SciDAC
Scientific Discovery through Advanced Computing

UNIVERSITY OF MINNESOTA
Driven to Discover℠
COLLEGE OF
Science & Engineering

SciDAC PI Meeting, July 2013

Charge Transfer and Charge Transport in Photoactivated Systems: *Challenges in Modeling Chromophore Solvation, Aggregation, and Flexibility*

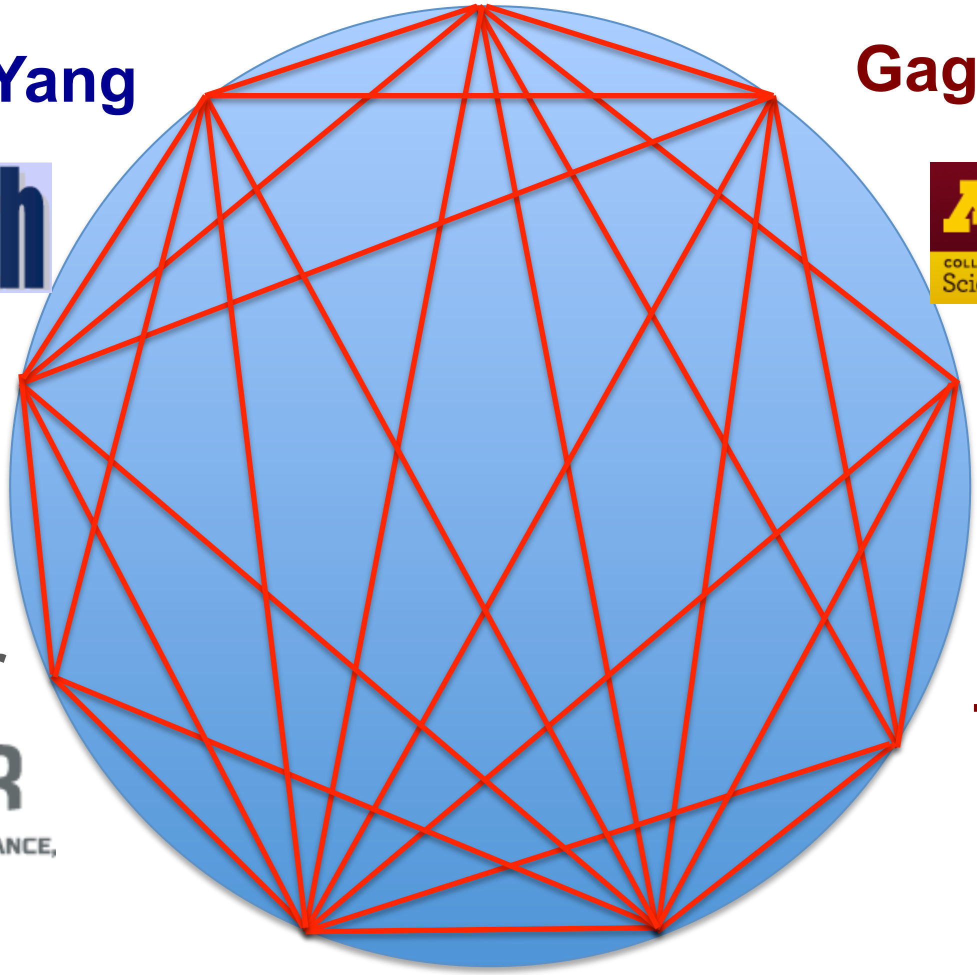
Presenter: J. Ilja Siepmann

SciDAC Partnership
Charge Transfer and Charge Transport in Photoactivated Systems:
Developing Electron-Correlated Methods for Excited State Structure and Dynamics in the NWChem Software Suite
Director: Christopher J. Cramer

Pacific Northwest
NATIONAL LABORATORY

BERKELEY LAB
LAWRENCE BERKELEY NATIONAL LABORATORY

Team Composition



Cramer

Chao Yang

Gagliardi

FASTMath

UNIVERSITY OF MINNESOTA
Driven to Discover℠
COLLEGE OF Science & Engineering

Esmond Ng

Siepmann

Lenny Oliker

SUPER
INSTITUTE FOR SUSTAINED PERFORMANCE, ENERGY, AND RESILIENCE

Truhlar

Bert DeJong

Niri Govind

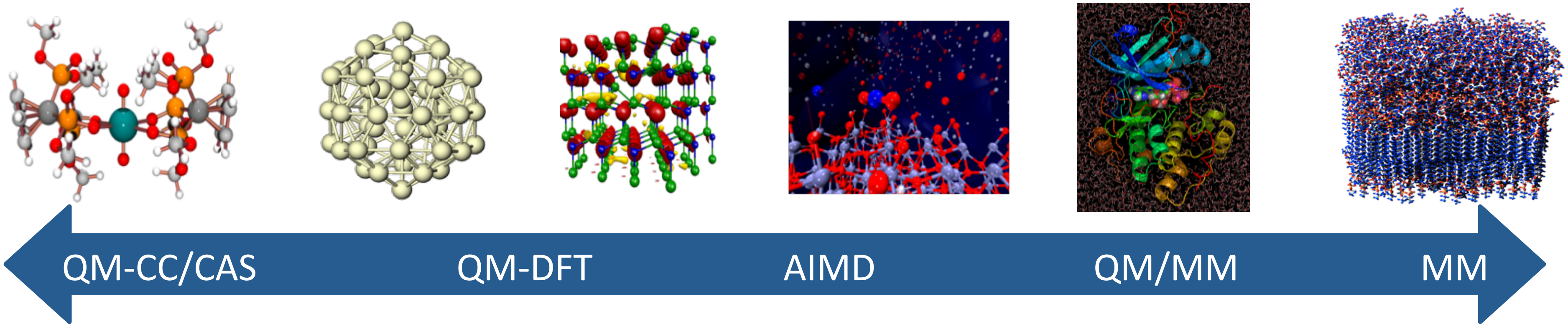
QUEST

NWCHEM
HIGH-PERFORMANCE COMPUTATIONAL CHEMISTRY SOFTWARE

SDAV

Charge Transfer and Charge Transport in Photoactivated Systems

Developing Electron-Correlated Methods for Excited State Structure and Dynamics in the NWChem Software Suite



QM-CC/CAS QM-DFT AIMD QM/MM MM

Investigators will develop methods, algorithms, and improved software tools for the reliable modeling of charge transfer and charge transport in photoactivated systems on leadership class computational platforms. Such processes are fundamental in solar energy devices.

NWChem
HIGH-PERFORMANCE COMPUTATIONAL CHEMISTRY SOFTWARE

Pacific Northwest
NATIONAL LABORATORY

University of Minnesota
Driven to Discover℠
College of Science & Engineering

BERKELEY LAB
LAWRENCE BERKELEY NATIONAL LABORATORY

Mission and Goals

Implement a suite of methods in the NWChem software suite in order to perform electronically excited-state dynamics in solution and to provide* improved *capabilities for excited-state dynamics in the gas phase.

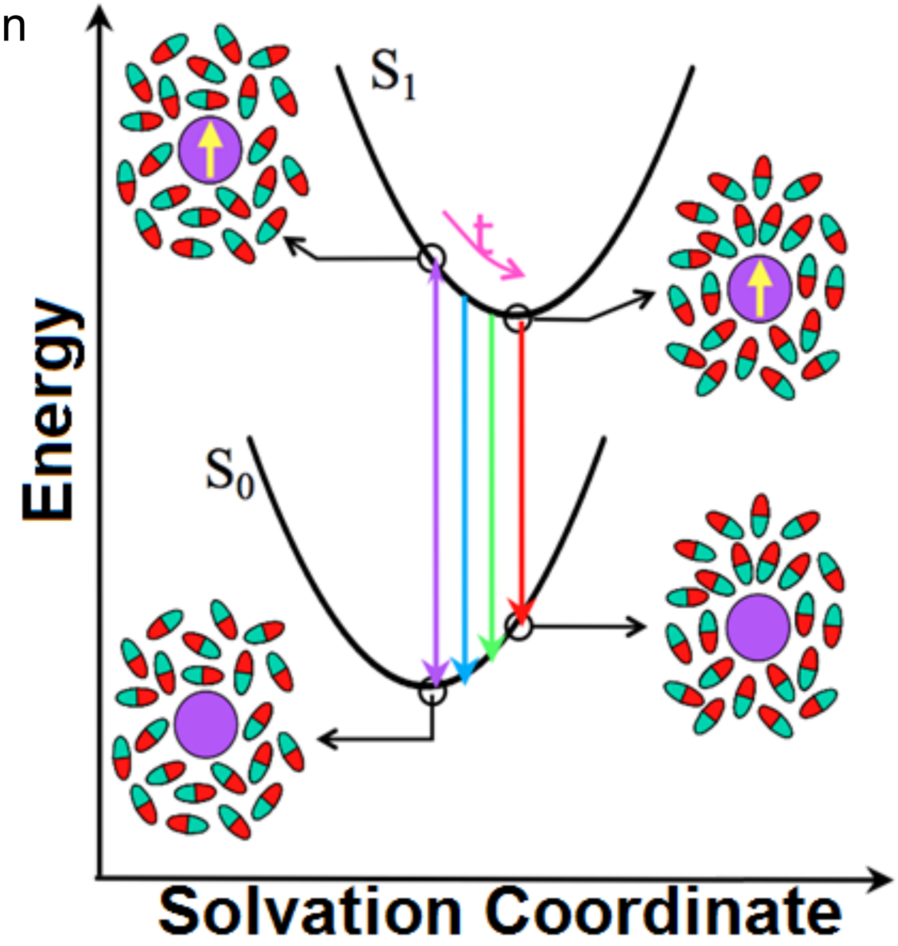
1. Multistate complete-active-space second-order perturbation theory including relativistic effects
2. **State-specific non-equilibrium and equilibrium continuum solvation effects for the computation of excited-state wave functions**
3. Algorithms for the treatment of electronically nonadiabatic and ultrafast dynamics in both the gas-phase and solution
4. Electrostatically embedded multiconfiguration molecular mechanics and molecular mechanics (EE-MCMM/MM) schemes
5. **Multiscale approaches for the treatment of explicit *local* solvation environments with embedding to include longer-range solvent effects**
6. **Monte Carlo strategies for efficient conformational sampling of large and flexible chromophores**

