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6. AUTHOR(S)
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13. ABSTRACT *(Maximum 200 words)*

Large scale computer simulations are being performed to study heterogeneous electron transfer processes and related phenomena across the electrode/electrolyte interface. This research introduces microscopic computer simulation methods into the field of electrochemistry, impacting such important technologies as advanced power sources, sensors, displays, corrosion prevention, and electrochemical synthesis. A specific goal is to explicitly characterize the interplay of the solvent reorganization required for the electron transfer event near an electrode surface with chemically reactive (e.g., bond-breaking) processes. Novel "first principles" simulations are being carried out with Car-Parrinello molecular dynamics techniques to treat the electronic structure of the system while computing the nuclear motions of the solvent molecules using no empirical approximations. Newly developed theoretical methods are also being implemented in the simulations which employ quantum path integral approaches. All of these methods are required to fully characterize highly complex condensed matter problems such as heterogeneous electron transfer.

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OFFICE OF NAVAL RESEARCH

END–OF–YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT: N00014-97-J-0265

PR Number: 97PR03964-01

"Computer Simulation of Electrochemical Processes"

Principal Investigator: Gregory A. Voth

University of Utah

Department of Chemistry
University of Utah
Salt Lake City, UT 84112

Submitted: June 1, 1998

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OFFICE OF NAVAL RESEARCH
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

PR Number: 97PR03964-01
Contract/Grant Number: N00014-97-J-0265
Contract/Grant Title: Computer Simulation of Electrochemical Processes
Principal Investigator: Gregory A. Voth

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Salt Lake City, UT 84112

Phone Number: (801) 581-7272
Fax Number: (801) 581-4353
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http address: N/A

a. Number of papers submitted to refereed journals, but not published (list attached): 7

b. Number of papers published in refereed journals (list attached): 3

c. Number of books or chapters submitted, but not yet published (list attached): 0

d. Number of books or chapters published (list attached): 0

e. Number of printed technical reports/non-refereed papers (list attached): 0

f. Number of patents filed: 0

g. Number of patents granted: 0

h. Number of invited presentations (list attached): 10

i. Number of submitted presentations: 0

j. Honors/Awards/Prizes for contract/grant employees (list attached): 2

k. Total number of **Full-time equivalent** Graduate Students and Post-Doctoral associates supported during this period, under this R&T project number:

Graduate Students: 1.0

Post-Doctoral Associates: 0.5

including the number of,

Female Graduate Students: 0

Female Post-Doctoral Associates: 0.0

the number of

Minority Graduate Students: 0

Minority Post-Doctoral Associates: 0

and, the number of

Asian Graduate Students: 0

Asian Post-Doctoral Associates: 0

l. Other funding (list attached)

a. List of Papers Submitted to Refereed Journals, but Not Yet Published

1. Y. Boroda and G. A. Voth, "A Theory for Electron Transfer between an Electrode and a Multilevel Acceptor/Donor Species in an Electrolyte Solution," (submitted).

2. A. Calhoun and G. A. Voth, "The Computer Simulation of Electron Transfer Processes Across the Electrode/Electrolyte Interface: The Role of Polarizability," (submitted).

3. M. T. M. Koper and G. A. Voth, "A Three-Dimensional Potential Energy for Dissociative Adsorption and Associative Desorption at Metal Electrodes," J. Chem. Phys. (in press).

4. A. Calhoun and G. A. Voth, "The Computer Simulation of Correlated Electron Transfer Across the Electrode/Electrolyte Interface Involving Multiple Redox Species," J. Chem. Phys. (submitted).

5. A. Calhoun and G. A. Voth, "Isotope Effects in Electron Transfer Across the Electrode/Electrolyte Interface: A Measure of Solvent Mode Quantization," J. Phys. Chem. (submitted).

6. A. Calhoun, M. T. M. Koper, and G. A. Voth, "A Direct Calculation of the Rates of Electrochemically Catalyzed Chemical Reactions," Science (to be submitted).

7. A. Calhoun, M. T. M. Koper, and G. A. Voth, "A Comparison of Simulation and Theory for the Rates of Bond-Breaking Electron Transfer Reactions at Metal Electrodes: ," J. Am. Chem. Soc. (submitted)

b. List of Papers Published in Refereed Journals

1. C. P. Ursenbach, A. Calhoun, and G. A. Voth, "A First-Principles Simulation of the Water/Semiconductor Interface", J. Chem. Phys. **106**, 2811-2818 (1997).

