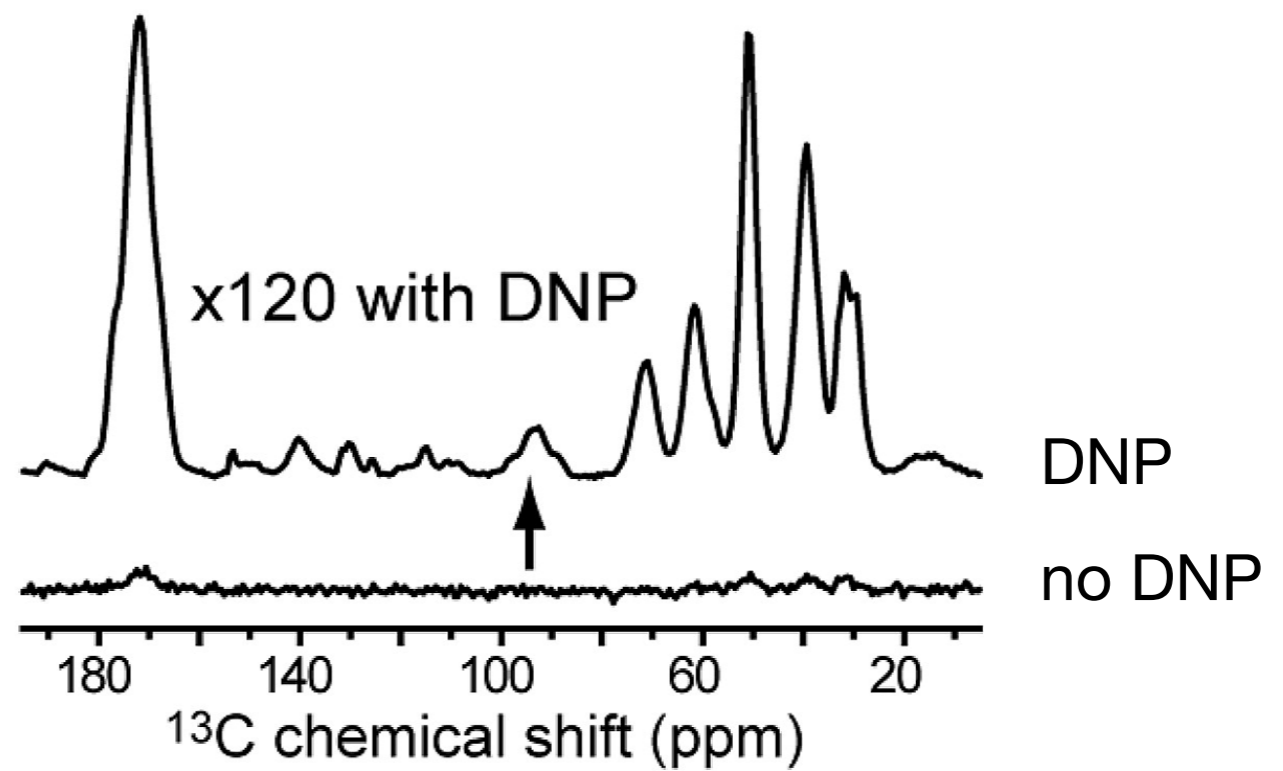


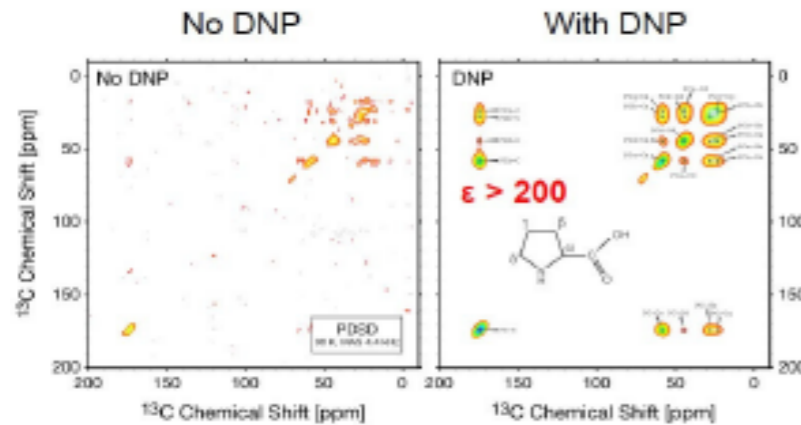
Applications of Dynamic Nuclear Polarisation



Józef Lewandowski

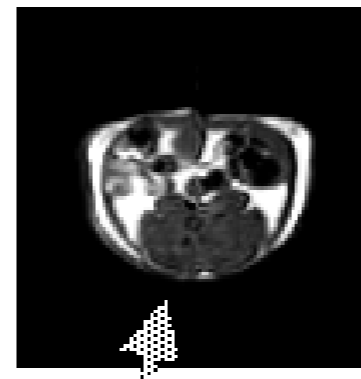
April 10 2013

Why to do DNP?



T. Maly/ R. Griffin, MIT

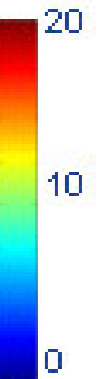
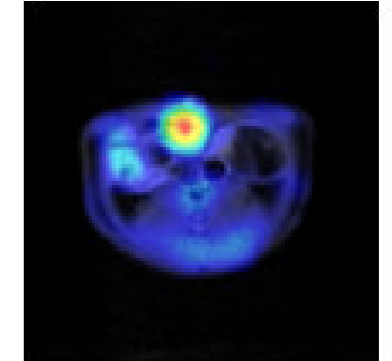
Anatomical ¹H image



¹³C image



DNP ¹³C-lactate



Klaes Golman, René in't Zandt, Mathilde Lerche, Rikard Pehrson,
and Jan Henrik Ardenkjaer-Larsen

- more signal
- faster acquisition
- new, previously not possible applications, now within the reach

What do you need for DNP?

1. source of large polarisation
2. way to transfer it to the species you care about
(relaxation or coherent process)
3. detect the high signal for your hyperpolarised species
(they have to live long enough)



- laser polarised noble gases (^3He and ^{129}Xe)
- chemical induced dynamic nuclear polarization (CIDNP)
- parahydrogen induced polarization (PHIP)
- microwave driven dynamic nuclear polarization (DNP)

Laser polarised noble gases (^3He and ^{129}Xe)



^3He and ^{129}Xe hyperpolarised using spin-exchange optical pumping (SEOP).

SEOP:

Circularly polarised infrared laser light excites e^- in Cs or Rb



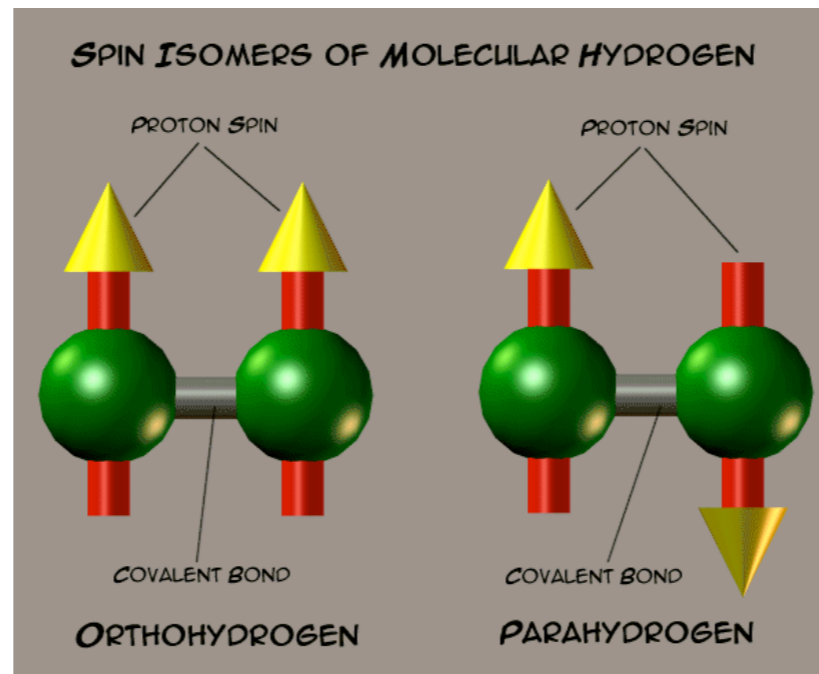
The angular momentum is transferred from metal e^- to noble gas nuclei through collisions.

- Using a thermal or photochemical reaction to create hyperpolarisation
- Powerful but not general

example:

photo-CIDNP effect in entire cells of cyanobacteria

Janssen, G. J.; Daviso, E.; van Son, M.; de Groot, H. J. M.; Alia, a; Matysik, J. *Photosynthesis research* **2010**, *104*, 275–82.

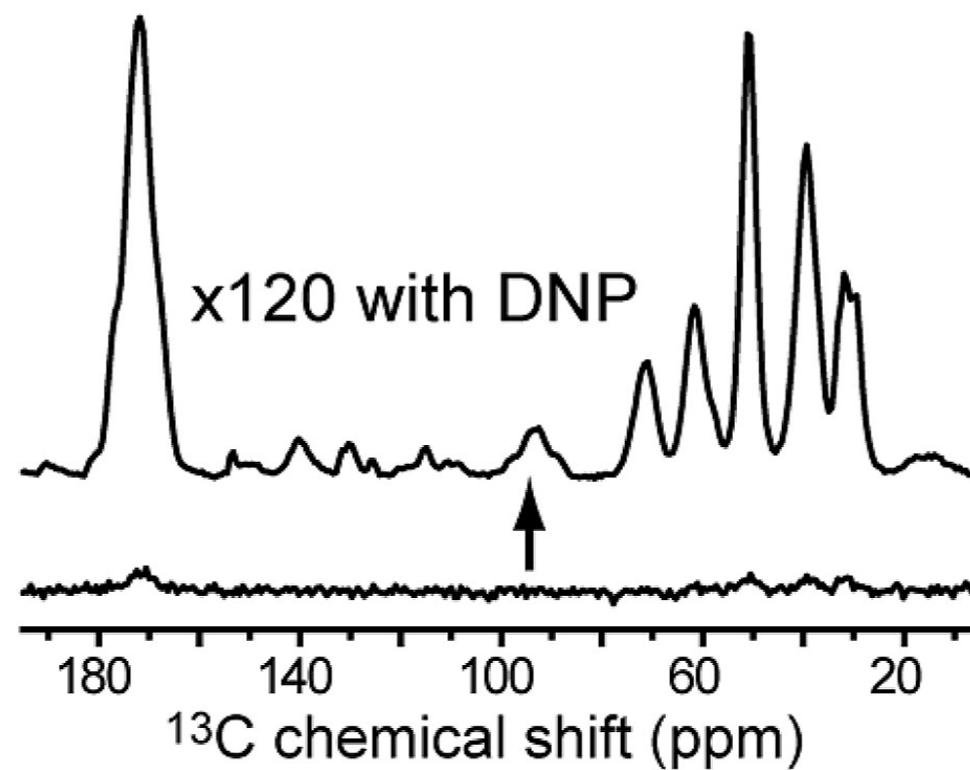


- Using parahydrogen in hydrogenation reactions to create hyperpolarisation
- Also known as PASADENA (Parahydrogen and Synthesis Allow Dramatically Enhanced Nuclear Alignment)

Mine is bigger than yours.

Enhancements

enhancement (ϵ)?



Mine is bigger than yours.

Enhancements

DNP enhancement; same sample at the same temperature

$$\varepsilon \rightarrow \text{SNR microwave on / SNR microwave off}$$

DNP enhancement; same sample at the room temperature

$$\varepsilon^\dagger \rightarrow \varepsilon \times \text{Boltzmann factor}$$

sensitivity enhancement; compared to a non-DNP sample at the same temperature

$$\Sigma \rightarrow \varepsilon \times \theta \times \sqrt{(\kappa)}$$

← ratio of T_1 for dry material and impregnated with radical solution

↑ paramagnetic quenching

sensitivity enhancement; compared to a non-DNP sample at the room temperature

$$\Sigma^\dagger \rightarrow \varepsilon \times \theta \times \sqrt{(\kappa)} \times \text{Boltzmann factor}$$

What do you need for microwave driven DNP?

polarizing agent/
unpaired electrons

e^-

+

microwave source



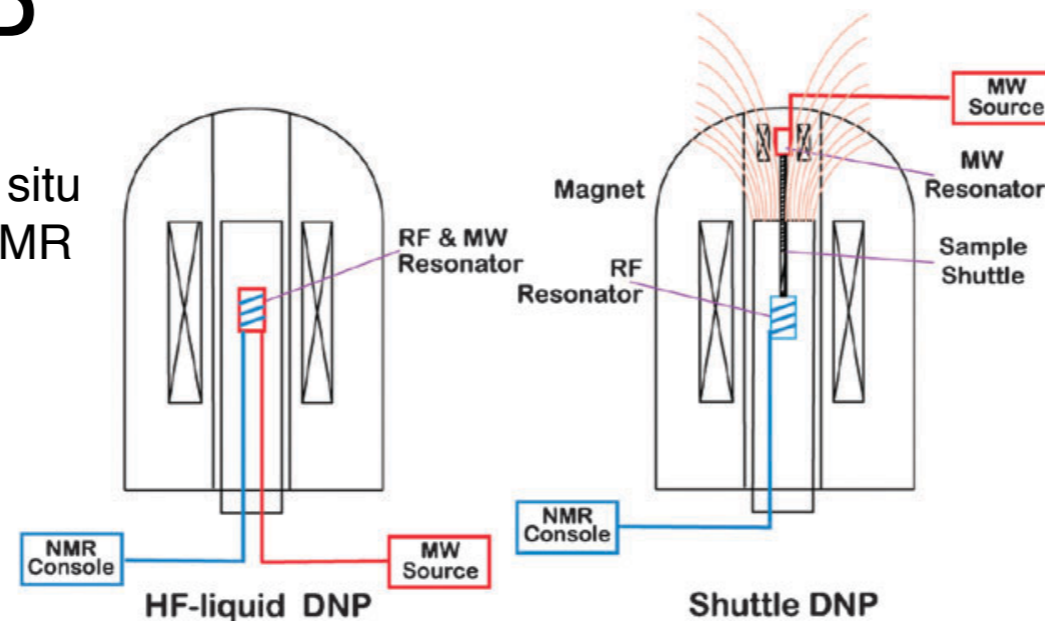
NMR/MRI set up



oh, and a sample,
off course...

HF-liquid DNP

high frequency liquid DNP: in situ microwave excitation at the NMR detection field

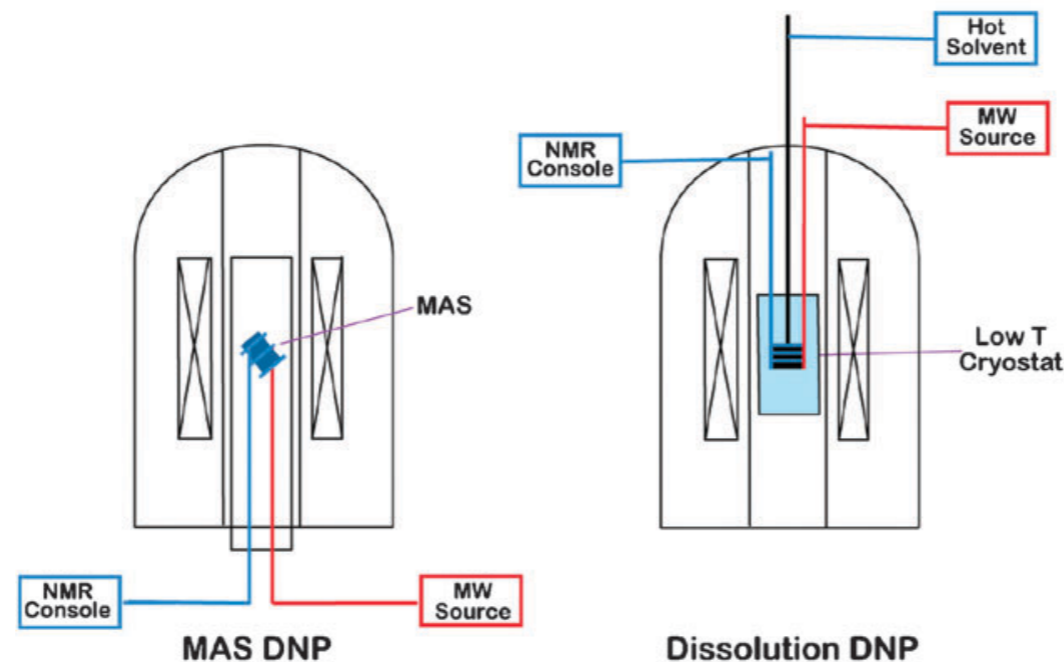


Shuttle DNP

liquid sample is rapidly moved from the low field, where the polarization is performed, to a high field region for NMR detection

High Field MAS DNP

gyrotron as a microwave source, solid sample irradiated with microwaves at the NMR detection field



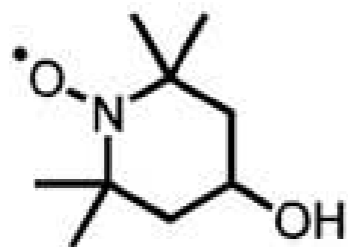
Dissolution DNP

the sample is polarized in the solid state at very low temperatures (typically 1–4 K) and magnetic fields of 3–7 T, rapidly dissolved, and finally transferred to either a high resolution NMR spectrometer or a MR imager

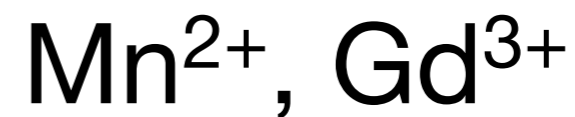
e^-

- naturally occurring in some samples (e.g. paramagnetic proteins)
- but most of the time you have to add it to the sample, e.g. dissolve it in a solution including the sample

Radicals



Transition Metals



What mechanism is used for DNP?

