Nuclear Magnetic Resonance Spectroscopy

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Outline

1. Introduction

2. NMR, the vector model and the relaxation

3. Chemical shift, scalar coupling and NOE

5. Two dimensional NMR.

5. Introduction to solid-state NMR.

Introduction

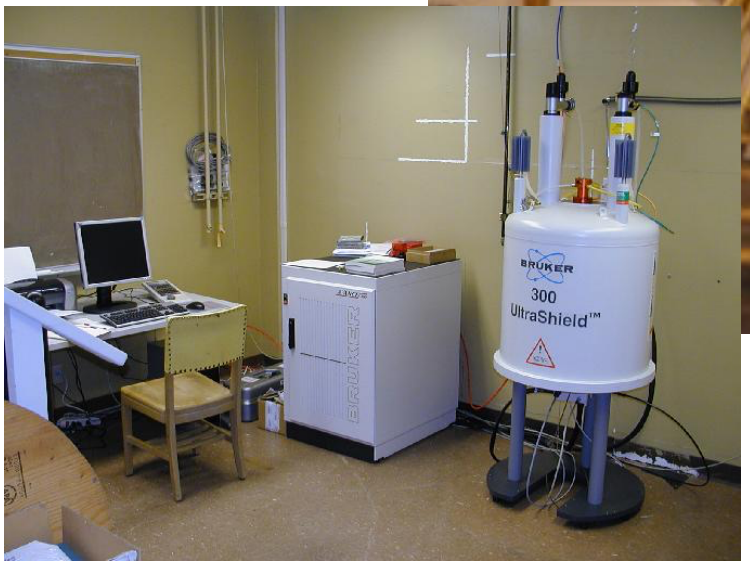
Questions to be answered during this lecture:

What is NMR spectroscopy? Do I known the origin of the methods, its backgrounds?
Could I recognize an NMR Spectrum? Analyze an NMR spectrum?
Do I know the applications? Why is this important?
What it is that I don't know yet?

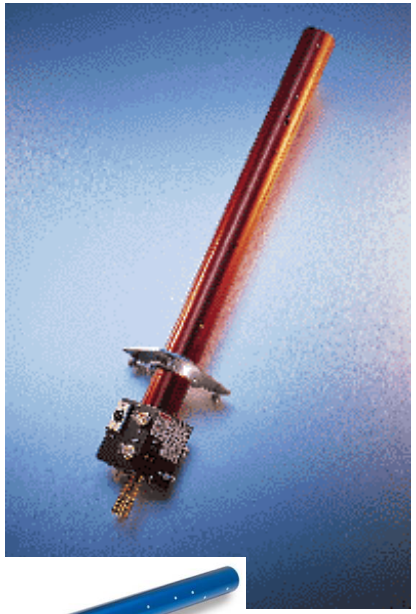
Readings:

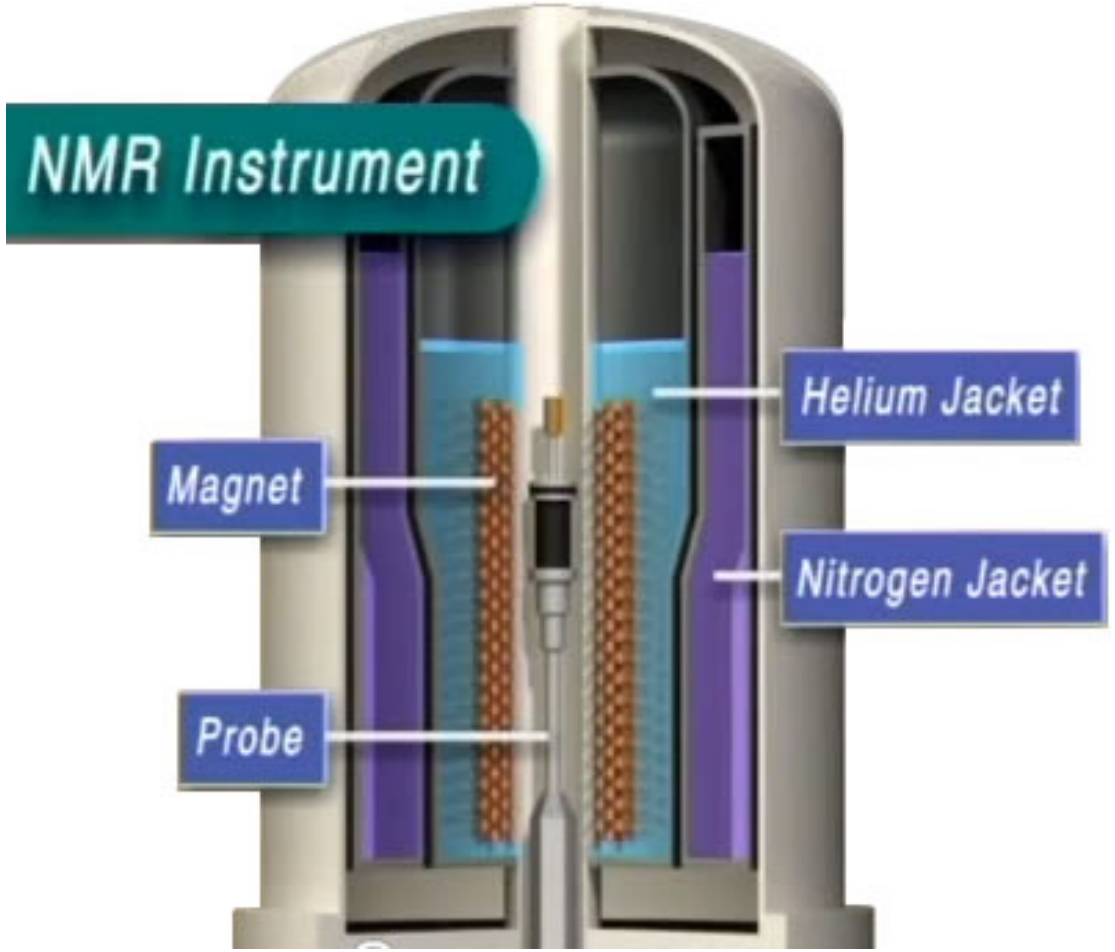
Spin Dynamics, Basics of NMR, **Wiley**, *Levitt*
Understanding NMR Spectroscopy, **Willey**, *Keeler*

What is NMR spectroscopy?



What is NMR spectroscopy?

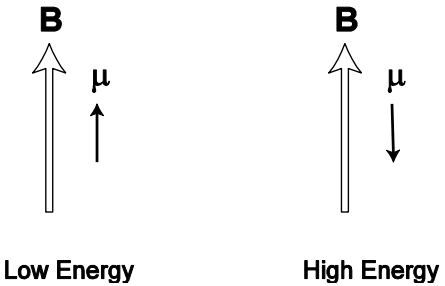




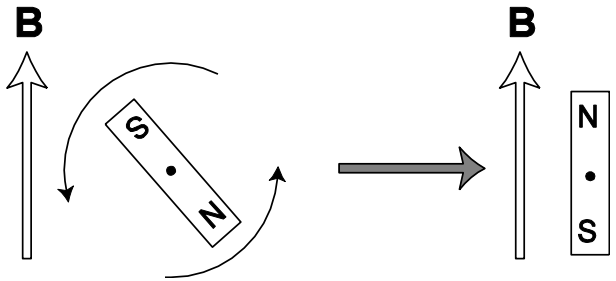
Effect of the Magnetic Field on Matter

Interaction of Magnetic Field and Matter: Macroscopic Magnetism

$$E = -\mu \cdot B$$



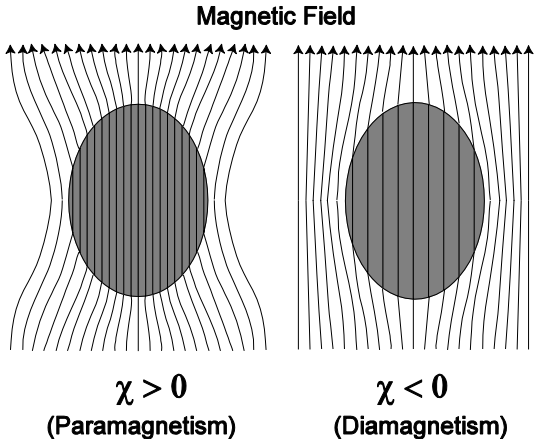
Permanent magnetic moment, *e.g.* magnets:



