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Practicalities of Molecular Computational Modeling Relevant to Renewable Energy Technologies

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CHEMISTRY

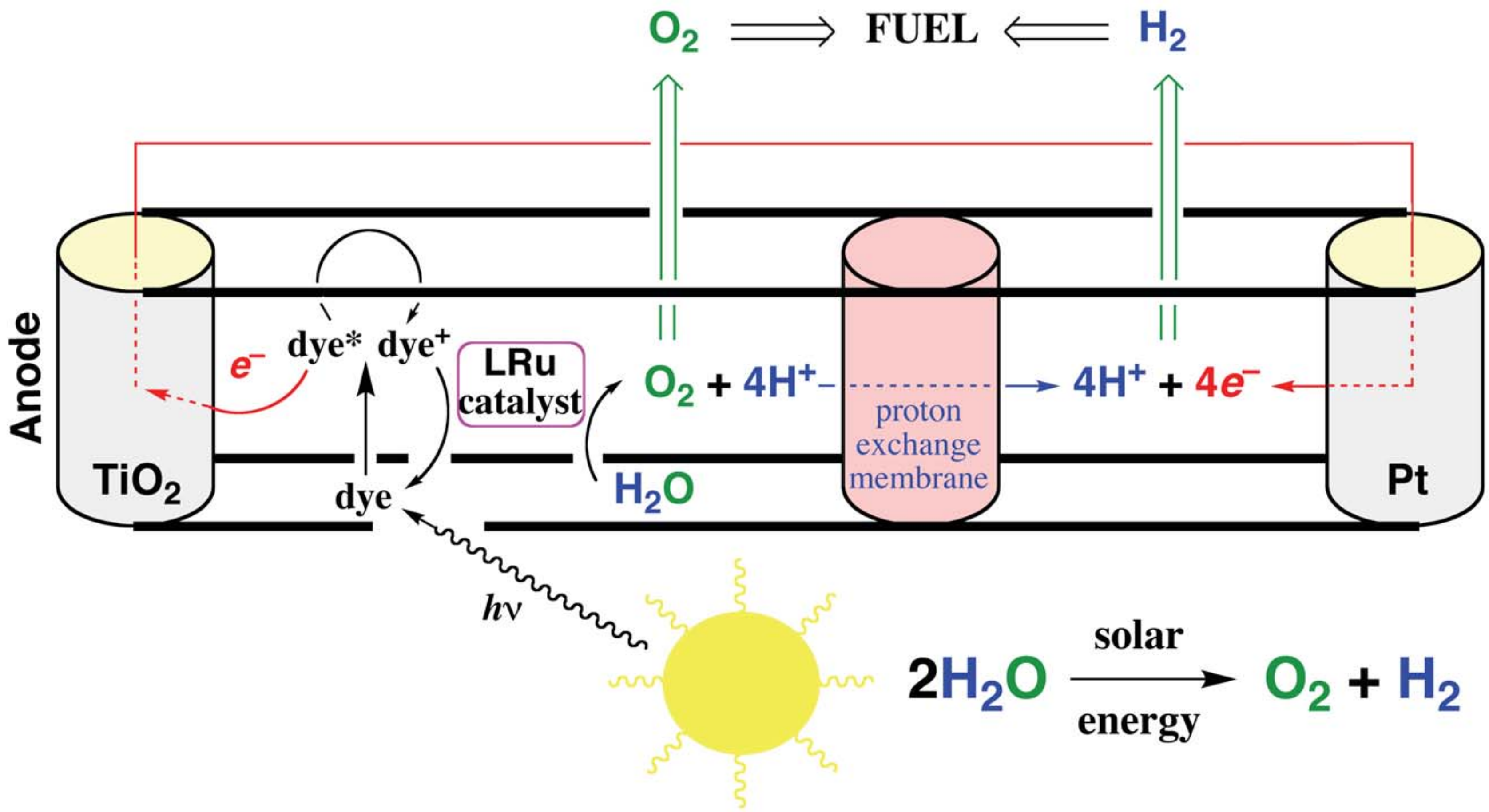
Practicalities of Molecular Computational Modeling Relevant to Renewable Energy Technologies

Christopher J. Cramer

Trieste, October 18, 2011

Conversion of Solar Energy to Green Fuel

Schematic of the Dye-Sensitized Solar Cell

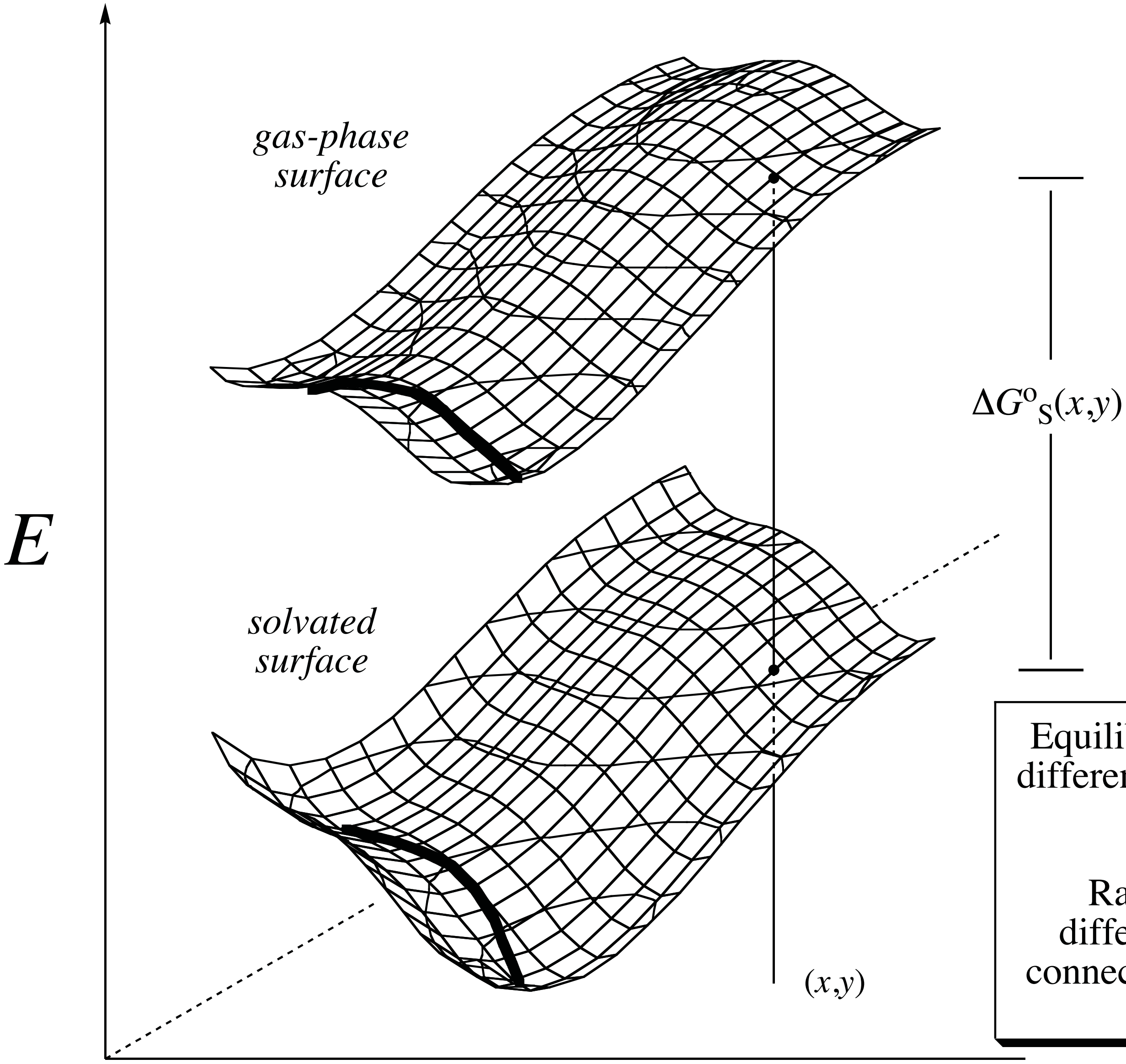


Possible Computational Goals

- Excited-state energy (of dye); nature of excited state
- Electron-transfer rate
- Standard reduction potential
- pKa
- Pourbaix diagram
- Molecular (catalytic) reaction mechanisms

Essentially all processes require quantum mechanical modeling; most if not all also require an accounting for the bulk and possible specific effects of a condensed phase (e.g., aqueous solvation)

Potential Energy Surface Perspective of Solvation



Phase partitioning from separation between the surfaces themselves

Equilibrium constants from differences in energy of local minima

Rate constants from differences in energy of connected local minima and saddle points

SM*x* Bulk Electrostatic Effects

Generalized Born (GB) equation

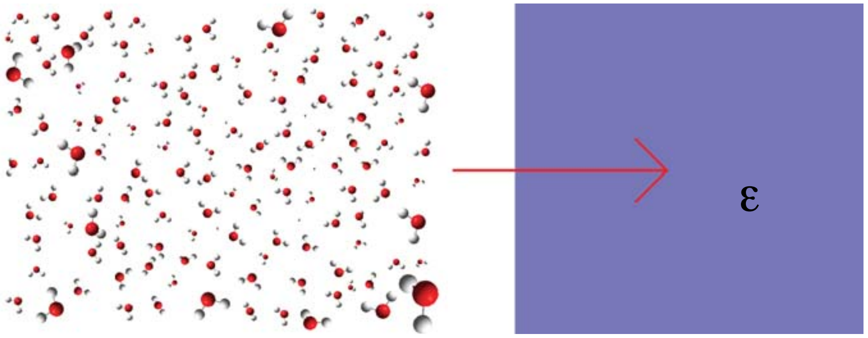
$$G_{\mathrm{P}} = -\frac{1}{2}\left(1-\frac{1}{\varepsilon}\right)\sum_{kk'}^{\text{atoms}} q_k \gamma_{kk'} q_{k'}$$