(This will affect the efficiency of the polarisation enhancement.
Need to consider the magnetic field and temperature.)

Does it dissolve in the solvent I want to use?

(Well, it has to somehow get near the sample that you try to enhance.)

Liquids

Overhauser effect (OE)

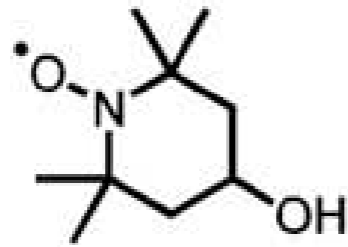
$$\epsilon \sim 1/B_0^2$$

Solids

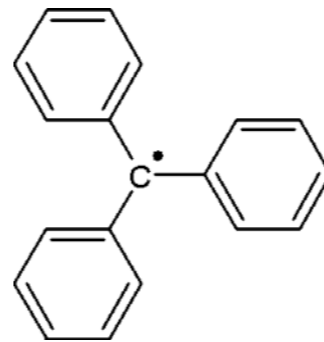
OE, solid effect (SE), cross effect (CE), thermal mixing (TM)

$$\epsilon \sim 1/B_0^2$$

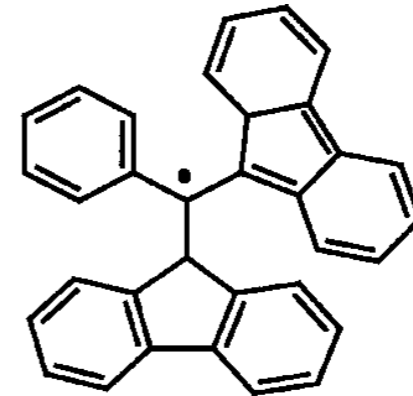
$$\epsilon \sim 1/B_0^1$$



4-hydroxy-TEMPO

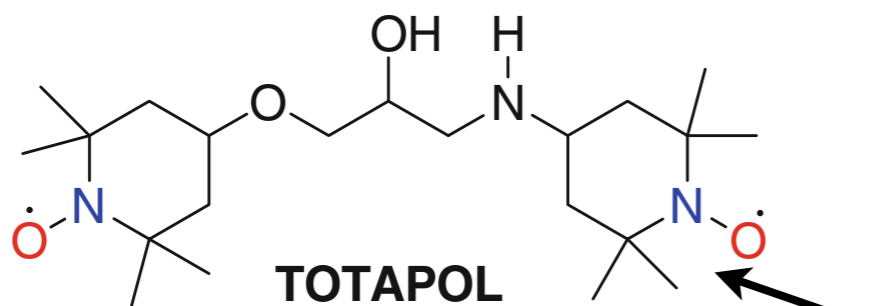
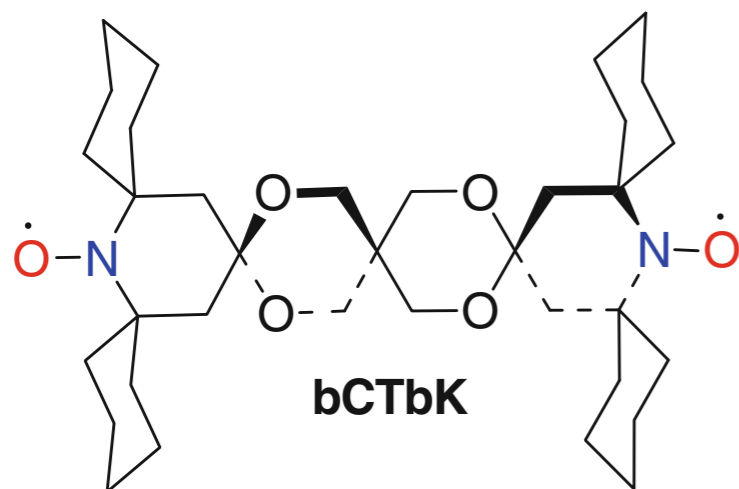
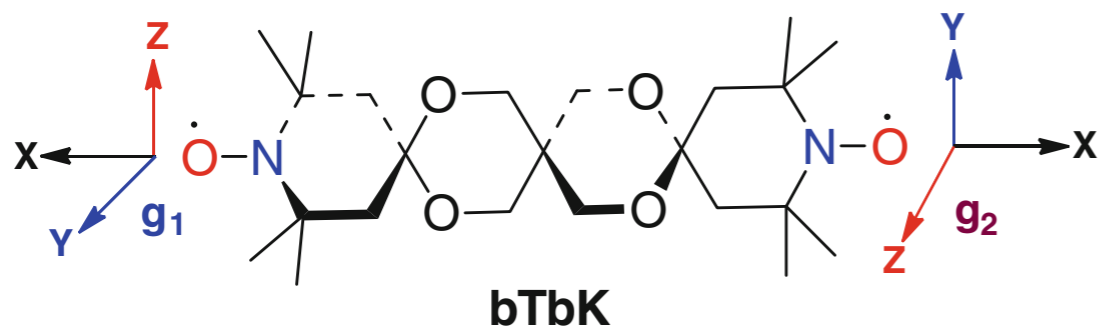


trityl radical



BDPA

- DNP in solids based on solid effect (SE); two spin process
- irradiating a forbidden transition at $\omega_n + \omega_e$ or $\omega_n - \omega_e$
- enhancement, $\epsilon \sim 1/B_0^2$
- requires polarising agent with relatively narrow EPR linewidth
- ($\omega_n \gg$ EPR line width)



water soluble



Paul Tordo

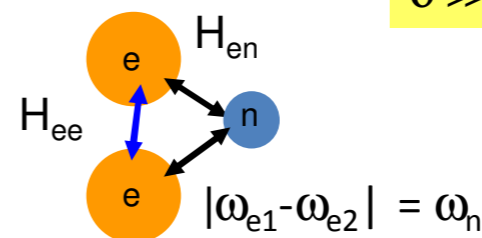


Tim Swager



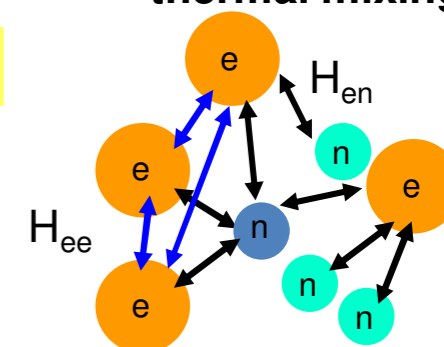
Bob Griffin

cross effect



$\delta \gg \omega_n$

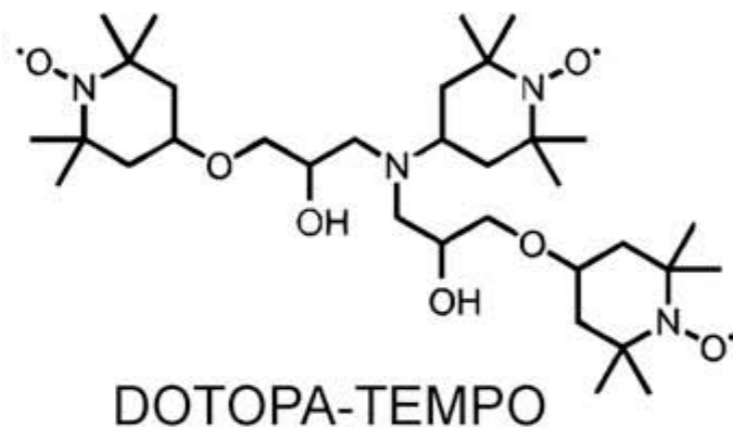
thermal mixing



Multi-spin model

- DNP based on cross-effect (CE) and thermal mixing (TM); ≥ 3 spin spin processes
- $\omega_{e1} + \omega_{e2} \approx \omega_n$
- enhancement, $\epsilon \sim 1/B_0^1$
- ($\omega_n < \text{EPR line width}$)

Thurber, K. R., Yau, W.-M. & Tycko, R. *J. Magn. Reson.* **204**, 303–13 (2010).



Rob Tycko
/rob tee-ko/

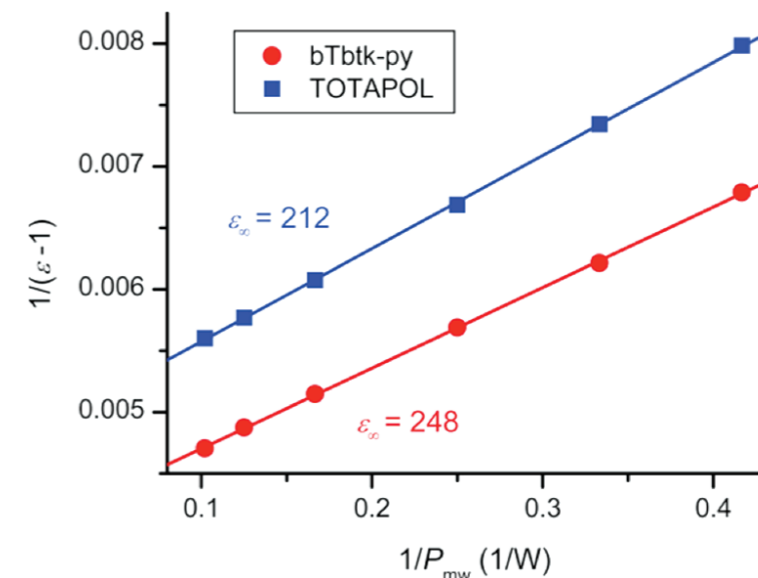
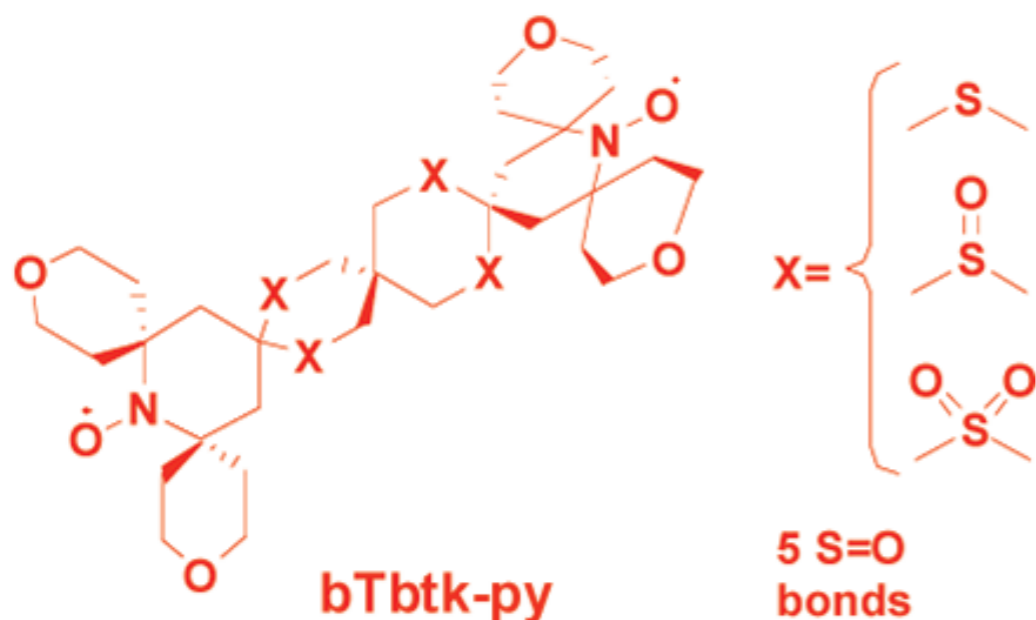
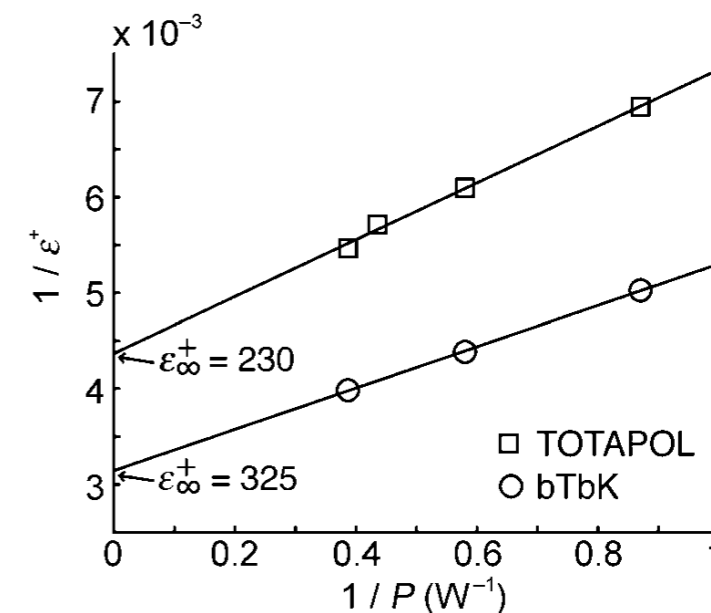
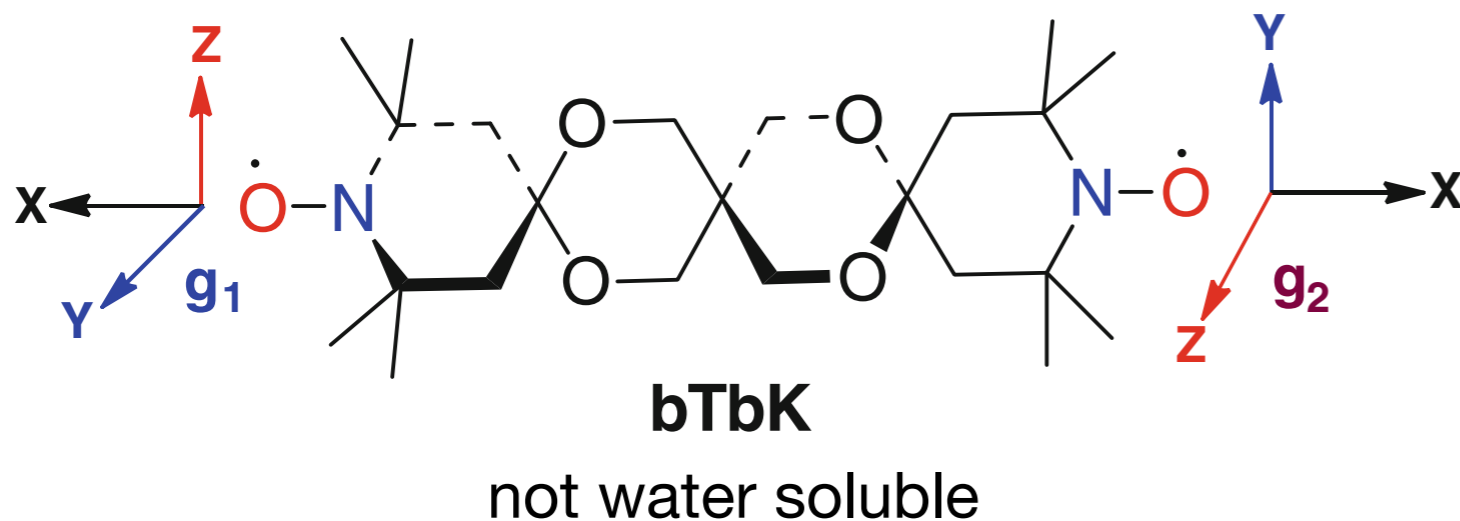
Temperature (K)	Dopant	Dopant concentration ^a (mM)	DNP signal enhancement ^b	DNP-enhanced signal ^c (arb. units)	T_{DNP} (s)	DNP-enhanced signal $\times (T_{\text{DNP}})^{-1/2}$
80	DOTOPA-TEMPO	20	12×	18	2.7 ± 0.7	11
	DOTOPA-TEMPO	30	10×	17	1.4	14
	TOTAPOL	20	6×	12	8.3	4.1
	4-Amino-TEMPO	40	11×	12	50 ± 15	1.8
	4-Amino-TEMPO	80	13×	17	7.0	6.5
	4-Amino-TEMPO	160	15×	9.4	1.2 ± 0.2	8.5
	4-Amino-TEMPO	320	9×	3.4	<1	
35	DOTOPA-TEMPO	20	34×	114	5.6	48
	DOTOPA-TEMPO	30	26×	114	2.4	73
	TOTAPOL	20	11×	57	18.5	13
	4-Amino-TEMPO	40	13×	33	90 ± 30	3.6
	4-Amino-TEMPO	80	41×	118	14.1	31
	4-Amino-TEMPO	160	34×	65	2.4	43
	4-Amino-TEMPO	320	15×	57	0.8 ± 0.2	63
16	DOTOPA-TEMPO	20	75×	578	10.6	177
	DOTOPA-TEMPO	30	59×	563	4.5	265
	TOTAPOL	20	26×	333	41	52
	4-Amino-TEMPO	40	29×	168	126	15
	4-Amino-TEMPO	80	82×	579	27	111
	4-Amino-TEMPO	160	54×	245	3.4	133
	4-Amino-TEMPO	320	15×	57	0.8 ± 0.2	63
7	DOTOPA-TEMPO	30	81×	1666	8.2	580
	4-Amino-TEMPO	40	48×	232	>200	

Kiesewetter, M. K., Corzilius, B., Smith, A. a, Griffin, R. G. & Swager, T. M. *J. Am. Chem. Soc.* **134**, 4537–40 (2012).

