



Recoupling in solid state NMR using γ prepared states and phase matching

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ABSTRACT

The paper describes two-dimensional solid state NMR experiments that use powdered dephased anti-phase coherence (γ preparation) to encode chemical shifts in the indirect dimension. Both components of this chemical shift encoded gamma-prepared states can be refocused into inphase coherence by a recoupling element. This helps to achieve sensitivity enhancement in 2D NMR experiments by quadrature detection. The powder dependence of the gamma-prepared states allows for manipulating them by suitable insertion of delays in the recoupling periods. This helps to design experiments that suppress diagonal peaks in 2D spectra, leading to improved resolution. We describe some new phase modulated heteronuclear and homonuclear recoupling pulse sequences that simplify the implementation of the described experiments based on γ prepared states. Recoupling in the heteronuclear spin system is achieved by matching the difference in the amplitude of the sine/cosine modulated phase on the two rf-channels to the spinning frequency while maintaining the same power on the two rf-channels.

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1. Introduction

Nuclear magnetic resonance (NMR) spectroscopy opens up the possibility of studying insoluble protein structures such as membrane proteins, fibrils, and extracellular matrix proteins which are difficult to analyze using conventional atomic-resolution structure determination methods, including liquid-state NMR and X-ray crystallography [1–5]. Sensitivity and resolution is a critical issue in all these applications. The most advanced solid-state NMR equipment and techniques still requires hours and days of signal averaging for a simple two-dimensional (2D) spectroscopy of peptides and proteins in a noncrystalline solid form. The resolution of solid state NMR experiments is limited by increased line widths of the powder samples. The present paper describes some new methodology development aimed at making improvements in resolution and sensitivity.

In [6], we addressed a fundamental problem of coherence transfer in solid-state NMR of “powder” samples. We showed how to design experiments that are insensitive to orientations of the crystallite in a powder sample and simultaneously transfer both components of transverse magnetization of spin S to a coupled spin I , in the mixing step of the 2D solid state NMR experiment under magic angle spinning. Simultaneous transfer of both components of the magnetization has been used to develop sensitivity enhanced experiments widely used in liquid-state NMR [7–10]. Pulse sequences for simultaneous transfer of transverse component of

magnetization have recently appeared in solid state NMR literature [11]. Transfer schemes presented in [6] are independent of the orientations of the crystallite in a powder sample.

In this paper [13], we show how the powdered dephased coherences (γ prepared states) can be used to develop recoupling experiments with improved resolution and sensitivity. The peaks in the 2D spectrum arising from the chemical shifts encoded on the γ prepared states are shifted in the indirect dimension by the rotor frequency (given that t_1 increments sample the rotor period). The NMR signal arising from these γ prepared states can be manipulated by inserting half rotor period delays in these experiments or suitable phase cycling as described in the paper. In principle, this makes it possible to retain only the peaks arising from the γ prepared states. We describe some methods for achieving this in the paper. These methods could aid in the chemical shift assignment of large molecules, especially for resolving cross-peaks close to the diagonal.

The paper is organized as follows. In Section 2, we describe some homonuclear recoupling experiments that recouple dipolar coupled spins under MAS experiments. These experiments are broadband and robust to rf-inhomogeneity and form the building block for preparation and refocusing of γ prepared states. This work extends recently developed techniques for broadband homonuclear recoupling as reported in the [15–17]. In Section 3, we show how these recoupling blocks can be used to prepare a powder dephased antiphase coherence and refocus both components of the chemical shift encoded γ prepared states (following t_1 evolution) into inphase coherence. In Section 3.1, we show how to design 2D experiments that only retain correlations encoded on the γ pre-

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pared states. This then helps to generate 2D spectra, where diagonals are in principle completely suppressed leading to improved resolution. In Section 4, we describe these methods in the context of heteronuclear experiments. In the context of heteronuclear spins, the recoupling is achieved by matching the phase modulations on the two rf-channels (analogous to Hartmann-Hahn matching of the rf-power commonly seen in heteronuclear recoupling experiments). Section 5 describes experimental verification of the proposed techniques. The results are discussed in the conclusion Section 6.

