

# Chemistry 210 -- Winter Semester 1997

## Chapter 10

### Basis of Spectroscopy

The characteristic frequency of the absorption (or emission) between two states is measured.

The “two states” can be due to many different causes

electronic states	UV/Vis spectroscopy
vibrational states	IR spectroscopy
rotational states	Microwave spectroscopy
NMR	nuclear magnetic moment alignment
ESR	electron magnetic moment alignment

1. Draw a picture of two states and indicate transition.
2. A **spectrum** records the intensity of the absorption as a function of wavelength or frequency or some parameter derived from the frequency.

## Physical Basis of NMR Spectroscopy

### Introduction

- 1946 First observation of effect  
Bloch, Hansen, Packard  
Purcell, Torrey, Pound
- 1952 Nobel Prize for Bloch and Purcell
- 1970 Two-dimensional methods (two frequency axes)
- 1991 Nobel Prize for Ernst

### Nuclear Angular Momentum and Magnetic Moment

Angular momentum  $P$  is quantized according to  $P = [I(I+1)]^{0.5} h/2$

$I$  = angular momentum quantum number or nuclear spin

Allowed values:  $I = 0, 0.5, 1, 1.5, \dots 6$

$I$  and  $P$  cannot be predicted.

The magnetic moment  $\mu$  is proportional to the angular momentum and the proportionality is given by the gyromagnetic ratio .

$$\mu = \gamma P$$

No spin, no magnetic moment

$^{12}\text{C}$  and  $^{16}\text{O}$  do not have spins, that is just too bad!

The sign of the gyromagnetic ratio can be negative

for the electron      for  $^{15}\text{N}$       for  $^{29}\text{Si}$

**Table 1-1.**

Properties of some nuclides of importance in NMR spectroscopy.

Nuclide	Spin $I$	Electric quadrupole moment <sup>a)</sup> [ $eQ$ ] [ $10^{-28} \text{ m}^2$ ]	Natural abundance <sup>a)</sup> [%]	Relative sensitivity <sup>b)</sup>	Gyromagnetic ratio $\gamma^a)$ [ $10^7 \text{ rad T}^{-1} \text{ s}^{-1}$ ]	NMR frequency [MHz] <sup>b)</sup> ( $B_0 = 2.3488 \text{ T}$ )
<sup>1</sup> H	1/2	–	99.985	1.00	26.7519	100.00
<sup>2</sup> H	1	$2.87 \times 10^{-3}$	0.015	$9.65 \times 10^{-3}$	4.1066	15.351
<sup>3</sup> H <sup>c)</sup>	1/2	–	–	1.21	28.5350	106.664
<sup>6</sup> Li	1	$-6.4 \times 10^{-4}$	7.42	$8.5 \times 10^{-3}$	3.9371	14.716
<sup>10</sup> B	3	$8.5 \times 10^{-2}$	19.58	$1.99 \times 10^{-2}$	2.8747	10.746
<sup>11</sup> B	3/2	$4.1 \times 10^{-2}$	80.42	0.17	8.5847	32.084
<sup>12</sup> C	0	–	98.9	–	–	–
<sup>13</sup> C	1/2	–	1.108	$1.59 \times 10^{-2}$	6.7283	25.144
<sup>14</sup> N	1	$1.67 \times 10^{-2}$	99.63	$1.01 \times 10^{-3}$	1.9338	7.224
<sup>15</sup> N	1/2	–	0.37	$1.04 \times 10^{-3}$	-2.7126	10.133
<sup>16</sup> O	0	–	99.96	–	–	–
<sup>17</sup> O	5/2	$-2.6 \times 10^{-2}$	0.037	$2.91 \times 10^{-2}$	-3.6280	13.557
<sup>19</sup> F	1/2	–	100	0.83	25.1815	94.077
<sup>23</sup> Na	3/2	0.1	100	$9.25 \times 10^{-2}$	7.0704	26.451
<sup>25</sup> Mg	5/2	0.22	10.13	$2.67 \times 10^{-3}$	-1.6389	6.1195
<sup>29</sup> Si	1/2	–	4.70	$7.84 \times 10^{-3}$	-5.3190	19.865
<sup>31</sup> P	1/2	–	100	$6.63 \times 10^{-2}$	10.8394	40.481
<sup>39</sup> K	3/2	$5.5 \times 10^{-2}$	93.1	$5.08 \times 10^{-4}$	1.2499	4.667
<sup>43</sup> Ca	7/2	$-5.0 \times 10^{-2}$	0.145	$6.40 \times 10^{-3}$	-1.8028	6.728
<sup>57</sup> Fe	1/2	–	2.19	$3.37 \times 10^{-5}$	0.8687	3.231
<sup>59</sup> Co	7/2	0.42	100	0.28	6.3015	23.614
<sup>119</sup> Sn	1/2	–	8.58	$5.18 \times 10^{-2}$	-10.0318	37.272
<sup>133</sup> Cs	7/2	$-3.0 \times 10^{-3}$	100	$4.74 \times 10^{-2}$	3.5339	13.117
<sup>195</sup> Pt	1/2	–	33.8	$9.94 \times 10^{-3}$	5.8383	21.499

