



NMR & MRI User Facility, Tallahassee

Tim Cross, Director

Ashley Blue, Bill Brey, Kyle Chen, Richard Desilets, Riqiang Fu, Zhehong Gan, Peter Gor'kov, Sam Grant, Yan-Yan Hu, Ivan Hung, Jason Kitchen, Ilya Litvak, Wenping Mao, Fred Mentink, Joana Paulino, Steve Ranner, Jens Rosenberg, Victor Schepkin,

Faith Scott, Robert Silvers, Sungsool Wi

Joanna Long, AMRIS Director

Lucio Frydman, Chief Scientist for Chem/Bio



FLORIDA STATE
UNIVERSITY



NMR/MRI User Program, Tallahassee

*In House Users: these people help to **drive new technology** and to **test new capabilities** so that when it is made available for external users, the technology works*

Lucio Frydman, Prof. of Chem & Bio Physics, Weitzman Inst. of Tech. Chief Scientist for Chemistry and Biology, MagLab

Tim Cross, Director of NMR & MRI User Program, Dept. of Chem & Biochem – Oriented Sample and MAS membrane protein spectroscopy

Yan-Yan Hu, Dept. of Chem & Biochem – Materials Research solid state NMR spectroscopy and MR Imaging

Sam Grant, Dept. of Chem & Biomed Eng. – MRI Probe Technology, Imaging & Spectroscopy

Robert Silvers, Dept. of Chem & Biochem – Solution & Solid State MAS Spectroscopy

Numerous other faculty from FSU, UF, and FAMU are occasional if not significant users

Joanna Long, Director of AMRIS, UF, Dept. of Biochem & Mol. Biol. – MAS & DNP Spectroscopy

NMR/MRI User Program, Tallahassee

These are some of the critical people who have been responsible for getting NMR spectroscopy operational on the SCH

Bill Brey, Associate Director of NMR & MRI User Program, NMR RF Technology, specialty in HTS RF coils

Ilya Litvak, NMR Technology, implementing NMR technology including Schiano's & Brey's Cascade Field Regulation System on the SCH

Peter Gor'kov, NMR Probe Technology & Engineering, specialty in designing and engineering the world's best solid state NMR probes

Zhehong Gan, Associate Director for Solid State NMR Spectroscopy specializing in spin physics & materials solid state NMR spectroscopy

Ivan Hung, specializing in spin physics & materials solid state NMR spectroscopy

Joana Paulino, specializing & facilitating bio applications on the SCH

Kyle Chen, specializing & facilitating materials applications on the SCH

NMR/MRI User Program, Tallahassee

These are other NMR & MRI Research Faculty and Staff that help the NMR & MRI Program Function

Riqiang Fu, Specializing in spin physics and both bio and materials ssNMR

Fred Mentink, Specializing in DNP spectroscopy

Sungsool Wi, Overhauser DNP, solution and ssNMR spectroscopy

Jens Rosenberg, Magnetic Resonance Imaging

Jason Kitchen, Probe development engineer and repair

Wenping Mao, PD RF engineer

Faith Scott, PD DNP Probe Engineer

Richard Desilets, Engineer and machinist

Ashley Blue, infrastructure oversight

Karol Bickett, oversees all things financial

Kim Mozolic, helps with all things financial

Mary Desilets, travel

NMR/MRI User Program, Tallahassee

User Report for 2017

Users: 280 Users

168 Senior Personnel:	120 US,	48 international
38 Postdocs:	32 US,	6 international
64 Students:	56 US,	8 international
10 Technicians	8 US,	2 international

Users:

Present:	96
Operating Remotely:	35
Sending Samples:	51
Off-Site Collaborations	98

Users:

Male	168
Female	53
Not Identifying	59

NMR/MRI User Program Instrumentation, Tallahassee

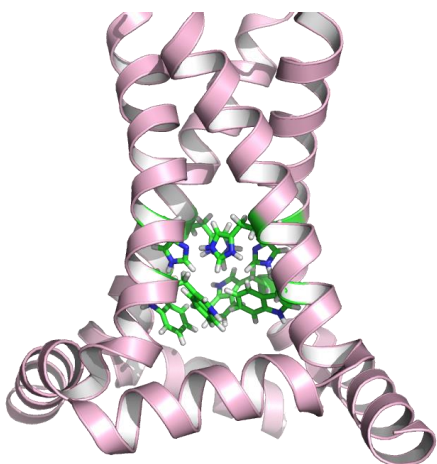
- **1500 MHz SCH Magnet**, - Materials and Bio ssNMR
 - Neo console**, Resistive & Ferro shims, Bruker Lock & Cascade Field Regulation
 - 3 probes – OS HX solenoid & Low-E RF coils, external lock & pick-up coils
 - X 3.2 mm MAS, external lock & pick-up coils
 - HX 2.0 mm MAS, external lock & pick-up coils
 - 500 hours at field for NMR so far this year***
- **900/105** – primarily MRI & some ssNMR
 - **NEO console and gradients on order**, MAS HXY 3.2 mm, OS HX probes
 - various MRI coils and probes
- **830/31** – primarily quadrupolar nuclei / materials research / STRAFI
 - double resonance **NEO console**, kW 1H & kW X channel
- **800/63 #1** – ssNMR/ MAS - bio & materials
 - **Avance III-HD** console, Low-E 3.2 mm MAS HXY; Bruker 1.3 MAS HCN
- **800/63 #2** – solid state NMR / MAS & OS - bio
 - **Avance I** console, #1 probes + OS Low-E probe (interchangeable coils)
- **800/52** – solution Instrument with **Avance II** console, TCI cryo probe

