Chemical shift powder spectra enhanced by multiple-contact cross-polarization under slow magic-angle spinning

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ABSTRACT

A simple multiple-contact cross-polarization (CP) scheme is applied to a powder sample of ferrocene and β-calcium formate under static and magic-angle spinning (MAS) conditions. The method is described analytically through the density matrix formalism. We show that multiple equilibrations–re-equilibrations with the proton spin bath improves the polarization transfer efficiency at short contact times and provides higher signal enhancements than state-of-the art techniques such as adiabatic passage through the Hartmann–Hahn condition CP (APHH-CP) when MAS is applied. The resulting chemical shift powder spectra then are identical to the ones obtained by using ROtor-Directed Exchange of Orientations CP (APHH-RODEO-CP) with intensity gains of a factor 1.1–1.3.

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1. Introduction

Cross-polarization (CP) of spins S with a low gyromagnetic ratio γ_S such as ^{13}C and ^{15}N from abundant spins I with a higher gyromagnetic ratio γ_I (e.g., ^1H) is a popular way of obtaining high sensitivity NMR spectra of solids [1–5]. In the Hartmann–Hahn (HH) version of the CP experiment (HHCP), efficient polarization transfer through heteronuclear zero quantum transitions is obtained at the HH condition $\omega_{1I} = \omega_{1S}$, where ω_{1I} and ω_{1S} are the amplitudes of the radiofrequency (RF) fields applied to the I and S spins [1,2,6]. It has been shown that the efficiency of HHCP is highly dependent on mismatch of the HH condition, RF-field inhomogeneity and resonance offset. To overcome these problems, several techniques such as mismatch-optimized IS transfer (MOIST) [7], variable-amplitude CP (VACP) [8], ramped-amplitude CP (RAMP-CP) [9], adiabatic passage through the HH condition (APHH) [10], variable-effective-field CP (VEFCP) [11], frequency-modulated CP (FMCP) [12], nuclear integrated CP (NICP) [13], simultaneous adiabatic spin-locking CP (SADIS-CP) [14] and composite zero CP (COMPO-ZER-CP) [15] have been developed. CP dynamics are very dependent on the relative sizes of the homonuclear (I–I) and heteronuclear (I–S) dipolar interactions [16]. When the fluctuations of the local field governing the spin diffusion process among the abundant spins are faster than the exchange of magnetization between the two spin systems, the spin-temperature hypothesis can be applied and CP proceeds exponentially as cross-relaxation (classical I–S model) [2,3,16]. This is typically the case of non-protonated carbons in organic solids. For a dilute-abundant spin system, the magnetization enhancement factor G_{CP} at thermal equilibrium for the single-contact HHCP experiment is equal to γ_I/γ_S [3]. Thus for CP from ^1H to ^{13}C or to ^{15}N, enhancement factors of 4 or 10, respectively, can be obtained. On the other hand, the presence of strong heteronuclear interactions, as in the case of protonated carbons, leads to coherent energy transfer, i.e., an oscillating behavior of the CP dynamics (I–I^*–S model) [7,16,17]. The resulting two-stage character of the polarization transfer for rigid or semi-rigid CH_n groups (n = 1, 2 and 3) has been previously observed and analyzed in both static and rotating samples [18–23]. A quasi-equilibrium state yielding a S-spin magnetization enhancement proportional to $n/(n + 1)$ is then rapidly established within the S–I_n subsystem, i.e., $G_{CP} = \gamma_I/(2\gamma_S)$ for n = 1. Hence, only half of the initial polarization of the I spin is transferred to the S spin in an isolated I–S spin pair. In this case, Hediger et al. [10] have shown that the CP efficiency can be improved by sweeping the RF amplitude adiabatically through the HH condition (APHH-CP). However, for an optimized pulse shape, knowledge of the HH level and of the heteronuclear dipolar coupling constant are desired. The CP process is also known to be an important source of lineshape distortions due to the orientation dependence of the dipolar coupling [3,24]. In particular, there is often a «magic-angle hole» (MAH) in the lineshape corresponding to the magic angle orientation of the I–S vector. We have recently developed a new simple and robust CP scheme under slow magic-angle spinning (MAS), called ROtor-Directed Exchange of Orientations CP (RODEO-CP) [25], which permits to obtain undistorted chemical shift (CS) powder spectra with short contact times, i.e., when a (quasi-)equilibrium state polarization is not reached. Moreover, a higher overall signal intensity has been obtained by using