State Specific Continuum Solvation

Alek Marenich, Chris Cramer & Don Truhlar

Non-equilibrium Excited State Solvation
Only the environment dynamic (electronic) response adjusts, the inertial (nuclear) part remains frozen in pre-excitation configuration

Equilibrium Excited State Solvation
Both electronic and nuclear parts adjust to being in excited state (solvent reorganization energy)



Non-equilibrium Ground State Solvation
Only the environment dynamic (electronic) response adjusts, the inertial (nuclear) part remains frozen in excited state configuration

State-Specific Continuum Solvation Effects

Challenges:

Computation of solvatochromic shifts in liquid-phase absorption and emission spectra requires a proper treatment of

- *non-equilibrium* electrostatic polarization using fast and slow time scales,
- changes in solvent−solute dispersion, and
- changes in solvent−solute hydrogen-bonding.

Plan:

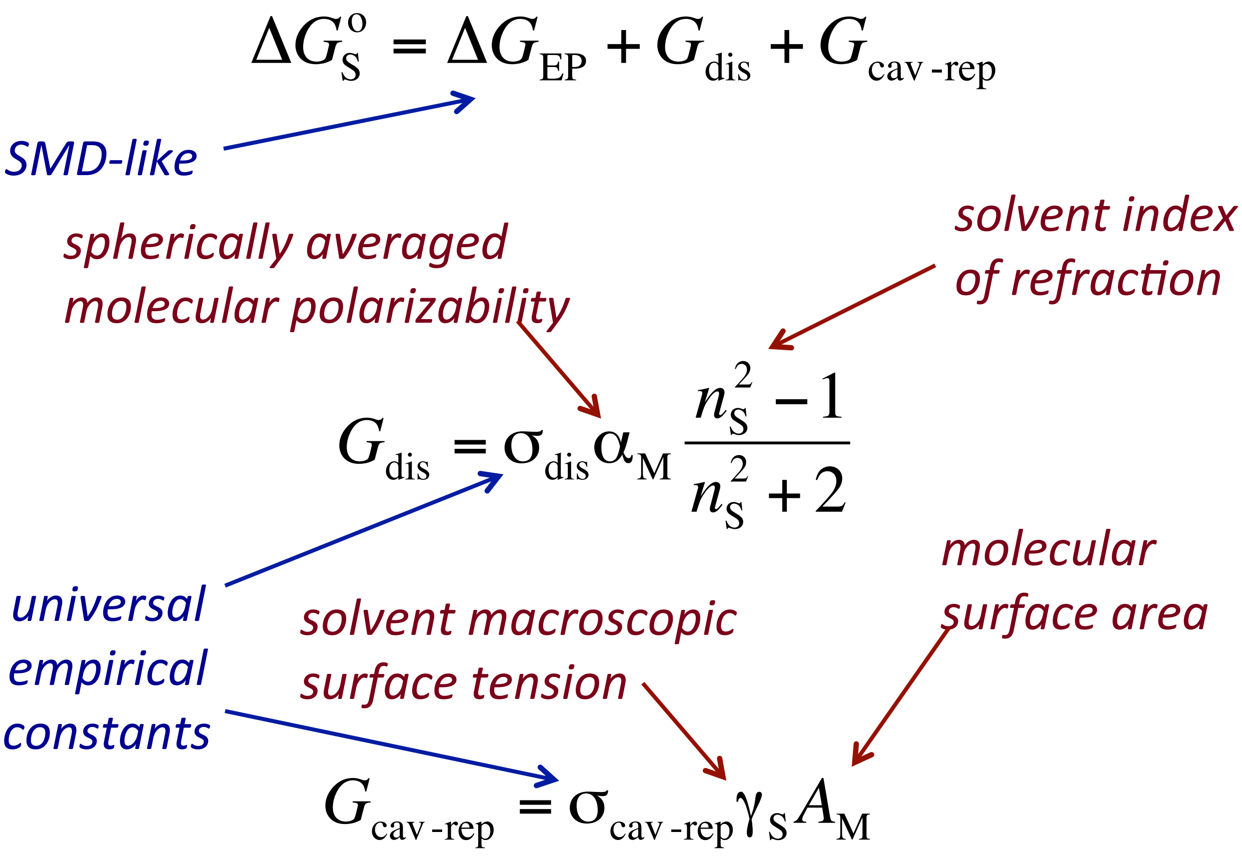
- to implement Vertical Electrostatic Model (VEM) based on Polarized Continuum Model (PCM) or Generalized Born Model for absorption, emission, and evolution (*underway*);
- to develop and implement a uniform treatment of dispersion (*essentially completed*)

Solvation Model with State-Specific Polarizability

A uniform treatment of solute−solvent dispersion contribution (***G*$_{\text{disp}}$**) in the ground and excited electronic states of the solute. To evaluate ***G*$_{\text{disp}}$**, the SMSSP approach uses only two descriptors:

- the spherically averaged dipole polarizability of the solute molecule (either in its ground or excited electronic state)
- the refractive index of the solvent.

MUE = 0.46 kcal/mol
643 data for 231 solutes
in 14 solvents
(electronic ground state)



$$\Delta G_{\mathrm{S}}^{\mathrm{o}} = \Delta G_{\mathrm{EP}} + G_{\mathrm{dis}} + G_{\text{cav-rep}}$$

SMD-like

spherically averaged molecular polarizability

solvent index of refraction

$$G_{\mathrm{dis}} = \sigma_{\mathrm{dis}} \alpha_{\mathrm{M}} \frac{n_{\mathrm{S}}^2 - 1}{n_{\mathrm{S}}^2 + 2}$$

universal empirical constants

solvent macroscopic surface tension

molecular surface area

$$G_{\text{cav-rep}} = \sigma_{\text{cav-rep}} \gamma_{\mathrm{S}} A_{\mathrm{M}}$$

Marenich, Cramer & Truhlar, *J. Chem. Theory Comput.* **2013**, in press; DOI:10.1021/ct400329u

Dispersion Contribution to Solvatochromic Shifts

The solvent−solute dispersion contribution ($\Delta\omega_{\text{disp}}$) to the solvatochromic shift, $\omega_{\text{gas}} - \omega_{\text{solvent}}$, can now be treated as

$$\Delta\omega_{\text{disp}} = -\sigma_{\text{disp}}(\alpha^{\text{ES}} - \alpha^{\text{GS}})\frac{n^2 - 1}{n^2 + 2}$$

Examples: The solvent−solute dispersion shifts for some solutes in cyclohexane (given in cm^{-1})

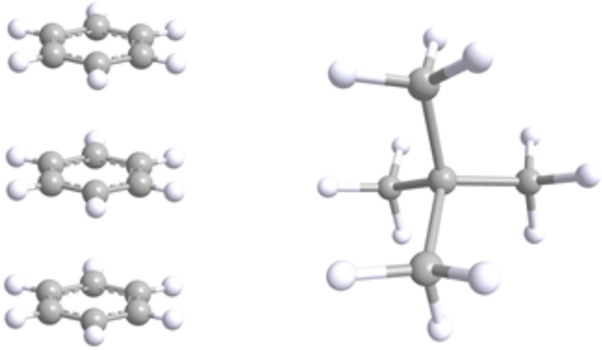
Solute	Transition	Our TD M06-2X calculation	Model of Rösch & Zerner	Experimental estimate
benzene	**$S_0 \rightarrow L_b$**	**127**	**316**	**209-308**
	$S_0 \rightarrow L_a$	**542**	**598**	**1070**
azulene	**$S_0 \rightarrow L_b$**	**-123**	**-162**	**-105**
	$S_0 \rightarrow L_a$	**234**	**288**	**340**
naphthalene	**$S_0 \rightarrow L_b$**	**307**	**332**	**275-389**
	$S_0 \rightarrow L_a$	**1344**	**879**	**367-902**

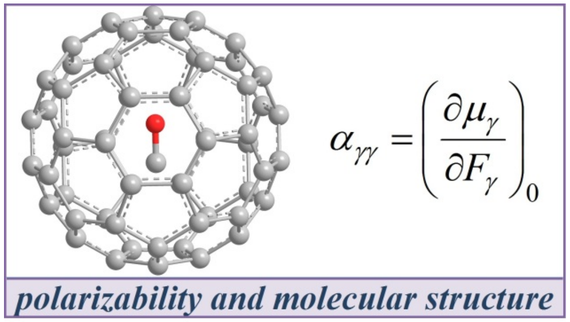
For details see Marenich et al., *JCTC* **2013**, in press; DOI:10.1021/ct400329u
Rösch & Zerner, *JPC* **1994**, *98*, 5817

A New Method for Distributed Polarizability Calculations

Partitions molecular polarizabilities based on Hirshfeld analysis and shows that the polarizability of the same functional group (for example, CO or OH) can differ substantially, depending on the position of this group in a molecule, but a general trend does emerge.
Our calculations for a diverse set of molecules show that

