Universidad Autónoma de Madrid

Institute for Advanced Research in Chemistry

MoBioChem
Modeling Biology and Chemistry

CONSEJERÍA DE EDUCACIÓN E INVESTIGACIÓN
Comunidad de Madrid

Programa de Atracción de Talento Investigador 2018

Simulation of Biological Systems

Day 8 – Computer Exercises: Computation of Absorption Spectra

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Clarification on Redox Potentials

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$$\Delta G_{red} = < E_R > - < E_O > - [\Delta G_{e,solv}]$$

Ensemble Averages

Solvated e^-

Should actually be

$$\Delta G_{red} \approx < E_R > - < E_O > - [\Delta G_{e,solv}]$$

Assuming small variations in V and S

$$A_R - A_O \approx < E_R > - < E_O >$$

Helmholtz Free Energies

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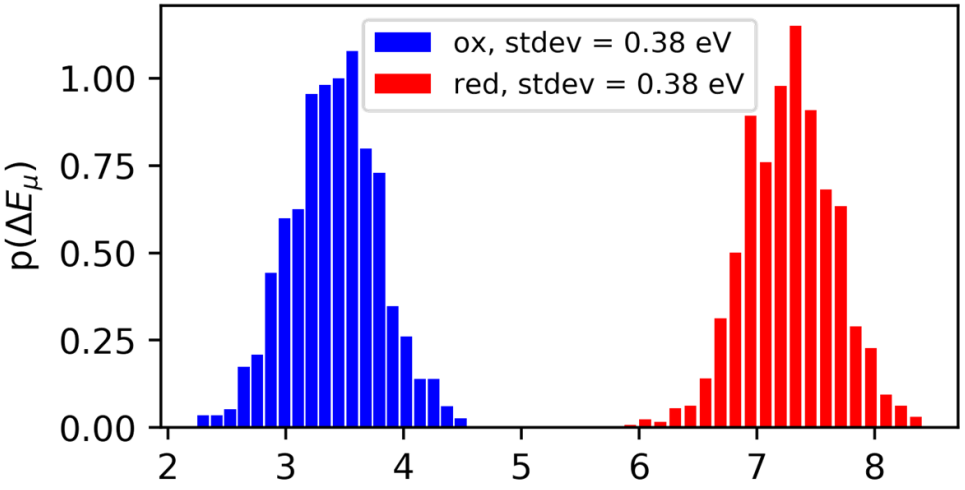

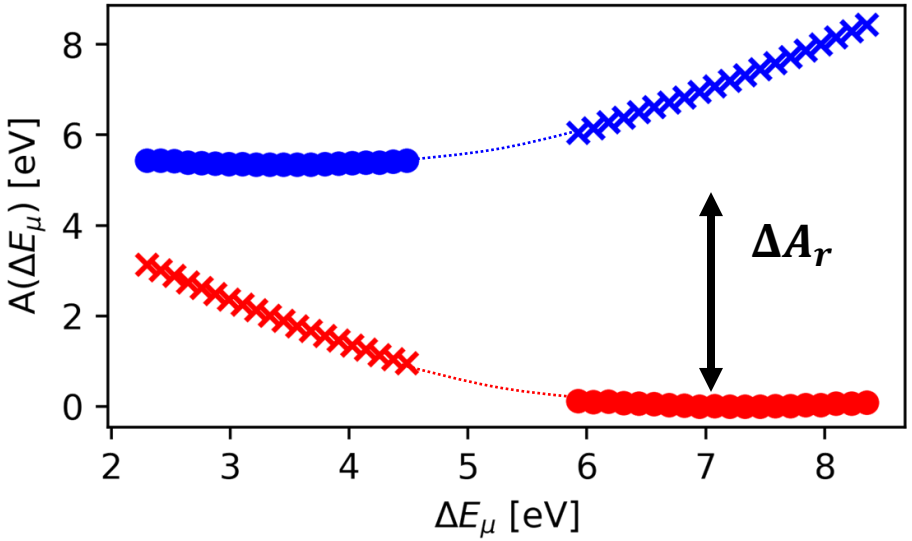

A can be computed by using the vertical energy differences ΔE as the reaction coordinate

$$\Delta A_R = -k_B T ln(p(\Delta E_{\mu,R}))$$

$$\Delta A_O = -k_B T ln(p(\Delta E_{\mu,O}))$$

Useful References

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Derivation of the working equations

Gregory King and Arieh Warshel., *The Journal of Chemical Physics,* 1990, **93**, 8682

Application to oxidation half reactions

Blumberger, J.; Tavernelli, I.; Klein, M. L.; Sprik, M., *The Journal of Chemical Physics,* 2006, **124**, 064507.

Diamantis, P.; Tavernelli, I.; Rothlisberger, U. *Journal of Chemical Theory and Computation,* 2020, **16**, 6690–6701,.

