

THE DYNAMICS OF CHEMICAL REACTIONS
PROGRESS REPORT
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CHICAGO, ILLINOIS

January 1, 1973 - December 31, 1973

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THE UNIVERSITY OF CHICAGO

TECHNICAL PROGRESS REPORT

AEC GRANT AT (11-1) 2092

January 1, 1973 - December 31, 1973

ABSTRACT

In this period, significant progress has been made in the studies of:

- A) Interactions and reactions of metastable rare gas atoms and atoms and molecules.
- B) The dynamics of collision induced dissociation of diatomic molecules.
- C) Translational to vibrational rotational energy transfers of linear triatomic molecules by rare gas atoms.
- D) Scattering of state selected molecules.
- E) Improvement in the velocity analysis of scattered molecules and the method of atomic beams production.
- F) Intramolecular energy transfers and unimolecular decomposition.

THE UNIVERSITY OF CHICAGO
TECHNICAL PROGRESS REPORT
AEC CONTRACT AT(11-1) 2092

January 1, 1973 - December 31, 1973

- I. Approximate percentage of time the principal investigator has devoted to the project: 40%.

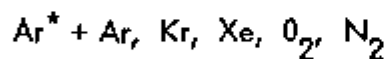
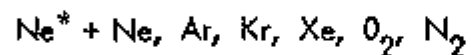
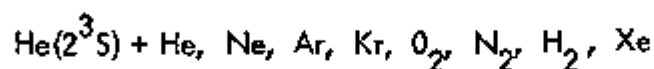
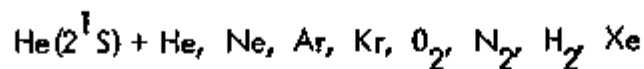
The amount of effort which is expected to be devoted during the remainder of current term: 40%.

- II. Programs undertaken during the current term:

A.) Interactions and reactions of metastable rare gas atoms and atoms and molecules.

A major effort, both in terms of manpower and resources, has been put into the measurements of differential cross sections of metastable rare gas atoms in order to understand the nature of interactions and reactions of metastable rare gas atoms with ground state rare gas atoms and simple molecules. The exceptional effort which was put into these studies is mainly due to the recent interest in the AEC laboratories (Livermore and Los Alamos) as well as in other institutions (MIT and Stanford Research Institute) in the development of high power vacuum UV rare gas lasers. In order to develop these lasers and optimize laser operation, detailed information on the interaction potentials and the process of electronic energy¹ transfers is urgently needed. Since we are in a unique position and capable of obtaining this information from differential scattering cross sections, we have been asked by these laboratories to investigate these properties.

During the past year we have obtained preliminary results for the systems listed below:



Several papers are in preparation at present, and the work was also presented at a conference on "Jesse Effect and Related Phenomena," organized by Argonne and Oak Ridge National Laboratories, held at Gatlinburg, Tennessee in November 1973.

One of the most unexpected results, and what is also the most important information related to the development of the vacuum UV laser, is the existence of the potential hump between van der Waals well at long distance and deeper "chemical" well at short distance for almost all combinations of excited and rare gas atoms. Although it has been recognized for quite some time, there exists a potential hump in $\text{He}^* + \text{He}$ interaction. This hump is regarded to be something special for this system. For other systems, especially for heavier homonuclear and heteronuclear systems, it is generally assumed that the attractive dispersion forces smoothly continue into chemical forces.

The existence of the potential hump in these systems is very important in the understanding of many elementary processes because the height of the potential

barrier determines whether a collision of $X^* + Y$ with a given translational energy and a given impact parameter will be able to overcome the hump to become a molecular state; $(XY)^*$, and proceed by radiating a photon from excited molecular state or ejecting an electron as in the processes of Penning and associative ionizations. Once the height of the potential hump is determined, an optimum laser operation temperature can be determined since, in the operation of vacuum UV laser, it is necessary to convert metastable rare gas atoms to radiative "metastable" molecules efficiently.

Through the measurement of temperature dependence of differential cross sections we have determined the height of potential humps of many of the systems. We have been able to elucidate the nature of Penning and associative ionization processes and explained the reasons for the failure of the previous theoretical prediction of temperature dependence of the rate constant of these processes. We have obtained preliminary information on van der Waals' interaction of these systems. For the symmetric system, we have not only observed oscillations in angular distributions caused by resonant excitation transfer, but also derived gerade and ungerade potentials for $Ar^* + Ar$. The effort in this area will be continued in the next period.

B.) Collision induced dissociation of diatomic molecules.

