Emerging trends in NMR of materials

Marek Pruski

U.S. DOE Ames Laboratory, Ames, Iowa 50011, U.S.A

Department of Chemistry, Iowa State University, Ames, Iowa 50011, U.S.A.

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THE Ames Laboratory

Research needs in materials science

Understanding the structure-property relations in novel materials is an unanswered scientific challenge, which prevents rational design. A few examples:

- heterogeneous catalysts: supports, catalytic sites, reaction mechanisms
- energy related materials: batteries, fuel cells, hydrogen storage, thermoelectrics, photovoltaics, …
- construction materials: cements, polymers, composites
- glasses and ceramics
- semiconductors, ion-conducting solids, and dielectric materials
- materials for environmental remediation and CO_2 sequestration
- biomaterials
- pharmaceuticals

(more examples are given in Task Force Summaries, p. 25-26)

Solid-state NMR

SS-NMR spectroscopy has an unparalleled ability to provide atomic-level characterization of materials:

- most elements have NMR-active isotopes
- nuclear spins are excellent, site-dependent "reporters" of local structure and dynamic processes

Challenges:

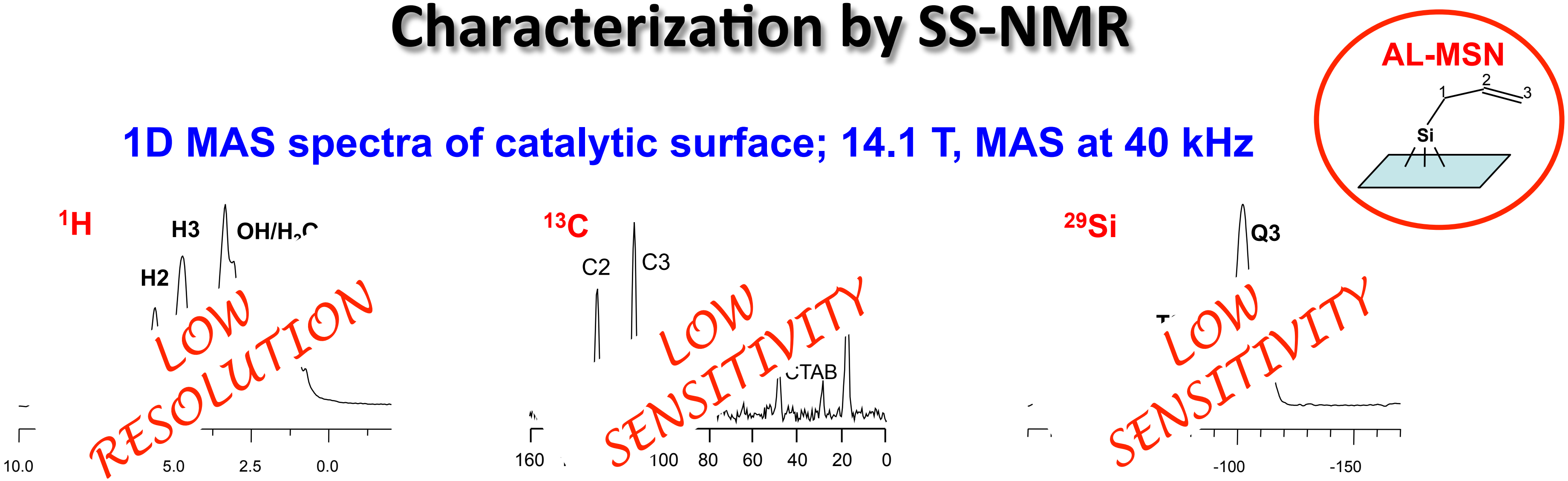
- intrinsically low sensitivity of NMR
- low resolution; homogeneous and inhomogeneous line broadening in solids

Transformational role of ultrahigh field in SS-NMR:

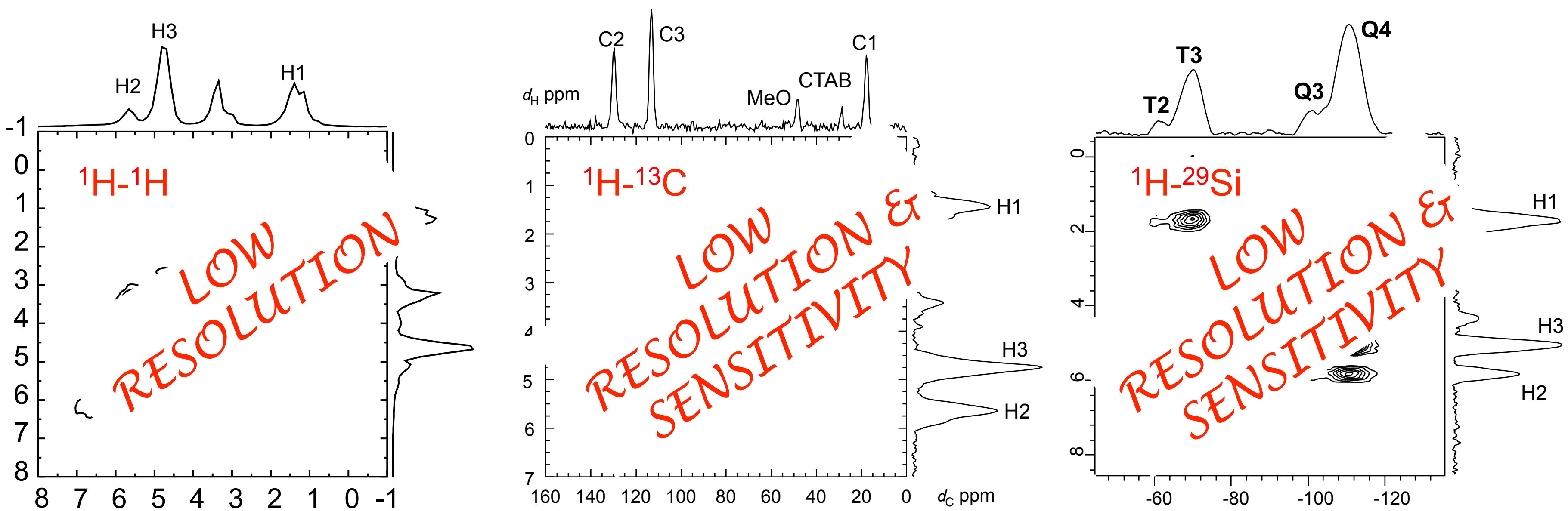
- ultrafast MAS; indirect detection
- low-gamma nuclei
- half-integer quadrupolar nuclei
- high-field DNP

Characterization by SS-NMR

1D MAS spectra of catalytic surface; 14.1 T, MAS at 40 kHz



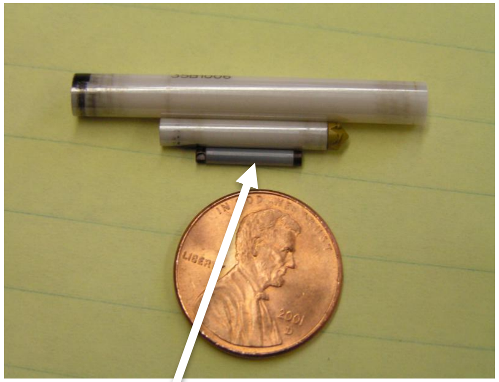
2D correlation spectra of the same system



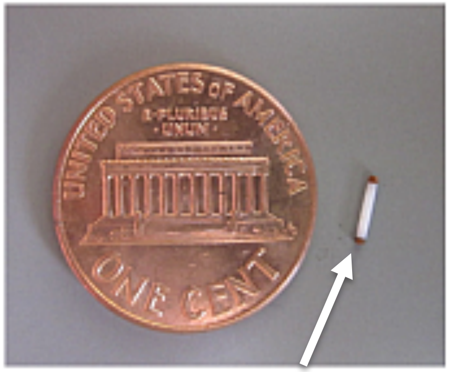
J. Trebosc, et al., *J. Am. Chem. Soc.*, **2005**, *127*, 3057-3068;
J. Am. Chem. Soc., **2005**, *127*, 7587-7593.

