Analyses of molecular dynamics trajectories

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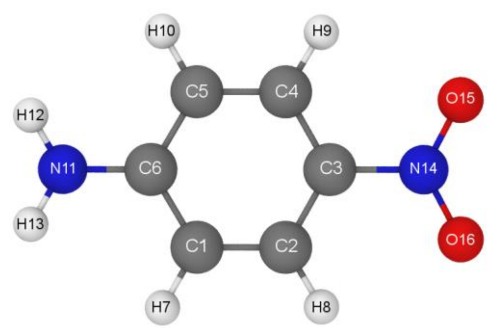


Wrocław, 2014-06-25

1. The motion of the molecule

Translation (diffusion)

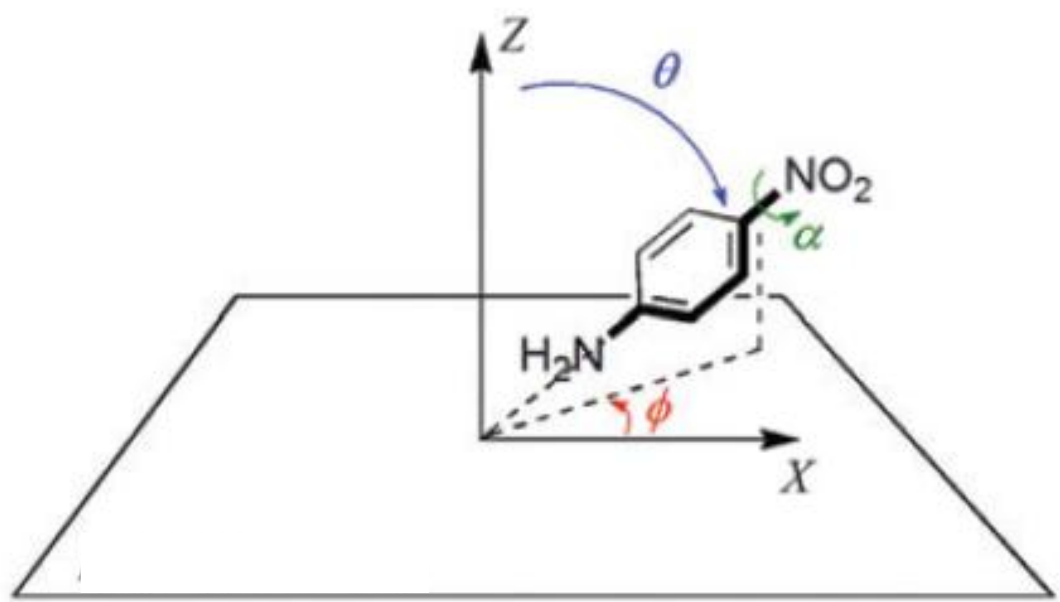
- The Einstein relation

$$6D_{\text{ion}} = \lim_{t\to\infty}\frac{d}{dt}\langle|\vec{R}(t) - \vec{R}(0)|^2\rangle$$

- D_{ion} is the self-diffusion coefficient
- The factor of 6 arises for 3D system
- D_{ion} is obtained from linear fitting of the mean square deviation (MSD) – time plot

Rotation (isotropic tumbling)

- Spatial rotation of the molecule described by the vector along or perpendicular to the molecule



