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Rotational echo double resonance without proton decoupling under fast spinning condition

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ABSTRACT

We show that rotational echo double resonance (REDOR) experiments can be carried out without proton decoupling under the conditions of fast spinning and strong rf field. Numerical simulations on a five-spin systems show that no significant attenuation of the reference signal (S_0) is observed at a spin rate of 25 kHz, provided that the rf power is larger than 100 kHz. This approach has been validated by ^{31}P{^{13}C} REDOR measurements on isotopically labeled glyphosate. The obtained van Vleck's second moment is in favorable agreement with the value calculated based on the crystal structure.

1. Introduction

The importance of the rotational echo double resonance (REDOR) technique [1] is evident by its widespread applications in the fields of biological research and material science [2–4]. The advantages of REDOR are several-fold: (i) the experimental setup is straightforward; (ii) the data analysis is simple; (iii) the amplitude of the corresponding average Hamiltonian is relatively large [5]. Recently, REDOR has been applied to the regime of fast spinning [6,7]. Under the fast spinning condition, the line broadenings due to rotational resonance could be avoided [8] and the signal-to-noise ratio of species with sizable chemical shift anisotropy (CSA) can be enhanced by suppressing the spinning side bands [9]. The most useful version of REDOR for biological samples contains a train of π pulses applied to the observed and dephasing channels at the time points of integral and half-integral number of rotor periods, respectively, [10]. For ^{13}C uniformly labeled systems, however, the π pulses applied to the ^{13}C channel may recouple the ^{13}C homonuclear dipole–dipole interaction when the pulse width is comparable with the rotor period [11,12], rendering the analysis of the REDOR data not trivial. Although one may alleviate the finite-pulse effect by increasing the B_1 field of the ^{13}C π pulses, it may, on the other hand, present a stringent requirement for proton decoupling. Consequently, several modifications based on windowless rf irradiations or symmetry-based pulse sequences have been proposed to extend the original REDOR pulse sequence to the fast spinning regime [13–19]. However, the scaling factors of these modifications, which measure the amplitudes of the resultant average Hamiltonians, are usually smaller than the original REDOR approach.

Very recently, it has been shown that the radio-frequency driven dipolar recoupling (RFDR) technique can be implemented for biological systems without proton decoupling under fast spinning condition [20,21], provided that the rf field of the π pulses is strong enough ($\sim$100 kHz) [22]. For RFDR, homonuclear dipolar recoupling is achieved by modulating the homonuclear dipole–dipole interaction by the chemical shift difference of the interacting spins. Although the underlying spin dynamics of RFDR and REDOR are completely different, both techniques are based on the delta pulse approximation and the rotor-synchronized pulse train suggested by Gullion et al. [23]. In this study, we show that REDOR measurements can indeed be carried out without proton decoupling under the conditions of fast spinning and strong rf power. Numerical simulations and experimental measurements on glyphosate were carried out to validate our approach. The ^{13}C{^{31}P} heteronuclear van Vleck's second moment obtained for glyphosate is in favorable agreement with the value calculated based on the X-ray crystallographic data.

2. Experimental methods

[2-^{13}C, ^{15}N] glyphosate, $\mathrm{HPO_3CH_2^{15}NH_2^{13}CH_2COOH}$, was used as received from Isotec. All NMR experiments were carried out at ^{31}P, ^{13}C, and ^{1}H frequencies of 121.5, 75.5, and 300.1 MHz, respectively, on a Bruker DSX300 NMR spectrometer equipped with a commercial 2.5 mm probe. The measurements were carried out at ambient temperature. The sample was confined to the middle one-third of the rotor volume using Teflon spacers. The magic-angle spinning (MAS) was carried out at a frequency of

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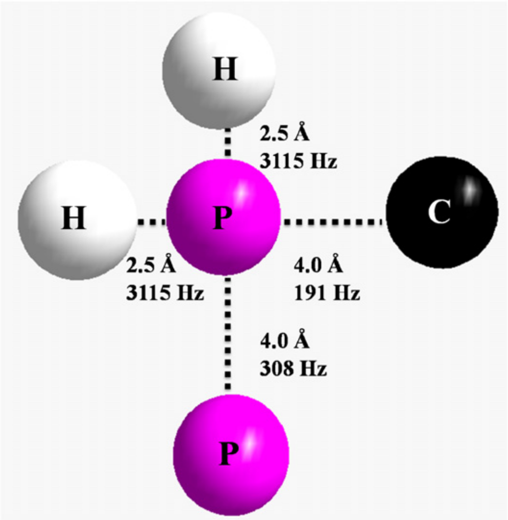

Fig. 1. Model spin system constructed for our numerical simulations. The most important dipolar coupling constants are indicated in the figure. Other coupling constants of the dipolar network are not indicated for brevity. Chemical shift interactions are not considered.

