EMSP
Environmental Management Science Program

High Level Waste Workshop

Mechanisms and Kinetics of Organic Aging and Characterization of Intermediates in High Level Waste
(#81883)

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Pacific Northwest National Laboratory
Operated by Battelle for the U.S. Department of Energy

Background

- The project started with first HLW call in 1998, renewed in 2002 and 2004; it builds on the PI's experience with Hanford Waste Tank Safety programs since 1993 and collaborations with EMSP projects:
  - *Interfacial Radiolysis Effects in Tank Waste Speciation* (54646), 9/96-9/99, T Orlando
  - *The NOx System in Nuclear Waste* (55229), D Meisel, 9/96-9/99, 2001-2004
- At start of the original project, there were unresolved questions about the safety of stored HLW, specifically the potential for releases from uncontrolled increases in temperature or pressure.
- Organic waste constituents and their degradation in HLW were central to many of these questions.
  - Radiolytic and thermochemical processes degrade organic solutes into smaller fragments of lower energy content, thereby reducing hazards associated with deflagration of organic complexants-nitrate salt mixtures
  - Organic degradation contributes to generation of toxic, flammable and potentially explosive gases, e.g., NH_3, H_2, and N_2O and myriad volatile organic compounds.
- Now the sites face questions about how the wastes react to mixing, heating, and chemical treatments during and pretreatment operations, such that understanding of HLW chemistry is still relevant.

Objective

- Develop fundamental understanding of the significant chemical changes that HLW undergoes during storage, retrieval and treatment operations and computational capabilities to model that chemistry

Approach:

- Combine experimental observation, electronic structure computations, and theoretical methods development to achieve this goal
- Exchange information with site operations staff … contribute to resolving technical issues

Research Activities

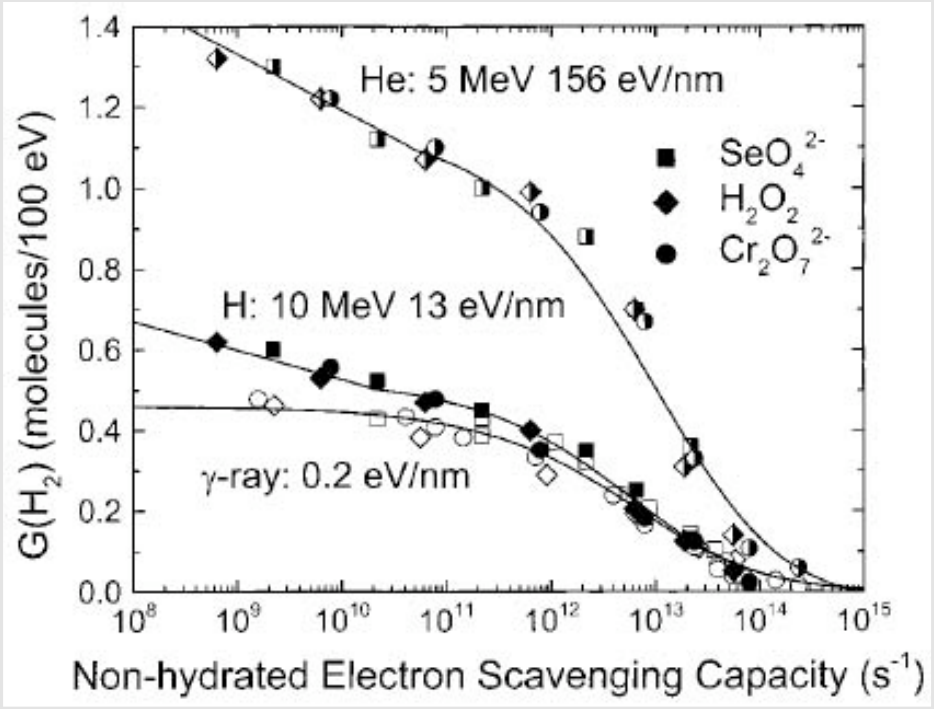
- Mechanistic elucidation of “waste aging” reactions
  - Reactions of organic complexants catalyzed by aluminate ions
  - Reactions in aerated wastes
  - Mechanisms of N_2O and NH_3 generation
- Charaterization of intermediates
  - Thermochemistry of radical reactions in water by photo-acoustic calorimetry
  - Theoretical characterization of intermediates
    - Electronic structure characterizations
    - Definition of aqueous solute cavities for continuum solvation theory
- Kinetic model development
  - H_2 generation rate models