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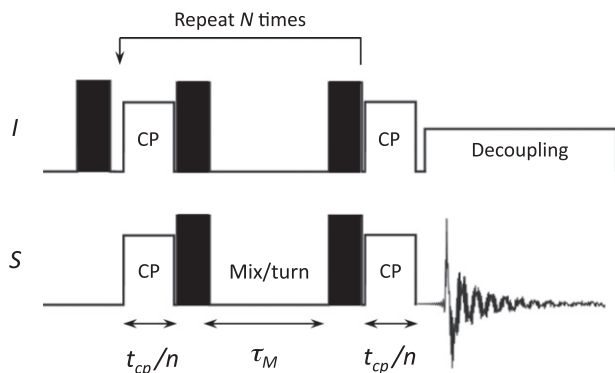 E-mail address: hirschinger@unistra.fr (J. Hirschinger).

Fig. 1. Pulse sequence for multiple-contact isotropic cross-polarization (MCI-CP). The filled rectangles indicate $\pi/2$ pulses.
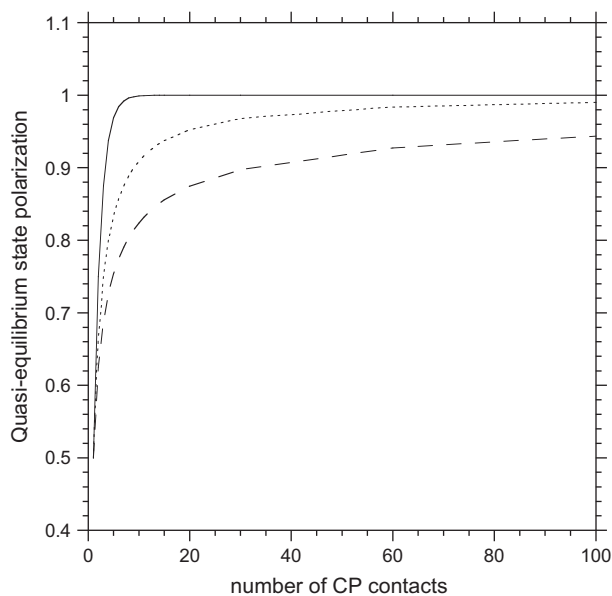

