



ELSEVIER

Contents lists available at ScienceDirect

Solid State Nuclear Magnetic Resonance

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

Simulating spin dynamics in organic solids under heteronuclear decoupling

Ilya Frantsuzov^{a,1}, Matthias Ernst^b, Steven P. Brown^c, Paul Hodgkinson^{a,*}^a Department of Chemistry, Durham University, South Road, Durham DH1 3LE, United Kingdom^b Laboratory of Physical Chemistry, ETH Zürich, Wolfgang-Pauli-Strasse 10, 8093 Zürich, Switzerland^c Department of Physics, University of Warwick, Coventry CV4 7AL, United Kingdom

ARTICLE INFO

Article history:

Received 9 December 2014

Received in revised form

14 April 2015

Available online 15 May 2015

Keywords:

Decoupling

Magic-angle spinning

Numerical simulation

Solid-state NMR

ABSTRACT

Although considerable progress has been made in simulating the dynamics of multiple coupled nuclear spins, predicting the evolution of nuclear magnetisation in the presence of radio-frequency decoupling remains challenging. We use exact numerical simulations of the spin dynamics under simultaneous magic-angle spinning and RF decoupling to determine the extent to which numerical simulations can be used to predict the experimental performance of heteronuclear decoupling for the CW, TPPM and XiX sequences, using the methylene group of glycine as a model system. The signal decay times are shown to be strongly dependent on the largest spin order simulated. Unexpectedly large differences are observed between the dynamics with and without spin echoes. Qualitative trends are well reproduced by modestly sized spin system simulations, and the effects of finite spin-system size can, in favourable cases, be mitigated by extrapolation. Quantitative prediction of the behaviour in complex parameter spaces is found, however, to be very challenging, suggesting that there are significant limits to the role of numerical simulations in RF decoupling problems, even when specialist techniques, such as state-space restriction, are used.

© 2015 The Authors. Published by Elsevier Inc. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Effective decoupling of the ¹H nuclear spins is essential for achieving high resolution ¹³C NMR spectra from typical organic molecules. Such heteronuclear decoupling is particularly difficult in the solid state due to the strong dipolar interactions between the different magnetic nuclei, which are not averaged out by molecular motion as they are in the solution state. While considerable progress has been made in developing approaches to decoupling and understanding how they work [1,2], there is not a comprehensive theory that allows decoupling performance to be predicted.

In principle, exact numerical simulation of nuclear spin systems [3–5] ought to allow the prediction of decoupling performance. The multi-spin nature of the dipolar-coupled network in solid systems is not necessarily an obstacle; we have, for example, shown that simulations on modest numbers (9–10) of spins are sufficient to predict exactly the ¹H spin dynamics under magic-

angle spinning (MAS) [6,7], and numerical solutions have proved invaluable in understanding how decoupling sequences work [8–15]. We show here, however, that predicting the performance of decoupling sequences, particularly in regions of interest around optimal conditions, would require very large numbers of spins to be included to obtain quantitative agreement with experiment. This number is larger than the practical limit for exact simulation, which is typically less than 12 spins (although this can be extended using artificial model geometries with additional symmetry [16]).

Recently a number of groups have demonstrated simulations of much larger numbers of coupled nuclear spins by restricting the size of the state space used for the simulations [17–21]. Different researchers have used slightly different methods for restricting the evolution of the spin system to coherences below a certain order, but it is argued that the success of such calculations relies on the populations of higher spin orders (i.e. the number of correlated spins involved in a coherence) remaining relatively small [22]. This is clearly the case in solution-state NMR, where high spin order coherences relax relatively quickly, and some promising results have also been obtained for simulations of ¹H spin-diffusion in powder samples under MAS [23–25]. It is not obvious, however, that state-space restriction is generally appropriate in the solid

* Corresponding author.

