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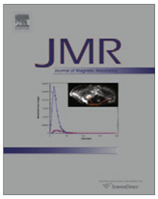

Communication

Distance measurement between a spin-1/2 and a half-integer quadrupolar nuclei by solid-state NMR using exact analytical expressions

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ABSTRACT

We show that the S-RESPDOR NMR method can be used to measure distances between spin-1/2 and half-integer quadrupolar nuclei, and that a general analytical formula describes its dephasing curve for all spin values. We demonstrate the method on the C^4–O^4 spin pair of L-tyrosine·HCl, with ^{13}C natural abundance and 30% ^{17}O enrichment, using a moderate magnetic field (9.4 T), a moderate ^{17}O rf-field (40 kHz) and a fast spinning speed (22 kHz). It is shown that S-RESPDOR is much more robust and accurate than previous methods.

1. Introduction

Nuclear magnetic resonance (NMR) is a powerful tool for the structural characterization of solid samples. It is especially qualified for chemical systems not amenable to conventional diffraction techniques. Specific techniques have been developed to extract different types of structural information. The first step consists in determining the chemical composition by resolving the different signals and measuring their relative proportions. Then, when the *S*/*N* is sufficient, the local environment of atoms can be probed by using homo- and hetero-nuclear correlations (HOMCOR and HETCOR) [1–4]. These experiments are based on coherence transfers through either *J*-coupling (*J*-HOMCOR [1] and *J*-HETCOR [2]) or dipolar coupling (*D*-HOMCOR [3] and *D*-HETCOR [4]). The *J*- and dipolar couplings reveal through-bond connectivities and through-space proximities, respectively. *D*-HOMCOR and *D*-HETCOR experiments require the use of dipolar recoupling sequences to impede the averaging effect of magic-angle spinning (MAS) on dipolar interaction. In general, *D*-HOMCOR and *D*-HETCOR only provide qualitative estimation of proximities. However, in the case of isolated spin pairs, the dipolar interaction can provide an accurate measurement of inter-nuclear distances. Therefore, a wide array of techniques has been developed to measure distances between spin-1/2 pairs of identical or different isotopes. For instance, the most popular MAS method to determine the distances between two different spin-1/2 isotopes is the rotational-echo double-resonance (REDOR) sequence [5]. This technique consists of rotor-synchronized π-pulses, which invert the spin magnetization. Hence, this method requires radio-frequency (rf) fields larger than internal spin interactions. This condition is usually fulfilled for spin-1/2 nuclei, which only experience chemical shift, *J*- and dipolar couplings. Conversely, for the nuclei with spin $I > ½$, the quadrupole interaction generally exceeds the rf-field and the use of REDOR is then prevented.

Distance measurements between spin-1/2 and quadrupolar nuclei are challenging. MAS pulse sequences include the transfer of population in double-resonance (TRAPDOR) [6], the rotational-echo adiabatic-passage double-resonance (REAPDOR) [7], and the rotary resonance-echo saturation-pulse double-resonance (R-RESPDOR) [8] experiments.

TRAPDOR and REAPDOR use an adiabatic-passage pulse to change the spin states of the quadrupolar nuclei to reintroduce the hetero-nuclear dipolar coupling. Therefore, the rf-field experienced by the quadrupolar nuclei must fulfill the condition: $\alpha = \nu_{1I}^2/(\nu_R\nu_Q) \geqslant 1$, where α is the adiabaticity parameter, ν_{1I} the rf-field amplitude on the quadrupolar *I* channel, $\nu_R = 1/T_R$ the MAS frequency, and $\nu_Q = 3C_Q/2I(2I-1)$ with $C_Q = e^2qQ/h$ [6,9,10]. This condition requires high-power rf-field, especially in the case of large quadrupole interactions and high spinning frequencies. Therefore,

