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FINAL REPORT

Theory of Electron Transfer Reactions

by

Rudolph A. Marcus
California Institute of Technology
Division of Chemistry and Chemical Engineering
Pasadena, CA

July 1, 1994

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I. Research Objectives and Conclusions

An objective of the research performed on this grant is the understanding of the detailed behavior of a variety of electron transfer processes. Theories were developed for (a) the rate of electron transfer between a reagent in one liquid phase and another in a second (immiscible) liquid or polymer, (b) the rate of long distance electron transfer in proteins, (c) charge transfer spectra in frozen media, (d) scanning tunneling microscopy (STM) of molecular adsorbates, and (e) analysis of models of solvents used in computer simulations of electron transfer, particularly examining the error incurred by their common neglect of the electronic and vibrational contributions of the solvent's dielectric response.

The results of these studies were published in a series of articles and technical reports and are listed later in this report.

II. Highlighted Presentation and Award

Of the various presentations and awards listed below, the most significant one during this contractual period has been the 1992 Nobel Prize in Chemistry. This prize was given for the P.I.'s theory of electron transfer reactions, research for which the Office of Naval Research has provided vital support in the early and subsequent years. The award address was described in several ONR Technical Reports (Technical Report No. 27, for example). The P.I.'s Nobel address has also been reprinted in the Naval Reviews 45, No. 4 (1993) - 46, No. 1 (1994), which was edited by Dr. Peter Schmidt of ONR. An article by Dr. Schmidt describes events surrounding the awarding of this

prize, and the volume also contains related research contributions by a number of ONR grantees.

III. Three Significant Publications

In one sense, the most unusual publication was the principal investigator's Nobel address (*e.g.*, Technical Report No. 27, *Rev. Mod. Phys.* 65, 599 (1993)). It is largely a historical review of the P.I.'s previous theoretical work on electron transfer. Instead, the three publications selected below describe new research by the P.I and his group:

1. Theory of Electron-Transfer Rates Across Liquid-Liquid Interfaces.

2. Relationships and Application (Technical Report No. 16)

In this study a theoretical treatment of the rate of electron transfer from a reactant in one liquid phase to a reactant in a second, immiscible phase is described. The factors which influence the electron transfer rate were included in the theory and are of two types, geometrical and solvent reorganizational. The theory itself was prompted by new experiments in which the rate of this type of electron transfer was measured for the first time. Electron transfer from a reactant in a liquid to a reactant embedded in a polymer that coats an electrode represents another type of system to which the theory can be applied.

2. Correlation Between Theory and Experiment in Electron-Transfer Reactions in Proteins: Electronic Couplings in Modified Cytochrome c and Myoglobin Derivatives (Technical Report No. 31)

A theoretical treatment of long range electron transfer in proteins is given in this report. It combines a simple quantum chemistry method ("extended Hückel") and an artificial intelligence (AI) method for

implementing it. The AI method permitted the identification of the most important regions of the protein for the electron transfer. The results on the rates of electron transfer from a donor to acceptor in the protein correlated well with the experimental results of Harry Gray and co-workers of this Institute. In those studies, electron transfer in modified cytochrome c and myoglobin was treated.

3. A Theoretical Model of Scanning Tunneling Microscopy: Application to the Graphite (0001) and Au(111) Surfaces (Technical Report No. 23)

In this study a theory of scanning tunneling microscopy (STM) was formulated. It describes a method related to that used by the P.I. and others to treat long-range electron transfer in proteins (item 2 above) and in electron donor-acceptor pairs that are separated by rigid organic spacers (Technical Report No. 13). It combines that method with a correspondingly simple model used frequently in the solid state physics literature for the discussion of the electronic structure of solids ("tight binding method"). This Report, together with Technical Reports 20 and 22, represent the first steps in one of the new directions of research of the P.I. and his coworkers: electronic properties of solid surfaces and adsorbates of interest in long-range electron transfer. Using these methods it is planned to see whether a simple quantum chemistry model (extended Hückel/tight binding) will serve to explain some unusual results found in the STM of various adsorbates on graphite: moiré patterns, and the dependence of the STM image on the bias voltage (pattern of graphite *vs.* pattern of adsorbate).

