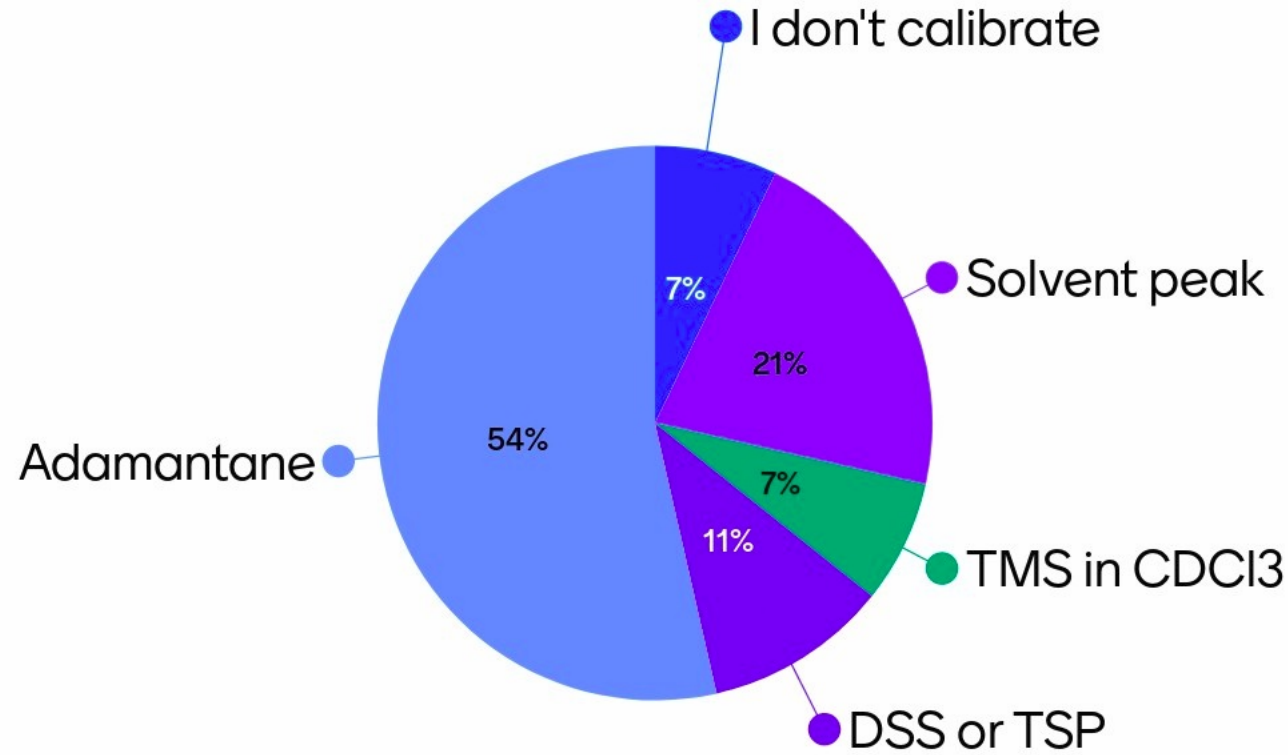


How to calibrate all your experiments with a single reference ?

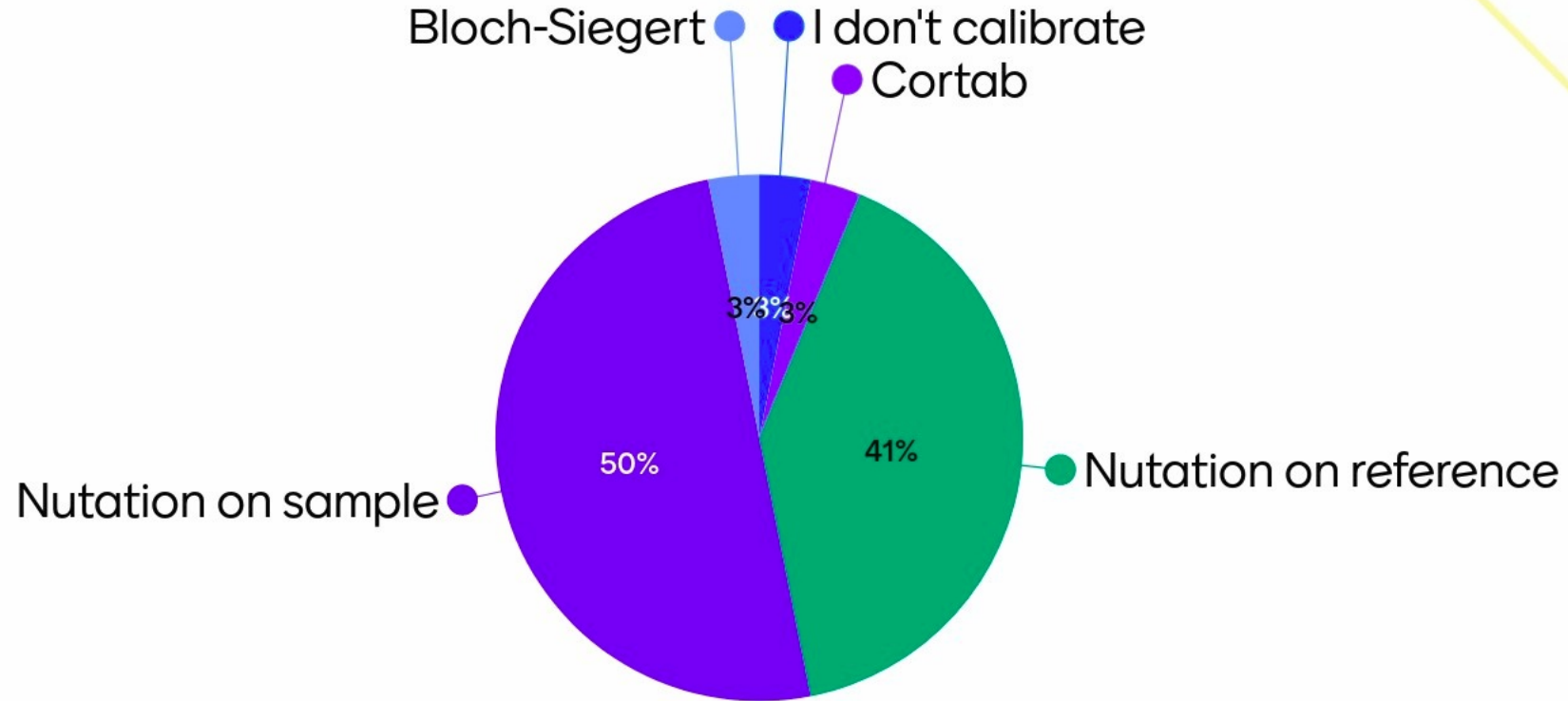
Guillaume Laurent

Laboratoire de Chimie de la Matière Condensée de Paris
Sorbonne Université, 4 place Jussieu, 75005 Paris, France
guillaume.laurent@sorbonne-universite.fr

