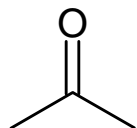


Nuclear magnetic resonance spectroscopy

nuclear spin transitions



^1H , ^{13}C , 2-dimensional

- which transitions?

wavelength and intensity; ppm

- what happens if we change the environment of the nucleus?

substituent effects on the chemical shift, ...

- prediction of a chemical shift

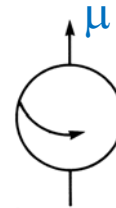
Reading:
Pavia
Chapter 5.1-5.7

1. General

- region of radio frequency: least energetic radiation
- absorption leads to a nuclear spin transition

nucleus (e.g. ^1H): - charged particle

- has angular momentum (behaves like a spinning particle)
- creates a magnetic field
- has a magnetic moment, μ



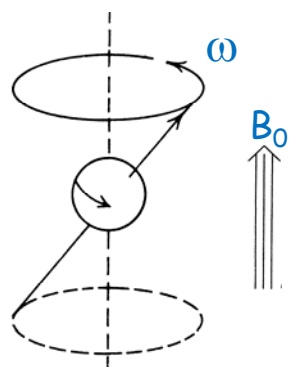
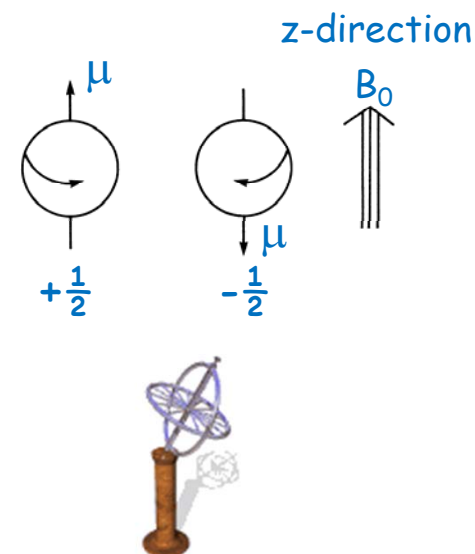
- has a spin quantum number, I (for ^1H , $I = \frac{1}{2}$)
- has allowed spin states $2I + 1$ (e.g. two for ^1H , $+\frac{1}{2}$ and $-\frac{1}{2}$)
 - states are degenerate
 - \Rightarrow spin transition not possible
 - \Rightarrow need to remove degeneracy to get an NMR signal

1. General continued

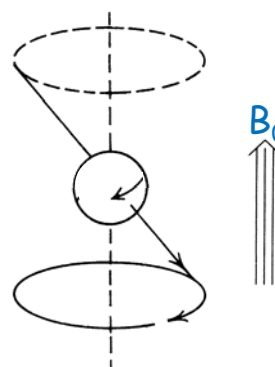
to get an NMR signal

- need to apply an external magnetic field, B_0
- ⇒ leads to two orientations: parallel and antiparallel
- ⇒ μ -vector rotates about the z-direction:

