

Cross-Polarization from the Dipolar Reservoir under the Mismatched Hartmann–Hahn Condition

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Cross-polarization from the dipolar reservoir for a range of mismatched Hartmann–Hahn conditions has been considered. Experiment, in general, agrees with the dispersive Lorentzian behavior expected on the basis of quasi-equilibrium theory. It is observed that inclusion of additional mechanisms of polarization transfer lead to an improvement of the fit of the experimental results. The utility of extending the technique to the case of ordered long chain molecules, such as liquid crystals, for the measurement of the local dipolar field is also presented. © 2002 Elsevier Science (USA)

Cross-polarization experiments are routinely used in several solid-state NMR studies where polarization transfer from abundant I spins to rare S spins is utilized to enhance S spin intensity. These studies utilize Hartmann–Hahn polarization transfer (I) between the Zeeman reservoirs of the I and S spins. The effect of the mismatch of the Hartmann–Hahn condition has been dealt with in detail by Levitt *et al.* (2). Polarization transfer from the dipolar reservoir using a Hartmann–Hahn type pulse sequence has been reported earlier (3). On the basis of quasi-equilibrium theory, a dispersive Lorentzian behavior has been predicted for the S spin intensity under mismatch and supportive experimental results have been provided by measurement of intensity for three different values of ω_{1S} such that $\omega_{1S} = \omega_{1I}$, $\omega_{1S} < \omega_{1I}$, and $\omega_{1S} > \omega_{1I}$ where ω_{1S} and ω_{1I} are the magnitudes of the spin-lock RF fields applied on resonance to the S and I spins respectively. In this communication the above polarization transfer process has been considered in detail by measuring S spin intensity for a wide range of mismatch conditions. The overall dependence of the S spin intensity on $\Delta\omega = \omega_{1S} - \omega_{1I}$ does indeed reveal a dispersive Lorentzian behavior. However, the detailed fit of the experimental points to a dispersive Lorentzian is not satisfactory, since the curve is not exactly antisymmetric showing higher intensity for larger values of ω_{1S} . We have considered possible mechanisms contributing to these deviations. The effect of adding additional terms has been presented and discussed. Another aspect of the study has been the application

of the method to the study of molecular motions in the case of long chain molecules exhibiting partial order.

The experiment (Fig. 1) consists of an ADRF pulse sequence on the I spins, which creates a dipolar order from the I spin Zeeman order during the period τ_a . During τ_{CP} , a Hartmann–Hahn cross-polarization pulse sequence is used, which results in transfer of polarization from the dipolar bath to the S spin Zeeman bath. The S spin intensity depends on the Hartmann–Hahn match condition and can be calculated using the quasi-equilibrium theory (2) as described below.

At the start of the experiment, the I spin Hamiltonian is given by

$$\mathcal{H}_{0I} = -\omega_{0I} \sum_{k=1}^N I_{kz} + \mathcal{H}_D, \quad [1]$$

where ω_{0I} is the I spin Larmor frequency and \mathcal{H}_D represents local fields such as those due to dipolar couplings between the I spins. The initial density matrix is given by

$$\sigma(0) = \alpha_{0I} \sum_{k=1}^N I_{kz}. \quad [2]$$

Here $\alpha_{0I} = -\omega_{0I}/kT_L$ with T_L being the lattice temperature. During the ADRF process (τ_a), the Zeeman and the dipolar reservoirs exchange energy and at the end of the process the entire magnetization is transferred to the dipolar bath. The new density matrix is given by

$$\sigma(\tau_a) = \beta \mathcal{H}_D, \quad [3]$$

where $\beta = \alpha_{0I}/\gamma H_D$.

During τ_{CP} , on-resonance radiofrequency pulses are applied on I and S spins for a short time, so that a Hartmann–Hahn type transfer process is established between the I and S spins. This is described by considering the I and S spin Zeeman interactions and the homonuclear I–I interactions as reservoirs and the heteronuclear coupling between the I and S spins as a perturbation bringing these reservoirs into contact with one another. The Hamiltonian of the system in the tilted rotating frame (2) is

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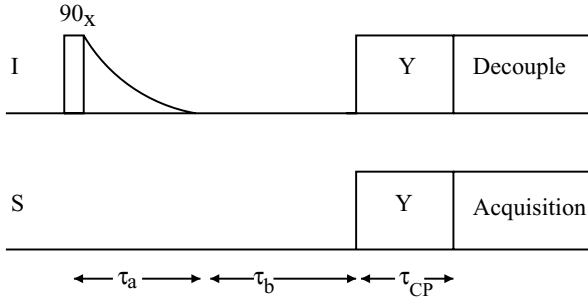