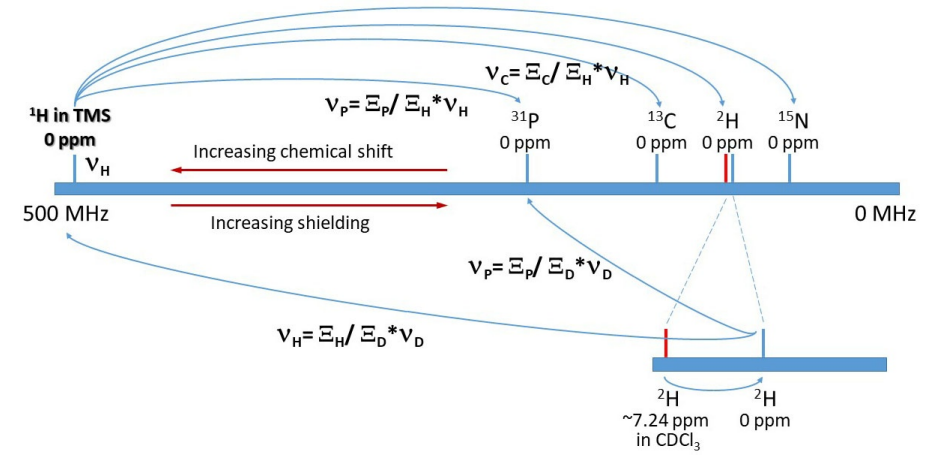
How do you calibrate the chemical shifts ?



How do you calibrate radiofrequency ?

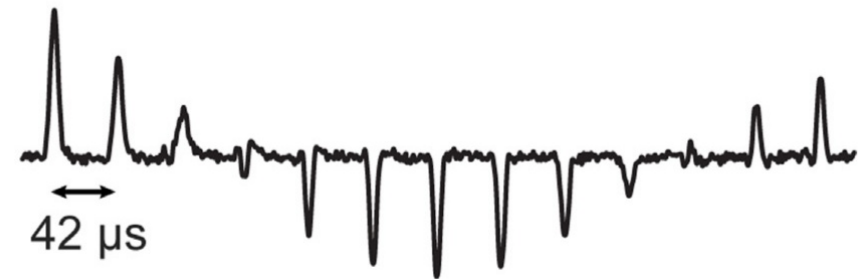


Outline

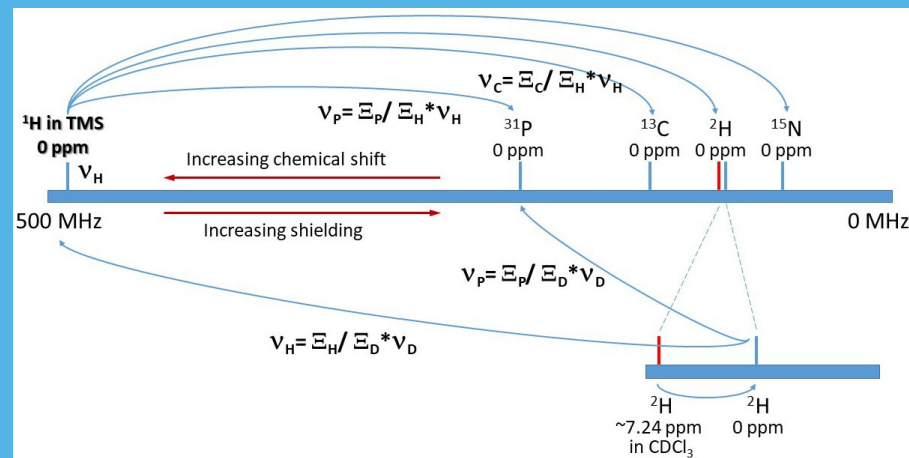


CHEMICAL SHIFT CALIBRATION

RADIOFREQUENCY CALIBRATION



Chemical shift calibration



How we used to calibrate chemical shifts

One reference sample per studied nucleus

Chemical Shift Ranges and Standards for Selected Nuclei

Nucleus	Spin	Chemical Shift Range δ [ppm]	Standard	Nucleus	Spin	Chemical Shift Range δ [ppm]	Standard
^1H	1/2	12 to -1	SiMe_4	^{43}Ca	7/2	40 to -40	CaCl_2
^6Li	1	5 to -10	1M LiCl in H_2O	^{51}V	7/2	0 to -2000	VOCl_3
^7Li	3/2	5 to -10	1M LiCl in H_2O	^{67}Zn	5/2	100 to -2700	ZnClO_4
^{11}B	3/2	100 to -120	$\text{Bf}_3 \cdot \text{OEt}_2$	^{77}Se	1/2	1600 to -1000	SeMe_2
^{13}C	1/2	240 to -10	SiMe_4	^{93}Nb	9/2	0 to -2000	NbCl_6
^{15}N	1/2	1200 to -500	MeNO_2	^{99}Ru	3/2	3000 to -3000	$\text{RuO}_3/\text{CCl}_4$
^{17}O	5/2	1400 to -100	H_2O	^{119}Sn	1/2	5000 to -3000	SnMe_4
^{19}F	1/2	100 to -300	CFCl_3	^{121}Sb	5/2	1000 to -2700	$\text{Et}_4\text{NSbCl}_6$
^{23}Na	3/2	10 to -60	1M NaCl in H_2O	^{129}Xe	1/2	2000 to -6000	XeOF_4
^{27}Al	5/2	200 to -200	$[\text{Al}(\text{H}_2\text{O})_6]^{3+}$	^{133}Cs	7/2	300 to -300	CsBr
^{29}Si	1/2	100 to -400	SiMe_4	^{195}Pt	1/2	9000 to -6000	Na_2PtCl_6
^{31}P	1/2	230 to -200	H_3PO_4	^{199}Hg	1/2	500 to -3000	HgMe_2

Unified scale for chemical shifts

NMR NOMENCLATURE. NUCLEAR SPIN PROPERTIES AND CONVENTIONS FOR CHEMICAL SHIFTS

(IUPAC Recommendations 2001)

