



The influence of the molecular system on the performance of heteronuclear decoupling in solid-state NMR

Guillaume Gerbaud^{a,1}, Stefano Caldarelli^{a,*}, Fabio Ziarelli^b, Stéphane Gastaldi^c

^a Aix Marseille Université, ISM2 UMR 6263, Campus de Saint Jérôme, Service 511 F-13013 Marseille, France

^b Spectropole, Fédération de Sciences Chimique de Marseille Université d'Aix Marseille III, Site de Saint Jérôme Service 511, France

^c Equipe de Chimie Moléculaire Organique, LCP UMR 6264, Boite 562, Université Paul Cézanne, Aix-Marseille III, Faculté des Sciences St Jérôme, Avenue Escadrille Normandie-Niemen, 13397 Marseille Cedex 20, France

ARTICLE INFO

Article history:

Received 3 December 2010

Revised 9 February 2011

Available online 17 February 2011

Keywords:

Solid-state NMR

Heteronuclear decoupling

CPMAS

TPPM

GTn

ABSTRACT

The intensity of the carbon signal in a CPMAS experiment has been measured for two CH and three CH₂ moieties in four test molecules under different phase-modulated proton decoupling conditions and as a function of the spinning rate. The proton decoupling schemes investigated were the golden standard TPPM and three of the GTn family.

Aim of this analysis was to better describe experimentally the impact and limitations of phase-modulated decoupling.

Sizeable differences in the response to decoupling were observed in otherwise chemically identical molecular fragments, such as the CHCH₂ found in tyrosine, phenyl-succinic acid or 9-Anthrylmethyl-malonate, probably due to differences in spin-diffusion rates.

In keeping with known facts, the efficiency of the decoupling was observed to decrease with the MAS rate, but with somewhat different trends for the tested systems.

© 2011 Elsevier Inc. All rights reserved.

1. Introduction

The impressive technological advances experienced by NMR of solids may induce the vision of a natural convergence of this domain of applications with its relative field, solution-state NMR. In fact, methods from this latter are becoming available for solids while concepts arisen in the solid-state area, such as the use of the anisotropy of the magnetic interactions, are becoming widespread tools in solution studies. However, one should not underestimate the specificities of organic solids, some of which are not yet dominated by the current status of technology. The main factor in cause here is the intimate structure of the proton dipolar coupled network, generically dubbed the proton “bath” in loose analogy with a thermostat. The size and the characteristics of this latter depend on the molecular shape, as well as on the crystal packing. In fact, the proton–proton dipolar interaction dies out relatively slowly, covering a few bond distances [1]. Therefore, an extended number of actor spins are to be taken into account for the description of an organic material. The frequency spectrum of the resulting Hamiltonian is a particularly intertwined combination of contributions from the original coupled spins.

This situation is usually described as a “homogeneous” interaction, a term that often translates into a reluctance to be manipulated by RF pulses, due to the facility of exchange of spin polarization terms among the protons (fast spin–diffusion regime) and to the increased rotary resonance conditions available in the overall Hamiltonian. A first consequence arising from this situation is the difficulty to achieve high-resolution proton spectra. Consequently, diluted nuclei are still a major target for NMR in solids.

Thus, proton heteronuclear decoupling remains a crucial and delicate step in NMR spectroscopy of organic solids towards optimum spectral sensitivity and resolution.

To this respect, the influence of the proton bath at the level of heteronuclear decoupling is particularly intriguing. On one hand the proton–proton interaction lends a helpful self-decoupling effect [2], while on the other hand it still hampers a “clean” manipulation of the proton spins by RF pulses. Also, the presence of interferences with the averaging from the proton CSA has been proposed from the very early times [3] to be a further major source of trouble for decoupling. As a consequence, the discovery of effective ways of performing proton decoupling in solids has lagged behind the achievements of solution-state NMR, where the question is basically solved.

A substantial leap forward to this respect has been the introduction of phase/amplitude modulated irradiation techniques [4]. The proposed methods are based on angle or amplitude modulation of

* Corresponding author.

E-mail address: s.caldarelli@univ-cezanne.fr (S. Caldarelli).

¹ Present address: BIP CNRS – UPR 9036, 31, Chemin Joseph Aiguier 13402, Marseille Cedex 20, France.

the applied decoupling field [5–18] on symmetry rules [19], or just on experimental searches directly on the spectrometer [20,21].

Although generally convenient and up to the task, these methods have been shown to suffer from the need of parametric optimization for best performances. Hence, a constant effort is observed to produce new experimental decoupling procedures increasingly robust [15,17,22]. This outstanding experimental progress has been accompanied by the search of a theoretical description suitable to reproduce the key aspects of the phase-modulated decoupling, namely their sensitivity (or lack of) to the periodicity and amplitude of the modulation, or to the influence of the irradiation offset.

Theoretical analysis of the behavior of multiparametric decoupling sequences have been performed by several authors [23–27].

The improvement of modulated RF pulses over continuous-wave (CW) irradiation is apparent in numerical simulation, and the positive role of a sizeable proton spin-diffusion was highlighted from the early studies [24]. Multimodal Floquet analysis was applied to try to decode the interplay of the three averaging fields (MAS, the decoupling RF and its modulation). This kind of analysis reveals and quantifies well the destructive interferences of the three fields, showing that the most negative effects on decoupling come from resonances between the RF irradiation and its modulation [23].

