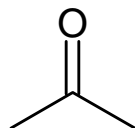# Nuclear magnetic resonance spectroscopy

nuclear spin transitions



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

• which transitions?

   wavelength and intensity; ppm

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

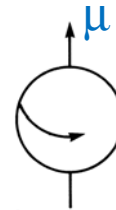   substituent effects on the chemical shift, …


• prediction of a chemical shift

# 1. General

• region of radio frequency: least energetic radiation

• absorption leads to a nuclear spin transition

nucleus (e.g. $^1$H): - charged particle
- has angular momentum (behaves like a spinning particle)
- creates a magnetic field
- has a magnetic moment, $\mu$

- has a spin quantum number, I (for $^1$H, I = $\frac{1}{2}$)
- has allowed spin states 2I + 1 (e.g. two for $^1$H, +$\frac{1}{2}$ and -$\frac{1}{2}$)

- states are degenerate
$\Rightarrow$ spin transition not possible
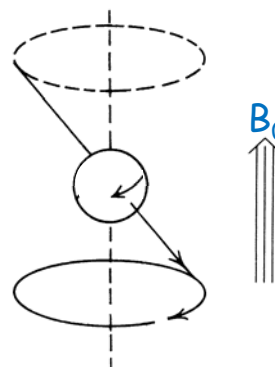$\Rightarrow$ need to remove degeneracy to get an NMR signal

# 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

z-direction

$B_0$

μ    μ
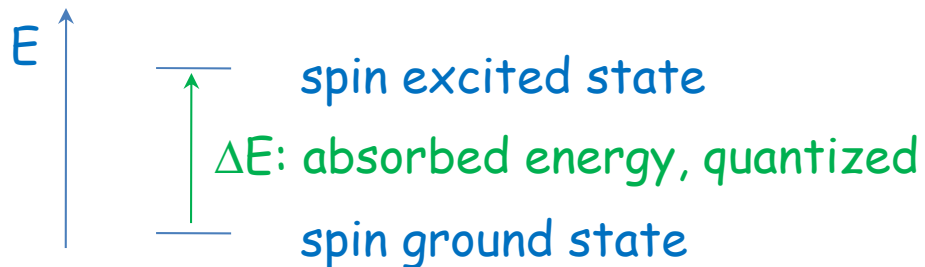
$+\frac{1}{2}$    $-\frac{1}{2}$

ω

$B_0$
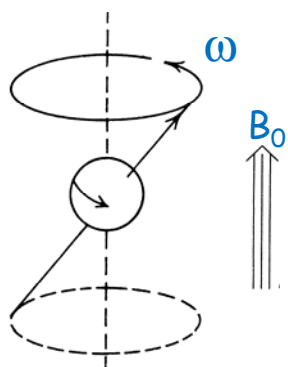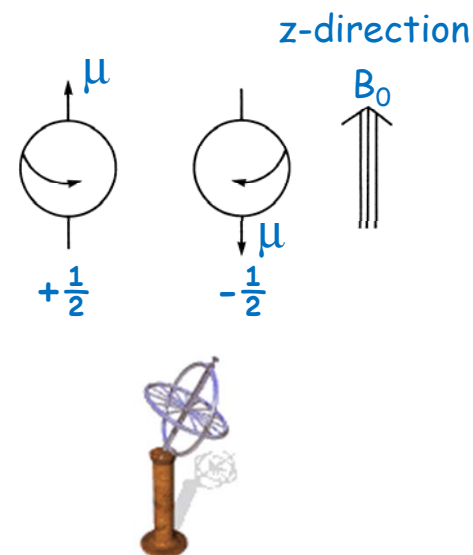
state I = $+\frac{1}{2}$
- parallel with external field
- lower E state

$B_0$

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

⇒ states are no longer degenerate

E

spin excited state

ΔE: absorbed energy, quantized

spin ground state

http://www.cem.msu.edu/~reusch/
VirtualText/Spectrpy/nmr/nmr2.htm

# 1. General continued

ΔE depends on $B_0$, E = f($B_0$)