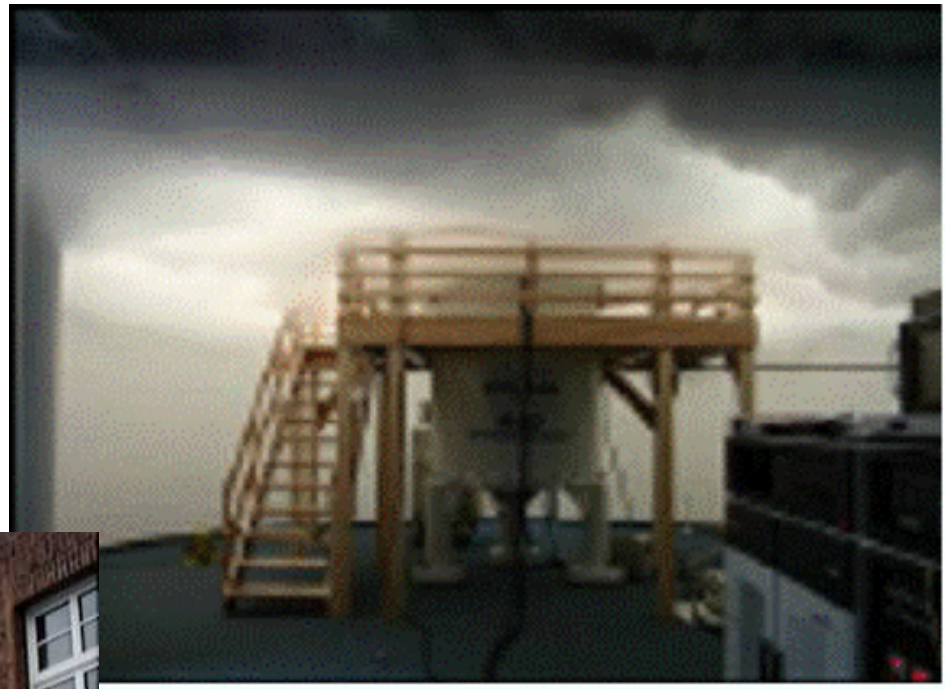
Induced magnetic moment

$$\mu_{induced} = \frac{\chi}{\mu_0} \times VB$$

V: Volume
χ: Magnetic susceptibility
B: Applied field
$\mu_0 = 4\pi \times 10^{-7}$ H/m



Really?



magnet quench

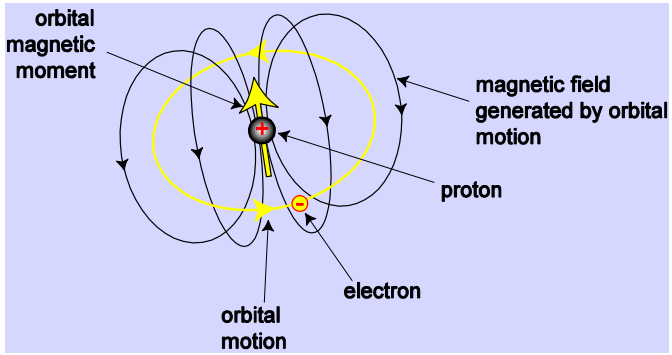
Effect of the Magnetic Field on Matter

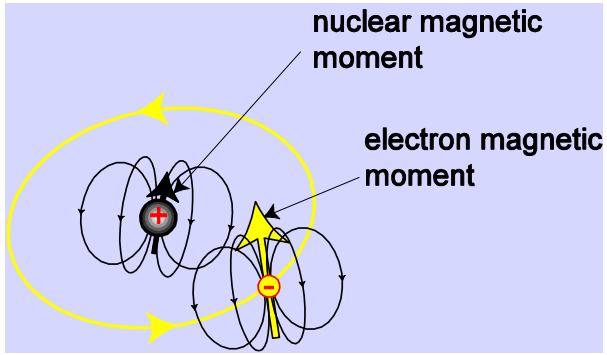
Interaction of Magnetic Field and Matter: Macroscopic Magnetism

Source of magnetism:

1) circulation of electron currents (negative contribution to susceptibility)
2) magnetic moments of electrons (positive contribution to susceptibility)
3) magnetic moments of nuclei (positive contribution to susceptibility)

with 1 and 2 > 3

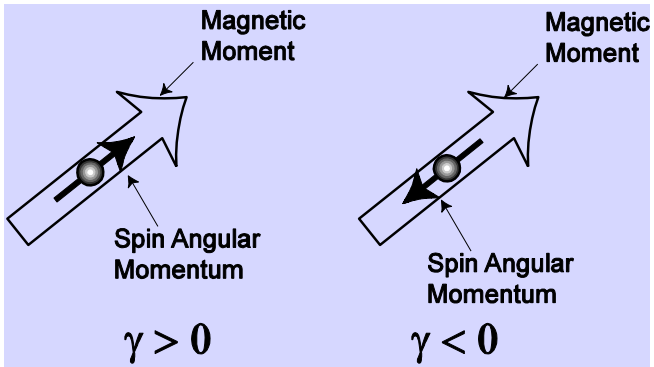




Spins and magnetism:

$$\hat{\mu} = \gamma \hat{S}$$

γ = gyromagnetic (or magnetogyric) ratio (positive or negative and characteristic of the nuclei).



The magnetic moment of the electron has been predicted by Dirac.

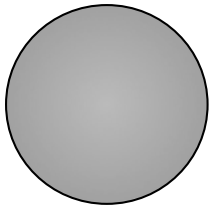
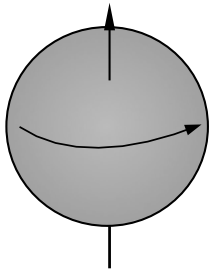
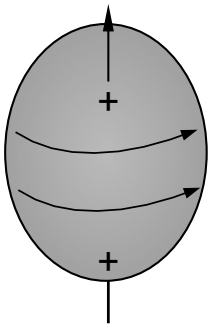
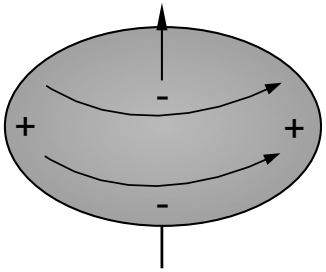
However, today the magnetic moments of quarks and nucleons, and thereby nuclei, are not year understood.

Effect of the Magnetic Field on Nuclei

Properties at the atomic level: *Nuclear Spin Quantum Number, I*

NMR Periodic Table

For protons and neutrons: I = ½
For atoms: I depends on how spin are paired or unpaired:

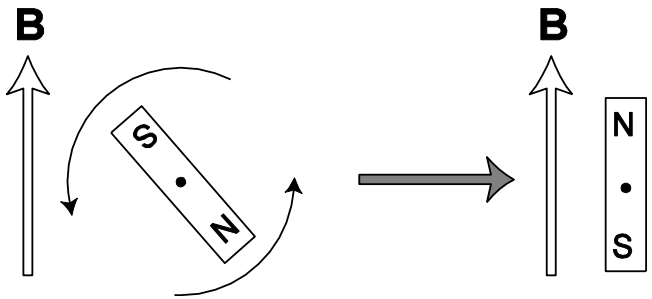
I = 0, $\mu_N = 0$	I = ½, $\mu_N \neq 0$, eQ = 0	I ≥ 1, $\mu_N \neq 0$, eQ > 0	I ≥ 1, $\mu_N \neq 0$, eQ < 0
			
No nuclear spin Nuclei with even numbers of both protons and neutrons (A and Z are even) e.g. ^{12}C, ^{16}O, ^{32}S…	Distribution of positive charge in the nucleus is spherical (spinning sphere) e.g. ^{1}H, ^{13}C, ^{19}F, ^{31}P… as well as ^{195}Pt…	Non-spherical distribution of charges (electric dipole, eQ) eQ = 0 in spherical environment *e.g.* ^{2}D, ^{14}N, ^{17}O… A = even, Z = odd, I = integer A = odd, I = half integer	

Unpaired nuclear spins (I ≠ 0) → nuclear magnetic moment (μ_N).
Spinning charges → angular momentum (*I*).
The allowed orientation of m are indicated by *nuclear spin angular momentum quantum number, m_I with m_I = I, I-1, …, -I+1 and I, a total of $2m_I$+1 states*

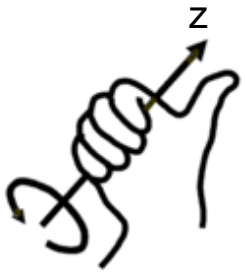
This is associated with a magnetic moment μ, a characteristic of the nuclei: $\vec{\mu}_N = \gamma\hbar\vec{I}$

Effect of the Magnetic Field on Nuclei

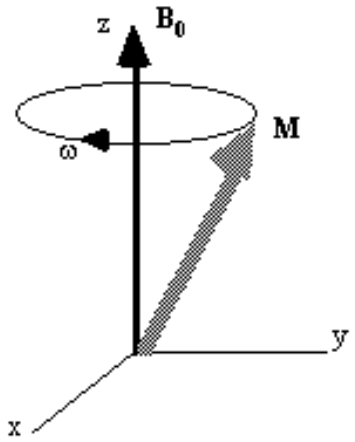
Macroscopic Magnetism



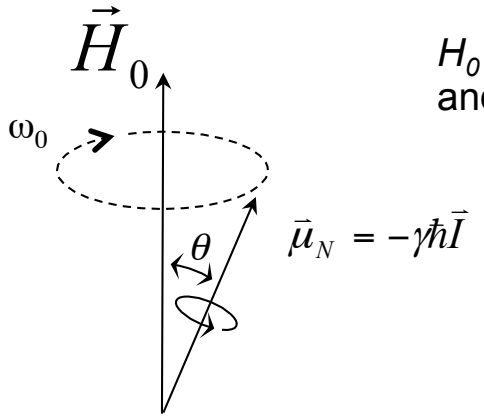
Microscopic Magnetism



In such an axis system, a positive rotation is defined by the curl of the fingers



