, D , of 451 Hz (31). The methyl deuterons in the zinc acetate dihydrate sample undergo fast methyl rotation. Hence, these deuterons will experience a smaller QCC ($\frac{1}{3}$ the rigid-lattice value) of approximately 55 kHz (32, 33). The ^{13}C - ^2D distance is 2.13 Å and results in a dipolar coupling of 310 Hz when only the fast methyl group rotation is taken into account. However, the ^{13}C - ^2D dipolar coupling is also motionally averaged by high-frequency librational motion of the entire molecule and has been previously measured to be 250 Hz for zinc acetate dihy-



FIG. 1. ^{13}C - and ^2D -labeled molecules: (a) alanine and (b) zinc acetate dihydrate.

drate (28). The 250-Hz dipolar coupling will be used in this work for zinc acetate dihydrate.

Experiments were performed on a homebuilt spectrometer using a Tecmag Libra pulse programmer and a 3.55-T magnet. The triple-channel probe uses a Chemagnetics 7.5-mm pencil rotor spinning assembly. Radiofrequency field strengths were 120 kHz for proton decoupling, 50 kHz for proton-carbon cross-polarization (CP), 50 kHz for carbon pulses, and 48.5 kHz for deuterium pulses. The spinning speed was 3.125 kHz and was stabilized with a homebuilt controller to within 0.2 Hz.

Figure 2 shows the ^{13}C -observe pulse sequence used to recouple the ^{13}C - ^2D dipolar interaction (26, 34). Protons were used for CP and were decoupled subsequently by a strong RF field. A train of rotor-synchronized xy -4 (35)-phased π pulses lasting for N_c rotor cycles is applied to the ^{13}C channel during the dipolar evolution period. The time between adjacent π pulses is one-half of a rotor period. The deuterium channel consists of a single pulse of flip angle θ , and the REDOR experiment is generated by setting θ to π . If $\theta \neq \pi$, the pulse sequence is the θ -REDOR experiment.

During the dipolar evolution time, the ^{13}C signal will decay from T_2 processes and will also dipolar dephase if the deuterium pulse is applied. The T_2 decay can be taken into account by performing an additional experiment that omits the deuterium pulse. Hence, for each value of the evolution time, two experiments are performed: one with the deuterium pulse and one without the deuterium pulse. The ratio of these two signals will be called S_d and the evolution of this normalized signal is due solely to dipolar dephasing.

The ^{13}C resonances will contain contributions from ^{13}C spins coupled to ^2D spins and from ^{13}C spins that have no deuterium neighbor because of the dilution of the labeled molecules in their respective natural-abundance matrices. Consequently, S_d is not what is obtained directly from the experimental spectra. Instead, the measured ratio is S_d^m . Two effects cause S_d and S_d^m to differ. First, because of the spin dilution only a fraction ρ of ^{13}C spins has a ^2D neighbor; this fraction can be calculated from the quantities of labeled and natural-abundance material used to make the samples. The value of ρ is 0.80 for the alanine sample and is 0.82 for the zinc acetate dihydrate sample. Second, the CP dynamics for ^{13}C spins on deuterated molecules may differ from the CP dynamics for ^{13}C spins on natural-abundance molecules. The differences in CP properties is not easy to calculate but will be noted by an empirical parameter ϵ . A simple model used in previous REDOR and REAPDOR experiments is assumed where the fraction of the ^{13}C signal

arising from ^{13}C spins with ^2D neighbors is $\alpha = \rho\epsilon$ (18, 36). It can be shown that S_d and S_d^m are related by

$$S_d = 1 - (1 - S_d^m)/\alpha. \quad [1]$$

For the experimental data presented below, α was set to 0.70 ($\epsilon = 0.88$) and 0.82 ($\epsilon = 1$) for the alanine and zinc acetate dihydrate samples, respectively.

Calculation of ideal (delta-function pulses) REDOR and θ -REDOR dephasing curves described by Eqs. [2]–[5] were performed by the Mueller method (37) with a program written in MATHEMATICA. For finite pulse widths, numerical simulations of the ^{13}C dipolar dephasing were performed by evaluating the time-dependent matrix elements of the evolution operator of the ^{13}C - ^2D spin pairs during the pulse sequence. The time-dependent spin Hamiltonian contained the deuterium quadrupolar interaction and heteronuclear dipolar interaction, and RF terms were added to the Hamiltonian during the pulses. Details of this stepwise numerical integration procedure have been described elsewhere (29).

