MRI-MRS Centre, Department of Chemistry
Indian Institute of Technology Madras

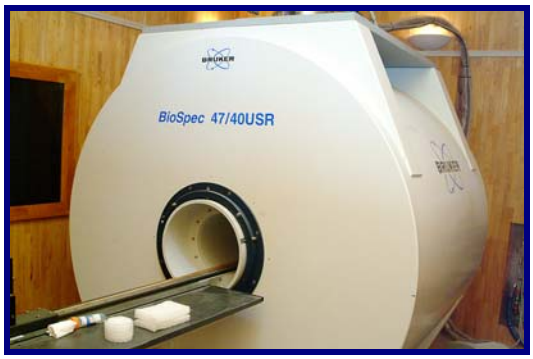
The MRI-MRS Centre was established late 2006 with support from the Department of Science and Technology and IIT Madras. The focus of the Lab is spatially resolved Magnetic Resonance (MR) and includes methodology development, as well as applications to a wide variety of systems. Spatially resolved Magnetic Resonance deals with the characterization of inhomogeneous, multi-component systems. In such systems, MR parameters are functions of spatial co-ordinates; spatial distributions of MR parameters are the primary object of investigation. Studies include MR imaging and microscopy (MRI/MRM), volume localized spectroscopy (MRS), and the measurement of transport, including self-diffusion, flow, etc. A state-of-the-art multi-band time domain DNP system, one of its kind worldwide, was added to the Centre in 2013, offering significant sensitivity enhancement for NMR work.

Current Facilities for Spatially Resolved NMR

The MRI-MRS Centre is currently equipped with three facilities

Bruker Avance II 500 MHz Microimaging system with Ultrashield Plus 89 mm bore magnet; imaging capability on a number of isotopes

200 MHz Bruker Biospec 47/40 USR system, with 4.7 T/40 cm bore MRI magnet



Multi-band Time Domain Dynamic Nuclear Polarization system for several isotopes

Research Interests

- Methodology development for spatially resolved MR and MR Spectroscopy
- Sensitivity enhancement
- Resolution enhancement
- Characterization of foodstuffs, membranes, fuel cells, etc., and *in vivo* studies by spatially resolved NMR
- Multivoxel MRS in Hadamard mode
- NMR self diffusion characterization of confined systems and micelles
- Diagonal suppressed homonuclear correlation spectroscopy
- Dynamic Nuclear Polarization (DNP) – Applications to sensitivity enhancement in NMR spectroscopy and in spatially resolved NMR
- Development of special purpose software and hardware sub-systems (*eg*., optimal control excitations; resonators)
- Optimal rare spin NMR correlation spectroscopy in solution and in solid state
- Ensemble quantum computing with electron-nuclear coupled spin systems
- Evolution of homonuclear zero and multiple quantum coherences under spin lock
- Ultrafast NMR methods

Recent Research

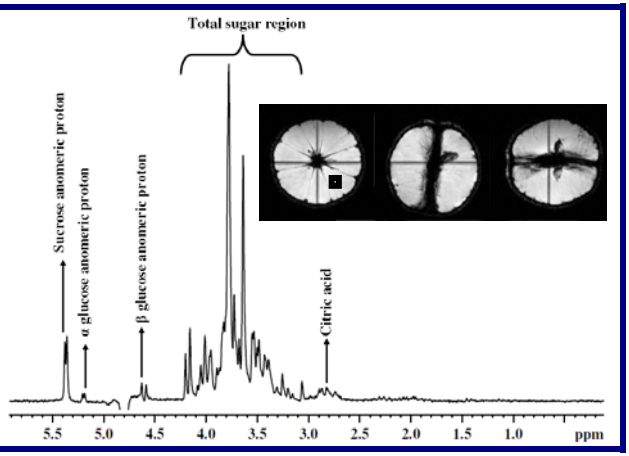
Spatially Resolved NMR

- Process Monitoring by Magnetic resonance Imaging and Spectroscopy
  - Permeability of fuel cell membranes
    - ✓ water permeability by NMR imaging/Microimaging (MRI/MRM)
    - ✓ Methanol permeability by Volume localized spectroscopy (MRS)
  - Measurement of self diffusion coefficients of water and methanol in fuel cell membranes
  - Monitoring the molecular imprint of Fruit Ripening (natural and artificial) by volume localized NMR

MRS studies of postharvest fruit ripening – natural ripening *vs.* acetylene induced ripening

On the right: Volume localized spectrum obtained from a cubic voxel of 4 mm edge in an intact sweet lime. Experiments were performed on the 200 MHz Biospec MRI system

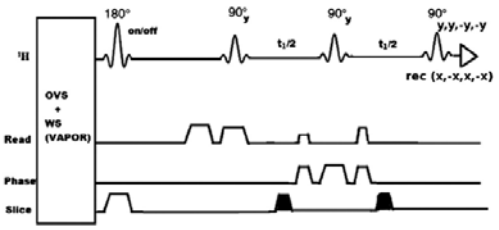
J Agri Food Chem (*ACS*), **2009,** *57*, 1183–87



