2

AD-A215 022

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
11 March 1981

3. REPORT TYPE AND DATES COVERED
Final

4. TITLE AND SUBTITLE
THE QUANTUM DYNAMICS OF CHEMICAL REACTIONS

5. FUNDING NUMBERS
61102F
2303/B1

. AUTHOR(S)
Aron Kuppermann

. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
California Institute of Technology
Division of Chemistry & Chemical Engineering
Pasadena, California 91125

8. PERFORMING ORGANIZATION REPORT NUMBER
AFOSR.TR. 89-1522

. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AFOSR
BLDG 410
BAFB DC 20332-6448

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
61102F
2303/B1

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release;
distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

DTIC
ELECTE
DEC 05 1989
S E D

14. SUBJECT TERMS

15. NUMBER OF PAGES
16

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT
unclassified

18. SECURITY CLASSIFICATION OF THIS PAGE
unclassified

19. SECURITY CLASSIFICATION OF ABSTRACT

20. LIMITATION OF ABSTRACT

NSN 7540-01-280-5500

Standard Form 298 (890104 Draft)
Prescribed by ANSI Std. 239-18
298-01

148

AFOSR-TR- 89-1522

APPLICATION FOR RENEWAL OF A RESEARCH CONTRACT FROM THE AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

Institution:	Division of Chemistry and Chemical Engineering California Institute of Technology Pasadena, California 91125
Title of Project:	The Quantum Dynamics of Chemical Reactions
Time Period for Which Support is Requested:	1 July 1981 through 30 June 1982
Contract Number:	F49620-79-C-0187

Principal Investigator:

Aron Kuppermann
Professor of Chemical Physics
(Social Security No.: 303-38-1510)

Approved:

Harry B. Gray, Chairman, Division of
Chemistry and Chemical Engineering

A. J. Lindstron, Director
Sponsored Research

Date: 11 March 1981

TABLE OF CONTENTS

1. PROJECT ABSTRACT

The aim of the proposed research is the performance of quantum mechanical calculations of an exact and approximate nature of the cross sections and rate constants of elementary chemical reactions. These calculations are of importance for the fundamental understanding of the nature of chemical reactions and for advanced technologies of interest to the United States Air Force, such as high-energy chemical lasers, plume technology. and the chemical effects of high-energy radiation. The calculations include processes involving three atoms, such as exchange reactions, collision-induced dissociation, three-body recombination, electronic branching ratios, tunneling, and vibrational quenching by reaction. The goal of this work is to develop a detailed understanding of such processes and to generate benchmark results which can serve as a basis for testing the validity of approximate methods.

2. SUMMARY OF PROGRESS

We summarize here the progress of the last year in the work supported by this contract.

2.1 Quantum Mechanical Calculations of Three-Dimensional Reactive Scattering

We have previously developed[1] the conceptual and numerical methodology for performing accurate three-dimensional quantum-mechanical calculations of the corss sections of triatomic exchange reactions of the type $A + BC \rightarrow AB + C$, $AC + B$ and applied it to the $H + H_2$ system.[2] These are the only accurate three-dimensional differential reaction cross sections published so far. A modified version of the code was developed for systems of the type A_2B, in which one of the three atoms could be distinct from the other two. During the last year we have performed extensive test calculations on the H_2D system, i.e., on the reaction $H + DH \rightarrow H_2 + D$, $HD + H$, and studied in detail the number of rotational and vibrational basis sets and the matching program parameters required for achieving convergence of the results. This testing work was done on our VAX 11/780 computer. The production calculations that must be performed in the future are two lengthy for such a computer, and, as a result, we are transferring them to an IBM 3032 machine available for this purpose. This transfer required further modifications of the code, as the size of its fast memory is smaller than that of the VAX. The necessary modifications have been made and are currently being tested. We expect to reach production stage on the IBM computer for zero total angular momentum in the next few months. The process is lengthy and painstaking in view of the size and complexity of the codes.

2.2 The Use of Hyperspherical Coordinates for Collinear Exchange Reactions

We had previously developed a new method for performing quantum mechanical calculations on collinear triatomic collisions. Over the last year this method has been extensively tested on the H + H_2 and F + H_2 systems, and found to be significantly more efficient than previous ones. A description of it and new results on the H + H_2 system have been published,[3] and a reprint is appended. In particular, it requires fewer vibrational channels for convergence, compared with other methods. For the two systems just mentioned, about 1/2 the usual number is sufficient, and for a heavy-light-heavy type system, such as I + HI, 1/6 of the usual number does the job. Since the time required for such calculations typically increases with the cube of the number of coupled channels, the new method achieves time economies of 2^3 or more, which is a substantial improvement.