Emerging technique: ultrafast MAS

New probes (e.g. ultrafast MAS): new pulse sequences/theory; improved resolution & sensitivity



- MAS rate: 45 kHz
- volume: ~9 µl
- introduced: ~2005



- MAS rate: 100+ kHz
- volume: ~0.3 µl
- introduced: ~2012

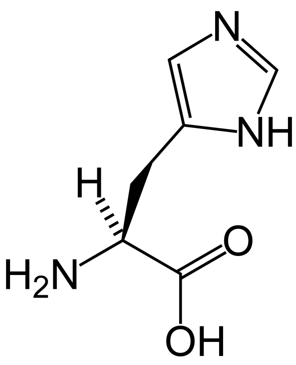
Transformational role of ultrafast MAS in SS-NMR:

- improved ^{1}H resolution ($\Delta\nu \sim (\nu_{MAS})^{-1}$)
- indirect detection
- sideband-free spectra
- better sensitivity/spin
- higher RF fields
- improved decoupling/recoupling
- dipolar truncation

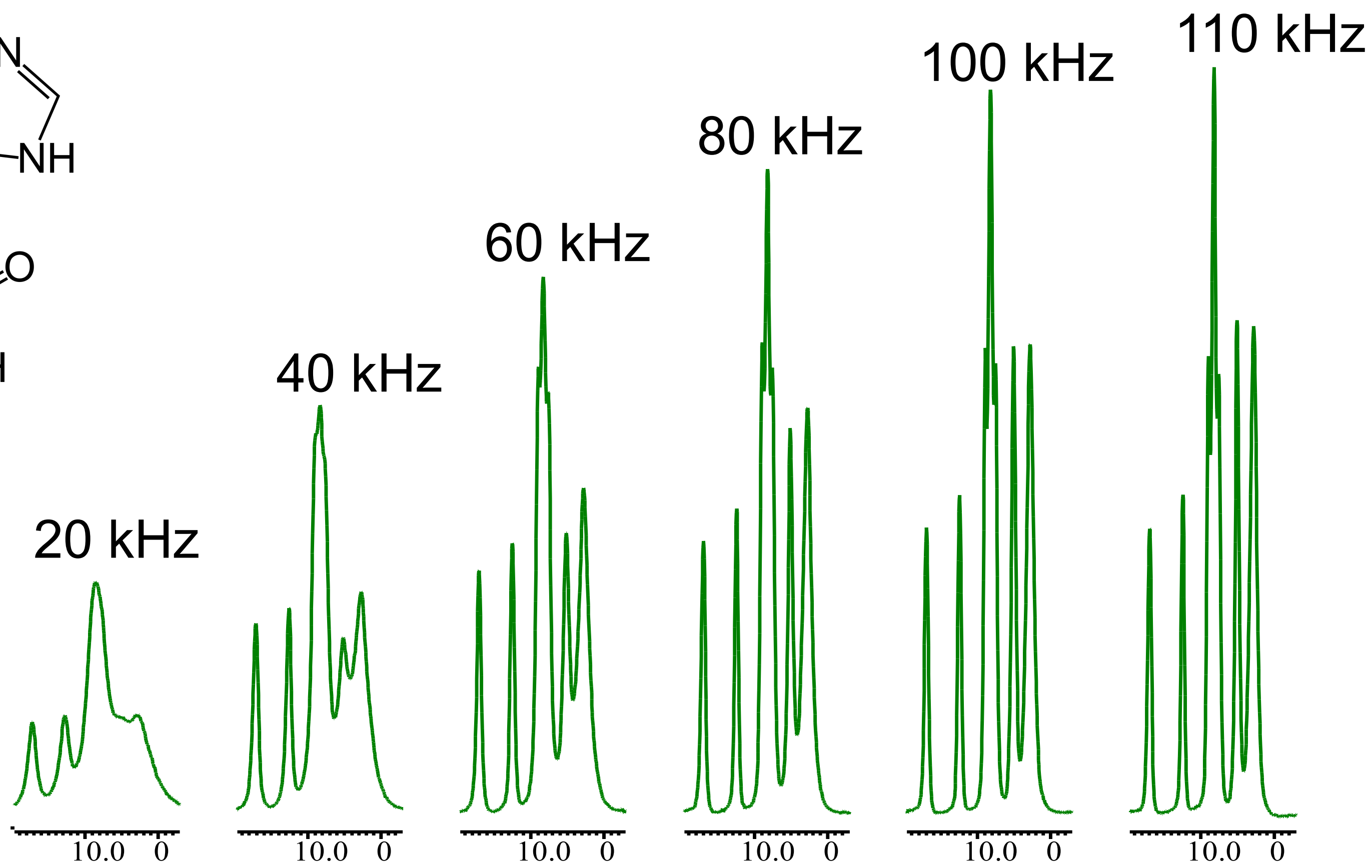
Need higher magnetic field!!!

^1H resolution under ultrafast MAS

L-histidine HCl H_2O



^1H MAS at 14.1 T

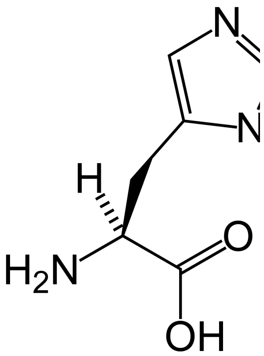


- ^1H resolution and SNR are greatly enhanced by fast MAS
- CRAMPS-like resolution approached at 100 kHz