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the use of TRAPDOR and REAPDOR may be prevented under fast MAS owing to the limited rf-field. Note that TRAPDOR is more demanding than REAPDOR since the adiabatic-passage irradiation lasts for one-half of the dipolar evolution period in the former instead of a fraction of the rotor period in the latter. Another limitation of REAPDOR and TRAPDOR is that their dephasing curves do not depend only on the dipolar coupling constant, b_{IS}, but are influenced by the quadrupole interaction [10–13]. Therefore, the determination of inter-nuclear distances by REAPDOR and TRAPDOR requires using simulation software. Compared to TRAPDOR, REAPDOR benefits from a weaker dependence of the dephasing curve on the quadrupole interaction [11], and approximate analytical expressions of REAPDOR curve have been proposed for spin values $I = 1$, 3/2, 5/2 and 7/2. These expressions are valid when $\alpha \geqslant 0.25$, 0.5, 0.55, and 1.6 for $I = 1$, 3/2, 5/2 and 7/2, respectively [10,13]. However, these empirical expressions are only applicable for short recoupling time. Finally, REAPDOR and REDOR suffer from the same drawbacks, especially under fast MAS: (i) they recouple the homo-nuclear dipolar interaction between the spin-1/2 nuclei [14], and (ii) their dephasing curves depend on the ratio between the π-pulse length and T_R [15]. It must be mentioned that another type of experiment, called RIDER, has been proposed, where distances between ^{13}C and ^{14}N nuclei were measured using the relaxation properties of the quadrupolar nucleus [16].

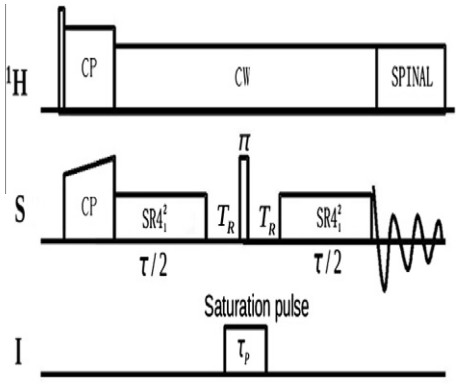

Fig. 1. S-RESPDOR pulse sequence. The nuclear spins are such as $S = 1/2$ and $I > 1/2$. The magnetization of S-spin nuclei can be enhanced by employing cross-polarization (CP) transfer from protons. Continuous-wave (CW) and SPINAL-64 decoupling have been applied to the ^{1}H channel before and during the acquisition. As the $SR4_1^2$ sequence is not γ-encoded, the interval between the first and the second $SR4_1^2$ sequences must be a multiple of $2T_R$. The distance determination requires the acquisition of two separate spin-echo signals as function of the dipolar evolution period τ: the dipolar-dephased signal, S, recorded with the pulse sequence displayed in the figure, and the reference signal, S_0, recorded by omitting the I pulse in the middle of τ. The phase of the initial ^{1}H 90° pulse and that of the receiver are cycled over $y/-y$ and $x/-x$, respectively.

2. Saturation pulses

Recently, an alternative was proposed [8], which consists in replacing adiabatic-passage pulses by saturation pulses. These are advantageous since they only need moderate rf-fields, even at high MAS speed. Saturation pulse was first incorporated in R-RESPDOR experiment [8], which uses rotary-resonance recoupling (R^3) [17] sequence as a hetero-nuclear dipolar method. The R^3 technique has the advantage to be γ-encoded and compatible with high MAS frequency [18]. However, R-RESPDOR presents several drawbacks: (i) it is very sensitive to rf-field inhomogeneity [19], (ii) it is influenced by chemical shift anisotropy (CSA) which does not commute with hetero-nuclear dipolar terms [20], (iii) it is sensitive to homo-nuclear dipolar interactions of the observed nuclei, (iv) it suffers from dipolar truncation, which prevents the measurement of medium- and long-range distances [21], and (v) it is not describable by analytical formula in the general case. We have shown very recently that the above limitations of R-RESPDOR can be circumvented by replacing the R^3 recoupling by $SR4_1^2$ sequence.[20,22] This symmetry-based resonance-echo saturation-pulse double-resonance (S-RESPDOR) method was applied to determine ^{13}C–^{14}N distance in uniformly ^{13}C-labeled amino acid.[20] In this communication, we demonstrate that S-RESPDOR can also be used to measure distances between spin-1/2 and half-integer quadrupolar nuclei, and that a general analytical formula describes its dephasing curve for all spin values.