<sup>a)</sup> Values from [1, 2].<sup>b)</sup> Values from the Bruker Almanac, 1992; sensitivity is expressed relative to <sup>1</sup>H (= 1) for constant field and equal numbers of nuclei.<sup>c)</sup> <sup>3</sup>H is radioactive.

## Nuclei in a Static Magnetic Field

The **angular momentum  $\mathbf{P}$**  can have only certain **components  $\mathbf{P}_z$**  along the direction of the magnetic field.

$$P_z = m h/2$$

$$m = I, I-1, \dots -I$$

(2I+1) possibilities

Example 1: Show schematic for half-spin nuclei such as  $^1\text{H}$  and  $^{13}\text{C}$ .

Example 2: Show schematic for full-spin nuclei such as  $^2\text{H}$  and  $^{14}\text{N}$ .

The **magnetic moment  $\mu_z$**  in the field direction (the component of the magnetic moment that matters for the energy) is

$$\mu_z = \gamma P_z$$

$$\mu_z = m \gamma h/2$$

Example 1: Show schematic for half-spin nuclei such as  $^1\text{H}$  and  $^{13}\text{C}$ .

In the classical picture, the magnetic dipole precesses around the direction of the magnetic field in any direction with the Larmor frequency,  $\omega_L = \gamma B_0$ . In the quantum-picture only some directions are allowed.

## **Zeeman Effect**

Energy of a magnetic dipole in a magnetic field:  $E = -\mu B_0$

The nuclear Zeeman levels:  $E = -\mu_z B_0 = - (m \hbar/2) B_0$

For spin  $I = 0.5$  nuclei (draw energy level diagram)

Level 1:  $m = 1/2$ ,  $\mu_z$  is parallel to field ( )

Level 2:  $m = -1/2$ ,  $\mu_z$  is antiparallel to field ( )

For  $I = 1$  nuclei (draw energy level diagram)

$m = +1, 0, -1$

Draw picture showing the B-field dependency of  $E = -\mu B_0$

Populations of the energy levels

$$N_1/N_2 = \exp(-E/k_B T) = 1 - E/k_B T = 1 - (\hbar/2 B_0) / (k_B T)$$

The population difference is in the ppm region. Very small.

Macroscopic Magnetization

$N_1$  with magnetic moment up  $>$   $N_2$  with magnetic moments down

$N_1$  and  $N_2$  nicely distributed, resulting magnetization to top:  $M_0$ .

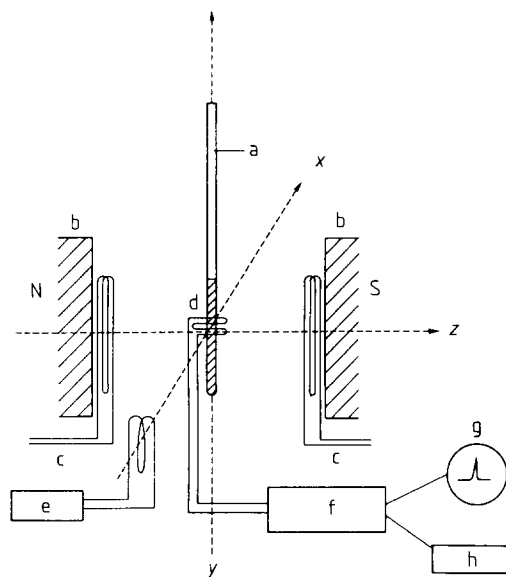
## Basic Principles of the NMR Experiment

