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Two Dimensional NMR and NMR Relaxation Studies
of Coal Structure

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PROGRESS REPORT

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Kurt W. Zilm
Department of Chemistry
Yale University
New Haven, CT 06511

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ABSTRACT

This report covers the progress made on the title project for the project period. Four major areas of inquiry are being pursued. Advanced solid state NMR methods are being developed to assay the distribution of the various important functional groups that determine the reactivity of coals. Special attention is being paid to methods that are compatible with the very high magic angle sample spinning rates needed for operation at the high magnetic field strengths available today. Polarization inversion methods utilizing the difference in heat capacities of small groups of spins are particularly promising. Methods combining proton-proton spin diffusion with ^{13}C CPMAS readout are being developed to determine the connectivity of functional groups in coals in a high sensitivity relay type of experiment. Additional work is aimed at delineating the role of methyl group rotation in the proton NMR relaxation behavior of coals.

Introduction

During the last quarter we have concentrated on further improvements in cross polarization (CP) sequences with a goal of making the CP process insensitive to the magic angle spinning (MAS) rate. In order to be able to use fields the order of 7.0 T or higher, CP efficiency must be maintained at MAS rates of over 10 kHz. The standard sequences have severe limitations at these rates which lead to intensity distortions in ^{13}C CPMAS spectra. Thus in order to be able to take advantage of the increases in sensitivity and resolution that accompany high field operation, improvements in the NMR methods are required. Since our last grant we have revised and further refined our theoretical model of the cross polarization process under high speed MAS. The attached preprint (to be submitted to J. Magn. Reson.) details the new theory.

Cross Polarization with High Speed Magic Angle Spinning

Xiaoling Wu and Kurt W. Zilm

a contribution from the Department of Chemistry, Yale University

225 Prospect Street, New Haven, CT 06511

ABSTRACT

Cross polarization magic angle spinning ^{13}C NMR has become an important analytical method for the study of organic solids. At high field strengths the high magic angle sample spinning (MASS) rates required to suppress spinning sidebands can substantially suppress the dipolar couplings among the abundant protons. This results in dramatic changes in the cross polarization (CP) dynamics. For samples with both weak homonuclear and heteronuclear dipolar couplings, the matching condition is only 1-2 kHz wide at 10 kHz MASS rates. The maximum CP signal for the rare spins S is also rather weak with an amplitude which is nearly the same as the Bloch decay signal. In addition, intensity distortions are observed in CP spectra due to the resonance offset effects. In this paper it is shown that if the phases of the two RF channels are simultaneously inverted many times during the CP contact, the matching width can be broadened to about 8 kHz, the S magnetization doubled, and intensity distortions significantly reduced. These useful features of rapid simultaneous phase inversion CP with high speed MASS are theoretically shown to be the result of different spin dynamics than encountered in static samples where slower phase inversion is employed.

INTRODUCTION

The combination of cross polarization (CP) (1) and magic angle sample spinning (MASS) (2) NMR has become one of the most powerful analytical tools for the study of solid samples. Perhaps the most widespread application involves CPMAS ^{13}C NMR of organic solids. In this instance it is usually desirable to spin at rates equivalent to at least 150 ppm at the field strength used, primarily to avoid the complications due to spinning sidebands. Although a number of elegant methods have been devised to suppress spinning sidebands without resorting to very high MASS rates, it is often the simplest solution when complex samples are studied, very high dynamic range is required, or quantitation is important. A decade ago these criteria lead many workers in the area to consider fields the order of 2.35 T (100 MHz for ^1H) optimum for many ^{13}C CPMAS applications. Since then MASS technology has made significant strides, and spin rates in excess of 15 kHz and even 20 kHz are routine with commercially available equipment. These advances have made it possible to perform high resolution solids and solution NMR experiments on the same instrument without sacrificing the high field strength desirable for solution work. This in turn has made routine solids NMR accessible to many more laboratories as it is often difficult to justify a separate low field spectrometer for solids work.

The remaining difficulty in making applications of CPMAS NMR truly routine at high fields is that the high MASS rates can interfere with the cross polarization process. This difficulty was recognized early in the development of CPMAS NMR and has been studied by several authors (3-5). The effects of high MASS rates on CP dynamics can be best described by considering a plot of the rare S spin, e.g. ^{13}C , signal intensity versus the

mismatch parameter defined as $\Delta\omega = (\omega_{1C} - \omega_{1H})$. For static samples this so-called Hartmann-Hahn (6) spectrum or matching curve is usually gaussian in shape and fairly broad. As long as MASS rates are less than the ^1H - ^1H dipolar couplings, this curve is relatively unaffected by MASS. However, when the MASS speed is larger than or comparable to the ^1H - ^1H dipolar couplings the Hartmann-Hahn spectrum breaks up into a series of sidebands. Maximal polarization transfer then occurs when $\Delta\omega$ is equal to an integer multiple of the MASS rate ω_r . At high MASS rates these peaks in the Hartmann-Hahn spectrum can be very narrow and the most efficient transfer is found for $\Delta\omega$ equal to either $\pm\omega_r$ or $\pm 2\omega_r$.

Experience in our laboratory with samples such as adamantane or hexamethylbenzene, where the ^1H - ^1H coupling is substantially suppressed by high-speed MASS, shows that the width of the peaks in the matching curve can be narrower than 1 kHz. This sensitivity of the matching condition to the spin rate can make it difficult to maintain an optimum CP match for an extended period of time. In addition, the maximum enhancements observed at 10 kHz MASS are much smaller than obtained for stationary samples. Resonance offset effects are also important in this regime and can result in intensity distortions if the required spectral width is large. Similar results, though not as dramatic, are also found for many samples such as glycine where the MASS does not have as substantial an effect on the ^1H - ^1H dipolar couplings.

Mechanical solutions that avoid these problems with using high speed MASS in CPMAS spectroscopy have been developed. One can flip the rotational axis away from the magic angle during CP (4) or use a combination of low-speed CP and high-speed data acquisition (7). Such methods require additional moderately specialized hardware and may not be easily adapted for use with the very highest MASS rates. We have been interested in devising

pulse sequences that will overcome this problem that can be implemented using standard CPMAS probeheads.

Experimentally it has been found that the simultaneous phase inversion CP (SPICP) sequence can be utilized at fast MASS rates for cross polarization in samples with small II and IS dipolar couplings. This method is much less sensitive to the Hartmann-Hahn matching condition than standard CP and results in an S spin signal enhancement closer to the theoretical maximum. The effectiveness of RF phase inversion under the mismatched Hartmann-Hahn conditions for a stationary or slow MAS sample has been discussed from different points of view by Levitt et. al.(8), Zhang et. al.(9,10), and recently by Wu et. al.(11). It will be shown that the CP dynamics for solids with weak II dipolar couplings is similar to that in liquids, which has been discussed by Levitt recently (12).