3. S-RESPDOR method

In the S-RESPDOR sequence [20], the $SR4_1^2$ recoupling is only applied to the observed spin-1/2 nucleus (Fig. 1). There are two pulses in the middle of the sequence: a π-pulse on S observed channel that refocuses CSA, and a saturation-pulse lasting τ_p on I quadrupolar channel. We have found with numerous simulations that its optimized length is about $\tau_p \approx 1.5T_R$, and that an rf-field in the range of 50–60 kHz is most of the time sufficient to saturate the whole nuclear magnetization of I-spin nuclei, even in the case of large C_Q values and/or fast spinning speeds. These values are similar to those recently proposed to improve the efficiency of the REAPDOR method [23]. However, it must be noted that the middle-pulse on the quadrupolar channel is then no more an adiabatic pulse, but a saturation pulse. It must also be noted that saturation can also be generated by the application of multiple-pulses on the quadrupolar nucleus, as in the SPIDER experiment [24]. Following a similar approach to that used for an isolated ^{13}C–^{14}N spin pair [20], we introduce a general formula describing the S-RESPDOR dephasing curves for a spin-1/2 nucleus coupled to any spin-I nucleus:

$$\frac{\Delta S}{S_0} = f\,\frac{1+\delta_{I,1/2}}{2I+1}\left\{2I - \frac{\pi\sqrt{2}}{4(2I+1)}\sum_{k=1}^{2I}[4I-2(k-1)]J_{1/4}\left(\frac{k\pi\lambda}{4}\right)\times J_{-1/4}\left(\frac{k\pi\lambda}{4}\right)\right\} \tag{1}$$

The parameter $\lambda = b_{IS}\tau$ is dimensionless with τ the dipolar dephasing period, and the fraction $\Delta S = S_0 - S$ is the difference signal, obtained by subtracting the dipolar-dephased signal S from the reference signal S_0. $J_{\pm 1/4}$ denotes the ±1/4-order Bessel function of the first kind. The pre-factor f represents the fraction of crystallites containing I-nuclei that are saturated by the pulse. Hence, f is the product of the isotopic abundance of this nucleus by the efficiency of the saturation pulse. It must be noted that Eq.1 also describes results observed with the symmetry-based resonance-echo double-resonance (S-REDOR) method [20], which is the analog of S-RESPDOR for a pair of spin-1/2 nuclei.

The validity of Eq. (1) was verified by comparison with numerical PULSAR simulations [25]. Fig. 2 displays the S-RESPDOR fraction in the case of $I = 1$, 3/2, 5/2, 7/2 and 9/2, as well as the S-REDOR ($I = ½$) fraction. The simulated fractions were fitted with Eq . (1), and are in good agreement with those obtained with PULSAR. One observes that a moderate (50–65 kHz) rf-field is sufficient in S-RESPDOR to saturate correctly the quadrupolar nucleus, as the f factor then always remains close to one and the fitted dipolar value is close to its introduced value. One also observes a steeper original slope for larger I-spin values (Fig. 2). This means that for identical b_{IS} and irreversible T_2' constant-time, losses effects decrease with increasing I values, as most of the time only the initial rising parts of the fraction curves are measurable. Moreover, it must be noted that the maximum S-RESPDOR fraction increases from c.a. 0.64 to 0.90 when I increases from 1 to 9/2.

