MR Spectroscopy

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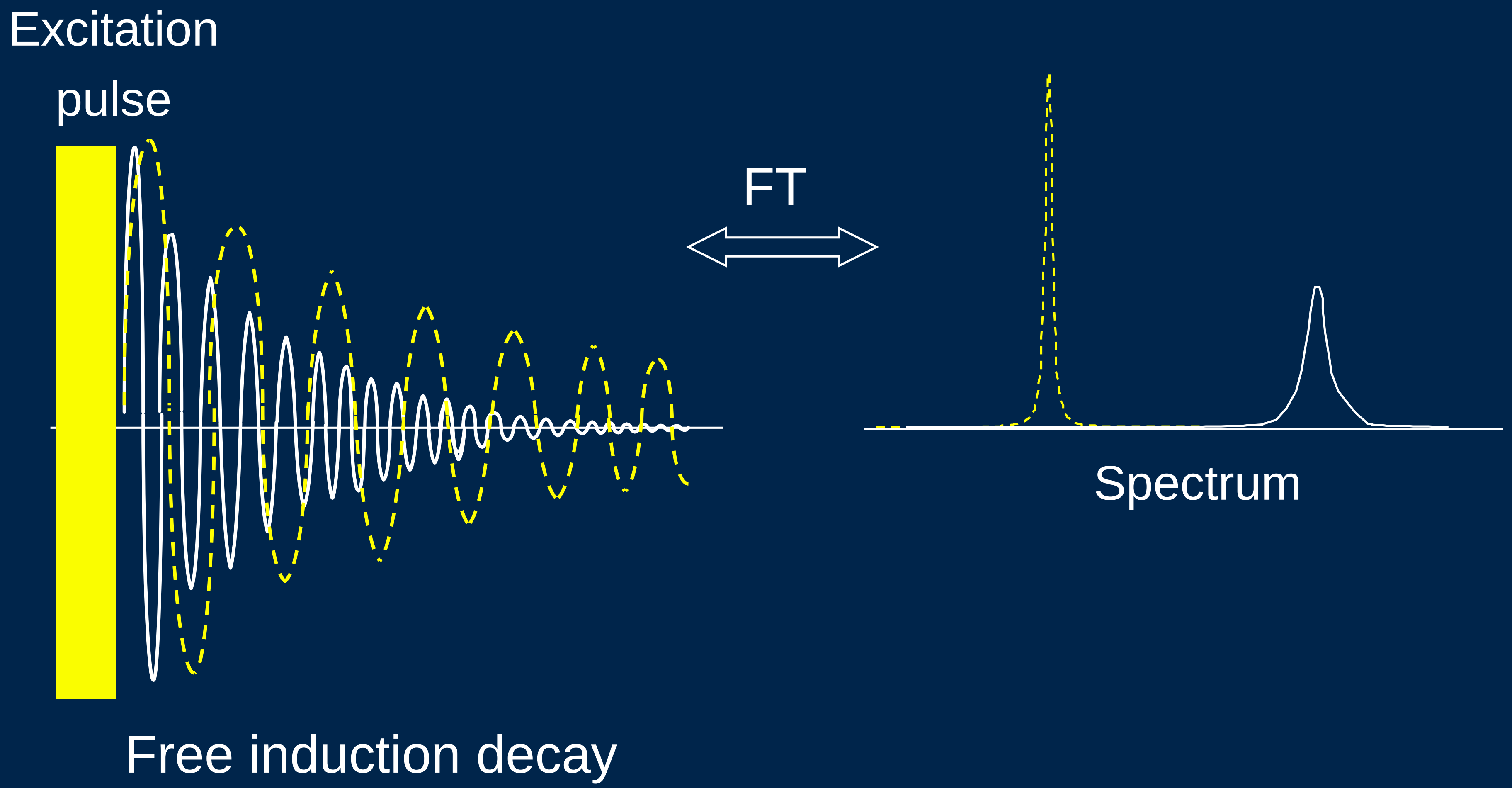
FID and Spectrum



Magnetic Resonance Larmor Frequency

$\nu_0 = \gamma^* \times B_0$

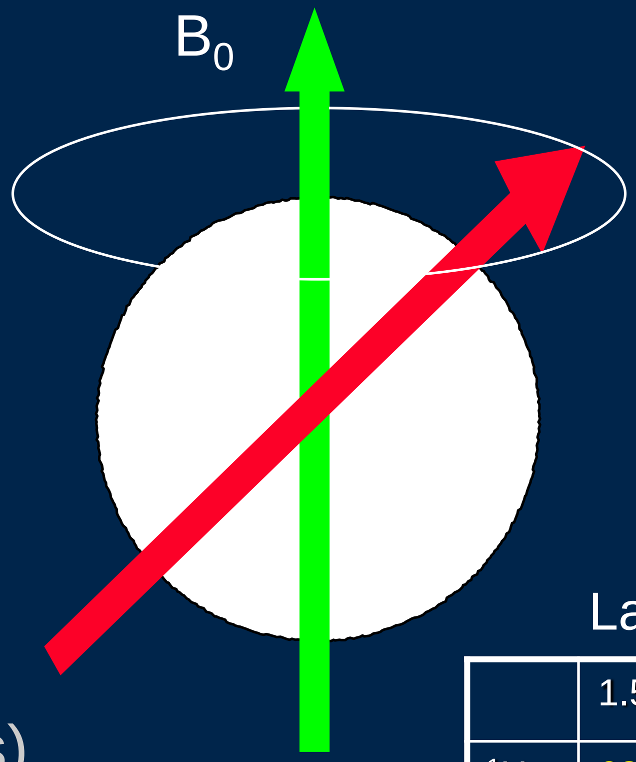
$(\gamma^* = \frac{\gamma}{2\pi})$

γ: gyromagnetic ratio

(property of nucleus)

$\gamma^*_H = 42.577$ Mhz/T

$\gamma^*_P = 17.235$ Mhz/T



Lamor frequency:

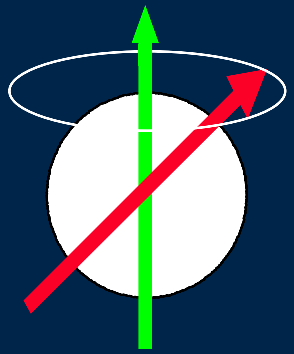
	1.5 T	3 T
^1H	63.86 MHz	127.73 MHz
^{31}P	25.85 MHz	51.7 MHz

Biologically Important NMR-Visible Nuclei

Relative Sensitivity ~ $|\gamma|^3 \cdot NA$ (NA = natural abundance)

	Spin-quantum number	Gyro-magnetc ratio $\gamma^* = \gamma / 2\pi$	Natural abundance [%]	Relative sensitivity for equal number of spins and constant magnetic field strenght	Relative sensitivity corrected for natural abundance
^{1}H	1/2	42.58	99.98	1.00	**1.00**
^{13}C	1/2	10.71	1.11	$1.59\ 10^{-2}$	**$1.8\ 10^{-4}$**
^{14}N	1	3.08	99.64	$1.01\ 10^{-3}$	**$1.0\ 10^{-3}$**
$^{17}0$	5/2	5.77	0.04	$2.91\ 10^{-2}$	**$1.1\ 10^{-5}$**
^{19}F	1/2	40.06	100.00	$8.30\ 10^{-1}$	**$8.3\ 10^{-1}$**
^{23}Na	3/2	11.26	100.00	$9.27\ 10^{-2}$	**$9.3\ 10^{-2}$**
^{31}P	1/2	17.24	100.00	$6.64\ 10^{-2}$	**$6.6\ 10^{-2}$**
^{39}K	3/2	1.99	93.08	$5.08\ 10^{-4}$	**$4.7\ 10^{-4}$**
^{43}Ca	7/2	2.87	0.14	$6.40\ 10^{-3}$	**$9.3\ 10^{-6}$**

Nuclei of Biological Interest



^{1}H

metabolites: 1-100 mmol/l in the body, high sensitivity

Problems: water suppression (110 mol/l !!),
fat suppression
overlapping of metabolite peaks

^{31}P

~ 10 mmol/l, important for studying energy metabolism

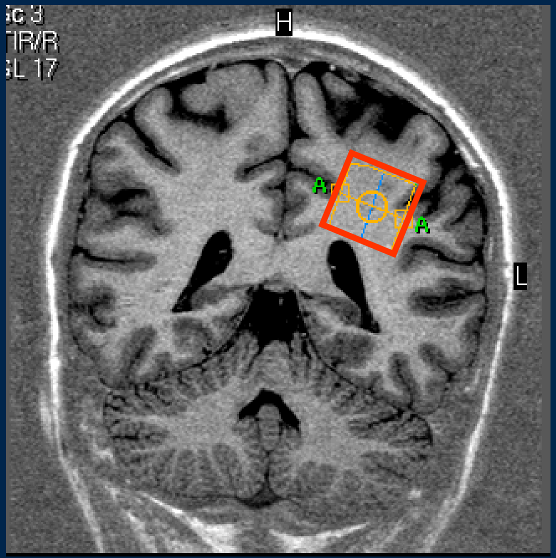
Problems: low sensitivity (100* lower than ^{1}H MRS)
fast T2 relaxation

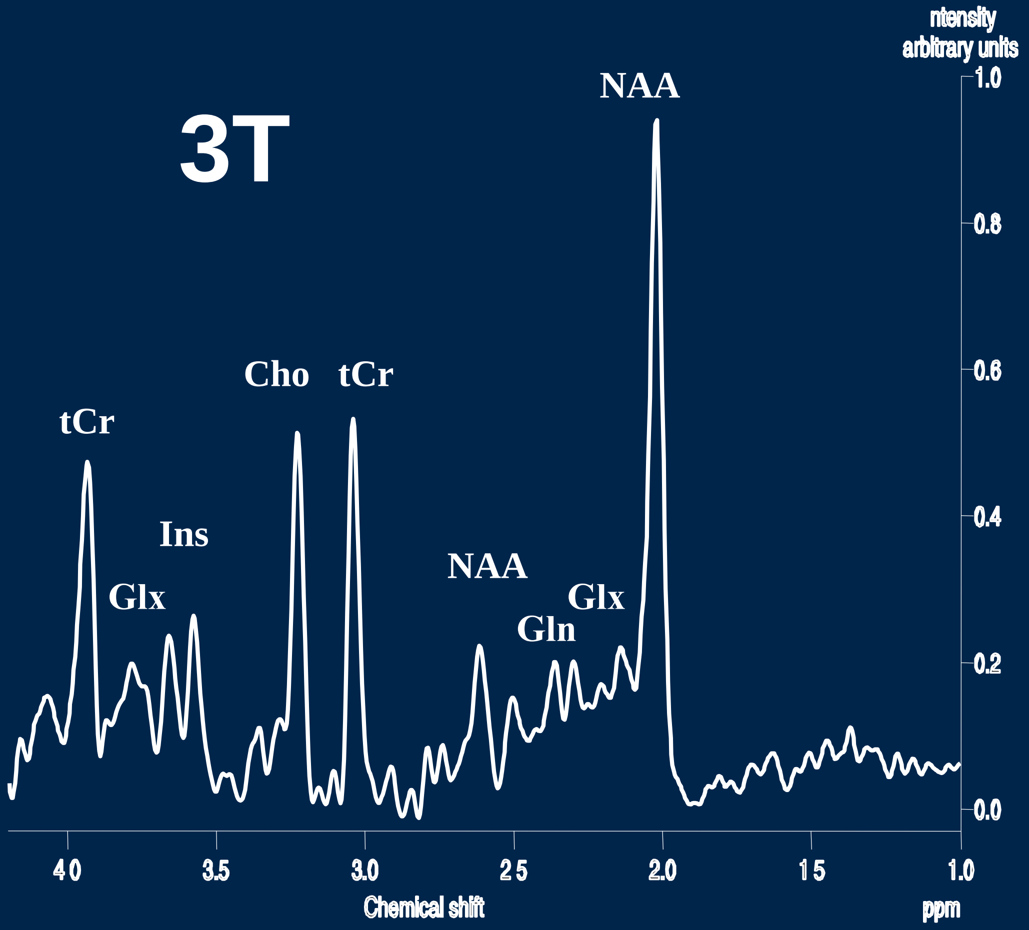
^{13}C

basic atom in organic molecules

Problems: only 1% natural abundance of ^{13}C
very low sensitivity
→ Sensitivity can be enhanced with hyperpolarization!

