MR Spectroscopy I : Basics and Single-voxel localization

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Nuclear Magnetic Resonance

Nuclear spin moment

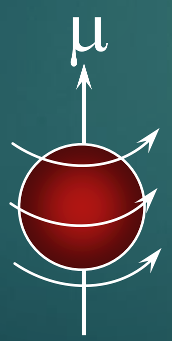
$$\mu = \gamma \hbar I$$

μ - magnetic moment

γ - gyromagnetic ratio

I - spin quantum number

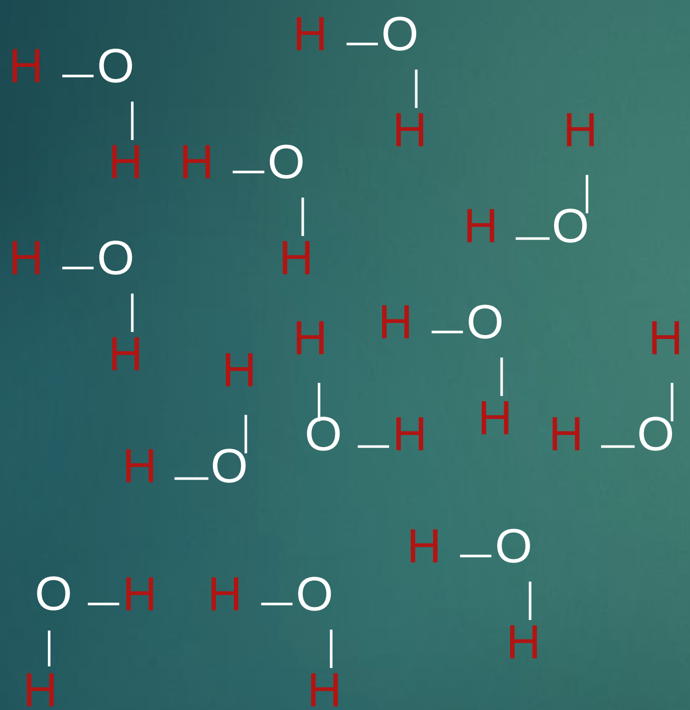
ħ - Planck's constant



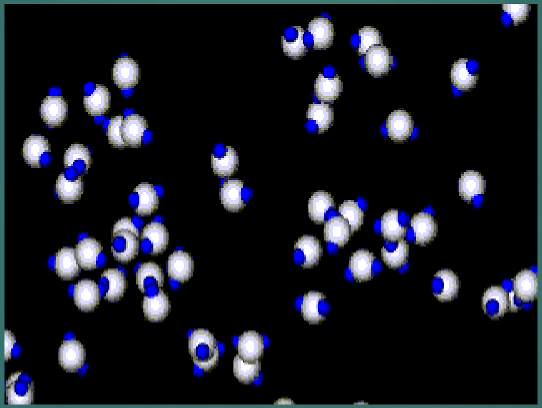
I is a property of the nucleus

Mass #	Atomic #	I
Odd	Even or odd	1/2, 3/2, 5/2,…
Even	Even	0
Even	Odd	1, 2, 3

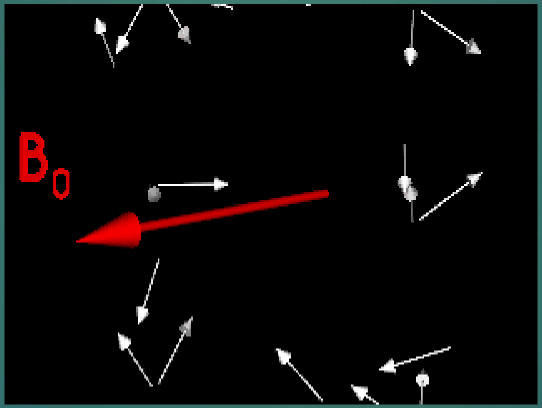
Water Molecule



Isotropy of Spin Polarization in the Absence of an External Magnetic Field

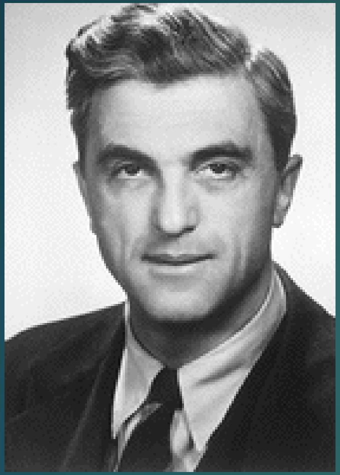


Presence of an External Magnetic Field, B_0



Magnetic Resonance

Nobel Prize in Physics 1952

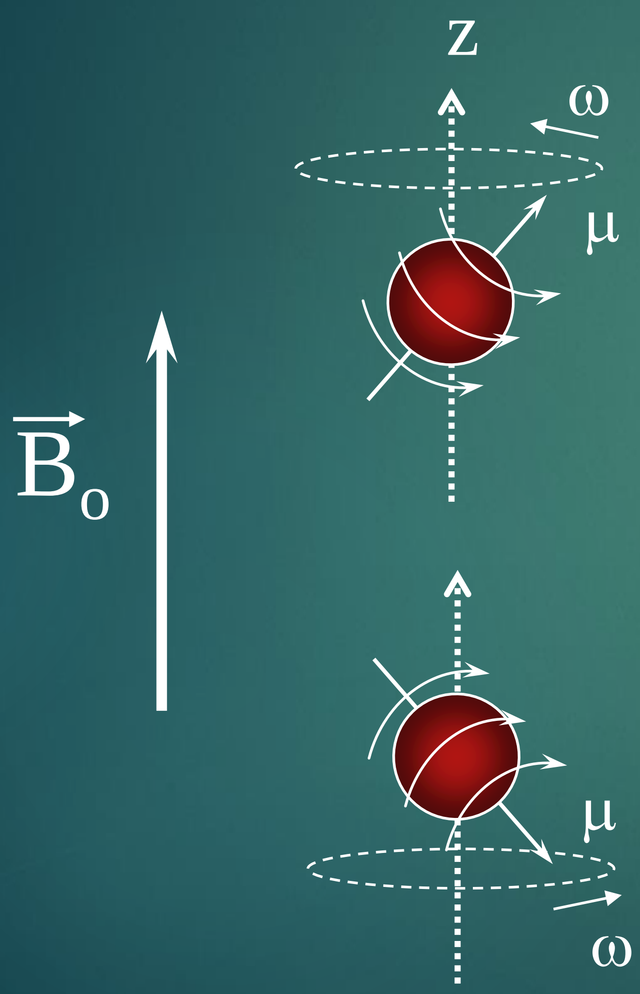


Felix Bloch Ph.D.

Edward Purcell Ph.D.

Apply an external magnetic field

(i.e., put your sample in the magnet)



$\omega = \gamma\, B_o = \nu/2\pi$

ω - resonance frequency
in radians per second,
also called Larmor frequency

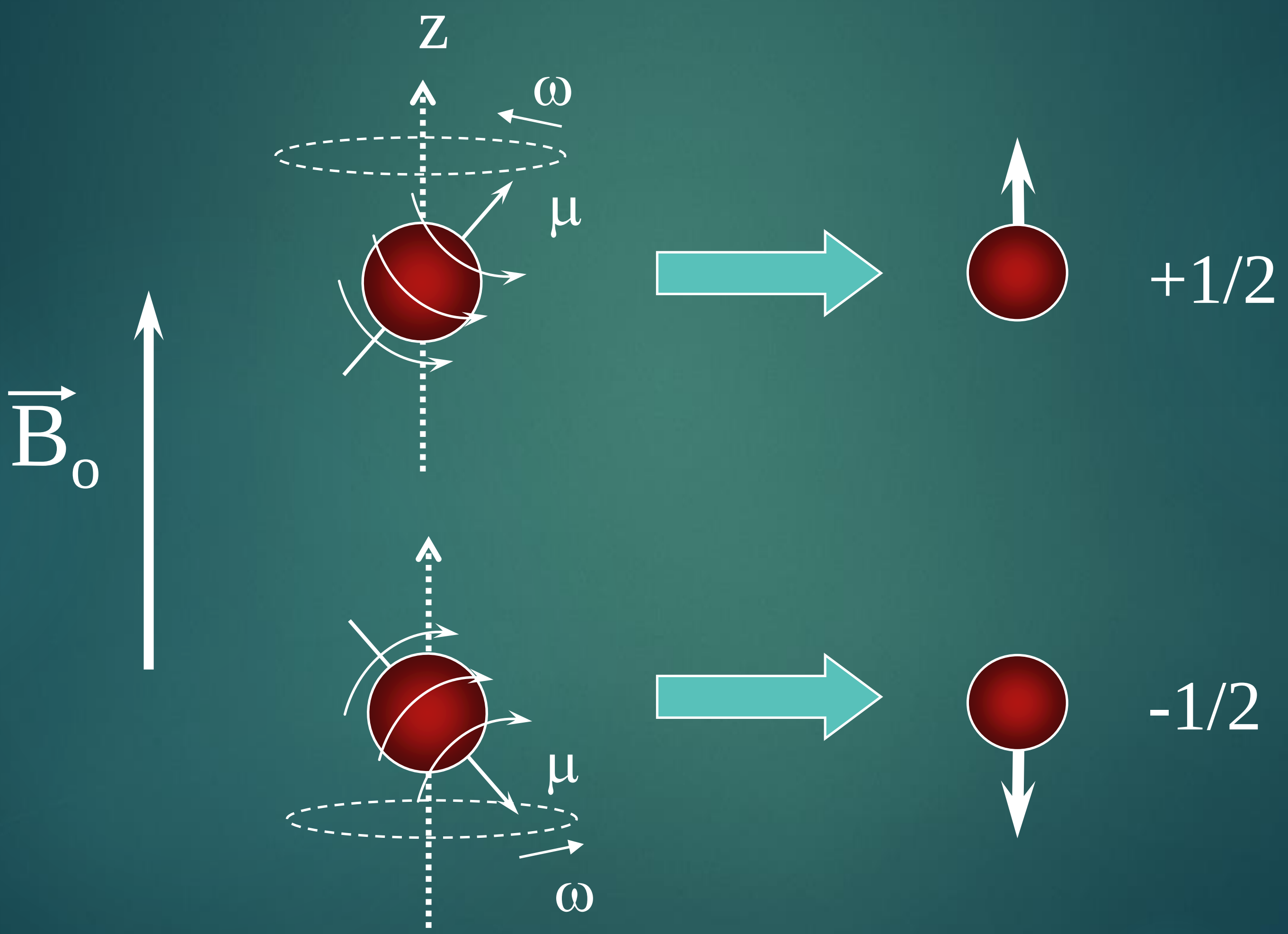
ν - resonance frequency
in cycles per second, Hz

γ - gyromagnetic ratio

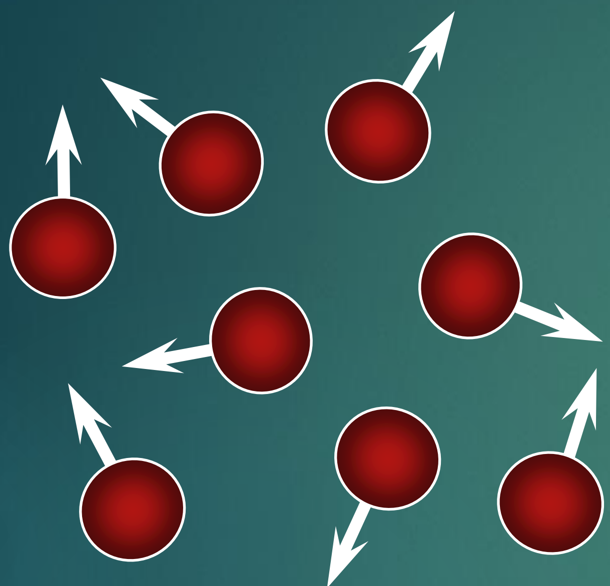
B_o - external magnetic
field (the magnet)

Spin 1/2 nuclei will have two orientations in a magnetic field +1/2 and -1/2.

Net magnetic moment

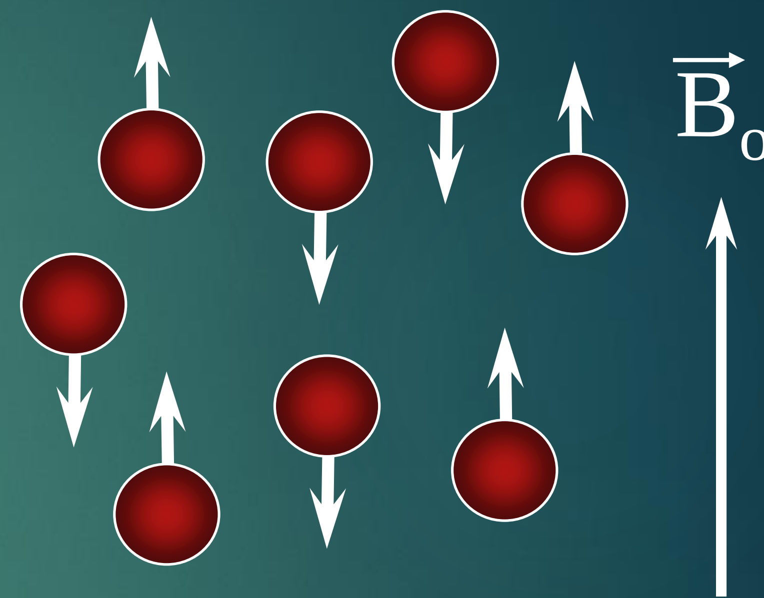


Ensemble of Nuclear Spins



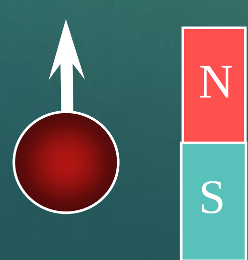
$\vec{B}_o = 0$

Randomly oriented



$\vec{B}_o > 0$

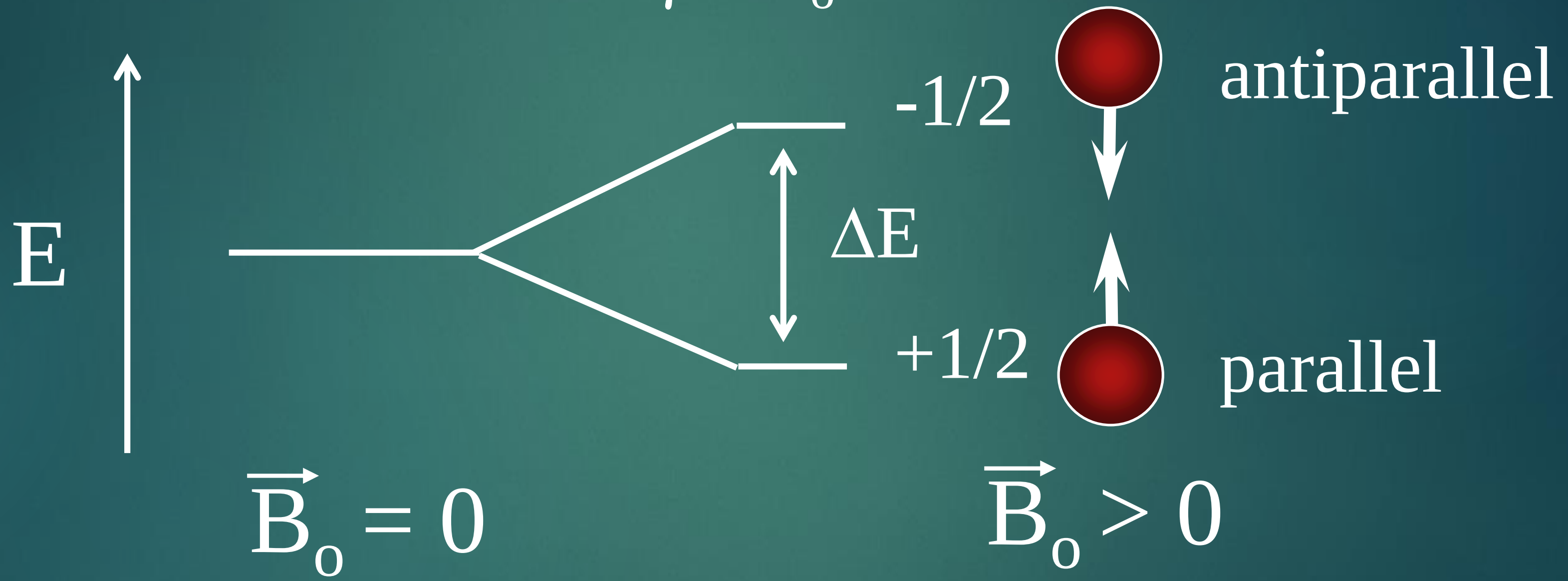
Highly oriented



Each nucleus behaves like a bar magnet.

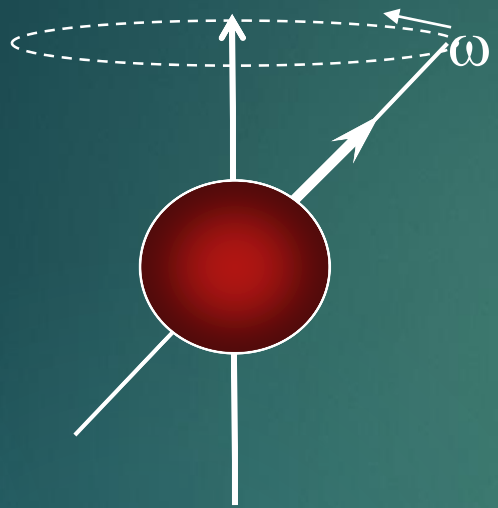
Allowed Energy States for a Spin 1/2 System

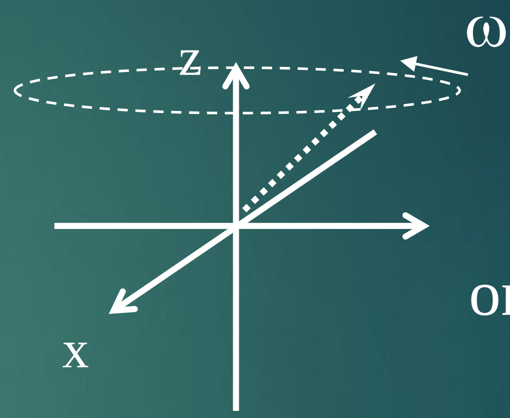
$$\Delta E = \gamma \hbar \vec{B}_o = \hbar \nu$$



Therefore, the nuclei will absorb light with energy ΔE resulting in a change of the spin states.

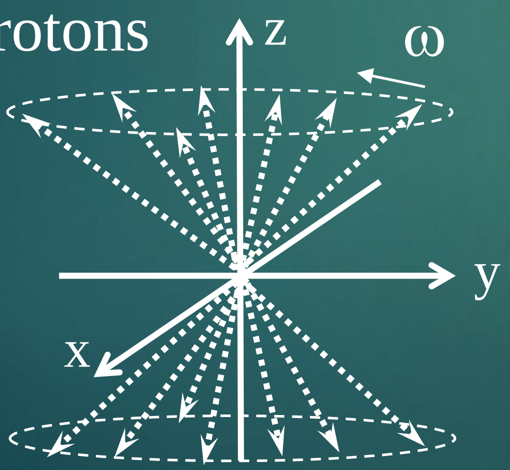
The net magnetization vector



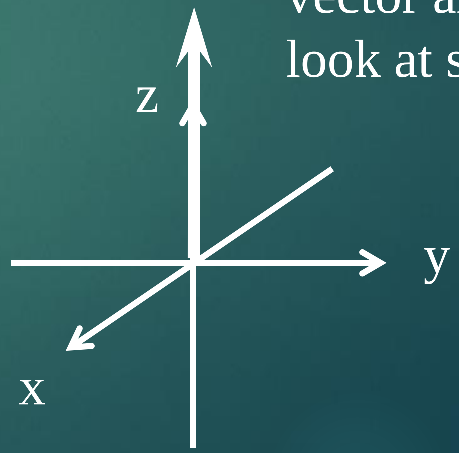


one proton

many protons



M_o - net magnetization vector allows us to look at system as a whole



MR Imaging

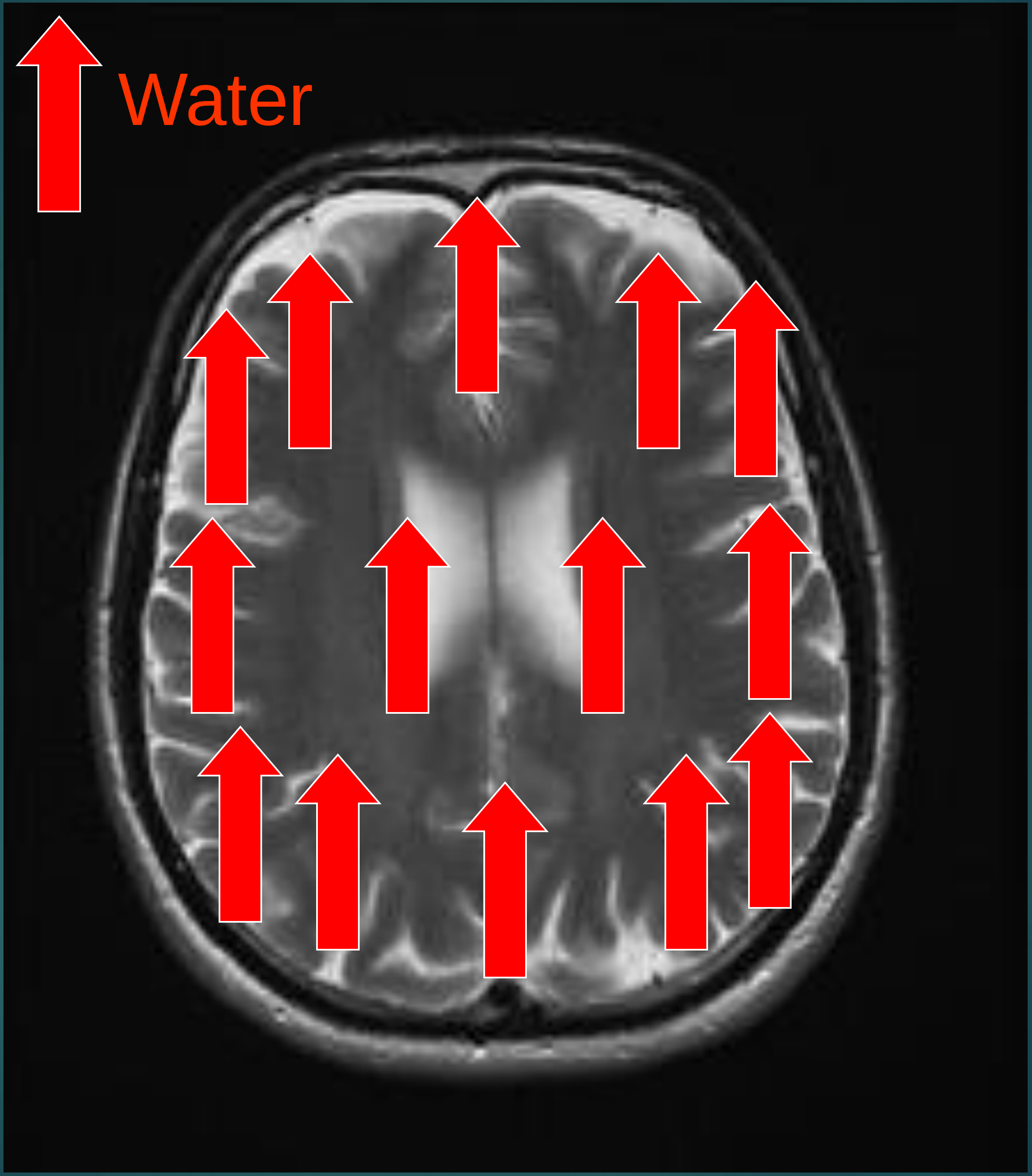
Larmor Equation:

$$\omega = \gamma B_0$$

Larmor Frequency

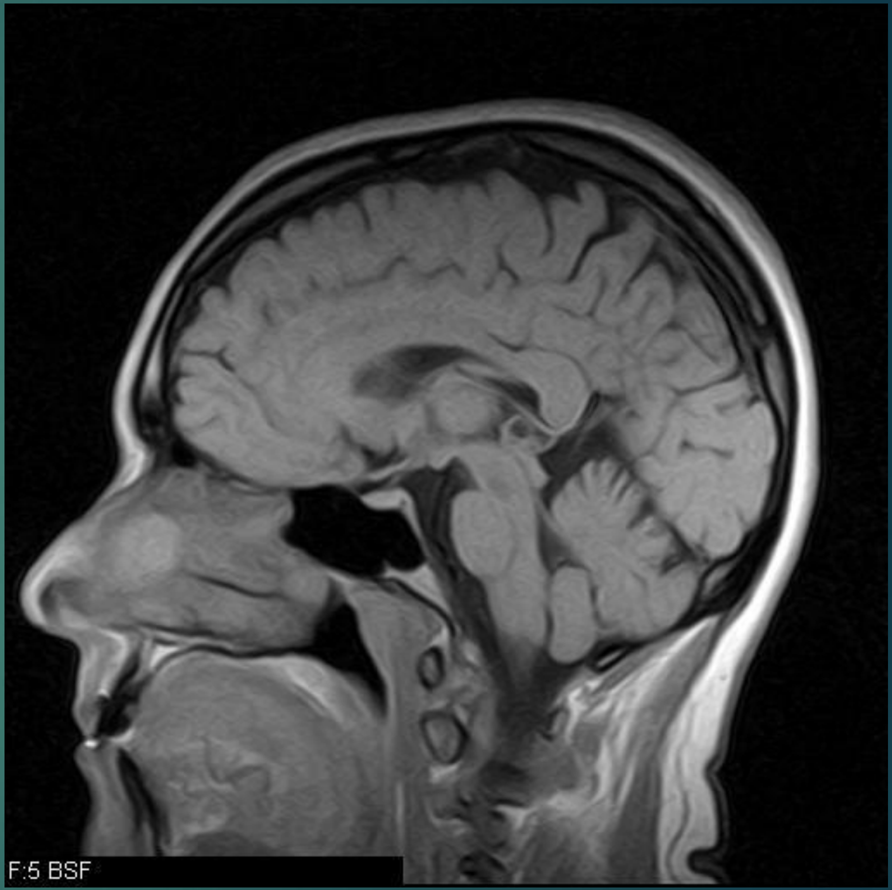
gyromagnetic constant

Apply spatially varying frequency and phase encoding magnetic field gradients


Water

Magnetic Resonance Imaging (MRI)

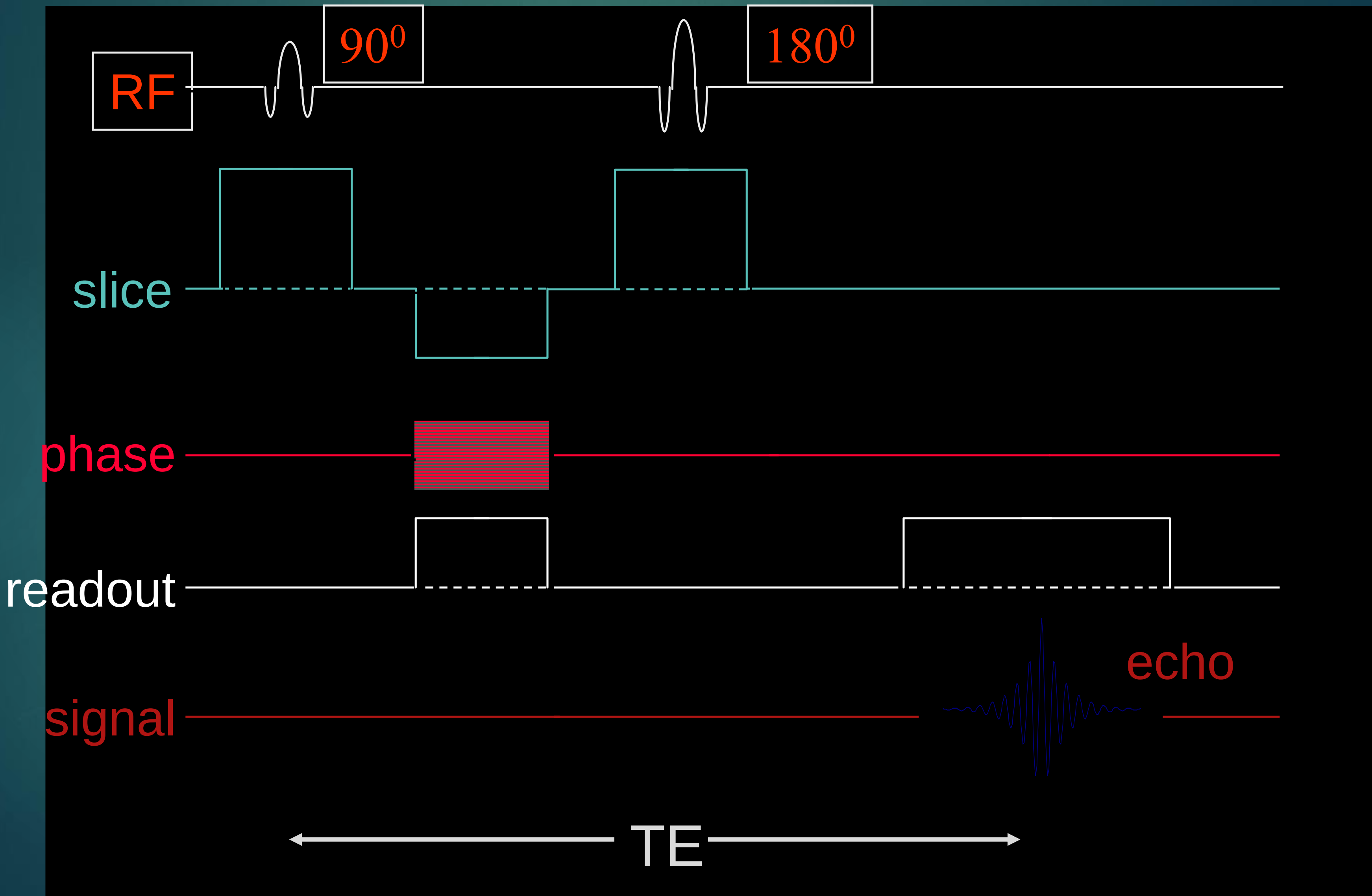
- MRI exploits Nuclear Magnetic Resonance (NMR) to produce water-based images
  - Signal from ^{1}H in water
  - Gray scale caused by T1/T2 relaxation and ^{1}H density within a voxel
- Structural differences cause T1/T2 relaxation variation among voxels
  - No biochemical information
- MRI resolution
  - 512x512 voxels in a slice
  - Sub-millimeter voxel volume

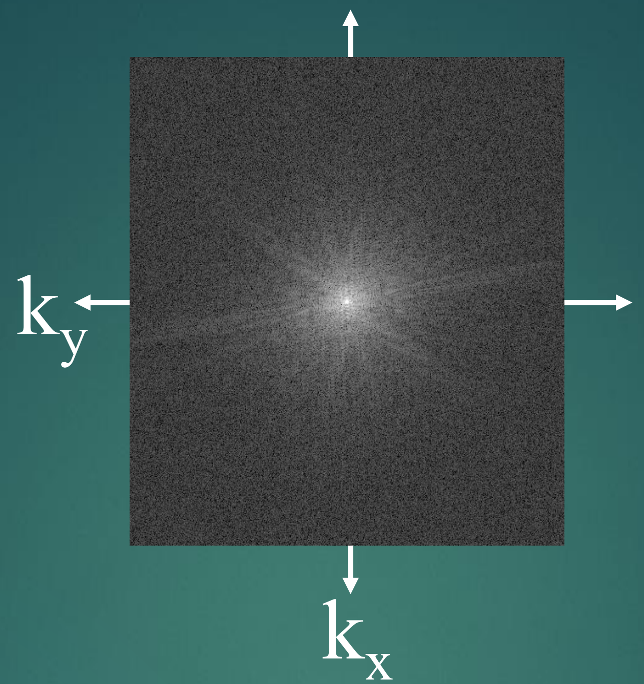


Magnetic Resonance Imaging Purpose:

- provide anatomical images
- T1 and T2 Weighted MRI
- Contrast enhanced MRI
- MR Angiography (MRA)
- Interventional MRI (iMR)
- functional MRI (fMRI)
- Perfusion MRI
- Magnetization transfer (MT) MRI and Spin-locking
- Diffusion-weighted MRI (DWI) and DTI

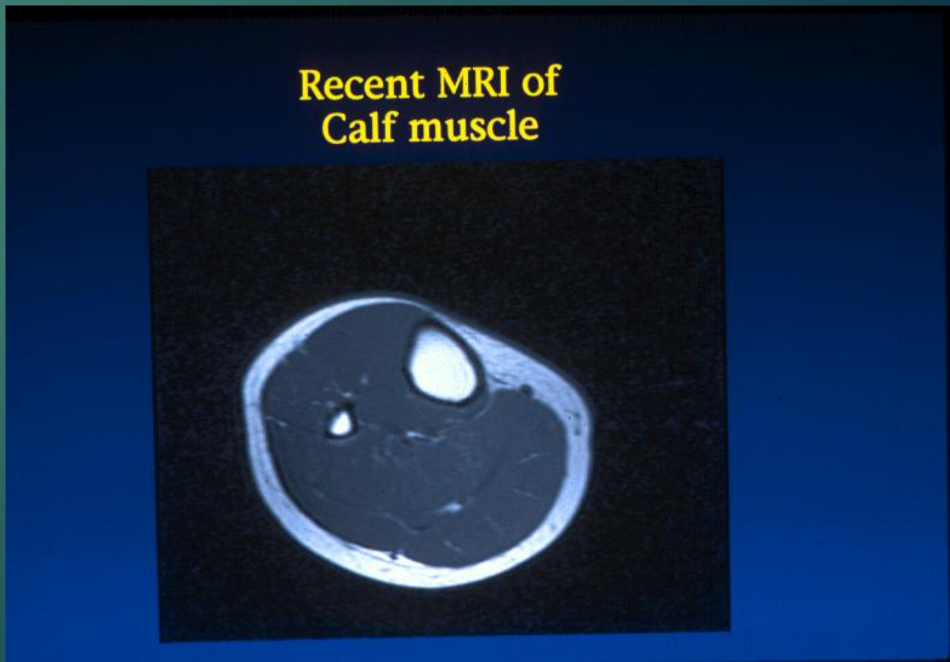
Spin Echo MRI *pulse timing*





k_y
k_x

MRI: Day one



Recent MRI of
Calf muscle

Problems with Anatomical Imaging

- Despite its superb soft tissue contrast and multiplanar capability, anatomical MRI is largely limited to depicting morphological abnormality.
- Anatomical MRI suffers from nonspecificity. Different disease processes can appear similar upon anatomic imaging, and in turn a single disease entity may have varied imaging findings.
- The underlying metabolic or functional integrity of brain cannot be adequately evaluated based on anatomical MRI alone. To that end, several physiology-based MRI methods have been developed to improve tumor characterization.