R. K. Harris *et al.*, *Pure Appl. Chem.* 73, 1795–1818 (2001).

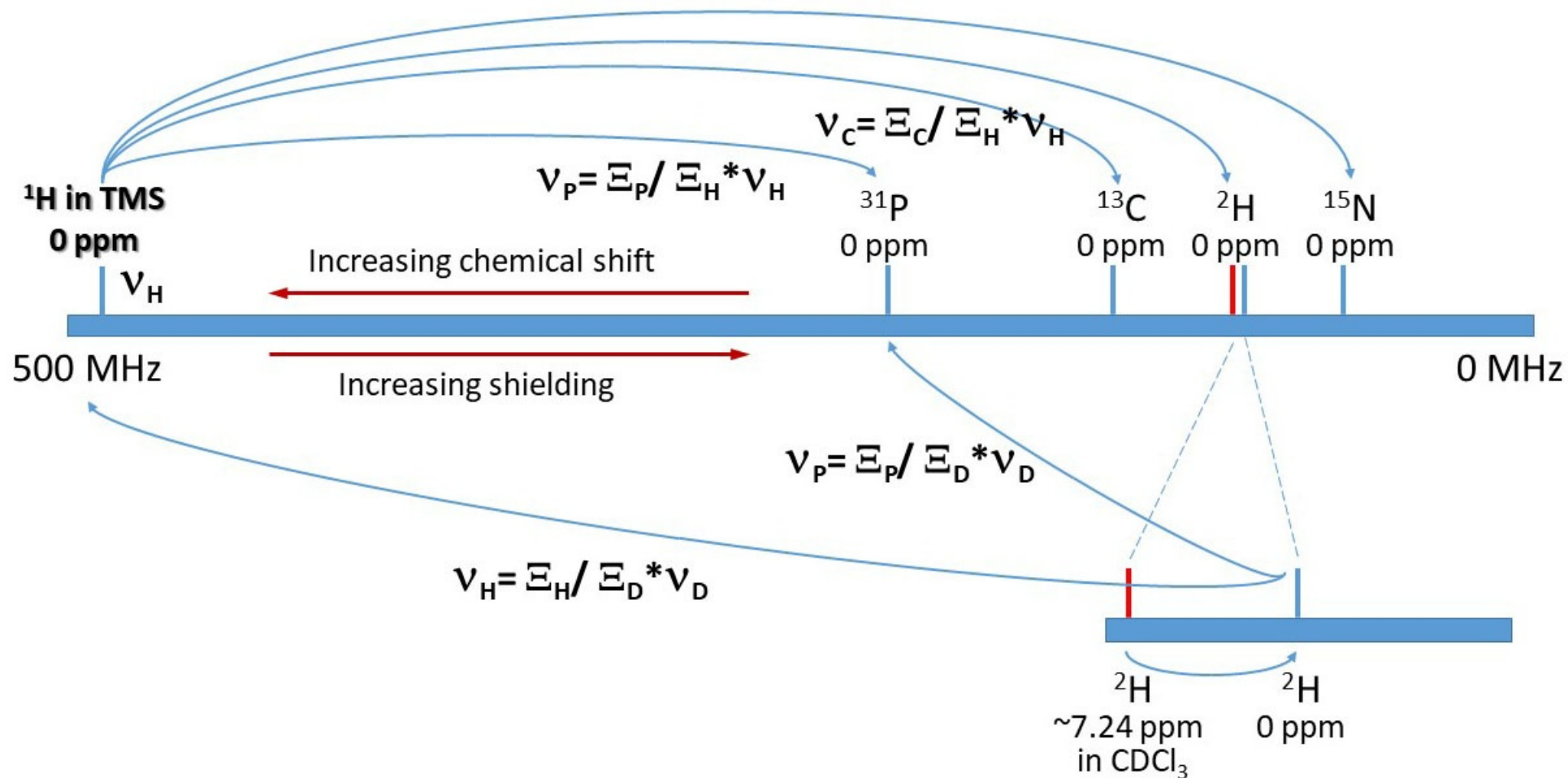
Further conventions for NMR shielding and chemical shifts
IUPAC recommendations 2008[☆]

R. K. Harris *et al.*, *Pure Appl. Chem.* 80, 59–84 (2008).

APPENDIX 1: RECOMMENDED VALUES OF ν FOR VARIOUS NUCLIDES^a

Isotope	Frequency ratio, ν / %	Reference compound	Reference compound conditions ^a
¹ H	100.000 000	Me ₄ Si	CDCl ₃ , $\phi = 1$ %
	100.000 000 ^b	DSS methyl signal	D ₂ O
² H	15.350 609	(CD ₃) ₄ Si	neat
³ H	106.663 974	Me ₄ Si- <i>t</i> ₁	
³ He	76.178 976 ^c	He	gas
⁶ Li	14.716 086	LiCl	D ₂ O, 9.7 mol/kg
⁷ Li	38.863 797	LiCl	D ₂ O, 9.7 mol/kg
⁹ Be	14.051 813	BeSO ₄	D ₂ O, 0.43 mol/kg
¹⁰ B	10.743 658	BF ₃ .Et ₂ O	CDCl ₃ , $\phi = 15$ %
¹¹ B	32.083 974	BF ₃ .Et ₂ O	CDCl ₃ , $\phi = 15$ %
¹³ C ^d	25.145 020	Me ₄ Si	CDCl ₃ , $\phi = 1$ %
	25.144 953 ^b	DSS methyl signal	D ₂ O
¹⁴ N	7.226 317	MeNO ₂	neat/CDCl ₃ ^e
¹⁵ N	10.136 767	MeNO ₂	neat/CDCl ₃ ^e
	10.132 912 ^b	NH ₃ (liquid)	external
¹⁷ O	13.556 457	D ₂ O	neat
¹⁹ F	94.094 011	CCl ₃ F	
²¹ Ne	7.894 296	Ne	gas, 1.1 MPa

Relations between nuclei



<https://nmr.chem.ucsb.edu/protocols/refppm.html>

Xi-referencing

$$SR_2 = [BF_1 * 10^6 + SR_1] * \frac{\nu_2}{\nu_1} - BF_2 * 10^6$$

	nucl	SR (Hz)	BF (MHz)	Xi (MHz)
Spectrometer	1H		300,290000	100,000000
nucl1	13C	-75,81	75,507981	25,145020
nucl2	1H	-301,49	300,290000	100,000000

