THE DYNAMICS OF CHEMICAL REACTIONS
PROGRESS REPORT
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January 1, 1972 - December 31, 1972

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TECHNICAL PROGRESS REPORT
AEC GRANT AT (11-1) 2092 MOD 1-1
January 1, 1972 - December 31, 1972

ABSTRACT

Substantial progress has been made on all five (5) programs listed below:

- 1.) Dynamics of atom molecule reactions.
- 2.) Intermolecular potentials.
- 3.) Inelastic scattering of atoms and molecules.
- 4.) High energy collisions --- hot atom chemistry.
- 5.) Collisions of metastable atoms and molecules.

The operation of ⁰time-of-flight velocity analyzer and monoenergetic metastable atom beam source added experimental sophistication.

TECHNICAL PROGRESS REPORT

AEC GRANT AT-(11-1) 2092 MOD 1-1

JANUARY 1, 1972 - DECEMBER 31, 1972

- I. Approximate percentage of time the principal investigator has devoted to the project: 60%.

The amount of effort which is expected to be devoted during the remainder of the current term: 60%.

- II. Programs undertaken during the current term:

A. Dynamics of atom molecule reactions

During this contract period, we have put into operation a time-of-flight velocity analyzer for product velocity distribution measurements. Product velocity distributions were measured for the following reactions

In reaction 1), different vibrational states of DF are resolved in velocity space, which confirm our earlier analysis on angular distribution. In reaction 2), our experiment clearly establishes the fact that in contrast to RRKM theory, the internal energy distribution is not statistical during the lifetime of collision complex. Similar phenomena were observed in reaction 3), 4) and many other reactions of fluorine atoms with unsaturated hydrocarbons. Results of $\text{F} + \text{D}_2$ work have been described in the Ph. D thesis of T. P. Schafer; further work at a different collision energy will be performed in the next period. The work of

reactions of fluorine atom and unsaturated hydrocarbons, which is mainly designed to study the process of intramolecular energy transfer and unimolecular decompositions, has been summarized in six papers and has been submitted for publication in J. Chem. Phys. These six papers are listed in Section III. B. [Papers submitted for publication: No. 4, 5, 6, 7, 8 and 9.] The preprints of these papers are included in this progress report.

B. Intermolecular potentials

Differential cross sections of scattering of para- H_2 with para- H_2 were measured at low collision energy. The effect of Bose statistics which para- H_2 followed was observed in differential cross sections. The intermolecular potential was obtained for $(H_2)_2$. The work is summarized in a paper listed in Section IV. A. [Paper published during contract period, No. 9.]

Ne_2 potential was further investigated at lower collision energy and now we have a reliable potential which gives good agreement with transport properties, solid properties, second virial coefficient as well as spectroscopic observation. The work is summarized in a paper listed in Section III. B. [Paper submitted for publication, No. 3.]

We have also started the project of studying the interaction with open shell atoms. The first two systems studied are $H_2 + 1$ and $Ne + 1$. The energy of interaction for H_2I was found to be much smaller than the value used in trajectory calculation by Richard Porter. The NeI interaction is essentially the same as that of $NeXe$. The manuscript is under preparation for these results. Also, see Section III. B, No. 1 and No. 2.

C. Inelastic scattering of atoms and molecules

We have successfully observed single rotational quantum transition in $\text{HD}(J=0) + \text{He} \rightarrow \text{HD}(J=1) + \text{He}$ process from the measurements of velocity of scattered HD. The cross section of this process appears to be smaller than $1 \text{ \AA}^2$ at collision energy of 0.4 kcal/mole. This value is much smaller than the recent theoretical calculation of Takayanagi ($5 \text{ \AA}^2$). The main reason for the discrepancy is due to the lack of reliable information on potential between He and H_2 molecule rather than inadequacy of theory. Since we have obtained this part of potential from elastic differential cross section measurements, this process will be extensively investigated theoretically.