IV. Undergraduate, graduate and post-doctoral associates funded through the grant

Graduate students: C. P. Hsu, X. Song

Post-doctoral Associates: A. Stuchebrukov, P. Siddarth, and H. Ou-Yang

V. Publications and Technical Reports

1. Reorganization Free Energy for Electron Transfers at Liquid-Liquid and Dielectric Semiconductor-Liquid Interfaces, R. A. Marcus, *J. Phys.Chem.* **94**, 1050(1990), (Technical Report No. 10).
2. Dynamics of Electron Transfer for a Nonsuperexchange Coherent Mechanism. I., R. Almeida and R. A. Marcus, *J. Phys.Chem.* **94**, 2973(1990), (Technical Report No. 11).
3. Dynamics of Electron Transfer for a Nonsuperexchange Coherent Mechanism. II. Numerical Calculations, R. Almeida and R. A. Marcus, *J. Phys.Chem.* **94**, 2978(1990), (Technical Report No. 12).
4. On the Theory of Electron-Transfer Rates Across Liquid-Liquid Interfaces, R. A. Marcus, *J. Phys.Chem.* **94**, 4152, 7742(1990), (Technical Report No. 13).
5. Vibrational Energy Redistribution Across a Heavy Atom, S. M. Lederman, V. López, V. Fairén, G. A. Voth, and R. A. Marcus, *Chem. Phys.* **139**, 171(1989), (Technical Report No. 14).
6. On the Theory of Charge-Transfer Spectra in Frozen Media, R. A. Marcus, *J. Phys.Chem.* **94**, 4963(1990), (Technical Report No. 15).

7. Theory of Electron-Transfer Rates Across Liquid-Liquid Interfaces. 2. Relationships and Application, R. A. Marcus, *J. Phys.Chem.* **95**, 2010(1991), (Technical Report No. 16).
8. Schrödinger Equation for Strongly Interacting Electron Transfer Systems, R. A. Marcus, *J. Phys.Chem.* **96**, 1753(1992), (Technical Report No. 17).
9. Calculation of Electron Transfer Matrix Elements for Bridged Systems Using a Molecular Fragment Approach, P. Siddarth and R. A. Marcus, *J. Phys.Chem.* **96**, 3213(1992), (Technical Report No. 18).
10. Theory of Electron Transfer Reactions and Comparison with Experiments, R. A. Marcus and P. Siddarth, In *Photoprocesses in Transition Metal Complexes, Biosystems and Other Molecules: Experiment and Theory*, E. Kochanski, ed. (Kluwer, Norwall, Massachusetts, 1992) p. 49, (Technical Report No. 19).
11. Tight-Binding Approximation for Semi-Infinite Solids. Application of a Transform Method and of Delta Function Normalization, R. A. Marcus, *J. Chem. Phys.* **98**, 5604(1993), (Technical Report No. 20).
12. Electron Transfer Reactions in Proteins: An Artificial Intelligence Approach to Electronic Coupling, P. Siddarth and R. A. Marcus, *J. Phys. Chem.* **97**, 2400(1993), (Technical Report No. 21).

13. Surface Properties of Solids Using a Semi-Infinite Approach and the Tight-Binding Approximation, H. Ou-Yang, B. Källebring and R. A. Marcus, *J. Chem. Phys.* **98**, 7405(1993), (Technical Report No. 22).
14. A Theoretical Model of Scanning Tunneling Microscopy: Application to the Graphite (0001) and Au (111) surfaces, H. Ou-Yang, B. Källebring and R. A. Marcus, *J. Chem. Phys.* **98**, 7565(1993), (Technical Report No. 23).
15. Electron-Transfer Reactions in Proteins: Electronic Coupling in Myoglobin, P. Siddarth and R. A. Marcus, *J. Phys. Chem.* **97**, 6111(1993), (Technical Report No. 24, 29*).
16. Outer-Sphere Electron Transfer in Polar Solvents: Quantum Scaling of Strongly Interacting Systems, Xueyu Song and Alexei A. Stuchebrukhov, *J. Chem. Phys.* **99**, 969(1993), (Technical Report No. 25).
17. Electron Transfer Reactions in Chemistry. Theory and Experiment, R. A. Marcus, *Angew. Chem.* **105**, 1161 (1993), (Technical Report No. 26).
18. Electron Transfer Reactions in Chemistry: Theory and Experiment, R. A. Marcus, *Rev. Mod. Phys.* **65**, 599 (1993), (Technical Report No. 27).
19. Electron Transfer Reactions in Chemistry. Theory and Experiment, R. A. Marcus, *Angew. Chem. Intl. Ed. Engl.* **32**, 1111(1993), (Technical Report No. 28).
20. Electron Transfer Reactions in Chemistry: Theory and Experiment, including biographical sketch, R. A. Marcus, In *Les Prix Nobel*, T. Frangsmyr,

ed., Nobel Foundation (Almqvist & Wiksell, Stockholm Sweden 1993) p. 63, (Technical Report No. 29A).