Functional Imaging

- Four physiology-based MRI methods have been developed to improve tissue characterization:
- Diffusion Weighted (DW) MRI: In addition to early diagnosis of cerebral ischemia, DW MRI is extremely sensitive in detecting other intracranial disease processes, including cerebral abscess, traumatic shearing injury, etc.
- Perfusion Imaging: Dynamic susceptibility-weighted contrast-enhanced (DSC) perfusion MRI of the brain provides hemodynamic information.
- CEST/Para-CEST/APT: Recently developed new class of MR contrast agents
- MR Spectroscopy

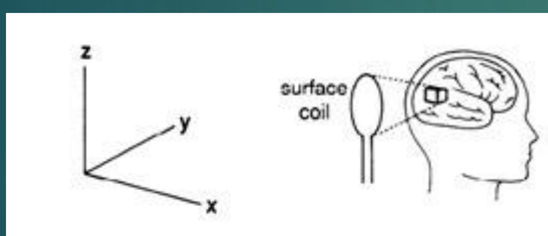
In Vivo NMR Spectroscopy

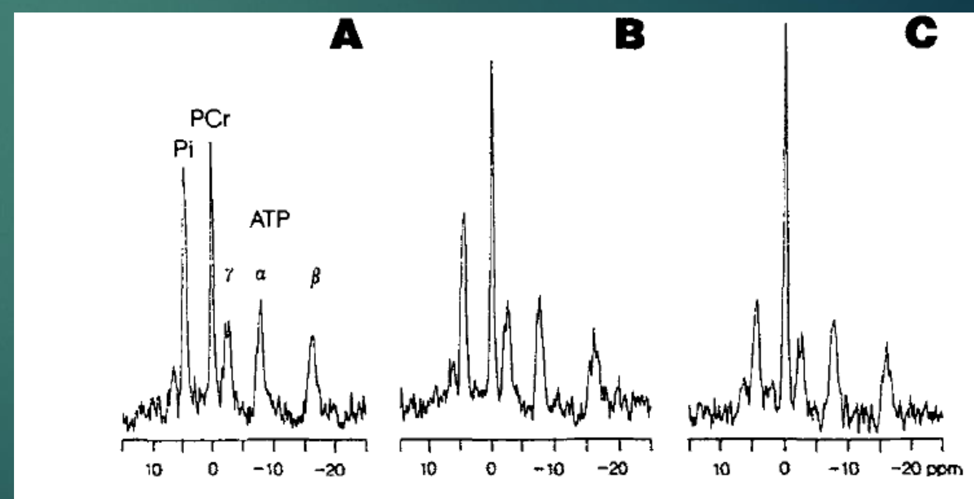
1987, *The British Journal of Radiology*, 60, 367–373 APRIL 1987

The study of human organs by phosphorus-31 topical magnetic resonance spectroscopy

By Rolf D. Oberhaensli, M.D., Graham J. Galloway, Ph.D., David Hilton-Jones, M.R.C.P., Peter J. Bore, F.R.C.S., Peter Styles, D.Phil., Bheeshma Rajagopalan, M.R.C.P., D.Phil., Doris J. Taylor, D.Phil. and George K. Radda, D.Phil., F.R.S.

MRC Clinical Magnetic Resonance Facility, John Radcliffe Hospital, Headington, Oxford OX3 9DU

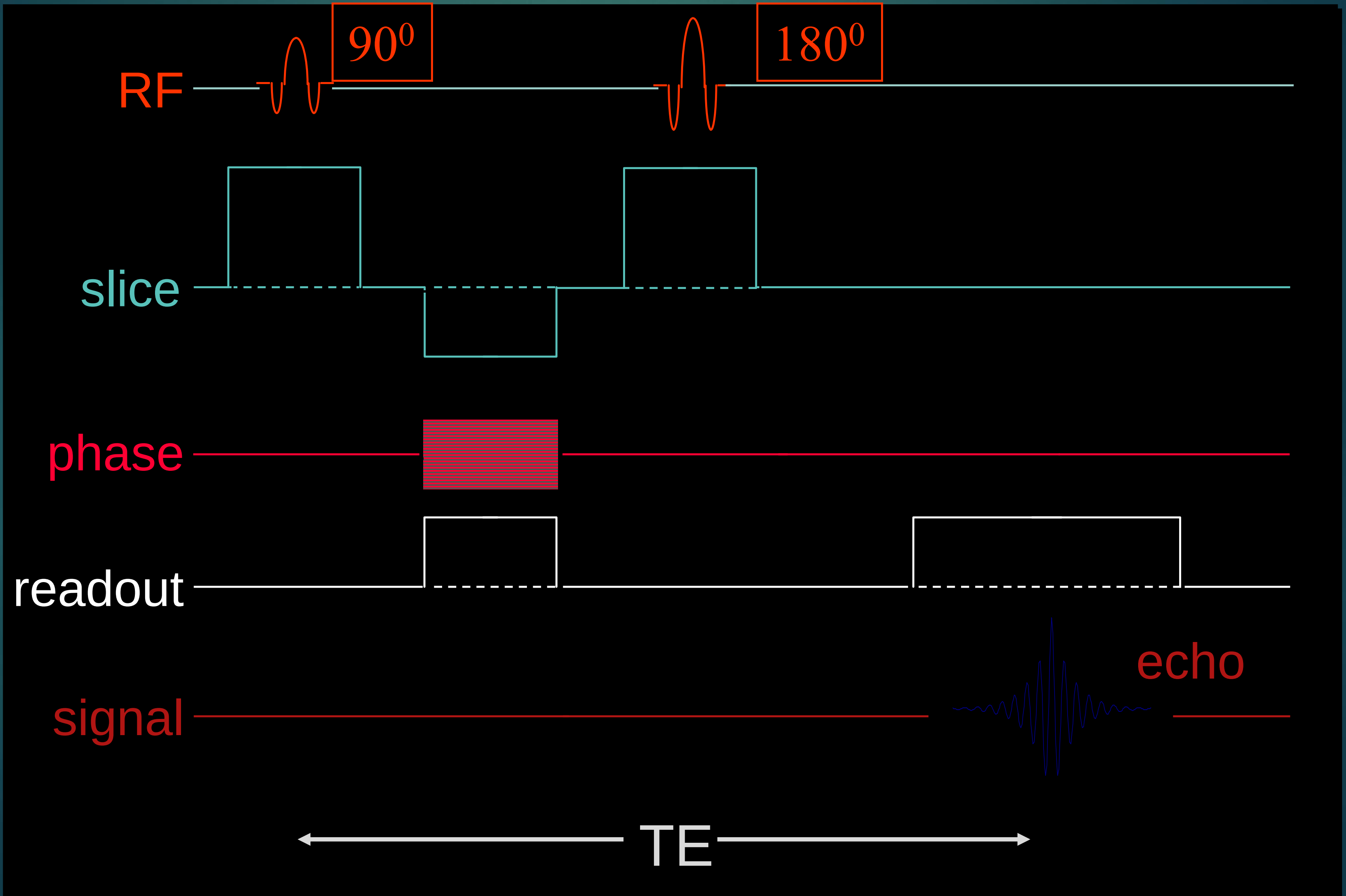




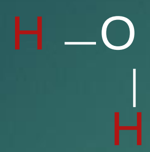
Typical 10-second spectra (2 FIDs) obtained from a single subject at the end of exercise (A) and at 15 (B) and 35 seconds (C} into the recovery period (different levels of work :2-18; 10 + 3.6) and reached different end-exercise force levels (64-599 J/min; 274 -+ 125).

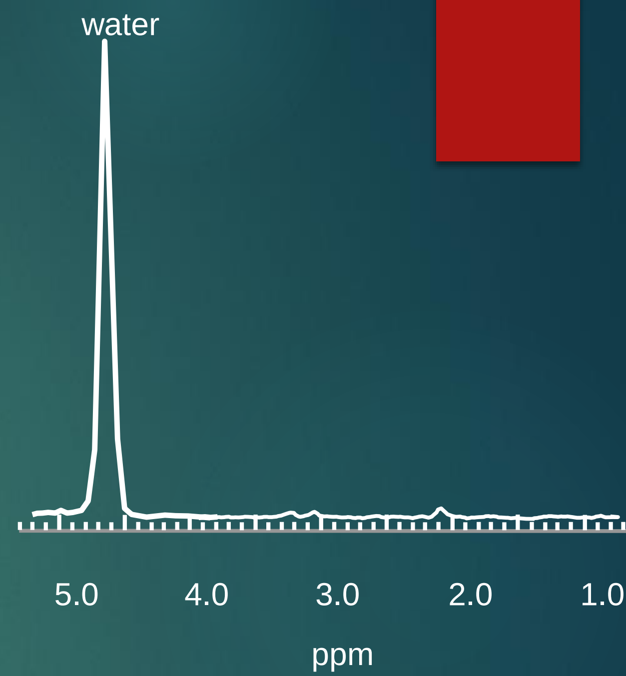
Lodi et al MAGMA 1997

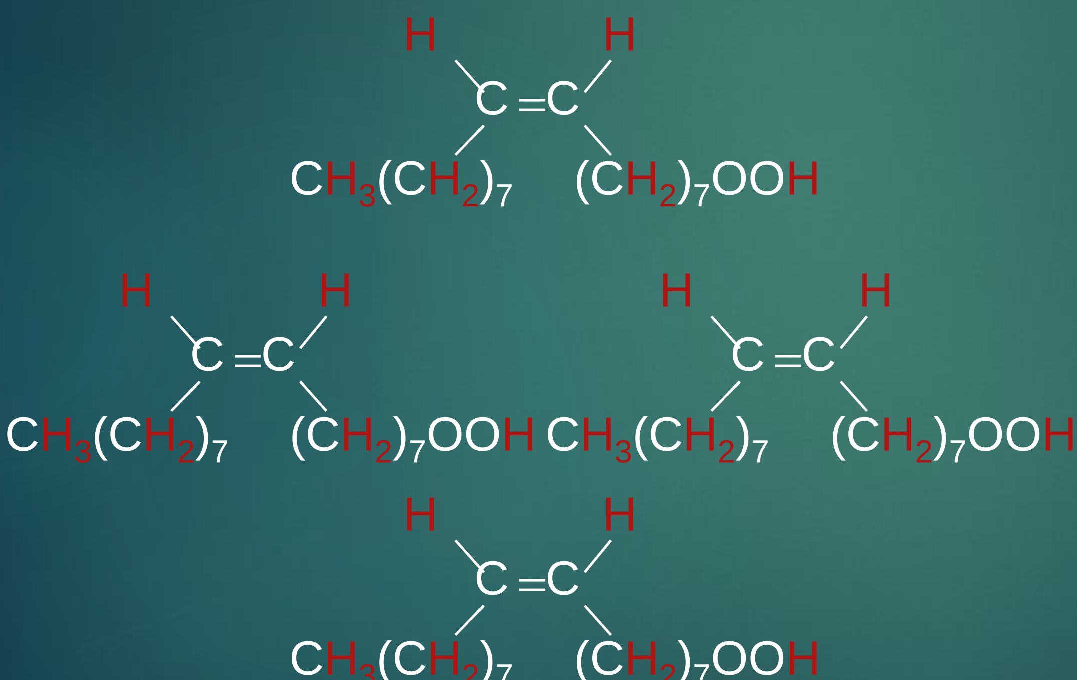
Spin Echo MR Spectroscopy
pulse timing

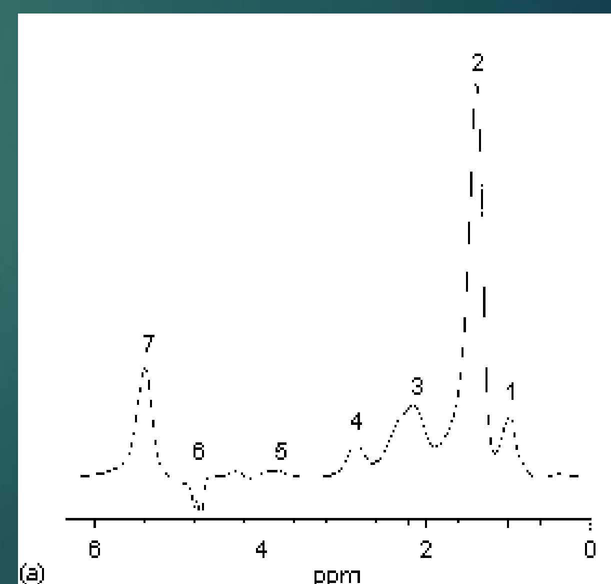


Water









Oleic Acid (Corn Oil)

MR Spectroscopy

Larmor Equation:

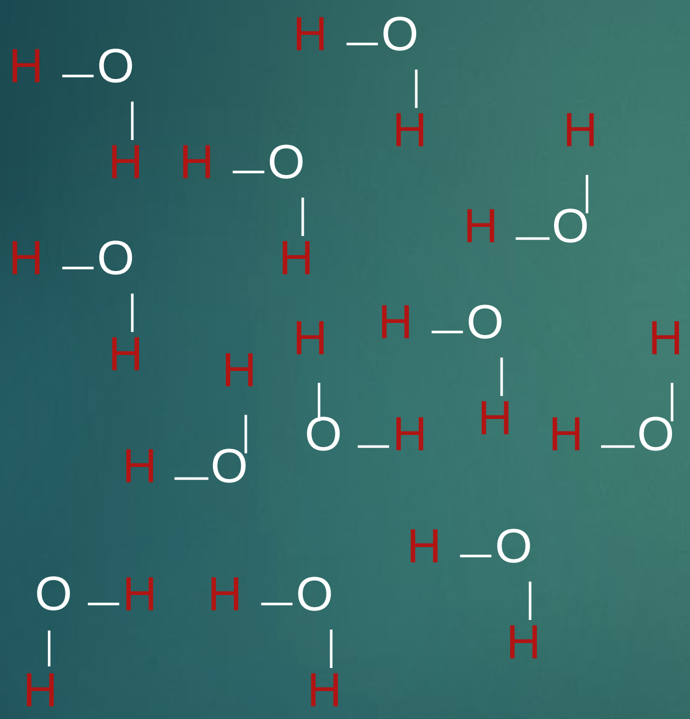
$$\omega = \gamma B_0$$

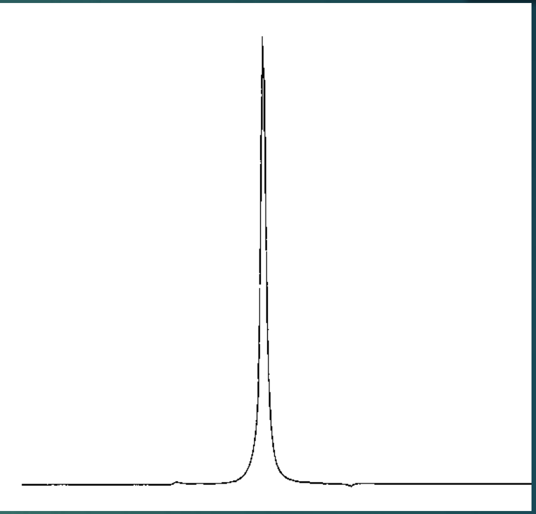
Larmor Frequency

gyromagnetic constant

Constant applied external magnetic field

MR Spectrum

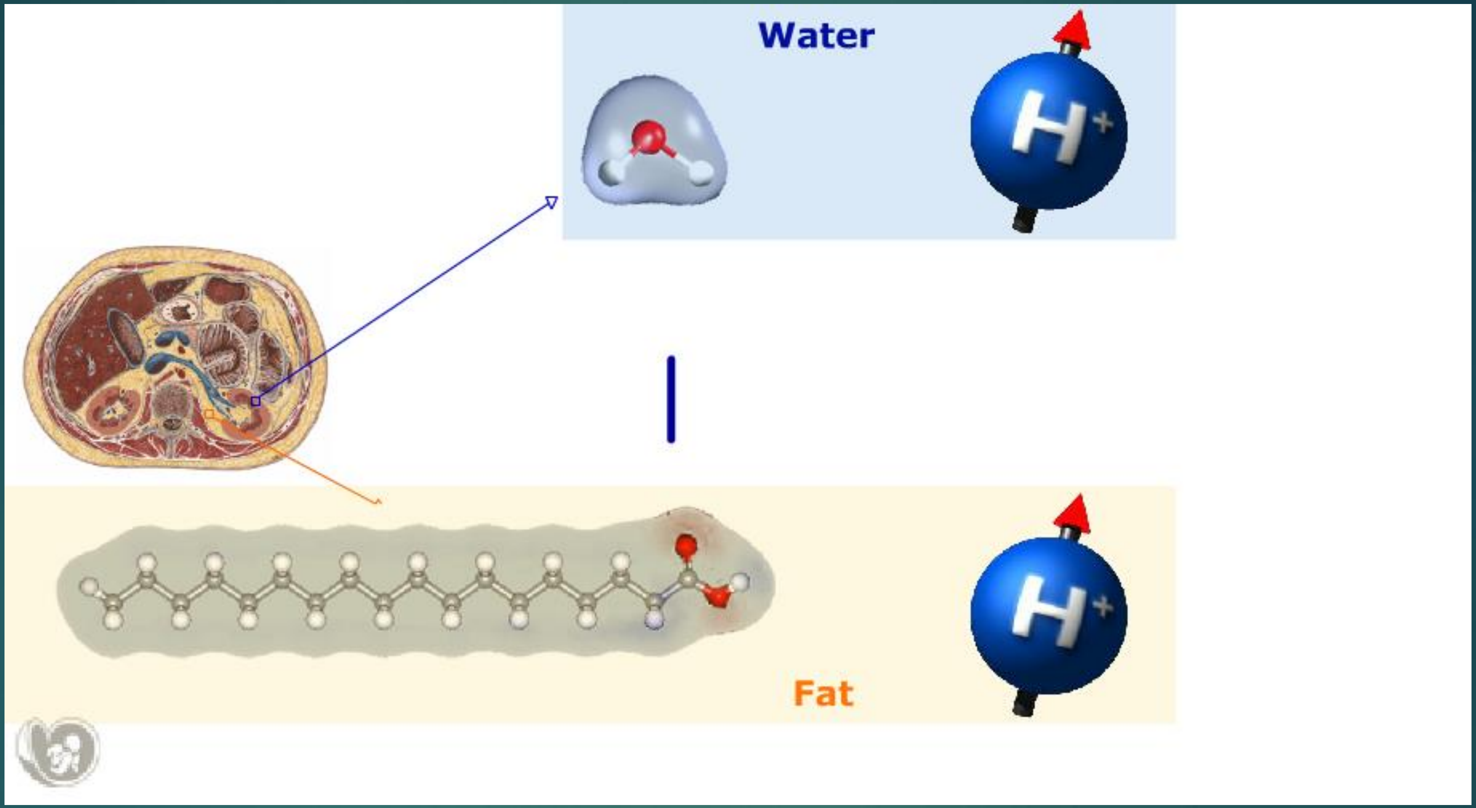


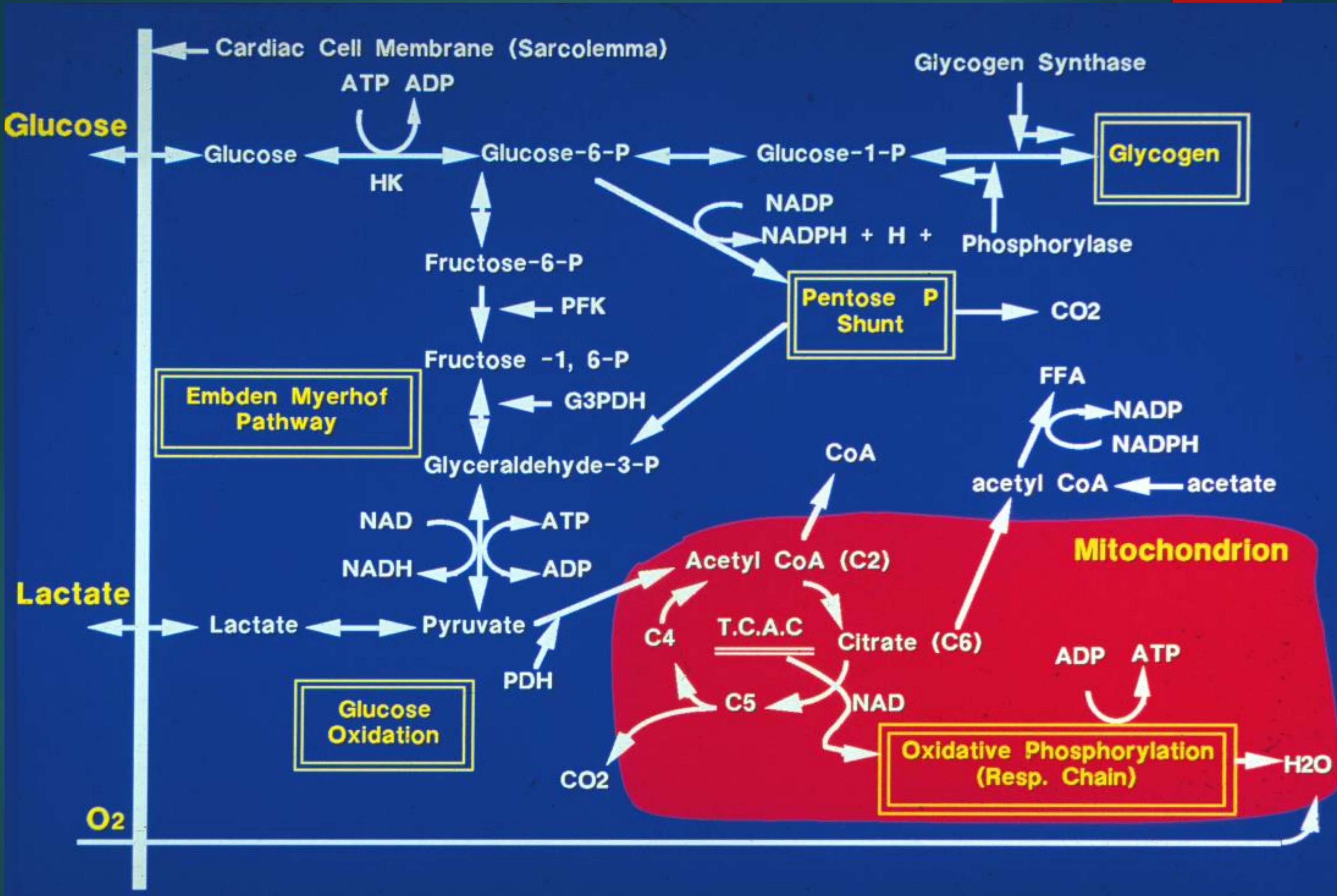


Area α # of spins

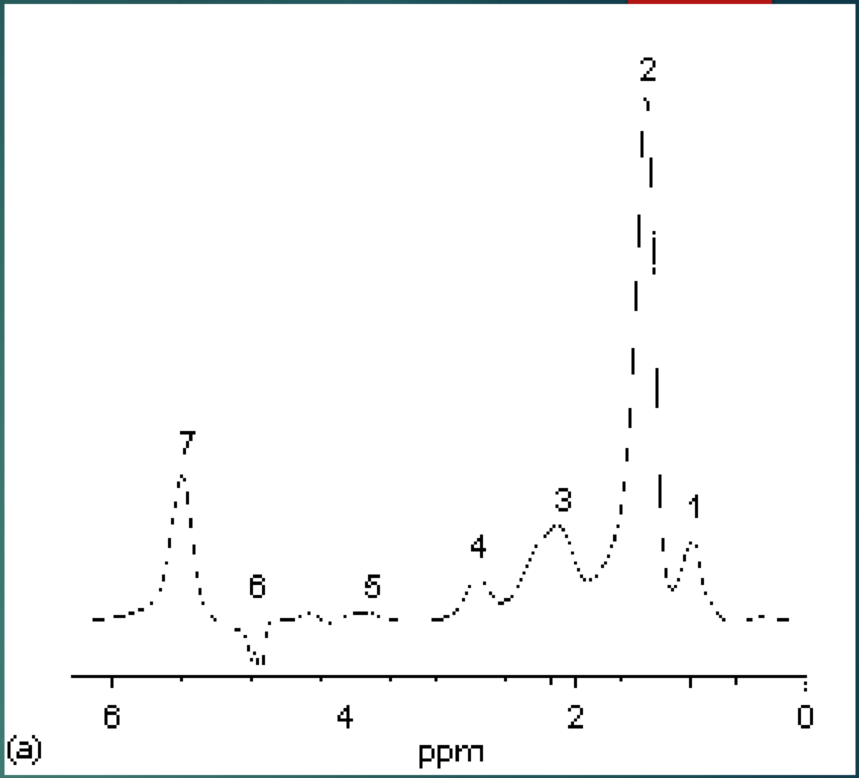
FWHM α $1/T_2^*$

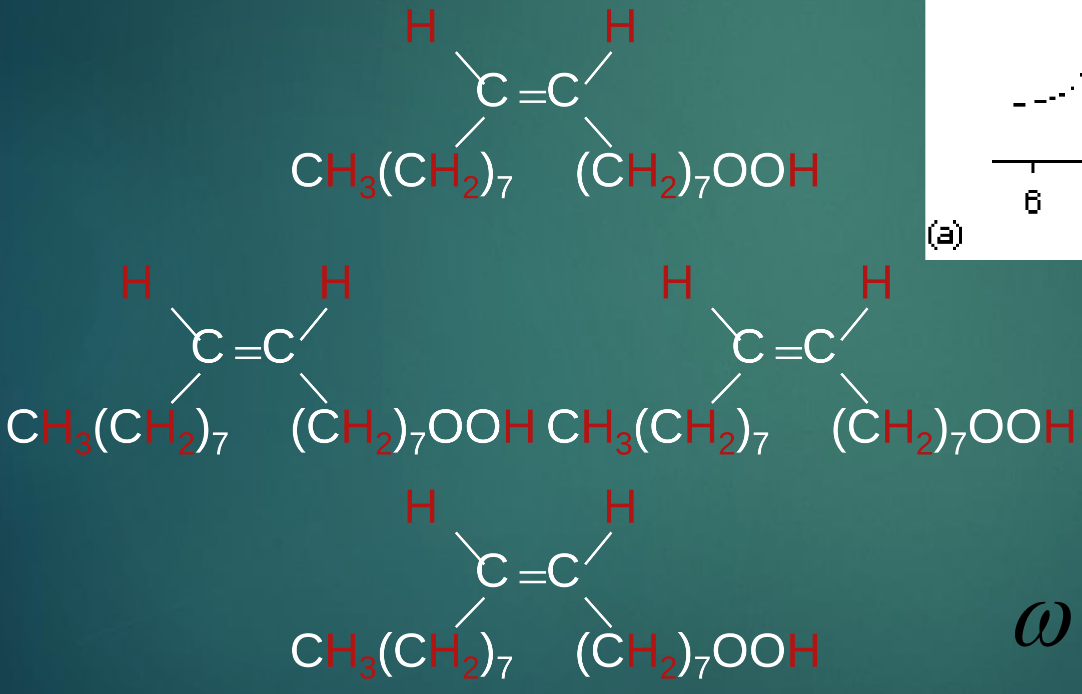
$$\omega = \gamma B_0 = \text{constant}$$