For $\gamma > 0$



$\vec{\mu}_N = -\gamma\hbar\vec{I}$

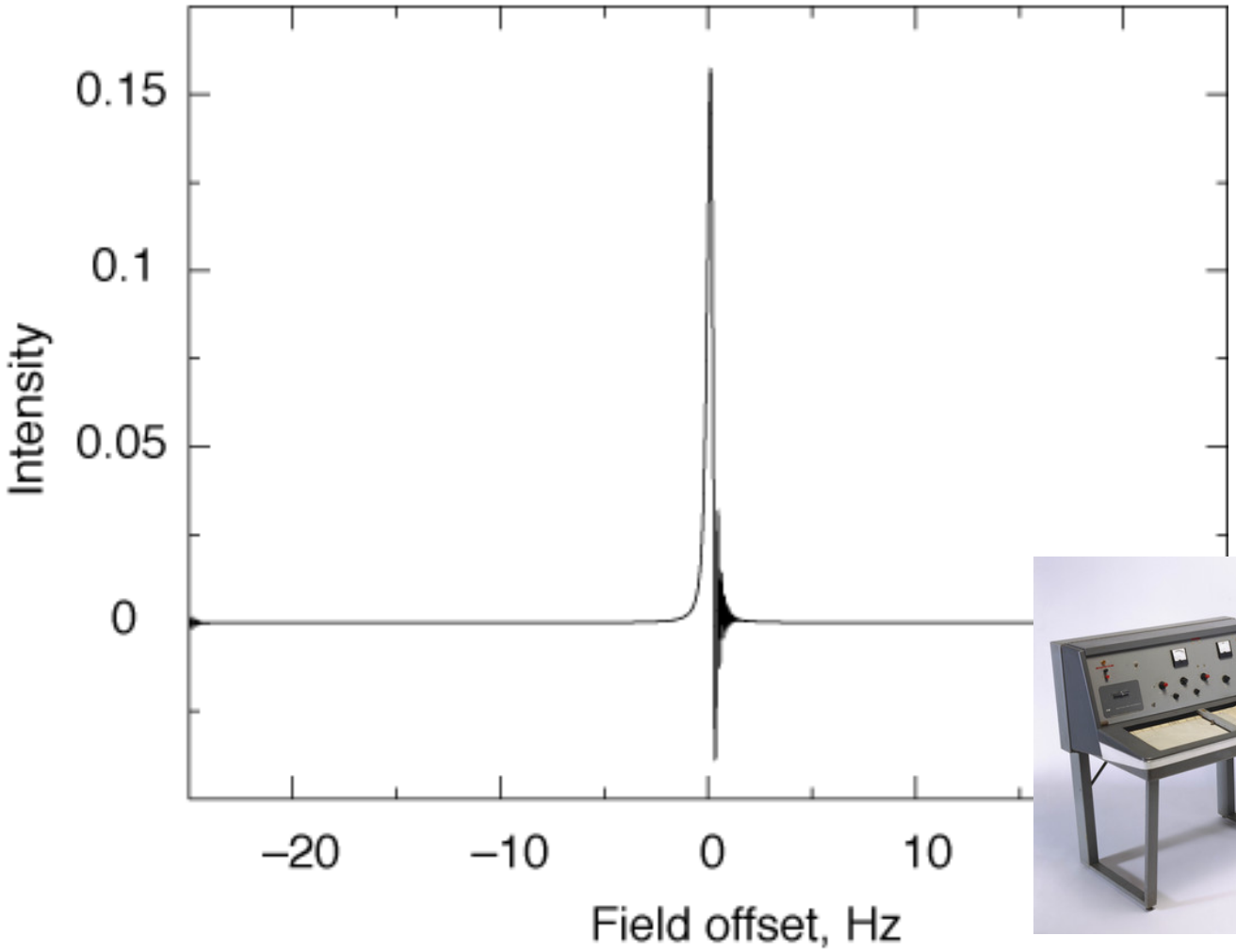
H_0 exerts a force (torque) on μ_N, causing a precession, perpendicular to μ_N and H_0, with a frequency ω_0 (Larmor frequency):

$$\vec{\tau} = \vec{\mu} \times \vec{H}_0 \qquad \omega_0 = -\gamma H_0$$

γ = gyromagnetic (or magnetogyric) ratio, associated with the angular momentum *I and a characteristic of the nucleus*

^{1}H, I =½; γ = 267.522×10^{6} rad/s/T (-500 MHz at 11.74 T)
^{2}H, I =1; γ = 41.066×10^{6} rad/s/T (-76.75 MHz at 11.74 T)
^{13}C, I =½; γ = 67.283×10^{6} rad/s/T (-125 MHz at 11.74 T)
^{29}Si, I =½; γ = - 53.190×10^{6} rad/s/T (99.34 MHz at 11.74 T)

Analysis of the movement: Continuous-Wave (CW) Spectrometers



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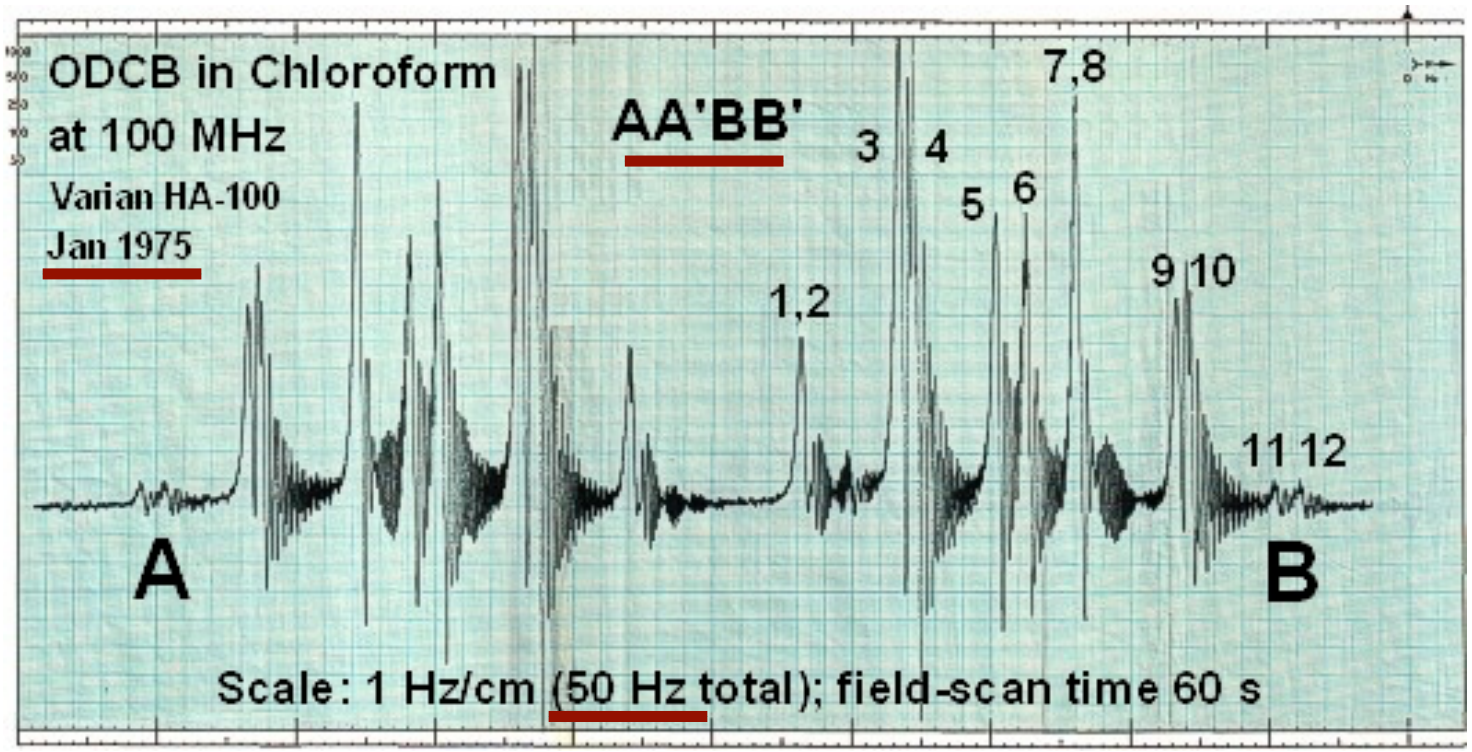
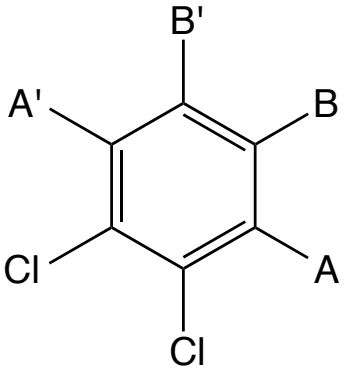