1H Spectrum of Brain at High Field



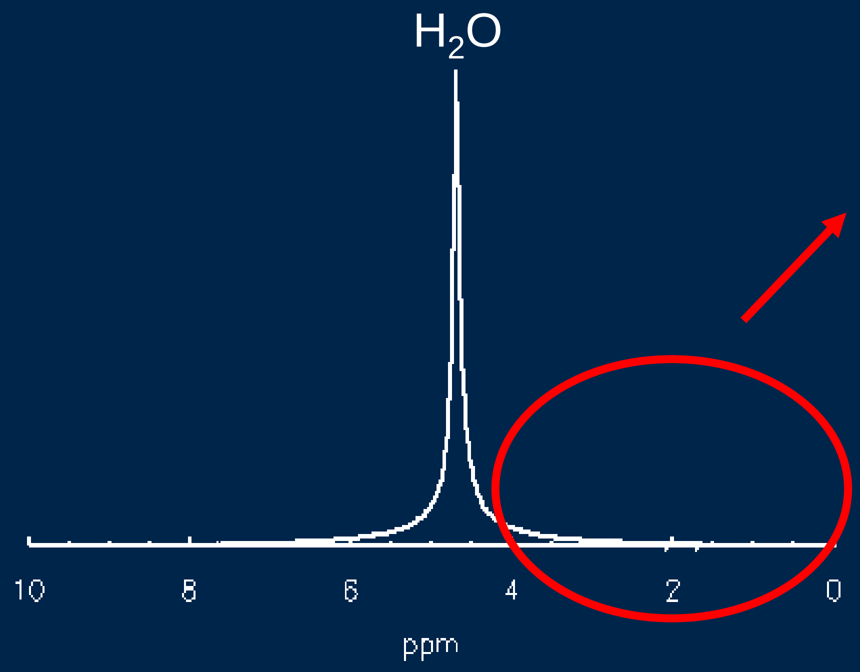


Courtesy: Dept. of Radiology, University of Bonn, Germany

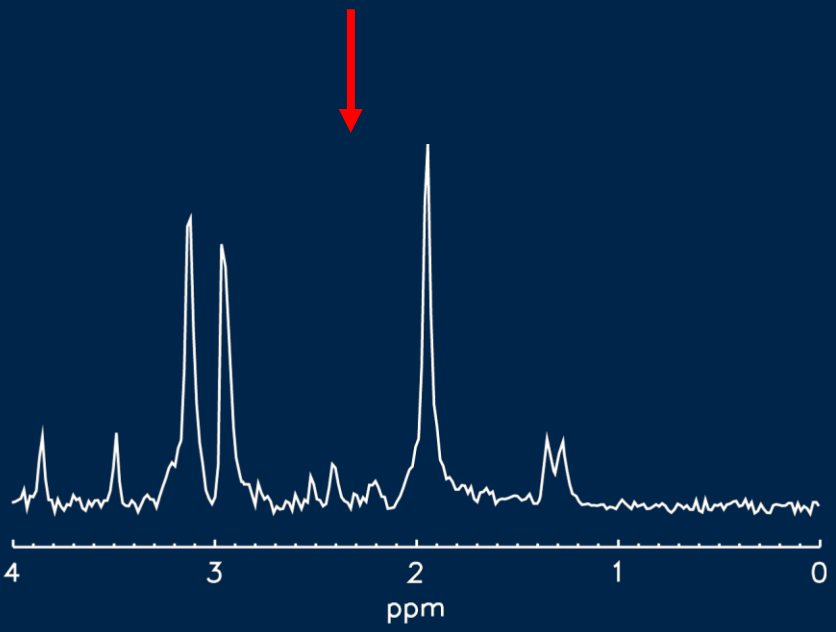
In vivo MRS

Water concentration ~ 10^4 times higher than metabolite concentrations

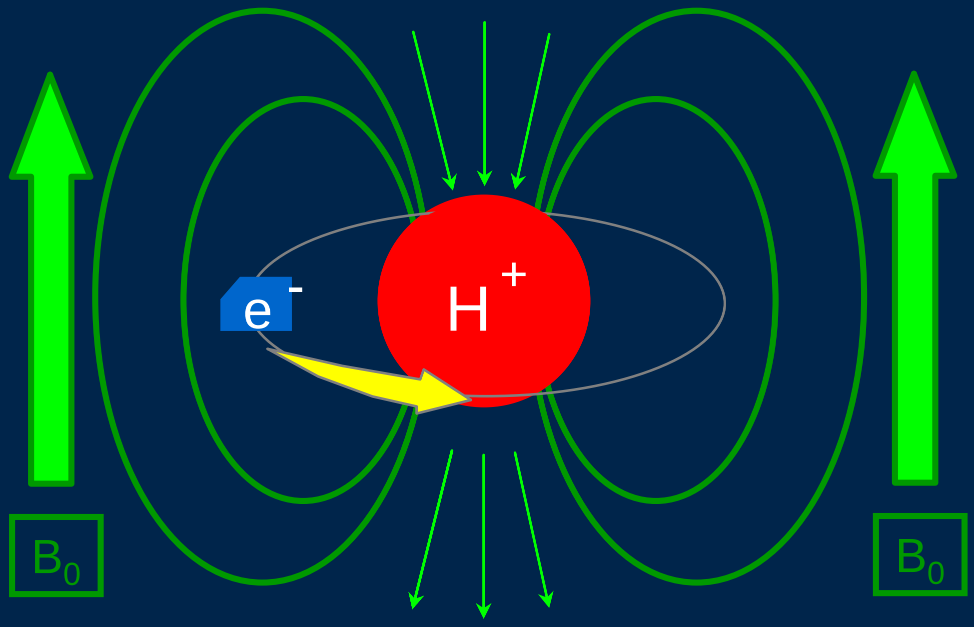
=> We are interested in the *small* peaks



Water suppression



Chemical Shift - Shielding effect of the electron shell

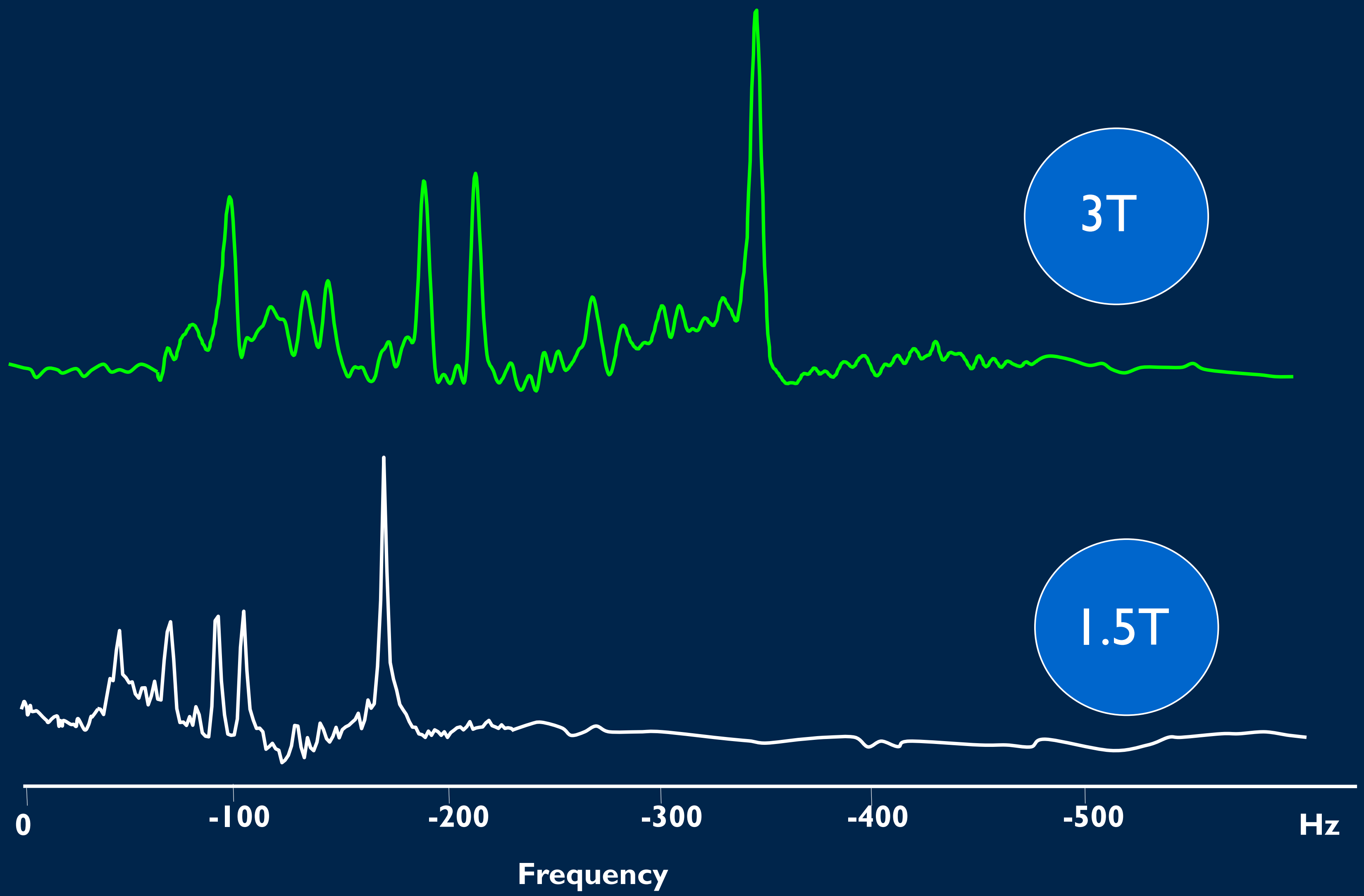


Shielding/deshielding of the nucleus by the electron shell:

=> different chemical environment for nuclei of same species
=> slightly different local magnetic field
=> slightly different Larmor frequency

The chemical shift scales with B_0 and therefore also with the Larmor frequency!

Hz Scaling

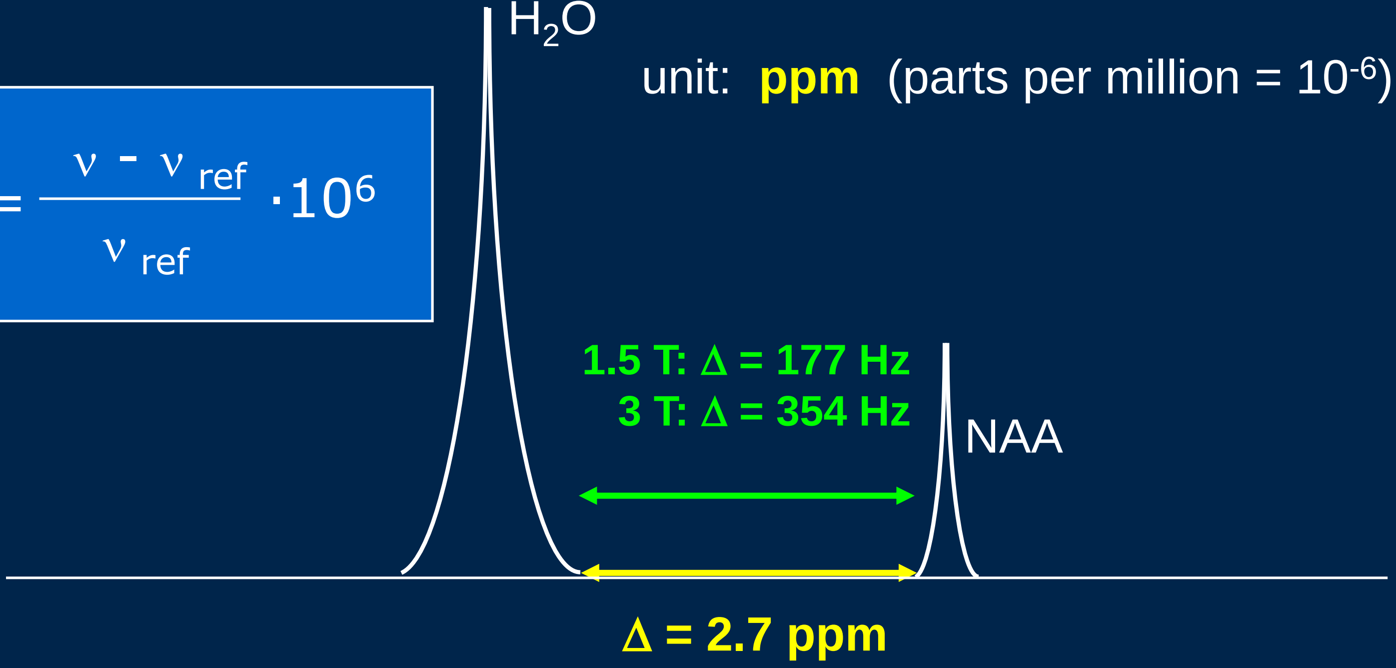


Chemical Shift

δ [Hz] $= \nu - \nu_{ref}$

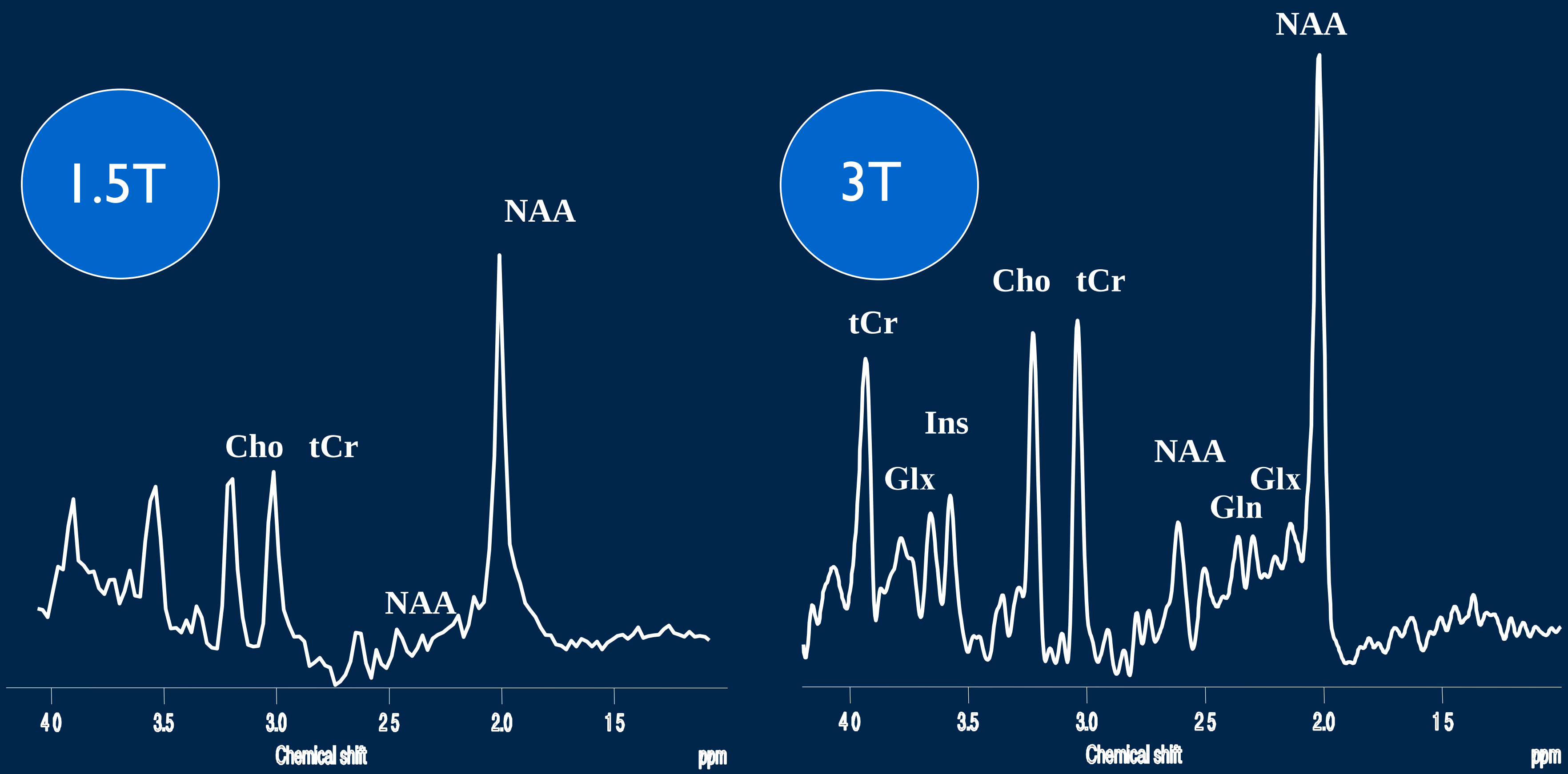
$$\boxed{\delta\ [\text{ppm}] = \frac{\nu - \nu_{ref}}{\nu_{ref}} \cdot 10^6}$$

unit: **ppm** (parts per million = 10^{-6})