Auto-correlation function

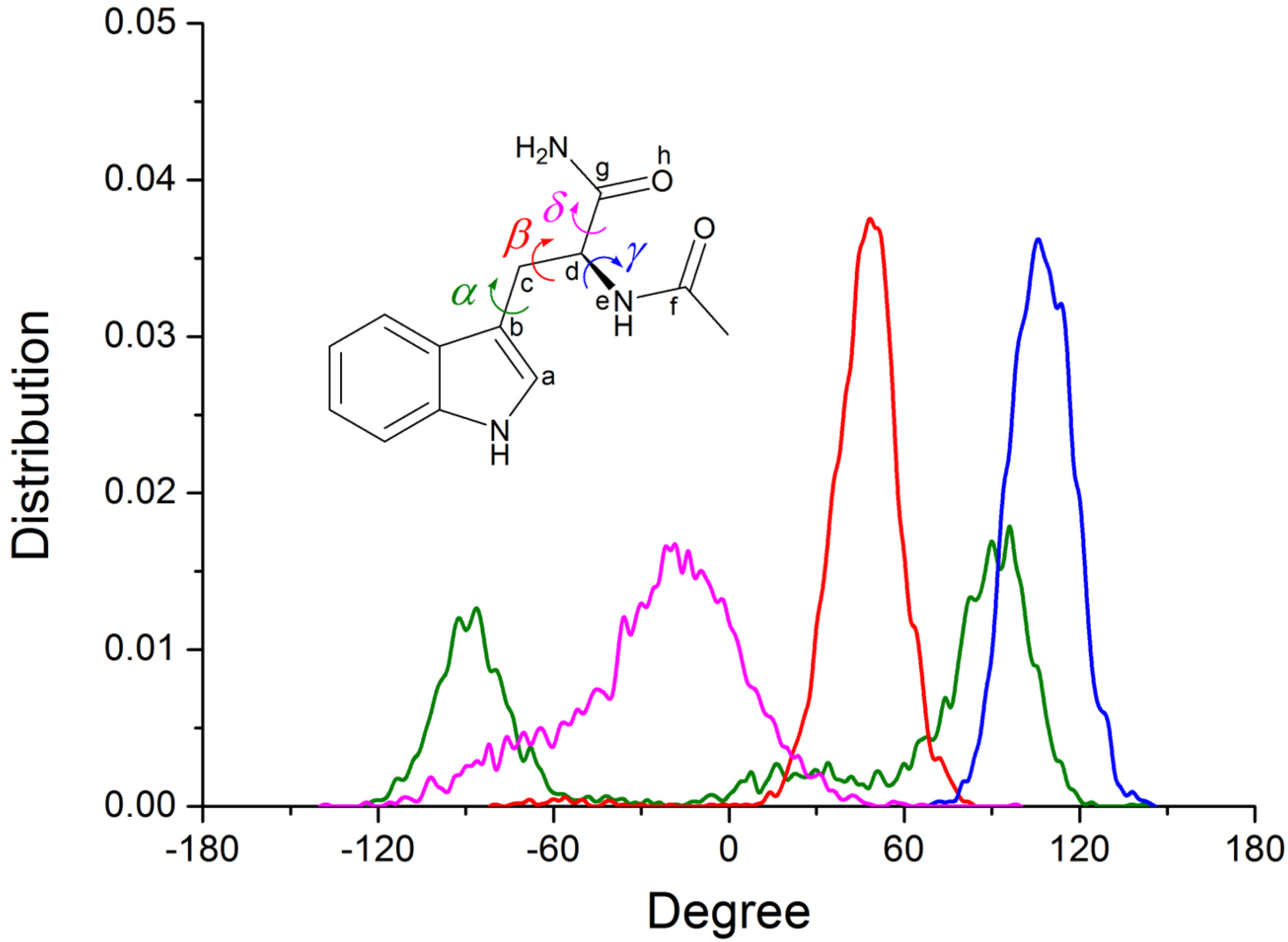
- For a vector $\boldsymbol{p}$

$$C_{\boldsymbol{p}}(t) = \int_0^{\infty} P_n(\cos\angle(\boldsymbol{p}(\xi), \boldsymbol{p}(\xi + t))\,\mathrm{d}\xi$$

- P_n is n-th order Legendre polynomial. Usually n = 2.

