Journal of Magnetic Resonance 268 (2016) 18–24

Contents lists available at ScienceDirect

Journal of Magnetic Resonance

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

Site-resolved ^{2}H relaxation experiments in solid materials by global line-shape analysis of MAS NMR spectra

E.L. Lindh [a,b,c], P. Stilbs [a], I. Furó [a,*]

[a] Division of Applied Physical Chemistry, Department of Chemistry, KTH Royal Institute of Technology, SE-10044 Stockholm, Sweden
[b] Wallenberg Wood Science Center, KTH Royal Institute of Technology, SE-10044 Stockholm, Sweden
[c] Innventia AB, Box 5604, SE-114 86 Stockholm, Sweden

ARTICLE INFO

Article history:
Received 16 February 2016
Revised 20 April 2016
Accepted 25 April 2016
Available online 26 April 2016

Keywords:
Solid state NMR
Magic angle spinning
Spectral resolution
Chemical shift
Longitudinal relaxation

ABSTRACT

We investigate a way one can achieve good spectral resolution in ^{2}H MAS NMR experiments. The goal is to be able to distinguish between and study sites in various deuterated materials with small chemical shift dispersion. We show that the ^{2}H MAS NMR spectra recorded during a spin-relaxation experiment are amenable to spectral decomposition because of the different evolution of spectral components during the relaxation delay. We verify that the results are robust by global least-square fitting of the spectral series both under the assumption of specific line shapes and without such assumptions (COmponent-REsolved spectroscopy, CORE). In addition, we investigate the reliability of the developed protocol by analyzing spectra simulated with different combinations of spectral parameters. The performance is demonstrated in a model material of deuterated poly(methacrylic acid) that contains two ^{2}H spin populations with similar chemical shifts but different quadrupole splittings. In ^{2}H-exchanged cellulose containing two ^{2}H spin populations with very similar chemical shifts and quadrupole splittings, the method provides new site-selective information about the molecular dynamics.

1. Introduction

Deuterium (^{2}H) has several advantageous features that facilitate its use when investigating the molecular structure and dynamics of solid materials [1]. First, its dominant spin coupling is quadrupolar and therefore ^{2}H relaxation reports about the relatively simple re-orientational (as opposed to coupled translational/re-orientational dynamics relevant for ^{1}H–^{1}H dipole–dipole coupling) dynamics of the spin-bearing species. Hence, quadrupolar relaxation lends itself well to molecular dynamics (MD) simulations. Secondly, ^{2}H has a relatively weak quadrupole moment that presents no excessive methodological demands (such as radiofrequency power). Thirdly, ^{2}H has a low natural abundance yet suitable isotope-enriched compounds are readily available. Hence, ^{2}H NMR permits the user to assess site selectivity via, for example, exchange processes. This last feature has been extensively exploited in structural biochemistry [2].

A large number of studies have been performed using ^{2}H as the probe of molecular properties; examples are dynamics of silanol groups in silica gels and nanoparticles [3,4], methylene group dynamics [5], conformations of membrane lipids [6], dynamics of different segments of polymer chains [7], distinguishing among and characterizing polymorphs [8] and hydrogen-bond arrangements in various materials [9,10]. Typically, such studies concerned ^{2}H populations at respective single sites in which case the whole spectrum reported on the same phenomenon. In solid or semisolid materials with non-zero static quadrupole coupling [1], the spectral intensities at particular frequencies correspond to molecules/regions with particular orientation; hence, anisotropy of spin relaxation may lead to a more complex behavior [11], even with single sites.

In systems with more than one ^{2}H spin populations, the large static quadrupolar broadening of the signal components typically masks features arising from small chemical shift differences between the involved sites. Therefore, except cases where the sites exhibit large differences among their quadruple coupling constants [12], information may not be obtained on a site-resolved manner. For such systems, magic angle spinning (MAS) can yield beneficial line narrowing. Indeed, it has been demonstrated recently that on this way one may gain access to site-specific information to molecular dynamics in deuterated solids [13–15]. In addition, MAS also suppresses the effect of relaxation anisotropy on the obtained line shapes [16]. One should note that 2D quadrupole echo with suitable phase cycling is also capable to resolve sites with different chemical shifts [17,18].

* Corresponding author.
E-mail address: furo@kth.se (I. Furó).

http://dx.doi.org/10.1016/j.jmr.2016.04.014
1090-7807/

In previous work, spectral information for different sites was easily resolved since the involved chemical-shift differences were at least 2–3 ppm [15]. In many interesting systems, the available chemical shift range is much smaller; as one example, the total hydrogen chemical shift range for various carbohydrates like cellulose or starch or chitin but also simple sugars [19–22] is in the order of one ppm. In this paper we extend the ^{2}H MAS methodology to systems with small chemical-shift differences. With application to cellulose and related materials in mind, we show that ^{2}H MAS NMR in combination with relaxation experiments, here specifically inversion recovery, can resolve sites with small or insignificant chemical shift differences. The relaxation module in the experiment has a dual purpose: (i) for sites with different relaxation rates, it aids the separation of their respective signals and (ii) provides access to site-specific information about molecular dynamics. Here, we are going to emphasize the first of those features and demonstrate the performance of the methodology in both a model material and in deuterium-exchanged microcrystalline cellulose (MCC). In addition, we also show that the methodology is robust by comparing the results obtained by different spectral deconvolution techniques such as direct spectral fitting and COmponent-REsolved (CORE) analysis [23].