NMR/MRI User Program Instrumentation, Tallahassee

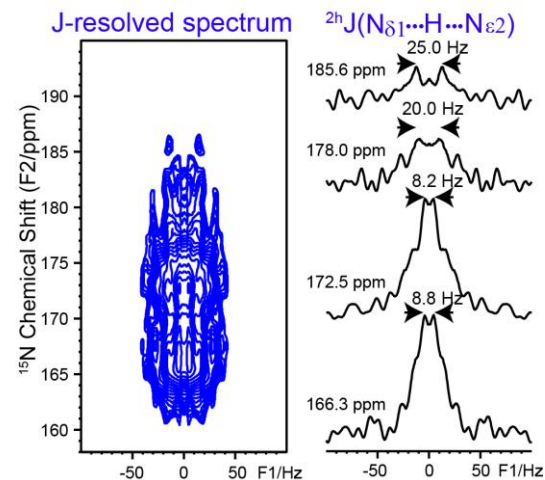
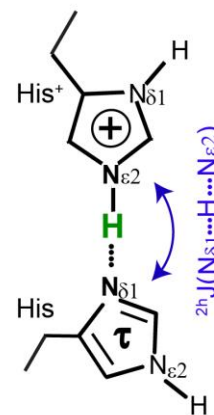
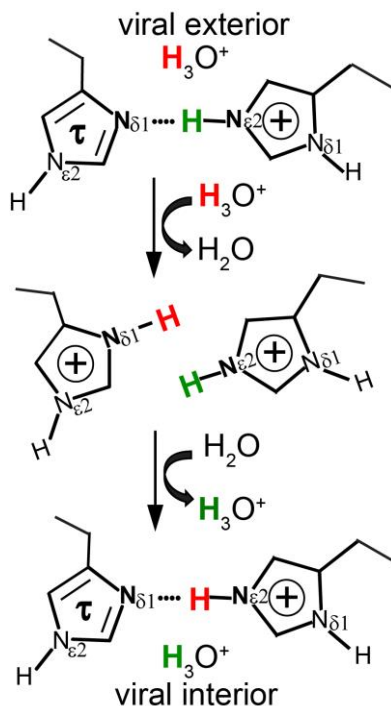
- **600/89 #1** – ssNMR MAS + OS – bio
 - **Bruker Neo**, kW 1H/19F & kW X
- **600/89 #2**– ssNMR MAS + OS – bio
 - **Avance 1**, 4 RF channels, 1-1H/19F kW amp & 2-1 kW amps for X
 - 1.3mm Bruker HCN, 2.5mm Bruker HCN, 3.2mm Low-E HXY and 4.0mm HXY, HF
- **600/89** Sweepable – DNP
 - **Avance III** 3 RF channels: 1kW 1H/19F & 2 1kW amps for X&Y channels
 - 3.2 mm MAS probe – LN cooled, Gyrotron and Quasi-optic table
- **600/53** Overhauser DNP – *solution NMR technology in development*
- **500/89** – ssNMR bio and materials
 - **Avance III** – 2.5 mm Bruker HXY probe
 - High temperature ssNMR laser probe –up to 700°C
- **400/89** – ssNMR – materials
 - **Avance I console**, *in situ* battery and STRAFI
- **300/89** – ssNMR
 - **Bruker DRX console** – 4 mm HX Bruker, 7 mm HCN Bruker, OS HP probe

SSNMR: 2D *J*-Resolved Spectrum Confirms Imidazole-Imidazolium Hydrogen Bonds in His-Tetrad of Full Length M2 Proton Channel

M2 protein from the *Influenza A* virus is a 97-residue membrane protein with a 22-residue N-terminal and a 51-residue C-terminal segment connected by a single transmembrane (TM) helix of 24 residues.



Model for proton conductance



Hydrogen Bond Mediated *J*-Couplings confirm the presence of imidazole-imidazolium hydrogen bonds

Fu & Cross, to be submitted

Formation and Breakage of Hydrogen Bonds monitored by SSNMR;

Miao et. al. *Structure*, 2015

Proton Conduction Rates determined by Chemical Exchange measurements



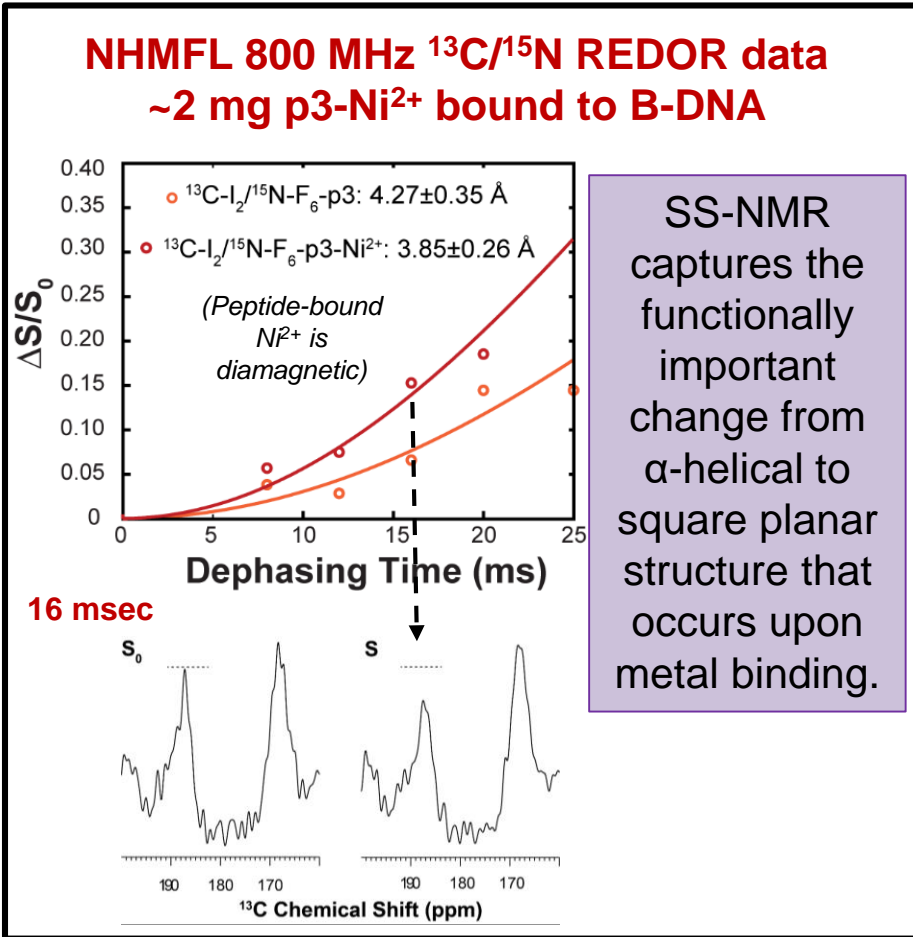
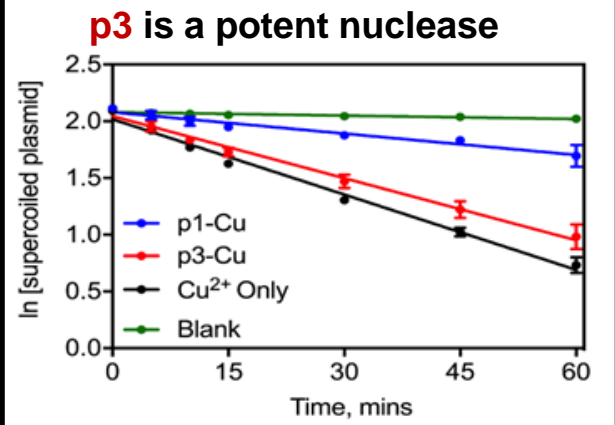
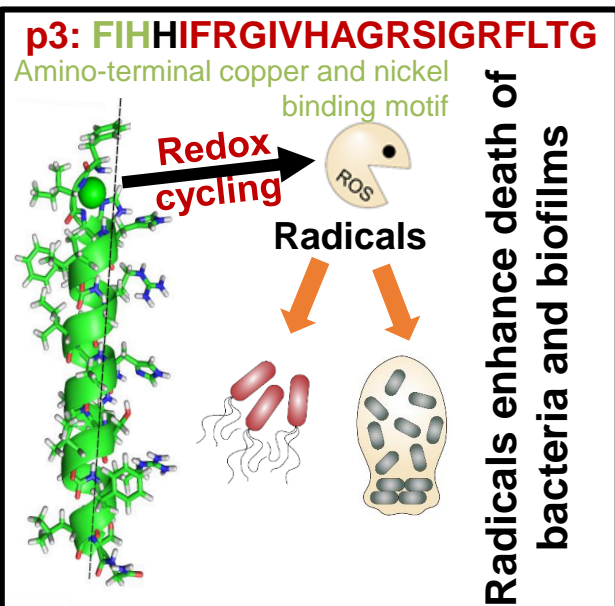
Structural Studies of Nuclease Activity by Host-Defense Peptide