Water
Fat



Cardiac Cell Membrane (Sarcolemma)
ATP ADP
Glucose
Glucose
HK
Glucose-6-P
Glucose-1-P
Glycogen Synthase
Glycogen
NADP
NADPH + H +
Phosphorylase
Fructose-6-P
PFK
Pentose P Shunt
CO2
Fructose -1, 6-P
Embden Myerhof Pathway
G3PDH
FFA
NADP
NADPH
Glyceraldehyde-3-P
CoA
acetyl CoA
acetate
NAD
ATP
NADH
ADP
Mitochondrion
Acetyl CoA (C2)
Lactate
Lactate
Pyruvate
C4
T.C.A.C
Citrate (C6)
ADP ATP
PDH
C5
NAD
Glucose Oxidation
Oxidative Phosphorylation (Resp. Chain)
H2O
CO2
O2



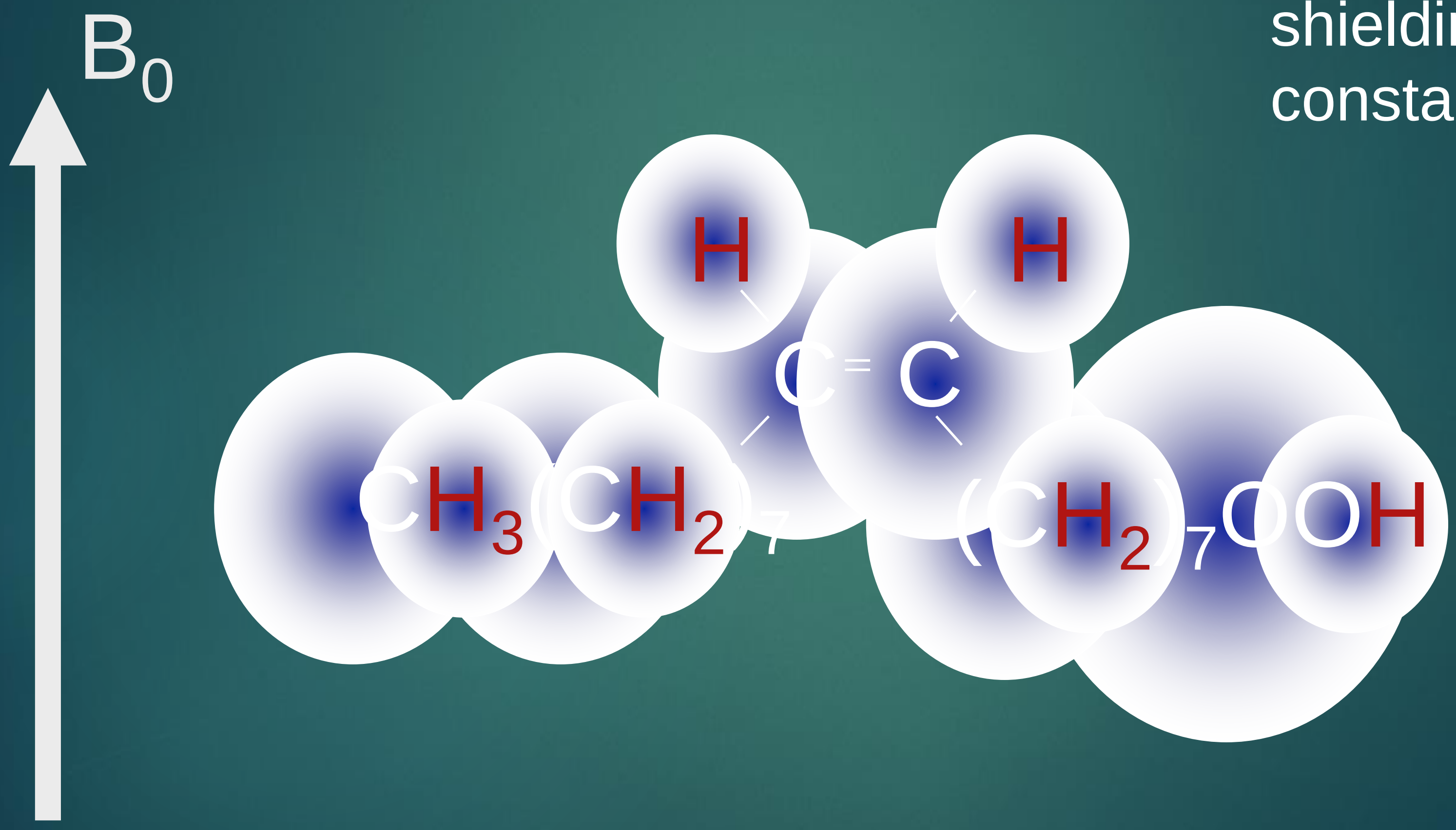


Oleic Acid (Corn Oil)

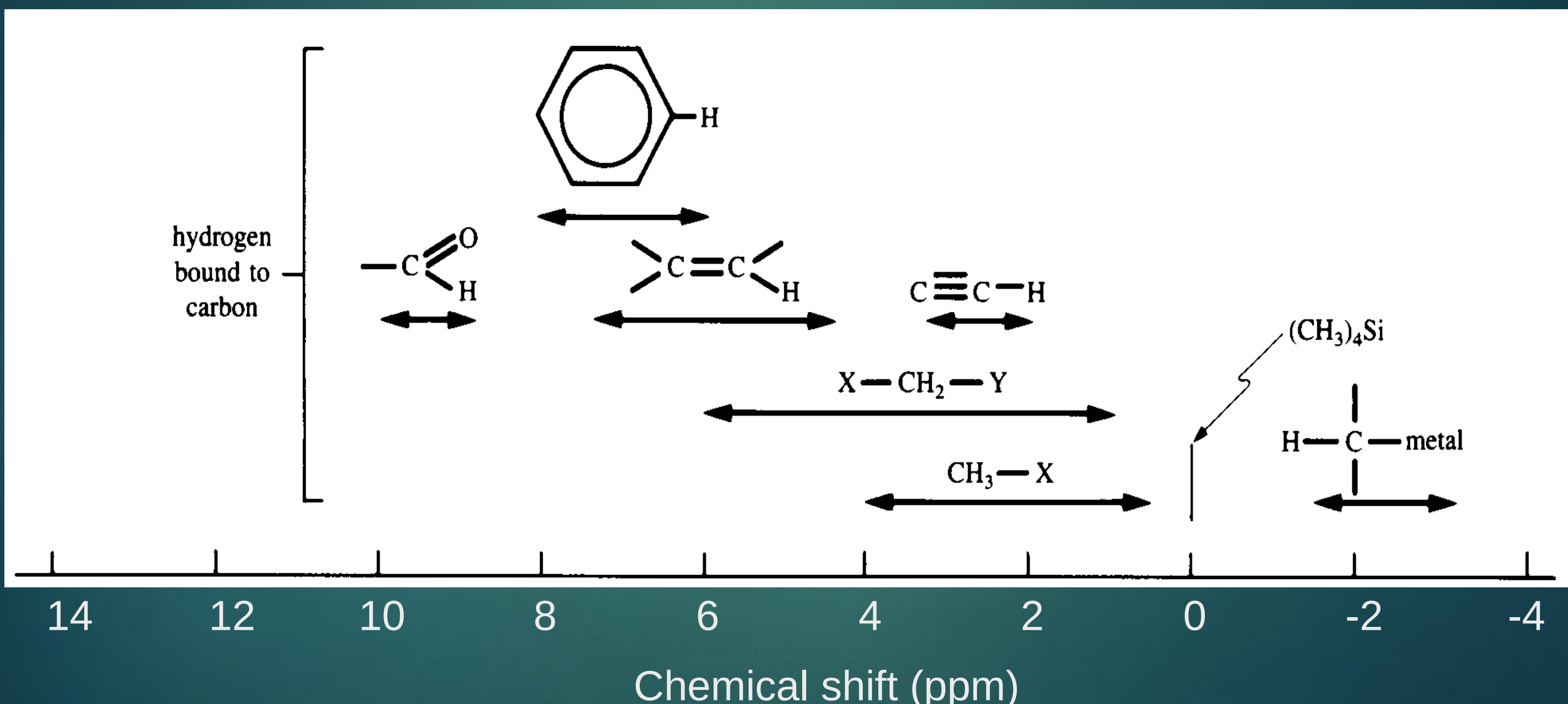
$$\omega = \gamma B_0 \neq \text{constant}$$

$$\omega = \gamma B_0(1 - \sigma)$$

shielding constant



Chemical shifts of H bound to C



Chemical Shift

- The frequency shift increases with field strength. For example, shift difference between water and fat

  $(\omega_{water} - \omega_{fat})$ at 1.5 T is 255 Hz at 3.0 T is 510 Hz

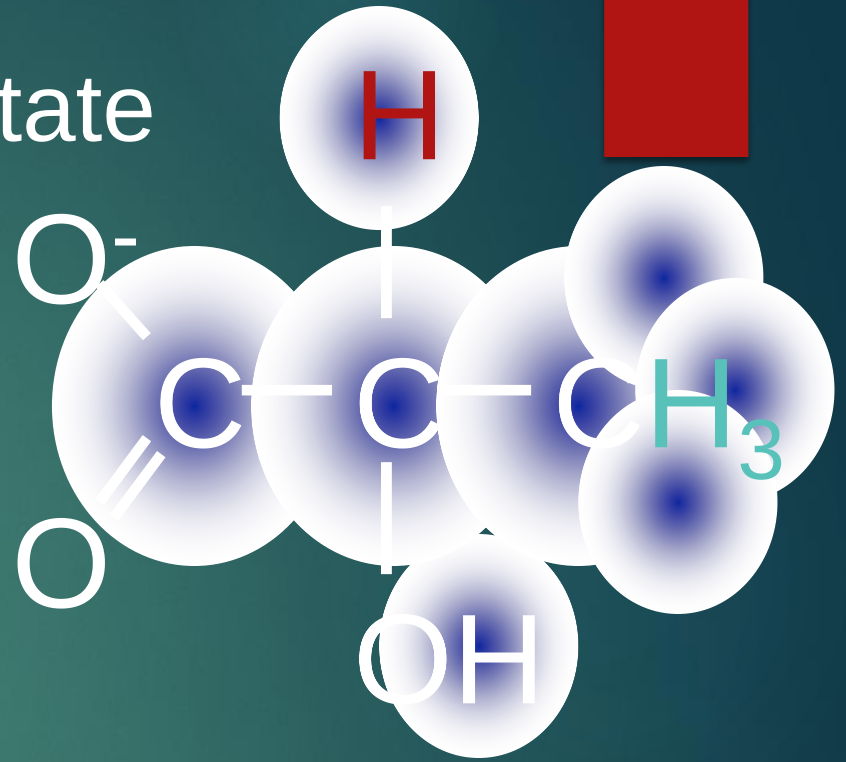
  $$\delta = (\omega_{water} - \omega_{fat})\ 10^6/\gamma Bo\text{, in ppm units}$$

  $\delta_{water\text{-}fat}$ is 3.5 ppm independent of field strength

- By convention
  - Signals of weakly shielded nuclei with higher frequency are on the left
  - Signals of more heavily shielded nuclei with lower frequency are on the right
- Chemical shift of water is set to 4.7 ppm at body temperature

Spectrum with shielding

Lactate



$$\omega = \gamma B_0$$

↓

$$\omega = \gamma B_0 (1 - \sigma)$$

Indirect Spin-Spin Coupling (J-coupling)

$$\omega = \gamma B_0$$

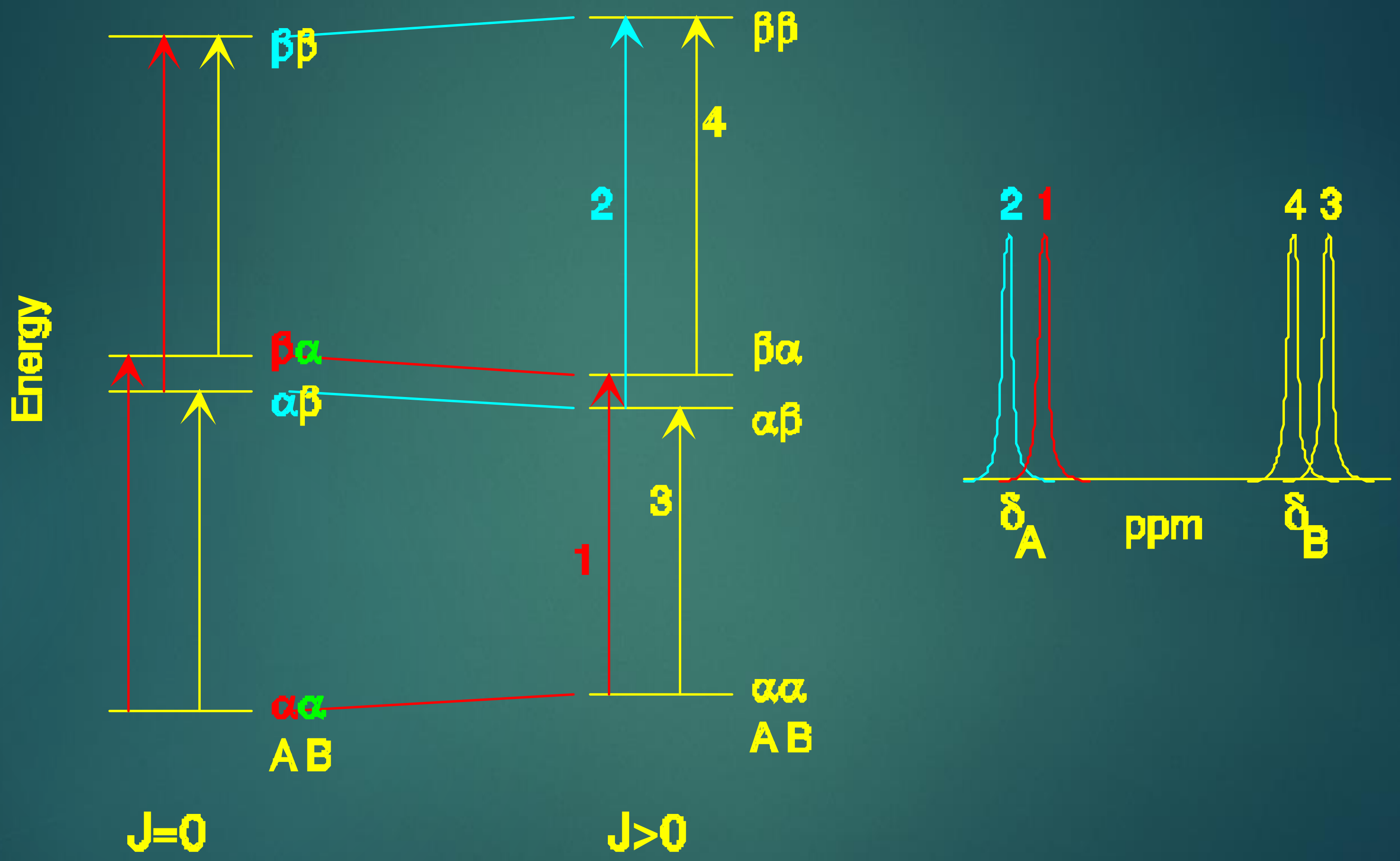
↓

$$\omega = \gamma B_0 (1 - \sigma)$$

↓

$$\omega = \gamma B_0 (1 - \sigma) + \mathrm{f}(J)$$

Stationary Energy States

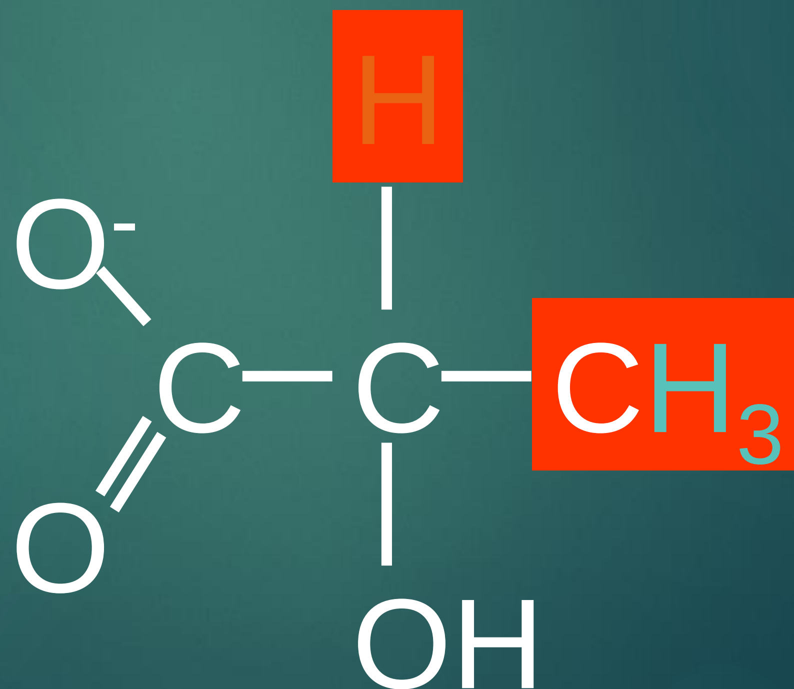


$$\omega = \gamma B_0$$

↓

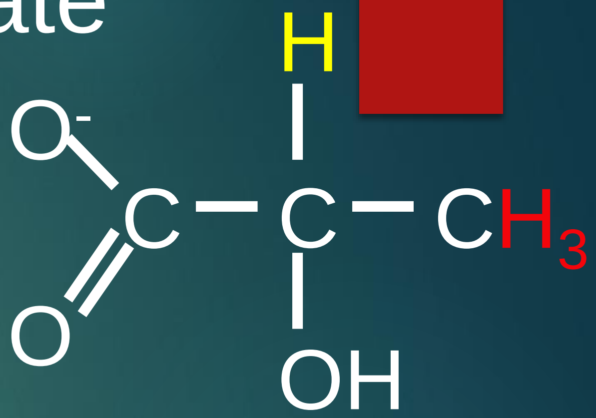
$$\omega = \gamma B_0 (1 - \sigma)$$

Lactate



Spin-spin coupling: The n+1 rule

Lactate

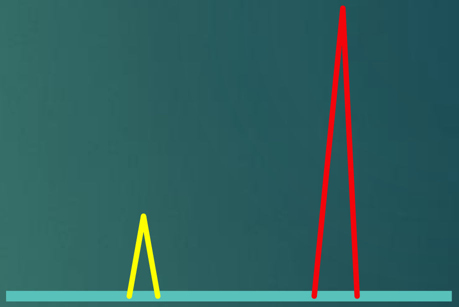


H_3 has n=1 neighbor H
which is in n+1=2 states :

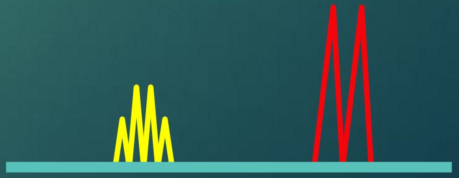
α, 1
β 1

H has n=3 neighbors H_3
which are in n+1=4 states :

ααα, 1
ααβ, αβα, βαα, 3
αββ,ββα, βαβ, 3
βββ 1

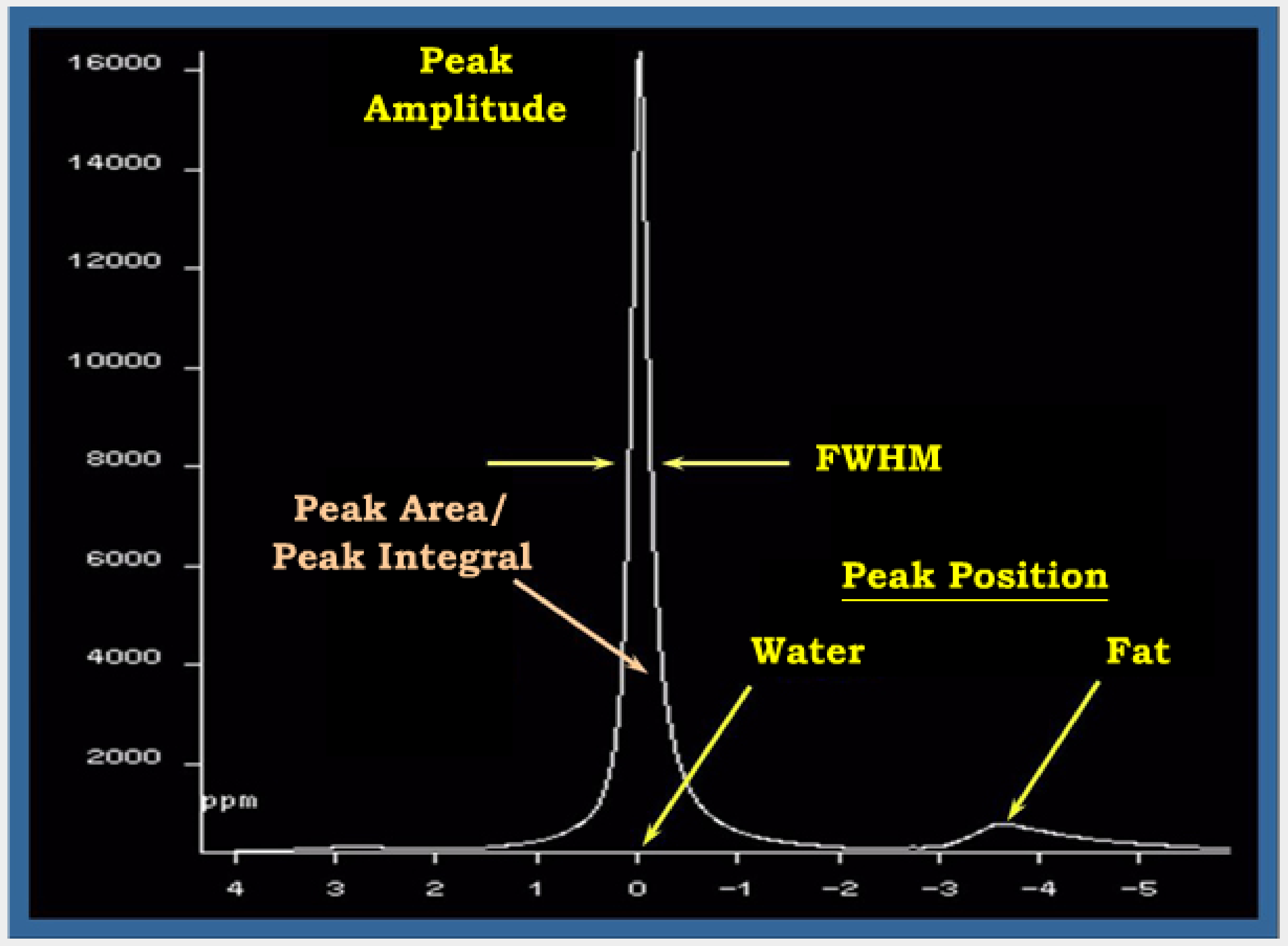


Spectrum w/o coupling



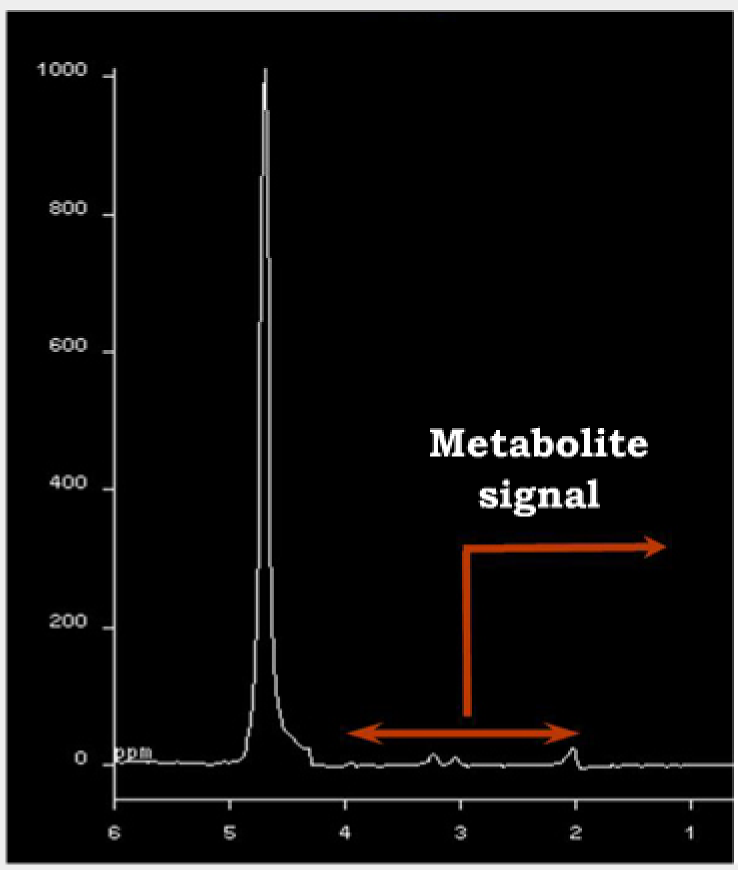
Spectrum with coupling

MR Spectrum: Peak Characteristics

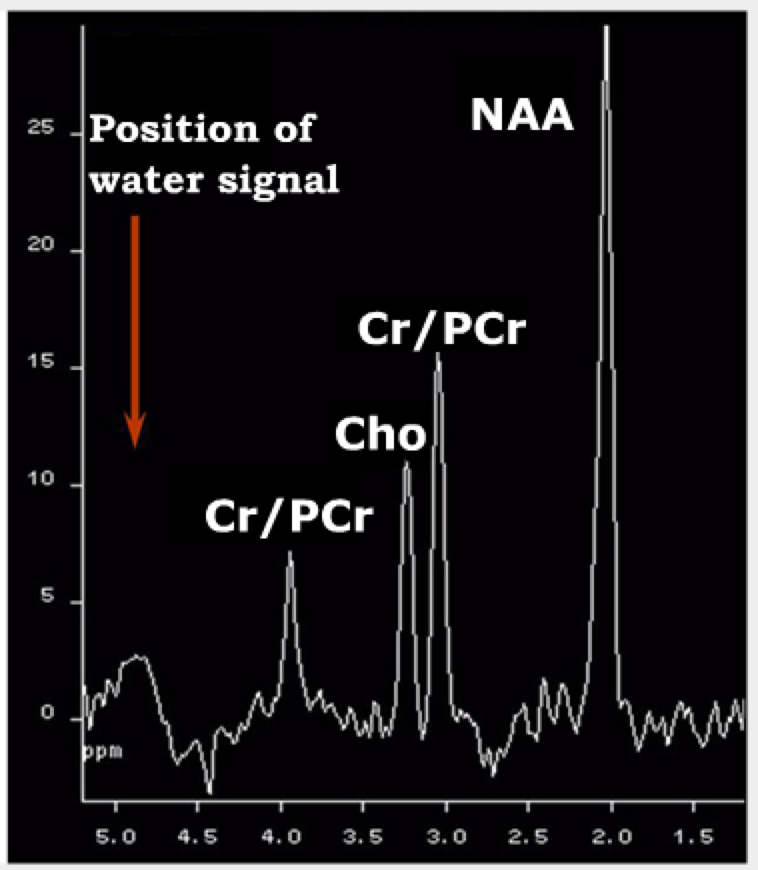


[1]H MR Spectrum from Brain

Water Signal



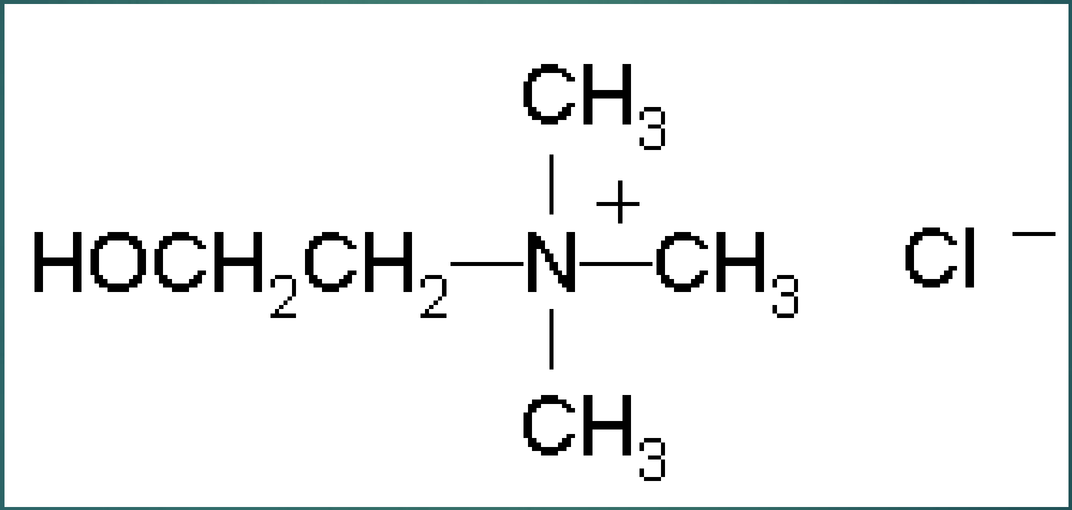
Metabolite Signals



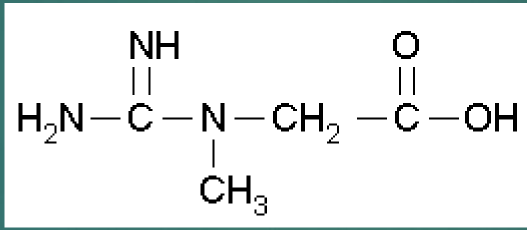
Cerebral metabolites

N-acetyl aspartate Neuronal marker	Glutamate Excitatory neurotransmitter
Creatine/Phosphocreatine Supplier of phosphate to convert ADP to ATP	Glutamine Product of reaction of Glu with ammonia.
Choline Total cerebral choline including neuro-transmitter acetylcholine, phospho-choline, and phosphotidylcholine	Glucose Energy source.
Myo-inositol Storage form of hormonal messenger inositol diphosphate	Lactate End product of anaerobic glycolysis

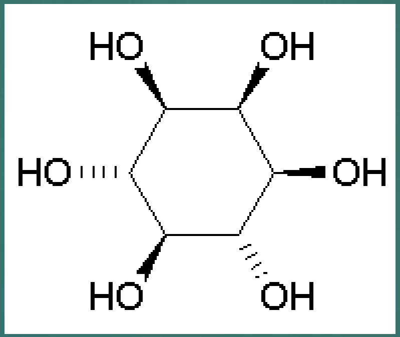
Choline



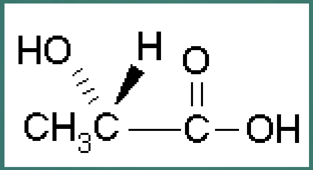
Creatine



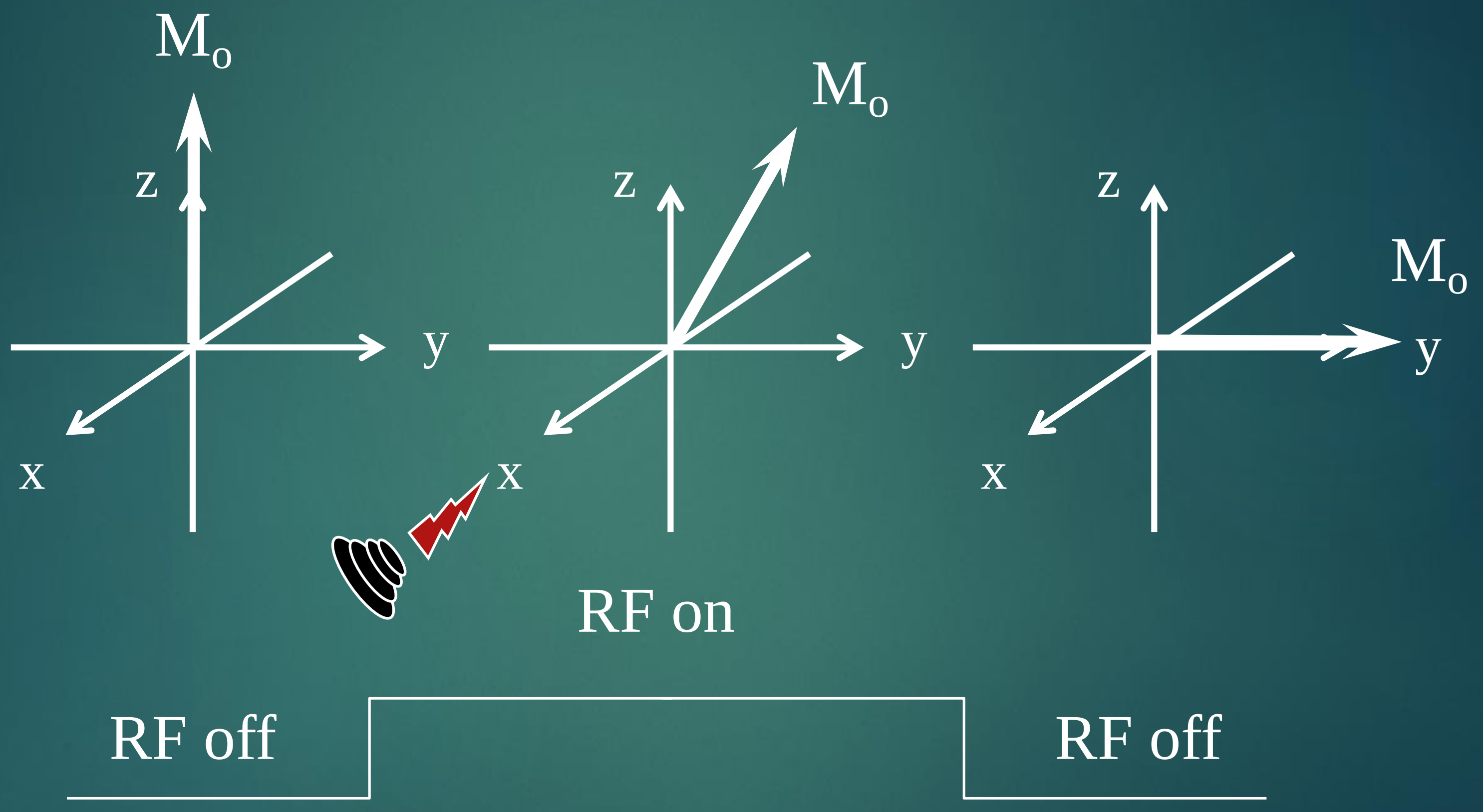
Myo-Inositol



Lactate



Nuclear Spin Dynamics



Effect of a 90^o x pulse

Excitation

- When a nucleus is in B_0 the initial population of energy levels are determined by thermodynamics as described by the Boltzmann distribution
  - Lower energy levels will contain slightly more nuclei than the higher level

- Nuclear magnetization can only be observed by rotating the net longitudinal magnetization towards or onto the transverse plane
  - This can be accomplished by applying a second magnetic field in the transverse plane oscillating at the Larmor frequency

Free Induction Decay

The signals decay away due to interactions with the surroundings.