Bruker TopSpin

1H in first procno

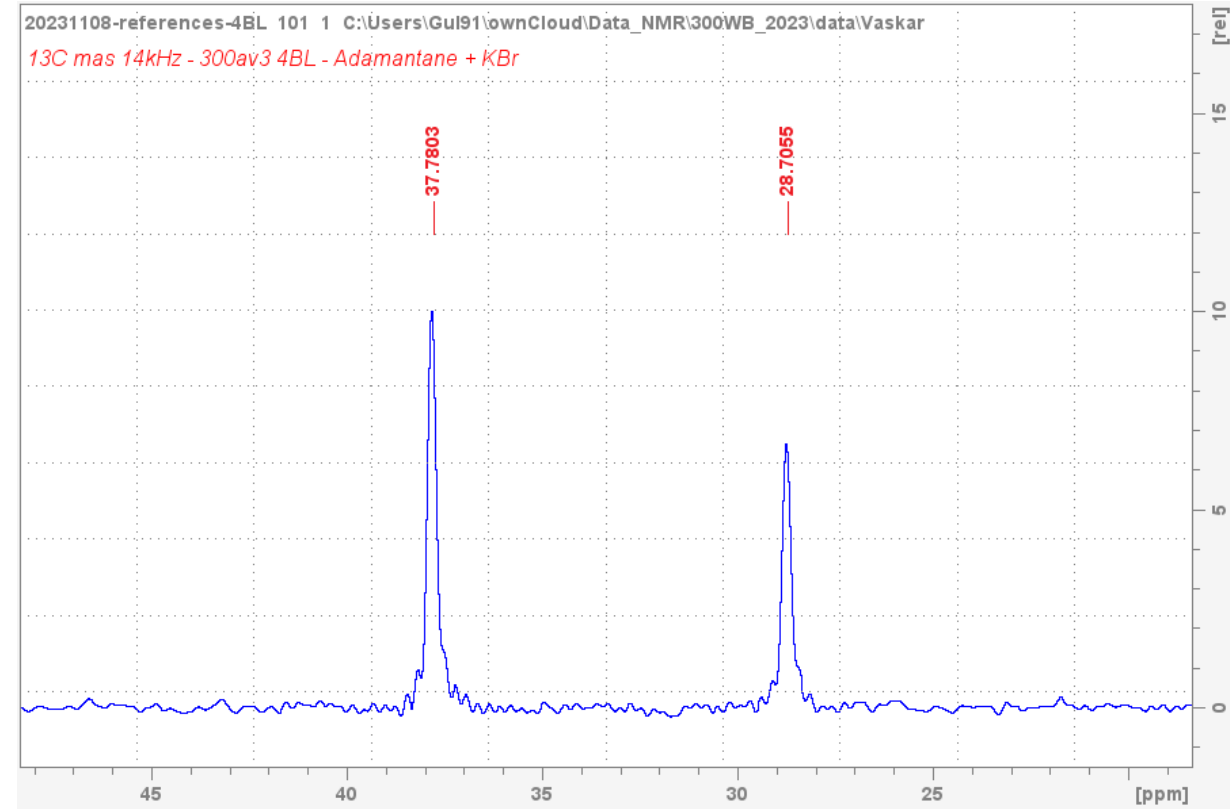
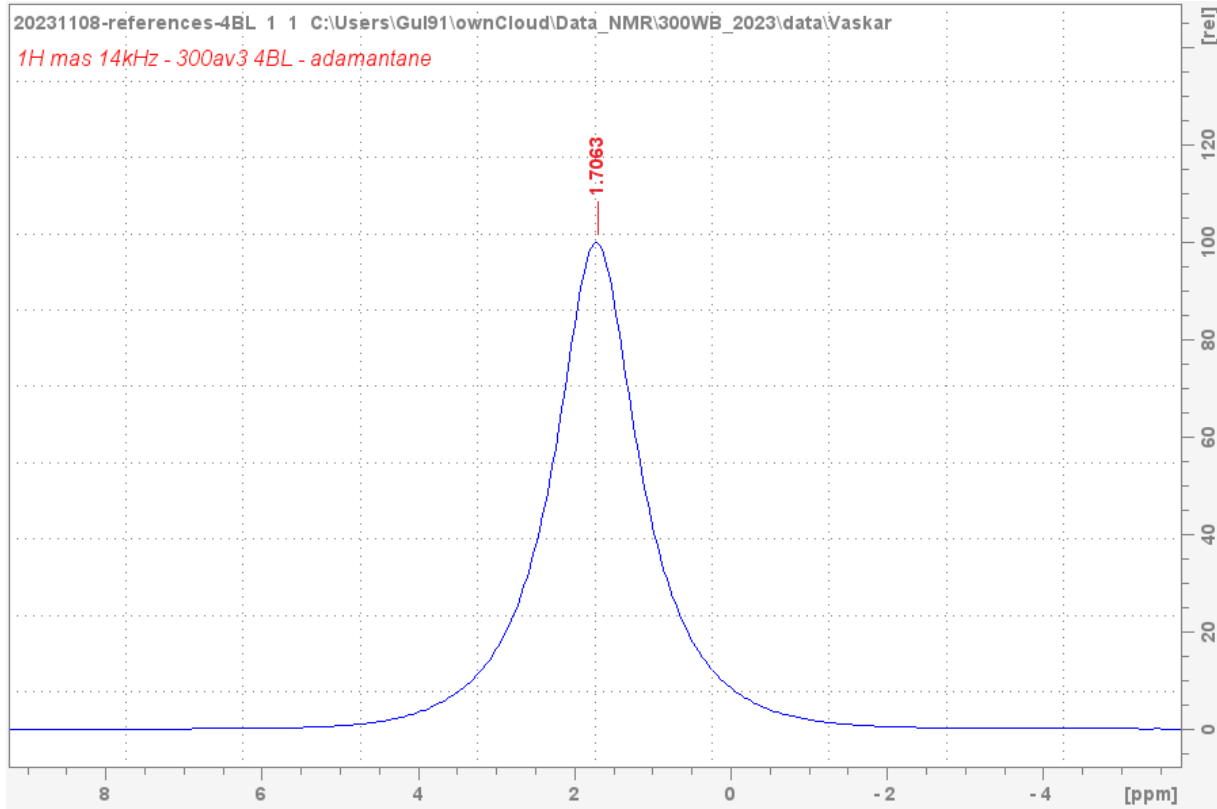
xiref → **SR** for all other procnos