Myriam Cotten
William & Mary



Riqiang Fu
NHFML



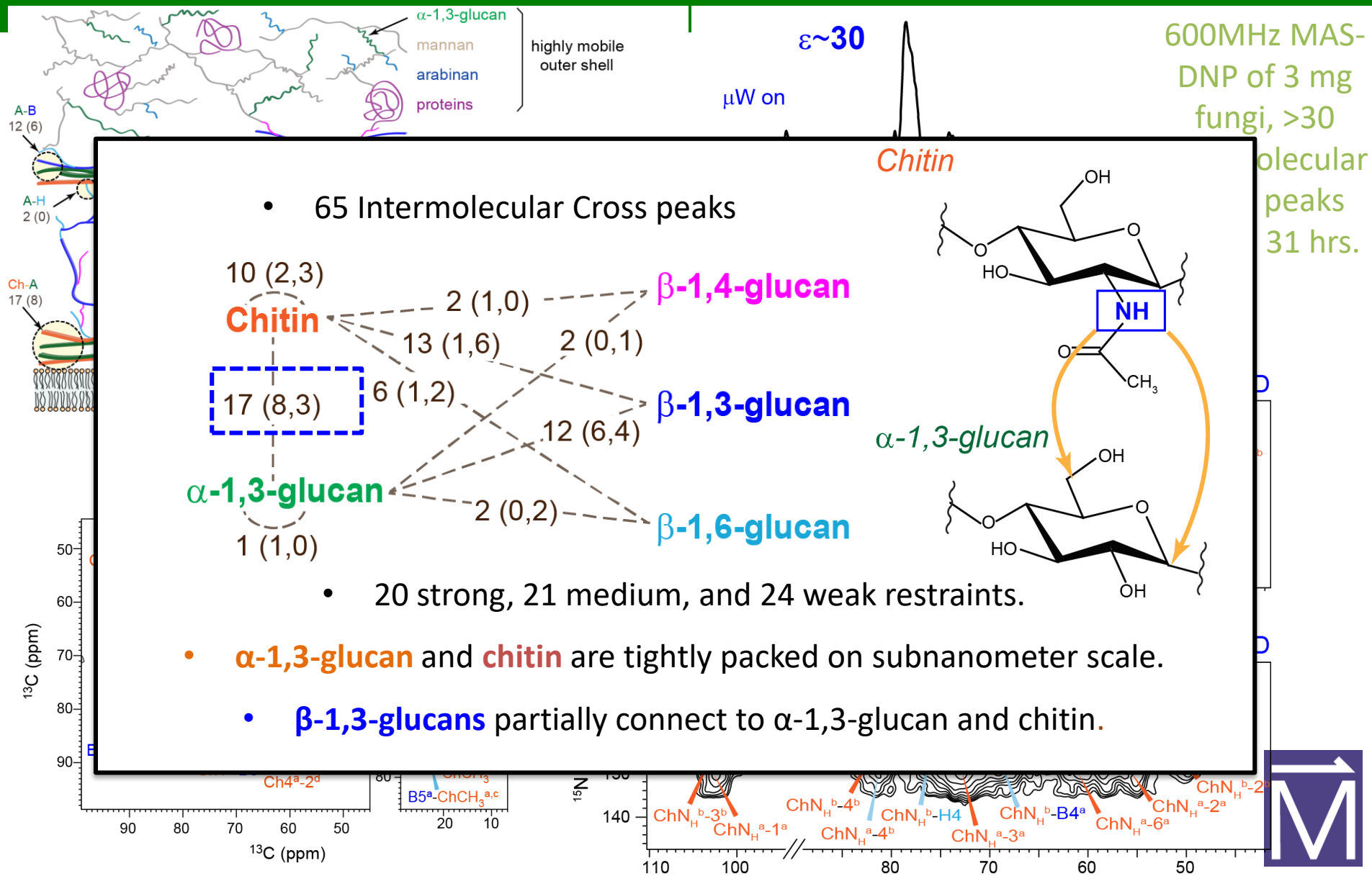
MD of aggregated p3-DNA complexes suggested an α-helical dimeric peptide structure but force field issues prevented MD of the p3-Ni²⁺-DNA complex

C-term
N-term.

