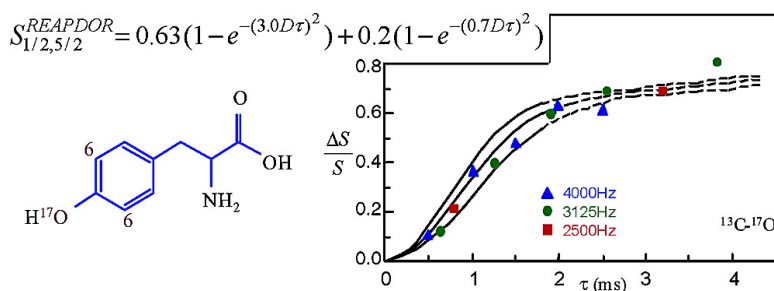


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J. Am. Chem. Soc., **2003**, 125 (37), 11194-11195 • DOI: 10.1021/ja0360642 • Publication Date (Web): 20 August 2003

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Interatomic Distance Measurement in Solid-State NMR between a Spin- $1/2$ and a Spin- $5/2$ Using a Universal REAPDOR Curve

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Measuring internuclear distances by high-resolution solid-state NMR has provided much needed structural information in solids that have been difficult to characterize by more traditional methods such as X-ray diffraction and solution-state NMR. Dipolar recoupling methods are used in magic-angle-spinning (MAS) NMR to provide structural information by measuring the dipolar interaction between nuclear spin-pairs.¹ An array of popular homonuclear recoupling experiments is available for measuring dipolar couplings between pairs of spin- $1/2$ nuclei such as ^{13}C - ^{13}C .¹ Currently, most quantitative distance measurements on heteronuclear pairs of spin- $1/2$ nuclei, such as ^{13}C - ^{15}N , use rotational-echo, double-resonance (REDOR) spectroscopy.² When one of the nuclei has spin ≥ 1 , its quadrupole interaction usually prevents the use of REDOR and requires the application of alternative experimental protocols such as rotational-echo, adiabatic-passage double-resonance (REAPDOR) spectroscopy.³ Unfortunately, interpretation of REAPDOR results presents a major difficulty in that the dipolar evolution depends on many NMR parameters, so that extensive density matrix calculations are required every time internuclear distances are to be determined. This is in contrast to the REDOR experiment, where dephasing depends only on the dipolar interaction and can be described by a universal dephasing curve. REAPDOR experiments were indeed combined with density matrix calculations for the determination of internuclear distances between ^{17}O - ^{13}C pairs in asparagine monohydrate,⁴ ^{23}Na - ^{29}Si pairs in the ETS-10 Zeolite,⁵ ^1H - ^{27}Al pairs in ZSM-5 and IFR,⁶ ^{13}C - ^{11}B ⁷ and ^{29}Si - ^{11}B pairs in ceramic materials,⁸ and ^{31}P - ^{59}Co pairs in a hexaminecobalt:AMP complex.⁹

The aim of our work is to provide an easy-to-apply quantitative interpretation tool enabling a wider use of REAPDOR for structural studies in inorganic glasses, catalysts, zeolites, and biological systems. In this Communication, we demonstrate the existence of a universal REAPDOR curve, which allows estimation of distances in solids between any observable NMR nucleus and atoms having spin- $5/2$ nuclei. The advantages and limitations of the use of this empirical curve will be discussed and REAPDOR results will be shown for ^{13}C - ^{67}Zn and ^{13}C - ^{17}O spin pairs. A forthcoming publication will present the spin- $3/2$ analogue.

First, consider the REDOR experiment shown in Figure 1. The pulse sequence consists of a rotor-synchronous train of radio frequency (RF) π pulses designed to manipulate the spin states in a coherent manner. A REDOR curve is obtained by comparing a reference signal S_0 to a dipolar dephased signal S . The reference signal can be acquired, for example, by applying two π pulses every rotor period on the I channel (the detected spin), while omitting the single S -channel (the coupled spin) π pulse. The dipolar-dephased signal is obtained by including the S -channel π pulse

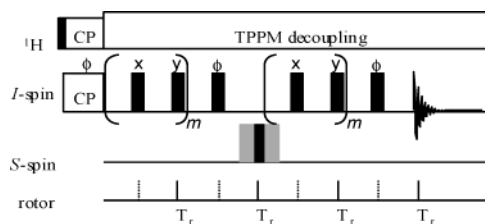


Figure 1. REDOR (black color π pulse on S -channel) and REAPDOR (gray pulse of length $T_r/3$) sequences. Initial spin magnetization is transferred from the abundant proton spins to the I -spin via cross polarization, or alternatively created by a $\pi/2$ pulse with a phase $\phi = 90^\circ$.