Irradiate with radiowaves that fulfill the *resonance condition*  $\nu = \gamma |m| B_0$  causes *spin inversions* or *spin flips* until *saturation* occurs (e.g.  $N_{\uparrow} = N_{\downarrow}$ ).

In systems with  $I > 0.5$ , there are more than two levels. Transitions can occur only with  $|\Delta m| = 1$ .  
Example:  $^{14}\text{N}$  with  $I=1$ , three levels, no transition from bottom to very top.

## The CW Spectrometer

Suitable for sensitive nuclei with  $I=0.5$  with large magnetic moments ( $^1\text{H}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$ )



**Figure 1-6.**

Schematic arrangement of an NMR spectrometer of the continuous wave (c. w.) type  
a sample tube; b magnet;  
c sweep coils; d receiver coil;  
e transmitter; f amplifier; g oscilloscope; h recorder.

In principle this diagram also serves to illustrate the arrangement in a pulse spectrometer, with the modifications that "e" becomes a radiofrequency pulse generator, and "f" is replaced by a more complex system of electronic units and a computer for recording, storing and processing the NMR signals (see also Section 1.5.3).

a magnet

a radiofrequency transmitter

a receiver (at right angle to transmitter)

Modes of operation

vary magnetic field (field sweep)

vary the transmitter frequency (frequency sweep)

$^1\text{H}$  and  $^{13}\text{C}$  resonance frequencies at different magnetic flux densities

	H	$^{13}\text{C}$
1.41	60	15.1
2.35	200	50.3
5.87	250	62.9
7.05	300	75.4
11.74	500	125.7
14.09	600	150.9

## The Chemical Shift

The field at the nucleus depends on its chemical environment

$$B_{\text{eff}} = B_0 - \sigma B_0 = (1 - \sigma) B_0$$

$\sigma$  is the shielding constant (order of magnitude  $10^{-5}$ )

The resonance frequency depends on the shielding

$$\nu_1 = \gamma / 2\pi (1 - \sigma) B_0$$

The 90 MHz  $^1\text{H}$ -NMR spectrum at  $B_0 = 2.11 \text{ T}$  (1 T = 10,000 Gauss)

For comparison, the static magnetic field of the earth is about 500 mG.

TMS frequency	90,000,000 Hz	(TMS is Tetramethylsilane, $\text{Me}_4\text{Si}$ )
$\text{CH}_3\text{Br}$	90,000,237 Hz	
$\text{CH}_2\text{Br}_2$	90,000,441 Hz	
$\text{CHBr}_3$	90,000,614 Hz	

### The Chemical Shift $\delta$ -scale

Advantage 1: The  $\delta$ -scale uses relative values rather than absolute resonance frequency so as to become independent of the magnetic field of the device.

Advantage 2: The  $\delta$ -scale adjusts the magnitude such that we can use “normal numbers” to talk about the chemical shifts.

$$\delta = [( \nu_{\text{sample}} - \nu_{\text{reference}}) / \nu_{\text{reference}}] * 10^6$$

The 90 MHz  $^1\text{H}$ -NMR spectrum at  $B_0 = 2.11 \text{ T}$  (1 T = 10,000 Gauss)

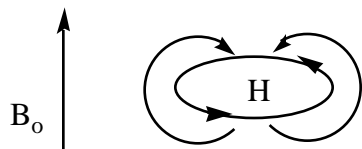
	<u>Absolute Freq.</u>	<u><math>\delta</math>-Scale</u>
TMS frequency	90,000,000 Hz	0.00 by definition
$\text{CH}_3\text{Br}$	90,000,237 Hz	2.63 ppm
$\text{CH}_2\text{Br}_2$	90,000,441 Hz	4.90 ppm
$\text{CHBr}_3$	90,000,614 Hz	6.82 ppm