FIG. 1. Pulse sequence for cross polarization from dipolar reservoir. Dipolar order is created by the ADRF pulse sequence during τ_a and τ_b . Polarization transfer from the dipolar reservoir to the S spin is achieved by the Hartmann-Hahn type cross polarization during τ_{CP} .

given by

$$\mathcal{H}_{CP} = \omega_{1I} \sum_{k=1}^N I_{kZ} + \omega_{1S} S_z + \mathcal{H}_D. \quad [4]$$

Taking into consideration that for high RF fields the Zeeman and dipolar baths do not exchange energy, quasi-equilibrium constants Q_1 and Q_2 have been defined as follows such that $(\sum_k I_{kZ} + S_z)$ is a constant of motion,

$$Q_1 = \left[\frac{(N\omega_{1I} + \omega_{1S})}{N+1} \right] \left(\sum_{k=1}^N I_{kZ} + S_z \right) \quad [5]$$

$$Q_2 = \mathcal{H}_{CP} - Q_1 = \left[\frac{\Delta\omega}{N+1} \right] \left(N S_z - \sum_{k=1}^N I_{kZ} \right) + \mathcal{H}_D. \quad [6]$$

The density matrix at the end of the cross polarization period is given by

$$\begin{aligned} \sigma(\tau_{CP}) &= \frac{\langle \sigma(\tau_a) | Q_1 \rangle}{\langle Q_1 | Q_1 \rangle} Q_1 + \frac{\langle \sigma(\tau_a) | Q_2 \rangle}{\langle Q_2 | Q_2 \rangle} Q_2 \\ &= \left[\frac{\beta\lambda^2}{\frac{\Delta\omega^2 N}{(N+1)} + \lambda^2} \right] \left[\left(\frac{\Delta\omega}{N+1} \right) \left(N S_z - \sum_{k=1}^N I_{kZ} \right) + \mathcal{H}_D \right]. \end{aligned} \quad [7]$$

Here $\lambda^2 = \langle \mathcal{H}_D | \mathcal{H}_D \rangle / \langle I_{kZ} | I_{kZ} \rangle$ is related to the I spin second moment. The measured S spin magnetization for large values of N is given by

$$\langle S_z \rangle = \frac{\beta\lambda^2 \Delta\omega}{\Delta\omega^2 + \lambda^2}. \quad [8]$$

The above equation predicts an S spin intensity, which has a dispersive Lorentzian dependence on $\Delta\omega$. It may be noted that the number of quasi-equilibrium constants to be considered may depend upon the details of the particular system. For example, if the two spin interaction between the S spin and one of the I spins is relatively stronger than the I-I interaction, then considering three quasi-equilibrium constants may be appropriate (2). These would correspond to (i) the two-spin zero quantum manifold, (ii) the two-spin double-quantum levels in combination with all the other I spin Zeeman levels separated by $\Delta m = \pm 2$, and (iii) the rest of the energy reservoir terms including the I-I dipolar couplings. We observe that in this case also, a dispersive Lorentzian relation similar to Eq. [8] is obtained for the S spin intensity with a width which is a numerical multiple of λ .

Figure 2 shows experimental results obtained by observing ^{31}P resonance on a powder sample of ammonium dihydrogen phosphate, using the pulse scheme shown in Fig. 1. The experimental details are given in the figure caption. The continuous line in Fig. 2a represents the best fit of the experimental results to Eq. [8], where β and λ have been kept as variable parameters. It is observed that in general the experimental results follow a dispersive Lorentzian behavior. However, a close examination of Fig. 2a reveals that the fit of the calculated curve to experimental data is not very good. The experimental intensities are not antisymmetric about the center and are higher for larger values of ω_{1S} . This leads us to consider possible additional mechanisms that could lead to an understanding of the deviation of the experimental data from the expected behavior. Particularly we are interested in the effect such additional terms might have on λ^2 which is related to the second moment of the I spins which can provide a handle on the local dipolar fields. For example, the conventional model [4] of treating the total Hamiltonian as the constant of motion leads to an S magnetization that depends linearly on ω_{1S} and can be obtained from

$$\begin{aligned} \sigma(\tau_{CP}) &= \frac{\langle \sigma(\tau_a) | \mathcal{H}_{CP} \rangle}{\langle \mathcal{H}_{CP} | \mathcal{H}_{CP} \rangle} \mathcal{H}_{CP} \\ &= \frac{\beta\lambda^2}{N\omega_{1I}^2 + \omega_{1S}^2 + \lambda^2} \left[\omega_{1I} \sum_{k=1}^N I_{kZ} + \omega_{1S} S_z + \mathcal{H}_{CP} \right] \end{aligned} \quad [9]$$

so that,

$$\begin{aligned} \langle S_z \rangle &= \frac{\beta\lambda^2}{N\omega_{1I}^2 + \omega_{1S}^2 + \lambda^2} \omega_{1S} \\ &\approx \frac{\beta\lambda^2}{N\omega_{1I}^2} \omega_{1S} \end{aligned} \quad [10]$$

for very large values of N.