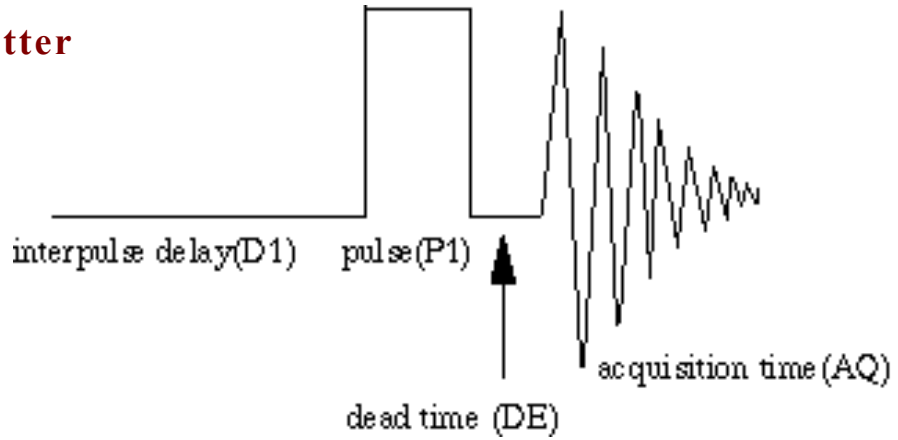


A simple molecule leads to many peaks… with a pattern that is difficult to rationalize?

We will try to understand what is happening with problem set IV

Introduction of the pulsed NMR

Problem set II should help better understanding the pulsed NMR



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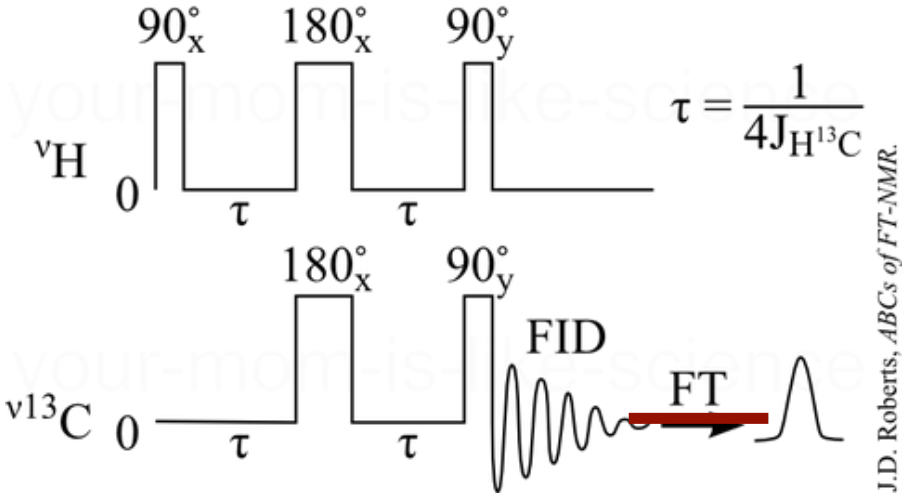
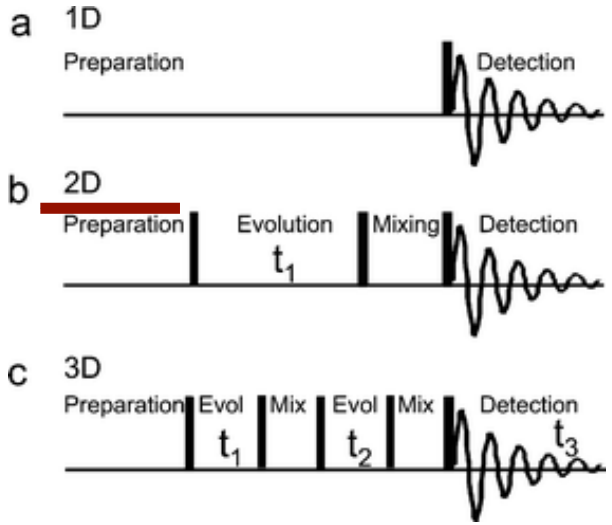
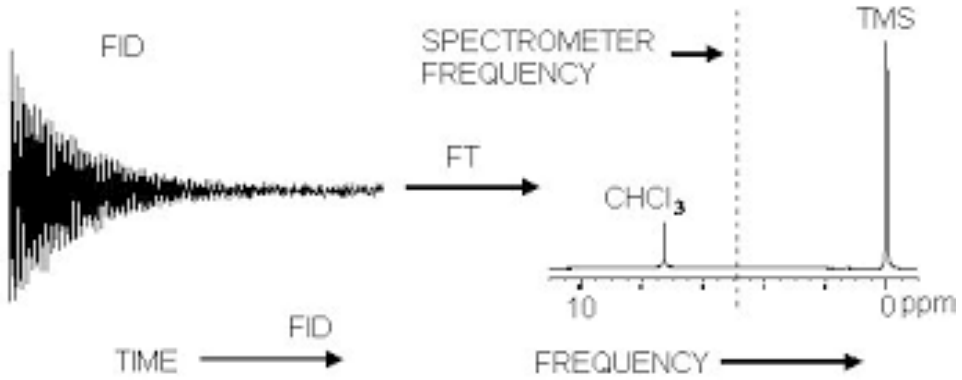
INEPT (Insensitive Nuclei Enhanced by Polarization Transfer) pulse sequence





From a FID to a readable spectrum

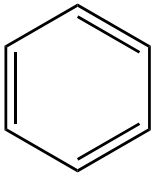


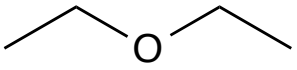
What are the practical problems that may occur?

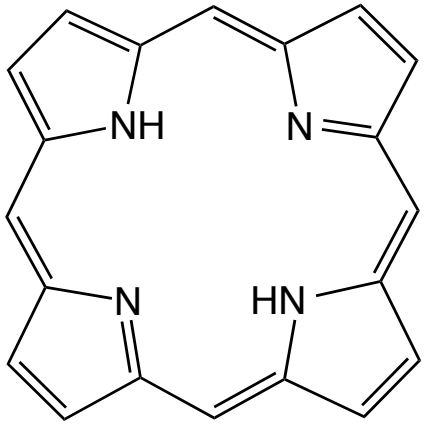
Set up the right frequency, locking…
Making sure the filed at the sample is homogeneous, shimming…
Having the base line right?
Is the phase correct?
What about the integration of the resonances?

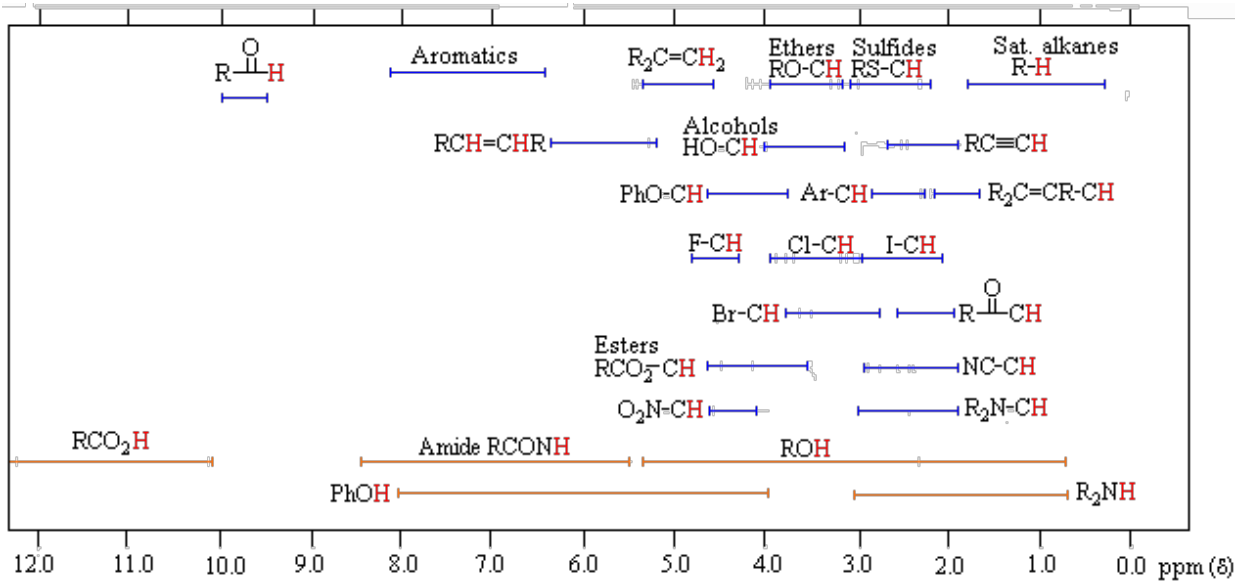
Problem set III will help making sure we know each step and understand how a spectrum is obtained?