The studies of collision induced dissociation of alkali halides by high energy rare gas atoms have made a big step forward in this period. The studies of this process have been limited to a relatively high collision energy, and also the energy loss of incident particle has been the only information available for speculation of the dynamics of collisional dissociations.

In order to understand the detailed dynamics of collisional dissociation processes of diatomic molecules by high energy atoms, it is necessary to obtain the dynamic information of two of the three atoms involved. We have successfully measured angular and energy distributions of both positive and negative ions dissociated from alkali halides as a function of collision energies for Xe + CsI, CsBr, RbI, KI and Kr + CsI, CsBr, RbI, KI, and made some very interesting observations.

When collision energies are near the threshold of dissociation of alkali halides, the most effective orientation of alkali halides for dissociation by impact of xenon is found to be near collinear configuration when three atoms are lying along the direction of the relative velocity of atoms and molecules. We also discovered that when Xe/atom collides with the heavy end of alkali halides, the probability of dissociation is higher than when Xe collides with the lighter end of the molecule. This observation is just contrary to what one would expect from the theory of translational-vibrational energy transfers by using the impulse approximation.

The theoretical investigation assisted by trajectory calculations was also carried out in order to understand our observations. In these systems, since Xe is heavier than lighter atoms of alkali halides, although the initial impact of Xe transfers more energy to the molecule when the lighter atom is hit, the secondary collision between the lighter atom and xenon essentially transfers most of the energy back to the Xe atoms.

When the collision energy is much higher than the threshold of dissociation, the contribution from non-collinear contribution becomes more and more important. The effect of internal energy is also investigated. The impact from Kr atoms has

shown a dramatic mass effect.

This work has been summarized in Dr. Frank Tully's Ph. D. thesis completed in December 1973. Several papers are now in preparation for publication.

C.) Translational to vibrational-rotational energy transfers in atom and linear triatomic molecules by rare gas atoms.

The translational to vibrational-rotational energy transfer processes have been investigated by analyzing velocities of scattered molecules for $\text{Kr} + \text{CO}_2$, N_2O at various energies. The velocity analysis of scattered molecules was carried out by using the cross-correlation method. In these experiments, we have observed an excitation of ^{the} bending mode of CO_2 when the collision energy is about twice the bending mode excitation. The bending mode excitation occurs when Kr collides with the center carbon atom and the peak of angular distribution appears at the backward hemisphere. On the other hand, rotational excitation occurs at a larger impact where the parameter and most of the rotationally excited molecules scatter in the forward hemisphere. Translational to rotational energy transfers of linear triatomic molecules are found to be very efficient. Not surprisingly, in some collisions, nearly 100% of the translational energy is converted to rotational energy. The highly rotationally excited molecules were found to have a wider angular distribution.

D.) Scattering of state selected molecules.

In order to understand the unisotropy of the interaction potential, the processes of the energy transfer, and the dynamics of chemical reaction better, we have initiated a new project where a beam of the rotational state (j, m) selected molecules was used in the crossed molecular beam investigation.

The first phase of investigation includes the construction of elastic quadrupole

field to select a specific rotational state of the polar diatomic molecules, such as hydrogen halides. The selection of low j states of hydrogen halides is quite favorable, since the beam produced by supersonic expansion has a very low rotational temperature. For example, in the beam of HCl more than 30% of the molecules are on the $J = 1$ state.

We have tested our electric quadrupole field and successfully carried out differential cross section measurements of HCl ($J = 1$) with Kr. The rainbow and a supernumerary rainbow are observed. The locations of the rainbows are very similar to the Ar-Kr scattering, indicating that there is no strong hydrogen bonding between hydrogen atomic HCl with Kr.

Further investigation of energy transfers and reaction dynamics of the rotational state selected molecules will be performed in the next period.

E.) Improvement in the velocity analysis of scattered molecules and the method of atomic beam production.

Until recently, the velocity distribution of scattered molecules was analyzed by the conventional time-of-flight method. Since the scattered molecules were introduced into the detector for a very short period of time, which was followed by a relatively long flight time measuring period, the duty cycle of this method is only about 2%. In order to increase the duty cycle, a cross-correlation time-of-flight velocity analyzer was installed in this period. The duty cycle of ^{the} cross-correlation velocity analyzer is approximately 50% and provides immense improvement in the efficiency of the velocity analysis of scattered molecules. The time-of-flight spectra, which previously took more than ten hours to develop, can now be obtained in one hour.

The experiments of the translational to vibrational-rotational energy transfers are performed with this new velocity analyzer.

