Applications of DFT with the help of ASE: Non-resonant Raman spectra and molecular forces

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Agenda

- (Resonant) Raman spectra
  - Derivation from Kramers/Heisenberg/Dirac
  - Placzek vs Albrecht approximations
- Molecular forces
  - Mechanochromophors
  - 3 segment COGEF

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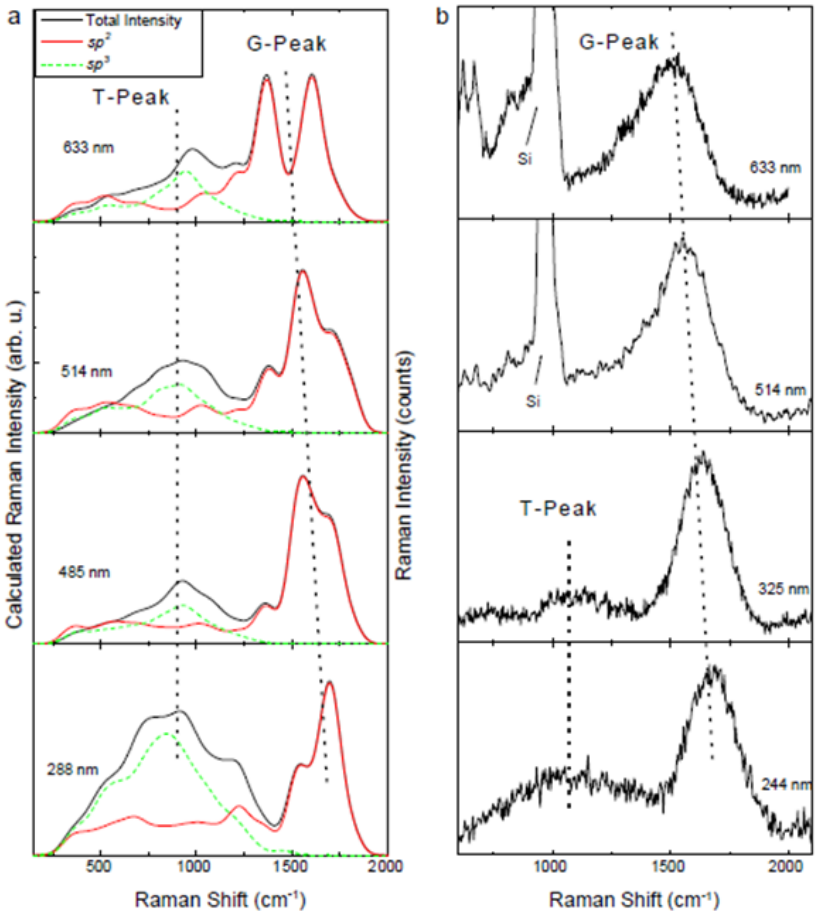
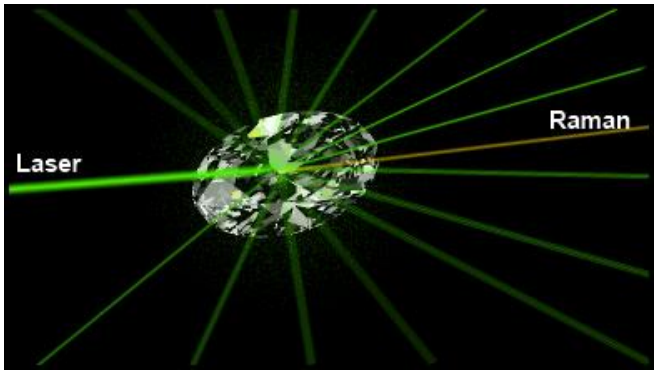
Raman spectra of amorphous C



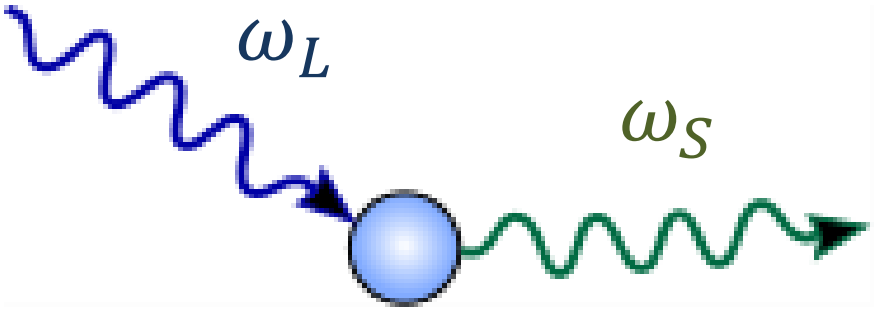
Raman spectra vary with excitation wavelength



Profeta *PRB* 2001
Piscanec *DiamRelMat* 2005

Cross section and matrix element

Scattering matrix element



$$\frac{d\sigma}{d\Omega} = \frac{\omega_L \omega_S^3}{\hbar^2 c^4} |V_{FI}|^2 \delta(E_I + \omega_L - E_F - \omega_S)$$

Kramers-Heisenberg-Dirac

$$V_{FI} = \sum_{K \neq I} \left(\frac{\langle F|\boldsymbol{u}_S \cdot \boldsymbol{D}|K\rangle\langle K|\boldsymbol{u}_L \cdot \boldsymbol{D}|I\rangle}{E_I + \omega_L - E_K} + \frac{\langle F|\boldsymbol{u}_L \cdot \boldsymbol{D}|K\rangle\langle K|\boldsymbol{u}_S \cdot \boldsymbol{D}|I\rangle}{E_I - E_K - \omega_S} \right)$$

Born-Oppenheimer to Placzeck

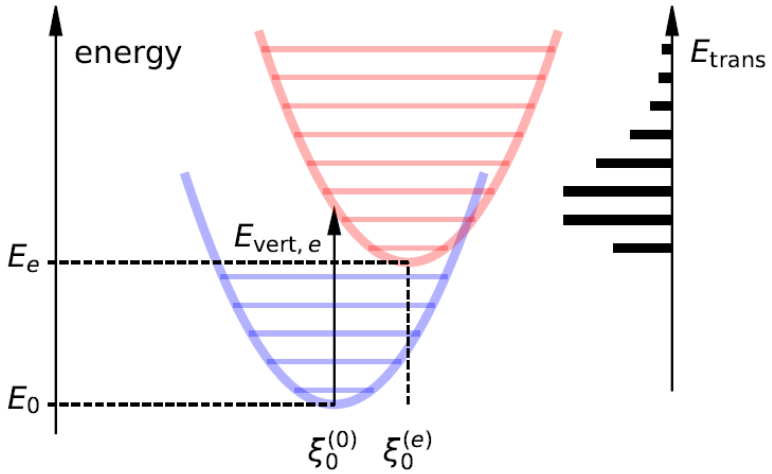
Separation of nuclear and electronic terms

$$\langle I|\boldsymbol{u}\cdot\boldsymbol{D}|K\rangle = \langle 0,0|m_u^e(\boldsymbol{R})|e,k\rangle$$