For heavy-light-heavy systems, such as I + HI, I + HCl, etc., the usual methods not only require large numbers of coupled channels (40 or more), but also have great difficulty in yielding reliable results. The central reason is the smallness of the skew angle of the corresponding potential energy surfaces, which is only 7° for the I + HI system (as compared with 60° for H + H_2). The hyperspherical coordinate method has no special difficulties with such a system and has yielded high quality results for I + HI using only six coupled channels. The corresponding results and discussion have been published recently,[4] and a reprint is appended.

The method of hyperspherical coordinates permits calculations to be done at high energies without deterioration of the quality of the results. We have calculated from such results deactivation rates for vibrationally excited H_2 (v) molecules by reactive and nonreactive collinear collisions with H atoms over the temperature range 200°K to 2000°K for v = 1 through 5. The corresponding Arrhenius plots show noticeable curvature at high temperatures and obey an exponential gap law quite well.

A system of considerable experimental[5] and theoretical[6] interest is the Cl + HCl → ClH + Cl, another heavy-light-heavy system, with a skew angle of 13.5°. We have performed reaction probability and rate constant calculations on this system on two LEPS surfaces, with barrier heights of 6.2 and 1.9 kcal/mole, respectively. We found that the rate constant for reaction of HCl (v = 1) is higher than that of HCl (v = 0) for the larger barrier height surface, but that the reverse is true for the lower one. In fact, the HCl (v = 1) rate on the low barrier surface is smaller than on the high barrier one. This is an unusual result, related to the heavy-light-heavy nature of the system.

Reactions of the general type X + HY(v) → XH + Y, where X and Y are halogens, are of substantial experimental interest.[7] We have also performed some preliminary calculations on the Cl + HBr system, which has a skew angle of 11.5°. Convergence to about 1% in the translational energy range 0 to 0.4 eV was achieved with six basis functions only, whereas the use of a previous method based on the one developed in our laboratory required 40 basis functions,[8] an additional demonstration of the superior efficiency of the hyperspherical method.

2.3 The Use of Hyperspherical Coordinates for Collinear Collision-Induced Dissociation

We had previously developed a method for rigorously discretizing the dissociation continuum in collision-induced dissociation and three-body recombination processes. During the last year we obtained accurately converged calculations for the collision-induced dissociation probabilities on a model symmetric collinear potential energy surface. The method has functioned remarkably well, the probabilities having converged to within ±0.02 for reagent translation energies up to three times the dissociation energy with only eight channels of each parity used to represent the continuum. The results are in press,[9] and a preprint is appended.

2.4 Collinear Reaction Probabilities for the $H + HI \rightarrow H_2 + I$ Reaction

This reaction is of considerable interest because its exothermicity is sufficient to produce electronically excited I atoms. As a preliminary step in its study, we have done calculations on a single electronically adiabatic potential energy surface, preparatory to a two-surface investigation. In a previous study of this system,[10] a potential energy surface having unrealistic wells in the reagent and product channel regions was used and resulted in pronounced sharp resonant structure. To avoid this, we constructed a more realistic surface, of the rotating Morse-cubic spline type,[11] devoid of such unphysical wells. The sharp resonances disappeared, as expected, and it was found that the bulk of the H_2 product was formed in the $v = 2$ state. This finding may be a useful guide for the deisgn of crossed beam experiments on this important system.

2.5 Three-Dimensional Reactive Scattering Calculations Using Symmetrized Hyperspherical Coordinates

Over the last year substantial progress was achieved in the application of the hyperspherical coordinate method to the three-dimensional $H + H_2$ reaction. The changes indicated in the last progress report, involving a modification of the method used for calculating the surface functions, were implemented. They resulted in conservation of flux for zero angular momentum quantum number of 1% or better, converged with respect to the number of basis functions. We find that ten such channels are sufficient over the 0.3 to 0.7 eV total energy range, whereas previously 30 to 40 channels were necessary.[2] This is a significant improvement of efficiency, which can result in a decrease of computer time by a factor in excess of 10. However, the results differ by about 10% from those obtained previously. We believe that this difference is due to a deterioration of the quality of the surface functions for hyperdistances in excess of 5 bohr, and we are currently implementing a change in this calculation for such distances aimed at correcting this defect. It is expected that the code will become operational in the not too distant future.

