AD-A058 855   PURDUE UNIV LAFAYETTE IND PROJECT SQUID HEADQUARTERS   F/G 21/2
EXPERIMENTAL AND THEORETICAL STUDIES OF CHEMICAL DYNAMICS AND I--ETC(U)
AUG 78 J ROSS   N00014-75-C-1143

UNCLASSIFIED   SQUID-MIT-90-PU   NL

1 OF 1
AD
A058855

END
DATE
FILMED
11-78
DDC

PROJECT SQUID

TECHNICAL REPORT MIT-90-PU

EXPERIMENTAL AND THEORETICAL STUDIES OF CHEMICAL DYNAMICS AND INSTABILITIES IN IRREVERSIBLE PROCESSES

BY

JOHN ROSS
CHEMISTRY DEPARTMENT
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASSACHUSETTS 02139

PROJECT SQUID HEADQUARTERS
CHAFFEE HALL
PURDUE UNIVERSITY
WEST LAFAYETTE, INDIANA 47907

AUGUST 1978

Project SQUID is a cooperative program of basic research relating to Jet Propulsion. It is sponsored by the Office of Naval Research and is administered by Purdue University through Contract N00014-75-C1143, NR-098-038.

(14) SQUID-MIT-9Ø-PU

(12)

Technical Report MIT-90-PU

PROJECT SQUID

A COOPERATIVE PROGRAM OF FUNDAMENTAL RESEARCH
AS RELATED TO JET PROPULSION
OFFICE OF NAVAL RESEARCH, DEPARTMENT OF THE NAVY

CONTRACT (15) N00014-75-C-1143 / NR-098-038

(6)

EXPERIMENTAL AND THEORETICAL STUDIES OF CHEMICAL DYNAMICS AND INSTABILITIES IN IRREVERSIBLE PROCESSES.

by

(10) John/Ross
Chemistry Department
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

(9) Final rept. 1 Oct 67-31 Dec 77,

Project SQUID Headquarters
Chaffee Hall
Purdue University
West Lafayette, Indiana

(11) Aug[redacted]978 (12) 2Øp.

ABSTRACT

The final report summarizes the work accomplished under the subcontract. The overall objectives of the investigation were as follows: The determination of molecular properties of chemical dynamics for reactions of importance to combustion and propulsion. Molecular beam techniques were used for the experimental part of this work and were accompanied by theoretical studies in chemical dynamics. The second purpose was the study of the interaction of chemical reactions with transport processes and flows in gases in which instabilities may occur.

PROJECT SQUID FINAL REPORT

A. Identification

Principal Investigator: John Ross, F. G. Keyes Professor of Chemistry

Contractor: Massachusetts Institute of Technology

Contract No.: Sub 4965-10 under Contract N00014-67-0226-0005

Title: Experimental and Theoretical Studies of Chemical Dynamics and Instabilities in Irreversible Processes

B. Duration:

October 1, 1967 - December 31, 1977

C. Participation

Other Support: Work has been supported in part by the National Science Foundation (30%) and M. I. T. (20%).

Names of Investigators who contributed to research:

†Robert K. Brown	*Jennifer Makowski
*Randolph H. Burton	*David L. McFadden
Rashmikant C. Desai	Charles Mims
*Michele Flicker	Abraham Nitzan
George P. Flynn	Peter Ortoleva
*John A. Gracki	*Lawrence G. Piper
Hong-sup Hahn	Itamar Procaccia
Raymond Kapral	George Schatz

†M. A.

*Ph. D.

D. Object

Purpose of Research: The determination of molecular properties of chemical dynamics for reactions of importance to combustion and propulsion. Molecular beam techniques were used for the experimental part of this work and were accompanied by theoretical studies in chemical dynamics. The second purpose was the study of the interaction of chemical reactions with transport processes and flows in gases in which instabilities may occur.

E. Achievements

1. Transport Processes: We developed a new method of solving the Boltzmann equation which describes transport processes in dilute gases (47). The method is similar to a WKB-type solution and at any stage of approximation is better than a sonine polynomial expansion. Experimental work was completed on measurements of the viscosity of gases as a function of temperature and pressure. The precision and accuracy of these measurements has not been superceded (54).

