

Lesson 9: Response properties: NMR

- Widely used structure determination method
- Uses very high magnetic fields to probe magnetically active nuclei
- Each type of nucleus gives specific signal in spectrum
- Position and shape of the signal is given by electronic and nuclear structure of the surroundings of the nucleus

What can be obtained

- Isotropic chemical shifts
- Chemical shift tensors
- J -coupling
- g -tensor (EPR)

- NMR properties are very sensitive to:
 - Chosen geometry
 - Wavefunction (tighten convergence criteria, if possible)
 - Solvent effects/crystal effects (especially exchangeable moieties)
 - Dynamic effects

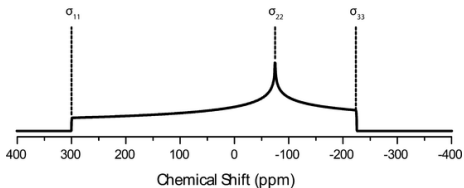
- Difference between states is $\Delta E = \gamma h B_0$
- Where:
 - γ is the magnetogyric ratio of a nucleus
 - h is Planck's constant
 - B_0 is the external magnetic field
- Small energies for excitations - perturbation to the wavefunction

Chemical shielding (σ)

- Difference in frequency of bare nucleus and nucleus under investigation
- $\sigma(ppm) = 10^6 * (\nu_{NUC} - \nu_{COM})/\nu_{NUC}$
- Magnetic field felt by the nucleus is $(1 - \sigma) * B_0$

- IUPAC convention:

$$\sigma_{11} \geq \sigma_{22} \geq \sigma_{33} \quad (1)$$



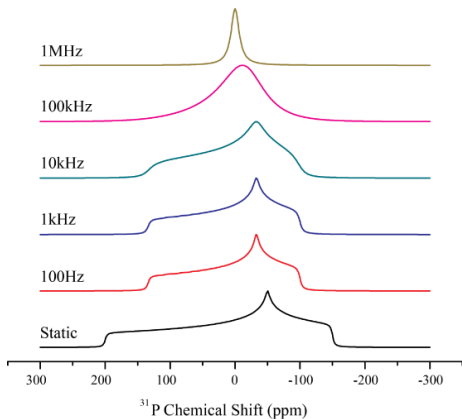
- σ_{11} : direction of least shielding
- σ_{33} : direction of highest shielding

Chemical shift (δ)

- Difference between the shielding of nucleus under investigation and nucleus in reference compound:
- $\delta(ppm) = 10^6 * (\sigma_{COM} - \sigma_{STD}) / (1 - \sigma_{STD})$

Isotropic tumbling

- In solution the dipolar couplings caused by CSA vanish
- In solid state the dipolar couplings are reduced by magic angle spinning (MAS)



- For DFT improved results with climbing Jacob's ladder
- Always try to use as high basis set as possible
- Make sure you wavefunction is well converged
- Increase the convergence criteria
- Calculate the chemical shifts against well-behaving reference

- Calculate the NMR properties of acetic acid
- Consider
 - Equilibrium geometry
 - Dimer
 - Microsolvated acetic acid with 2 water molecules
 - Use the preoptimized geometries distributed in IS
 - Calculate the spin-spin J -couplings as well

- In your inputfiles 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
- $\delta^{13}\text{C} = 127.83$, $\delta^1\text{H} = 7.15$
- $\delta_{COM}(ppm) = \sigma_{STD} - \sigma_{COM} + \delta_{STD}$

- 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?