

REPORT DOCUMENTATION PAGE

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4. TITLE AND SUBTITLE Final Report: Enabling Computational Technologies for the Accurate Prediction/Description of Molecular Interactions in Condensed Phases			5a. CONTRACT NUMBER W911NF-09-1-0377		
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			5c. PROGRAM ELEMENT NUMBER 611102		
6. AUTHORS Christopher J. Cramer			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES University of Minnesota - Minneapolis 450 McNamara Alumni Center 200 Oak Street SE Minneapolis, MN 55455 -2070				8. PERFORMING ORGANIZATION REPORT NUMBER	
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14. ABSTRACT We developed and applied models to compute accurately the molecular interactions between a mobile or stationary phase and a target substrate or analyte, which are fundamental to diverse technologies, e.g., sensor or separation design. With these models we achieved good success in predicting key chemical properties in condensed phases, including, inter alia, optical spectra, acidity/basicity (including at multiple sites), and electrochemical redox potentials.					
15. SUBJECT TERMS solvation, reduction potential, thermochemistry, electronic structure					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Christopher Cramer
UU	UU	UU	UU		19b. TELEPHONE NUMBER 612-624-0859

## **Report Title**

Final Report: Enabling Computational Technologies for the Accurate Prediction/Description of Molecular Interactions in Condensed Phases

### **ABSTRACT**

We developed and applied models to compute accurately the molecular interactions between a mobile or stationary phase and a target substrate or analyte, which are fundamental to diverse technologies, e.g., sensor or separation design. With these models we achieved good success in predicting key chemical properties in condensed phases, including, inter alia, optical spectra, acidity/basicity (including at multiple sites), and electrochemical redox potentials.

**Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:**

**(a) Papers published in peer-reviewed journals (N/A for none)**

<u>Received</u>	<u>Paper</u>
03/18/2013 10.00	Aleksandr V. Marenich, Abir Majumdar, Michelle Lenz, Christopher J. Cramer, Donald G. Truhlar. Construction of Pourbaix Diagrams for Ruthenium-Based Water-Oxidation Catalysts by Density Functional Theory, <i>Angewandte Chemie International Edition</i> , (12 2012): 12810. doi: 10.1002/anie.201206012
03/18/2013 11.00	Aleksandr V. Marenich, Christopher J. Cramer, Donald G. Truhlar. Generalized Born Solvation Model SM12, <i>Journal of Chemical Theory and Computation</i> , (01 2013): 609. doi: 10.1021/ct300900e
04/08/2012 7.00	Aleksandr V. Marenich, Steven V. Jerome, Christopher J. Cramer, Donald G. Truhlar. Charge Model 5: An Extension of Hirshfeld Population Analysis for the Accurate Description of Molecular Interactions in Gaseous and Condensed Phases, <i>Journal of Chemical Theory and Computation</i> , (02 2012): 0. doi: 10.1021/ct200866d
08/10/2011 3.00	Christopher J. Cramer, Donald G. Truhlar, Aleksandr V. Marenich. Sorting Out the Relative Contributions of Electrostatic Polarization, Dispersion, and Hydrogen Bonding to Solvatochromic Shifts on Vertical Electronic Excitation Energies, <i>Journal of Chemical Theory and Computation</i> , (09 2010): 2829. doi: 10.1021/ct100267s
08/10/2011 5.00	Aleksandr V. Marenich, Christopher J. Cramer, Donald G. Truhlar, Ciro A. Guido, Benedetta Mennucci, Giovanni Scalmani, Michael J. Frisch. Practical computation of electronic excitation in solution: vertical excitation model, <i>Chemical Science</i> , (12 2011): 0. doi: 10.1039/c1sc00313e
08/10/2011 4.00	Raphael F. Ribeiro, Aleksandr V. Marenich, Christopher J. Cramer, Donald G. Truhlar. The solvation, partitioning, hydrogen bonding, and dimerization of nucleotide bases: a multifaceted challenge for quantum chemistry, <i>Physical Chemistry Chemical Physics</i> , (07 2011): 10908. doi: 10.1039/c0cp02784g
08/13/2012 8.00	Aleksandr V. Marenich, Wendu Ding, Christopher J. Cramer, Donald G. Truhlar. Resolution of a Challenge for Solvation Modeling: Calculation of Dicarboxylic Acid Dissociation Constants Using Mixed Discrete–Continuum Solvation Models, <i>The Journal of Physical Chemistry Letters</i> , (06 2012): 1437. doi: 10.1021/jz300416r
08/13/2012 9.00	Varinia S. Bernales, Aleksandr V. Marenich, Renato Contreras, Christopher J. Cramer, Donald G. Truhlar. Quantum Mechanical Continuum Solvation Models for Ionic Liquids, <i>The Journal of Physical Chemistry B</i> , (08 2012): 9122. doi: 10.1021/jp304365v
09/10/2010 2.00	Raphael F. Ribeiro, Aleksandr V. Marenich, Christopher J. Cramer, Donald G. Truhlar. Prediction of SAMPL2 aqueous solvation free energies and tautomeric ratios using the SM8, SM8AD, and SMD solvation models, <i>Journal of Computer-Aided Molecular Design</i> , (04 2010): . doi:
09/10/2010 1.00	Junjun Liu, Casey P. Kelly, Alan C. Goren, Aleksandr V. Marenich, Christopher J. Cramer, Donald G. Truhlar, and Chang-Guo Zhan. Free Energies of Solvation with Surface, Volume, and Local Electrostatic Effects and Atomic Surface Tensions to Represent the First Solvation Shell (Reprint), <i>Journal of Chemical Theory and Computation</i> , (01 2010): . doi:

