Theory of electron transfer
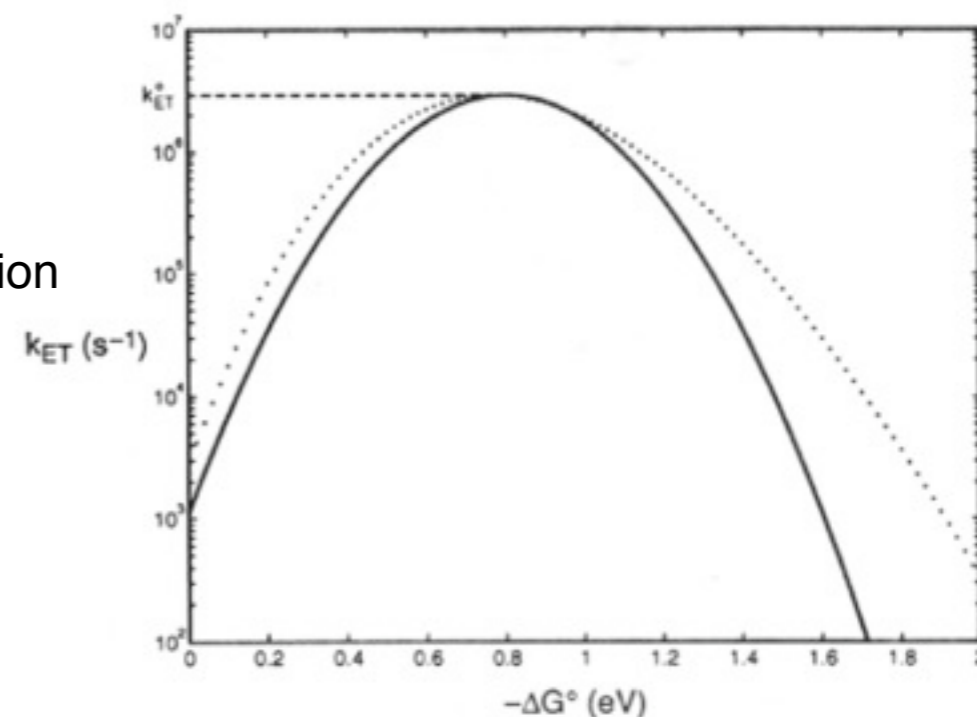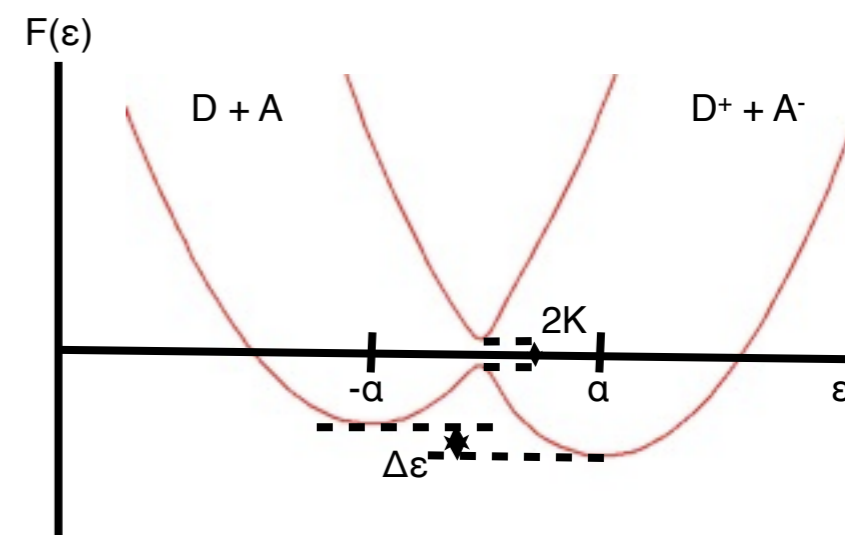
Winterschool for Theoretical Chemistry and Spectroscopy
Han-sur-Lesse, Belgium, 12-16 December 2011

Summary Part 1

Marcus theory of Electron transfer

$$k_{et} = \frac{2\pi}{\hbar}|H_{AB}|^2 \frac{2}{\sqrt{4\pi\lambda k_B T}} \exp{-\frac{(\lambda + \Delta G_0)^2}{4\lambda k_B T}}$$

1. reaction rate theory (Eyring) or vibronic excitation (Franck-Condon)
2. Gaussian potentials when polarization is the reaction coordinate
3. λ = inner sphere (harmonic vibrations) plus outer sphere (central limit theory) reorganization
4. dependence of activation energy on driving force ΔG_0 and reorganization free energy
5. inverted region when $\lambda < \Delta G_0$
6. adiabatic vs diabatic picture (energy gap versus Fermi's golden rule)
7. quantum tunneling

Electron transfer

How can we compute all this in practice?

Molecular model for aqueous ferrous–ferric electron transfer

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We present a molecular model for studying the prototypical ferric–ferrous electron transfer process in liquid water, and we discuss its structural implications. Treatment of the nonequilibrium dynamics will be the subject of future work. The elementary constituents in the model are classical water molecules, classical ferric ions (i.e., Fe^{3+} particles), and a quantal electron. Pair potentials and pseudopotentials describing the interactions between these constituents are presented. These interactions lead to ligand structures of the ferric and ferrous ions that are in good agreement with those observed in nature. The validity of the tight binding model is examined. With umbrella sampling, we have computed the diabatic free energy of activation for electron transfer. The number obtained, roughly 20 kcal/mol, is in reasonable accord with the aqueous ferric–ferrous transfer activation energy of about 15 to 20 kcal/mol estimated from experiment. The Marcus relation for intersecting parabolic diabatic free energy surfaces is found to be quantitatively accurate in our model. Due to its significance to future dynamical studies, we have computed the tunnel splitting for our model in the absence of water molecules. Its value is about 1 $k_B T$ at room temperature for ferrous–ferric separations around 5.5 Å. This indicates that the dynamics of the electron transfer are complex involving both classical adiabatic dynamics and quantal nonadiabatic transitions. The dynamics may also be complicated due to glassy behavior of tightly bound ligand water molecules. We discuss this glassy behavior and also describe contributions to the solvation energetics from water molecules in different solvation shells. Finally, the energetics associated with truncating long ranged forces is discussed and analyzed.

J. Chem. Phys. 89, 3248-3257 (1988)

Times cited: 333

model

$$Fe^{3+} + Fe^{2+} \rightleftharpoons Fe^{2+} + Fe^{3+}$$
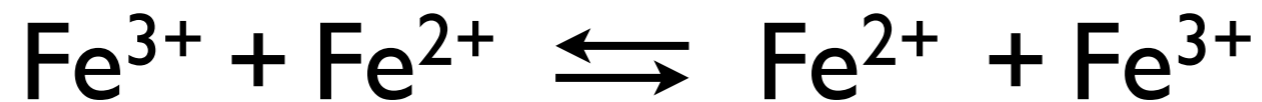
- 430 SPC water

  LJ_{O-O} + q_H=0.41e + q_O=-0.82e

- 2 Fe^{3+} ions

- one electron (Coulombic pseudopotential)

$$U_{\text{Fe3+}-\text{H}_2\text{O}} = \frac{A}{|r - r_O|^9} + 3e \sum_{\alpha} \frac{q_\alpha}{|r - r_a|}$$
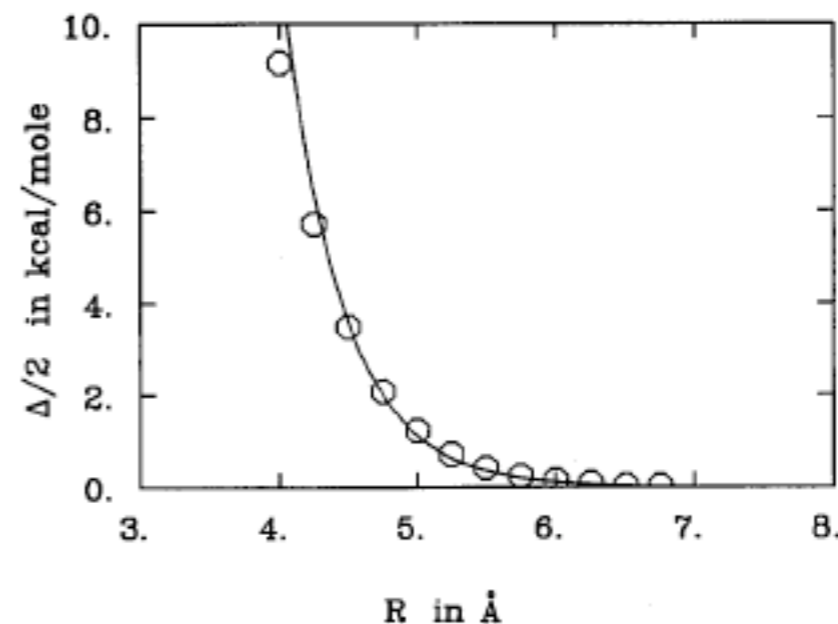
model

- rigid water model (no polarization)

- spherical pseudopotentials (no d-orbitals)

- octahedral iron coordination, Fe-O distance

- solvation energy of Fe^{3+} does not match

quantum mechanics

- Path integral MC calculations of aqueous system

- one electron Schrodinger equation calculation of Fe^{2+}--Fe^{3+} in vacuum

tunnel splitting

electron tunneling

Electron transfer free energy

- Molecular dynamics, NVT (T=298 K)

- Spherical cut-off

- Umbrella Sampling, z={0.0, 0.17, 0.33, 0.5}

  - z = [0,1] electron charge transfer

  - $E(R^N)$ electric potential energy difference at iron sites

  - $V_z(R^N)$ is the total potential energy

- 2.5 ps trajectories

umbrella sampling

distribution of the electric potential field difference at redox sites, *E*

$$P(E) = \int \int dR^N d\dot{R}^N \exp[-\beta V_0(R^N)]\delta[E(R^N) - E]$$

activation free energy

$$\Delta F = -k_B T \ln[P(0)/P(E_{\min})]$$

Biased sampling

$$P(E) = \int \int dR^N d\dot{R}^N \exp[-\beta V_z(R^N)] \exp[-\beta V_0(R^N) + \beta V_z(R^N)]\delta[E(R^N) - E]$$