2. Experimental section

2.1. Materials

Deuterated poly(methacrylic acid)-d$_5$ from Polymer Source Inc. (PMAA-d5, see molecular structure in Fig. 1), ^2H_2O (99.9 atom% ^{2}H), microcrystalline cellulose (MCC, S5504) cotton linter powder, and tetramethylsilane (TMS, 99.95%) all from Sigma–Aldrich, were used as obtained. The MCC was placed for a couple of days in a vessel with a heavy-water atmosphere of relative humidity of roughly 91%, established by saturated solution of KNO_3 in ^2H_2O placed in the vessel. Under such conditions at room temperature, the accessible hydroxyl groups, such as the ones on the surface of cellulose fibrils [24], become deuterated. Finally, after having been deuterated the sample was dried in a vacuum oven operating at 50 °C; this treatment removed the water adsorbed on the MCC and left –O^{2}H groups of cellulose as the dominant source of the ^{2}H NMR signal.

2.2. NMR experiments

The ^{2}H NMR spectra were recorded on a Bruker Avance HD 500 MHz spectrometer operating at a resonance frequency of 76.1 MHz and equipped with a 4 mm MAS probe. The sample spinning speed was set to 10 kHz and the 90° pulse length to 3 μs. The spectra presented were recorded at 25 °C with 256 scans (PMAA) respectively 4096 scans (MCC) and recycle times of 1 s (PMAA) respectively 5 s (MCC). The relaxation delays for inversion recovery (IR) were roughly logarithmically arranged between 0.6 ms and 4.8 s. All spectra were phase-corrected according to the spectrum recorded with the longest relaxation delay; the results obtained in the PMAA sample are shown in Fig. 2 (see MCC spectra in Supplementary Material). The TMS signal, used for chemical-shift referencing, was recorded separately for TMS filled in a rotor and with a spinning speed of 10 kHz.

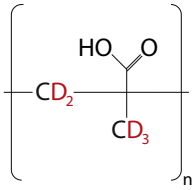

Fig. 1. The molecular structure of PMAA-d5.

2.3. Spectral analysis

The MAS-peak manifold contains a central peak and numerous spinning sidebands (SSB) that flank the central peak at set frequencies. Within all peaks, the relative position of signal from different sites is governed by the respective isotropic chemical shift. In our case, the central peak in the cellulose sample (see Supplementary Material) has clearly a contribution from a component that was absent in the cellulose sideband spectra. The corresponding total signal was negligible (we tentatively assign this mobile peak to remaining heavy water molecules), but because of this feature we excluded the cellulose central peak from the data-treatment procedure outlined below.

In the procedure termed "component fitting", we least-square fitted both to the central line and all SSBs (for PMAA-d5) or to the SSBs only (for MCC) a theoretical expression representing the sum of Lorentzian peaks as

$$S(\tau, \nu, n) = \sum_i I_{i,n}^{\infty}\left(1 - E_n e^{-\frac{\tau}{T_{1,i}}}\right)\frac{T_{2,i}}{1 + \left(2\pi T_{2,i}(\nu - \nu_i - n\nu_{rot})\right)^2} \quad (1)$$

where τ is the IR delay time, ν the spectral frequency, and n the SSB index while E_n is the inversion efficiency (<2, because of limited radiofrequency power) at frequencies $n\nu_{rot}$ relative to the central frequency. In addition, $I_{i,n}^{\infty}$ is the thermal equilibrium intensity of a spectral component i in a given SSB [25] that is also characterized by a chemical shift defined as $\delta_i = (\nu_i - \nu^0)/\nu^0$, where ν_i and ν^0 the is the resonance frequencies of the spectral component i and TMS, respectively. Finally, $T_{1,i}$ (strictly speaking, T_{1z} that characterizes the relaxation of Zeeman order) and $T_{2,i}$ are the component-specific longitudinal and transverse spin relaxation times, respectively. The relaxation parameters are global because all SSBs are signal averages over the whole sample [26]. For both samples, the fits performed with the Levenberg–Marquardt algorithm with two spin populations (an assumption for the cellulose sample); the results obtained are presented in Table 1.

In contrast to the procedure above with set Lorentzian line shapes, the other procedure used for analyzing the spectral manifold exploits the CORE [23] analysis (software available at https://www.kth.se/en/che/divisions/tfk/staff/emeriti/stilbs/core-data-processing-downloads-1.193738). The CORE processing is also a global least-square fitting of the spectral data, but without an assumed line shape. Instead, the CORE analysis assumes that the spectrum consists a set number of components and each component exhibits a variation by a specific mathematical function along an extra experimental variable, in our case the evolution time in the inversion recovery experiment. This translates into having fitted the variation of the spectral intensity with the evolution time at each frequency point by a two-exponential function (that is, one assumes two components) where the time constants were global as

$$S(\tau, \nu, n) = \sum_i I_{i,n,\nu}^{\infty}\left(1 - Ee^{-\frac{\tau}{T_{1,i}}}\right) \quad (2)$$

In other words, for each frequency point it is the relative contribution of the two involved relaxation procedures that is allowed to vary. In CORE, we simply approximate the same inversion efficiency for the whole spectral range.

The band shapes resulting from the CORE analysis are illustrated in Supplementary Material. Because the CORE analysis does not assume any particular band shape, the chemical shift is