$\omega$ = 60 MHz

$\nu$ = 60 MHz

$h\nu$
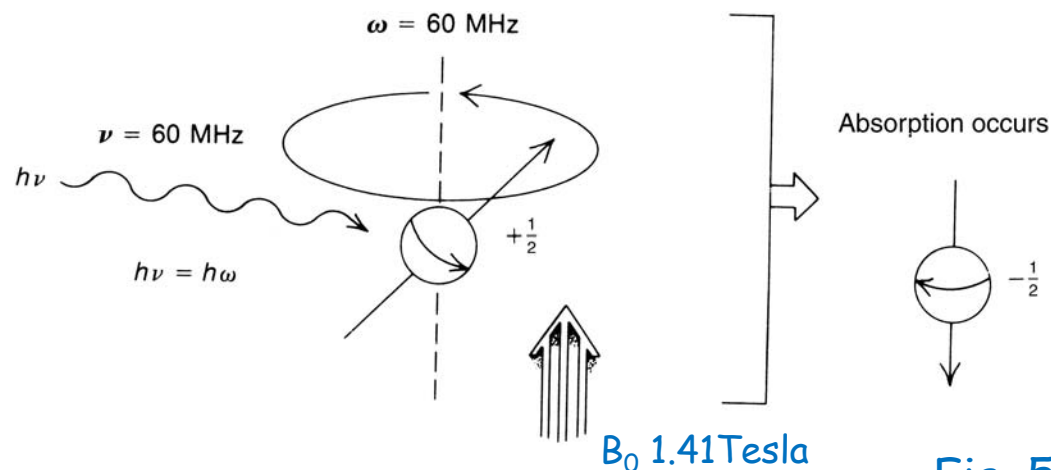
$h\nu = h\omega$

Absorption occurs

$B_0$ 1.41Tesla
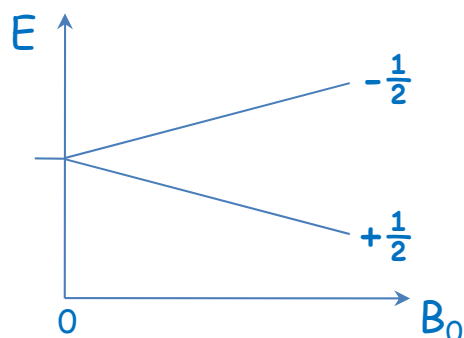
Fig. 5.8

more precisely,

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

$\gamma$: gyromagnetic ratio, constant for a nucleus  see Table 5.2

$^1H$ $\quad \gamma$ 267.53

$^{13}C$ $\quad \gamma$ 67.28 $\quad$ unit: radians/T

$^{19}F$ $\quad \gamma$ 251.7 $\quad$ or $10^6$ rad/sT

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

resonance condition: for $^1H$: $\quad$ $B_0$ 1.41 T $\Rightarrow \omega$ 60 MHz, $\nu$ 60 MHz

$B_0$ 7.05 T $\Rightarrow \omega$ 300 MHz, $\nu$ 300 MHz

$\lambda$?

# 1. General continued

Problem: $\Delta E$ is very small: at 1.41 T, $\Delta E$ is $\approx 0.02$ 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?