## Local Contributions to Shielding

$\sigma_{\text{dia}}$  = **diamagnetic shielding**

external field induces ring current which produces a magnetic field that counteracts.



diamagnetic shielding increases with number of electrons.

for H atom:  $17.8 \cdot 10^{-6}$

for C atom:  $260.7 \cdot 10^{-6}$

for P atom:  $961.1 \cdot 10^{-6}$

$\sigma_{\text{para}}$  = **paramagnetic shielding**

opposite sign compared to diamagnetic contribution

always smaller in magnitude  $|\sigma_{\text{para}}| < \sigma_{\text{dia}}$

depends on excitation energies and number of low lying excited states

large excitation energies for H atom, paramagnetic contribution very small

small excitation energies for C atom, paramagnetic contribution can dominate trends

### Charge dependence of the shielding

Only the diamagnetic shielding depend on the electron density around the nucleus.

A relation between the charge of an atom and its chemical shift exists only in cases where the paramagnetic shielding is clearly unimportant. This is true for H-atoms but it is not usually true for other atoms.

For the H-atoms, the paramagnetic contributions do not play any significant role because the excitation energies into C-H antibonding orbitals have low probabilities.

## Non-Local Contributions to Shielding

$\sigma_N$  = magnetic anisotropy of neighboring groups

Multiply bonded systems cause anisotropic shielding behaviour

Can be described with **double-cones** where

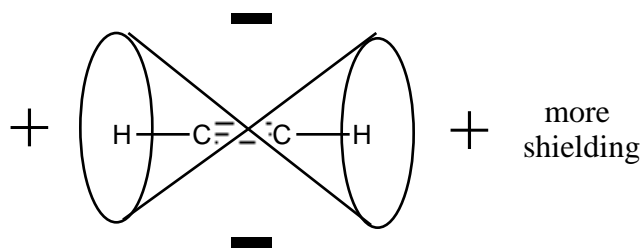
- positive region is additionally shielded
- negative region is shielded less

### Example 1: Acetylene

+ region at the H atoms

small shielding expected (acidic H) with  $\delta = 5.28$  ppm

large shielding actually found with  $\delta = 2.88$  ppm

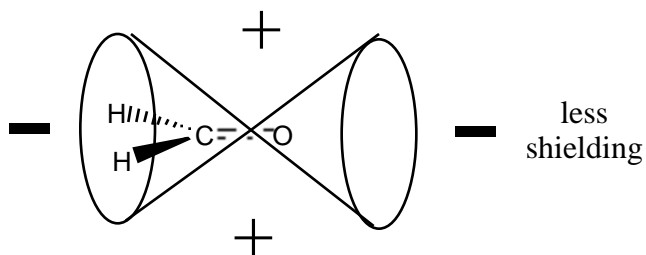


### Example 2: CC Double Bonds and Carbonyls

+ region perp. to multiple bond

- region includes the H atoms

aldehyde hydrogens are very deshielded and appear at  $\delta = 9 - 10$  ppm



### Example 3: Cyclohexane

+ region perp. to single bond

axial protons are more strongly shielded

## $\sigma_R$ = Ring Current Effects

### Example 1: Benzene

protons in alkenes occur already at higher chemical shifts than expected

protons in benzene (7.27) are even less shielded than in alkenes (ethene 5.28)

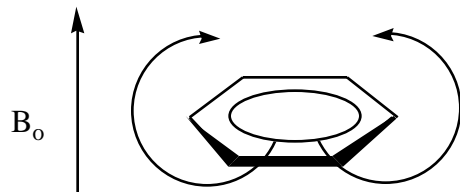
B field aligned with symmetry axis and induced ring current

that is field enforcing outside the ring

that is field reducing inside the ring

+ region on top of the ring

- region in the equator of the ring

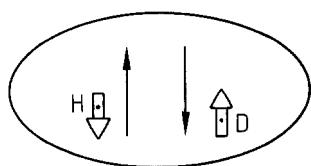


## Spin-Spin Coupling

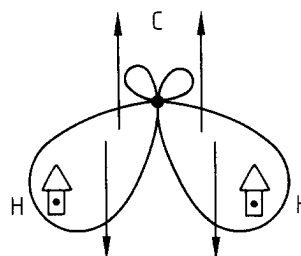
### Coupling between Nuclei because of Electron-Nuclear Interactions

Interaction between the electrons and the nucleus: Fermi contact term.