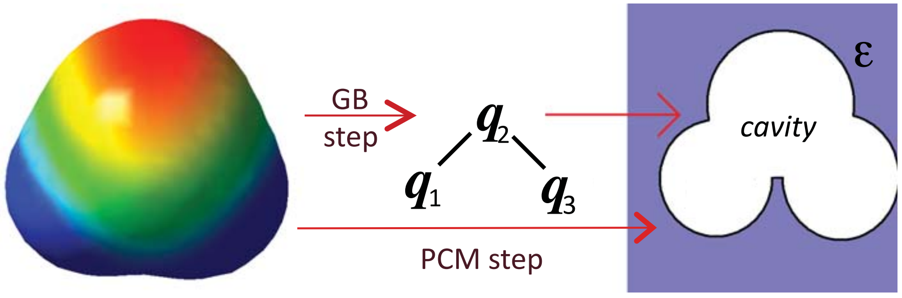
Polarized Continuum Model (PCM) equation

$$G_{\mathrm{P}} = -\frac{1}{2}\left(\langle\Psi|V_{\mathrm{RF}}|\Psi\rangle + \sum_{k}^{\text{nuclei}} Z_k V_{\mathrm{RF}}\right)$$

Reaction field—usually

$$V_{\mathrm{RF}}(\mathbf{r}) = \sum_{k'} \frac{q'_{k'}}{|\mathbf{r}-\mathbf{r}_{k'}|}$$





Limiting behaviors…

$$r_{kk'} >> 0$$

$$G_{\mathrm{P}} = -\frac{1}{2}\left(1-\frac{1}{\varepsilon}\right)\frac{q_k q_{k'}}{r_{kk'}}$$

Coulomb's Law

$^1/_2$(–gas + solution)

$$r_{kk'} = 0$$

$$G_{\mathrm{P}} = -\frac{1}{2}\left(1-\frac{1}{\varepsilon}\right)\frac{q_k^2}{\alpha_k}$$

Born's Equation

monatomic ion

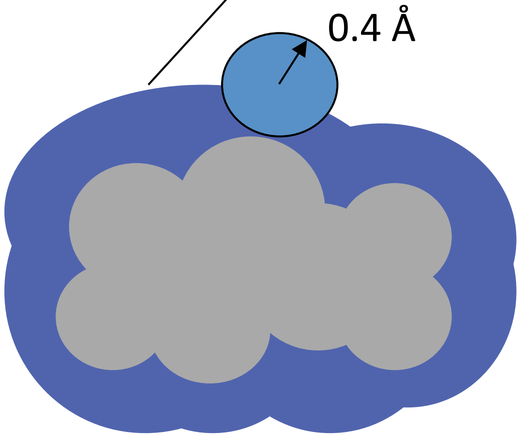
First-Solvation-Shell Contributions

Cavitation, **D**ispersion, **S**tructural rearrangement of solvent

$$G_{\mathrm{CDS}} = \sum_{k}^{\text{atoms}} A_k \left(\sigma_k + \sum_{k'}^{\text{atoms}} \sigma_{kk'}(\mathbf{R}) \right)$$

atomic-number-dependent parameters

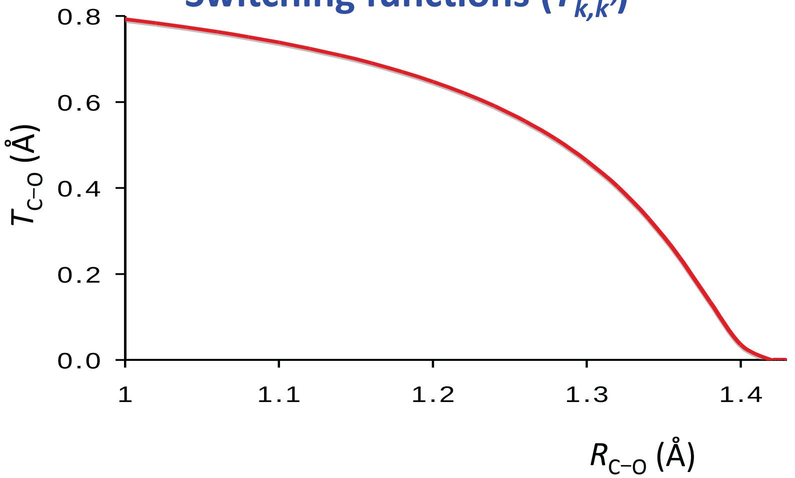
atomic surface tension designed to account for the effect of solute geometry

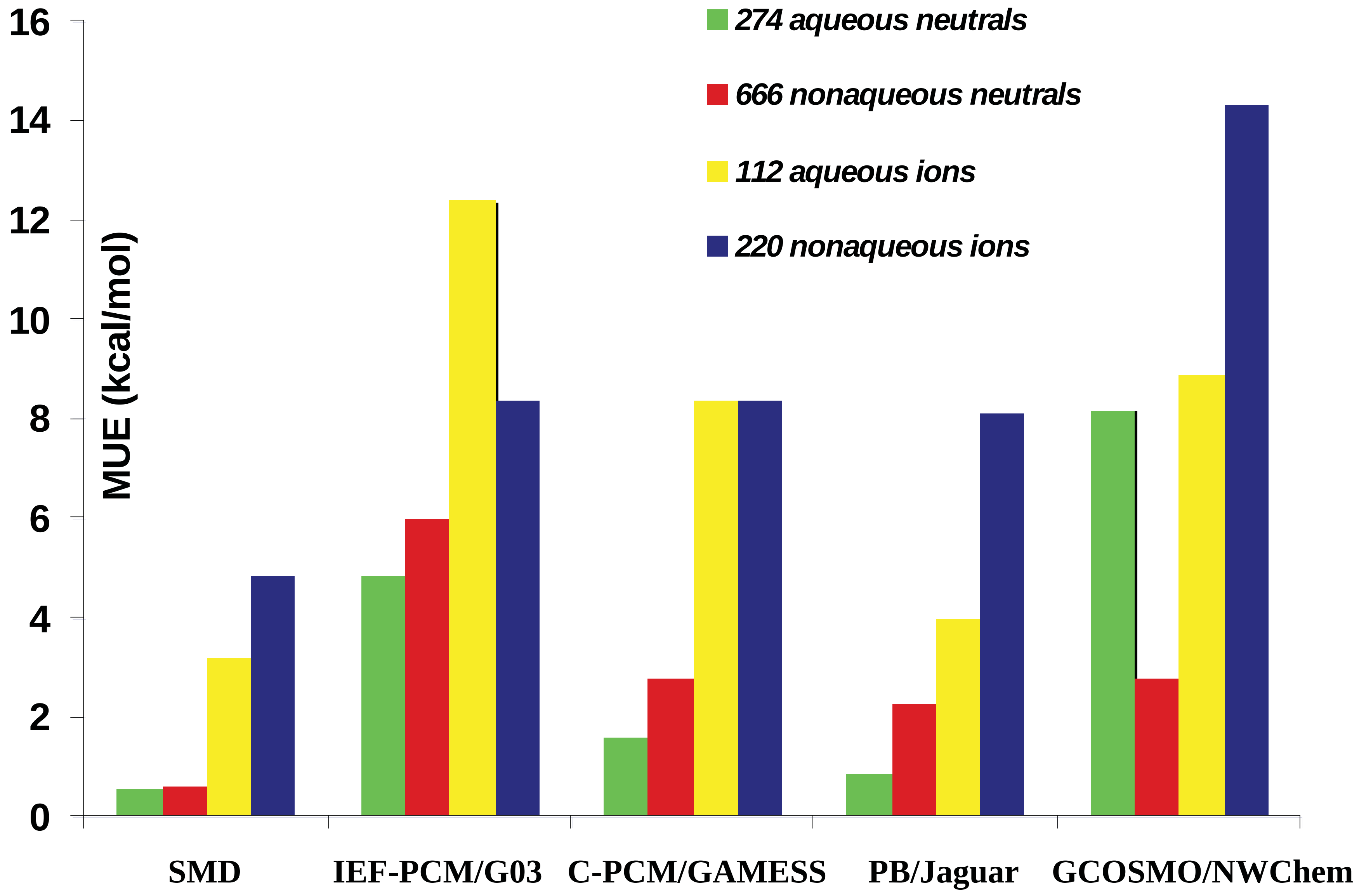


Solvent **A**ccessible **S**urface **A**rea

(defines the first solvation shell)

Switching functions ($T_{k,k'}$)





274 aqueous neutrals
666 nonaqueous neutrals
112 aqueous ions
220 nonaqueous ions
MUE (kcal/mol)
16
14
12
10
8
6
4
2
0
SMD
IEF-PCM/G03
C-PCM/GAMESS
PB/Jaguar
GCOSMO/NWChem

Equilibria: Thema mit Veränderungen

pK_a *(Born-Haber cycle)*

$$\begin{tikzcd}
AH_{(g)} \arrow[r, rightleftharpoons, "\Delta G^{o}_{g}"] \arrow[d, "\Delta G^{o}_{S}(AH)"'] & A^{-}_{(g)} \arrow[d, "\Delta G^{o}_{S}(A^{-})"'] & + & H^{+}_{(g)} \arrow[d, "\Delta G^{o}_{S}(H^{+})"] \\
AH_{(s)} \arrow[r, rightleftharpoons, "\Delta G^{o\prime}_{aq}"'] & A^{-}_{(s)} & + & H^{+}_{(s)}
\end{tikzcd}$$

$$\mathrm{p}K_a = -\log\left(e^{-\Delta G^{o\prime}_{aq}/RT}\right)$$

$$= \frac{\Delta G^{o\prime}_{aq}}{2.303RT}$$

1) Need diffuse functions in basis set and good theory to get accurate gas-phase deprotonation free energy
2) Can't compute *E* for H^{+} (no electrons!) so electronic structure programs are reluctant to compute thermal contributions to *G* (but a good spreadsheet will)
3) ΔG^{o}_{S} of proton is an experimental quantity (–264.0 kcal mol^{-1})
4) Standard-state concentration-change free energy must be included
5) Each non-cancelled error of 1.4 kcal mol^{-1} in any step will lead to an error in pK_a of 1 p*K* unit — errors in ionic solvation free energies are potentially *much* larger than this…
6) Can correct for functional-group systematic errors, see: Klicic et al. *J. Phys. Chem. A* **2002,** *106*, 1327.