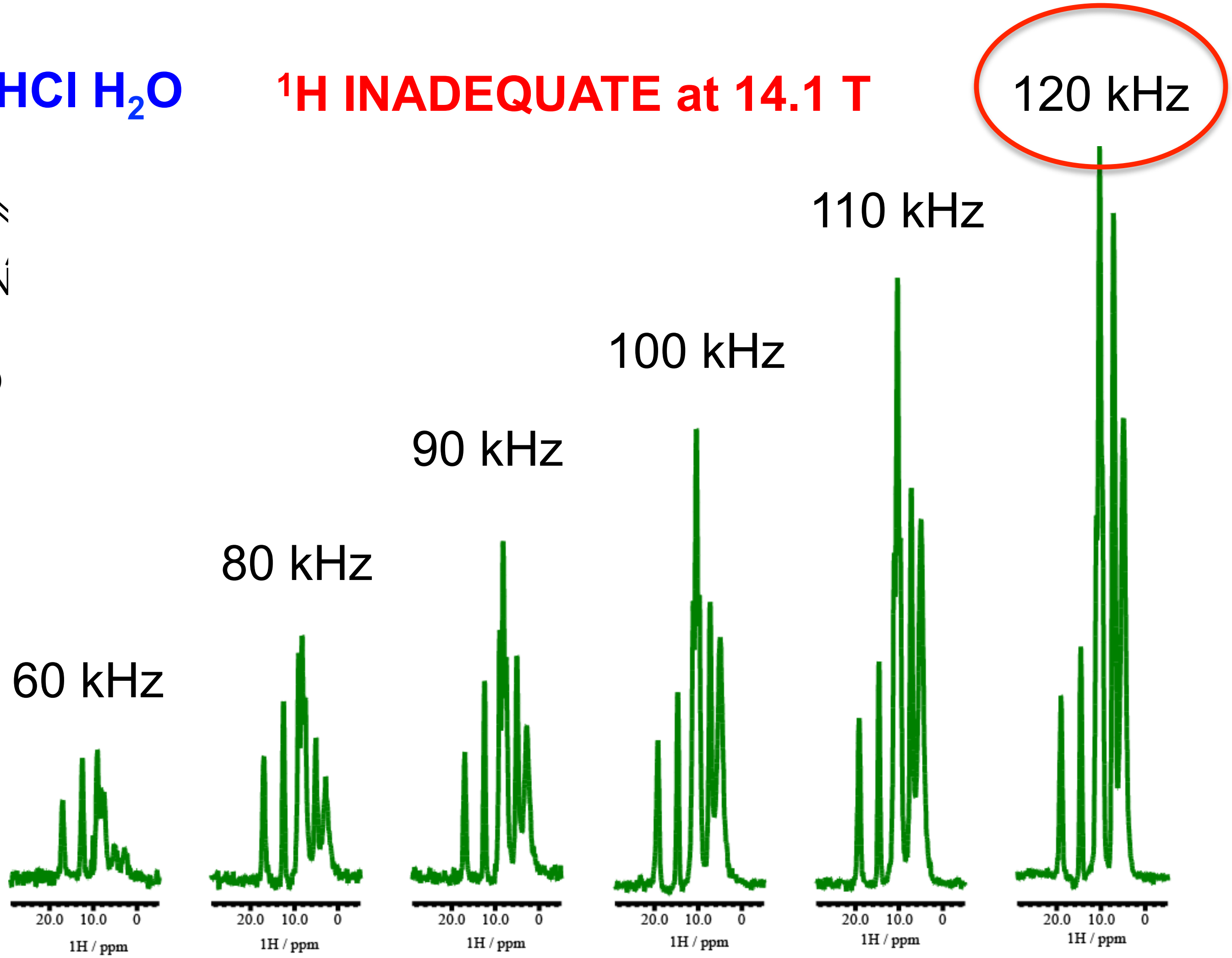
Y. Nishiyama, JEOL Resonance.

^{1}H resolution under ultrafast MAS

L-histidine HCl H_2O



^{1}H INADEQUATE at 14.1 T



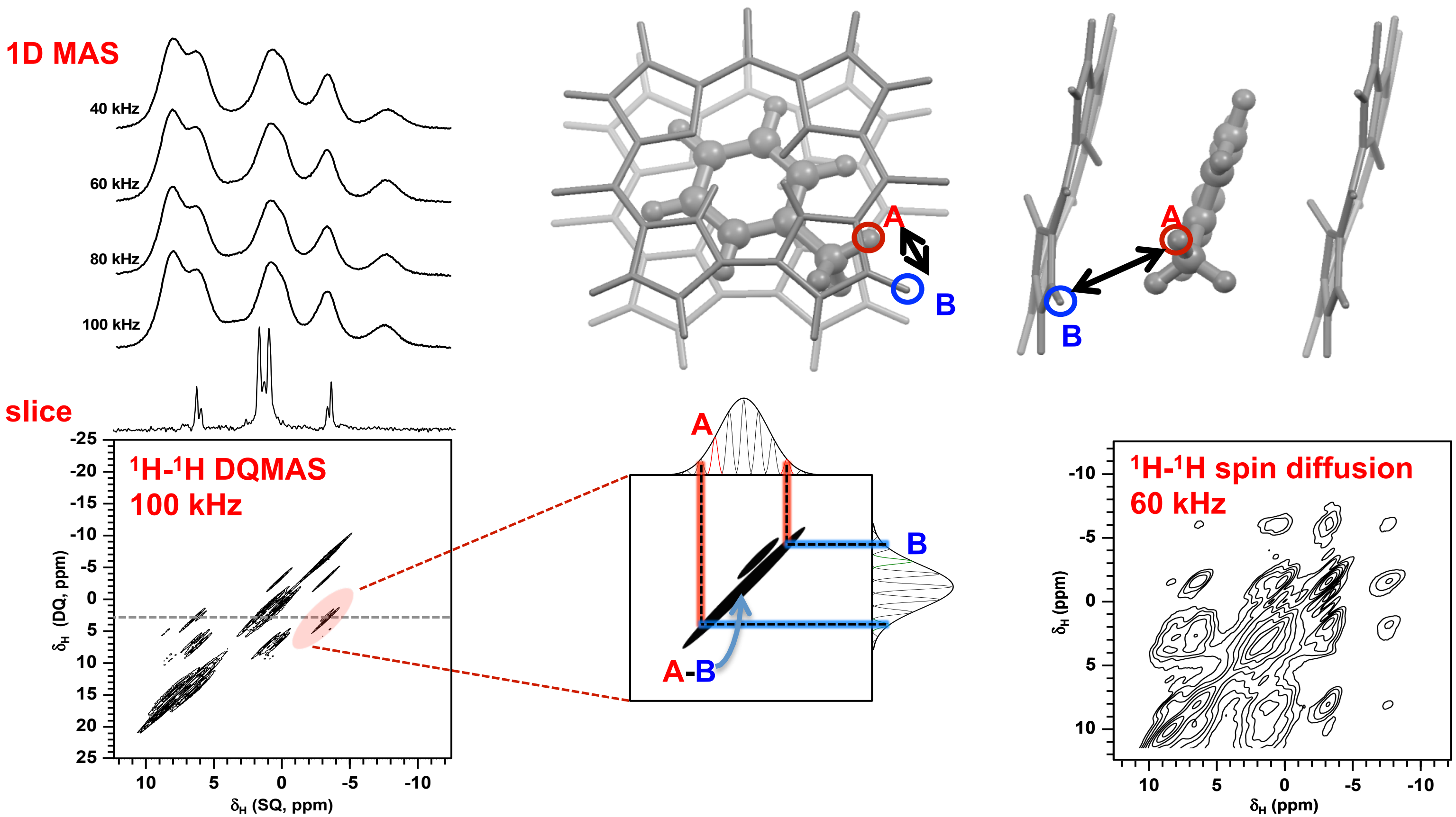
- ^{1}H resolution and SNR are greatly enhanced by fast MAS

Y. Nishiyama, JEOL Resonance.

^{1}H-^{1}H correlations under MAS at 100 kHz

Ultrafast MAS at 100 kHz: improved resolution in 2D ^{1}H-^{1}H NMR

- Host-guest interaction in corrole/toluene system

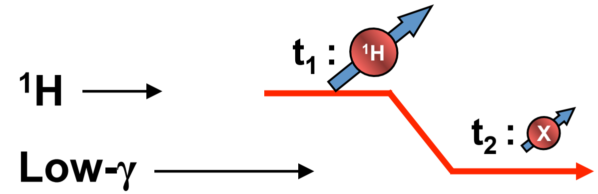


Polymers, supramolecular systems, catalysts, …

T. Kobayashi, et al., *Angew. Chem. Int. Ed.*, 2013, *52*, 14108.
S.P. Brown, *Macromol. Rapid. Commun*. 2009, 30, 688-716