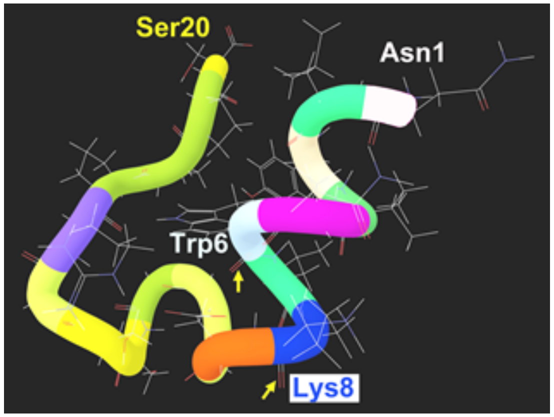
- the polarizabilities of interior atoms and groups are greatly quenched, and
- the outermost atoms and functional groups in molecules are in general much more polarizable than their buried counterparts.





$$\alpha_{\gamma\gamma} = \left(\frac{\partial \mu_\gamma}{\partial F_\gamma}\right)_0$$

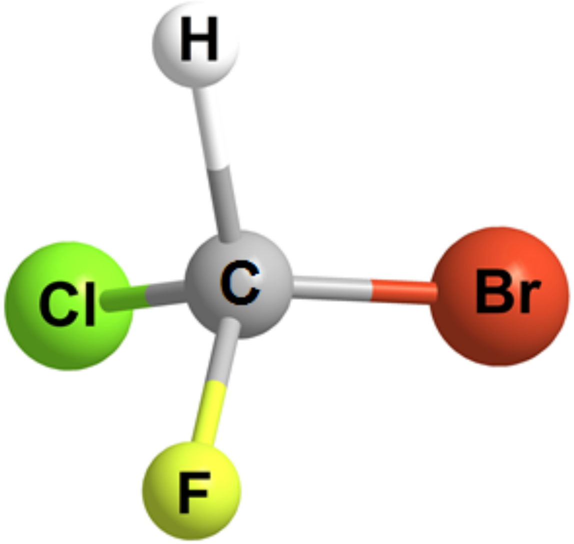
polarizability and molecular structure



Marenich, Cramer & Truhlar, *Chem. Sci.* **2013**, *4*, 2349; DOI: 10.1039/C3SC50242B

Distributed Polarizabilities

Some numerical example: Distributed atomic polarizabilities (α_i, in a. u.) and CM5 partial atomic charges (q_i, in a.u.) in the ground and in the first excited electronic state of the CFClBrH molecule in the gas phase



	Ground state		Excited state	
Atom *i*	α_i	q_i	α_i	q_i
C	**1.7**	**+0.09**	**2.0**	**-0.00**
F	**6.3**	**-0.09**	**6.7**	**-0.11**
Cl	**16.9**	**-0.05**	**24.0**	**-0.08**
Br	**18.6**	**-0.09**	**28.8**	**+0.08**
H	**5.2**	**+0.14**	**9.8**	**+0.11**
Total	**48.6**	**0.00**	**71.2**	**0.00**

Methods: M06-2X for the ground state and TD M06-2X for the excited state, with MG3 on H, F, Cl and ma-Def2-TZVP on Br.

Conclusion: The polarizability of the buried carbon is reduced in comparison with the remaining (external) atoms in CFClBrH.

Explicit Local Solvation Environments

Tiannan Chen, Hannah Leverentz, Ilja Siepmann, Don Truhlar & Niri Govind

Multiscale approaches for the treatment of explicit local solvation environments with embedding to include longer-range solvent effects

Challenge: Strong interactions (e.g., hydrogen-bonding) cause **preferential solvation** and require explicit local solvation environments; other examples of non-uniform solvent environments include **highly compressible fluids** (e.g., supercritical CO_2) and **interfaces**

Plan: Develop MC procedures for the efficient generation of **minimal sets of representative explicit solvent configurations** (MC-MSREX) and additional embedding in a polarizable continuum model; planned collaboration with Youssef Marzouk (QUEST Inst) to find best fitness function and to quantify uncertainty

Automatic generation of a large number of uncorrelated explicit solvent configurations using MD/MC with KS-DFT or MM description

Development of a fitness function to measure whether a subset of these configurations is representative of the entire ensemble

MC simulated annealing/genetic evolution algorithm for pruning of subsets

OR Development of “graphical” similarity search (potential collaboration with SDAV Inst) to distill structural motives that are weighted by occurrence in large-scale simulation

NWChem program: Computation of ground- and excited-state wave functions and convergence control

Scientific issue: Can pruned subset describe ensemble of solvent configurations?

Mathematical issues: Provide mathematical definition of fitness function and uncertainty quantification

Algorithmic issues: What are the most efficient ways to prune or find structural motives and to check for convergence?

Choice of “Minimal” Set of Configurations

Unbiased selection of configurations from trajectory of large-scale MD/MC simulation

- Find longest relaxation time to determine frequency (number) of uncorrelated configurations, N_{con}
- Determine size of minimal set (number of configurations, N_{set}) that can be afforded for electronic structure calculations
- Select from uncorrelated configurations at equal intervals
- Select from uncorrelated configurations at random

Problem: May not be representative when the size of the set is relatively small.

Biased Selection of Minimal Set

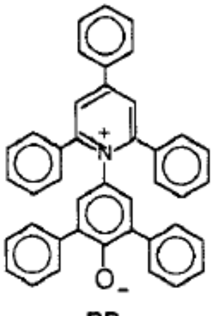
Fitness Function Based Approaches

- Use structural analysis of trajectory to develop fitness function
- **Exhaustive search** of all possible sets of configurations
  - guaranteed to find the best set (for a given fitness function)
  - combinatorial problem with computational cost that scales as power law with size of set
  - approach to be used when N_{set} is small due to high cost of electronic structure calculation
- **Monte Carlo simulated annealing/genetic algorithm** to search for optimal representative set and use unweighted averages for property calcultions

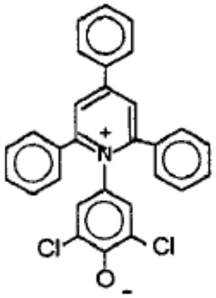
Similarity Based Approach

- Use structural/**IMAGE** analysis tools to find distinct structural motives (i.e., collections of configurations with high similarity) and determine their statistical weights
- Pick one example from N_{set} structural motives and use weighted averages for property calculations

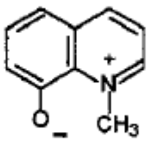
Strong Non-Idealities for Solvatochromic Probes in Water/Organic Solvent Mixtures



RB



WB



QB

$$E_T^r = (E_T^{mix} - E_T^{org}) / (E_T^{wat} - E_T^{org})$$

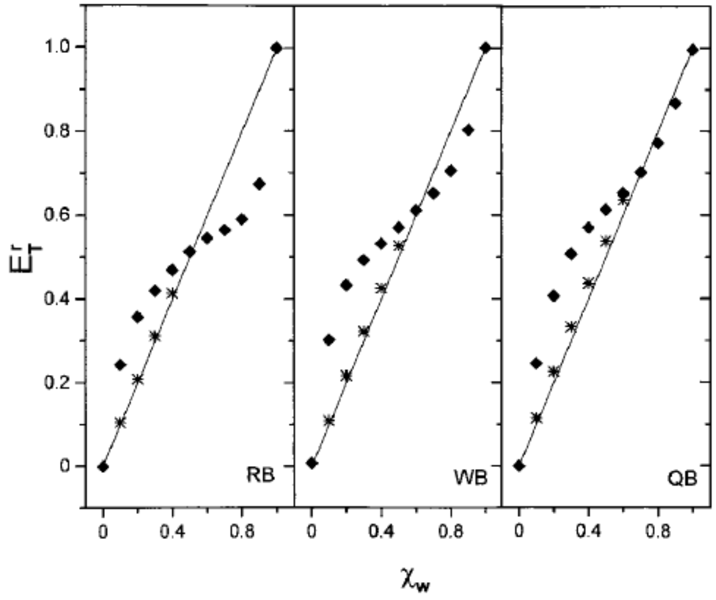
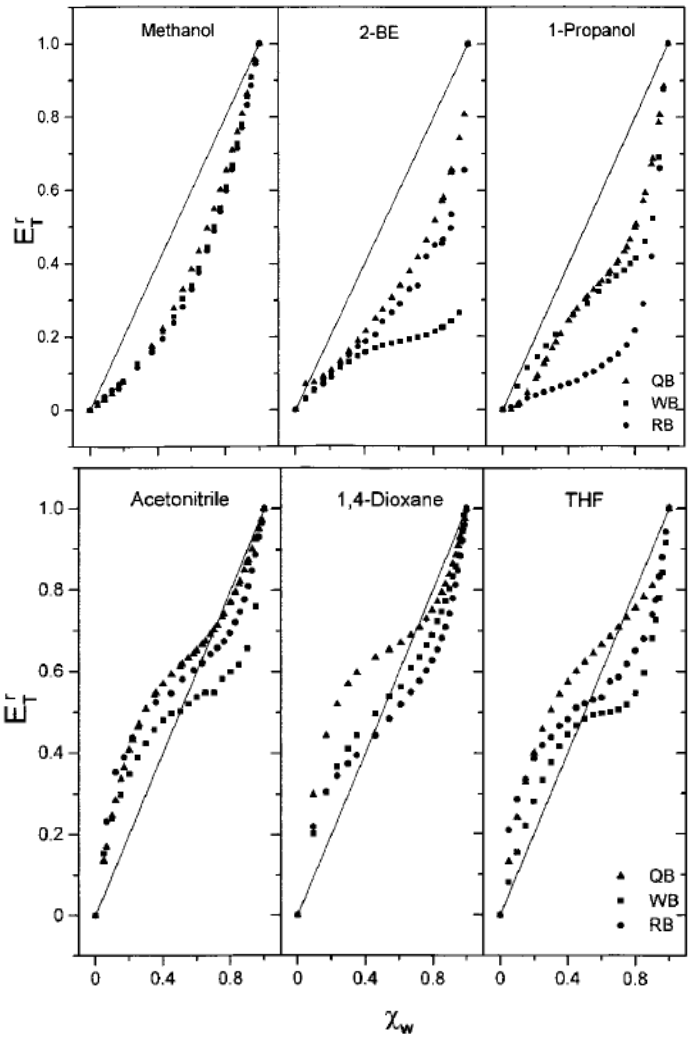


