

## Lesson 9: Response properties: NMR

- 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

# What can be obtained

- Izotropic 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:
  - $\gamma$  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

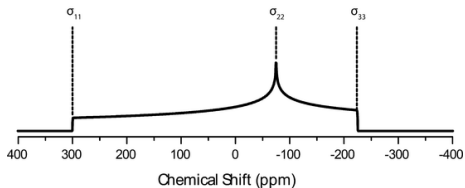
# Chemical shielding ( $\sigma$ )

- 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  $(1 - \sigma) * B_0$

# Chemical shielding tensor

- IUPAC convention:

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



- $\sigma_{11}$ : direction of least shielding
- $\sigma_{33}$ : direction of highest shielding

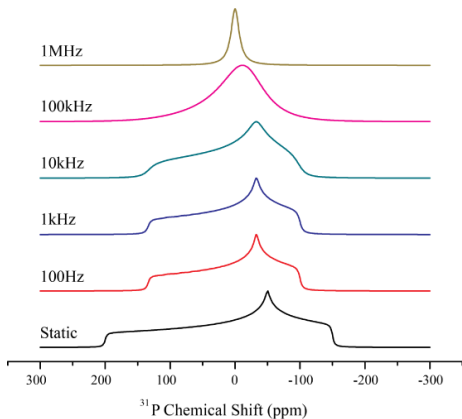
# Chemical shift ( $\delta$ )

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



# Isotropic tumbling

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



- 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

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

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