The Fermi contact term is the direct interaction between the magnetic moment of the nucleus and the bonding electrons in s-states. (H: 1s; C: 2s) The Dirac Vector model is based on the assumption that there is a preference for the magnetic moments of the nucleus and the close electron to be antiparallel. By this mechanism, **the nuclei know about each other, they are coupled**. If the coupling is over one bond, then the nuclei will be anti-parallel (positive coupling). With the “modified Hund’s rule”, we find by the same model that  $^2J$  coupled H nuclei are parallel to each other (negative J value).



**Figure 3-4.**  
Indirect spin-spin coupling in the HD molecule, transmitted through the bonding electrons. The sketch shows the energetically preferred configuration of the nuclear and electron spins.



**Figure 3-5.**  
Indirect spin-spin coupling through two bonds in a  $\text{CH}_2$  group. The sketch shows the energetically preferred configuration of the nuclear and electron spins.

### Nomenclature for Coupling

$^nJ(X,Y)$  where n is the number of bonds between the coupled nuclei X and Y.

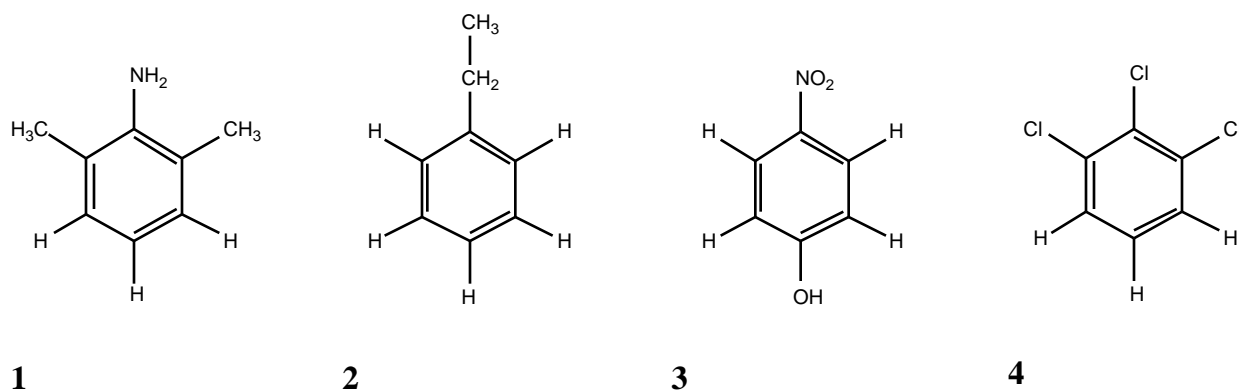
### Coupling Mechanism

- \* Independent of applied field
- \* Indirect (that is through bonds not space)

The spin-spin coupling between nuclei that are chemically and magnetically equivalent does not affect the spectrum.

The spin-spin coupling between nuclei that are chemically and magnetically **not** equivalent **does affect** the spectrum.

## Chemical and Magnetic Equivalence



Chemical Equivalence: Two nuclei are equivalent if they have the same resonance frequency.

- \* equivalent by symmetry (H2/H6 and H3/H5 in **3**; H4/H6 in **4**)
- \* accidentally equivalent (isochronous)
- \* H-atoms in 1,1 dichloro and 1,1 difluoroethene are chemically equivalent

Magnetic Equivalence: Chemical equivalence and their couplings with other nuclei in the molecule are the same (couple to **the same** atoms).