Free Energy Cycles and Ions

No explicit water molecules

$$\begin{tikzcd}
\mathrm{AH(g)} \arrow[r, "\Delta G_{\mathrm{g}}^{\circ}(\mathrm{AH})"] \arrow[d, "\Delta G_{\mathrm{S}}^{*}(\mathrm{AH})"] & \mathrm{A^{-}(g)} \arrow[d, "\Delta G_{\mathrm{S}}^{*}(\mathrm{A^{-}})"] & + & \mathrm{H^{+}(g)} \arrow[d, "\Delta G_{\mathrm{S}}^{*}(\mathrm{H^{+}})"] \\
\mathrm{AH(aq)} \arrow[r, "2.303RT\mathrm{p}K_{\mathrm{a}}"'] & \mathrm{A^{-}(aq)} & + & \mathrm{H^{+}(aq)}
\end{tikzcd}$$

$$2.303RT\mathrm{p}K_{\mathrm{a}} = \Delta G_{\mathrm{g}}^{\circ}(\mathrm{AH}) - \Delta G_{\mathrm{S}}^{*}(\mathrm{AH}) + \Delta G_{\mathrm{S}}^{*}(\mathrm{A^{-}}) + \Delta G_{\mathrm{S}}^{*}(\mathrm{H^{+}})$$

Free Energy Cycles and Ionic Clusters

Treat the ion as a cluster

$$\begin{tikzcd}
\mathrm{AH\ (g)} \arrow[d, "\Delta G_S^*(\mathrm{AH})"] & + & \mathrm{H_2O\ (g)} \arrow[r, "\Delta G_g^\circ(\mathrm{AH})"] \arrow[d, "\Delta G_S^*(\mathrm{H_2O})"] & \mathrm{H_2O \bullet A^-(g)} \arrow[d, "\Delta G_S^*(\mathrm{H_2O \bullet A^-})"] & + & \mathrm{H^+(g)} \arrow[d, "\Delta G_S^*(\mathrm{H^+})"] \\
\mathrm{AH\ (aq)} & + & \mathrm{H_2O\ (aq)} \arrow[r, "2.303RT\mathrm{p}K_a"'] & \mathrm{H_2O \bullet A^-(aq)} & + & \mathrm{H^+(aq)}
\end{tikzcd}$$

$$2.303RT\mathrm{p}K_a = \Delta G_g^\circ(\mathrm{AH}) - \Delta G_S^*(\mathrm{AH}) - \Delta G_S^*(\mathrm{H_2O}) + \Delta G_S^*(\mathrm{H_2O \bullet A^-}) + \Delta G_S^*(\mathrm{H^+})$$

For additional details on cluster solvation free energies and their use to set the absolute solvation free energy of the proton and the absolute potential of the normal hydrogen electrode (NHE), see Kelly, C. P.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2006**, *110*, 16066.

Example: pK_a of Methanol (Expt. 15.5)

$MeOH / MeO^-$

(Cycle 1)

Experimental data:

$\Delta G_g^\circ = +375.0$ kcal/mol

$\Delta G_S^*(H^+) = -265.9$ kcal/mol

$\Delta G_S^*(MeOH) = -5.11$ kcal/mol

Calculated (SM6) data:

$\Delta G_S^*(MeO^-) = -88.3$ kcal/mol

$pK_a = 20.4$

$MeOH / H_2O \bullet MeO^-$

(Cycle 2)

Experimental data:

$\Delta G_g^\circ = +358.0$ kcal/mol

$\Delta G_S^*(H^+) = -265.9$ kcal/mol

$\Delta G_S^*(MeOH) = -5.11$ kcal/mol

$\Delta G_S^*(H_2O) = -6.32$ kcal/mol

Calculated (SM6) data:

$\Delta G_S^*(H_2O \bullet MeO^-) = -81.8$ kcal/mol

$pK_a = 16.0$

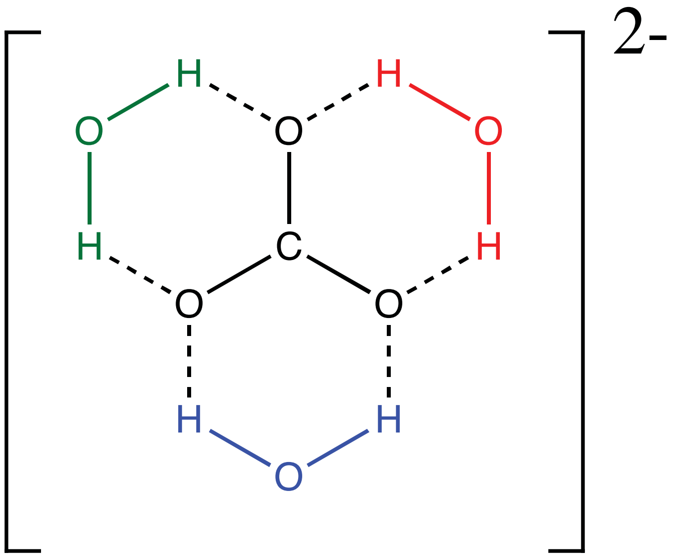
Adding More Waters

Experimental pK_a's

$$H_2CO_3 \underset{pK_{a_1} = 6.4}{\rightleftharpoons} HCO_3^- \underset{pK_{a_2} = 10.3}{\rightleftharpoons} CO_3^{2-}$$

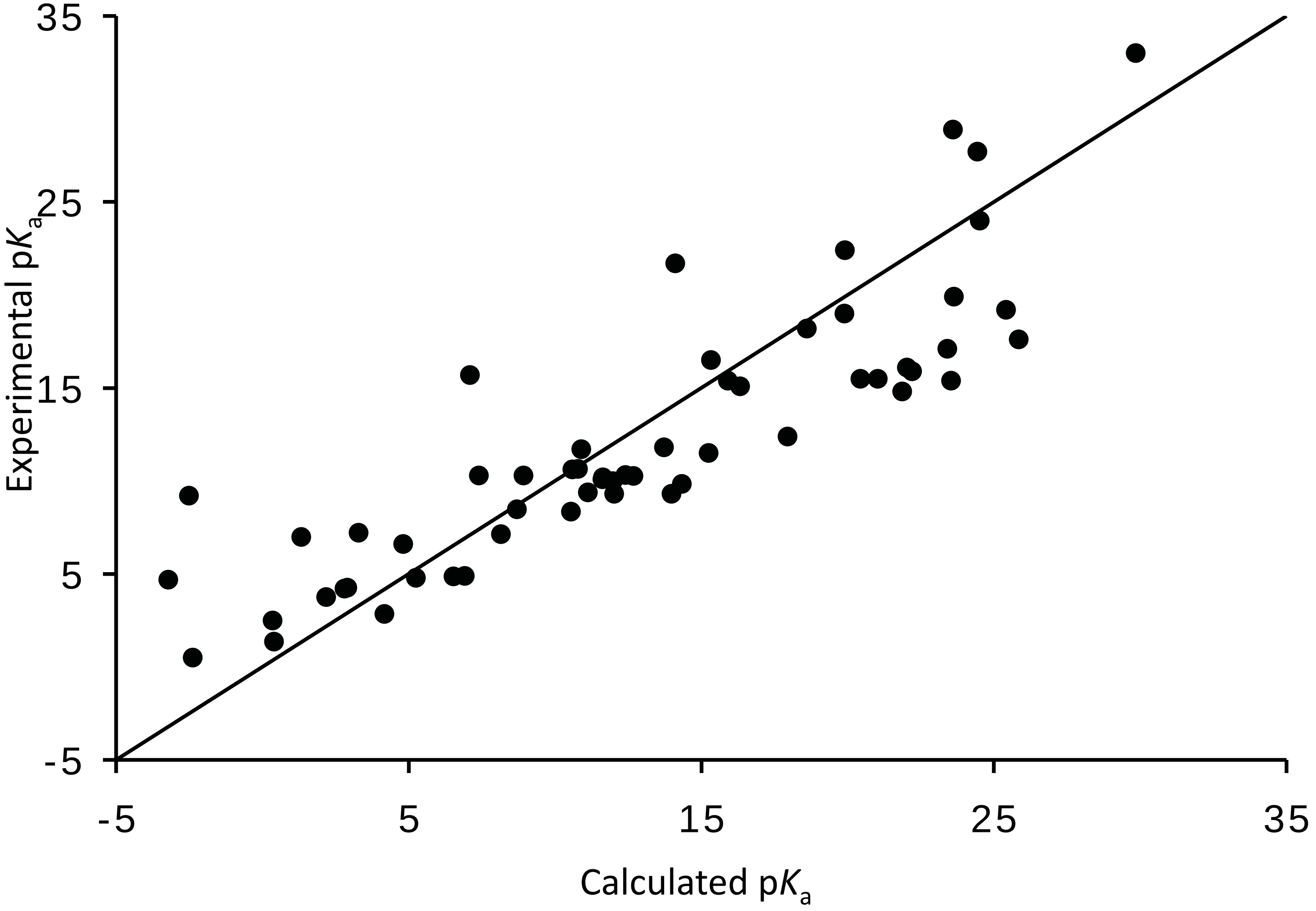
Calculated pK_a's

No. H_2O	pK_{a_1}	pK_{a_2}
0	−0.6	1.6
1	**1.3**	**5.0**
2	**2.3**	**7.8**
3	**4.2**	**9.0**