E-mail address: paul.hodgkinson@durham.ac.uk (P. Hodgkinson).¹ Current address: Department of Chemistry, Kansas State University, Manhattan, KS 66506-0401, USA.

state, where very high spin orders can be observed amongst ^1H nuclei [26–28], and so we also investigate the role of higher spin orders in heteronuclear decoupling.

2. Methods

The decoupling performance is quantified experimentally by measuring the T_2' decay constant of the ^{13}C magnetisation, that is, the time constant for the decay of ^{13}C magnetisation where a 180° pulse is applied on ^{13}C at the mid-point of the decay period [29,30]. The spin-echo refocuses decay due to inhomogeneous effects, such as B_0 inhomogeneity and magnetic susceptibility broadenings [31]. As a result, T_2' is much more sensitive to decoupling quality than T_2^* values obtained from measured linewidths; linewidths are often not particularly sensitive to changes in decoupling quality [30,32]. T_2' values continue to increase as the RF decoupling power is increased, tending towards the fundamental limit set by true T_2 relaxation [33], well after the limiting linewidth is observed. We use T_2^C here to refer to the *coherent* decay of ^{13}C magnetisation in the absence of a spin-echo, to distinguish it from true (incoherent) T_2 relaxation and the overall time constant for magnetisation decay, T_2^* , which includes inhomogeneous contributions associated with the sample and any instrumental factors. The mechanisms for the decay of ^{13}C magnetisation are different for T_2^C and T_2 , but they both result in loss of the original coherence which cannot be readily refocused. Decoherence is used here to refer to this magnetisation decay. In contrast to T_2' and T_2^* , T_2^C is not directly measurable, while both T_2' and T_2^C can, in principle, be directly observed in numerical simulations of magnetisation decay with or without a spin echo. It is important to note, however, that all the T_2 values used here are phenomenological quantities obtained by fitting experimental or simulated magnetisation decays to exponential functions. The absence of molecular tumbling in the solid state means that the magnetisation decays will generally be orientation dependent, and their powdered-averaged sum may not fit well to a single exponential.

2.1. Experimental

Experimental measurements of T_2' were performed on a polycrystalline sample of glycine- $2\text{-}^{13}\text{C},^{15}\text{N}$ (99% ^{13}C , 98% ^{15}N) purchased from CortecNet. The sample was confirmed to be α -glycine based on the ^{13}C carbonyl peak at 176.5 ppm, which is sensitive to polymorphic changes [34,35]. As expected from the stability range of this form, 5–500 K [36], no transformations were observed during experiments. For measurements of TPPM [37] and CW performance, the sample was packed into a Bruker 2.5 mm o.d. MAS rotor and data obtained at a ^1H Larmor frequency of $\nu_0^{\text{H}} = 600$ MHz and MAS frequency of $\nu_r = 12$ kHz on a Bruker Avance II+ console. The XiX [32,63] measurements were performed at $\nu_0^{\text{H}} = 500$ MHz on an InfinityPlus console using a Bruker 1.3 mm o.d. rotor spinning at $\nu_r = 25$ kHz. ^{13}C magnetisation was created using cross-polarisation ramped on the ^1H RF power using either the centreband matching condition with a contact time of 1.2 ms, for $\nu_r = 12$ kHz, or the $\nu_1^{\text{H}} - \nu_1^{\text{C}} = \nu_r$ sideband with a contact time of 2.7 ms for $\nu_r = 25$ kHz. These represent typical conditions for acquiring ^{13}C spectra of natural abundance samples under TPPM and XiX decoupling. The ^{13}C magnetisation was then measured after a spin-echo period, $\tau\text{-}\pi\text{-}\tau$, during which either CW, TPPM or XiX proton decoupling was applied, as shown in Fig. 1. For both the CW and TPPM experiments, the acquisition and recycle delay times were 30.77 ms and 4 s respectively, while under XiX decoupling they were 25.6 ms and 5 s respectively. Note that the TPPM pulse width, τ_p , is generally parameterised below in terms of the corresponding nutation angle, $\theta = \tau_p \nu_1 360^\circ$.

