Excellent!

JIGSAW 5B

18 November 2024

Question 1

[Week 1 Slides 18-25] The complete NMR Hamiltonian for a molecule in a diamagnetic condensed sample is:

$$\mathcal{H}_{\text{NMR}} = \mathcal{H}_Z + \mathcal{H}_Q + \mathcal{H}_D + \mathcal{H}_{\text{CS}} + \mathcal{H}_J$$

a. Name all the terms. For each term, determine if it will be observable in solid state NMR, in liquid state NMR, or in both. Justify your answers. Also state which units the corresponding values are usually reported in (e.g., Hz, MHz, ppm, etc.).

$\mathcal{H}_Z$ corresponds to the Zeeman spitting, and is measured around 100 MHz. The energy split depends only on the B-field, so is almost independant of geometry, so is visible in solid and liquid state.

$\mathcal{H}_Q$ is the quadrupole interaction and is also in MHz. It is not observable in the liquid states because of motion averaging.

$\mathcal{H}_D$ is the dipolar coupling, and is in kHz. It can be observed in solid NMR only, as the anisotropy is averaged-out in liquid state.

$\mathcal{H}_{CS}$ is the chemical shift, and is in ppm. It is seen in solid and liquid (averaging is non-zero) states.

$\mathcal{H}_J$ is the scalar coupling, and is in Hz. Scalar coupling does not depend on the instantaneous fields, so is observed in liquid and solid states.

b. Explain the main differences between scalar couplings and dipolar couplings. Why does one produce splittings in NMR spectra of liquids and the other one does not?

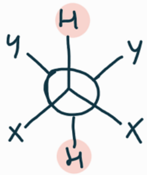
Dipolar interaction is caused by the magnetic fields generated by nuclear spins interacting with each other. On the other hand, scalar coupling (or J-coupling) is due to nuclear magnetic moments in the same molecule affecting each other through the electron cloud. Thus, the main difference between the couplings is that dipolar interaction is the result of direct interaction between the nuclear magnetic moments, whilst the scalar coupling is an indirect interaction via the bonding electrons.

The dipolar coupling depends on spatial distance and orientation of the nuclei relative to the external field. Therefore, in liquid NMR, the quick isotropic movements of molecules averages dipolar couplings to zero. Dipolar coupling does not produces splittings in NMR spectra of liquids, but scalar coupling does, as it doesn't depend on spatial orientation.

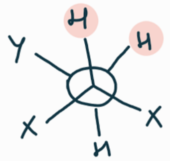
Question 2

According to the lecture : $\begin{cases} J_{HH} = P_g J_g + P_t J_t \\ P_g + P_t = 1 \end{cases}$

Where $J_{HH} = 3.27$ Hz is the ^1H-^1H J coupling in $CH_2X_2-CH_2Y_2$ and P_t, P_g are successively the population fractions of the trans and gauche conformers of this molecule. These two rotamers are represented below:



trans conformation



gauche conformation

Knowing the coupling constants for each conformation $J_t = 8.7$ Hz and $J_g = 2.0$ Hz one can determine P_t and P_g using the previous equations.

$$\longrightarrow \quad P_t = 1 - P_g$$

$$\longrightarrow \quad J_{HH} = P_g J_g + (1 - P_g) J_t$$

$$\Leftrightarrow \quad J_{HH} = P_g J_g - P_g J_t + J_t$$

$$\Leftrightarrow \begin{cases} P_g = \dfrac{J_{HH} - J_t}{J_g - J_t} = \dfrac{3.27 - 8.7}{2.0 - 8.7} = 0.81 \\ \\ P_t = 1 - 0.81 = 0.19 \end{cases}$$

Great work!

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Jigsaw 5B

1. [Week 1 Slides 18-25] The complete NMR Hamiltonian for a molecule in a diamagnetic condensed sample is:

$$\mathcal{H}_{NMR} = \mathcal{H}_Z + \mathcal{H}_Q + \mathcal{H}_D + \mathcal{H}_{CS} + \mathcal{H}_J$$

   a. Name all the terms. For each term, determine if it will be observable in solid state NMR, in liquid state NMR, or in both. Justify your answers. Also state which units the corresponding values are usually reported in (e.g., Hz, MHz, ppm, etc.).