A free induction decay, FID, is the result.

Fourier transformation, FT, of this time domain signal produces a frequency domain signal.

Signal detection

- In principle, Signal intensity generated by a class of nuclei is linearly proportional to the number of nuclei in the sample
- In NMR peaks may be broadened by T2* losses, which is caused by spin-spin coupling and B_0 in-homogeneities

Signal detection

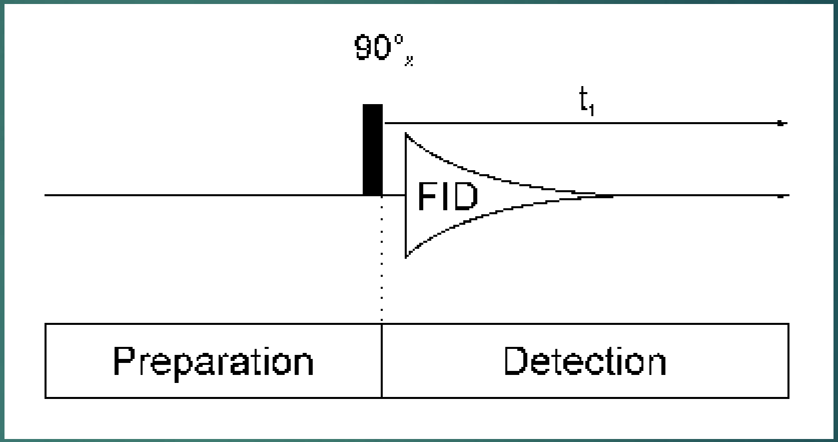
- Spectral Resolution

$$Spectral\ Resolution = \frac{1}{(\#complex\ points)*\Delta t}$$

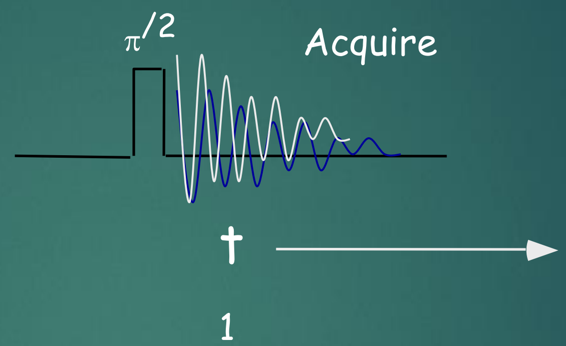
- MRI
  - 64,128 or 256 complex points, short acquisition time
  - Low spectral resolution (~350 Hz)
    - Limited to water and lipid concentration
- MRS
  - 256-2048 complex points
  - Much high spectral resolution (8-25 Hz)

1D NMR

Pulse Sequence



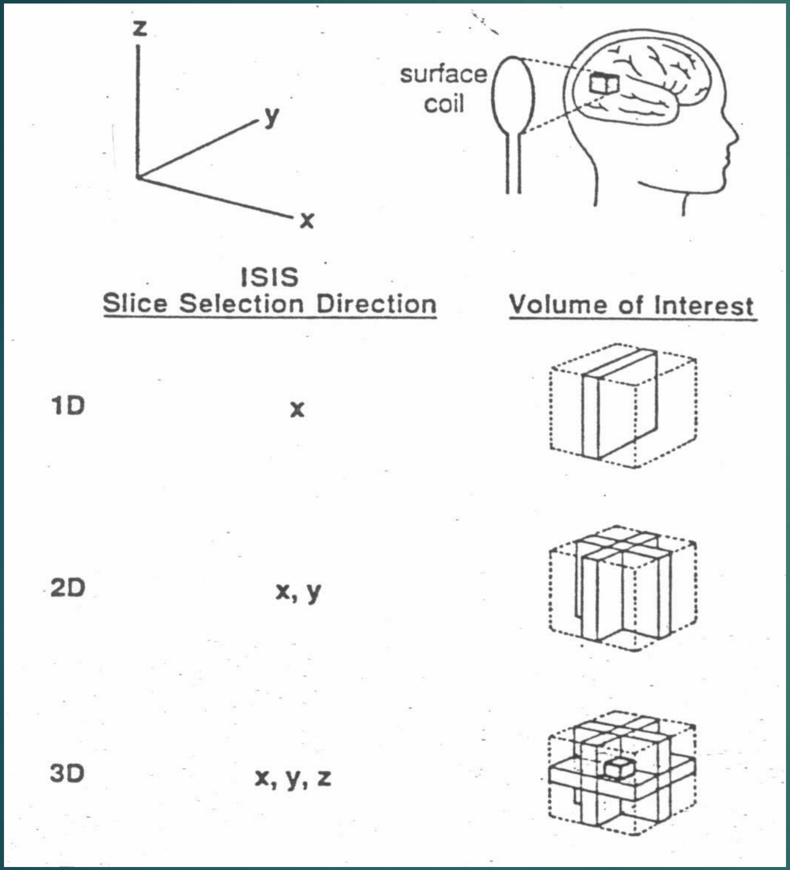
General One Dimensional Experiment

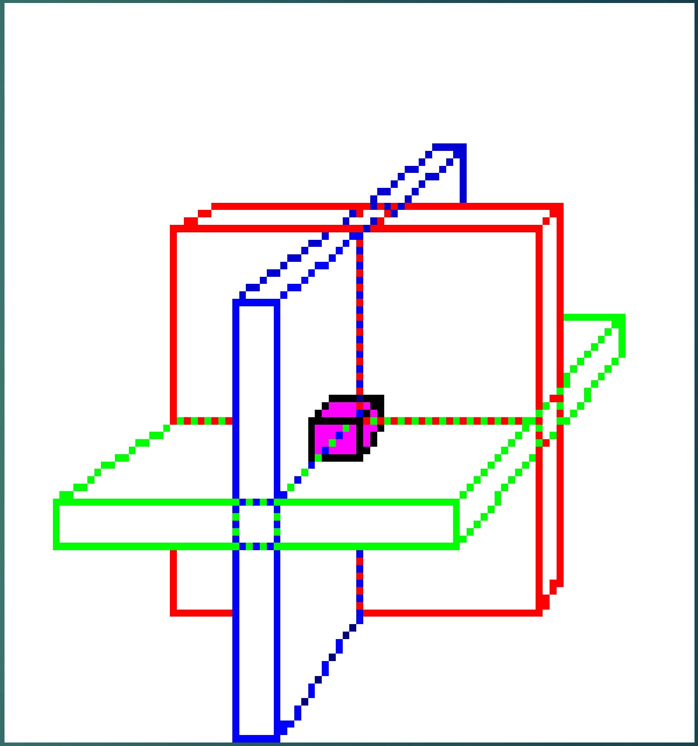


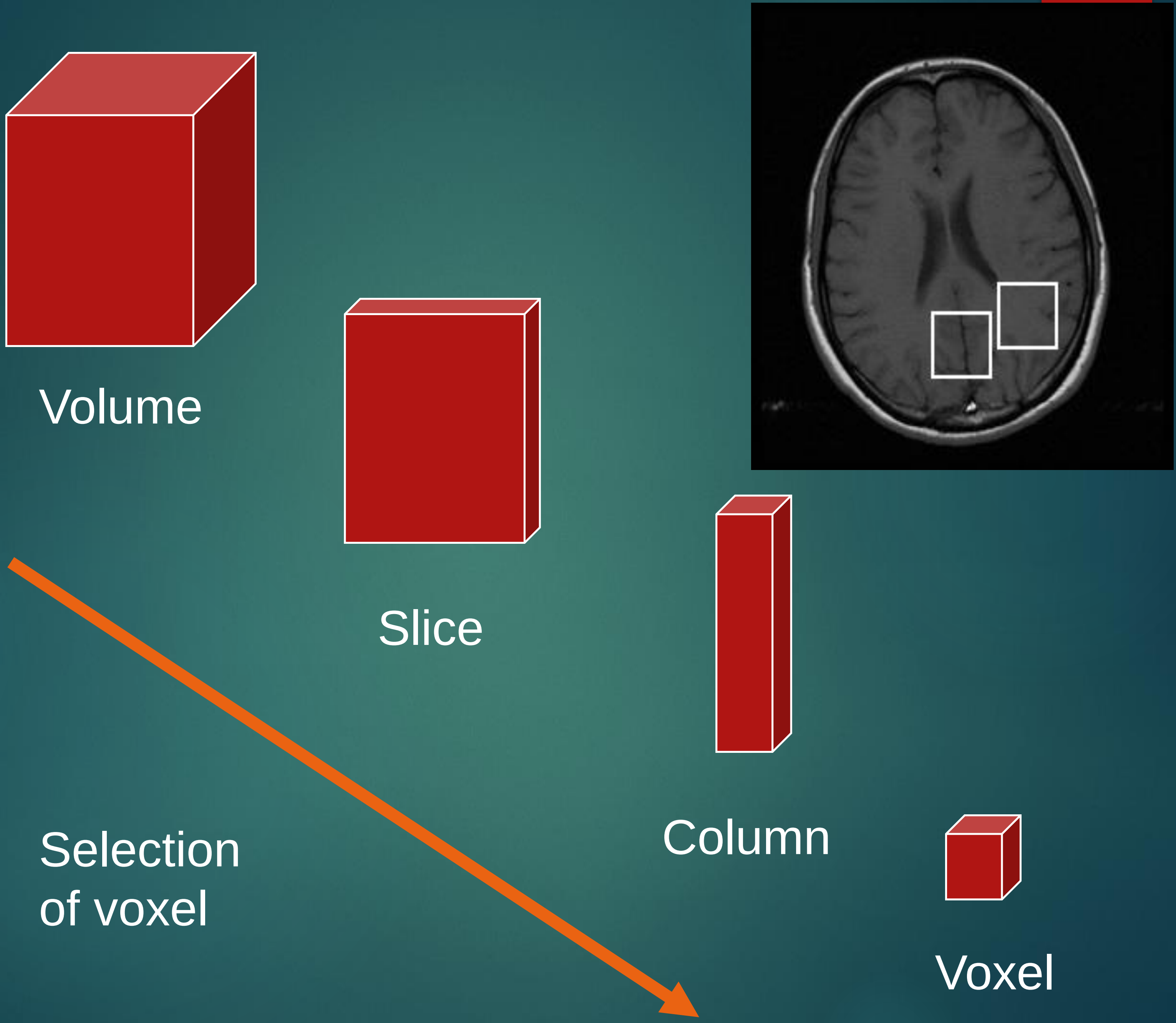
Fourier Transformation resolves multiple frequencies that overlap in the time domain

Fourier Transform
t_1 -> f_1

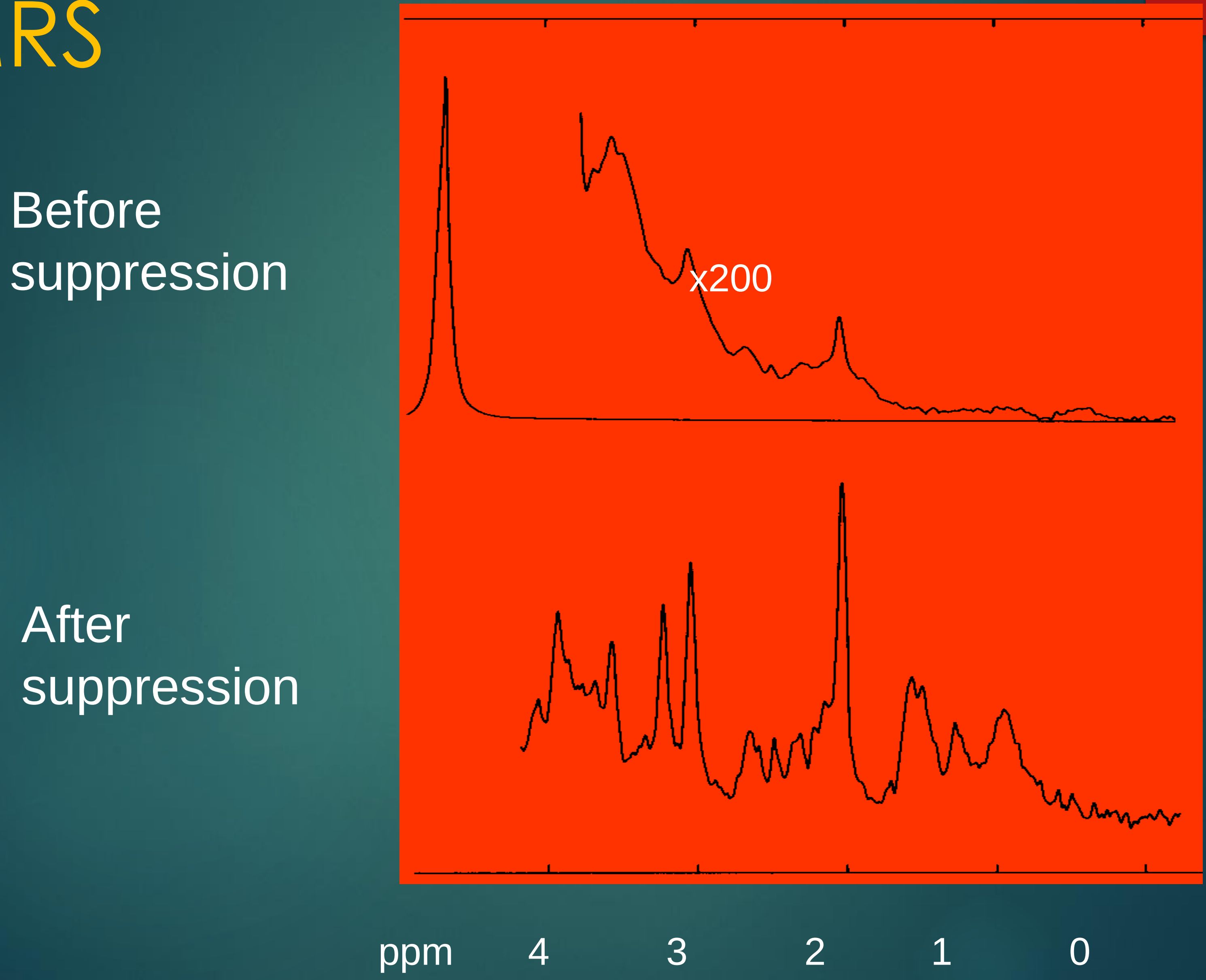
Localization






Volume
Slice
Column
Voxel
Selection
of voxel

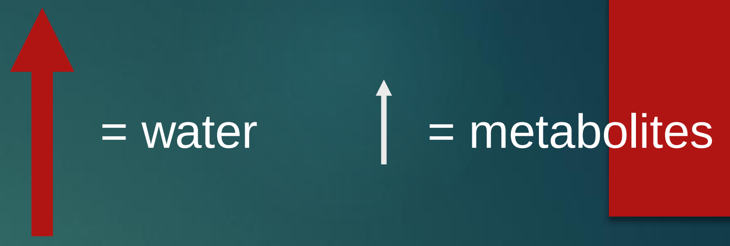
Water: + for MRI, - for MRS

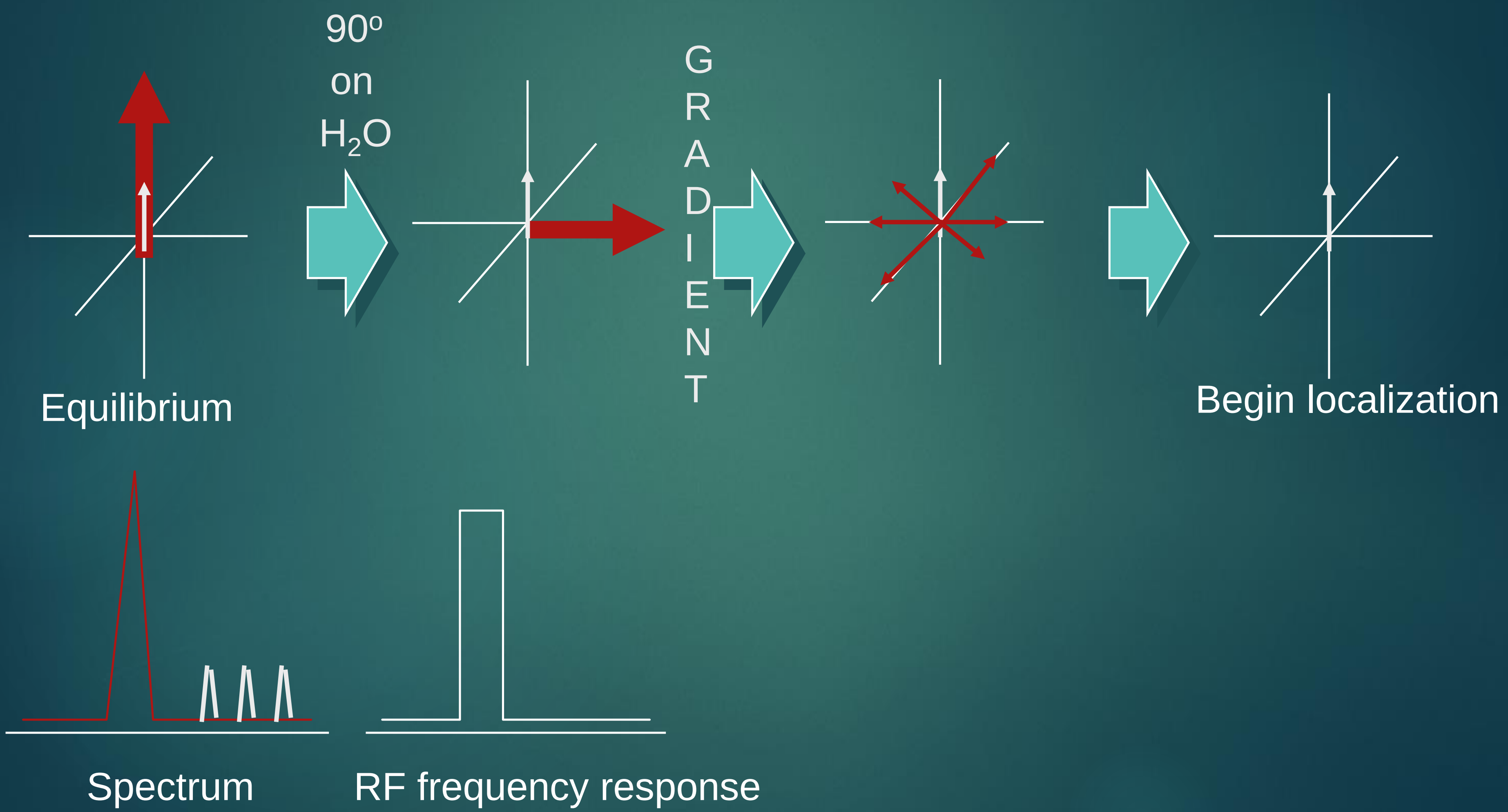


CHESS

(global)

Water suppression





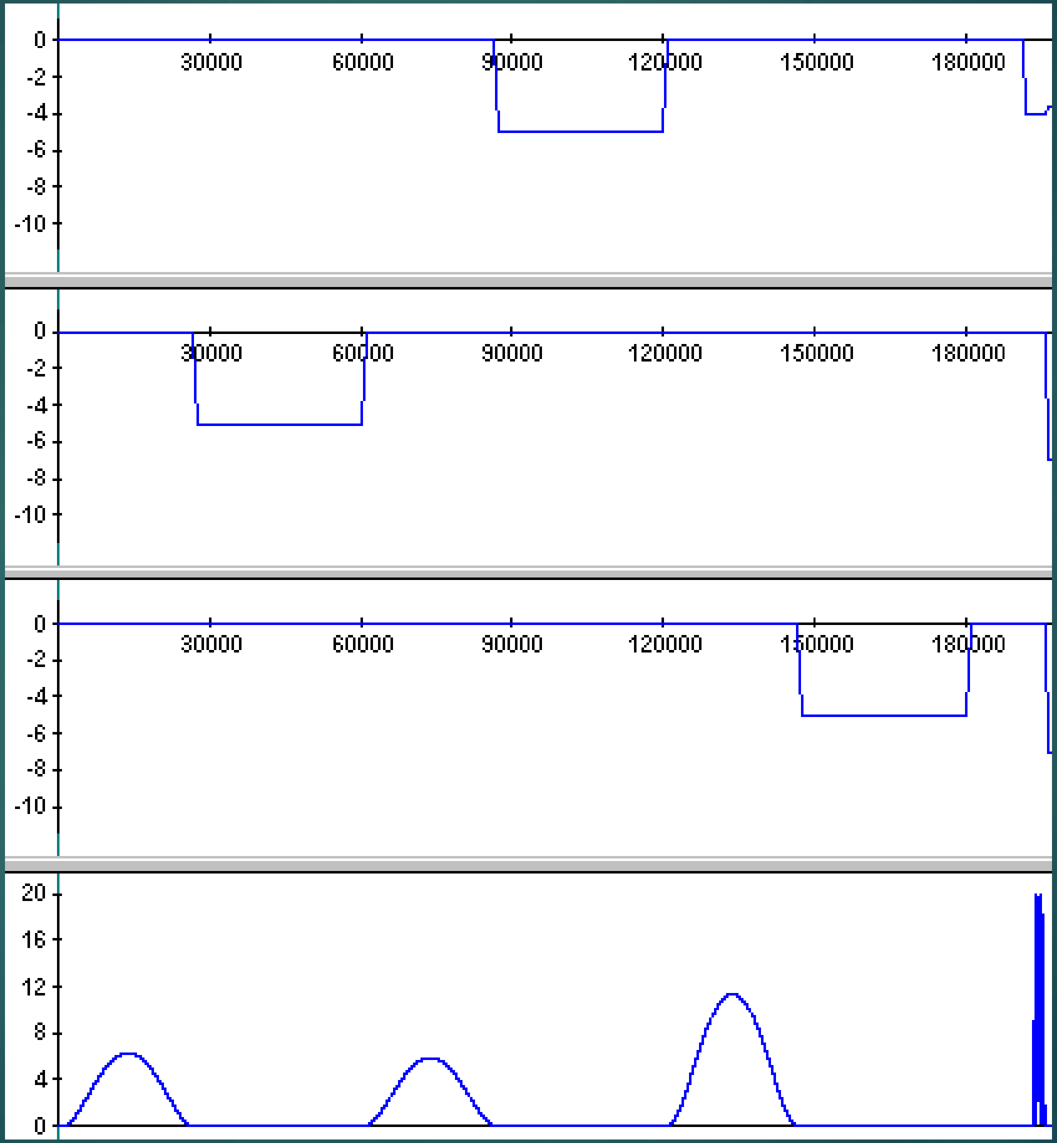
CHESS (global)

Gx

Gy

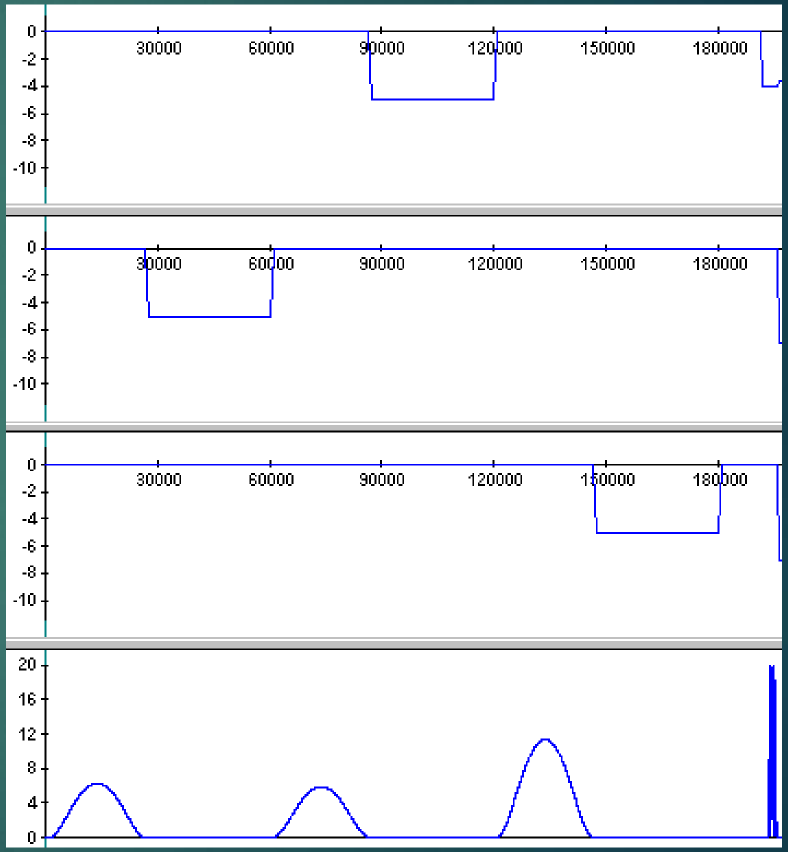
Gz

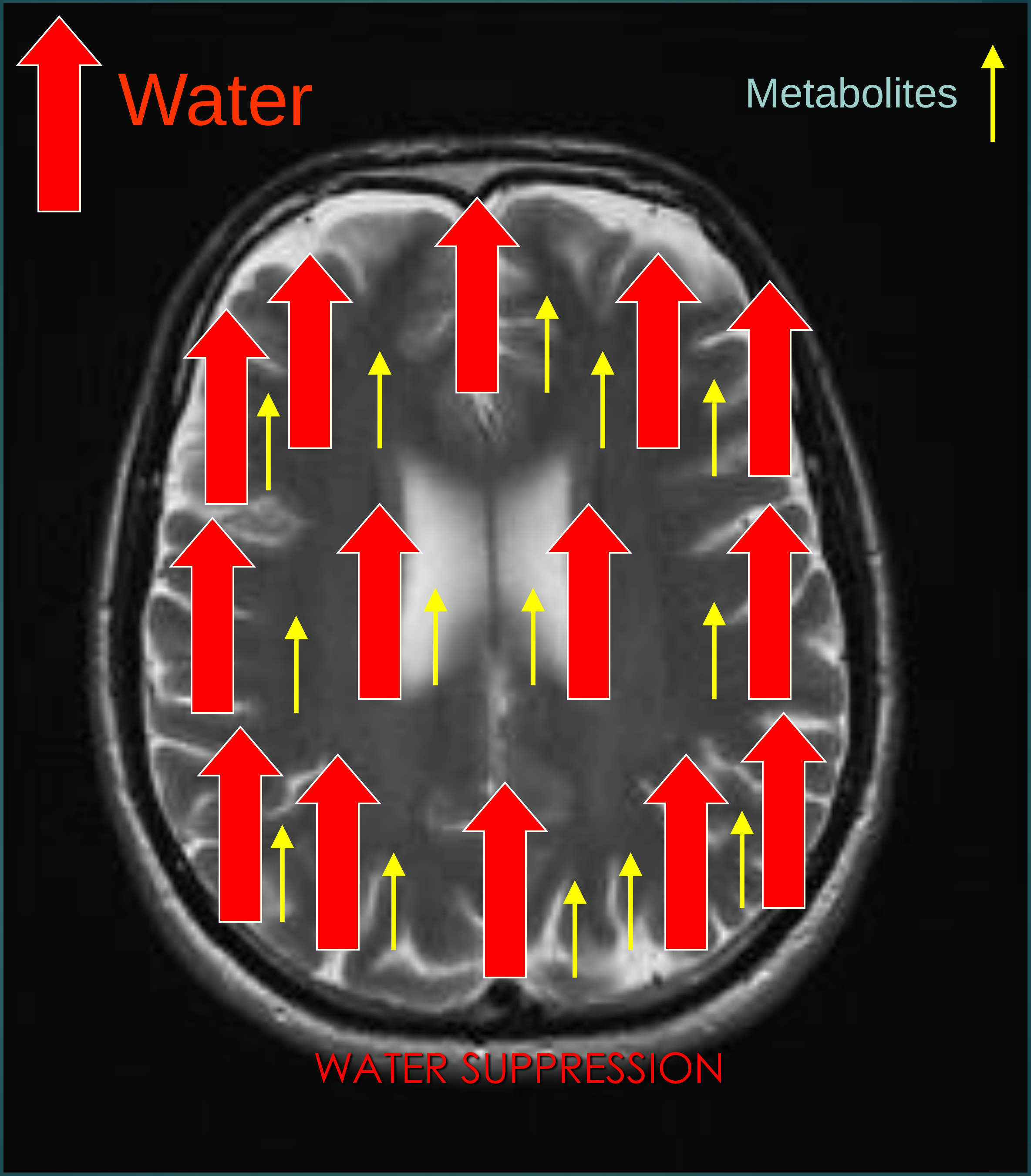
RF



Water Suppression

- Nomal water signal is ~ 5000 times stronger than metabolites
- Need to reduce it at least by 1000 times to get the right dynamic range.
- Common way is by frequency selective pulses followed by dephasing gradient.