$$V_0(R^N) - V_z(R^N) = -zeE(R^N)$$
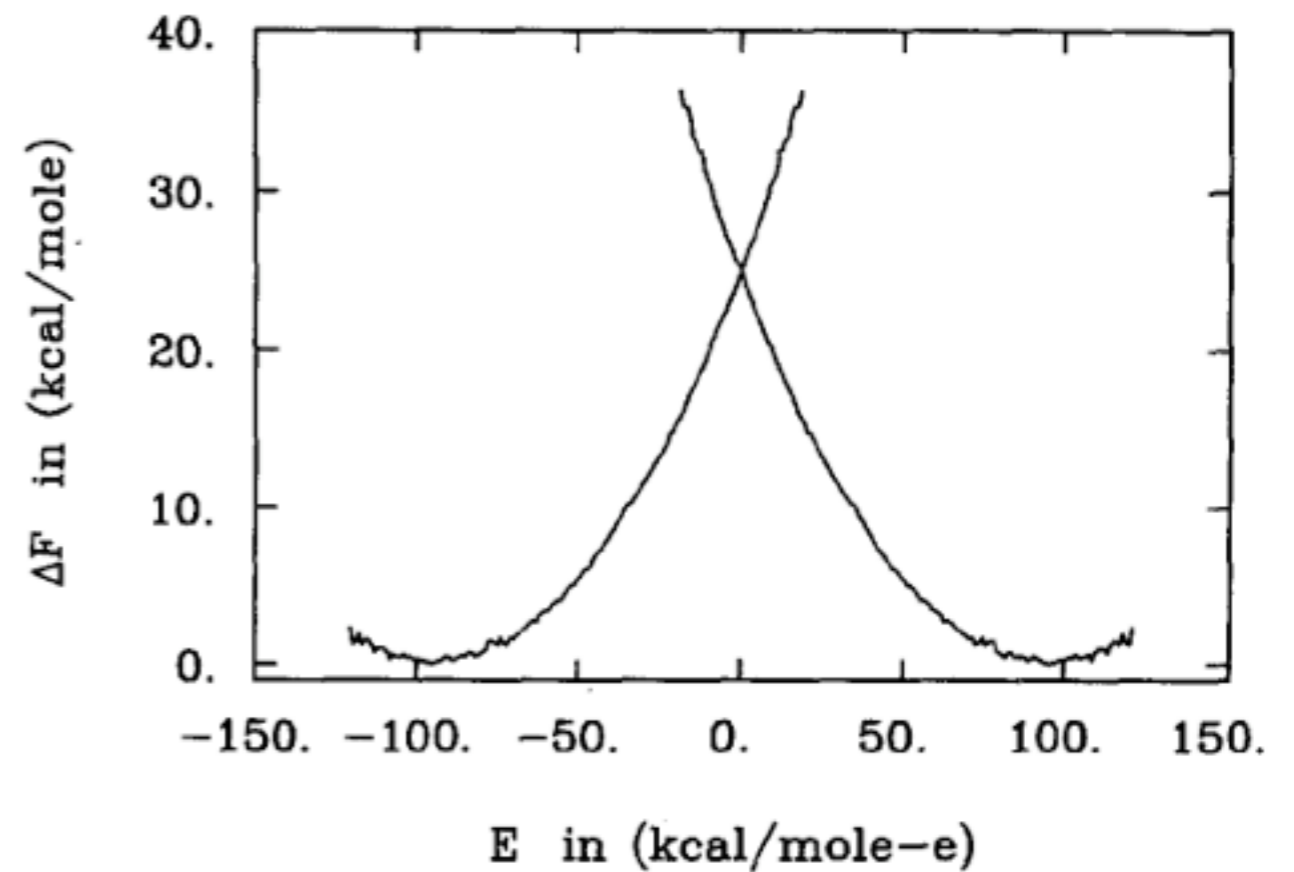
$$P(E) = c_z e^{\beta zeE} < \delta[E - E(R^N)] >_z$$

4 windows: z = 0.0, 0.17, 0.33, and 0.5

reversible work
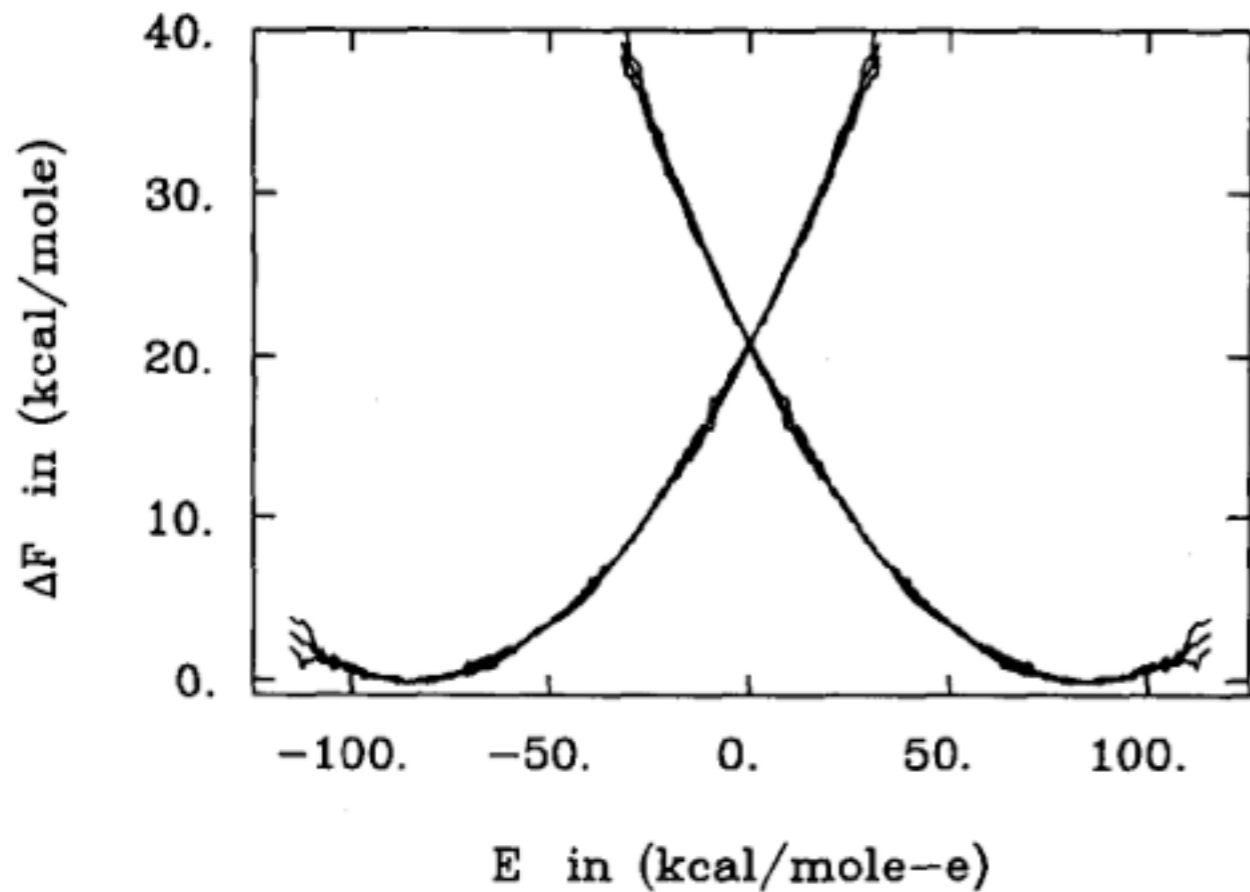
$d(Fe^{(2+z)+} - Fe^{(3-z)+}) = 5.5A$ $d(Fe^{(2+z)+} - Fe^{(3-z)+}) = 6.5A$

Solvent structure

Analysis of trajectories

The inner sphere reorganization is understood from the radial distribution functions of Fe^{2+}, $Fe^{2.5+}$, and Fe^{3+}.

System size comparison shows that the outer sphere reorganization is rather short ranged.

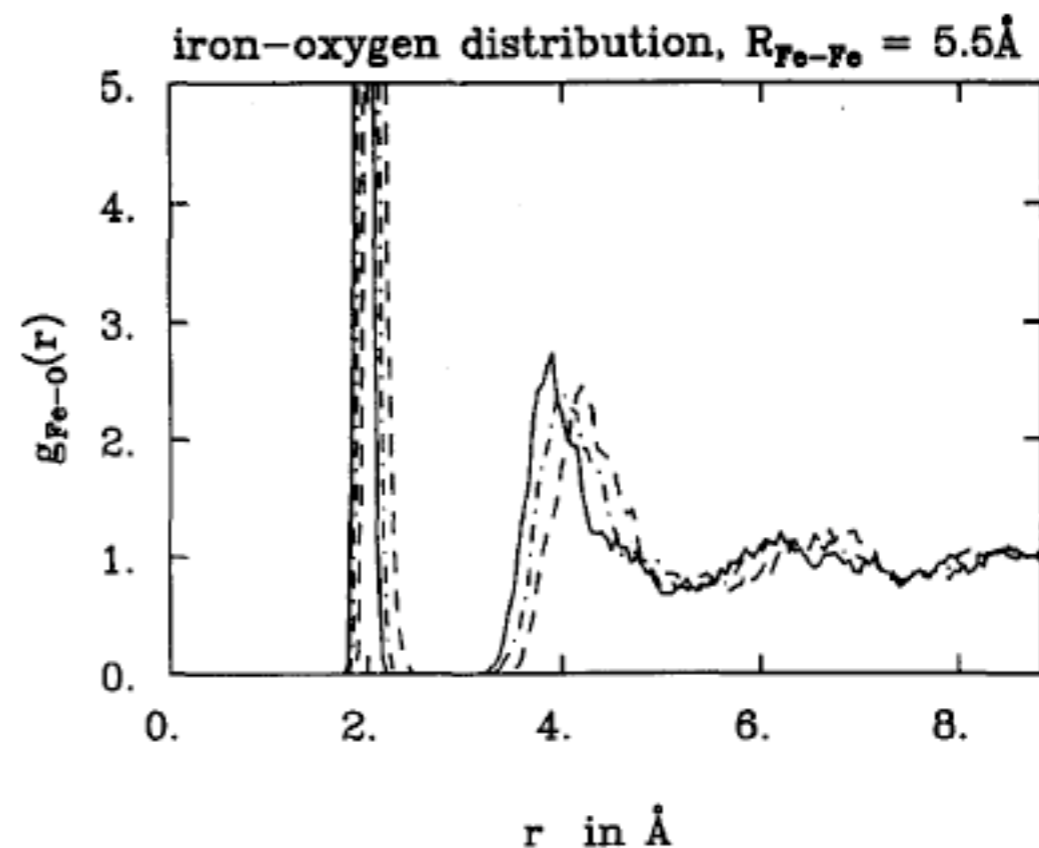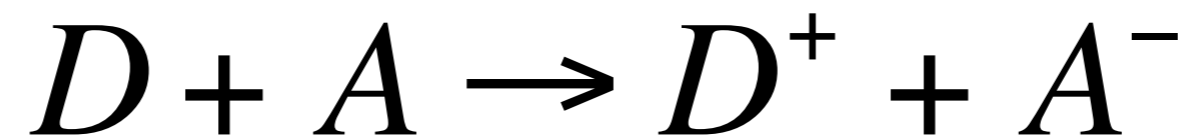iron−oxygen distribution, $R_{Fe-Fe} = 5.5Å$

$g_{Fe-O}(r)$

r in Å

TABLE III. Finite size effects studied with interionic separation 5.5 Å.