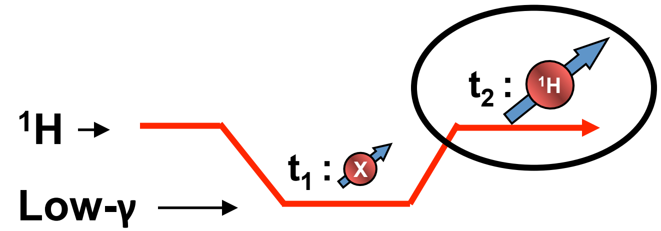
Indirect detection of low-γ nuclei

Traditional SSNMR approach: <u>direct detection</u> of low-γ nuclei (e.g. ^{13}C, ^{15}N)



- ^{1}H homonuclear RF decoupling
- low sensitivity

<u>Indirect detection</u> of low-γ nuclei



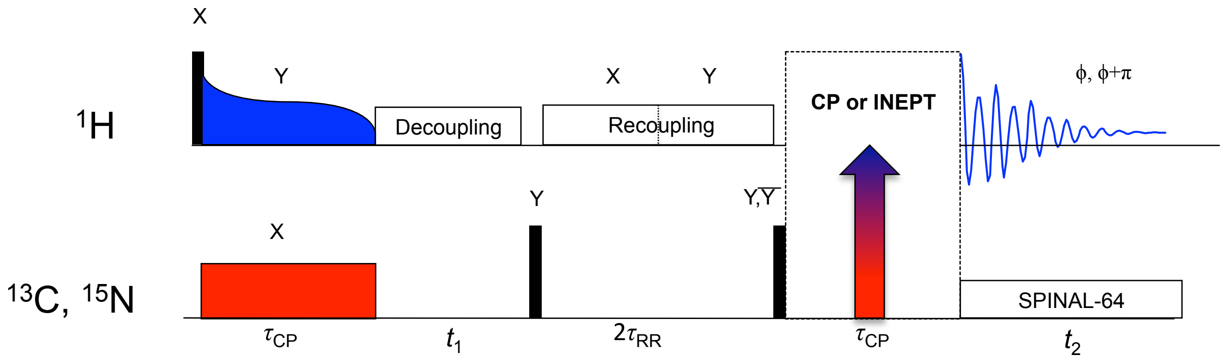
- ^{1}H decoupling by fast MAS
- high sensitivity

S/N gain:

$$\frac{(S/N)_{ID}}{(S/N)_{DD}} \approx \alpha \left(\frac{\delta\nu_X}{\delta\nu_H}\right)^{1/2} \left(\frac{\gamma_H}{\gamma_X}\right)^{3/2}$$

For ^{15}N: $\left(\frac{\gamma_H}{\gamma_N}\right)^{3/2} = 31$ ⟹ **time performance improves by ~10^3!**

^{1}H-^{13}C HETCOR under fast MAS: catalytic surface

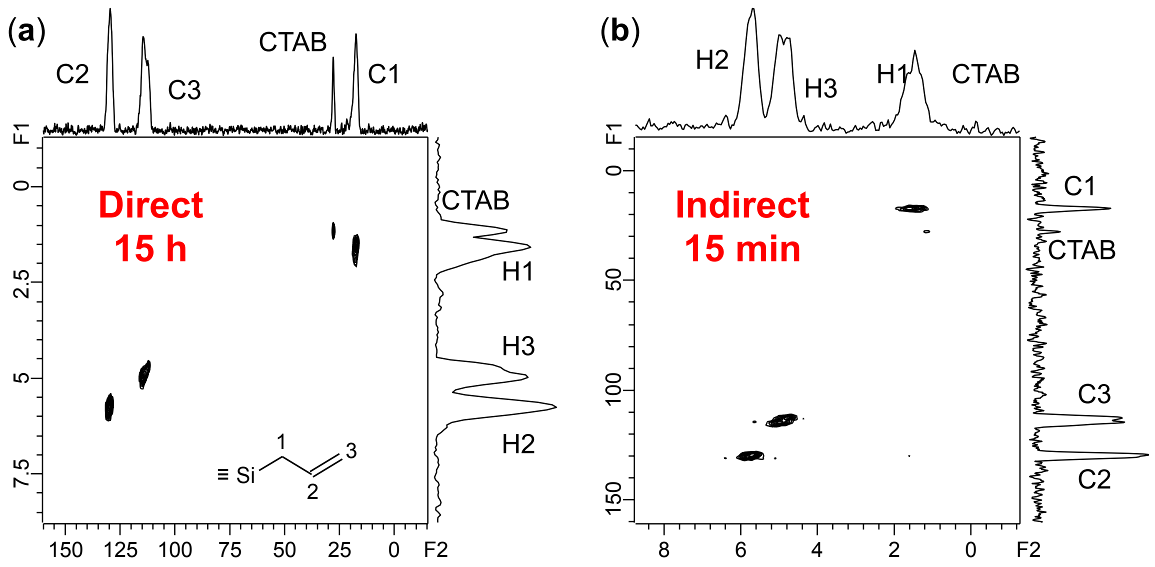


Through space correlations:

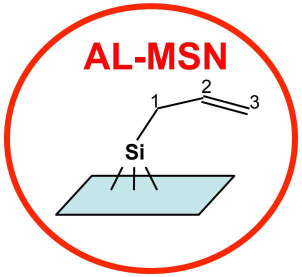
Ishii, Y.; Tycko, R. *JMR,* 2000, *142*, 199;
Wiench, J.W. et al. *JACS* 2007, *129*, 12077;
Zhou D.G. et al., *JACS* 2007, *129*, 11791

Through-bond correlations:

Elena, B. et al. *JACS*, 2005, *127*, 17296;
Mao, K.; Pruski, M. JMR, 2009, 201, 165;