The remainder of this paper is organized as follows. First, a short description of the standard continuous wave cross polarization (CWCP) and the simultaneous phase inversion CP (SPICP) experiments are given. We then present an analysis of CP dynamics under fast MASS using a density operator approach based on a simple model SI spin pair. This analysis is compared to what is termed the "flip-flop" picture. Predictions from these models on CP dynamics under high speed MASS are then compared to experimental results obtained for several different types of samples.

THEORY

The simultaneous phase inversion cross polarization (SPICP) and the standard continuous wave CP (CWCP) pulse sequences are sketched in Fig. 1.a and 1.b respectively. In both cases the protons are spinlocked by an RF

field B_{1I} at a frequency ω_I close to the larmor frequency ω_{0I} . A second RF field B_{1S} is also applied to the S spins at a frequency ω_{0S} which again is close to resonance. In the SPICP sequence the phases of the two RF fields are shifted by π between the periods τ_{cp1} and τ_{cp2} which are repeated for a total of N times.

To compare the CP efficiencies of these two schemes with high speed MASS we will take an isolated SI spin pair as our basic spin system. This is a useful model as neither the I spin system nor the S spin system behaves as a reservoir with a homogeneous spin temperature on the timescale of interest here. This is especially true for the rare S spin system (11). A qualitative extension of this description to systems including II dipolar interactions can be done using the flip-flop picture of CP dynamics (vide infra).

During cross polarization the rotating frame Hamiltonian of the SI spin pair can be written as

$$\mathcal{H} = -\omega_{1I} I_x - \Delta\omega_I I_z - \omega_{1S} S_x - \Delta\omega_S S_z + b I_z S_z + \mathcal{H}_{II}. \quad [1]$$

where $\omega_{1I} = \gamma_I B_{1I}$ and $\omega_{1S} = \gamma_S B_{1S}$ are the amplitudes of the applied RF fields and $\Delta\omega_I$ and $\Delta\omega_S$ are the resonance offsets. The heteronuclear dipolar coupling constant for the SI pair b is given by

$$b = \frac{\gamma_I \gamma_S \hbar^2}{r^3} (3\cos^2\theta - 1), \quad [2]$$

where r is the internuclear distance and θ the angle between the internuclear vector and the static magnetic field. $\mathcal{H}_{II}$ is the homonuclear interaction among the abundant protons. The heteronuclear interaction

between the S spin and protons other than the directly bonded one will be suppressed for the moment. When the RF fields used are large enough to produce good decoupling, it is convenient to transform the Hamiltonian to a doubly tilted frame since the spin locked magnetizations we are interested in will lie along the effective fields in this frame. Defining the effective field angles with $\tan\theta_I = \omega_{1I}/\Delta\omega_I$ and $\tan\theta_S = \omega_{1S}/\Delta\omega_S$, the following Hamiltonian is obtained:

$$\begin{aligned} \mathcal{H}^T = & -\omega_{\bullet I} I_z - \omega_{\bullet S} S_z + b I_x S_x \sin\theta_I \sin\theta_S + b I_z S_z \cos\theta_I \cos\theta_S \\ & - b I_z S_x \cos\theta_I \sin\theta_S - b I_x S_z \sin\theta_I \cos\theta_S + \mathcal{H}'_{II} \end{aligned} \quad [3]$$

where the effective fields $\omega_{\bullet I} = [\omega_{1I}^2 + (\Delta\omega_I)^2]^{1/2}$ and $\omega_{\bullet S} = [\omega_{1S}^2 + (\Delta\omega_S)^2]^{1/2}$. $\mathcal{H}'_{II}$ is the homonuclear dipolar interaction transformed to this frame and it may be separated into a secular, $\mathcal{H}_{II}^{(0)}$, and nonsecular, $\mathcal{H}_{II}^{(ns)}$ term (13). For the moment we will restrict ourselves to an isolated IS pair and also drop these terms.

Close to resonance or in systems with a weak IS coupling, $|\omega_{1I}|, |\omega_{1S}| \gg |b|, |\Delta\omega_I|$, and $|\Delta\omega_S|$ making $\cos\theta_I \approx \cos\theta_S \approx 0$. In this instance the effective Hamiltonian is approximately

$$\mathcal{H}^T = -\omega_{\bullet I} I_z - \omega_{\bullet S} S_z + b \sin\theta_I \sin\theta_S (I_x S_x) \quad [4]$$

On resonance of course the effective fields become ω_{1I} and ω_{1S} and $\sin\theta_I \approx 1$. For simplicity then the on resonance Hamiltonian

$$\mathcal{H}^T = -\omega_{1I} I_z - \omega_{1S} S_z + b I_x S_x \quad [5]$$

will be used recognizing that any results obtained will be valid for small

resonance offsets provided the effective fields and the effective heteronuclear coupling $b \sin \theta_I \sin \theta_S$ are used to replace ω_{II} , ω_{IS} and b .

For the case of a pair of spin 1/2 nuclei it is convenient to further recast its Hamiltonian as

$$\mathcal{H}^T = -\Delta I_z^\Delta - \Sigma I_z^\Sigma + b(\Sigma_{++} + \Delta_{+-}) , \quad [6]$$

where $\Delta = \omega_{II} - \omega_{IS}$, $\Sigma = \omega_{II} + \omega_{IS}$ and the operators I_z^Δ , I_z^Σ , Σ_{++} and Δ_{+-} are defined by:

$$I_z^\Delta = \frac{I_z - S_z}{2} , \quad I_z^\Sigma = \frac{I_z + S_z}{2} , \quad [7]$$

$$\Sigma_{++} = I_+ S_+ + I_- S_- , \quad \text{and} \quad \Delta_{+-} = I_+ S_- + I_- S_+ .$$

In this way the Hamiltonian can be written in two parts as $\mathcal{H}^T = \mathcal{H}^{\Sigma T} + \mathcal{H}^{\Delta T}$ which commute with each other. In the product basis the Hamiltonian then can be written in simple block diagonal matrix form as:

	$ ++\rangle$	$ --\rangle$	$ +-\rangle$	$ -+\rangle$
$\langle ++ $	$-\Sigma/2$	b		
$\langle -- $	b	$\Sigma/2$		
$\langle +- $			$-\Delta/2$	b
$\langle -+ $			b	$\Delta/2$

[8]

As the magnetizations we are interested in will be spinlocked along the effective fields, we will primarily be interested in linear combinations of the I_z^Δ and I_z^Σ operators and their time development. Within the approximations made here, these two operators can be readily seen to evolve independently in the 2x2 subspaces of the above matrix representation of $\mathcal{H}^T$ as noted previously by Levitt in his treatment of J cross polarization (12). Therefore the problem reduces to the independent evolution of two pseudo-

spin 1/2 systems. In each case the effective Hamiltonian then is equivalent to

$$H_{eff} = -\Omega I_z + b I_x, \quad [9]$$

which is simply that for a spin 1/2 subject to an off resonance RF field. In the following, the component of the operator I_z^Δ in the Δ subspace is referred to $I_{\Delta z}$ and, similarly, the component of I_z^Σ in the Σ subspace is referred to $I_{\Sigma z}$.