Adding explicit water molecules improves the accuracy of the calculation

Clustering Other Ions

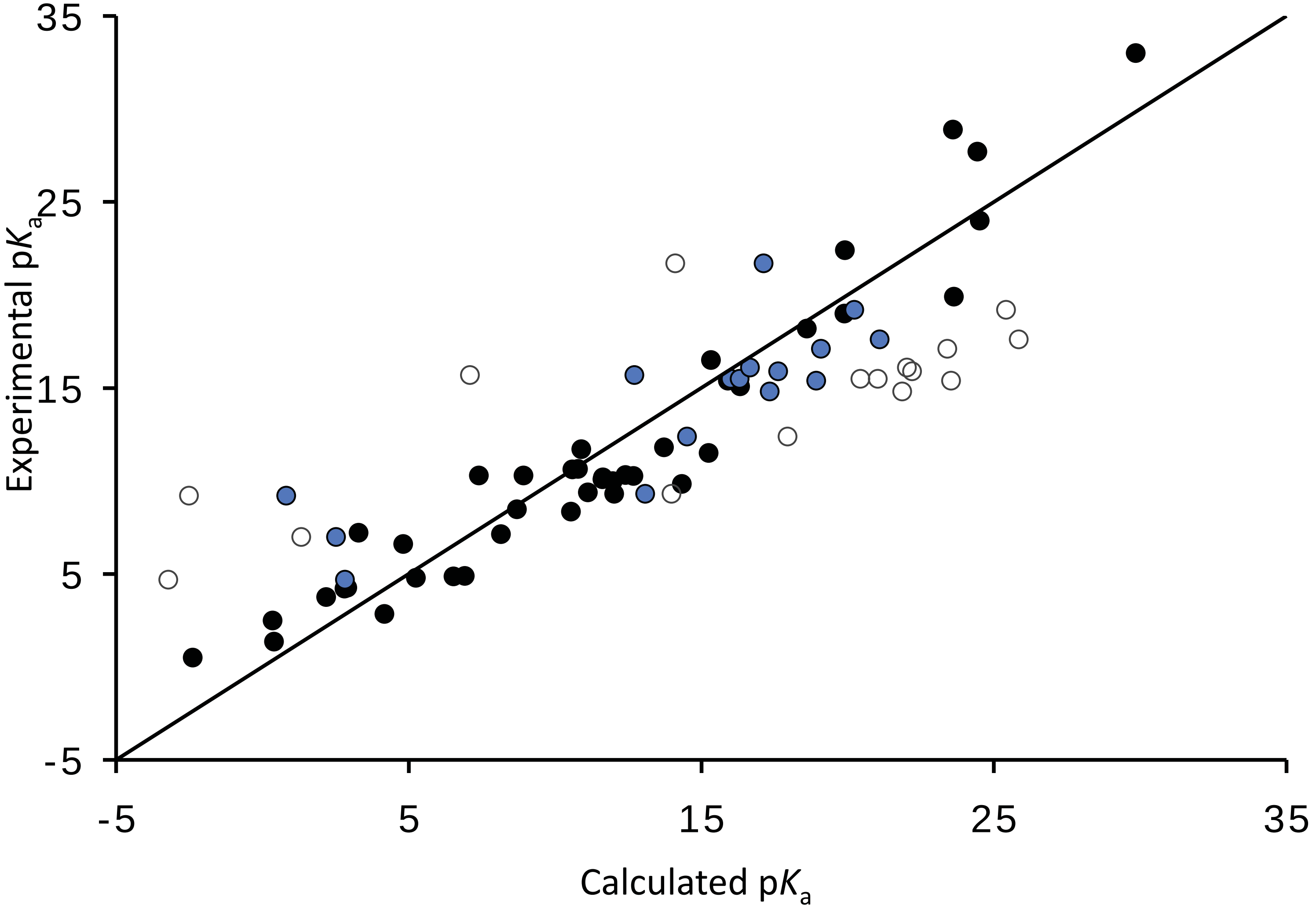


● , ○ : bare ion used

● : clustered ion used

Kelly, C. P.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. A.* **2006**, *110*, 2493

Clustering Other Ions



● , ○ : bare ion used

● : clustered ion used

Kelly, C. P.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. A.* **2006**, *110*, 2493

Equilibria: Tema e Variazioni

Oxidation and Reduction Potentials

$$\begin{tikzcd}
A^{+\bullet}_{(gas)} \arrow[d, "\Delta G^o_S(A^{+\bullet})"'] & + & e^-_{(gas)} \arrow[d, "\Delta G^o = 0"] & & A_{(gas)} \arrow[llll, "\Delta G^o_{(gas)}"'] \arrow[d, "\Delta G^o_S(A)"'] \\
A^{+\bullet}_{(sol)} & + & e^-_{(gas)} & & A_{(sol)} \arrow[llll, "\Delta G^o_{(sol)}"']
\end{tikzcd}$$

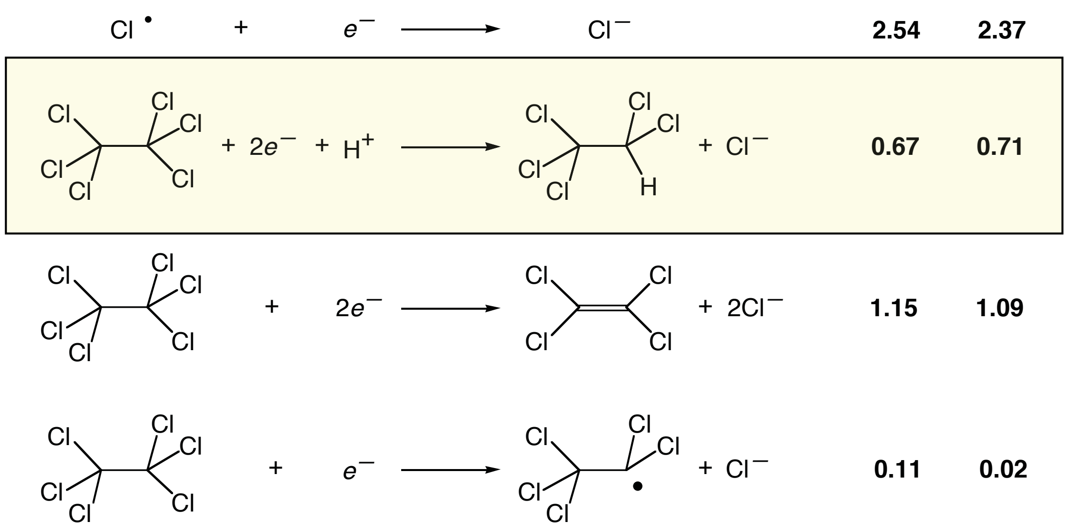
$$\begin{tikzcd}
A_{(gas)} \arrow[d, "\Delta G^o_S(A)"] & + & e^-_{(gas)} \arrow[d, "\Delta G^o = 0"] \arrow[rr, "\Delta G^o_{(gas)}"] & & A^{-\bullet}_{(gas)} \arrow[d, "\Delta G^o_S(A^{-\bullet})"] \\
A_{(sol)} & + & e^-_{(gas)} \arrow[rr, "\Delta G^o_{(sol)}"] & & A^{-\bullet}_{(sol)}
\end{tikzcd}$$

$$E^o = -\frac{\Delta G^o}{nF}$$

1) Need diffuse functions in basis set and good theory to get accurate gas-phase electron affinity
2) Can’t compute E for e^- (no nuclei!) so electronic structure programs are reluctant to compute thermal contributions to G (but a good spreadsheet will)
3) ΔG^o_S of electron is not an issue as it is a gas-phase species in the electrochemical standard state
4) Beware of standard-state concentration issues, especially buffered ions
5) To place on standard scale, must add (or subtract) absolute potential for the normal hydrogen electrode (NHE: 4.28 V)
6) Can correct for functional-group systematic errors again
7) Consider specific first solvation shell

Example: Reductive Dechlorination of Haloalkanes

Winget et al. *Theor. Chem. Acc.* **2004**, *112*, 217.



Reaction	E^o expt	E^o calc
$Cl^\bullet + e^- \longrightarrow Cl^-$	2.54	2.37
$+ 2e^- + H^+ \longrightarrow$ $+ Cl^-$	0.67	0.71
$+ 2e^- \longrightarrow$ $+ 2Cl^-$	1.15	1.09
$+ e^- \longrightarrow$ $+ Cl^-$	0.11	0.02

$$\Delta G^{o'} = \Delta G^o + RT\ln\left[\frac{\dfrac{(1\,\mathrm{M}\;C_2Cl_5H)(10^{-3}\,\mathrm{M}\;Cl^-)}{(1\,\mathrm{M}\;C_2Cl_6)(10^{-7}\,\mathrm{M}\;H^+)(1\,\mathrm{M}\;e^-)^2}}{\dfrac{(1\,\mathrm{M}\;C_2Cl_5H)(1\,\mathrm{M}\;Cl^-)}{(1\,\mathrm{M}\;C_2Cl_6)(1\,\mathrm{M}\;H^+)(1\,\mathrm{M}\;e^-)^2}}\right]$$

$$= \Delta G^o + 5.5\ \mathrm{kcal\ mol^{-1}}$$

Protocol: E *from CCSD(T)/aug-cc-pVDZ//BPW91/aug-cc-pVDZ (thermal contributions from geometry level), solvation from SM5.42R/BPW91/DZVP, standard state* pH *7, all species 1 M but* Cl^- *buffered to 1 mM*

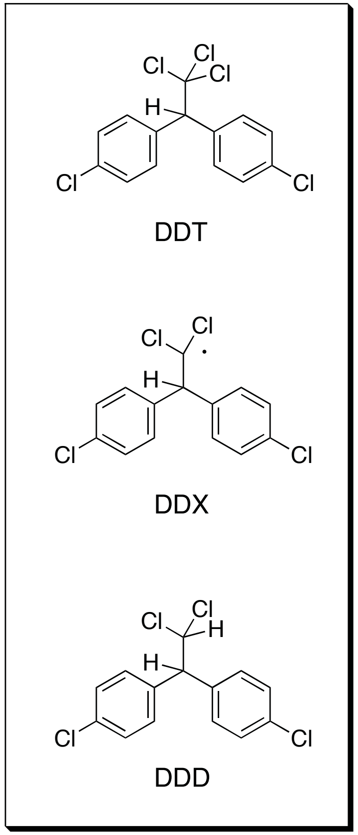
Example: Reductive Dechlorination of DDT

Lewis et al. *J. Chem. Ed.* **2004**, *81*, 596 (erratum **2007**, *84*, 934).