H_Z: Zeeman interaction: SS + LS (MHz) → because interaction between nuclear spin and external field
H_Q: Quadrupolar interaction: SS (MHz) → because nuclei with spin >1/2 overlap and averaged in liquid
H_D: Dipolar interaction: SS (kHz) → dipolar coupling, overlap and averaged in liquid
H_{CS}: Chemical Shift: SS + LS (ppm) → because shift → shielding effect of environment, occurs in both phases
H_J: Scalar Coupling: SS +LS (Hz) → because interaction between nuclear spin is transmitted through chemical bonds and is present in both states

   b. Explain the main differences between scalar couplings and dipolar couplings. Why does one produce splittings in NMR spectra of liquids and the other one does not?

Scalar coupling	Dipolar Coupling
Indirect interaction	Direct interaction
Long range through bond effect	Very distance dependent ($1/r^3$)
Magnitude ~Hz	Magnitude~kHz

Scalar	Dipolar
indepent of molecular orientation relative to the magnetic field	strong dependancy on tge relative orientation of the nuclei and the magnetic field

since molecular motion is rapid and isotropic, all of the orientation dependent components average out, cancelling put the dipolar coupling

2. [From Past Exam] [Hore Section 3.7] The ^1H-^1H J-coupling in CHX_2–CHY_2 is measured to be 3.27 Hz. If J_g = 2.0 Hz and J_t = 8.7 Hz, determine the population fractions of the two rotamers. J_g and J_t are the ^1H-^1H coupling constants for the gauche and trans conformations, respectively.

$^2J=P_gJ_g+P_tJ_t$
$3.27=P_g*2.0+P_t*8.7$
$P_g+P_t=1$
$3.27= P_g*2.0+(1-P_g)*8.7$
$P_g=0.81$
$P_t=0.19$

Good job!

Question 1

a) $H_{NMR} = H_Z + H_Q + H_D + H_{CS} + H_J$

H_Z : Zeeman interaction (~100 MHz)

H_Q : quadrupolar interaction (0 - 100 MHz)

H_D : Dipolar interaction (0 - 20 kHz)

H_{CS} : Chemical shift (0 - 2000 ppm)

H_J : scalar coupling (0 - 200 Hz)

Liquid state NMR: only quadrupolar and dipolar interactions are average out ⇒ they are not visible on the spectrum

This is because H_Q and H_D have orientation dependancy that average out in liquid due to rapid tumbeling

Solid state NMR: All interactions are observable on the spectrum

b)

Scalar couplings:

- It arises from the interaction between the magnetic moment of two coupled nuclei through chemical bond.
- It is independant of the internuclei distance
- It has a range of a few Hz.
- ~~It is isotropically averaged in solution state NMR~~
- Not very affected by molecular motion
- It manifests on the spectrum as multiplet patterns

Dipolar couplings:

- It arises from the interaction of the magnetic dipole moment of 2 nuclei that have an non uniforme charge distribution, through space.
- It depends on the distance between the nuclei.
- The magnitude of the dipole can be large. In particular for solid state NMR or in sample with partially ordered structure
- In liquid-state NMR, coupling are rapidly isotropical average due to molecular motion.
- In solid-state NMR on the other hand, coupling may not completly average and can provide more info on the structure
- Line breadning may appear as well as spin side bands on the spectrum

Question 2

$^{+}H-^{+}H$ J coupling in CHX_2-CHY_2

$J_g = 2$ Hz $J_t = 8{,}7$ Hz $J = 3{,}27$ Hz

$$\left.\begin{aligned} J &= P_g J_g + P_t J_t \\ P_g + P_t &= 1 \Rightarrow P_t = 1 - P_g \end{aligned}\right\} J = P_g J_g + (1-P_g) J_t = P_g (J_g + J_t) + J_t \Rightarrow P_g = \frac{J - J_t}{J_g + J_t} = \frac{3{,}27 - 8{,}7}{2 - 8{,}7} = 0{,}811 = 81{,}1\ \%$$

We can substitute $P_t = 1 - P_g = 1 - 0{,}811 = 0{,}189 = 18{,}9\ \%$