Cross polarization of a static sample where $b \neq f(t)$ is then quite simply understood. As long as the sum of the RF fields $\Sigma \gg b$, the sum of the spinlocked I and S magnetizations, $I_{\Sigma z}$ is a constant of the motion. If the initial density operator $\rho(0)$ corresponds solely to I spin magnetization $I_z = I_z^\Sigma + I_z^\Delta$, maximal polarization transfer can be achieved by inverting $I_{\Delta z}$. In the Δ subspace this amounts to rotating $I_{\Delta z}$ about an effective field, and maximal inversion by the effective RF field b is obtained if the effective resonance offset Ω is zero. This effective resonance offset in this subspace is just the difference between ω_{1I} and ω_{1S} and thus the usual Hartmann-Hahn condition, $\omega_{1I} = \omega_{1S}$, is obtained as providing the greatest enhancement of the S spin magnetization. For small resonance offsets the condition can be easily seen to be equality in the amplitudes of the effective RF fields.

The role of the size of the heteronuclear coupling b is also made clear by the above treatment. As long as b is large compared to the mismatch parameter, cross polarization still takes place. The sensitivity of the limiting amount of coherent magnetization transfer at the beginning of cross polarization to a given mismatch is determined by the ratio of b to Δ . In systems with small IS dipolar interactions like adamantane, the sensitivity of the signal amplitude to the matching parameter is then as much due to a

small b value as to the small II interactions.

When the sample is spun at the magic angle, b becomes time dependent (14):

$$b(t) = \sum_{k=-2}^2 b_k e^{-i\omega_r t}, \quad [10]$$

where

$$\begin{cases} b_{\pm 1} = \frac{\gamma_I \gamma_S \hbar^2}{2r^3} \sqrt{2} \sin(2\beta) e^{\pm i\gamma}, \\ b_{\pm 2} = \frac{\gamma_I \gamma_S \hbar^2}{2r^3} \sin^2 \beta e^{\pm 2i\gamma}. \end{cases} \quad [11]$$

The situation in each subspace then becomes analogous to having two linearly polarized RF fields applied simultaneously. When the b_i are small compared to $|\Delta|$ and ω_r , the situation is familiar; only under a resonance condition will the effective "transverse field" $b(t)$ have an effect on the magnetization spin locked along the z axis. If neither Σ nor $|\Delta|$ is nearly equal to $n\omega_r$ ($n = 1$ or 2), both I_{zz} and $I_{\Delta z}$ are time independent, which means that there is no polarization transfer between the I and S spins. If $|\Delta|$ is equal to $n\omega_r$, $I_{\Delta z}$ will rotate around a "transverse field", while I_{zz} is kept constant. The polarization is transferred through flip-flop, and a positive S magnetization is created, as in the usual cases. On the other hand, if Σ is equal to $n\omega_r$, I_{zz} will rotate, while $I_{\Delta z}$ is kept constant. The polarization is also transferred from the I spin to the S spin. However, it is through flop-flop, and a negative S magnetization is created. This prediction has been confirmed by the recent observations by Meier (15). If the b_i are large enough, i.e. $b_i > \omega_r$, cross polarization can still take place at the unmodified Hartmann-Hahn condition $\Delta = 0$. This will

be true even if the II interactions are averaged by MASS as long as the IS interactions are larger than ω_r .

In this paper, we restrict ourselves to the situations where $b_1 < \omega_r$, and ω_r is much smaller than Σ . The theoretical treatment is similar to that of a pseudo-spin which was dealt with by Gan and Grant (16). The general form of the effective Hamiltonian in the Δ subspace is

$$\mathcal{H}_\Delta^T = a(t)I_{\Delta z} + b(t)I_{\Delta x} \quad , \quad [12]$$

The pseudo-magnetic fields, $a(t)$ and $b(t)$, are cyclicly dependent on time and have Fourier components:

$$\begin{cases} a(t) = \sum_k a_k \exp(ik\omega_{cp}t), \\ b(t) = \sum_{k=-2}^2 b_k \exp(ik\omega_r t). \end{cases} \quad [13]$$

The term $a(t)$ is the mismatch parameter Δ in our case. Under the simultaneous RF phase inversion, the frequency ω_{cp} may be different from ω_r , the rotor frequency, and may have infinite Fourier components.

For the standard CPMAS experiments, $\Delta = \omega_{1I} - \omega_{1S}$ is time independent so that a_k 's are all zero except a_0 . The zeroth-order average Hamiltonian is

$$\mathcal{H}_\Delta^{av} = \text{Re}(b_k)I_{\Delta x} + \text{Im}(b_k)I_{\Delta y} + (\Delta - k\omega_r)I_{\Delta z} \quad , \quad [14]$$

where k is chosen according to the condition $k\omega_r \approx \Delta$. It can be calculated that the time-dependence of the transferred S spin polarization is (12):

$$\langle S_x \rangle(\tau) = \frac{|b_k|^2}{|b_k|^2 + (\Delta - k\omega_r)^2} \sin \left\{ \frac{\tau}{2} \sqrt{|b_k|^2 + (\Delta - k\omega_r)^2} \right\} \quad [15]$$

The transferred S magnetization falls off, when $|\omega_\Delta - k\omega_r| \gg |b_k|$. The smaller the heteronuclear coupling, the narrower the matching width.

When the phases of both RF irradiations are inverted periodically, the situation becomes quite different. Under the condition $\tau_{cp1} = \tau_{cp2} = \tau_{cp}$, $a_0 = 0$. We will not use the same approach as Gan's, since the zeroth-order average Hamiltonian gives no difference for the different cases $|\Delta| = 0$, ω_r and $2\omega_r$. If, for example, during the first duration of CP, τ_{cp1} , $\Delta \approx \omega_r$, a rotating frame R is used which is defined by the transformation:

$$A^R = \exp(i\omega_r t I_{\Delta z}) A^T \exp(-i\omega_r t I_{\Delta z}). \quad [16]$$

When the phase inversion is synchronous with the MASS, for example $\tau_{cp} = \tau_r$, the average Hamiltonian during the period of τ_{cp1} in the frame R is :

$$\mathcal{H}^R(\tau_{cp1}) = \text{Re}(b_1) I_{\Delta x} - \text{Im}(b_1) I_{\Delta y} - (\Delta - \omega_r) I_{\Delta z}. \quad [17]$$

During the second duration τ_{cp2} , after the phase is inverted at the end of time τ_{cp1} , a new frame R' has to be used, because another component with frequency $-\omega_r$ is now effective. The frame R' is defined by

$$A^{R'} = \exp(-i\omega_r t I_{\Delta z}) A^T \exp(i\omega_r t I_{\Delta z}). \quad [18]$$

The average Hamiltonian during τ_{cp2} in the frame R' is

$$\mathcal{H}^{R'}(\tau_{cp2}) = \text{Re}(b_{-1}) I_{\Delta x} - \text{Im}(b_{-1}) I_{\Delta y} + (\Delta - \omega_r) I_{\Delta z}. \quad [19]$$

The time evolution operator at the end of $2\tau_r$ is

$$U^T(2\tau_r) = \exp(-i\tau_r \mathcal{H}^{R'}(\tau_{cp2})) * \exp(-i\tau_r \mathcal{H}^R(\tau_{cp1})). \quad [20]$$

The zeroth order average Hamiltonian during this period of time is:

$$\mathcal{H}^T(2\tau_r) = -\frac{I_{\Delta x}}{2} [\text{Re}(b_1) + \text{Re}(b_{-1})] + \frac{I_{\Delta y}}{2} [\text{Im}(b_1) + \text{Im}(b_{-1})]. \quad [21]$$

The "Zeeman term" disappears. The averaging Hamiltonian is independent of the mismatch amount $(|\Delta| - \omega_r)$, and the polarization is effectively transferred under the driving of the components b_1 and b_{-1} .

