MASTER

COO-3129-4

**EXPERIMENTAL CHEMICAL KINETICS ;
A STUDY OF CHEMICAL REACTIONS BY MEANS OF
MOLECULAR BEAM TECHNIQUES**

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Final Report

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May 1978

Prepared for

THE U.S. DEPARTMENT OF ENERGY

UNDER CONTRACT NO. EY-76-5-02-3129.A001

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I. RESUME OF RESEARCH CONDUCTED

This report gives a brief summary of the work which has been accomplished during the 19 years that Brown University has received support under this contract first with the U. S. Atomic Energy Commission, then the U. S. Energy Research and Development Administration and finally the U. S. Department of Energy. Because most of the work is described in published papers listed in Section II, only a brief description is included here.

Support from the contract helped Brown University to set up one of the first laboratories concerned with studying the reactive and non-reactive scattering of molecular beams at thermal energies. Paper 1 reports the first velocity selected thermal beam used in a chemical scattering experiment. Paper 3 describes the first study of the rainbow structure in the differential cross section for molecular scattering. Subsequent work of this kind in many laboratories has contributed significant information about intermolecular potentials. Papers 4, 6, 7, 13, 15, 17, and 22 contain results of measurements of differential cross sections for many systems and show how non-reactive scattering can be interpreted to give detailed information about chemical reactions such as total reaction cross sections and the probability of reaction as it varies with impact parameter or the distance of closest approach during a collision. Papers 8, 24, and 27 describe the use of shock waves for the study of the kinetics of gas reactions which are often inaccessible by other techniques.

Relatively little work has been published on the formation of negative ions at surfaces. Paper 21 and to some extent Paper 25 report the study of

some systems where negative ions are formed and propose a mechanism to account for deviations from the simplest equilibrium theory. The object of several other papers (Nos. 19, 20, and 31) has been to clarify for the non-specialist the nature of molecular scattering measurements and their interpretation in terms of quantities of concern to chemical kineticists.

The use of a beam of electrons to control the motions of neutral molecules is the subject of Paper 32. This work is supplemented by a thesis by H. D. Lambropoulos of which the abstract is appended to this report. The mechanism responsible for the effect is likely to involve the shift of the energy levels (Stark effect) of atoms and molecules in the electric field produced by the electrons, but the magnitude calculated is not sufficient to give a quantitative fit to the experiments. If further work leads to better understanding, the effect may be useful by permitting the collection of small numbers of neutral molecules so they can be detected efficiently.

Papers 34, 35, and 37 concern experiments on the inelastic scattering of alkali halides by rare gases. A simple model involving a short-lived complex can be used to interpret measurements from 3 laboratories which show that the transfer of large amounts of energy between translation and internal modes occurs with large cross sections.

Paper 36 proposed a simple classical model for the interpretation of the elastic scattering of atoms from crystalline surfaces. Work is underway to test the usefulness of the model by comparison with an experiment in which Kr is scattered from graphite.

Two more projects are currently being studied but have not advanced enough to be ready for publication. The first seeks to find the relative importance of kinetic energy and internal energy in a molecule when it reacts after suddenly hitting a solid surface. Molecules of C_2Cl_6 are seeded into an excess of carrier gas H_2 , He, Ar or Kr and accelerated as the gas flows from a nozzle into a vacuum. The internal energy of the C_2Cl_6 is varied by changing the temperature of the nozzle. Pyrolysis alone at 300 C gives negligible decomposition but with acceleration to kinetic energies in the range $E = 50-180 \text{ kJ mol}^{-1}$ from a source at 300 C as much as 6% of the molecules react to form C_2Cl_4 and CCl_4 . Similar experiments in which the seed molecules are C_2HCl_5 produce appreciable quantities of C_2Cl_6 showing perhaps that the C-C bond is broken as a result of the impact. Work is continuing with the objective of learning about the mechanism of the decomposition and specifying how it may change as the amounts of kinetic and internal energy are varied.