Water
Metabolites
WATER SUPPRESSION

CHESS

(global)

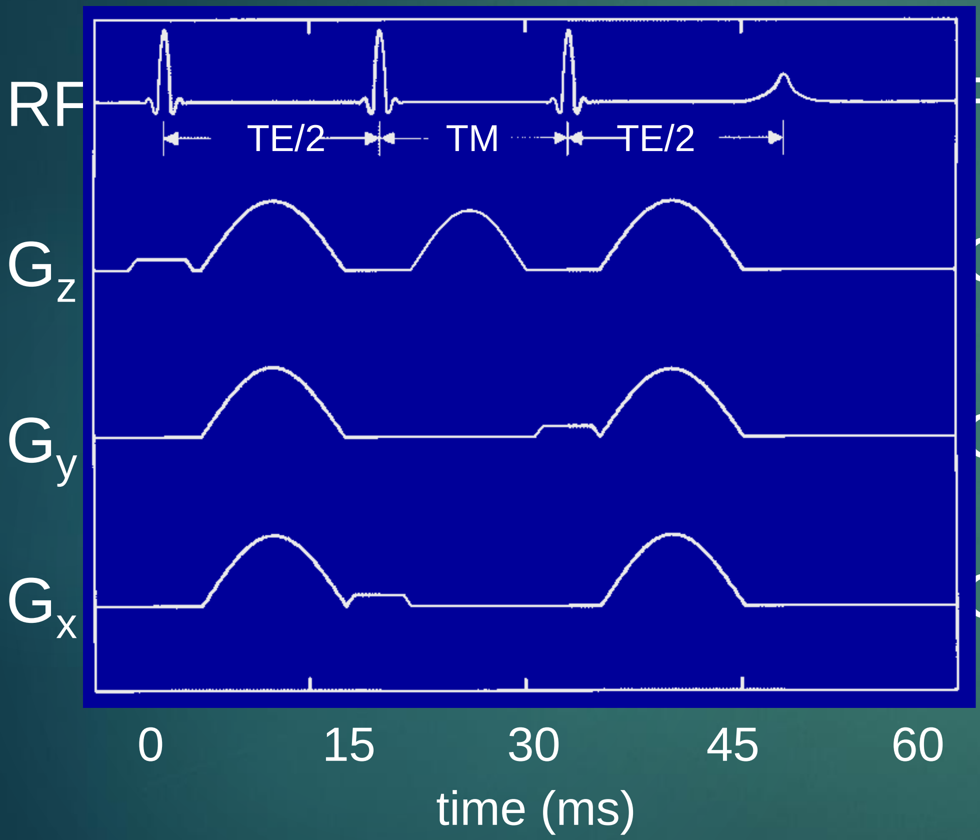
1D

STEAMSV

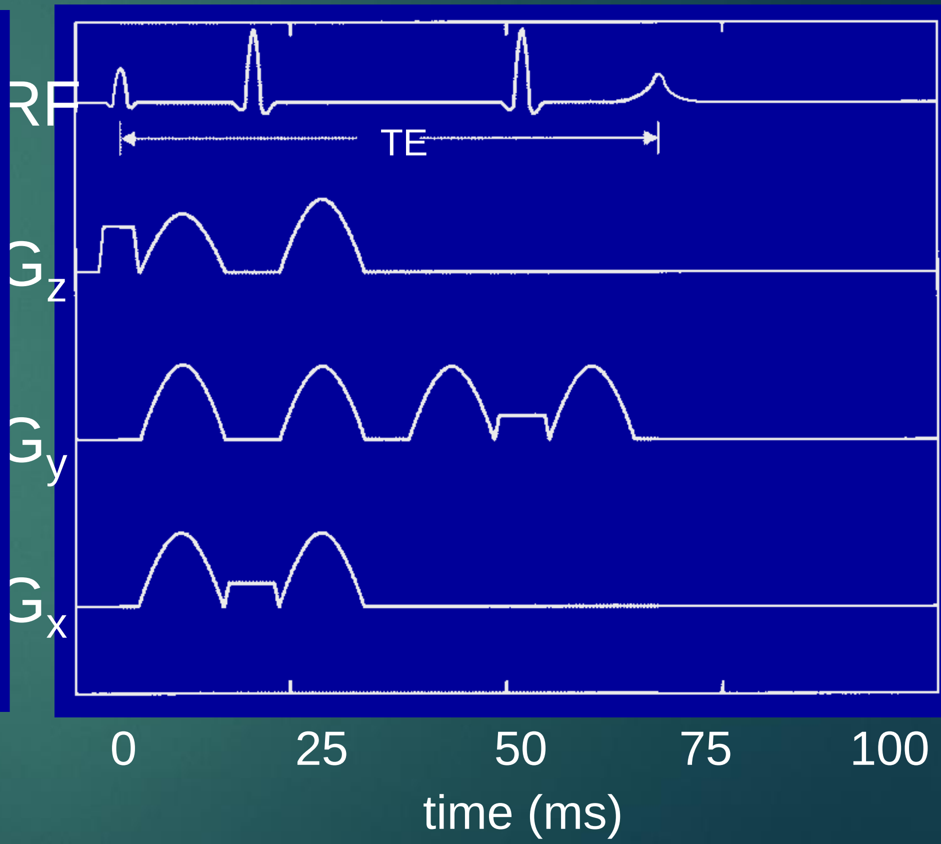
PRESSSV

Localization

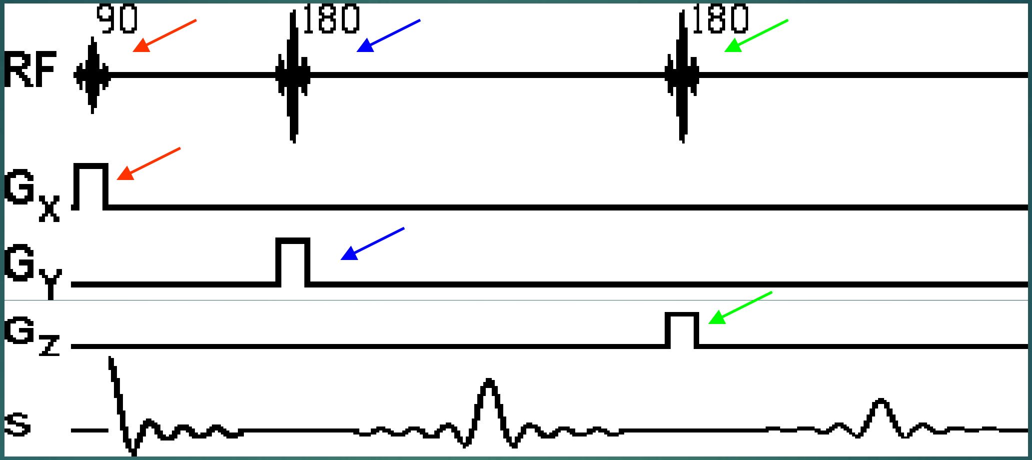
STEAM



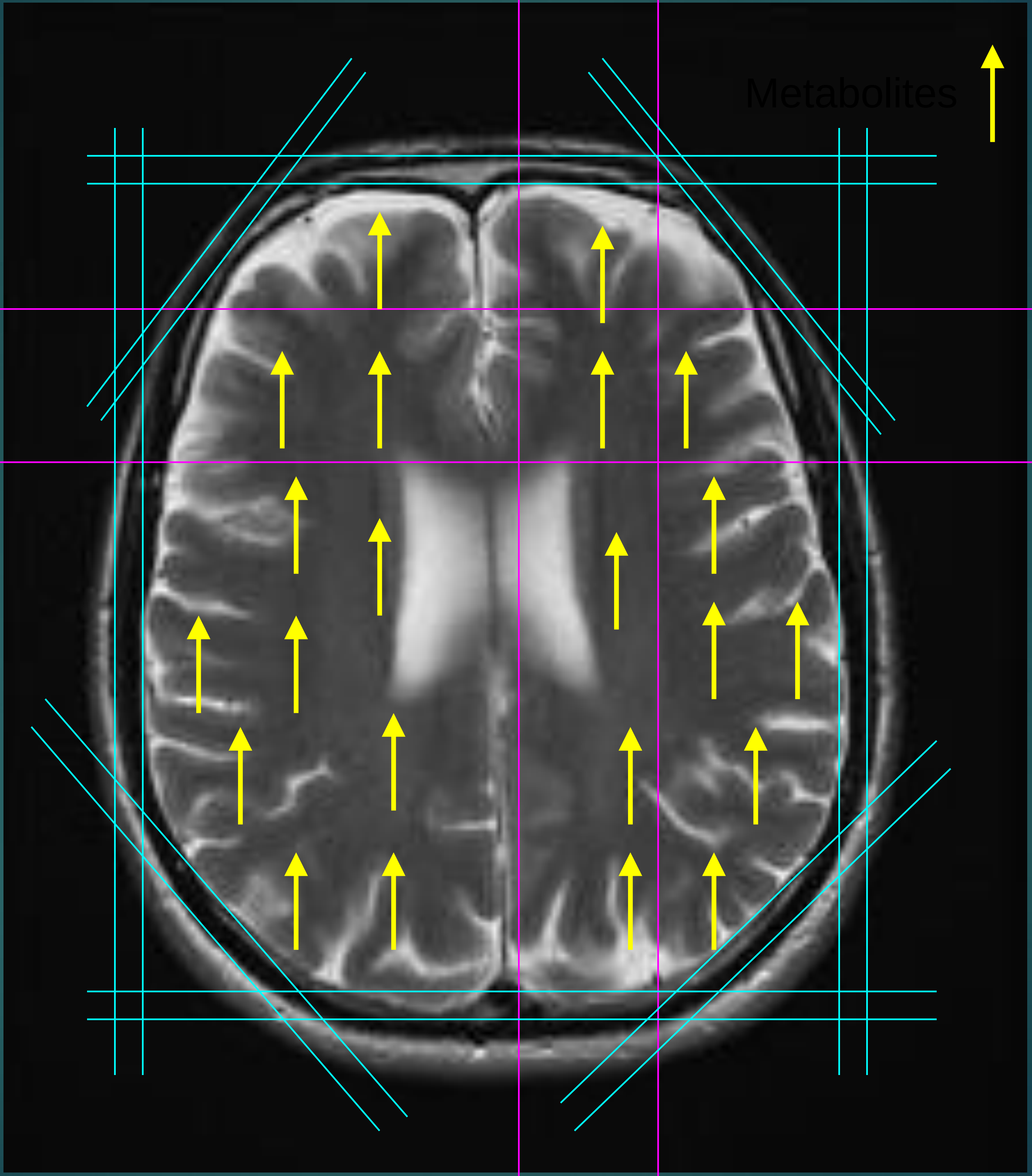
PRESS



PRESS-SV Sequence

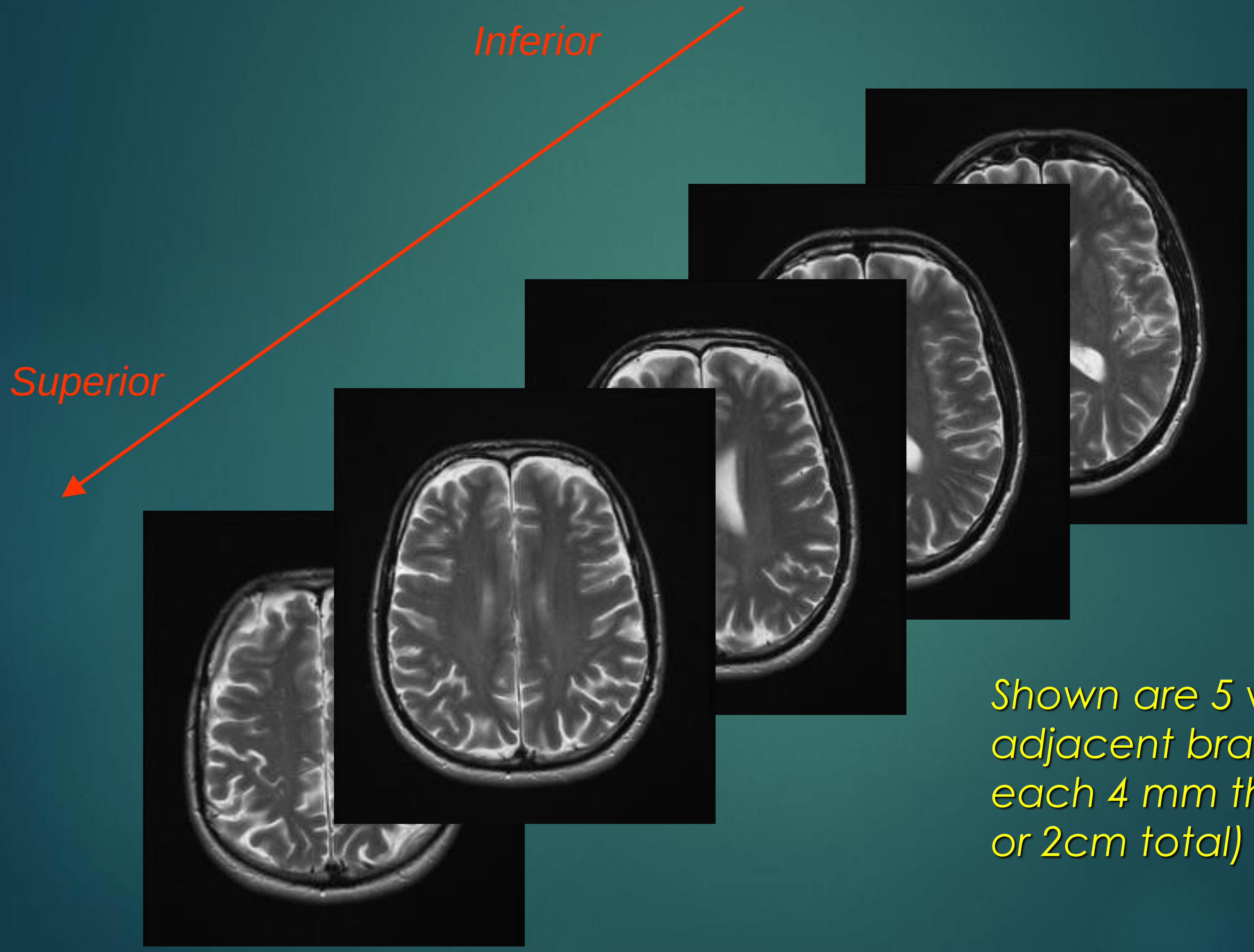


A second echo is recorded as the signal.
FT the echo to produces an NMR spectrum.



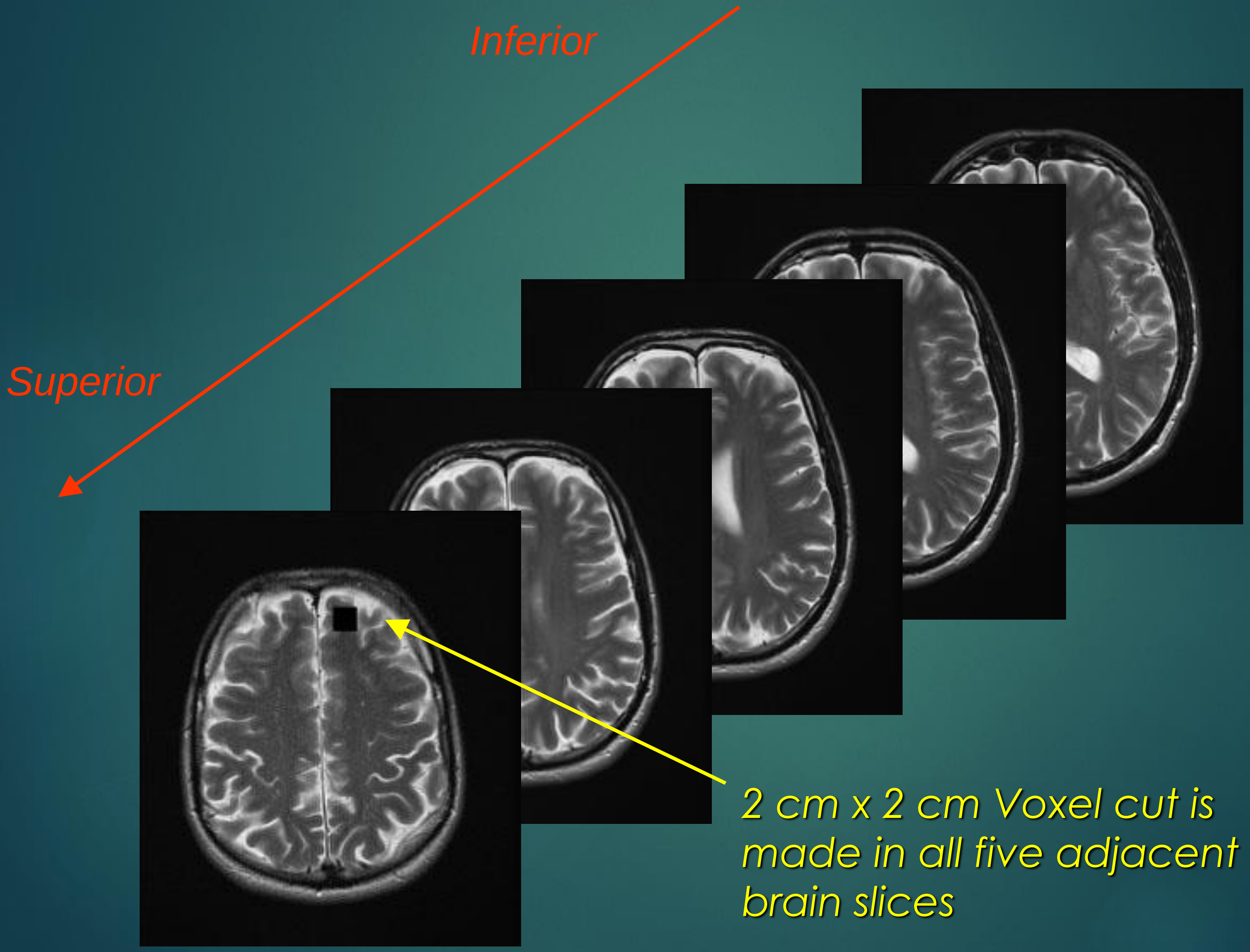
$2 \times 2 \times 2\ cm^3$
Voxel
Measured

2x2x2 cm³ Voxel, 5 Slices

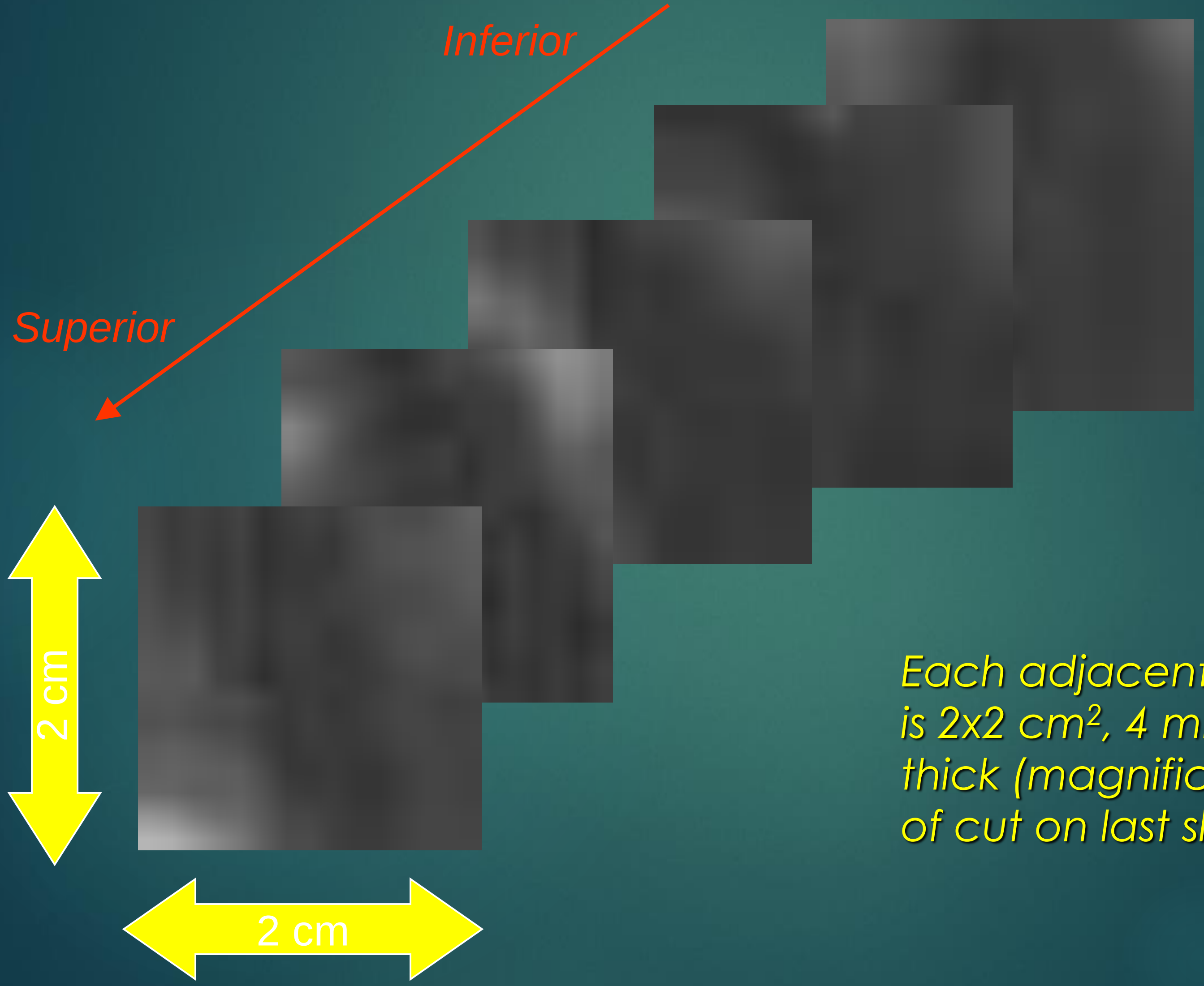


Shown are 5 vertically adjacent brain slides, each 4 mm thick (20 mm or 2cm total)

2x2x2 cm³ Voxel, 5 Slices

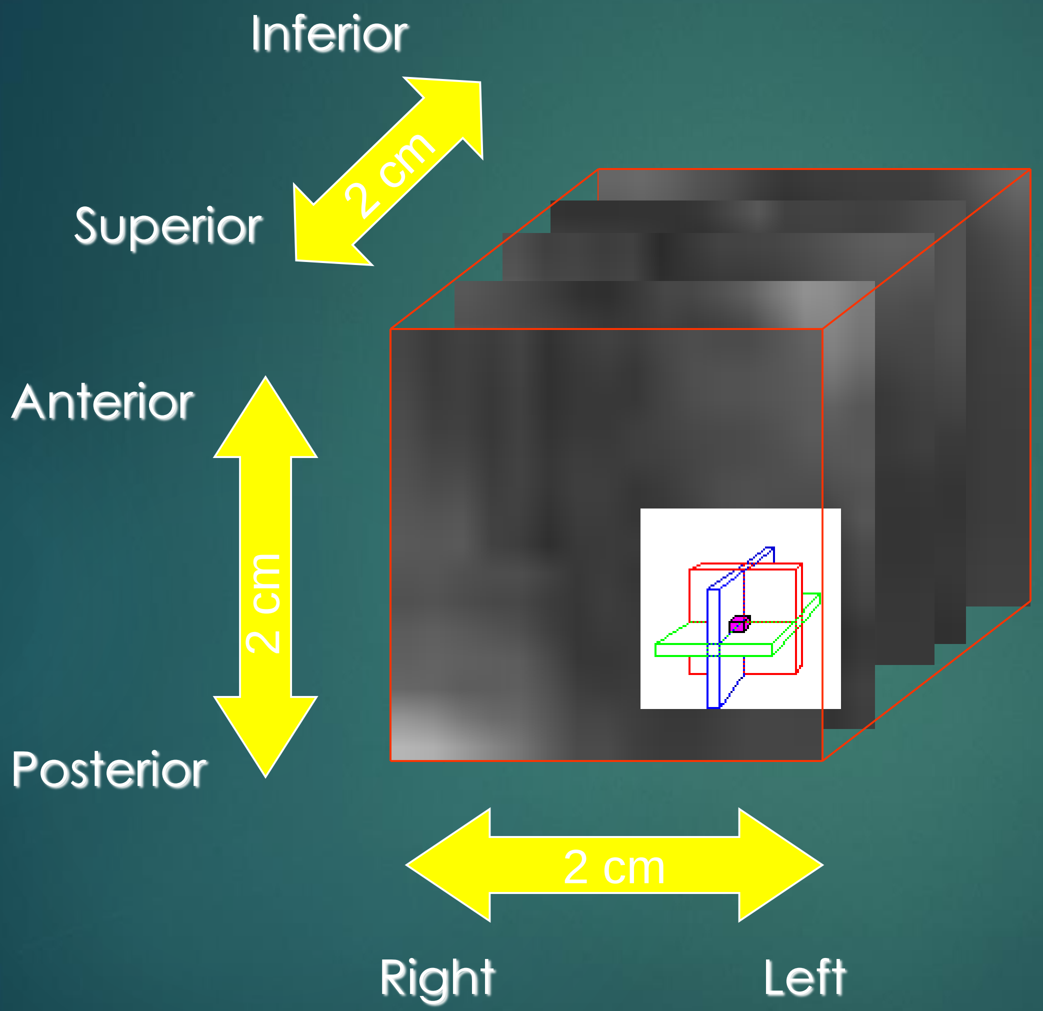


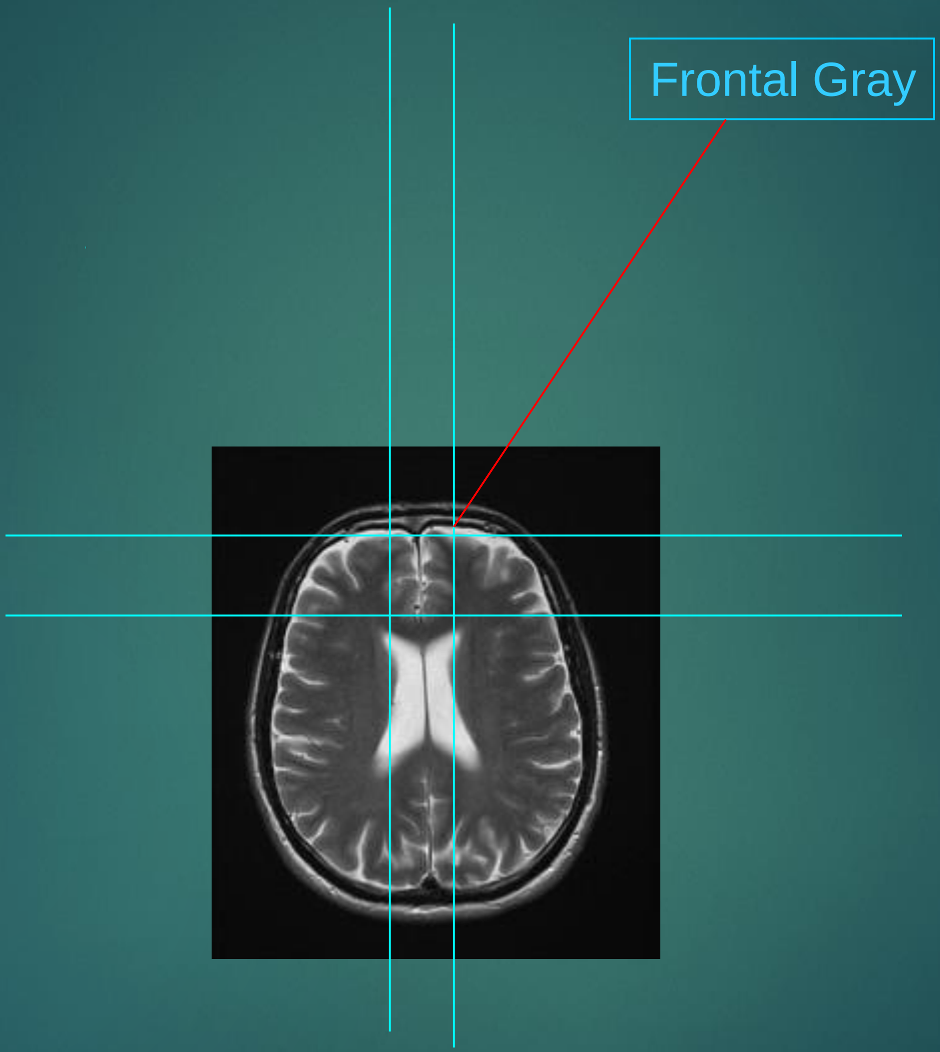
5 Adjacent Voxel Slices

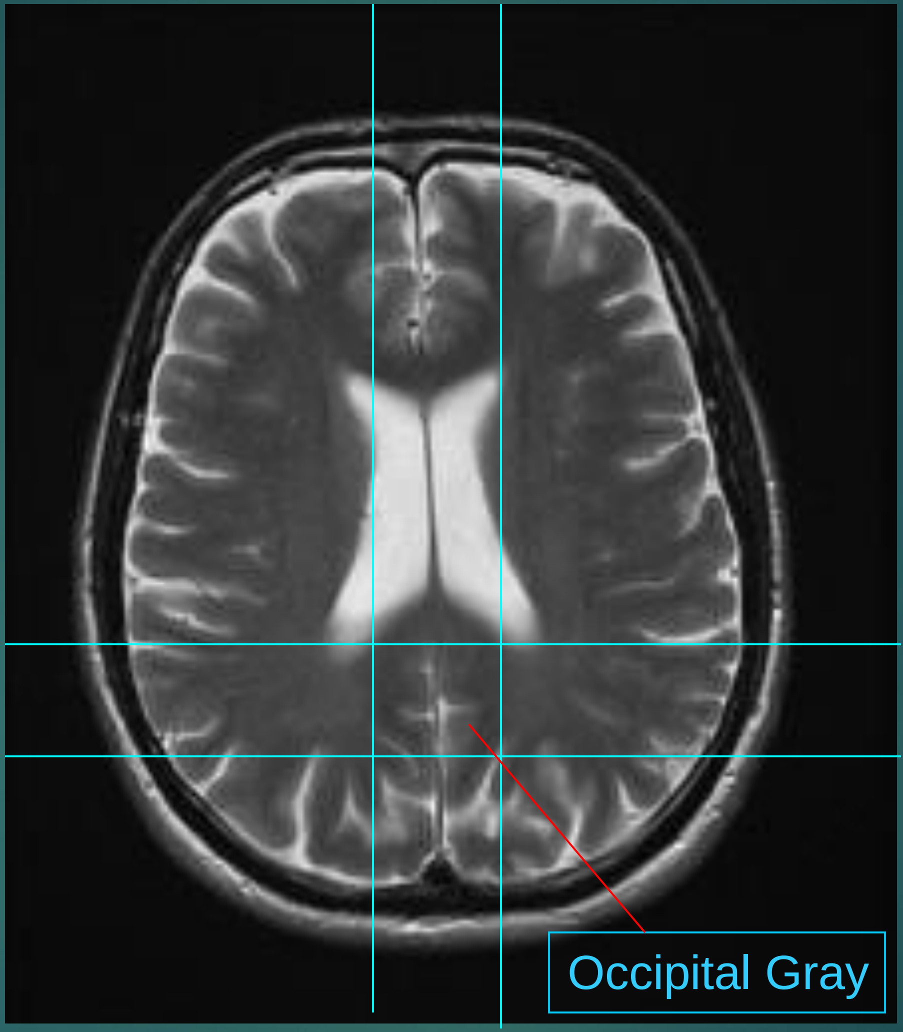


Each adjacent slice is 2x2 cm^2, 4 mm thick (magnification of cut on last slide)