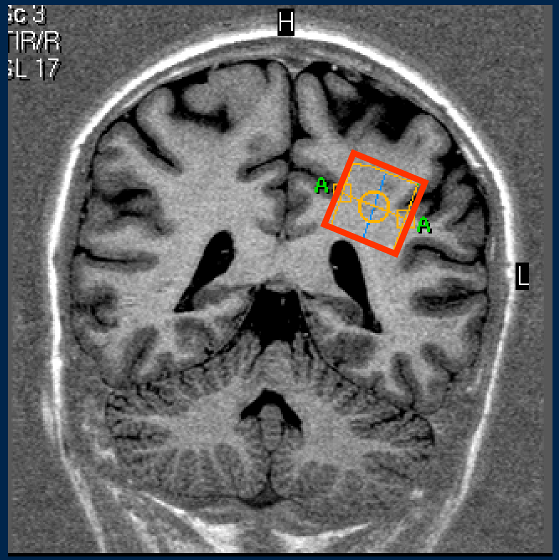
1H: $\nu_{ref} = \nu_{TMS}$ (TMS: tetramethylsilane $Si(CH_3)_4$)

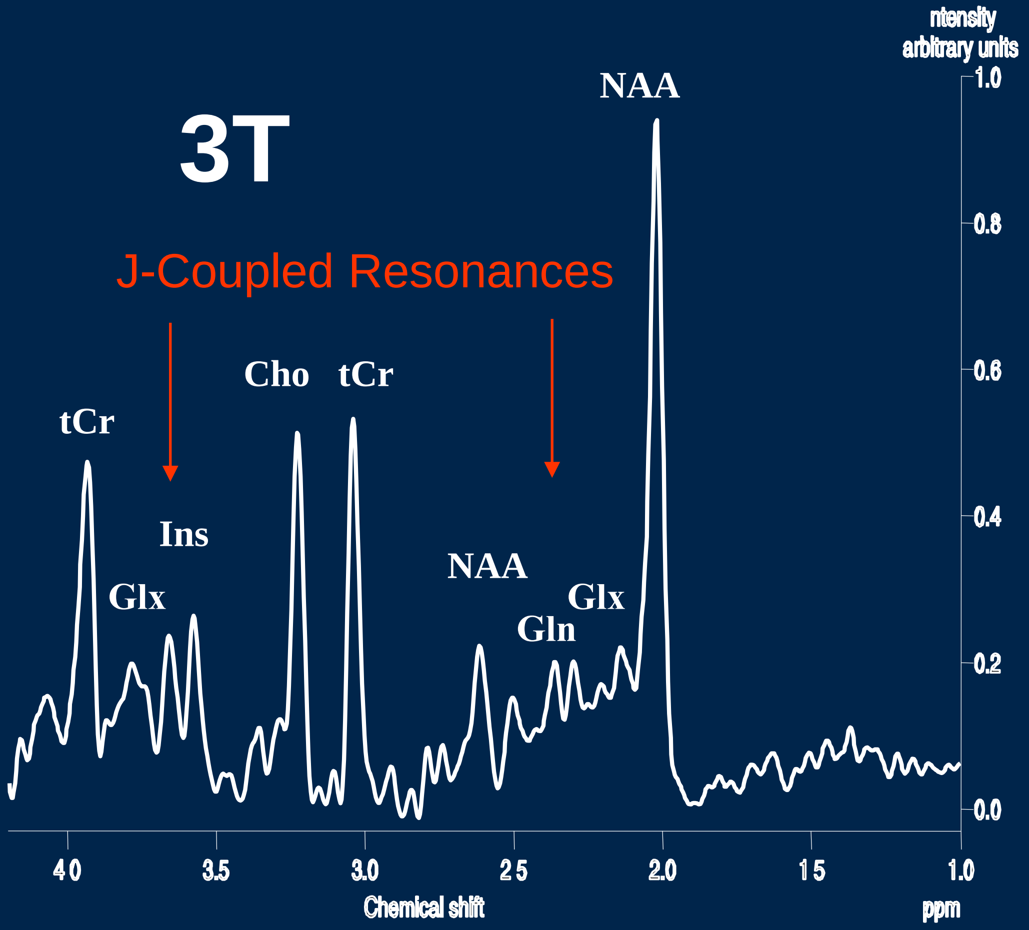
ppm Scaling



1.5T
NAA
Cho
tCr
NAA
4.0
3.5
3.0
2.5
2.0
1.5
Chemical shift
ppm
3T
NAA
Cho
tCr
tCr
Ins
Glx
NAA
Glx
Gln
4.0
3.5
3.0
2.5
2.0
1.5
Chemical shift
ppm

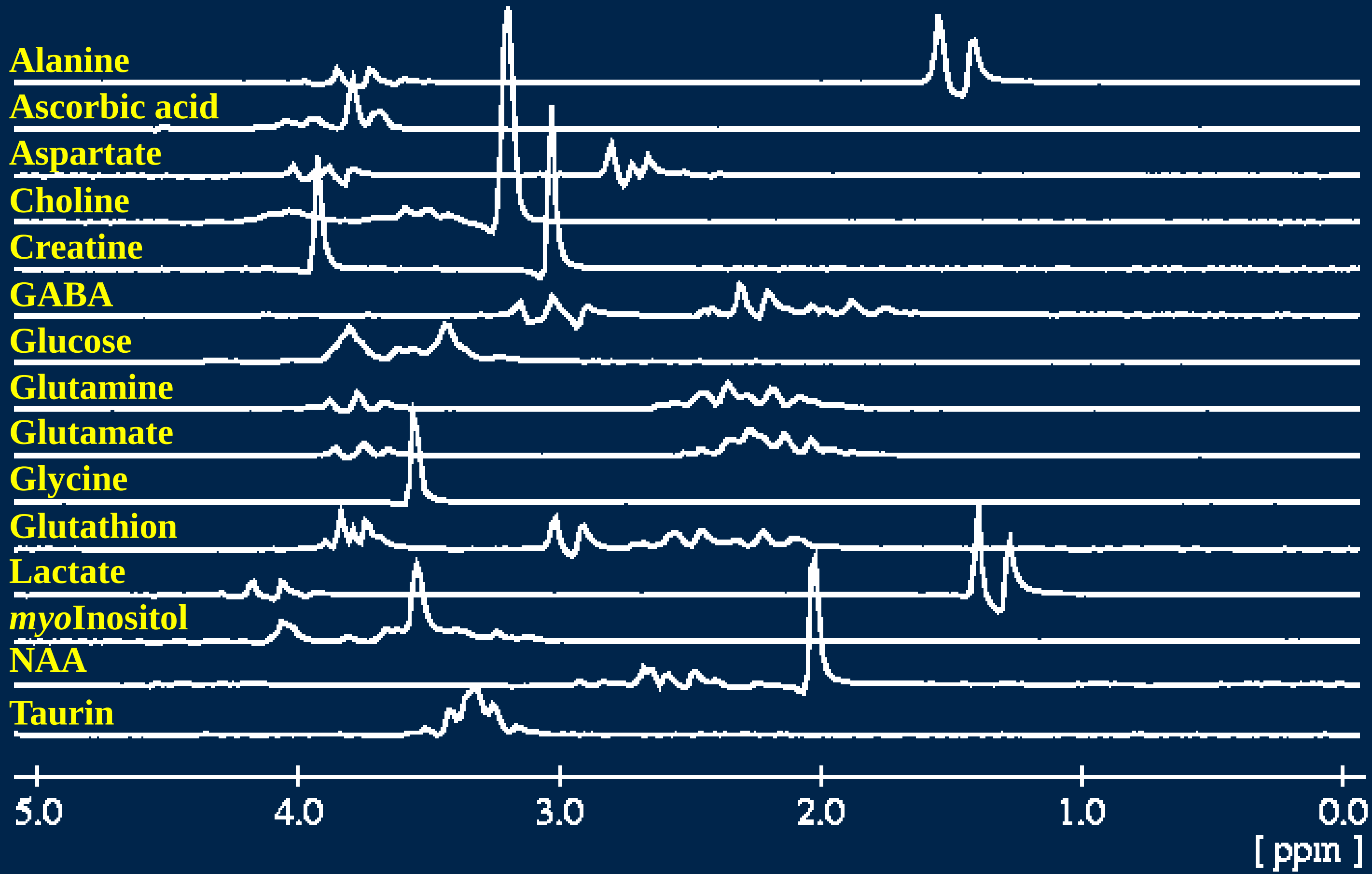
Hydrogen Spectrum of Brain at High Field



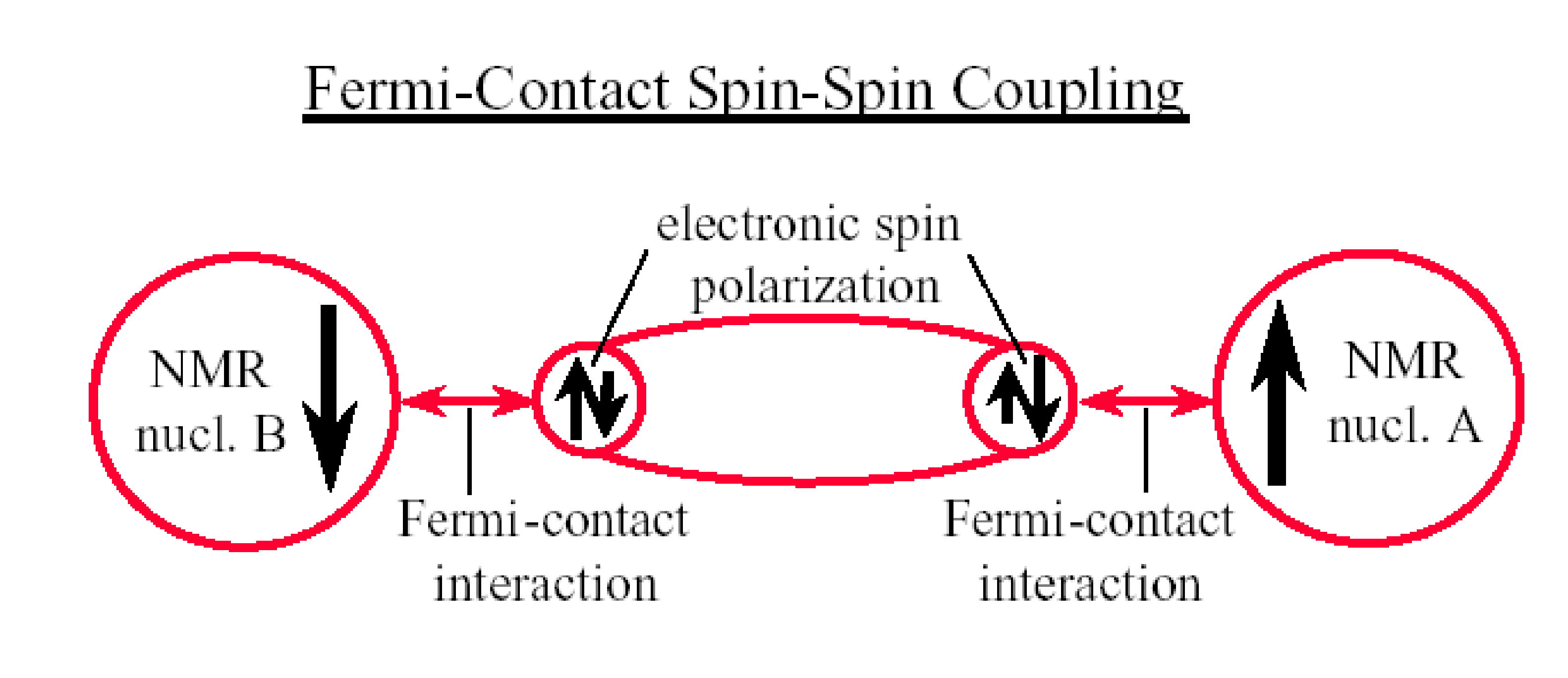


Courtesy: Dept. of Radiology, University of Bonn, Germany

Metabolites seen in ^{1}H MR Spectroscopy



J-coupling

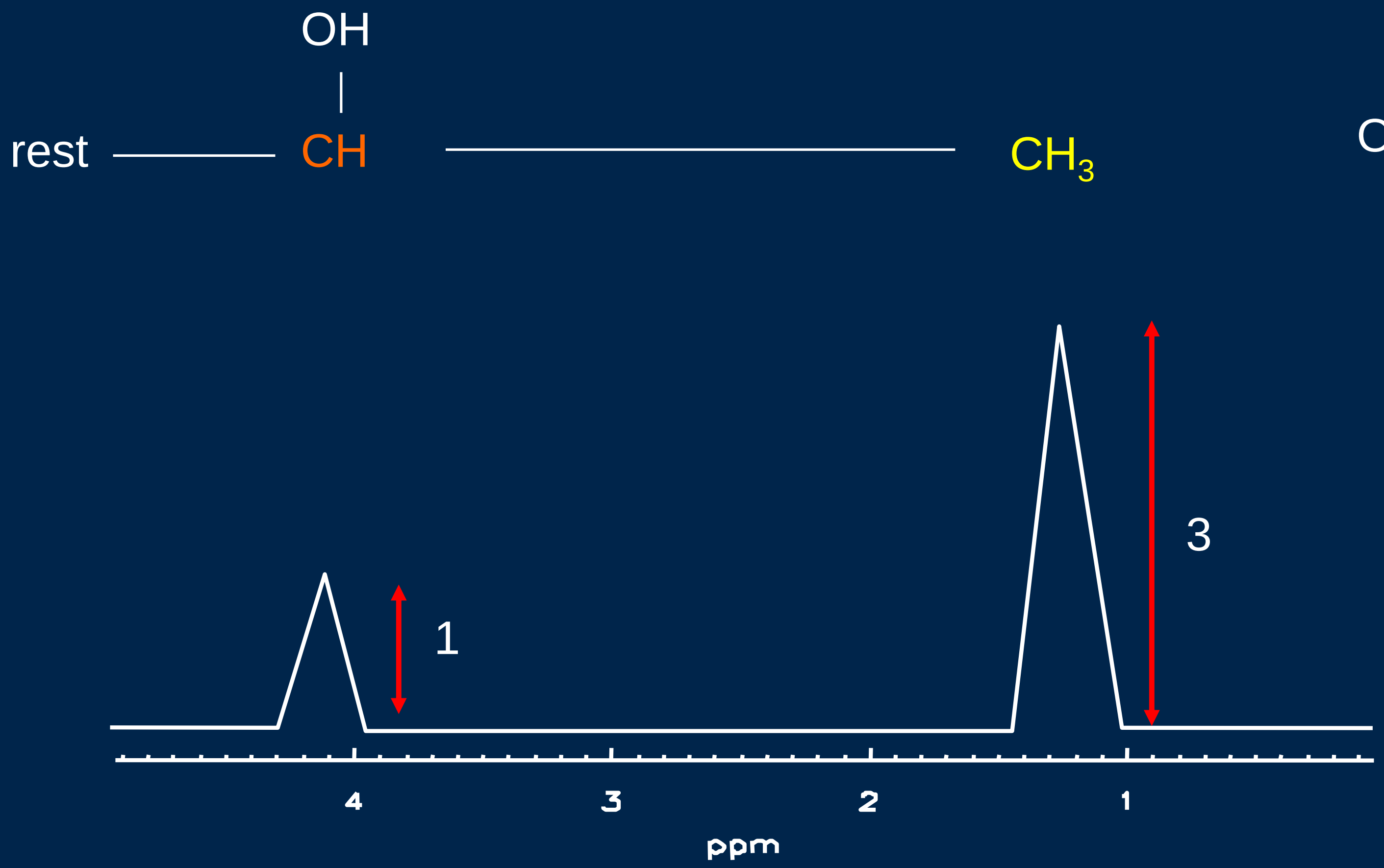


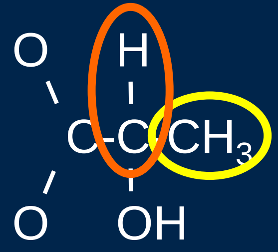
$\rightarrow$ Intramolecular interaction

J-coupling is equal at all field strengths !