But why do we study this?



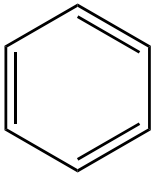


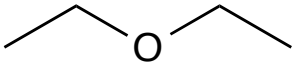


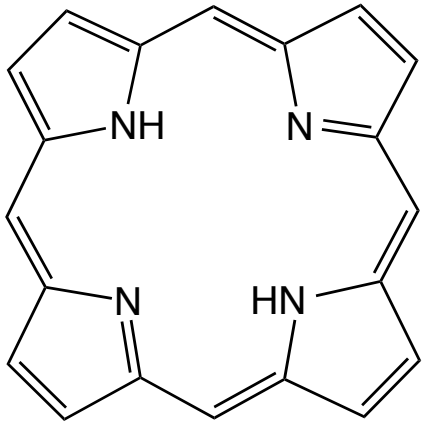


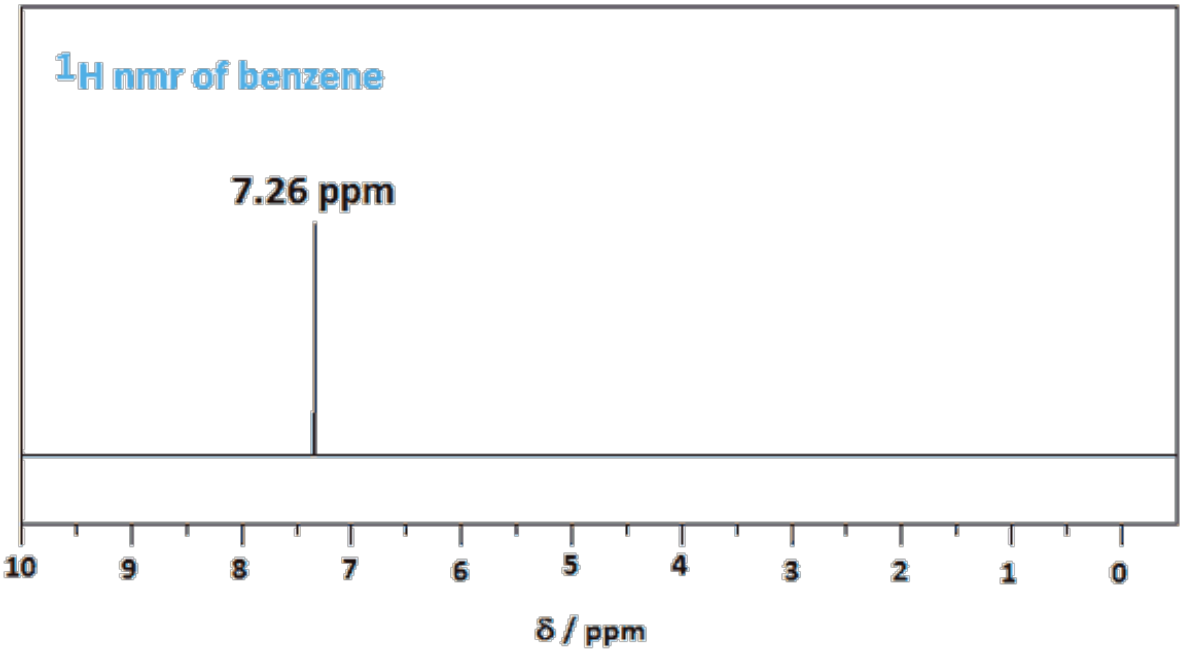
This is what you should know… and we will remember tis together with problem set I

