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Summary report for the second year.

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

Electronic energy, 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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Annual Summary Report

Research Grant N-00014-78-G-0036

ELECTRONIC EXCITATION IN MOLECULAR COLLISIONS: STRUCTURAL, DYNAMIC AND KINETIC CONSIDERATIONS

R. D. Levine
Principal Investigator

Contents*

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

1. <u>Principal Investigator</u>

   R. D. Levine

   Professor of Physical and Theoretical Chemistry

   The Hebrew University of Jerusalem.

2. <u>Contract Description</u>

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

3. <u>Scientific Problem</u>

   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. <u>Technical Approach</u>

   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. <u>Progress</u>

   During the second year the work has been directed at the development of the required theoretical tools and at several novel applications. Progress can be summarised along the following lines:

   a. <u>Chemiluminescent ion-molecule reactions</u>

   Ion-molecule reactions which produce electronically excited products have been subjected to a (state of the art) surprisal analysis* [12]. In addition, the direct simulation of the spectral emission using information-theoretic procedures has been discussed [12]. The most important aspect of the analysis is the taking of proper cognizances of experimental errors. An explicit, practical expression for placing error bars on the surprisal parameters has been applied. In this fashion it was possible to show, e.g. that to within experimental error the $C^{+}+H_2$ and $C^{+}+D_2$ reactions have the same set of surprisal parameters and that both the vibrational and the rotational surprisals are linear.

b. Structure-reactivity correlations

The progress in this direction, discussed in the previous report has been maintained in the second year. Much of the work has by now appeared in the literature, [1,4,5-9] and several reviews have been accepted for publication [13-15]. The most significant finding is the unified formulation [14] where both the microscopic-dynamical questions ('how do changes in the energy of the reactants correlate with changes in the reaction probability') and the macroscopic questions ('how do changes in the chemical structure of the reactants correlate with changes in the reaction probability') can be discussed within the same framework.

c. Multiphoton ionization

The earliest evidence for multiphoton excitation of polyatomic molecules was the observation of electronically excited species.

*References are to the list of publications, paragraph 6 below.

It was therefore deemed appropriate to develop an approach where the branching fractions for formation of all possible species, following multiphoton pumping, could be readily estimated. As a test case we have selected to study the extensive fragmentation of polyatomic molecules which is observed following resonance enhanced multiphoton ionization. A simple statistical theory where the fragmentation pattern is governed by the mean energy uptake per parent molecule has been formulated and compared with experimental results for benzene. (The only input are the standard thermodynamic functions of all neutral and ionic dissociation products and the major uncertainties are in the heats of formation of some of the ions.) By varying the mean energy absorbed it is found possible to span the range of different observed fragmentation patterns, from the production of primarily C_6 and C_4 ions at low energies up to the dominance of C_1 ions above 37 eV/molecule. A preliminary account has just been published [11]. The method is eminently suitable for estimating the branching fractions for the production of neutral but electronically excited species. We plan such applications in the near future.

d. Surprisal synthesis as a dynamical approach

Work has started on the direct computation of the surprisal from a realistic potential energy surface. The first test case is going to be the $F+H_2$ reaction using a collinear collision geometry and classical mechanics. The very preliminary studies are promising but no firm conclusions can be drawn at this stage. We very much hope however to be able to say much more about this novel venture during the forthcoming project year.

e. Quenching of electronically excited atoms and molecules

Work is in progress on the systematics of the role of the quencher in electronic energy transfer. The method used is that developed for structure-reactivity correlations (See 5.b above and [8,13-15]) with suitable modifications made necessary by the fact that such quenching processes typically lead to a wide variety of products. The data base employed are experimental results on quenching of excited rare gas atoms and laser-excited diatomic molecules.

RDL/vms

g. Publications

Published papers

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

2. R. D. Levine and C. E. Wulfman, Energy Transfer to a Morse Oscillator, Chem. Phys. Letters 60, 372 (1979).

3. R. D. Levine, An Information Theoretic Approach to Inversion Problems, J. Phys. A13, 91 (1980).

4. N. Agmon and R. D. Levine, Empirical Triatomic Potential Energy Surfaces Defined Over Orthogonal Bond Order Coordinates, J. Chem. Phys. 71, 3034 (1979).

5. N. Agmon, An Analytical Approximation for the Number of States Along the Reaction Coordinate, Chem. Phys. 45, 249 (1980).

6. E. Pollak and R. D. Levine, The Reactivity-Selectivity Principle: The Derivation of Bounds and A Computational Study, J. Chem. Phys. 72, 2484 (1980).

7. E. Pollak and R. D. Levine, Statistical Theories for Molecular Collisions: A Maximum Entropy Derivation, J. Chem. Phys. 72, 2990 (1980).

8. N. Agmon and R. D. Levine, Structural Considerations in Chemical Kinetics: Gas Phase H-Atom Transfer Reaction Series, Isr. J. Chem. 19, 330 (1980).

9. N. Agmon, Is There A Nitroalkane Anomaly? J. Am. Chem. Soc. 102, 2164 (1980).

10. G. L. Hofacker and R. D. Levine, On Maximizing The Information from an Indirect Experiment, Zeit. f. Naturf. 35a, 490 (1980).

11. J. Silberstein and R. D. Levine, Fragmentation Patterns in Multiphoton Ionization: A Statistical Interpretation, Chem. Phys. Letts. 74, 6 (1980).

Papers accepted for publication

12. E. Zamir, R. D. Levine and R. B. Bernstein, The Practice of Surprisal Synthesis: Products' State Distribution in Chemiluminescent Ion Molecule Reactions, Chem. Phys.

13. N. Agmon, Structure Reactivity Correlations, in "Lectures on Biological and Chemical Physics, A Symposium in Honour of S. Lifson on his 65th Birthday". An invited review of papers 1 and 4.

14. R. D. Levine, The Reactivity-Selectivity Principle, in "Lectures on Biological and Chemical Physics, A Symposium in Honour of S. Lifson on his 65th Birthday".

15. N. Agmon, From Energy Profiles to Structure-Reactivity Correlations, Int. J. Chem. Kinet.

7. Special circumstances

Surprisal analysis for reactions producing electronically excited products was initially carried out by Dr. E. Keren (cf. paragraph 9 below). The quality of Keren's work and his rate of progress left much to be desired. He has left us after a stay of ten months. The topic was assigned (6/79) to Mr. E. Zamir. Although inexperienced, he has done very well and we have recovered some of the lost time, (see item 6.12).

8. Budget

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

9. Personnel

R. D. Levine, principal invesitgator

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

Dr. J. Rookstool, postdoctoral fellow.

U. S. citizen from Dallas, Texas. Working on implementing surprisal synthesis as a practical computational procedure.

Mr. N. Agmon, advanced graduate student.

Mr. A. Heilperin, advanced graduate student

Mr. E. Zamir, graduate student

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

Mr. H. Almagor, programming assistant

10. Other Current or Requested Federal Grants and Other Contract Support of R. D. Levine at the Hebrew University.

a. Studies in Molecular Disequilibrium

The US-Israel Binational Science Foundation, April 1980-March 1981, ~$8000. J. L. Kinsey, I. Oppenheim, R. Silbey, and J. I. Steinfeld cooperating investigators.

b. Multiphoton Ionization

The US-Israel Binational Science Foundation, April 1980 March 1981. ~$9000. R. B. Bernstein cooperating investigator.

Both (a) and (b) are lower cost grants primarily to enable the cooperating investigators to spend time with the research group of R. D. Levine in Jerusalem.