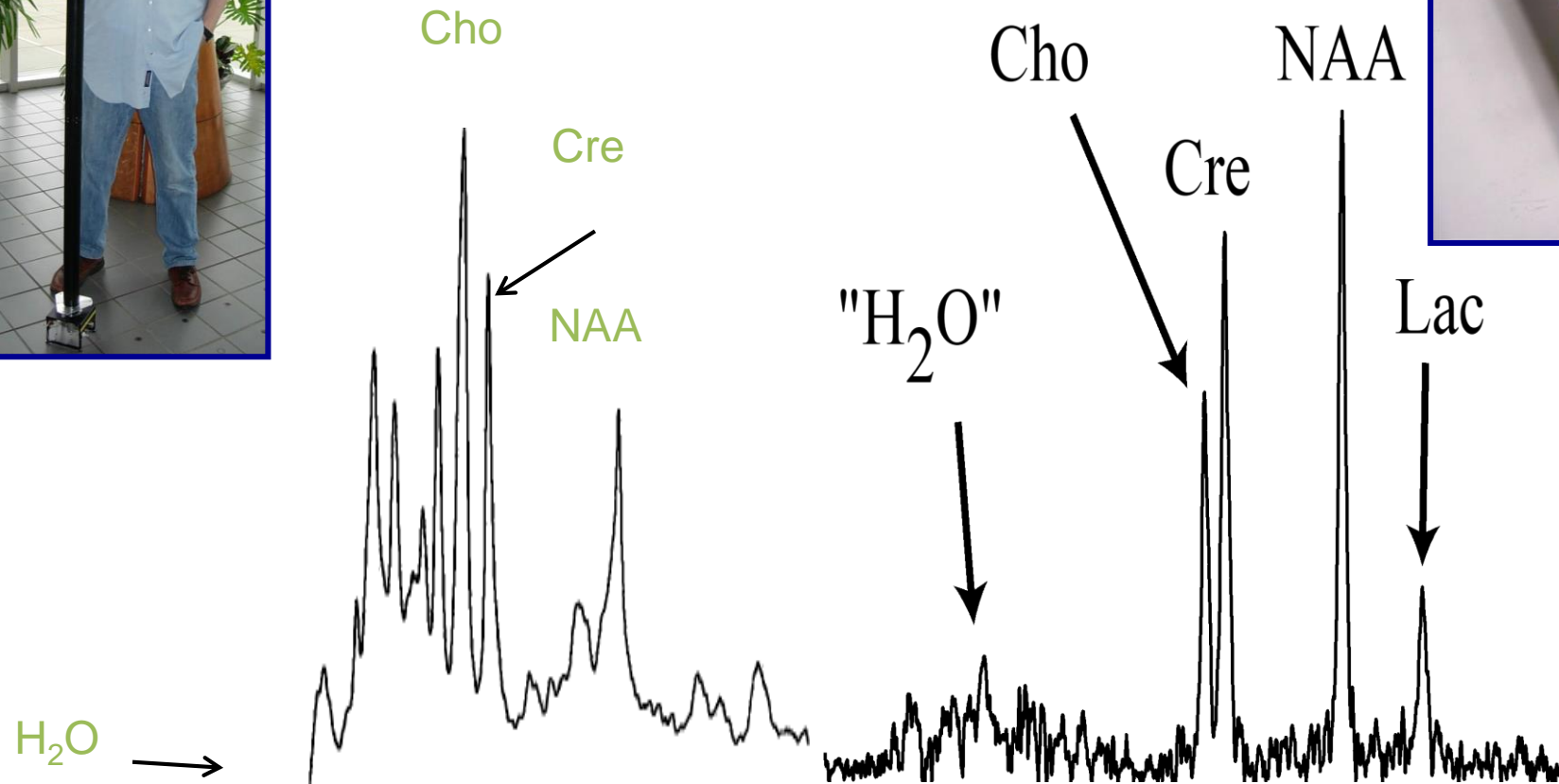
Libardo et al., *FEBS. J.*, 2017, 284:3662-83.



DNP-enhanced SSNMR of Pathogenic Fungal Cell Walls (Kang...Mentink-Vigier and Wang *Nat Comm*, 2018)



Once again – the quality of the system depends on the quality of its coils/probes



PRESS sequence w/Vapor
S/N (NAA) ≈ 40 for $\approx 125\mu\text{L}$
9.4 T MRI w/Cryoprobe; 5 min acq.

RE ¹H MRS sequence
S/N (NAA) ≈ 60 for $\approx 125\mu\text{L}$
21.1 T MRI; 6 sec acq.

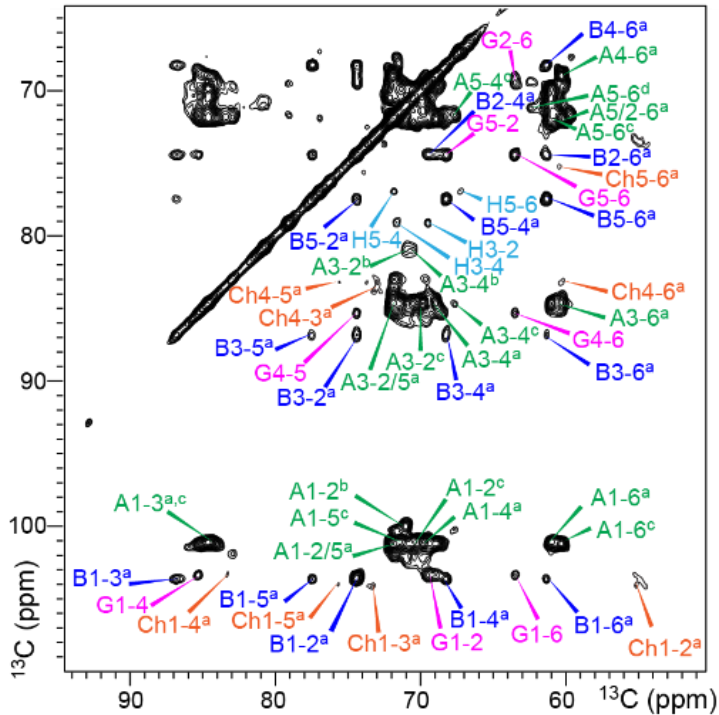


Welcome to the Magnet Lab
and to the
NMR & MRI User Program

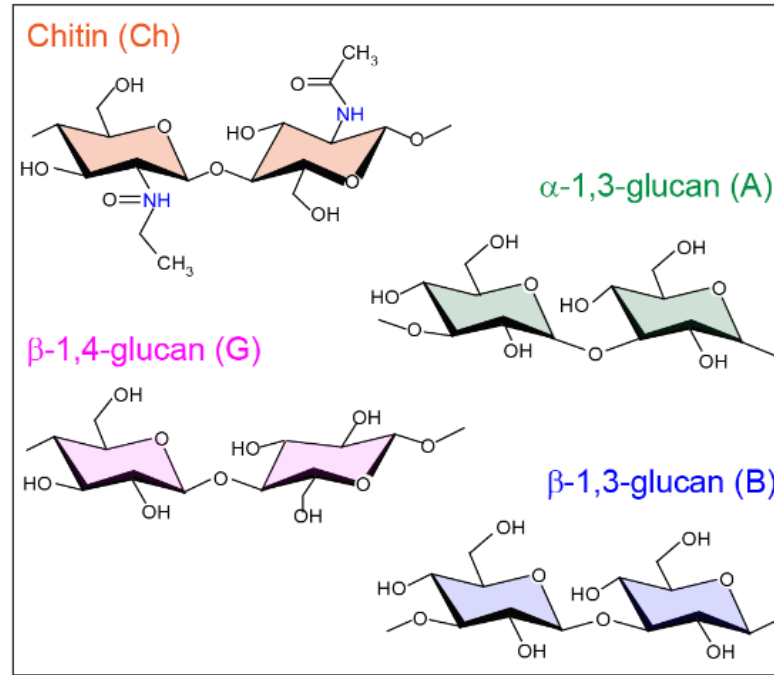
Structural Characterization of Intact Fungal Cell Walls

