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Extracting intramolecular dynamics informations from conventional and remote protons CP/MAS NMR build-up curves

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An ^{13}C Solid-State Nuclear Magnetic Resonance Spectroscopy (SS-NMR) procedure for extracting structural and dynamical information in organic molecules is introduced. The method combines numerical simulations with two kinds of NMR experiments namely conventional CP-MAS (cross-polarisation magic angle spinning) and remote protons CP-MAS. The former is mostly sensitive to dipolar couplings between directly bonded ^{13}C-^{1}H nuclei, whereas the latter prepares a state of non-uniform polarization, where these particular spin pairs are de-polarized prior to recording the CP buildup curve. This curve is then expected to quantify the polarization transfer from remote protons only. The method is demonstrated for the specific NH_3 group of L-alanine and it shows that the remote protons polarization transfer curve can be used in combination with the conventional CP/MAS curve to get additional structural and dynamical information in molecular systems with relevance for biology and advanced materials.

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1. Introduction

The combination of cross-polarization (CP) [1] with high-power proton decoupling and magic angle spinning (MAS) [2] is routinely used for increasing sensitivity in high-resolution solid-state nuclear magnetic resonance (SS-NMR) spectroscopy of low-γ nuclear spins (^{13}C, ^{15}N) in organic materials. CP is performed under simultaneous irradiation with strong resonant *rf* fields of ^{1}H and low-γ nuclei (designated here by the *I* and *S* spin, respectively). An optimum polarization transfer between the two spin species is attained at exact Hartmann-Hahn matching [1,3].

The transfer process has been described using thermodynamic [4,5] as well as quantum-mechanical treatments [6-10]. The thermodynamic picture is usually applied to systems with strong *I-I* couplings, where the evolution of the transferred polarization with the CP contact time can be described through a single exponential function. By contrast, when the dipolar coupling between directly bonded *I-S* spins exceeds the *I-I* couplings, as in the case of protonated ^{13}C, the CP curve evolves in a damped oscillatory fashion, giving rise to the so-called transient oscillations [11]. This phenomenon is considered a clear indication of the coherent nature of the polarization transfer process, and it has been extensively used for extracting structural and dynamical information in organic solids, liquid crystals, and oriented membrane proteins. Most of the applications rely on measuring heteronuclear dipolar couplings with ^{13}C chemical site resolution by means of 2D separated local field (SLF) spectroscopy [12]. For every ^{13}C chemically distinct site, the dipolar spectra measured through 2D SLF spectroscopy are dominated by the strongest C-H couplings, with smaller effects coming also from more distant protons. In principle, each individual contribution can be separated according to its ^{1}H chemical shift value by means of 3D LG-CP HETCOR [13, 14-15]. However, this is not a generally valid procedure due to the strong dependence on the achievable proton resolution. In this work we use a simplified scheme, based on CPPI [16] sequence, for separating distinct contributions to the CP/MAS curve (thus, implicitly, to the C-H dipolar spectrum), which relies on the large difference in polarization dynamics between directly bonded, and remote ^{1}H spins, respectively. The experiments were performed on L-alanine, an aminoacid which presents three resonances in a ^{13}C NMR spectrum for CH3, CH and the carbonyl group, respectively.

2. Experimental

Solid state ^{13}C NMR spectra were recorded at 100 MHz ^{13}C Larmor frequency with a Bruker AVANCE-400 spectrometer at the NMR Facility of Physics Department, Babes-Bolyai University. All NMR experiments were performed on L-alanine at room temperature. The sample was purchased from Alfa Aesar and used without further purification. It was center-packed to minimize the effect of rf field inhomogeneity. Standard cross-polarization magic-angle-spinning (CP/MAS) experiments were performed at a spinning frequency of ν_R = 8 kHz, using a ^{1}H 90^0 pulse length of 3.8 μs. The ^{13}C NMR spectra were acquired under two-pulse phase-modulated (TPPM) ^{1}H decoupling at 70 kHz by averaging 256 scans with a recycle delay of 3 s.

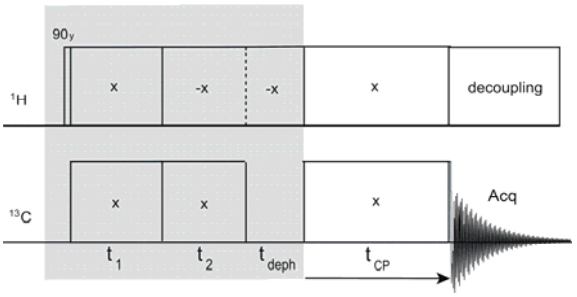

Fig. 1. The pulse sequence employed for the remote protons polarization transfer scheme. It consists of a preparation period (shaded area), followed by a standard CP/MAS sequence. The remote protons CP/MAS curve is recorded by incrementing the value of the third contact time, τ_{CP}.