→ **1D, 2D,...**

Varian VnmrJ

set_ref

Solid-state NMR calibration

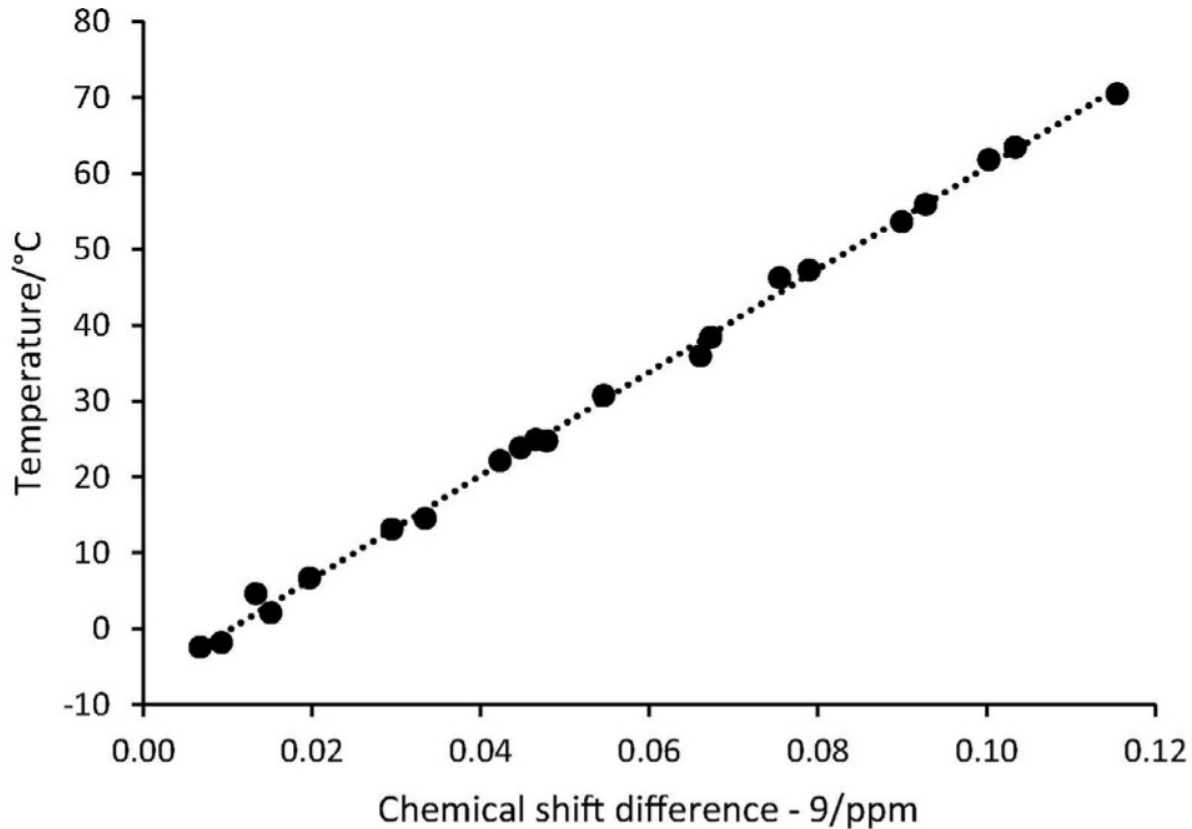


^1H : broad peak, imprecise \rightarrow ^{13}C : narrow peaks, more precise

1.82 ppm / 38.48 ppm ? No, values from neat TMS

1.71 ppm / 37.77 ppm ? OK, values from 1 % TMS in CDCl_3

Adamantane temperature



$$T = -7.15 + 686.9(\Delta\delta - 9) - 0.72(\Delta\delta - 9)^2$$

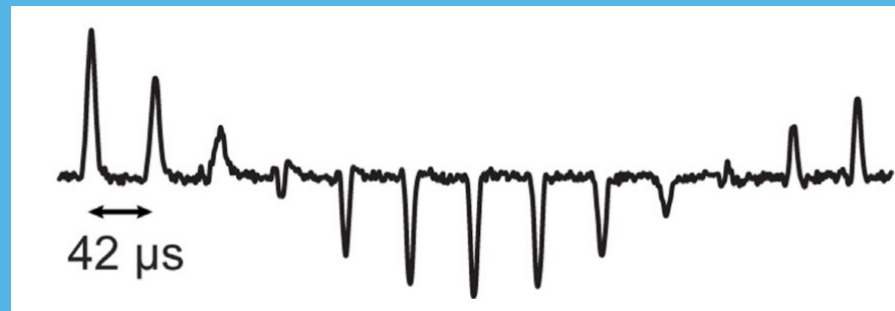
$$\delta(CH) = 37.7531 + 8.14 \times 10^{-4} * T + 4.91 \times 10^{-6} * T^2$$

$$\delta(CH_2) = 28.7425 - 6.33 \times 10^{-4} * T + 4.55 \times 10^{-6} * T^2$$

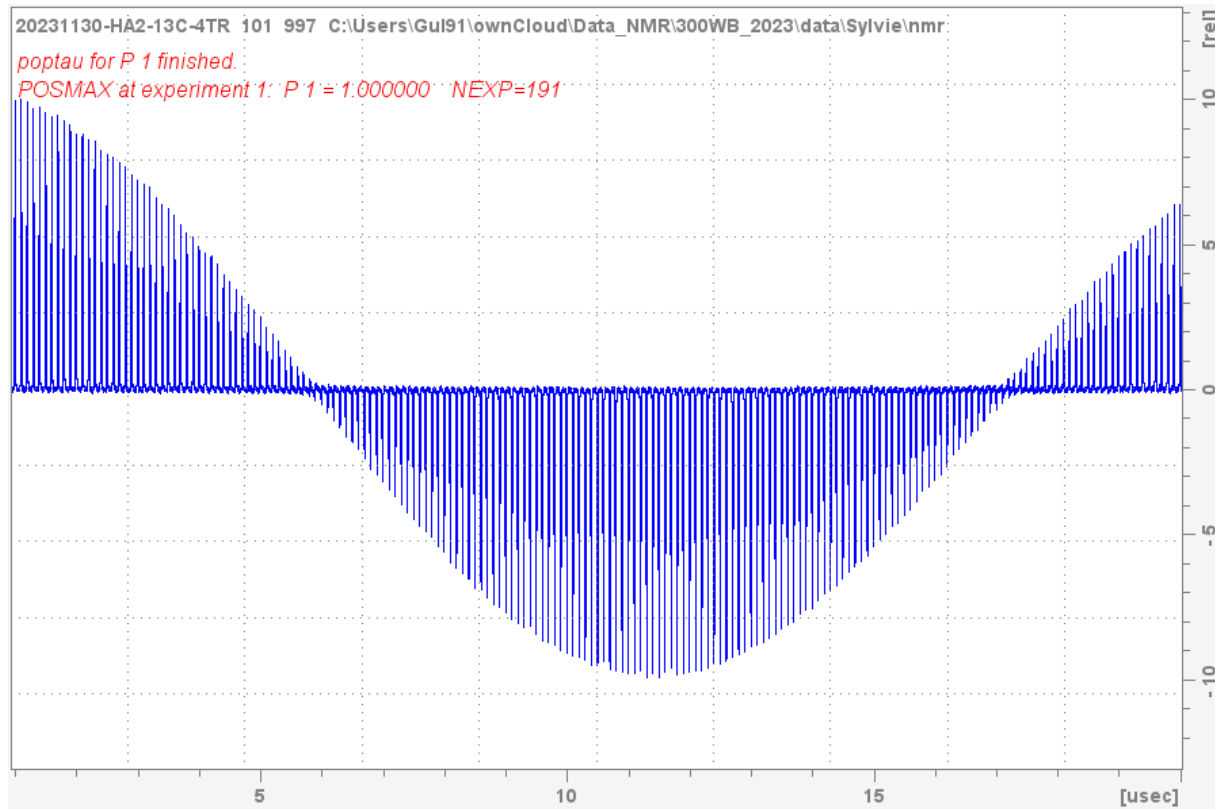
	experimental	corrected
δ_{CH} (ppm)	37,7676	37,7767
δ_{CH_2} (ppm)	28,7205	28,7294
$\Delta\delta$ (ppm)	9,0471	9,0473
T (°C)	25,2	

R. Hoffman, J. Magn. Reson. 340, 107231 (2022).

Radiofrequency calibration



How we used to calibrate radiofrequency



- **Nutation on X nucleus**
- **Reference sample**
- **Difficult for low gamma and/or low abundance**
- **Direct polarization or polarization transfer**

Is there another way ? Yes !

Using the heteronuclear Bloch-Siegert shift of protons for B_1 calibration of insensitive nuclei not present in the sample

I. Hung, P. Gor'kov, Z. Gan, *J. Magn. Reson.* 310, 106636 (2020).

(c) ^{14}N



What is the Bloch-Siegert shift ?

Magnetic Resonance for Nonrotating Fields

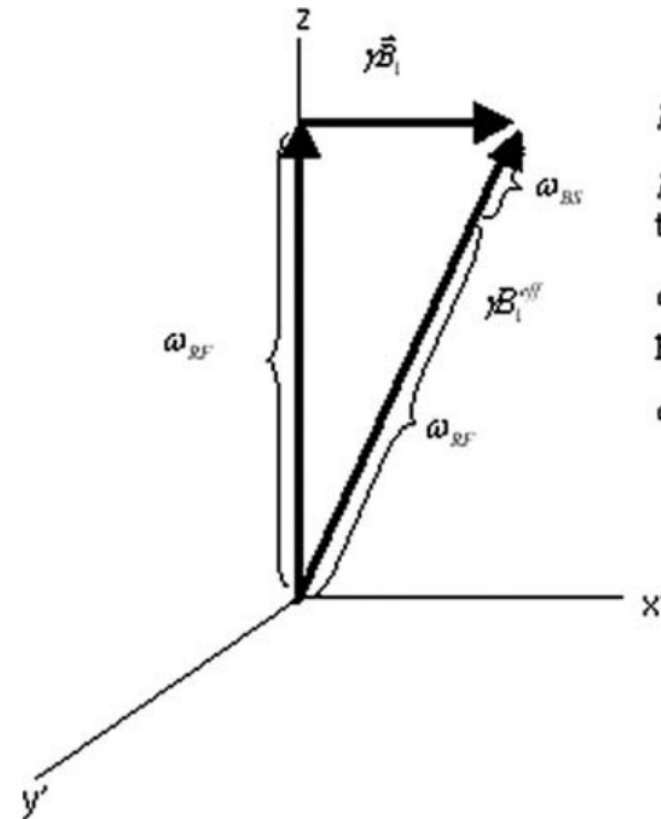
F. BLOCH AND A. SIEGERT*

Department of Physics, Stanford University, Stanford University, California

(Received January 19, 1940)

It is shown that in the lowest order correction the shape of the resonance curve is unchanged but that it is **shifted by a percentage amount** $H_1^2/16 H_0^2$ where H_1 is the effective amplitude of the oscillating field.