precession, with Larmor frequency, ω

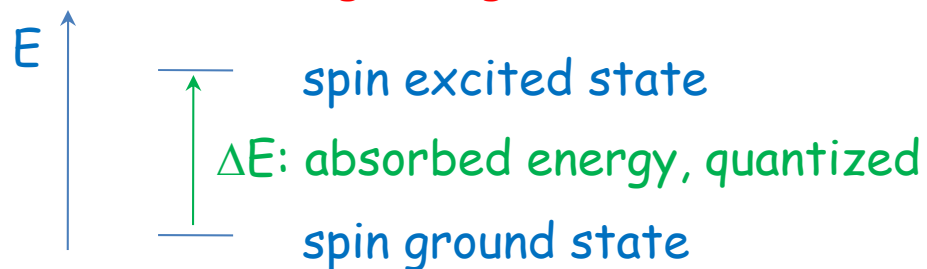


state $I = +\frac{1}{2}$
 - parallel with external field
 - lower E state



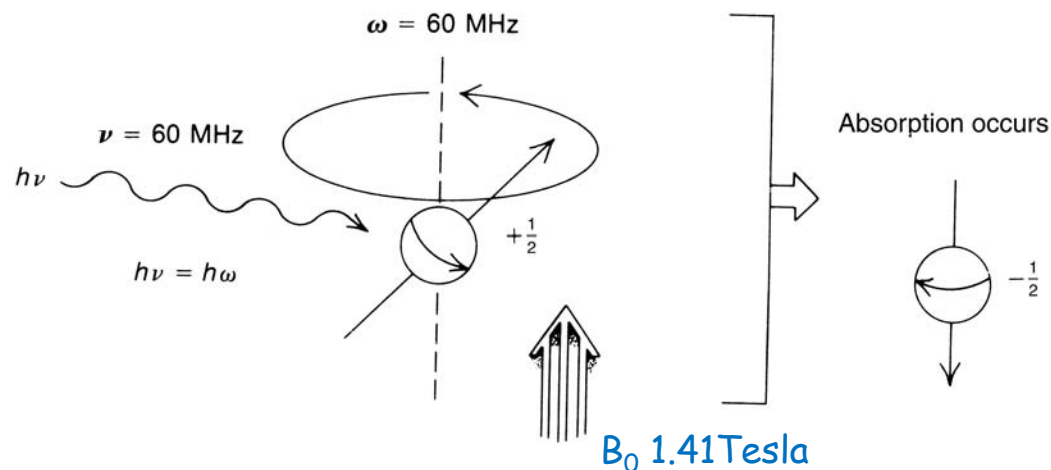
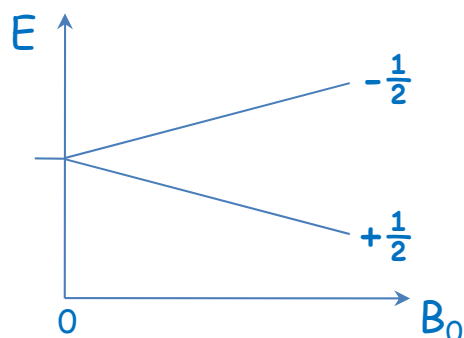
state $I = -\frac{1}{2}$
 - against external field
 - higher E state

⇒ states are no longer degenerate



1. General continued

ΔE depends on B_0 , $E = f(B_0)$



more precisely,

$$E = h\nu = \gamma \frac{h}{2\pi} B_0$$

γ : gyromagnetic ratio, constant for a nucleus see Table 5.2

$$\nu = \omega = \frac{\gamma}{2\pi} B_0$$

^1H γ 267.53

^{13}C γ 67.28

^{19}F γ 251.7

unit: radians/T

resonance condition: for ^1H :

B_0 1.41 T \Rightarrow ω 60 MHz, ν 60 MHz

B_0 7.05 T \Rightarrow ω 300 MHz, ν 300 MHz

$\lambda?$

1. General continued

Problem: ΔE is very small: at 1.41 T, ΔE is ≈ 0.02 J/mol

Question: How large is the energy gap needed (let's say at 60 MHz) and what does that imply for the population of the two states?

$$E = h\nu = 6.624 \cdot 10^{-34} \text{ Js} \cdot 60 \cdot 10^6 \text{ s}^{-1} = 3.9744 \cdot 10^{-26} \text{ J}$$

$$\begin{array}{l} \text{upper level} \longrightarrow N_u \\ \text{lower level} \longrightarrow N_l \end{array} \longrightarrow \frac{N_u}{N_l} = e^{-\frac{\Delta E}{kT}} = e^{-\frac{3.96 \cdot 10^{-26} \text{ J}}{1.38 \cdot 10^{-23} \text{ J/K} \cdot 298 \text{ K}}} = 0.9999904 \approx \frac{1,000,000}{1,000,010}$$

↑
Don't miss the negative sign!

read:

⇒ only a very small overpopulation of the lower level

⇒ poor signal strength

Solution: use stronger magnets

2. Spectrometer

Solution: use stronger magnets

300 MHz



600 MHz



900 MHz



1 GHz NMR (2009, Lyon)
23.5 T
4.5 m
12 tonnes

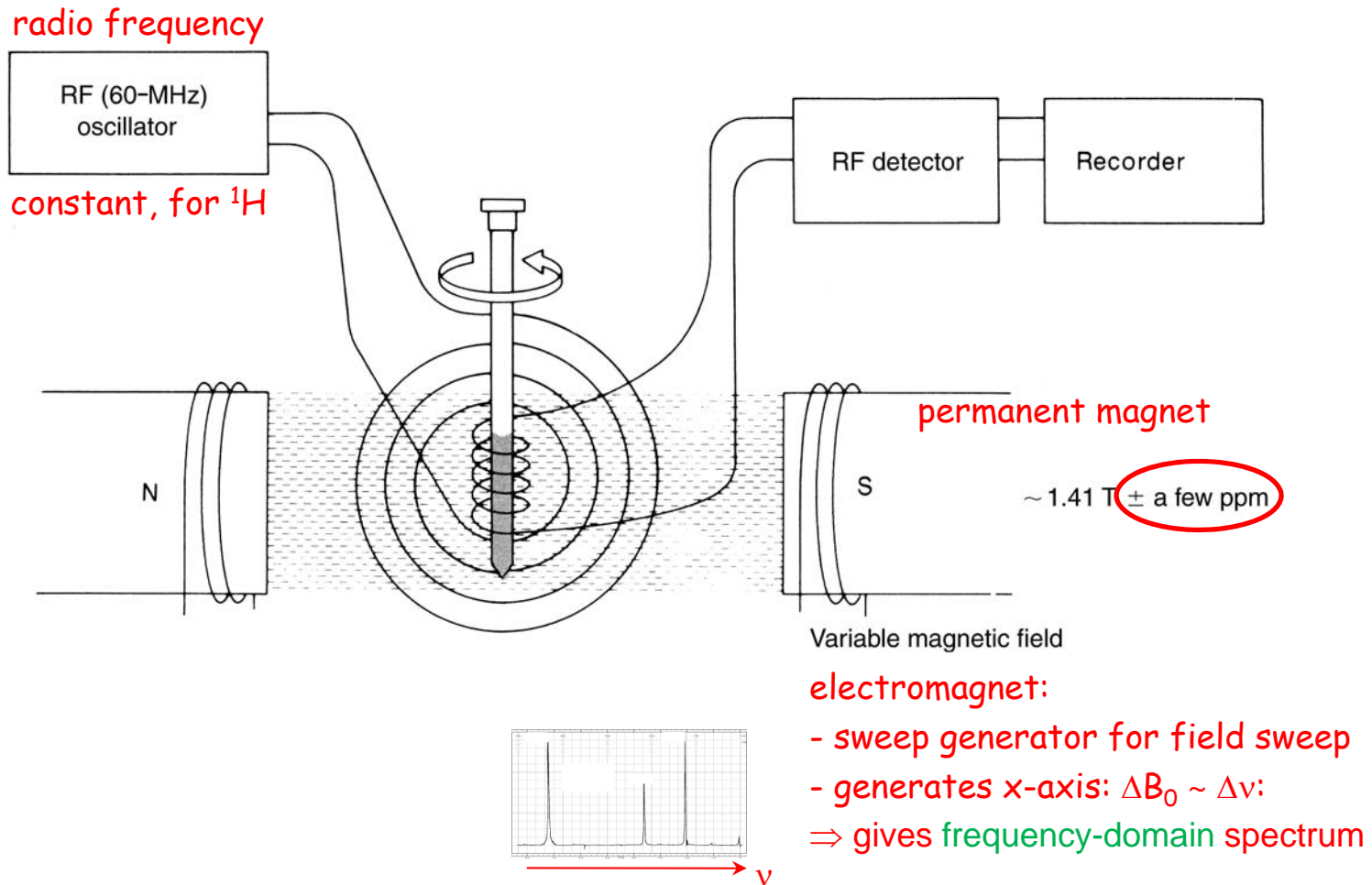


<http://www.tcu.edu>
<http://www.chemie.tu-berlin.de>
<http://nmrresource.ucsd.edu>