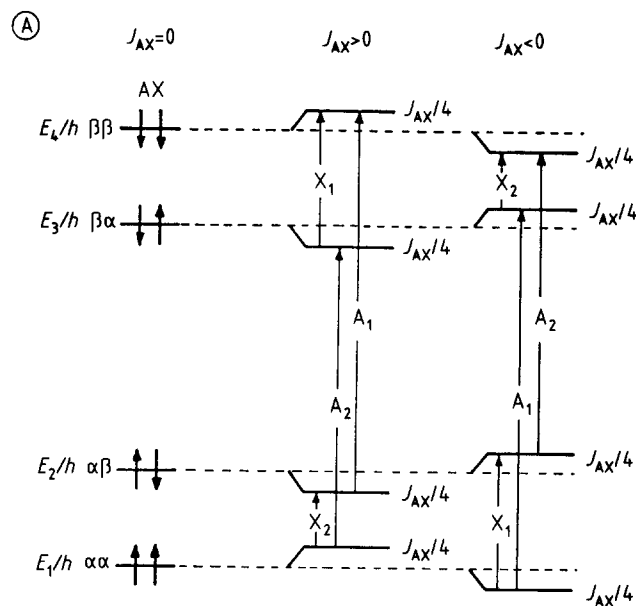
- \* H4/H6 in **4** because they couple the same with H5.
- \* NOT the pairs in **3**! Because the couplings  ${}^2J(\text{H3},\text{H2})$  and  ${}^5J(\text{H5},\text{H2})$  are different.
- \* H atoms in 1,1-dichloroethene are magnetically equivalent
- \* H atoms in 1,1-difluoroethene are NOT magnetically equivalent because they couple in different ways with the two F-atoms present.  ${}^3J_{\text{cis}}$  and  ${}^3J_{\text{trans}}$  differ.

Nomenclature: Chem. equivalent but magn. non-equivalent nuclei are distinguished by a prime.

- \* **1** is a AX<sub>2</sub> system (or AB<sub>2</sub>)
- \* **2** is a ABB'CC' system
- \* **3** is a AA'XX' system
- \* **4** is a AX<sub>2</sub> system (or A<sub>2</sub>B)
- \* 1,1-dichloroethene is an A<sub>2</sub> system, 1,1-difluoroethene is a AA'XX' system.

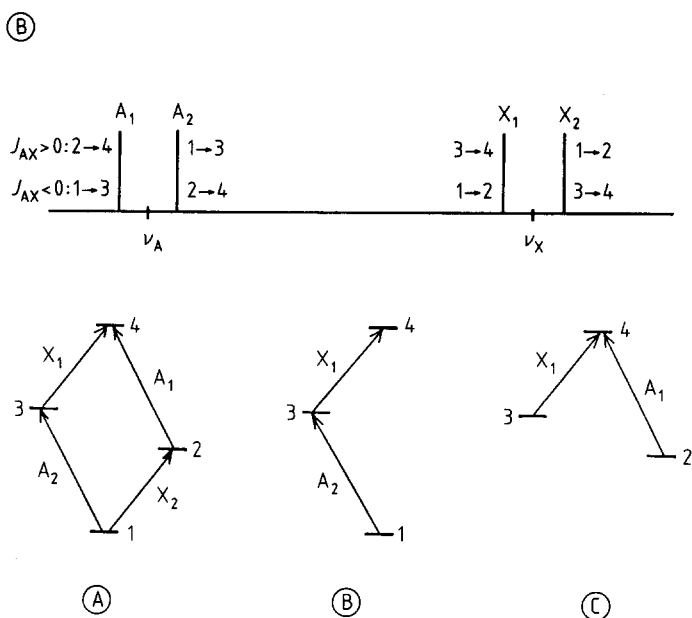
## The AX Spin System

Note the selection rule  $m = +/- 1$ .



**Figure 4-3.**

A: Energy level scheme for a two-spin AX system for the cases  $J_{AX} = 0$ ,  $J_{AX} > 0$  and  $J_{AX} < 0$ . The arrows indicate the spin orientations (z-components).  $A_1$ ,  $A_2$ ,  $X_1$  and  $X_2$  are the allowed nuclear resonance transitions for the A and X nuclei; B: stick spectrum and signal assignments for positive or negative  $J_{AX}$ .