Semiclassical approximation for transition energies

$$E_e - E_0 + (\varepsilon_k^e - \varepsilon_i^0) \approx E_{\text{vert}}$$

$$V_{FI} \propto \langle 0,i|\alpha(\omega_L)|0,f\rangle$$



Placzek aproximation

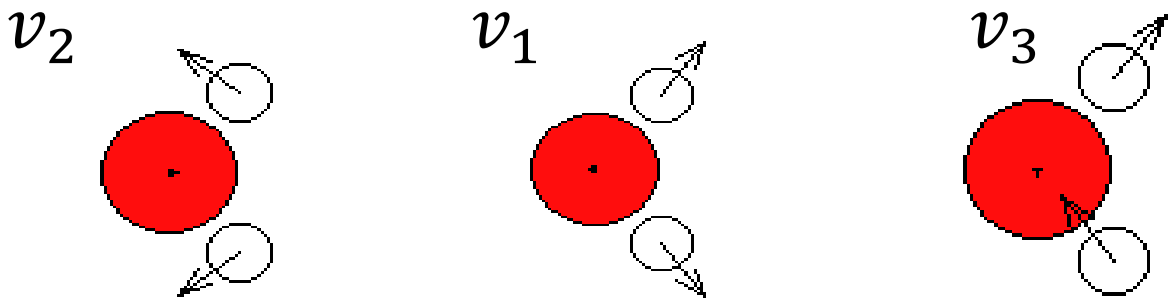
Expansion in normal coordinates

$$\alpha_{LS}(\omega, \boldsymbol{R}) = \alpha_{LS}(\omega, \boldsymbol{R}_0) + \sum_v \frac{\partial \alpha_{LS}(\omega, \boldsymbol{R}_0)}{\partial Q_v} Q_v + O({Q_v}^2)$$

"Absolute" Raman intensity

$$I_{Ram} \sim \left| \frac{\partial \alpha_{LS}(\omega = 0, \boldsymbol{R}_0)}{\partial Q_v} \right|^2$$

Example: water



„Static“ Raman intensities

mode	I_{Ram} ours	I_{Ram} others	I_{Ram} exp
v_2 bend	3	0.9	0.8
v_1 symmetric	95	108	120
v_3 asymmetric	26	19	30

Beyond Placzek: Albrecht approx.

Taylor expansion of electronic ME

$$m(\boldsymbol{Q}) = m(\boldsymbol{R}_0) + \boldsymbol{Q}\left.\frac{\partial m(\boldsymbol{Q})}{\partial \boldsymbol{Q}}\right|_{\boldsymbol{Q}=0} + O(\boldsymbol{Q}^2)$$

A term

$$V_{fi}^0 = \sum_{e,k}\left(\frac{\langle 0,i|e,k\rangle\langle e,k|0,f\rangle m_L^e m_S^{e*}}{E_e - E_0 + (\varepsilon_k^e - \varepsilon_i^0) - \omega_L} + \frac{\langle 0,i|e,k\rangle\langle e,k|0,f\rangle m_S^e m_L^{e*}}{E_e - E_0 + (\varepsilon_k^e - \varepsilon_i^0) + \omega_S}\right)$$

B and C terms

$$V_{fi}^B = \sum_{e,k}\sum_{v}\frac{\langle 0,i|e,k\rangle\langle e,k|Q_v|0,f\rangle m_L^e m_{S,v}^{e*} + \langle 0,i|Q_v|e,k\rangle\langle e,k|0,f\rangle m_{L,v}^e m_S^{e*}}{E_e - E_0 + (\varepsilon_k^e - \varepsilon_i^0) - \omega_L}$$

$$V_{fi}^C = \sum_{e,k}\sum_{v}\frac{\langle 0,i|e,k\rangle\langle e,k|Q_v|0,f\rangle m_S^e m_{L,v}^{e*} + \langle 0,i|Q_v|e,k\rangle\langle e,k|0,f\rangle m_{S,v}^e m_L^{e*}}{E_e - E_0 + (\varepsilon_k^e - \varepsilon_i^0) + \omega_S}$$