It can be shown that the higher order terms of the average Hamiltonian result in non-zero Zeeman terms, which will reduce the polarization transfer efficiency. The higher correction $\mathcal{H}^{(n)}$ contains factors $(\tau_{cp}|b_k|)^n$ and $(\tau_{cp}|\Delta - k\omega_r|)^n$. Thus for Eq. [21] to hold true, it is required that

$$(\tau_{cp}|b_k|), (\tau_{cp}|\Delta - k\omega_r|) \ll 1. \quad [22]$$

For the weakly coupled SI, $|b_k|$ is smaller than several kHz. The matching width that we want is about 5 kHz. So τ_{cp} should be in the time scale of several hundred μs .

For SPICP with $\tau_{cp1} = \tau_{cp2} = \tau_{cp}$, $\Delta(t)$ can be expressed as a Fourier Series (17):

$$\Delta(t) = \frac{4|\Delta|}{\pi} \sum_k \frac{1}{(2k+1)} \sin\left[\frac{(2k+1)\pi t}{\tau_{cp}}\right] \quad [23]$$

If the phase inversion is not synchronized with the MASS, for example, when $\tau_{cp} = \tau_r(1+\epsilon)$, where ϵ is the measurement of the deviation, a non-zero Zeeman term is created, which is:

$$\bar{\Delta}(2\tau_{cp}) I_{\Delta z} = I_{\Delta z} \frac{4|\Delta|}{\pi^2} \sum_k \frac{1}{(2k+1)^2} \sin^2 \frac{(2k+1)\pi}{1+\epsilon}. \quad [24]$$

It turns out from Eq. [24] that the synchronization is more important under

the conditions $|\Delta| \sim \omega_r$ or $2\omega_r$ than $|\Delta| \sim 0$ and for weaker couplings b .

As mentioned before, the resonance offset is equivalent to changing the ω_{eI} , ω_{eS} , and reducing the heteronuclear coupling constant by a factor $\sin\theta_I \sin\theta_S$. In SPICP, these effects on CP efficiency are much smaller than in the CWCP.

The quantum mechanics calculation by using the density operator theory is a strict one. Nevertheless, it becomes quite complicated, when the number of the protons in the SI_n subsystem is increased and the I-I coupling is included. Actually, the enhancement of the CP efficiency under SPI, can be partially explained by using a flip-flop picture. The energy level diagram for the SI pair is schematically shown in Fig. 2 (11). For the I spin, the Zeeman splitting is determined by the strength of the RF irradiation ω_{II} . For the S spin, the splitting is determined by ω_{IS} . We shall denote the eigenenergies of the proton as E_a and E_b with corresponding wave functions $|a\rangle$ and $|b\rangle$. The eigenenergies of the S spin are likewise E_1 and E_2 , with corresponding wave functions $|1\rangle$ and $|2\rangle$.

The elemental step in the CP is a flip-flop process that interchanges the polarization within a pair of dipolar coupled spins. From perturbation theory, the flip-flop, i.e., the transition between the product state $|a2\rangle$ and $|b1\rangle$, will occur with a probability (18):

$$W_{a2 \leftrightarrow b1} = \frac{2\pi b^2}{\hbar} |\langle a2 | I_+ S_- + I_- S_+ | b1 \rangle|^2 \delta[(E_a + E_2) - (E_b + E_1) \pm \omega\hbar], \quad [25]$$

where $b(I_+ S_- + I_- S_+)$ is the flip-flop term of the heteronuclear interaction, $(E_a + E_2)$ and $(E_b + E_1)$ are the energies of the spin pair before and after flip-flop, and ω is the frequency contained in the perturbation b .

When the sample is spun, the imbalance of the Zeeman energies can be compensated for by the sample spinning, since the heteronuclear coupling

contains frequencies ω_r and $2\omega_r$. As a result, the most effective flip-flop occurs when

$$\omega_{IS} - \omega_{II} = \pm n\omega_r, \text{ with } n = 1 \text{ or } 2. \quad [26]$$

When $(\omega_{IS} - \omega_{II})$ is not exactly equal to $\pm n\omega_r$, there is an amount of energy imbalance

$$(\omega_{IS} - \omega_{II} \mp n\omega_r), \quad [27]$$

which needs to be compensated for. When the homonuclear interaction is effectively averaged by fast MASS, the energy balance can be maintained by the heteronuclear coupling, $b(I_x S_x + I_y S_y)$, if it is strong enough. This is confirmed by Eq. [14], where the variation of $(\Delta - k\omega_r) \langle I_{\Delta z} \rangle$ represents the Zeeman energy imbalance during the polarization transfer (after being compensated for by the spinning). This imbalance can be compensated for by the term $[\text{Re}(b_k) I_{\Delta x} - \text{Im}(b_k) I_{\Delta y}]$, since the total energy is a constant of motion. When $\mathcal{H}_{II}$ and $\mathcal{H}_{IS}$ both are weak, the matching width is extremely narrow.

SPICP can increase the CP efficiency when $\mathcal{H}_{II}$ and $\mathcal{H}_{IS}$ both are weak. The reason is that the fast simultaneous phase inversion in the two channels averages the difference of two Zeeman energies, $[(E_a + E_2) - (E_b + E_1)]$, eliminating the obstacle for the flip-flop of the spin pair SI. As shown in Fig. 2, before the phase inversion, the transition from state $|a2\rangle$ to state $|b1\rangle$ will, for example, relieve an amount of energy $(\omega_{II} - \omega_{IS})$. When RF phases are inverted, the Zeeman energies for states $|a2\rangle$ and $|b1\rangle$ are inverted. The same transition now needs to absorb the same amount of energy. When the phase inversion is fast enough compared with the difference $|\omega_{II} - \omega_{IS}|$, the net energy change before and after flip-flop will be averaged to zero, which is similar to the phenomena known as motional averaging. As a result, a much bigger mismatch amount is tolerable,

corresponding to a much broader matching width and a much less offset dependence. And more SI pairs are allowed to flip-flop rapidly, resulting in a stronger signal. This picture can be easily applied to SI_n subsystems coupling to other I spins.