Fig. 2. Quasi-equilibrium state polarization as a function of the number n of CP contacts for the MCI-CP (solid line) and MC-CP (broken line) sequences deduced from Eq. (3). The dotted line shows the quasi-equilibrium state polarization $n/(n+1)$ obtained by single-contact HHCP for a $S–I_n$ subsystem.
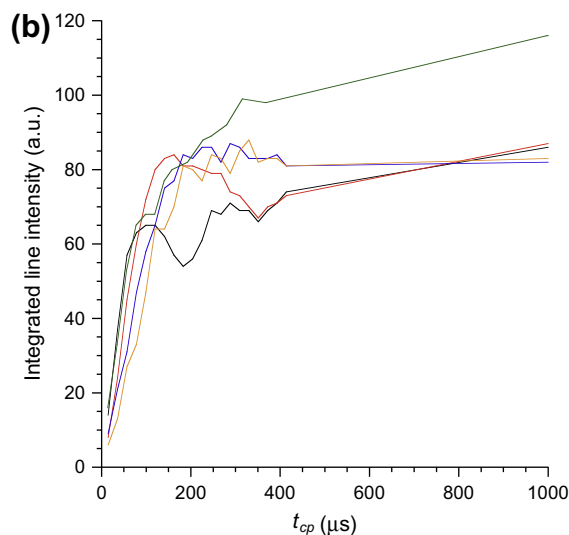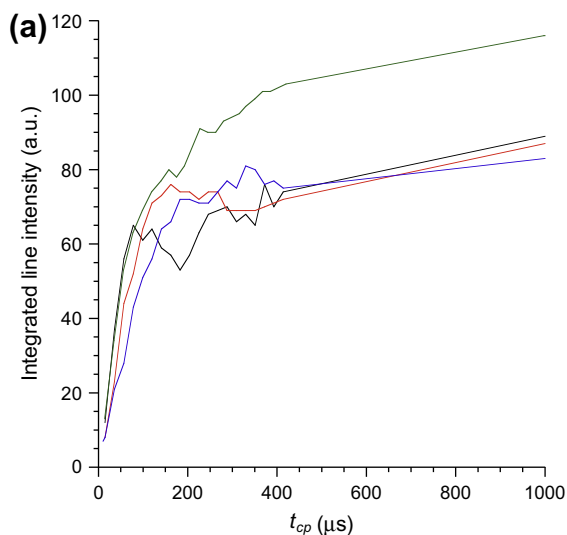
APHH-CP as the initial CP step in the RODEO-CP sequence [25]. (APHH)-RODEO-CP is expected to be particularly useful in mobile samples such as liquid crystalline materials, polymers, membrane-associated peptides or small proteins characterized by a short spin–lattice relaxation time in the rotating frame ($T_{1\rho}$) [26,27].

In this paper, we investigate the CP dynamics of a multiple-contact pulse scheme originally proposed in the textbook by Gerstein and Dybowski [4] under static and MAS conditions and compare the results with the ones obtained with the APHH-CP and APHH-RODEO-CP sequences. To our knowledge, this Multiple-Contact CP (MC-CP) technique has been first used in order to study the nature of CP under mismatched HH condition [28]. The same pulse sequence applied under MAS, the so-called Multiple-Contact Isotropic CP (MCI-CP) experiment [24], has then been used to partially diminish spinning sideband patterns distortions. Although MCI-CP is merely the MAS version of MC-CP we will keep both denominations throughout the text. Recently, an improved version of MC-CP including synchronous phase reversals of the two spin-locking RF fields termed as REP-CP [29] has been shown to yield an enhancement of the magnetization transfer as compared to HHCP and MOIST-CP in ^{15}N NMR of membrane proteins reconstituted in magnetically aligned bicelles. In the following, we analyze MC-CP and MCI-CP experiments in ferrocene and β-calcium formate with particular emphasis on the polarization transfer efficiency and the distortions of CS powder spectra observed at short contact times.

2. Theory

In order to describe spin dynamics during the MCI-CP [24] pulse sequence, we use the $I–I^*–S$ model [16] originally introduced by Müller, Kumar, Baumann, and Ernst (MKBE) [17]. Indeed, we have shown previously that this model accounts successfully for CP results in molecular crystals, polymers and liquid crystals [22,23,30,31]. The system is then treated as a tightly coupled ^{13}C–^{1}H spin pair immersed in a thermal bath consisting of the remaining protons. The interaction of this particular I^* spin with the bath or infinite reservoir of I spins is considered in a phenomenological way. Neglecting spin–lattice relaxation ($T_{1\rho}$), the reduced density operator in Liouville space $|\hat{\sigma}(t)\rangle$ describing the

Fig. 3. Integrated intensity of the ^{13}C NMR spectrum of ferrocene as a function of the total contact time t_{cp} for the HHCP, APHH-CP, MC-CP (τ_M = 10 ms) and MCI-CP (τ_M = 3 ms) experiments. (a) static sample: HHCP (black line), APHH-CP with ϕ = 88° (green line), MC-CP N = 1 (red line), MC-CP N = 2 (blue line); (b) MAS sample: HHCP (black line), APHH-CP with ϕ = 88° (green line), MCI-CP N = 1 (red line), MCI-CP N = 2 (blue line), MCI-CP N = 3 (orange line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)