RESULTS AND DISCUSSION

A. An Isolated ^{13}C - ^2D Spin Pair with a Large Deuterium Quadrupolar Coupling Constant

First, the case where a ^{13}C spin is coupled to a single ^2D spin with a large QCC is examined. Large deuterium quadrupolar coupling constants are found for deuterons having little or no motion and typically range from 160 to 220 kHz. When a deuterium pulse is applied, the ^2D spins may change their magnetic quantum numbers. For example, using the unitary rotation operator for spin-1 nuclei and assuming a delta-function π pulse, the transformation of the three possible ^2D spin states are $|1, +1\rangle \xrightarrow{\pi} |1, -1\rangle$, $|1, 0\rangle \xrightarrow{\pi} |1, 0\rangle$, and $|1, -1\rangle \xrightarrow{\pi} |1, +1\rangle$; each of these transformations

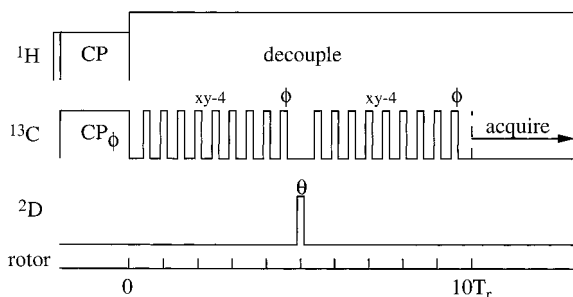


FIG. 2. The REDOR/ θ -REDOR pulse sequence. The pulse sequence shown is for a 10 rotor cycle dipolar evolution period. The deuterium pulse flip angle is $\theta = \pi$ for REDOR and $\theta \neq \pi$ for θ -REDOR. All ^{13}C pulses following the CP pulse are xy -4-phased π pulses except for the two specifically marked with the CP phase ϕ .

TABLE 1
Fraction of ^2D Spins Having $|\Delta m| = 0, 1,$ or 2
for Delta-Function Pulses

^2D pulse $\setminus \Delta m $	0	1	2
π	$\frac{1}{3}$	0	$\frac{2}{3}$
$\pi/2$ or $3\pi/2$	$\frac{1}{6}$	$\frac{2}{3}$	$\frac{1}{6}$

correspond to changes in the magnetic quantum number, $|\Delta m|$, of 2, 0, and 2, respectively. Thus, $\frac{1}{3}$ of the deuterons have $|\Delta m| = 0$, no deuterons have $|\Delta m| = 1$, and $\frac{2}{3}$ of the deuterons have $|\Delta m| = 2$. Table 1 shows the fraction of ^2D spins having a given $|\Delta m|$ for the REDOR experiment ($\theta = \pi$) and for the θ -REDOR experiment with $\theta = \pi/2$ or $3\pi/2$. All entries in the table were obtained using a ^2D delta-function pulse and the method just described for the π pulse. The table shows that the REDOR experiment makes use of ^2D spins having $|\Delta m| = 2$ whereas the θ -REDOR experiment works primarily through ^2D spins having $|\Delta m| = 1$.

The dipolar decay of the ^{13}C magnetization along the axis that the magnetization was initially prepared during CP of a single ^{13}C spin coupled to a single ^2D spin with a particular change in its spin state is described by $\cos \Delta\Phi$, where $\Delta\Phi = |\Delta m| \bar{\omega}_d \tau$ (16). The dipolar evolution time, τ , is the product of the number of rotor cycles, N_c , and the rotor period, T_r . The average dipolar frequency, $\bar{\omega}_d$, depends on the spatial orientation of the spin pair and on the dipolar coupling, D . The dipolar coupling (in units of Hz) is equal to $\gamma_D \gamma_C \hbar / 2 \pi r^3$. The average dipolar frequency for a given orientation of a ^{13}C - ^2D internuclear vector is $\bar{\omega}_d = 2\sqrt{2} D \sin 2\beta \sin \alpha$, where α and β are the azimuthal and polar angles of the internuclear vector with respect to the rotor frame, respectively (16). The dipolar-dephased signal of a collection of ^{13}C - ^2D spin pairs with identical average dipolar frequencies is given by $\sum_{|\Delta m|} f_{|\Delta m|} \cos(|\Delta m| \bar{\omega}_d \tau)$, where $f_{|\Delta m|}$ is the fraction of ^2D spins having a given $|\Delta m|$ during the dipolar evolution period.

