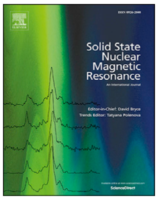
Solid State Nuclear Magnetic Resonance 91 (2018) 1–8

Contents lists available at ScienceDirect

Solid State Nuclear Magnetic Resonance

journal homepage: www.elsevier.com/locate/ssnmr



Separation of ^{2}H NMR spectra assisted by molecular dynamics in diamagnetic and paramagnetic solids

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ARTICLE INFO

Keywords:
Deuterium
CPMG
Hyperfine
Molecular motion
RAS

ABSTRACT

The relaxation-assisted separation method was applied to overlapping ^{2}H nuclear magnetic resonance (NMR) spectra of diamagnetic and paramagnetic solids to separate them based on the different relaxation behaviors caused by molecular motion. Carr–Purcell–Meiboom–Gill sequences for ^{2}H NMR were adopted to build two-dimensional data sets from one-dimensional NMR experiments. For diamagnetic α-glycine, the ^{2}H NMR spectrum collected at 198 K was separated into two components from static $–CD_2–$ and dynamic $–ND_3$. In addition, for the paramagnetic $Sm(NO_3)_3$·6D2O, the asymmetric ^{2}H NMR spectra obtained at 213 K due to the hyperfine coupling was also separated into two components, which corresponded to coordinated and crystal water molecules undergoing a 180° flip motion with different correlation times.

1. Introduction

Solid-state nuclear magnetic resonance (SSNMR) spectroscopy is a well-known and powerful tool for investigating the local structures of molecules. Deuterium (^{2}H, $I=1$) is a quadrupole nucleus with spin $I>1/2$, which exhibits a nuclear quadrupole moment that interacts with the electric field gradient (EFG) at the nucleus, resulting in a nuclear quadrupole interaction [1,2]. Thus, ^{2}H SSNMR spectra are governed by the first-order quadrupole interaction, which measures up to a few hundred kilohertz and, in powdered samples, these spectra exhibit a symmetric line shape produced by transitions of $|1\rangle \leftrightarrow |0\rangle$ and $|0\rangle \leftrightarrow |-1\rangle$ [3–6]. These spectra are particularly useful for the study of not only the static but also the dynamic properties of crystalline and non-crystalline solids, as the principal axis of an EFG tensor is almost parallel to the chemical bond direction in the majority of cases, and the spectral line shape can vary depending on the molecular motion taking place within a molecule [7–9]. In addition to one-dimensional (1D) spectra, a variety of ^{2}H SSNMR techniques also exist, such as magic-angle-spinning (MAS) [10,11] and off-MAS (OMAS) spectroscopy [12–14], two-dimensional (2D) exchange NMR [15–17], Carr–Purcell–Meiboom–Gill (CPMG) NMR [18–20], double quantum NMR [21,22], and spin–lattice relaxation studies (T_1) [23–26], which render it possible to monitor molecular dynamics with a correlation time ranging from nanoseconds to seconds.

Both diamagnetic and paramagnetic compounds can be target materials for ^{2}H SSNMR spectroscopy [4,27–38]. In the case of paramagnetic compounds, the spectra are frequently shifted or broadened by additional contributions from hyperfine interactions [39–42]. Indeed, experimentally, the conventional quadrupole echo (QE) sequence for static samples [43] fails to produce distortion-free spectra, due to these hyperfine interactions. As a potential solution to this issue, a π-pulse-inserted QE (PIQE) sequence [44], which refocuses the dephasing due to the quadrupole and paramagnetic shift interactions, has been developed to yield ^{2}H in-phase spectra of paramagnetic solids. An alternative sequence that discards unwanted coherence-transfer pathways [45] can also be used. The acquired ^{2}H spectra can then be analyzed by simulations upon considering the above interactions. In addition, for paramagnetic compounds, ^{2}H SSNMR methods have also been reported to measure separated pure-quadrupole and/or -shift spectra under MAS [46], OMAS [47], and static conditions [48–50].