J-coupling - Fine structure

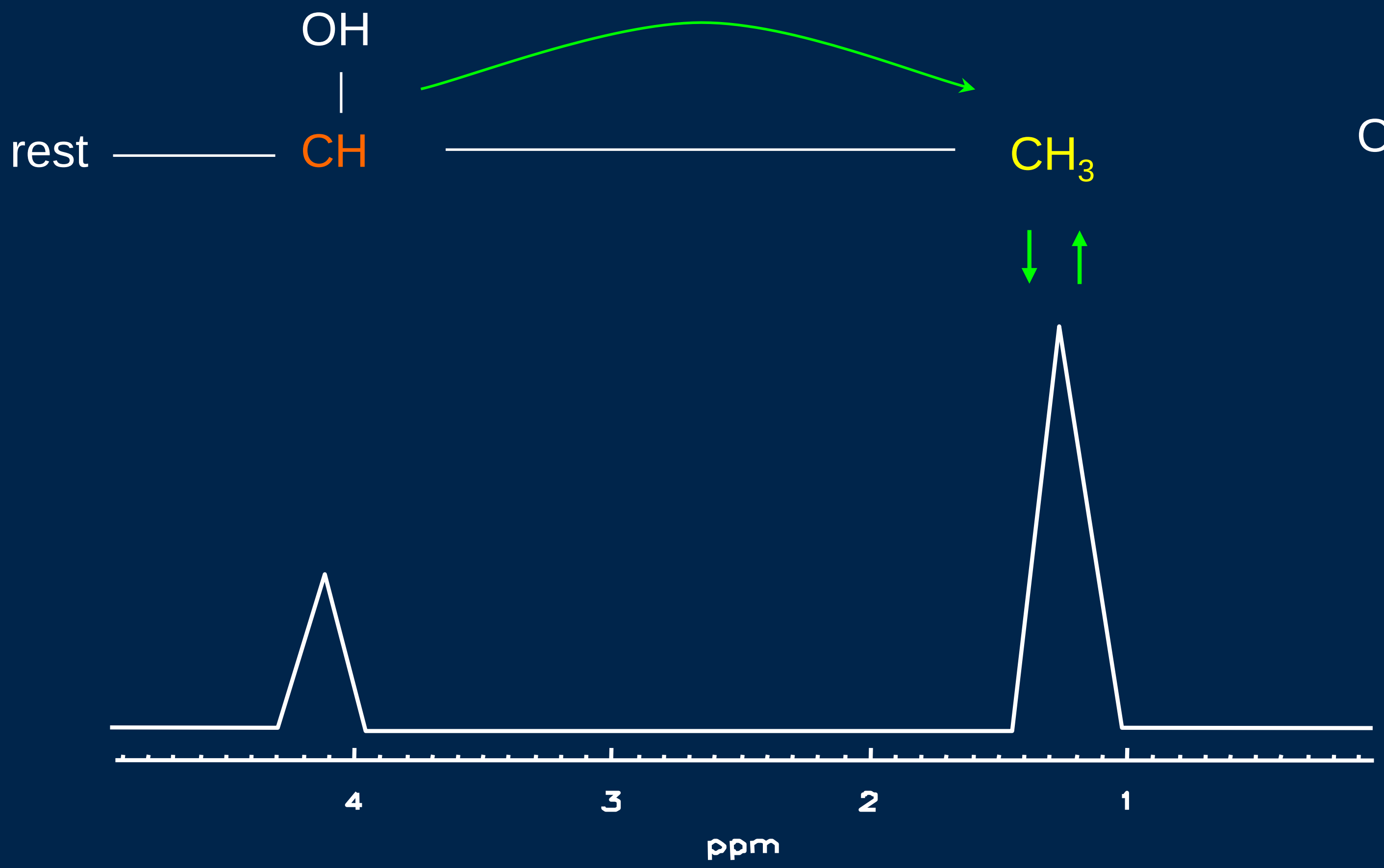
1H SPECTRUM OF LACTATE

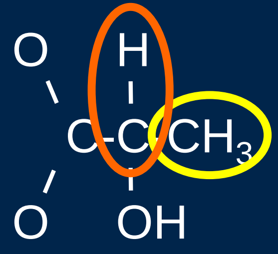




J-coupling - Fine structure

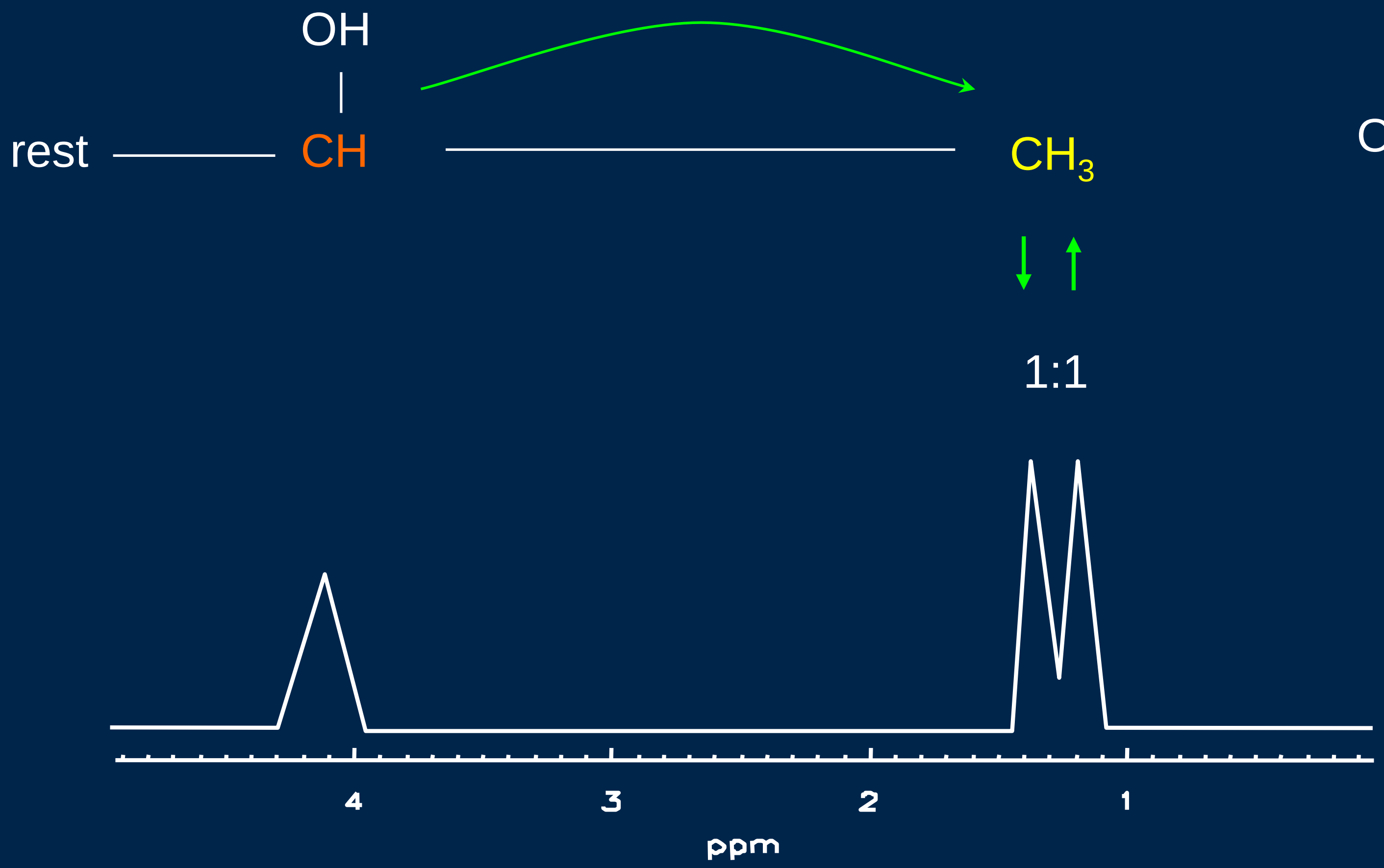
1H SPECTRUM OF LACTATE

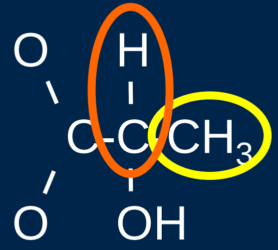




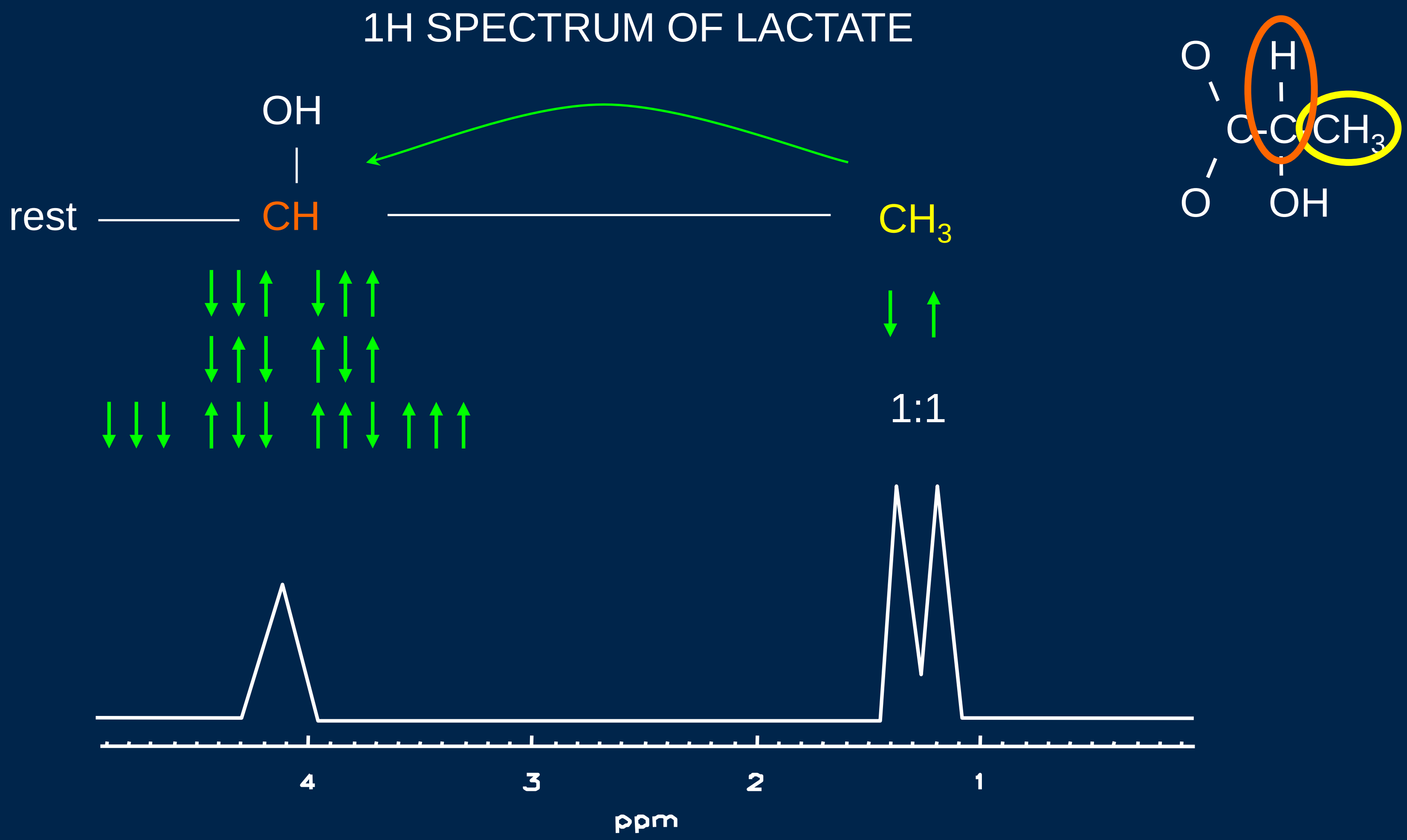
J-coupling - Fine structure

1H SPECTRUM OF LACTATE

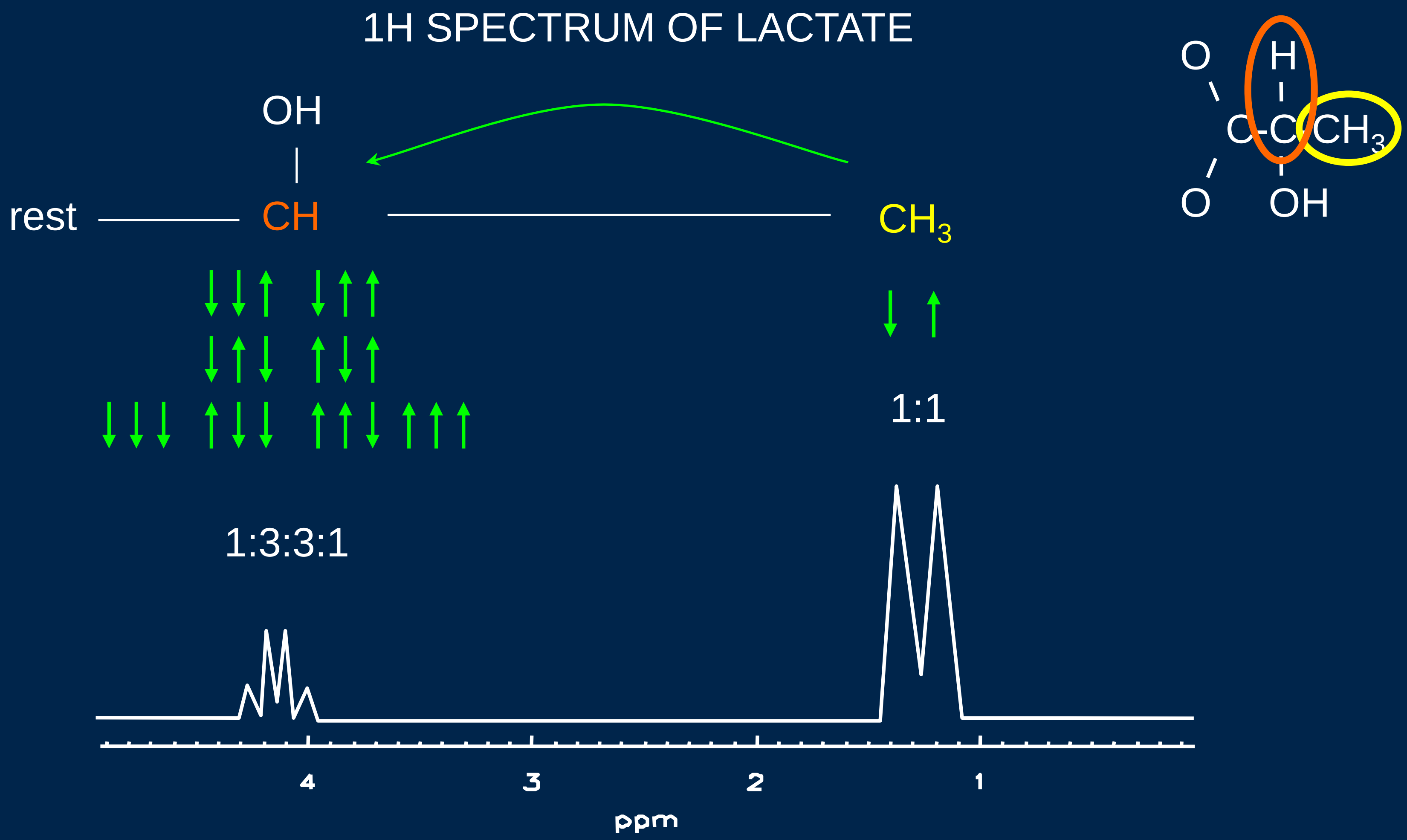




J-coupling - Fine structure

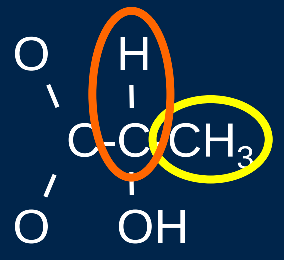


J-coupling - Fine structure



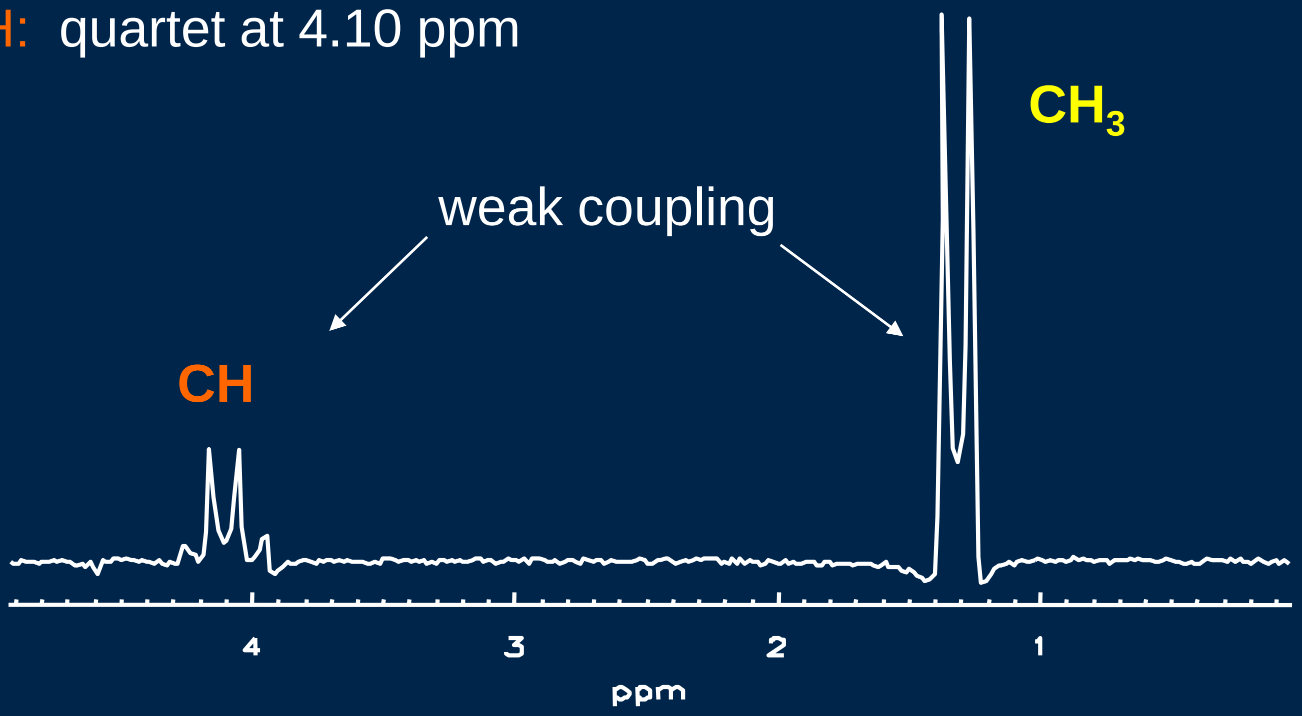
J-coupling - Fine structure

1H SPECTRUM OF LACTATE



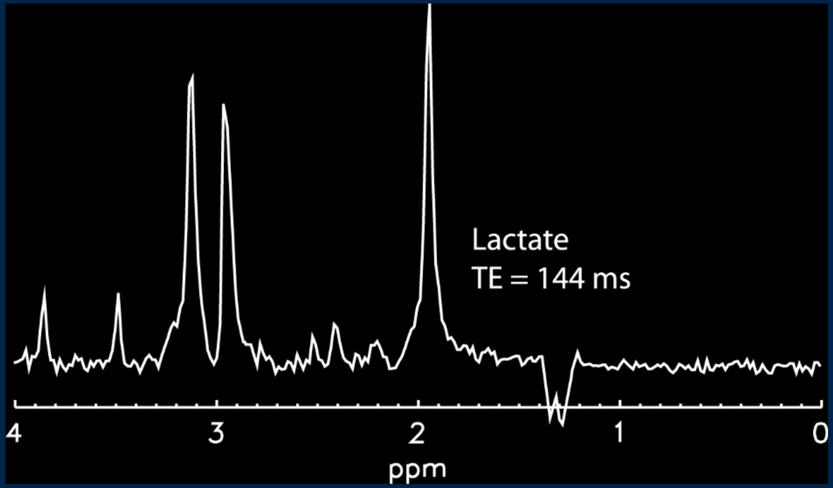
CH_3: doublet at 1.31 ppm

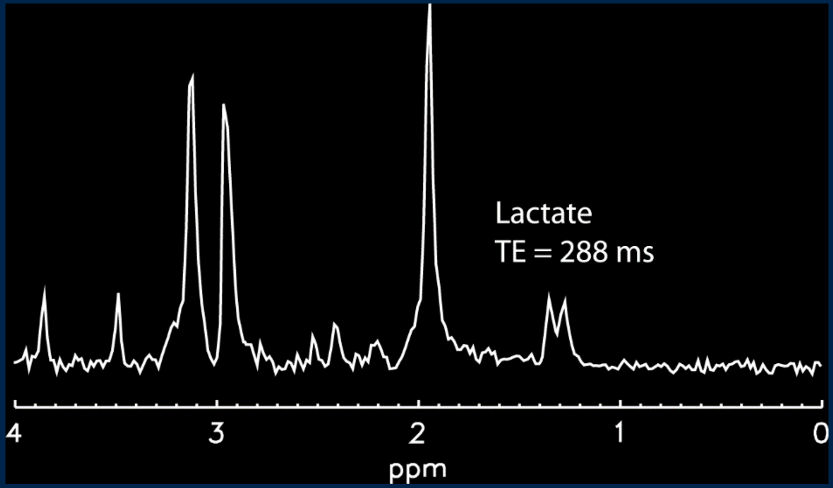
CH: quartet at 4.10 ppm



J-coupling - Evolution

Resonance shape is echo time dependent:





=> multiplet looks

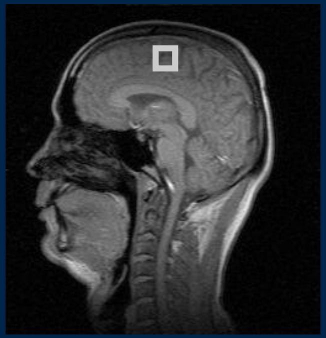
up at TE = n/J with even n

down at TE = n/J with odd n

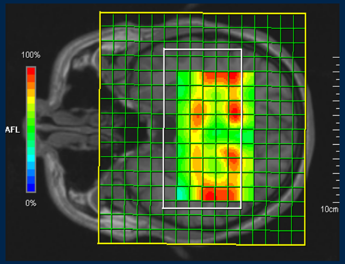
Localisation Techniques