3. DESCRIPTION OF PROPOSED RESEARCH

We intent to continue in the next year or two to do research along the lines described in the proposal dated 31 August 1976, as follows:

1. Continue the three-dimensional calculation on the D + H_2 system in order to generate differential and integral cross sections and rate constants, comparing them with those for H + H_2, to obtain accurate isotope effects on the same potential energy surface. Also, we will test the validity of isotope effect theories.
2. Perform three-body recombination calculations on the same collinear surface for which collision-induced dissociation calculations were performed last year. Also, study the partitioning of reagent translational energy among the products of collision-induced dissociation.
3. Do a systematic study on the dynamic characteristics of the X + HY → XH + Y collinear reactions, where X and Y are halogen atoms, as a function of features of the potential energy surface, using the new hyperspherical coordinate method.
4. Study the electronic branching ratio for the collinear H + HI → H_2 + I ($^2P_{3/2}$, $^2P_{1/2}$) reaction for model coupling surfaces, to elucidate the conditions under which the production of electronically excited products is formed.
5. Continue the development of the three-dimensional hyperspherical coordinate code and apply it to the H + H_2 and D + H_2 reactions as benchmark systems. Also, extend it to the T + HD one. Evaluate its convergence with respect to size of basis set and its computational efficiency.
6. Perform j_z-conserving three-dimensional approximate calculations based on the older arrangement channel method[1,2] and the newer

hyperspherical method, as well as corresponding first-order perturbation calculations whose reference potential contains the important dynamic features of the correct potential.

7. Perform accurate three-dimensional calculations on the Cl + H_2 reaction at low energies by either the arrangement channel or hyperspherical coordinate methods.

8. Perform calculations on streamlines of probability current density and tunneling fractions in order to assess the reaction pathways on the potential energy surface for the reactions mentioned in 3 above.

The order in which these several projects will be pursued will depend on available manpower and relative progress, but it is expected that a significant effort will be carried on on most, if not all, of them.

4. SCIENTIFIC PERSONNEL

The Project Director will continue to be Professor Aron Kuppermann, whose curriculum vitae and publications list were included in the proposal dated 31 August 1976. The following additional personnel are currently working on different facets of the project.

Dr. Joseph K. C. Wong, postdoctoral fellow, full-time
Dr. Nancy M. Harvey, postdoctoral fellow, 1/3 time
Mr. Jack A. Kaye, graduate student
Ms. Diane M. Hood, graduate student
Mr. Huey-Jenn Chiang, graduate student
Mr. Loudon L. Campbell, undergraduate student.

5. BUDGET (AFOSR): 1 July 1981 through 30 June 1982

Salaries		
Aron Kuppermann, Principal Investigator		$ 5,600
One Postdoctoral Research Fellow, full-time, 12 months @ $13,500/year		13,500
Two Graduate Research Assistants, full-time 12 months @$6060/year		12,120
Secretary, 12 months, 1/4 time		4,800
	Total Salaries	$36,020
Staff Benefits		
24.6% of Total Salaries		8,861
Supplies and Expense		
Stationery supplies, photocopying, graphic arts, illustrations		1,700
Page charges and reprint costs for publications		1,200
Computing Costs		
700 hours @ $14/hour (DEC VAX 11/780)		9,800
Travel - Domestic		
Meetings and Conferences		1,500
	Total Direct Costs	$59,081
Overhead		
48% of Total Direct Costs		28,359
	TOTAL COSTS	$87,440

6. REFERENCES

1. G. C. Schatz and A. Kuppermann, J. Chem. Phys., **65**, 4642 (1976).
2. A. Kuppermann and G. C. Schatz, J. Chem. Phys., **62**, 2502 (1975); G. C. Schatz and A. Kuppermann, ibid., **65**, 4668 (1976).
3. A. Kuppermann, J. A. Kaye, and J. P. Dwyer, Chem. Phys. Lett., **74**, 257 (1980).
4. J. A. Kaye and A. Kuppermann, Chem. Phys. Lett., **77**, 573 (1981).
5. M. Kneba and J. Wolfram, J. Phys. Chem., **83**, 69 (1979).
6. I. W. M. Smith, J. Chem. Soc. Faraday Trans. II, **71**, 1970 (1975).
7. M. R. Levy, Prog. React. Kin., **10**, 1 (1979).
8. M. Baer, J. Chem. Phys., **62**, 305 (1975).
9. J. A. Kaye and A. Kuppermann, Chem. Phys. Lett., in press.
10. F. M. Chapman, Jr., and E. F. Hayes, J. Chem. Phys., **66**, 2554 (1977).
11. J. M. Bowman and A. Kuppermann, Chem. Phys. Lett., **34**, 523 (1975.).

7. LIST OF PUBLICATIONS

The following are publications describing work performed under this project which appeared in print or have been submitted/accepted for publication since the original contract application dated 31 August 1976:

Quantum Mechanical Reactive Scattering for Planar Atom Plus Diatom Systems. I. Theory.
A. Kuppermann, G. C. Schatz, and M. Baer.
J. Chem. Phys., **65**, 4596 (1976).