When more than one chemically distinct ^{2}H site is present in the sample, the isotropic shift of each site can be resolved feasibly by MAS, while the envelope of the ^{2}H powder-pattern spectrum splits into spinning sideband (SSB) manifolds [51,52]. Information on molecular dynamics can again be obtained by spectral simulation of the SSB pattern upon considering the internal nuclear interactions that may be present [32–34]. Even for paramagnetic materials, separation of the isotropic-anisotropic interactions may be performed through use of the rotor synchronization of MAS by 2D SSNMR techniques, including 2D

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https://doi.org/10.1016/j.ssnmr.2018.03.001
Received 28 December 2017; Received in revised form 5 March 2018; Accepted 5 March 2018

one pulse [53], double quantum [54–56], and improved two- or three-pulse spectroscopy [57]. However, to examine the molecular dynamics, static conditions are advantageous to the MAS conditions, as it is easier to vary the temperature and calculate the theoretical NMR signals.

While 2D exchange spectroscopy is capable of analyzing molecular dynamics [3,58], chemically distinct sites can also be detected on the basis of differences in exchange, relaxation, or diffusion behavior. This can be achieved through the application of an inverse Laplace transformation (ILT) instead of a Fourier transformation (FT) [59–65]. In a 2D relaxation-assisted separation (RAS) method [62], NMR spectra for components with different relaxation rates are separated in the indirect dimension by ILT with respect to the interpulse delay of the relaxation experiments. Indeed, structural studies into cage compounds by ^{7}Li RAS NMR spectroscopy have been reported [66], and the RAS technique has been adapted to electron paramagnetic spectroscopy to separate overlapping hyperfine spectra [67]. Very recently, RAS has been conducted using the CPMG sequence for ultra-wideline NMR spectra based on differences in transverse relaxation times [68], where a non-negative Tikhonov fitting was efficiently used to process data in ILT.

In the present work, we explore the application of the RAS method for overlapping ^{2}H NMR static spectra, where the indirect dimension is employed to encode the transverse relaxation behavior caused by molecular dynamics. ^{2}H CPMG sequences [18,69] are applied to build 2D data sets, and the feasibility of the method is confirmed for diamagnetic and paramagnetic solids. In addition, ^{2}H RAS spectra are theoretically calculated to simulate the different relaxation behaviors caused by the molecular motions. Deuterated diamagnetic glycine and paramagnetic samarium nitrate hexahydrate ($\mathrm{Sm(NO_3)_3}\cdot$6H2O) are employed as model samples for the NMR measurements.

Under ambient conditions, glycine is known to crystallize in three different forms, namely α-, β-, and γ-glycine [70–72], where the polymorph stability decreases in the order: $\gamma > \alpha > \beta$. As such, the β form is metastable, and transforms spontaneously into either α- or γ-polymorphs, in which the glycine molecule exists in the zwitterionic form ($\mathrm{H_3N^+CH_2COO^-}$). Although the $\mathrm{–CH_2–}$ group is rigid, the $\mathrm{–NH_3}$ group can undergo rotational motion about the pseudo three-fold axis [73–81].

$\mathrm{Sm(NO_3)_3\cdot 6H_2O}$ forms a triclinic crystal with the $P\overline{1}$ space group at 298 K [82]. In this complex, four of the six water molecules are coordinated, while the other two constitute crystal water molecules [82–84]. As such, both the ^{2}H NMR spectrum and T_1 have been analyzed through superposition of the two components, which arise from the two different types of $\mathrm{H_2O}$ exhibiting different correlation times for the 180° flipping motion.

2. Experimental

Fully deuterated glycine (glycine-d_5, $\mathrm{D_3N^+CD_2COO^-}$, 98% atom D) was purchased from Cambridge Isotope Laboratories, Inc. and was used without further purification. Samarium nitrate hexadeuterate ($\mathrm{Sm(NO_3)_3\cdot 6D_2O}$) was prepared by repeated recrystallization of the corresponding hydrated compounds from heavy water. The obtained samples were ground into fine powders using a mortar and pestle.