Matsuki, Y. *et al. Angewandte Chemie* **121**, 5096–5100 (2009).

$$CE: \omega_{e1} + \omega_{e2} \approx \omega_n$$

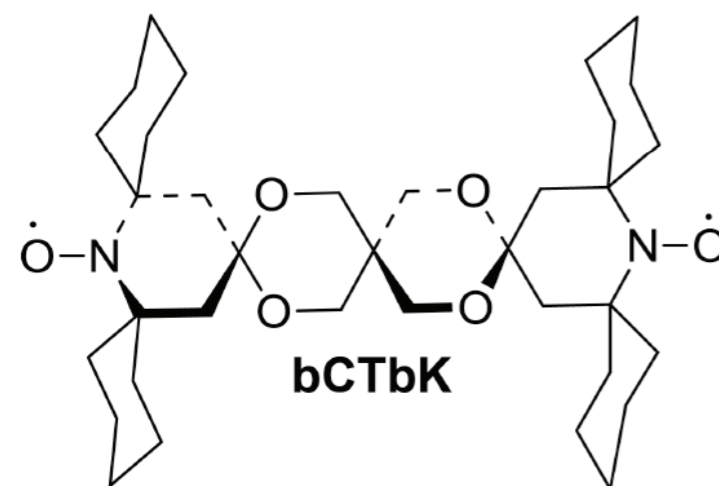
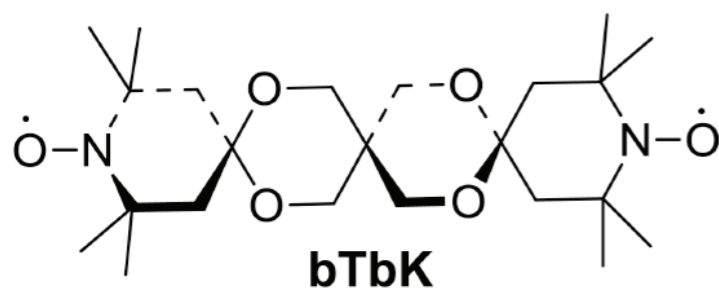
The effective electron resonance frequency can depend strongly on the molecular orientation with respect to the external magnetic field, and in a biradical the matching condition is controlled by the relative orientations of the electron g tensors.



Zagdoun, A.; Casano, G.; Ouari, O.; Lapadula, G.; Rossini, A. J.; Lelli, M.; Baffert, M.; Gajan, D.; Veyre, L.; Maas, W. E.; Rosay, M. M.; Weber, R. T.; Thieuleux, C.; Coperet, C.; Lesage, A.; Tordo, P.; Emsley, L. *J. Am. Chem. Soc.* **2012**, *134*, 2284–91.

Table 1. DNP Efficiency Comparison and Electron Spin–Lattice Relaxation Times for the TOTAPOL, bTbK, and bCTbK Biradicals under Optimal Conditions

biradical	solvent	$\epsilon_H^{a,b}$	$\epsilon_{Si,CP}^{a,c}$	$\Sigma_{Si,CP}^{a,c}$	$H_m(^{13}C)^{b,d}$	T_{1e}^e (μs)	T_{2e}^e (μs)
TOTAPOL	water	$\sim f$	31(3)	15(4)	0.75(3)	554(4)	1.6(1)
bTbK	tetrachloroethane	26(3)	21(3)	12(5)	0.51(2)	453(4)	1.5(1)
bCTbK	tetrachloroethane	105(3)	52(3)	38 (7)	1.00(4)	762(4)	2.8(1)



not water soluble

- longer electron spin-lattice relaxation time helps to get higher enhancements



Lyndon Emsley



Melanie Rosay



Anne Lesage



Björn Corzilius

Corzilius, B. *et al.* *J. Am. Chem. Soc.* **133**, 5648–51 (2011).

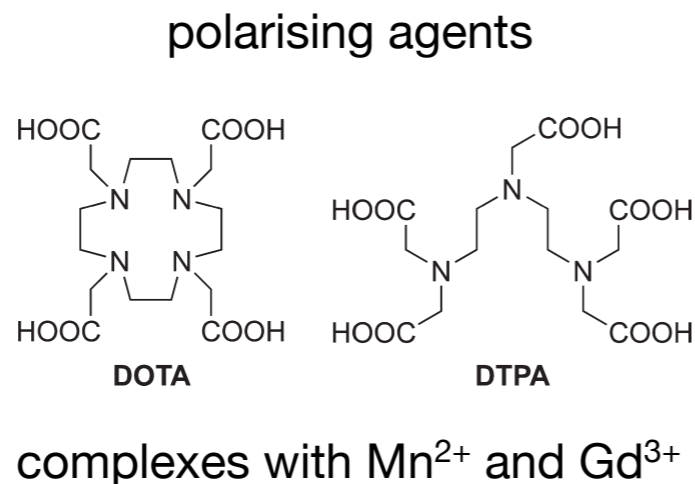
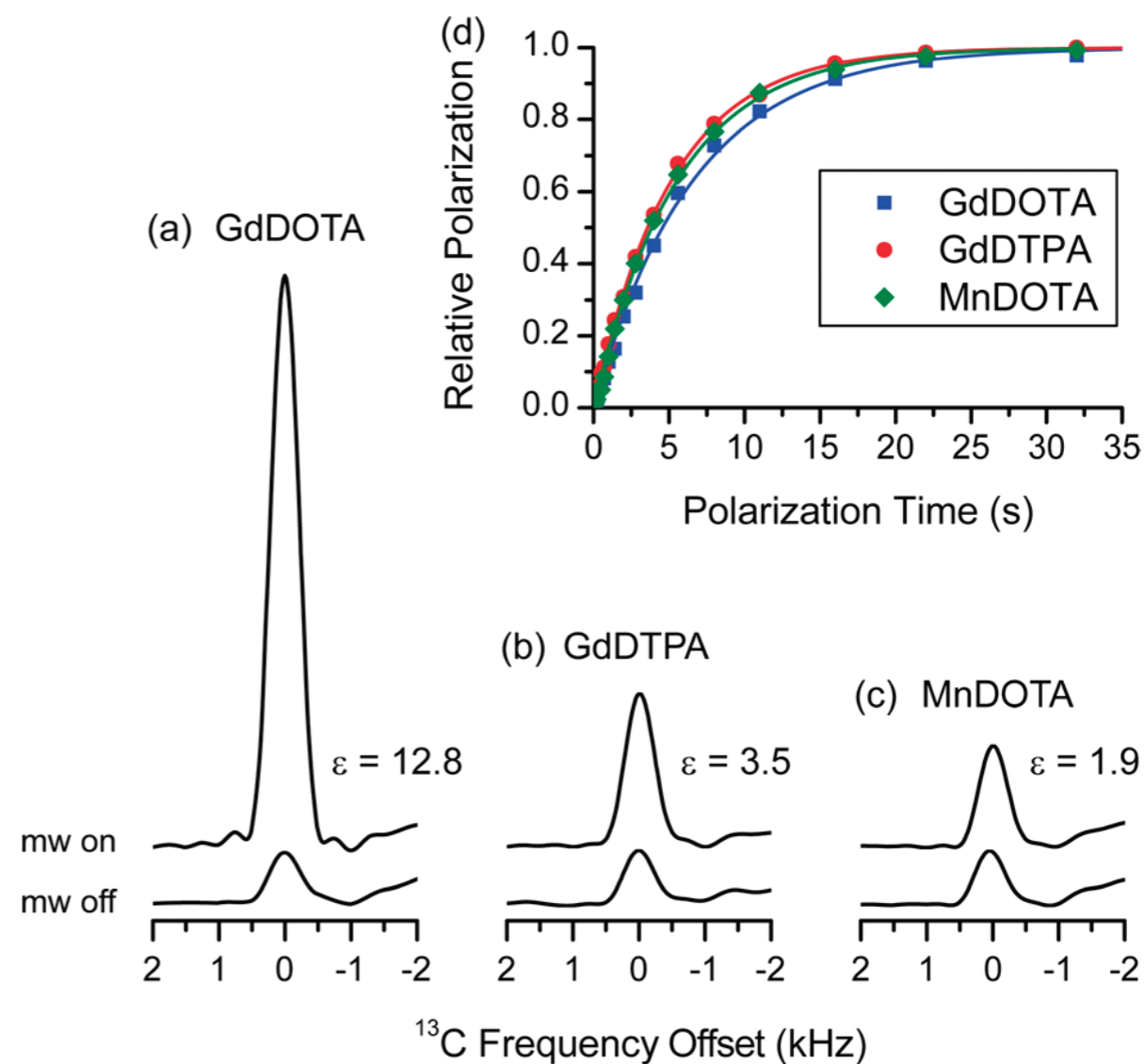


Table 1. Experimental DNP Parameters

sample	enhancement	integral enhancement	buildup time (s)
GdDOTA ^a	12.8	0.98	6.6
GdDTPA ^a	3.5	0.70	5.2
MnDOTA ^b	1.9	0.89	5.6

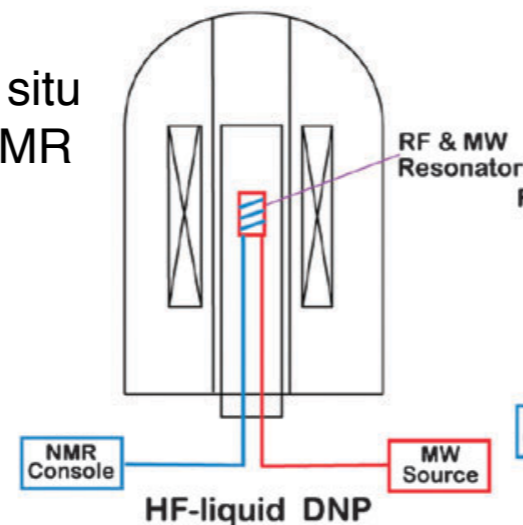
^aAt 6 W microwave power. ^bAt 5 W microwave power. For further details, see the text.



- modest enhancements achievable (up to $\epsilon \sim 13$)
- enhancement related to the effective line width of the central EPR transition

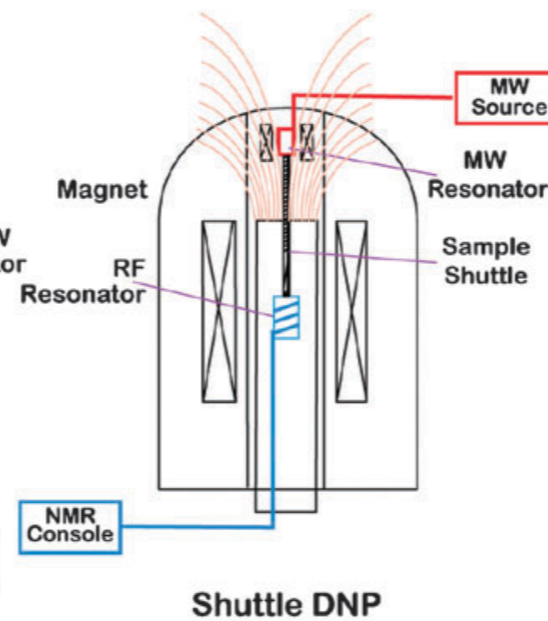
HF-liquid DNP

high frequency liquid DNP: in situ microwave excitation at the NMR detection field



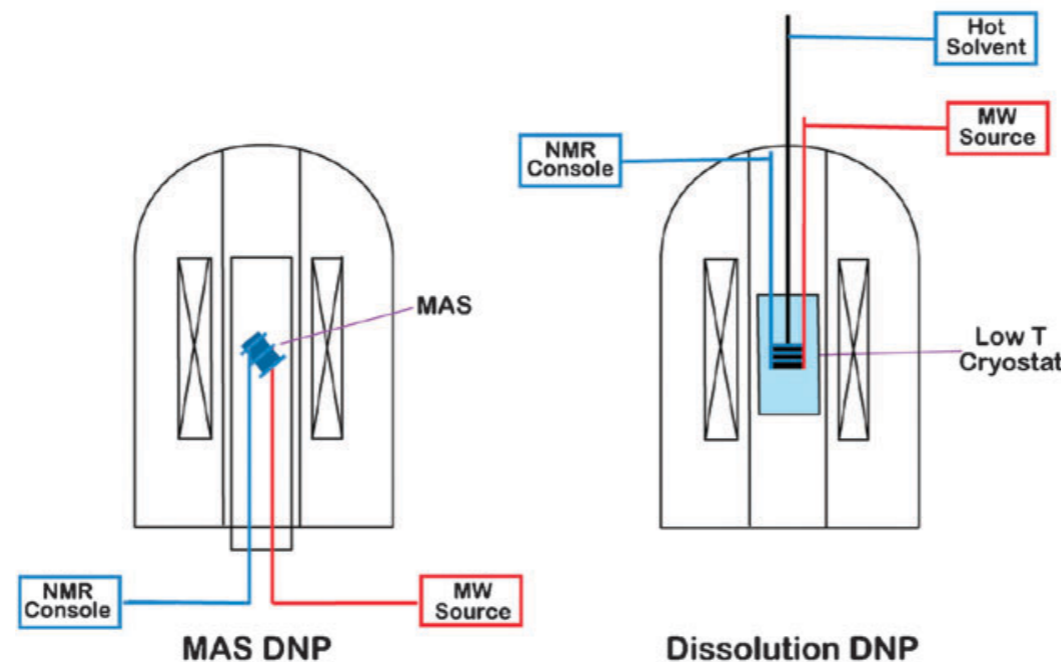
Shuttle DNP

liquid sample is rapidly moved from the low field, where the polarization is performed, to a high field region for NMR detection



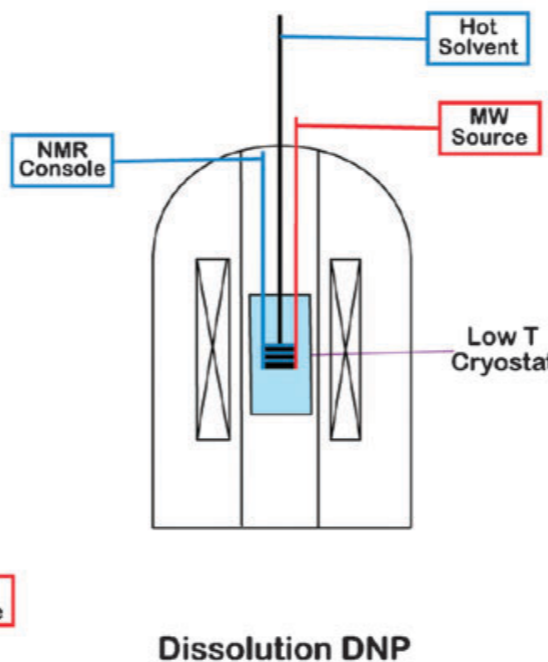
High Field MAS DNP

gyrotron as a microwave source, solid sample irradiated with microwaves at the NMR detection field



Dissolution DNP

the sample is polarized in the solid state at very low temperatures (typically 1–4 K) and magnetic fields of 3–7 T, rapidly dissolved, and finally transferred to either a high resolution NMR spectrometer or a MR imager



- frozen solution (aqueous and non-aqueous)
- frozen solution containing macroscopic particles and aggregates
- sedimented solutes
- porous materials with non-aqueous solvents
- crystals?

An aqueous solvent mixture consisting of **deuterated glycerol**, D_2O , water, and a **soluble radical** polarizing agent provides a **glass-forming matrix** that **distributes the polarizing agents uniformly** and at the same time acts as a cryoprotectant.



➡ enhancements in deuterated/protonated solvent mixtures are higher because relaxation is reduced and spin diffusion preserved

- fast nuclear relaxation destroys the enhanced signal

(Why do they always start with proline and not alanine? How about the temperature?)