Number of water molecules	Length of box side (Å)	Cutoff of potentials (Å)	ΔF (kcal/mol)	Number of runs at each z	Length of runs (ps)
248	19.55	9.0	20.1	1	1.5
430	23.46	9.0	20.8	4	2.5
430	23.46	11.73	20.6	1	0.6

Redox Potential

Electron transfer reaction

$$D + A \rightarrow D^+ + A^-$$

$$\Delta\varepsilon = \varepsilon_{LUMO}^{A} - \varepsilon_{HOMO}^{D}$$

DFT

HOMO-LUMO gap is not a good estimate of the redox potential

$$\Delta \varepsilon = IP_D + EA_A$$

- electronic issue

One-electron gap in exact DFT

$$\varepsilon_{HOMO} = -IP$$

$$\Delta \varepsilon = \varepsilon_{HOMO}^{A^-} - \varepsilon_{HOMO}^{D}$$

DFT

HOMO-LUMO gap is not a good estimate of the redox potential

$$\Delta\varepsilon = IP_D + EA_A$$

molecular relaxation

difference in redox free energy of two half reactions:

difference in
vertical excitation

difference in
reorganization free energy

$$\Delta\Delta A = \Delta\Delta E_R - \Delta\lambda$$

$$\Delta\varepsilon = \Delta\Delta A + \Delta\lambda = F\Delta RP + \Delta\lambda$$

Faraday's constant

difference in
reduction potentials

DFT

long range interactions

cubic box, L=10-15A, pbc
neutral charge background

not ideal solution

$$X^{m+1} + Y^m \rightarrow X^m + Y^{m+1}$$
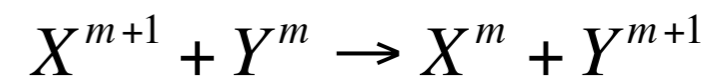
$$RP^O_{X^{m+1}} = RP^*_{X^{m+1}} - \frac{RT}{F} \ln \frac{\gamma_{X^m}}{\gamma_{X^{m+1}}} + v_0$$

$$RP^O_{X^{m+1}} - RP^O_{Y^{m+1}} = RP^*_{X^{m+1}} - RP^*_{Y^{m+1}} - \frac{RT}{F} \ln \frac{\gamma_{X^m}\gamma_{Y^{m+1}}}{\gamma_{X^{m+1}}\gamma_{Y^m}}$$

DFT

- *electronic issue*
- *molecular relaxation*
- *long range interactions*

- *sampling (10-100 ps)*
- *pseudopotentials*
- *DFT radical states*

- *breakdown of Marcus theory*

Results

Redox free energies and one-electron energy levels in density functional theory based ab initio molecular dynamics

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[b] *Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom*

List of the redox reactions discussed in this work

	Redox reaction	Solv.	Ref.
1	$MnO_4^{2-} + RuO_4^{1-} \rightarrow MnO_4^{1-} + RuO_4^{2-}$	H_2O	[1]
2	$Ru(CN)_6^{4-} + RuCl_6^{3-} \rightarrow Ru(CN)_6^{3-} + RuCl_6^{4-}$	H_2O	[10]
3	$Ru^{2+}(NH_3)_5Py + Ru^{3+}(NH_3)_6$ $\rightarrow Ru^{3+}(NH_3)_5Py + Ru^{2+}(NH_3)_6$	H_2O	[9]
4	$TH + TTF^{\cdot+} \rightarrow TH^{\cdot+} + TTF$	MeCN	[11]
5	$BQ^{\cdot-} + DQ \rightarrow BQ + DQ^-$	MeOH	[12]

The reactions were studied by partitioning in half reactions as outlined in Section 2.1. The solvent which is treated in our calculations at the same level of theory as the redox active solute is indicated in the second column (MeCN stands for acetonitrile and MeOH for methanol). Reactions **1**, **2** and **3** involve transition metal aqua ions (Py is pyridine). TH (thianthrene) and TTF (tetrathiafulvalene) are two organosulfur compounds which can be ox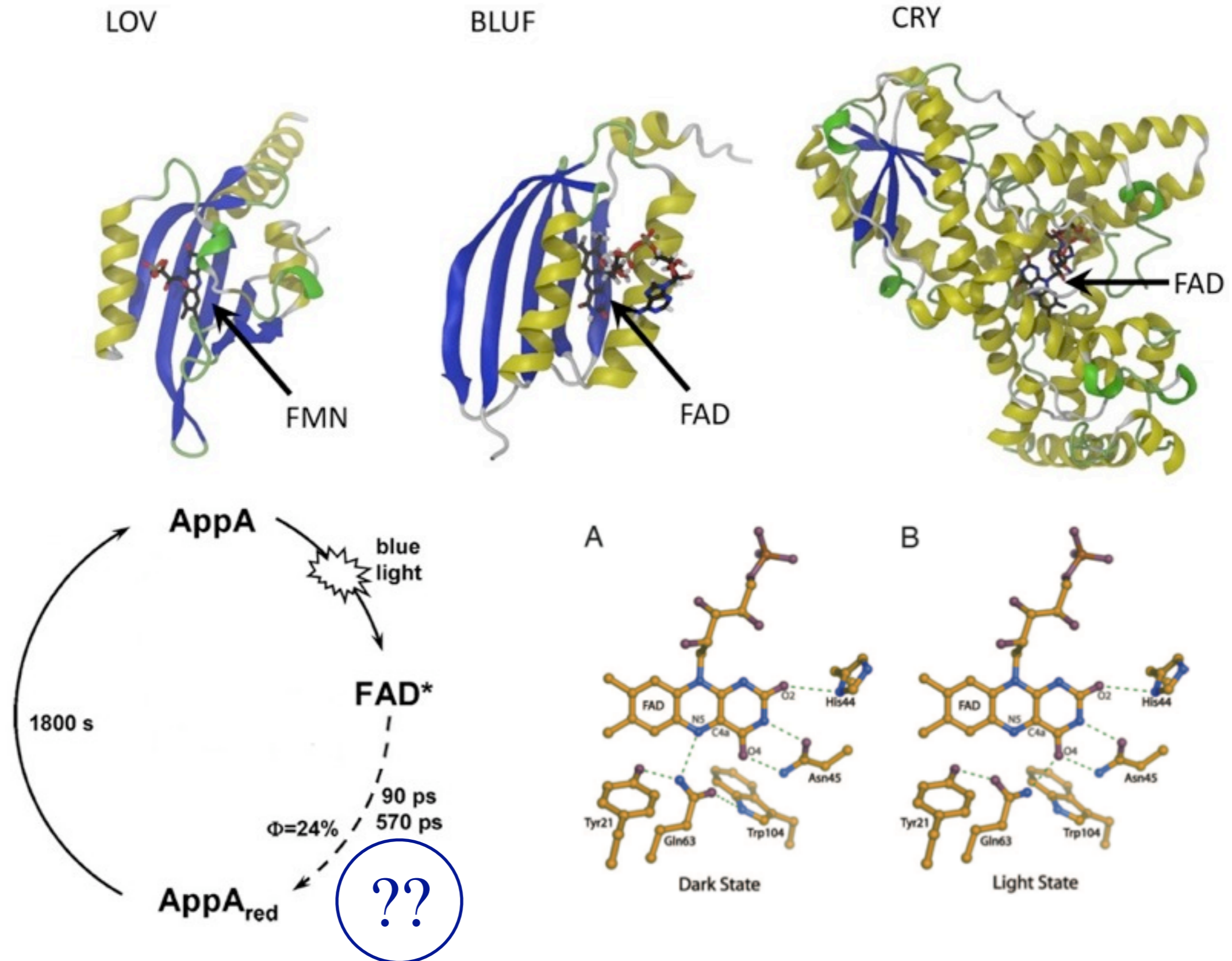idized to stable radical cations. BQ (benzoquinone) and DQ (duroquinone) are small quinones forming radical anions. The final column gives the reference to the original papers.

Energetics in units of eV of the five model redox reactions of Table 1

React.	$\Delta\epsilon$	$\Delta\Delta E_R$	$\Delta\lambda$	$\Delta\Delta A$	ΔG(exp.)
1	0.66	0.37	+0.15	0.3	0.04
2	1.6	1.2	−0.2	1.4	1.78
3	0.3	0.02	−0.25	0.27	0.23
4	1.00	0.94	−0.02	0.9	0.93
5	0.30	0.39	−0.14	0.43	0.46

$\Delta\epsilon$ is the difference in HOMO energy of the reduced acceptor and donor as defined in Eq. (15). $\Delta\Delta E_R$ is the relative vertical energy gap (Eq. (6)) averaged over a MD equilibrium trajectory of the reduced systems. $\Delta\lambda$ is the corresponding difference in reorganization energy of the half reactions and $\Delta\Delta A$ is the reaction free energy of the full reaction computed by subtracting the free energy ΔA of the corresponding half oxidation reactions. ΔG(exp.) is the literature value for the standard free energy change of the reaction.

Free energy

- half reaction: $R \rightarrow O + e^-$

$$\Delta A = \left\langle \Delta E(R^N) \right\rangle_R - \lambda$$

$$\Delta A = \left\langle \Delta E(R^N) \right\rangle_O + \lambda$$

- Activation free energy

$$\Delta A^* = \frac{(\lambda + \Delta A_0)^2}{4\lambda}$$

- Vertical ionization

$$\Delta E(R^N) = E_O(R^N) - E_R(R^N)$$

- reorganisation free energy

from fluctuations of the gap

$$2k_B T \lambda = \sigma_R^2 = \sigma_O^2$$

$$\sigma_R^2 = \left\langle \left(\Delta E(R^N) - \Delta E_R \right)^2 \right\rangle_R$$

Linear Response

Marcus theory

$$2k_B T \lambda = \sigma_R^2 = \sigma_O^2$$

- Linear response to a change in charge
- Equal variance of the fluctuations
- Gaussian distribution

$$A_R = \frac{1}{2}\left(\Delta E_R + \Delta E_O\right)$$

$$\lambda = \frac{1}{2}\left(\Delta E_R - \Delta E_O\right)$$

$$A_R(\Delta E) = A_R^* + \frac{k}{2}\left(\Delta E - \Delta E_R\right)^2$$

Molecular Dynamics
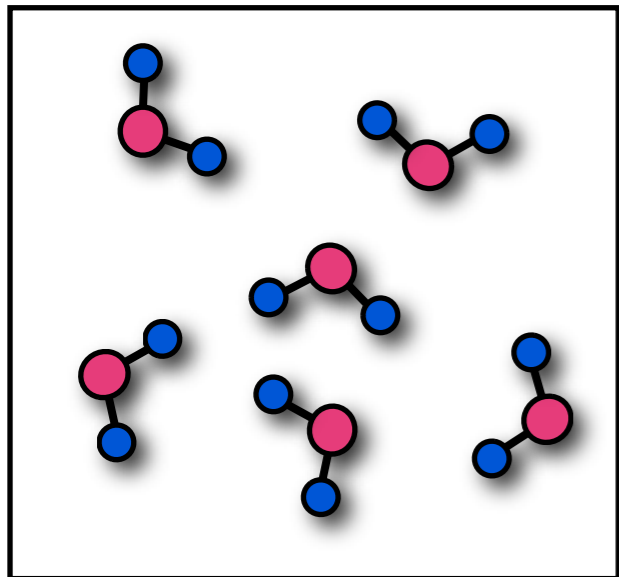
$$r(t + \Delta t) = r(t) + v(t + \Delta t/2)\Delta t$$

$$v(t + \Delta t/2) = v(t - \Delta t/2) + \Delta t \frac{f(t)}{m}$$

$$F = m\frac{d^2 r}{dt^2} = ma$$

The force *F* is given by the gradient of the potential *V(r)*

$$F = -\frac{dV(r)}{dr}$$

Given the potential, one can integrate the trajectory *r(t)* of the whole system as a function of time.