It might be expected that Eq. [8] is the appropriate one to use when high values of RF are used and Eq. [10] for values of

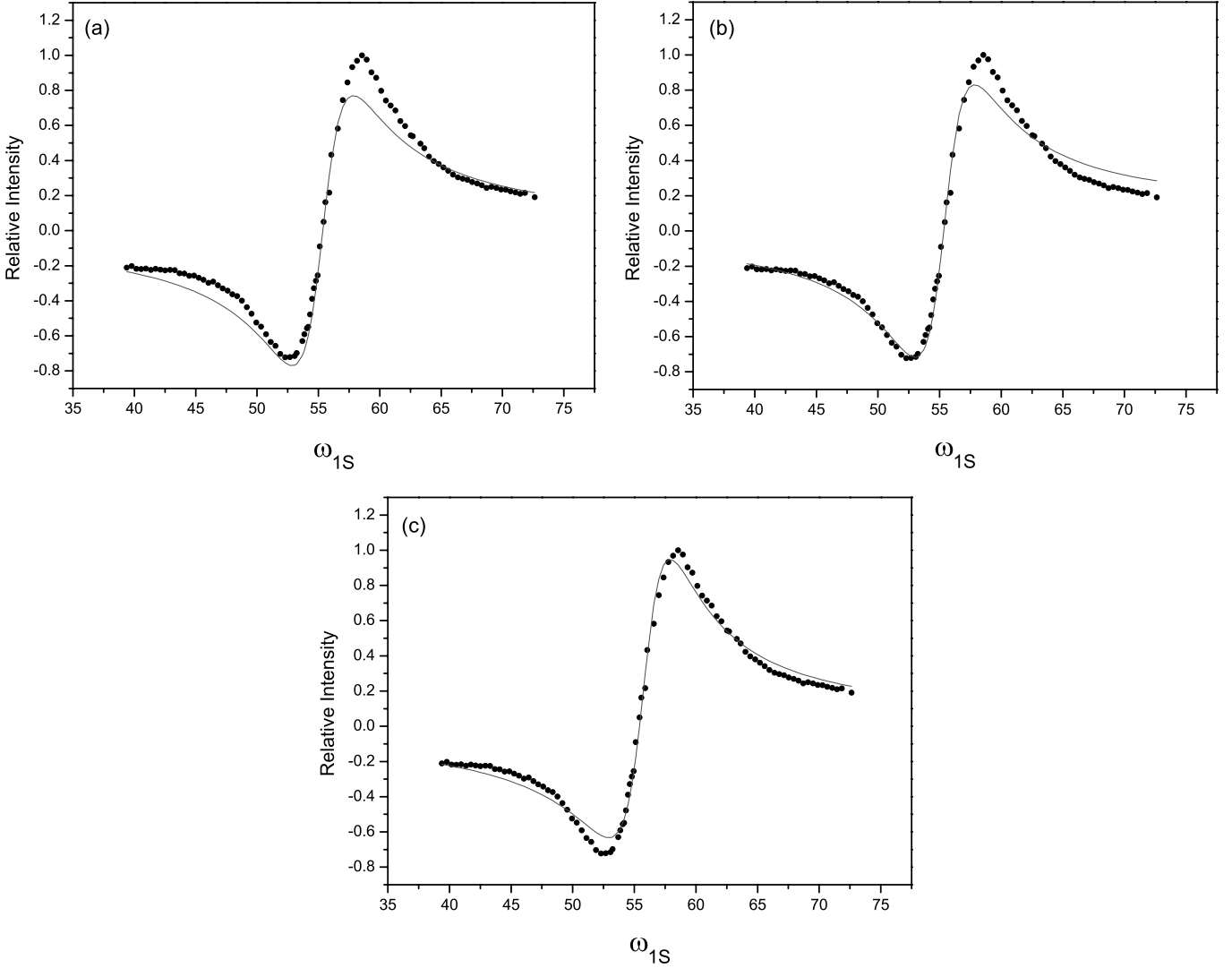


FIG. 2. Variation of cross polarized signal intensity from dipolar bath of protons to ^{31}P in ammonium dihydrogen phosphate (ADP) for different RF powers (ω_{1S}) on ^{31}P obtained using the pulse sequence shown in Fig. 1 with $\tau_a = \tau_b = 1$ ms and $\tau_{CP} = 400$ μs . The spectra were obtained on a Bruker DSX-300 NMR spectrometer at a ^{31}P resonance frequency of 121.442 MHz. ω_{1I} was kept constant at 55 kHz. Continuous lines in the figures show fit of the experimental data to (a) a dispersive Lorentzian function (Eq. [8]), (b) a dispersive Lorentzian function and a term proportional to ω_{1S} (Eq. [11]), and (c) a mixture of dispersive and absorptive Lorentzian functions.