- spin diffusion transfers polarisation from the directly polarized protons to the protons that are too far from the polarising agent to experience direct enhancement of polarisation

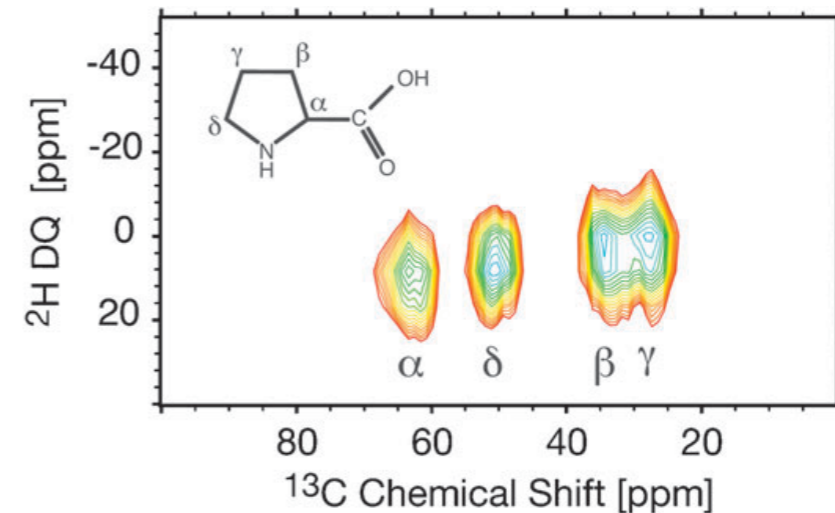
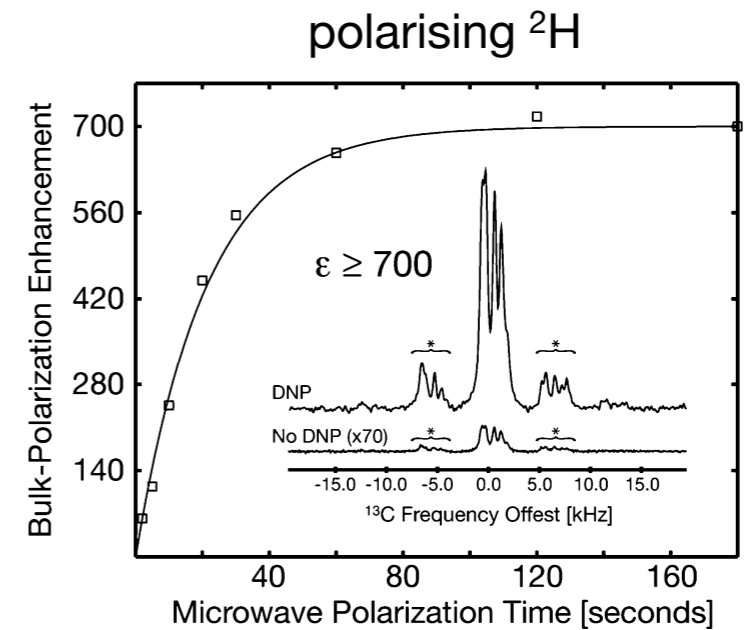
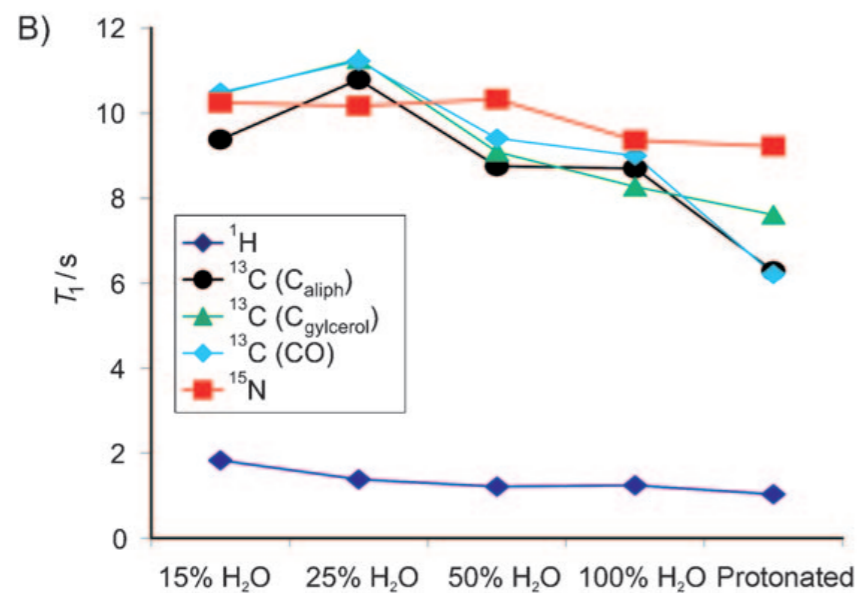
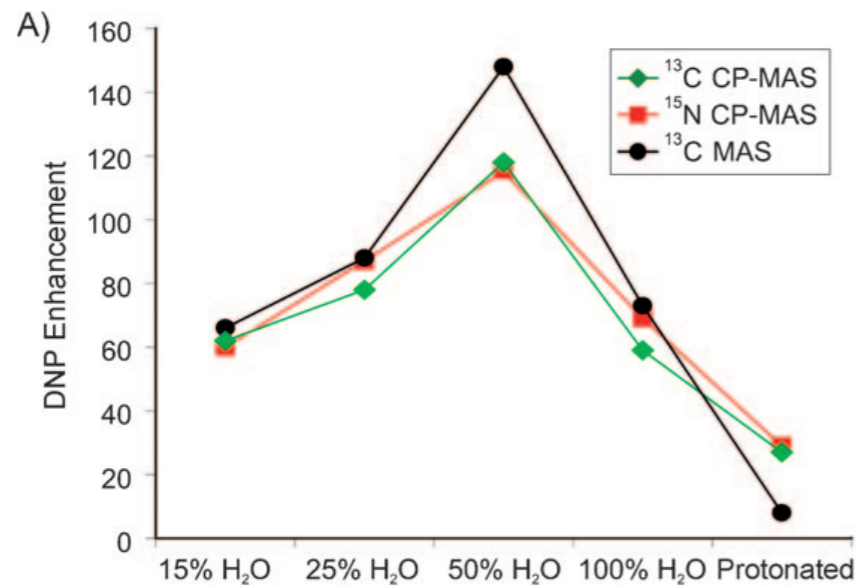
(Do you know what spin diffusion rate depends on?)

➡ typical conditions: $[D_6]$ DMSO or $[D_8]$ glycerol/
 D_2O/H_2O in 6:3:1 ratio

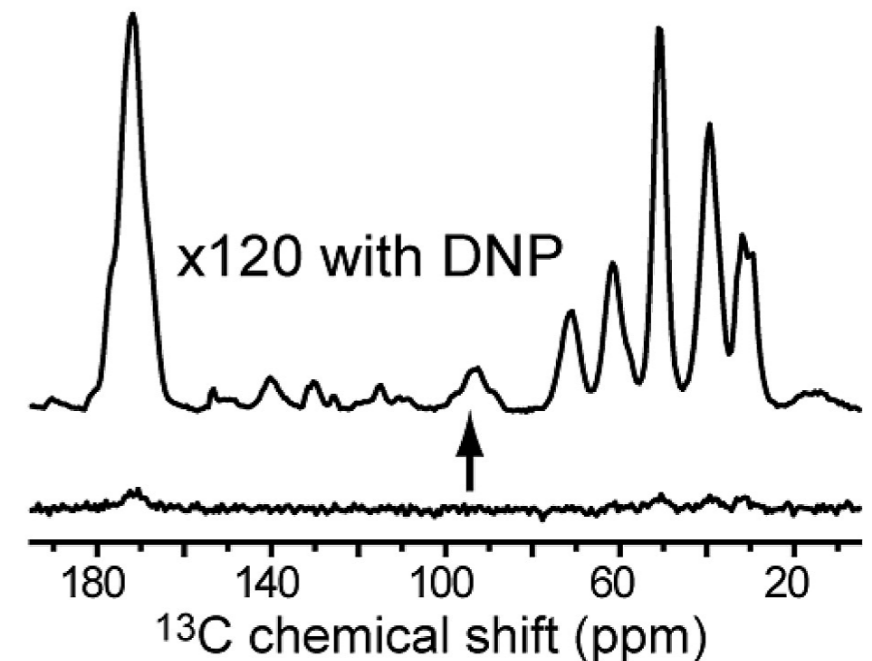
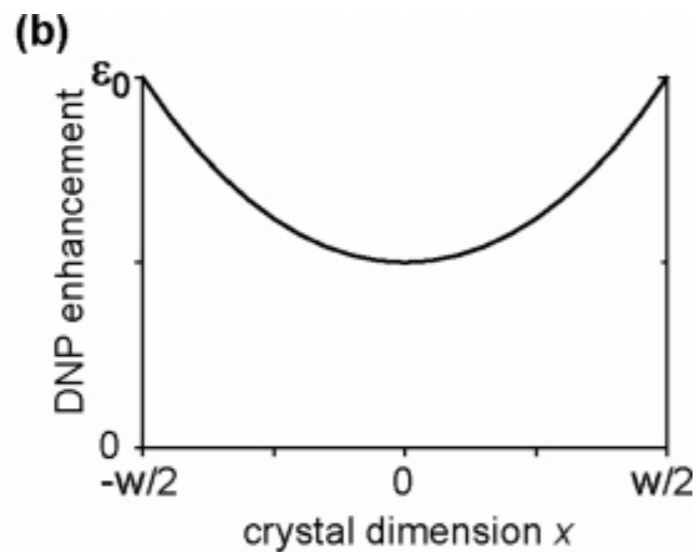
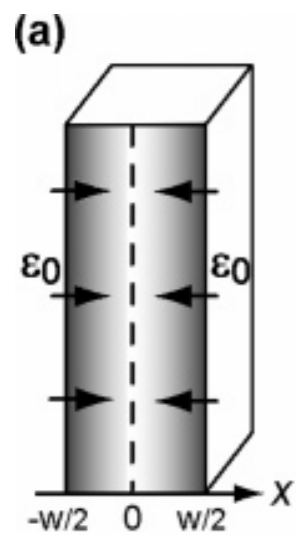
Perdeuteration may be also good for the sample itself

Akbey, Ü.; Franks, W. T.; Linden, A.; Lange, S.; Griffin, R. G.; van Rossum, B.-J.; Oschkinat, H.; Rossum, B. *Van Angew. Chem.* **2010**, *49*, 1–5.

Maly, T.; Andreas, L. B.; Smith, A. A.; Griffin, R. G. *Phys. Chem. Chem. Phys.* **2010**, *12*, 5872–8.



➡ establish balance between reduction of relaxation and retention of spin diffusion

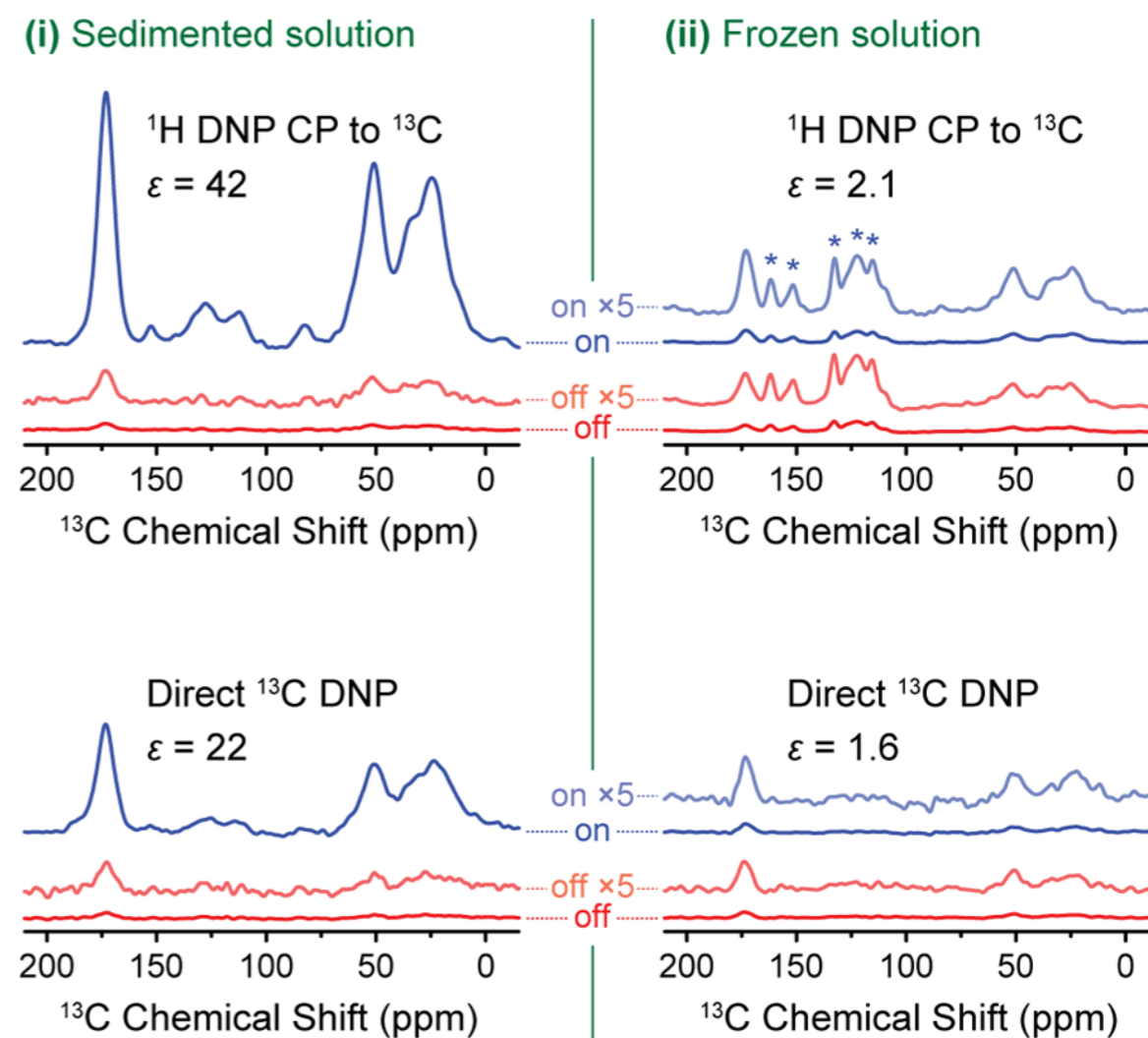


➡ we can also use spin diffusion to transfer polarisation into the particles that are not penetrated by the radicals

Table 1. Summary of DNP Enhancements and ^1H , ^{13}C Polarization Buildup Time Constants for All Samples

sample	^1H T_B (s)	^{13}C T_B (s)	ϵ ($^1\text{H}/^{13}\text{C}$)
frozen sediment, 2 mM TOTAPOL (i)	1.2	12.4	42/22
frozen solution, 2 mM TOTAPOL (ii)	2.1	13.4	2.1/1.6
frozen sediment sans TOTAPOL (iii)	2.1 ^a	12.1 ^a	– ^b /– ^b
cryoprotected 2 mM TOTAPOL (A)	20.4/1.1 ^c	– ^d	70/– ^d
cryoprotected 15 mM TOTAPOL (B)	5.0/0.6 ^c	3.5	100/~10

^a T_B equals nuclear T_1 for non-DNP enhanced signals. ^b $\epsilon = 1$ by definition for non-DNP-enhanced signals. ^cSlow and fast component of biphasic buildup. ^dNot determined.