$$V(\mathbf{r}) = \sum_{bonds} k_r(r - r_{eq})^2 + \sum_{angles} k_\theta(\theta - \theta_{eq})^2 + \sum_{dihedrals} \frac{1}{2}\nu_n(1 + cos(n\phi - \phi_0)) + \sum_{i<j}\left(\frac{a_{ij}}{r_{ij}^{12}} - \frac{b_{ij}}{r_{ij}^6} + \frac{q_i q_j}{\epsilon r_{ij}}\right)$$

bonds   bends   torsions   non-bonded

Ab Initio Molecular Dynamics

$$\mathcal{H}\Psi = E\Psi$$

$$\mathcal{H}^{\mathrm{DFT}}\psi_i = \left[-\frac{\hbar^2}{2m}\nabla^2 + \sum_\alpha \frac{eZ_\alpha}{R_{i\alpha}} + \frac{e^2}{2}\int dr\frac{\rho(r')}{|r-r'|} + \frac{\delta E_{xc[\rho]}}{\delta\rho(r)} \right]\psi_i = \epsilon_i\psi_i$$
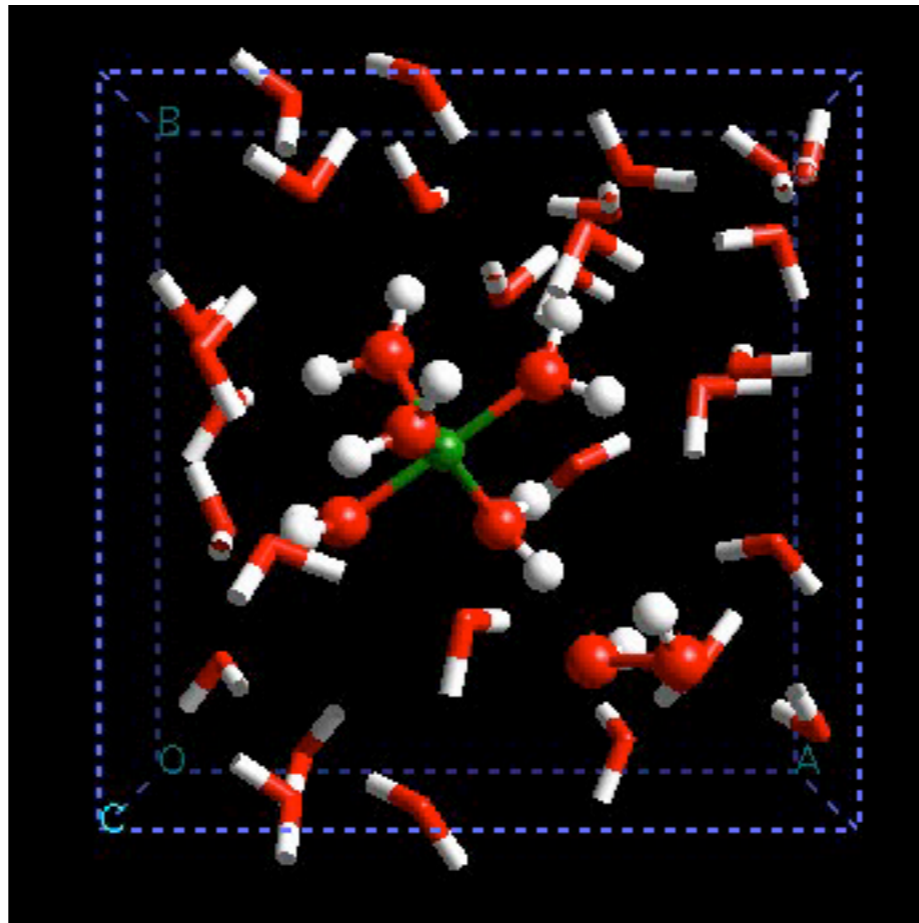
Signal transduction in photoreceptors

LOV

BLUF

CRY

FMN

FAD

FAD

AppA

blue light

1800 s

FAD*

90 ps
570 ps
Φ=24%

??

AppA$_{red}$

A

FAD

His44

O2

N5

C4a

O4

Asn45

Tyr21

Gln63

Trp104

Dark State

B

FAD

His44

O2

N5

C4a

O4

Asn45

Tyr21

Gln63

Trp104

Light State

LF $\xrightarrow{\text{e}^-}$ LF$^-$

LF$^-$ $\xrightarrow{\text{H}^+}$ LFH

LFH $\xrightarrow{\text{e}^-}$ LFH$^-$

LFH$^-$ $\xrightarrow{\text{H}^+}$ LFH$_2$
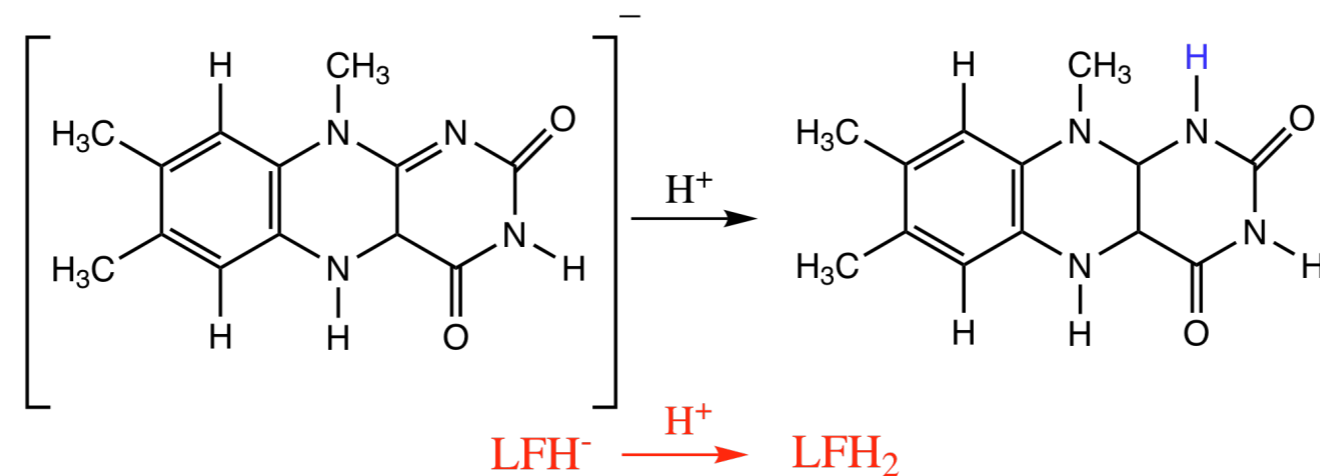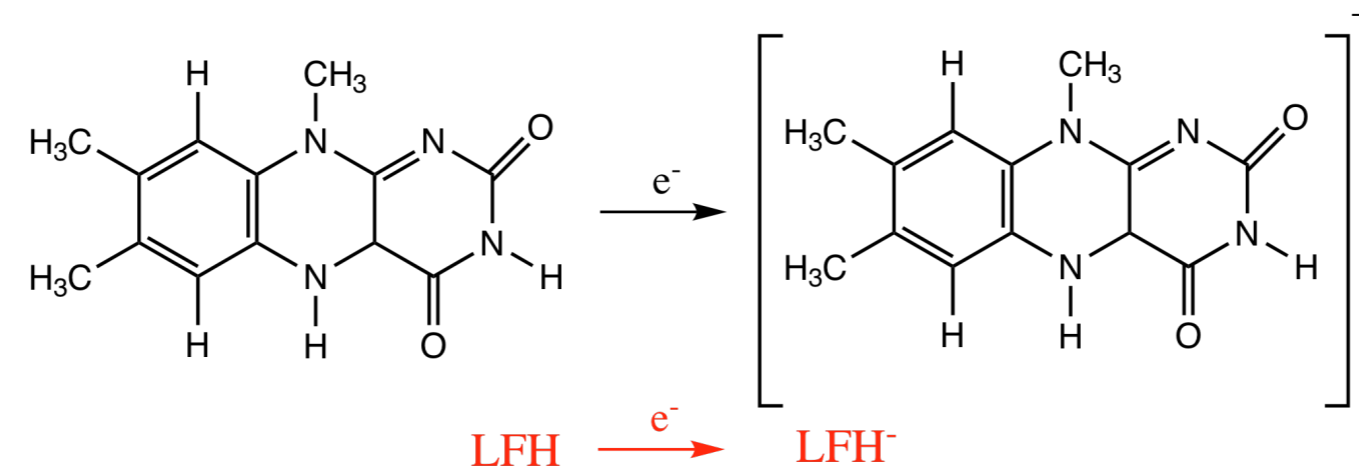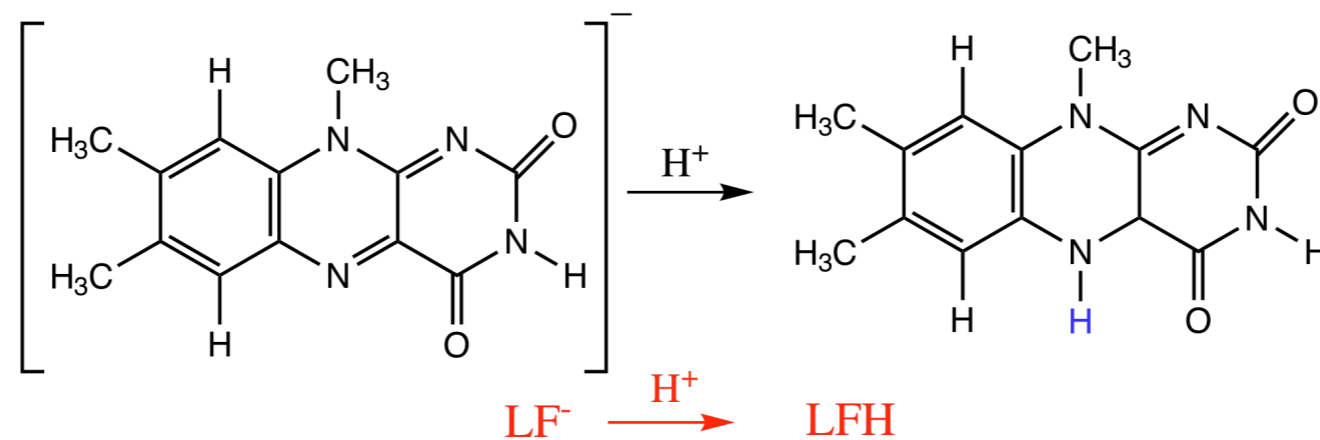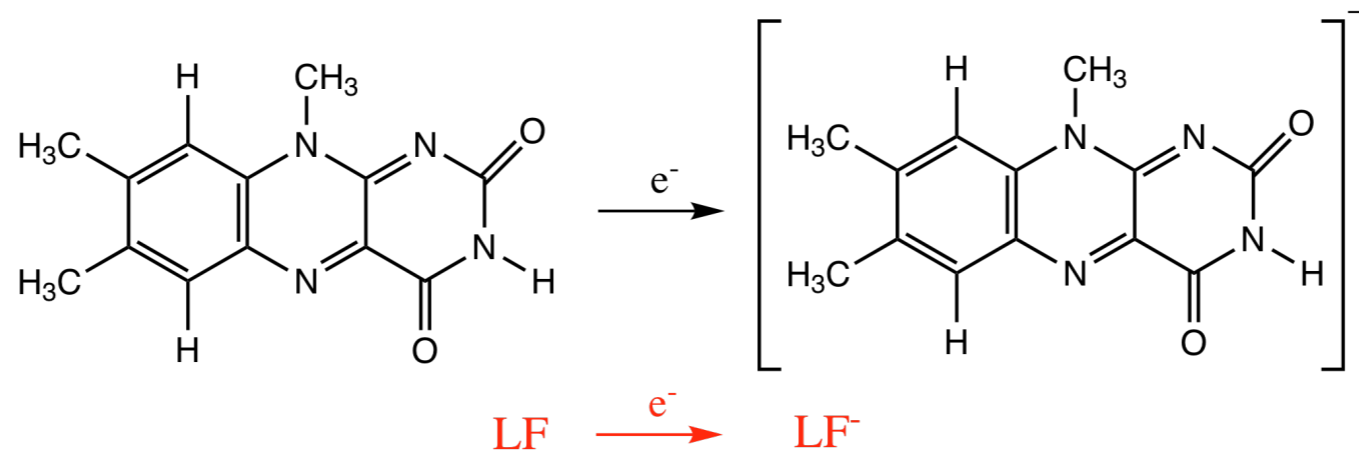
Redox potential of flavin