(shown in black in Figure 1). The REDOR fraction following $n = 2m + 2$ rotor cycles of cycle time T_r is $S_{1/2,1/2}(\lambda) = (S_0 - S)/S_0$. The dimensionless parameter λ is the product of the dipolar evolution time, nT_r , and the dipolar coupling, $D = \hbar\gamma_I\gamma_S/2\pi r^3$, in units of hertz. This fraction becomes larger as the dipolar evolution period increases and achieves an eventual value of 1.

Applying the REDOR sequence for a quadrupolar spin with $S \geq 1$ introduces several complications. When the quadrupolar frequency $\omega_Q = 3e^2qQ/[2S(2S - 1)\hbar]$ is larger than or of the order of the strength ω_1 of the S -spin RF pulse, the nutation behavior of the quadrupolar spin during that pulse is complex.¹⁰ This results in incomplete dephasing that depends not only on the dipolar interaction but also on ω_Q and the orientation of the quadrupolar tensor.

In the REAPDOR experiment, adiabatic transfer of populations between spin states is exploited during the RF irradiation on the quadrupolar nucleus.¹⁰ An optimal adiabatic pulse is obtained when the S -spin pulse length equals $T_r/3$ ¹¹ (gray shaded pulse in Figure 1) and $\omega_1^2/(\omega_Q\omega_r)$ is of the order of 1 or larger. These conditions give rise to a REAPDOR dephasing signal that is stronger than that found for the REDOR experiment.⁴ There is always a subset of crystallites for which the spin transitions are not adiabatic, or are unaffected by the pulse. As a result, the shape of the REAPDOR fraction as a function of λ depends on a number of parameters that vary from sample to sample and thus requires a comprehensive analysis to extract dipolar couplings. Despite the above-mentioned complications, it has lately been shown¹² that under certain experimental conditions the REAPDOR signal of isolated spin pairs with $I = 1/2$ and $S = 1$ can be effectively described by a universal curve that provides internuclear distances to within 4% of their true value. In search of a similar universal curve for spin- $5/2$ nuclei, we numerically calculated a large set of REAPDOR curves for a large variety of experimental parameters using the SIMPSON program.¹³ The results show that within certain conditions all of the dephasing curves fall in a narrow range and do not deviate more than 15% from the proposed universal curve given by the equation

$$S_{1/2,5/2}^{\text{REAP}}(\lambda) = 0.63(1 - e^{-(3.0\lambda)^2}) + 0.2(1 - e^{-(0.7\lambda)^2}), \quad (1)$$

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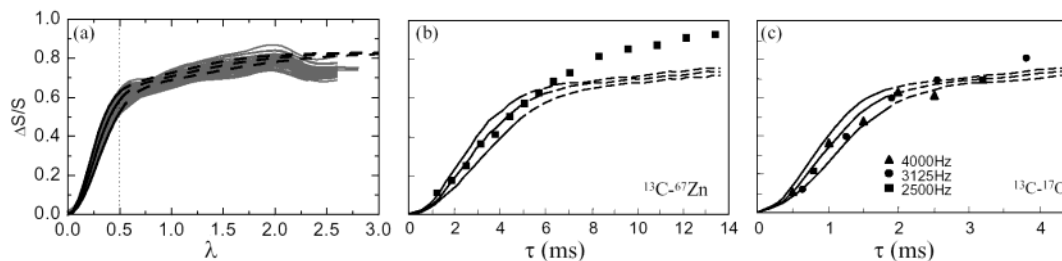


