

Lesson 9: Response Properties: NMR

NMR Spectroscopy

- widely used structure determination method
- uses very high magnetic fields to probe magnetically active nuclei
- typical nuclei: ^1H , ^{13}C , ^{15}N , ^{31}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 ($\alpha - \beta$)

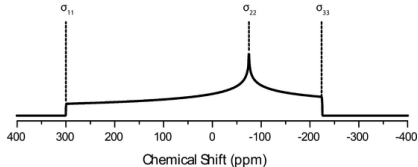
- difference between states is $\Delta E = \gamma \hbar B_0 = -\gamma \omega$
- where:
 - γ is the magnetogyric ratio of a nucleus
 - h is Planck's constant
 - B_0 is the external magnetic field
 - ω is the Larmor precession frequency
- small energies for excitations - perturbation to the wavefunction

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 σ
- 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

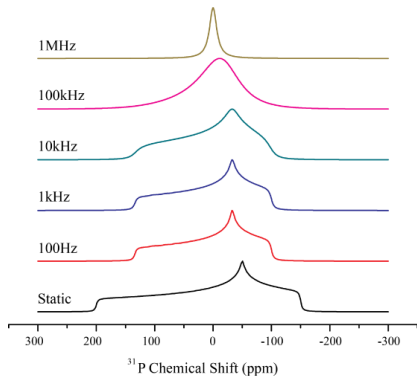
- IUPAC convention:
 - $\sigma_{11} \geq \sigma_{22} \geq \sigma_{33}$
 - σ_{11} : direction of least shielding, σ_{33} : direction of highest shielding



- 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 (δ)

- difference between the shielding of nucleus under investigation and nucleus in reference compound:

$$\bullet \delta(\text{ppm}) = 10^6 * (\sigma_{COM} - \sigma_{STD}) / (1 - \sigma_{STD})$$

- *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

ACTIVITY I - Acetic Acid

- use the series of optimize geometries provided (**Acetic Acid**)
- for NMR calculation your input files must include:
 - b3lyp 6-311++g(d,p) method
 - tighten the SCF convergence to 10^{-8}
 - 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
- NOTE: $\delta^{13}\text{C}_{ref} = 127.83$, $\delta^1\text{H} = 7.15$
- $\delta_{com}(ppm) = \sigma_{ref} - \sigma_{com} + \delta_{ref}$

Assesment - Acetic Acid

- 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?

END