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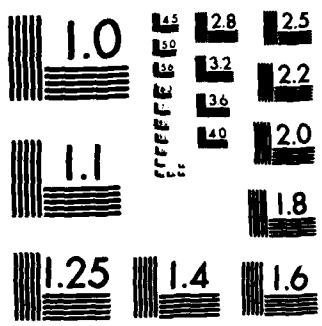

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER / 2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE *(and Subtitle)* Electronic Excitation in Molecular Collisions: Structural, Dynamic and Kinetic Considerations	5. TYPE OF REPORT & PERIOD COVERED 9/1978-12/1983 -Final Report 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) R.D. Levine	8. CONTRACT OR GRANT NUMBER(s) N-00014-78-C-0036
PERFORMING ORGANIZATION NAME AND ADDRESS Department of Physical Chemistry The Hebrew University of Jerusalem Jerusalem 91904, Israel	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Arlington, Virginia	12. REPORT DATE August, 1984 13. NUMBER OF PAGES 9
MONITORING AGENCY NAME & ADDRESS*(if different from Controlling Office)*	15. SECURITY CLASS. *(of this report)* unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

DISTRIBUTION STATEMENT *(of this Report)*

Approved for public release; distribution unlimited

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

18. SUPPLEMENTARY NOTES

Final report for the project

1984

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Electronic Luminescence, Potential energy surfaces, Branching ratio, Surprisal analysis, Information theory, Inversion procedures, Structure-reactivity correlations, Linear free energy relations, Chemiluminescent ion-molecule reactions, Multiphoton dissociation.

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

The factors governing chemical reactivity with special reference to the role of electronic energy in promoting the reaction and to the production of electronically excited species are examined. The problem is studied both in general terms (i.e., the development of the required theoretical framework) and in application to specific systems.

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S/N 0102-LF-014-6601

unclassified
SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

Research Grant N-00014-78-G-0036

1978 - 1983

Electronic Excitation in Molecular Collisions: Structural, Dynamic and Kinetic Considerations

FINAL REPORT

by

R.D. Levine
Principal Investigator

Contents*

*Arranged according to the 'Summary Questionnaire' of the ONR Physics Program.

1. Principal Investigator

R.D. Levine
Professor of Physical and Theoretical Chemistry
The Hebrew University of Jerusalem

2. Contract Description

The acquisition, storage and disposal of electronic energy by molecular collisions.

3. Scientific Problem

The factors governing chemical reactivity with special reference to the role of electronic energy in promoting the reaction and to the production of electronically excited species are examined. The problem is studied both in general terms (i.e., the development of the required theoretical framework) and in application to specific systems.

4. Technical Approach

Much of the work is based either directly or indirectly on the information theoretic approach to molecular collision theory, as pioneered and developed in Jerusalem.

5. Summary of Work

The annual progress has been presented in the four 'annual summary reports' issued during the project. Here therefore we shall discuss the five major areas where our efforts were mainly concentrated. Details are provided in the papers published under the support of this project which are listed in paragraph 6 below. Reference numbers are to that list.

(a) Multiphoton Dissociation

The framework for predicting and analyzing the fragmentation patterns in multiphoton ionization by visible/uv photons [11,18,19,20,29,30] seems to us to be the major practical development of the project. The theory has been subjected to many experimental tests and several of its predictions are yet to be verified. The 80/81 and 81/82 summary reports list many of the then verified predictions. Of special relevance are those studies dealing with the formation of electronically excited products [19,20,29,30]. Invited lectures on this work have been presented at both the 1982 and 1984 Gordon Research Conferences on Multiphoton Ionization/Dissociation.

(b) Potential Energy and Free Energy

During the earlier part of the project considerable attention was given to the correlation of structure (potential energy surface) and reactivity [1,4,5,6,7,8,9,13,14,15,21,24]. The 78/79 and 79/80 reports deal mainly with these developments. The reactivity-selectivity principle as discussed and documented in these papers has been followed up by several other workers. It offers a way of correlating large amounts of experimental data over many decades of variations.

(c) Surprisal Analysis of Chemiluminescent Reactions

The procedure proposed in [12] has now been incorporated in many other laboratories as part of their analysis of the raw data for reactions producing electronically excited products (and also when laser induced fluorescence is used as the method of detection).