2. Spectrometer continued

Continuous-wave (CW) NMR spectrometer

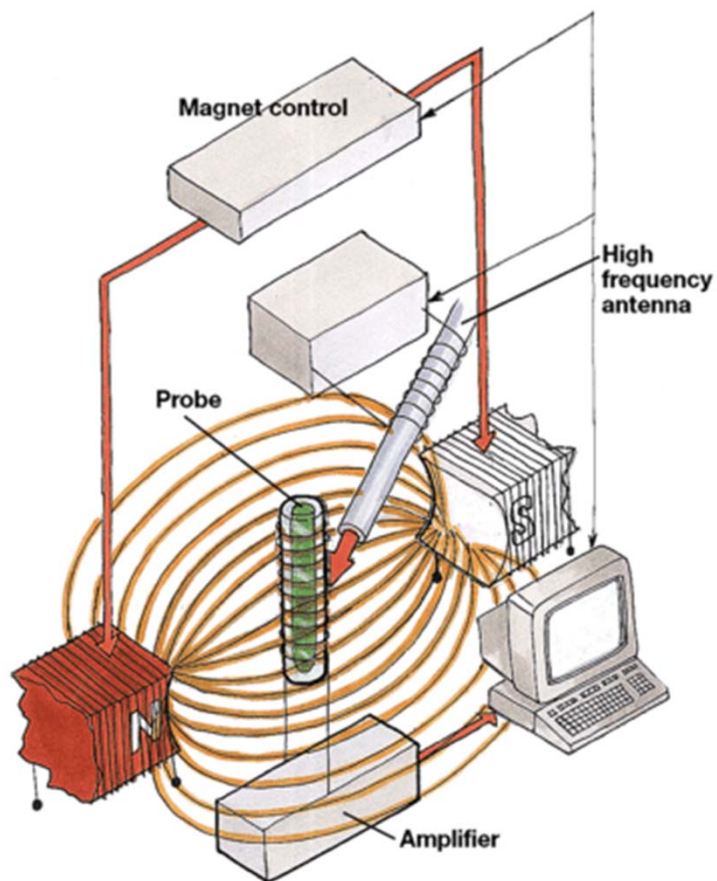
- field-sweep at constant frequency



also possible: opposite configuration: frequency-sweep at constant field

2. Spectrometer continued

Fourier-transform (FT) NMR spectrometer



http://hiq.aga.cl/international/web/lg/spg/likegspg.nsf/docbyalias/anal_nmr

magnet: superconducting cryomagnet:

- cooled to $-269\text{ }^{\circ}\text{C}$ by $\text{He}_{(l)}$ that is cooled to $-196\text{ }^{\circ}\text{C}$ by $\text{N}_{2(l)}$
- for B_0 up to 23.5 T ($\sim 1000\text{ MHz}$ for ^1H)

The danger of the cryogenics:

- 600 MHz, maybe 60 L of $\text{He}_{(l)}$:  ~2 min

The danger of high field strengths:

- 60 MHz, only 1.5 T:  10 s  90 s

The 5-G line safety:



https://www.youtube.com/watch?v=tPqduF5xB-o&index=4&list=PLYwOwW_K_SUUFetmnSVezDqIhiJ6RyA_

<https://www.youtube.com/watch?v=7g5UVrOt2CI>

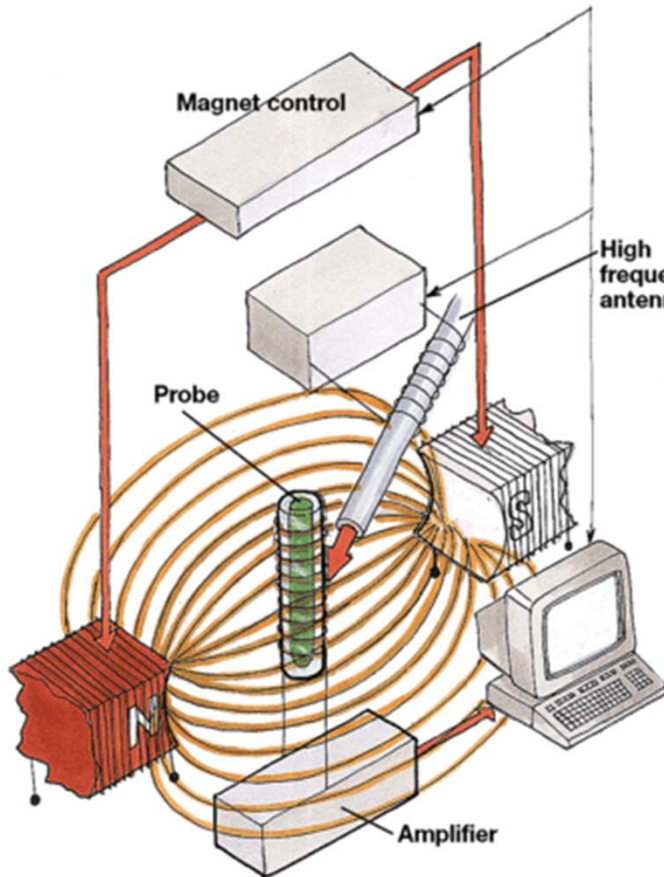
<https://www.youtube.com/watch?v=byRIwDk21sw>

http://voo-mokinha.blogspot.ca/2011/02/really-really-nerdy-stuff_02.html

2. Spectrometer continued

Fourier-transform (FT) NMR spectrometer

Advantage? Disadvantage?



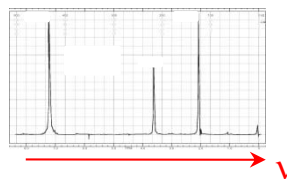
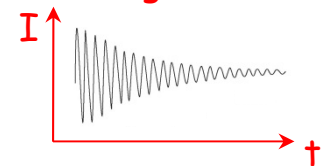
provides RF pulse:

- short (μs), intense burst ("pulse")
- wide enough to cover the spectrum for a certain type of nucleus
- all these nuclei are excited at once
- all these nuclei relax to the ground state after the pulse

records the emission and its decay: a time-domain signal ("FID": free induction decay signal)

⇒ Fourier-transform

⇒ frequency-domain spectrum



3. General ^1H spectrum

Question: sweeps: why do we need a small change from 1.41 T at 60 MHz?