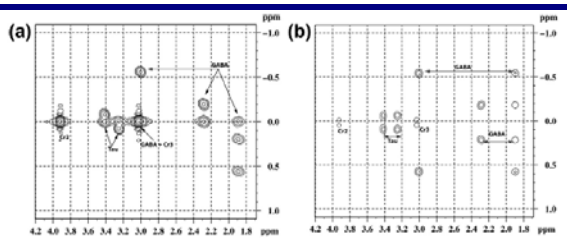
- *In vitro* Drug release studies by MRS
- Fuel cell flow field imaging *in situ*, under load
- Development and application of chemical shift selective volume localized ^{13}C MRS in direct and indirect detection modes

❖ Volume Localized DIagonal Suppressed Spin Echo Correlation specTroscopy (LDISSECT)

Volume Localized DISSECT pulse sequence



J Magn Reson, **2014**, *239*, 69-74



2D spectrum of a phantom (15 mM each of Cr, GABA and Taurine in 1% agar gel) obtained with volume localized (a) SECSY and (b) LDISSECT

High Resolution NMR Spectroscopy

❖ Multiply selective RF pulse sequences for 1D exchange spectroscopy-Applications to NQR, MAS NMR and solution state NMR

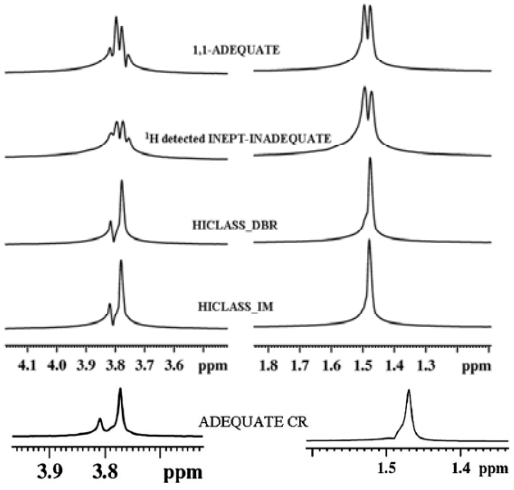
❖ Novel optimal experiments for 2D homonuclear correlation spectroscopy of rare spins – application to ^{13}C (CLASSY), ^{29}Si, $^{119/117}Sn$, … (LASSY); single transition selectivity reduces measurement time typically by a factor of 2; patented and technology transferred to international NMR equipment manufacturer

❖ Novel optimal experiments for ^{1}H indirect detected rare spin homonuclear correlation spectroscopy – Application to ^{13}C (HICLASS, ADEQUATE CR); partial transition selectivity in resulting ^{1}H multiplets, and reduction of measurement time typically by a factor of 2

HICLASS and ADEQUATE CR: Novel optimal experiments for indirect detected 2D homonuclear correlation spectroscopy of rare spins – application to ^{13}C; measurement time is typically halved

On the right: 400 MHz HICLASS and ADEQUATE CR spectra of alanine in D_2O (different scales). Partial transition selectivity achievable with our methods may be noted, unlike other known experiments.

Org Lett, **2011**, *13*, 5448-5451;
Magn. Reson. Chem., **2014**, *52*, 241-246



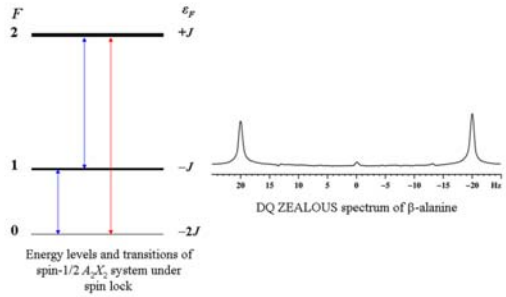
❖ Studies on ensemble quantum computing by rotating frame coherence transfer – improvement of efficiency

❖ Sensitivity enhanced multiple quantum filtered ^{23}Na spectroscopy–Applications to the discrimination of intracellular, extracellular and interstitial sodium in 'biological' systems

- Transition selective double quantum filtered deuterium NMR in systems with residual quadrupolar coupling
- 'Amplification' of scalar homonuclear couplings under multiple quantum spin lock (ZEALOUS) – potential applications *in vivo* and to measurement of unresolved couplings for structure elucidation

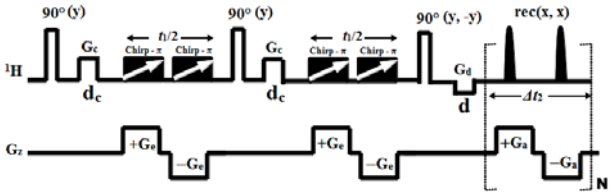
ZEALOUS: *On the right*: ZEALOUS spectrum of β–alanine. Homonuclear scalar couplings are amplified by a factor of 3.