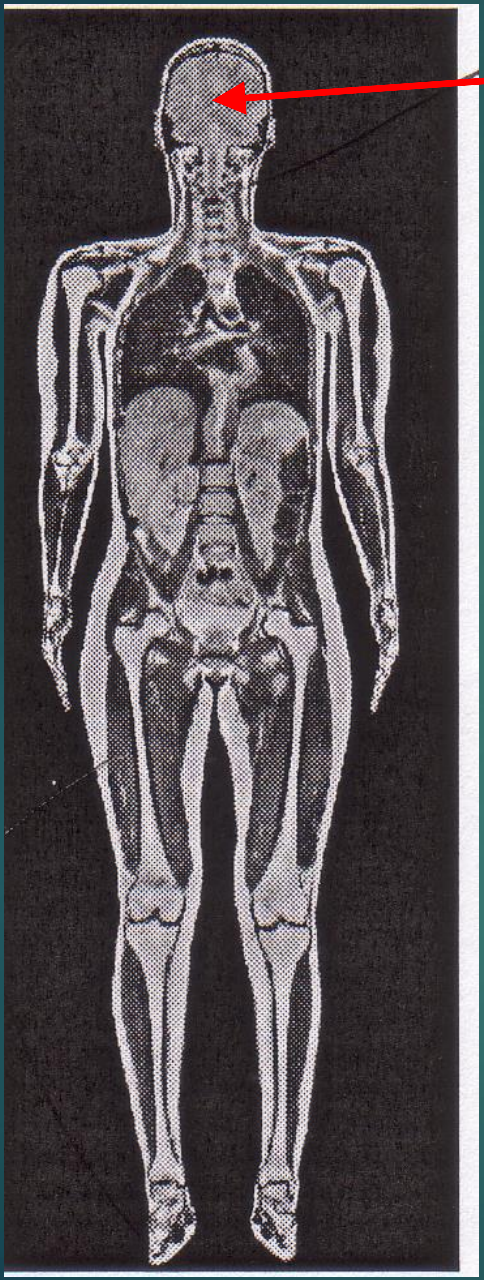
2 x 2 x 2 cm^3 Voxel




Frontal Gray


Occipital Gray

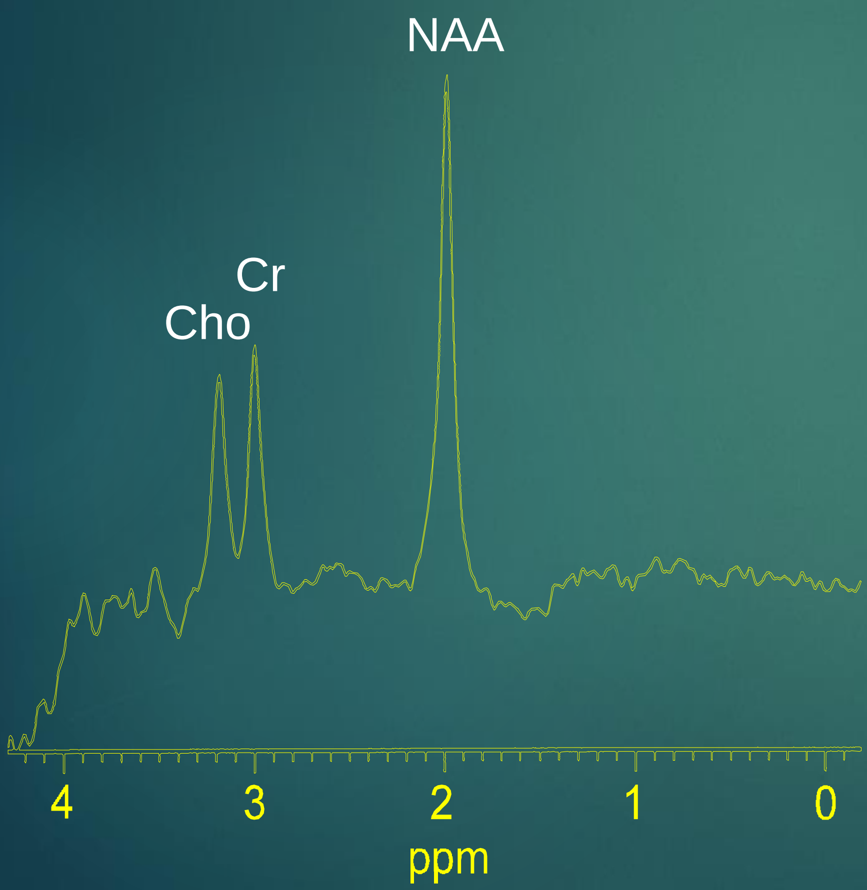

CHESS
(global)
1D
STEAMSV
PRESSSV
Data
Acquisition
(N*Δt)
Recovery
Time
(TR)



Brain MRI and MRS

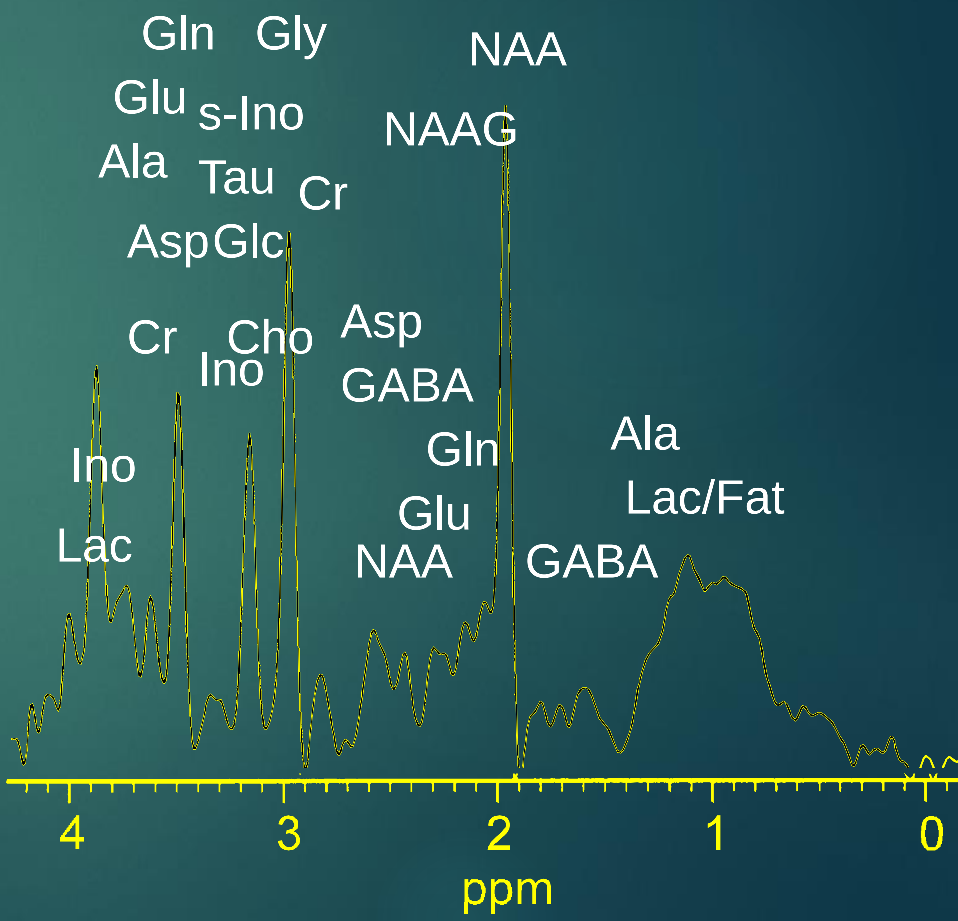
That was then ...

STEAM, TE=270ms, TR=1500ms



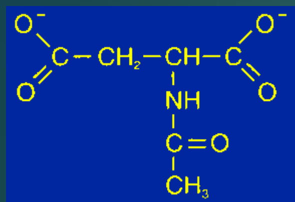
This is now.

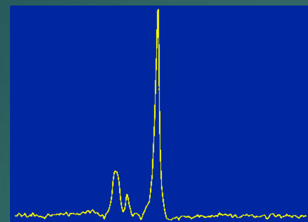
STEAM, TE=20ms, TR=1500ms



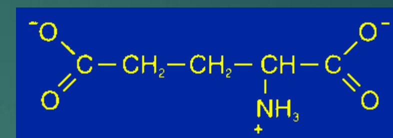
Cerebral metabolites

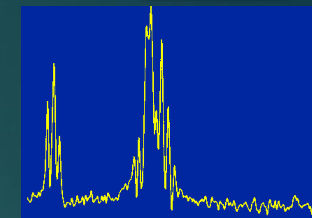
N-acetyl aspartate



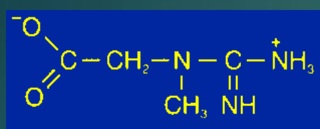


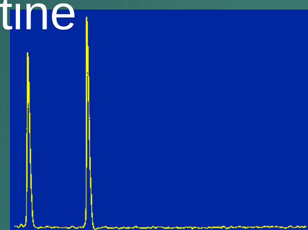
Glutamate



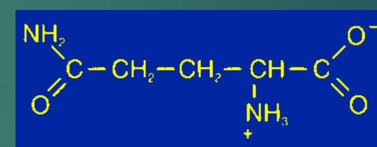


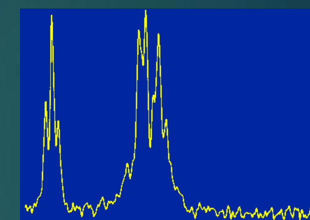
Creatine/Phosphocreatine



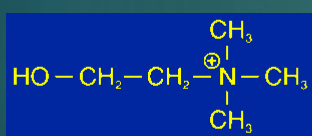


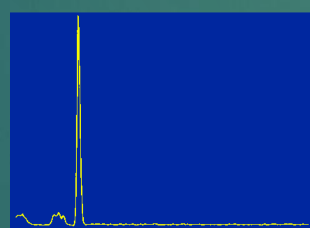
Glutamine



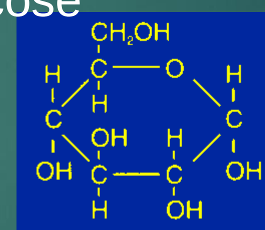


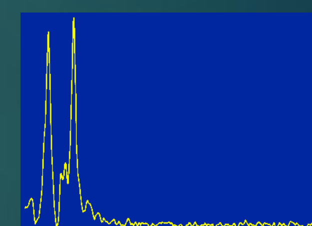
Choline



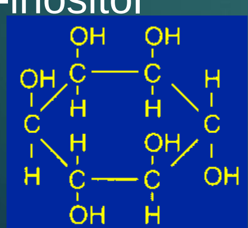


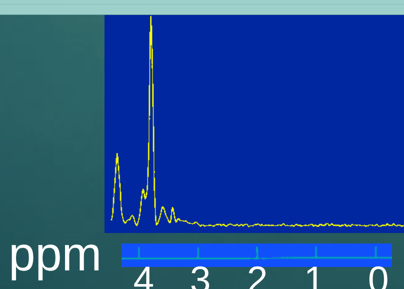
Glucose



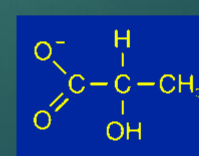


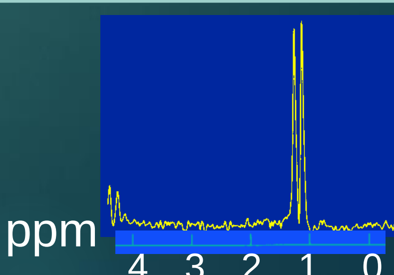
Myo-inositol





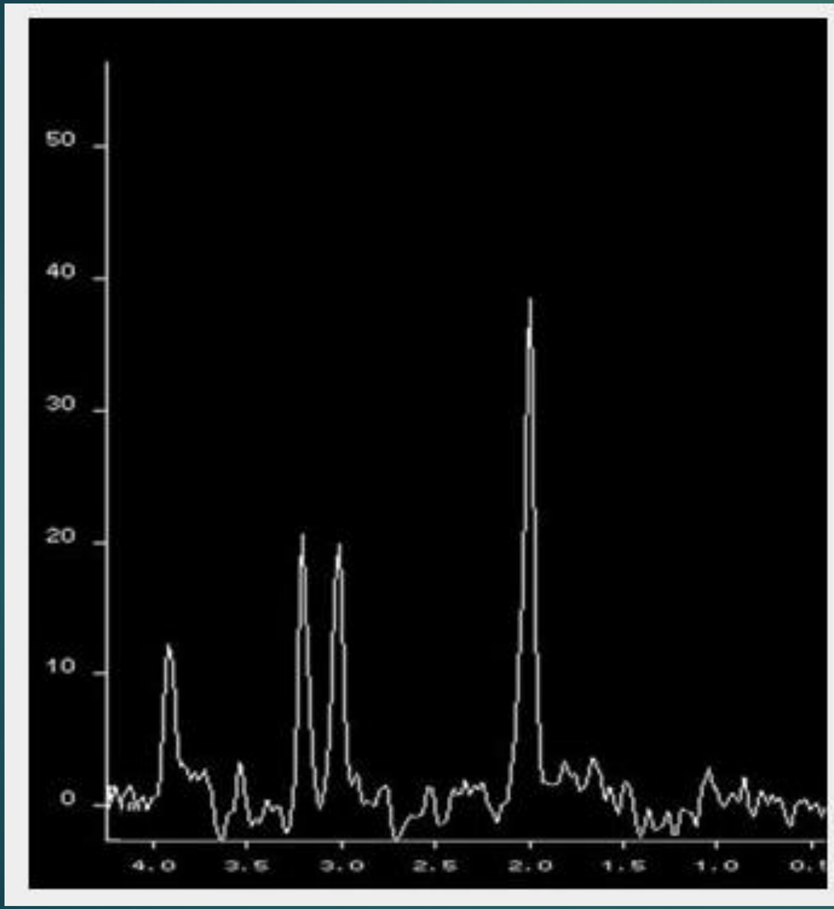
Lactate



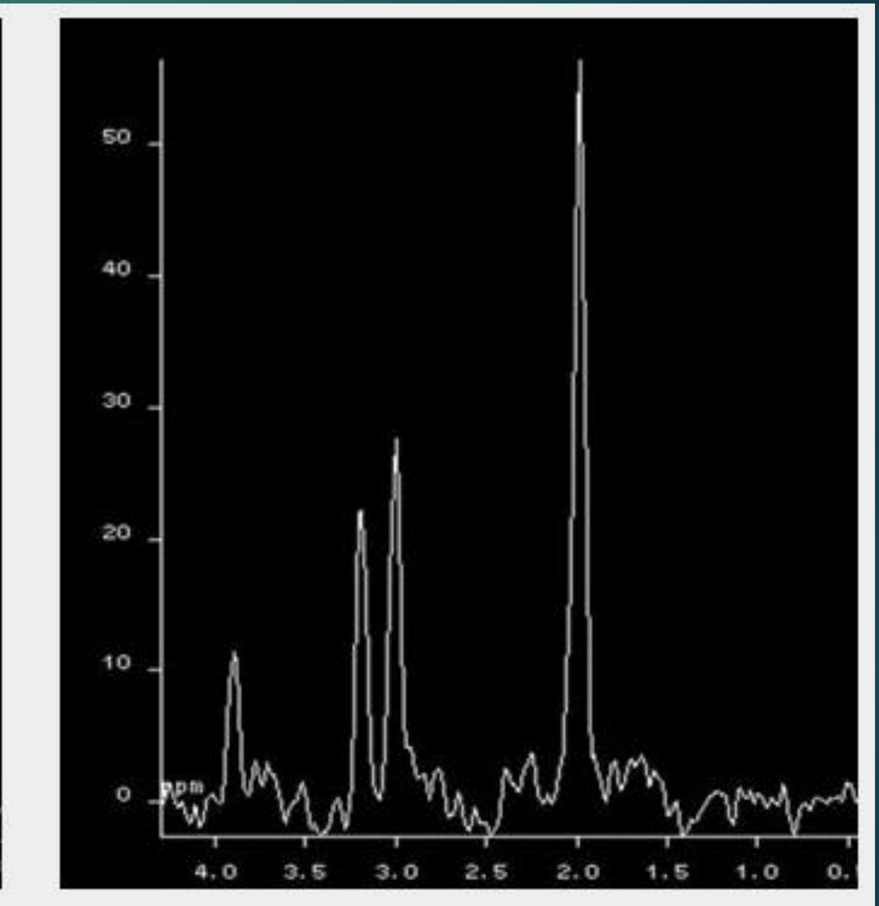


Effect of Repetition Time (TR)