Purpose: Data collection from a well-defined volume of interest (VOI)

- Gradient localization with conventional pulses:
  - PRESS: Point RESolved Spectroscopy
    (Bottomley PA, Ann N Y Acad Sci. 1987;508:333-48)
  - STEAM: STimulated Echo Acquisition Method
    (Haase et al., Radiology 1986;160:787-790)

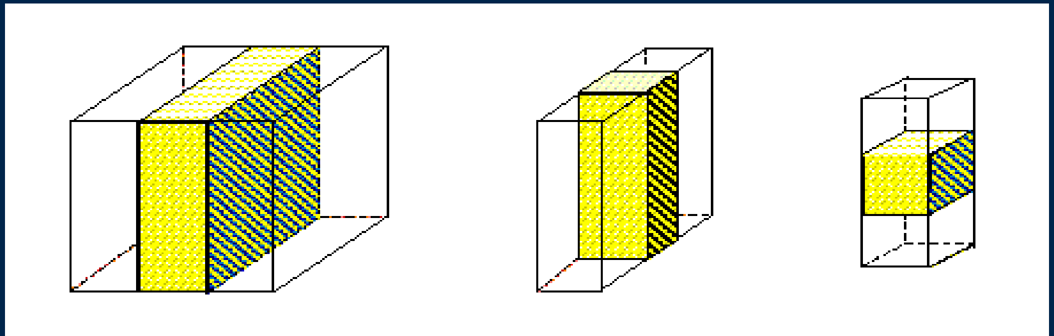


- Gradient localization with adiabatic pulses:
  - LASER: Localization by Adiabatic SElective Refocusing
    (Garwood M et al., J Magn Reson 2001 Dec;153(2):155-77)
- Localization via phase encoding: Chemical Shift Imaging (CSI)

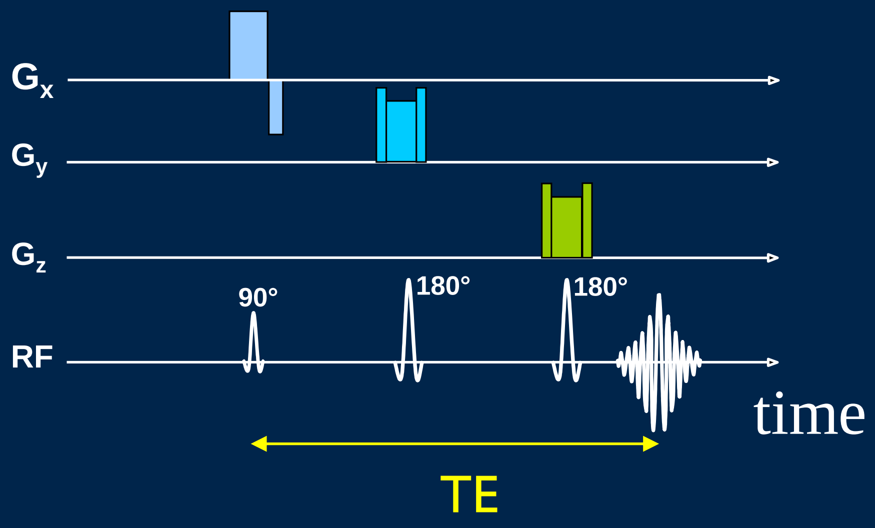


Localisation by Gradients

In each direction a pulse in combination with a gradient field defines one slice
=> the intersection of these slices is the selected volume of interest



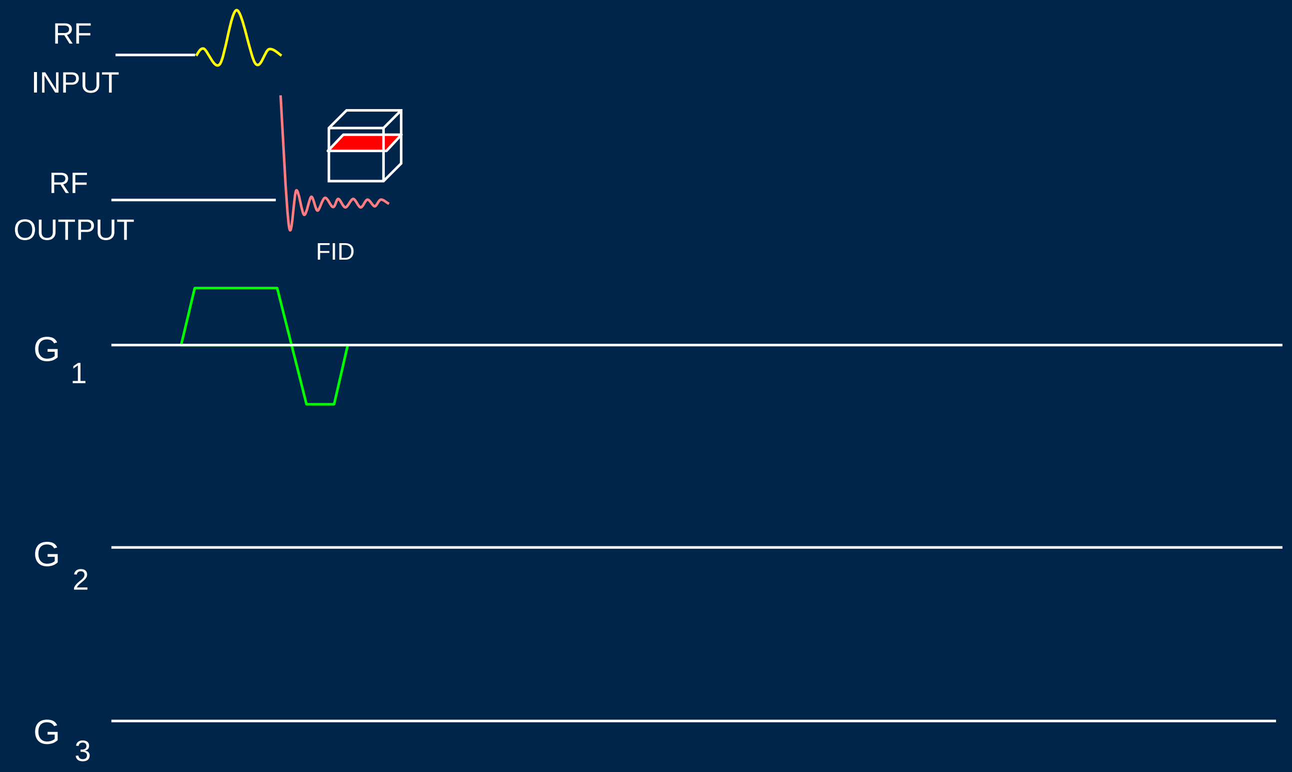
PRESS



- (Point RESolved Spectroscopy)
- *selective excitation:*
  double spin echo sequence: 90° - 180° - 180° - echo acquisition
- spoiler/crusher gradients: eliminate unwanted coherences from outside the selected volume