Connection to Placzek

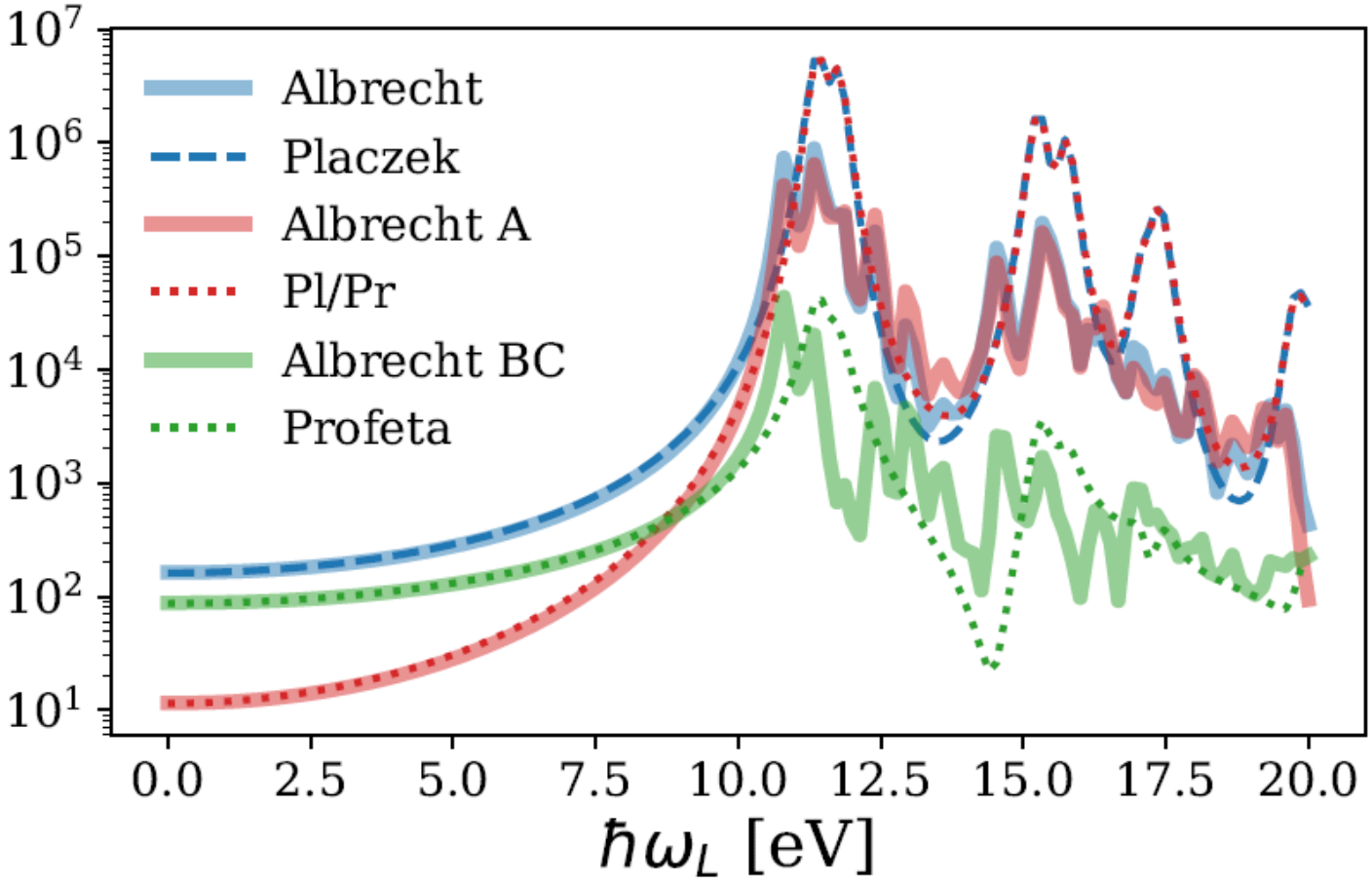
Sum over states form of polarizability

$$\alpha_{LS}(\omega) = \sum_e \frac{2E_{e,\mathrm{vert}}\, m_L^e m_S^e}{E_{e,\mathrm{vert}}^2 - (\hbar\omega)^2}$$

Derivative

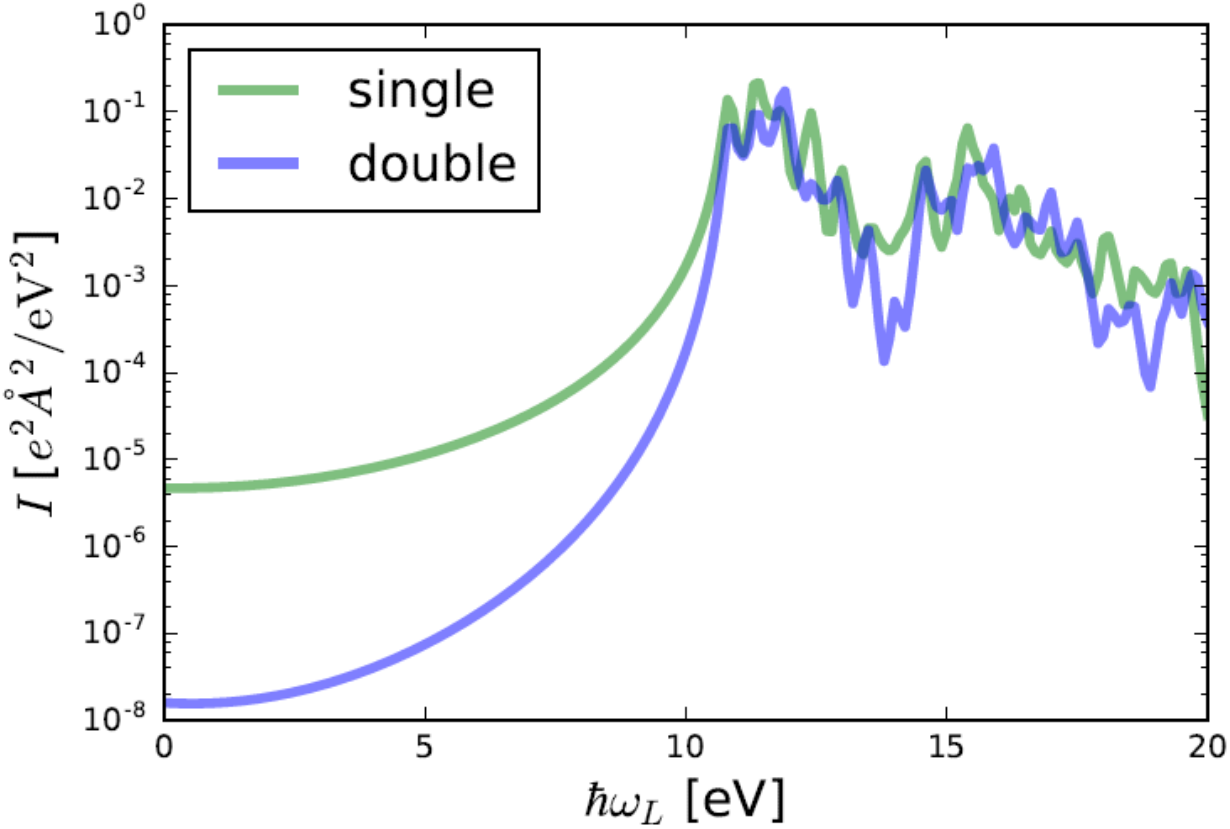
$$\frac{\partial \alpha}{\partial Q} = \underbrace{\frac{\partial \alpha}{\partial E_{\mathrm{vert}}} \frac{\partial E_{\mathrm{vert}}}{\partial Q}}_{\textbf{Albrecht A}} + \underbrace{\frac{\partial \alpha}{\partial m} \frac{\partial m}{\partial Q}}_{\textbf{Albrecht B/C}}$$