In previous experiments, the velocity of reactant atoms were selected by the mechanical velocity selector after effusing from the orifice by a molecular flow. The mechanical velocity selector imposes two serious limitations on the maximum intensity obtainable from the effusive beams. The space needed by a mechanical velocity selector sets the minimum distance required between a beam source and a collision region, and the low acceptance angle and the low transmission of the velocity selector further cut down the intensity of the selected beam. In addition to the low intensity obtained, there is an additional formidable shortcoming when the cross-correlation velocity analyzer is used for the analysis of the velocity of scattered molecules. The mechanical velocity selection introduces a high frequency modulation of beam intensity which interferes with the cross-correlation velocity analysis of scattered molecules.

Extensive effort was made in this period to continue the development of the high intensity atomic beams with narrow velocity distributions. We recognize that the best method to obtain a high intensity beam with narrow velocity distribution is by high pressure isentropic expansion, but in order to obtain a high fraction of dissociation of a given molecule, the pressure of molecules to be dissociated, i. e. H_2 , F_2 , Cl_2 and I_2 , etc., has to be low. These contradictory conditions can be overcome by preparing an appropriate mixture of dissociating molecules with rare gases, expanding it from an oven at a temperature which is sufficiently high for the near complete dissociation of the molecule. The rare gas atom not only serves the purpose of achieving a high degree of translational relaxation to give a narrow velocity distribution, but also serves to vary the velocity of beams from the same

temperature by changing the masses of mixing rare gas atoms.

F and Cl atom beams produced by this method have been tested. The performance is as good as expected. $F + C_2H_4 \rightarrow C_2H_3F + H$ reaction studied previously was used for comparison. With the present arrangement of the new beam source and the new velocity analyzer, we have obtained a much better signal to noise ratio with the same experimental resolution in less than one-tenth of the time it required in the previous arrangement. This new improvement will allow us to investigate the dynamics of chemical reaction in greater detail in the next period.

F.) Intramolecular energy transfers and unimolecular decomposition.

Five papers concerned with this subject have been published in J. Chem. Phys. this year; the sixth paper will appear in the December issue of J. Chem. Phys. In addition, a paper will appear in the Faraday Society Discussion 55, 1973, and another paper in Berichte Bunsengesellschaft für Physikalische Chemie. Reprints and preprints are attached in place of the description of the progress in this field.

III. Publication List

A. Papers published during contract period

1. Spectroscopic Information on Homonuclear Inert Gas Diatomics, Kate K. Docken and Trudy P. Schafer, J. Mol. Spectroscopy (1973).
2. Neon Interatomic Potentials from Scattering Data and Crystalline Properties, J. M. Farrar, Y. T. Lee, V. V. Goldman and M. L. Klein, Chem. Phys. Letters 19, 359 (1973).

3. Unimolecular Decomposition of the Long-Lived Complex Formed in the Reaction of $F + C_4H_8$, J. M. Parson, K. Shobatake, Stuart A. Rice, and Y. T. Lee, *J. Chem. Phys.* 59, 1402 (1973).
4. The Unimolecular Decomposition of Long-Lived Complexes of Fluorine and Substituted Mono-Olefins, Cyclic Olefins and Dienes, K. Shobatake, S. A. Rice and Y. T. Lee, *J. Chem. Phys.* 59, 1416 (1973).
5. The Laboratory Angular Dependence and the Recoil Energy Spectrum of the Products of the Reaction $F + C_6D_6 \rightarrow D + C_6D_5F$, J. M. Parson, K. Shobatake, S. A. Rice and Y. T. Lee, *J. Chem. Phys.* 59, 1427 (1973).
6. The Reactions of F atoms and Aromatic and Heterocyclic Molecules: Energy Distribution in the Reaction Complex, K. Shobatake, S. A. Rice and Y. T. Lee, *J. Chem. Phys.* 59, 1435 (1973).
7. Substitution Reactions of Fluorine Atoms and Unsaturated Hydrocarbons: Crossed Molecular Beam Studies of Unimolecular Decompositions, J. M. Parson, K. Shobatake S. A. Rice and Y. T. Lee, *Discussions Faraday Society*, Vol. 55 (1973).
8. An ITFITS Model for Vibration-Translation Energy Partitioning in Atom-Polyatomic Molecule Collisions, K. Shobatake, S. A. Rice, and Y. T. Lee, *J. Chem. Phys.* 59, 2483 (1973).
9. A crossed Molecular Beams Study of the Reaction $F + C_2H_2Cl_2 \rightarrow Cl + C_2H_2ClF$, K. Shobatake, S. A. Rice, and Y. T. Lee, *J. Chem. Phys.* 59, 12 (1973).
10. Rotational Excitation of Linear Triatomic Molecules: $Ar + CO_2$, $Ar + N_2O$, J. M. Parson, J. M. Farrar and Y. T. Lee, *Proceeding of the Fourth International Symposium on Molecular Beams*, Cannes, France (1973).