Figure 4. Dependence of E_T^r on χ_w (aqueous acetonitrile) for RB, WB and QB. (◆) Experimental results; (⁎) calculated contribution to experimental E_T^r by preferential solvation of the probe by dielectric enrichment (see Calculations section)



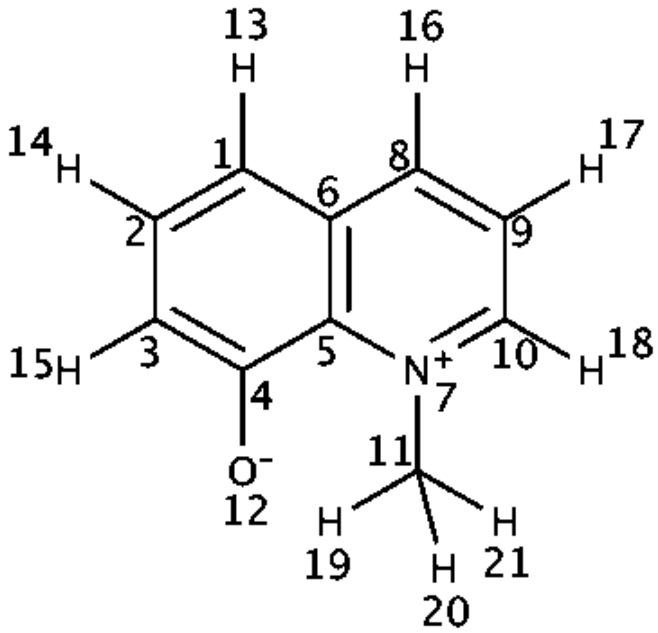
Observations:

- Deviations from ideal behavior depend on probe
- enrichment of protic solvent
- mixtures with aprotic solvents exhibit **"azeotropic"** behavior with initial water enrichment

Tada, Novaki and El Seoud,
J. Phys. Org. Chem. **13**, 679 (2000)

Simulation Details: QB Force Field

CM5 charges for QB were determined from optimized structure at M06-2X/6-31+G(d,p) level with SM8 implicit solvent model using 1-octanol as solvent



Atom No.	Element	CM5 Charge	Atom No.	Element	CM5 Charge
1	C	-0.135	**12**	**O**	**-0.514**
2	C	-0.108	13	H	0.101
3	C	-0.149	14	H	0.105
4	C	0.062	15	H	0.087
5	C	0.085	16	H	0.139
6	C	-0.014	17	H	0.135
7	**N**	**-0.195**	18	H	0.152
8	C	-0.022	19*	H	0.120
9	C	-0.080	20*	H	0.115
10	C	0.100	21*	H	0.119
11*	C	-0.103			

CM5 Dipole Moments:
X: -8.4; *Y*: -5.8; *Z*: 0.0; Total: 10.1 D

*: The methyl group is treated as united atom at C(11) position with the partial charge being the sum of the four atoms (0.251)

Lennard-Jones parameters for aromatic ring and methyl group taken from TraPPE-EH and TraPPE-UA force fields

Simulation Details: Solvents, State Point, Trajectories

Solvent force fields

- TIP4P [1] for water, TraPPE-UA [2] for acetonitirle, and TraPPE-EH [3] for benzene

State Point

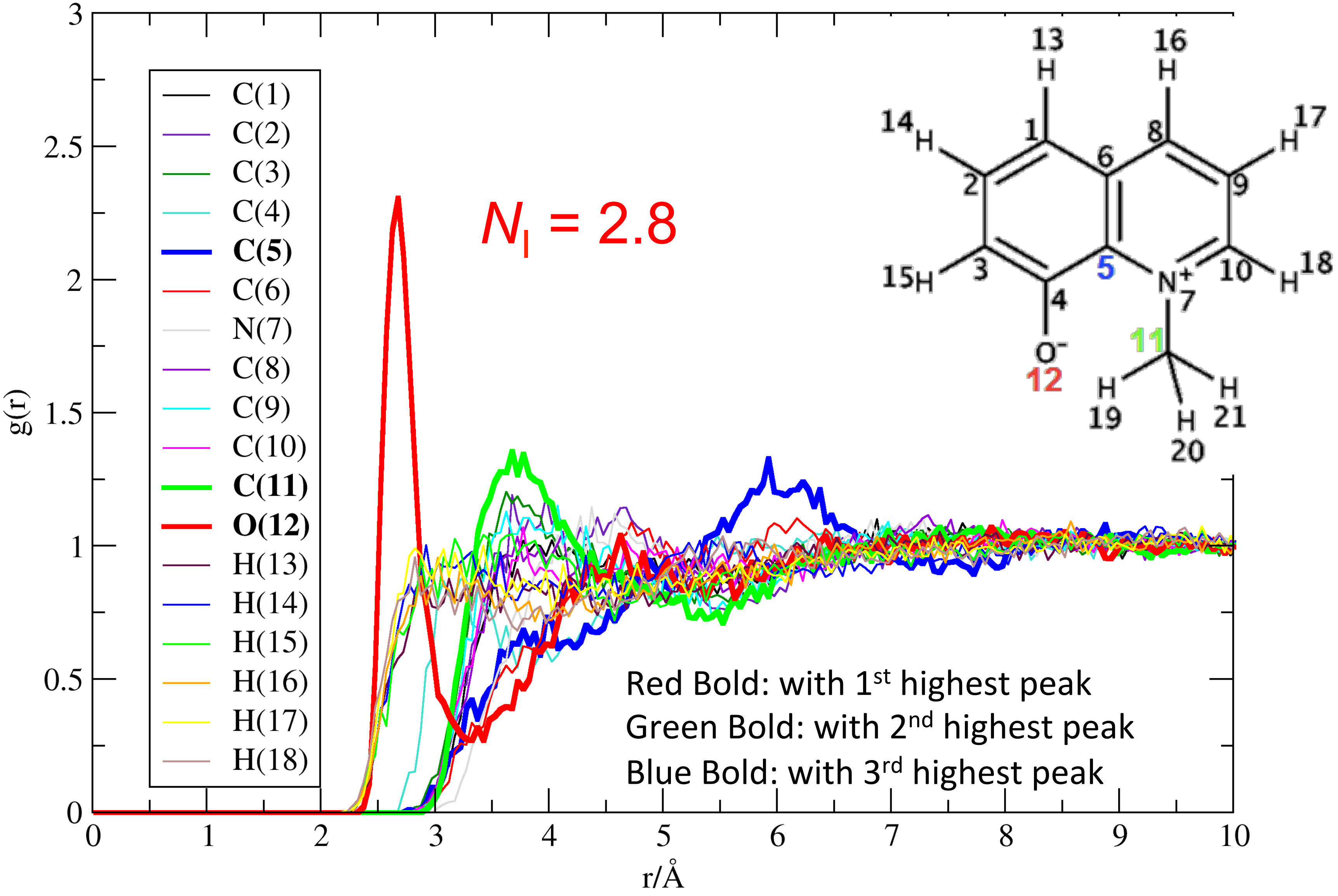
- *NpT* ensemble: $T = 298.15$ K and $p = 1$ bar

Trajectories

- 1 QB molecule + 1000 water/400 ACN/200 BEN molecules
- 16 independent runs consisting each of 10^5 Monte Carlo cycles (using MCCCS−MN software [4])
- Configurations taken every 10^3 MC cycles for a total of 1600 uncorrelated configurations

[1] Jorgensen *et al*., *J. Chem. Phys*. **79**, 926 (1983)
[2] Wick *et al*., *J. Phys. Chem. B* **109**, 18974 (2005)
[3] Rai, & Siepmann, *J. Phys. Chem. B*, **111**, 10790 (2007)
[4] Monte Carlo for Complex Chemical Systems−Minnesota