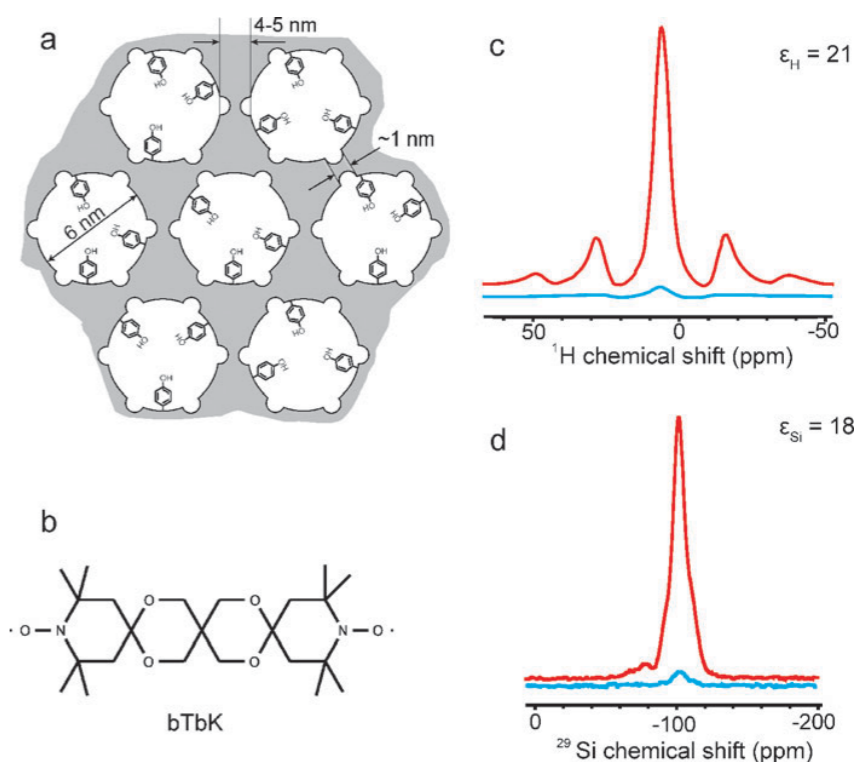
- ➡ sedimented solutes - “microcrystalline glass”
- ➡ use low (< 5mM) concentration of TOTAPOL

Table 1 Proton and silicon-29 enhancements measured for **I** impregnated with a 10 mM solution of bTbK in different solvents

Category ^a	Solvent	ϵ_{Si} ^b	ϵ_{H} ^b
1 good candidate →	Chloroform	10	16
	1,1,2,2-Tetrachloroethane	18	21
	<i>trans</i> -Dichloroethene	8	9
	1,2-Dichlorobenzene	16	19
	1,2-Dichloroethane	18	23
	1,2-Dibromoethane	11	11
	1,3-Dibromobutane	12	19
	1,1,2,2-Tetrabromoethane	14	12
2	Hexafluoropropan-2-ol	9	6
	2,2,2-Trifluoroethanol	7	5
	Isopropanol	7	6
	Mesitylene	5	6
3	Tetrahydrofuran	1	4
4	Methyl-ter butylether (MTBE)	1	3
	Dimethylformamide (DMF)	3	3
	Dimethylsulfoxide (DMSO)	4	4
	Acetonitrile	7	5
5	1,1,1-Trichloroethane	3	3
	Dichloroethane	3	9

^a See text for discussion. ^b Sample preparation and definition of ϵ are in ESI.

hybrid silica material

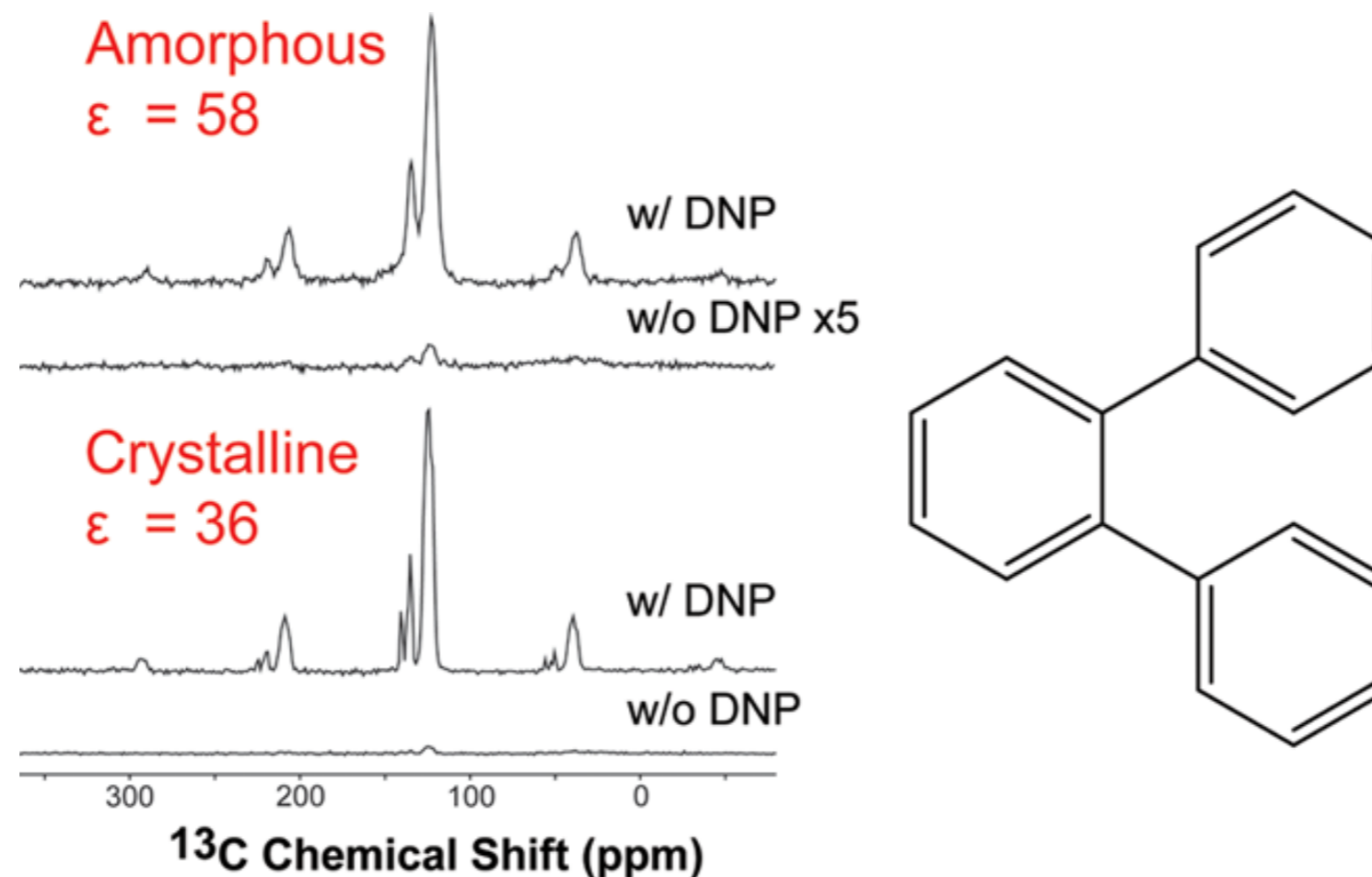


➔ a lot of inorganic systems require non-aqueous solvents

Do we have to have solvent?

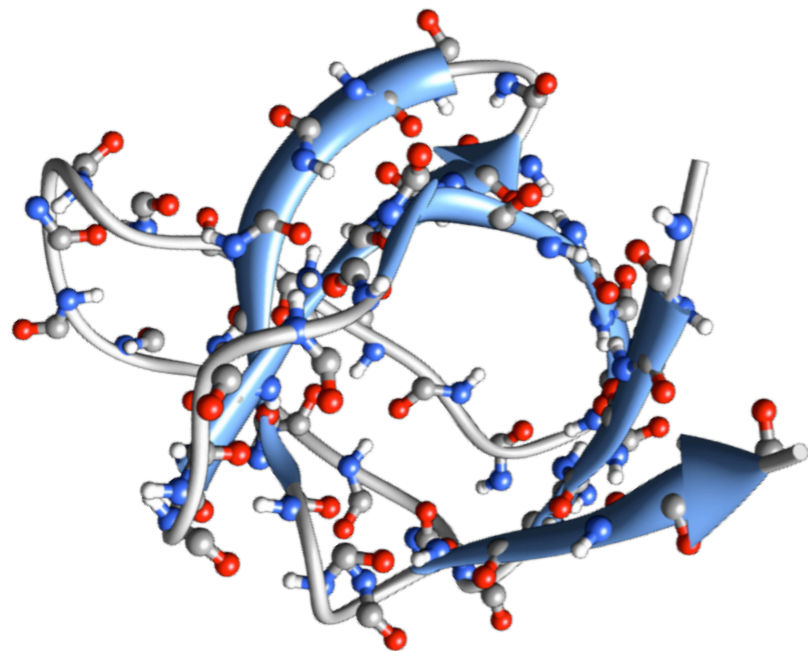
Ong, T.-C.; Mak-Jurkauskas, M. L.; Walish, J. J.; Michaelis, V. K.; Corzilius, B.; Smith, A. a; Clausen, A. M.; Cheetham, J. C.; Swager, T. M.; Griffin, R. G.

J. Phys. Chem. B **2013**, *117*, 3040–6.

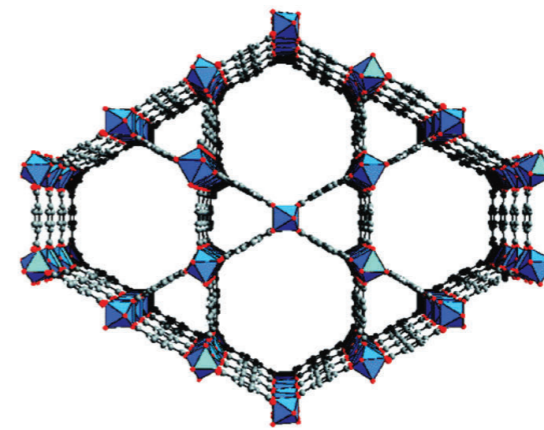


➡ having glass helps but DNP can provide large enhancements in dry, solvent-free crystalline systems, while maintaining excellent spectral resolution (in spite of clustering of radicals)

Biomolecules



Materials



see also: Rossini, A. J.; Zagdoun, A.; Hegner, F.; Schwarzwälder, M.; Gajan, D.; Copéret, C.; Lesage, A.; Emsley, L. *J. Am. Chem. Soc.* 2012, 134, 16899–908.

NMR Spectroscopy

Rapid Natural-Abundance 2D ^{13}C - ^{13}C Correlation Spectroscopy Using Dynamic Nuclear Polarization Enhanced Solid-State NMR and Matrix-Free Sample Preparation**

Hiroki Takahashi, Daniel Lee, Lionel Dubois, Michel Bardet, Sabine Hediger, and Gaël De Paëpe*

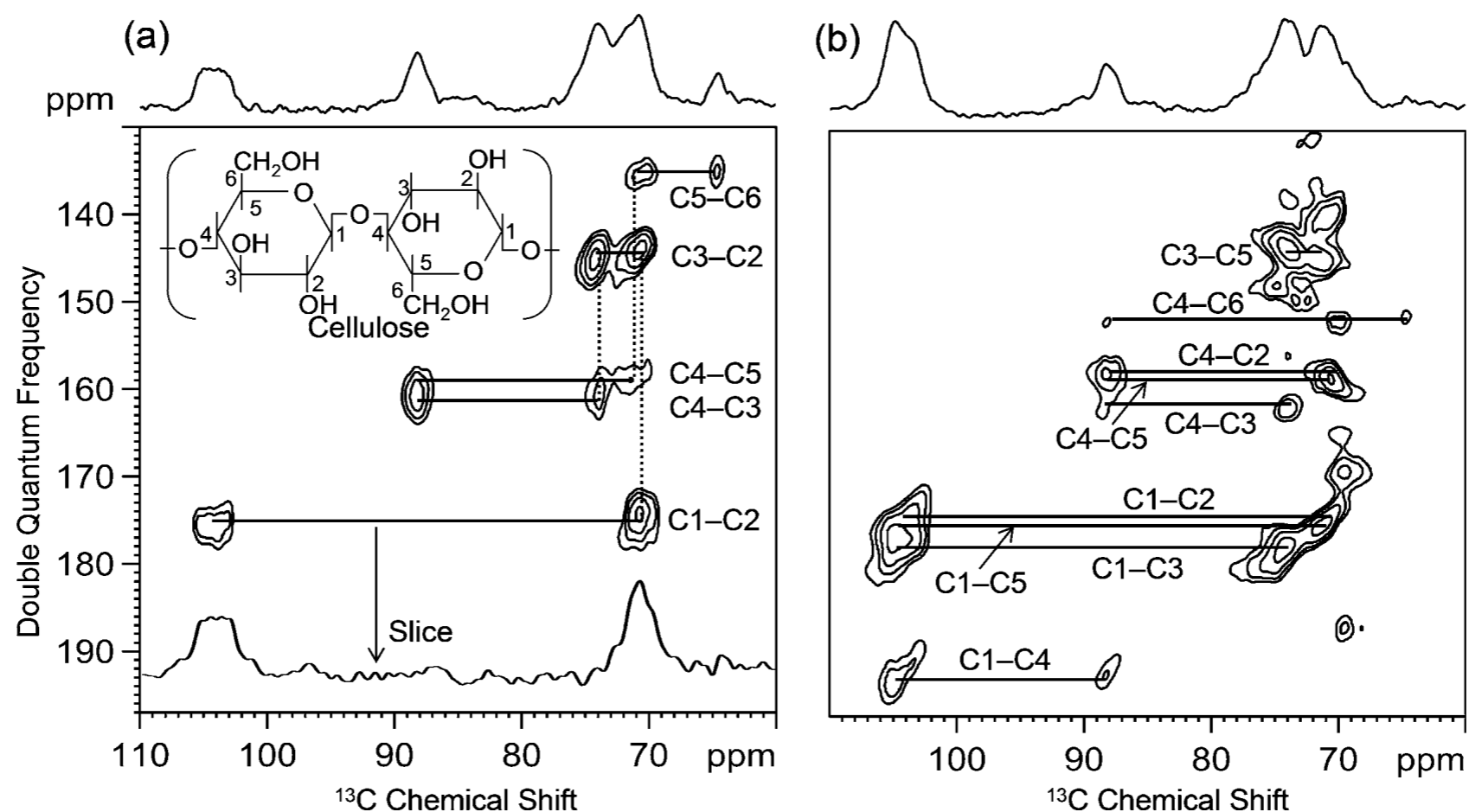


Figure 2. DNP-enhanced 2D DQ-SQ ^{13}C - ^{13}C POST-C7 dipolar correlation spectra of MF NA microcrystalline cellulose recorded at 105 K. MAS frequency and the number of scans are 8 kHz and 16, respectively. a) The spectrum is obtained in 20 min with a recycle delay of 0.9 s, 1.4 ms evolution time, and 1 ms POST-C7 mixing. b) The experimental time is 2 h with a recycle delay of 3.4 s, 2.3 ms evolution time, and 3.5 ms of POST-C7 mixing. Projections are shown on the top.

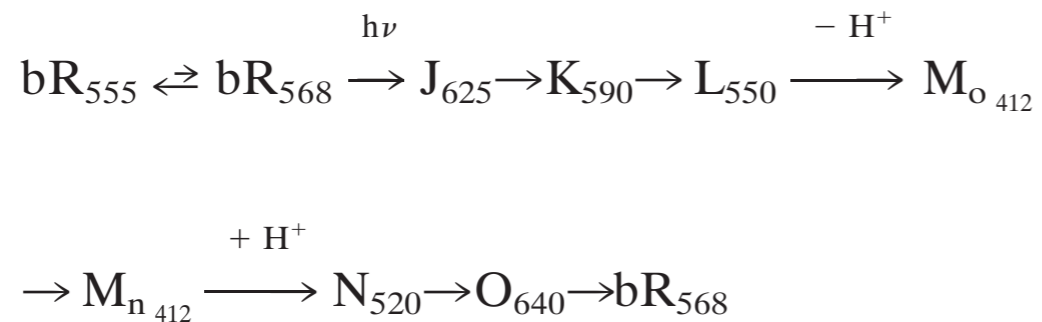
Functional and shunt states of bacteriorhodopsin resolved by 250 GHz dynamic nuclear polarization-enhanced solid-state NMR

Vikram S. Bajaj^{a,1}, Melody L. Mak-Jurkauskas^{a,b}, Marina Belenky^b, Judith Herzfeld^b, and Robert G. Griffin^{a,2}

^aDepartment of Chemistry and Francis Bitter Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, MA 02139; and ^bDepartment of Chemistry, Brandeis University, Waltham, MA 02454

