

NMR & NQR

www.hyperfinecourse.org

1

Classification of nuclear methods

These 3 energy scales distinguish 3 different classes of experimental methods:

- 1 • Nuclear Magnetic Resonance (NMR)
• Nuclear Quadrupole Resonance (NQR)
- 2 • laser spectroscopy
• Electron Paramagnetic Resonance (EPR)
- 3 • Low-Temperature Nuclear Orientation (LTNO)
• NMR on Oriented Nuclei (NMR/ON)
• forward scattering of synchrotron radiation
• Mössbauer Spectroscopy (MS)
• Conversion Electron Mössbauer Spectroscopy (CEMS)
• Perturbed Angular Correlation spectroscopy (PAC)

2

2

nuclear magnetic resonance

nuclear quadrupole resonance

stefaan.cottenier@ugent.be

3

Pedagogical assumptions:

- nuclei with $I=1/2$ ($\rightarrow Q=0$, hence no complications due to quadrupole interaction. Relevant examples are ^1H , ^{19}F , ^{31}P)
- no hyperfine field present (\rightarrow the nucleus feels only the applied field)

- 1 Apply an external magnetic field
- 2 This leads to a weak orientation of the nuclear ensemble.

4

4

Pedagogical assumptions:

- nuclei with $I=1/2$ ($\rightarrow Q=0$, hence no complications due to quadrupole interaction. Relevant examples are ^1H , ^{19}F , ^{31}P)
- no hyperfine field present (\rightarrow the nucleus feels only the applied field)

- 1 Apply an external magnetic field
- 2 This leads to a weak orientation of the nuclear ensemble.
- 3 Determine the level-splitting by monitoring absorption of radiowaves :
Apply an external field, scan the rf-frequency
or
Apply a constant rf-field, and scan the external field strength

5

5

Work flow followed by the early (nuclear physics) NMR-researchers :

- Take a homogenous externally applied magnetic field B_0
- We'll measure the NMR signal of a H-nucleus ("proton NMR").
- Put a H-containing environment (say H_2O) inside the field.
- The H-nucleus feels the applied field, and a hyperfine splitting appears.
- By scanning the frequency, you determine the frequency that corresponds to the hyperfine splitting.
- This determines the magnetic moment (or g-factor) of the H-nucleus.
- What happens if you do the same measurement for another molecule, say CH_4 ?

It's different ...!

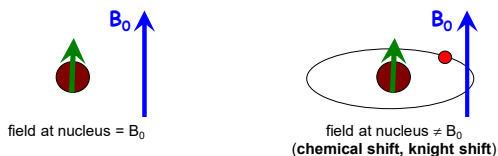
Why?

6

6

Work flow followed by the early (nuclear physics) NMR-researchers :

- Take a homogenous externally applied magnetic field B_0
- We'll measure the NMR signal of a H-nucleus ("proton NMR").
- Put a H-containing environment (say H_2O) inside the field.
- The H-nucleus feels the applied field, and a hyperfine splitting appears.
- By scanning the frequency, you determine the frequency that corresponds to the hyperfine splitting.
- This determines the magnetic moment (or g-factor) of the H-nucleus.
- What happens if you do the same measurement for another molecule, say CH_4 ?



7

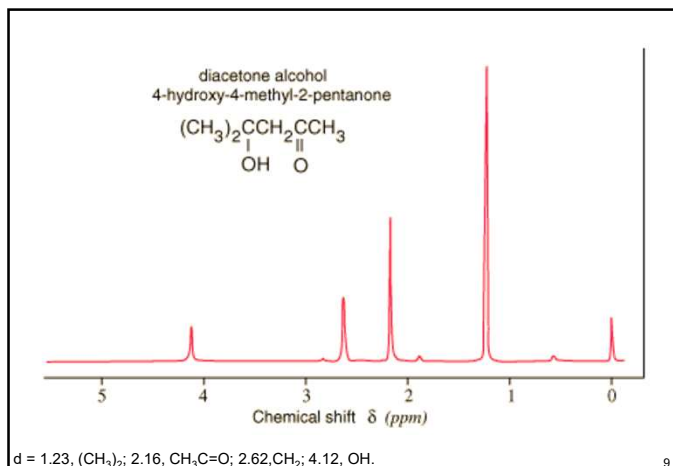
Work flow followed by the early (nuclear physics) NMR-researchers :

- Take a homogenous externally applied magnetic field B_0
- We'll measure the NMR signal of a H-nucleus ("proton NMR").
- Put a H-containing environment (say H_2O) inside the field.
- The H-nucleus feels the applied field, and a hyperfine splitting appears.
- By scanning the frequency, you determine the frequency that corresponds to the hyperfine splitting.
- This determines the magnetic moment (or g-factor) of the H-nucleus.
- What happens if you do the same measurement for another molecule, say CH_4 ?

It's different ...!

- Annoying for the early nuclear physicists, measuring g-factors.
- An opportunity for chemistry: sensitivity to the local environment.