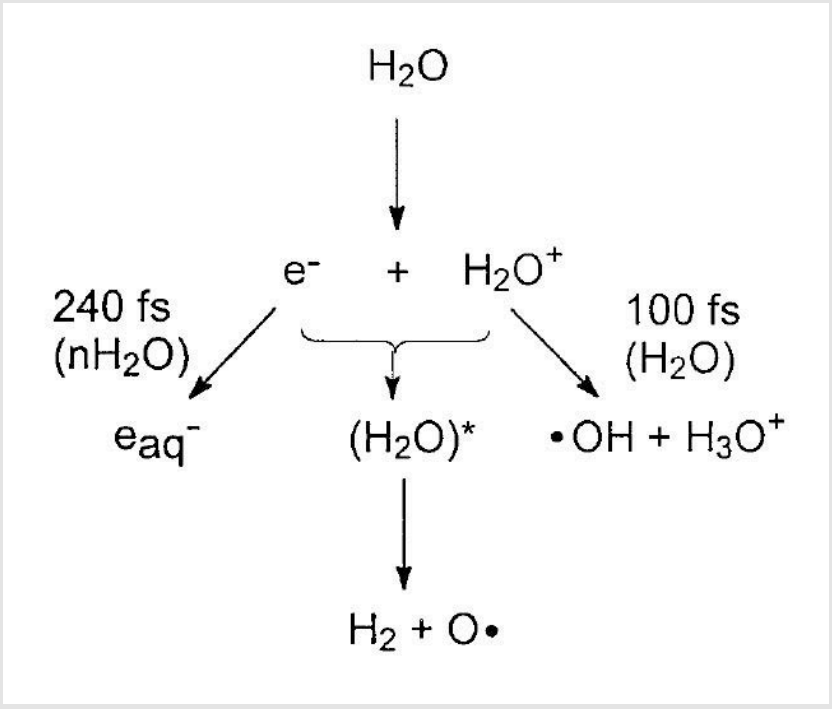
Predicting H_2 Generation in Hanford Tank Waste and WTP Treatment Streams

- Estimates of H_2 generation rates in Hanford Waste Treatment and Immobilization Plant process streams were needed to complete designs of mixing and ventilation systems.
- Camaioni worked with David Sherwood (Washington Group) and Leon Stock (WTP consultant) to perform technical analysis of available data and advance new models for estimating H_2 generation rates.
- Camaioni advised Albert Hu (CH2MHill) on how to adapt the new models for use by Hanford Tank Farm Operations.

New Mechanism for H_2 Formation in Water

LaVerne, J. A.; Pimblott, S. M. *J. Phys. Chem. A,* 2000, *104*, 9820





$$G(\mathrm{H_2}) = G_0(\mathrm{H_2})\frac{\tau^{-1}}{\tau^{-1} + k[\mathrm{S}]}$$

New Equations for Radiolytic Yield of H_2

- Hanford Waste Treatment Plant process streams
  (DJ Sherwood and LM Stock, 2490-WTP-RT-04-0002, Rev 0)

$$G_{(H_2)}{}^{\beta/\gamma} = \frac{0.34}{1+2.4\left[NO_3^-\right]+0.62\left[NO_2^-\right]} + \frac{0.11}{1+120\left[NO_3^-\right]+43\left[NO_2^-\right]} \text{ molecules/100eV}$$

$$G_{(H_2)}{}^{\alpha} = \frac{1.05}{1+2.4\left[NO_3^-\right]+0.62\left[NO_2^-\right]} + \frac{0.35}{1+3900\left[NO_3^-\right]+1400\left[NO_2^-\right]} \text{ molecules/100eV}$$