TR = 1500 ms

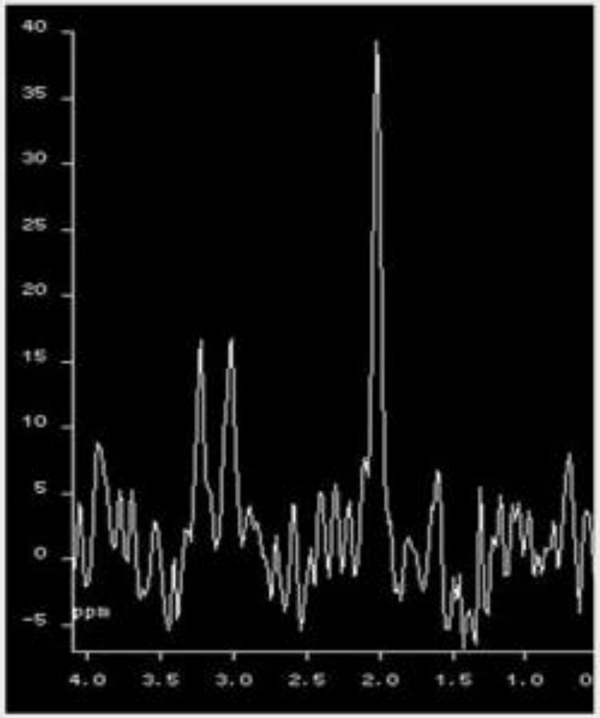


TR = 5000 ms

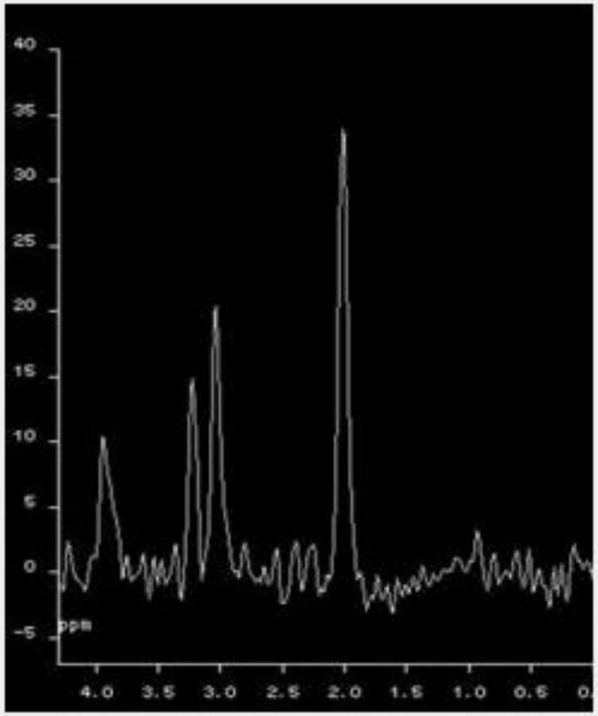


Effect of Signal Averaging

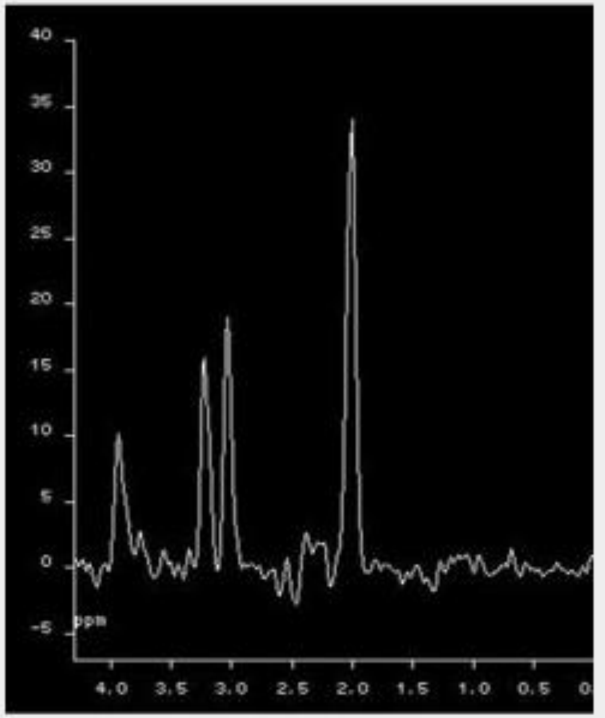
8 Averages



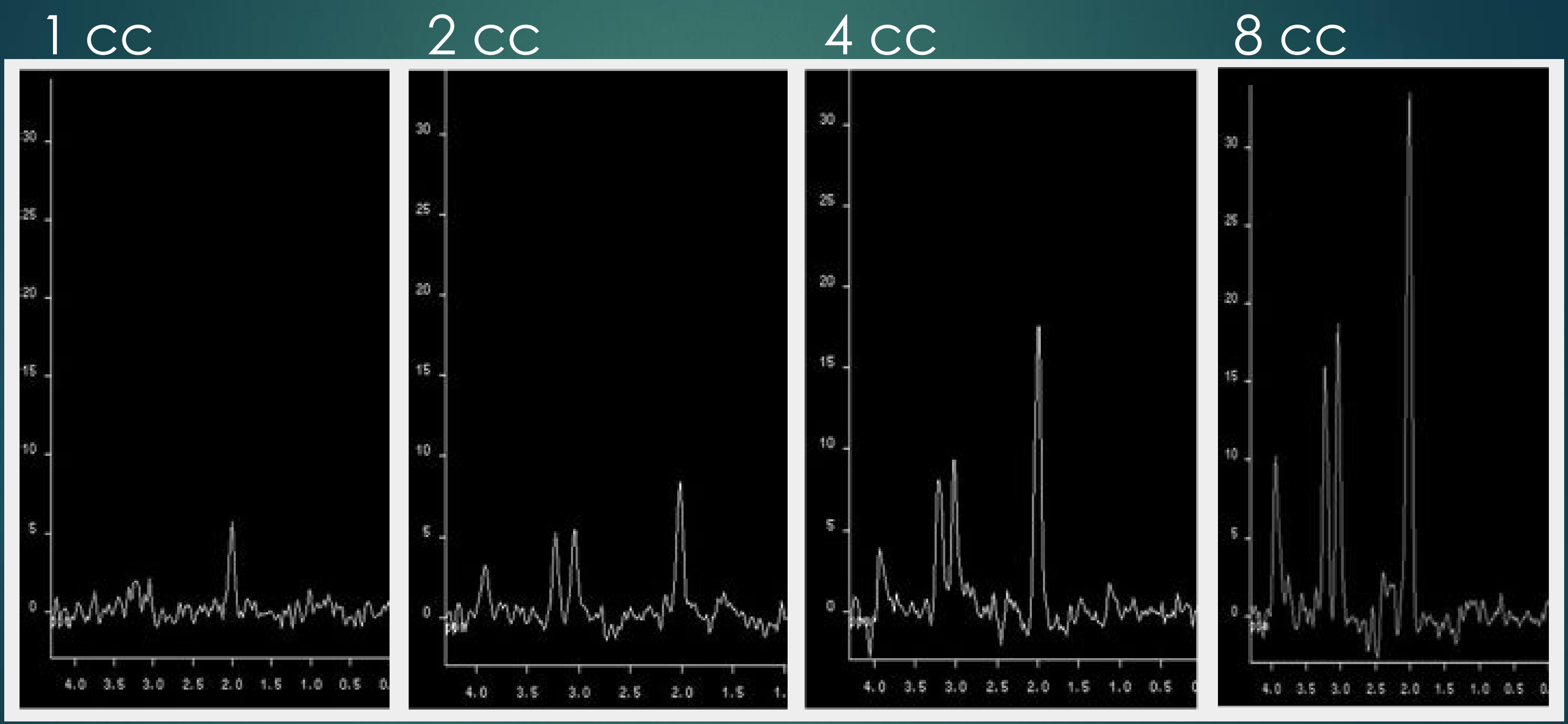
64 Averages



256 Averages

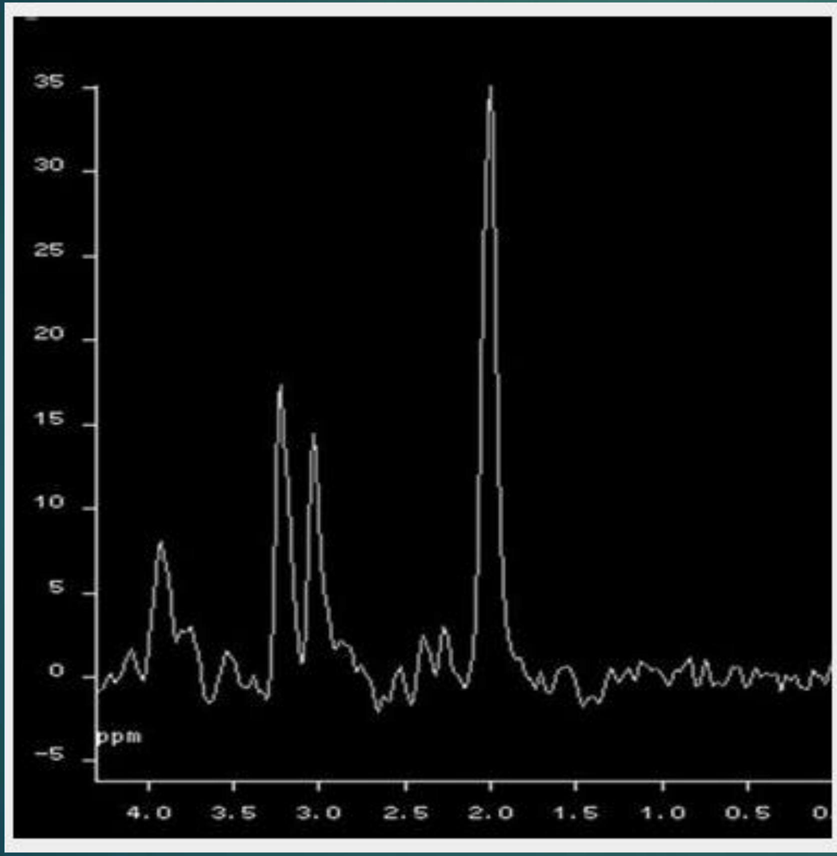


Effect of Voxel Size

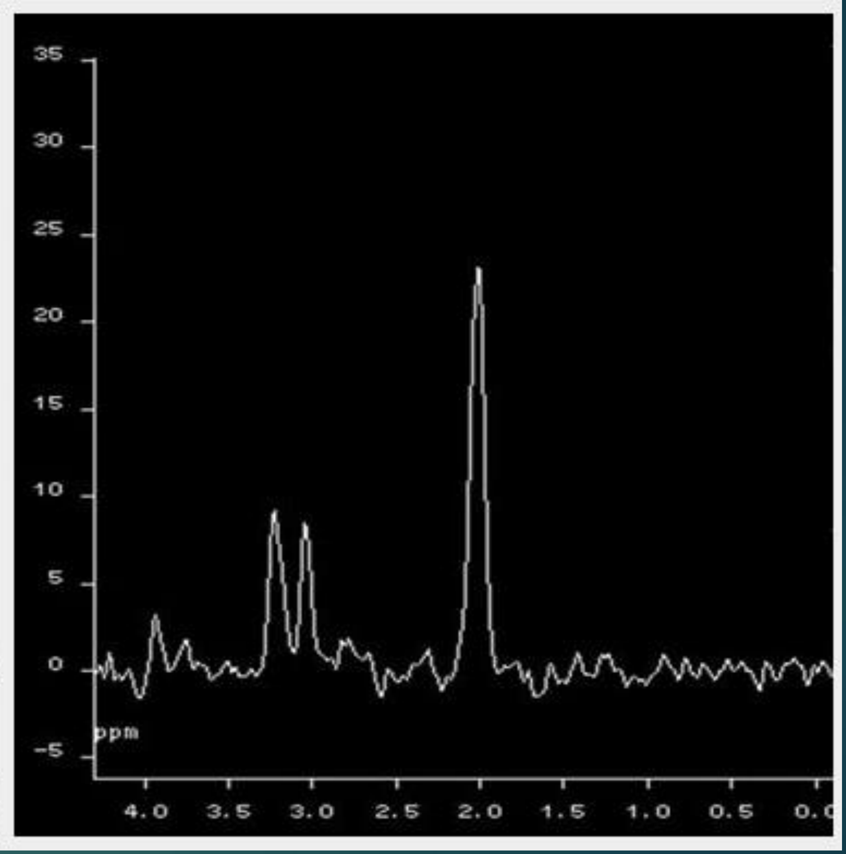


Effect of Echo Time, TE

TE = 144 ms

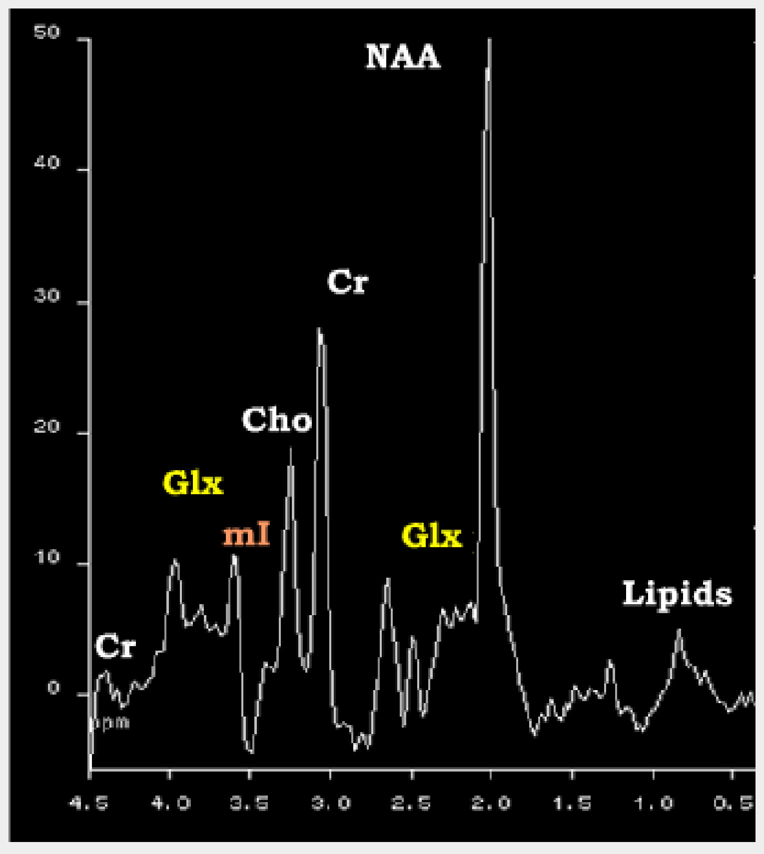


TE = 288 ms



Short TE ¹H Brain Spectrum

Healthy volunteer



Additional Peaks

Glx	2.05-2.45 ppm 3.6 - 3.8 ppm
mI	3.56 ppm
Glucose	3.43 ppm 3.8 ppm
And more	

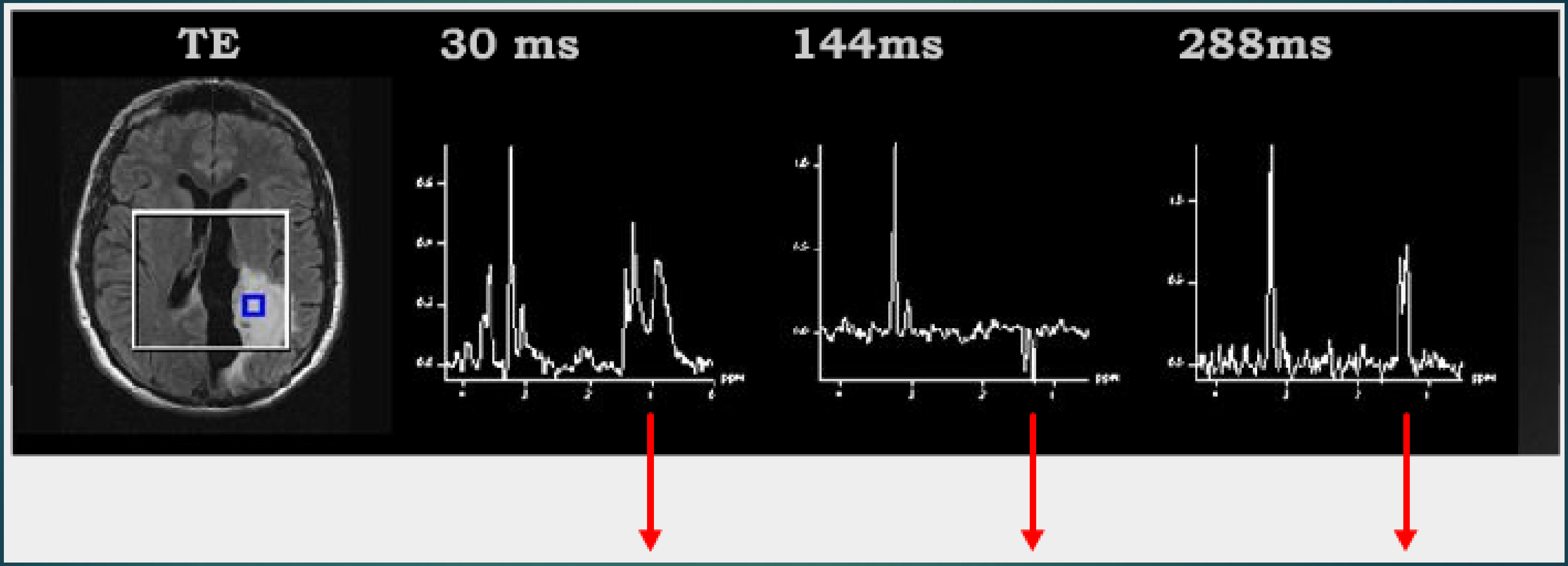
Table 2. Short-TE Neuro-MRS: Differential Diagnosis[1]

Metabolite (normal cerebral concentration)	Increased concentration	Decreased concentration
Myoinositol (mI) (5 mM)	normal neonatal brain, Alzheimer disease, diabetes mellitus, recovered hypoxia, hyperosmolar states	chronic hepatic encephalopathy, hepatic encephalopathy, stroke, neoplasms
Creatine (Cr) and Phosphocreatine (PCr) (8 mM)	head trauma, hyperosmolar states, increases with age	hypoxia, stroke, neoplasms, infant brain
Glucose (G) (1 mM)	diabetes mellitus, ? parenteral feeding, ?hypoxic encephalopathy	not detectable
Choline (Cho) (1.5 mM)	head trauma, diabetes, neonatal brain, post liver transplant, neoplasms, chronic hypoxia, hyperosmolar states, ? Alzheimer disease	asymptomatic liver disease, hepatic encephalopathy, stroke, nonspecific dementia
Aceto-acetate, acetone, ethanol, aromatic amino acids, propane-diol	detectable in specific settings	not detectable

[1] *Behavior of lactate, N-acetylaspartate, glutamate and glutamine same as in Table 1*

The Lactate Doublet

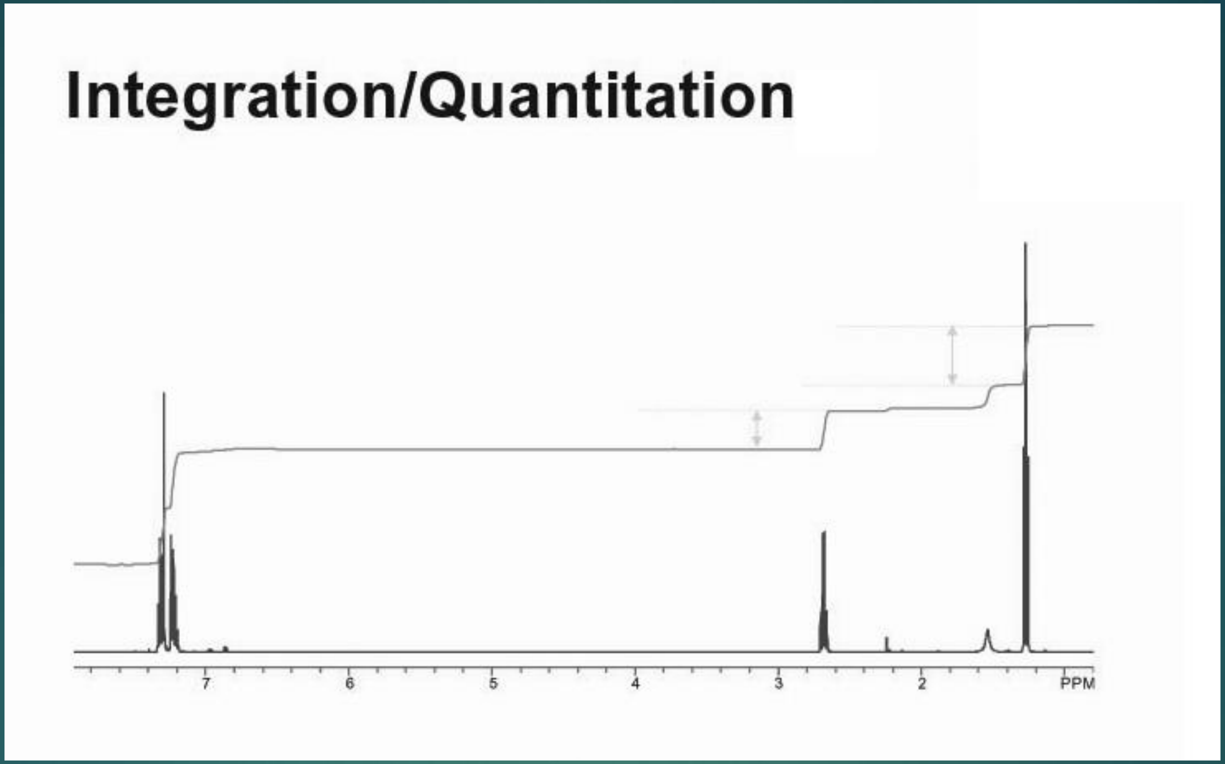
Tumor spectra: showing no NAA, ↑ Cho, ↑ mI, ↑ lactate



Lipids and lactate

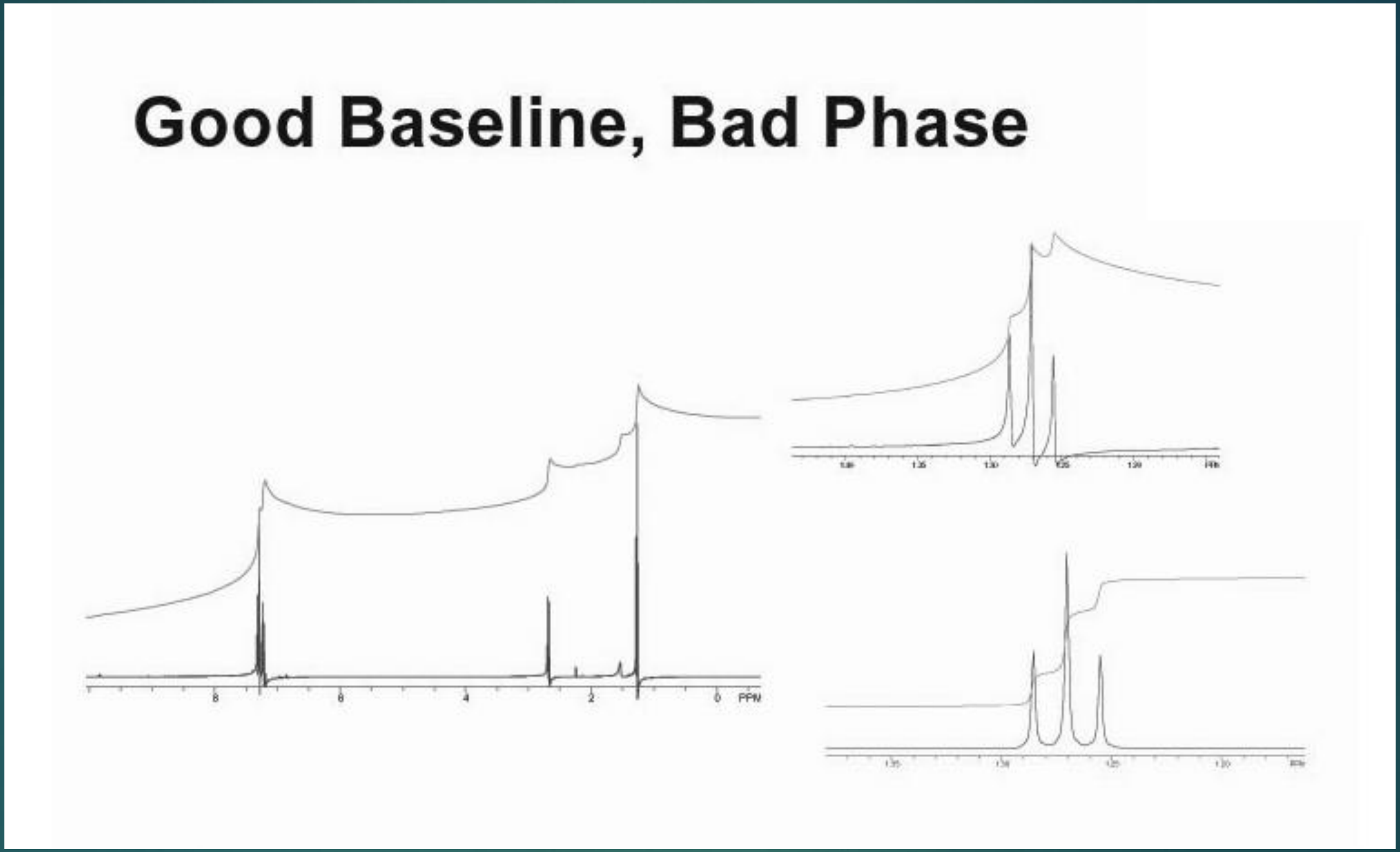
Inverted lactate

Upright lactate



When you have resonances which are not overlapping with each other then the integral (area) of the spectral resonances (peaks) can be used to calculate the number of protons under each peak.

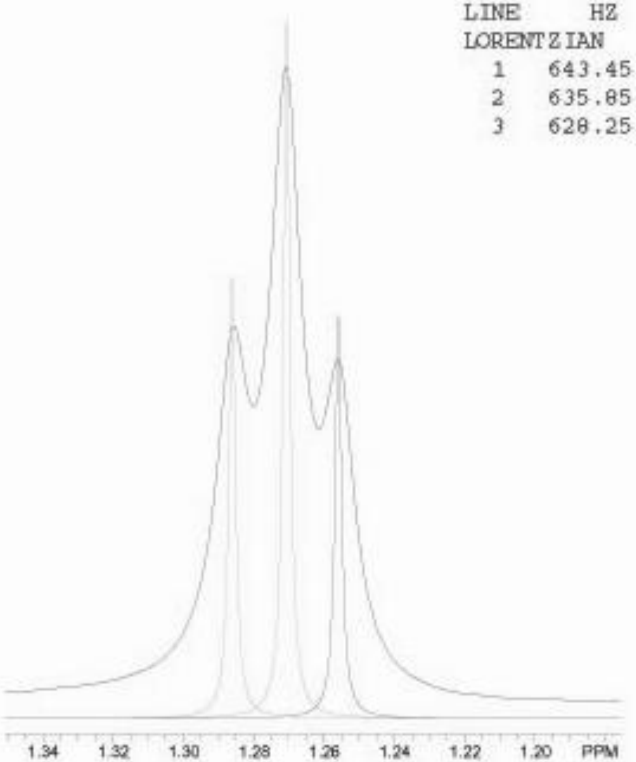
You need good baseline and correct phase

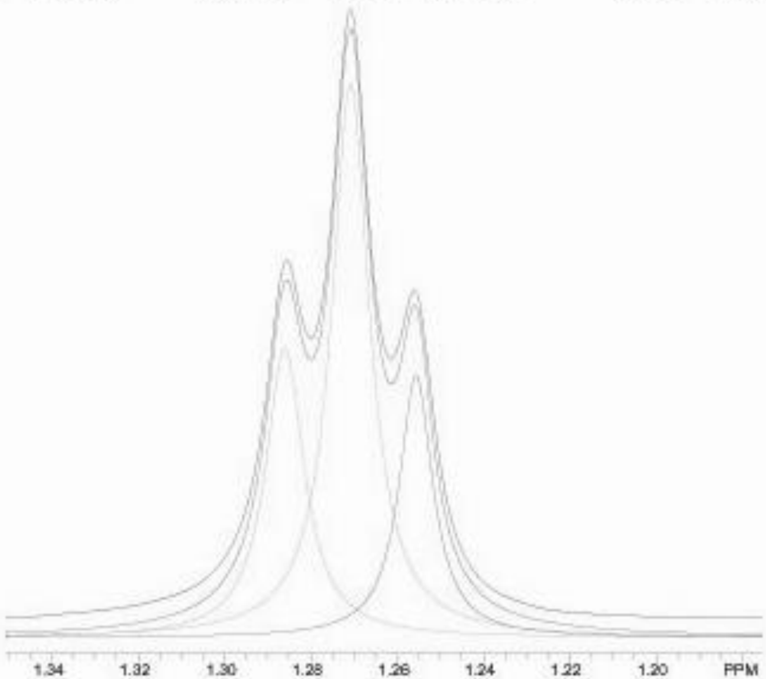


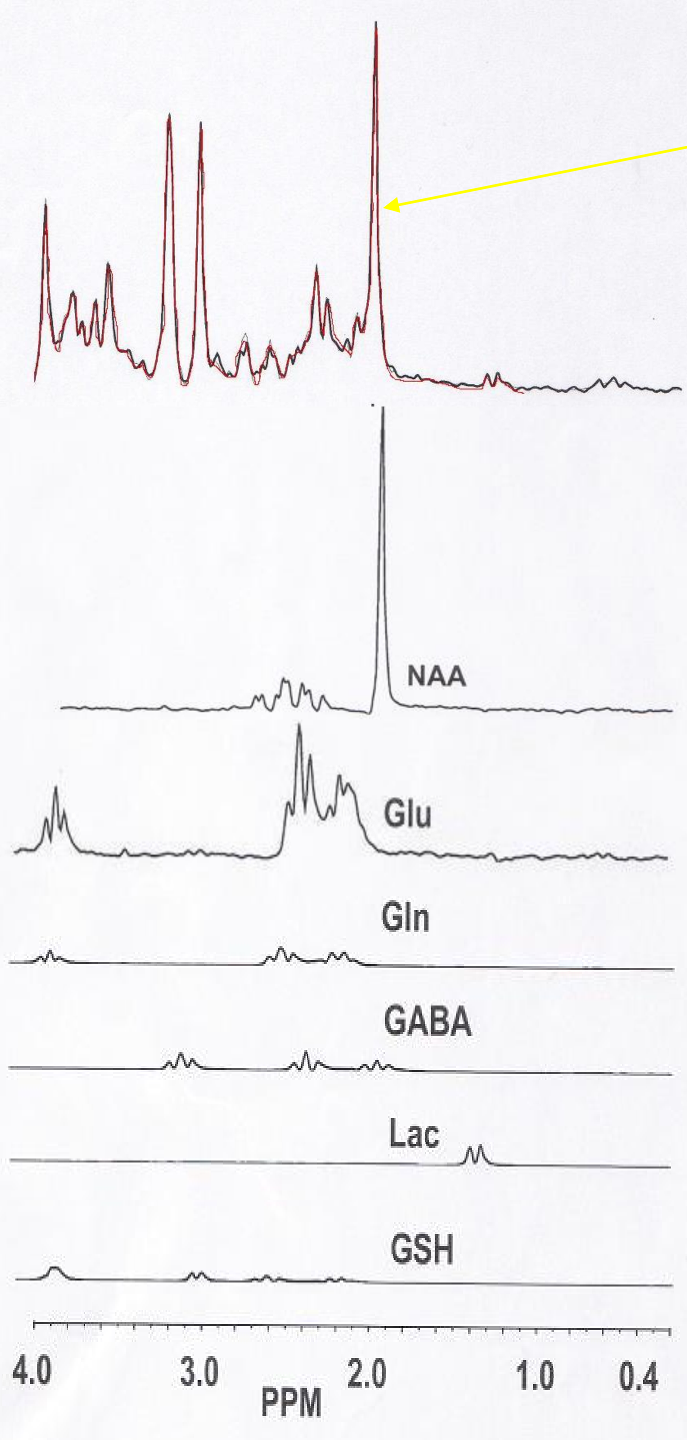
You need sophisticated spectral fitting algorithms for quantification

Deconvolution...line-fitting

LINE	HZ	PPM	HEIGHT	REL_HT	WIDTH	AREA	REL_AREA	FRACTION
LORENTZIAN								
1	643.45	1.286	720384	46.132	5.23	3766398	1.01	1.000
2	635.85	1.271	1395686	89.377	5.36	7481549	2.00	1.000
3	628.25	1.256	668149	42.787	4.97	3318865	0.89	1.000



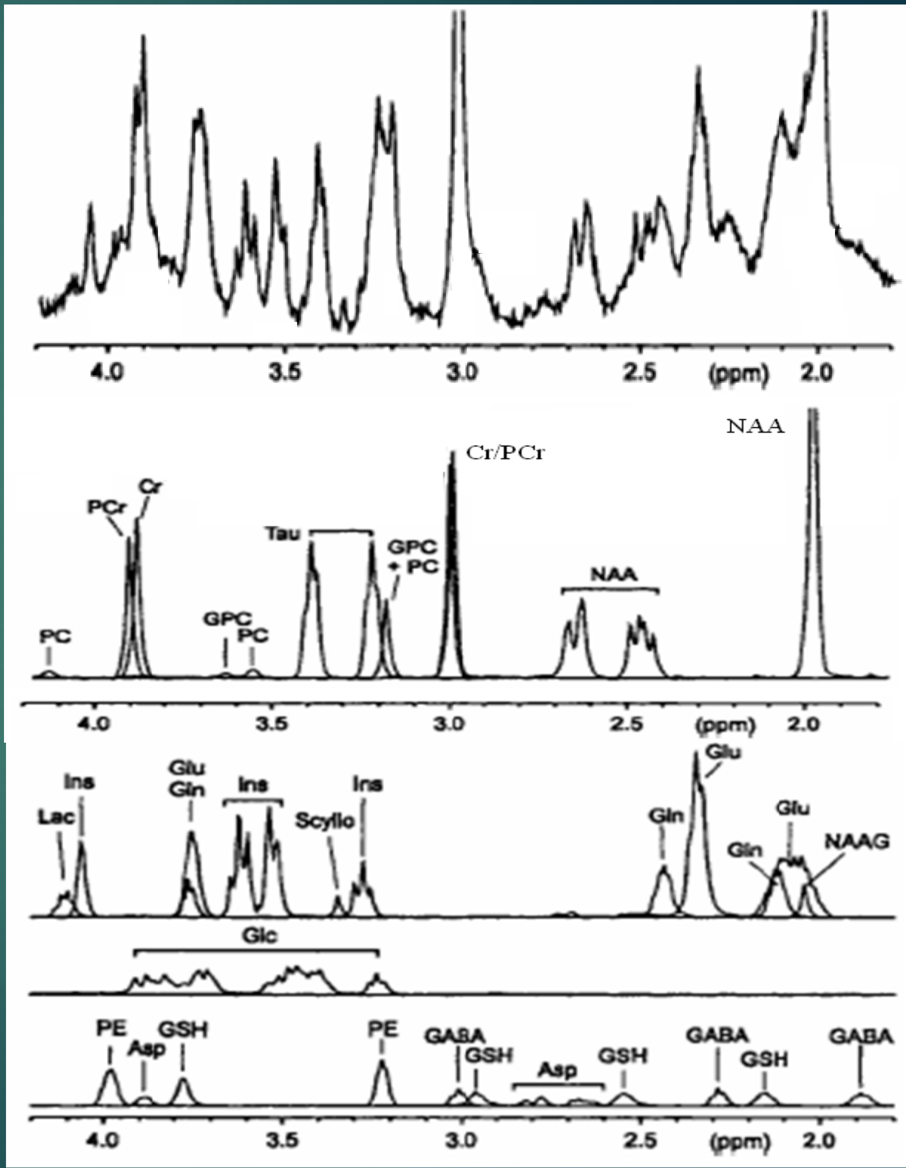


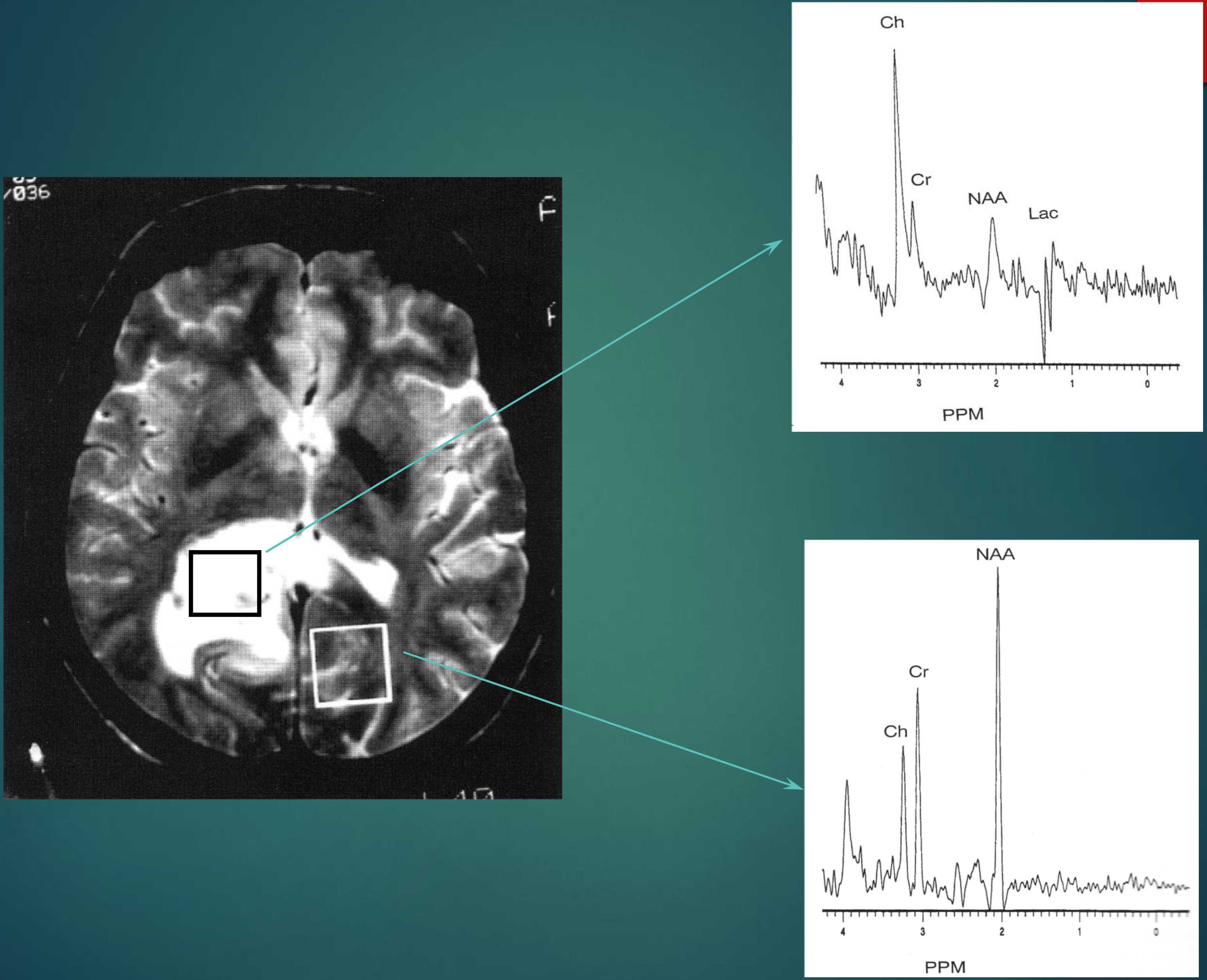

LCModel Fitting
NAA
Glu
Gln
GABA
Lac
GSH
4.0
3.0
2.0
1.0
0.4
PPM

1D MRS Quantitation

- LC-Model for 1D MRS quantitation.
- Works in frequency domain using prior knowledge

Provencher (2001)




Ch
Cr
NAA
Lac
4 3 2 1 0
PPM
NAA
Cr
Ch
4 3 2 1 0
PPM

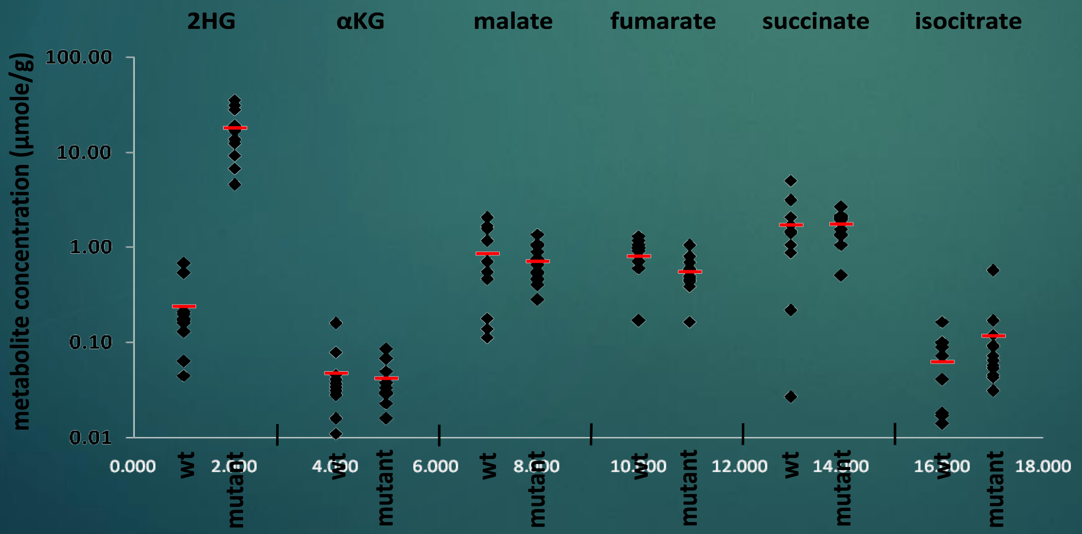
IDH1 R132H mutation and 2-HG

- Somatic mutations of the isocitrate dehydrogenase 1 and 2 genes (IDH1 and IDH2) have recently been implicated in gliomagenesis and are found in approximately 80% of World Health Organization (WHO) grade II-III gliomas and secondary glioblastomas (WHO grade IV) in humans.

- Vast majority of IDH1 mutant, high-grade gliomas have evolved from lower grade lesions.