Ab Initio MD

- density functional theory
- classical dynamics of atoms (nuclei)
- 100 H_2O
- 20 ps simulation time
- CP2K program
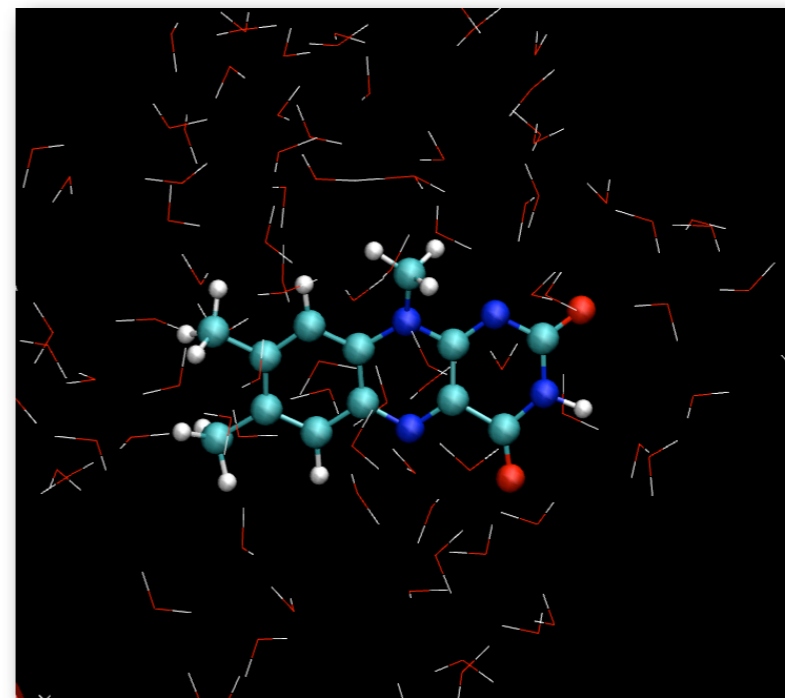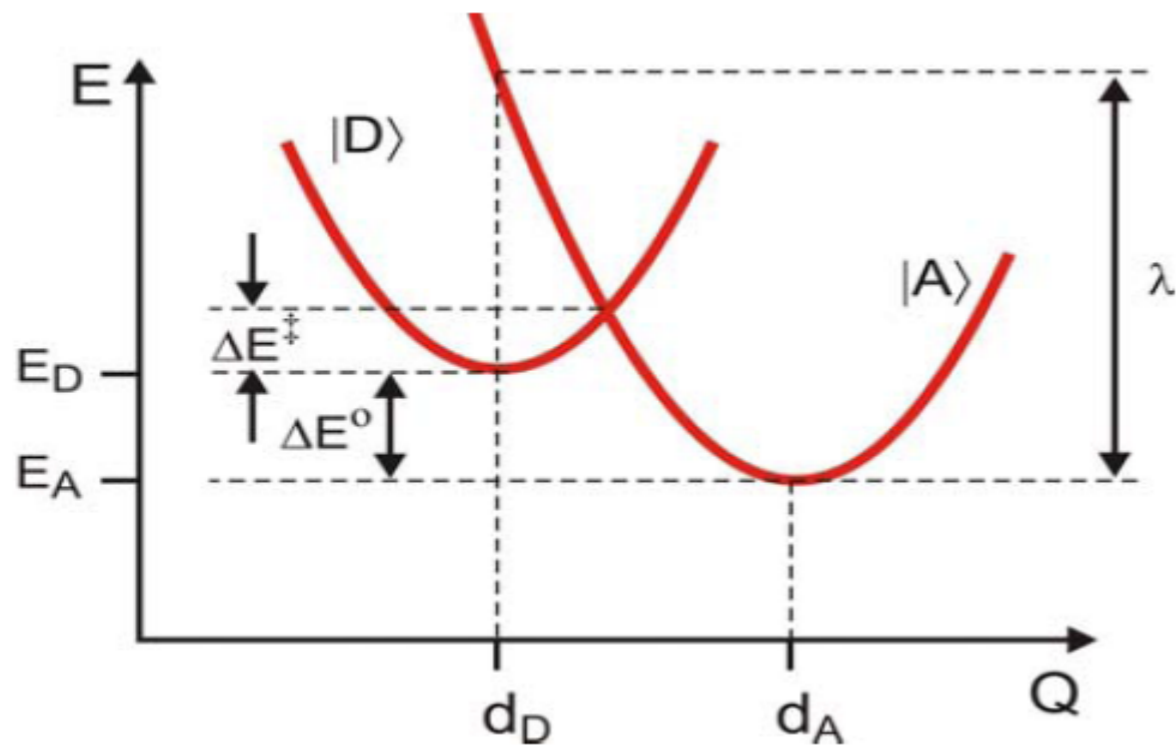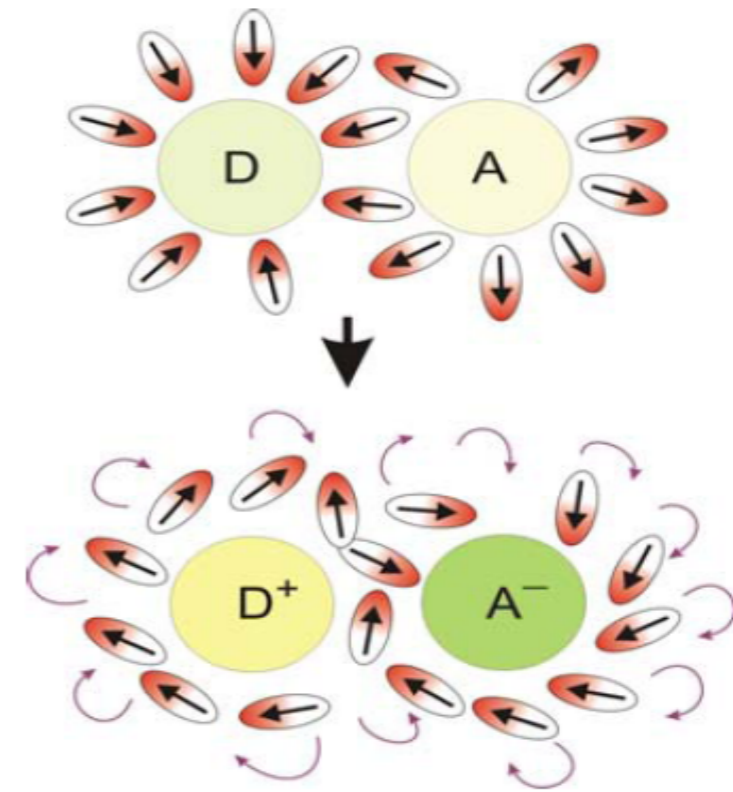
Redox potential of flavin

Electron transfer half reaction:

$$LF \xrightarrow{e^-} LF^-$$
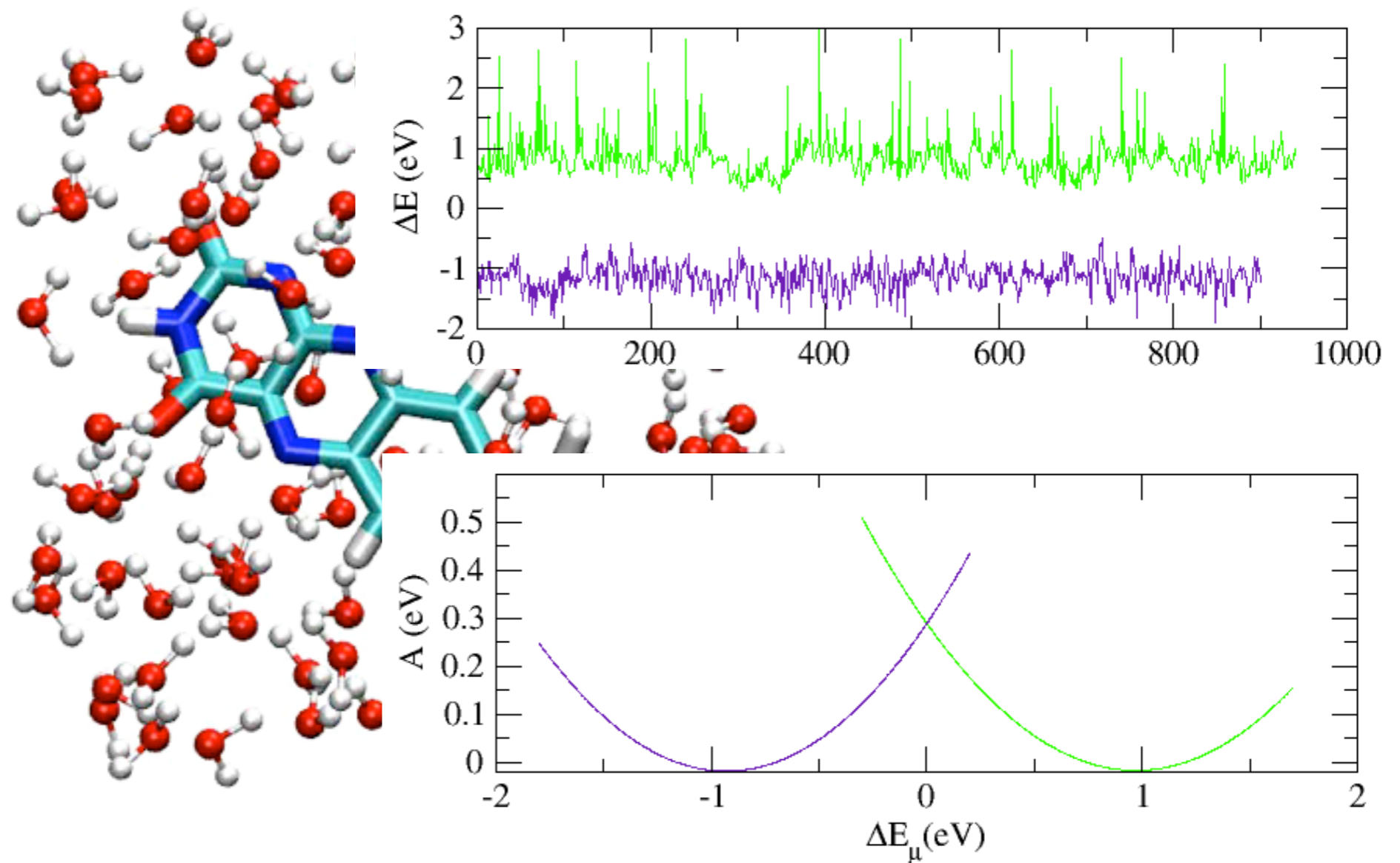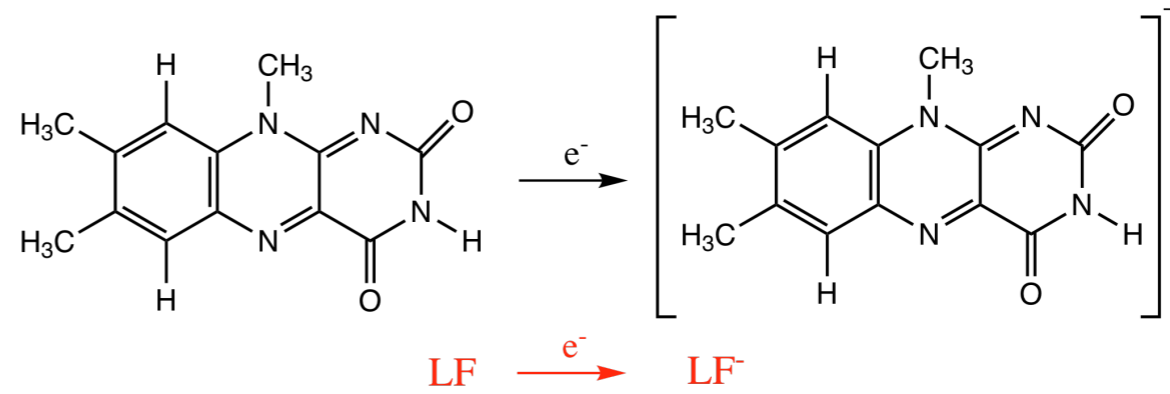
Redox potential of flavin

Rudolph A. Marcus:
take ΔE as reaction coordinate!