QB Bead – Water COM Radial Distribution Functions



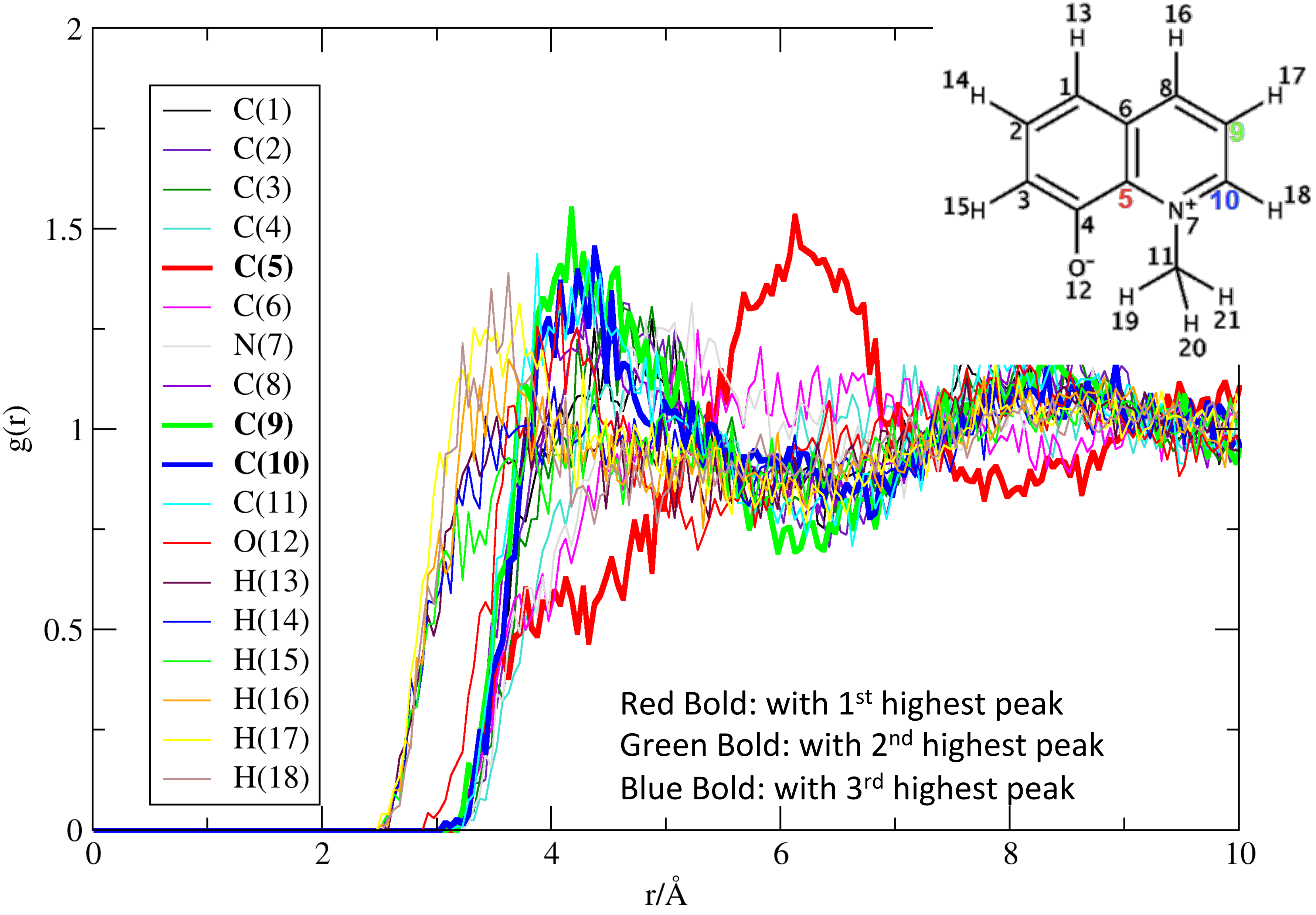
$N_I = 2.8$

Red Bold: with 1st highest peak

Green Bold: with 2nd highest peak

Blue Bold: with 3rd highest peak

QB Bead − Acetonitrile COM RDFs

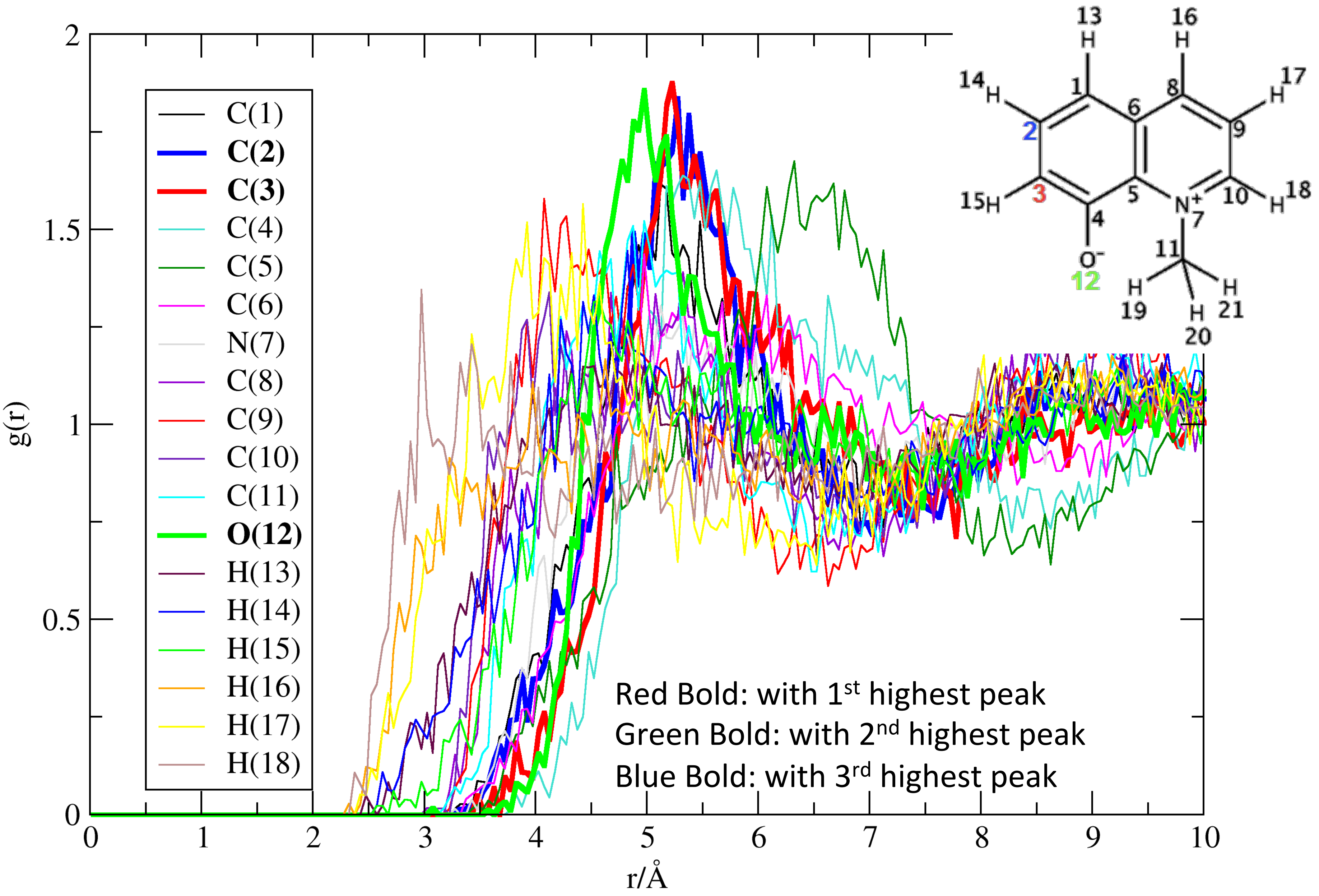


Red Bold: with 1st highest peak

Green Bold: with 2nd highest peak

Blue Bold: with 3rd highest peak

QB Bead – Benzene COM RDFs



Red Bold: with 1st highest peak

Green Bold: with 2nd highest peak

Blue Bold: with 3rd highest peak

Selection of Minimal Set

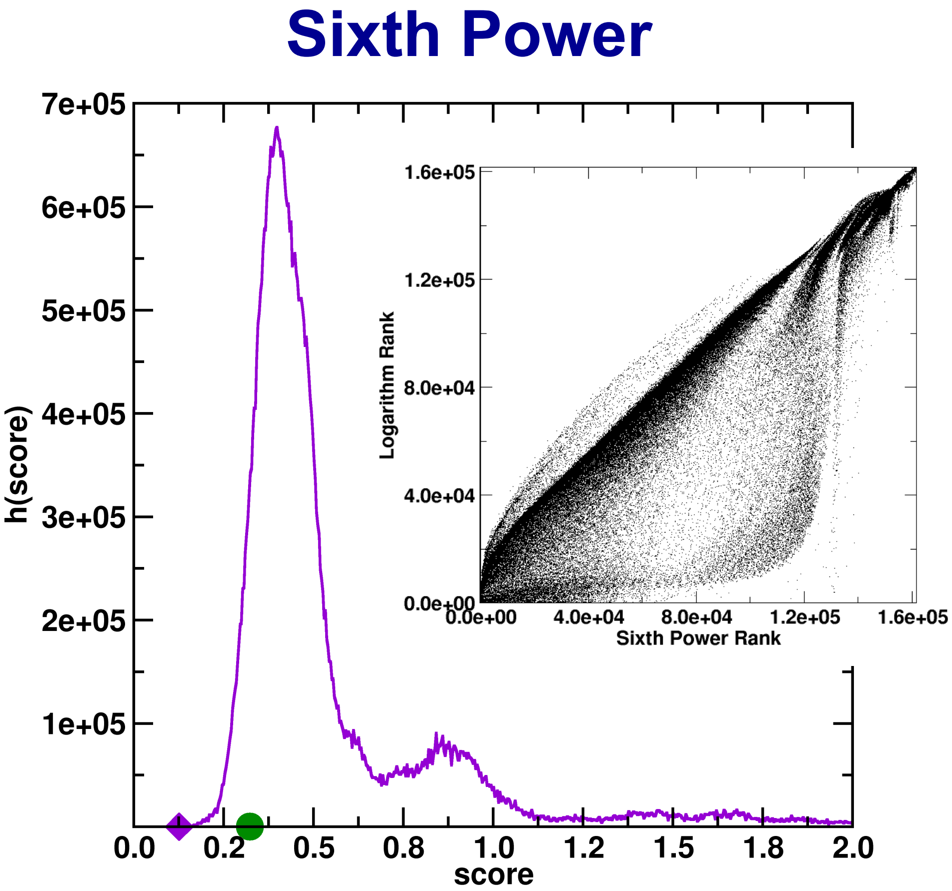
- **Exhaustive search** for set of 3 most representative configurations of water solvation shell
- Explore two fitness functions involving 1st and 2nd moments:

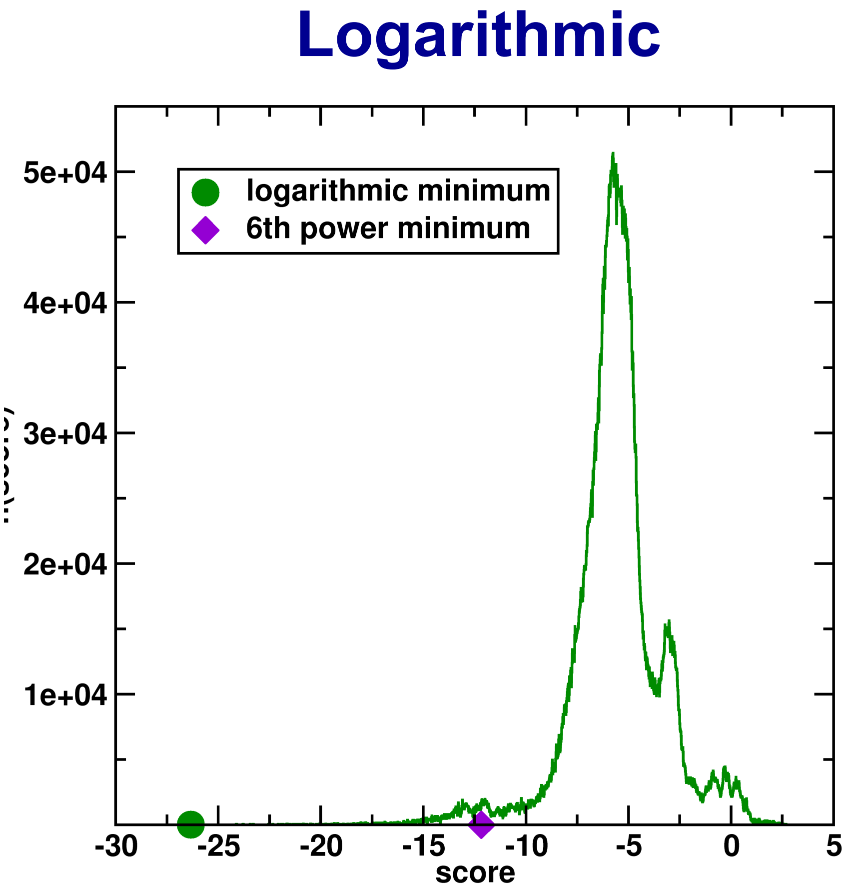
$$S_6 = \left\{ \left[\frac{\langle d_1 \rangle^* - \langle d_1 \rangle}{\langle d_1 \rangle} \right]^6 + \left[\frac{\langle {d_1}^2 \rangle^* - \langle {d_1}^2 \rangle}{\langle {d_1}^2 \rangle} \right]^6 + \left[\frac{\langle d_2 \rangle^* - \langle d_2 \rangle}{\langle d_2 \rangle} \right]^6 + \left[\frac{\langle {d_2}^2 \rangle^* - \langle {d_2}^2 \rangle}{\langle {d_2}^2 \rangle} \right]^6 \right\}^{1/6}$$

$$S_{\ln} = \ln \left| \frac{\langle d_1 \rangle^* - \langle d_1 \rangle}{\langle d_1 \rangle} \right| + \ln \left| \frac{\langle {d_1}^2 \rangle^* - \langle {d_1}^2 \rangle}{\langle {d_1}^2 \rangle} \right| + \ln \left| \frac{\langle d_2 \rangle^* - \langle d_2 \rangle}{\langle d_2 \rangle} \right| + \ln \left| \frac{\langle {d_2}^2 \rangle^* - \langle {d_2}^2 \rangle}{\langle {d_2}^2 \rangle} \right|$$

Where d_1 and d_2 denote the distances from O in QB to the closer H atom from two closest water molecules;
<>* and <> stand for the averages for the 3-configuration sets and for the average over all 1600 configurations from large-scale simulation

Sensitivity to Fitness Function





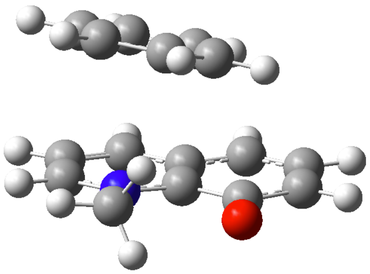
Different fitness functions lead to different 3-configuration minimal set → need UQ help

Sixth power minimum is ranked 2891 in logarithmic ranking and logarithmic minimum is ranked 12959 in sixth power ranking.

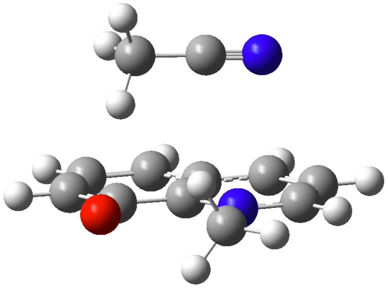
QB Excitation Energies

Sensitivity to Inclusion of an Explicit Solvent Molecule

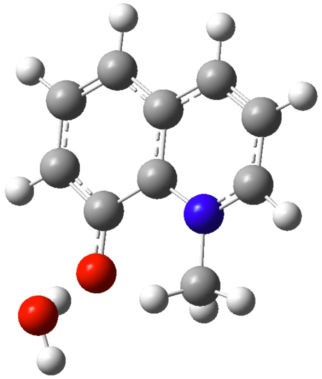
- Optimized geometry of QB alone and QB + 1 explicit solvent model using SMD/M06-2X/6-31G(d,p) in benzene, acetonitrile, and water.
  For explicit solvent optimizations, starting geometry was based on "chemical intuition" and a preliminary AM1 (benzene and water) or AM1-D (acetonitrile) geometry optimization.
- Used VEM-SM8/TD-M06-2X/6-31G(d,p) single-point calculations to compute the visible-range excitation energy (and corresponding solvatochromic shifts) of the QB dye in benzene, acetonitrile, and water.
  VEM = vertical excitation model, see Marenich, Cramer, Truhlar, Guido, Mennucci, Scalmani & Frisch, *Chemical Science* **2011**, *2*, 2143.



QB and explicit benzene



QB and explicit acetonitrile



QB and explicit water

QB Excitation Energies

Sensitivity to Inclusion of an Explicit Solvent Molecule

Solvent	# of Explicit Solvent Molecules	Excitation Energy (eV)	λ_{max} (nm)	Solvato-chromatic Shift (eV)[a]
Benzene (experiment)[b]	**---**	**2.16**	**574**	---
Benzene (VEM[c]-SM8[d]/TD-M06-2X/6-31G(d,p))	0	2.26	548	---
Benzene (VEM-SM8/TD-M06-2X/6-31G(d,p))	1	2.31	536	---
Acetonitrile (experiment)[b]	**---**	**2.38**	**521**	**0.22**
Acetonitrile (VEM-SM8/TD-M06-2X/6-31G(d,p))	0	2.54	488	0.28
Acetonitrile (VEM-SM8/TD-M06-2X/6-31G(d,p))	1	2.63	471	0.32
Water (experiment)[b]	**---**	**2.80**	**443**	**0.64**
Water (VEM-SM8/TD-M06-2X/6-31G(d,p))	0	2.62	473	0.36
Water (VEM-SM8/TD-M06-2X/6-31G(d,p))	1	2.80	443	0.49

[a] Relative to the excitation energy in benzene.

[b] Tada, Novaki & El Seoud, *J. Phys. Org. Chem.* **2000**, *13*, 679.

[c] Marenich *et al.*, *Chem. Sci*. **2011**, *2*, 2143.

[d] Marenich *et al.*, *J. Chem. Theory Comput*. **2007**, *3*, 2011.

QB Excitation Energies

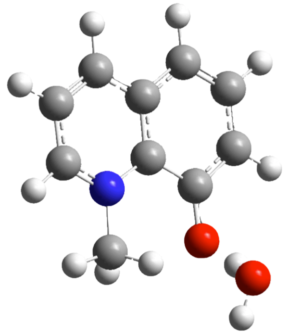
VEM-SM8/TDDFT[a]/6-31G(d,p) single-point energy calculations

	M06-2X		CAM[b]-B3LYP	
System Description	**Excitation Energy (eV)**	**λ_{max} (nm)**	**Excitation Energy (eV)**	**λ_{max} (nm)**
QB in water, experiment[c]	**2.80**	**443**	**2.80**	**443**
QB in implicit water	2.62	473	2.57	482
QB(H_2O) [optimized geometry] in implicit water	2.80	443	2.75	451
QB(H_2O) [averaged over 3 representative configurations] in implicit water	2.66	465	2.62	474
QB$(H_2O)_2$ [averaged over 3 representative configurations] in implicit water	2.71	458	2.66	466

[a] Casida, in Recent Advances in Density Functional Methods, Part I, edited by Chong (World Scientific, Singapore, 1995), p. 155.