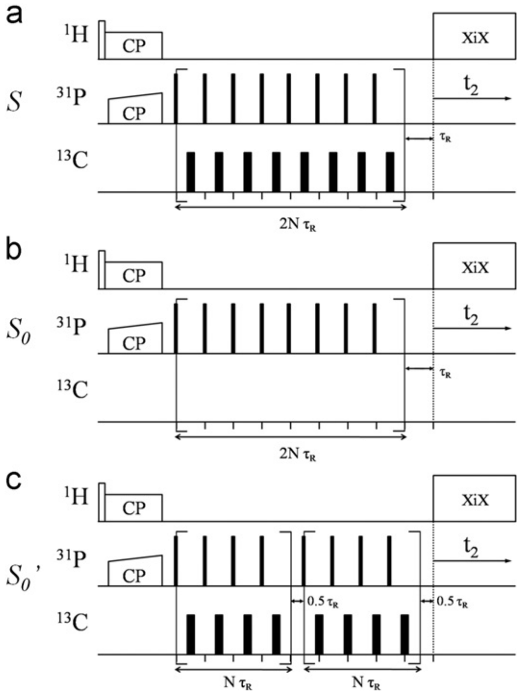

Fig. 2. Pulse sequences used in this study. The corresponding signals measured by the pulse sequences (a), (b), and (c) are denoted as S, S_0, and S_0', respectively. The difference signal fractions, $(S_0-S)/S_0$, as a function of the dephasing time constitute the ordinary REDOR curve. Pulse sequence (c) serves to provide an empirical correction for the REDOR curve, abbreviated as dummy echo in the text. The open and filled rectangles represent hard $\pi/2$ and π pulses, respectively.

25 kHz and its variation was limited to ± 3 Hz using a commercial pneumatic control unit (Bruker, MAS II). During the contact time (2.5 ms) of the cross polarization, the ^{1}H rf field was set to 50 kHz and that of ^{31}P was adiabatically ramped through the Hartmann–Hahn matching condition [24,25]. Recycle delay was set to 12 s. During the REDOR recoupling period, the ^{31}P and ^{13}C π pulses were set to 4 and 10 μs, respectively. The π pulse trains in the ^{31}P and ^{13}C channels were individually phase cycled according to the xy-16 scheme [23]. The tachometer signals for pulse sequence synchronization were filtered with a home-built phase-locked loop circuit. The rf field of XiX proton decoupling was set to 100 kHz during the acquisition period [26]. Typically, for each spectrum of glyphosate, a total of 16 transients were accumulated.

Numerical simulations were carried out using SPINEVOLUTION (version 3.4.1) [27]. The maximum time step over which the Hamiltonian is approximated to be time-independent was set to 1 μs. Typically, a powder averaging scheme containing 168 REPULSION angles (α and β) [28] and 20 γ angles was chosen. Relaxation effects were ignored. The calculations were done on a five-spin system at 7.05 T. For simplicity, the geometry of the spins was set arbitrarily as illustrated in Fig. 1. The initial and detected density operators were set on the central phosphorus nucleus. Simulation parameters were matched to the experimental conditions wherever applicable. Typical input files are provided in the supporting information.

3. Results and discussion

3.1. Pulse sequence design

Fig. 2 shows the pulse sequences used in this study. If the rf field of the π pulses is large enough, proton decoupling during the REDOR dephasing period may become unnecessary. The REDOR signal (S) is generated by the sequence shown in Fig. 2(a), whereas the reference signal (S_0) is obtained without rf pulses in the dephasing channel (Fig. 2b). In principle, the REDOR curve can be obtained by calculating the fractions $(1-S/S_0)$ as a function of the dephasing time. However, the amplitudes of the REDOR fractions may be affected by a number of experimental imperfections. Previously, it has been shown that the fidelity of the REDOR curve of a multiple-spin system can be greatly improved by an empirical correction [29]. The idea is to measure another echo signal obtained by a pulse sequence as similar to that for the REDOR signal as possible. For convenience, this echo signal is henceforth referred to as the dummy echo (S_0'). Under perfect experimental conditions, S_0 and S_0' are identical. In practice, however, these two echo signals are usually different and their difference signal could be used to correct the REDOR fractions. In this work, the dummy echo is obtained by the sequence shown in Fig. 2c, which is identical to that of Fig. 2a except for the fact that the second half of the REDOR dephasing period is displaced by half the rotor period. The time modulations of the heteronuclear dipolar interaction by the three pulse sequences are illustrated in Fig. 3, where it is clearly shown that S_0 and S_0' are identical under perfect experimental conditions.

3.2. Numerical simulations

To evaluate the practicability of our approach, we have carried out a series of simulations on a five-spin system based on the pulse sequences shown in Fig. 2. As depicted in Fig. 4a, the S_0 signal calculated under our experimental conditions, where the π pulses in the ^{31}P channel were set to 125 kHz, shows no significant decay up to a dephasing time of 5 ms, indicating that both the homonuclear and heteronuclear dipole–dipole interactions are well suppressed. Nevertheless, the decay of S_0 becomes appreciable as the rf power in the ^{31}P channel decreases. This phenomenon could be ascribed to the finite pulse effect and to the reintroduced requirement of proton decoupling when the recoupling rf field is relatively weak. The calculated S_0' signals also show a similar trend to the S_0 signal, verifying that the ^{31}P–^{13}C