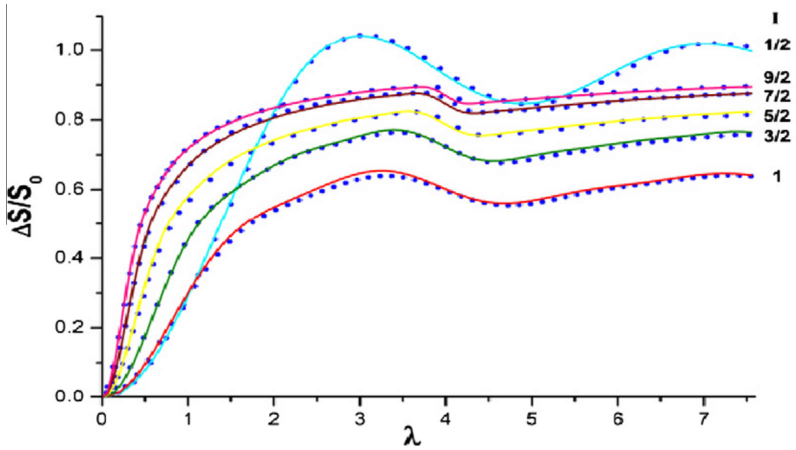

Fig. 2. S-REDOR and S-RESPDOR signal fraction as function of the dimensionless parameter λ. The (blue) points represents the simulated $\Delta S/S_0$ values calculated with PULSAR [23] at $\nu_R = 20$ kHz and $B_0 = 9.4$ T for an $S = {}^{13}C$–I spin pair. We use an infinitely short central π-pulse on the ^{13}C-observed channel. For S-RESPDOR, the saturation pulse lasts 75 μs = $1.5T_R$. The anisotropic chemical deshielding constant, δ_{aniso} (^{13}C), is equal to 8 kHz and η_{CSA} (^{13}C) = 0. The continuous lines represent the fits of simulated $\Delta S/S_0$ values using Eq. (1). For each curve, the simulation and fit parameters are given below: (a) $I = 1/2$ (^{15}N). PULSAR: $b_{IS} = 937$ Hz, ideal central π-pulse on non-observed ^{15}N channel. Fit: $b_{IS} = 924$ Hz, $f = 1.0$. (b) $I = 1$ (^{14}N). PULSAR: $b_{IS} = 674$ Hz, $C_Q = 1.14$ MHz, $\eta_Q = 0.24$, $\nu_{14N} = 50$ kHz. Fit: $b_{IS} = 659$ Hz, $f = 0.96$. (c) $I = 3/2$ (^{11}B). PULSAR: $b_{IS} = 800$ Hz, $C_Q = 2.5$ MHz, $\eta_Q = 0.8$, $\nu_{11B} = 60$ kHz. Fit: $b_{IS} = 793$ Hz, $f = 1.02$. (d) $I = 5/2$ (^{17}O). PULSAR: $b_{IS} = 300$ Hz, $C_Q = 8.52$ MHz, $\eta_Q = 0.74$, $\nu_{17O} = 65$ kHz. Fit: $b_{IS} = 290$ Hz, $f = 0.99$. (e) $I = 7/2$ (^{51}V). PULSAR: $b_{IS} = 270$ Hz, $C_Q = 1.73$ MHz, $\eta_Q = 0.37$, $\nu_{51V} = 50$ kHz. Fit: $b_{IS} = 267$ Hz, $f = 1.0$. (f) $I = 9/2$ (^{73}Ge). PULSAR: $b_{IS} = 320$ Hz, $C_Q = 5$ MHz, $\eta_Q = 1$, $\nu_{73Ge} = 50$ kHz. Fit: $b_{IS} = 319$ Hz, $f = 0.98$. There are two parameters introduced into the fit: f and b_{IS}. These two parameters can be fully determined as long as the recoupling time τ is long enough to reach the plateau of the signal fraction. When it is not the case, these two parameters are strongly correlated, and then the pre-factor f must be fixed as in Fig. 3. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4. Experimental verification

In order to test the sequence, we have measured the shortest C-O distance (C^4–O^4) in [30%-$^{17}O^4$]-L-tyrosine·HCl sample. S-RESPDOR spectra were recorded at 9.4 T on an AVANCE-II WB Bruker spectrometer, with a triple resonance 3.2 mm MAS probe spinning at $\nu_R = 22$ kHz. Quadrupolar parameters of O^4 atom have been determined previously and are equal to $C_Q = 8.52$ MHz and $\eta_Q = 0.74$ [26]. It must be mentioned that the pre-factor f and the dipolar coupling constant b_{IS} are strongly correlated into the fitting of the experimental data, as long as the plateau of the S-RESPDOR fraction is not reached. Therefore, the experimental $^{13}C^4$–$^{17}O^4$ data, shown in Fig. 3, were fitted with the pre-factor fixed to $f = 0.24$, in agreement with the level of $^{17}O^4$-labeling, and the actual rf-field amplitude of the saturation pulse ($\nu_{1I} \approx 40$ kHz), which is slightly insufficient to fully saturate the ^{17}O density matrix with such a strong quadrupole interaction. The continuous line corresponds to a C^4–O^4 distance of 136.6 pm, which is in perfect agreement with that determined by X-ray diffraction: 137.4 pm [27].

5. Conclusions

We have demonstrated the application of S-RESPDOR sequence for the inter-nuclear distance measurements between spin-1/2 and half-integer quadrupolar nuclei. In the case of our sample, the challenge was not so easy to fulfill, as only 0.3% of the C^4–O^4 spin pairs of L-tyrosine.HCl contributed to the signal, and as we have used a moderate magnetic field (9.4 T), a moderate rf-field ($\nu_{1I} = 40$ kHz) and a fast spinning speed ($\nu_R = 22$ kHz). With such a spinning speed, it would have been impossible using the REAPDOR method with its approximate analytical expressions. Indeed, these would have required the rf-field amplitude on the oxygen channel to be larger than 125 kHz [10]. More generally, the S-RESPDOR method