2. Y. Boroda, A. Calhoun, and G. A. Voth, "A Theory for Electron Transfer across the Electrode/Electrolyte Interface Involving Multiple Redox Ions," J. Chem. Phys. **107**, 8940-8954 (1997).

3. M. T. M. Koper and G. A. Voth, "A Theory for Adiabatic Bond Breaking Electron Transfer Reactions at Metal Electrodes," Chem. Phys. Lett. **282**, 100-106 (1998).

c. List of books or chapters submitted, but not yet published

None

d. List of books or chapters published

None

e. List of Printed Technical Reports/Non-Refereed Papers

None

h. List of Invited Presentations

1. "The Theory and Simulation of Condensed Phase Quantum Dynamics", James Franck Institute Seminar, University of Chicago, May, 1997.

2. "Theoretical and Computational Approaches for Electron Transfer Across the Electrode/Electrolyte Interface", Invited Seminar for the Electrochemical Double Layer Symposium Commemorating 50 Years of D. C. Grahame's Ground-Breaking Paper, 1997 National Spring Meeting of the Electrochemical Society, Montreal, Canada, May, 1997.

3. "Path Integral Centroid Methods in Condensed Phase Quantum Dynamics", Invited Lecture, International Summer School on the Computer Simulation Of Rare Events And The Dynamics Of Classical And Quantum Condensed Phase Systems, Lerici, Italy, July, 1997.

4. "Including Quantum Effects in Molecular Dynamics Simulations", Department of Defense CHSSI Workshop, Dayton, Ohio, August, 1997.

5. "The Quantum Dynamics of the Excess Proton in Water", Invited Lecture at the Deutsche Bunsen-Gesellschaft für Physikalische Chemie International Discussion Meeting on "Hydrogen Transfer: Experiment and Theory," Freie Universität, Berlin, Germany, September, 1997

6. "The Theory and Simulation of Condensed Phase Quantum Dynamics", Kansas Center for Advanced Scientific Computing Seminar, University of Kansas, October, 1997.

7. "Proton Translocation in Water and Biomolecular Systems", Joint Chemistry and Physics Colloqium, Swarthmore College, November, 1997

8. "The Theory and Simulation of Condensed Phase Quantum Dynamics", Invited Lecture in the Symposium on Time Propagation Methods in Chemistry, Fifth Chemical Congress of North America, Cancun, Mexico, November, 1997.

9. "Feynman Path Centroid Methods for Condensed Phase Quantum Dynamics", Invited Lecture at the Los Alamos Workshop on Novel Monte Carlo Algorithms and Their Applications, Los Alamos National Lab, New Mexico, January, 1998.

10. "Nonadiabatic Transitions and Quantum Rate Processes", International Conference on Molecular Science of Excited States and Nonadiabatic Transitions, Institute for Molecular Science, Okazaki, Japan, March, 1998.

j. List of Honors/Awards/Prizes for Contract/Grant Employees

1. Elected Fellow of the American Physical Society, 1998
2. IBM Corporation Faculty Research Award, 1997

l. Other Funding

1. The National Science Foundation (CHE-9712884), "Theoretical and Computational Studies of Quantum Dynamical Processes in Condensed Matter": $354,000 total costs for three years, 1/1/98 – 12/31/00. A total of $118,000 was received this year.

   This research funding is unrelated to the ONR grant.

2. The Office of Naval Research (AASERT Training Grant): $124,583 total costs for three years, 6/1/95 – 5/31/98. $41,528 was received this year.

   This research funding is for charge (primarily proton) transfer and is complementary to the core ONR project as stipulated by the AASERT Program.

3. The Air Force Office of Scientific Research (F49620-97-1-0023), "Computational Studies of High Energy Density Materials: Stability and Synthesis": $360,000 total costs for three years, 1/1/97– 12/31/99 $120,000 was received this year.

   This research funding is for atomic impurities in solid hydrogen and solvent effects in high energy density matter and is unrelated to the ONR grant.

4. The National Institutes of Health (1R01-GM-53148), "Simulations of Proton Translocation in Biomolecules": $395,585 total costs for three years, 5/1/96 – 4/30/99. $121,837 was received this year.

   This research funding is for proton transfer in biomolecular systems and is unrelated to the ONR grant.