Asst. Prof. Tuo Wang, LSU

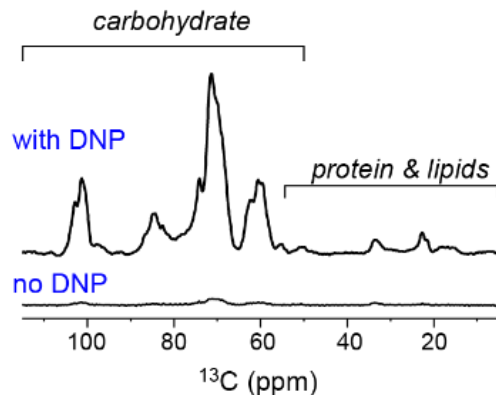
2D ^{13}C - ^{13}C spectra



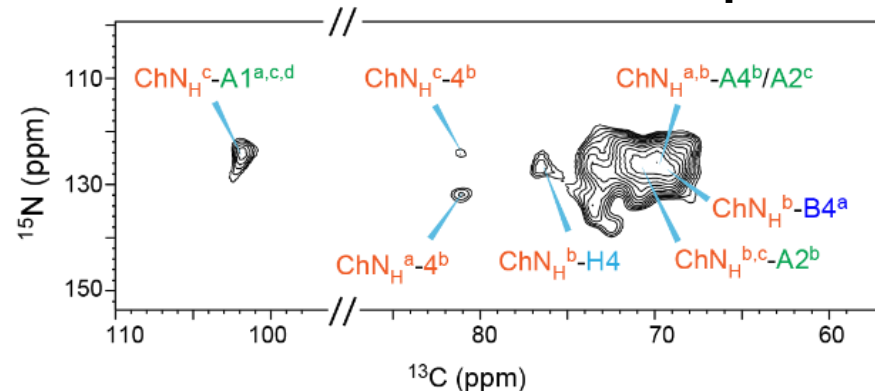
Glycan Structure



30-fold MAS-DNP enhancement



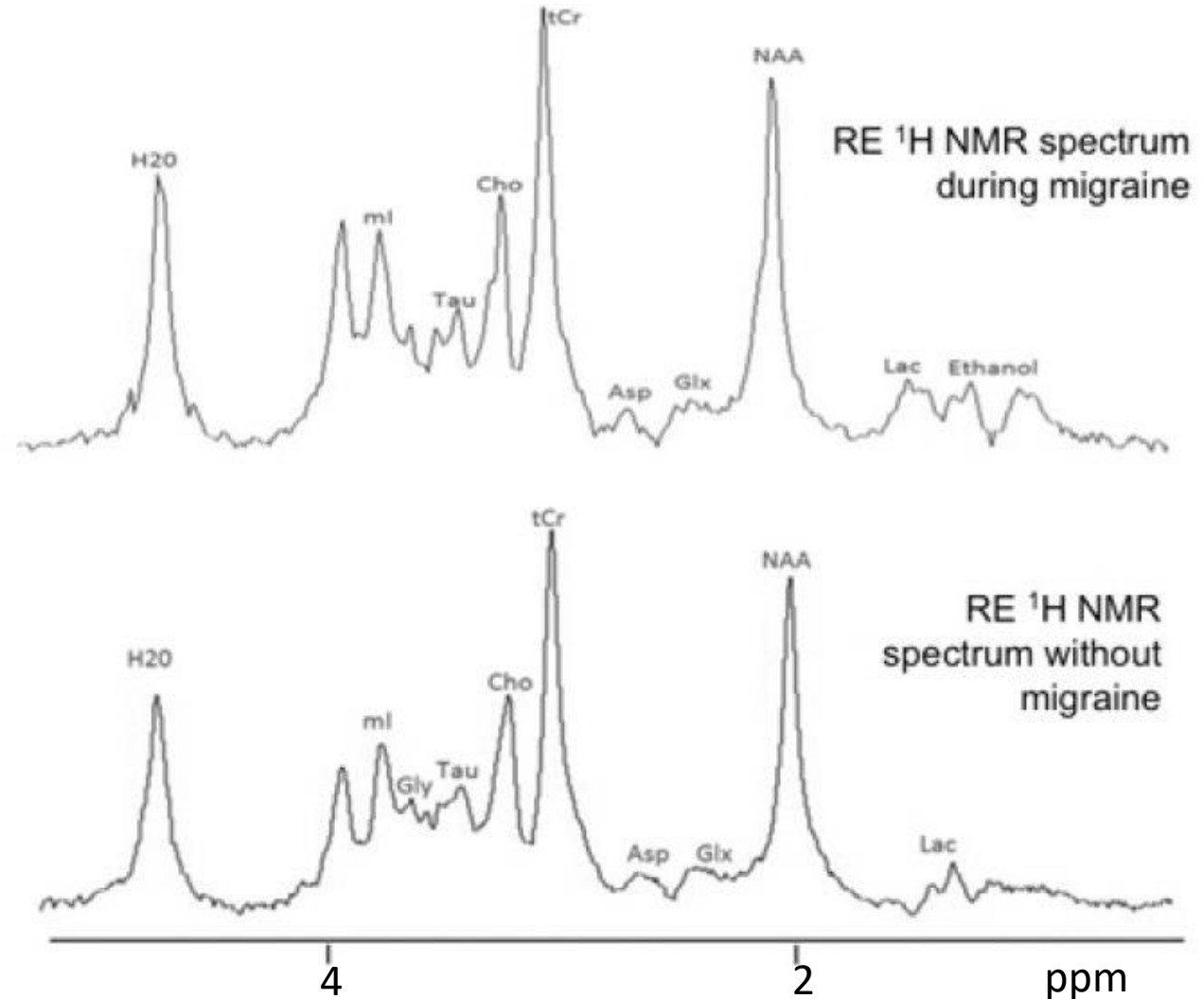
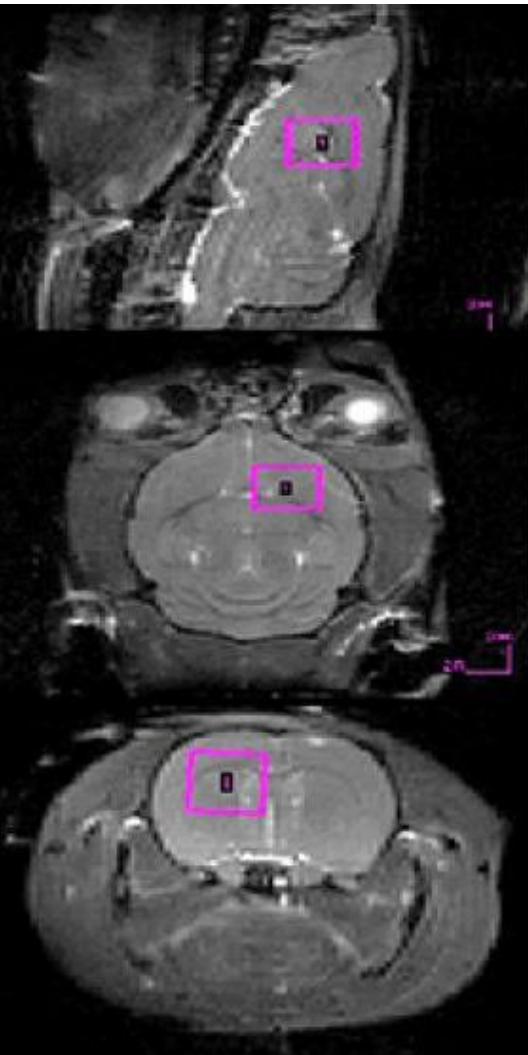
^{15}N - ^{13}C DNP Correlation Spectrum –



sub-nm
contacts

Metabolic Assessment of Migraines using Ultra-High B₀

- Significant Lactate and Creatine increases pointed to remodeling of energy usage, while Sustained Taurine also evidenced increased ion release during **migrane progression**.