- Hanford Tank Waste (TA Hu, *HNF-3851, Rev 1)*

$$G_{(H_2)}{}^{\beta/\gamma} = \frac{0.32}{1+2.4\left[NO_3^-\right]+0.62\left[NO_2^-\right]+0.31\left[Na^+\right]_{ex}^2} + \frac{0.13}{1+139\left[NO_3^-\right]+54\left[NO_2^-\right]} \text{ molecules/100eV}$$

Future Directions: Gas Generation Models

- Explore improving water radiolysis equations by correcting for fraction of radiation absorbed by water in wastes with sodium in high excess over nitrate/nitrite
- Equations for predicting thermal generation rates of H_2 are empirical; basic understanding is needed of
  - Catalysis by aluminate ion:

    $R = k[\text{TOC}][\text{Al(III)}]^{0.4}$ or $R = k_1[\text{TOC}] + k_2[\text{TOC}][\text{Al(III)}]$
  - Rate enhancements by O_2
  - Catalysis by transition metal ions (Cr, Mn, etc.)
  - Organic reactivity factors
- Mechanisms/rates of generation of other gases, volatile chemicals

Thermal Degradation of Complexants

- Complexants such glycolate and HEDTA undergo aluminum-catalyzed thermal degradation
- Our evidence suggest the following mechanism

$$^{-}OCH_2CO_2^{-} + \equiv AlOH^{-} \leftrightarrows \equiv AlOCH_2CO_2^{-}$$

H-Atom Transfer:

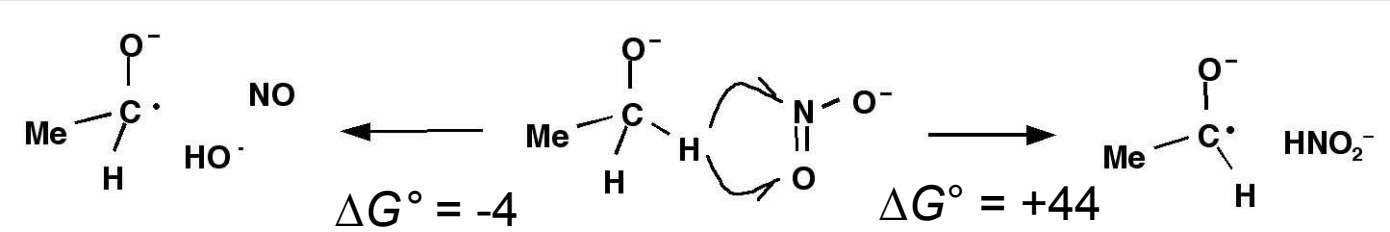
$$\equiv AlOCH_2CO_2^{-} + ONO^{-} \longrightarrow \equiv AlOCHCO_2^{-} + HO^{-} + NO$$

Electron Transfer:

$$\equiv AlOCH_2CO_2^{-} + ONO^{-} \rightarrow \left[\begin{array}{c} | \\ ^{-}ONOAlOCHCO_2^{-} \\ | \end{array} \right] \rightarrow \begin{array}{c} | \\ ^{-}OAlO{=}CH_2 \\ | \end{array} + CO_2 + NO^{-}$$