EXPERIMENTS

The CWCP and SPICP experiments have been performed on several samples. The samples used fall into three different categories: (A) with strong $\mathcal{H}_{II}$ even at high-speed MASS such as glycine, (B) with weak $\mathcal{H}_{II}$ but strong $\mathcal{H}_{IS}$ such as ferrocene, (C) with both weak $\mathcal{H}_{II}$ and $\mathcal{H}_{IS}$ such as adamantane and HMB. The results are quite different.

The experiments have been performed on a homebuilt NMR spectrometer controlled by a Tecmag data system and using an Oxford instrument 7.05 T, 89-mm room temperature bore superconducting solenoid. The proton RF channel of the spectrometer is configured such that all four quadrature phase are available at two independently adjustable power levels. In the most of the experiments, a fixed proton RF level, $\omega_{II}/2\pi = 45$ kHz, has been used for the 90° pulse and decoupling. In the SPICP experiments, the RF strength $\omega_{II}^{(1)}/2\pi$ for the protons during τ_{cp1} is fixed to the same strength. The mismatch amount $\Delta\omega^{(1)} = \omega_{IS}^{(1)} - \omega_{II}^{(1)}$ can be finely adjusted by using a fine in-line attenuator with the smallest step of 0.1 db. The RF strength $\omega_{IS}^{(2)}$ during τ_{cp2} is determined by the same attenuator. Once $\omega_{IS}^{(2)}$ is fixed, the mismatching condition $\Delta\omega^{(2)} = \omega_{IS}^{(2)} - \omega_{II}^{(2)}$ can be finely adjusted by using another in-line attenuator. In this way, the mismatch amounts $\Delta\omega^{(1)}$ and $\Delta\omega^{(2)}$ can be independently controlled. The RF intensities are measured by using the single pulse experiment.

A Doty CP MASS probe with a high speed spinning system has been used. The inner diameter of the rotor is 3.5 mm, while its effective sample length is 10 mm. The MASS speed is controlled by changing the air pressure which drives the spinner and is stabilized by using a pair of standard air pressure regulators. The speed is monitored with a digital speed counter as well as the oscilloscope. The fluctuation of the speed at 10 kHz is smaller than ± 100 Hz.

RESULTS

1. CWCP experiments on adamantane

Figure 3 shows the plot of M_s versus $\Delta\omega/2\pi = (\omega_{1S} - \omega_{1I})/2\pi$ using a contact time of 8 ms and $\omega_{1I}/2\pi$ set to 45 kHz. The maximum S signal is obtained under the conditions $(\omega_{1S} - \omega_{1I})/2\pi = \pm 0, 10, 20$ kHz. The CWCP behavior has the following features:

A. The maximum peaks are very sharp. They are much sharper than that at 2.2 kHz MASS (3). The matching width is only about 1 ~ 2 kHz. This feature puts a very strict requirement on the high stability of the RF irradiations, which is difficult to maintain for a long period of time in practice. This is also the underlying element for other phenomena observed at high-speed MASS.

B. The optimum CP rate is the same order of magnitude as in a stationary sample. Figure 4 shows the S magnetization as the function of cross polarization time τ_{cp} under the conditions $\omega_{1I}/2\pi = 45$ kHz, while $\omega_{1S}/2\pi = 25, 35$ and 45 kHz, respectively. The data for $\omega_{1S}/2\pi = 55$ and 65 kHz are similar to that for $\omega_{1S}/2\pi = 35$ and 25 kHz, respectively. As a comparison, the CWCP curve, scaled down to 3/10, for a stationary sample

under the matched condition $\omega_{IS} = \omega_{II}$ is also displayed. It turns out that when $\omega_{IS} - \omega_{II} = \pm n\omega_r$ ($n = 1, 2$), the initial CP rates at 10 kHz MASS has also a time constant of about 1 ms.

C. The maximum CP MASS S signal is relatively weak. It is only about 35% of that of a stationary sample. The CP gain can be measured by the ratio of the CP S signal to the Bloch decay signal, which is obtained by using a 90° pulse in the S channel instead of the CP. For a stationary sample, the CP gain can reach 3.3 in our experiments. However, it is only about 1.0 at 10 kHz MASS.

It is noticed in passing from Fig. 4 that though the CP rate for $n = 0$ (i.e., $\omega_{IS} \approx \omega_{II}$) is about 1/7 of that for $n = \pm 1$, the maximum S magnetization obtained after 8 ms of contact time is still quite large, being about 60 % of that for $n = \pm 1$.

D. The matching condition is very sensitive to the size of the resonance offset. The experimental observations are as follows. The optimum matching condition was first adjusted under the condition that the carrier frequencies in both I and S channels were set on resonance. Then the carrier frequencies were shifted and the S signals were recorded. It turns out that the optimum matching condition is spoiled by the change of the offset. The weaker the RF irradiation, the bigger the signal drop as expected. Under condition $\omega_{II}/2\pi = 45$ kHz, $\omega_{IS}/2\pi = 35$ kHz, 3 kHz offset in proton channel (~ 10 ppm) results in a signal drop by about 20 %, 7.5 kHz offset in ^{13}C channel (~ 100 ppm) results in a signal drop by about 50 %. When $\omega_{IS}/2\pi = 55$ kHz, for 7.5 kHz offset in the ^{13}C channel, the signal drop is about 30%.

2. SPICP experiments on adamantane

A. Simultaneous phase inversion cross polarization (SPICP) can enhance the CP effectiveness dramatically. Figure 5 shows a part of the M_S vs $\Delta\omega/2\pi$ curves (o) obtained by using SPICP. As a comparison, the M_S vs $\Delta\omega/2\pi$ curve under CWCP (+) is also displayed and the Bloch decay signal is taken as 100 %. The total contact time is 8 ms in the both CP experiments. The durations for SPICP are: $\tau_{cp1} = \tau_{cp2} = 200 \mu s$. It turns out that, by using SPICP, the matching width is much broadened, the HHW being now about 8 kHz, and the maximum M_S signal is enhanced up to 250 %. The offset effect is also less severe than in CWCP. The signal drops are about 10, 30, and 10 %, respectively, under the same conditions mentioned above for CWCP. For bigger offset, the effectiveness of SPICP is more obvious. For example, when $\omega_{IS}/2\pi = 35$ kHz and the resonance offset in the S channel is 9 kHz, the residual signal for CWCP is only 20 %, while for SPICP, it is 60 %.

The much broader matching width is very important from the point of view of practice, because it means that a much bigger irradiation intensity error or shift in time is tolerable.

B. In SPICP, the phase inversion frequency should be high. The faster the phases are inverted, the broader the matching widths are, as shown in figure 6, where M_S vs $\Delta\omega/2\pi$ curves obtained for different τ_{cp1} are displayed. The total contact time was 8 ms. For stationary or slow MASS CP, τ_{cp1} is taken to be about one millisecond, and the second or later phase inversion does not contribute to the signal a lot (11).