For translational-rotational energy transfer, as well as for the study of reaction dynamics, a rotational state selector for dipolar diatomic molecules has been constructed during this period. The state selector is just in the process of testing with HCl molecules.

D. High energy collisions --- hot atom chemistry

Reaction of $\text{I} + \text{HCl} \rightarrow \text{H} + \text{ICl}$ has been studied in this period. The threshold observed for this reaction is somewhat higher than endoergicity, and the cross section is only $\sim 10^{-20} \text{ cm}^2$ even at 5 kcal/mole above the threshold of this reaction. Experimental results are under analysis.

We have also made significant progress in the study of collisional dissociation. Angular distributions and energy distributions for both positive and negative ions have now become possible. After completion of this work, it will give us the opportunity of understanding the dynamics of collisional dissociation more thoroughly.

E. Collisions of metastable atoms and molecules

The beam of monoenergetic metastable beam source has been successfully constructed and operated. We have studied the scattering of metastable He with ground state He and Ar, metastable Ar with Ar. Differential cross sections measured provides information on resonant excitation energy transfers, as well as Penning ionization process in $\text{He}^* + \text{Ar} \rightarrow \text{He} + \text{Ar}^+$ as a function of impact parameter. Preliminary results have been published, Section III, A. [Paper published during contract period, No. 7.] Preprints of this paper are included in this report. [Reprints were not available at the time of preparation of this report] At present we are trying to improve our metastable beam source both in intensity and selectivity. A quenching lamp is now installed for removing $\text{He}^*(^1\text{S})$ from the beam, such that pure $\text{He}^*(^3\text{S})$ remains.

III. Publication List

A. Papers published during contract period.

1. Intermolecular Potentials from Crossed Beam Differential Elastic Scattering Measurements IV. Ar + Ar, J. M. Parson, P. E. Siska and Y. T. Lee J. Chem. Phys. 56, 1511 (1972).
2. Reactive Scattering of Atoms and Molecules: Crossed Molecular Beam Experiments Y. T. Lee, VIIth ICPEAC Book of Invited Talk and Progress Reports, North-Holland Publishing Co. (1972) p. 357.
3. Crossed Molecular Beam Study of $\text{F} + \text{C}_2\text{H}_4$, C_2D_4 , J. M. Parson and Y. T. Lee, J. Chem. Phys. 56, 4658 (1972).

4. Hyperthermal Xe Beam from Free Jets of 1% Xe and 99% H₂.
H. Haberland and F. P. Tully, VIII International Symposium of Rarefied Gas Dynamics, Palo Alto, California (1972).
  5. Intermolecular Potentials from Crossed Beam Differential Elastic Scattering Measurements V. The Attractive Well of He₂, J. M. Farrar and Y. T. Lee, J. Chem. Phys. 56, 5801 (1972).
  6. Intermolecular Potentials from Crossed Beam Differential Elastic Scattering Measurements VI. Atoms and Diatomic Molecules. Ar + N₂, Ar + O₂, Kr + N₂ and Kr + O₂, F. P. Tully and Y. T. Lee, J. Chem. Phys. 57, 866 (1972).
  7. Differential Cross Sections for Metastable He and Ar, H. Haberland, C. H. Chen and Y. T. Lee, Atomic Physics III. Plenum Publishing Co. (1972) p. 359.
  8. Comments on the Interatomic Potential for Argon, H. J. M. Hanley, J. A. Barker, M. Klein, J. M. Parson and Y. T. Lee, J. Mol. Phys. 24, 11 (1972).
  9. Intermolecular Potentials from Crossed Beam Differential Elastic Scattering Measurements VII Para-H₂ + Para-H₂, J. M. Farrar and Y. T. Lee, J. Chem. Phys. 57, 5492 (1972).
- B. Papers submitted for publication (to appear in 1973 Journals)
1. Spectroscopic Information on Homonuclear Inert Gas Diatomics, Kate K. Docken and Trudy P. Schafer, J. Mol. Spectroscopy (1973).
  2. Comment on Inert Gas Potentials for Mixed Interactions, T. P. Schafer and Y. T. Lee, J. Chem. Phys.

