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Double-quantum filtered ^{1}H MAS NMR spectra

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Abstract

It is shown that straightforward double-quantum filtered ^{1}H MAS NMR experiments yield spectral lineshapes that permit to estimate the minimum number of ^{1}H spins in a cluster. The approach may offer an alternative to multiple-quantum experiments for the characterisation of ^{1}H spin clusters of moderate size. The duration of the double-quantum excitation period has to be chosen suitably, it is necessary to find a practical compromise between optimum double-quantum filtration efficiency and optimum information content of the spectral lineshapes. Some ^{1}H MAS NMR experiments on partially deuterated maleic acid are reported as well as numerical simulations.
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Keywords: MAS NMR; Rotational resonance; Double-quantum filtration; Numerical simulations; ^{1}H spin systems

1. Introduction

Of all NMR active spin-$\frac{1}{2}$ isotopes commonly used ^{1}H has the largest gyromagnetic ratio and is nearly 100 percent naturally abundant. In principle, these properties lead to high sensitivity and render spin systems involving ^{1}H spins suitable for probing relatively large internuclear distances by measurements based on the exploitation of direct dipolar coupling. In solid-state NMR, however, these promising properties are usually counterbalanced by less desirable side effects such as lack of spectral resolution and and/or complications caused by very large spin systems unless one is confronted with samples in which dilute ^{1}H spin systems occur naturally, as is sometimes found in inorganic solid materials. Generally speaking, however, conventional ^{1}H MAS NMR spectra are not sufficiently informative

and many efforts have been devoted to improve spectral resolution by the application of multiple pulse sequence under MAS conditions [1–8]. Another area of activity in ^{1}H solid-state NMR has been the characterisation of the cluster size of networks of coupled spins [9,10]. Such spin-counting experiments usually involve the excitation of multiple coherences and provide an estimate of the minimum number of coupled spins in a cluster. A difficulty with this approach is a rapidly decaying signal amplitude when recording the signatures of high(er) order coherences. More recently, patterns of spinning sidebands in ^{1}H MAS NMR spectra have been exploited to determine internuclear ^{1}H–^{1}H distances and thus to characterise the topologies in supramolecular solid materials [11,12].

Here we will investigate how spectral ^{1}H MAS NMR lineshapes under conditions of double-quantum filtration (DQF) reflect the size of ^{1}H spin clusters. We use a straightforward COSY-like pulse sequence [13]. Our model compound is maleic acid in which all acid protons have been replaced by deuterium (Fig. 1), **1**, and will consider the ^{1}H spin system of the olefinic protons in **1**. The single-crystal structure of maleic acid is known

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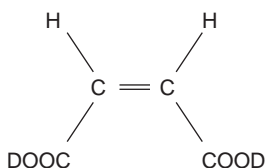*E-mail addresses:* a.sebald@exeter.ac.uk, angelika.sebald@uni-bayreuth.de (A. Sebald).

Fig. 1. Schematic representation of the molecular structure of partially deuterated maleic acid, **1**.

[14,15] and also the ^{1}H spin system in solid maleic acid has been fully characterised [16,17].

2. Experimental

2.1. Preparation of samples

The starting materials, D_2O, maleic acid anhydride (Aldrich Chemicals) and fully deuterated maleic acid anhydride (Isotec Inc.), are commercially available. Fully deuterated maleic acid and maleic acid with only the acid protons replaced by deuterium, **1**, are obtained by dissolving deuterated maleic acid anhydride or maleic acid anhydride, respectively, in D_2O at ambient conditions. Deuterium-diluted versions of **1** were obtained by co-crystallization of **1** and fully deuterated maleic acid in a 1:3 ($\mathbf{1}_{1:3}$) molar ratio. After isolation of the crude material from D_2O by evaporation, the sample was recrystallised from acetone as described in the literature [14,15].

2.2. ^{1}H MAS NMR

^{1}H MAS NMR spectra were recorded on Bruker MSL 300 and Avance 600 NMR spectrometers using standard 4 mm MAS probes. The corresponding ^{1}H Larmor frequencies, $\omega_0/2\pi$ are -300.1 and -600.1 MHz. ^{1}H shielding is quoted with respect to $\omega_{iso}^{CS} = 0$ ppm for the ^{1}H resonance of SiMe$_4$. MAS frequencies were $\omega_r/2\pi = 10$ kHz and were actively controlled to within ± 2 Hz. ^{1}H $\pi/2$ pulse durations were 2.7 µs, recycle delays were 600 s. The straightforward COSY-like pulse sequence $\pi/2_{(x)}$-τ-$\pi/2_{(y)}$-$\varDelta$ -$\pi/2_{(\phi)}$-τ-acquisition [13] with 16-step phase cycling according to standard procedures [18] was used to record ^{1}H DQF MAS NMR spectra of **1** and $\mathbf{1}_{1:3}$. The duration of $\varDelta$ was set to 3 µs.