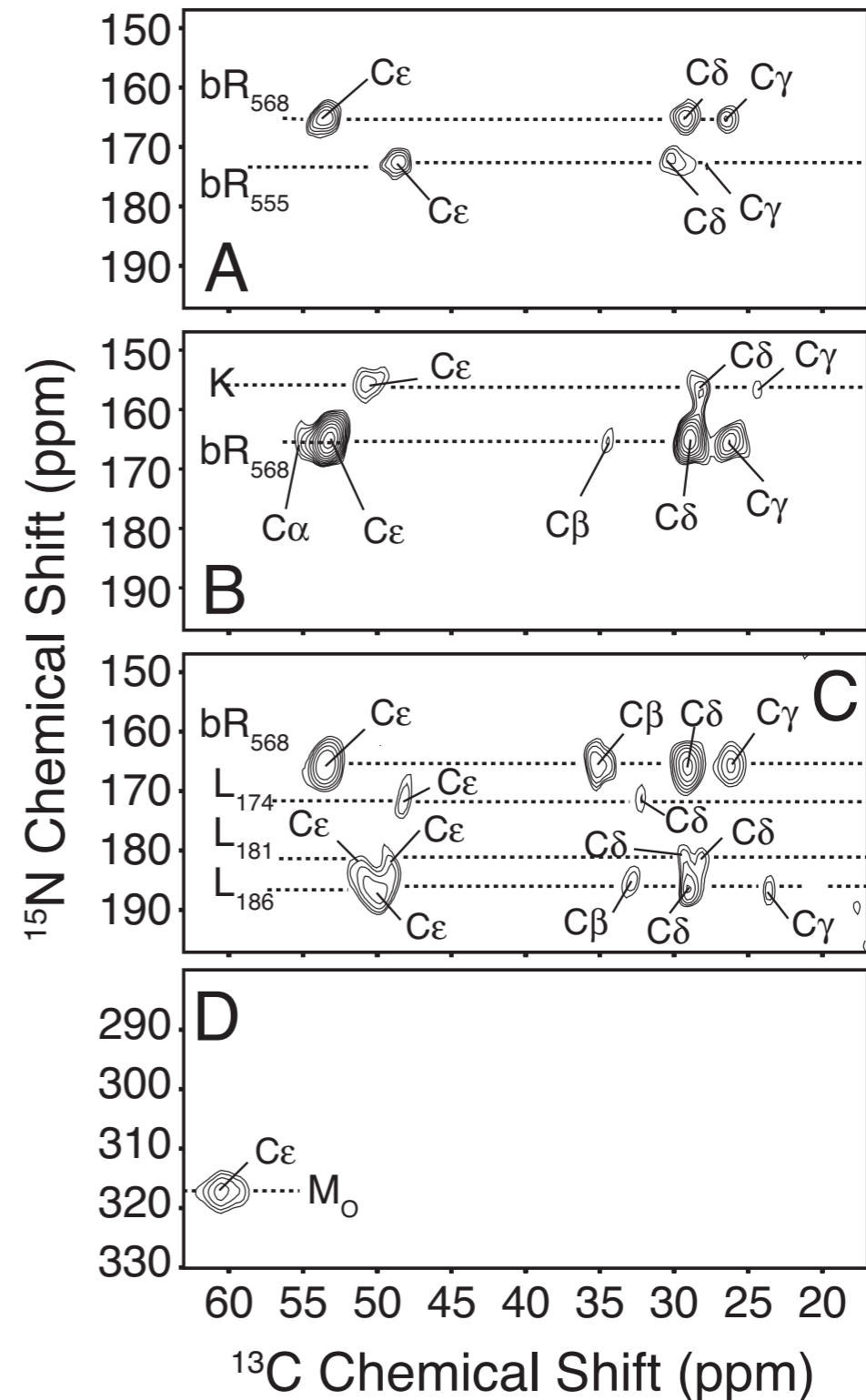
Edited by Brian M. Hoffman, Northwestern University, Evanston, IL, and approved April 13, 2009 (received for review January 27, 2009)

9244–9249 | PNAS | June 9, 2009 | vol. 106 | no. 23



Observation and structural studies of reaction intermediates of proteins are challenging because of the mixtures of states usually present at low concentrations. Here, we use a 250 GHz gyrotron (cyclotron resonance maser) and cryogenic temperatures to perform high-frequency dynamic nuclear polarization (DNP) NMR experiments that enhance sensitivity in magic-angle spinning NMR spectra of cryo-trapped photocycle intermediates of bacteriorhodopsin (bR) by a factor of ≈ 90 . Multidimensional spectroscopy of U-¹³C,¹⁵N-labeled samples resolved coexisting states and allowed chemical shift assignments in the retinylidene chromophore for several intermediates not observed previously. The correlation spectra reveal unexpected heterogeneity in dark-adapted bR, distortion in the K state, and, most importantly, 4 discrete L substates. Thermal relaxation of the mixture of L's showed that 3 of these substates revert to bR₅₆₈ and that only the 1 substate with both the strongest counterion and a fully relaxed 13-*cis* bond is functional. These definitive observations of functional and shunt states in the bR photocycle provide a preview of the mechanistic insights that will be accessible in membrane proteins via sensitivity-enhanced DNP NMR. These observations would have not been possible absent the signal enhancement available from DNP.

Magic Angle Spinning DNP on a membrane protein



DNP on oriented membrane proteins

Appl Magn Reson (2012) 43:91–106
DOI 10.1007/s00723-012-0338-5

Applied
Magnetic Resonance

Salnikov, E. S.; Ouari, O.; Koers, E.; Sarrouj, H.; Franks, T.; Rosay, M. M.; Pawsey, S.; Reiter, C.; Bandara, P.; Oschkinat, H.; Tordo, P.; Engelke, F.; Bechinger, B.
Applied Magnetic Resonance **2012**, *43*, 91–106.

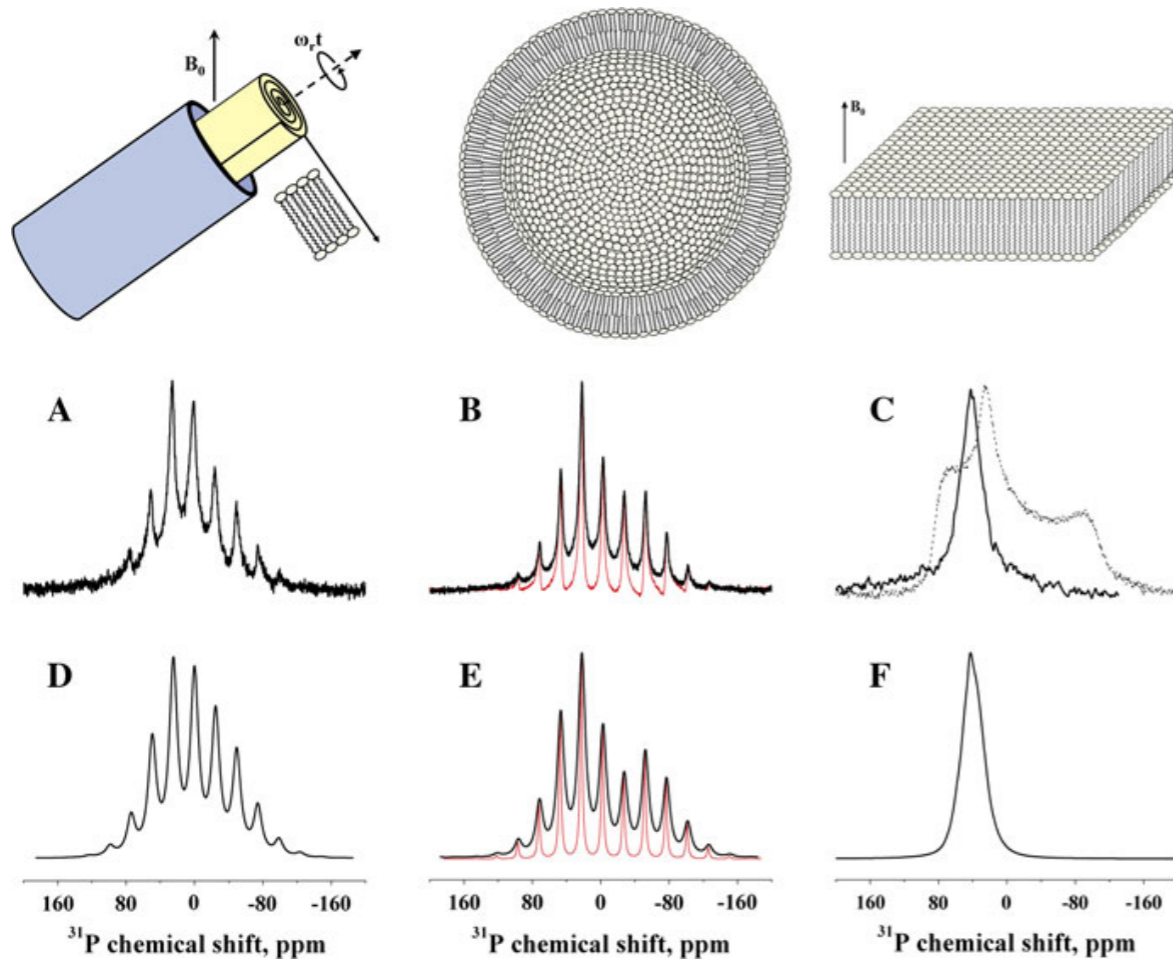
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Developing DNP/Solid-State NMR Spectroscopy of Oriented Membranes

Evgeniy S. Salnikov · Olivier Ouari · Eline Koers · Hiba Sarrouj · Trent Franks · Melanie Rosay · Shane Pawsey · Christian Reiter · Priyanga Bandara · Hartmut Oschkinat · Paul Tordo · Frank Engelke · Burkhard Bechinger

vesicles

bilayers



Hartmut Oschkinat



Burkhard Bechinger

Magic Angle Spinning DNP on a virus

Chemical Shifts for the Unusual DNA Structure in Pf1 Bacteriophage from Dynamic-Nuclear-Polarization-Enhanced Solid-State NMR Spectroscopy

Ivan V. Sergeyev,[†] Loren A. Day,[‡] Amir Goldbourt,[§] and Ann E. McDermott^{*,†}

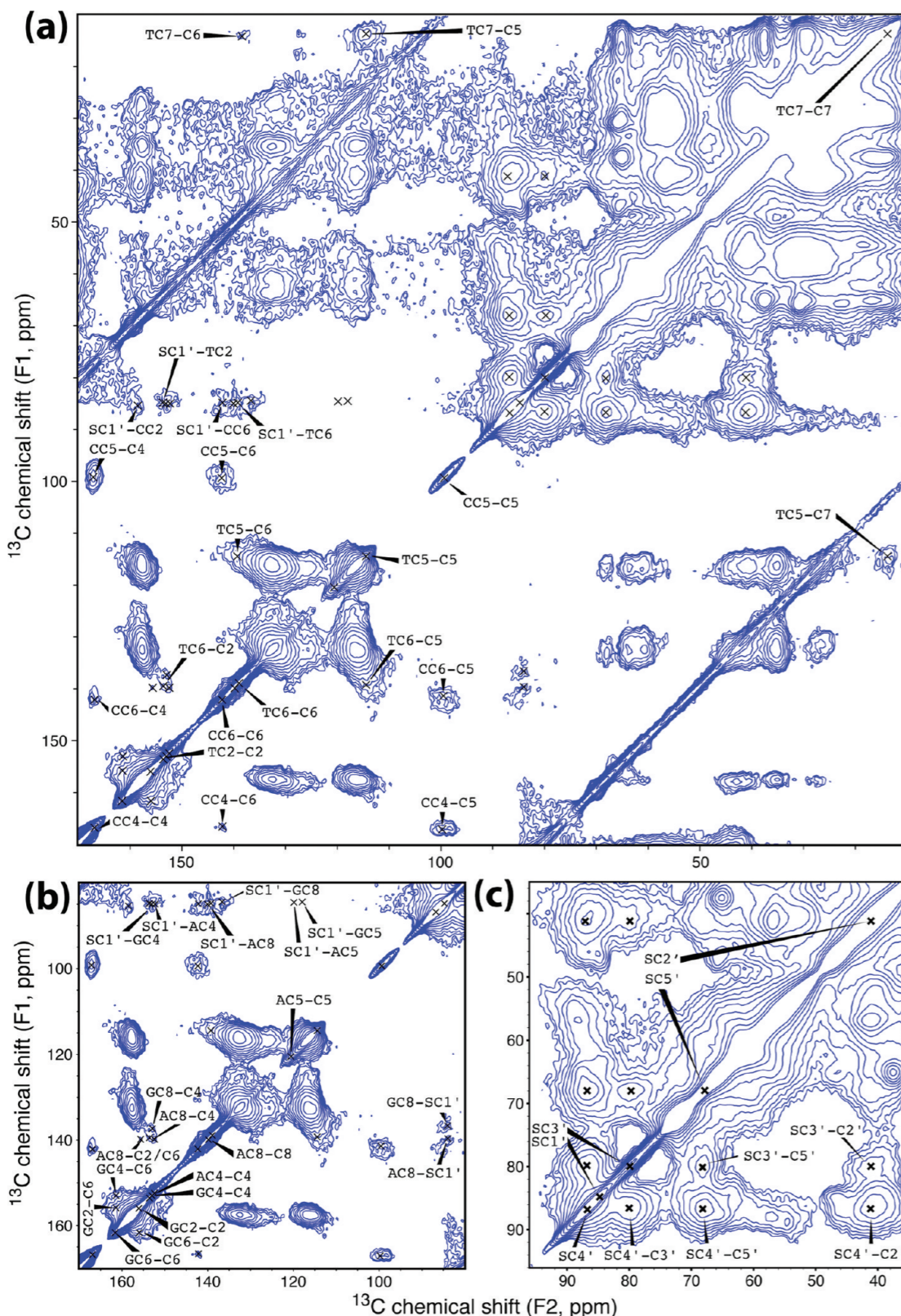
[†]Department of Chemistry, Columbia University, 3000 Broadway, New York, New York 10027, United States

[‡]The Public Health Research Institute of the University of Medicine and Dentistry of New Jersey, 225 Warren Street, Newark, New Jersey 07103, United States

[§]School of Chemistry, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel Aviv University, Ramat Av



Ann McDermott



CONCLUSIONS

The mere presence of the DNA peaks, and especially of those corresponding to the bases, indicates a well-ordered DNA structure. A number of DNA peaks are split into multiple resonances, consistent with the idea that each nucleotide type in each strand has an environment shared by all nucleotides of that type in that strand. These unique environments share common features, namely 2'-endo/*gauche* deoxyribose ring conformations and *anti* glycosidic bond orientations, corroborating conclusively results from other methods.²³ Extreme DNA chemical shift values, in some cases falling outside of BMRB chemical shift ranges, indicate an unusual DNA structure. The DNA lacks hydrogen bonding, also corroborating previous findings,^{11,14,70} yet there is some sort of stacking present, consistent with predicted base–tyrosine interactions¹⁹ and the presence of Y40-DNA (base and sugar) crosspeaks. Overall, these initial high-resolution NMR results support the Pf1 DNA model put forth by Liu and Day and subsequently refined by Tsuboi et al.^{12,21}

Figure 2. DNP-enhanced SSNMR spectra of Pf1 showing (a) the assignments of the dC/dT base resonances, (b) the dA/dG base resonances, and (c) the sugar spin systems. Data were collected using a 400 MHz wide-bore AVANCE III spectrometer at cryogenic temperatures (100 K), with a mixing time of 22 ms. See Table S1 for additional acquisition and processing parameters.

Solid-State NMR on Bacterial Cells: Selective Cell Wall Signal Enhancement and Resolution Improvement using Dynamic Nuclear Polarization

Hiroki Takahashi,[†] Isabel Ayala,[‡] Michel Bardet,[†] Gaël De Paëpe,[†] Jean-Pierre Simorre,[‡] and Sabine Hediger^{*†}

[†]Laboratoire de Chimie Inorganique et Biologique, UMR-E3 (CEA/UJF) and CNRS, Institut Nanosciences et Cryogénie, CEA, 38054 Grenoble, France

[‡]Institut de Biologie Structurale, UMR5075 (CEA/CNRS/UJF), 38027 Grenoble, France

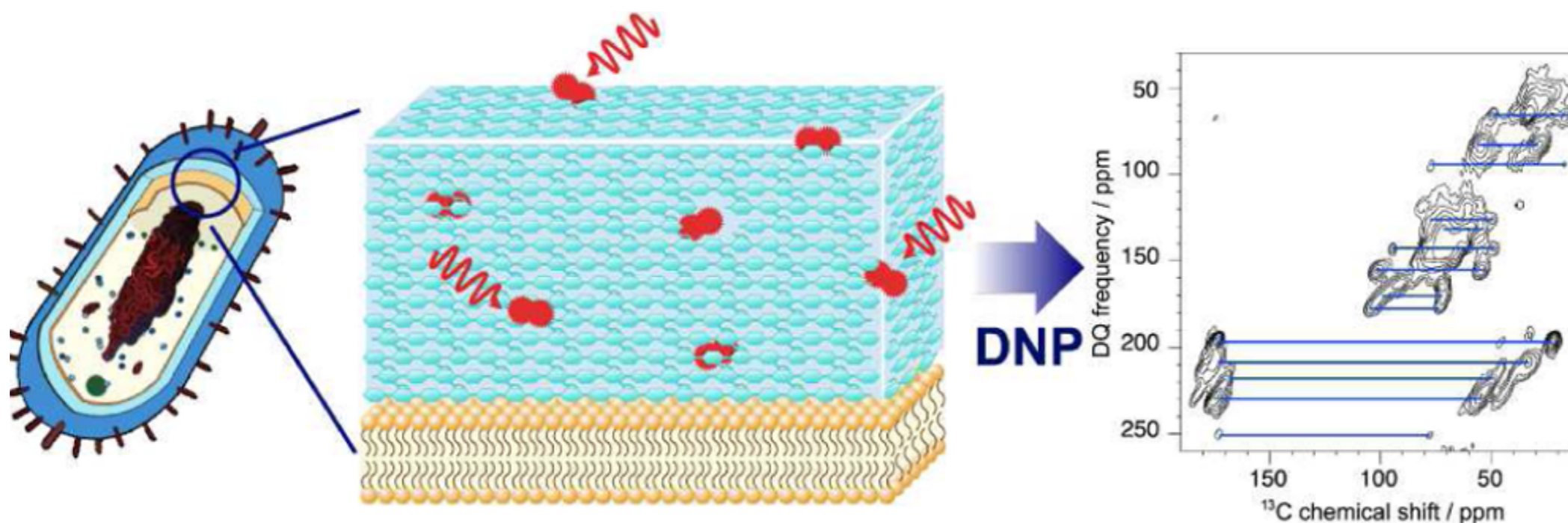


Gaël de Paëpe



Sabine Hediger

- DNP used for selective enhancement of the cell walls



Solid-State NMR Spectroscopy on Cellular Preparations Enhanced by Dynamic Nuclear Polarization**