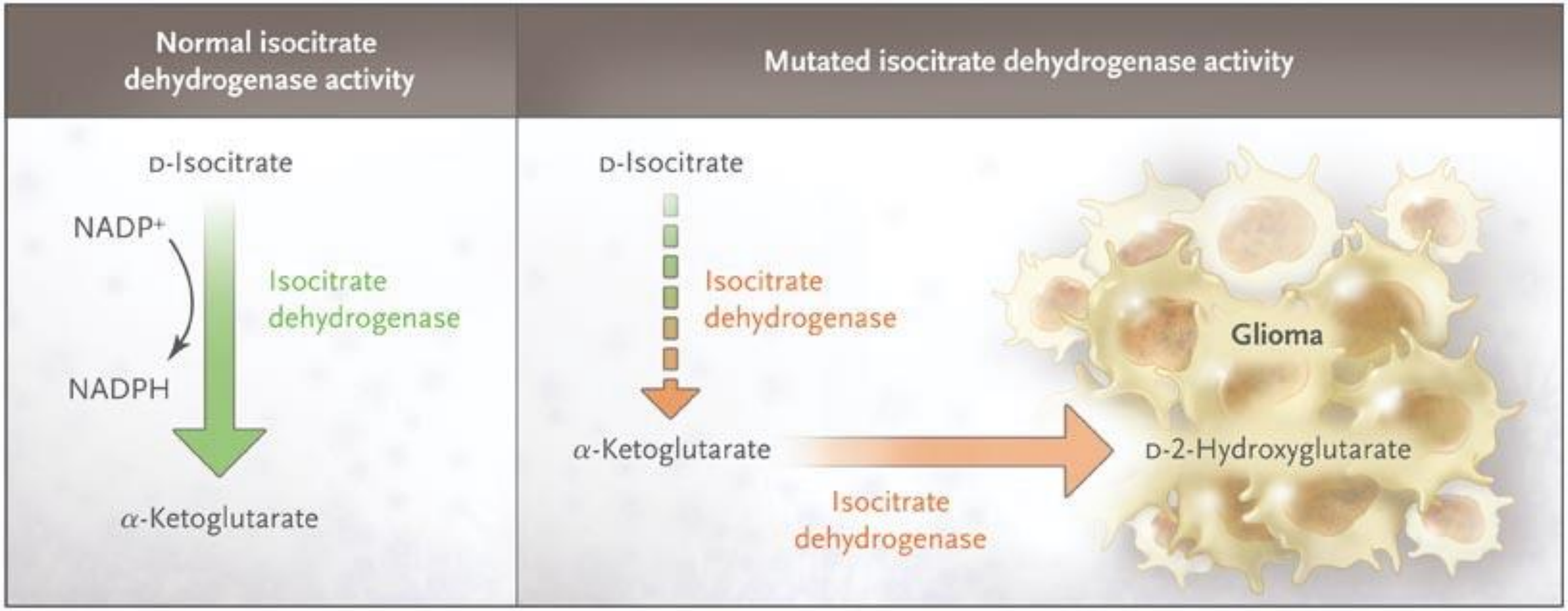
IDH1 R132H mutation and 2-HG

A recent work by Dang and co-workers reported a mutation observed in the isocitrate dehydrogenase1 (IDH1*)* gene, which occurs in the majority of grade II and grade III gliomas and secondary glioblastomas, resulting in significant elevation of 2HG in these tumors.



Dang et al. 2010, Nature

IDH1 R132H mutation produces 2-HG



Smeitnik, J. "Metabolism, Gliomas, and IDH1," N Eng J Med 362: 1144-45, 2010

Pope et al. 2012
Andrenosi et al. 2012
Elkhaked et al. 2012
Choi et al. 2012

Scanner : Siemens 3T Trio-Tim

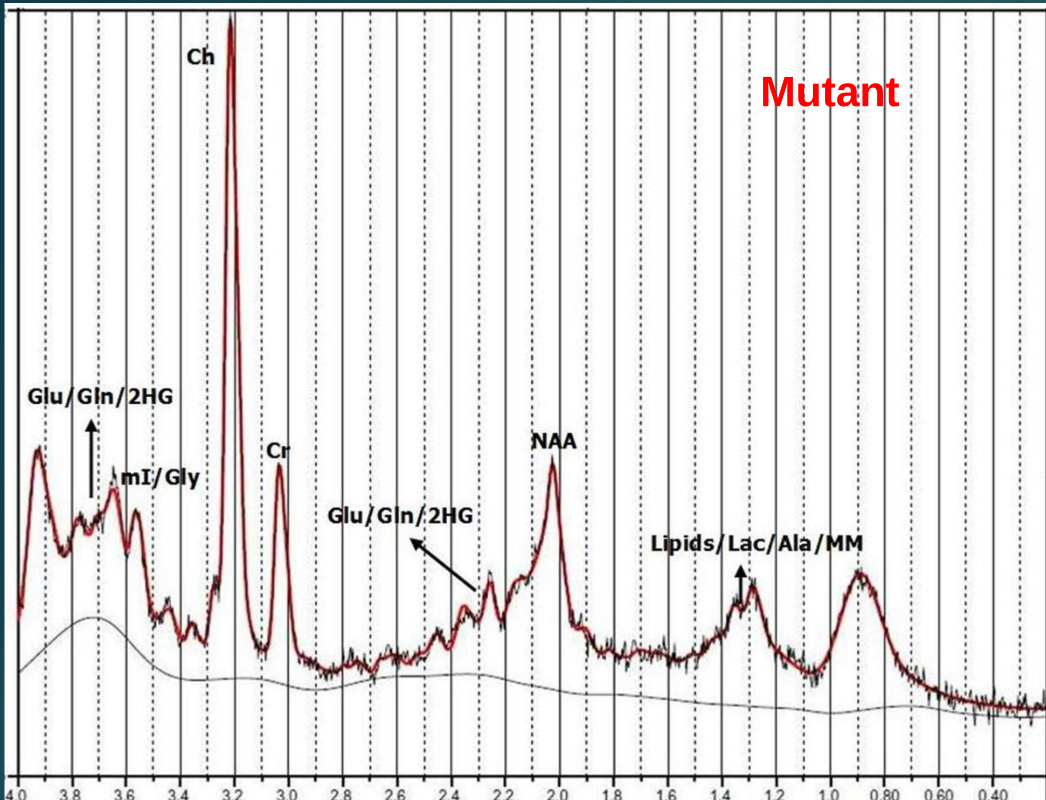
Coil : 12 Channel receive

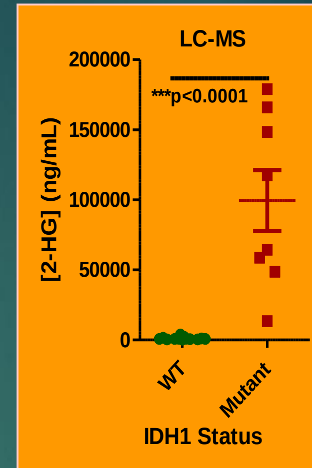
Subjects : 24 brain tumor

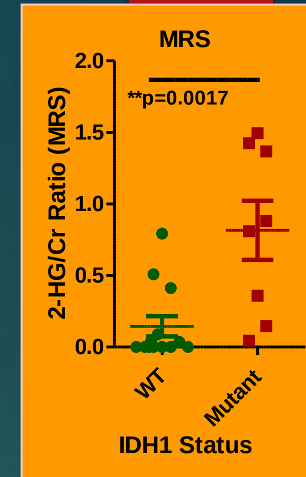
Mutant Tumor : 9 (Mean age 43 years)

Wild Tumor : 15 (Mean age 59 years)

Tumor Grade : 14 primary GBM (grade IV), 6 oligodendroglioma (grade III), and 4 low grade (grade II)







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Non-invasive detection of 2-hydroxyglutarate and other metabolites in *IDH1* mutant glioma patients using magnetic resonance spectroscopy

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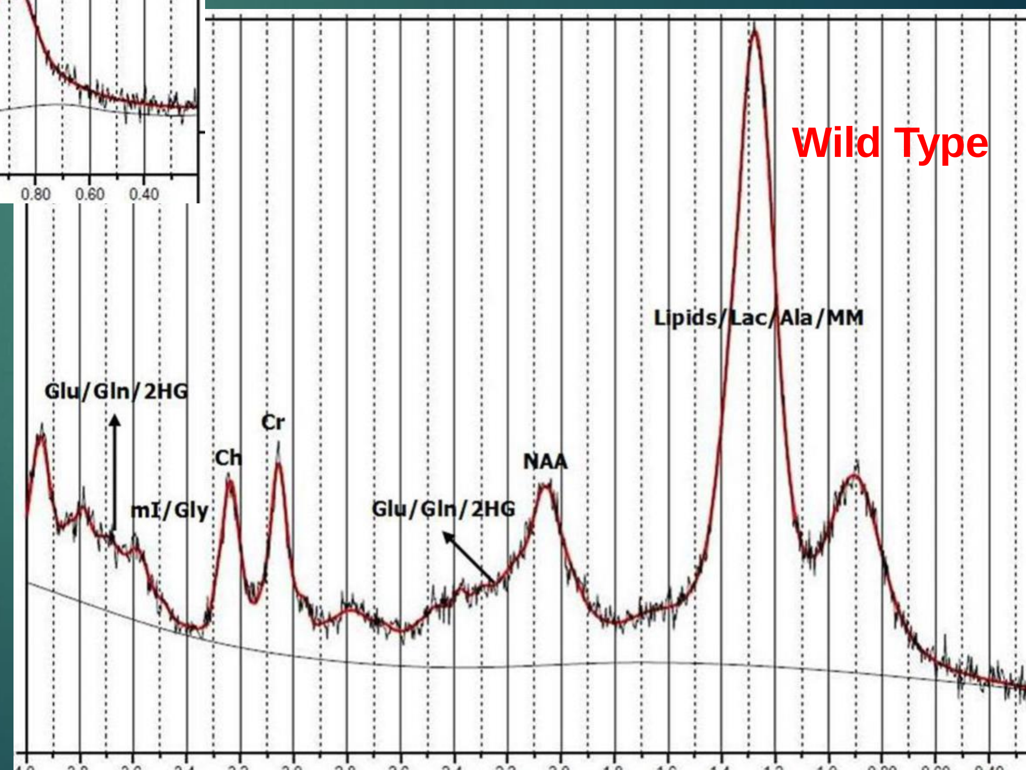
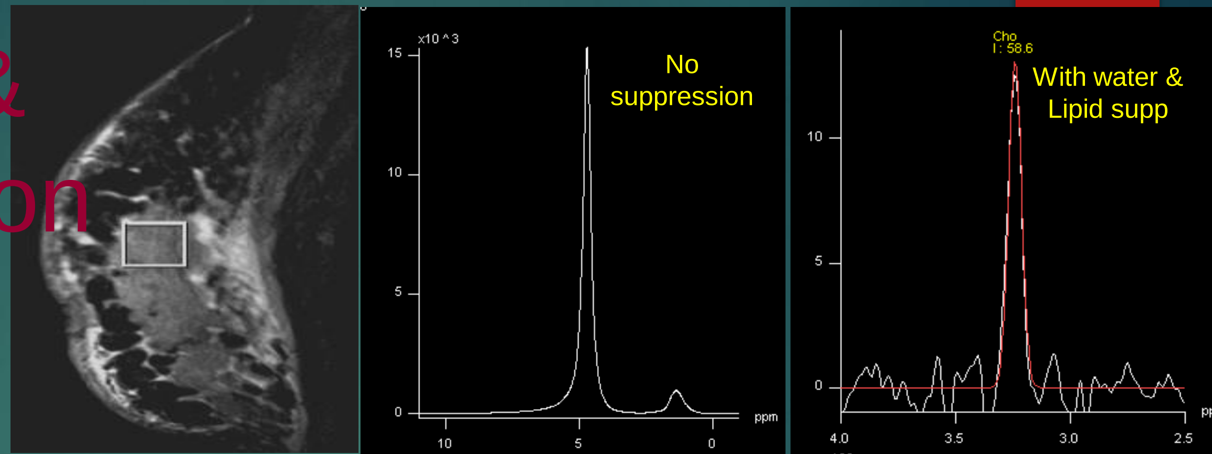
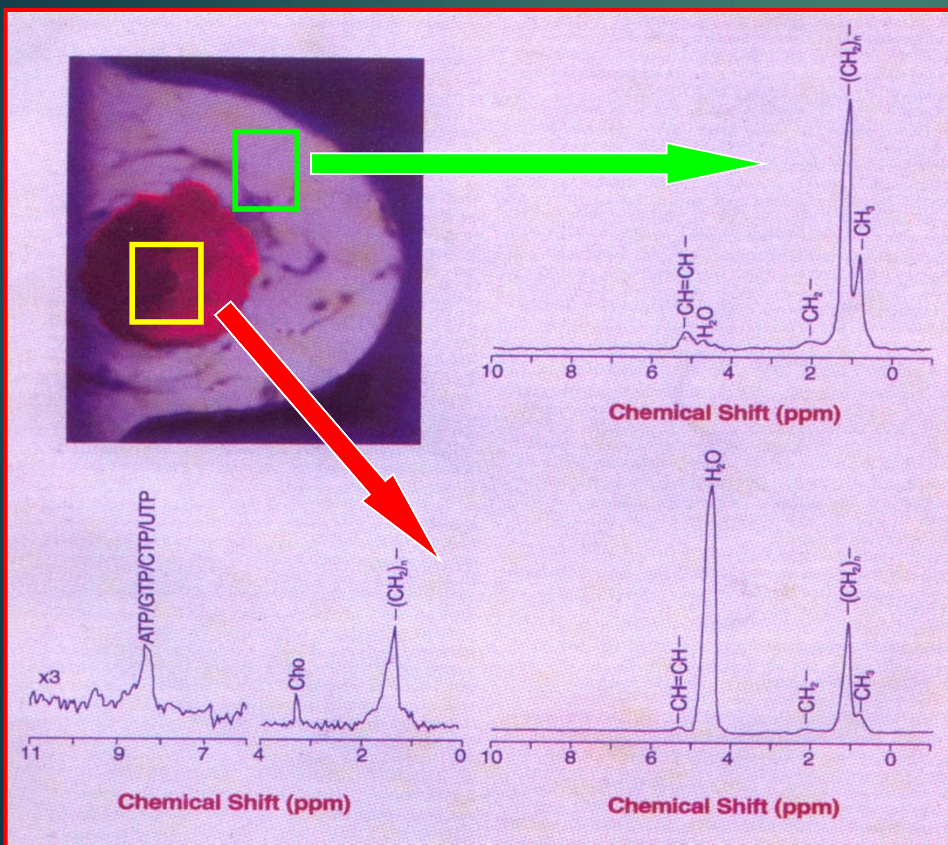


Single voxel MRS – Detection of tCho

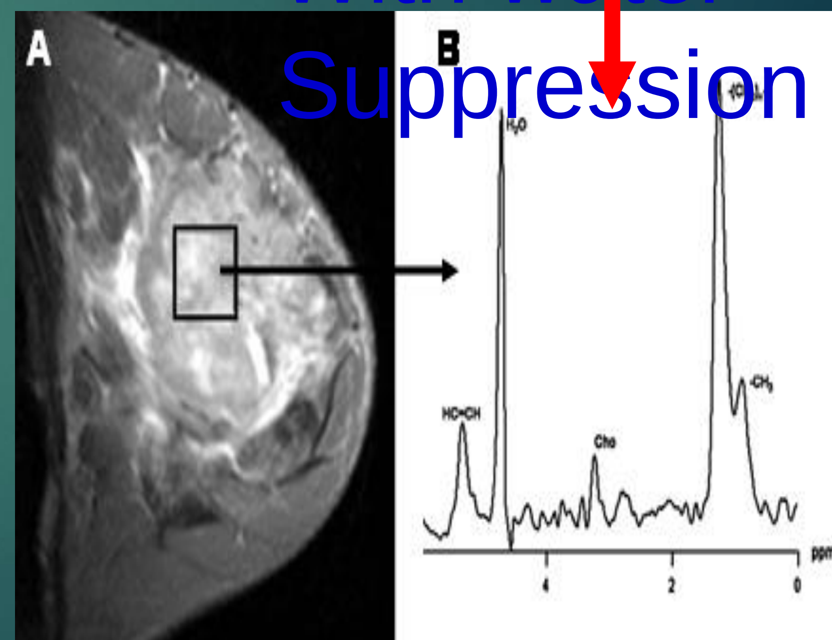
With water & fat suppression



Spectra from tumor & Normal portion with only Water suppression

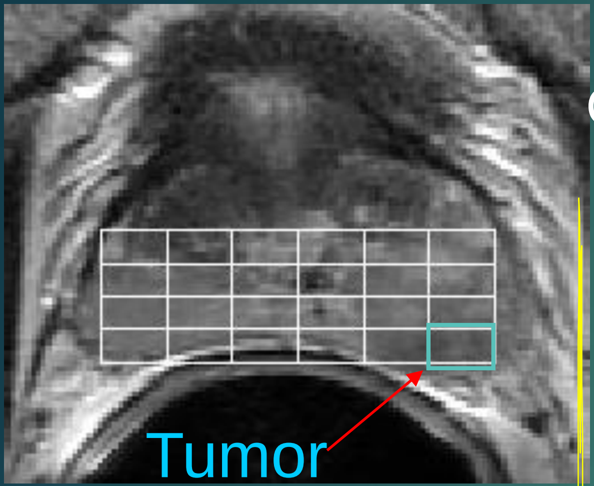


With water Suppression

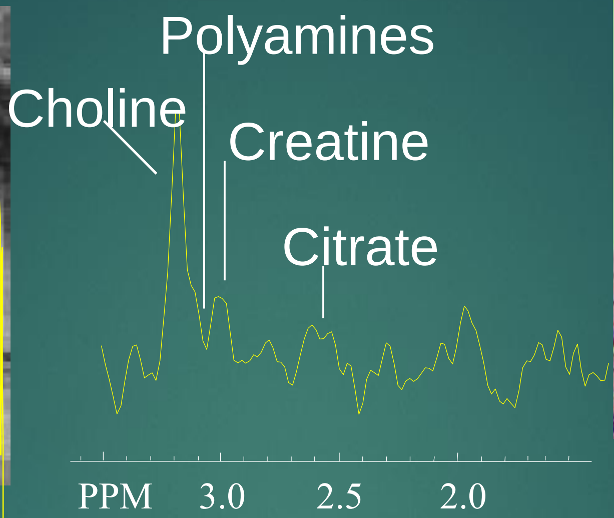


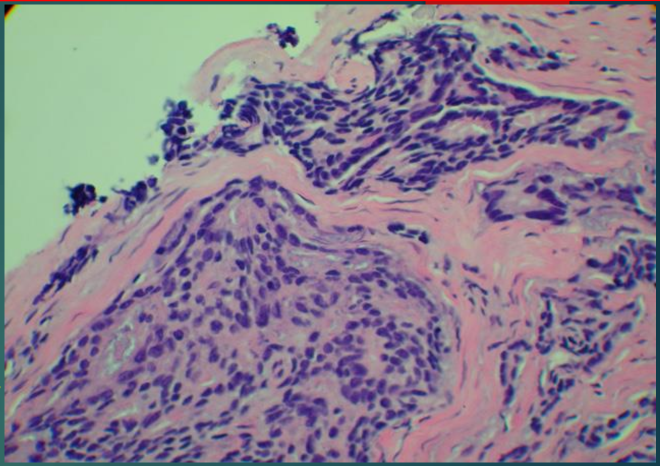
Jagannathan et al Br. J. Cancer 84; 1016-22, 2001

Malignant Prostate Metabolism



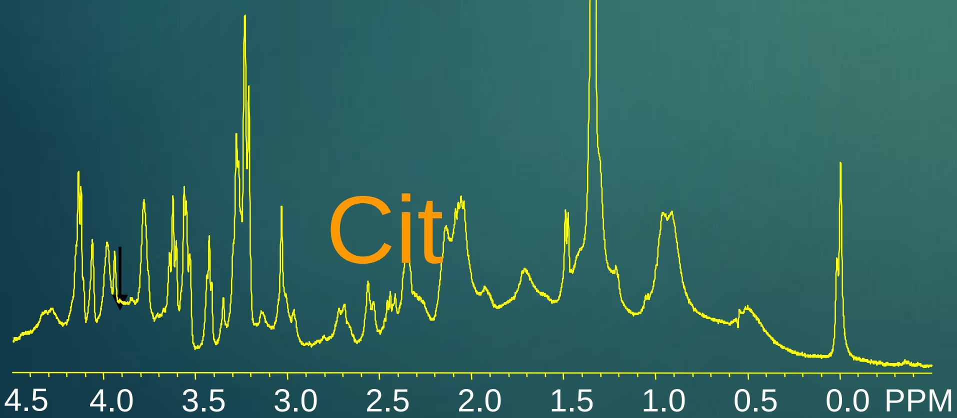
T2W MR image

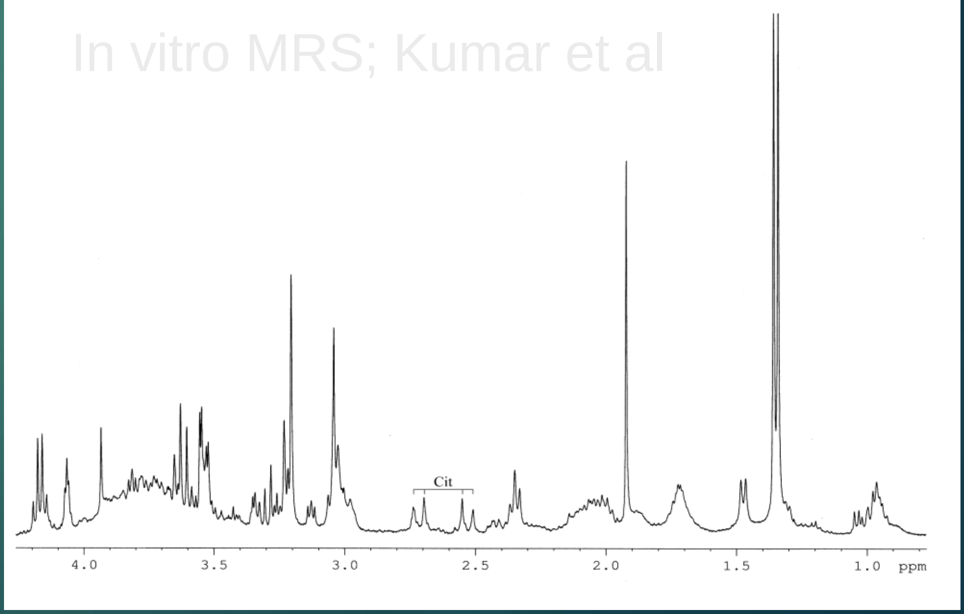




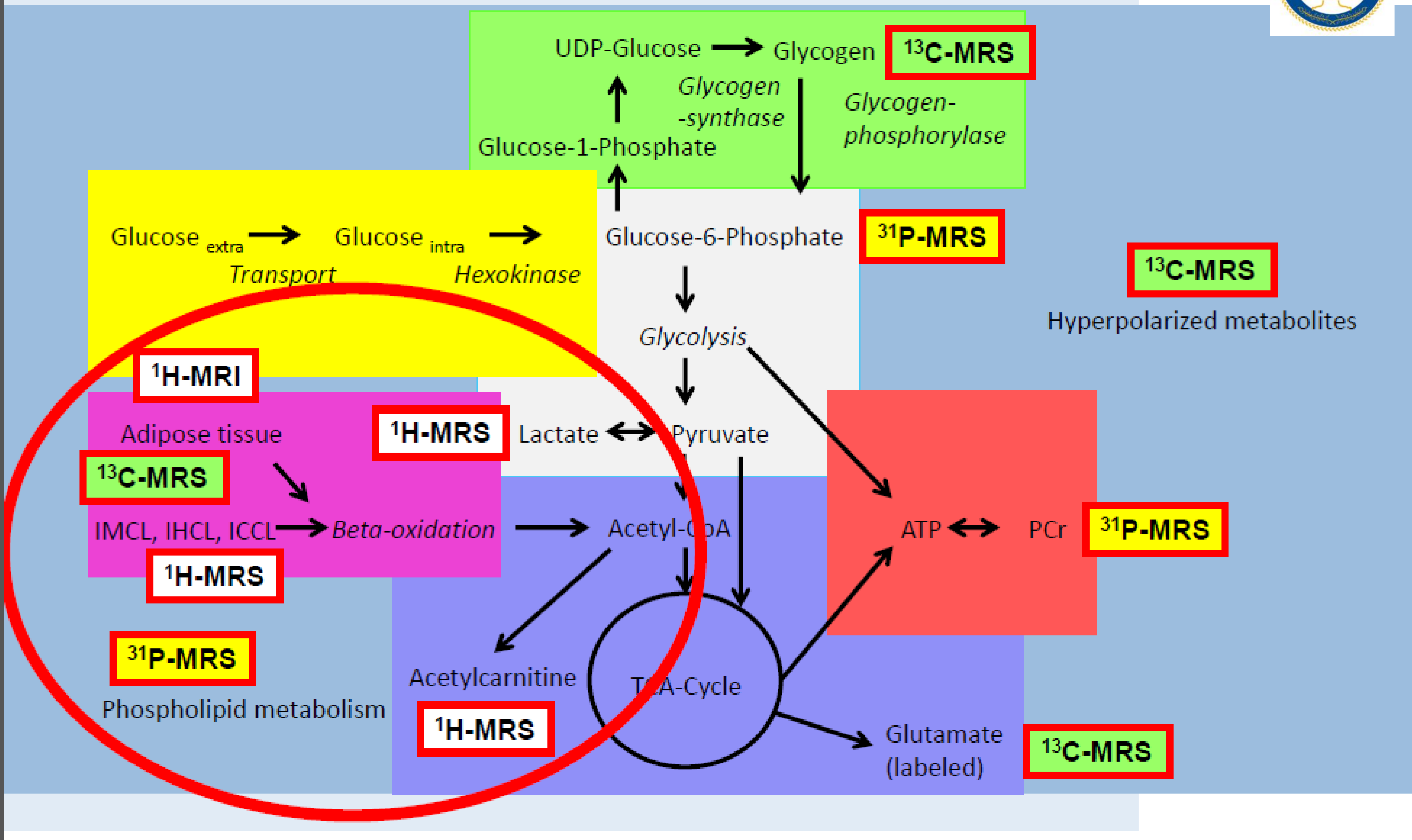
50% G(4+4), 50% HS

1D HR-MAS Spectrum (500 MHz)





Courtesy: Prof. John Kurhanewicz



UDP-Glucose
Glycogen
13C-MRS
Glycogen
-synthase
Glycogen-
phosphorylase
Glucose-1-Phosphate
Glucose extra
Glucose intra
Transport
Hexokinase
Glucose-6-Phosphate
31P-MRS
13C-MRS
Hyperpolarized metabolites
Glycolysis
1H-MRI
Adipose tissue
1H-MRS
Lactate
Pyruvate
13C-MRS
IMCL, IHCL, ICCL
Beta-oxidation
Acetyl-CoA
ATP
PCr
31P-MRS
1H-MRS
31P-MRS
Phospholipid metabolism
Acetylcarnitine
TCA-Cycle
1H-MRS
Glutamate
(labeled)
13C-MRS

UCLA

Important Nuclei for Biomedical MR

^{1}H – **Neurotransmitters, amino acids, membrane constituents**

^{2}H – **Perfusion, drug metabolism, tissue and cartilage structure.**

^{13}C – **Glycogen, metabolic rates, substrate preference, drug metabolism, etc.**

^{19}F – **Drug metabolism, pH, Ca^{2+} and other metal ion concentration, pO_2, temperature, etc**

^{23}Na – Transmembrane Na^{+} gradient, tissue and cartilage structure.

^{31}P – **Cellular energetics, membrane constituents, pH_i, [Mg^{2+}], kinetics of creatine kinase and ATP hydrolysis.**

Important Nuclei for Biomedical MR

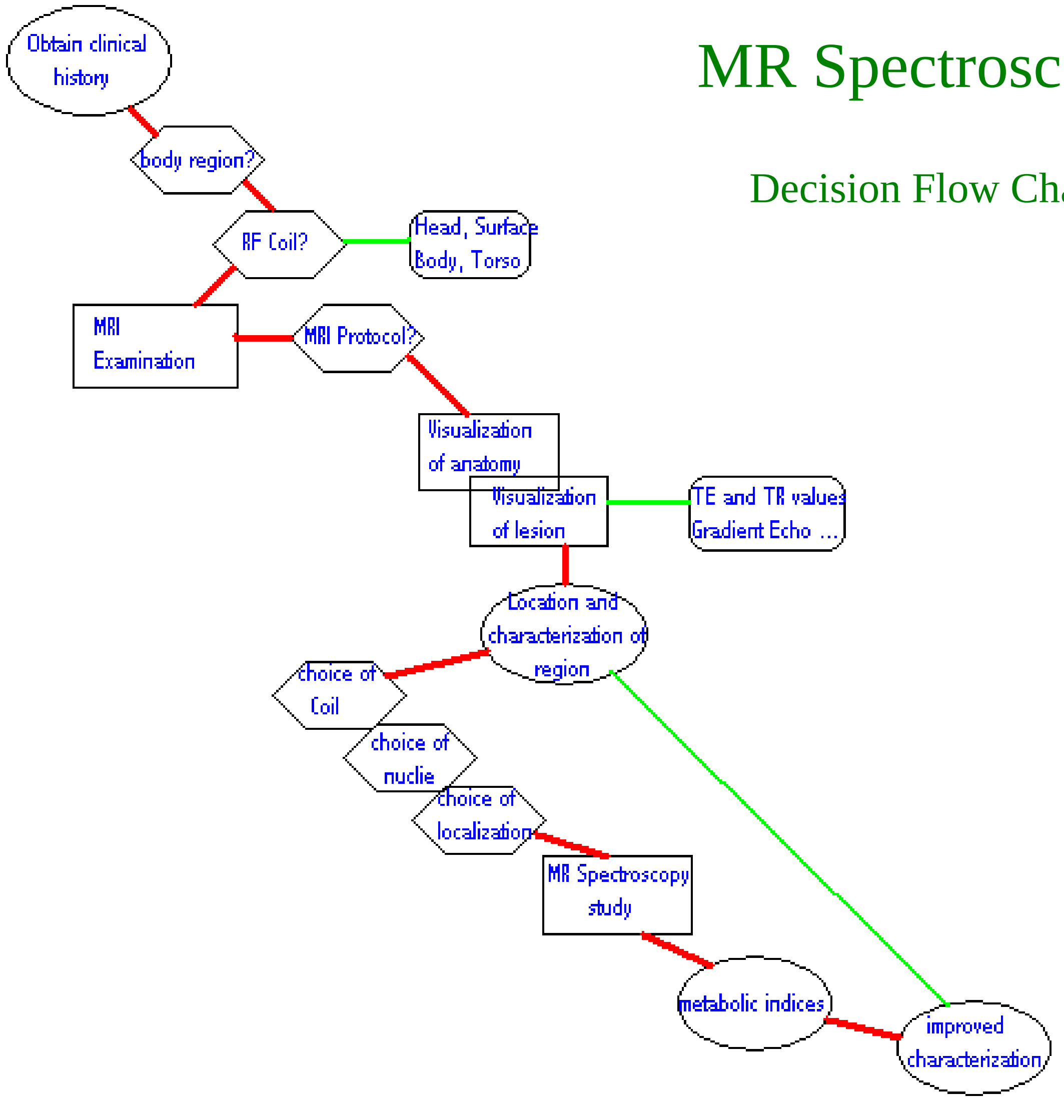
Nucleus	Spin	γ, MHz/T	Natural Abundance	Relative Sensitivity
^{1}H	1/2	42.576	99.985	100
^{2}H	1	6.536	0.015	0.96
^{3}He	1/2	32.433	.00013	44
^{13}C	1/2	10.705	1.108	1.6
^{17}O	3/2	5.772	0.037	2.9
^{19}F	1/2	40.055	100	83.4
^{23}Na	3/2	11.262	100	9.3
^{31}P	1/2	17.236	100	6.6
^{39}K	3/2	1.987	93.08	.05

How long it takes to perform a single voxel MR Spectroscopy?

Steps	Long ago	Now-a-days
Prescription	2-5 min.	1 min
Adjustment: frequency	2 min	2 min
Adjustment: shim	5-15 min	
Adjustment: suppression	5-10 min	
Acquisition	4-16 min	2-8 min
Data reconstruction	10 min	1 min

MR Spectroscopy

Decision Flow Chart




Thank You