Wavelength dependent Raman of H_2



Walter and Moseler *arXiv*:1806.03840

Albrecht only: overtones



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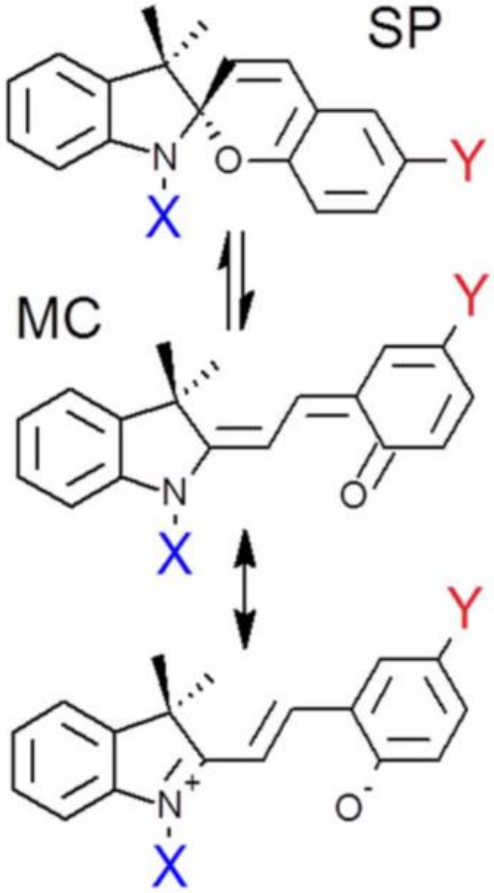
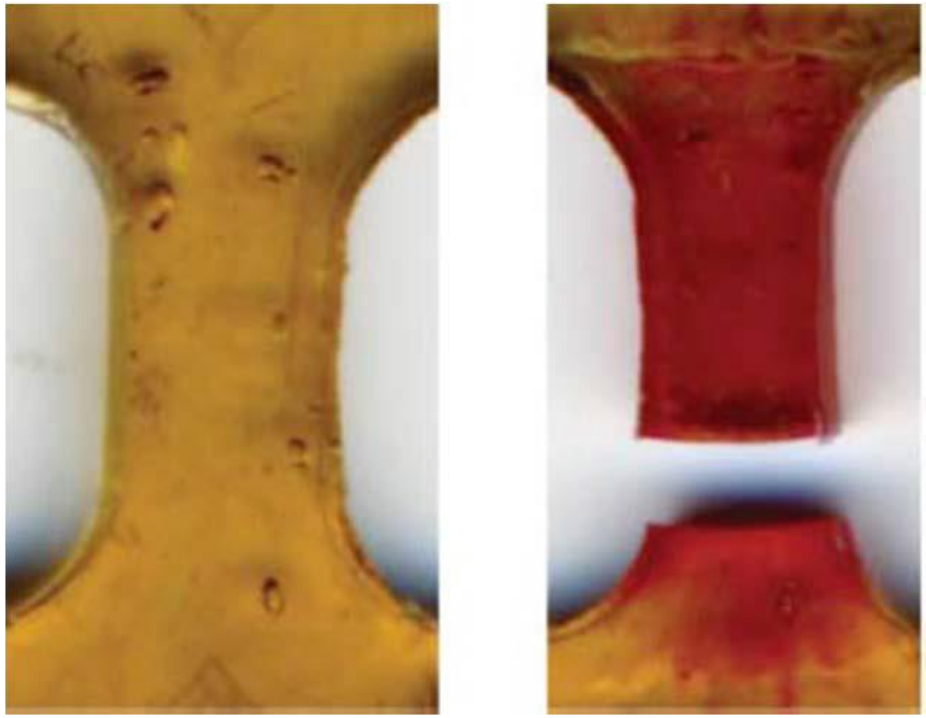
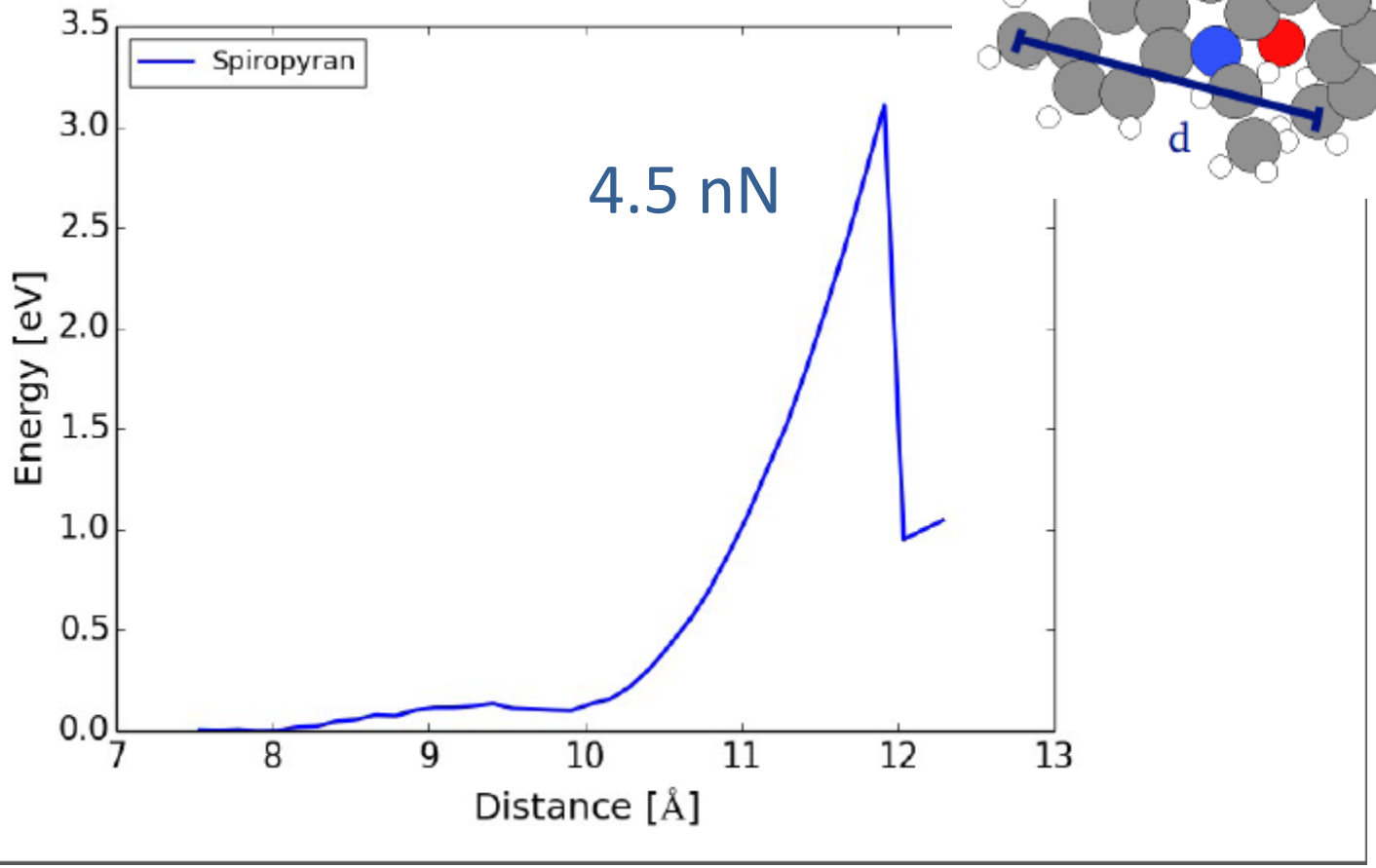
Molecular force sensors





