Surface-Mediated Hyperpolarization of Liquid Water from Parahydrogen

Zhao, E.W.; Du, Y.; Zhao; Bowers, C.R. (UF Chemistry), Collins, J. (NHML AMRIS); Maligal-Ganesh, R.; Huang, W.; Ma, T.; Zhou, L.; Goh, T.-W.; Huang, W. (Iowa State Chemistry, AMES Lab)

Introduction

We discovered that Pt_3Sn intermetallic nanoparticles (iNPs), synthesized within a protective mesoporous silica shell ($Pt_3Sn@mSiO_2$), catalyze alignment of the proton magnetic moments in water as well as methanol and ethanol molecules using parahydrogen. In this SWAMP effect (Surface Waters Are Magnetized by Parahydrogen), a negative proton spin temperature is induced simply by bubbling parahydrogen through a suspension of the iNP catalyst in the neat liquid. The polarization transfer is mediated by symmetry-breaking surface interactions on $Pt_3Sn@mSiO_2$ nanoparticles. The hallmark of SWAMP is intense stimulated emission NMR signals of the exchangeable hydroxy protons. Non-exchangeable methyl or methylene protons also become hyperpolarized, an observation that provides insight into the molecular mechanism for polarization transfer. SWAMP has a myriad of potential applications, ranging from low-field MRI to drug discovery.

Experimental

A 10mm NMR tube was pressurized to 7 bar and heated to 120°C in the earth's magnetic field and p-H_2 was bubbled through the liquid suspension for about 20 s. The sample was then rapidly transferred by hand (in about 10s) from the lab bench to the field center of the 9.4 T or 17.6 T (750 MHz AMRS spectrometer). The ^{1}H NMR spectrum (**Fig.1**, right) or image was immediately acquired. For the image, the SPIRAL-EPI pulse sequence was used.

Results and Discussion

Insight into the surface interactions that mediate the SWAMP effect can be gleaned from the high-vacuum surface science literature on well-defined Pt(111), Pt_3Sn(111) and Pt_2Sn(111) surface alloys formed under high-vacuum conditions. The surface structure of the $Pt_3Sn@mSiO_2$ iNPs optimizes the balance between facile H_2 dissociation and restriction of H ad-atom surface diffusion.

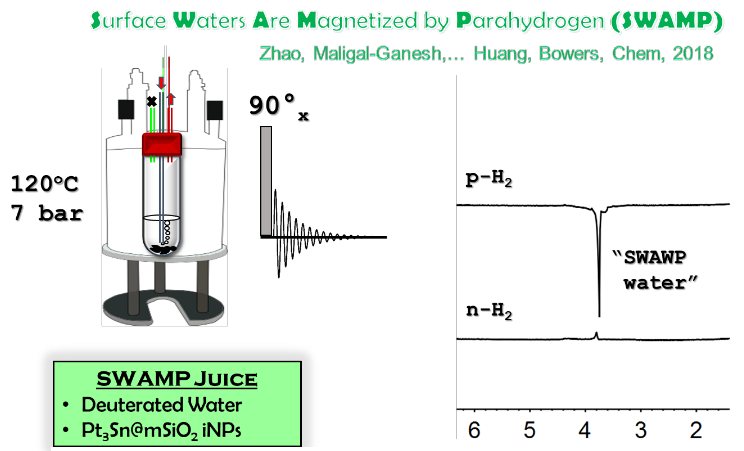

Fig.1 After bubbling parahydrogen through a suspension of .01% HDO/D_2O containing 50 mg of the insoluble Pt3Sn@mSiO_2 solid, the NMR tube was quickly placed into the 400 MHz or 750 MHz spectrometer. The spectrum exhibits a hyperpolarized HDO signal.

Conclusions

A key advantage of our heterogeneous $Pt_3Sn@mSiO_2$ catalyst is its insolubility, which allows it to be quickly and completely separated from the hyperpolarized water without any leaching, as previously shown. This remains a non-trivial problem for dissolved catalyst complexes. SWAMP can generate NMR-observable hyperpolarization of liquids that are free of free radicals, catalyst residues or other additives at low magnetic field. This could enable low field MRI without superconducting magnets which could enable wider access of this powerful medical diagnostic technique in remote or impoverished regions.

Acknowledgements

Supported by NSF grants CHE-1507230 and CHE- 1808239 (CRB). The work at Ames Lab (TM, LZ) was supported in part by the U.S. DOE BES, Contract DE-AC02-07CH11358. The 750 MHz magnetic resonance images were acquired in the McKnight Brain Institute at the NHMFL's AMRIS Facility, which is supported by National Science Foundation Cooperative Agreement No. DMR-1644779 and the State of Florida.

References

[1] Zhao, EW, *et al.,* Chem. **4**, 1387-1403 (2018).
[2] Zhao, EW, *et al.*, Chemie International Edition, **129**, 3983-3987 (2017).
[3] Bowers, CR and Weitekamp, DP, Physical Review Letters, **57**, 2645 (1986)