

# Introduction to Magnetic Response Properties

## Lesson 9: Intro. to Magnetic Response Properties



# Magnetic Response Spectroscopy

- widely used structure determination method
- uses very high magnetic fields to probe magnetically active nuclei
- typical nuclei:  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$ ,  $^{31}\text{P}$
- each type of nucleus gives specific signal in spectrum
- position and shape of the signal is given by electronic and nuclear structure surrounding the nucleus

# Properties that can be obtained

- isotropic Chemical Shifts
- chemical Shielding Tensors
- $J$ -coupling
- $g$  and A-tensors (EPR, paramagnetic NMR)

# *In Silico* NMR Properties

- calculated NMR atomic properties are very sensitive to:
  - chosen geometry
  - wavefunction (tighten convergence criteria, if possible)
  - solvent effects/crystal effects (especially exchangeable moieties)
  - dynamic effects

## Energy Levels ( $\alpha - \beta$ )

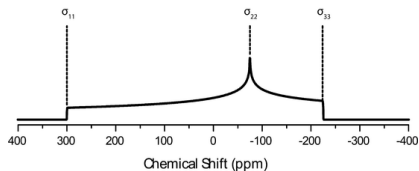
- difference between states is  $\Delta E = \gamma \hbar B_0 = -\gamma \omega$
- where:
  - $\gamma$  is the magnetogyric ratio of a nucleus
  - $\hbar$  is Planck's constant
  - $B_0$  is the external magnetic field
  - $\omega$  is the Larmor precession frequency
- small energies for excitations - perturbation to the wavefunction

# NMR Chemical Shift

- $\Delta E = \gamma \hbar (1 - \sigma) B_0 = -\gamma \omega$ 
  - magnetic field felt by the nucleus is  $(1 - \sigma) * B_0$  as a result of chemical shielding  $\sigma$
- difference in frequency of bare nucleus and nucleus under is:
  - $\sigma(ppm) = 10^6 * (\nu_{nuc} - \nu_{com}) / \nu_{nuc}$
- chemical shift:
  - $\delta(ppm) = 10^6 * (\sigma_{ref} - \sigma_{sample})$

# Chemical Shift Anisotropy

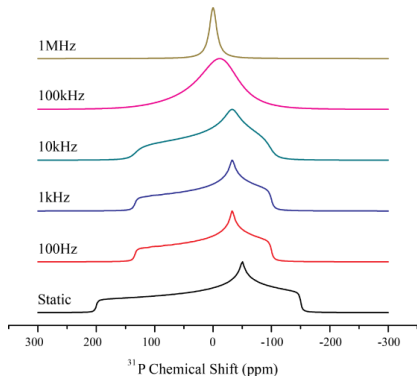
- IUPAC convention:
  - $\sigma_{11} \geq \sigma_{22} \geq \sigma_{33}$
  - $\sigma_{11}$ : direction of least shielding,  $\sigma_{33}$ : direction of highest shielding



- the average of these is the "isotropic" value

# Isotropic Tumbling

- due to fast tumbling in solution, the shielding gets isotropically distributed
- in solid state the anisotropy is reduced by magic angle spinning (MAS)





# Chemical shift ( $\delta$ )

- difference between the shielding of nucleus under investigation and nucleus in reference compound:
  - $\delta(ppm) = 10^6 * (\sigma_{COM} - \sigma_{STD}) / (1 - \sigma_{STD})$
- *In Silico* Methods
  - improved results with climbing Jacob's ladder (DFT and *ab initio*)
  - always try to use as high basis set as possible
  - STO are superior to GTO
  - make sure you wavefunction is well converged
  - increase the SCF convergence criteria
  - calculate the chemical shifts against well-behaving reference

# Practical task (NMR)

- Calculate the NMR properties of acetic acid
- Consider
  - Equilibrium geometry
  - Dimer
  - Microsolvated acetic acid with 2 water molecules
  - Calculate the spin-spin J-couplings as well

- In your input files include:
  - b3lyp 6-311++g(d,p) method
  - Very tight linear equations for SCF
  - D3 dispersion correction
  - Ultrafine integration grid
  - PCM water solvation model
  - Calculation of only J-couplings for nonoxygen atoms of acetic acid (see documentation of NMR in Gaussian, do NOT calculate for dimer)

# Reference compound

- Good reference from computational point of view:
  - Small and symmetric
  - Rigid molecule (elimination of dynamic effects)
  - Only electrostatic interactions with surroundings (elimination of charge transfer effects)
- Benzene in benzene
- Use the very same setup as for acetic acid (except PCM),
- use “tight” convergence for optimization
- $\delta^{13}C = 127.83, \delta_1H = 7.15$
- $\delta_{COM}(ppm) = \sigma_{STD} - \sigma_{COM} + \delta_{STD}$

# Results

- Compare the experimental values with predicted ones:
- $^1H$  : 2.08 and 11.7 ppm
- $^{13}C$  : 20.0 and 180.0 ppm
- Why Some geometries give better results?