Quadrupolar Nuclei are Ubiquitous in Chemical and Materials Sciences

Opening up the Periodic Table: It has started

IA													IIIA	IVA	VA	VIA	VIIA	VIIIA
H	IIA												B	C	N	O	F	He
Li	Be												Al	Si	P	S	Cl	Ne
Na	Mg	IIIB	IVB	VB	VIB	VIIIB	VIII B			IB	II B	Al	Si	P	S	Cl	Ar	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
Fr	Rd	Ac																

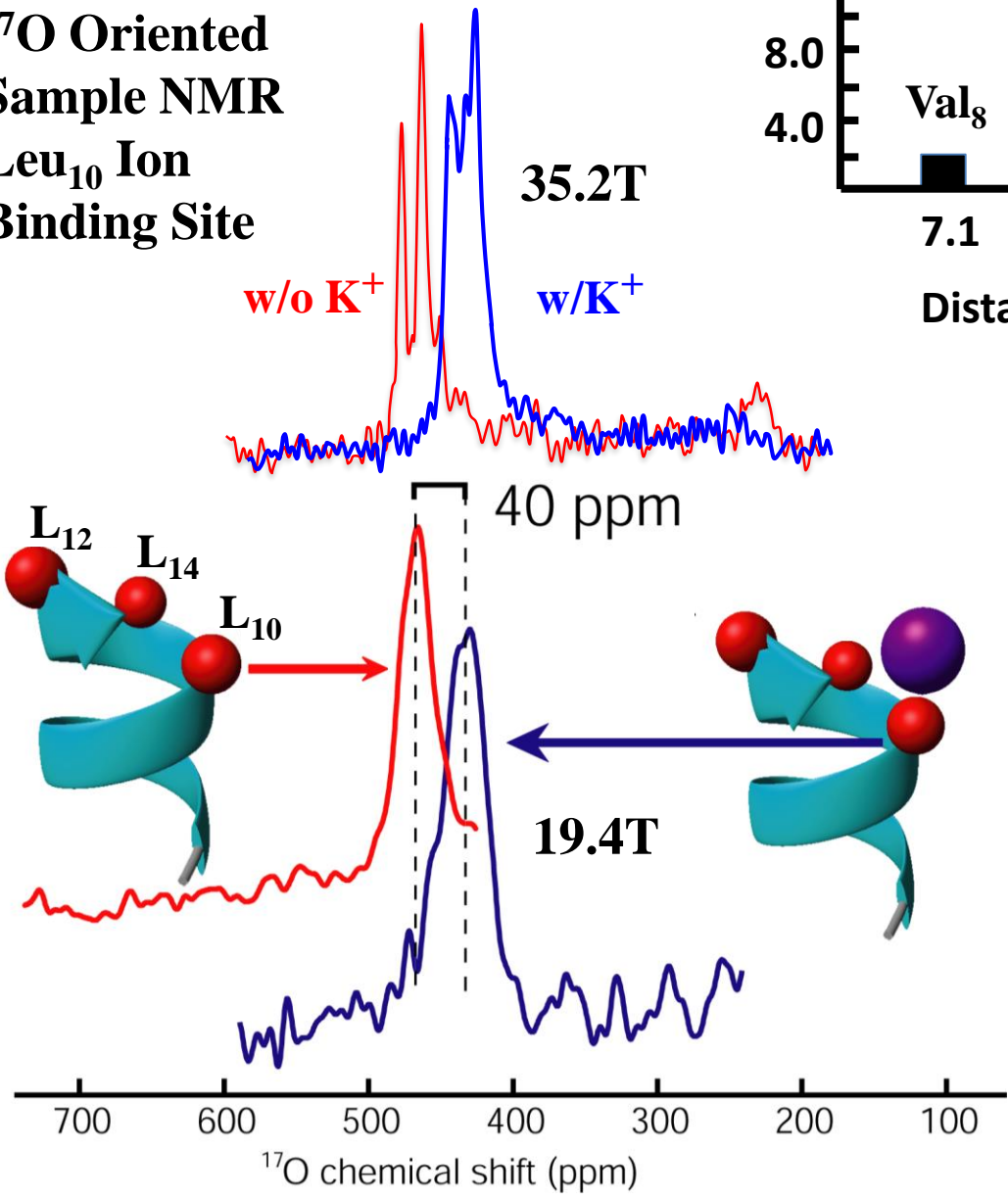
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

NMR active nuclei are found throughout the periodic table

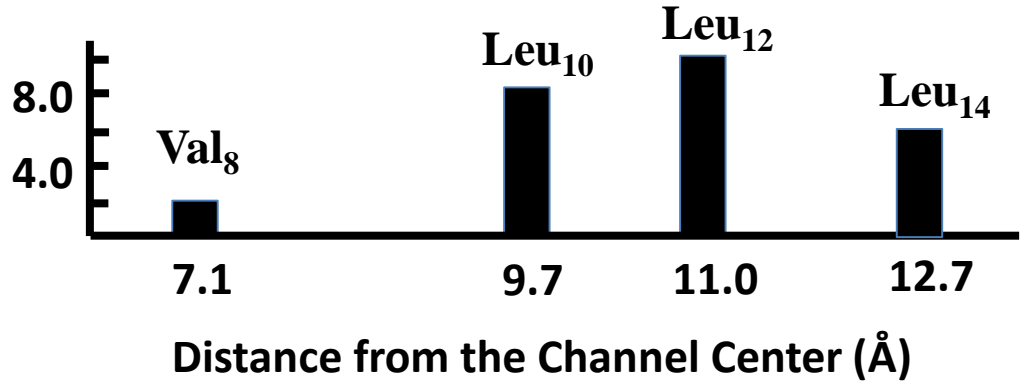
<http://www.grandinetti.org/Research/NMR>