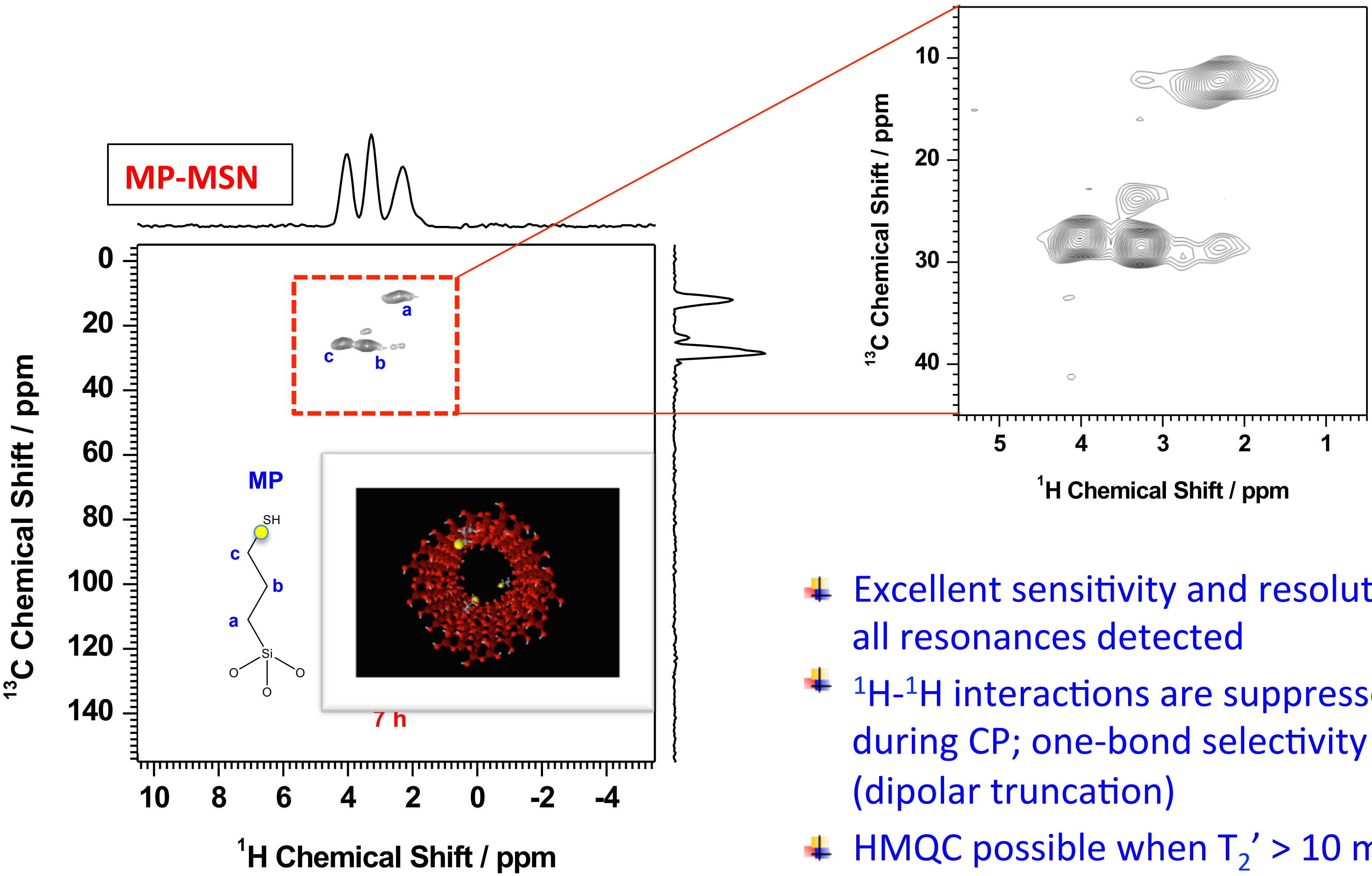


40 kHz MAS



^{1}H-^{1}H homonuclear RF decoupling → INEPT

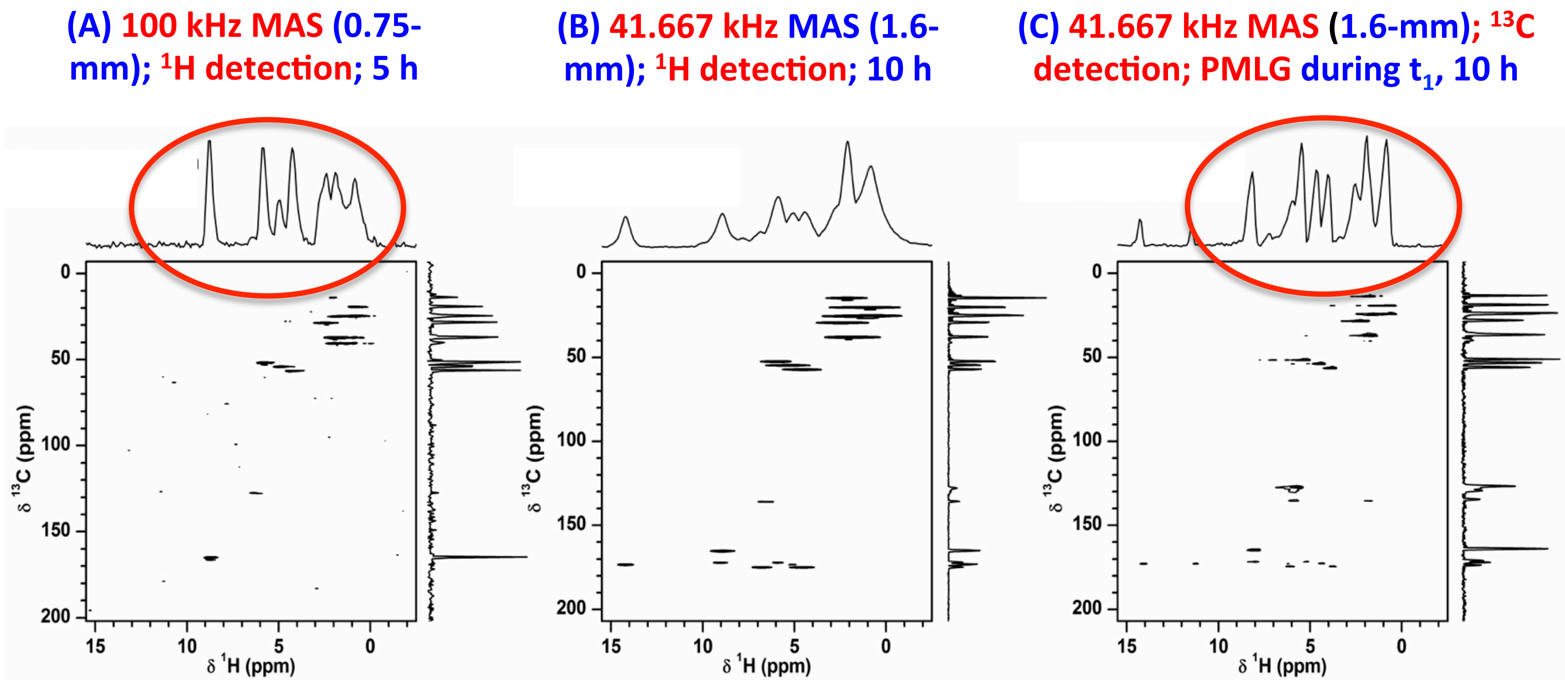
^{1}H-^{13}C HETCOR under MAS at 100 kHz

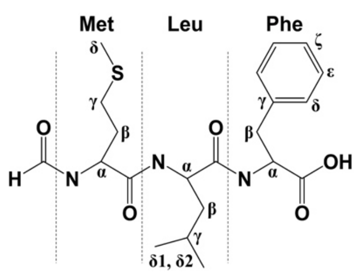


- Excellent sensitivity and resolution; all resonances detected
- ^{1}H-^{1}H interactions are suppressed during CP; one-bond selectivity (dipolar truncation)
- HMQC possible when $T_2' > 10$ ms