Answer:

- nuclei are "shielded" to a different extent:
 - a nucleus is surrounded by electrons
 - electrons are moving charges that create magnetic fields
 - create a "diamagnetic shielding" opposing B_0
- shielded nucleus feels less of B_0
 - has a smaller Larmor frequency, ω
 - if we supply a constant RF, B_0 needs to be adjusted

adjustments are small:

	1.41 T	
$(\text{CH}_3)_4\text{Si}$	60,000,000 Hz	
$\text{CH}_3\text{-R}$	60,000,060 Hz	\Rightarrow 1 ppm difference
CHCOR	60,000,480 Hz	\Rightarrow 8 ppm difference
adjustment:	1.41 T \pm "a few" ppm	
	normal ^1H range is about 10 ppm	

3. General ^1H spectrum continued

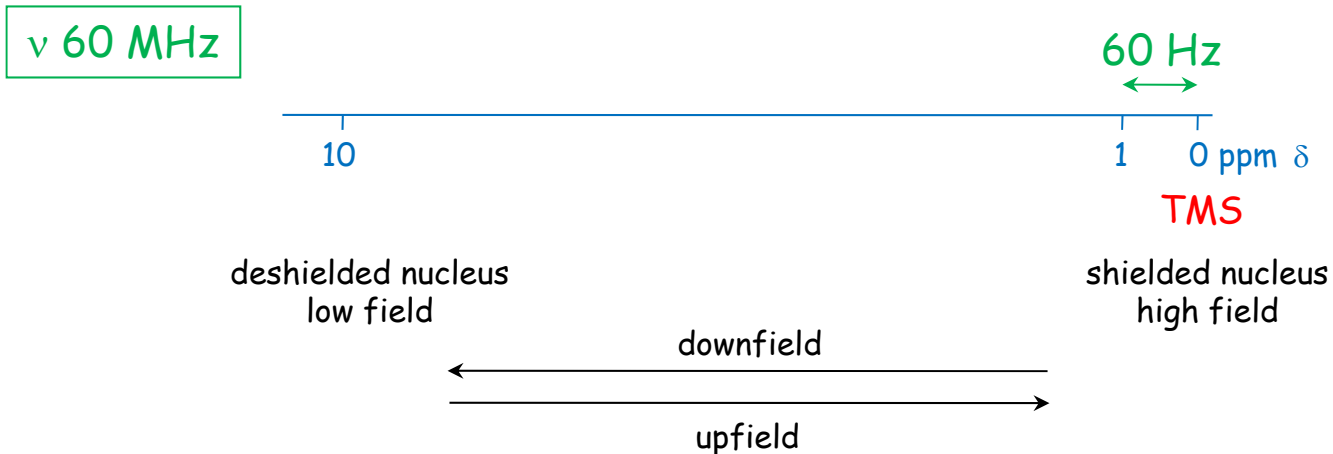
Use of the ppm scale

	1.41 T (60 MHz)	7.05 T (300 MHz)
$(\text{CH}_3)_4\text{Si}$	60,000,000 Hz	300,000,000 Hz
$\text{CH}_3\text{-R}$	60,000,060 Hz	300,000,300 Hz
	\Rightarrow 60 Hz difference	300 Hz difference
	\Rightarrow 1 ppm difference	1 ppm difference

chemical shift $\delta = \frac{\text{changes in Hz}}{\nu \text{ in MHz}}$

δ is independent of ν !

ppm-changes in ω on the order of Hz in a MHz (10^6 Hz)



4. Materials

standard: - depends on the solvent

- usually TMS: tetramethylsilane, $(\text{CH}_3)_4\text{Si}$
- ^1H are considered "most shielded"

solvents: - usually deuterated organic solvents: CDCl_3 , $(\text{CD}_3)_2\text{CO}$, C_6D_6 , CD_3OD , D_2O

- or CCl_4

- usually dry, otherwise H_2O signal [see p. 478, bottom](#)

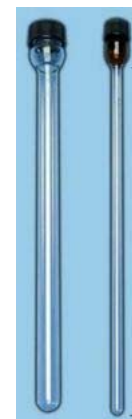
sample tubes: - depend on the application

- different glasses
- different diameters



~\$10

moisture-sensitive
samples



\$20 \$30

UV-sensitive
samples



\$30 \$40

4. Materials continued

- signals from solvents and other nuisances