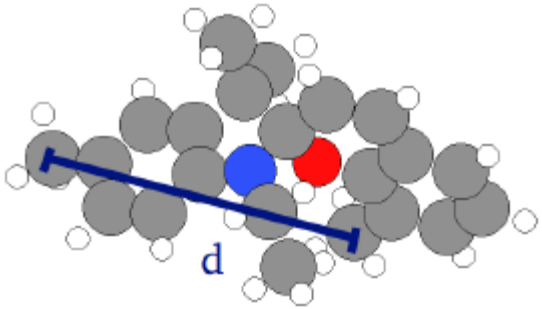
Davis *Nature* **459** (2009) 68

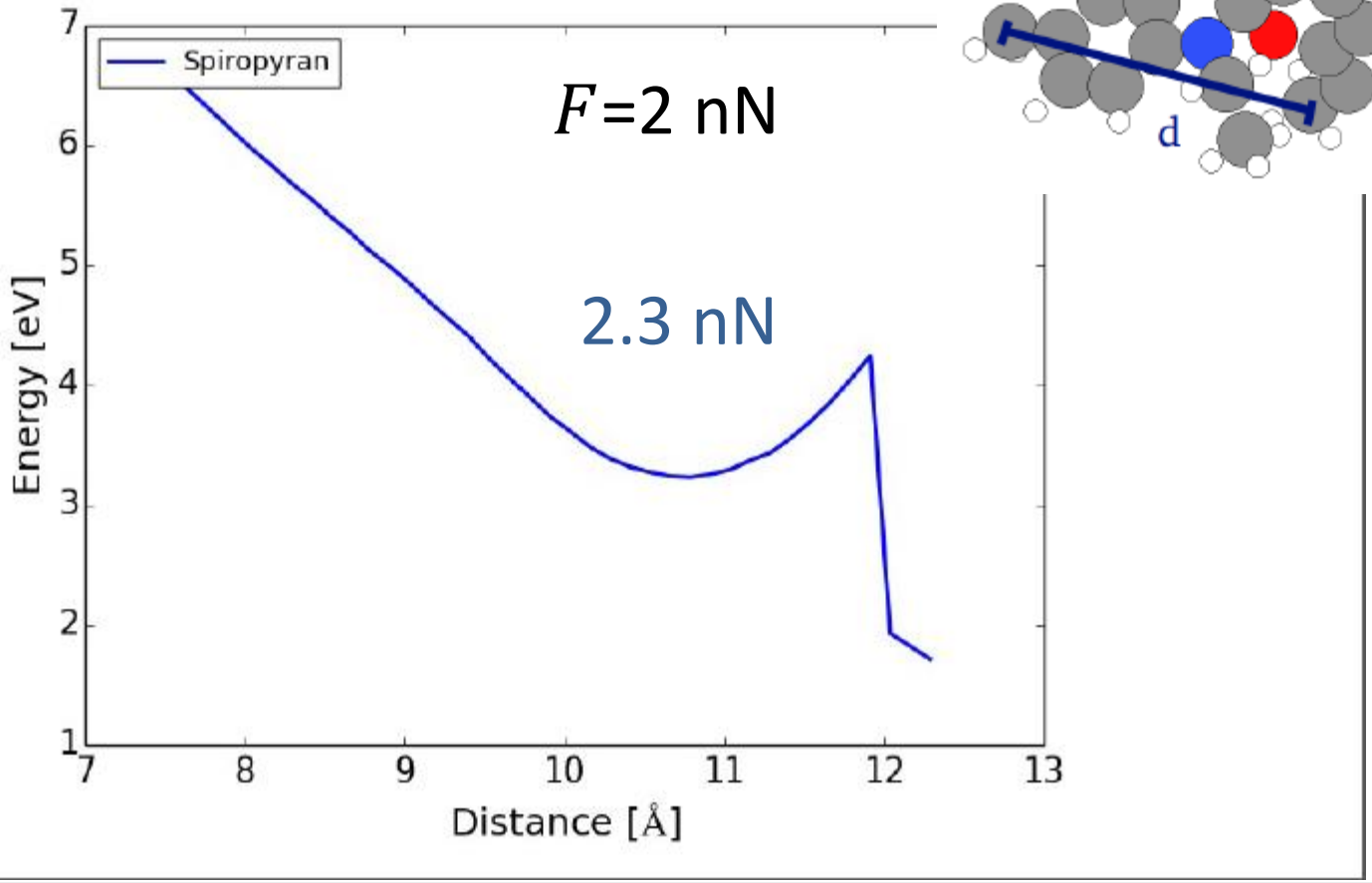
Forces on atomic scale



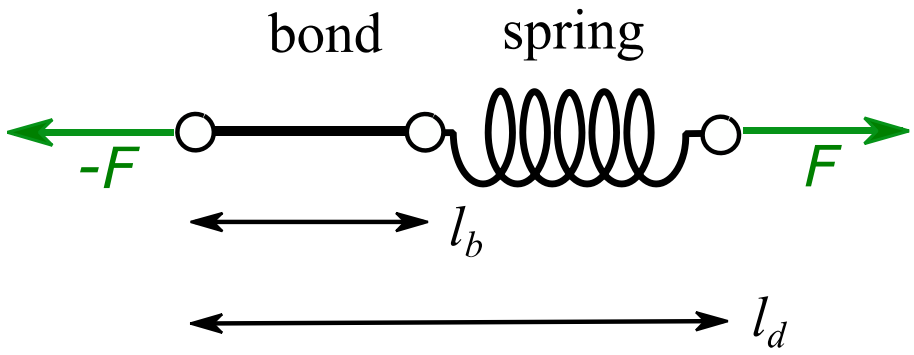
Energy contribution of the force

$$\bar{U}(d) = U(d) - F\,[d - d_0]$$

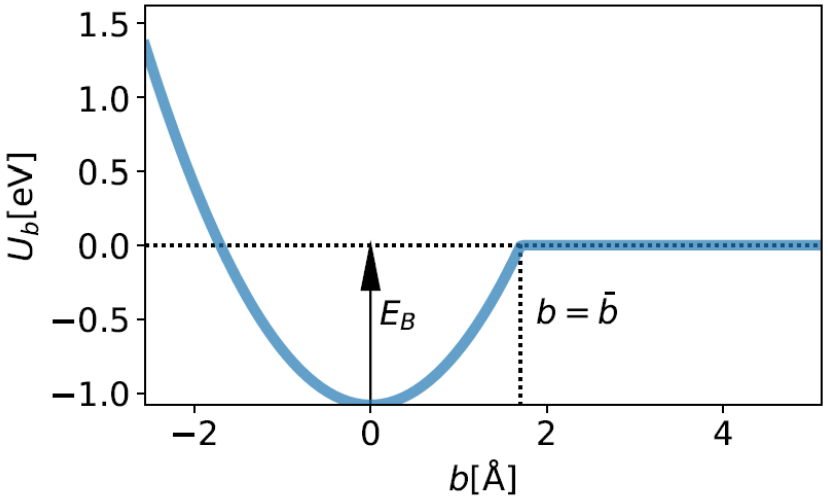