T. Kobayashi, et al., *Angew. Chem. Int. Ed.*, 2013, *52*, 14108.

HSQC of f-MLF-OH under natural abundance at 14.1 T

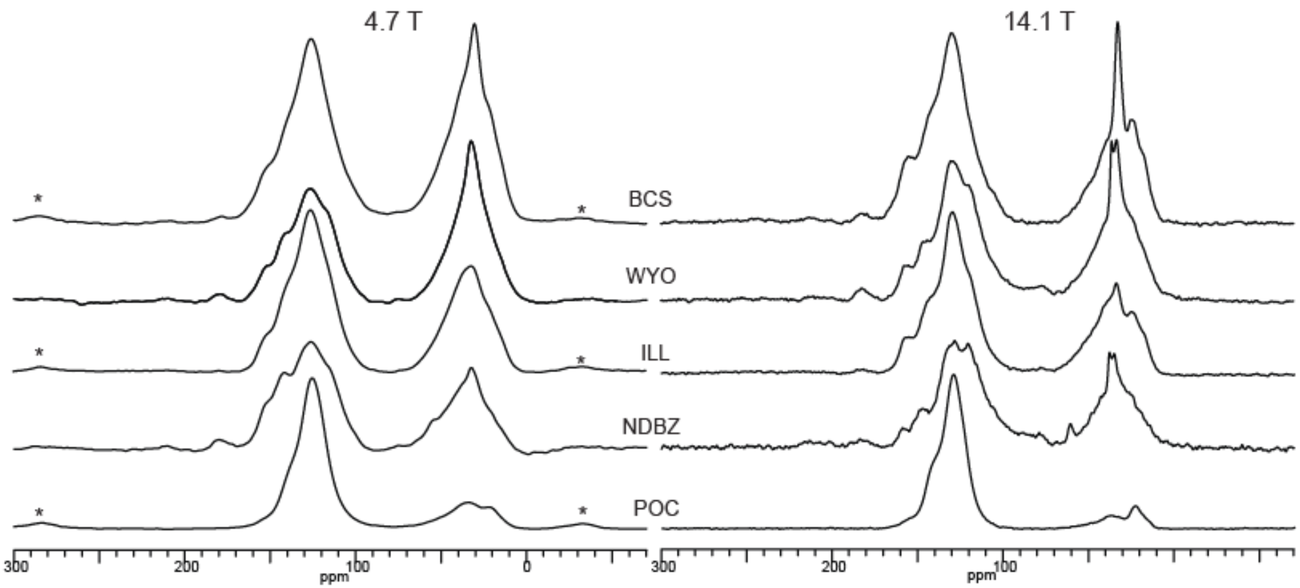




- Sensitivity/scan at 100 kHz close to that of 1.6-mm probe (>50% in terms of SNR), in spite of 20x smaller volume
- Resolution in (A) similar to PMLG (C)

Y. Nishiyama, T. Kobayashi, et al., SSNMR, 66-67, 56-61 (2015)

^{13}C CPMAS NMR of Argonne Premium Coals at low and high magnetic field

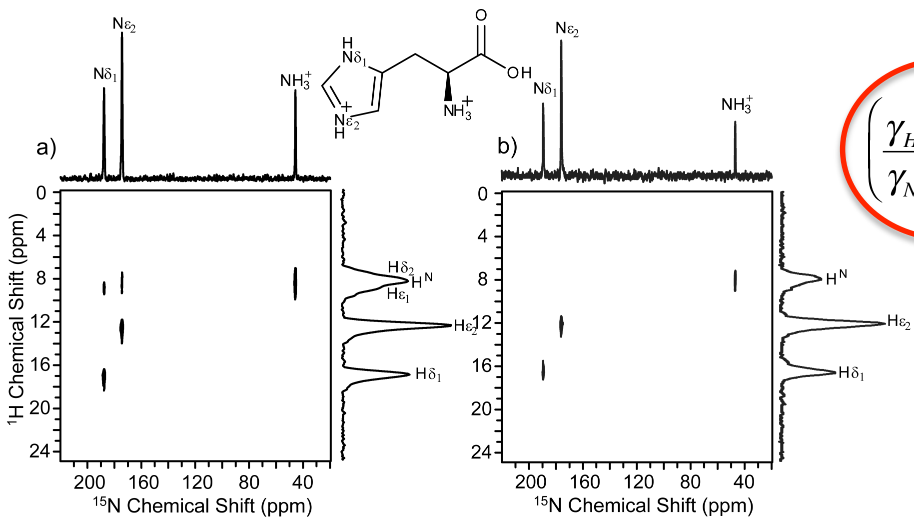


Sample weight:	**150 mg**	**8 mg**
Acquisition time:	**8 h**	**8 h**
MAS rate:	**8 kHz**	**42 kHz**
Sensitivity (per scan):	**1.5-2.0**	**1**
Resolution:	**-**	**+**

^{15}N or ^{33}S??

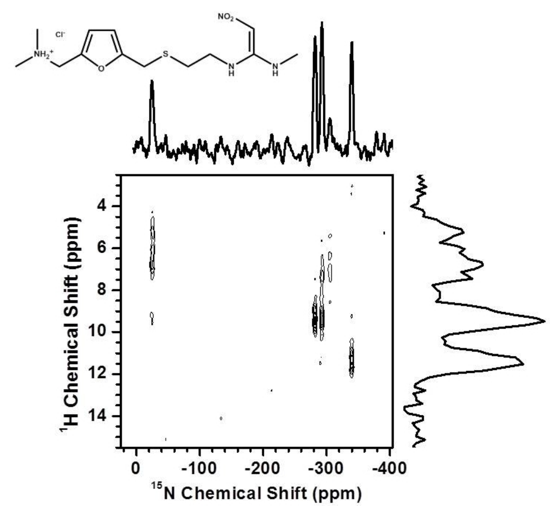
Studies of low-γ nuclei: ^{15}N under natural abundance

^{15}N-^{1}H HETCOR of amino acids
through space through bond



$$\left(\frac{\gamma_H}{\gamma_N}\right)^{3/2} = 31$$

^{15}N-^{1}H HETCOR of pharmaceuticals
through space



Similar techniques can be used/developed for other low-γ nuclei in many classes of materials

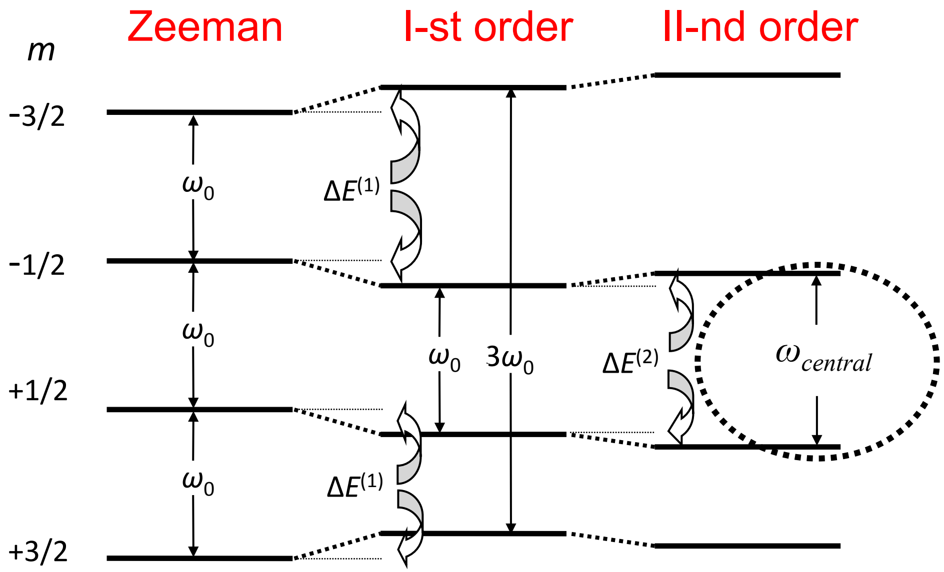
Need higher magnetic field!!!

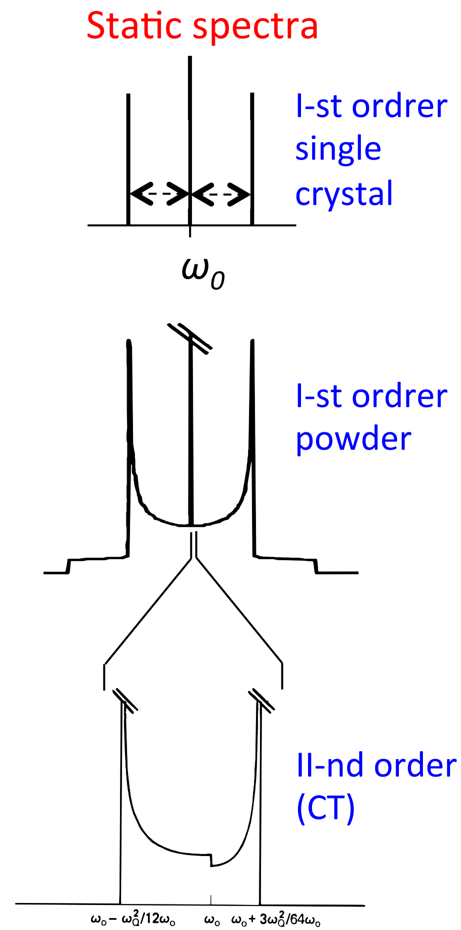
Althaus et al., SSNMR, 57-58, 17-21 (2014); collaboration with R. Schurko, University of Windsor