F. Bloch, A. Siegert, *Phys. Rev.* 57, 522–527 (1940).



$\gamma \vec{B}_1$: RF field

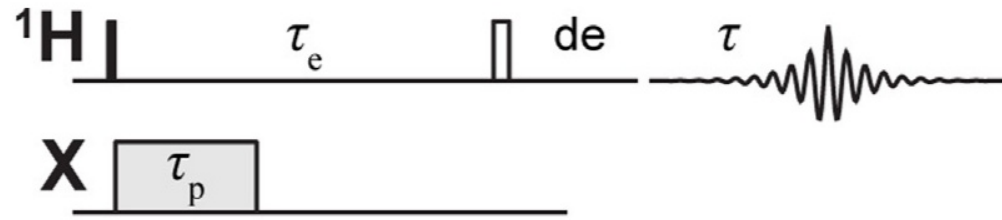
$\gamma \vec{B}_1^{eff}$: effective RF field vector in the rotating frame of the RF

ω_{RF} : Frequency offset of the RF pulse from resonance frequency ω_0 .

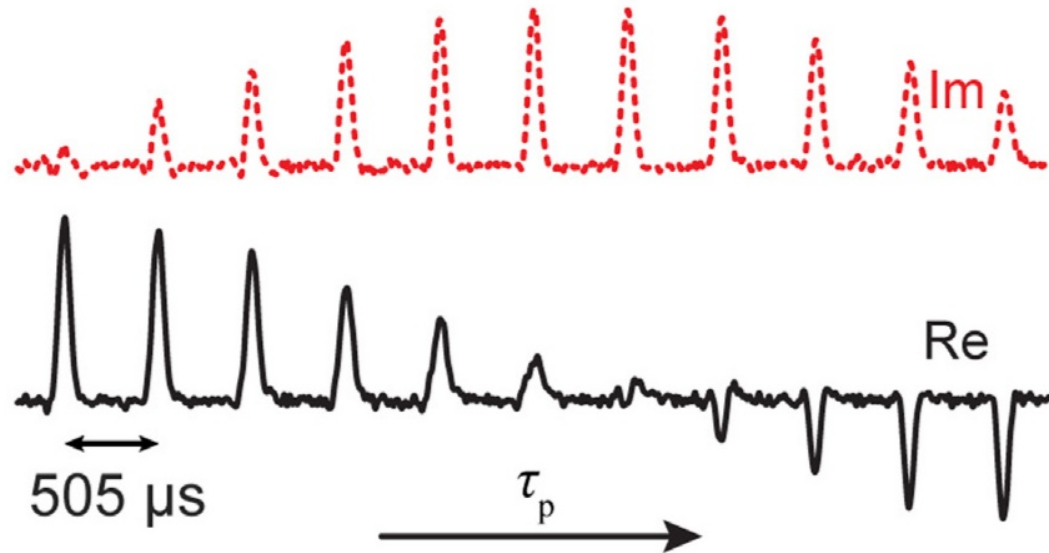
ω_{BS} : Bloch-Siegert frequency shift.

L. I. Sacolick *et al.*, *Magn. Reson. Med.* 63, 1315–1322 (2010).

Echo and irradiation



(a) ^{13}C 300 kHz off-resonance

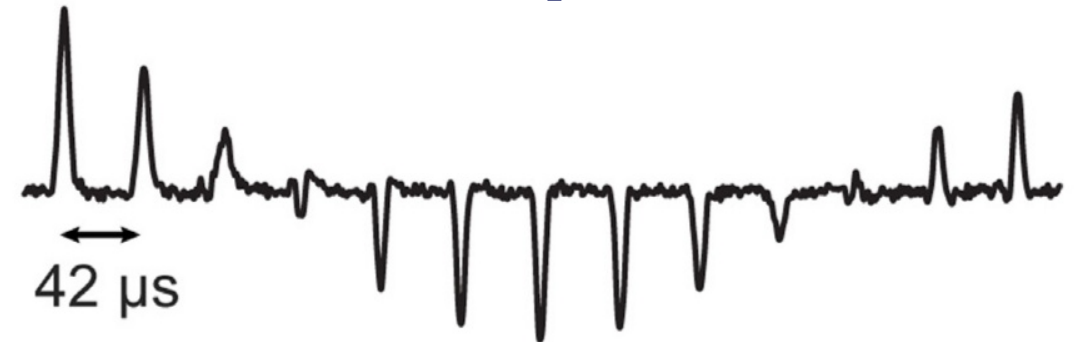


(b) ^{13}C on-resonance



(c) ^{14}N

**Nucleus not needed
in sample**



RF field strength

$$RF_2 = \frac{SF_2}{SF_1} * \sqrt{\frac{SF_1}{\tau * 4 * 10^{-6}} * \left[1 - \left(\frac{SF_2}{SF_1} \right)^2 \right]}$$

	SF (MHz)	tau (μs)	RF (kHz)	t90 (μs)
nucl1	300,2900000	1300,0000000		
nucl2	79,430000		61,30019497	4,078290454