- The rotational correlation time is obtained through integration of the auto-correlation function from zero to infinity

Dihedral angle dynamics



Auto-correlation function

- For a dihedral angle φ

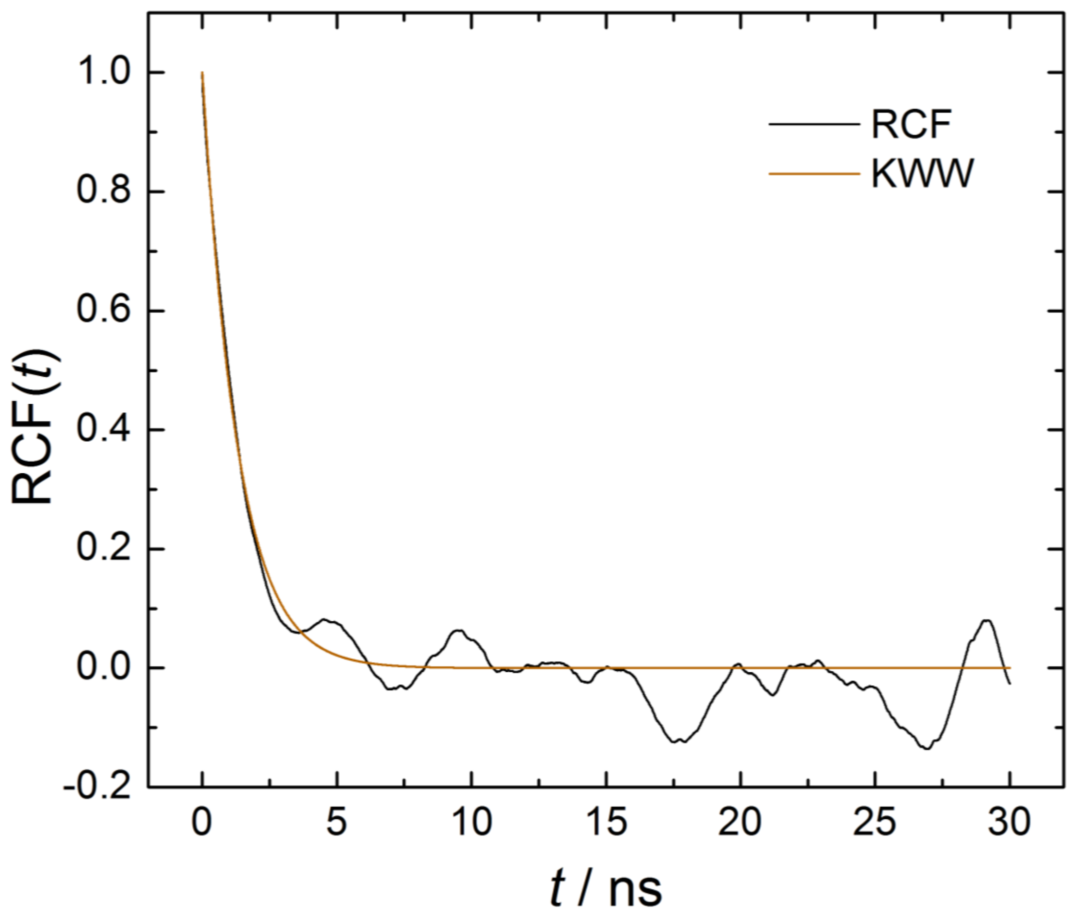
$$C(t) = \left\langle \cos[\varphi(t_0) - \varphi(t_0 + t)] \right\rangle_{t_0}$$

- Can be fitted to the Kohlrausch-Williams-Watts relaxation function

$$KWW(t) = \exp(-\alpha t^{\beta})$$

- The rotational correlation time is obtained through integration of the *KWW* function from zero to infinity

Rotational correlation function



Nonlinear fitting:

Use Matlab Or Gauss-Newton method

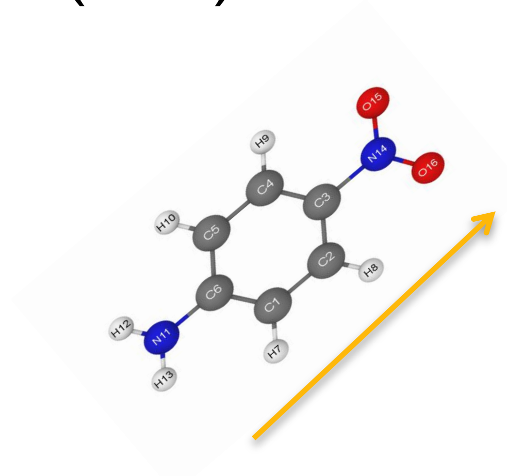
2. The orientation of the molecule

Orientation (long axis)

- The molecular inertia tensor (3x3)

$$I_{\alpha\beta} = \sum_i m_i \left(r_i^2 \delta_{\alpha\beta} - r_{i\alpha} r_{i\beta} \right)$$

$$\alpha, \beta \in \{x, y, z\}$$



- The molecular long-axis is defined as the eigenvector associated with the **smallest** eigenvalue of $\boldsymbol{I}$.