In a standard 2D NMR experiment [18], the initial coherence on spin S evolves under the chemical shift ω_S for time t_1 to $S_x \rightarrow S_x \cos(\omega_S t_1) + S_y \sin(\omega_S t_1)$. During the mixing step, the x magnetization on spin S is transferred to a coupled spin I , and assuming perfect transfer, $S_x \rightarrow I_x$, the spin I precesses under its chemical shift, i.e.,

$$I_x \cos(\omega_S t_1) \rightarrow \cos(\omega_S t_1) \{I_x \cos(\omega_I t_2) + I_y \sin(\omega_I t_2)\}.$$

The precession is recorded and the experiment is repeated by incrementing t_1 , finally leading to a two dimensional signal in t_1 and t_2 that encodes for ω_I and ω_S . Simultaneous transfer of both components of the transverse magnetization during the mixing step, i.e.,

$$S_x \cos(\omega_S t_1) + S_y \sin(\omega_S t_1) \rightarrow I_x \cos(\omega_S t_1) + I_y \sin(\omega_S t_1),$$

is desirable as it enhances the sensitivity of the experiment by a factor of $\sqrt{2}$. Such sensitivity enhanced experiments are performed routinely in liquid-state NMR [7–10]. The simultaneous transfer of both transverse components of the magnetization is usually achieved by synthesizing an isotropic Hamiltonian or a Unitary propagator,

$$U_{iso} = \exp(-i\pi\{I_x S_x + I_y S_y + I_z S_z\}).$$

However in solid state NMR experiments under MAS, the dispersion in the coupling strengths arising due to the orientation dependence of the couplings makes the task of synthesizing U_{iso} for all coupled spin pairs (independent of the orientation) a non-trivial task. This problem can be alleviated by suitably transforming the initial magnetization on spin S , before the t_1 evolution period. This is called γ preparation, as the transformed state depends on angle γ that denotes the rotation of the crystallite around the rotor axis. This transformed state is then made to evolve under the chemical shift of spin S . Because of the initial preparation, it becomes possible to simultaneously transfer both components of the transverse magnetization of spin S after the t_1 precession. The paper proposes many new techniques for creation, manipulation and application of these γ prepared states for design of multidimensional NMR experiments.

Notation: Let $S_\alpha(\beta, \gamma)$ denote the rotation of operator S_α around the axis β by angle γ , where $\alpha, \beta \in \{x, y, z\}$, i.e., $S_\alpha(\beta, \gamma) = \exp(-i\gamma S_\beta) S_\alpha \exp(i\gamma S_\beta)$. For example $S_x(z, \gamma) = S_x \cos \gamma + S_y \sin \gamma$. It is straightforward to verify relations of the following kind

$$[-iS_x(\beta, \gamma), -iS_y(\beta, \gamma)] = -iS_z(\beta, \gamma).$$

It also follows from definition that for any unitary transformation U ,

$$US_\alpha(\beta, \gamma)U' = S_{U\alpha U'}(U\beta U', \gamma),$$

where $S_{U\alpha U'}(U\beta U', \gamma)$, denotes rotation of operator $US_\alpha U'$ around $U\beta U'$.

Let the unit vectors l, m, n constitute a right handed coordinate system ($l \times m = n$). Then

$$\mathcal{H}_{DQ}^l(\gamma) = I_m S_m(l, \gamma) + I_n S_n(l, \gamma) = S_m I_m(l, -\gamma) + S_n I_n(l, -\gamma), \quad (1)$$

and

$$\mathcal{H}_{DQ}^l(\gamma) = I_m S_m(l, \gamma) - I_n S_n(l, \gamma) = S_m I_m(l, \gamma) - S_n I_n(l, \gamma), \quad (2)$$

are used to denote the zero quantum and multiple (double) quantum operators.