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

upper level $\longrightarrow$ $N_u$
lower level $\longrightarrow$ $N_l$

$$\frac{N_u}{N_l} = e^{-\frac{\Delta E}{kT}} = e^{-\frac{3.96 \cdot 10^{-26}\,J}{1.38 \cdot 10^{-23}\,J/K \cdot 298K}} = 0.9999904 \approx \frac{1,000,000}{1,000,010}$$

Don't miss the
negative sign!

read:
$\Rightarrow$ only a very small
overpopulation of
the lower level
$\Rightarrow$ poor signal strength

Solution: use stronger magnets

# 2. Spectrometer

Solution: use stronger magnets

300 MHz

600 MHz

900 MHz



see Table 5.2

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

# 2. Spectrometer continued

Continuous-wave (CW) NMR spectrometer

 - field-sweep at constant frequency

radio frequency

RF (60−MHz) oscillator

constant, for $^1H$

RF detector

Recorder

N

S

permanent magnet

~1.41 T ± a few ppm

Variable magnetic field

electromagnet:

 - sweep generator for field sweep

 - generates x-axis: $\Delta B_0 \sim \Delta\nu$:

$\Rightarrow$ gives frequency-domain spectrum

$\nu$
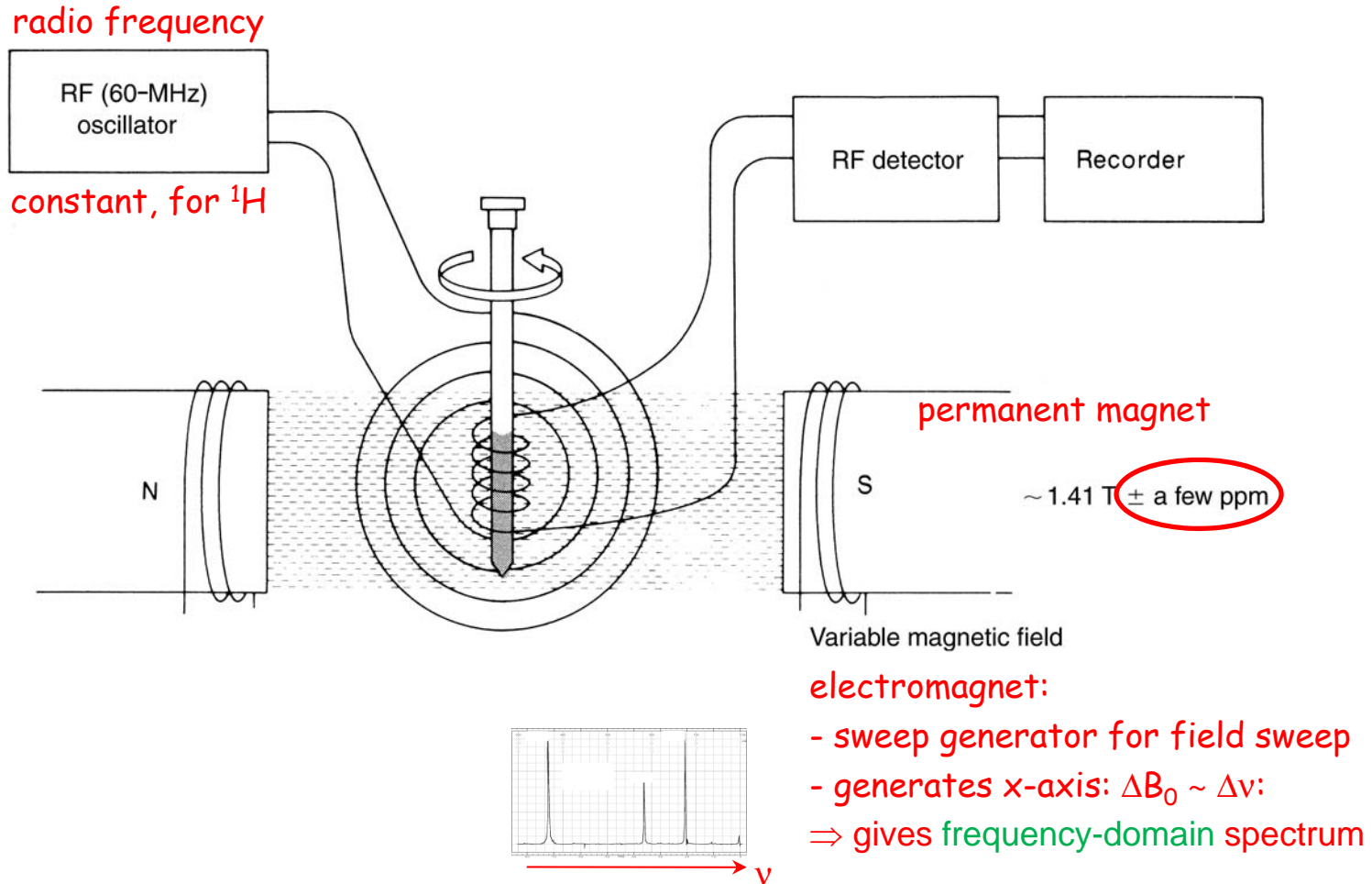
also possible: opposite configuration: frequency-sweep at constant field