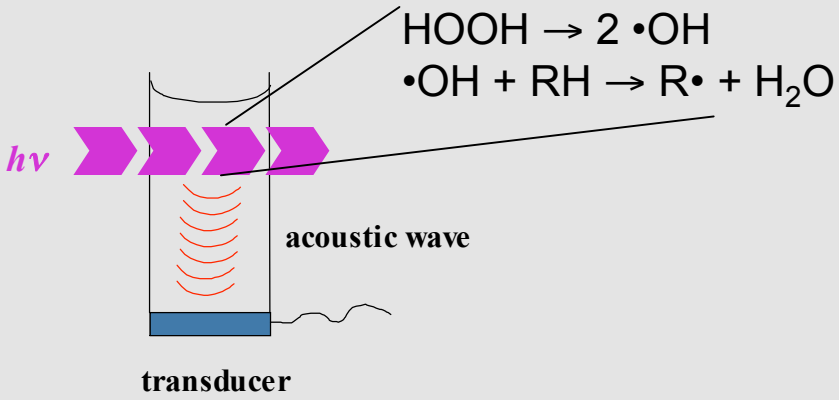
Some Thermochemistry

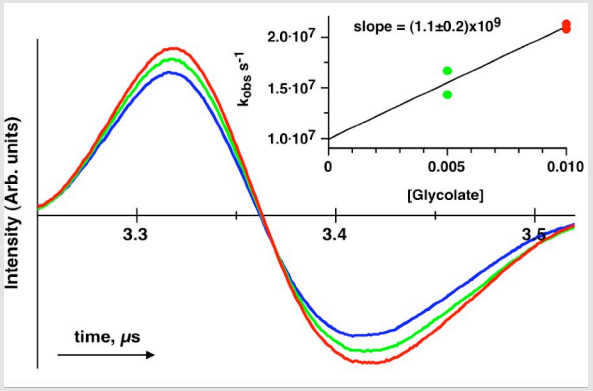
- Recently found that HNO_2^- had lifetime in water of 200 μs, but NO_2H^- dissociates spontaneously to NO + OH^-
  - SV Lymar, HA Schwarz, G Czapski, *J Phys Chem A,* **2002**, *106*, 7245
  - GL Hug, DM Camaioni, I Carmichael, *J Phys Chem A*, **2004**, *108*, 65994
- As illustrated by ethoxide, reduction of nitrite ion by glycolate should be favorable when H atom is transferred to nitrite oxygen.



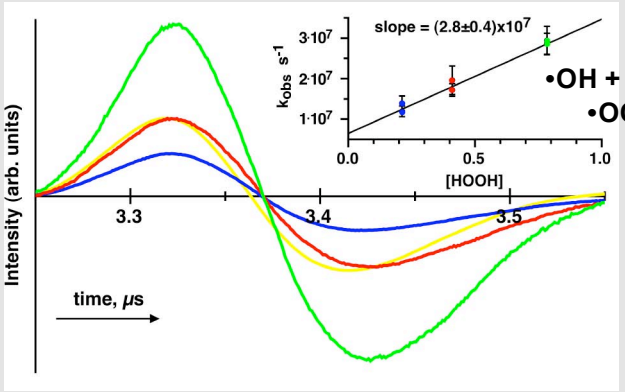
- Complexation with Al(III) may weaken α-C-H bond, which could explain the catalytic effect, but need to determine the activation barrier.

Kinetics and Thermochemistry of Radicals in Aqueous Solution: Time-Resolved Photoacoustic Calorimetry



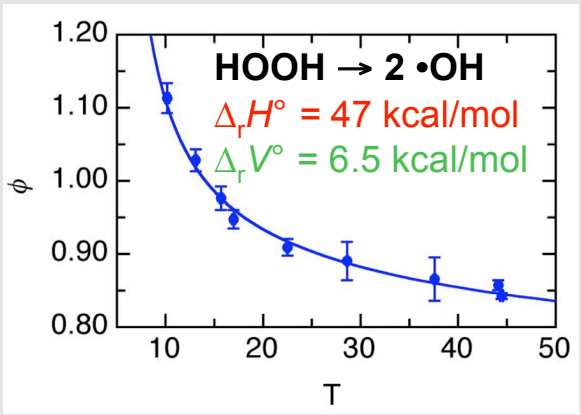


•OH + $HOCH_2CO_2^-$ → $HOC•HCO_2^-$ + H_2O



•OH + HOOH → •OOH + H_2O

- Signal depends reaction rate and changes in enthalpy and volume
- Analysis gives
  - Bond Dissociation Enthalpies
  - Enthalpies of formation
  - Enthapies of solvation
  - Partial molar volumes



Autrey, Brown, Camaioni, Foster and Getty *J Am Chem Soc* **2004**, *126*, 3680

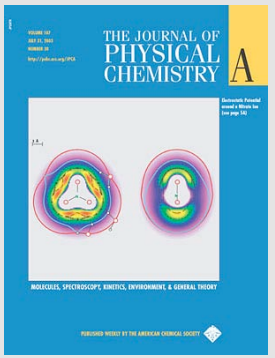
Ab Initio-Based Characterization of Intermediates in High Level Waste

Motivation:

- After extensive experimental characterization of stored HLW during the 1990s, theoretical input based on ab initio theories is now needed:
  - to obtain an improved understanding of chemical reactions in aqueous phase
  - to provide fundamental data of intermediates that cannot be easily measured and yet is needed for the development of reliable kinetic models.