The second project which is well underway but not yet complete is a study of the efficiency with which ions are formed when neutral atoms hit the surfaces of metals, semiconductors, and insulators. Most of the work has been done with Si (100) surfaces. A clean Si surface is an excellent ionizer for beams of alkali metals and would make a good detector for them. Silicon's high work function ($\phi = 5.5 \text{ eV}$) means that even Li is ionized with about 10% efficiency. Values of the work function for Si obtained from the Richardson equation agree with those from the temperature dependence of the yield of positive ions interpreted with the Saha-Langmuir equation, an equilibrium model. When the surface becomes contaminated, the work function changes.

A particularly striking example occurs when Si previously exposed to a K beam is then used to ionize Li. At temperatures below 1500 K Li appears to be ionized as it is on a clean surface; at higher temperatures the current of Li^+ recorded by the mass spectrometer suddenly drops while a current of K^+ , which had been small but noticeable at lower temperatures, suddenly rises. Apparently the fraction of the surface covered by K increases abruptly as the K emerges from the bulk. The K lowers the work function of the Si and greatly decreases the yield of Li^+ . A simple kinetic analysis suggests that the activation energy for bringing K from the bulk to the surface is 4.4eV.

In contrast to Si a surface of Al_2O_3 does not form ions according to the equilibrium model. The dynamics of the process seem to be of importance and perhaps can be revealed by proper study of the system. A further point to note is that visible radiation shining on the Al_2O_3 surface can lead to an increase of up to 30% in the yield of Na^+ and Li^+ from incident beams of Na and Li. Possibly the excited atoms produced by the absorption of the light can lose an electron to the nearly empty conduction band of the Al_2O_3 while the resulting ion, at an energy lower by the ionization potential, cannot easily be reneutralized because few electrons are available unless they come from the valence band which lies at a much lower energy. Variation of the frequency and intensity of the light should give information useful for understanding the mechanism.

II. PUBLICATIONS

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3. "Wide Angle Scattering in Molecular Beams. The Rainbow Effect", J. Chem. Phys., 37, 2884 (1962) D. Beck.
4. "A Study of the Reaction of K with HBr in Crossed Molecular Beams", J. Chem. Phys., 37, 2895 (1962) D. Beck, E.F. Greene and J. Ross.
5. "The Study of Chemical Reactions in Crossed Molecular Beams" in Proceedings of the XII Solvay Congress in Chemistry, Transfert, d'Energie dans les Gaz. (Interscience Publishers, New York, 1962), p. 363 J. Ross and E.F. Greene.
6. "A Study of the Reaction of K with CH₃Br in Crossed Molecular Beams" IX Symposium (International) on Combustion. (Academic Press, New York, 1963) p. 669 M. Ackerman, E.F. Greene, A.L. Moursund and J. Ross.
7. "Elastic and Reactive Scattering of K by HCl and HI in Crossed Molecular Beams", J. Chem. Phys., 41, 1183 (1964) M. Ackerman, E.F. Greene, A.L. Moursund and J. Ross.
8. "Vibrational Relaxation of HI, 1400°-2300°K", J. Chem. Phys., 43, 324 (1965), C.C. Chow and E.F. Greene.
9. "Semiclassical Theory of Rotational Excitation of a Diatomic Molecule by an Atom", J. Chem. Phys. 43, 2930 (1965) K.P. Lawley and J. Ross.
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11. "Calculation of Chemical Reaction Probabilities from Elastic Scattering Data", J. Chem. Phys. 44, 188 (1966) J.L.J. Rosenfeld and J. Ross.
12. "Some Applications of the R-Matrix Theory to Reactive and Elastic Molecular Scattering", J. Chem. Phys. 44, 2467 (1966) B.C. Eu and J. Ross.
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28. "Physical Interpretation of Glory Undulations in Scattering Cross Sections", J. Chem. Phys., 57, 2065 (1972) E.F. Greene and E.A. Mason.
29. "Linear Least-Squares Fitting of Molecular-Beam Differential Cross Section Data Using Spline Functions" J. Chem. Phys., 58, 1321 (1973) R.P. Creaser, R.P. English and J.L. Kinsey.
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31. "A Molecular Beam Apparatus for Student Experiments on Reactive Scattering", J. Chem. Ed., 51, 620 (1974) R.J. Conley, E.F. Greene and S.M. McInnis.

