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

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**Summary Report:**

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.
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
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*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. **Progress**
During the first year much of the work has been directed at the development of the required theoretical tools. Progress to date can be summarised along the following lines.

a. **Electronic potential energy surfaces.**
The basis for a fundamental understanding of the dynamics of molecular collisions is the potential energy surface. We have
begun exploring two routes to the construction of such surfaces:

(a.1) Inversion of experimental data.

A general information theoretic algorithm for the inversion of data was developed* [3]. It is intended to apply this approach to concrete problems during the second project year. The inversion algorithm [3] has however many other potential applications some of which may well be of direct interest to the Department of the Navy.** We therefore intend to explore potentially significant implications of the approach even when these are not strictly within the technical description of the contract as given in paragraph 2.

(a.2) Semi-empirical approach

A semi-empirical approach procedure which has, thus far, given very accurate results has been developed [4]. Further work is in progress. The introduction of this method is based on work carried out to elucidate the systematics of chemical reactivity [1,4]. It is expected that developments in these two directions will continue to be mutually beneficial.

b. Chemical reactivity with special reference to branching ratios.

This direction is the major thrust of the project. Work has been carried out along several lines.

(b.1) The theory of branching ratios

The reactivity-selectivity principle has been derived on general grounds [6] and has been applied [7] to derive previous
theories (RRKM, the phase space theory, transition state theory, the unified statistical theory) and extension thereof. It is intended to use this formulation first in the analysis of experimental data and then as a predictive tool. In this connection, an explicit solution of a nontrivial dynamical problem by information-theoretic techniques was carried out [2].

(b.2) **Structure-reactivity correlations**

This is a semi-empirical version of (b.1) which has proven to be a versatile (cf. 5(a.2) above) and useful tool [1,5]. We expect to devote considerable attention to this development, even if it might lead us somewhat away from the strict technical description of the contract.

c. **Surprisal analysis**

Surprisal analyses for reactions which produce electronically excited diatomic molecules have been carried out and are in preparation for publication. A technically useful development has been the use of surprisal synthesis which enables one to place confidence limits and to simulate the chemiluminescent spectra.

d. **Summary**

The most significant work during the first year appears to be the development of the information-theoretic inversion algorithm (5(a.1)) and the semi-empirical structure-reactivity correlations (5(b.2)). We intend a follow-up of these directions in addition to other lines of enquiry as outlined in the original proposal.
6. **Publications**

   a. **Published papers**


   b. **Papers accepted for publication**


   Additional papers have been submitted but not yet accepted.

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 will be leaving 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.
8. **Budget**

At the end of the first year we have some unspent but encumbered funds (e.g. page charges which are committed but not yet paid). There are no significant amounts of unspent funds.

9. **Personnel**

a. Prof. R. D. Levine, principal investigator. Awarded the Weizmann Prize*, April 1979 for his work on fundamental processes in chemical laser systems.

*bPrevious recipients include C. Pekeris (Applied Mathematics), Y. Nee'man (Elementary Particle Physics), E. Katzir (Biophysics) and M. Sela (Immunology) all of whom are members of the (US) National Academy of Science.

b. Dr. E. Pollak, senior postdoc. Previously with Professor P. Pechukas at Columbia. Left 7/31/79 to accept a tenure-track position.

c. Dr. E. Keren, postdoc. Previously with Prof. R. A. Marcus at Illinois. Started 12/1/78.

d. Mr. N. Agmon, advanced graduate student.

e. Mr. E. Zamir, beginning graduate student.

f. 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

b. Multiphoton Ionization

The US-Israel Binational Science Foundation, applied for April 1980 starting date but not yet approved. R. B. Bernstein cooperating investigator.

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