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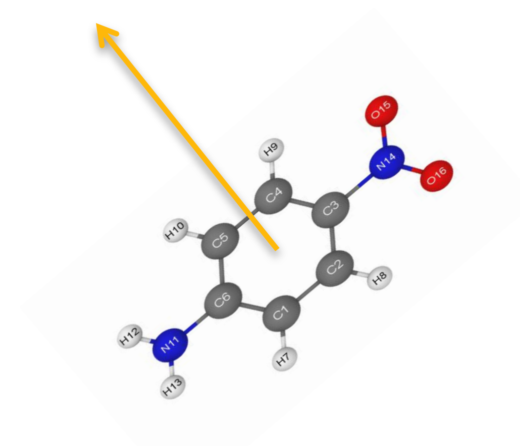
Orientation (normal direction)

- The molecular inertia tensor (3x3)

$$I_{\alpha\beta} = \sum_i m_i \left(r_i^2 \delta_{\alpha\beta} - r_{i\alpha} r_{i\beta} \right)$$

$$\alpha, \beta \in \{x, y, z\}$$



- The eigenvector associated with tne **<u>largest</u>** eigenvalue of inertia tensor $\boldsymbol{I}$ is perpendicular to the molecular plane.

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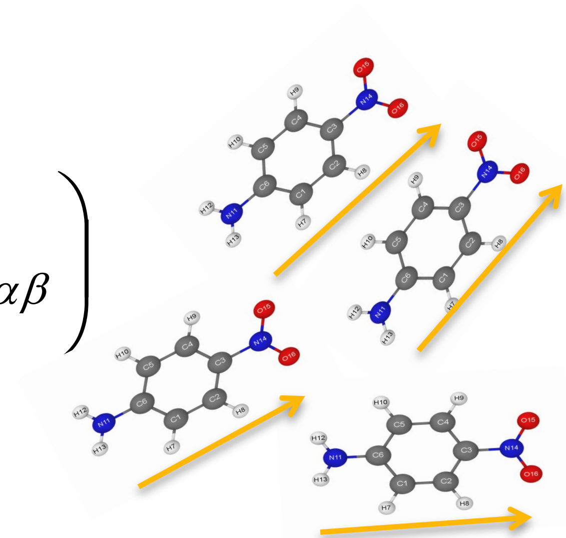
Order-parameter (self-assembly)

- The ordering tensor (3x3)

$$Q_{\alpha\beta} = \frac{1}{N}\sum_{j=1}^{N}\left(\frac{3}{2}a_{j\alpha}a_{j\beta} - \frac{1}{2}\delta_{\alpha\beta}\right)$$

$$\alpha, \beta \in \{x, y, z\}$$



  - N is number of molecules
  - $\boldsymbol{a}_j$ is the molecular long-axis of the j-th molecule
- The largest eigenvalue of $\boldsymbol{Q}$ is the uniaxial order parameter

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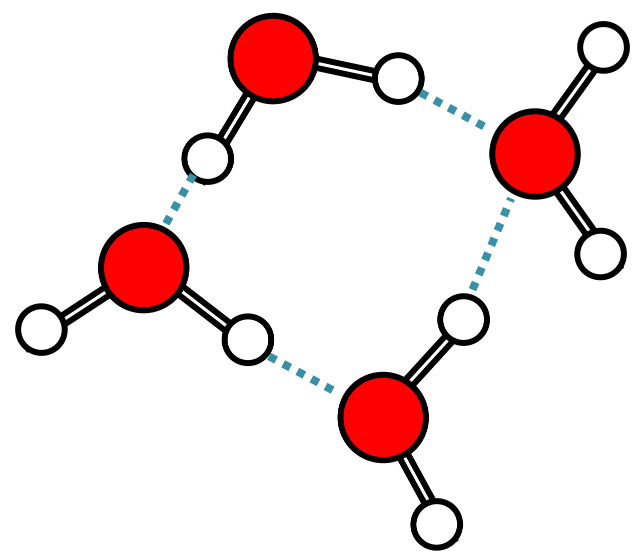
3. Molecule-environment interaction

Hydrogen bonds

- Formed between hydrogen atoms and electronegative atoms (N, O, F, etc.)