Significance of Research:

- We traced limitations regarding computationally-derived data to the accuracy of continuum models for describing hydration free energies and in particular to the definition of molecular cavities not reflecting well the solute electronic structure.
- This finding causes us to derive chemically-based approaches to the definition of molecular cavities.



"Theoretical Characterization of Oxoanion XO_m^{n-} Solvation,"
DM Camaioni, M Dupuis, and J Bentley, *J Phys Chem A,* **2003**, 107, 5778

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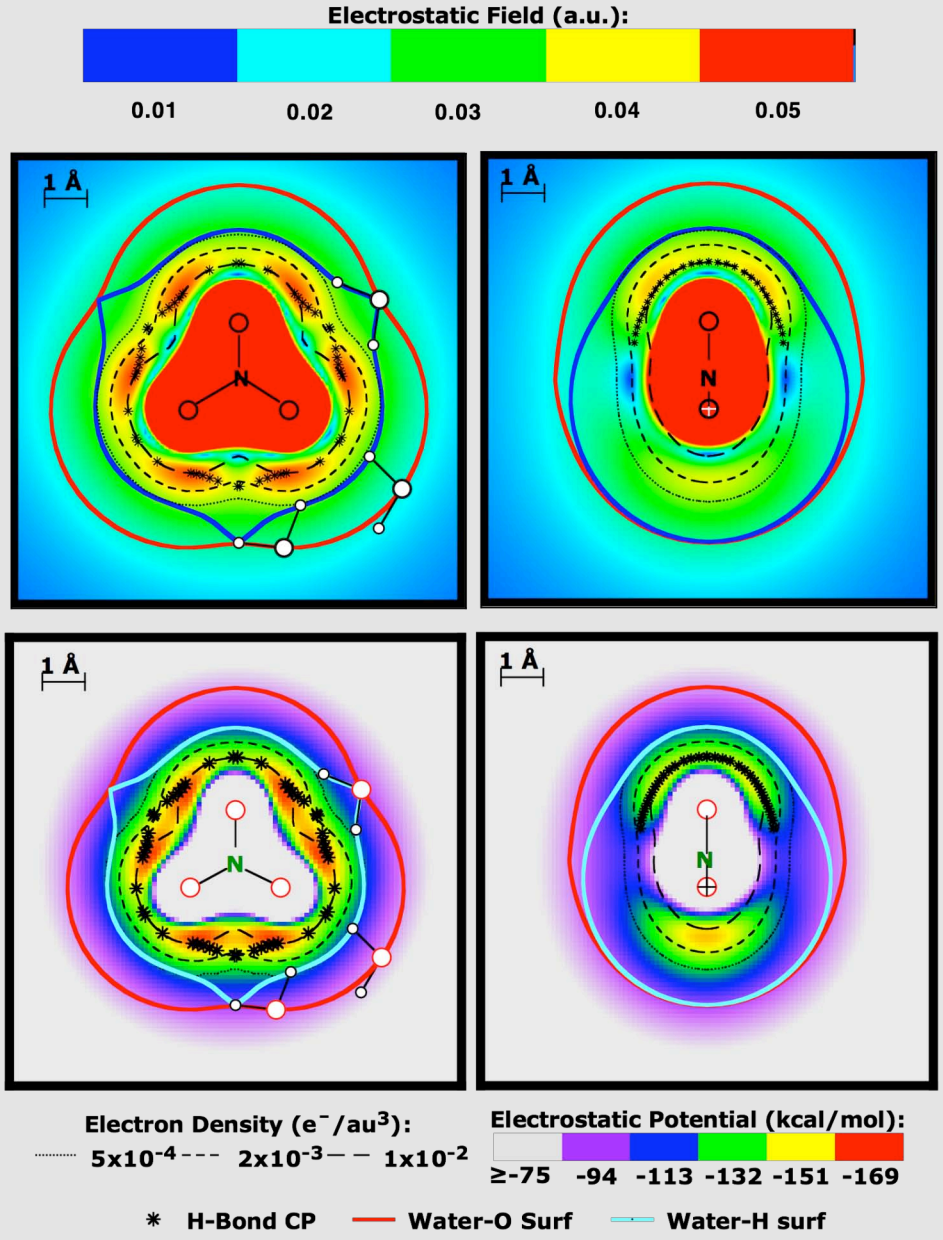
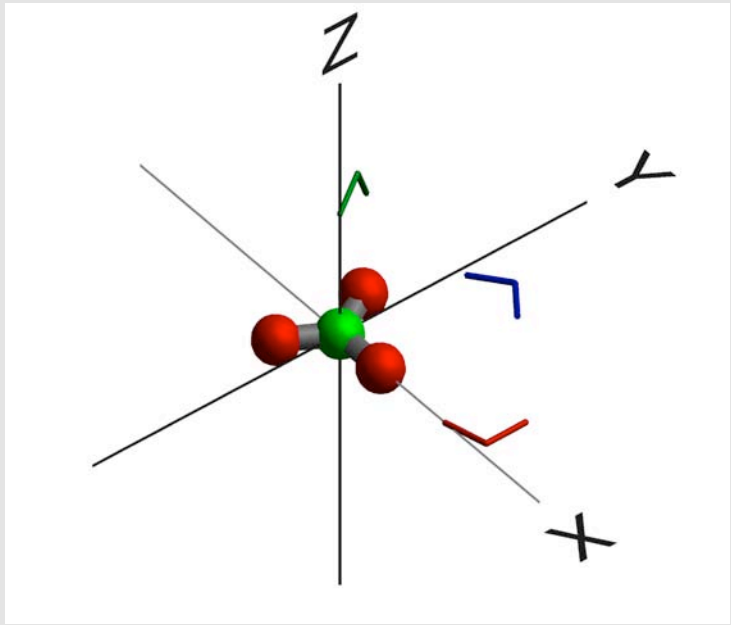
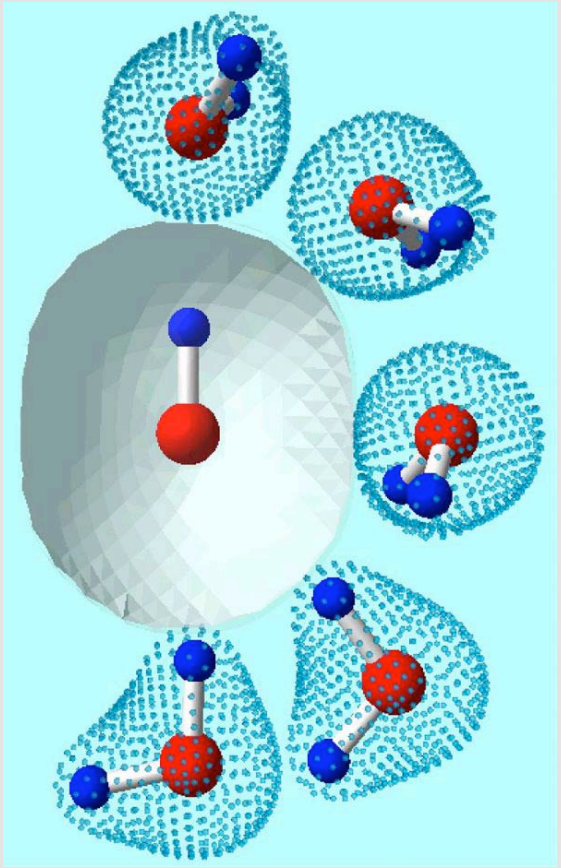