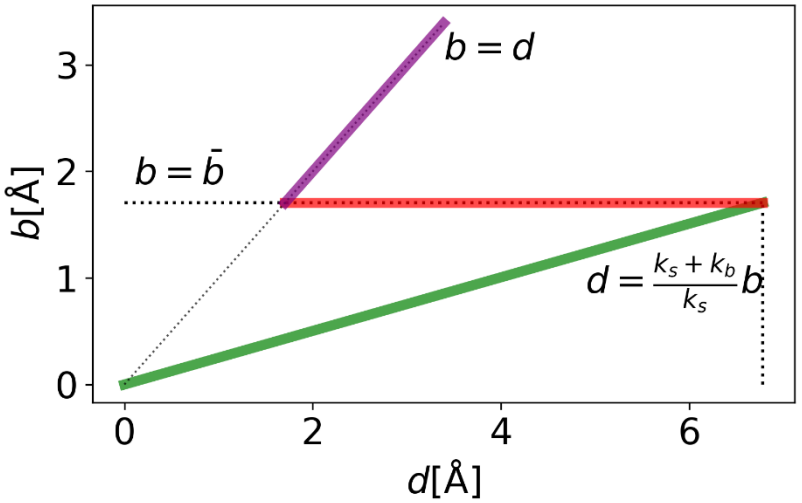
Simplified model: definition



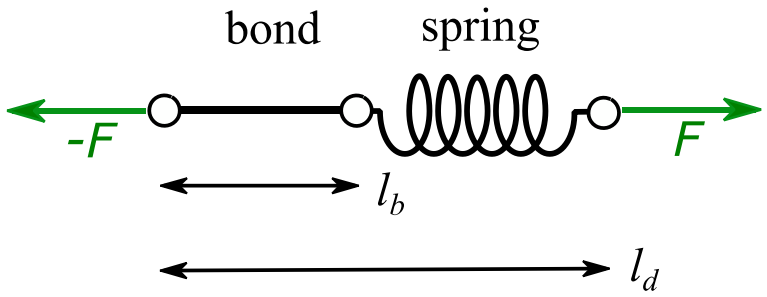
Bond-potential



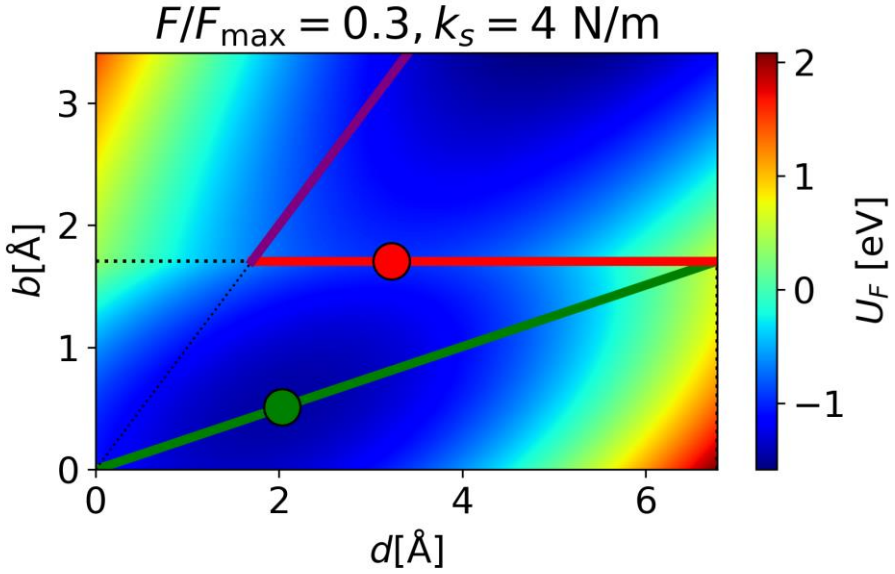
Universal extrema

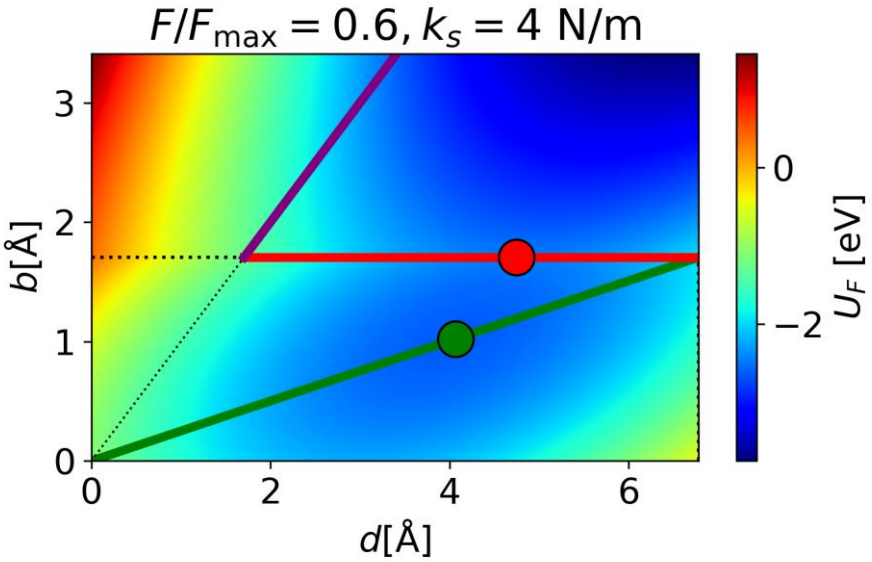


Simplified model: external force

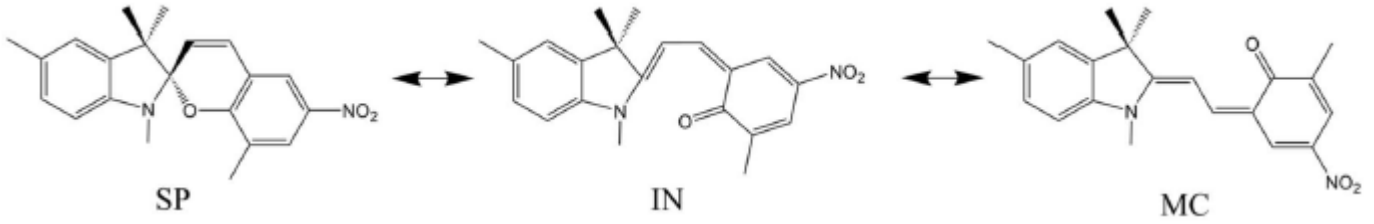