Of particular interest, the dominance of the proton CSA Hamiltonian as the limiting factor in determining a largely non-uniform parametric response has been highlighted [23].

The challenge for the experimentalist is to determine whether a single set of parameters can be chosen for a specific experiment to provide acceptable improvement over non-modulated (CW) decoupling.

In fact, most calculations and demonstrations of decoupling methods concern model systems, the current consensus being that the decoupling behavior is mostly influenced by small molecular motifs, typically the immediate surrounding of the target nucleus, while the influence of the extended proton homonuclear couplings (spin-diffusion, spin-bath) has not been assessed exactly.

In fact, the structure of the internal Hamiltonians, as well as their degree of interference, it is likely to be at variations for any combination of spin system, MAS and decoupling conditions, which may have an impact on the optimal parametrization of the decoupling. It is noteworthy that this kind of reasoning led to the development of experimentally optimized continuously modulated decoupling pulses [15,21].

In this context, the reaction of a given molecular site to decoupling is believed to be determined by its multiplicity (thus different for CH₂, CH or CH₃). The role of the surrounding proton spins is usually summarized to a single parameter, for instance the “strength” of the spin bath or the spin-diffusion rate constant. This approximation does provide some agreement with the experimental results, but it does not yield a satisfactory explanation of the spin dynamics, especially because it is not easy to evaluate *a priori* the proton bath parameters for a solid [24].

One important issue for the experimentalist is to know how much effort should be put in the parametric optimization, a task that is particularly demanding for sample with an intrinsic low signal to noise. To this respect, the crucial point is to determine if it is possible to transfer safely a parameter set optimized for a test sample to the case of interest. As a corollary, it is important to assess the intensity gain introduced by the use of phase-modulated decoupling.

In this work we characterized the heteronuclear decoupling behavior in a few molecular fragment, some of which serve as typical NMR standards for setting up the decoupling conditions and the rest of which bear similar chemical functions, all carrying CH₂ or CH groups. We submitted this ensemble of compounds to

a parametric comparison of the decoupling performance of some phase-modulated pulse. The methods tested were the widespread forerunner TPPM and Gaussian-envelope cosine modulations (GTn), which have shown to be more robust than TPPM with respect to the parametric response [15]. The parameter explored were the MAS frequency, the irradiation offset and the ones describing the phase modulation.

2. Materials and methods

All experiments were performed on a Bruker DRX-400 spectrometer at a B₀ field of 9.4 T in a commercial Bruker probehead using 2.5 mm rotors. Cross-polarization experiments were performed with a variable amplitude contact time [28]. The decoupling field was set at 96.0 kHz. All the decoupling pulses were written in a unique shaped pulse, of a duration corresponding to eight modulation periods, in order to minimize the effect of possible deformation of the shape pulse repetition in the pulse timing. Line intensities were measured directly with the spectrometer software. The influence of the CP on the line intensities was taken into account by using a calibration single-pulse carbon experiment for each molecule at any given MAS frequency. The value obtained this way was normalized to the number of carbon-13 moles, deduced by weighing the sample. We arbitrarily set to 1 the value for glycine recorded under MAS at 10 kHz (on-resonance irradiation).

2.1. Samples

The test molecules, as well as the three-letter code used for reference in the text, are depicted in Fig. 1.

Glycine and L-tyrosine hydrochloride salt were obtained from commercial sources, and used as such.

9-Anthrylmethyl-2-¹³C-malonate was synthesized according to Ref. [29], using 99.9% ¹³C-enriched diethylmalonate.

Phenyl-succinic acid, selectively ¹³C labeled at the CH₂ position, was synthesized according to the procedure described in Appendix A. Both labeled compounds were confirmed to be more than 99% enriched by solution-state NMR.

2.2. Decoupling pulse sequences

The sequences used in this work belong to the family of periodically phase-modulated pulses, which can be described in terms of

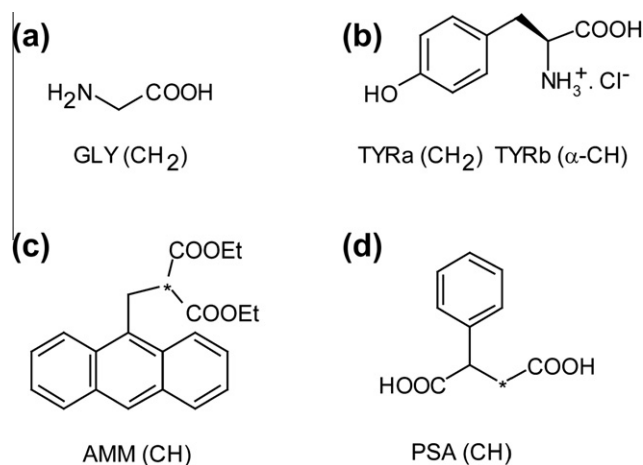


Fig. 1. The samples used in this work, together with the acronyms used throughout the text. (a) Glycine. (b) L-tyrosine hydrochloride. (c) Anthrylmethyl 2-¹³C malonate. (d) 2-Phenyl-succinic 3-¹³C acid. The analyzed carbons are the CH and CH₂ elements, indicate by the asterisks for the ambiguous cases.

Download English Version:

<https://daneshyari.com/en/article/5406340>

Download Persian Version:

<https://daneshyari.com/article/5406340>

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