Adding K^+ to the Gramicidin

^{17}O Oriented
Sample NMR
Leu₁₀ Ion
Binding Site

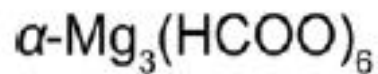
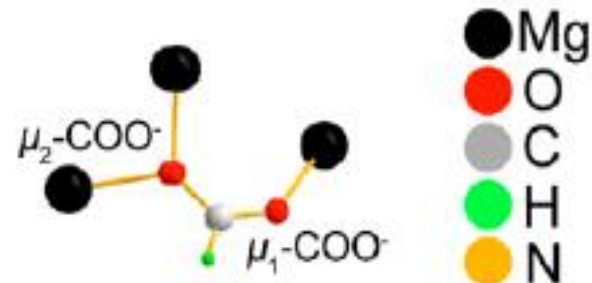
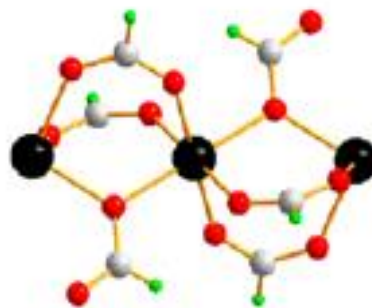
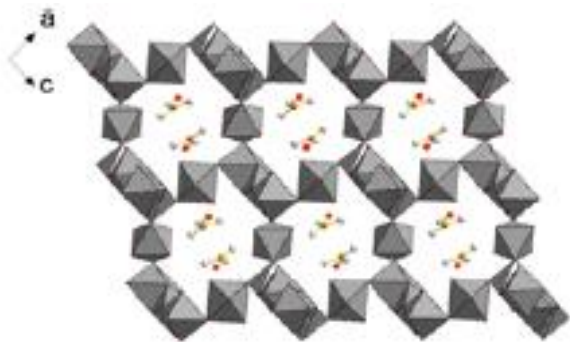


Anisotropic ^{15}N Chemical Shift in the Presence of Cations

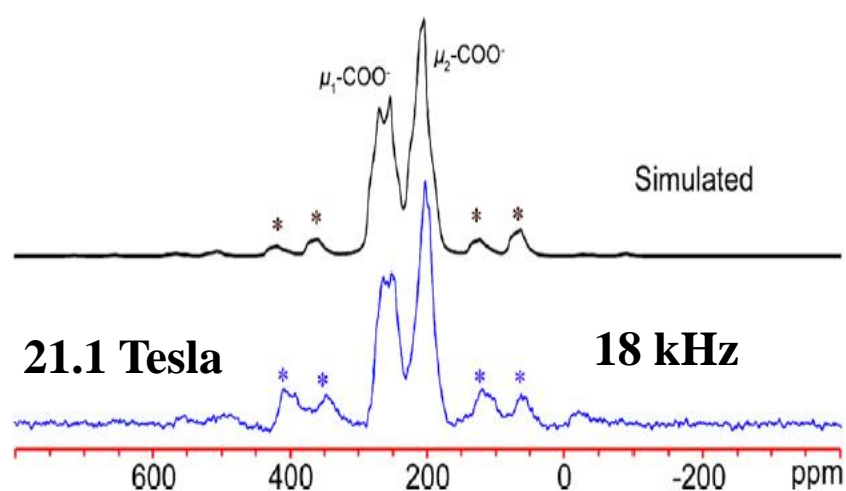
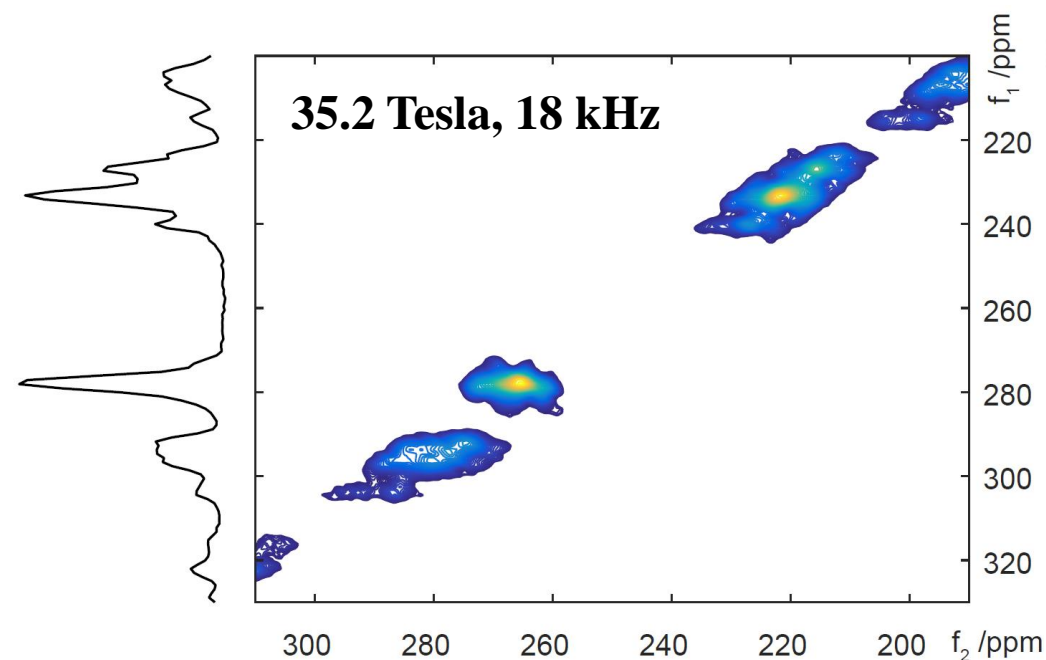


- Same shift seen at 19.4 T and at 35.2 T for K^+ in cation binding sites.
- Consistent with ^{15}N Results
- Reflecting multiple binding configurations in the binding site –

^{17}O NMR of Metal-Organic Frameworks: 1.5GHz vs 900MHz



The high-field and MQMAS reveal more ^{17}O peaks in $\alpha\text{-Mg}_3(\text{HCOO})_6$ MOF that were not observed at 900MHz