2. Phase alternating modulated recoupling

Consider two homonuclear spins I and S under magic angle spinning condition [19]. In a rotating frame, rotating with both the spins at their common Larmor frequency, the Hamiltonian of the spin system takes the form

$$H(t) = \omega_I(t)I_z + \omega_S(t)S_z + \omega_{IS}(t)(3I_z S_z - I \cdot S) + 2\pi A(t) \times (\cos \phi(t)F_x + \sin \phi(t)F_y), \quad (3)$$

where the operator $F_x = I_x + S_x$, and $\omega_I(t)$ and $\omega_S(t)$ represent the chemical shift for the spins I and S respectively and $\omega_{IS}(t)$ represents the time varying couplings between the spins under magic-angle spinning. These interactions may be expressed as a Fourier series

$$\omega_\lambda(t) = \sum_{m=-2}^2 \omega_\lambda^m \exp(im\omega_r t), \quad (4)$$

where ω_r is the spinning frequency (in angular units), while the coefficients $\omega_\lambda(\lambda = I, S, IS)$ reflect the dependence on the physical parameters like the isotropic chemical shift, anisotropic chemical shift, the dipole-dipole coupling constant and through this the internuclear distance [22].

The term $I \cdot S$ in (3), commutes with the rf-Hamiltonian, and in the absence of the chemical shifts, it averages to zero under MAS. We will, therefore, drop this term in the subsequent treatment, where we truncate the chemical shift Hamiltonian with a strong rf-field.

Consider the rf irradiation on homonuclear spin pair whose amplitude is chosen as $A(t) = \frac{C}{2\pi}$ and the offset $\Delta\omega(t)$

$$\dot{\phi}(t) = -\Delta\omega(t) = \omega_r \cos(Ct + \theta). \quad (5)$$

This offset is implemented as a phase modulation

$$\phi(t, \theta) = \frac{\omega_r}{C} \{\sin(Ct + \theta) - \sin(\theta)\}. \quad (6)$$

In the modulation frame, which transforms the density matrix from

$$\rho \rightarrow \exp(i\phi(t)F_z) \rho \exp(-i\phi(t)F_z),$$

the rf-Hamiltonian takes the form

$$H^{rf}(t) = CF_x - \dot{\phi}F_z = CF_x - \omega_r \cos(Ct + \theta)F_z, \quad (7)$$

where C is in the angular frequency units and we choose $C \gg \omega_I(t), \omega_S(t), \omega_{IS}(t), \omega_r$. In the interaction frame of the irradiation along x -axis, with the strength C , the chemical shifts of the spins are averaged out. The coupling Hamiltonian of the spin system takes the form

$$H_I^{DD}(t) = \frac{3}{2}\omega_{IS}(t)(I_z S_z + I_y S_y) + \frac{3}{2}\omega_{IS}(t)((I_z S_z - I_y S_y) \cos(2Ct) + (I_z S_y + I_y S_z) \sin(2Ct)), \quad (8)$$

and the rf-Hamiltonian of the spin system transforms to

$$H_I^{rf}(t) = -\frac{\omega_r}{2} \{ (2F_z \cos^2(Ct) \cos \theta + 2F_y \sin^2(Ct) \sin \theta) - \sin(2Ct)(F_y \cos \theta + F_z \sin \theta) \}, \quad (9)$$

which averages over a period $\tau_c = 2\pi/C$ to

$$H_I^{rf} = -\frac{\omega_r}{2} (\cos \theta F_z + \sin \theta F_y). \quad (10)$$

We have therefore an effective field along the direction m , where $m = -\sin \theta \hat{y} - \cos \theta \hat{z}$. For $\theta = 0$, we have an effective rf-field along the $-z$ direction. For $\theta = \frac{\pi}{2}$, we have an effective field along $-y$ direction.

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