... but...
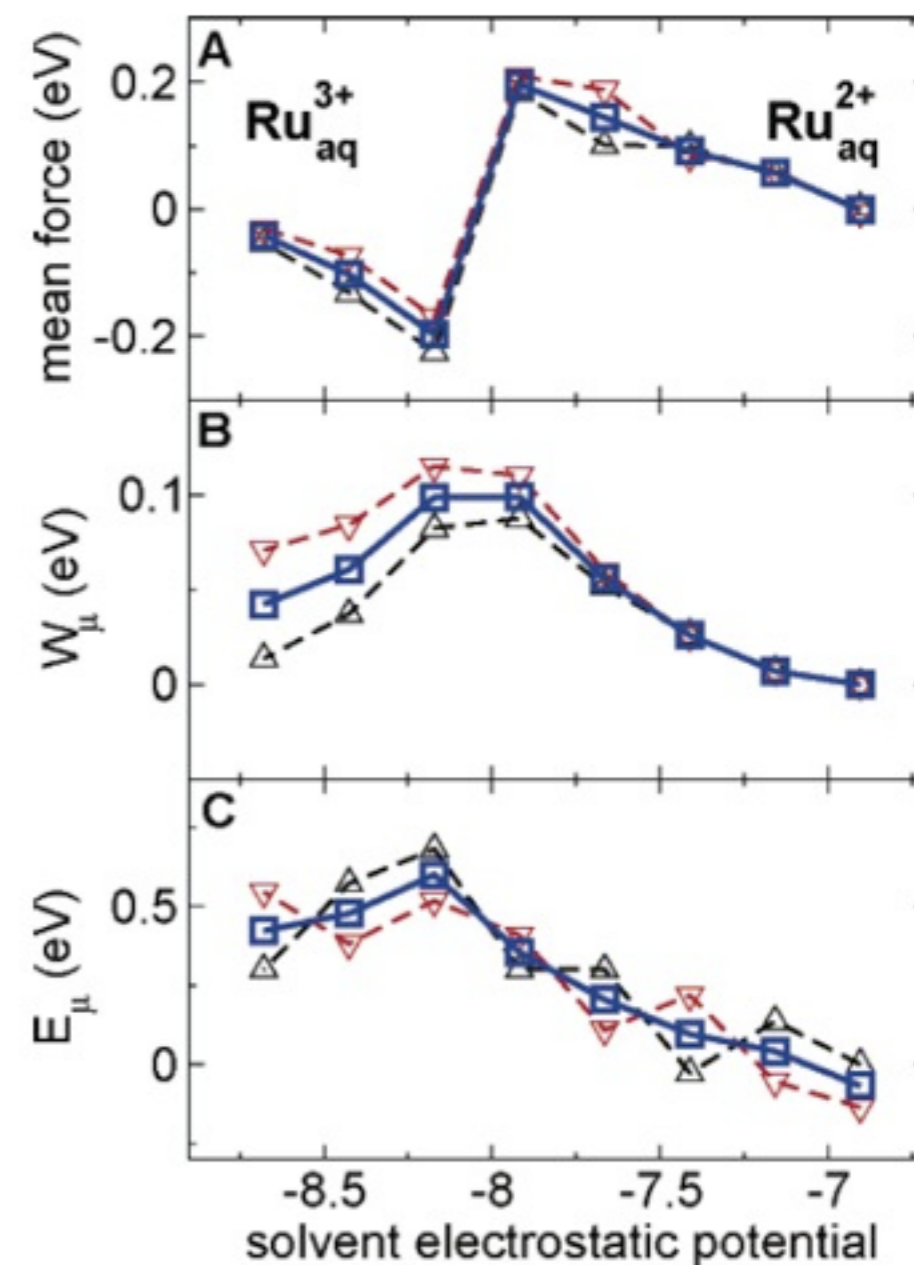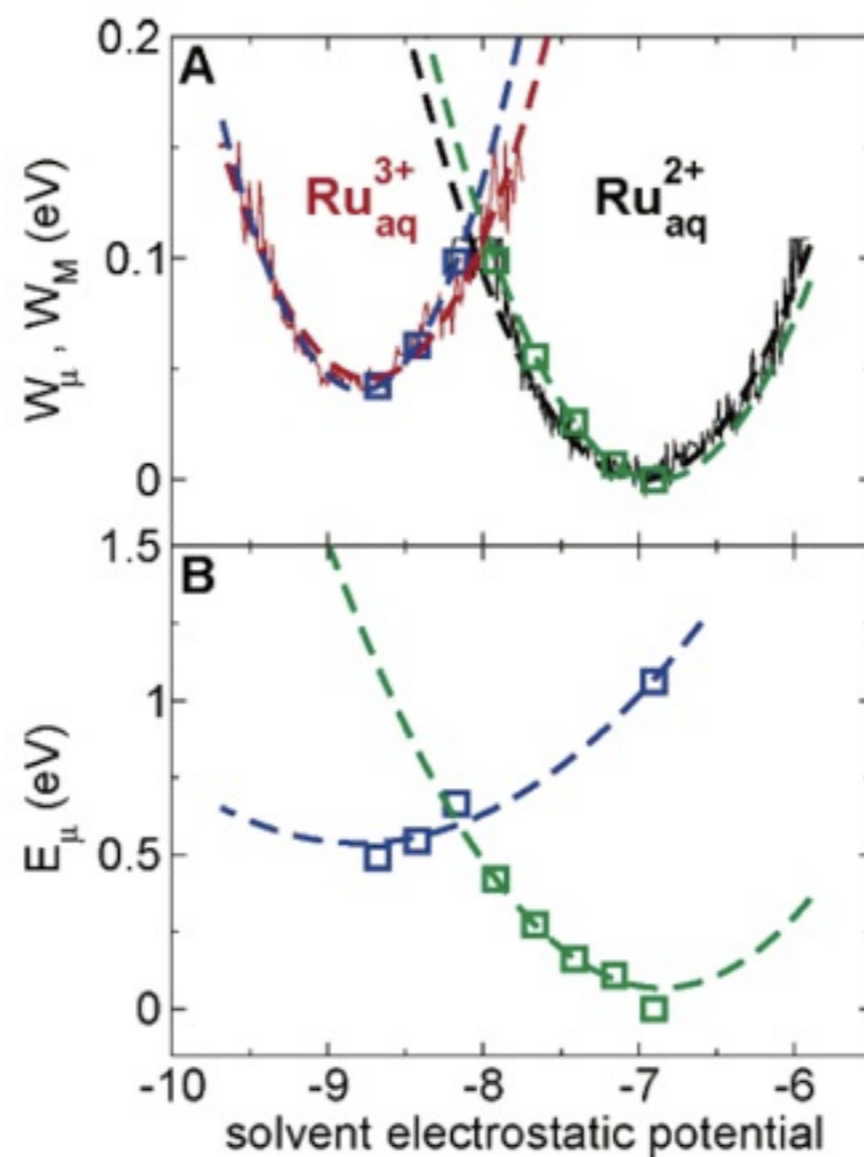with which structural changes
does ΔE correlate?
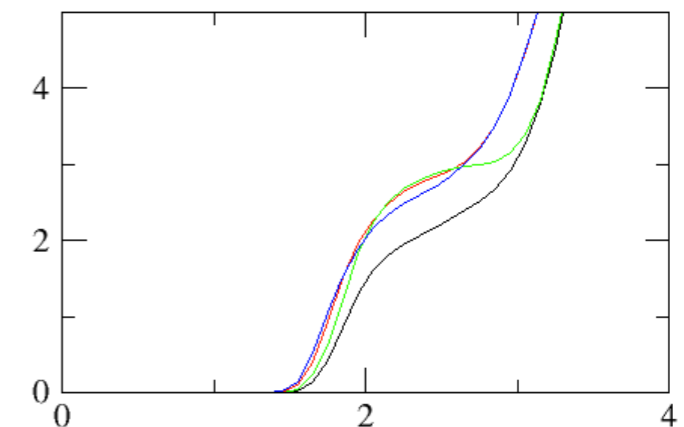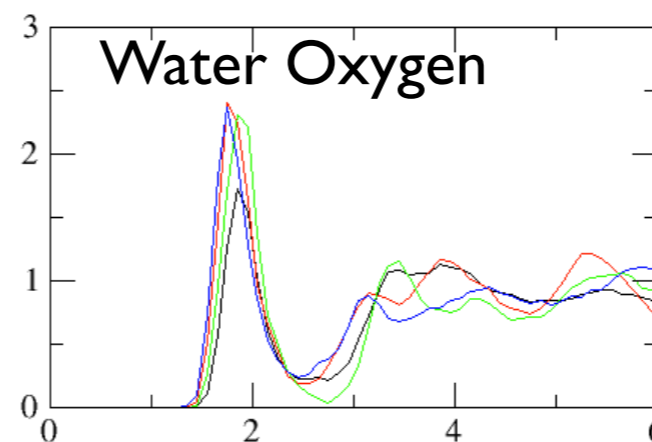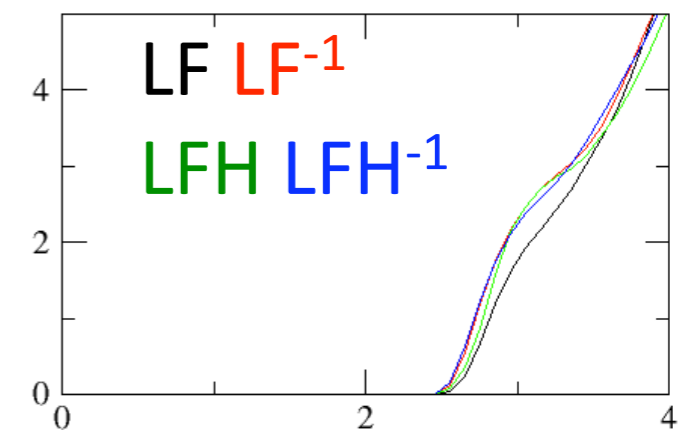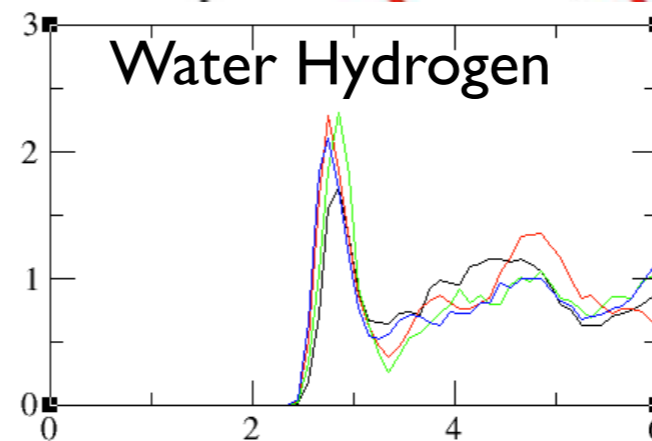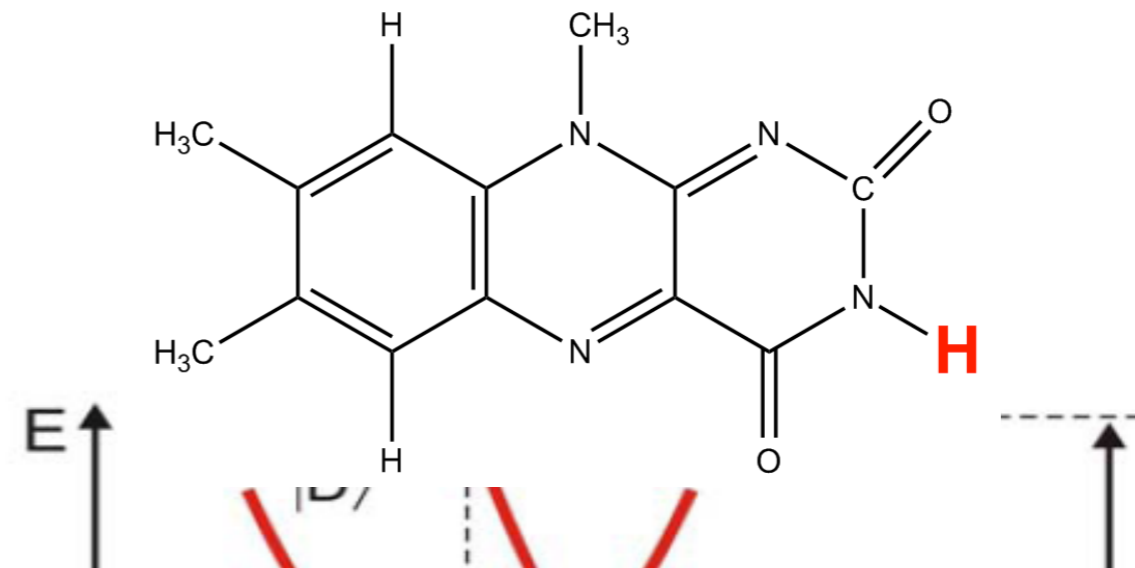
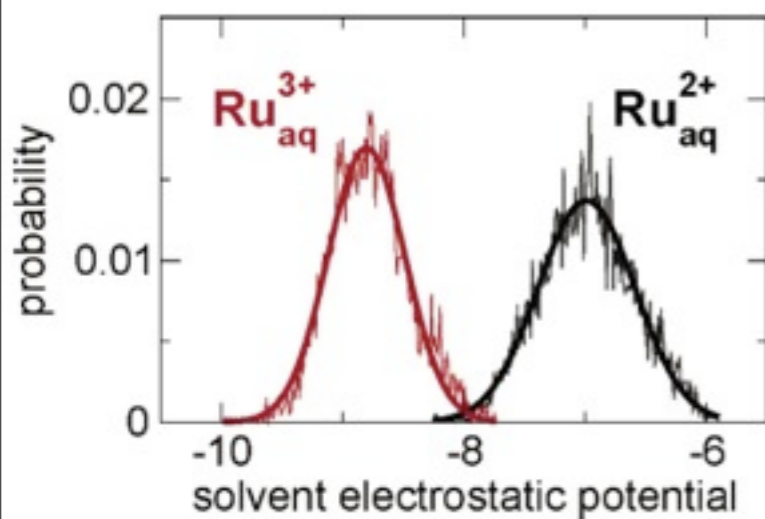difference map of mulliken charges