- Donor(D)-Hydrogen(H)...Acceptor(A)

- Geometry criteria:
  - distance D-A ≤ 3.5 Å
  - angle H-D-A ≤ 30°



Lifetime of hydrogen bonds

- Auto-correlation function

$$C(t) = \langle s_i(t_0) s_i(t_0 + t) \rangle$$

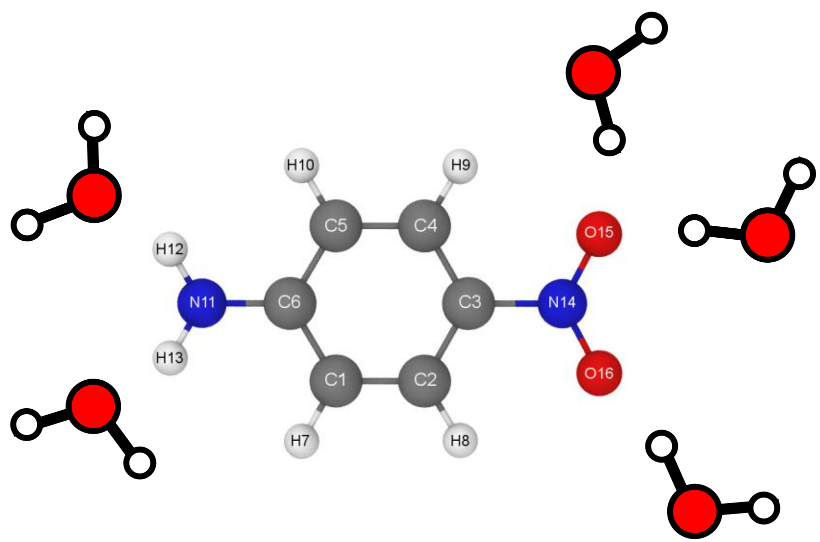
  - $s_i(t_0) = 0$ or 1 for H-bond i at time t_0