Chemical attribution

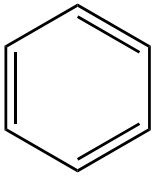


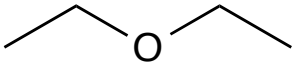


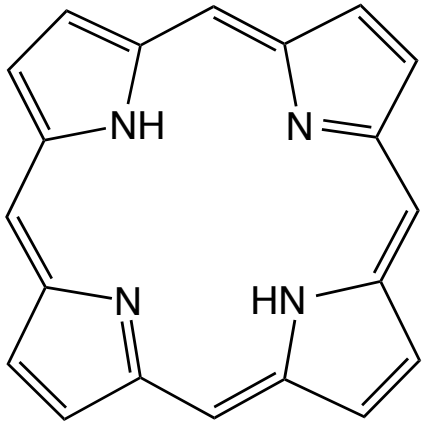


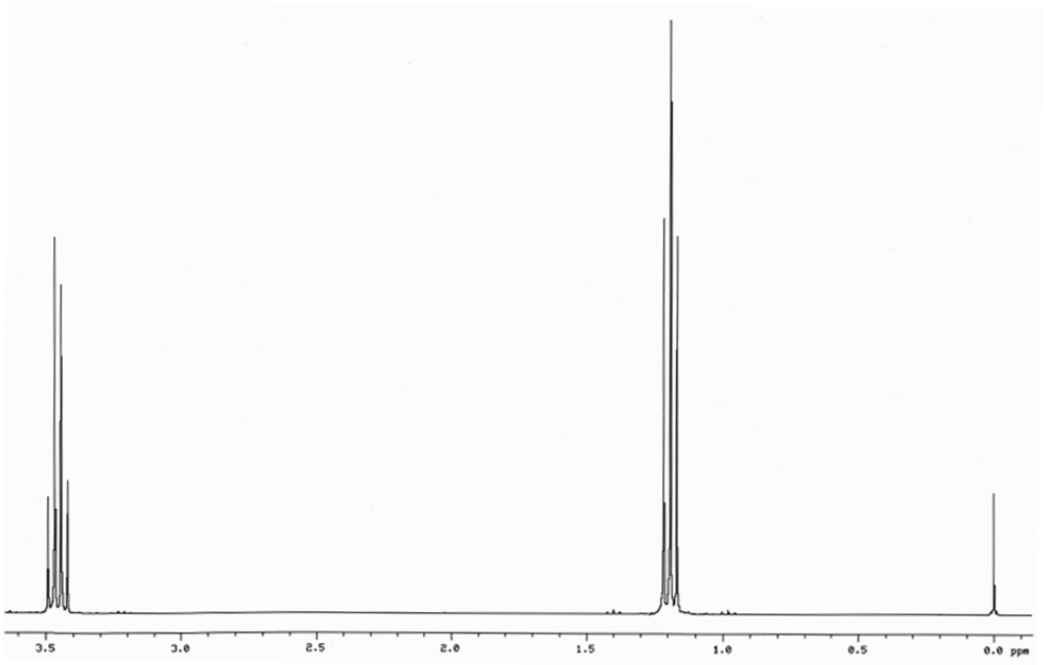


Chemical attribution

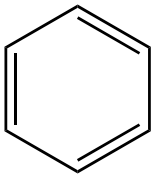


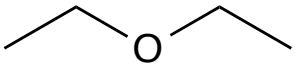


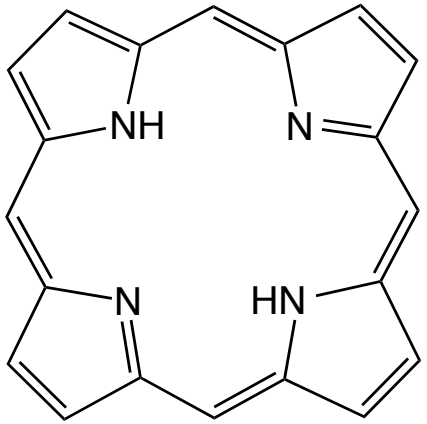


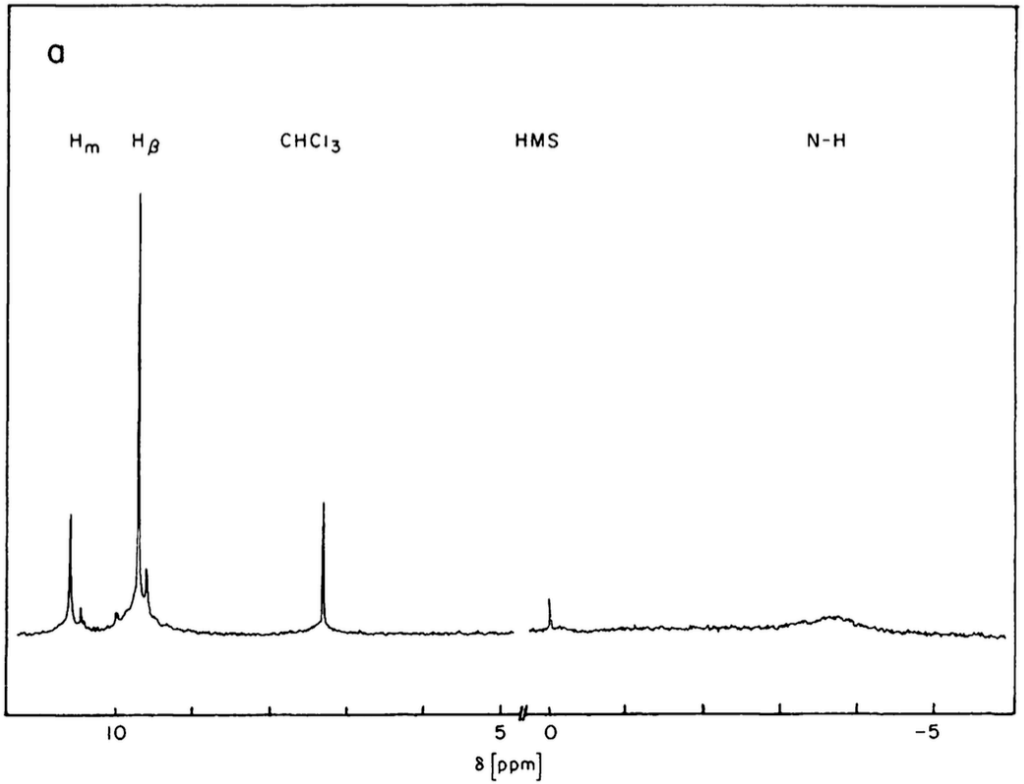


Chemical attribution

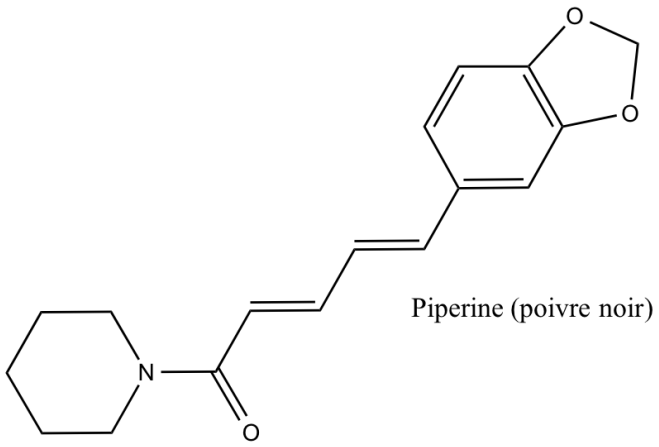




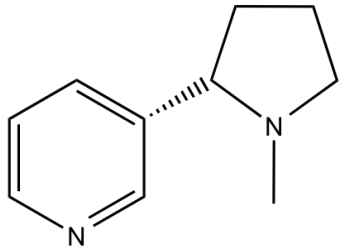




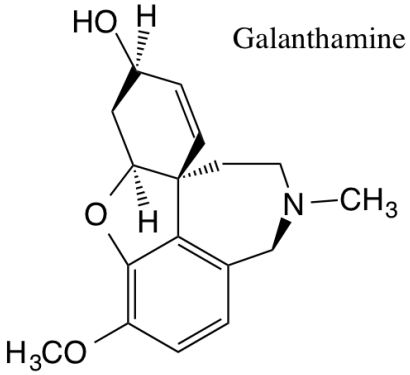
Chemical attribution: Problem set I



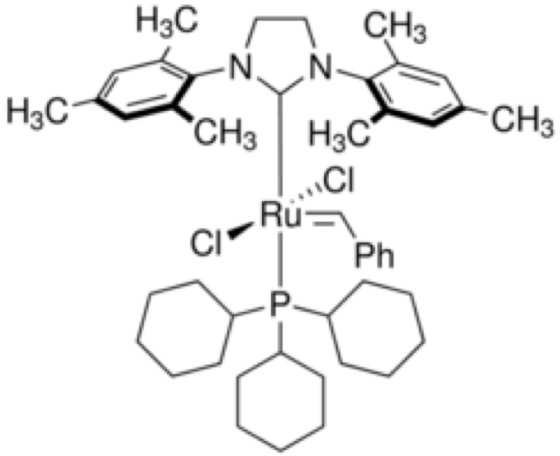
Piperine (poivre noir)



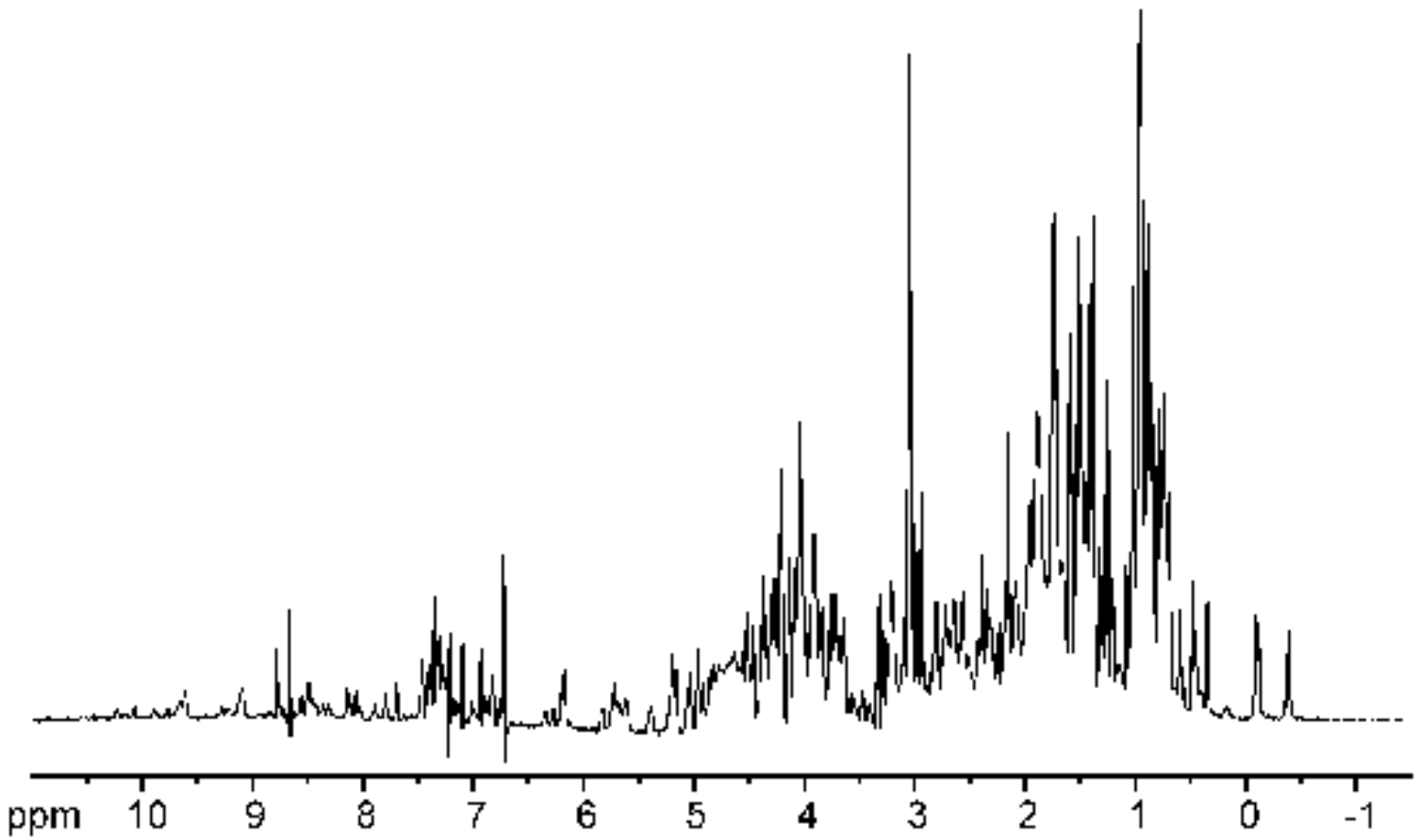
Nicotine (Tabac)