# 2. Spectrometer continued

## Fourier-transform (FT) NMR spectrometer



Magnet control

High frequency antenna

Probe

Amplifier

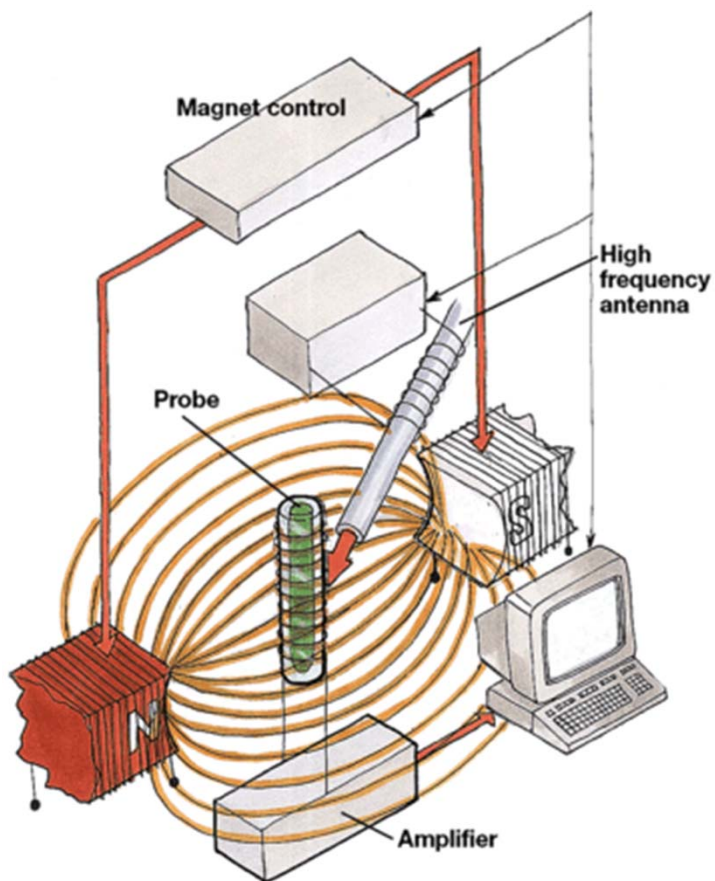magnet: superconducting cryomagnet:
- cooled to -269 °C by $He_{(l)}$ that is cooled to -196 °C by $N_{2(l)}$
- for $B_0$ up to 23.5 T ($\nu$ 1000 MHz for $^1H$)