Figure 2. (a) The band of curves in gray color represents full density matrix REAPDOR simulations for a large range of values of e^2qQ/h (1–13 MHz), $\omega_1/2\pi$ (40–150 kHz), and $\omega_r/2\pi$ (3–20 kHz), keeping $\omega_1^2/(\omega_q\omega_r) > 0.55$. In addition, the asymmetry parameter of the quadrupolar tensor, η , and the polar angles defining the direction of the internuclear vector in the quadrupolar PAS were modified. Efficient proton decoupling was assumed. The universal curve of eq 4 is drawn with its upper and lower 15% boundaries. The region beyond $\lambda = 0.5$, where the fitting is not accurate, is shown as a dash line. (b) ^{13}C – ^{67}Zn REAPDOR results for the carbonyl carbons in Zn–acetate (■) overlaid by the best fit of the universal curve ($\pm 15\%$). The experiment was performed on a home-built spectrometer with a ^1H Larmor frequency of 151 MHz using a transmission-line triple-channel MAS NMR probe. RF field strengths were 50 kHz for cross-polarization, 120 kHz for proton decoupling, and 40 kHz for ^{67}Zn . The values of $\omega_1/2\pi = 3125$ Hz and $e^2qQ/h = 5.2$ MHz¹⁶ for ^{67}Zn give $\omega_1^2/(\omega_q\omega_r) = 0.64 > 0.55$. The 10 mg Zn–acetate sample was prepared by reacting acetic acid (^{13}C ; Cambridge Isotopes, Inc.), acetic acid (^{13}C ; Cambridge Isotopes, Inc.), and zinc oxide (^{67}Zn , 90%; Trace Science International) together. REAPDOR fraction for ^{67}Zn was recalculated so that $(\Delta S/S_0) = (\Delta S/S_0)_{\text{exp}}/0.9$. (c) ^{13}C – ^{17}O REAPDOR results on the C6 carbon in L-tyrosine (100 mg, 35–40% ^{17}O ; Cambridge Isotopes, Inc.). REAPDOR fraction for ^{17}O was recalculated so that $(\Delta S/S_0) = (\Delta S/S_0)_{\text{exp}}/0.35$. Experimental parameters were as in (b), except that the ^{17}O RF field strengths ranged from 52 to 56 kHz.

provided that the adiabaticity constraint $\omega_1^2/(\omega_q\omega_r) > 0.55$ is met. Calculated dephasing curves are shown as a gray band in Figure 2a. The universal curve is drawn in black, together with its upper and lower 15% bounding curves. The simulated curves fan out widely for $\lambda > 0.5$ due to the increasing dependence on the quadrupolar interaction and its orientation in the molecular frame. Hence, the fit between the universal and the simulated curves holds only for $\lambda < 0.5$. Beyond this boundary, eq 1 provides a “guide” (dashed line) to detect the presence of couplings of the observed nuclei to additional quadrupolar spins at larger distances.

Experimental REAPDOR results for a ^{13}C – ^{67}Zn spin pair in Zn–acetate are plotted and fitted to the universal curve in Figure 2b. A simple least-squares fit routine of the first seven data points yields a dipolar coupling $D_{\text{fit}} = 92$ Hz and an internuclear distance of 2.51 Å. The shortest ^{13}C – ^{67}Zn distance of 2.62 Å in the crystal¹⁴ corresponds to a dipolar coupling of $D = 105$ Hz. The ratio $D_{\text{fit}}/D = 0.88$ (4.2% error in $r_{\text{Zn-C}}$) is within the theoretical tolerance for the fittings to our universal curve. The importance of the extension of the universal curve beyond $\lambda = 0.5$ is also illustrated in this experiment. The deviation of the data from the universal curve at large λ values is due to the presence of additional zinc atoms in the vicinity of the carbonyls at distances of 4.5–5.5 Å.

The advantage of performing spinning-frequency-dependent REAPDOR experiments is demonstrated on a sample of tyrosine, Figure 2c. Because the validity of the universal curve is limited to $\lambda = nDT_r < 0.5$, the useful number of rotor cycles for each experimental setup is limited by $n < v_r/(2D)$. Hence, applying REAPDOR in the traditional way by fixing the spinning frequency and incrementing the number of rotor cycles $n = 2, 4, \dots$ can sometimes provide only a small number of valuable data points, particularly when D is large. This can be overcome by performing the experiment at more than one spinning speed. While normally such an approach would require a larger set of simulations, in the universal curve approach all data points can be used in the same fit routine. For the tyrosine sample, ^{13}C – ^{17}O REAPDOR fractions were measured at three different spinning frequencies. The combined first six points were fitted simultaneously to eq 1, yielding $D_{\text{fit}} = 278$ Hz ($r_{\text{C-O}} = 2.45$ Å). The average of the X-ray diffraction determined distances is 2.39 Å¹⁵ ($D = 300$ Hz, $D_{\text{fit}}/D = 0.92$).

In conclusion, we have presented a convenient tool for probing distances of single pairs of atoms with spin- $1/2$ and spin- $5/2$, using a simple fit of REAPDOR data points to a universal formula. The limitations on the experimental parameters are well within the capabilities of solid-state NMR probes. The use of a universal curve enables the performance of a spinning-frequency-dependent experiment without any extra calculations for the data analysis. The validity of this approach is supported by experimental evidence. Its implications as a probe for localizing quadrupolar nuclei in inorganic and biological samples are apparent.

Acknowledgment. This work was supported by the US-Israel Binational Science Foundation. T.G. acknowledges support from NSF Grant CHE-0091663.

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JA0360642