TECHNICAL PROGRESS REPORT

AEC Grant AT-(11-1) 2092

CDD-2092-1

THE DYNAMICS OF CHEMICAL REACTIONS

- I. Dynamics of Fluorine Atom Reactions,
- II. Intermolecular Potentials From High Resolution
Differential Cross Sections, and
- III. Collision Induced Dissociations of Diatomic Molecules

Effective Date: April 1, 1970
To Present Date: December 31, 1970
Principal Investigator: Yuan Tseh Lee
Institution: The University of Chicago
James Franck Institute
5640 South Ellis Avenue
Chicago, Illinois 60637
312/753-8208

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

TECHNICAL PROGRESS REPORT

AEC Grant AT-(11-1) 2092

(For the period April 1, 1970 to December 31, 1970)

- I. Approximate percentage of time the principal investigator has devoted to the project:

75%.

The amount of effort which is expected to be devoted during the remainder of the current term:

75%.

- II. Programs undertaken during the current term:

1). Dynamics of Fluorine Atom Reactions

Fluorine is one of the most important and fascinating elements in the periodic table. It is the most reactive oxidizing element and forms stronger single bond than any other elements with carbon atom. Much attention has been paid in the past to fluorine chemistry due to its importance in the separation of uranium isotopes.

Hot atom chemists have also investigated some elementary chemical processes involving fluorine atoms. More recently, hydrogen fluoride chemical lasers have been studied extensively in many laboratories and it has now become possible to produce first continuously operating chemical laser. The important dynamic information of these reactions was not available in the past. During the current contract period we have successfully obtained many valuable dynamics information of fluorine atom reactions.

A). Crossed Molecular Beam Study of F + D₂ Reactions [See Reprint No. 3 for partial results]

This is one of the most significant chemical reactions producing chemical lasers. Detailed information on internal states distribution of product molecules and their angular distributions were obtained at various collision energies by crossed molecular beam technique. This was the first experiment in which the products vibrational states were resolved from angular measurements. Differences in angular distributions were observed for different vibrational states produced in the reaction from different reactant kinetic energies.

B). Reactions of Fluorine Atoms and Unsaturated Hydrocarbons

In hot atom chemistry, unsaturated hydrocarbons have often been used as scavenger of free fluorine atoms, because fluorine atoms add to double bonds readily and eventually replace hydrogen atoms from activated complex, or deactivated to stable radicals. Many experimental studies of unimolecular decomposition of this type have been carried out in the past, but all experiments were performed in homogeneous gas phase and did not provide any dynamical information on molecular decomposition or intramolecular energy transfer processes.

A series of experiments involving fluorine atom and unsaturated hydrocarbons were studied by crossed beam technique, in which angular distributions and energy distributions have been obtained. This information obtained so far will be the key to the understanding of molecular mechanics of intramolecular energy transfer processes and the theory of unimolecular decomposition.

Reactions listed below have been studied with velocity selected fluorine atoms and supersonic beams of unsaturated hydrocarbons:

Product molecules of all these reactions are found to have isotropic angular distributions implying formation of long-lived complexes with life-times which are many times of the rotational periods of collision complexes. Average kinetic energies of product molecules, nevertheless, appears to be much larger than that would be expected from statistical or free flow model of PRKM theory of unimolecular decomposition. For example, for the reaction of $\text{F} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_3\text{F} + \text{H}$, more than 50% of total energy appears as kinetic energy of relative motion.

Theoretical understanding of the decomposition of activated collision complexes and the detailed mechanism of intramolecular energy transfer are now under intensive study in collaboration with Professor Rice's group at our University.

2). Intermolecular Potentials from High Resolution Differential Cross Sections. [See reprint Nos. 1,2, and 4 for partial results.]

Tremendous effort has been made during the last decade for the understanding of intermolecular potentials. Although it is well known that high resolution differential cross sections will provide the most accurate information on intermolecular potentials,

the high resolution molecular beam results have been limited only to the systems containing alkali atoms. For non-alkali systems, the information has been mainly obtained from macroscopic quantities, such as virial coefficients, thermal conductivities and viscosities. The information obtained usually contains a large amount of uncertainties.

We have successfully constructed a universal crossed molecular beam machine which is sensitive enough to provide reliable high resolution differential cross sections of non-alkali systems efficiently. Consequently, the valuable information of detailed knowledge of intermolecular potentials of various non-alkali systems has first become available.

Since all macroscopic phenomena are based on detailed microscopic molecular interactions, this information will become extremely useful, not only in the understanding of various phenomena, but also in the prediction of many processes, such as the efficiency of separation of rare gas isotopes by thermal diffusion.

All the structures in angular distribution which would be expected from scattering theory, rainbows, supernumerary rainbows, fast quantum mechanical oscillations and oscillations caused by nuclear symmetry are observed in our differential scattering cross sections.

The systems studied are listed below.