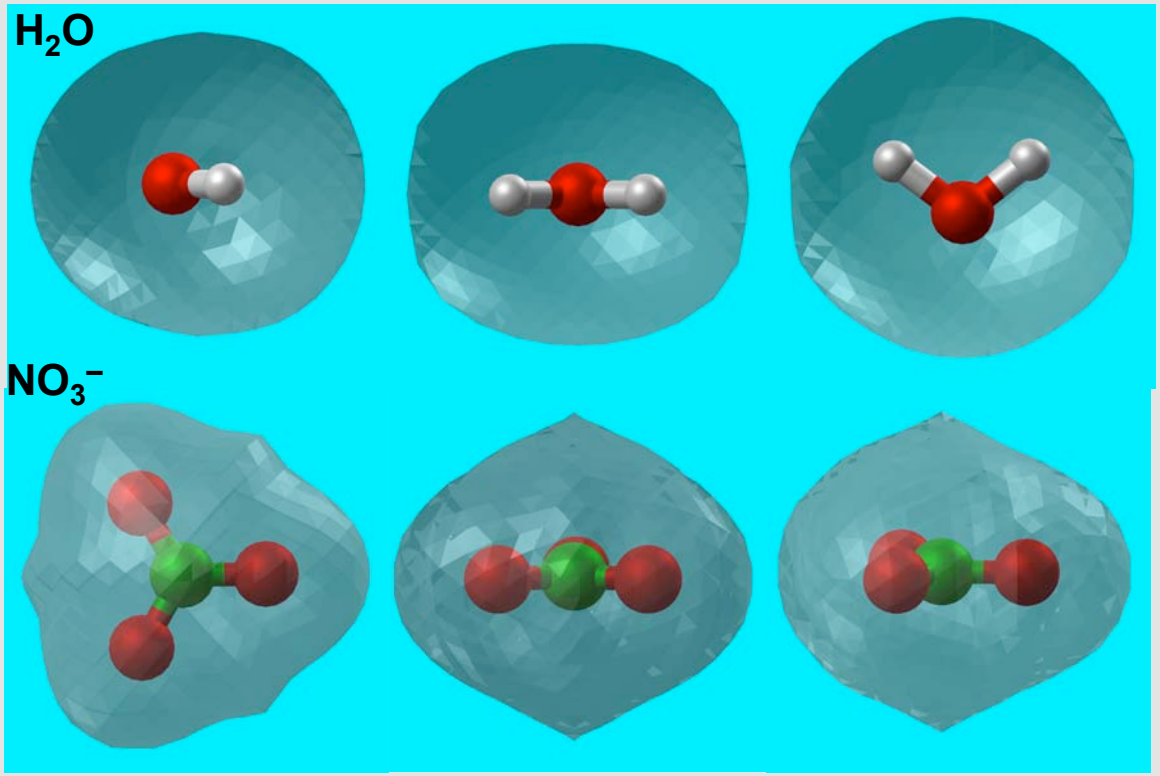


A cavity for nitrate ion with large radius over nitrogen and small radii over oxygens is most consistent with the Electrostatic Potential/Field around nitrate ion and with the nitrate-water surface of minimum interaction energy.

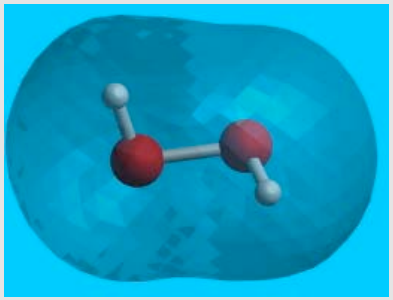
Ab Initio Cavities Defined by Rolling Water Around the Solute

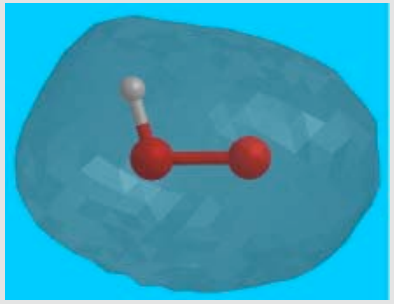


T Autrey, AK Brown, DM Camaioni, M Dupuis, NS Foster, and A Getty, *J Am Chem Soc*, **2004**, *126*, 3680



H_2O_2





HO_2

Hydration Free Energies (kcal/mol) … Ab Initio Cavity Continuum Model

Solute	$\Delta_s G^*$ Electro-static	$\Delta_s G^*$ cav, dis-rep	$\Delta_s G^*$	$\Delta_s G^*$ Expt
OH	-6.3	1.9	-4.4	-3.5 ± 1.5
H_2O	-8.4	2.1	-6.3	-6.32
HO_2	-8.8	2.8	-6.0	-7 ± 2
H_2O_2	-10.8	2.0	-8.8	-8.6
NO_3^-	-67.2	2.6	-64.6	-65 ± 1