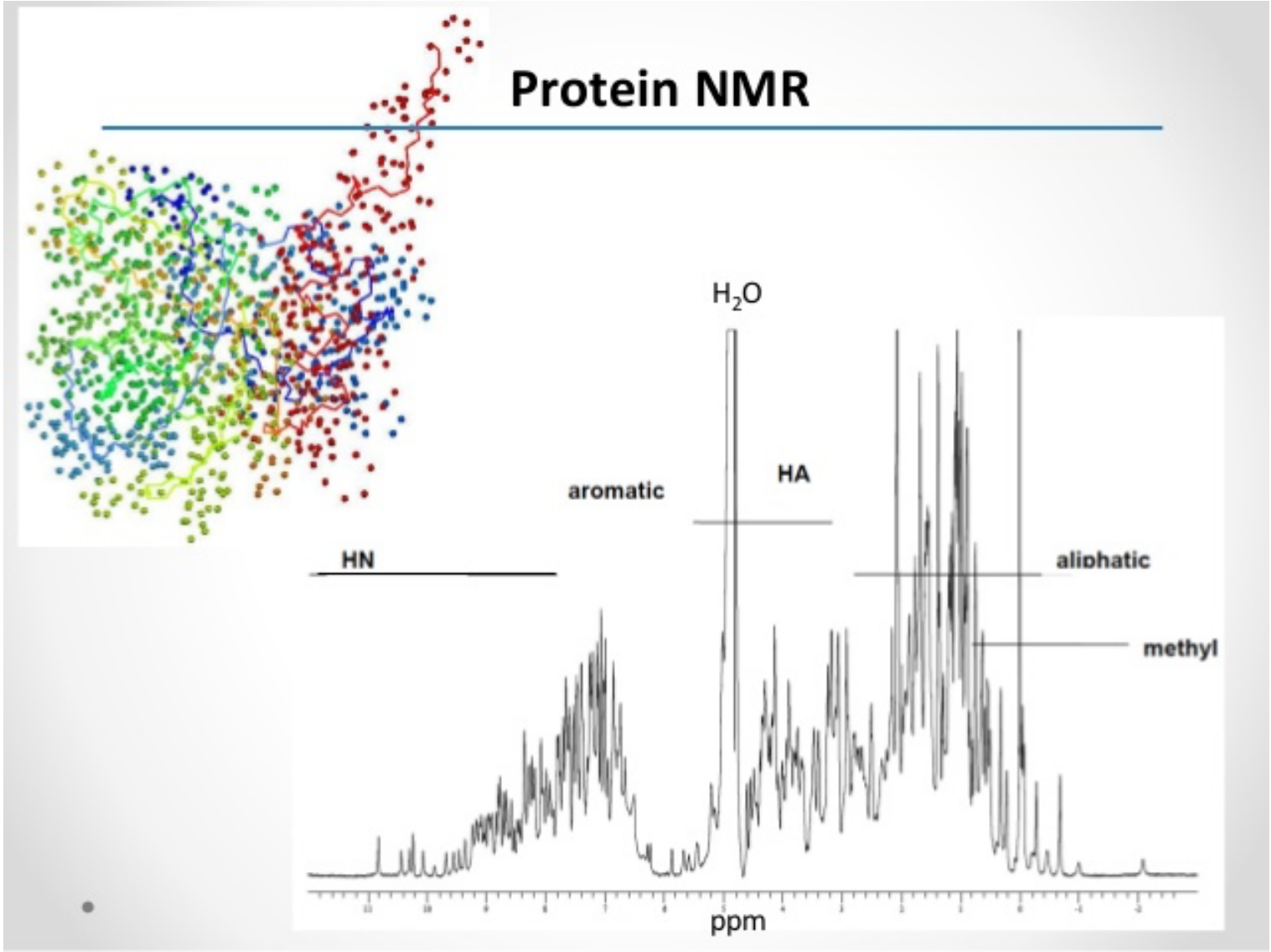
Galanthamine



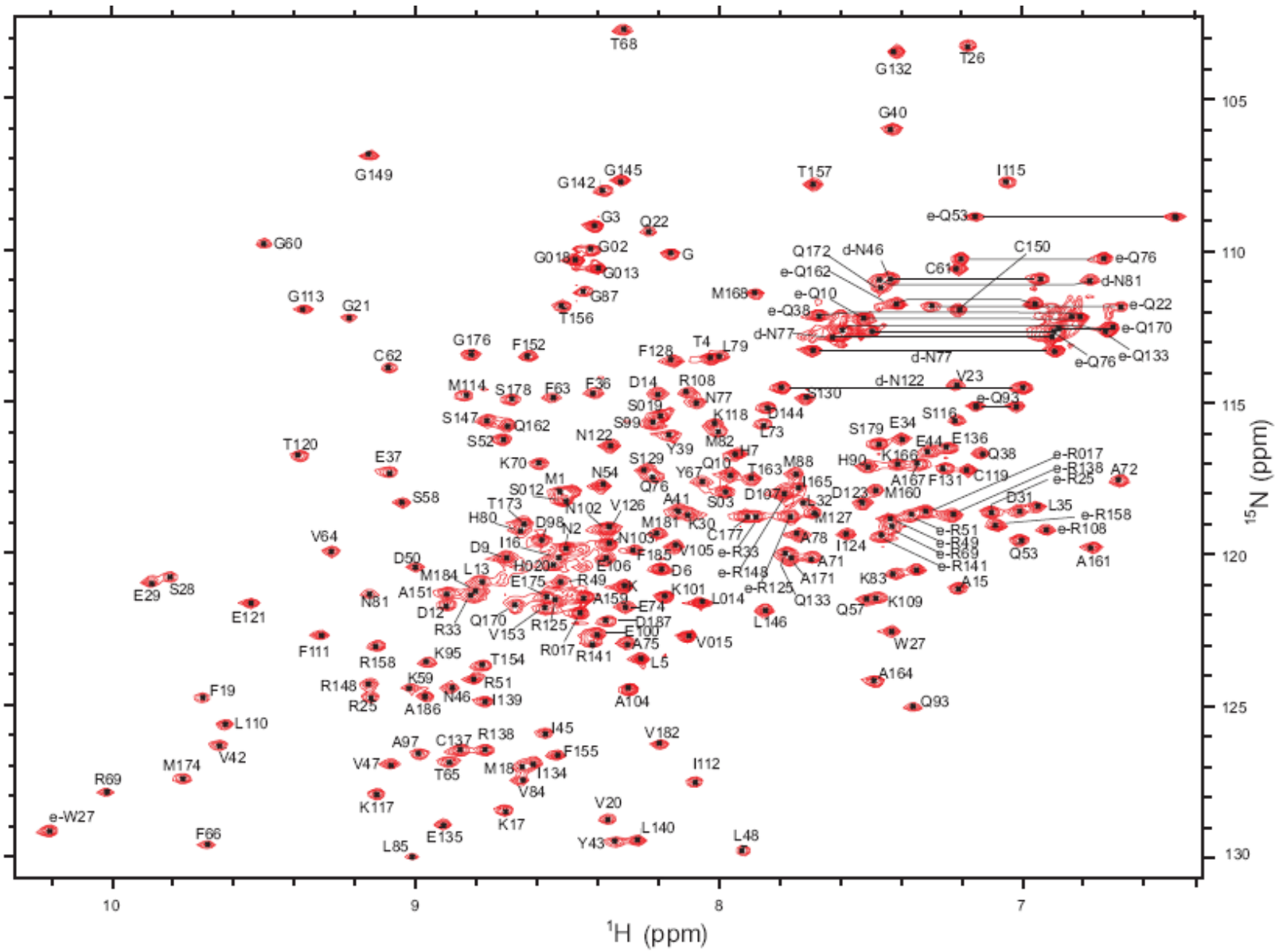
Structural Chemistry using NMR



Structural Chemistry using NMR



Structural Chemistry using NMR



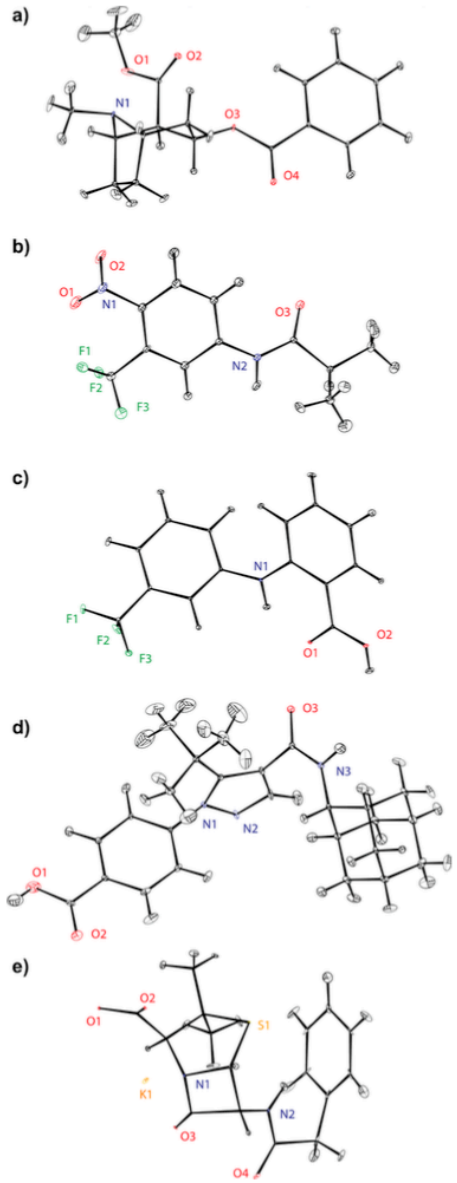


Figure 1. ORTEP plots drawn at the 90% probability level for the NMR-determined crystal structures of (a) cocaine, (b) flutamide, (c) flufenamic acid, (d) AZD8329, and (e) the K salt of penicillin G. The ellipsoids correspond to positions within a ^{1}H chemical shift RMSD of 0.49 ppm.