The CP transfer was optimized for the first Hartmann – Hahn matching condition ($\nu_{1C} = \nu_{1H} - \nu_R$), where the rf fields on the ^{1}H and ^{13}C channels have been calibrated to 50 and 42 kHz, respectively. The conventional CP curves were acquired through the standard CP/MAS sequence, whereas the experimental setup illustrated in Fig. 1 has been employed for acquiring the remote protons CP/MAS curves.

In both cases, the evolution of spin polarization is obtained by incrementing the length of the appropriate contact pulse from 0 to 5 ms: this was done in steps of 5 μs at short times, while at longer times the increment value has been progressively increased, so that in the end a total number of 64 points was employed to define the measured CP build-up curves.

The conventional ^{13}C CP/MAS curves have been acquired in a single experiment, with the carrier frequency set in the middle between the CH and CH_3 resonances. Since they are separated by only 3 kHz, the induced offset effect can be considered negligible. In the case of the remote protons CP/MAS curves, two distinct experiments were carried out, because of the different preparation conditions characteristic to the two aliphatic moieties. Corresponding to the CH and CH_3 groups, the duration of the contact pulses in the CPPI sequence were found to be τ_1 = 70, and 175 μs, and τ_2 = 47, and 80 μs, respectively. The former was determined as the short-time maximum of the conventional CP/MAS curve, whereas the latter represents the inversion time of the ^{13}C signals in the corresponding CP polarization inversion experiment (performed separately, for each resonance). The dephasing period was set to τ_{deph}=50 μs.

3. Results and discussion

The computations were performed using the Spinevolution program [17]. To get reliable conclusions, however, a high accuracy level is required for describing the polarization transfer process by means of numerical simulations on suitably selected spin subsystems. From this point of view, L-alanine represents an ideal model system. In particular, the precise value of the proton positions (± 0.003 Å) determined by neutron diffraction [21] removes possible errors due to uncertainties in the involved C-H and H-H dipolar couplings. Also, the fast (compared with the CP time-increment, $\Delta\tau_{CP}$ = 5 μs) methyl rotation around its symmetry axis has been explicitly accounted for in computations, as described in the Spinevolution reference manual.

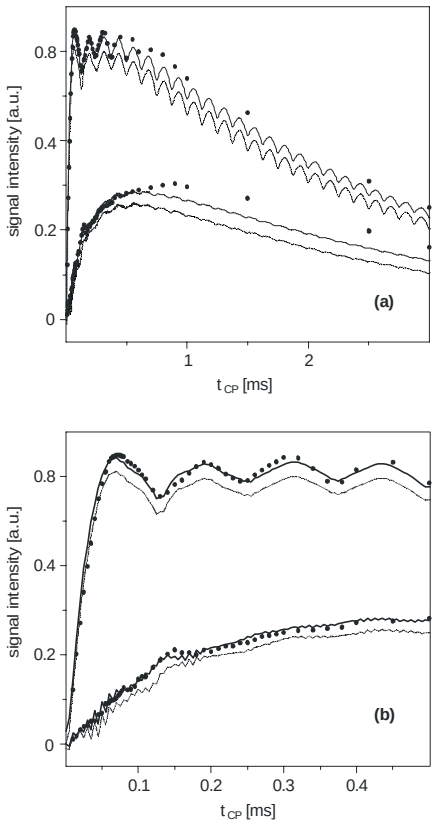

Fig. 2. Comparison between the experimental and computed buildup curves of the CH carbon in L-alanine acquired by conventional- (the upper curves), and remote protons CP/MAS (the lower curves). Measured data are represented by filled symbols. Simulations performed in representative C-H7 (dashed line) and C-H9 (continuous line) spin subsystems. . Rapid rotation around the trigonal axis is considered here only for the CH_3 moiety, whereas the contribution of the NH_3 group to CP dynamics is treated in the rigid approximation. The illustrated dependencies for τ_{CP} in the range 0 – 3, and 0 – 0.5 ms, are shown in the figures (a), and (b), respectively.