B3LYP/6-311+G*//B3LYP/6-31G*
+ SM5.42R/BPW91/6-31G*

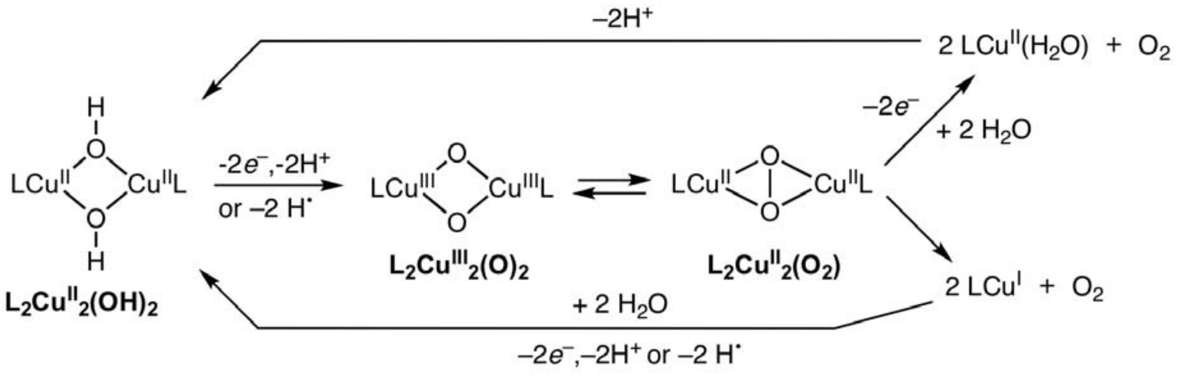
$$\begin{tikzcd}
\mathrm{DDT}_{(g)} \arrow[d, "\Delta G^{o}_{S}\ (\mathrm{DDT})"] & + & e^{-}_{(g)} \arrow[d, "\Delta G^{o} = 0"] \arrow[r, "\Delta G^{o}_{(g)}"] & \mathrm{DDX}_{(g)} \arrow[d, "\Delta G^{o}_{S}\ (\mathrm{DDX})"] & + & \mathrm{Cl}^{-}_{(g)} \arrow[d, "\Delta G^{o}_{S}\ (\mathrm{Cl}^{-})"] \\
\mathrm{DDT}_{(aq)} & + & e^{-}_{(g)} \arrow[r, "\Delta G^{o}_{(1e)}", "\boxed{\mathbf{0.58\ V}}"'] & \mathrm{DDX}_{(aq)} & + & \mathrm{Cl}^{-}_{(aq)}
\end{tikzcd}$$

$$\begin{tikzcd}
\mathrm{DDT}_{(g)} \arrow[d, "\Delta G^{o}_{S}\ (\mathrm{DDT})"] & + & \mathrm{H}^{+}_{(g)} \arrow[d, "\Delta G^{o}_{S}\ (\mathrm{H}^{+})"] & + & 2e^{-}_{(g)} \arrow[d, "\Delta G^{o} = 0"] \arrow[r, "\Delta G^{o}_{(g)}"] & \mathrm{DDD}_{(g)} \arrow[d, "\Delta G^{o}_{S}\ (\mathrm{DDD})"] & + & \mathrm{Cl}^{-}_{(g)} \arrow[d, "\Delta G^{o}_{S}\ (\mathrm{Cl}^{-})"] \\
\mathrm{DDT}_{(aq)} & + & \mathrm{H}^{+}_{(aq)} & + & 2e^{-}_{(g)} \arrow[r, "\Delta G^{o}_{(2e)}", "\boxed{\mathbf{0.86\ V}}"'] & \mathrm{DDD}_{(aq)} & + & \mathrm{Cl}^{-}_{(aq)}
\end{tikzcd}$$

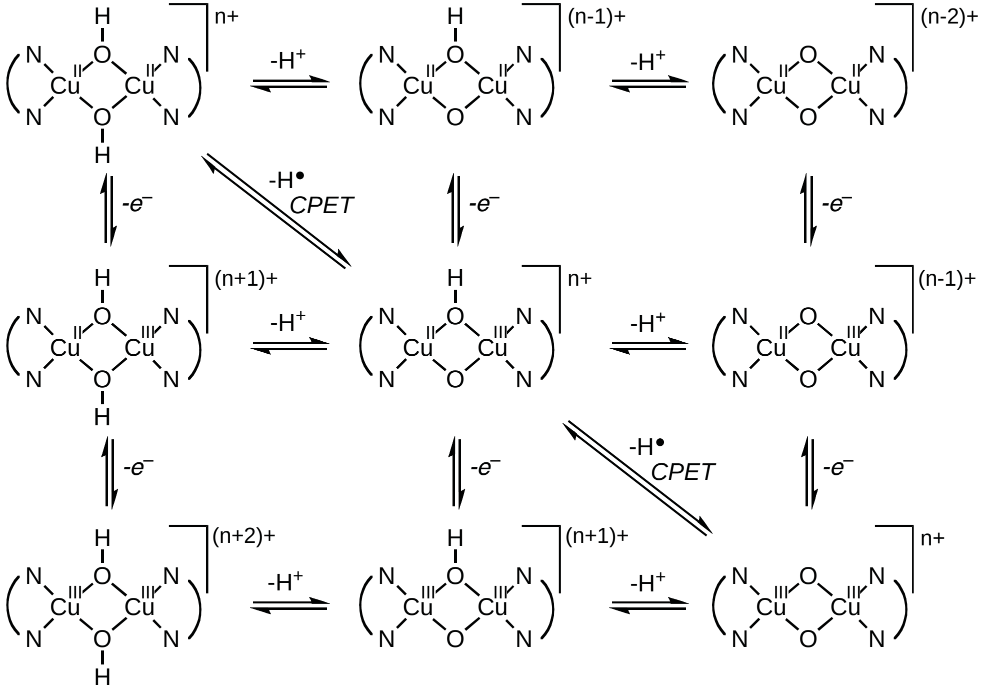


Conversion of Solar Energy to Green Fuel

Catalyst Activation



What are the reduction potentials and pK_a values for microscopic steps leading to an activated dioxo species? These are free energy questions, and they refer to free energies in solution.



Pourbaix Diagrams

Inorg. Chem. **2009,** *48,* 4372−4383

Inorganic Chemistry Article

Characterization of Redox States of $Ru(OH_2)(Q)(tpy)^{2+}$ (Q = 3,5-di-*tert*-butyl-1,2-benzoquinone, tpy = 2,2′:6′,2″-terpyridine) and Related Species through Experimental and Theoretical Studies

Ming-Kang Tsai,[†] Jonathan Rochford,[†] Dmitry E. Polyansky,[†] Tohru Wada,[§] Koji Tanaka,[§] Etsuko Fujita,*[,†] and James T. Muckerman*[,†,‡]

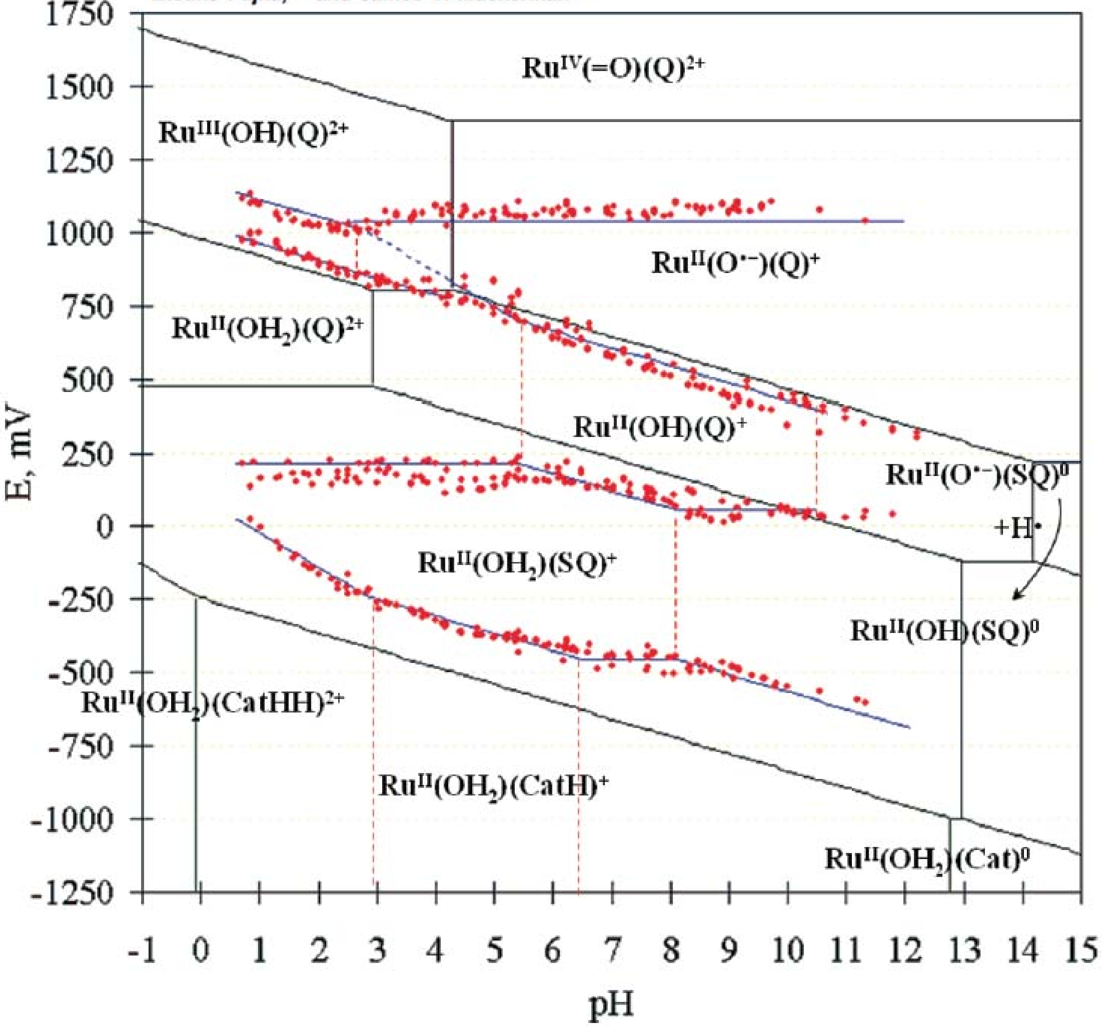
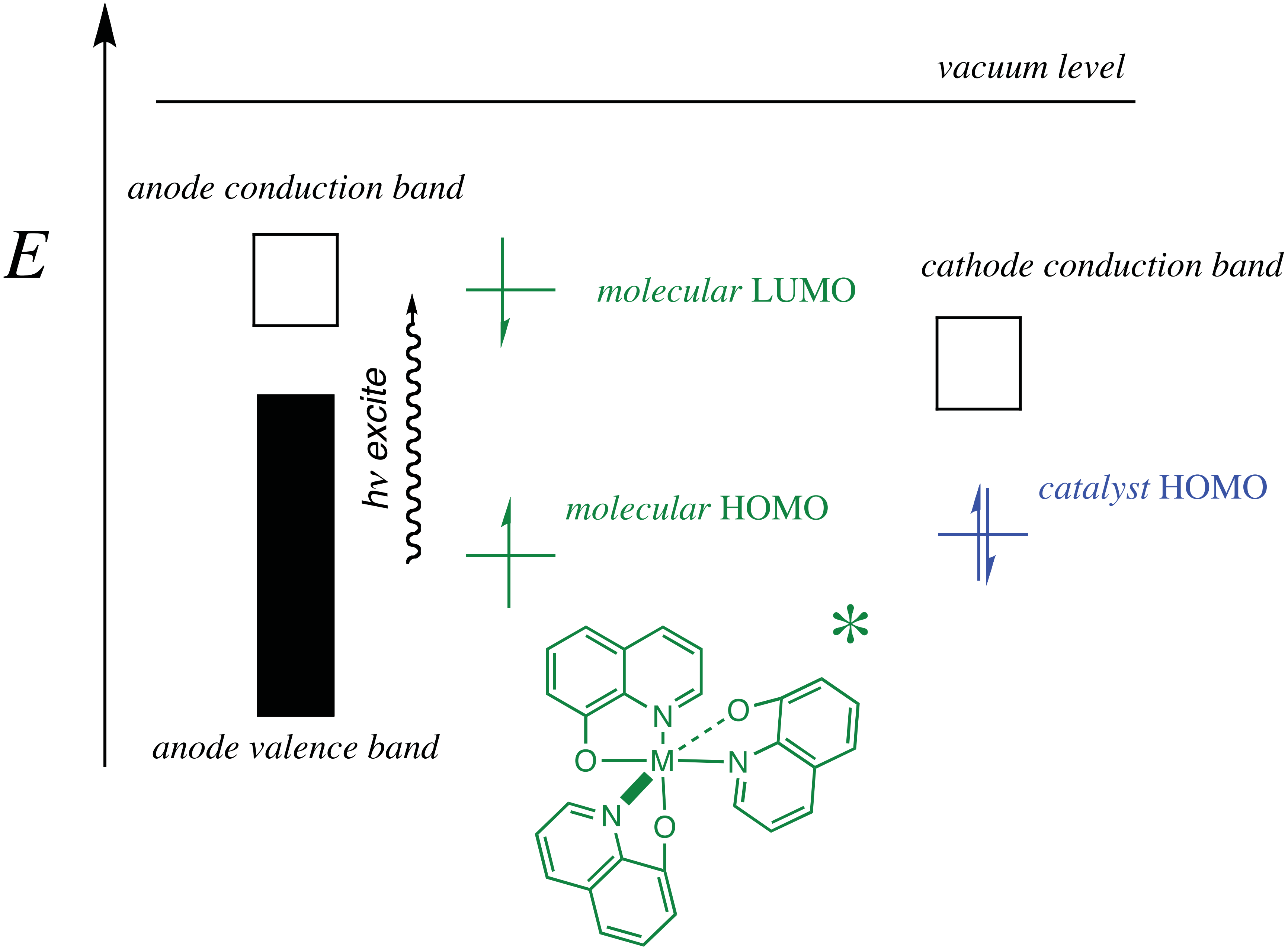


