NMR II

Chemical Shift

Ref 9 : 5, 6; 8th ed.
9 : 6, 7; 9th ed.

Prob HMWK #2

Adv Rdg 9: 7 (8^{th}) / 9: 8 (9^{th})

Local Magnetic Field, B_{local}

External Field B_0

- interacts with e^-'s of molecule, incl. valence e^- s
- induces **opposing** small local magnetic field, B_{local} (making B_{eff} smaller)

$$B_{local} = \sigma B_0$$

where σ is "shielding const."

high e^- density causes:

Shielding Constant, σ

- depends principally on local e^- density (+ other factors)
- if neighboring atoms are e/n then,
- and v.v if neighboring atoms are **not** e/n then,

Effective Mag. Field Strength, B_{eff}

B_{eff} = "B, actually felt by nucleus"

Effect on Resonance Frequency, ν_{res}

must use B_{eff} (*not* B_0)

ν_{res} =

Practice

neighbor atoms	are e/n (e.g., Cl)	are less e/n (e.g., Si)
e^- density at H atom		
shielding, σ		
B_{local}		
B_{eff}		
ν_{res}		

Example

1.) TMS, tetramethylsilane, $Si(CH_3)_4$

- Si is “electropositive”,
- increases e^- density at H,
- H becomes “e^- rich” = “shielded”

2.) bromoform, $CHBr_3$

- Br is “electronegative”,
- decreases e^- density at H,
- H becomes “e^- poor” = “deshielded”

shielding effects ...

variable	TMS	$CHBr_3$
e^- density		
nucleus		
σ (shielding const)		
B_{local}		
B_{eff}		
ΔE		
ν_{res}		
resonance occurs		
traditional term		
peak occurs on		

Quantitative Example

B_0						
ν	100 MHz		300 MHz		500 MHz	
cmpd	TMS	$CHBr_3$	TMS	$CHBr_3$	TMS	$CHBr_3$
B_{eff} (T)						
ν_{res} (Hz)						
$\Delta\nu$ (Hz)						
δ (ppm)						

$\Delta\nu$, absolute shift; δ, relative ("chemical") shift

Explanatory Notes

A.) at 100 MHz

1.) "ν", nominal operating frequency,

as required for PMR

2.) B_0, associated mag. field strength, from

$$\nu = \gamma \frac{B_0}{2\pi} \text{ (use } \gamma \text{ for } {}^1H)$$

3.) TMS used for calibration,

ν_{res} set at 100 000 000 Hz (= ν_{ref})

($\therefore B_{eff}$ = 2.350 000 00 T)

4.) ν_{res} for $CHBr_3$, (X), experimentally observed

5.) $\Delta\nu = \nu_X - \nu_{ref} = 674$ Hz

6.) $\delta = \frac{\Delta\nu}{\nu_{ref}} \times 10^6 = 6.74$ ppm

Explanatory Notes ...

B.) at 300 MHz

1.) $B_o \propto \nu$

2.) $B_{eff} = B_o(1 - \sigma)$

$\propto B_o$

$\therefore B_o$ triples $\rightarrow B_{eff}$ triples

3.) similarly, $\nu_{res} \propto B_o$

$\Delta\nu_o \propto B_o$

} also triple; convince yourself

4.) at 100 MHz: $\delta = \frac{\Delta\nu}{\nu_{ref}} \times 10^6$

at 300 MHz: $\delta = \frac{3\,\Delta\nu}{3\,\nu_{ref}} \times 10^6$

$\therefore$ δ value does **not** change w/ instrument

C.) at 500 MHz ? Do as HMWK!