C. For the conditions $\omega_{IS} - \omega_{II} \approx \pm n\omega_r$, $n = 1$ or 2 , the phase inversion should be synchronous with the sample spinning. For $\omega_r/2\pi = 10$ kHz, $\omega_{IS} \approx \omega_{II} - \omega_r$, and $\tau_{cp1} = 200 \mu s$, the tolerable error in the synchronization is $\pm 5 \mu s$. As shown in Fig. 6, when $\tau_{cp1} = 220 \mu s$, the M_S nearly disappears completely. For $\omega_{IS} \approx \omega_{II}$, the synchronization is not important. When τ_{cp1}

increases from 200 μ s to 220 μ s, the M_s vs $\Delta\omega/2\pi$ curve near $\Delta\omega \approx 0$ changes only slightly.

D. The mismatch amounts for the two durations of contact time should be kept as the similar as possible, i.e., $\Delta\omega^{(1)} = \omega_{IS}^{(1)} - \omega_{II}^{(1)}$ during τ_{cp1} should be equal to $\Delta\omega^{(2)} = \omega_{IS}^{(2)} - \omega_{II}^{(2)}$ during τ_{cp2} . For adamantane, if $\Delta\omega^{(2)}$ differs from $\Delta\omega^{(1)}$ by 2 kHz, the M_s will drop more than one half.

3. SPICP experiments on other samples.

The 10 kHz SPICP MASS experiments have been performed on several different samples. The results are summarized in the Table 1. Where M_0 is the signal intensity obtained by CWCP with $t_{cp} = 8$ ms, M_s is that of SPICP with the same total contact time and with each duration of 200 μ s.

For hexamethylbenzene, the SPICP is almost equally effective as for adamantane. But the requirement of the synchronization of the phase inversion is not so critical. When $\Delta\omega = \pm \omega_r$, the tolerable error of the duration is about ± 10 μ s for the aromatic carbon, and is about ± 15 μ s for the methyl group. For ferrocene, the SPICP can increase the M_s only by 24 %, and the synchronization is less critical. For glycine, SPICP does not increase the signal intensity at all.

DISCUSSIONS

1. Comparison of experimental results with theory.

The different results of SPICP are caused by the different IS heteronuclear interaction as well as the different II dipolar interaction, as analyzed above. Table 2 lists some parameters which are important in determining the CP dynamics.

The proton linewidth (HHW) is the measurement of the II dipolar

interaction. As the MASS rate is increased, the proton linewidth for adamantane, HMB and ferrocene decreases rapidly, because of the small homogeneous contributions to the static linewidth (19). At 10 kHz MASS, the residual HHW is less than 1 kHz. On the other hand, glycine has still broad proton line width with HHW of 4.8 kHz, so that the CWCP matching width is broad even for the nonprotonated ^{13}C , which are weakly coupled to protons. For glycine, the signal is actually smaller with SPICP than with CWCP, because there is bigger loss of order due to the stronger proton coupling when the proton Zeeman spin temperature periodically inverted, which will be discussed in more detail later.

CP is a two-stage process for protonated rare spins (20). Thus the initial CWCP rate, or the corresponding time constant T_{IS} , is the measurement of the strongest IS heteronuclear interaction. As is well known, adamantane is a typical sample with weak heteronuclear interactions as well as weak homonuclear couplings (21). Under stationary conditions, the CP time constant is roughly one millisecond, which corresponds to a coupling intensity of 1 kHz. As a result, the matching width at 10 kHz MASS is extremely narrow and SPICP is very effective. In SPICP, the synchronization of the phase inversion is also critical. For 10 kHz MASS, 5 μs of deviation corresponds to an error $\epsilon = 5\%$. It can be calculated from Eq. [24] that for $n \approx \pm 1$, i.e., for $|\omega_{\Delta}| \approx 10 \text{ kHz}$, $\bar{\omega}_{\Delta}(t) \approx 0.47 \text{ kHz}$, which is comparable with b_k , resulting in the drop of the CP efficiency.

For $n \approx 0$, the synchronization is not so critical. However, the effective heteronuclear interaction for polarization transfer is b_0 , which is much smaller than $b_{\pm 1}$ or $b_{\pm 2}$, resulting in a relatively slow CP rate and a small polarized S magnetization, as shown in Fig. 7.

The requirement that $\Delta\omega^{(1)}$ during τ_{cp1} should be equal to $\Delta\omega^{(2)}$

during τ_{cp2} can be analyzed in a similar way as for the synchronization.

HMB has also both weak κ_{II} and κ_{IS} so that it behaves like adamantane. Because its κ_{IS} and κ_{II} are slightly stronger than that of adamantane, HMB has slightly broader CWCP matching widths and less sensitive to the synchronization. The difference in the CP behaviors for the two groups (aromatic ^{13}C and $^{13}\text{CH}_3$) is also consistent with the theory.

However, directly bonded rigid SI_n groups such as CH_2 in glycine and CH in ferrocene display very strong heteronuclear coupling. Ferrocene rotates about the five-fold axis rapidly. As a result, the MASS can effectively average both homo- and heteronuclear interactions (19,22). However, when the mismatch amount ($\omega_{IS} - \omega_{II}$) is equal to $\pm \omega_r$ or $\pm 2\omega_r$, the heteronuclear coupling is recovered (3). Consequently, its initial CWCP rate is very fast with a time constant of 45 μs and its CWCP matching width is quite broad, being 7 kHz. SPICP provides very little additional signal enhancement. Ferrocene at 10 kHz MASS has almost the same proton line width as HMB at 6 kHz. But their CP behaviors are very different. The dependence of the matching width on the coupling intensity b was noticed before by Wind et al. (5). At that time, however, there was no theory available to explain it.

2. The nature of smaller CP gain at high-speed MASS.

The fast CP rate and the smaller CP gain suggest that there is only a small portion of ^{13}C spins which can be polarized at a fast rate, no matter how well the two RF field strengths are adjusted. To investigate whether the heterogeneity is macroscopic or microscopic, the following experiment was designed. The adamantane powder sample is put in the central part of the rotor, while HMB is at one end. Both samples have a thickness of 2.5 mm. The proton resonance frequencies for the two samples differ from each other only by tens of Hz, and the I channel RF frequency is set in between. The S

channel RF frequency is set in the middle between the aromatic ^{13}C signal of HMB, M_{HMB} , and the $^{13}\text{CH}_2$ signal of adamantane, M_{ada} , so that the offset effect on the matching conditions is removed. A CWCP experiment was performed, where the intensity $\omega_{\text{H}}/2\pi$ was fixed to be 48 kHz, while $\omega_{\text{S}}/2\pi$ was varied around 38 kHz. It turns out that when the matching condition is optimum for M_{ada} , the signal M_{HMB} disappears completely. After the RF strength $\omega_{\text{S}}/2\pi$ is reduced by about 2 kHz, M_{HMB} signal becomes maximum, while M_{ada} is reduced to 16%. Exchanging the positions of the two samples does not change the fact that the optimum matching condition for the sample at the end of the rotor needs a smaller S channel RF strength. In addition, the maximum signal for the sample at the end of the rotor is much weaker than in the center.