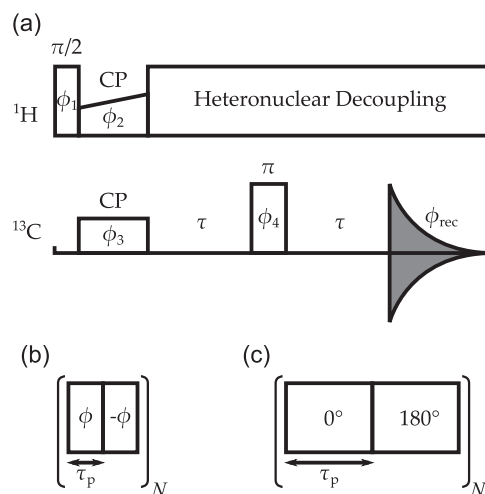


Fig. 1. (a) Spin-echo pulse sequence using the same decoupling during the 2τ and acquisition periods. Phases (combining spin-temperature inversion and EXOR-CYCLE): $\phi_1=0^\circ, 180^\circ, 0^\circ, 180^\circ$; $\phi_2=\phi_3=90^\circ$; $\phi_4=0^\circ, 0^\circ, 90^\circ, 90^\circ$; $\phi_{\text{rec}}=90^\circ, 270^\circ, 270^\circ, 90^\circ$. (b) TPPM decoupling element, with phase excursion ϕ and pulse width τ_p . (c) XiX decoupling element.

The same ^1H decoupling was used in both spin-echo and acquisition periods. Although using a fixed decoupling sequence for acquisition would lead to reasonably consistent line-shapes in the acquired spectra, significant mismatches between spin-echo and acquisition decoupling were observed to distort fitted T_2' values via the orientation dependence of decoupling efficiency [38]; magnetisation that has been preserved by efficient decoupling during the spin-echo period may rapidly decohere under the acquisition decoupling, leading to an underestimate of intensity at longer spin-echo times and hence an underestimation of T_2' . The variation of the orientation dependence of T_2' with decoupling parameters is illustrated in the [Supplementary Information, Fig. S2](#). The ^1H decoupling nutation rate, ν_1 , was measured using the same sequence with a zero-length spin-echo period, incrementing the initial ^1H pulse width to acquire a ^1H nutation spectrum and taking the peak position as the nominal ν_1 .

Full decay curves were obtained at selected decoupling conditions by incrementing the evolution time, 2τ , linearly in 41 steps from zero to approximately twice the maximum expected T_2' . The free induction decays were zero-filled and Fourier transformed (without apodisation) using matNMR [39]. The decay of the methylene ^{13}C peak height as a function of 2τ was fitted to a decaying exponential to obtain T_2' using MATLAB[®] [40]. Where detailed parameter maps as a function of the parameters of a decoupling sequence were acquired, T_2' values were inferred from a pair of experiments at $2\tau=0$ and $2\tau \approx T_{2,\text{max}}'$, assuming simple exponential decay of the peak height between these points. Discrepancies between the T_2' values obtained by this quick, but approximate, approach and those obtained from full decays were reduced by re-scaling the approximate values using a quadratic function fitted to approximate vs. accurate T_2' values at between three and five characteristic points in the parameter space. As illustrated in the SI, Fig. S1, this rescaling resulted in relatively modest changes in the T_2' values (up to 20% at maxima and 30% around minima), and allowed good T_2' estimates to be measured efficiently for a wide parameter space.

2.2. Numerical simulations

To explore how the spin dynamics change as a function of spin-system size, spin-systems containing different numbers of protons at increasing distance from a selected methylene C atom were created, based on the room temperature neutron structure of α -

Download English Version:

<https://daneshyari.com/en/article/5420272>

Download Persian Version:

<https://daneshyari.com/article/5420272>

[Daneshyari.com](https://daneshyari.com)