Half-integer quadrupolar nuclei

Most NMR-active nuclei are half-integer quadrupolar: 77 out of ~110, including ^{7}Li, ^{11}B, ^{17}O, ^{23}Na, ^{25}Mg, ^{27}Al, ^{33}S, ^{35}Cl, ^{39}K, ^{43}Ca, ^{55}Mn, ^{87}Rb, …

The challenge: SSNMR spectra are dominated by quadrupolar broadening





$$\omega_{central} = \omega_0 - \frac{\omega_Q^2}{16\omega_0}\{I(I+1) - 3/4\}(1 - 3\cos^2\beta)(9\cos^2\beta - 1)$$

Typical values for ^{27}Al: $\Delta E_m^{(1)}$ = 1 MHz, $\Delta E_m^{(2)}$ = 10 kHz

^{27}Al chemical shift range at 9.4 T: 10 kHz

Advances in NMR of quadrupolar nuclei: complete line-narrowing

Symmetric transition under fast rotation of the sample

$$\omega^{(2)}_{-m\leftrightarrow m} = \frac{\omega_Q^2}{\omega_0} A_0(I,p) B_0^Q(\eta_Q) +$$

isotropic

$$\frac{\omega_Q^2}{\omega_0} A_2(I,p) B_2^Q(\eta_Q,\alpha_Q,\beta_Q) P_2(\cos\theta) +$$

$$\frac{\omega_Q^2}{\omega_0} A_4(I,p) B_4^Q(\eta_Q,\alpha_Q,\beta_Q) P_4(\cos\theta)$$

anisotropic

where: $p = 2m$; α_Q, β_Q – angles between QPAS and rot. axis; θ - angle between rotation axis and B_0; $P_{2,4}(\cos\theta)$ – 2nd and 4th order Legéndre pol.; $A_i(I,p)$, $i = 0,2,4$ - coefficients

The resonance frequency also includes chemical shift

$$\omega_{-m\leftrightarrow m} = 2m\omega_0 + \omega^{(2)}_{-m\leftrightarrow m} + \omega^{cs}_{-m\leftrightarrow m}$$

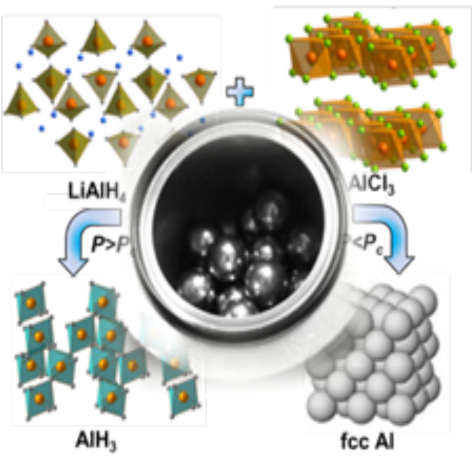
with $$\omega^{cs}_{-m\leftrightarrow m} = 2m\omega_0[\Delta\delta + B_2^{cs}(\eta_{cs},\alpha_{cs},\beta_{cs})P_2(\cos\theta)]$$

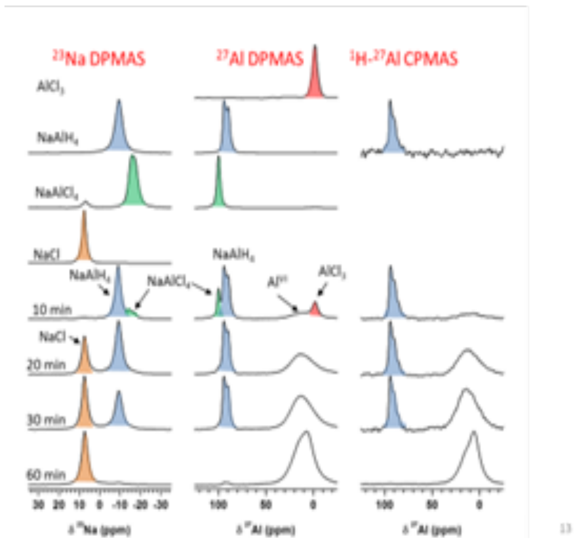
$P_2(\cos\theta)$ and $P_4(\cos\theta)$ do not have a common root; MAS narrows second order broadening only by a factor of ~3; DOR, DAS and MQMAS yield isotropic spectra

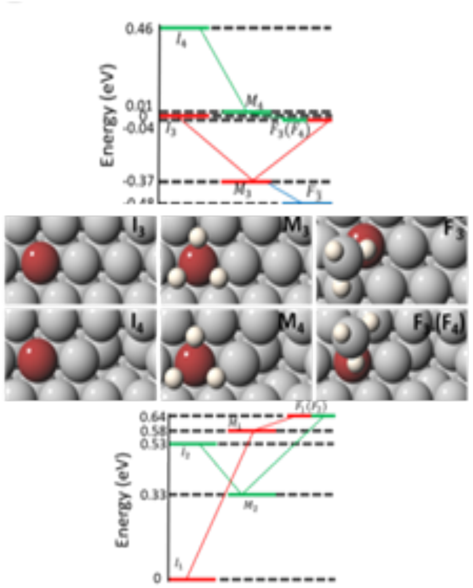
A. Pines et al., *Mol. Phys.* 65, 1013 (1988); *JMR*, 86, 470 (1990); L. Frydman et al., *JACS*, 117, 5367 (1995)

Example: mechanisms of dehydrogenation in metal hydrides

Mechanochemistry







Solid-state NMR
^{7}Li, ^{11}B, ^{23}Na, ^{27}Al

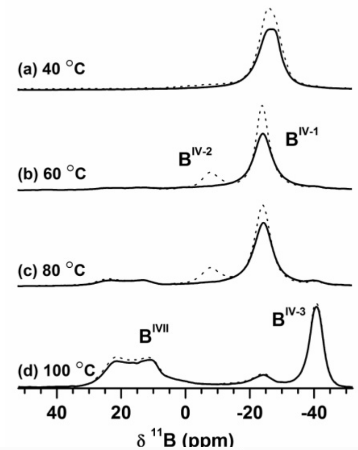
DFT Modeling

Example: mechanisms of dehydrogenation in metal hydrides

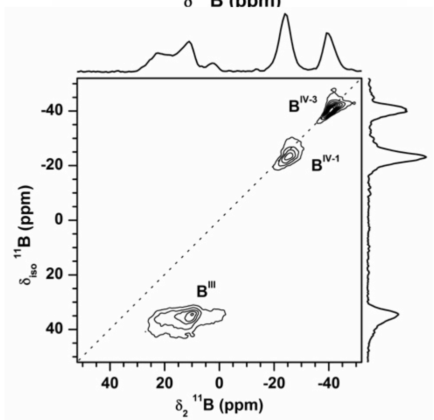
Our approach:

- measure 1D and 2D NMR spectra of ^{1}H, ^{7}Li, ^{11}B, ^{23}Na, ^{27}Al and other nuclei in hydrides processed under various conditions and in reference compounds
- obtain chemical shifts and quadrupolar parameters (for spins > 1/2) to identify the coordination geometries and chemical structures
- carry the out additional SSNMR experiments to probe interatomic correlations, molecular motions, etc.
- refine the structures using molecular modeling and DFT calculations

Need higher magnetic field!!!