Because the length of the coil is much shorter than the wave length of the RF irradiations used, it is reasonable to assume that the two RF fields have the same distribution across the coil, i.e., the ratio $\omega_{\text{H}}/\omega_{\text{S}}$ is a constant across the coil. Thus for stationary samples or slow-speed MASS, the optimum Hartmann-Hahn condition can be obtained for whole sample, not suffering from the inhomogeneity of the RF field strength. At high-speed MASS, the situation is different, since the optimum CP requires a mismatch amount $\omega_{\text{H}} - \omega_{\text{S}} = \pm \omega_r$. The actual mismatch amount varies from place to place when the RF field strengths are not homogeneous. It is measured that the 90° pulse of the proton channel is 5.2 μs for the sample in the center of the rotor, while it is 6.5 μs for the end of the rotor. That means the actual RF strength $\omega_{\text{H}}/2\pi$ in the center is 48.1 kHz, while it is 38.5 kHz at the end. Thus if the mismatch amount in the center is 10 kHz, it is 8.0 kHz at the end. It is necessary to reduce $\omega_{\text{S}}/2\pi$ by another 2 kHz to get an optimum CP condition for the end, which is just what we have observed. When the

matching width is very narrow, the variation of the actual mismatch amount due to the inhomogeneity of the RF field strength prevents the match from being established over the whole sample volume, resulting in a weak signal. This is also the reason why the CP signal after 8 ms of contact time is not much larger at $n = \pm 1$ than at $n = 0$, although the CP rates are quite different in the two cases. SPICP can increase the signal intensity for $n = \pm 1$ and ± 2 , because it broadens the matching width, increasing the effective volume of the sample.

The Doty probe used has a coil with a constant pitch. The diameter is 6.0 mm, while the length is 9.6 mm, which is slightly shorter than the effective length of the rotor. The theoretical calculation shows that, in this case, the homogeneity of the RF strength across the sample is less than optimal (23). Near the ends of the coil, there is an extremely large RF field gradient, so that it is not possible to achieve optimum CP conditions for a whole sample with a thickness of 2.5 mm. This is the reason why the sample at the end always contributes a much weaker CP signal. These facts show that the RF field homogeneity is important for a high-speed MASS probe. A variable pitch design is preferred (23).

3. The optimum phase inversion duration

The shortest τ_{cp} which can be used for SPICP at 10 kHz MASS is 100 μs if synchronization is necessary. However, shorter τ_{cp} means more phase inversions, if the total contact time is kept constant. Too many phase inversions will cause the attenuation of the S signal. One reason is technical: the phase shift between X and -X may not be exactly 180° . Another reason is physical. The dipolar "reservoir" in the I spin system will have different, often opposite "spin temperature" with respect to the "Zeeman reservoir". The orders in the two reservoirs can cancel one another,

reducing the spin locked I magnetization. This has been checked by the following experiments on adamantane. As shown in Fig. 1.c, before CWCP, the I magnetization is spin locked for 8 ms by a phase inverted irradiation. As the duration is decreased, the number of phase inversions is increased to keep the total spin locking time constant. It turns out that when the phase is inverted more rapidly, the polarized S signal becomes smaller, as shown in Table 3. The cancel of the orders during the phase inversion may be a reason why the S signal obtained by using SPICP does not reach the optimal value of 4 (corresponding to the γ 's ratio). For adamantane, the experiments show that the the maximum SPICP S signal can be obtained under the conditions: $t_{cp1} = 200 \mu s$ and the repeating time of the basic cycling N is 6 or 7, which corresponds to a total contact time 2.6 ~ 3.0 ms, as shown in Fig. 7.

4. The validity of some approximations taken in the theory.

Under our experimental conditions, $|\omega_{1I}|, |\omega_{1S}| \sim 40 \text{ kHz}$, $|\Delta\omega_{0I}| \leq 1.5 \text{ kHz}$, $|\Delta\omega_{0S}| \leq 5 \text{ kHz}$. For weakly or intermediately coupled IS pairs, $|b|$ ranges from 1 kHz to several kHz. Thus the dropping of $\cos\theta_I$ and $\cos\theta_S$ is reasonable.

The validity of the theoretical analysis starting from Eq.[17] requires the condition $|b(t)| \ll \omega_r$. The reason is similar to the case of the Bloch-Siegert shift, where the effect of the counter rotating part of the RF field can be neglected when the RF field strength is much smaller than the Larmor frequency (24). For 10 kHz MASS and weak IS coupling with a constant of a few kHz, this approximation is good enough. However, for the intermediate IS couplings where $|b(t)|$ is comparable with 10 kHz, the higher order terms in the Magnus expansion are needed (25). Consequently, all the five components have the contributions to the effective field. The theoretical prediction

expressed by Eqs. [17] etc. should be modified. For example, the efficient polarization transfer occurs also when the mismatch amount $\Delta\omega \approx n\omega_r$ with $n \geq 3$, as shown in figure 3 of the reference (3). In that case, the rotor speed is only 2.2 kHz, which is comparable with the IS coupling of adamantane. However, the inclusion of the higher order terms does not change the basic fact that the effective field driving the CP is quite large and the matching width is thus relatively broad compared with the weak IS coupling cases. When the IS coupling is larger than the rotor speed, the Magnus expansion does not converge. Thus some other approaches have to be applied. However, the basic trends obtained from the simplified analysis are consistent with the experimental observations under the strong IS coupling conditions.

CONCLUSION

When the sample spinning rate is larger than II dipolar coupling, the homonuclear interaction $\mathcal{H}_{II}$ will be averaged, and the Zeeman energy level broadening becomes very narrow. For some materials with fast molecular rotation, this will occur under lower spinning rate. When the II homonuclear interaction is suppressed,, the M_s vs $(\omega_{IS}-\omega_{II})$ curve for weakly coupled rare spins has very narrow peaks at $\omega_{II}-\omega_{IS} = \pm n\omega_r$ ($n = 0,1,2$). For the sample with a full rotor size, the cross polarization appears highly heterogeneous, and only a small portion of S spins can be polarized so that the CP S signal is relatively weak. The CP spectrum is also intensity distorted due to the resonance offset dependence of the matching condition. Fast simultaneous phase inversion of the RF irradiations eliminates the Zeeman energy imbalance resulting from the mismatched Hartmann-Hahn

condition and speeds up the polarization transfer. As a result, the matching width can be significantly broadened, the S signal can be doubled or more, and the resonance offset dependence is reduced. The most effective CP is obtained when the mismatch amount $\Delta\omega$ is equal to the rotor speed ω_r and the phase inversion is synchronous with the sample spinning. This requires a stable sample spinning rate. Non-synchronization of the phase inversion is also allowed when $\omega_{IS} \approx \omega_{II}$, but with lower CP efficiency. In SPICP, the requirement for very stable RF intensities as in CWCP is greatly reduced. This method is much easier to employ than flipping of the rotation axis or switching the rotor speed.

As mentioned by other authors(4), although the weak II dipolar interaction occurs mainly in contrived cases, one can expect to encounter such situations frequently in some special samples. Furthermore, since faster and faster spinning rate is available, the effects of fast MASS mentioned above will be encountered more frequently. In addition, the same principles also apply to the polarization transfer between rare spins.