Marie Renault, Shane Pawsey, Martine P. Bos, Eline J. Koers, Deepak Nand, Ria Tommassen-van Boxtel, Melanie Rosay, Jan Tommassen, Werner E. Maas, and Marc Baldus*



Marc Baldus

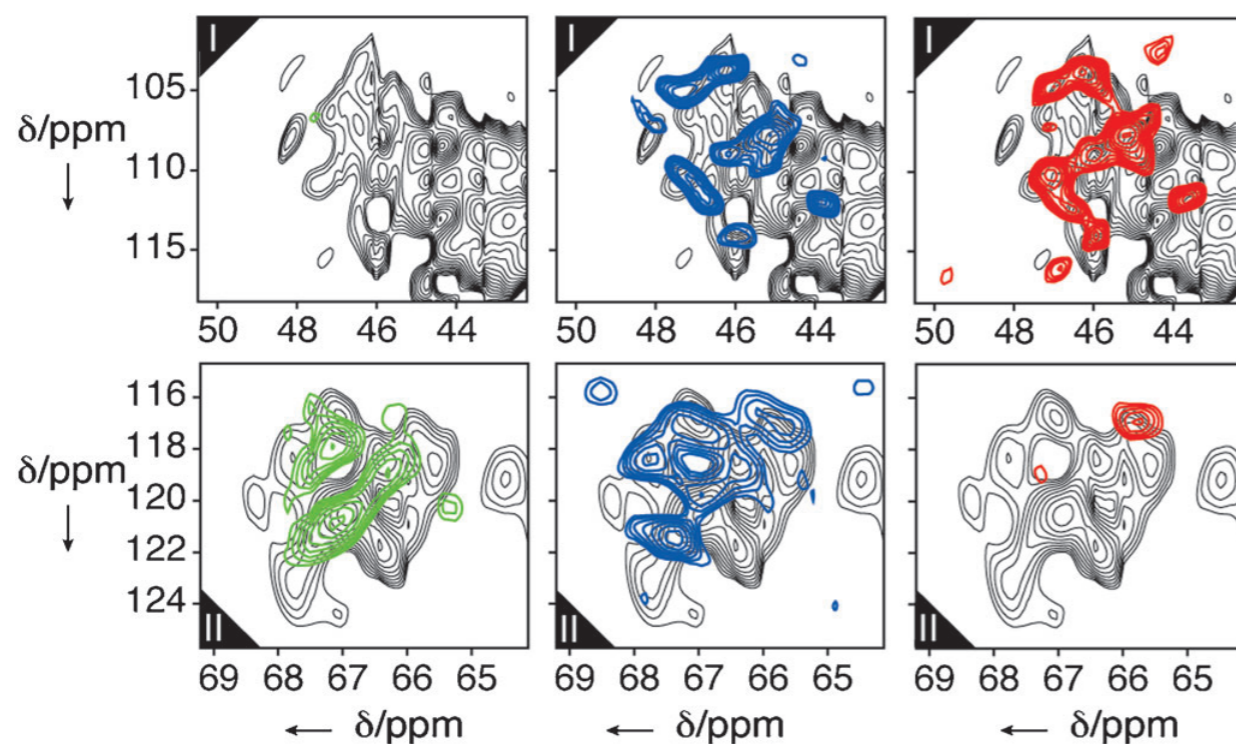


Figure 3. Overlay of the DNP-enhanced 2D (^{15}N , ^{13}C) NCA correlation spectra of ($\text{U-}^{13}\text{C}$, ^{15}N)-labeled WC (at 100 K, 8 kHz MAS) (black) and the 2D NCA of ($\text{U-}^{13}\text{C}$, ^{15}N)-labeled CE isolated from noninduced (green) or PagL-overexpressing (blue) cells and purified ($\text{U-}^{13}\text{C}$, ^{15}N)-PagL reconstituted in proteoliposomes (red) obtained at 271 K and 13 kHz MAS). Upper row: region I, lower row: region II.

Magic Angle Spinning DNP on a whole cells and cell extracts

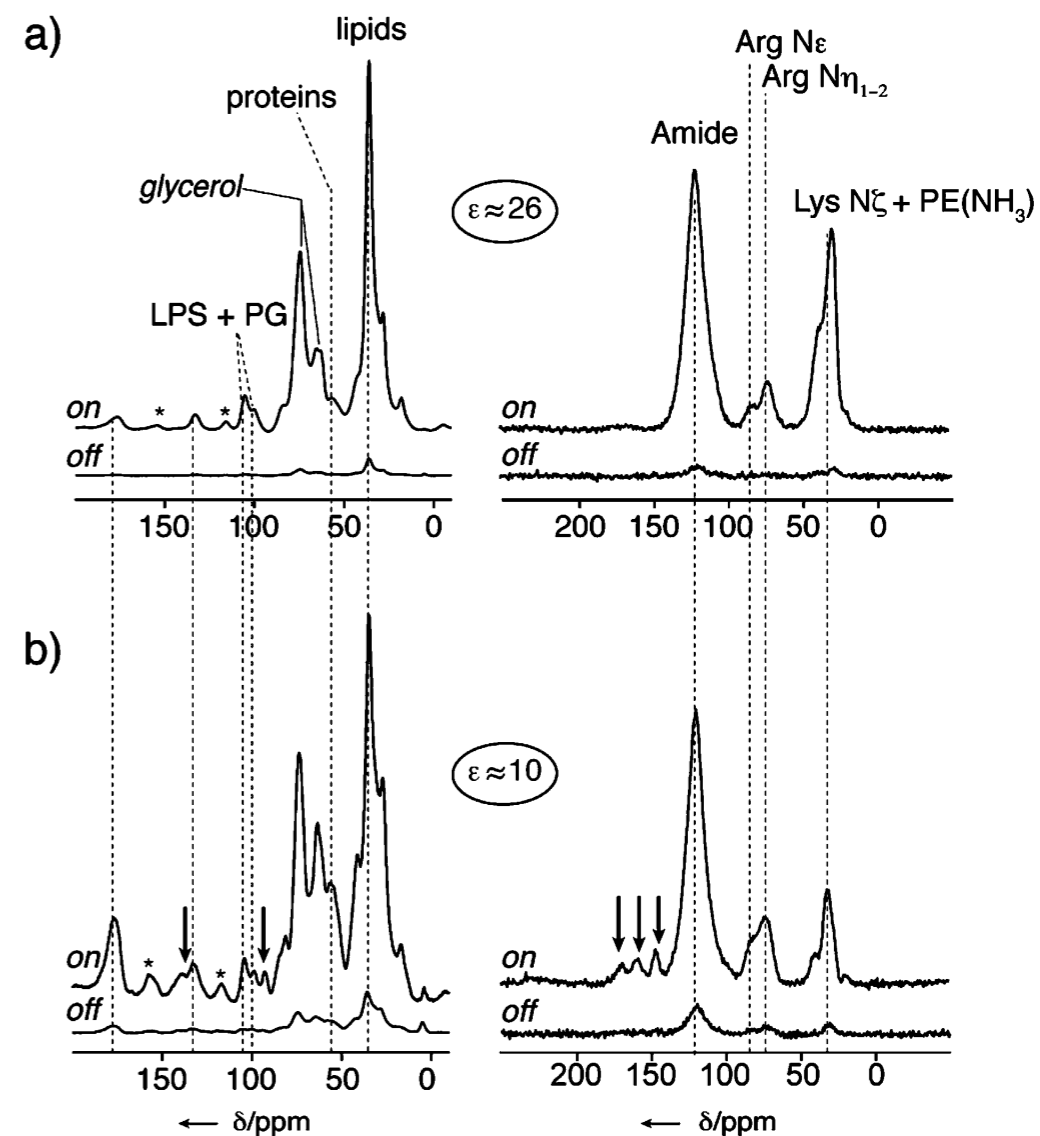
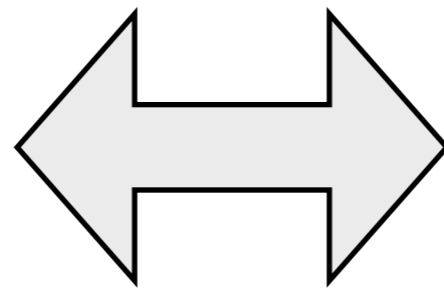


Figure 1. Comparison of ^{13}C (left) and ^{15}N (right) CP-MAS spectra of ($\text{U-}^{13}\text{C}$, ^{15}N)-labeled CE (a) and WC (b) with (top trace, “on”) and without (bottom trace, “off”) DNP, using a microwave irradiation time of 10 s. Significant differences in the spectra of the two preparations are denoted by arrows. Asterisks indicate MAS side bands. Assignments of major *E. coli* molecular components are, if available, annotated and signal enhancements are given. Natural abundance ^{13}C signals from glycerol ($\delta^{13}\text{C} \approx 73$ and 63 ppm) present in the glassy matrix and from the silicon plug ($\delta^{13}\text{C} \approx 4$ ppm) are visible in the ^{13}C CP spectra of the WC and CE preparations.

Can you see any problem/challenge in these biomolecular applications?

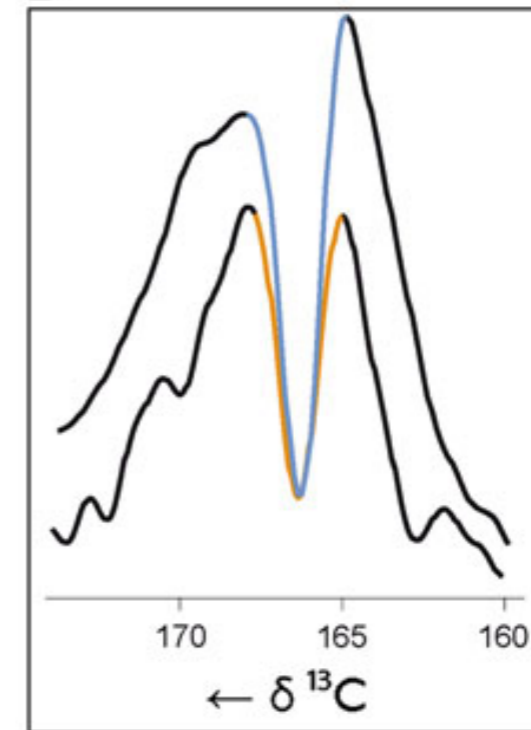
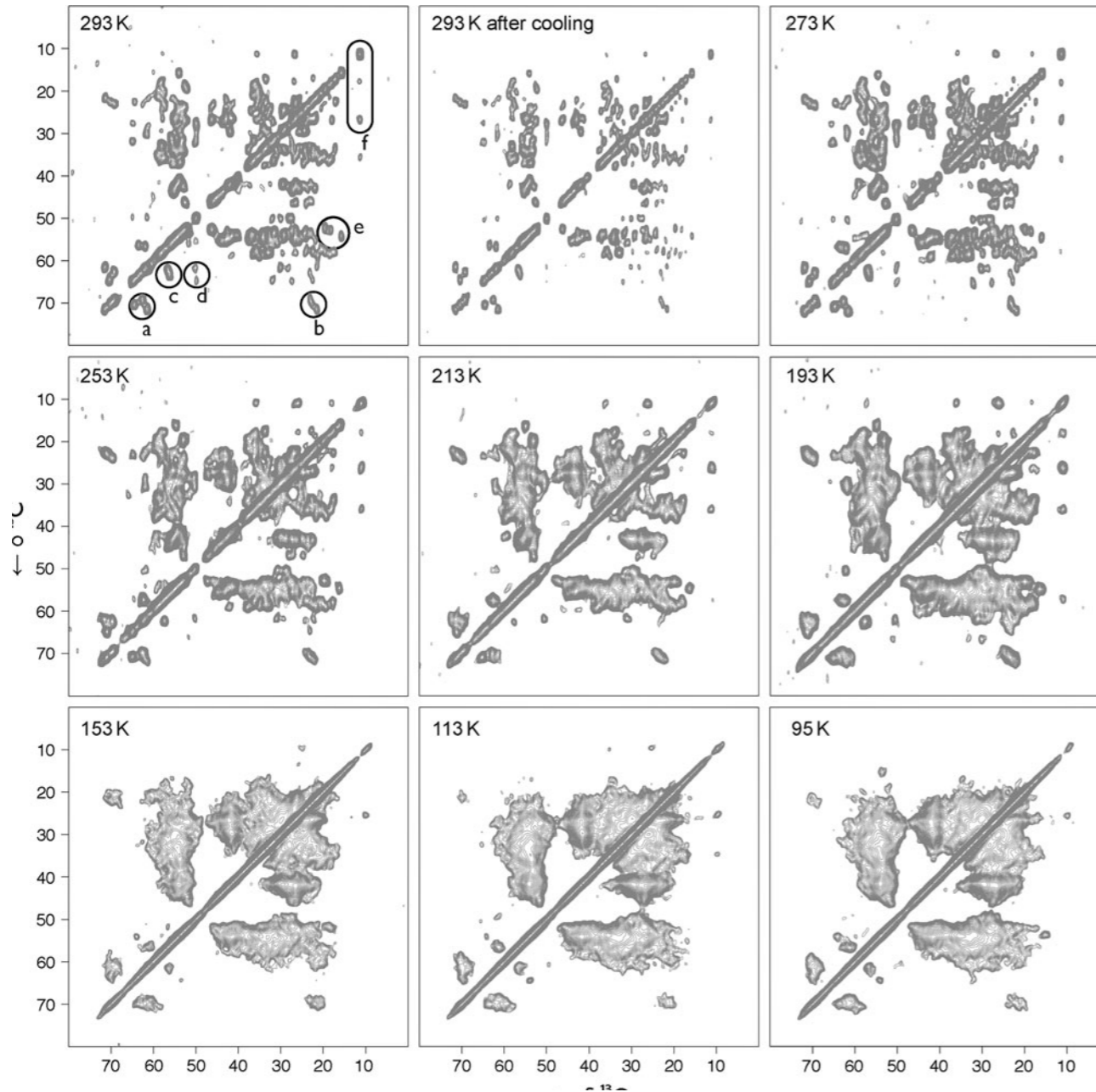
Lines generally broaden at low temperatures
(getting resolution may be a problem)

Inhomogeneous
broadening?



Relaxation?