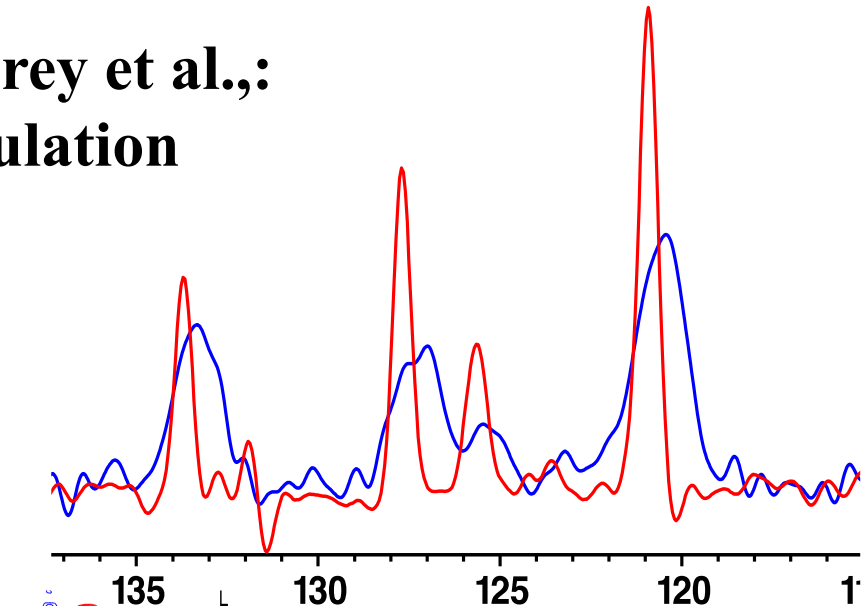
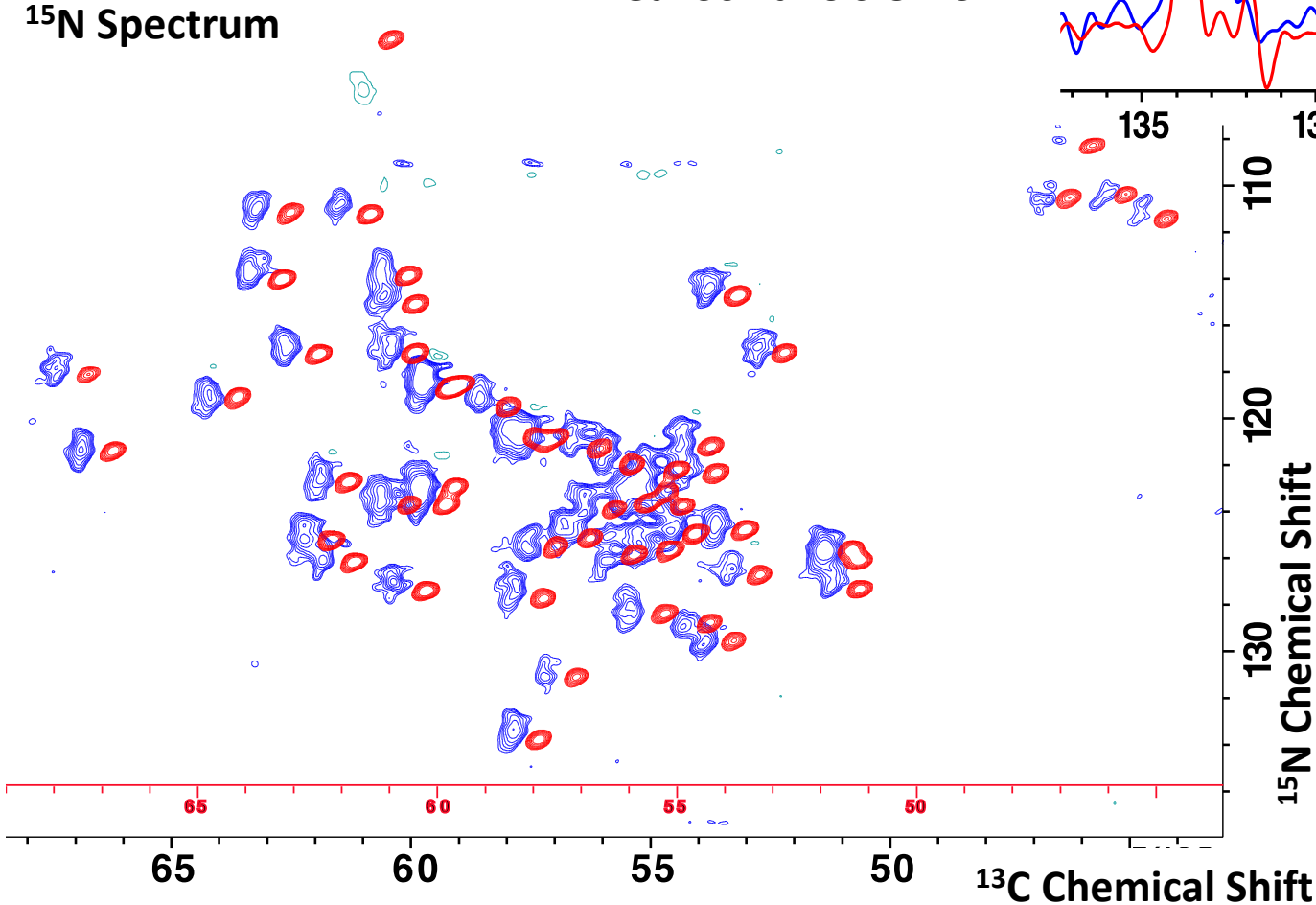
Y. Huang U. West Ontario

- Shown with permission

Prof. Jeff Schiano, Ilya Litvak, Bill Brey et al., Development of a Cascade Field Regulation System for 35 T NMR Spectroscopy

GB1 2D ^{13}C -
 ^{15}N Spectrum

Blue: Bruker's Lock
Red: Schiano's CFRS



^{15}N Chemical Shift
A Slice through 57.85
ppm of the ^{13}C
dimension of the 2D ^{13}C -
 ^{15}N Spectrum

SCH NMR Users – so far in 2018

- Nathaniel Traaseth – OS ssNMR EmrE membrane protein in bicelles - 1/18
- Gang Wu – ^{17}O MAS ssNMR of organic solids - 6/18
- Rob Schurko – ^1H - ^{103}Rh MAS ssNMR of catalysts and model compounds - 4/18
- Alex Nevzorov – OS ssNMR of Pf1 coat protein in bicelles - 1/18
- Len Mueller – ^{17}O MAS ssNMR of Tryptophan synthase
- Rachel Martin – MAS ssNMR of Droserasin – 4 & 9/18
- Francesca Marassi – OS ssNMR of *Y. pestis* Ail - 1/18
- Daniel Lee – MAS ssNMR metal oxide nanocrystals
- Danielle Laurencin - MAS ssNMR of biomaterials - 4/18
- Oliver Lafon – ^{71}Ga ssNMR of Ga_2Se_3 - 4 & 7/18
- Hans Jakobsen – ^{95}Mo ssNMR of tetraoxoanions – 2/18
- Yining Huang - ^{17}O ssNMR of metal organic frameworks – 4 & 5/18
- Sophia Hayes – ^{25}Mg of metal oxide thin films - 4/18
- Oc Hee Hahn – ^{79}Br and ^{81}Br NMR of Perovskite crystals - 2/18
- Robert Griffin – ^{17}O labeled water in amyloid forming peptide – 4 & 9/18
- Cecil Dybowski – ^{67}Zn of ZnO-based pigments in paint films – 1 & 3/18
- Myriam Cotten – OS ssNMR of metallopeptides bound to membrane surface - 3/18
- Brad Chmelka – ^{23}Na , ^{27}Al , ^{35}Cl , ^{39}K , ^{71}Ga , ^{95}Mo , and ^{115}In in nanostructured solids - 6/18
- Ed Chekmenev – ^{17}O gramicidin OS ssNMR (fill-in spectroscopy)
- David Bryce – Quadrupolar spectroscopy of various organics and inorganics - 2/18