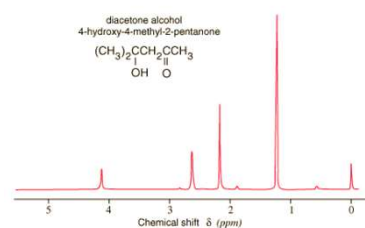
8



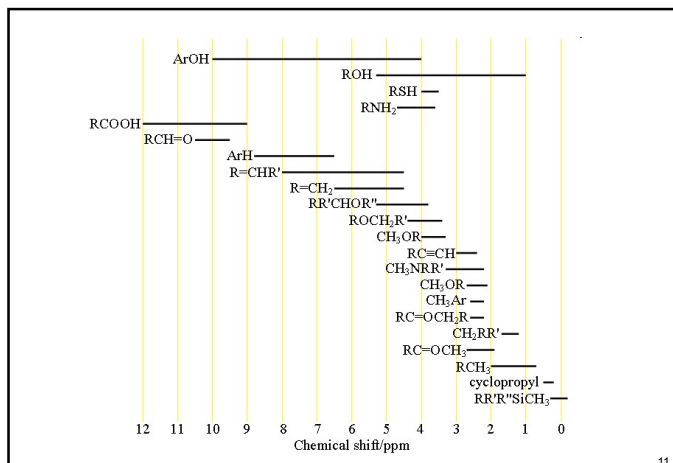
9

How to exploit this experimentally :

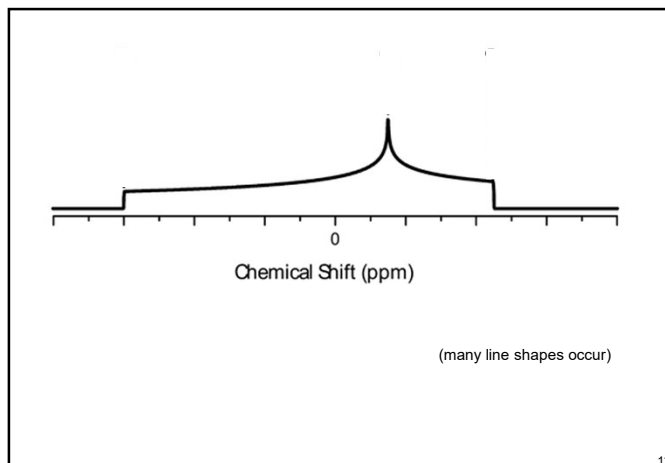
- Create a region with a know (and homogeneous) applied field
- Fill it with a reference molecule (TMS)
- Determine the frequency at which resonance occurs
- Fill the box now with the substance of interest
- Determine the resonance frequencies
- Their difference with the TMS resonance is characteristic for the environment of the nucleus



10



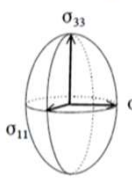
11

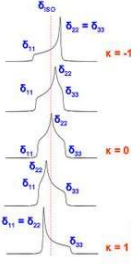


12

The chemical shift is a tensor of rank 2 (with non-vanishing trace):

Apply the external field along the x-, y- and z-axes, respectively. Measure the component of the induced field (or chemical shift) along each axis.


$$\sigma = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix}$$
$$\sigma^{\text{PAS}} = \begin{pmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{pmatrix}$$



Defining the Solid State Chemical Shift Line Shape Parameters for Spin $I = \frac{1}{2}$ Nuclei

$$\delta_{iso} = \frac{(\sigma_{11} + \sigma_{22} + \sigma_{33})}{3}$$
$$\text{SPAN } \Omega = (\sigma_{11} - \sigma_{22}) \quad (\Omega > 0)$$
$$\text{SKEW } K = \frac{3(\sigma_{22} - \sigma_{33})}{\Omega} \quad (-1 \leq K \leq 1)$$

The isotropic value (1/3 of the trace), the span and the skew are typical for a particular environment.

13

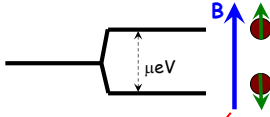
The Chemical Shift (CS) and Chemical Shift Anisotropy (CSA) are powerful tools for **chemical identification**: "which molecules or solids do I have in my sample".

NMR-spectroscopists have a toolbox of tricks to extract information on the **position in space** of the absorbing nuclei.


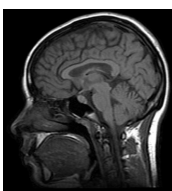
The combination of chemical identification and position information makes NMR useful as a medical imaging technique (usually called MRI).

14

Magnetic Resonance Imaging (MRI = NMR)




Generate a 4 T external field by a superconducting magnet.




If you do proton-NMR, you will "see" where all the protons in your "sample" are (when methods for *spatial resolution* are added – not a topic of this course).

15

Magnetic Resonance Imaging (MRI = NMR)



Generate a 4 T external field by a superconducting magnet.



If you do proton-NMR, you will "see" where all the protons in your "sample" are (when methods for *spatial resolution* are added – not a topic of this course).

16

nuclear magnetic resonance


nuclear quadrupole resonance

stefaan.cottenier@ugent.be

17

Nuclear Quadrupole Resonance (NQR)

The same principle can be applied to quadrupolar hyperfine levels. The electric-field gradient need not to be externally applied, you can use the EFG present in materials.



Sensitive to ^{14}N , and nitrogen is a constituent of almost any explosive (as NO_2 complexes – RDX, TNT and PETN are dominantly used).

- No external magnet needed → no safety problem to apply in e.g. airports (what happens if you scan a metal bottle...)
- Not applicable to liquids (EFGs wiped out)
- Detection of liquids: zero-field NMR (using small applied fields and sensitive squids for signal detection – is being rolled out)

18