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Table 1

Sample	$\omega_{1S} - \omega_{1I} \approx \pm \omega_r$			$\omega_{1S} \approx \omega_{1I}$	
	M_S/M_0	Matching width HHW(kHz)	Tolerable error in synchronization (μs)	M_S/M_0	Matching width HHW(kHz)
Adamantane	2.5	8.0	5	1.8	6.0
aromatic	2.5	8.0	10	1.3	8.0
HMB methyl			15	1.8	>10.0
Ferrocene	1.24	> 10.0	>50		
Glycine	< 1.0				

Table 2

Sample	^1H linewidth (HHW) (kHz)			CWCP T_{IS}^{-1} (kHz) at 10 kHz MASS	CWCP Matching width (HHW) (kHz)		$\frac{M_S(10 \text{ kHz})}{M_S(0 \text{ Hz})}$
	Spin rate				Spin rate		
	0 Hz	6 kHz	10kHz		0 Hz	10 kHz	
Adamantane	14	0.7	0.43	1.4	6	<1	0.30
aromatic				1.4	6	1	0.30
HMB	12.5	0.8	0.60				
methyl				6.0	6	2.4	
Ferrocene	15.6	1.42	0.86	22.0		7	0.55
COOH				1.7	9*	5	1
Glycine	30.5		4.80				
CH				56.0	14*	>10	

* at 1.7 kHz MASS

Table 3

Duration τ (ms)	Repeating times	S signal (%)
4.0	2	100
0.4	20	94.0
0.2	40	72.6
0.1	80	64.2
0.05	160	~ 0

Figure Captions:

Fig. 1. The pulse sequences utilized. (a) Standard Continue Wave Cross Polarization (CWCP). After a 90° pulse with phase Y or -Y is applied in the I spin channel, the I spins and the S spins are simultaneously irradiated with RF fields. Here $\omega_{II} = \gamma_I B_{II}$ and $\omega_{IS} = \gamma_S B_{IS}$ are the RF strengths for the I and S channel, respectively. (b) Simultaneous Phase Inversion Cross Polarization (SPICP), where τ_{cp1} and τ_{cp2} are two durations of CP with opposite phases in the both channels, and N is the repeating number of the basic phase inversion cycle. The mismatch amount during the two CP durations, i.e., $\Delta\omega^{(1)} = \omega_{IS}^{(1)} - \omega_{II}^{(1)}$ and $\Delta\omega^{(2)} = \omega_{IS}^{(2)} - \omega_{II}^{(2)}$, can be independently adjusted. (c) The I spin magnetization is spin-locked by a phase inverted irradiation before CP. The total spin locking time is 8 ms.

Fig. 2. The energies of the spin pair before and after the RF phase inversion. Before the phase inversion, $E_{a2} = +(1/2)(\omega_{II} - \omega_{IS})$, $E_{b1} = -E_{a2}$. After the phase inversion, E_{a2} and E_{b1} change their signs.

Fig. 3. The carbon-13 magnetization intensity of adamantane at 10 kHz MASS as a function of $\Delta\omega/2\pi = (\omega_{IS} - \omega_{II})/2\pi$ in a CWCP experiment. $\omega_{II}/2\pi$ is fixed to 45 kHz, while $\omega_{IS}/2\pi$ is varied. The matching width, i.e., the width of these maximum peaks, are very narrow, being 1 ~ 2 kHz.

Fig. 4. The CWCP carbon-13 magnetization intensity of adamantane at 10 kHz MASS as the function of the Cross Polarization time τ_{cp} under different Hartmann-Hahn mismatch conditions. $\omega_{II}/2\pi$ is fixed to 45 kHz, while $\omega_{IS}/2\pi$ is changed: o : 25 kHz, Δ : 35 kHz, + : 45 kHz. The CWCP curve for a stationary sample under the matched condition is also displayed (*), but scaled down to 30 % of its original intensity.

Fig. 5. The carbon-13 magnetization intensity of adamantane at 10 kHz

MASS as the function of $\Delta\omega/2\pi = (\omega_{1S} - \omega_{1H})/2\pi$ for the standard CWCP(+) and SPICP (o) with total contact time of 8 ms. The intensity obtained by using block decay is taken as the reference 100%. The durations for SPICP are: $\tau_{cp1} = \tau_{cp2} = 200 \mu s$. By using SPICP, the matching width is broadened to 8 kHz and the maximum signal is enhanced to 250 %.

Fig. 6. M_S vs $\Delta\omega/2\pi$ curves obtained by using SPICP with different τ_{cp1} for adamantane at 10 kHz MASS. $\bullet$: $\tau_{cp1} = 100 \mu s$, $\circ$: $200 \mu s$, $\square$: $400 \mu s$, and $+$: $220 \mu s$. The total contact time is about 8 ms. For the condition $\Delta\omega \approx -\omega_r$, the synchronization of the phase inversion with the sample spinning is important, while it is not for $\Delta\omega \approx 0$. The faster the phases are inverted, the broader the matching widths are.

Fig. 7. M_S vs N , i.e., the repeating number of the basic phase inversion cycle, in SPICP for adamantane at 10 kHz MASS. $\square$: $\omega_{1I} - \omega_{1S} = n\omega_r$ with $n = 1$, $\circ$: $n = 2$, while $+$: $n = 0$.

Table Captions

Table 1. The results of the simultaneous phase inversion CP at 10 kHz MASS on different samples. There M_0 is the Bloch decay signal obtained by using a single 90° pulse in the carbon channel instead of CP. For adamantane, SPICP is very effective. The matching width is broadened to 8 kHz and the maximum CP signal is enhanced to 250 %. When $\Delta\omega = \pm \omega_r$, the synchronization is very important with a tolerable error of 5 μ s. For hexamethylbenzene, SPICP is almost equally effective. But the tolerable error of the synchronization is larger due to the slightly stronger I-S and I-I couplings. For ferrocene, SPICP can increase the signal only a little. In the case of glycine, SPICP does not help at all.

Table 2. The important parameters in determining the CP dynamics. The proton linewidth (HHW) is the measurement of the I-I dipolar coupling intensity, while the initial CWCP rate, or the corresponding time constant T_{IS} , is the measurement of the I-S dipolar coupling intensity. $M_s(10 \text{ kHz})$ and $M_s(0 \text{ Hz})$ are the CWCP signal intensities obtained from the sample at 10 kHz MASS and at rest, respectively. At 10 kHz MASS, adamantane, HMB and ferrocene have very narrow proton linewidth due to the fast internal molecular motion. However, ferrocene has strong I-S coupling so that its CWCP matching width is still broad. In the case of glycine, the proton linewidth at 10 kHz MASS is still broad so that the CWCP matching width is broad even for the signal $^{13}\text{COOH}$ which has weak I-S coupling.

Table 3. The CWCP S magnetizations obtained by using the pulse sequence shown in Fig. 3c. Before CP, the I magnetization is spin-locked 8 ms by a irradiation with periodical phase inversion. The faster the phase inversion, the smaller the S signal.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

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