Part II

Principal Investigator: Gregory A. Voth

Telephone Number: (801) 581-7272

ONR Scientific Officer: P. P. Schmidt

Program Objective:

Large scale computer simulations are being performed to study heterogeneous electron transfer processes and related phenomena across the electrode/electrolyte interface. *This research introduces microscopic computer simulation methods into the field of electrochemistry, impacting such important technologies as advanced power sources, sensors, displays, corrosion prevention, and electrochemical synthesis.* A specific goal is to explicitly characterize the interplay of the solvent reorganization required for the electron transfer event near an electrode surface with chemically reactive (e.g., bond-breaking) processes. Novel "first principles" simulations are being carried out with Car-Parrinello molecular dynamics techniques to treat the electronic structure of the system while computing the nuclear motions of the solvent molecules using no empirical approximations. Newly developed theoretical methods are also being implemented in the simulations which employ quantum path integral approaches. All of these methods are required to fully characterize highly complex condensed matter problems such as heterogeneous electron transfer.

Significant Results during the Last Year

During the last year, there have been three significant developments in this research program. The first was the formulation and application of a computer simulation method to calculate the free energies for adiabatic heterogeneous electron transfer (ET) across the water/metal electrode interface for realistically high redox ion concentrations in which the electron transfer events become correlated. The second development was the first *ab initio* simulation of a water/metal interface. In the latter it was found that the electronic states of the electrode significantly mix with the water molecules and are transported some distance from the electrode surface through water hydrogen bonds, affecting the effective coupling between an electrode and an aqueous redox species. The third development is the formulation of a theoretical basis to describe electrochemical ET reactions which induce chemically reactive (e.g., bond-breaking) events in the redox species. The famous solvent free energy curve picture of Marcus must be generalized in this case to be multidimensional

free energy surface, and the resulting theory is now being implemented within the context of largescale computer simulations. In light of these three developments, the computational modeling many realistic electrochemical systems is now at hand.

Summary of Plans for Next Year's Work

In the next year, the focus will be primarily on two problems: (1) *ab initio* molecular dynamics simulations of the electronic states of the water/metal interface for Cu and Ag electrodes, including simulations of a redox ion in water near the metal electrode surface to determine the effective electronic exchange and the role of the perturbed electronic state densities on that exchange; and (2) the computer simulation of electron transfer processes across the electrode/electrolyte interface which induce chemical reactions (e.g., bond-breaking) using our new theoretical formalism. The focus in the first case will be to calculate both the electrode surface structure and the interface electronic state properties using first principles ("Car-Parrinello") computer simulation techniques, and to determine the effects of these properties on the ET rate constant. These simulations explicitly treat the electrons of both the electrode and the water molecules during the molecular dynamics simulation. The focus in the second case will be to explicitly characterize both the thermodynamic and dynamical nature of the electrochemically induced reactive processes of redox species near an electrode.