- Cavities defined by 0.073 ‘rolling’ water electron isodensity contour
- Electrostatic hydration energy – Chipman’s SSC(V)PE model (HONDO)
- Cavity, dispersion and repulsion energies from scaled particle theory and interaction potentials (Gaussian98 PCM)

New Parameterization … Free Energy of Solvation for Oxoanions and Related Neutral Compounds, XO_m^{n-}

DM Camaioni, M Dupuis, and J Bentley, *J Phys Chem A, **2003**, 107,* 5778

Training Set:

Anions:

O^-, O_2^-, HCO_2^-, O_3^-, NO_2^-, ClO_2^-, NO_3^-

Neutrals:

SO_2, ClO_2, O_3, CO_2, NO_2, O_2

Cavity Radii related to Potential-Derived Atomic Charges:

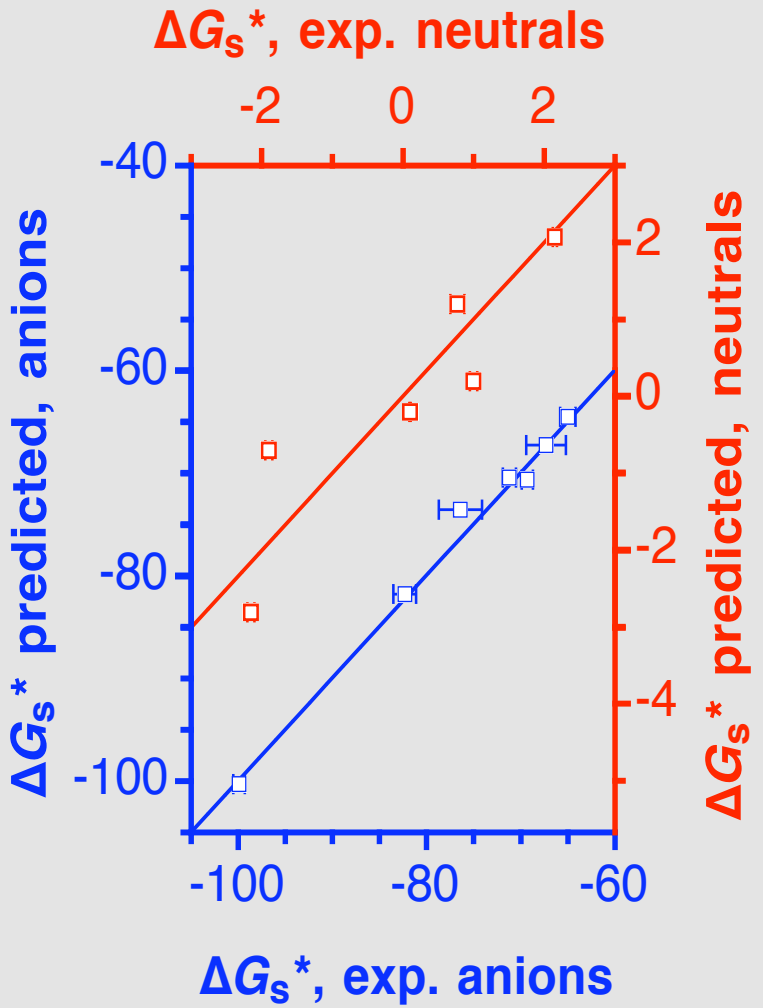
$$R_O = -0.24 \times |Q_O| + 1.69$$

$$R_X = +0.44 \times |Q_X| + a \times D_{X-O}$$

$$a = 1.37 \; for \; neutrals$$

$$a = 1.51 \; for \; anions$$

***Mean unsigned errors*: ≤ 1 kcal/mol**



Theoretical Characterizations … Current and Future Directions

- Extend protocol for defining continuum solvation cavities based on potential-derived charges and water interactions
  - Dianions, oxometalates
  - OH, NH and CH functional groups
- Explore applications to transition state structures
  - $HO\bullet + HOOH \rightarrow HOH + \bullet OOH$
- Use methods to model reactions of complexants
  - Al(III)-catalyzed oxidation by nitrite ion
  - Oxidations by O_2 and NO_2