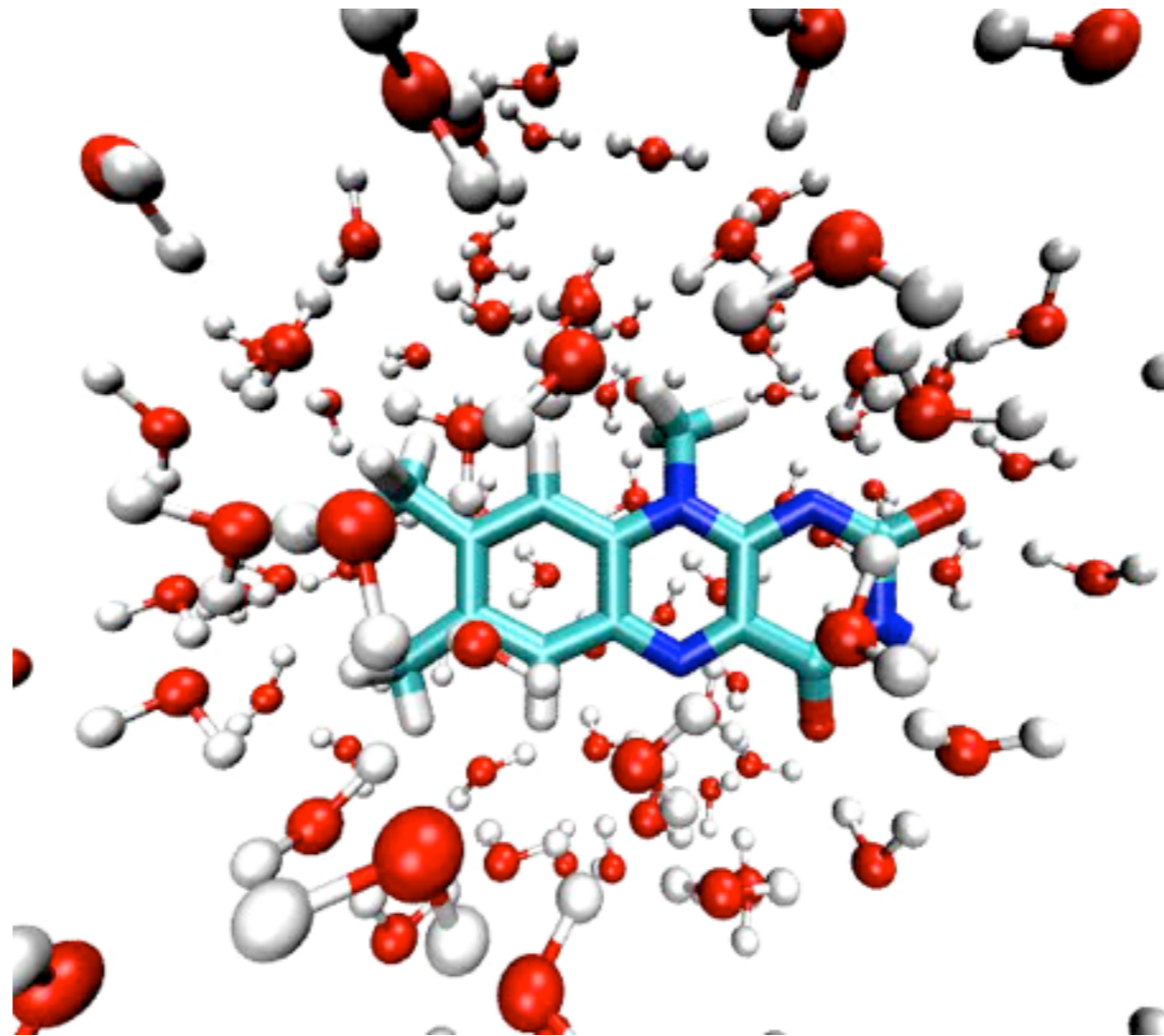
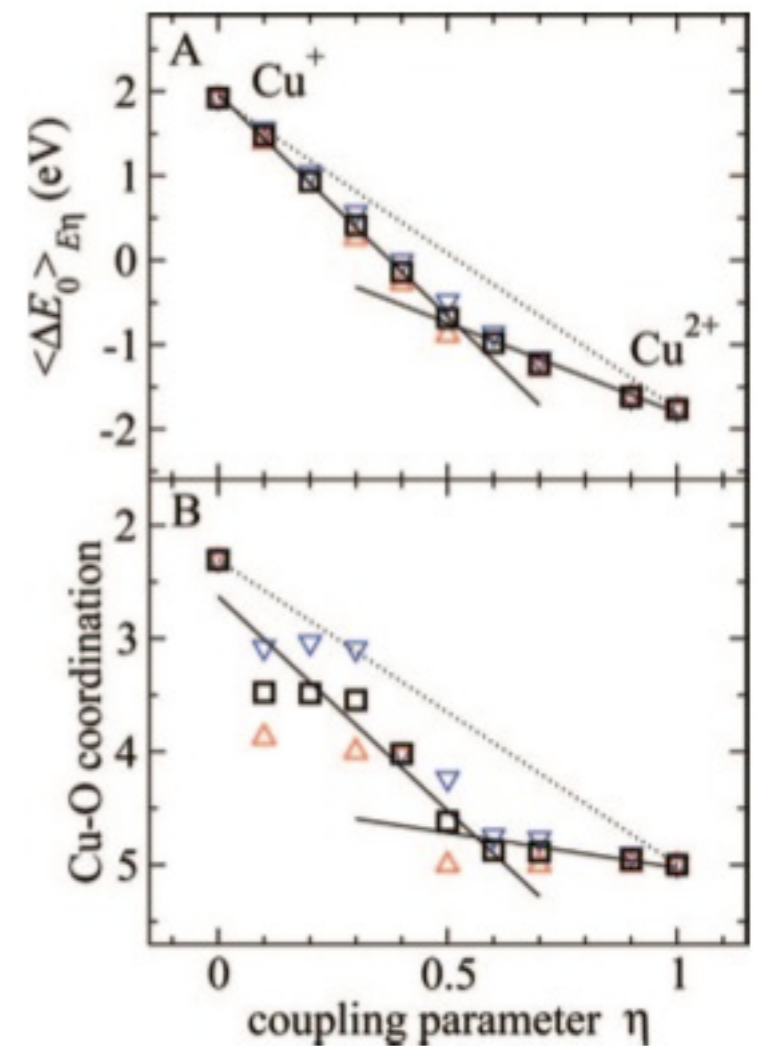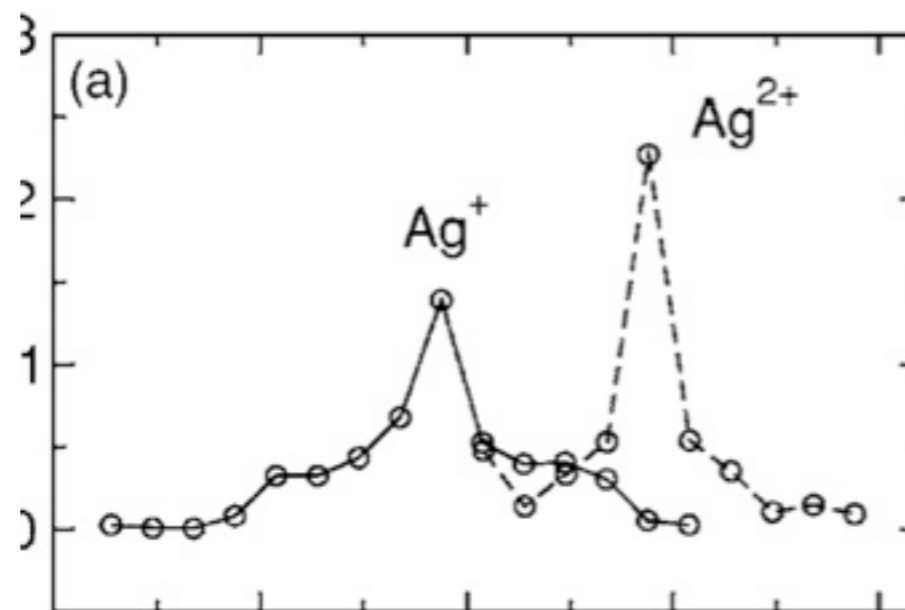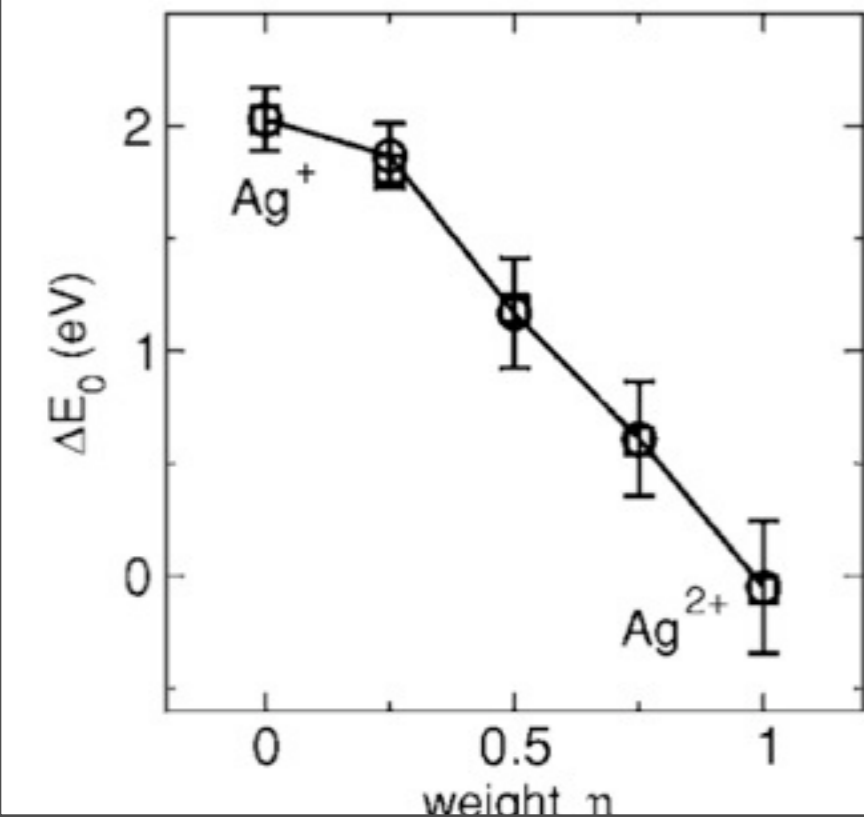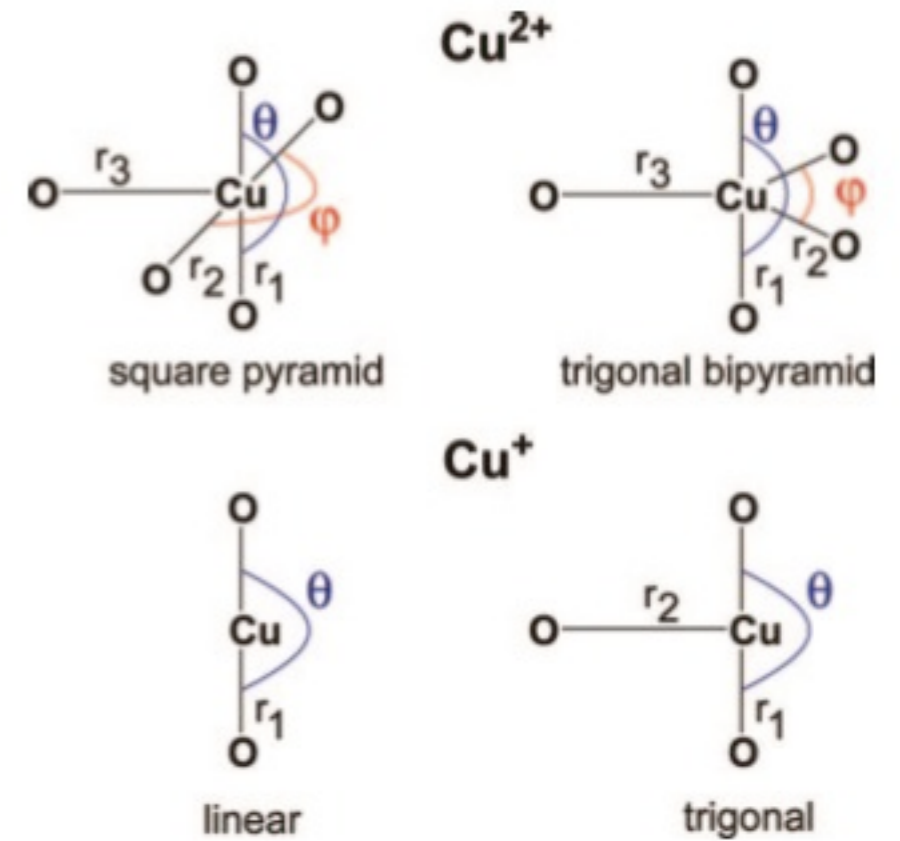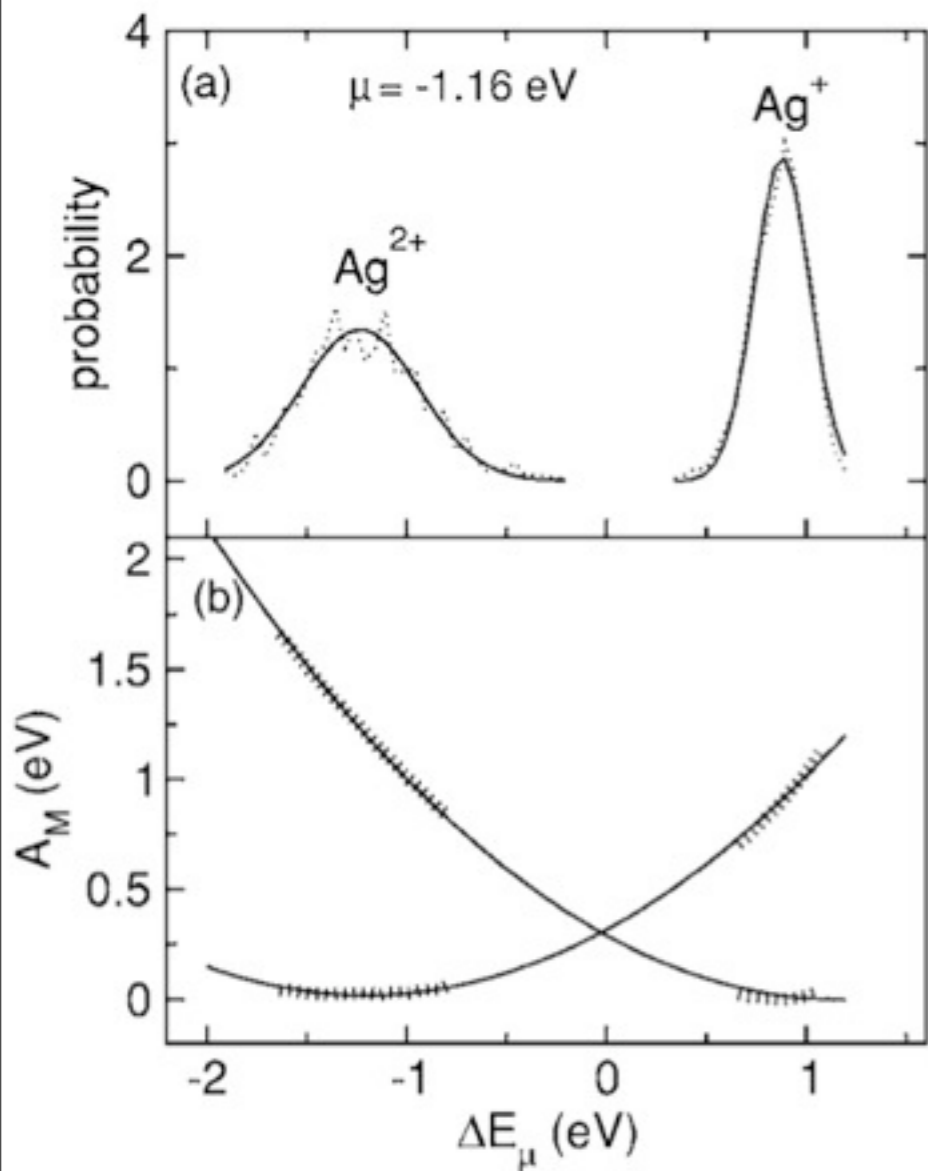# Ab Initio Molecular Dynamics Simulation of the Aqueous Ru^{2+}/Ru^{3+} Redox Reaction: The Marcus Perspective[†]