Graduate Students Working on the Project

(1) Mr. Brian Gau

Post-Doctorals Working on the Project

(1) Dr. Alain Mazzolo

The Computer Simulation of Electrochemical Processes

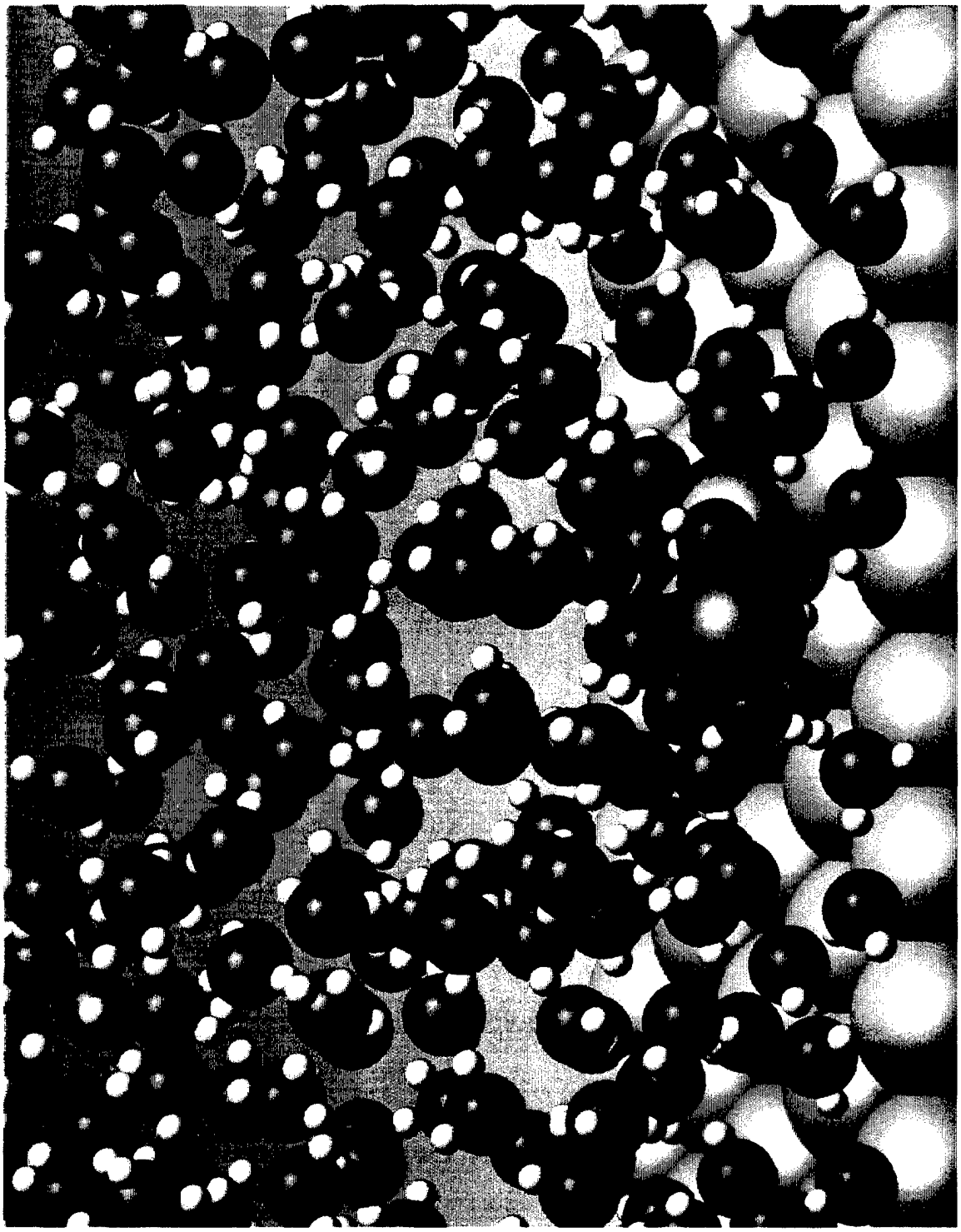
Gregory A. Voth
University of Utah

- **Objective**: To develop and implement largescale *computer simulations* of heterogeneous electron transfer processes across electrode/electrolyte interfaces and related phenomena.