Unlike CH_3, the strength of the hydrogen bonding network formed by NH_3^+ will generally determine high activation energies for its rotational motion and, implicitly, slower hoping rates around the symmetry axis. In the case of L-alanine [18], the corresponding hoping time becomes comparable with $\Delta\tau_{CP}$, so that special caution is needed when describing the NH_3 contribution to the CP dynamics. As such, the measured CP/MAS curves of the CH carbon are compared in the Figs. 2 and 3 with simulations performed under both, rigid approximation, and fast rotation limit of the NH_3 group, respectively.

To get a feeling about the errors one might expect when working on a reduced number of spins, the results on the C-H7 spin arrangement are supplemented with

simulations performed on an extended C-H9 system, which incorporates two extra CH intermolecular protons (located at 3.5 and 3.8 Å from the central CH ^{13}C spin). The effect of the spin-lattice relaxation in the rotating frame is accounted for by multiplying the computed buildup curves with exponential functions; their decay rates have been extracted from the exponential fit of the long-time evolution in the corresponding experimental curves.

The dependencies depicted in Figs. 2 and 3 clearly show that the correspondence between the theoretical and experimental data is much better in the rigid NH_3 approximation than in the fast rotational regime. However, small deviations still exist even in the former case. A possible cause is represented by the limited size of the simulated system.

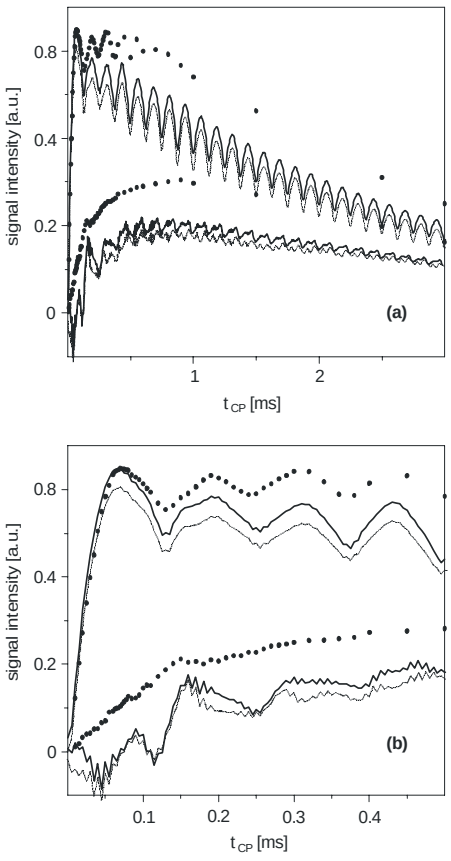

Fig. 3. The same as in Fig. 2, except that both, CH_3 and NH_3 moieties are assumed in a fast rotational regime.

However, this assumption seems rather implausible as it appears from comparing the seven and nine ^{1}H spins simulations (the dashed and continuous lines in the illustrated dependencies). Indeed, the additional two protons are seen to mostly affect the magnitude of the transferred polarization, while the overall shape of the buildup curve is kept almost unchanged (at least up to 0.5 ms – see Figs. 2b and 3b). Thus, the observed deviations are more likely indicative for NH_3 being in a slow rotational regime. Also, a small contribution coming from rf field inhomogeneity cannot be completely ruled out. Unfortunately, the employed simulation program is not yet adapted to incorporate slow molecular motion, so that the results illustrated in Fig. 2 set the accuracy level one can presently reach. Finally, it is worth mentioning that the C-H9 simulations also provide a higher accuracy level in describing the polarization inversion process. Specifically, a better correspondence between the measured and computed ^{13}C polarization inversion time is obtained on the C-H9 system (τ_2 = 46 μs), compared to C-H7 system (τ_2 = 42 μs).

4. Conclusions

The most important conclusion one can draw from the above analysis, is the increased sensitivity of remote protons CP/MAS to structural and dynamical details of distant protons. Indeed, very large deviations between simulated and measured remote protons polarization transfer curves have been obtained in this case under fast rotational assumption compared to a general good agreement that characterizes the rigid NH_3 approach. By contrast, the difference between the rigid-, and fast NH_3 rotation limit, is by far not so well pronounced in the case of conventional CP/MAS build up curves. Nevertheless, the fact that conventional CP/MAS is less sensitive to details of the NH_3 molecular motion is not completely surprising, as these details can be easily obscured under the dominant effect of bonded proton. From practical perspective, the two polarization transfer schemes can be thus combined together to provide more structural and dynamical information than would result from using standard CP/MAS alone.

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