4.1. RESEARCH RESULTS

A) Rare gas systems

B) Rare gas atoms and diatomic molecules

C) Rare gas atoms and polyatomic molecules

D) Polyatomic and polyatomic molecules

3). Collision Induced Dissociations of Diatomic Molecules.

Very little information is available on the detailed dynamics of dissociation of molecules in their ground state or low internal excitation by high energy collisions. It is generally assumed that collisional dissociation of molecules is not effective unless molecules under collision are highly internally excited. We chose the following processes

as examples to study the dynamic of collisional dissociation. High energy xenon beam is produced by seeded supersonic beam technique in these experiments.

The measured threshold energies of these processes are in good agreement with the value calculated from dissociation energies to atomic limits, electron ~~affinities~~ of halogen atoms and ionization potentials of alkali atoms. If collision energy is slightly above dissociation energy of the molecule, the cross section of dissociation is found to have pronounced dependence on the internal energy of the molecule. But when the collision energy is 30% higher than the dissociation energy, the collisional dissociation becomes very effective ($\sim 10^{-12}$) and does not depend strongly on internal energy.

The analysis of kinetic energy of dissociated ions has shown that at higher collision energy the collisions of xenon atoms approaching perpendicularly to alkali halide molecules contribute to most of dissociations. For RbI and CsBr, the efficiency of dissociation is found to be higher when xenon atoms approach lateral atoms of alkali halides.

The manuscript of this work is now under preparation.

III. Publication List

A) Papers in Print

1. Effect of Nuclear Symmetry in Atom-Atom Scattering
by P.E. Siska, J.M. Parson, T.P. Schafer, F.P. Tully,
Y.C. Wong, and Y.T. Lee, Phys. Rev. Letters 25, P271 (1970).
2. Intermolecular Potentials from Crossed Beam Differential
Elastic Scattering Measurements I, Ne + Ar, Ne + Kr,
and Ne + Xe, by J.M. Parson, T.P. Schafer, F.P. Tully,
P.E. Siska, Y.C. Wong, and Y.T. Lee, J. Chem. Phys. 53,
pp. 2123-2124 (1970).
3. Crossed Molecular Beam Study of F + D₂ by T.P. Schafer,
P.E. Siska, J.M. Parson, F.P. Tully, Y.C. Wong and
Y.T. Lee, J. Chem. Phys. 53, pp.3385-3387 (1970).

4. Intermolecular Potentials from Crossed Beam Differential Elastic Scattering Measurements II, Ar + Kr and Ar + Xe, by J.M. Parson, T.P. Schafer, F.P. Tully, P.E. Siska, Y.C. Wong, and Y.T. Lee, J. Chem. Phys. 53, pp. 3755-3756 (1970):

B) Seminars and Conference Speeches given during contract period.

1. Recent Development of Molecular Beam Technique
Amdur Conference of Dynamics of Molecular Collisions, August 31, to September 4, 1970,
Oak Ridge National Laboratory, Oak Ridge, Tennessee.
2. Dynamics of Molecular Collisions
Chemistry Division Seminar
October 14, 1970,
Argonne National Laboratory, Argonne, Illinois.
3. Crossed Molecular Beam Experiment
Physical Chemistry Seminar
November 16, 1970,
Ohio State University, Columbus, Ohio.
4. Molecular Beam Chemical Kinetics
Physical Chemistry Seminar
November 25, 1970,
Northwestern University, Evanston, Illinois.
5. Recent Molecular Beam Studies of Chemical Reactions
Departmental Colloquium
December 10, 1970,
The University of Iowa, Iowa City, Iowa.

C) The following list of seminars are scheduled to be given before March 31, 1970.

1. Crossed Molecular Beam Chemistry
Joint Physical Chemistry Seminar of Caltech,
January 18, 1971,
University of California, Los Angeles and
University of Southern California, Los Angeles, California.

2. Molecular Beam Chemical Kinetics
Physical Chemistry Seminar
January 21, 1971,
University of California, Irvine, California.
3. Recent Molecular Beam Studies of Elementary
Chemical Processes
Physical Chemistry Seminar
January 26, 1971,
University of Illinois, Chicago Circle
Campus, Chicago, Illinois.
4. Recent Molecular Beam Studies of Fluorine
Atom Reactions
Physical Chemistry Seminar
March 16, 1971,
Massachusetts Institute of Technology,
Cambridge, Massachusetts.
5. Crossed Molecular Beam Studies of Chemical Reactions
Chemistry Division Seminar
March 17, 1971,
Brookhaven National Laboratory, Upton, New York.

IV. List of Personnel working on the project, in addition to the
author:

	<u>NAME</u>	<u>POSITION</u>	
A)	Peter E. Siska	Research Associate	AEC-AT(11-1) 2092
B)	Albert Y.C. Wong	Research Assistant	AEC-AT(11-1) 2092
C)	John M. Parson	Research Assistant	NSF Traineeship
D)	Trudy P. Schafer	Research Assistant	Graduate Fellow-Fannie and John Hertz Foundation
E)	Frank P. Tully	Research Assistant	ARPA Student University of Chicago