Figure 4. An experimental and theoretical Pourbaix diagram of $Ru(OH_2)(Q)(tpy)^{2+}$. $E_{1/2}$ is relative to the SCE. The red dashed and solid blue lines correspond to the experimental pK_a and redox potentials. The black lines are the theoretical predictions.

Note apparent greater challenges in pK_a predictions compared to E^o values is optical illusion (ordinate spans 69 kcal/mol while abscissa spans 21.5 kcal/mol)

Conversion of Solar Energy to Oxidizing Power



E

vacuum level

anode conduction band

anode valence band

hν excite

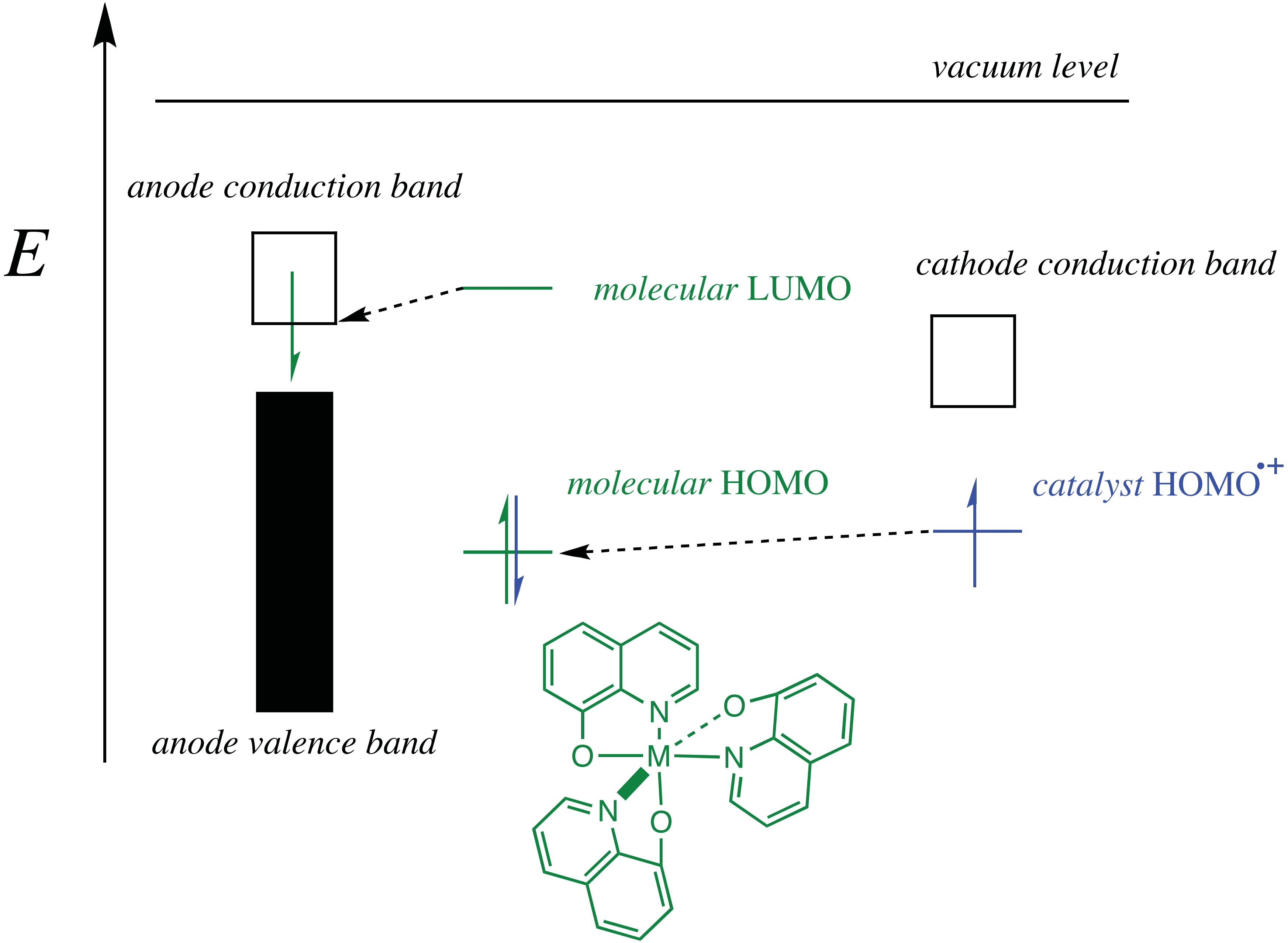
molecular LUMO

molecular HOMO

cathode conduction band

catalyst HOMO

Conversion of Solar Energy to Oxidizing Power



E

vacuum level

anode conduction band

molecular LUMO

cathode conduction band

molecular HOMO

catalyst HOMO$^{\bullet+}$

anode valence band

Issues

- Molecular orbital energy levels relative to electrodes
- Electron and hole transport efficiency
- Singlet vs. triplet excited-state generation
- Intersystem crossing rates
- Molecular excited-state energy levels
- Quantum efficiency of absorption

- What computational models are useful for the prediction of these quantities?
- Accuracy
- Cost

MO Energy Levels

- Commonly computed from Hartree-Fock (HF) or Density Functional Theory (DFT)
- The experimental quantities relevant to the HOMO and LUMO energies are ionization potential (IP) and electron affinity (EA)
- IP and EA may be computed for vertical (no geometric relaxation) or adiabatic (full relaxation of ionized state) processes
- Energy change from relaxation contributes to “reorganization energy” (a factor that affects electron/hole transport rates)
- The approximation $\varepsilon_{\mathrm{HOMO}} = -\mathrm{IP}$ is generally not bad
- The approximation $\varepsilon_{\mathrm{LUMO}} = \mathrm{EA}$ is generally *very* bad

Excited Electronic States

- We usually write the Schrödinger equation as
$$H\Psi = E\Psi$$

- However, that obscures the reality that there are infinitely many solutions to the Schrödinger equation, so it is better to write
$$H\Psi_n = E_n\Psi_n$$

- Hartree-Fock theory provides us a prescription to construct an approximate ground-state wave function (as a single Slater determinant)

- How do we build from there to construct an excited-state wave function?

Correlated Methods. I. Configuration Interaction

A Hartree-Fock one-electron orbital (wave function) is expressed as a linear combination of basis functions with expansion coefficients optimized according to a variational principle (where **S** is the overlap matrix)

$$|\,\mathbf{F} - E\mathbf{S}\,| = 0 \quad \Longrightarrow \quad \phi = \sum_{i=1}^{N} a_i \varphi_i$$

The HF many-electron wave function is the Slater determinant formed by occupation of lowest possible energy orbitals, *but, the HF orbitals are not “perfect” because of the HF approximation*

So, one way to improve things would be to treat the different Slater determinants that can be formed from *any occupation of HF orbitals* to *themselves* be a basis set to be used to create an improved many-electron wave function

$$|\,\mathbf{H} - E\mathbf{S}\,| = 0 \quad \Longrightarrow \quad \Psi = a_0\Psi_{\mathrm{HF}} + \sum_{i}^{\mathrm{occ.}}\sum_{r}^{\mathrm{vir.}} a_i^r\Psi_i^r + \sum_{i<j}^{\mathrm{occ.}}\sum_{r<s}^{\mathrm{vir.}} a_{ij}^{rs}\Psi_{ij}^{rs} + \cdots$$

CI in a Nutshell

	Ψ_{HF}	Ψ_i^a	Ψ_{ij}^{ab}	Ψ_{ijk}^{abc}
Ψ_{HF}	E_{HF}	**0**	dense	**0**
Ψ_i^a	**0**	dense	sparse	very sparse
Ψ_{ij}^{ab}	dense	sparse	sparse	extremely sparse
Ψ_{ijk}^{abc}	**0**	very sparse	extremely sparse	extremely sparse

The bigger the CI matrix, the more electron correlation can be captured.