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Positional Variance in NMR Crystallography

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But why do we study this?

Metathesis Activity Encoded in the Metallacyclobutane Carbon-13 NMR Chemical Shift Tensors

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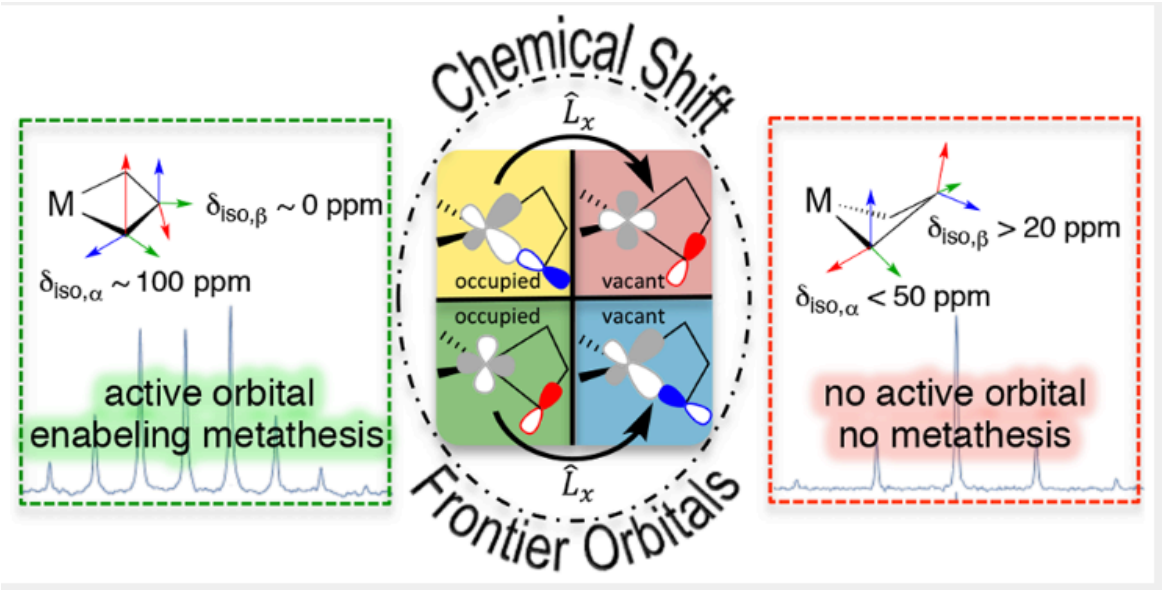

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NMR Spectroscopy

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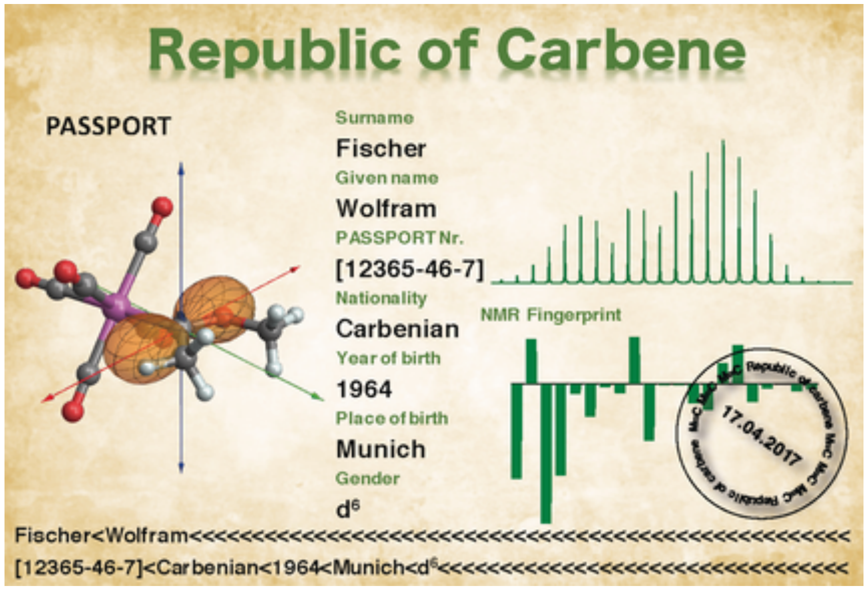
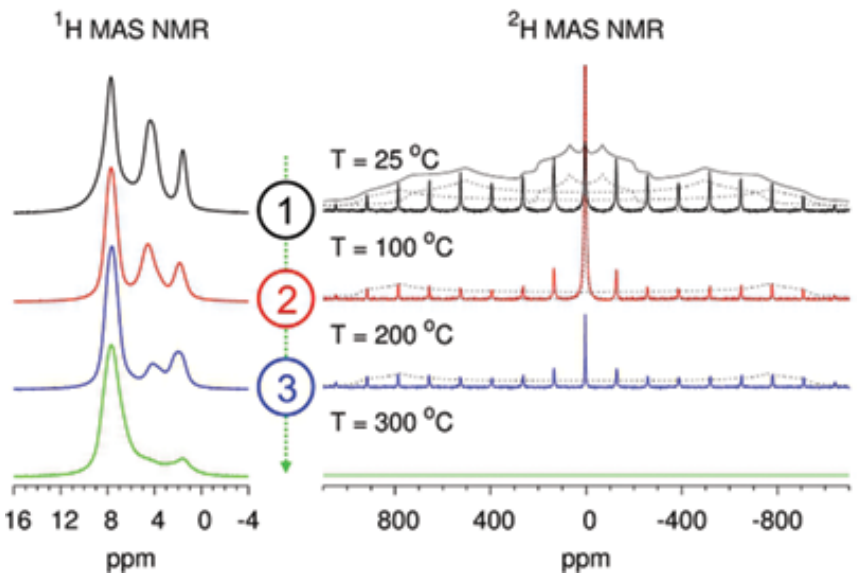
Orbital Analysis of Carbon-13 Chemical Shift Tensors Reveals Patterns to Distinguish Fischer and Schrock Carbenes

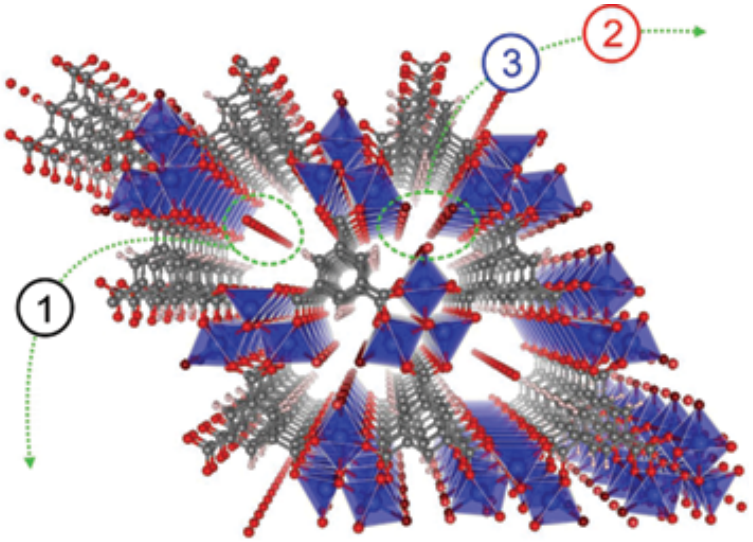
Keishi Yamamoto, Christopher P. Gordon, Wei-Chih Liao, Christophe Copéret, Christophe Raynaud,* and Odile Eisenstein**

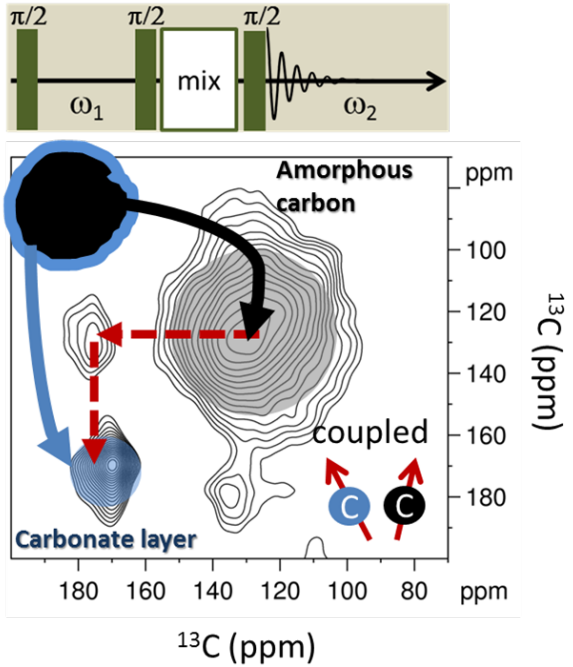
Dedicated to Professor Roald Hoffmann on the occasion of his 80th birthday



Characterization of advanced materials







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Tuning of the relaxation properties