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Symmetry-based recoupling of ^{17}O–^{1}H spin pairs in magic-angle spinning NMR

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Abstract

We have performed magic-angle-spinning solid-state NMR experiments in which protons are recoupled to oxygen-17 nuclei by applying a symmetry-based recoupling sequence at the proton Larmor frequency. Two-dimensional quadrupole-dipole correlation spectra are produced, in which the second-order quadrupolar shift of the oxygen-17 central transition is correlated with the recoupled heteronuclear dipole–dipole interaction. These spectra are sensitive to the relative orientation of the electric field gradient at the site of the oxygen-17 nucleus and the O–H internuclear vector. We also demonstrate experiments in which polarization is transferred from protons to oxygen-17, and show that oxygen-17 signals may be selected according to the protonation state of the oxygen site. We discuss the small observed value of the heteronuclear dipolar splitting in the central-transition oxygen-17 spectra.

Keywords: Solid-state NMR; Quadrupolar nuclei; Oxygen-17; Correlation spectroscopy; Symmetry-based recoupling; MAS; Brucite

1. Introduction

^{17}O solid-state NMR of isotopically enriched materials is an important method for studying a wide range of substances, including zeolites [1–3], glasses [4], battery materials [5], and membrane-bound peptides [6]. The NMR of ^{1}H–^{17}O pairs is of particular interest for the study of acidic sites and hydrogen-bonded systems [3,7,8] since the ^{17}O quadrupole interaction and chemical shift tensors are sensitive to local structural perturbations [9]. Furthermore, the magnitude of the ^{1}H–^{17}O dipole–dipole coupling, and its relative orientation with respect to the chemical shift and quadrupole coupling tensors of the ^{17}O nucleus [10] provide additional information.

The ^{1}H–^{17}O dipole–dipole coupling constant has a magnitude of around 15 kHz in a directly bonded hydroxyl moiety. Although this a considerable interaction, it is difficult to observe, since ^{17}O nuclei in hydroxyl sites experience a large electric field gradient, leading to a second-order quadrupolar broadening of the ^{17}O central transition by several kHz at typical magnetic fields. Furthermore, in many samples, strong ^{1}H–^{1}H interactions create additional complications. Nevertheless, the ^{1}H–^{17}O dipolar coupling has been resolved in static samples by performing Hartmann–Hahn cross-polarization from ^{1}H to ^{17}O, while spin-locking the ^{1}H nuclei by off-resonance irradiation satisfying the Lee-Goldburg condition, in order to reduce the effect of the ^{1}H–^{1}H couplings [10]. Two-dimensional spectroscopy was used to correlate the second-order quadrupolar shift of the ^{17}O central transition with the ^{1}H–^{17}O dipolar coupling, allowing determination of the relative orientation of the ^{1}H–^{17}O dipolar coupling and ^{17}O quadrupolar interaction tensors [10]. In this paper, such two-dimensional spectra are termed quadrupole-dipole (QD) correlation spectra.

It would be desirable to perform QD correlation experiments under magic-angle-spinning (MAS) conditions,

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since this would allow the ^{1}H–^{17}O dipolar coupling information to be combined with chemical site selectivity, particularly if multiple-quantum magic-angle-spinning (MQMAS) [11,12] or satellite-transition magic-angle-spinning (STMAS) [13,14] are used. Unfortunately, Hartmann–Hahn cross-polarization is problematic for quadrupolar nuclei in the presence of MAS, due to the breakdown of the central-transition spin-lock [15–17]. Alternative schemes, such as those based on REDOR [18–22] or TEDOR [19,23] also have problems, due to the strong homonuclear ^{1}H–^{1}H couplings present in many samples. Here we show that these difficulties may be avoided by using symmetry-based recoupling sequences [24–26]. A suitable choice of recoupling symmetry numbers implements ^{1}H–^{1}H dipolar decoupling at the same time as ^{1}H–^{17}O dipolar recoupling. We demonstrate quadrupole–dipolar (QD) correlation spectroscopy under MAS conditions for two different ^{17}O-labelled molecular systems. The QD correlation spectra have a strikingly different appearance, reflecting their sensitivity to the relative tensor orientations. We also demonstrate significant polarization transfer from the ^{1}H nuclei to the ^{17}O central transition, allowing the ^{17}O spectrum to be edited according to the protonation of the ^{17}O site.

Heteronuclear recoupling leads to splittings in the central-transition ^{17}O spectra. However, the observed splittings are significantly smaller than expected from the OH distance as estimated by neutron diffraction. We discuss various explanations for these discrepancies below but cannot yet provide a definitive explanation.