The information in Table 1 predicts that the ^{13}C signal will dephase at a faster rate for REDOR than for θ -REDOR because of the large fraction of ^2D spins with $|\Delta m| = 2$ in the REDOR experiment. However, the ^{13}C signal will dephase to a much lower baseline value (equal to $\frac{1}{6}$) for θ -REDOR than for REDOR (equal to $\frac{1}{3}$). For the REDOR experiment, the ^{13}C signal, S_d , for a *specific orientation* of the ^{13}C - ^2D dipolar vector is

$$s_d(\tau) = \frac{1}{3} (1 + 2 \cos 2\bar{\omega}_d \tau). \quad [2]$$

A normalized powder average of Eq. [2] provides the dipolar-dephased signal, S_d , arising from all ^{13}C spins. Similarly, the ^{13}C signal intensity arising from a specific orientation of the ^{13}C - ^2D vector for the θ -REDOR experiment is

$$s_d(\tau) = \frac{1}{6} (1 + 4 \cos \bar{\omega}_d \tau + \cos 2\bar{\omega}_d \tau), \quad [3]$$

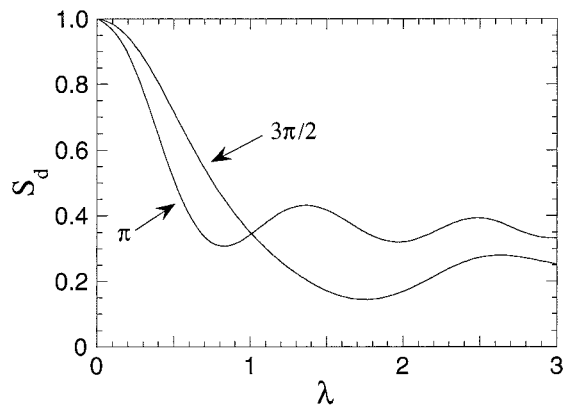


FIG. 3. Ideal behavior of the dipolar-dephased ^{13}C signal on λ for isolated ^{13}C - ^2D spin pairs. Delta-function pulses are assumed in the calculations. The REDOR and θ -REDOR curves are marked with a π and a $3\pi/2$, respectively. θ -REDOR dephasing for $\theta = \pi/2$ is identical to the $3\pi/2$ curve.

where the second term is due to deuterons making only one single-quantum transition. Figure 3 shows S_d as a function of $\lambda (= N_c T_r D)$ for the two experiments. It is clear from the figure that the REDOR experiment dephases the ^{13}C signal at a faster rate, and θ -REDOR reaches a lower baseline signal. Hence, for *very high* deuterium RF powers REDOR provides stronger initial dephasing; however, if the goal of the experiment is to maximize the number of ^{13}C spins that dephase, then the θ -REDOR experiment is preferable.

Experimentally it may be difficult to obtain very high RF powers with a triple-resonance solid-state probe. The NMR probe used in this work provided ^2D RF powers of 48.5 kHz at 23.239 MHz. Limited RF power on the deuterium channel may lead to inefficient single-quantum transitions which will have adverse effects on the ^{13}C dipolar dephasing. The experimental results presented in Fig. 4 show the dependence of the ^{13}C dipolar-dephased signal intensity on the deuterium pulse width.

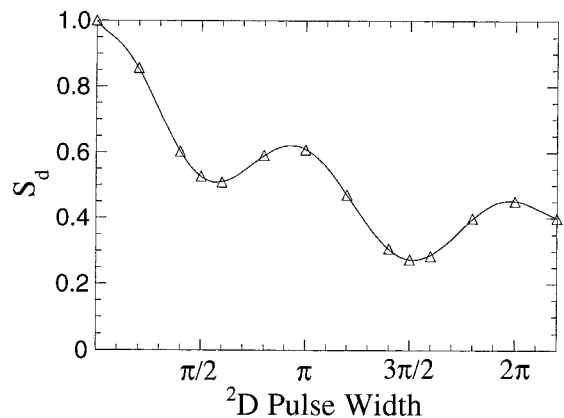


FIG. 4. Dependence of the dipolar-dephased ^{13}C signal on the deuterium pulse width for the alanine sample. Data taken with $\tau = 3.2$ ms. The solid line is a guide to the eye.