Conclusion

Conclusion

CHEMICAL SHIFT CALIBRATION

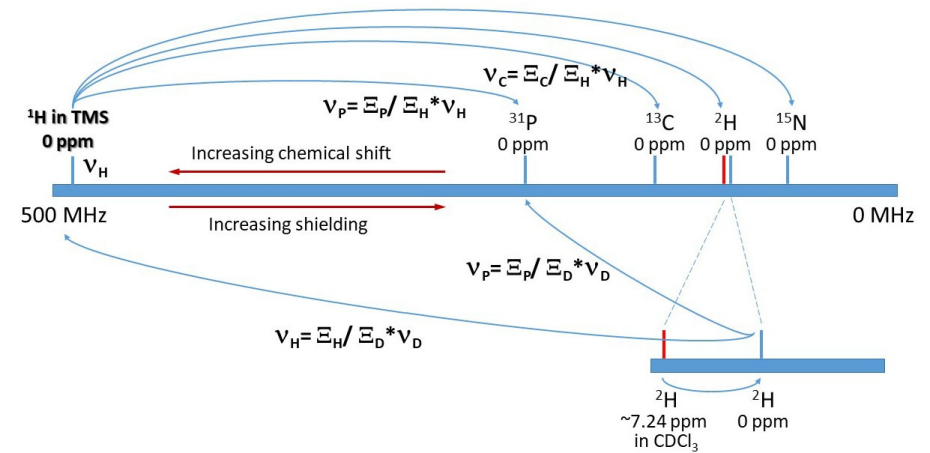
Absolute referencing with Xi

RADIOFREQUENCY CALIBRATION

Calibration without the nucleus

POSSIBLE EXPERIENCES

Post-C7, SR4₁², D-HMQC, PRESTO



NMR has strongly evolved

Acknowledgments



Frederic Perras
Takeshi Kobayashi
Alexander Paterson
Scott Southern

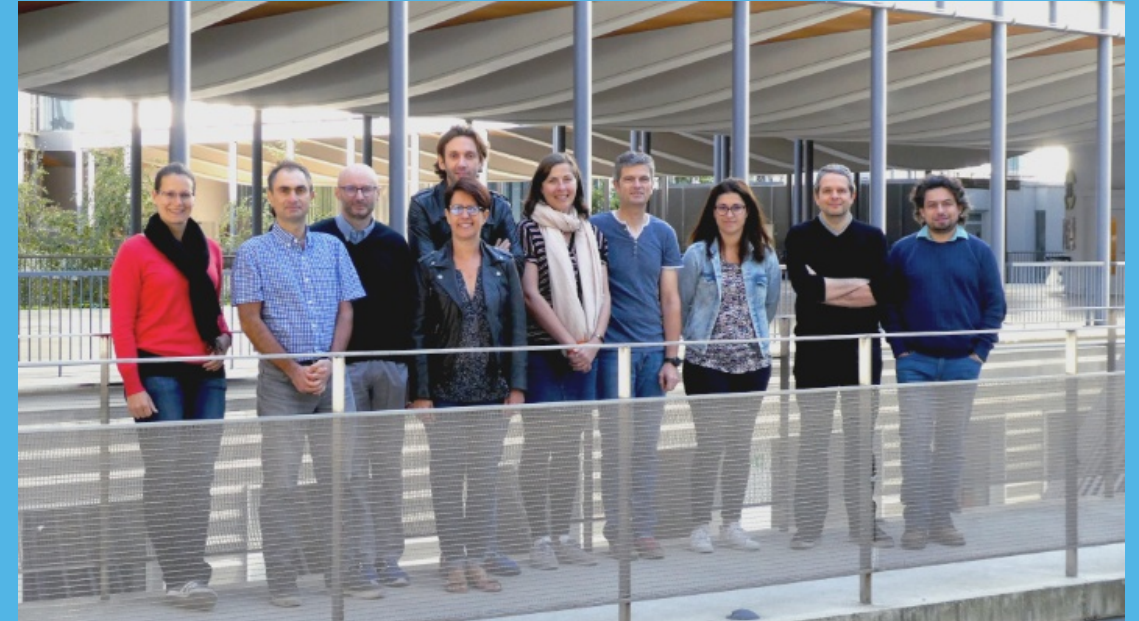


Aaron Rossini
Rick Dorn



Christian Bonhomme
Thierry Azais
Ieva Goldberga
Adam Nelson

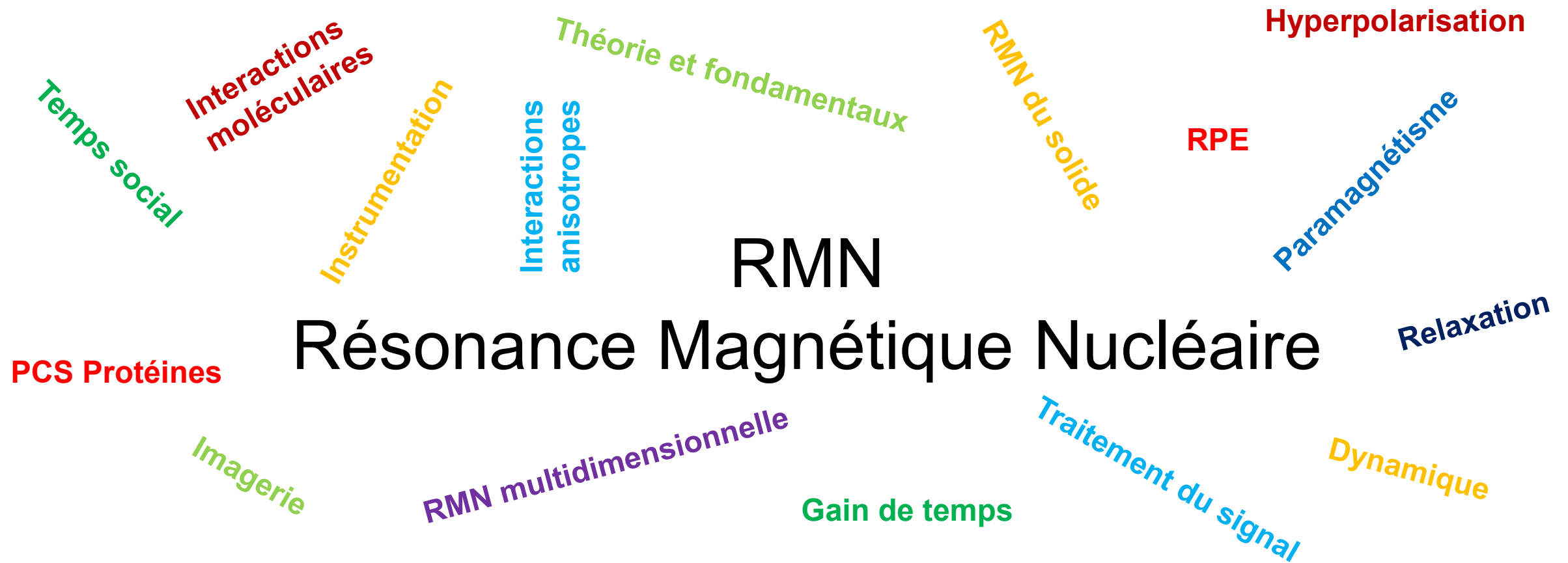
Baptiste Rigaud
Cristina Coelho
Claire Troufflard
Régina Maruchenko
Franck Lacour





GERM2024 : Ecole de RMN du GERM
18-22 mars 2024 Cargèse (France)