Absorption Spectrum: Azobenzene

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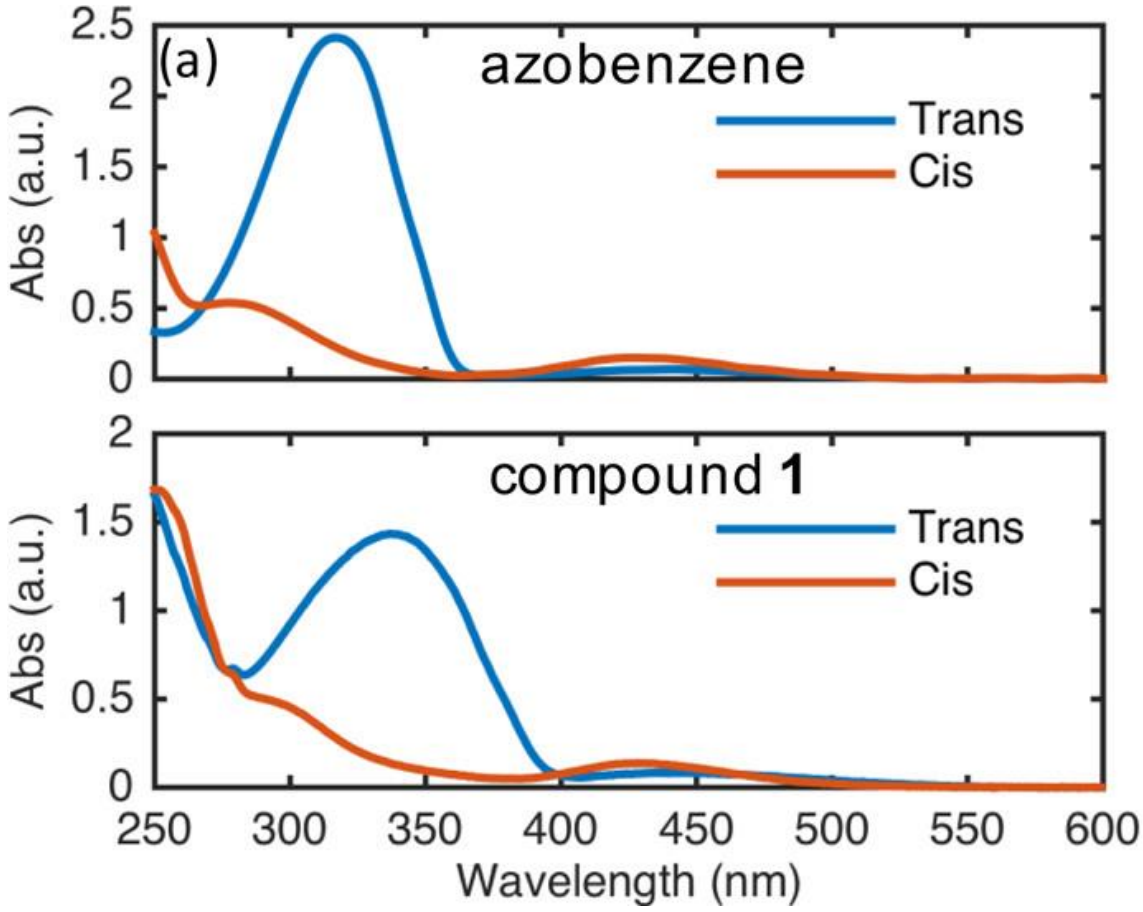

Eugene N. Cho, David Zhitomirsky, Grace G. D. Han, Yun Liu , and Jeffrey C. Grossman, *ACS Appl. Mater. Interfaces* 2017, 9, 10, 8679−8687

Computation of Absorption Spectra

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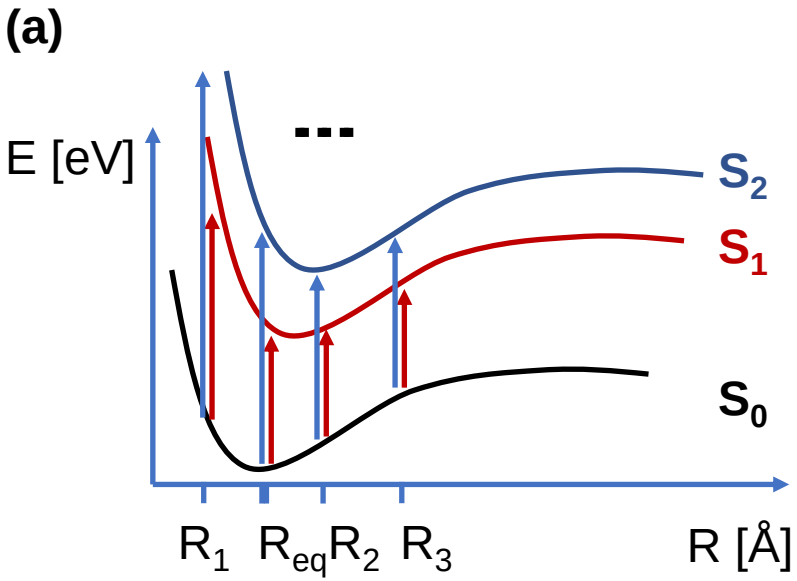
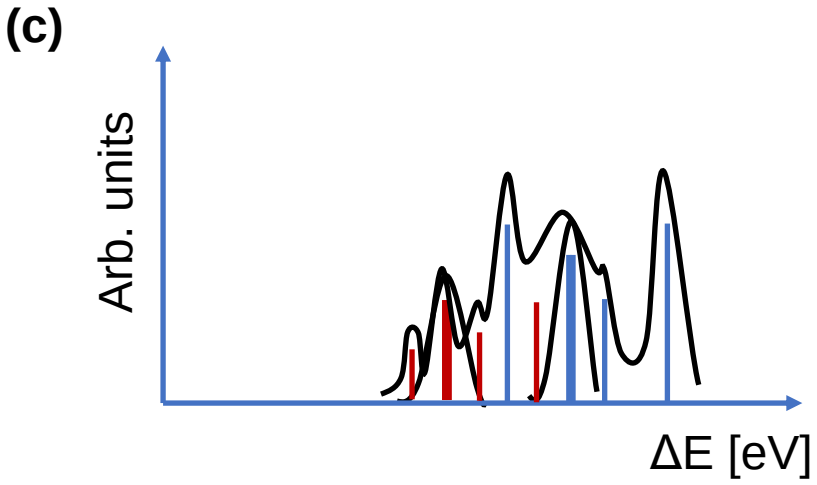
- Vertical excitations at the equilibrium geometry, R_{eq}
- Vertical excitations: ensemble