The CI matrix can be made bigger either by increasing basis-set size (each block is then bigger) or by adding more highly excited configurations (more blocks).

The ranked eigenvalues correspond to the electronic state energies.

Most common compromise is to include only single and, to lower ground state, double excitations (CISD)—not size extensive.

CI Singles (CIS)

$$\begin{array}{c|c|c|}
 & \Psi_{\mathrm{HF}} & \Psi_i^a \\
\hline
\Psi_{\mathrm{HF}} & E_{\mathrm{HF}} & \mathbf{0} \\
\hline
\Psi_i^a & \mathbf{0} & \text{dense} \\
\hline
\end{array}$$

There are *m* x *n* singly excited configurations where *m* and *n* are the number of occupied and virtual orbitals, respectively.

Diagonalization gives excited-state energies *and* eigenvectors containing weights of singly excited determinants in the pure excited state

Quality of excited-state wave functions about that of HF for ground state.

Efficient, permits geometry optimization; semiempirical levels (INDO/S) optimized for CIS method.

Time-Dependent Density Functional Theory

A perturbation theory formalism applied to density functional theory shows that excitation energies can be determined as poles of the polarizability matrix

$$\langle \alpha \rangle_{\omega} = \sum_{m>0} \left[\frac{\left| \langle \Phi_m | \mathbf{r} | \Phi_0 \rangle \right|^2}{\omega_{m0} + \omega} \pm \frac{\left| \langle \Phi_m | \mathbf{r} | \Phi_0 \rangle \right|^2}{\omega_{m0} - \omega} \right]$$

$$\omega = 2\pi\nu \qquad \omega_{m0} = \frac{E_m - E_0}{\hbar}$$

Qualitative points:

TD DFT tends to be more accurate than CIS but this is sensitive to choice of functional and certain special situations

<u>Charge-transfer</u> transitions are particularly problematic (hybrid functionals generally much preferred over local for such excitations)

No wave function is created, but eigenvectors analogous to those predicted by CIS are provided

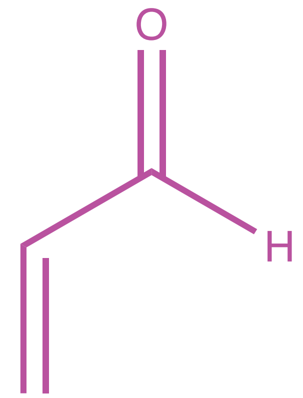
CI Singles (CIS) — Acrolein Example

```
Excited State   1:   Singlet-A"     4.8437 eV  255.97 nm  f=0.0002
     14 -> 16          0.62380
     14 -> 17          0.30035

Excited State   2:   Singlet-A'     7.6062 eV  163.01 nm  f=0.7397
     15 -> 16          0.68354

Excited State   3:   Singlet-A"     9.1827 eV  135.02 nm  f=0.0004
     11 -> 16         -0.15957
     12 -> 16          0.55680
     14 -> 16         -0.19752
     14 -> 17          0.29331

Excited State   4:   Singlet-A"     9.7329 eV  127.39 nm  f=0.0007
      9 -> 17         0.19146
     10 -> 16          0.12993
     11 -> 16          0.56876
     12 -> 16          0.26026
     12 -> 17         -0.11839
     14 -> 17         -0.12343
```



LUMO+1: π_4^*
LUMO: π_3^*
HOMO: π_2
HOMO–1: n_O

Eigenvectors CIS/6-31G(d)

Experiment 3.73 / 6.41 eV

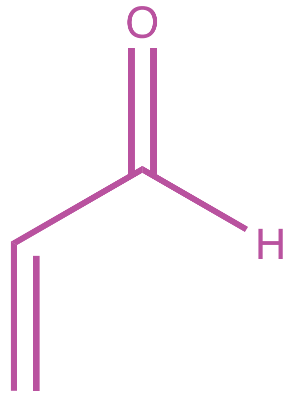
TDDFT — Acrolein Example

```
Excited State   1:   Singlet-A"     3.7829 eV  327.75 nm  f=0.0000
      15 -> 16         0.67412
      15 -> 17         0.10545

Excited State   2:   Singlet-A'     6.7142 eV  184.66 nm  f=0.3785
      14 -> 16         0.60530
      14 -> 17         0.12143

Excited State   3:   Singlet-A"     7.2723 eV  170.49 nm  f=0.0004
      13 -> 16         0.18077
      15 -> 16        -0.11786
      15 -> 17         0.66306

Excited State   4:   Singlet-A"     7.8041 eV  158.87 nm  f=0.0006
      13 -> 16         0.67088
      15 -> 17        -0.18640
```

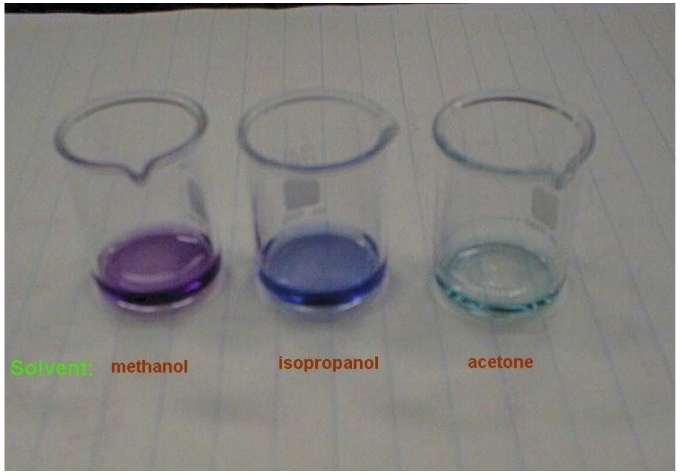


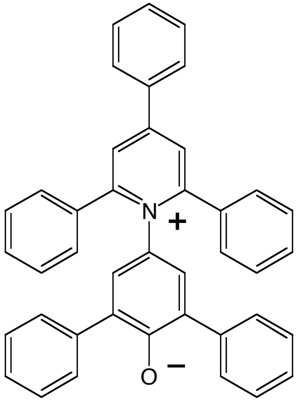
LUMO+1: π_4^*
LUMO: π_3^*
HOMO: n_O
HOMO–1: π_2

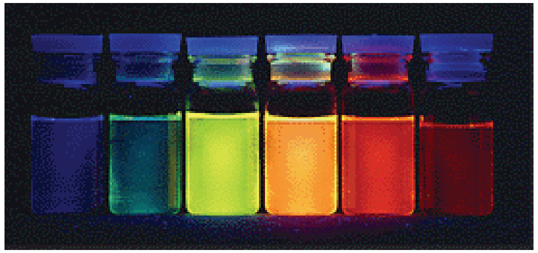
Eigenvectors PBE1/6-31G(d)

Experiment 3.73 / 6.41 eV

Solvatochromism of Dye E_T30 (S_1 – S_0)

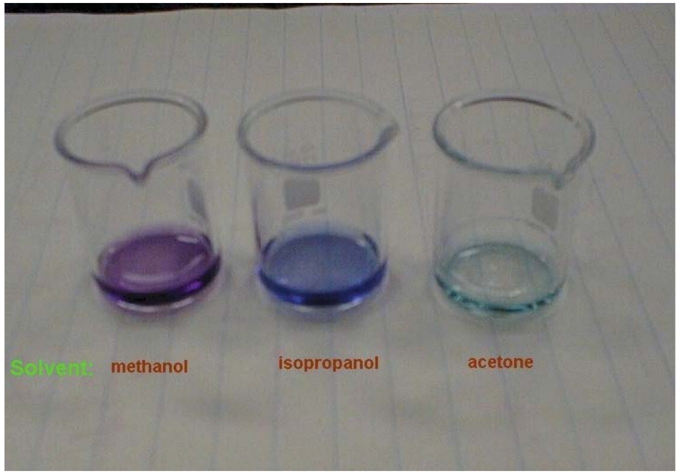


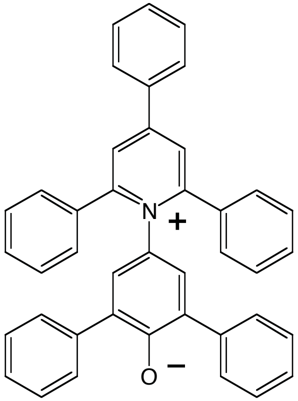


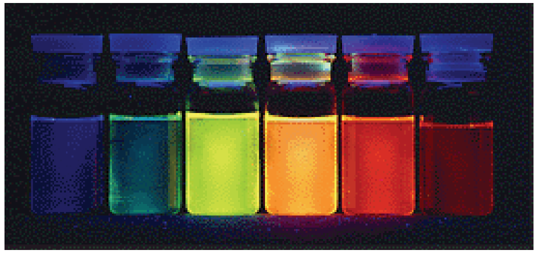


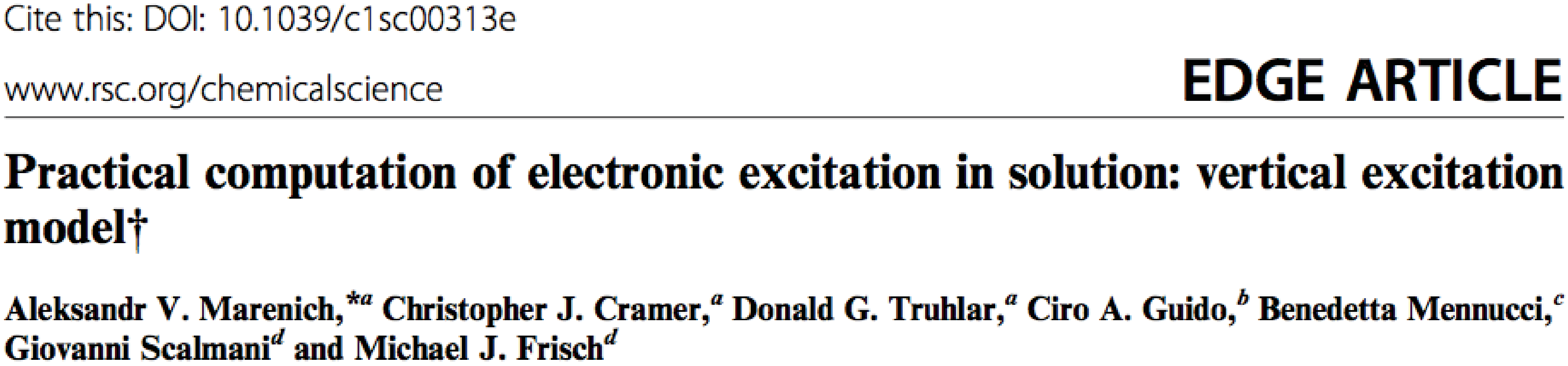
Solvent	Color	λ_{max}, nm
anisole	yellow	769
acetone	green	677
2-pentanol	blue	608
ethanol	violet	550
methanol	red	515