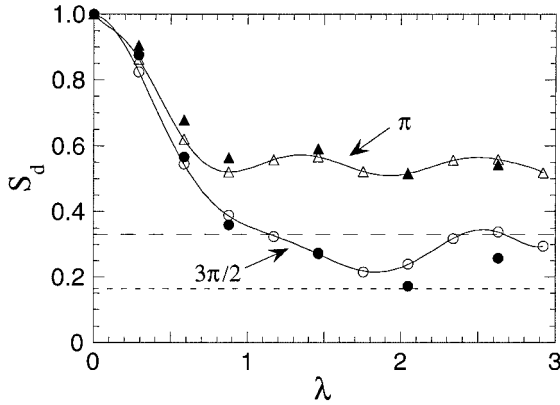


FIG. 5. Behavior of the dipolar-dephased ^{13}C signal on λ for isolated ^{13}C - ^2D spin pairs with modest deuterium RF power. The open triangles are numerical simulations for REDOR and the closed triangles are REDOR results obtained on the alanine sample. The open circles are θ -REDOR simulations and the closed circles are θ -REDOR results obtained on the alanine sample. The solid lines are guides to the eye for the numerical calculations. The upper and lower dashed lines are the ideal REDOR and θ -REDOR baselines of $\frac{1}{3}$ and $\frac{1}{6}$, respectively.

For perfect pulses, a deuterium 2π pulse causes no ^{13}C dipolar dephasing and S_d values for deuterium pulses of $\pi/2$ and $3\pi/2$ are identical. However, the results shown in the figure illustrate the poor performance of the deuterium pulse since there is significant dipolar dephasing for a 2π pulse and since the dipolar dephasing for a $\pi/2$ pulse differs substantially from that caused by a $3\pi/2$ pulse. Since it was found experimentally that the performance of θ -REDOR was better with $\theta = 3\pi/2$ than with $\theta = \pi/2$ for the alanine sample, all θ -REDOR results discussed henceforth are for $\theta = 3\pi/2$.

The dependence of REDOR and θ -REDOR on λ using finite-width ^2D pulses is compared through numerical simulations in Fig. 5. The simulations were performed by stepwise integration of the respective evolution operators. The calculations were performed using the alanine deuterium QCC of 167 kHz and a ^2D RF power of 48.5 kHz. The simulations suggest that REDOR deviates strongly from the ideal behavior described by Eq. [2] whereas the time evolution of the θ -REDOR experiment differs only slightly from that predicted by Eq. [3] under these conditions. For example, dipolar dephasing of the ^{13}C spins occurs more rapidly for θ -REDOR than for REDOR, which is in contrast to the calculations presented in Fig. 3 for infinite RF power. Furthermore, the θ -REDOR baseline almost reaches its theoretical asymptotic limit of $\frac{1}{6}$ whereas the REDOR baseline falls well short of its theoretical limiting value of $\frac{1}{3}$.

Also shown in Fig. 5 are experimental data obtained from the alanine sample. The experimental data shown in the figure have been corrected according to Eq. [1] using the value of $\alpha = \rho\epsilon$ mentioned earlier. For alanine, $\rho = 0.80$ but ϵ is not easy to measure. Instead, the raw uncorrected REDOR data (not shown) were corrected according to Eq. [1] until the corrected REDOR data (shown) fit the numerical simulation.

The experimental data and simulation are in good agreement with ϵ set to 0.88 for the alanine sample. This value of ϵ was then used to correct the θ -REDOR data which are clearly in good agreement with the θ -REDOR simulation. Because of the good agreement between the θ -REDOR data and simulation, this value of ϵ for alanine is considered to be reasonable and the numerical simulations do predict the behavior of the experiments correctly.