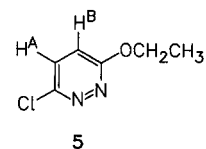
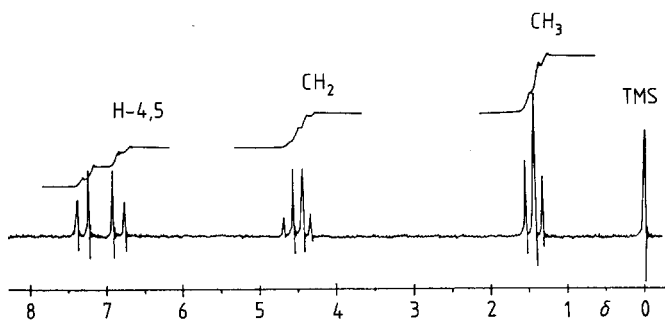
**Figure 4-4.**

Definition of progressively and regressively interconnected transitions. A: Energy level scheme for a two-spin AX system. B: Example of a progressively connected pair of transitions. C: Example of a regressively connected pair of transitions.

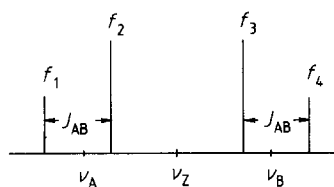
## The AB Spin System

close to  $J$  makes the AB system.

Example: 3-chloro-6-ethoxypyridazine



**Figure 4-5.**  
60 MHz  $^1\text{H}$  NMR spectrum of  
3-chloro-6-ethoxypyridazine (**5**)  
in  $\text{CCl}_4$  with integrated curve.



**Figure 4-6.**  
Sketch for analyzing a two-spin  
AB system.

The AX and AB systems show that the spin-spin coupling

- affects a “splitting” of the resonance signal and
- affects the intensity of the lines is affected.

## The Simple Spin-Spin Coupling Rules

Consider only  $^3J(\text{H},\text{H})$ . This is called **vicinal** coupling.

observe H'-C-C-H''

not observed H'-C-O-H'' and H'-C-N-H'' (fast proton exchange)

### Splitting Pattern

The chemically equivalent H-atoms do not cause a splitting.

The splitting pattern is related to the number of equivalent H-atoms at the neighboring atom.

0 H atoms as neighbor	singlet	
1 H atom as neighbor	dublet	(e.g. - <u>CH</u> -CH-)
2 H atoms as neighbors	triplet	(e.g. - <u>CH</u> -CH <sub>2</sub> -)
3 H atoms as neighbors	quartet	(e.g. - <u>CH</u> -Me)
4 H atoms as neighbors	quintet	(e.g. -CH <sub>2</sub> - <u>CH</u> -CH <sub>2</sub> -)
5 H atoms as neighbors	sextet	
6 H atoms as neighbors	septet	(e.g. Me- <u>CH</u> -Me)
....	...	
n H atoms as neighbors	n+1 lines	

### Intensity of the Multiplet Lines: Pascal Triangle

				1					
			1		1				
		1		2		1			
	1		3		3		1		
	1	4		6		4		1	
1		5	10		10		5		1

The intensity of all lines combined is proportional to the number of H-atoms responsible for the resonance.



## Spectrum Interpretation and Constitution Analysis

(Conformation analysis also is possible but will not be discussed here)

### Position of signal == chemical shift

use tables of typical chemical shifts for analysis

tells about connectivity to electronegative atoms, functional groups, aromatic rings

### Area of signal == integration

number of this type of H-atoms

### Splitting of signal == multiplicity

connectivity information

### ... and now: Lots of exercise

look up structures and predict their spectra (do this first)

look up spectra and deduce the structure (this is the ultimate goal)

Spectrum 1: Propanoic Acid (ethyl group, acidic H does not show)

Spectrum 3: Propanoic acid methyl ester (ethyl group plus singlet)

Spectrum 7: 2-Bromopropane (contains a septet)

Spectrum 17: Acetamide (singlet, amino H do not show)

### Pair of Structure Isomers

Spectrum 9: Phenylacetone

Spectrum 81: 3-Chloropropene (ABDX<sub>2</sub> system)

Spectrum 92: Me<sub>2</sub>C=CH-C(O)-Me (two non-equivalent terminal Me)