[b] Coulomb Attenuating Method: Yanai, Tew & Handy, *Chem. Phys. Lett.* **2004**, 393, 51.

[c] Tada, Novaki & El Seoud, *J. Phys. Org. Chem.* **2000**, *13*, 679.



Chromophore Conformation and Aggregation

Rajan Vatassery,Thilanga Liyana Arachchi,
Wayne Gladfelter, Chris Cramer, Ilja Siepmann & Niri Govind

Monte Carlo strategies for efficient conformational sampling of large and flexible chromophores and their aggregation

Challenge: Flexible chromophores can access multiple conformational states with the distribution influenced by solvation effects; conformational states are often separated by large free energy barriers requiring specialized sampling approaches

Plan: Develop MC procedure for the efficient generation of minimal sets of representative chromophore conformations (MC-MSCON) and of chromophore aggregates (MC-MSAGG)

Automatic generation of a large number of uncorrelated chromophore conformations using configurational-bias MC approaches and of aggregates using aggregation-volume-bias MC approaches
Development of a fitness function to measure whether a subset of these conformations is representative of the entire ensemble
MC simulated annealing/genetic evolution algorithm for pruning of subsets

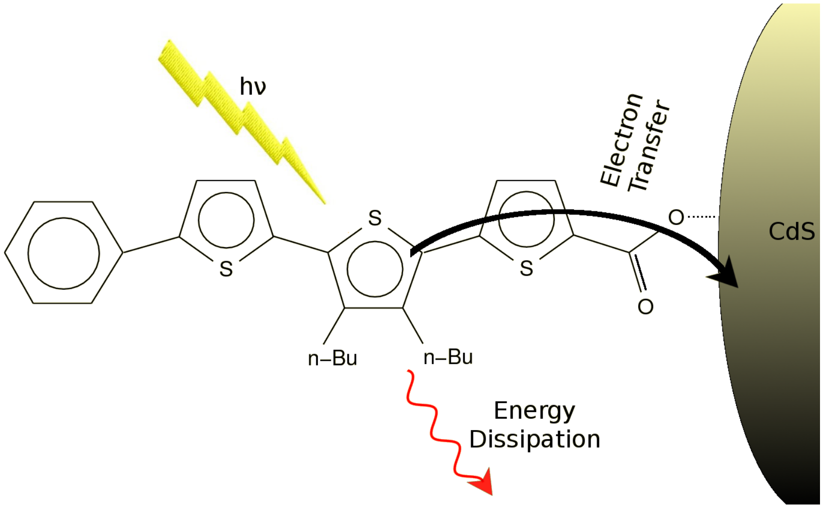
NWChem program: Computation of ground- and excited-state wave functions and convergence control

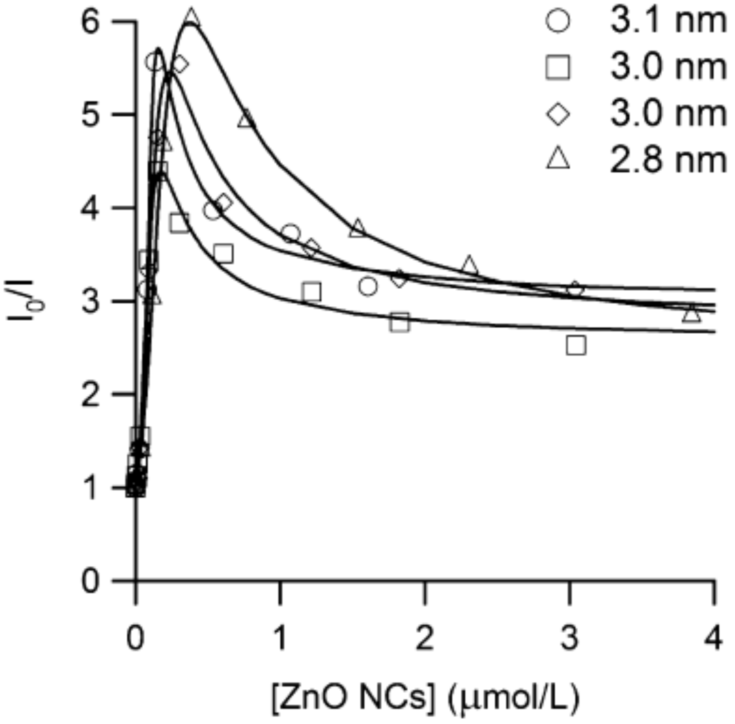
Mathematical issue: Provide mathematical definition of fitness function

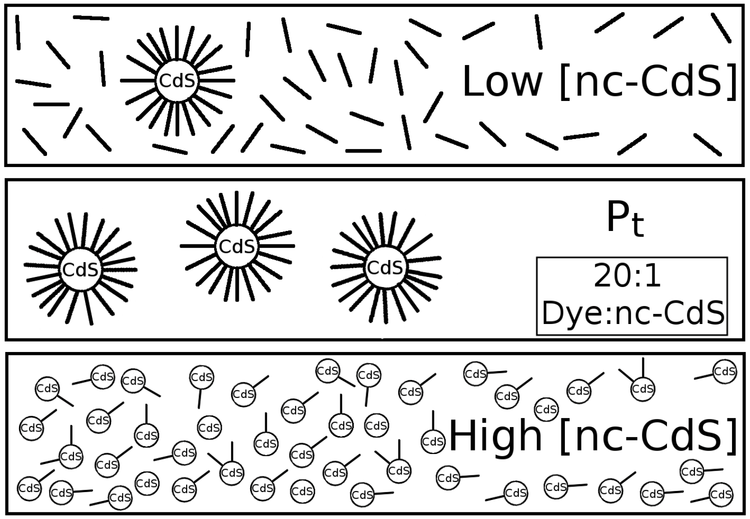
Scientific issue: Can pruned subset describe ensemble of chromophore conformations and aggregates?

Algorithmic issue: What is the most efficient way to prune and to check for convergence?