Jochen Blumberger and Michiel Sprik*

Department of Chemistry, University of Cambridge, Cambridge CB2 1EW, United Kingdom

non-linear behavior

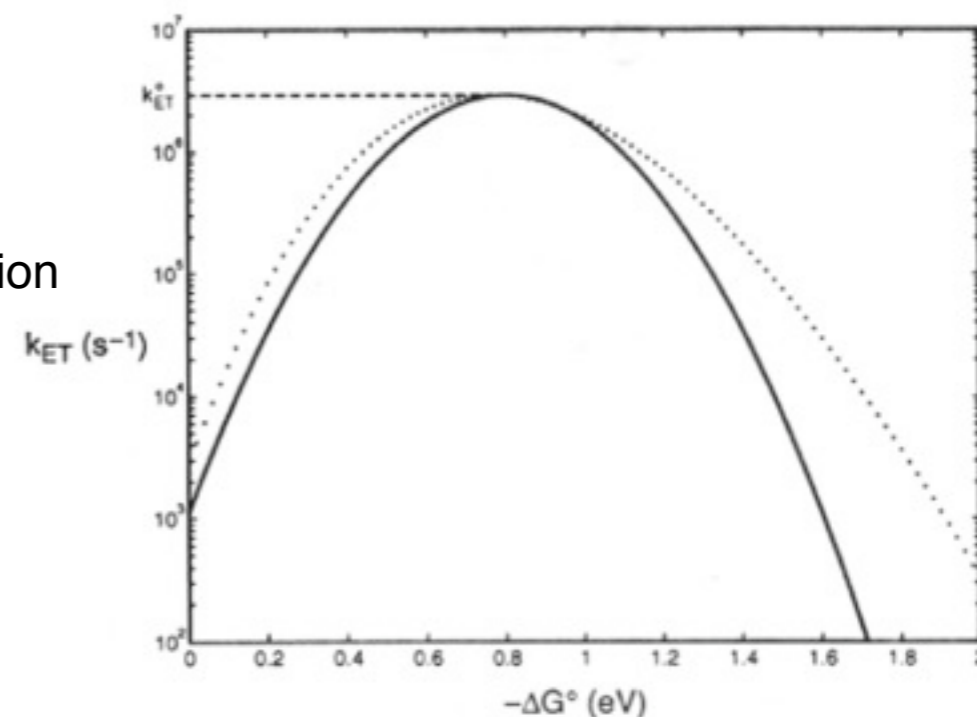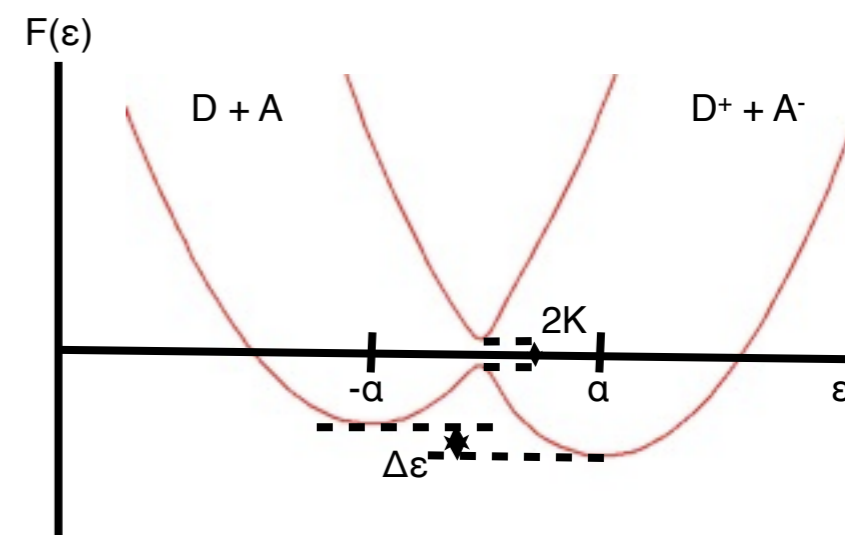Ag$^+$/Ag^{2+}
and
Cu$^+$/Cu^{2+}

Summary Part 1

Marcus theory of Electron transfer

$$k_{et} = \frac{2\pi}{\hbar}|H_{AB}|^2 \frac{2}{\sqrt{4\pi\lambda k_B T}}\exp-\frac{(\lambda + \Delta G_0)^2}{4\lambda k_B T}$$

1. reaction rate theory (Eyring) or vibronic excitation (Franck-Condon)
2. Gaussian potentials when polarization is the reaction coordinate
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4. dependence of activation energy on driving force ΔG_0 and reorganization free energy
5. inverted region when λ < ΔG_0
6. adiabatic vs diabatic picture (energy gap versus Fermi's golden rule)
7. quantum tunneling

Bibliography and further reading

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