Pré-inscription avant le 2 février 2024 sur <https://germ2024.sciencesconf.org/>



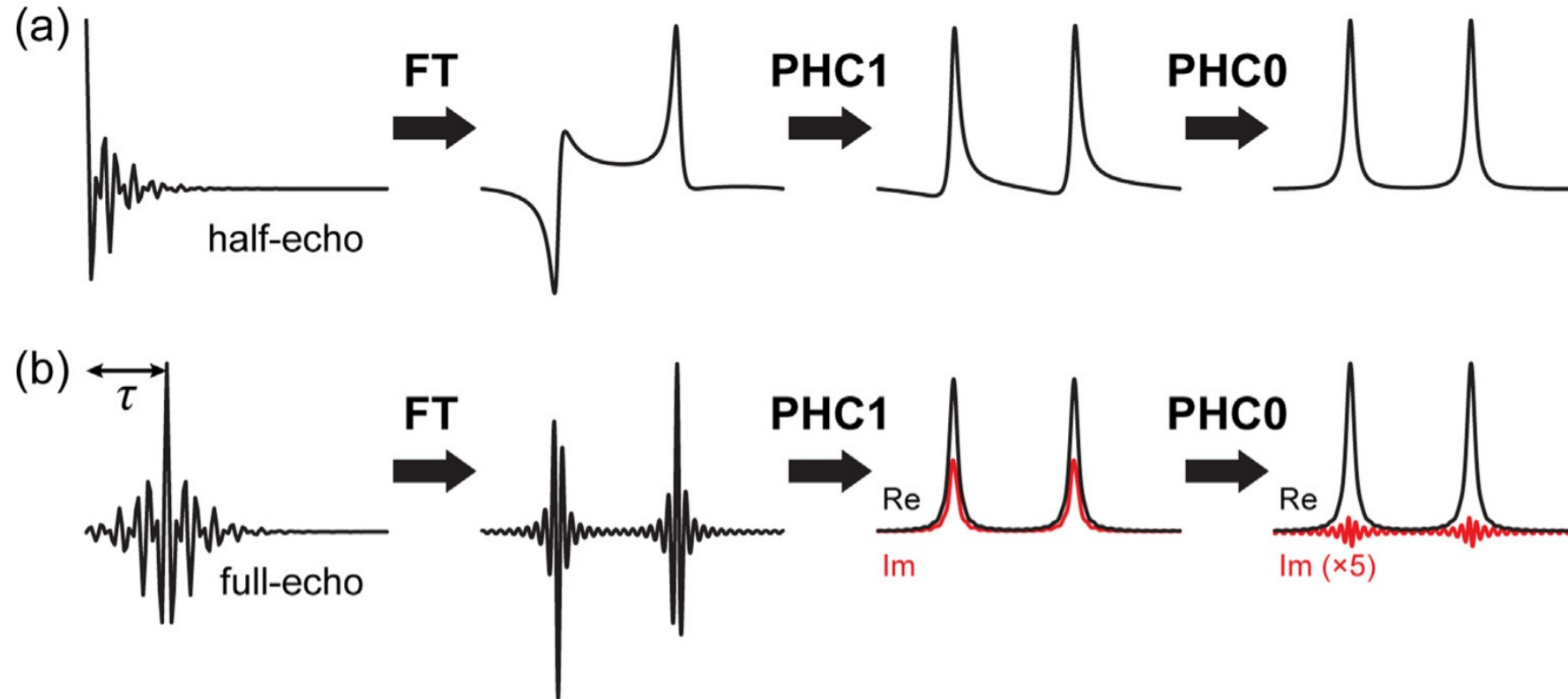
Supplementary materials

Corrected ^1H chemical shifts

 1 % TMS in CDCl_3 at 25°C

Sample	Peak	$\delta_{0^\circ\text{C}}$ ppm	Slope $^b 10^{-3}$ ppm $^\circ\text{C}^{-1}$	2nd Order $^b 10^{-6}$ ppm $^\circ\text{C}^{-2}$	$\sigma(\text{error})^d$ $^b 10^{-3}$ ppm	Shift at 25°C ppm	$d\delta/d(P_{\text{air}})$ $^b 10^{-3}$ ppm bar^{-1}
Acetone- d_6	TMS	-0.1692	0.084	-2.86	0.3	-0.1689	0.0014
	Acetone- d_5	1.8973	-0.414	-2.18	0.6	1.8856	0.0017
	H_2O	2.8459	-8.927	19.08	1.3	2.6346	0.0028
Acetonitrile- d_3	TMS	-0.0011	-0.522		0.6	-0.0141	-0.0002
	CHD_2CN	1.9520	-1.031		0.7	1.9262	0.0000
	H_2O	2.2278	-5.472	20.08	1.4	2.1036	-0.0008
Benzene- d_6	TMS	-0.5196	0.434		0.5	-0.5087	0.0000
	H_2O	-0.1527	1.296		1.0	-0.1203	-0.0014
	C_6HD_5	6.6354	0.522		0.6	6.6485	-0.0002
Chloroform- d	TMS	0.01225	-0.490		-	0.0000	0.0010
	H_2O					$\sim 1.55^c$	
	CHCl_3	7.2836	-0.925		0.1	7.2605	0.0010
Deuterium oxide	DSS d	-0.0833	0.595	-3.44	1.0	-0.0706	
	TMS d	-0.1099	0.905	-5.77	0.9	-0.0909	
	TSP- d_4	-0.0944	0.675	-4.56	0.8	-0.0804	
Dichloromethane- d_2	HOD	4.9920	-12.025	26.85	1.2	4.7081	0.0013
	TMS	-0.0122	-0.495		0.9	-0.0246	
	H_2O	1.5774	-3.372		1.8	1.5002	
DMSO- d_6	CHDCl_2	5.3260	-1.281		1.4	5.2940	
	TMS	0.0744	-0.545		0.5	0.0608	0.0017
	DMSO- d_5	2.5822	-0.833		0.7	2.5614	0.0012
	H_2O	3.4962	-4.994		2.5	3.3714	0.0015

Half-echo vs full-echo

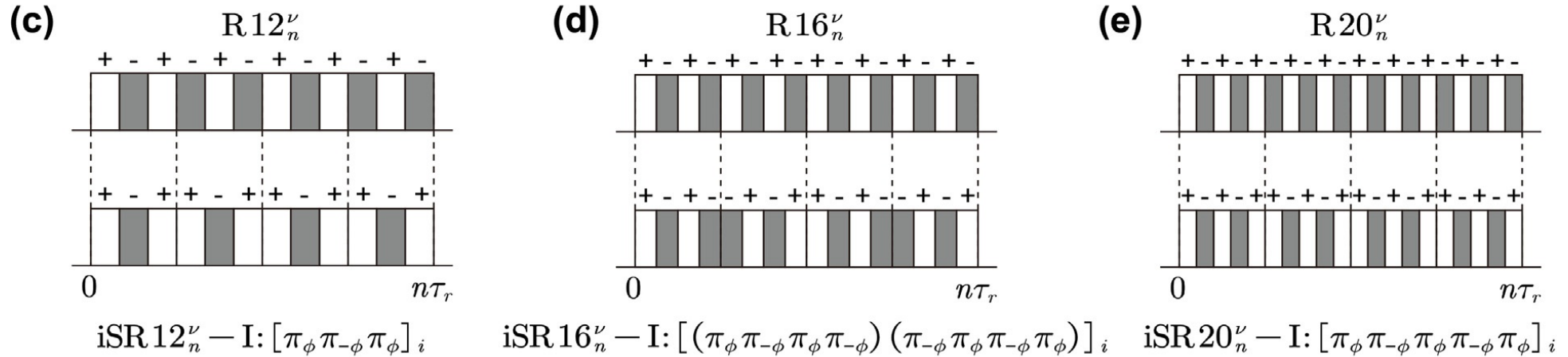


I. Hung *et al.*, *J. Magn. Reson.* 310, 106636 (2020).

Full echo is more sensitive but can present distortions

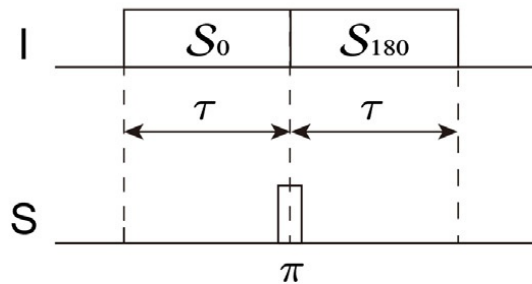
PRESTO

(a) $RN_n^\nu = [\pi_\phi \pi_{-\phi}]_{N/2}$ $RN_n^{-\nu} = [\pi_{-\phi} \pi_\phi]_{N/2}$ (b) $SRN_n^\nu = [RN_n^\nu RN_n^{-\nu}]$



(f) $iSRN_n^\nu - II: (iSRN_n^\nu - I) (iSRN_n^{-\nu} - I), N = 4k, k = 3, 4, 5, \dots$

(g) Spin echo



(h) PRESTO-III