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37. "Inelastic Scattering of Alkali Halides by Rare Gases", R.P. McGinnis and E.F. Greene, preprint attached.

III. PERSONNEL

Personnel whose work has been supported by the contract are as follows

Postdoctoral Research Associates

D. Beck	D. B. Sheen
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K. Kadera	M. J. Cardillo
J. R. Airey	S. M. Bobbio
G. P. Reck	S. E. Johnson
T. J. Rosenfeld	R. B. Hall
H. Y. Sun	C. T. Chiou
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Graduate Students Receiving Degrees

R. W. Roberts, Ph.D. 1960, The Scattering of a Potassium Atomic Beam by a Crossed Beam of Bromine Molecules.

C. H. Williams, Jr., Ph.D. 1964, The Dissociation of a Cesium Fluoride Molecule by Impact with a Fast Argon Atom.

A. L. Moursund, Ph.D. 1964, The Elastic and Reactive Scattering of K by HCl, CH₃Br, and HI in Crossed Molecular Beams.

B. C. Eu, Ph.D. 1966, R-Matrix Theory for Elastic and Reactive Molecular Scattering.

K. R. Westberg, 1969, The Dissociation of Br₂ and HBr in Shock Waves.

M. W. Lee, Ph.D. 1969, The Elastic Scattering of K and Cs for Reactive and Non-reactive Systems in Crossed Molecular Beams.

M. H. Lau, Ph.D. 1970, The Non-reactive Scattering of Cs by HBr and Neopentane.

T. C. Wang, Ph.D. 1970, Inelastic Non-reactive Scattering in Crossed Molecular Beams.

R. H. Hammond, Ph.D. 1970, A Study of Ionizing Collisions of Argon Atoms with Argon Atoms and of Helium Atoms with Helium Atoms.

R. J. Conley, Ph.D. 1971, The Elastic and Inelastic Scattering of CsI Molecules by a Crossed Beam of Argon Atoms.

M. S. Chou, Ph.D. 1972, Crossed Molecular Beam Study of the Scattering of CCl₄ by Kr and by Isooctane and of CH₂Cl₂ by Isooctane.

W. A. Armstrong, Ph.D. 1974, Elastic and Inelastic Scattering of Cesium, Cesium Iodide, and Arium Chloride by Argon and Xerion in Crossed Atomic and Molecular Beams.

N. A. Sondergaard, Ph.D. 1977, Energy Transfer in Diatom-Atom Collisions: The Elastic and Inelastic Scattering of Cesium Iodide by Argon and Xenon.

H. D. Lambropoulos, Ph.D. 1978, Control of the Motion of Neutral Molecules and Atoms by a Beam of Electrons.

F. J. Petrone, Jr., M. A. 1961

M. A. Pickering, M. A. 1978 (expected)

Master of Arts in Teaching

R. J. Couley, MAT, 1963, The Scattering of a Potassium Atomic Beam by a Crossed Beam of Methyl Iodide Molecules.

H. F. Pettengill, MAT, 1963, The Dissociation of CsF by a Neutral Ar Beam.

Undergraduate Senior Research

B. K. Annis,	1962
R. N. Nelson,	1963
A. B. Lees,	1964
S. S. Fried,	1966 - January
V. Vaida,	1973
W. Holber,	1976
C. Parks,	1978
P. Marzuk,	1978

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