2. Pulse sequences

Fig. 1 shows two pulse sequences suitable for ^{1}H–^{17}O dipolar recoupling in the presence of MAS. Both methods exploit symmetry-based recoupling sequences of the class $\mathrm{R}N_n^{\nu}$ applied at the ^{1}H Larmor frequency. The selection rule theorems [24–26] allow one to choose symmetry numbers N, n, and ν which implement recoupling of heteronuclear spin interactions, while removing the effect of ^{1}H–^{1}H spin interactions, to first order in average Hamiltonian theory. In all of the experiments described in this paper, we used a recoupling pulse sequence with the symmetry $\mathrm{R}18_2^5$, using the simplest possible basic element of a single 180° pulse. The $\mathrm{R}18_2^5$ sequence consists of a repetition of the two-pulse element $180_{50}180_{-50}$, where the pulse flip angles and phases are specified in degrees, and the rf field strength corresponds to a nutation frequency of 4.5 times the MAS frequency. This sequence may be shown on symmetry grounds [24–27] to recouple the heteronuclear ^{1}H–^{17}O dipole–dipole interactions whilst decoupling the homonuclear ^{1}H–^{1}H dipolar interactions. Note, however, that the $\mathrm{R}18_2^5$ sequence also recouples the ^{1}H chemical shift anisotropy (CSA): in high magnetic fields, the recoupled proton chemical shift anisotropy can interfere with the heteronuclear recoupling performance, as is described below.

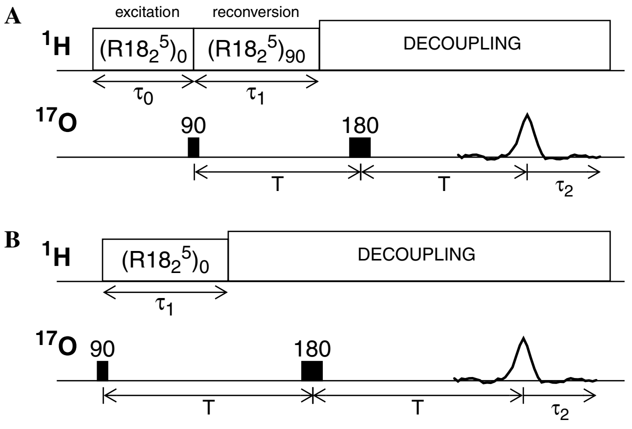

Fig. 1. (A) PRESTO-II pulse sequence. Recoupling periods are denoted by $\mathrm{R}18_2^5$, where 18, 2, and 5 denote the symmetry numbers N, n, and ν of the recoupling sequence. The subscript to the recoupling period denotes the overall rf phase in degrees. The ^{17}O flip angles correspond to rotations in degrees of the central transition and the echo intervals T correspond to a fixed integer number of rotor periods $\tau_r = 2\pi/\omega_r$. (B) Sequence for generating a dipolar oscillation for a 1Q coherence.

In practice the sequence $\mathrm{R}18_2^5$ is especially suitable for heteronuclear recoupling experiments at a magic-angle spinning frequency of around 15–20 kHz (requiring rf field strengths of 67.5–90 kHz). Symmetries with different ratios of nutation frequency to spinning frequency are available [24–26]. For example, the sequence $\mathrm{R}18_1^7$ was used at 10 kHz MAS frequency, yielding similar results to the ones presented here (not shown).

Fig. 1A shows the PRESTO-II (phase-shifted recoupling effects a smooth transfer of order) [27] pulse sequence. This method has already been used for heteronuclear polarization transfer in spin-1/2 systems. In the first interval, denoted τ_0, a $\mathrm{R}18_2^5$ sequence is applied to the Zeeman-polarized ^{1}H nuclei, to decouple the ^{1}H–^{1}H interactions and recouple the ^{1}H–^{17}O interactions. A state of transverse ^{1}H polarization, antiphase with respect to the ^{17}O spin states, is generated at the end of τ_0. A 90° pulse on the ^{17}O central transition is applied, followed by evolution under a second $\mathrm{R}18_2^5$ sequence for an interval τ_1. This second $\mathrm{R}18_2^5$ sequence has an overall phase shift of 90°, and need not be complete, so that in general it is not equal to an integer number of rotor periods. A 180° pulse is applied to the ^{17}O central transition, and centred around a time point which is T after the end of the ^{17}O 90° pulse. The interval T must be equal to a constant integer number of rotor periods, independent of the value of τ_1. ^{17}O signals are acquired starting from an interval T after the centre of the ^{17}O 180° pulse. The lower half of the PRESTO-II pulse sequence corresponds to a rotor-synchronized Hahn echo applied to the ^{17}O central transition, which refocuses the isotropic ^{17}O chemical shift, the ^{17}O chemical shift anisotropy, and the second-order ^{17}O quadrupolar interaction. TPPM-modulated ^{1}H irradiation [28] is used to suppress heteronuclear interactions during that part of the spin echo which is not occupied by the $\mathrm{R}18_2^5$ sequence, and during signal acquisition.