### The danger of the cryogens:

- 600 MHz, maybe 60 L of $He_{(l)}$: ~2 min

### The danger of high field strengths:

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

### The 5-G line safety:

# 2. Spectrometer continued

Fourier-transform (FT) NMR spectrometer

Advantage? Disadvantage?
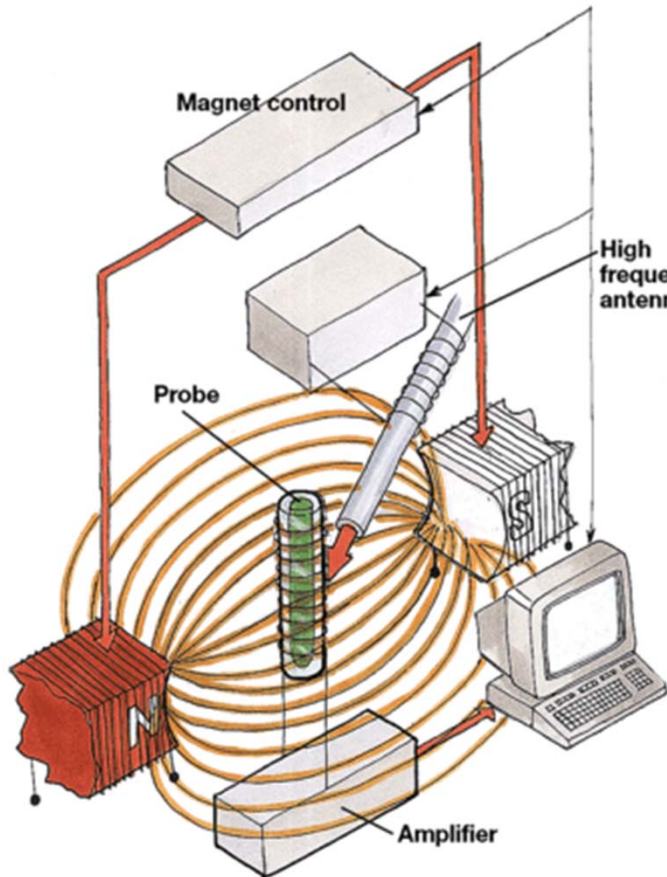


provides RF pulse:
- short (μs), intense burst ("pulse")
- wide enough to cover the spectrum for a certain type of nucleus
- all these nuclei are excited at once
- all these nuclei relax to the ground state after the pulse

records the emission and its decay: a time-domain signal
   ("FID": free induction decay signal)
⇒ Fourier-transform
⇒ frequency-domain spectrum

http://hiq.aga.cl/international/web/lg/spg/likelgspg.nsf/docbyalias/anal_nmr
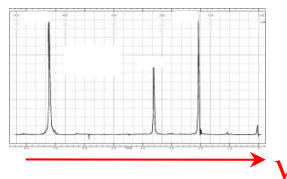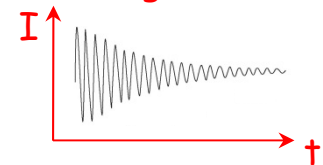
# 3. General $^1$H spectrum

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 $B_0$

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

- has a smaller Larmor frequency, $\omega$

- if we supply a constant RF, $B_0$ needs to be adjusted

adjustments are small:

**1.41 T**

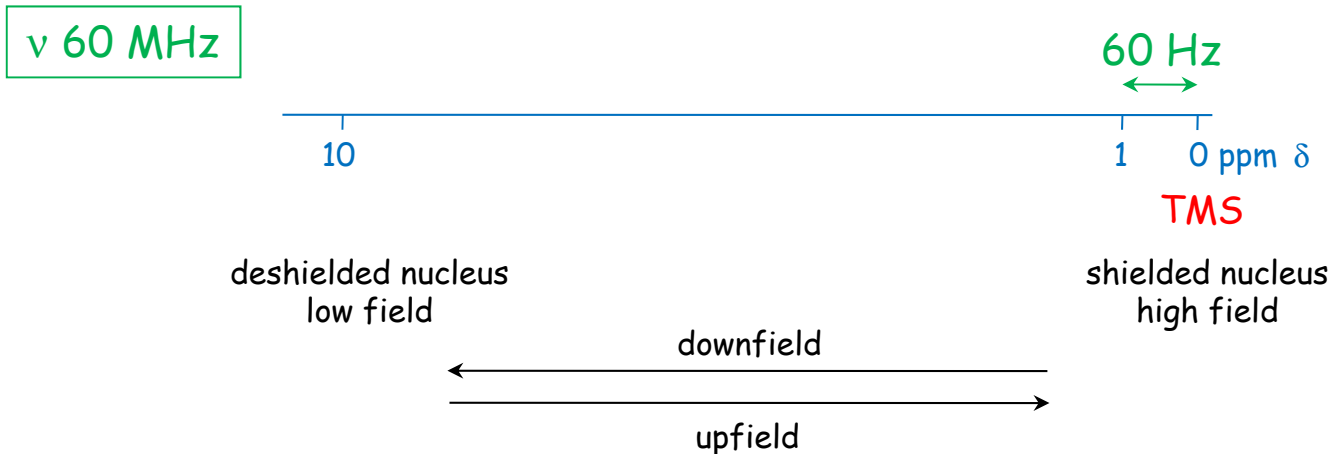| | | |
|---|---|---|
| $(CH_3)_4Si$ | 60,000,000 Hz | |
| $CH_3$-R | 60,000,060 Hz | $\Rightarrow$ 1 ppm difference |
| HCOR | 60,000,480 Hz | $\Rightarrow$ 8 ppm difference |
| adjustment: | 1.41 T $\pm$ "a few" ppm | |
| | normal $^1$H range is about 10 ppm | |

# 3. General $^1$H spectrum continued

**Use of the ppm scale**

|  | **1.41 T (60 MHz)** | **7.05 T (300 MHz)** |
|---|---|---|
| $(CH_3)_4Si$ | 60,000,000 Hz | 300,000,000 Hz |
| $CH_3$-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 $\delta = \dfrac{\text{changes in Hz}}{\nu \text{ in MHz}}$     $\boxed{\delta \text{ is independent of } \nu!}$

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

$\boxed{\nu \text{ 60 MHz}}$                                    60 Hz
                                                              $\longleftrightarrow$
———————————————————————————————————————
        10                                          1      0 ppm  $\delta$
                                                            TMS

  deshielded nucleus                              shielded nucleus
     low field                                       high field

                          downfield
              $\longleftarrow$
              $\longrightarrow$
                           upfield

# 4. Materials

standard: - depends on the solvent

　　　　- usually TMS: tetramethylsilane, $(CH_3)_4Si$

　　　　- $^1H$ are considered "most shielded"


solvents: - usually deuterated organic solvents: $CDCl_3$, $(CD_3)_2CO$, $C_6D_6$, $CD_3OD$, $D_2O$

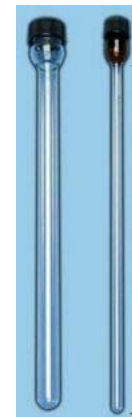　　　　- or $CCl_4$

　　　　- usually dry, otherwise $H_2O$ signal

sample tubes: - depend on the application

　　　　- different glasses

　　　　- different diameters

moisture-sensitive samples　　UV-sensitive samples



~$10

$20　$30　　$30　$40

http://www.newera-spectro.com/

# 4. Materials continued

- signals from solvents and other nuisances

always present as a
small signal with $CDCl_3$
as solvent:
from H-D exchange

CHCl₃

TMS

reference;
often a second signal
close by due to use of grease

solvent signal
from d6-acetone:
from H-D exchange

satellite bands:
$^1H$-$^{29}Si$ coupling

satellite bands:
$^1H$-$^{13}C$ coupling

R     R

$D_3C-CO-CHD_2$

$S_{Si}$  $S_{Si}$

rotational side bands:
sample spun too slowly

$S_C$

$S_C$     H₂O

R    R

7,27                          2,05                    0

δ_H

water in d6-acetone;
at 1.6 ppm in $CDCl_3$

Hesse, Meier, Zeeh, Spektroskopische Methoden in der Organischen Chemie, Thieme, 1987