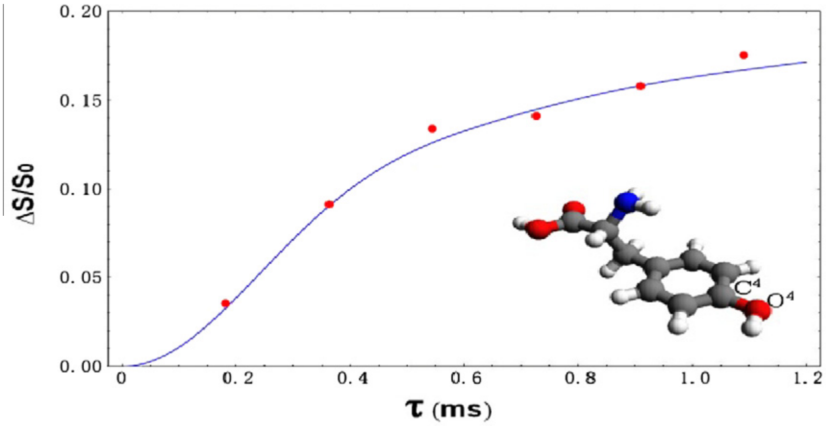

Fig. 3. S-RESPDOR signal fraction corresponding to the shortest C–O distance (C^4–O^4) in [30%-$^{17}O^4$]-L-tyrosine·HCl sample. The signal fraction was determined by integrating signal C^4. The experiment was performed at $B_0 = 9.4$ T and $\nu_R = 22$ kHz. The $^1H \rightarrow {}^{13}C$ CP transfer uses nutation frequencies of $\nu_H = 67$ kHz and $\nu_C = 45$ kHz, and a contact time of 1.8 ms The rf nutation frequencies of the ^1H $\pi/2$ and ^{13}C π-pulses were $\nu_{\pi/2\text{-}H} = 114$ kHz and $\nu_{\pi\text{-}C} = 50$ kHz. The saturation ^{17}O pulse with $\nu_{\tau p} = 40$ kHz, lasts $\tau_p = 1.5T_R$. Before the acquisition, CW ^1H decoupling with $\nu_{CW} = 100$ kHz was applied to the ^1H channel, whereas during the acquisition, the ^1H decoupling consists in SPINAL-64 irradiation with $\nu_{SPINAL} = 80$ kHz. The S-RESPDOR spectrum results from averaging 3072 transients and the recycling delay is 4 s, i.e. total experimental time of 68 h. The points represent the experimental signal fraction, whereas the continuous curve is the best fit to Eq. (1) with $b_{13C\text{–}17O} = 1606 \pm 100$ Hz, with the pre-factor fixed to $f = 0.24$. The error bar, 100 Hz, is an estimation deduced from several simulations with different $b_{13C\text{–}17O}$ values.

presents several advantages over the REAPDOR and R-RESPDOR methods. There is one single general analytical formula describing its fraction for all spin values. This leads to a fast determination of inter-nuclear distances from experimental data. Moreover, in addition to the dipolar interaction, this formula includes a single prefactor parameter, which takes into account the isotopic abundance and all pulse limitations (amplitude) or errors (timing and length). The method is not dipolar truncated, which means that short and long distances can simultaneously be determined. The method is very little sensitive to: (1) homo-nuclear dipolar interactions on the observed channel, (2) rf-field inhomogeneity, (3) offsets, (4) CSA, and (5) relative orientations of the various microscopic interactions. Moreover, the method is not very demanding as the rf-field amplitude is equal to twice the spinning speed on the observed spin-1/2 channel and must only be larger than c.a. 60 kHz on the non-observed quadrupolar channel for complete saturation, even in case of strong C_Q values and/or fast spinning speeds.

There are two parameters introduced into the fit: f and b_{IS}. These two parameters can be fully determined as long as the recoupling time τ is long enough to reach the plateau of the signal fraction. When it is not the case, as in Fig. 3, these two parameters are strongly correlated, and then the pre-factor f must be fixed. An *estimation* of this parameter is possible if the isotopic abundance and the C_Q value are known. When simultaneously: (i) only the initial rising part of the fraction curve is measured, and (ii) the isotopic abundance and/or the C_Q value are unknown, it is very difficult to determine the inter-nuclear distance with accuracy.

The second technical limitation of the sequence is that the spinning speed must be correctly regulated (c.a. ±2–3 Hz). This is also the case of the REAPDOR sequence due to the non-γ-encoding aspect of both sequences. This limitation can easily be overcome by either triggering all pulses with respect to the sample rotation, and/or by directly introducing into the pulse sequence the instantaneous actual spinning speed instead of the desired one.

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