Solvatochromism of Dye E_T30 ($S_1 – S_0$)









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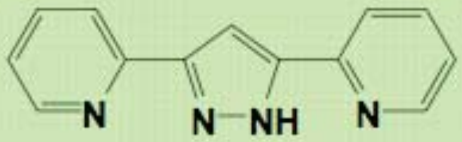
EDGE ARTICLE

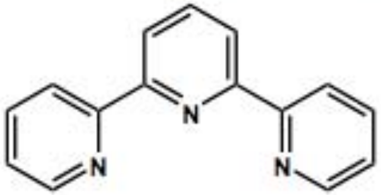
Practical computation of electronic excitation in solution: vertical excitation model†

Aleksandr V. Marenich,*[a] Christopher J. Cramer,[a] Donald G. Truhlar,[a] Ciro A. Guido,[b] Benedetta Mennucci,[c] Giovanni Scalmani[d] and Michael J. Frisch[d]

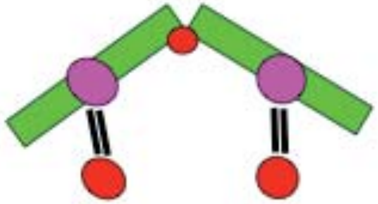
Ru FUNCTIONAL MODELS: Ru-HBPP

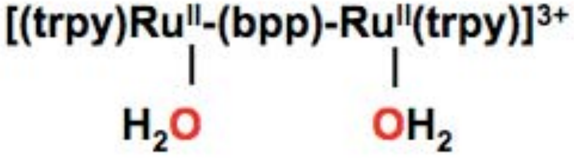


Hbpp

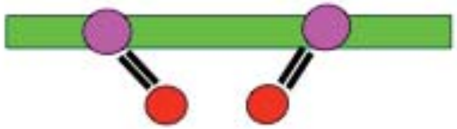


trpy



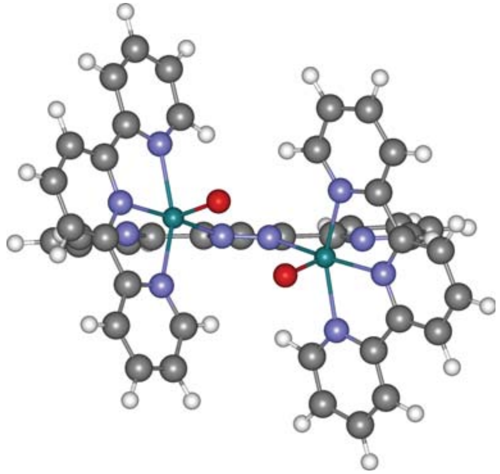


$[(trpy)Ru^{II}\text{-}(bpp)\text{-}Ru^{II}(trpy)]^{3+}$ with H_2O on the first Ru and OH_2 on the second Ru



Sens, C.; Romero, I.; Rodríguez, M.; Llobet, A. et al., *J. Am. Chem. Soc.*, **2004,** *126*, 7798
Sala, X.; Romero, I.; Rodriguez, M.; Escriche, L.; Llobet, A. *Angew. Chem. Int. Ed.* **2009**, *48*, 2842

The electronic structure of $[4,4]^{3+}$

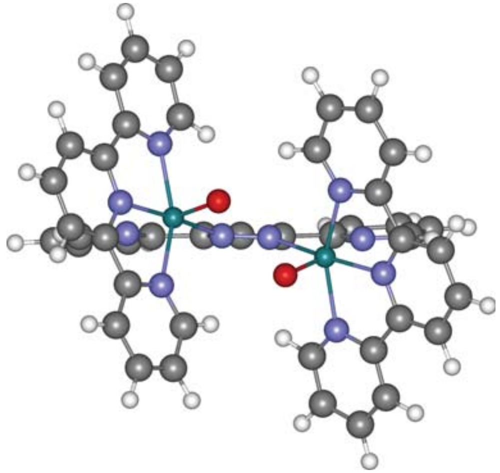


1. Ground state?
2. $Ru^{IV}=O$ vs. $Ru^{III}–O^{–\bullet}$

	Q	S_0 (AF)	S_1 (CS)	T
CASSCF	-0.8	0	26.5	-0.8/13.5
CASPT2	0.5	0	32.5	0.7/16.6
DFT/B3LYP	-0.8	0	44.8	7.2
DFT/M06L	-1.0	0		9.3

Q: 82 % weight
S_0: 15 % AF + mixture of 4 different closed-shell config. (15 % weight each)
S_1: 43 % CS + 11 % AF + some other CS config. with ~5 % weight each
T: two degenerate + 1 lower in energy: strongly multireference character

The electronic structure of $[4,4]^{3+}$



1. Ground state?
2. $Ru^{III}–O^{-\bullet}$ spins locally coupled triplet

	Q	S_0 (AF)	S_1 (CS)	T
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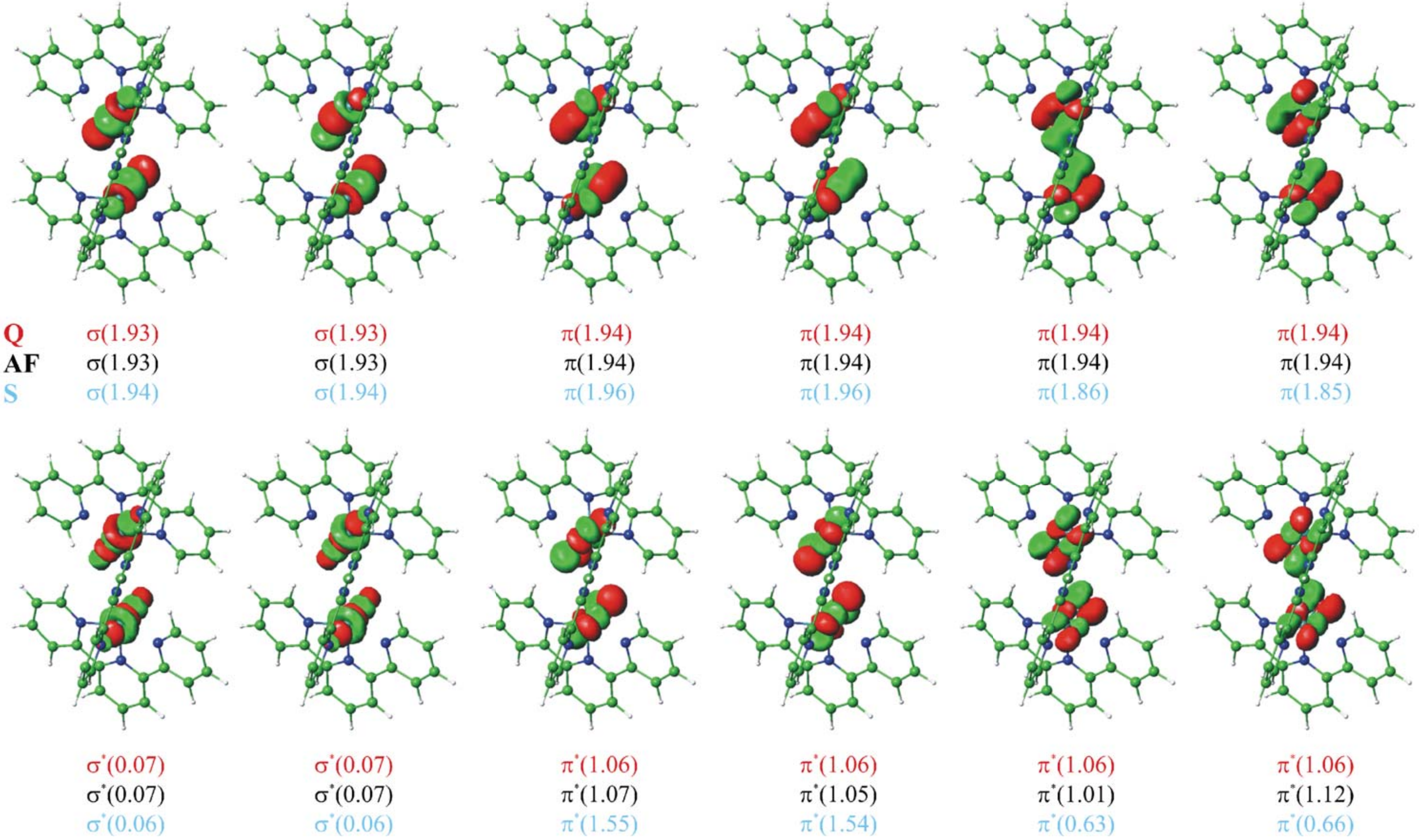
T: two degenerate + 1 lower in energy: strongly multireference character

The electronic structure of $[4,4]^{3+}$

CAS(16,12)

Ru$^{(IV)}$=O$^{(2-)}$ is not accurate, Ru$^{(III)}$–O$^{(-\bullet)}$ is better



Theory Considerations

- Dispersion really, really matters (DFT-D, M06 family, best choices at moment for DFT)
- Careful use of broken-symmetry DFT techniques may be necessary when non-innocent ligands are involved (an oxo is a ligand) or in other non-single-determinantal situations
- Benchmarking DFT with CASPT2 or CC approaches increases confidence
- Continuum and sometimes explicit solvation must be taken account of
- Thermochemistry, transition-state theory, and kinetic isotope effects are all sensitive to vibrational partition functions—quasiharmonic approximation helpful for very large or floppy molecular systems

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Zahid Ertem

Nora Planas

Stuart Kohl

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Prof. Antoni Llobet (ICIQ)

Prof. Piotr Piecuch (MSU)

Prof. Bill Tolman (Minnesota)