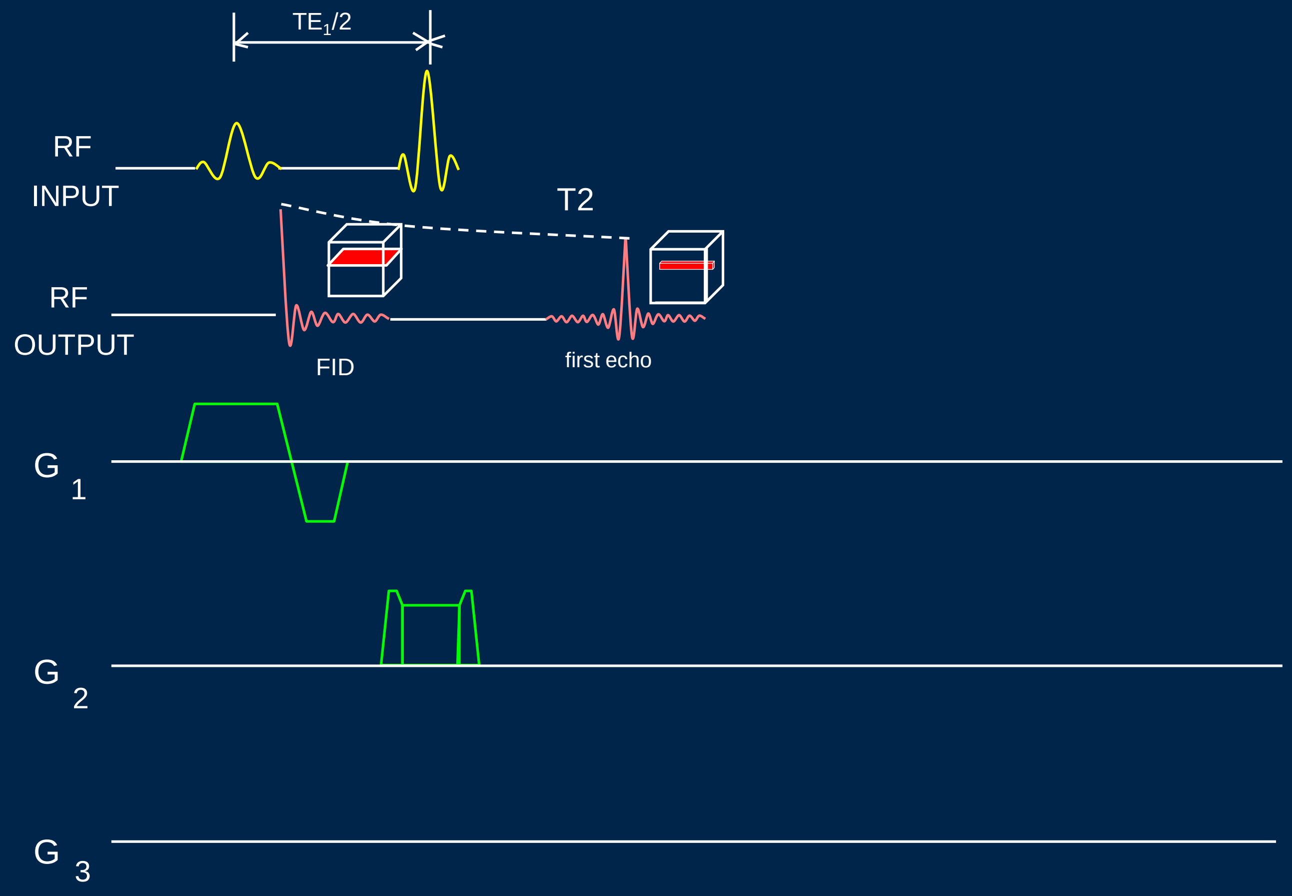
PRESS

Method of choice for 1H spectroscopy



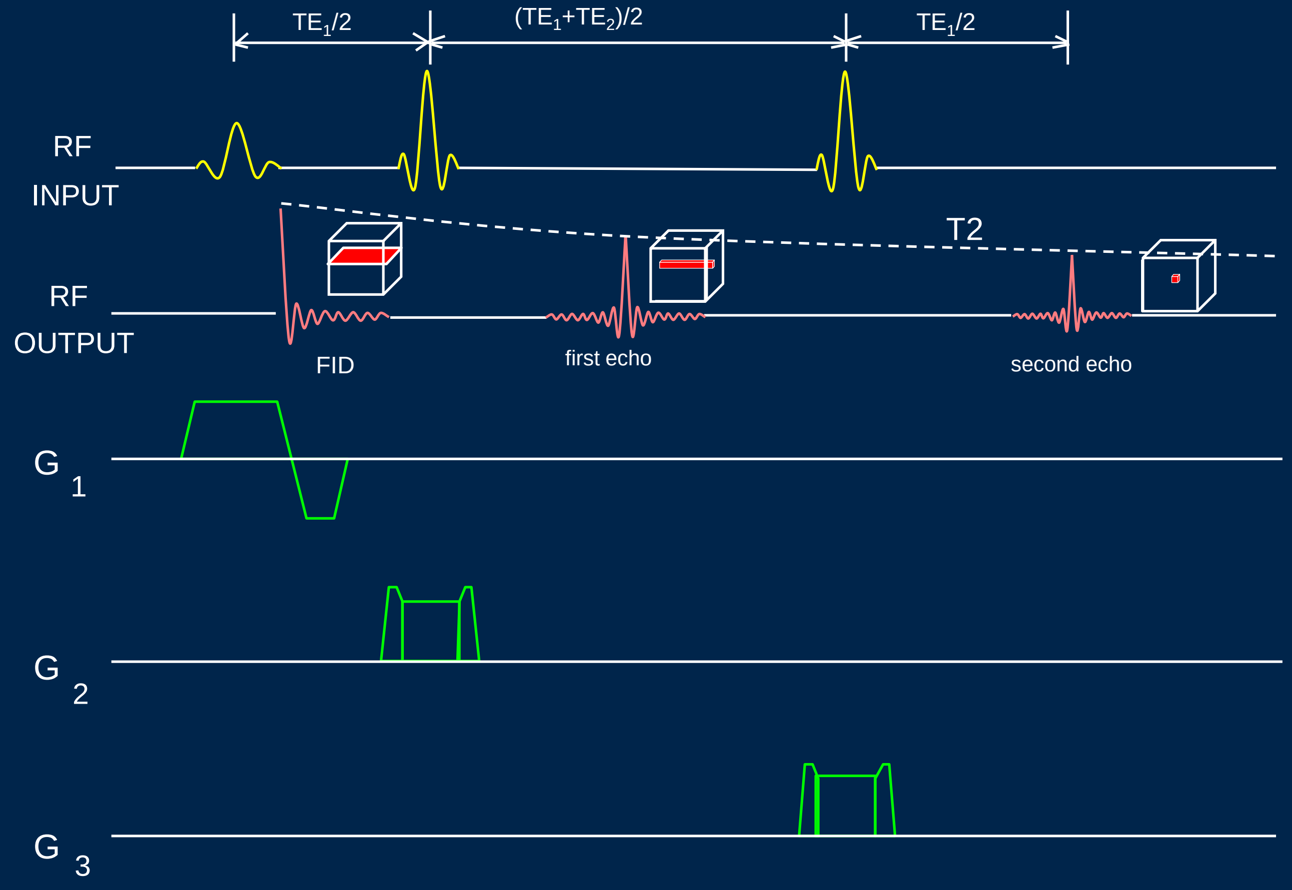
PRESS

Method of choice for 1H spectroscopy

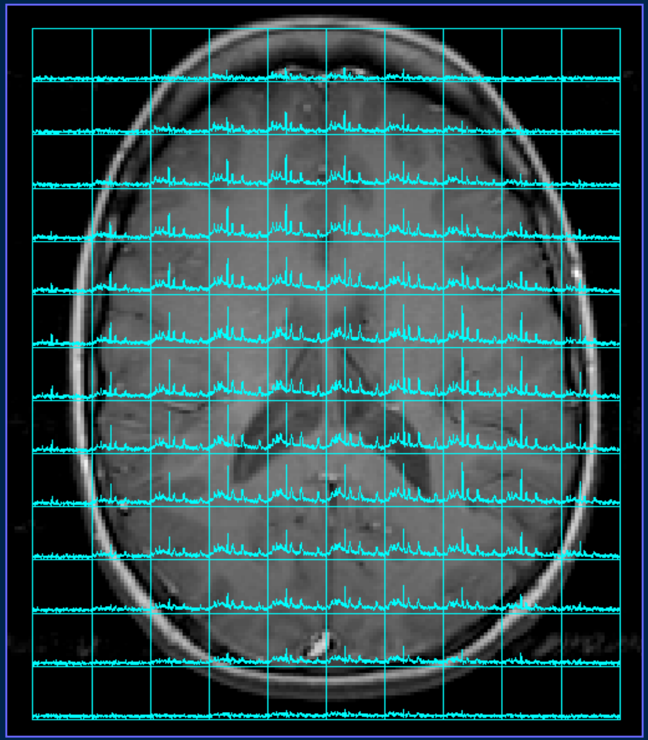


Echo Volume Selection

Method of choice for 1H spectroscopy

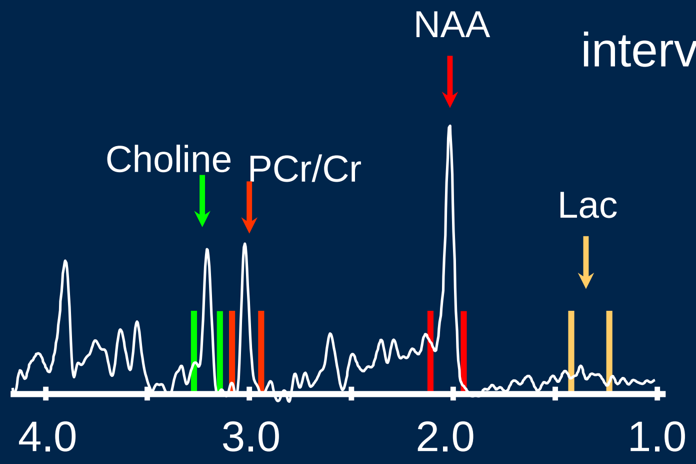


Spectroscopic Imaging

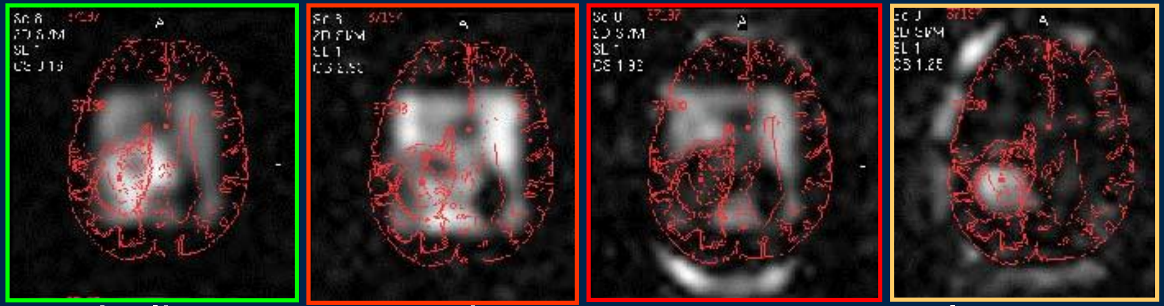


every voxel

a spectrum

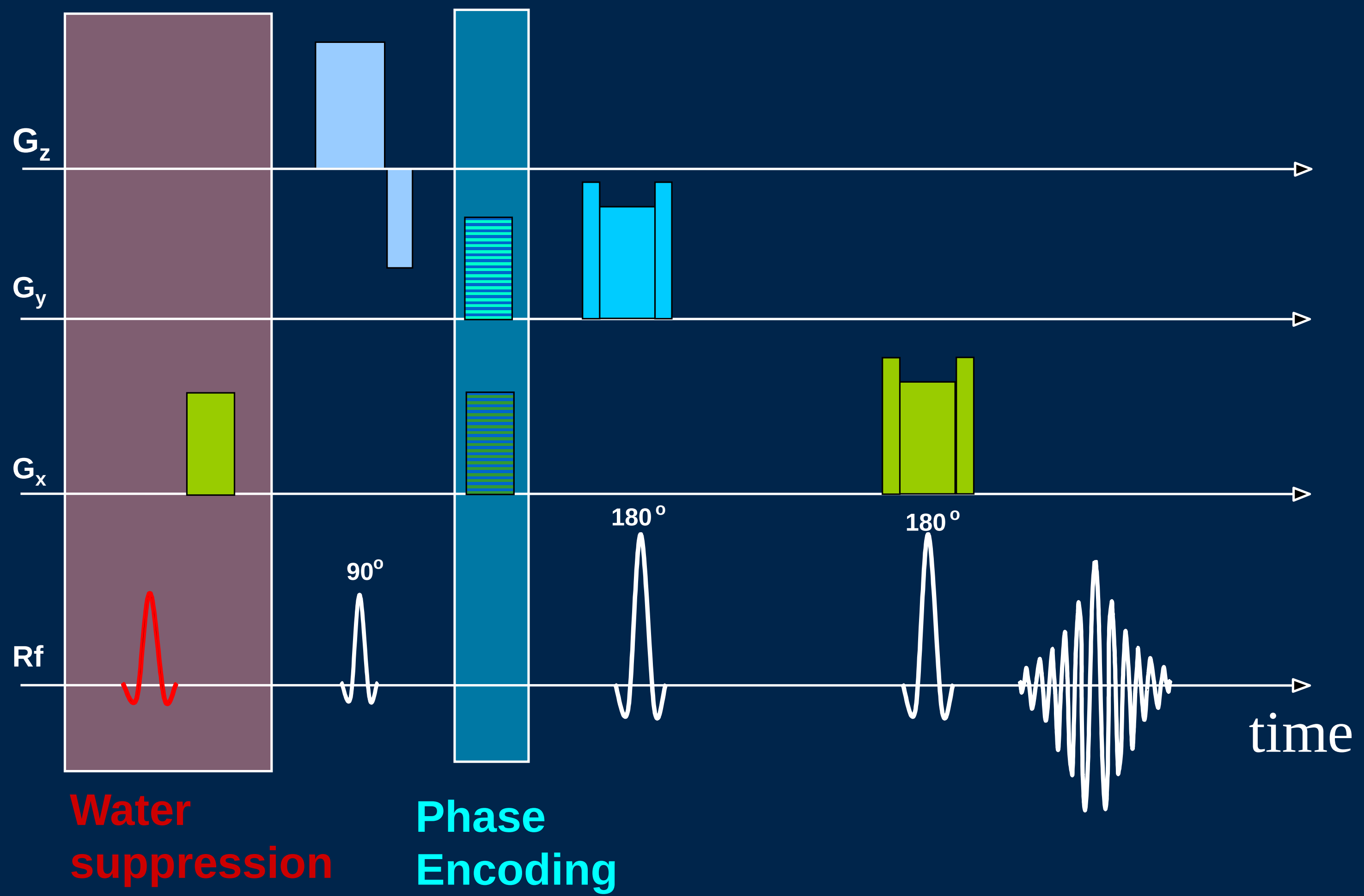


Chemical shift interval

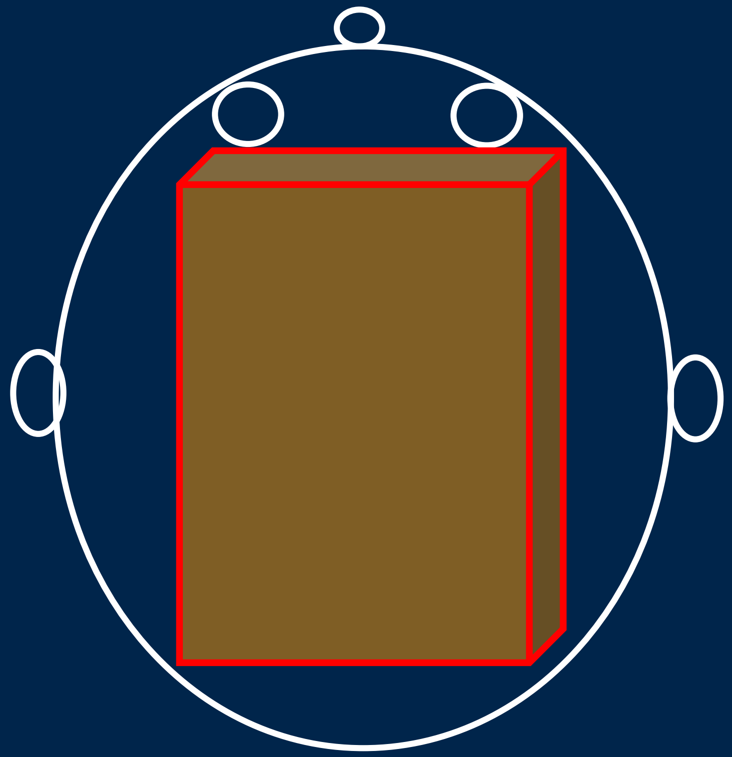


choline creatine NAA lactate

2D-SI Sequence with PRESS Localisation