- 10/08/2014 15.00 Aleksandr V. Marenich, Junming Ho, Michelle L. Coote, Christopher J. Cramer, Donald G. Truhlar. Computational electrochemistry: prediction of liquid-phase reduction potentials, *Physical Chemistry Chemical Physics*, (08 2014): 15068. doi: 10.1039/c4cp01572j
- 10/08/2014 12.00 Aleksandr V. Marenich, Christopher J. Cramer, Donald G. Truhlar. Reduced and quenched polarizabilities of interior atoms in molecules, *Chemical Science*, (03 2013): 2349. doi: 10.1039/c3sc50242b
- 10/08/2014 14.00 Aleksandr V. Marenich, Christopher J. Cramer, Donald G. Truhlar. Uniform Treatment of Solute–Solvent Dispersion in the Ground and Excited Electronic States of the Solute Based on a Solvation Model with State-Specific Polarizability, *Journal of Chemical Theory and Computation*, (06 2013): 3649. doi: 10.1021/ct400329u
- 10/08/2014 13.00 I-F. Will Kuo, Brice F. Ngouana W., Matthew J. McGrath, Julius N. Ghogomu, Christopher J. Mundy, Aleksandr V. Marenich, Christopher J. Cramer, Donald G. Truhlar, J. Ilja Siepmann. Calculation of the Gibbs free energy of solvation and dissociation of HCl in water via Monte Carlo simulations and continuum solvation models, *Physical Chemistry Chemical Physics*, (06 2013): 13578. doi: 10.1039/c3cp51762d
- 11/26/2011 6.00 Raphael F. Ribeiro, Aleksandr V. Marenich, Christopher J. Cramer, Donald G. Truhlar. Use of Solution-Phase Vibrational Frequencies in Continuum Models for the Free Energy of Solvation, *The Journal of Physical Chemistry B*, (11 2011): 0. doi: 10.1021/jp205508z

**TOTAL: 15**

**Number of Papers published in peer-reviewed journals:**

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**(b) Papers published in non-peer-reviewed journals (N/A for none)**

<u>Received</u>	<u>Paper</u>
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**TOTAL:**