RF comparable with the local dipolar field, when the Zeeman and dipolar baths freely exchange energy. For the case of the experimental results shown in Fig. 2, we recalculated the intensities using Eq. [8] adding the expression of Eq. [10] as a leakage term as

$$\langle S_z \rangle = k \frac{\beta \lambda^2 \Delta \omega}{\Delta \omega^2 + \lambda^2} + (1 - k) \frac{\beta \lambda^2}{N \omega_{1I}^2} \omega_{1S}. \quad [11]$$

Such an equation will be appropriate in a situation where the RF fields are different at different parts of the sample due to RF field inhomogeneity. In Eq. [11] factors like β , λ , N , and k have been

treated as variable parameters and the best fit obtained is shown in Fig. 2b as a continuous curve. It is observed that Eq. [11] provides a more improved fit of the experimental result than Eq. [8], the χ^2 parameters being respectively 0.005 and 0.008. We have also considered the possibility of transfer from remnant Zeeman magnetization of the I spins at the end of the ADRF period, cross polarizing directly to the S spin, in which case the transfer of magnetization will follow an absorptive Lorentzian as a function of mismatch (2). In this case Eq. [8] is modified to be a mixture of dispersive and absorptive Lorentzians and the χ^2 value of the fit (Fig. 2c) was obtained to be 0.003. Thus addition of such terms marginally improves the fit as seen in Fig. 2 and the results emphasize the essentially dispersive Lorentzian

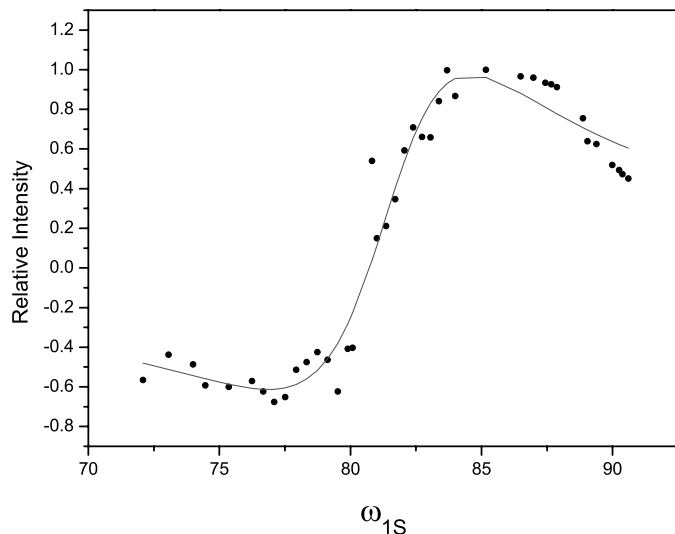


FIG. 3. Variation of cross polarized signal intensity from dipolar bath of protons to ^{13}C in the liquid crystal EBBA for different RF powers (ω_{1S}) on ^{13}C obtained using the pulse sequence shown in Fig. 1 with $\tau_a = \tau_b = 1$ ms and $\tau_{CP} = 200$ μs . The spectra were obtained on a Bruker DSX-300 NMR spectrometer at a ^{13}C resonance frequency of 75.432 MHz. ω_{1I} was kept constant at 83 kHz. The continuous curve corresponds to a fit of the experimental data to a mixture of dispersive and absorptive Lorentzian functions and yields a value for $\lambda^2 = 14.2$ kHz^2 for the α carbon.

nature of the polarization transfer from the dipolar bath. It also does not change significantly λ^2 which is 6.2, 5.7, and 5.9 kHz^2 for the three cases considered above. We notice that in long chain molecules such as liquid crystals for which we have carried out the above experiments, λ provides a handle on the local dipolar field and serves as an indicator of local order. A typical plot

of relative intensity versus ω_{1S} for one of the carbon atoms in the aliphatic chain in *N*-(4-ethoxybenzylidene)-4-n-butylaniline (EBBA) in oriented phase is shown in Fig. 3. The value of λ^2 obtained from such plots when compared for methylene carbons along the chain shows a variation similar to the one expected for local order parameters (5). The method, like the WISE (6) technique, provides another means of indirectly monitoring proton dipolar couplings using the heteronuclear chemical shift dispersion.

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