B. A Single ^{13}C Spin Coupled to Three Rotating Methyl Deuteriums with Modest Quadrupolar Coupling Strengths

The alanine data and simulations show that a REDOR experiment with a deuterium having a strong quadrupolar coupling constant performs poorly for modest deuterium RF powers. Deuterium spins in a methyl group undergoing fast rotation about the carbon-carbon bond have a quadrupolar coupling constant of about 55 kHz, which is significantly weaker than that for a static deuterium. For REDOR, the contribution to the dipolar-dephased ^{13}C signal for a specific carbon-methyl group orientation of a ^{13}C spin coupled to three equivalent methyl deuterons is

$$s_d(\tau) = \frac{1}{27} (7 + 12 \cos 2\bar{\omega}_d\tau + 6 \cos 4\bar{\omega}_d\tau + 2 \cos 6\bar{\omega}_d\tau). \quad [4]$$

Similarly, s_d for the θ -REDOR experiment is

$$s_d(\tau) = \frac{1}{1728} (308 + 624 \cos \bar{\omega}_d\tau + 414 \cos 2\bar{\omega}_d\tau + 248 \cos 3\bar{\omega}_d\tau + 108 \cos 4\bar{\omega}_d\tau + 24 \cos 5\bar{\omega}_d\tau + 2 \cos 6\bar{\omega}_d\tau). \quad [5]$$

Equations [4] and [5] were derived by the same method used to obtain Eqs. [2] and [3] and assume very strong deuterium RF power. The normalized powder averages of Eqs. [4] and [5] are plotted in Fig. 6. For large values of τ (or λ), the predicted baseline signal intensities are 0.259 and 0.178 for the REDOR and θ -REDOR experiments, respectively. REDOR dephases the ^{13}C signal at a faster rate than θ -REDOR, but θ -REDOR dephases a higher fraction of ^{13}C spins than REDOR.

The predictions of Eqs. [4] and [5] were tested by REDOR and θ -REDOR experiments performed on the zinc acetate dihydrate sample. The experimental data are also shown in Fig. 6 and are in good agreement with the calculations. Hence, the 48.5-kHz RF power used in these experiments is sufficient for the modest quadrupolar coupling constant often found for methyl deuterons, and the ^{13}C dipolar dephasing obeys the powder averages of either Eq. [4] or [5] for such cases, depending on the experiment performed.

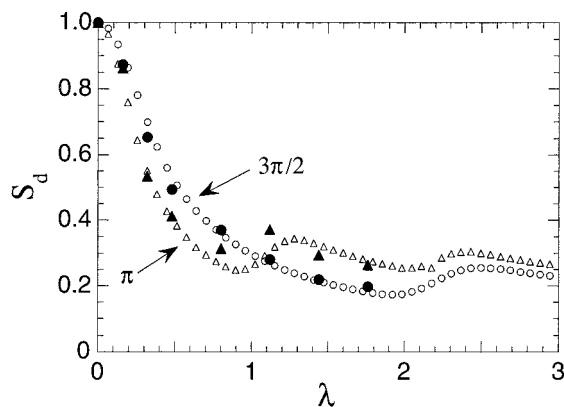


FIG. 6. Dependence of the dipolar-dephased ^{13}C signal on λ for a ^{13}C coupled to three methyl deuterons undergoing fast methyl rotation. The open triangles and open circles are calculated REDOR and θ -REDOR powder averages, respectively. The closed triangles and the closed circles are the respective REDOR and θ -REDOR results (corrected with $\epsilon = 1$) obtained on the zinc acetate dihydrate sample.

CONCLUSIONS

A comparison of the REDOR and the θ -REDOR experiments for ^{13}C - ^2D spin pairs has been performed. For modest ^2D RF powers the performance of REDOR is poor in comparison to θ -REDOR, as judged by the fraction of ^{13}C spins that dipolar dephase, when the deuterium quadrupolar coupling constant is large. For deuterons with modest quadrupolar coupling constants, both the REDOR and θ -REDOR experiments perform ideally. For deuterons with large quadrupolar coupling constants, numerical simulations will probably need to be performed to accurately describe the ^{13}C dipolar dephasing. However, for modest deuteron quadrupolar coupling constants, the ^{13}C dipolar dephasing is described by Eqs. [2]–[4], depending on the type of spin interaction and the experiment performed.

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