Quantum Mechanical Reactive Scattering for Planar Atom Plus Diatom Systems. II. Accurate Cross Sections for $H + H_2$.
G. C. Schatz and A. Kuppermann
J. Chem. Phys., **65**, 4624 (1976).

Quantum Mechanical Reactive Scattering for Three-Dimensional Atom Plus Diatom Systems. I. Theory.
G. C. Schatz and A. Kuppermann.
J. Chem. Phys., **65**, 4642 (1976).

Quantum Mechanical Reactive Scattering for Three-Dimensional Atom Plus Diatom Systems. II. Accurate Cross Sections for $H + H_2$.
G. C. Schatz and A. Kuppermann.
J. Chem. Phys., **65**, 4668 (1976).

Large Quantum Effects in a Model Electronically Nonadiabatic Reaction: $Ba + N_2O \rightarrow BaO^* + N_2$.
J. M. Bowman, S. C. Leasure, and A. Kuppermann.
Chem. Phys. Lett., **43**, 374 (1976).

Angular Momentum Decoupling Approximations in the Quantum Dynamics of Reactive Systems.
A. Kuppermann, G. C. Schatz, and J. P. Dwyer.
Chem. Phys. Lett., **45**, 71 (1977).

Validity of the Adiabatic Approximation for Vibrational Energy Transfer in Collisions Between Diatomic Molecules.
J. P. Dwyer and A. Kuppermann.
Chem. Phys. Lett., **44**, 499 (1976).

An Exact Quantum Mechanical Transition State Theory. I. An Overview.
A. Kuppermann.
J. Phys. Chem., **83**, 171 (1979).

Comment on "Theory of Collisions Between an Atom and a Diatomic Molecule in the Body-Fixed Coordinate System".
G. C. Schatz and A. Kuppermann.
J. Chem. Phys., **70**, 3151 (1979).

Vibrational Deactivation on Chemically Reactive Potential Surfaces: An Exact Quantum Study of a Low Barrier Collinear Model of H + FH, D + FD, H + FD, and D + FH.
G. C. Schatz and A. Kuppermann.
J. Chem. Phys., **72**, 2737 (1980).

Theoretical Aspects of the Mechanism of Simple Chemical Reactions.
A. Kuppermann.
In the *Proceedings of the Summer School on Chemical Photophysics, "Dynamique Réactionelle des Etats Excités"*, P. Glorieux, D. Lecler, and R. Vetter, Eds., Les Houches, France, 18-30 June 1979 (Editions due Centre National de la Recherche Scientifique, Paris, 1979), pp. 293-384.

Accurate Quantum Calculations of Reactive Systems.
A. Kuppermann
In *Theory of Scattering*, Volume VIII of *Theoretical Chemistry: Advances and Perspectives*, D. Henderson and H. Eyring, Eds. (Academic Press, Inc., New York, 1980), pp. 79-164.

Hyperspherical Coordinates in Quantum Mechanical Collinear Reactive Scattering.
A. Kuppermann, J. A. Kaye, and J. P. Dwyer
Chem. Phys. Lett., **74**, 257 (1980).

Quantum Mechanical Collision-Induced Dissociation Calculations with Hyperspherical Coordinates.
J. A. Kaye and A. Kuppermann
Chem. Phys. Lett., in press.

Few-Body Molecular Collisions: Theoretical.
A. Kuppermann.
In the Proceedings of the IXth International Conference on the Few-Body Problem, F. S. Levin, Ed. (North-Holland Publishing Co., Amsterdam, 1980), *Nuclear Physics A*, in press.

Collinear Quantum Mechanical Probabilities for the I + HI → IH + I Reaction Using Hyperspherical Coordinates.
J. A. Kaye and A. Kuppermann.
Chem. Phys. Lett., **77**, 573 (1981).

8. OTHER SOURCES OF SUPPORT

Department of Energy

Contract No.:	DE-AM03-76SF00767
Project Agreement No.:	DE-AT03-76ER72004
Title of Project:	Studies in Spectroscopy and Chemical Dynamics
Duration of Project:	1 March 1981 through 28 February 1982
Award:	$80,000 (including overhead)
Project:	Experimental investigations on electron impact and laser spectroscopy

National Science Foundation

Grant No.:	CHE77-26515
Title of Project:	Dynamic Resonances in Chemical Reactions
Duration of Project:	1 May 1980 through 30 April 1981
Award:	$35,000 (including overhead)
Project:	Theoretical investigations of dynamic resonances. This work is complementary to but does not overlap the studies supported by the AFOSR.