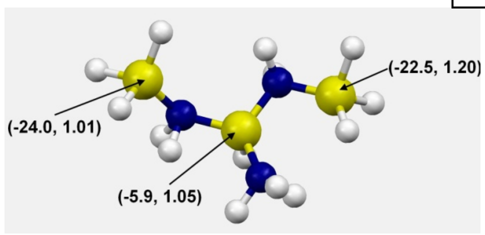


^{11}B MAS



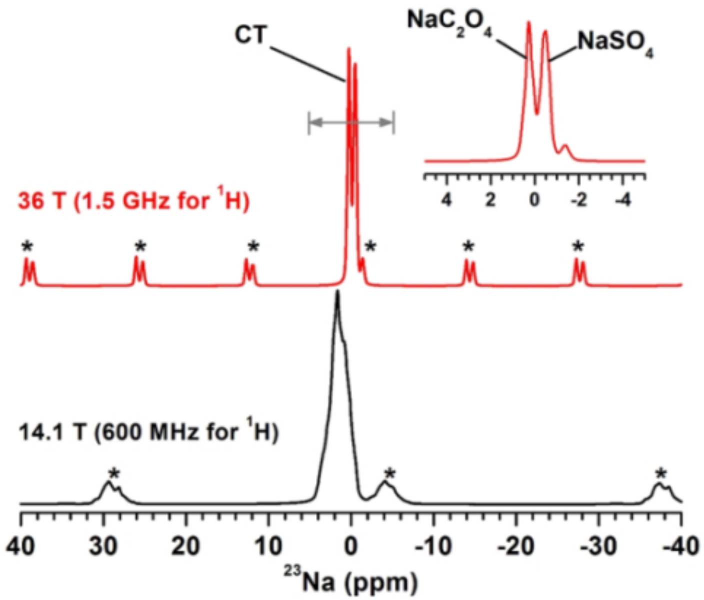
^{11}B MQMAS

DFT (δ_{CS}, P_Q)

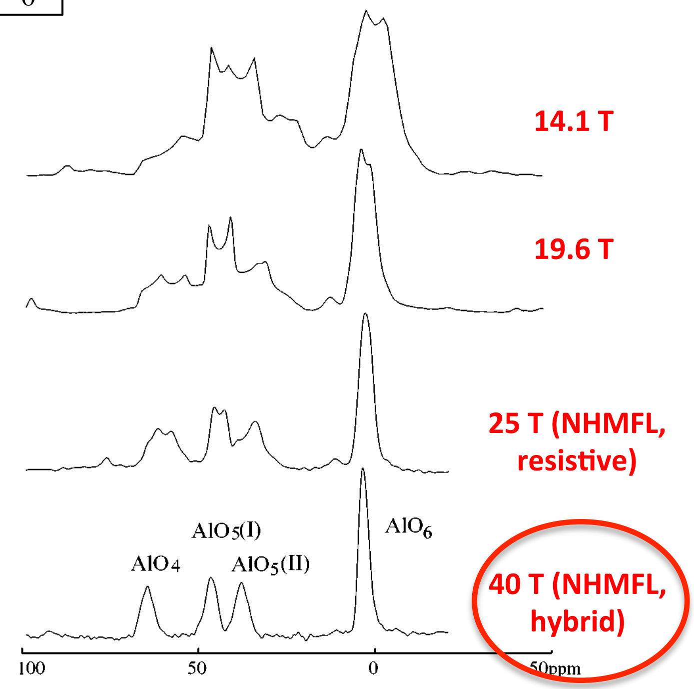


Spectra of quadrupolar nuclei at ultrahigh fields

$$\Delta E_m^{(2)}, \omega_{-m\leftrightarrow m}^{(2)} \propto B_0^{-1}$$



Simulated MAS spectra of ^{23}Na in NaC_2O_4/ $NaSO_4$ mixture at 14.1 T and 36 T

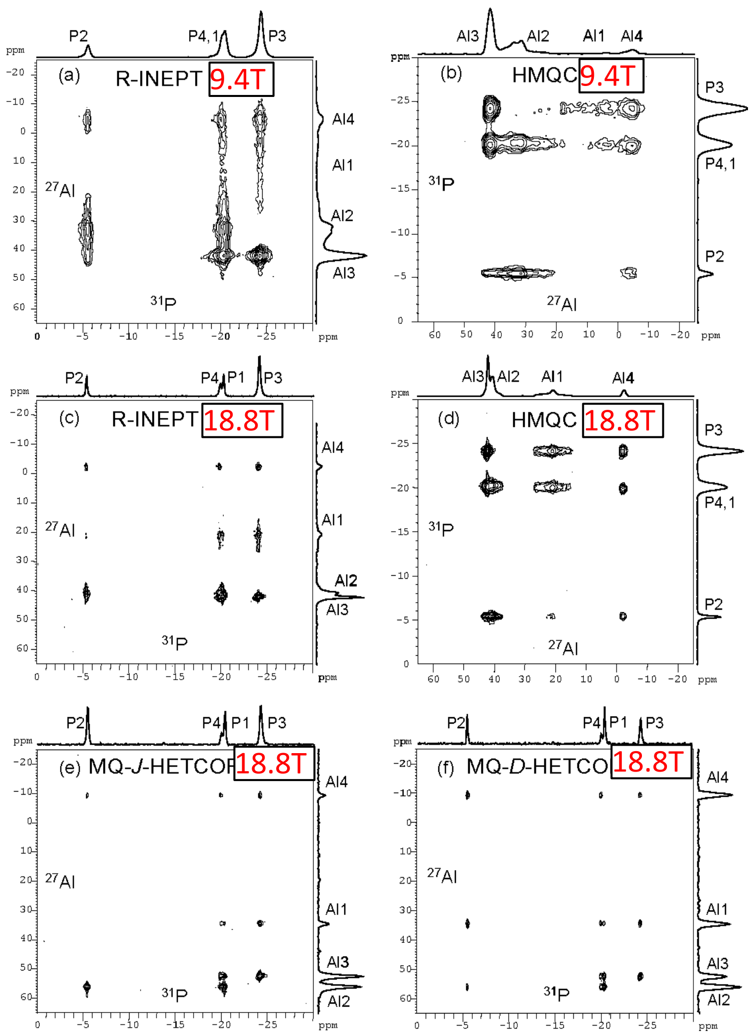


^{27}Al MAS spectra of aluminoborate $9Al_2O_3+2B_2O_3$

Transformational role of ultrahigh field: at 40 T, second order quadrupolar broadening and shift are diminished; the line width is mainly due to field drift

Z. Gan et al., *JACS*, 124, 5634 (2002)

2D HETCOR spectra of quadrupolar nuclei at high fields



2D ^{27}Al-^{31}P HETCOR spectra of $AlPO_4$-14:

- Resolution of MAS-based spectra at 18.8 T in (c) and (d) rivals that of MQ-HETCOR taken at 9.4 T! (not shown here) Assuming 20% efficiency of MQMAS, time performance at 36 T could improve by an incredible factor of $(36/9.4)^5$ times $5^2 \cong 2\text{x}10^4$

M. Pruski et al., *JMR*, *184*, 1 (2007)

Conclusion and acknowledgments

The role of ultrahigh field in SS-NMR and materials research will be transformational:

- dramatically expanded capabilities: resolution, detection limits, range of nuclei
- dramatically expanded range of applications to new materials

Thank you DOE, NSF and NIH for supporting our science!

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