21. Quantum Correction for Electron Transfer Rates: Comparison of Polarizable vs. Nonpolarizable Descriptions of Solvent, Xueyu Song and R. A. Marcus, *J. Chem. Phys.* **99**, 7768(1993), (Technical Report No. 30).

22. Correlation Between Theory and Experiment in Electron Transfer Reactions in Proteins: Electronic Couplings in Modified Cytochrome *c* and Myoglobin Derivatives, P. Siddarth and R. A. Marcus, *J. Phys.Chem.* **97**, 13078(1993), (Technical Report No. 31).

* Inadvertently duplicated. Later replaced by Technical Report 29A.

VI. Awards (1989-93)

National Medal of Science, 1989

Theodore William Richards Medal, American Chemical Society,
Northeastern Section, 1990

Member, American Philosophical Society, 1990-

William Lloyd Evans Award, Ohio State University, Columbus, 1990

Honorary Fellow, Royal Society of Chemistry, 1991

Edgar Fahs Smith Award, American Chemical Society, Philadelphia Section,
1991

Remsen Award, American Chemical Society, Maryland Section, 1991

Linus Pauling Award, American Chemical Society, Oregon, Portland, and
Puget Sound Sections, 1991

Nobel Prize in Chemistry, 1992

Joseph O. Hirschfelder Prize in Theoretical Chemistry, 1993

Foreign Fellow, Royal Society of Canada, 1993

D.Sc. h.c. University of New Brunswick, St. John, Canada 1993

D.Sc. h.c. Queen's University, Kingston, Canada 1993

American Academy of Achievement Golden Plate Award, 1993

VII. Invited Presentations (1989-93)

Plenary Lecture, Eighth International Congress on Photosynthesis,
Stockholm, Sweden, August 6 - 11, 1989

Lectures, Summer School on Molecular Sciences, Institute of Atomic and
Molecular Sciences, Academia Sinica, Taiwan, August 28 - 30, 1989

Lecture, Symposium on The Frontier of Electrochemistry, Sendai, Japan,
September 15 - 16, 1989

Plenary Lecture, International Society of Electrochemistry Meeting,
Sendai, Japan, September 17 - 22, 1989

Lecture, Symposium on Electron Transfer Reactions in Inorganic, Organic
and Biological Systems, International Chemical Congress of Pacific
Basin Societies, December 17 - 22, 1989

Lecture and Session Chairman, Royal Society Discussion Meeting on
Intramolecular Motion and Chemical Reaction, London, United
Kingdom, February 14 - 15, 1990

Lecture, Reilley Award Symposium, Pittsburgh Conference on Analytical
Chemistry and Applied Spectroscopy, New York, NY,
March 6, 1990

Theodore Williams Richards Lecture, American Chemical Society,
Northeastern Section, Harvard University, March 8, 1990

Lecture, International Energy Agency Executive Conference on Solar
Photoconversion Processes for Recycling Carbon Dioxide from the
Atmosphere, Colorado Springs, Colorado, March 13 - 16, 1990

Lecture, Symposium on Large Amplitude Motions in Vibrationally-Excited
Molecules, American Chemical Society, Boston, Massachusetts,
April 22 - 27, 1990

ONR Electrochemical Sciences Grantees Meeting, Naval Oceans System
Center, San Diego, CA, July 11 - 12, 1990

Lecture, American Conference on Theoretical Chemistry, San Diego, CA,
July 30 - August 3, 1990

Organizer and Lecture, Symposium on Electron Transfer Reactions in
Chemistry and Biology, American Chemical Society National
Meeting, Washington, D.C., August 26 - 31, 1990

John Howard Appleton Lecture, Brown University, Providence, RI,
October 16, 1990

William Lloyd Evans Award Lecture, Ohio State University, Columbus, OH,
October 19, 1990

Closing Lecture, Faraday Discussion on Structure and Dynamics of Reactive
Transition States, Nottingham, England, March 25-27, 1991

Edgar Fahs Smith Memorial Lecture, University of Pennsylvania,
Philadelphia, PA, April 2, 1991

Glenn Brown Lectures, Case Western Reserve University, Cleveland, Ohio,
April 4, 1991