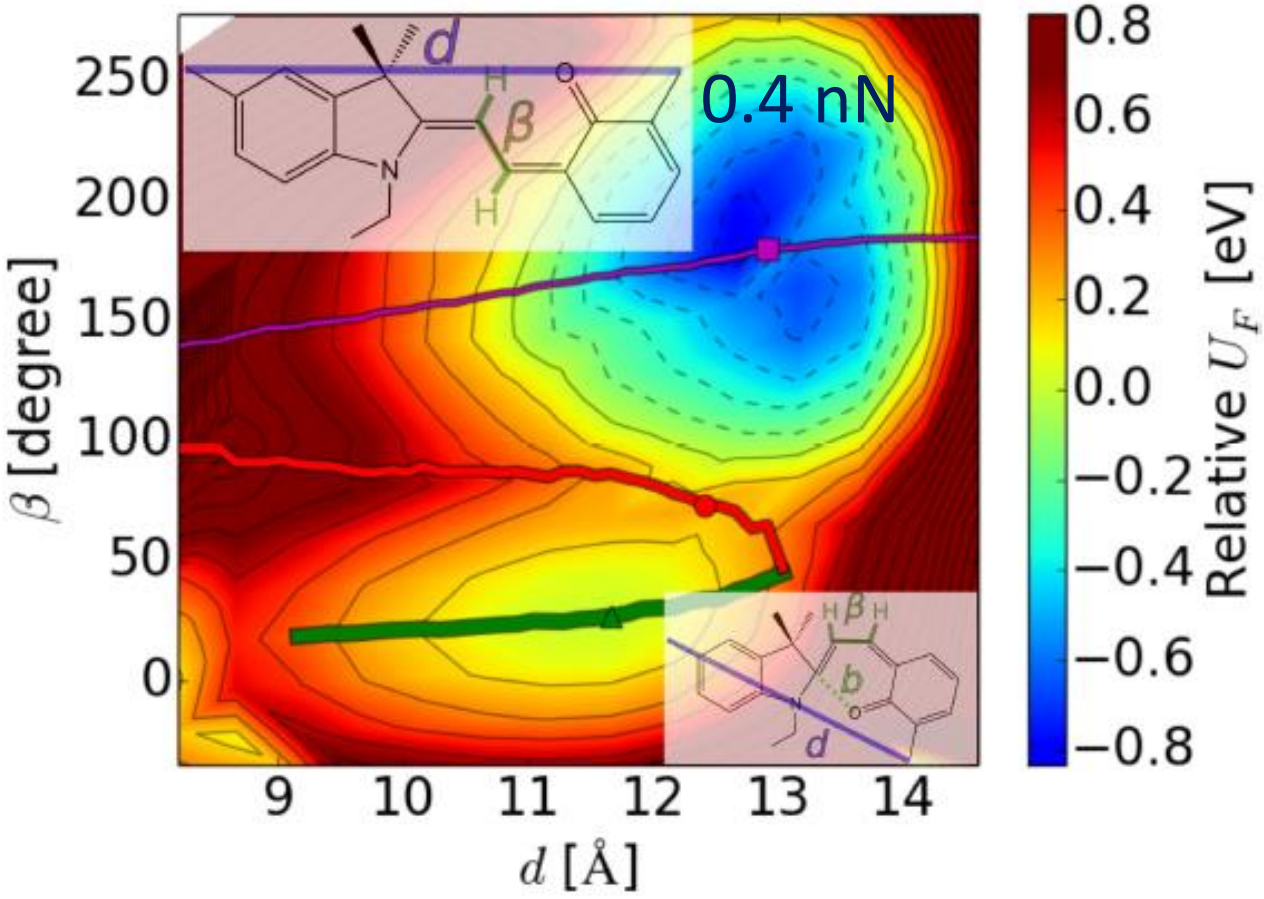
$$\bar{U}(d,b) = U(d,b) - F\,d$$





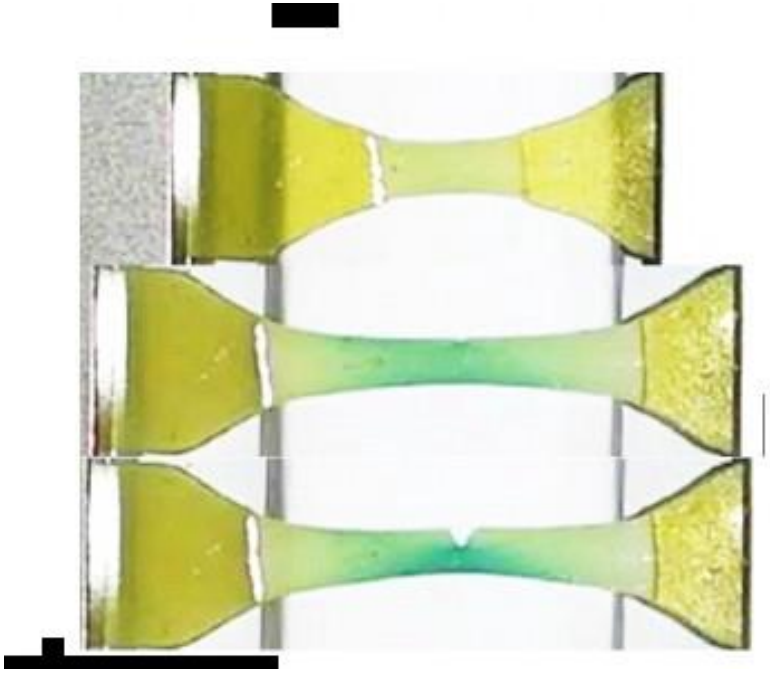
2D picture in spiropyran

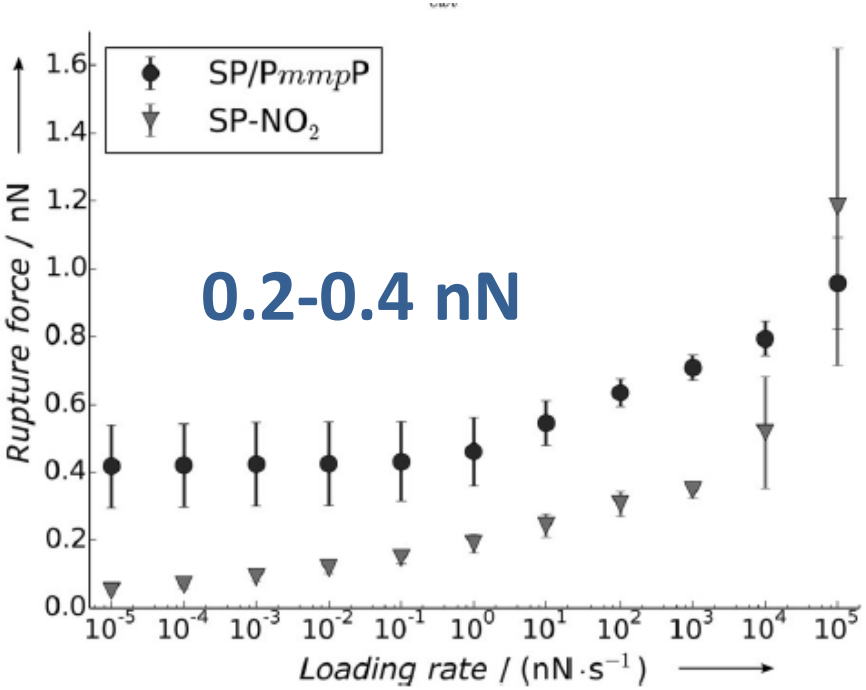




O. Brügner and MW
Phys. Rev. Mat.
2 (2018) 113603

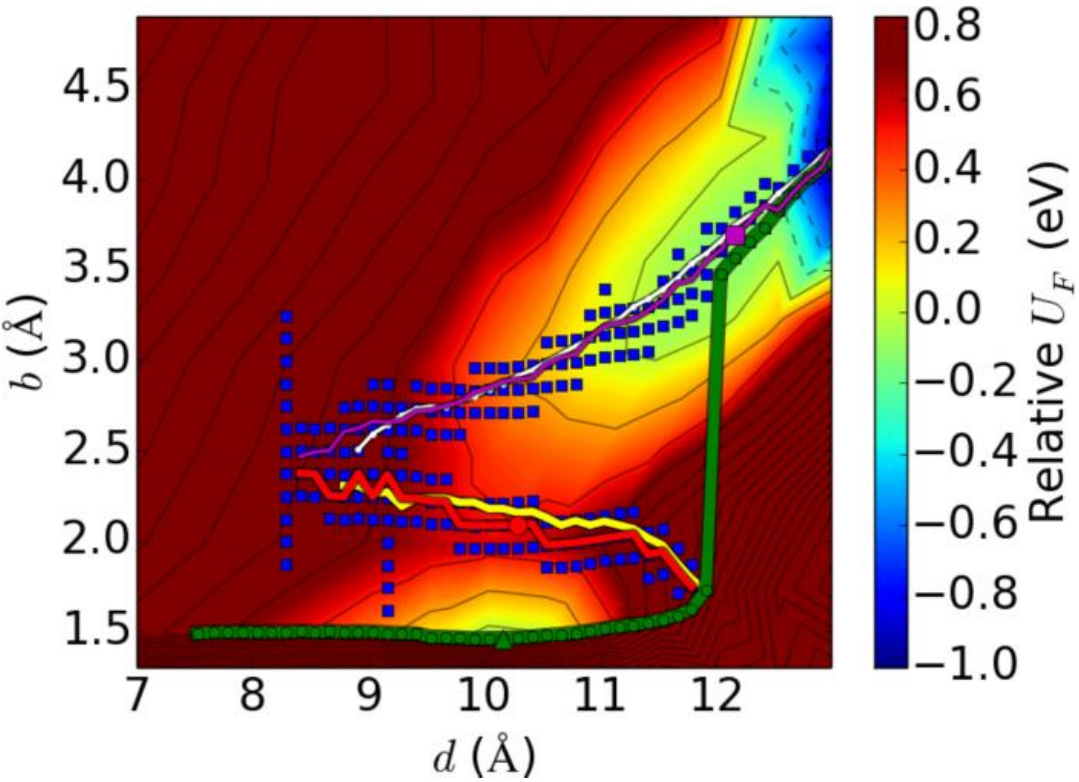
Tough polyarene + spiropyrane





F. Kempe, O. Brügner, H. Buchheit, S. Momm, F. Riehle, S. Hameury, MW, M. Sommer
Angew. Chemie **57** (2018) 997-1000

ASE-cogef module



Oliver Brügner

ase-cogef 1.0.0

```
pip install ase-cogef
```

Thanks

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