2.3. Definitions, notation, and numerical methods

Shielding notation [19] is used throughout. Homonuclear J coupling $^3J(^1H,^1H)$ is negligible for the spin system in **1**, for the interactions $\lambda = CS$ (chemical shielding) and $\lambda = D$ (direct dipolar coupling), the isotropic part ω_{iso}^{λ}, the anisotropy ω_{aniso}^{λ}, and the asymmetry parameter η^{λ} relate to the principal elements of the interaction tensor ω^{λ} as follows [20]: $\omega_{iso}^{\lambda} = (\omega_{xx}^{\lambda} + \omega_{yy}^{\lambda} + \omega_{zz}^{\lambda})/3$, $\omega_{aniso}^{\lambda} = \omega_{zz}^{\lambda} - \omega_{iso}^{\lambda}$, and $\eta^{\lambda} = (\omega_{yy}^{\lambda} - \omega_{xx}^{\lambda})/\omega_{aniso}^{\lambda}$ with $|\omega_{zz}^{\lambda} - \omega_{iso}^{\lambda}| \geqslant |\omega_{xx}^{\lambda} - \omega_{iso}^{\lambda}| \geqslant |\omega_{yy}^{\lambda} - \omega_{iso}^{\lambda}|$. For direct dipolar coupling $\eta^D = \omega_{iso}^D = 0$ and $\omega_{aniso}^{D_{ij}} = b_{ij} = -\mu_0\gamma_i\gamma_j\hbar/(4\pi r_{ij}^3)$, where γ_i, γ_j denote gyromagnetic ratios and r_{ij} is the internuclear distance between spins S_i, S_j. The Euler angles $\Omega_{IJ} = \{\alpha_{IJ}, \beta_{IJ}, \gamma_{IJ}\}$ [21] relate axis system I to axis system J, where I, J denote P (principal axis system, PAS), C (crystal axis system, CAS), R (rotor axis system, RAS), or L (laboratory axis system). For simulations of ^{1}H DQF MAS NMR spectra of **1** and $\mathbf{1}_{1:3}$ it is convenient to define the PAS of the intramolecular ^{1}H$_i$–^{1}H$_j$ dipolar coupling tensor as the CAS, $\Omega_{PC}^{D_{ij}} = \{0, 0, 0\}$. Our procedures for numerically exact spectral lineshape simulations and iterative fitting are fully described and discussed in detail elsewhere [22–24]. In general, these numerical procedures employ the REPULSION [25] schemes for the calculation of powder averages, implement some of the routines of the GAMMA package [26], use, where possible, the γ-COMPUTE approach [27–30], and take advantage of accelerated multi-processor computations in calculating powder averages [24]. Error minimisations employ routines from the MINUIT package [31].

3. Results and discussion

The solid-state structure of maleic acid is illustrated in Fig. 2. The acid hydrogen atoms form strong intra- and intermolecular hydrogen bonds, leading to a layered structure of ribbons of linked maleic acid molecules. The distance between the two olefinic protons in a molecule is 224 pm, corresponding to a dipolar coupling constant $b_{ij}/2\pi = -10,686$ Hz between these two protons. There are several further olefinic protons in neighbouring molecules in spatial proximity to each of these two olefinic protons, for instance within 322, 337, 410, and 583 pm. Accordingly, even in our sample **1** with all acidic protons replaced by deuterium atoms, the question arises whether the two olefinic protons per maleic acid molecule represent isolated ^{1}H spin pairs in solid **1**. Not only the crystal structure of maleic acid is known, also the ^{1}H spin system in solid maleic acid has been characterised by means of ^{1}H single-crystal NMR [16,17] and by ^{1}H multiple pulse experiments [1]. The ^{1}H chemical shielding parameters of the two olefinic protons are given in Table 1. With a difference in isotropic ^{1}H chemical shielding $\omega_{iso}^{\varDelta} = 0.2$ ppm and ^{1}H chemical shielding anisotropies $\omega_{aniso}^{CS_1} = \omega_{aniso}^{CS_2} = -3.0$ ppm, these two ^{1}H spins thus constitute a (more or less isolated) spin pair near the $n = 0$ rotational resonance (R^2) condition [32,33], with direct dipolar coupling being the largest anisotropic interaction