Terthiophene Dyes on Model Nano-Crystals



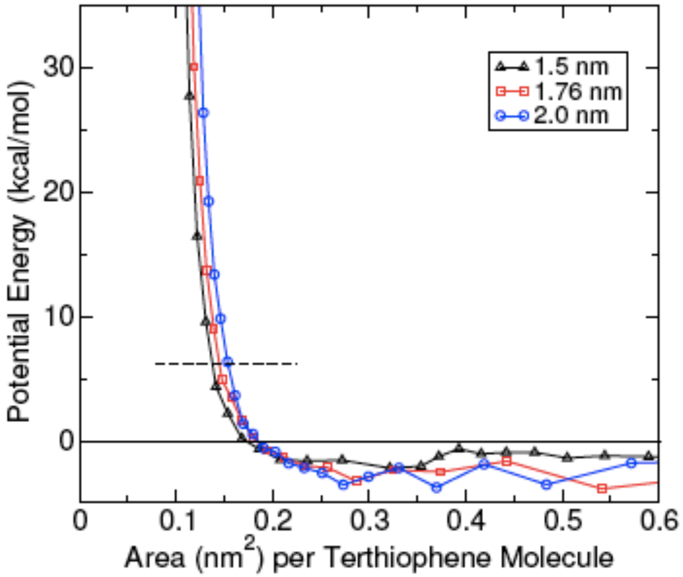


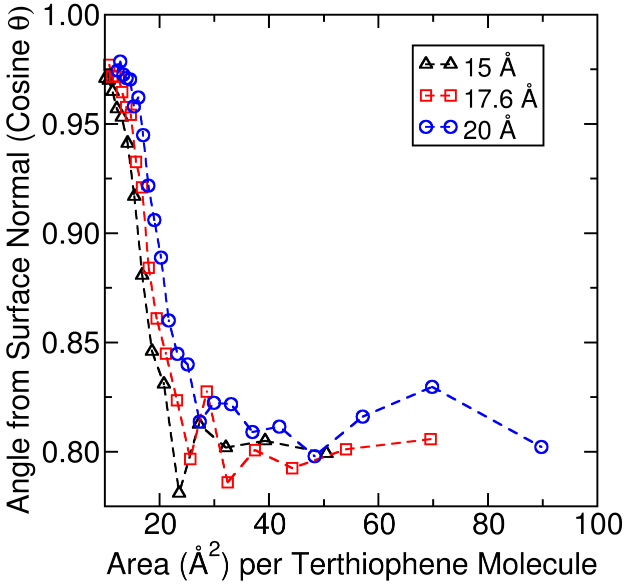


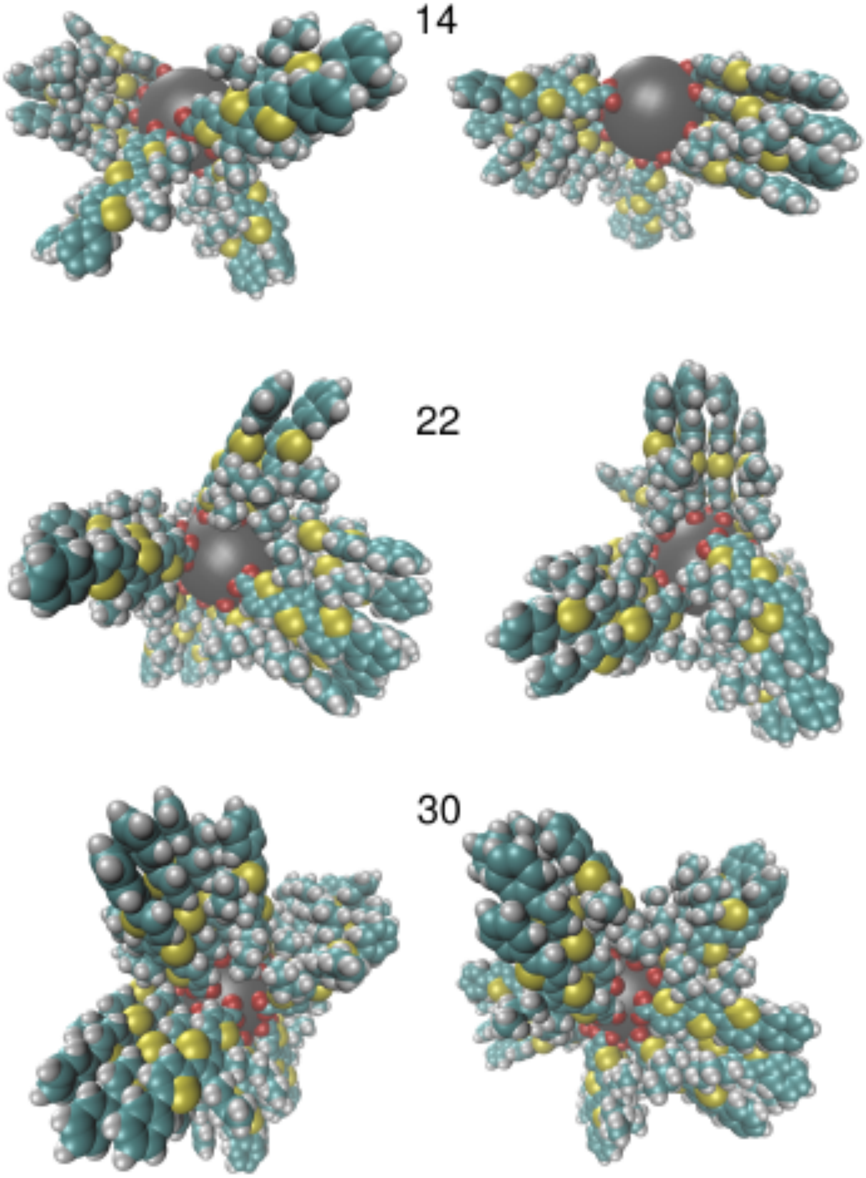
Questions:
Why is there a maximum in the Stern-Volmer plot of concentration quenching?
Is there an optimal packing for dye molecules?
Do dye molecules aggregate at low coverages?

Approach: Use large-scale MD simulations to probe dye structure in explicit solvent.

Terthiophene Dyes on Model Nano-Crystals

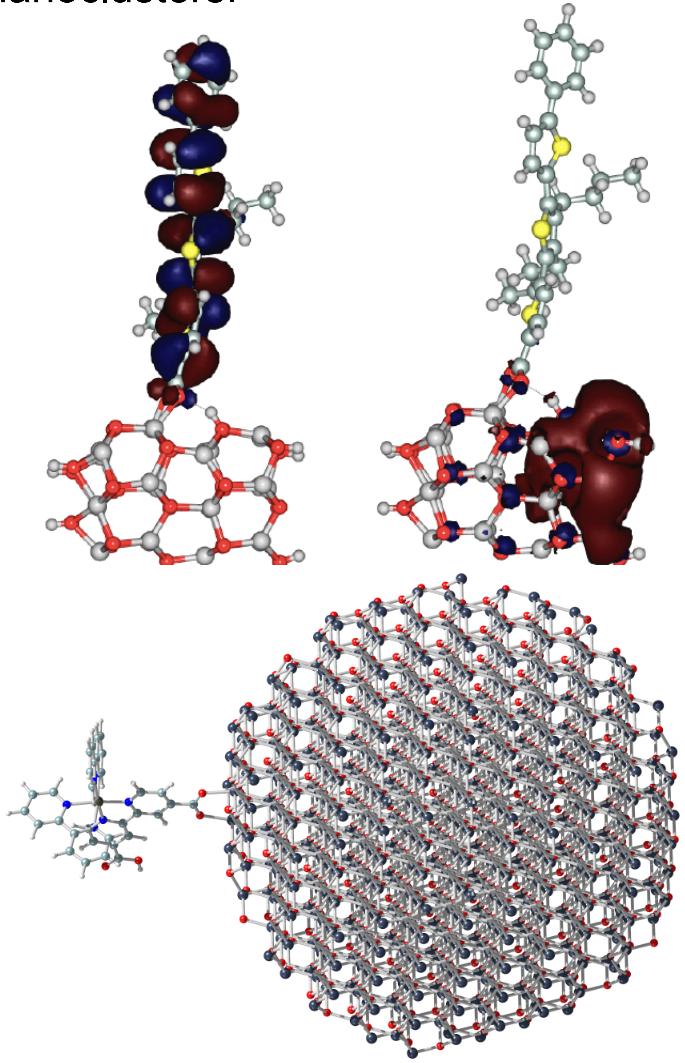






Quantum-chemical Modeling of Dye-sensitized Solar Cells

Question: Why are electron injection rates of dyes on ZnO nanoparticles relatively low compared to those on TiO_2 nanoparticles in spite of similar band-gap?
Challenge: Excited state relaxation dynamics on realistic nanoclusters.



Method Development and Validation from Small to Large

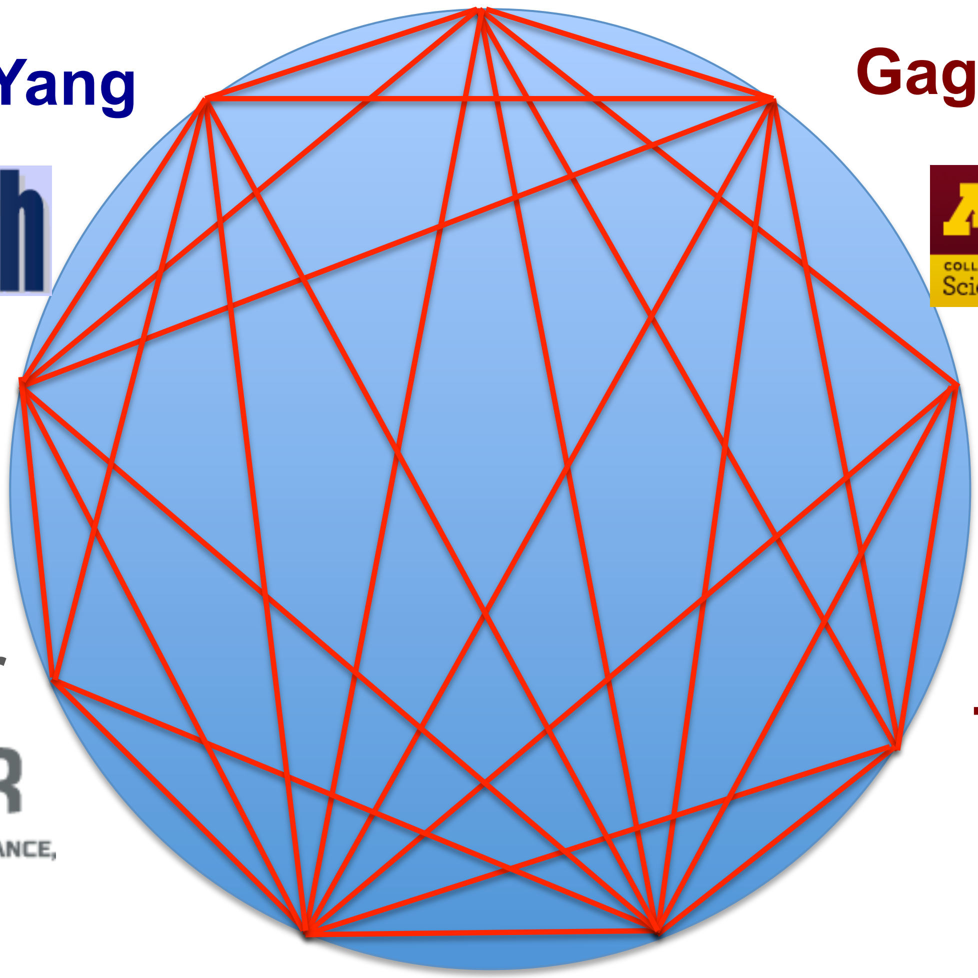
Small-sized nanocluster $(ZnO)_n(H_2O)_m$, $n \leq 32$

- **Ground state**. Full optimization of $(ZnO)_n(H_2O)_m$, dye molecules (LRu and terthiophene) and dye@$(ZnO)_n(H_2O)_m$ system using DFT-GGA.
- Single point calculations using hybrid DFT+solvation (CPCM): band-gap, HOMO-LUMO.
- **Excited states.** Linear response and real time TDDFT: Absorption spectrum, excited state optimization, relaxation dynamics.
- **Benchmark calculations**. Effect of basis set size, percentage of HF exchange.

Medium-sized nanocluster, $32 \leq n \leq 120$ (1.3 nm; ≈ 4,000 basis functions with SVP basis set)

Large-sized nanocluster with $120 \leq n \leq 1200$ (3 nm; ≈ 40,000 basis functions)

Questions ?



Cramer

Chao Yang

Gagliardi

FASTMath

UNIVERSITY OF MINNESOTA
Driven to Discover℠
COLLEGE OF Science & Engineering

Esmond Ng

Siepmann

Lenny Oliker

SUPER
INSTITUTE FOR SUSTAINED PERFORMANCE, ENERGY, AND RESILIENCE

Truhlar

Bert DeJong

Niri Govind

QUEST

NWCHEM
HIGH-PERFORMANCE COMPUTATIONAL CHEMISTRY SOFTWARE

SDAV