(d) Information Theory

Our most recent paper on this topic [32] has been the subject of a feature article in Nature (28 June 1984). Lest we blush, we do not cite from that article but refer the interested reader to the literature. The reviewer in Nature also compares our work to other studies from NRL. A full length version of that paper has been prepared for publication [33]. A forerunner of that approach has been an early contribution [3] under this project. Other contributions in this context were [10] and [17].

(e) Statistical Dynamics

The combination of an information theoretic point of view with dynamical equations of motion has received considerable attention under this project [2,16,22,23,25,31]. The object is to compute only those details which do not get averaged over. The main conclusion is that the time evolution can be characterized as being 'as statistical as possible subject to constraints'.

The first demonstration that such an approach can be implemented for a realistic problem was provided in [2]. That turned out to be a pivotal paper receiving numerous citations in the literature. The approach pioneered therein is now being followed by at least a dozen research groups. The final chapter under the present project is [31] where the self consistent field (Hartree Fock) procedure has been obtained as a very special case of the general approach.

6. Publications

Published papers

1. R.D. Levine, Free Energy of Activation: Definition, Properties and Dependent Variables, J. Phys. Chem. 83, 159 (1979).

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22. P. Pfeifer, All-Time vs. Asymptotic Reduced Dynamics and Entropy in Finite Quantum Systems, Adv. Chem. Phys. 53, 351 (1983).

23. P. Pfeifer and R.D. Levine, A Stationary Formulation of Time Dependent Problems in Quantum Mechanics, J. Chem. Phys. 79, 5512 (1983).

24. E. Pollak and R.D. Levine, Maximal Entropy Approach to Reactivity and Selectivity in Elementary Chemical Reactions, J. Phys. Chem. 86, 4931 (1982).

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31. N.Z. Tishby and R.D. Levine, A Self Consistent Field Procedure for Stationary States Using an Algebraic Approach and the Maximum Entropy Formalism, Chem. Phys. Letts. 104, 4 (1984).

32. Y. Tikochinsky, N.Z. Tishby and R.D. Levine, Consistent Inference and Probabilities for Reproducible Experiments, Phys. Rev. Letters 52, 1357 (1984).

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7. Special Circumstances

A VAX 11/750 Computer dedicated entirely to research in molecular dynamics and operated by our group has been installed in November 1981. The computer has worked essentially continuously (24 hours a day) with very few failures due to technical malfunctioning.

8. Budget

As allowed for in the budget, some of the funds allocated for post-doctoral support were used to increase the fraction of the time that the programmger spent on this project.

9. Personnel

R.D. Levine, Principal Investigator.

Dr. E. Pollak, senior postdoctoral fellow, left Aug. 79.

Dr. Y. Tikochinsky, senior postdoctoral fellow.

Dr. E. Keren postdoctoral fellow, left Oct. 1979.

Dr. J. Rookstool, postdoctoral fellow, left July 1981.
U.S. Citizen from Dallas, Texas, worked on implementing surprisal synthesis as a practical computational procedure.

Dr. P. Pfeifer, postdoctoral fellow, left July 1982.

Dr. N. Ohmichi, postdoctoral fellow working on multiphoton ionization.

Mr. N. Agmon, advanced graduate student, received his Ph.D. June 1981.

Mr. A.S. Heilperin, advanced graduate student, received his Ph.D. Aug. 1982.

Mr. E. Zamir, advanced graduate student, received his Ph.D. Aug. 1984.

Mr. J. Silberstein, graduate student working on multiphoton ionization.

Mr. N.Z. Tishby, advanced graduate student.

Mr. H. Almagor, programming assistant.

Mr. A. Malek, system operator (VAX 11/750).

10. The Future

Our own work in the coming immediate future is likely to be mostly in areas 5(a) and 5(e). We believe that both will have a strong bearing on experiments on the one hand and will also be interesting from the point of view of novel methodologies.

In particular, the combination of (Lie) algebraic techniques with an information theoretic point of view (e.g. [2] or [31]) will be vigorously pursued. We have recently been able to show (JCP, in press, 1984) that algebraic techniques can predict high lying spectra to unprecedented accuracy. Coupled with a practical dynamical approach (Phys. Rev., in press, 1984) we hope to be able to carry out computations for realistic dynamical problems. Work on energy transfer collisions is already in progress.