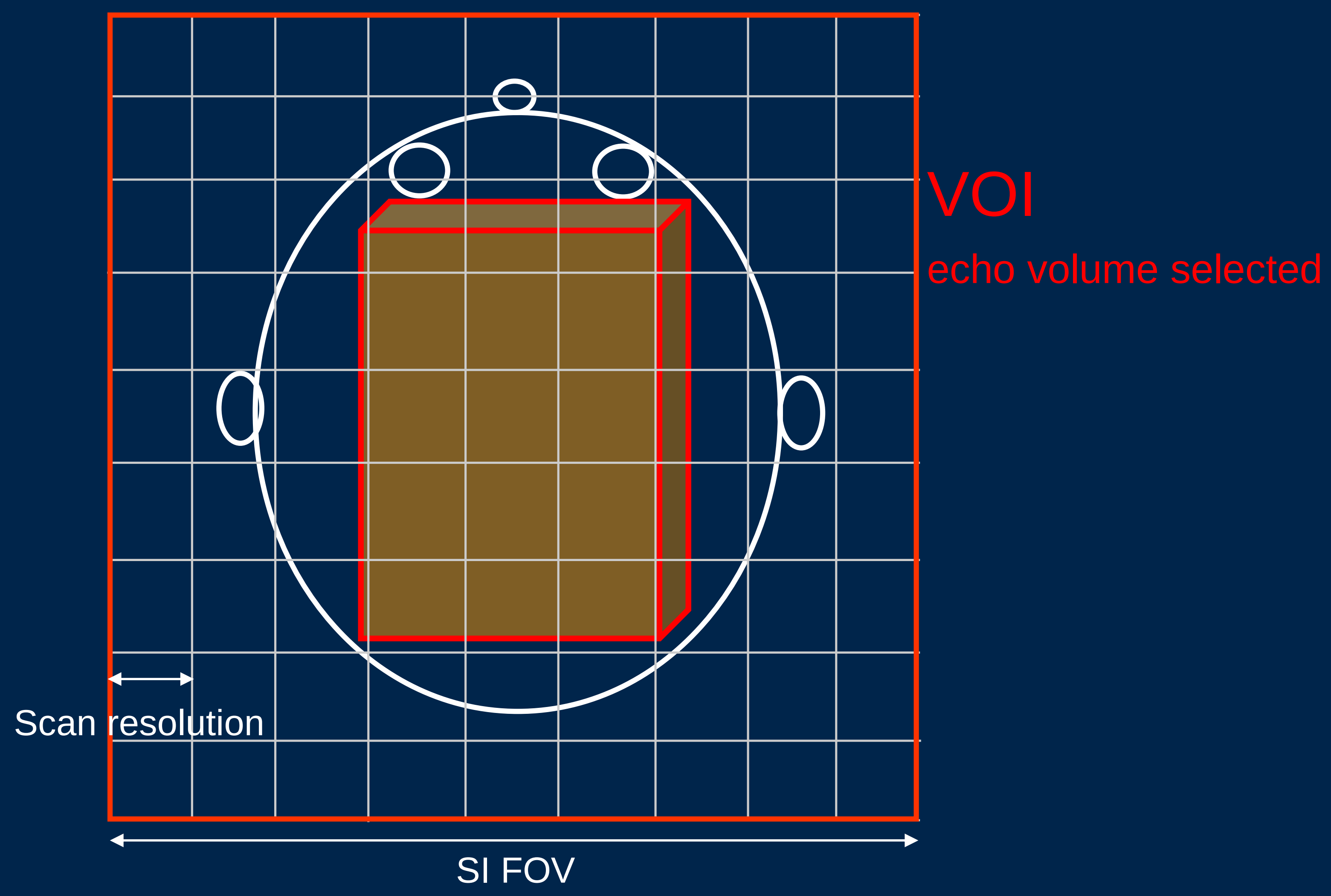
2D-Spectroscopic Imaging



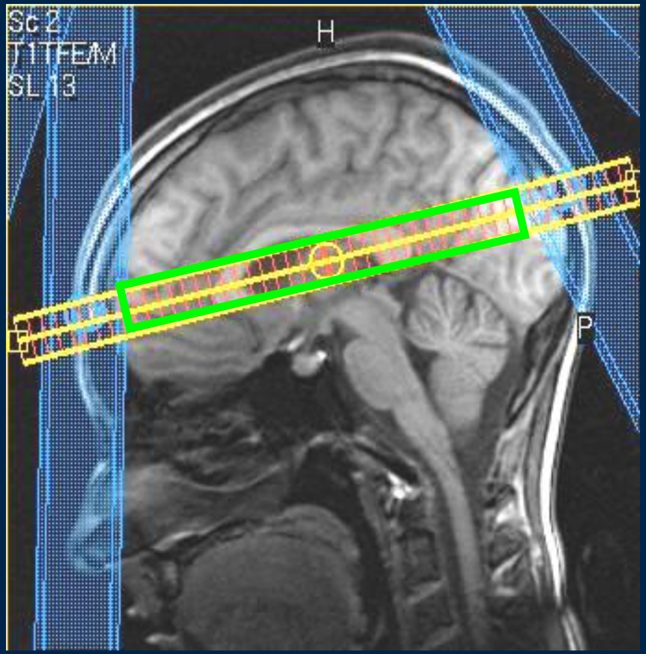
VOI

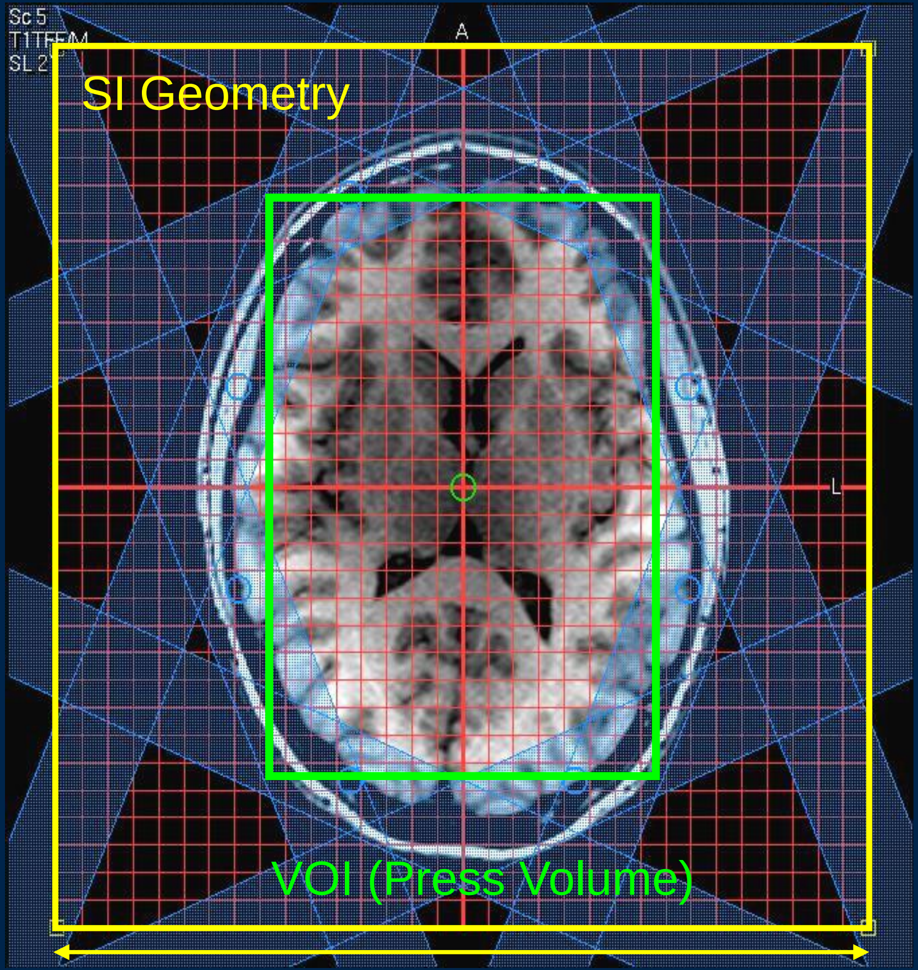
echo volume selected

2D-Spectroscopic Imaging



2D-SI: Outer Volume Suppression



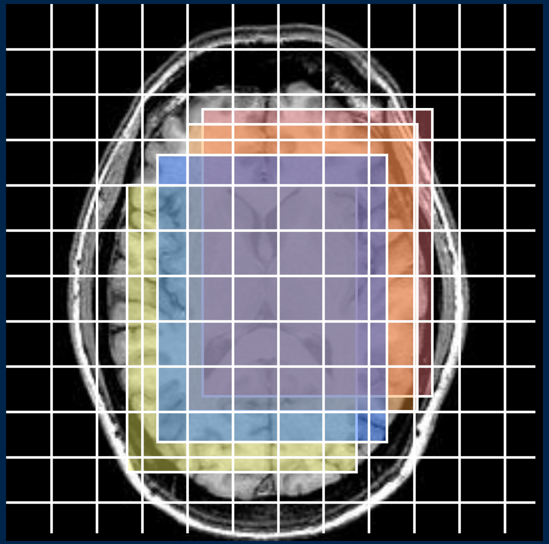


Outer Volume Suppression (OVS)

FOV

2D-SI Sequence with PRESS Localisation

- PRESS: localisation slightly different for different metabolites / chemical shifts!

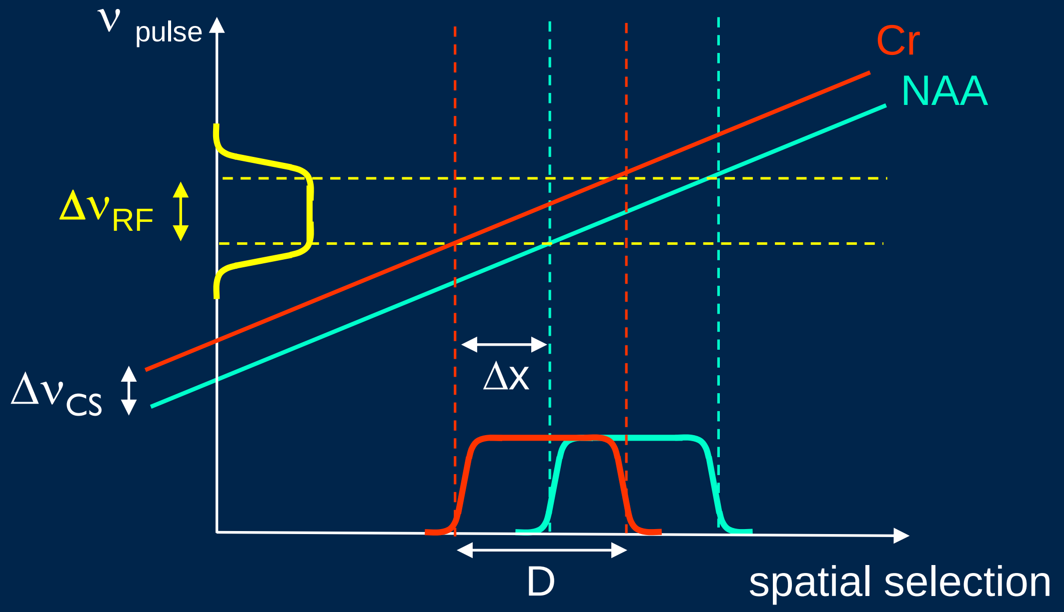


NAA
Cr
Cho
Lac/Lip

- Phase encoding: localisation equal for all metabolites / chemical shifts !