- The average H-bond lifetime

$$\tau_{HB} = \int_0^\infty C(t)dt$$

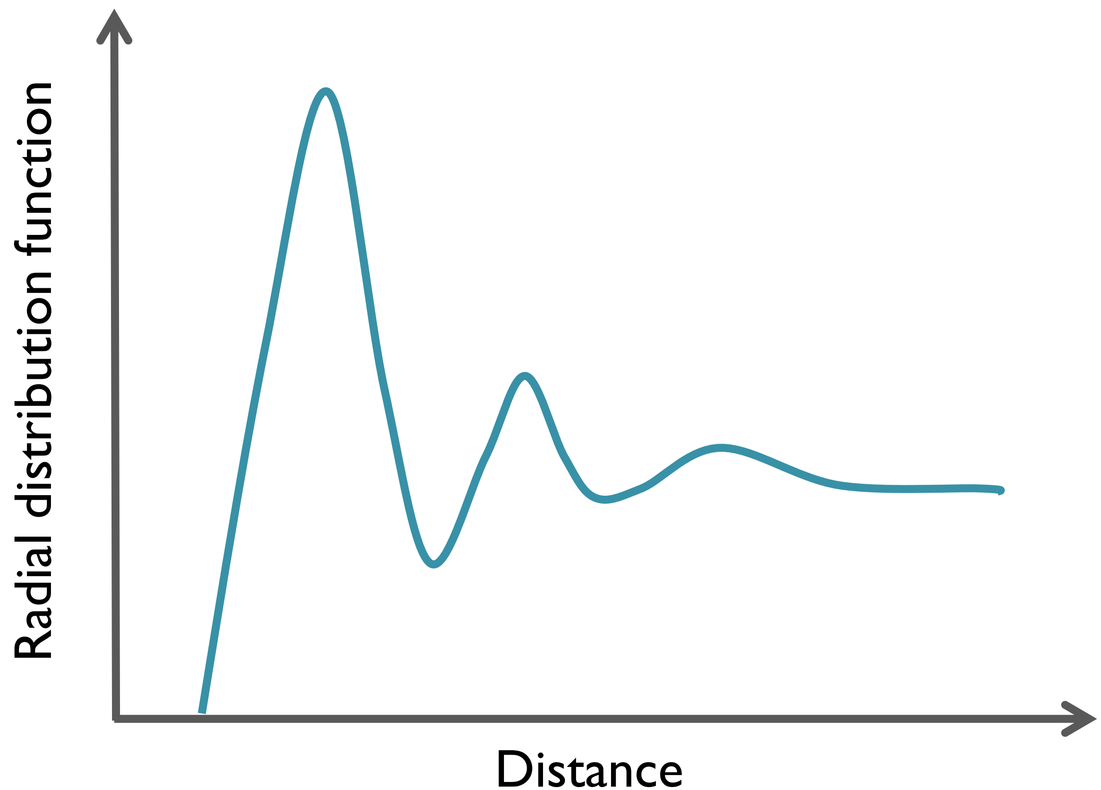
Radial distribution function

- Relative density of B around A with respect to bulk
- Non-uniform distribution of B in the vicinity of A



Radial distribution function

- First solvation shell
- Second solvation shell



4. Analyzing tools in GROMACS

GROMACS tools

- g_msd
  - Calculate mean square deviation and diffusion constant.
- g_rotacf
  - Calculate rotational correlation function for molecules.
- g_rdf
  - Calculate radial distribution function in several different ways.
- g_hbond
  - Calculate and analyze hydrogen bond number, distance, angle, lifetime, etc.

GROMACS tools

Refer to the manual

editconf
eneconv
g_anadock
g_anaeig
g_analyze
g_angle
g_bar
g_bond
g_bundle
g_chi
g_cluster
g_clustsize
g_confrms
g_covar
g_current
g_density
g_densmap
g_dielectric
g_dih
g_dipoles
g_disre
g_dist

g_dyndom
g_enemat
g_energy
g_filter
g_gyrate
g_h2order
g_hbond
g_helix
g_helixorient
g_lie
g_mdmat
g_membed
g_mindist
g_morph
g_msd
g_nmeig
g_nmens
g_nmtraj
g_order
g_polystat

g_potential
g_principal
g_protonate
g_rama
g_rdf
g_rms
g_rmsdist
g_rmsf
g_rotacf
g_rotmat
g_saltbr
g_sas
g_select
g_sgangle
g_sham
g_sigeps
g_sorient
g_spatial
g_spol
g_tcaf
g_traj

g_tune_pme
g_vanhove
g_velacc
g_wham
g_wheel
g_x2top
g_xrama
genbox
genconf
genion
genrestr
gmxcheck
gmxdump
make_edi
make_ndx
mdrun
mk_angndx
Pdb2gmx
tpbconv
trjconv
trjcat
trjorder

5. Computational models for absorption spectra

Computational models

- Molecule (QM) + PCM
- Molecule (QM) + Solvent (MM, point charges)
- Molecule (QM) + Solvent (MM, point charges and dipoles)
- Supermolecule: Molecule + surrounding solvent molecules (QM)

6. Analysis of computed spectra

A few words on TD-DFT

- Compute the absorption spectra (UV-Vis spectra)
- Only reliable for low-lying excited states
- Be careful with charge transfer cases
- Use polarization and diffusion functions