SH3

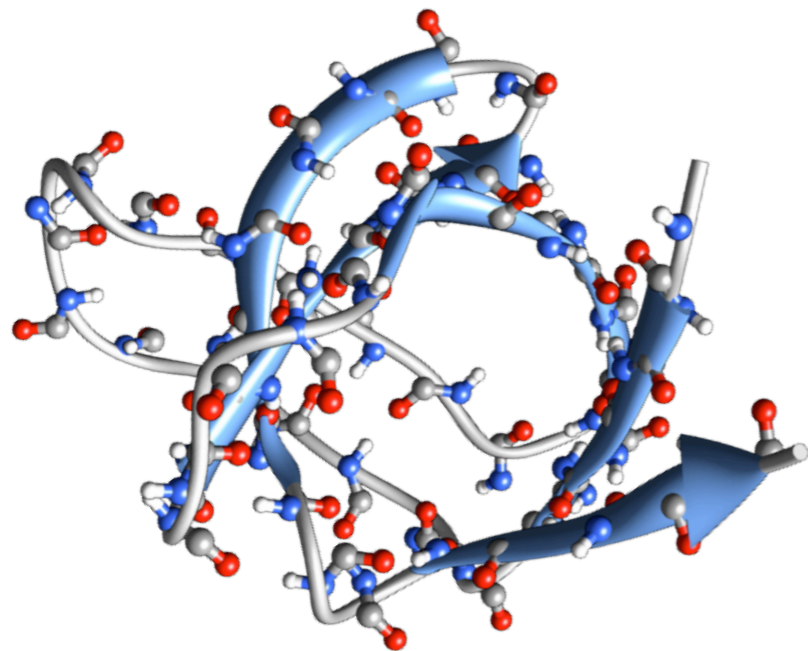


hole burning experiments show that the broadening is of inhomogenous nature

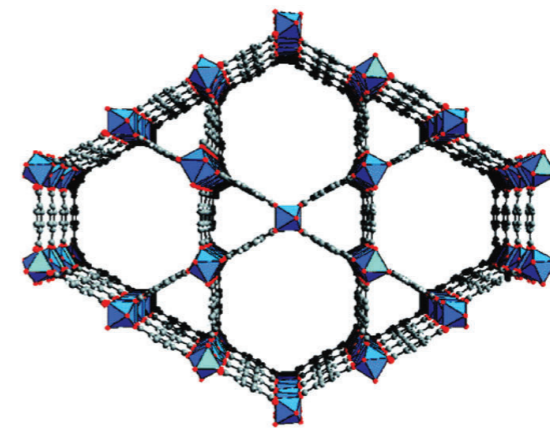


The line broadening at lower temperatures is of inhomogenous nature

Biomolecules

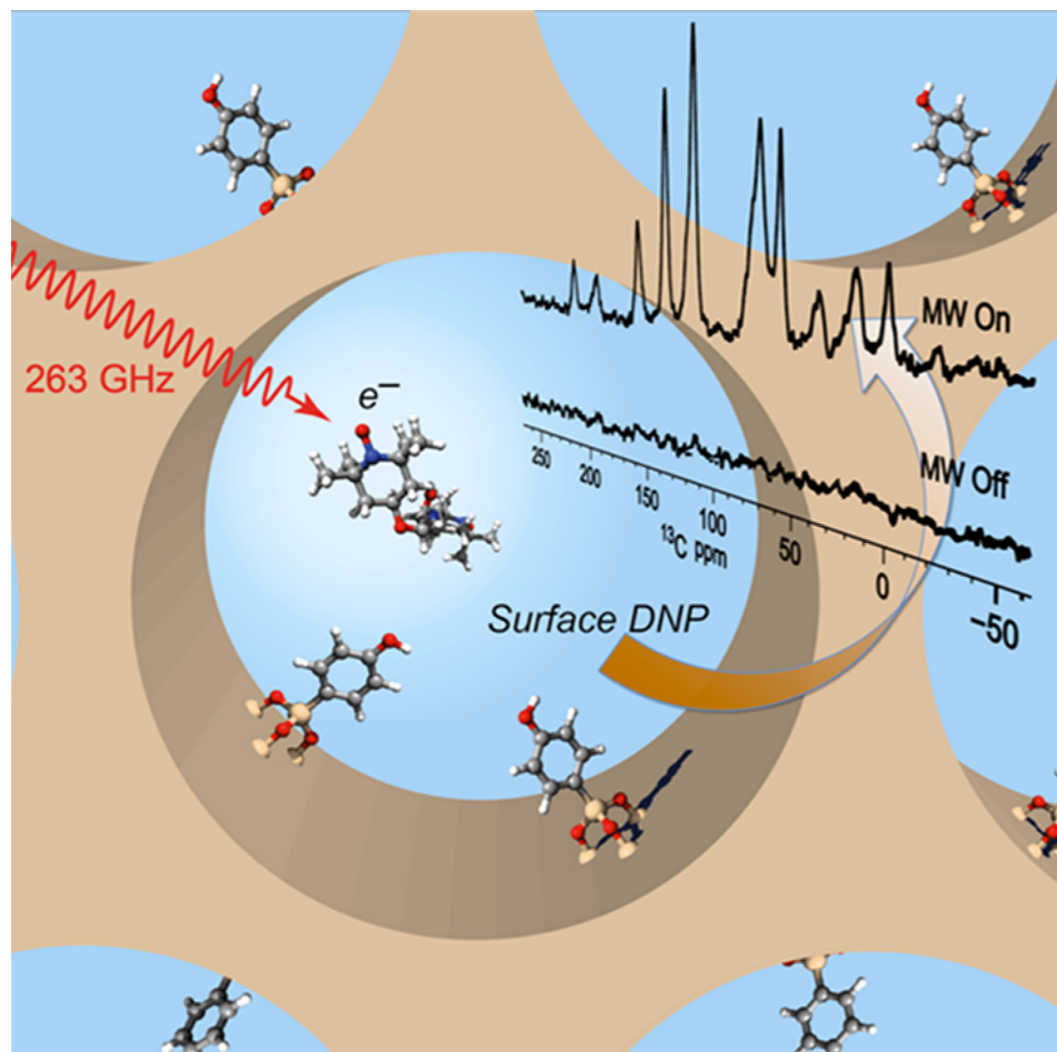


Materials

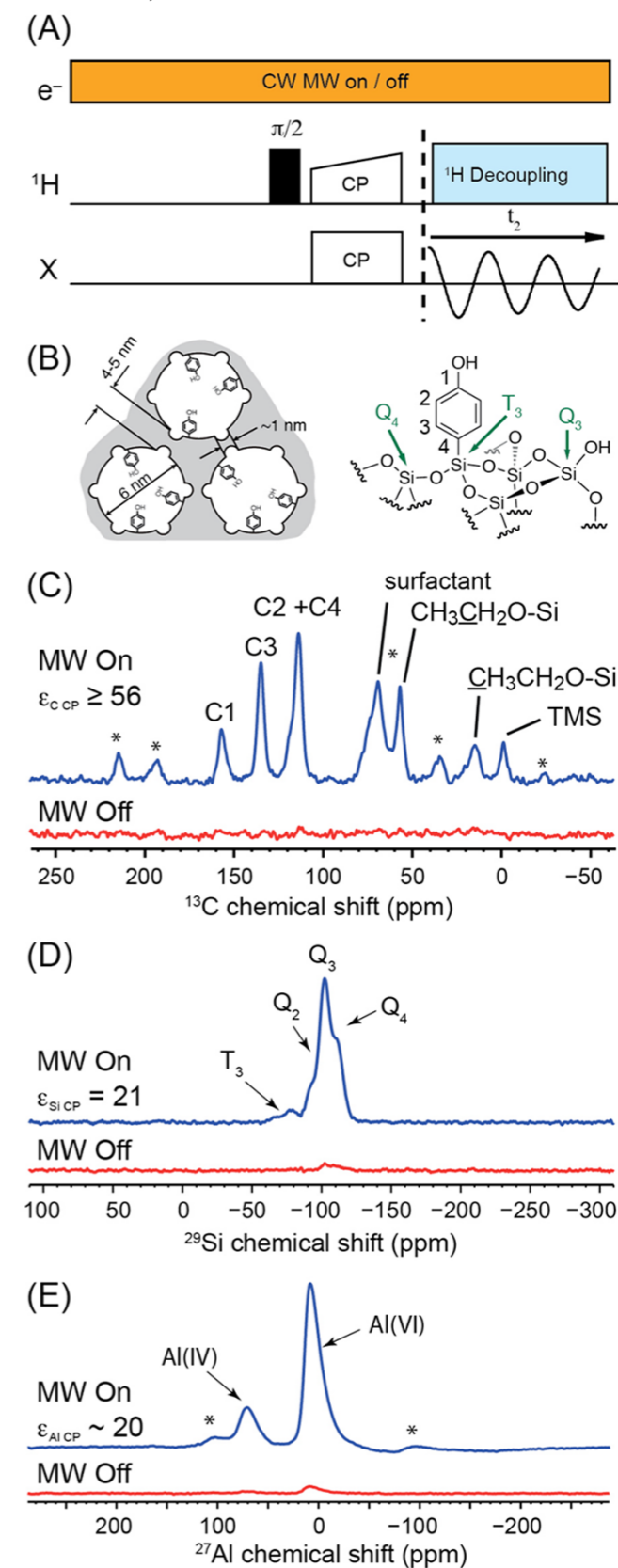


“Surface Enhanced DNP” -SENS

1. Rossini, A. J. *et al. Acc. Chem. Res.* (2013) 10.1021/ar300322x.



- hybrid materials
- organometallic species
- metal-organic frameworks
- enhancements up to 100



^{14}N DNP

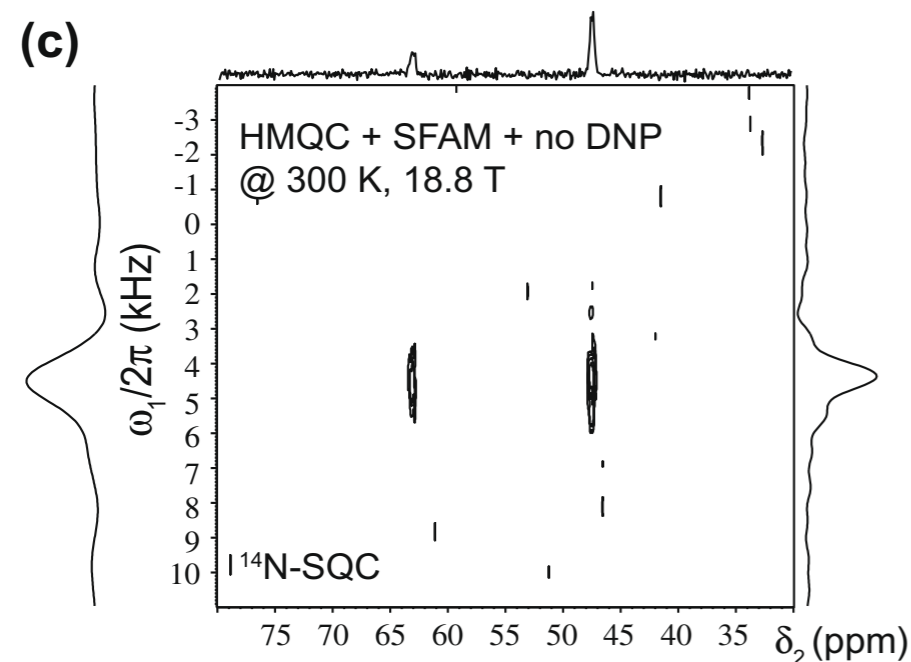
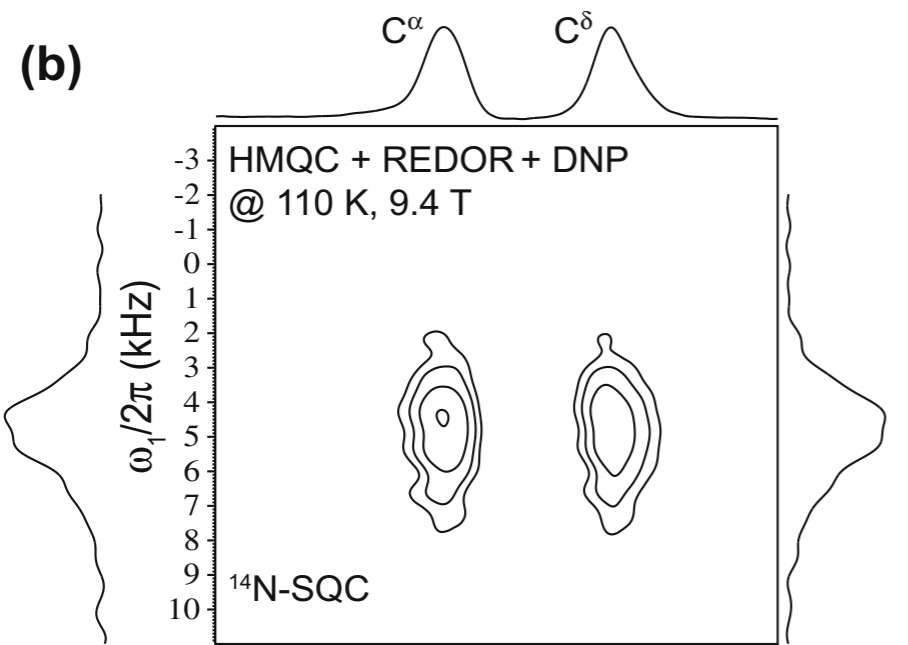
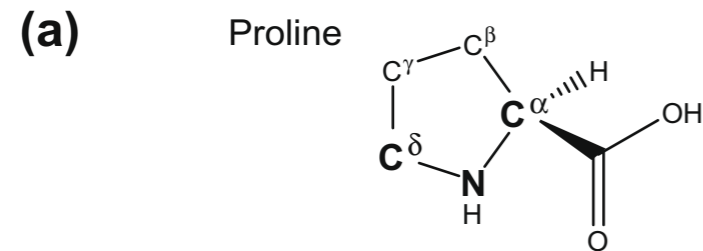
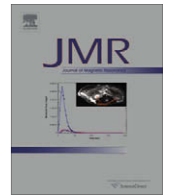


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Communication

Solid-state nitrogen-14 nuclear magnetic resonance enhanced by dynamic nuclear polarization using a gyrotron

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^a Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne, EPFL, Batochime, 1015 Lausanne, Switzerland
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$\epsilon \sim 40$



Geoffrey Bodenhausen

^{13}C -detected
 ^{13}C - ^{14}N 2D correlations

DNP of ^{27}Al

Dynamic nuclear polarization of quadrupolar nuclei using cross polarization from protons: surface-enhanced aluminium- ^{27}Al NMR†

Veronika Vitzthum,^a Pascal Miéville,^{*a} Diego Carnevale,^a Marc A. Caporini,^a David Gajan,^b Christophe Copéret,^b Moreno Lelli,^c Alexandre Zagdoun,^c Aaron J. Rossini,^c Anne Lesage,^c Lyndon Emsley^c and Geoffrey Bodenhausen^{adef}

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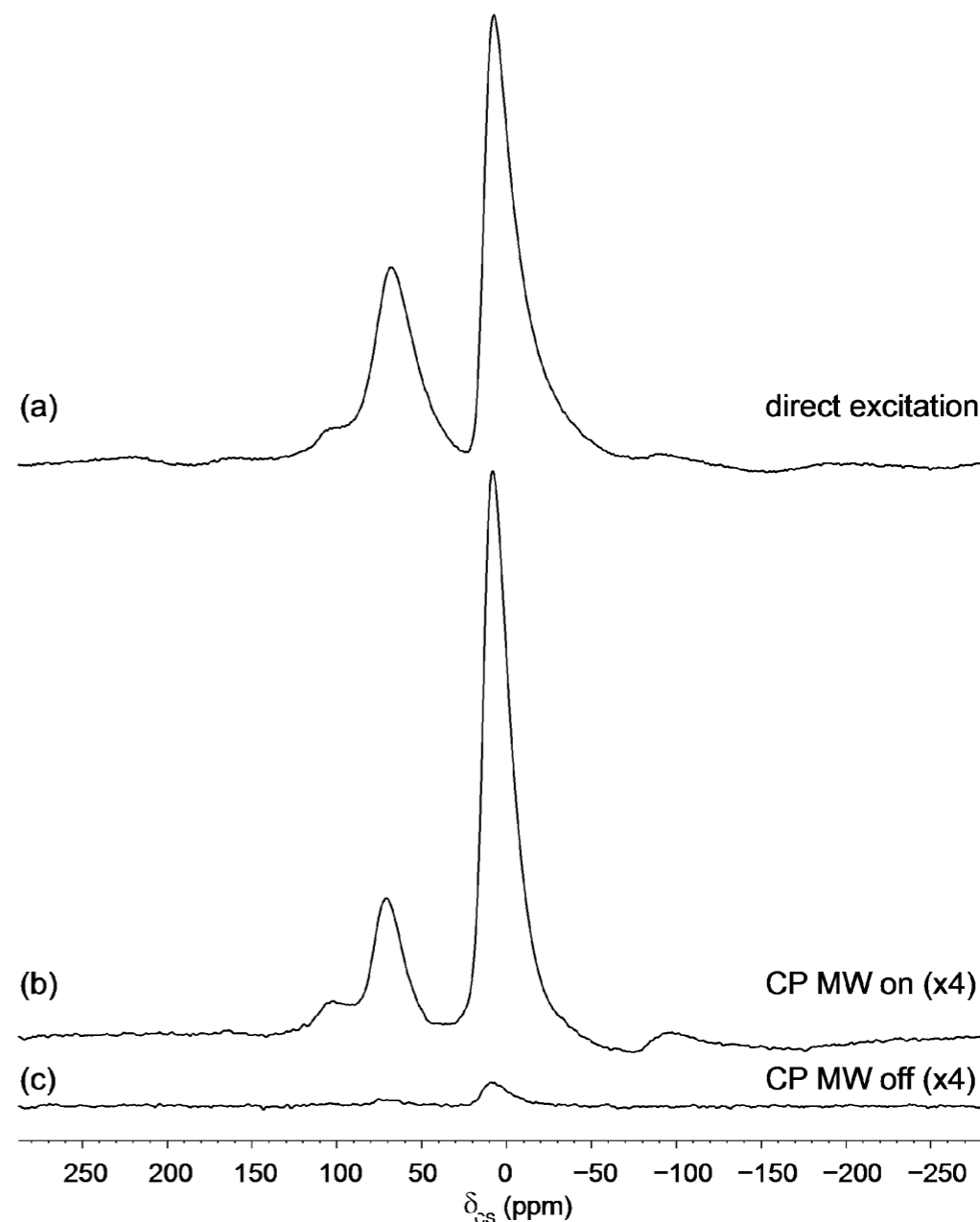


Fig. 1 ^{27}Al spectra of γ -alumina ($r = 0.45$, $c = 4$ mM and $x = 0.10$): (a) excited directly with a single *rf* pulse (signals from both surface and bulk); (b) excited by CP from protons with microwave saturation of the EPR transitions of the TOTAPOL radical (surface enhanced signals); and (c) CP without microwave irradiation (signals from surface only).

$\epsilon_{\text{CP}} \sim 20$

Dynamic Nuclear Polarization Enhanced Natural Abundance ¹⁷O Spectroscopy

Frédéric Blanc,^{*,†,‡} Luke Sperrin,[†] David A. Jefferson,[†] Shane Pawsey,[§] Melanie Rosay,[§] and Clare P. Grey^{†,⊥}

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dx.doi.org/10.1021/ja4004377 | *J. Am. Chem. Soc.* 2013, 135, 2975–2978

$\epsilon_{CP} \sim 17$

$\epsilon_{CPCPMG} \sim 3400$