Chemical Shift Displacement

Chemical shift displacement artifact:



Gradient strength for given pulse bandwidth $\Delta\nu_{RF}$ and slice thickness D :

$$G_x = \frac{\Delta\nu_{RF}}{\gamma^* \cdot D}$$

Spatial displacement:

$$\Delta x = \frac{\Delta\nu_{CS}}{\gamma^* \cdot G_x}$$

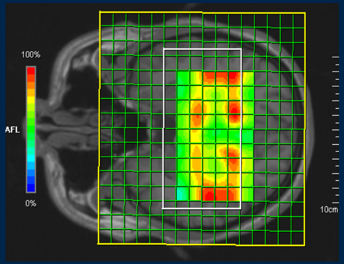
=> relative displacement: $\dfrac{\Delta x}{D} = \dfrac{\Delta\nu_{CS}}{\Delta\nu_{RF}}$

Spectroscopic Imaging vs. SVS

Single voxel spectroscopy:

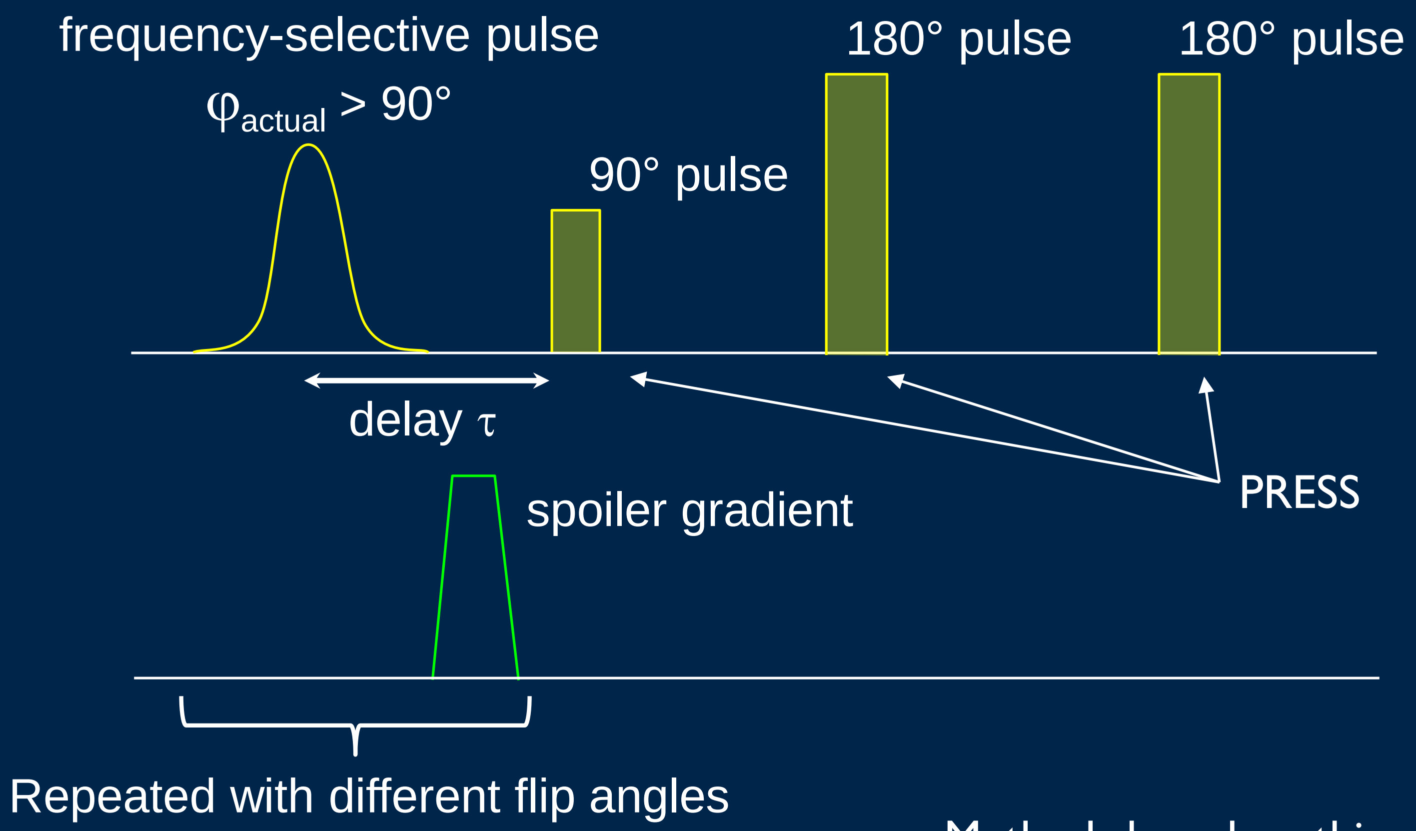
- ☺ good signal-to-noise ratio
- ☺ Rapid: ~2 to 6 min for 8 cc voxel
- ☹ selected volume is block-shaped ≠ anatomical shape
- ☹ only information on one location

Spectroscopic imaging:



- ☺ overview of spatial distribution of metabolites
- ☺ Usually higher resolution (~1 ml)
- ☹ mostly: longer acquisition times
- ☹ reduced signal-to-noise ratio (shim never as good as for SVS)
- ☹ signal leakage into neighbouring voxels (PSF)
- ☹ Slice should not go through air, bone, major vessels, fat

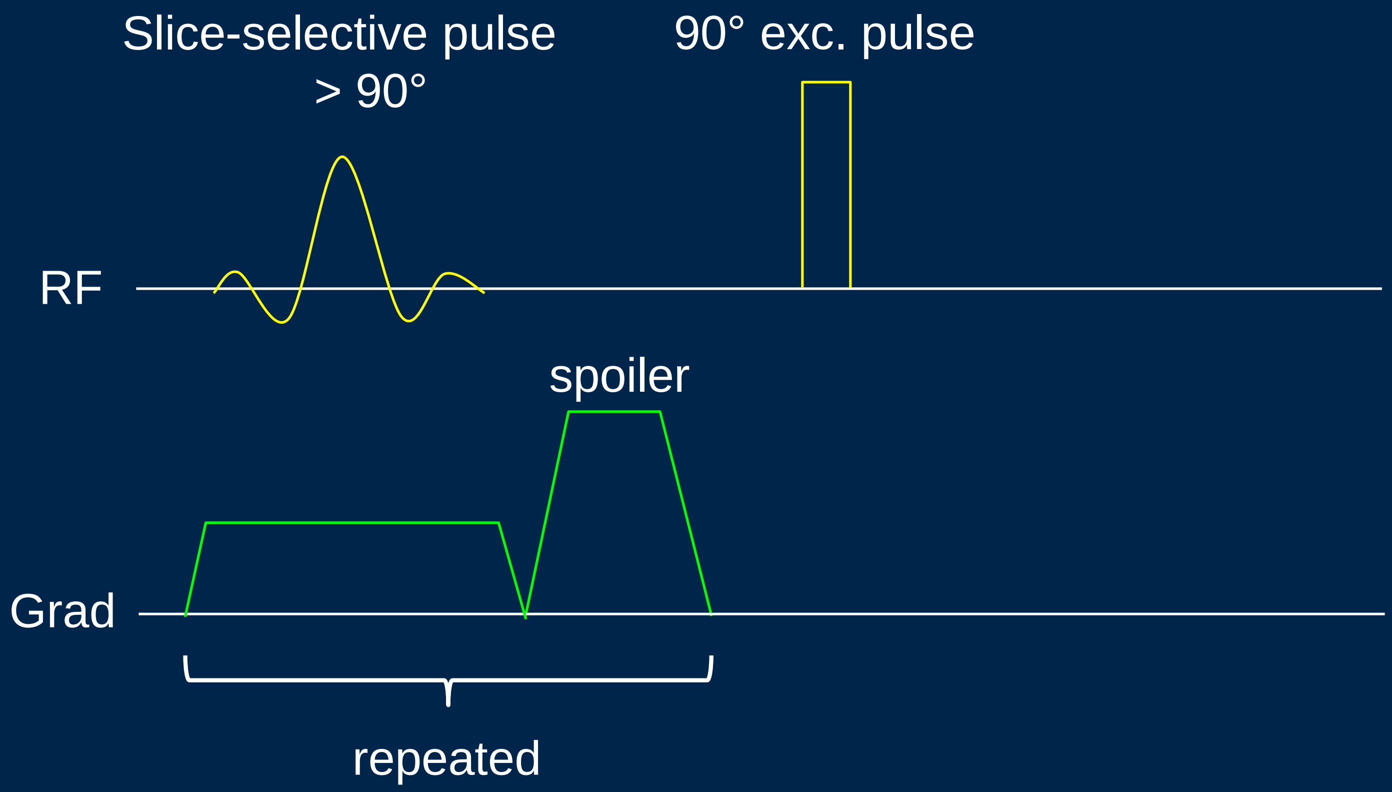
Water Suppression

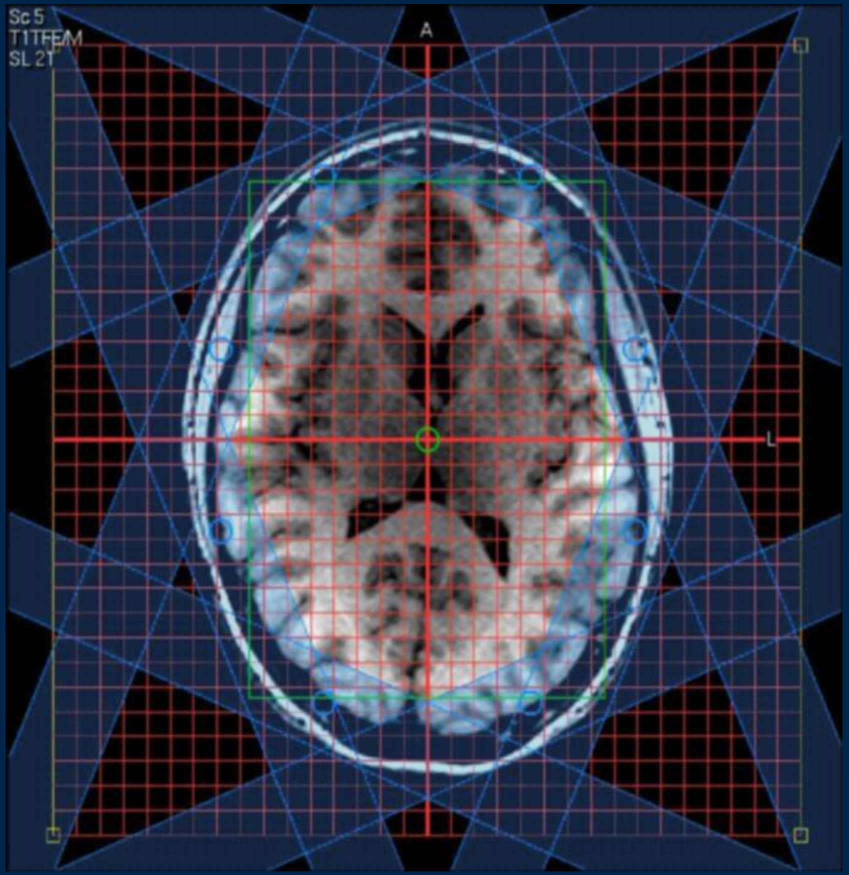


Methods based on this approach:

- CHESS (Chemical Shift Selective excitation)
- WET (Water Suppression enhanced through T_1 effects)

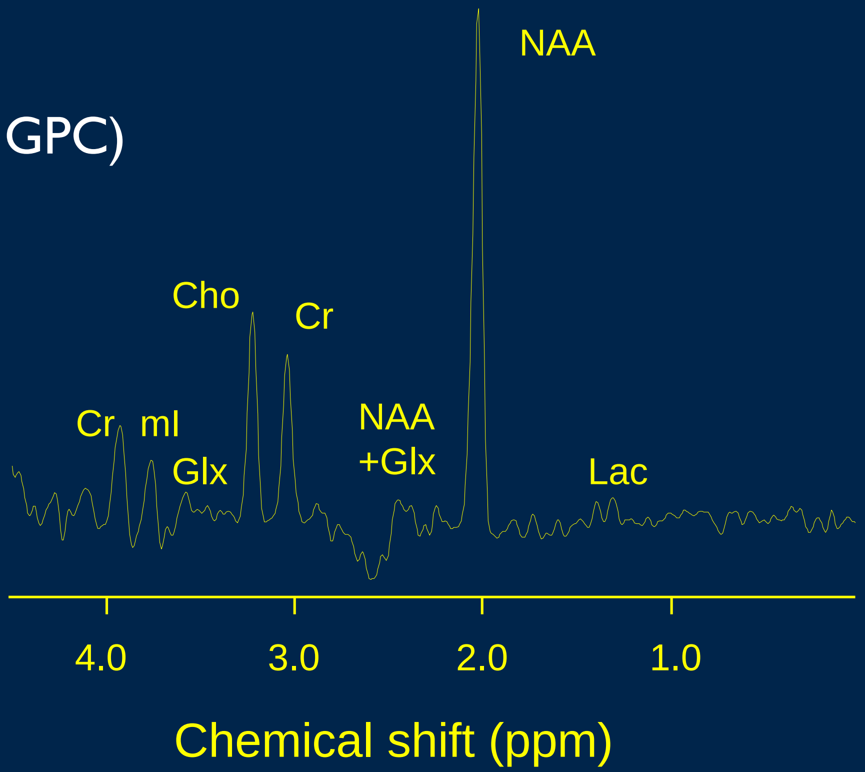
Outer Volume Suppression (OVS)

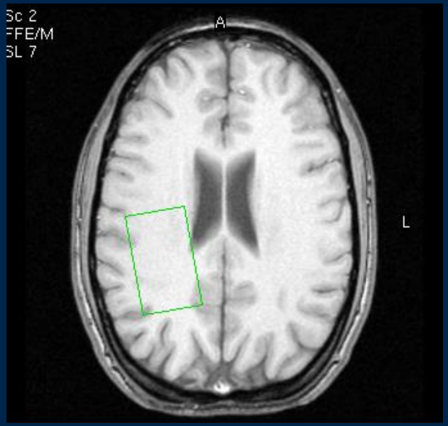




Brain Metabolites in ^{1}H MR Spectroscopy

NAA: N-acetylaspartate
Cr: creatine + phosphocreatine
Cho: choline-containing compounds (PCh, GPC)
Glx: glutamate + glutamine
mI: myo-inositol
Lac: lactate





Literature and Ressources

- Robin A. de Graaf:
  „In Vivo NMR Spectroscopy: Principles and Techniques“

- James Keeler:
  „Understanding NMR Spectroscopy“

- Malcolm H. Levitt:
  „Spin Dynamics: Basics of Nuclear Magnetic Resonance“

- Jeffrey C. Hoch and Alan S. Stern:
  „NMR Data Processing“

<u>Toolbox for MRS processing: FID-A</u>
https://www.opensourceimaging.org/project/fid-a-advanced-processing-and-simulation-of-mr-spectroscopy/