11. Crossed Molecular Beam Studies and Dynamics of Decomposition of Chemically Activated Radicals, Y. T. Lee, XIth International Symposium on Free Radicals, Munich, West Germany, September 4-8, 1973. (Paper will appear in *Berichte Bunsen-Gesellschaft für Physikalische Chemie.*)

B. Ph. D. Thesis completed during contract period

1. Crossed-Molecular Beam Study of the Collision-Induced Dissociation of Alkali Halides, Ph. D. Thesis, Frank Paul Tully, The University of Chicago, Chicago, Illinois, December 1973.

C. Seminars and Conference speeches given during contract period

1. International Centennial Boltzmann Seminar on Transport Phenomena, Brown University, Providence, Rhode Island, January 22-26, 1973.

Title: Intermolecular Potentials of Rare Gas Systems.

2. Third Winter Course in Gas Kinetics, Lake Arrowhead, California, February 18-24, 1973.

Title: 1) Method of Molecular Beam Experiments,

2) Molecular Beam Studies of Dynamics of Chemical Reactions, and

3) Intermolecular Potentials.

3. The Chemical Society Faraday Division General Discussion on Molecular Beam Scattering, University College, London, England, April 16-18, 1973.

Title: Substitution Reactions of Fluorine Atoms with Unsaturated Hydrocarbons: Crossed Molecular Beam Studies of Unimolecular Decomposition.

4. Fourth International Symposium on Molecular Beams, Palais des Festivals, Cannes, France, July 9-12, 1973.

Title: Rotational Excitation of Linear Triatomic Molecules: $\text{Ar} + \text{CO}_2$, $\text{Ar} + \text{N}_2\text{O}$
(Presented by J. M. Farrar).

5. VIIIth International Conference on the Physics of Electronic and Atomic Collisions, Beograd, Yugoslavia, July 16-20, 1973. (presented by H. Haberland).

Title: Dynamics of Collisional Dissociation: $\text{CsI} + \text{Xe} \rightarrow \text{Cs}^+ + \text{I}^- + \text{Xe}$.

6. Gordon Research Conference on Molecular Energy Transfer, Proctor Academy, Andover, New Hampshire, July 23-27, 1973.

Title: Rotational Energy Transfer (principle speaker).

7. XIth International Symposium on Free Radicals Berchtesgaden-Königssee, Germany, September 4-7, 1973.

Title: Crossed Molecular Beam Studies and Dynamics of Decomposition of Chemically Activated Radicals (main lecture).

8. VIIIth International Hot Atom Chemistry Symposium, Jülich, Germany, September 10-14, 1973.

Title: Chemical Dynamics of Hot Atom Reactions (invited talk).

9. 26th Annual Gaseous Electronics Conference, Madison, Wisconsin, October 16-19, 1973.

Title: Collision Induced Dissociation of Alkali Halides by High Energy Krypton and Xenon (presented by Frank P. Tully).

10. Symposium on the Jesse Effect and Related Phenomena, Gatlinburg, Tennessee, November 9-10, 1973.

Title: Scattering of Metastable Rare Gas Atoms.

11. National Research Council, Ottawa, Canada, May 24, 1973.

Title: Dynamics of Atomic and Molecular Processes by Molecular Beam Method.

12. Columbia University, Chemistry Department, New York, New York,
November 1, 1973.

Title: Crossed Beam Studies of Atomic and Molecular Processes.

13. Washington University, Department of Chemistry, St. Louis,
Missouri, November 15, 1973.

Title: Crossed Molecular Beam Studies of Chemical Reactions.

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

<u>NAME</u>	<u>POSITION</u>	
Trudy P. Schafer	Research Associate	Camille and Henry Dreyfus Foundation.
Daniel Auerbach	Research Associate	AEC-AT(11-1) 2092
Franco Vecchiocattivi	Research Associate	Summer Research Visiting Professor Univ. of Perugia, Perugia, Italy
Keith Jamieson	Research Associate	Sabbatical, 1 year Loyola University, Chicago, Ill.
Albert Wong	Research Assistant	AEC-AT(11-1) 2092
Frank P. Tully	Research Assistant	ARPA student University of Chicago
James Farrar	Research Assistant	NSF-Graduate Fellow Harper Fellow, University of Chicago
Winston C. Chen	Research Assistant	AEC-AT(11-1) 2092
James Valentini	Research Assistant	NSF - Graduate Fellow