Selective Homonuclear Hartmann-Hahn for ^{13}C-^{13}C Polarization Transfer in Solution State NMR

T. R. Eykyn[1], and M. O. Leach[1]

[1]Cancer Research UK Clinical Magnetic Resonance Group, Institute of Cancer Research, Sutton, Surrey, United Kingdom

Introduction

Polarization transfer has become a commonplace technique for the enhancement of a variety of nuclei in high field nuclear magnetic resonance (NMR). In this abstract we consider selective homonuclear Hartmann-Hahn (1) as a method for polarization transfer between two scalar coupled ^{13}C nuclei. The transfer is mediated via the one bond scalar coupling which is of the order $^{1}J_{CC} = 50$ Hz and a transfer duration of $^{1}J_{CC}^{-1} = 20$ ms. We have achieved a 90% transfer of polarization using this method in a sample of isotopically enriched glycine. This may show particular utility in the field of dynamic nuclear polarization (DNP) and could be used as an addendum to already established DNP techniques (2) allowing the favourable enhancement to be 'stored' on long-lived nuclei and subsequently transferred to short-lived nuclei prior to observation.

Theory and Methods

A major limitation for achieving homonuclear coherence transfer between ^{13}C nuclei by conventional cross-polarization is the large chemical shift range. Resonance frequencies may be several kHz apart requiring the use of high power RF to cover the entire chemical shift range and may lead to problems with overheating and power deposition when applying long RF pulses. Furthermore ^{13}C nuclei, with the exception of carbonyls and quaternary nuclei, invariably possess one or more directly bound protons with a large one bond heteronuclear coupling constant of the order $^{1}J_{CH} = 140$ Hz. To circumvent these problems we propose using a doubly selective spin-locking pulse that is resonant with the two ^{13}C nuclei. This is achieved by modulating the amplitude of a square pulse with the function $\cos(\Delta\Omega t)$ where $\Delta\Omega = 1/2(\Omega_1 - \Omega_2)$ and applying the carrier of the spin-locking field midway between the two

Fig 1. Pulse sequence for ^{13}C-^{13}C polarization transfer by selective homonuclear Hartmann-Hahn.

chemical shifts. This modulation causes the response of the spin-lock field to be split into two side bands at $\omega_0 \pm \Delta\Omega$, which will be resonant with the two chemical shifts. Figure 1 shows a pulse sequence that can be used to achieve cross-polarization between two spins S = ^{13}C. A selective $(\pi/2)_y$ gaussian pulse is applied to one of the ^{13}C nuclei. A clear advantage of homonuclear transfer over its heteronuclear counterpart is that there is no need to calibrate the Hartmann-Hahn condition since the same transmitter coil generates both RF fields.
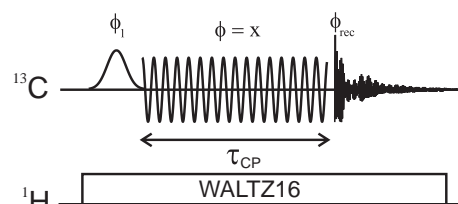
Results and Discussion

Coherence transfer functions have been simulated to examine the influence of heteronuclear ^{1}H-^{13}C couplings. A three spin system ^{13}C-^{13}C-^{1}H was assumed and the spin-lock amplitude set equal to the scalar coupling constant $\omega_1/2\pi = 50$ Hz. When the additional scalar couplings to ^{1}H were turned off, i.e. $^{1}J_{CH} = {}^{2}J_{CH} = 0$ Hz the coupling network reduces to a two-spin system with an optimum transfer observed for a spin-lock duration $\tau_{CP} = 1/{}^{1}J_{CC} = 20$ ms. When these heteronuclear ^{1}H-^{13}C scalar couplings were turned on they were found to be highly detrimental to the cross-polarization efficiency. This underlines the importance of ^{1}H decoupling during the Hartmann-Hahn period.

Figure 2 shows spectra for the optimum transfer from the carbonyl to the α carbon in uniformly ^{13}C labelled glycine. All spectra are acquired with co-addition of 4 transients, lb = 3 Hz and identical receiver gain. Fig. 2(a) shows a standard pulse acquire with ^{1}H decoupling during acquisition, i.e. no NOE enhancement. Fig. 2(b) shows a spectrum following selective excitation of the carbonyl ^{13}C with a 1ms gaussian pulse. Fig. 2(c) shows a spectrum following selective excitation of the carbonyl ^{13}C followed by cross-polarization to the alpha ^{13}C. The integrated signal in (c) is 91% that of the carbonyl signal in (b) and 88% of the alpha carbon from direct excitation in (a).

Experiments have also been carried out to examine the influence of spin-lock amplitude during the cross-polarization period. The optimum RF amplitude was observed for $\omega_1/2\pi \approx 200$ Hz. If the RF field strengths are less than this then the two components of the doublets are no longer efficiently locked. Conversely for RF fields with a much greater amplitude then there is cross-talk between the two side bands of the RF field which has a highly detrimental effect on the mechanism of cross polarization.

Conclusions

We have considered selective homonuclear Hartmann-Hahn as a method for ^{13}C-^{13}C polarization transfer. Under conditions of optimised RF field strength and ^{1}H decoupling the method was found to be highly efficient resulting in a 90% transfer of polarization. This technique may find utility in the field of dynamic nuclear polarization.

Acknowledgements

References

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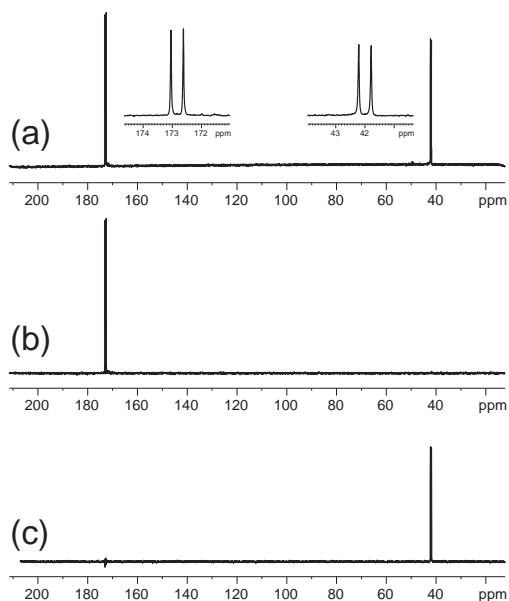
Fig 2. (a) ^{13}C spectrum of uniformly labelled glycine. Inset shows an expanded view of the two doublets. (b) Selective excitation of carbonyl carbon. (c) Resulting signal on the α-carbon following cross-polarization.