Coherent and incoherent magnetization transfer from hyperpolarised ^{129}Xe for enhancing secondary nuclei

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Introduction

The possibility of transferring the polarization from hyperpolarized ^{129}Xe to a secondary nucleus such as ^{13}C, ^{15}N, ^{19}F or ^{31}P would open up a wide variety of molecules that may be enhanced. In particular the ability to transfer the polarization to biologically active molecules and to follow the course of their metabolism would offer novel insights into a number processes that may otherwise be hindered by the sensitivity of conventional magnetic resonance.

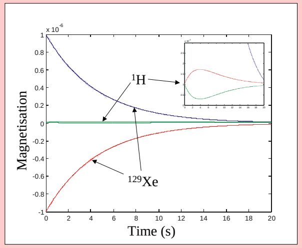
Magnetisation transfer from hyperpolarised ^{129}Xe has therefore been the subject of much interest in recent years (1). Polarisation transfer has been achieved to ^{13}C through low-field thermal mixing (2). This is achieved by reducing the external field to create a regime where difference in energies between the Zeemann levels of the two spin baths become matched. By analogy high-field RF driven polarisation transfer has been shown to be possible employing Hartmann Hahn cross-polarisation. Alternatively polarisation may also be transferred by cross relaxation between ^{129}Xe and ^{1}H in the solution state.

In this poster we present preliminary experiments for achieving polarisation transfer through cross-relaxation to ^{1}H in toluene. Differential enhancement factors for the benzene and methyl protons are tentatively attributed to differences in local correlation times and suggest the possibility of studying dynamic processes employing hyperpolarised ^{129}Xe. We also consider Hartmann Hahn cross polarisation as a potential technique for subsequently transferring the magnetisation from ^{1}H to ^{13}C and ^{15}N.

SPINOE magnetisation transfer

Polarization can be transferred from dissolved laser polarised xenon to surrounding solvent nuclei through cross-relaxation and is a manifestation of the nuclear Overhauser effect.

Below is shown a simulation of the decay of the ^{129}Xe polarisation and subsequent transient build-up, magnified inset, of the ^{1}H magnetisation on a neighbouring solvent spin assuming a two-spin system. The sign of the build-up depends on the sign of the hyperpolarisation and leads either to an enhancement or a reduction in the signal intensity with respect to the equilibrium signal.



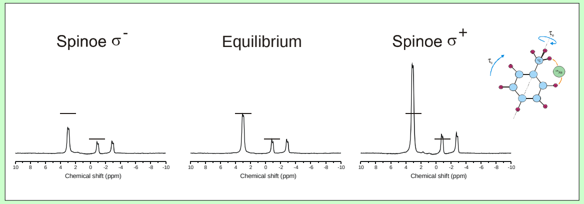
^{129}Xe → ^{1}H SPINOE enhancement in toluene

The figure (below) shows spectra recorded after SPINOE magnetization transfer from hyperpolarised ^{129}Xe to ^{1}H in toluene. The xenon, P ~ 10%, was initially frozen onto the surface of the toluene and then allowed to melt, forming ~ 1:1 mixture. Spectra were recorded with a single scan after 1 min to allow for cross-relaxation to occur.

Negative and positive polarization was achieved by reversing the sign of the current in the Helmholtz coil.

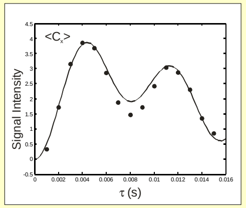
With positively polarized ^{129}Xe enhancement factors of 130% and 40% were observed for the benzene ring and methyl group, respectively.

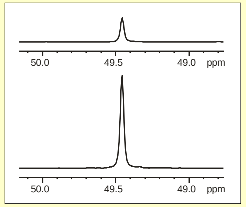
Different enhancement factors arise due to differences in cross relaxation rates. This is due to the difference in mobility of the methyl group compared to the benzene ring.



Coherent magnetization transfer from ^{1}H → ^{13}C by cross- polarization

Right shows the magnetisation transfer function from ^{1}H to ^{13}C in ^{13}C labelled methanol using Hartmann Hahn cross-polarisation. The pulse sequence employs two matched RF fields applied to the proton and carbon nuclei. Symbols correspond to the experimental signal intensity plotted as a function of the duration (3) of cross polarisation. The solid line is a numerical simulation employing MATLAB for an IS_3 spin system.

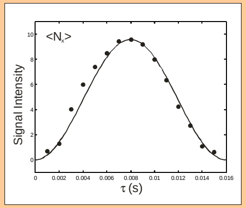


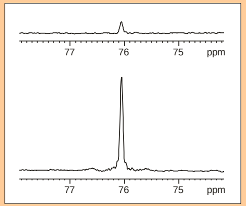


Left shows the enhanced ^{13}C signal in methanol acquired with a cross-polarisation duration of 4 ms and with ^{1}H decoupling. Top shows the equilibrium signal whereas the bottom is the signal after cross-polarisation. The integrated signal intensity is enhanced by a factor 3.9.

Coherent magnetization transfer from ^{1}H → ^{15}N by cross- polarization

Right shows the magnetisation transfer function from ^{1}H to ^{15}N in ^{15}N labelled urea using Hartmann Hahn cross-polarisation. The pulse sequence employs two matched RF fields applied to the proton and nitrogen nuclei. Symbols correspond to the experimental signal intensity plotted as a function of the duration (3) of cross polarization. The solid line is a numerical simulation employing MATLAB for an IS_2 spin system.





Left shows the enhanced ^{15}N signal in urea acquired with a cross-polarisation duration of 8 ms and with ^{1}H decoupling. Top shows the equilibrium signal whereas the bottom is the enhanced signal after cross-polarisation. The integrated signal intensity is amplified by a factor 9.6.

Conclusion

We have demonstrated preliminary results for achieving polarization transfer from hyperpolarised ^{129}Xe to ^{1}H through cross relaxation induced SPINOE. Differential enhancement factors were observed for the different protons in toluene.

We have also considered the possibility of subsequently transferring the polarisation from ^{1}H to ^{13}C or ^{15}N employing RF driven Hartmann Hahn transfer.

The next step will be to demonstrate the transfer ^{129}Xe to ^{1}H to ^{13}C.

Acknowledgements
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References

1) B. M. Goodson, J. Magn. Reson. **155**, 157-216 (2002).
2) A. Cherubini, G. S. Payne, M. O. Leach, A. Bifone, Chem. Phys. Lett. **371**, 640-644 (2003).
3) T. R. Eykyn, D. J. Philip, P. W. Kuchel, J. Chem. Phys. **118**, 6997 (2003),