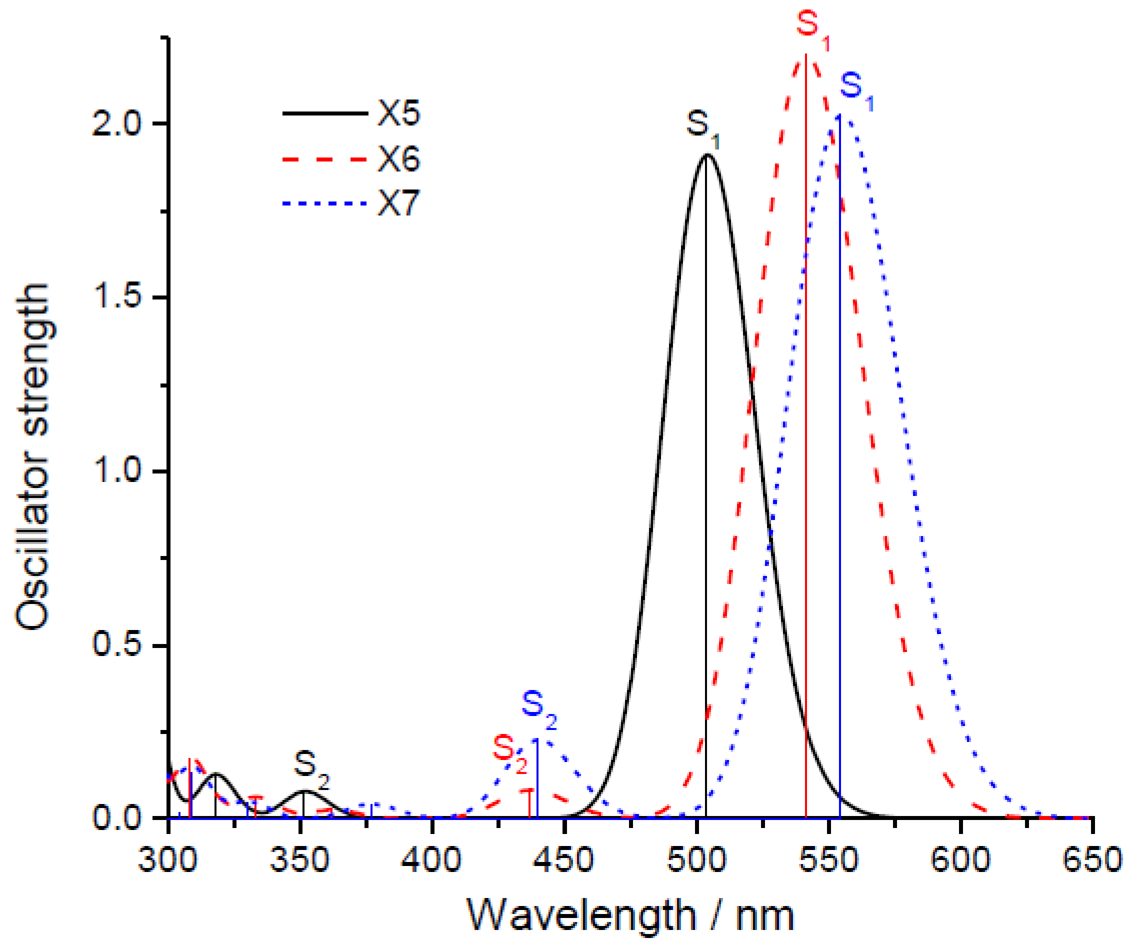
- `CAM-B3LYP/6-311+G(d,p)`
- `CAM-B3LYP/TZVP`

Output from Gaussian09

- Excitation energies ΔE
- Oscillator strengths f
- Transition dipole moment M
- $f = 2/3 \; \Delta E \; M^2$

- Molecular orbital composition
  - 2 x (CI coefficient)^2
  - e.g. coefficient = 0.7, composition = 98%

Broadening of stick spectra



Broadening of stick spectra

- Gaussian broadening

$$G(\omega) = \sum_{n=1}^{N} \frac{1}{\sqrt{\pi} \cdot \Delta} e^{-\left(\frac{\omega-\omega_n}{\Delta}\right)^2}$$

- Lorentzian broadening

$$L(\omega) = \sum_{n=1}^{N} \frac{1}{\pi \cdot \Delta \cdot \left[1+\left(\frac{\omega-\omega_n}{\Delta}\right)^2\right]}$$