**Number of Papers published in non peer-reviewed journals:**

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**(c) Presentations**

- 245th National ACS Meeting (COMP), Universal Solvation Models: Theory and Application, Marenich, A. V.; Cramer, C. J.; Truhlar, D. G., New Orleans, LA, April 9, 2013.
- 223rd Electrochemical Society Meeting, Continuum Solvation Models for Computational Electrochemistry: Recent Advances, Marenich, A.; Cramer, C. J.; Truhlar, D. G., Calgary, Canada, May 16, 2013 (co-senior author, not presenter).
- Midwest Theoretical Chemistry Conference, Modeling Condensed Phase Effects on Structure and Spectroscopy, Urbana, IL, May 31, 2013.
- Challenges in Computational Homogeneous Catalysis - 2013, Modeling Catalysis Relevant to Energy Sustainability, Cramer, C. J., Stockholm, Sweden, June 13, 2013.

Number of Presentations: 0.00

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**Non Peer-Reviewed Conference Proceeding publications (other than abstracts):**

Received      Paper

**TOTAL:**

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

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**Peer-Reviewed Conference Proceeding publications (other than abstracts):**

Received      Paper

**TOTAL:**

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

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**(d) Manuscripts**

Received      Paper

**TOTAL:**

Number of Manuscripts:

---

**Books**

Received      Book

**TOTAL:**

Received

Book Chapter

**TOTAL:**

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**Patents Submitted**

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**Patents Awarded**

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**Awards**

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**Graduate Students**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

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**Names of Post Doctorates**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Aleksandr V. Marenich	0.50
<b>FTE Equivalent:</b>	<b>0.50</b>
<b>Total Number:</b>	<b>1</b>

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**Names of Faculty Supported**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Donald G. Truhlar	0.04	Yes
Christopher J. Cramer	0.04	
<b>FTE Equivalent:</b>	<b>0.08</b>	
<b>Total Number:</b>	<b>2</b>	

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**Names of Under Graduate students supported**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

**Student Metrics**

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: ..... 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense ..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 0.00

**Names of Personnel receiving masters degrees**

NAME

**Total Number:**

**Names of personnel receiving PHDs**

NAME

**Total Number:**

**Names of other research staff**

NAME

PERCENT SUPPORTED

**FTE Equivalent:**

**Total Number:**

**Sub Contractors (DD882)**

**Inventions (DD882)**

## Scientific Progress

- 1) We developed a solvation model for primarily non-polar solvents (more accurately, solvents without significant hydrogen-bond donating or accepting capability) that replaced many empirical parameters with universal dispersion and cavitation terms, with the former deriving from computed spherically averaged molecular polarizabilities. This model is of special utility because it provides a means to estimate changes in dispersion interactions associated with electronic excitations, through analysis of changes in polarizabilities.
- 2) We showed that continuum solvent models, in combination with explicit simulations, can accurately predict acid dissociation equilibrium constants for strong acids in water over a wide range of state points.
- 3) We demonstrated the rather surprising phenomenon that atomic polarizability is NOT a transferable property and that molecular polarizabilities derive primarily from the sum of atomic effects at the periphery of a molecule, with interior atoms contributing very little to overall polarization.
- 4) Through our own work and a careful review of the literature, we established uncertainty estimates and provided guidance on best practices for the prediction of equilibrium reduction potentials of all sorts.

## Technology Transfer

The SMx models (and the underlying CMx charge models) were been coded into many software packages, including several distributed freely, under license, by the University of Minnesota (see [comp.chem.umn.edu/mccdir/software.htm](http://comp.chem.umn.edu/mccdir/software.htm)). Since 1996, many academic, governmental, and commercial organizations have successfully downloaded AMSOL (500+ licenses), GAMESSPLUS (300+ licenses), HONDOPLUS (150+ licenses), OMNISOL (125+ licenses), and SMXGAUSS (125+ licenses). We are continuing to incorporate all of our SMx developments into these codes and we anticipate continued brisk demand. We have ongoing developmental relationships with the commercial distributors of JAGUAR and Q-CHEM, and we will make our new developments available in this manner as well. Three years ago, SMD was incorporated into Gaussian 09, and it has already been cited more than 1000 times. We consider this to have been a major success of this project.