^{2}H NMR spectra were measured at a magnetic field B_0 of 11.7 T using a JEOL ECA 500 spectrometer at $\nu_0 = 76.78$ MHz. For the purpose of the NMR measurements, a Varian-Chemagnetics 3.2 mmϕ HX MAS probe or a Doty 7 mmϕ MAS probe that was slightly modified to have a 2 mmϕ sample coil (the axis of which was set to be perpendicular to the B_0 field) was employed. The radio frequency (RF) field strength ν_1 was 100 kHz for the 3.2 mmϕ probe and 160 kHz for the modified 2 mmϕ probe. Experiments were performed at ambient temperature (295 K) or at a controlled low temperature, and the temperature at the sample position was calibrated using a type-T (copper-constantan) thermocouple. The ^{2}H NMR spectra were obtained under static conditions using the $\mathrm{D_2O}$ peak at 0 ppm as a reference. The QE-CPMG sequence shown in Fig. 1 (a) was executed by eight-step phase-cycling of $4\phi_1 \times 2\phi_2$. The durations of τ, τ_{d1}, τ_{d2}, and τ_{acq} were 80, 5, 10, and 160 μs, respectively. The PIQE-CPMG sequence shown in Fig. 1(b) was executed by 32-step phase-cycling of $4\phi_1 \times 2\phi_2 \times 2\phi_3 \times 2\phi_4$. The durations of τ_1, τ_2, τ_3, τ_{d1}, τ_{d2}, and τ_{acq} were 51, 55, 55, 4, 10, and 100 μs, respectively. The dwell time was 1 μs, and the number of CPMG iterations was $M = 32$. The recycle delay (RD) ranged from 1 to 200 s depending on the T_1 value of the spectral component. The CPMG signals of 384 and 1024 transients measured with the 3.2 mmϕ probe were accumulated for glycine-d_5 and $\mathrm{Sm(NO_3)_3\cdot 6D_2O}$, respectively. The 1D spectra of glycine-d_5 recorded with an average of 16 transients were measured using the QE sequence where $\tau = 18$ μs. Gaussian line broadenings of 4 and 8 kHz were applied before FT for glycine-d_5 and $\mathrm{Sm(NO_3)_3\cdot 6D_2O}$, respectively.

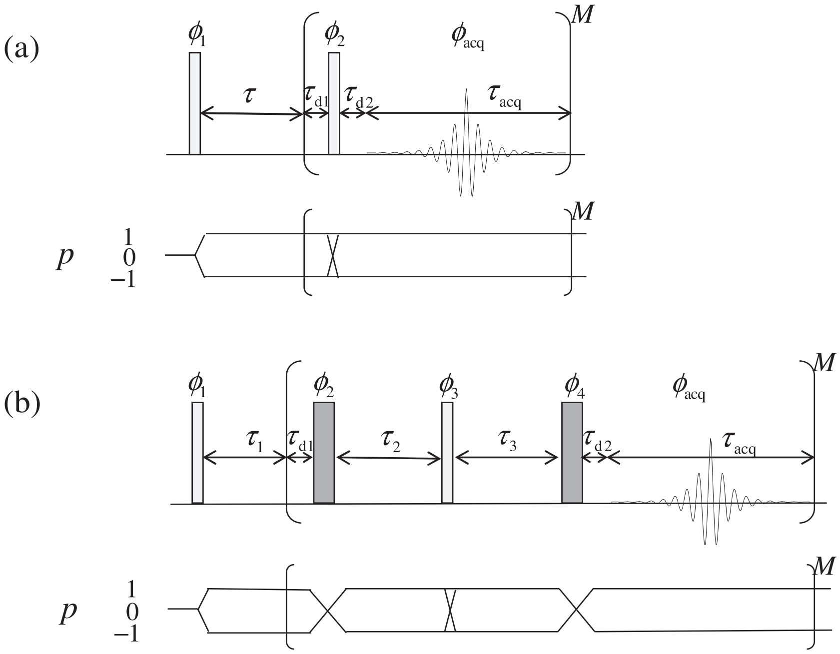

Fig. 1. The (a) QE-CPMG and (b) PIQE-CPMG pulse sequences employed in this work. The narrow and broad shaded areas indicate the 90° and 180° pulses, respectively. The desired coherence-pathway is shown below each sequence.