3. 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.

4. Unimolecular Decomposition of the Long-Lived Complex Formed in the Reaction of $F + C_4H_8$, John M. Parson, Kosuke Shobatake, Yuan T. Lee and Stuart A. Rice, J. Chem. Phys.

5. The Unimolecular Decomposition of Long-Lived Complexes of Fluorine and Substituted Mono-Olefins, Cyclo Olefins and Dienes, Kosuke Shobatake, Y. T. Lee and Stuart A. Rice, J. Chem. Phys.

6. The Laboratory Angular Dependence and the Recoil Energy Spectrum of the Products of the Reaction $F + C_6D_6 \rightarrow D + C_6D_5F$, John M. Parson, Kosuke Shobatake, Yuan T. Lee and Stuart A. Rice, J. Chem. Phys.

7. The Reactions of F Atoms and Aromatic and Heterocyclic Molecules: Energy Distribution in the Reaction Complex, Kosuke Shobatake, Yuan T. Lee and Stuart A. Rice, J. Chem. Phys.

8. A Classical Model of Collision Induced Vibration-Translation Energy Partitioning, K. Shobatake, Stuart A. Rice and Yuan T. Lee, J. Chem. Phys.

9. Substitution Reactions of Fluorine Atoms with Unsaturated Hydrocarbons: Crossed Molecular Beam Studies of Unimolecular Decompositions, John M. Parson, Kosuke Shobatake, Yuan T. Lee and Stuart A. Rice, Discussions Farraday Soc.

C. Ph. D. Thesis completed during contract period

1. Crossed-Molecular-Beam Scattering Studies with a Mass Spectrometric Detector, Ph. D. Thesis, John Morris Parson, The University of Chicago, Chicago, Illinois, June 1972.
2. Crossed Molecular Beam Studies of Elastic and Reactive Scattering, Ph. D. Thesis, Trudy Porter Schafer, The University of Chicago, Chicago, Illinois, December 1972.

D. Seminars and Conference speeches given during contract period

1. Recent Molecular Beam Studies of Chemical Reactions, Physical Chemistry Seminar, Univ. of California, Berkeley, California, Feb. 1972.
2. Reactive Scattering of Atoms and Molecules, Chemistry Department Seminar, National Taiwan Univ., Taiwan, CHINA, March 1972.
3. Intermolecular Potentials, Chemistry Department Seminar, National Tsinghua University, Taiwan, CHINA, April 1972.
4. Study of Reactive Scattering by Crossed Molecular Beam Method, Special Seminar Sponsored by the Chinese Chemical Society, Taiwan, CHINA, May 1972.
5. Reactive Scattering, Gordon Research Conference, Principal Sepaker, New Hampshire, July 1972.
6. Molecular Beam Chemical Kinetics, Physical Chemistry Seminar, University of Illinois, Urbana, Illinois, October 1972.

7. Atomic and Molecular Processes, Chemistry Division Seminar

National Bureau of Standards, December 1972.

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

<u>NAME</u>	<u>POSITION</u>	
Helmut Haberland	Research Associate	Fellowship, Forschungs-Gemeinschaft, Germany
John M. Parson	Research Assistant Research Associate*	NSF Trainee ACS - PRF
Trudy P. Schafer	Research Assistant Research Associate*	Fannie and John Hertz Foundation Graduate Fellow Camille and Henry Dreyfus Foundation
Albert Y. 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
Winston C. Chen	Research Assistant	AEC-AT(11-1) 2092
Chuck C. Ng	Research Assistant	AEC-AT(11-1) 2092
Cindy Denley	Under Graduate (Summer Student)	NSF - Summer Research Participant

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* Change of status during contract period.