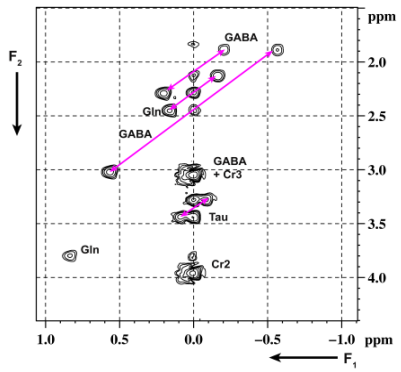
Chem Phys Lett, **2013**, *563*, 107-111



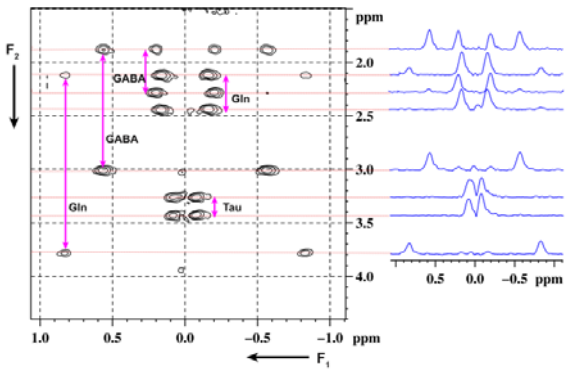
- Ultrafast Diagonal Suppressed Spin Echo Correlation Spectroscopy (UF-DISSECT) – 2D experiments in seconds instead of hours, with diagonal suppression; enables visualization of cross peaks between spins with close lying chemical shifts

Ultrafast DISSECT Pulse Sequence





Ultrafast SECSY



Ultrafast DISSECT

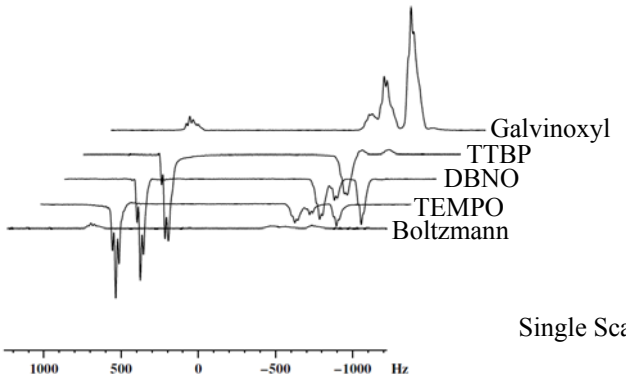
J. Chem. Phys.(Comm.), **2014,** *140 (#24), in press.*

Dynamic Nuclear Polarization

- ^{1}H, ^{19}F and ^{13}C DNP in solution state at low and moderate field strengths: 0.34 T, 1.2 T, 3.34 T; sensitivity enhancement corresponding to measurements at 4.7 T – 23.5 T
- Rare spin DNP by Polarization Transfer from abundant peripheral spins (*eg.* ^{13}C from ^{1}H/^{19}F)
- Spatially resolved DNP

❖ Differential DNP enhancement for structural information

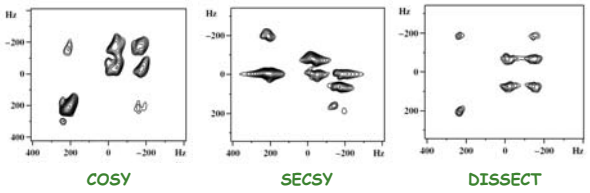
^{19}F differential DNP enhancements in octafluorotoluene obtained at *ca.* 13.7 MHz



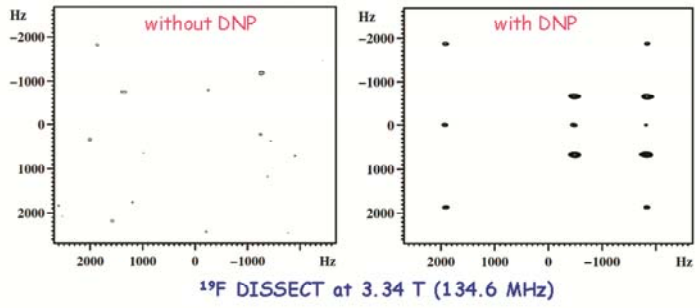
Single Scan

❖ DNP enhanced 2D homonuclear correlation spectroscopy, including DISSECT

DNP enhanced ^{19}F-^{19}F correlations at X-band



1,2,4-trifluorobenzene+C_6H_6 (1:4 v/v) with 20 mM TEMPO



1,2,4-trifluorobenzene + C_6H_6 (1:4 v/v) with 20 mM galvinoxyl; Sample volume ~2µl

Angew. Chem. Int. Ed., 2014, DOI: 10.1002/anie.201402320

Research positions for a Ph.D. degree are open for scholars with Chemistry/Physics/other relevant training, and CSIR/UGC Fellowship / GATE qualification. One year M.Sc./M.Tech./B.Tech. projects for students of IIT Madras can also be explored.
Contact: Prof. N. Chandrakumar (044-2257 4920; chandrakumar.iitm@gmail.com).