Nuclear Magnetic Resonance

NMR I

Physical Basis

Ref   9 : (1, 2), 3, 4;   8th ed.

         9.: (1), 2, (3), 4;   9th ed.

         Also: lab website:
         Handbook/Spectroscopy/^{1}HNMR

Prob   HMWK #2

Adv Rdg   9 : 6, 7; 8th ed.

         9 : 7, 8; 9th ed.

General

nmr happens in nucleus of atom

affected by

     • surrounding valence e^- 's

     • neighboring nuclei

∴   provides info. on

     • molecular structure (3D arrangement)

     • e^- distribution

     • chem. bonding

currently, most important analytical tool
in Org. Chem.

Physical Basis

Generally,

• nuclei in atoms are spinning

     (*"nuclear spin"*)

• spinning causes "magnetic moment"

• nuclei behave like little bar magnets

Exception

if (# of p's) and (# of n's) are both even ,

then nucleus has no nmr !

Practice

isotope	# of p's	# of n's	nmr active ?
^{12}C	6	6	no
^1H	1	0	yes
^2H	1	1	yes
^{13}C	6	7	yes
^{16}O	8	8	no

this course: ^{1}**H only !!**

        " PMR"

Nuclear Spin

^{1}H atom can have

2 different nuclear spin states (m_I)

$$m_I = +\frac{1}{2} \quad (\uparrow,\ \alpha)$$

$$m_I = -\frac{1}{2} \quad (\downarrow,\ \beta)$$

N		S
S		N

　　　α　　　　β
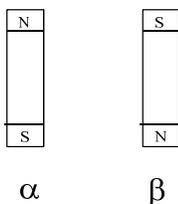
states α and β 　　have same energy

　　　　　　　　　　　　in absence of mag. field

Effect of External Mag. Field

• put sample inside a magnet

• now states α and β have different energy

• magnet must be very strong
  for this effect to be observable

Illustration
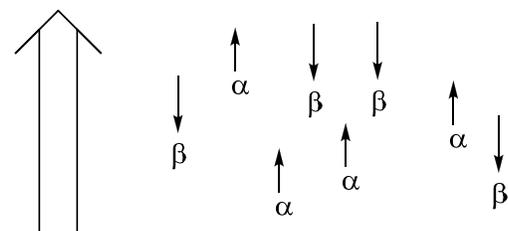
external
mag. field
(B_0)

　　　　α parallel to B_0

　　　　β antiparallel to B_0

$$E_\beta \ > \ E_\alpha$$

$$\Delta E \ = \ E_\beta - E_\alpha$$

---

effect ....

• transition $\alpha \ \rightarrow \ \beta$ possible

　if sample is irradiated w/ EMR

　that satisfies　　$\Delta E \ = \ h\nu$ (Planck's Equ^n)

• now absorption of energy occurs

• i.e., resonance condition exists

Magnitude of ΔE

depends on

  strength of **external** mag. field, B_0;

  actually, proportional to B_0

B_0 measured in   gauss (G) or

                      tesla (T)

                      $(1\ T\ =\ 10^4\ G)$

current technology uses

1.4 T ——————— 14 T (..... 20 T)

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magnitude ...

$$\Delta E\ =\ \text{const.}\ \times\ B_0$$

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

γ, "gyromagnetic ratio",

  "nucleus specific",

  determined by experiment

e.g. $^1H:\ \gamma\ =\ 26.8 \times 10^7\ T^{-1}\ s^{-1}$

       $^{13}C:\ \gamma\ =\ \ \ 6.7 \times 10^7\ T^{-1}\ s^{-1}$

Practice

"PMR" ; $B_0\ =\ 1.41\ T$; $\Delta E\ =\ ?$

$\Delta E\ =\ \ 26.8 \times 10^7\ T^{-1}\ s^{-1}\ \times$

$\qquad \dfrac{6.63 \times 10^{-34}\ Js}{2\pi}\ \times 1.41\ T$

$\qquad =\ \ 3.98 \times 10^{-26}\ J$ for 1 transition

on mole basis, multiply by N_A

$\qquad \times\ 6.02 \times 10^{23}\ mol^{-1}$

$\qquad =\ \ 2.40 \times 10^{-2}\ \ J\,/\,mol$

$\qquad =\ \ 2.40 \times 10^{-5}\ \ kJ\,/\,mol$

∴ very small, indeed

  (compare w/ ΔE of chem. rxns, $\approx 100\ kJ\,/\,mol$)

Resonance Frequency, ν_{res}

EMR required to cause

$\alpha \quad\xrightarrow{\hspace{2cm}}\quad \beta$

$\begin{bmatrix} \text{with } B_0 & \text{against } B_0 \\ \text{low E} & \text{high E} \end{bmatrix}\ ?$
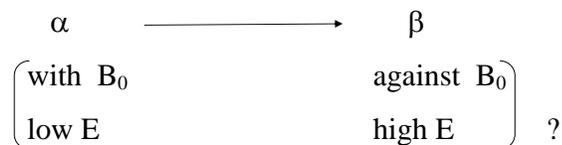
Ans. : $\Delta E, \nu$ related by Planck

$\qquad \Delta E\ =\ h\nu$

$\qquad \nu\ =\ \dfrac{\Delta E}{h}$

$\qquad\quad =\ \gamma\ \dfrac{h}{2\pi}\ B_0\ \dfrac{1}{h}\ =\ \gamma\ \dfrac{B_0}{2\pi}$

Previous example cont^d :

$\nu\ =\ \dfrac{3.98 \times 10^{-26}\ J}{6.63 \times 10^{-34}\ Js}\ =\ 6.00 \times 10^7\ s^{-1}\ =\ 60.0 \times 10^6\ Hz$

$\qquad\qquad\qquad\qquad\qquad\qquad\quad =\ 60\ MHz,$

i.e., range of FM radiowaves;

therefore often called **radiofrequency**

App^n to Org. Chem.

cmpd = assembly of nuclear magnets.

e.g.
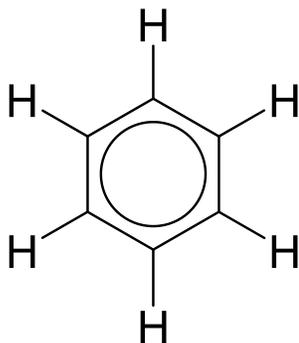
• any one H could be in α or β state

• any α could be "flipped" to β

  w/ proper radiofrequency

   (= "resonance frequency")

"Clincher"

• NMR would be of little use

  if all H's absorbed ("resonated") at same ν

• differences in "chem. environment",

  i.e., in local e$^-$ density &

       presence of neighboring atoms, esp. H's

  have an effect

Ex.
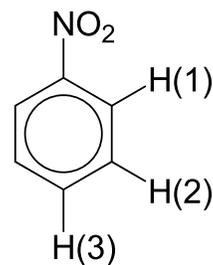
H(1), H(2), H(3) are different,

∴ resonate (absorb) at different ν values