Lecture, Bernstein Symposium, Chemistry Department, UCLA,
April 19 - 20, 1991

Seminar, Chemistry Department, Duke University, Durham, NC,

April 22, 1991

Fritz London Memorial Lecture, Duke University, Durham, North Carolina,

April 23, 1991

Remsen Memorial Lecture, John Hopkins University, Baltimore, Maryland,

May 9, 1991

Opening Lecture, Satellite Meeting on Electron Transfer, International

Congress of Quantum Chemistry, Sophia-Antipolis, France,

June 25 - 28, 1991

Lecture, International Congress of Quantum Chemistry, Menton, France,

July 2 - 5, 1991

Lectures, NATO Advanced Seminar Institute, Photoprocesses in Transition

Metal Complexes, Biosystems and Other Molecules, Experiment and

Theory, Aussois, France, September 1 - 13, 1991

Lecture, Weissberger - Williams Lecture Series, Eastman Kodak Company,

Rochester, NY, October 11, 1991

George Fisher Baker Lectures in Chemistry, Cornell University, Ithaca, NY,

September 24 - October 24, 1991 (12 lectures)

Lecture, Gordon Research Conference on Electrochemistry, Holiday Inn,

Ventura, CA, January 20 - 24, 1992

Dupont Lecture, Harvey Mudd College, Claremont, CA, April 1, 1992

Lecture, Symposium on Novel Structural Mechanical and Electrical Aspects

of Chemical Interfaces, American Chemical Society Meeting, San

Francisco, CA, April 5 - 10, 1992

Northwest Lectures in Physical Chemistry, Molecular Science Research

Center, Battelle Pacific Northwest Laboratories, Washington State

University, and University of Washington, May 6 - 8, 1992

1991 Pauling Award Address, American Chemical Society, Oregon State University, Corvallis, WA, May 9, 1992

Lecture, IUPAC Symposium on "Experimental and Theoretical Aspects of Excited State Electron Transfer and related Phenomena," Pultusk, Poland, September 27 - October 2, 1992

Opening Lecture, Symposium in Models of the Electrode/Electrolyte Interface and Closing Lecture, Charge Transfer Processes at Liquid-liquid Interfaces, The Electrochemical Society, Toronto, Canada, October 11 - 16, 1992 (one lecture served for both)

C.A. McDowell Lectures, University of British Columbia, Canada, October 19 - 20, 1992

Nobel Lecture, Royal Swedish Academy of Sciences, Stockholm, Sweden, December 8, 1992

Lecture, Chemical Society of Uppsala, University of Uppsala, Uppsala, Sweden, December 13, 1994

Lecture, Department of Chemistry, University of Göteborg, Göteborg, Sweden December 14, 1992

Lecture, Chemical Society of Lund, University of Lund, Lund, Sweden December 15, 1992

Lecture, Danish Chemical Society, University of Copenhagen, Copenhagen, Denmark December, 16, 1992

Lecture, The Associates of California Institute of Technology, Pasadena, CA, January 25, 1993

Institute Lecture, California Institute of Technology, Pasadena, CA, February 1, 1993

Keynote Address, Research Directors Conference, Industrial Associates, California Institute of Technology, Pasadena, CA, February 4 - 5, 1993

Lecture, Athenaeum Dinner, California Institute of Technology, Pasadena,
CA, March 18, 1993

J.O. Hirschfelder Lectures, Madison, Wisconsin, April 12 - 14, 1993

Sigma Xi Thomas A. Edison Memorial Lecture, Naval Research Laboratory,
Washington, D.C., April 27, 1993

Lecture, Physics Colloquium, California Institute of Technology, Pasadena,
CA, May 6, 1993

General Session Speaker, Seminar Day, California Institute of Technology,
Pasadena, CA, May 15, 1993

Convocation Address, University of New Brunswick, Saint John, NB,
Canada, May 28, 1993

Convocation Address, Faculty of Arts and Science, Queen's University,
Kingston, Ontario, Canada, June 4, 1993

Summer Undergraduate Research Fellowships Lecture, California Institute
of Technology, Pasadena, CA, June 7, 1993

Lecture, American Academy of Achievement, Glacier Park Lodge, Glacier
Park, Montana, June 24 - 26, 1993

Lecture, Conference on Molecular Structure and Dynamics in Honor of Max
Wolfsberg, University of California at Irvine, Irvine, CA, July 11 - 16,
1993

Opening Lecture, Cursos de Verano, Laser Spectroscopy and Molecular
Dynamics, Universidad Complutense, Aguadulce, Spain, July 30 -
August 7, 1993

Opening Lecture, NATO Advanced Research Workshop on Photoinduced
Electron Transfer Reactions, Albufeira, Portugal, September 5 - 10, 1993

Lecture, California Institute of Technology Associates, San Francisco, CA,
September 18, 1993

Lecture, Caltech Freshman Camp, Catalina, CA, September 22, 1993

Nobel Laureate Lectures, California State University at Long Beach, Long
Beach, CA, September 29 - 30, 1993

Lecture, The McGill Society of Southern California, Queen Mary, Long
Beach, CA, October 30, 1993