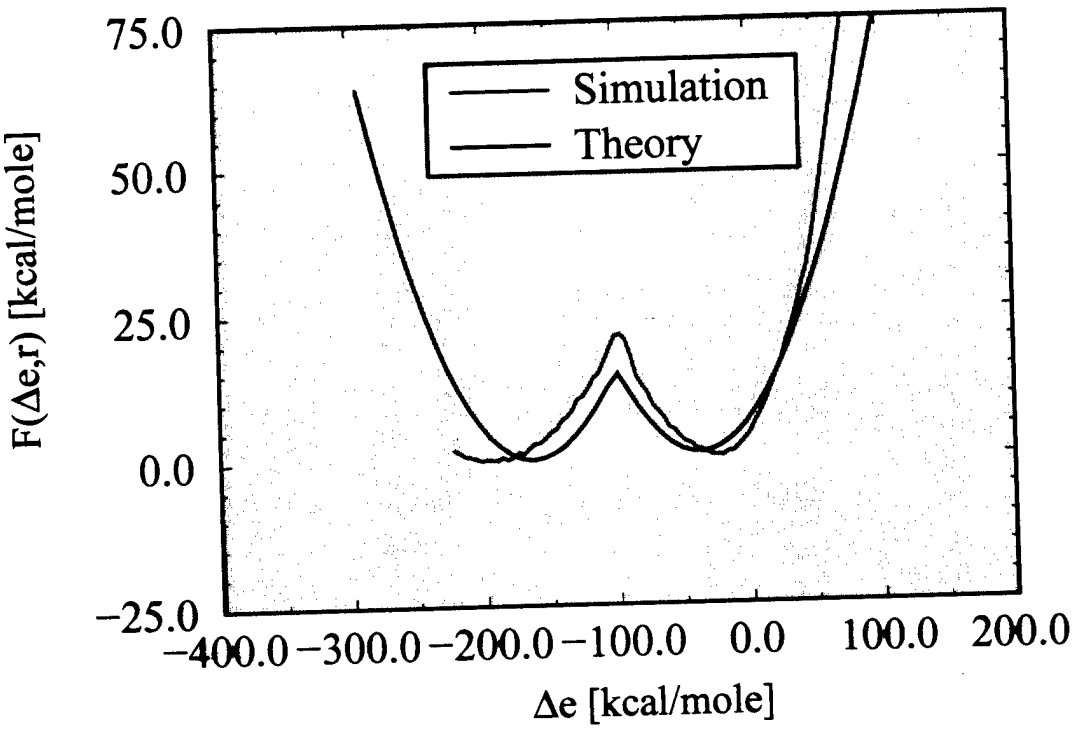
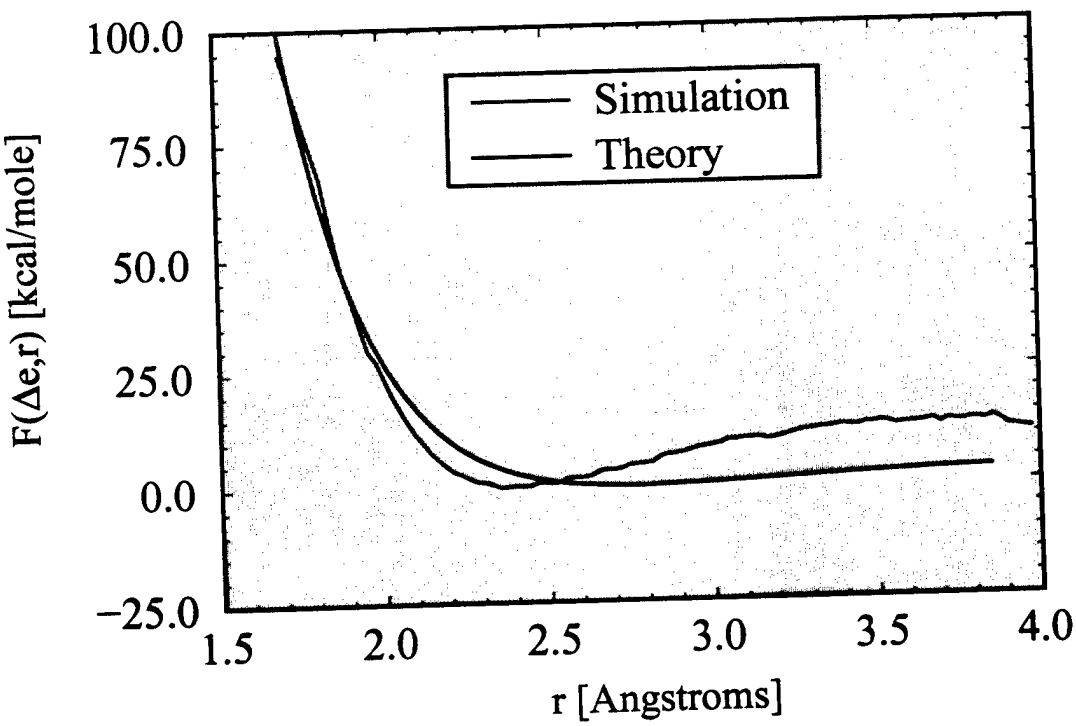
- **Approach**: Novel theoretical approaches are required to carry out this research program, including *ab initio* molecular dynamics methods to study the electronic properties of the electrode/electrolyte interface.

- **Accomplishment**: The first molecular dynamics study of a chemically reactive process (e.g., bond-breaking) induced by electrochemical electron transfer has been carried out (cf. figure next page for CH_3Cl dissociation at the interface with a Pt electrode). On the subsequent page is shown the theoretically predicted free energy surface in comparison with the one obtained through explicit computer simulation. The surface is a function of both the Marcus solvation coordinate and the C-Cl bond distance. The predictions of theory are quantitatively incorrect for the solvent reorganization contribution to the barrier, while they are qualitatively incorrect for the free energy curve along the dissociative C-Cl bond distance.

- **Impact**: The important tool of computer simulation has been introduced into the field of electrochemistry and related phenomena. These techniques will impact the development of such important technologies as advanced batteries, sensors, displays, corrosion prevention, and electrochemical synthesis and processing.



Bond Breaking ET Free Energy Barrier: Solvent Coordinate



Bond Breaking ET Free Energy Barrier: C-Cl Bond Dissociation Coordinate