2. Theory of Chemical Dynamics: We have made progress in this field along a number of lines. We developed the theory of optical potentials for reactive systems (43, 46); we treated reactions by distorted wave approximations (51), semiclassical analysis (56), direct interaction and complex formation approaches (65, 72). The optical potential method has proven best where applicable for the determination of total collision cross sections. In an analysis of symmetry effects in chemical reactions (67) we derived the theoretical basis of the important Woodward-Hoffmann rules and showed their limitations.

3. Molecular Beam Research: In a number of publications (50, 66, 73, 76) we measured angular distributions of both reactants and products in a chemically reactive system and derived from that total reaction cross sections, probabilities of reactions, threshold conditions, such as activation energy and threshold distances necessary for reaction, and distribution of exothermicity in reaction products. This work contributed to showing that a molecular beam approach yields valuable data not available by other techniques.

4. Chemical Instabilities: Chemical Instabilities occur when nonlinear reaction mechanisms, normally achieved with auto- or cross catalysis, are driven sufficiently far from chemical equilibrium. In that case a number of interesting events, such as multiple stationary

states, oscillations and formation of macroscopic spatial structures may occur. We have made pioneering contributions in a number of areas. We showed the existence of resonance-like phenomena due to boundary or external perturbations (69, 70); we showed the importance of local autocatalysis (71) and predicted new cooperative phenomena in a field of local sites at which autocatalytic reactions may occur (89); we investigated the interaction of mechanical (sound) modes with chemical reactions and showed how chemical reactions may amplify sound waves (75, 79), which is of particular importance in combustion; we have predicted the occurrence of instabilities in illuminated systems (82, 90) and proceeded to confirm our predictions with experiments; we analyzed a variety of waves in oscillatory chemical reactions (80, 93, 101); and we discussed the connection between fluctuations and transitions in chemical instabilities as compared to those in phase transitions. Much of this work is reviewed in Ref. 114. Instabilities and oscillatory phenomena occur in flames and other combustion processes and we believe that we have contributed to an understanding of these phenomena.

Publications of Professor John Ross

1. "Diffusion Coefficients of the Systems CO_2-CO_2 and CO_2-N_2O," J. Chem. Phys., 20, 436 (1952). (With I. Amdur, J. W. Irvine, Jr., and E. A. Mason.)

2. "Intermolecular Potentials for the Systems CO_2-CO_2 and CO_2-N_2O," J. Chem. Phys., 20, 1620 (1952). (With I. Amdur and E. A. Mason.)

3. "The Statistical-mechanical Theory of Transport Processes. VIII. Quantum Theory of Transport in Gases," J. Chem. Phys., 22, 1094 (1954). (With J. G. Kirkwood.)

4. "Statistical Mechanical Theory of Transport Processes. IX. Contribution to the Theory of Brownian Motion," J. Chem. Phys., 24, 375 (1956).

5. "Energy of Interaction Between a Hydrogen Atom and a Helium Atom," J. Chem. Phys., 25, 626 (1956). (With E. A. Mason and P. N. Schatz.)

6. "The Energy of Interaction of He^+ and H^-," The Astrophysical J., 124, 485 (1956). (With E. A. Mason.)

7. "Temperature Dependence of Distribution Functions in Quantum Statistical Mechanics," Phys. Rev., 107, 28 (1957). (With I. Oppenheim.)

8. "The Statistical Mechanical Basis of the Boltzmann Equation," Contribution to International Symposium on Statistical Mechanics and Transport Processes. Interscience Publishers, New York, 1958. (With J. G. Kirkwood.)

9. "Transport Equation in Quantum Gases," Phys. Rev., 109, 1877 (1958). (With H. Mori.)

10. "On the Calculation of Properties of Gases at Elevated Temperatures," Combustion and Flame, 2, 412 (1958). (With I. Amdur.)

11. "Statistical Mechanical Theory of Transport Processes. XII. Dense Rigid Sphere Fluids," J. Chem. Phys., 31, 575 (1959). (With S. A. Rice, J. G. Kirkwood, and R. W. Zwanzig.)

12. "Variation of a Chemical Reaction Cross Section with Energy," J. Chem. Phys., 32, 940 (1960). (With E. F. Greene and R. W. Roberts.)

13. "Quantum Corrections for Transport Coefficients," J. Chem. Phys., 33, 1324 (1960). (With S. Choi.)

14. "Some Deductions from a Formal Statistical Mechanical Theory of Chemical Kinetics," J. Chem. Phys., 35, 19 (1961). (With P. Mazur.)

15. "Some Topics in Quantum Statistics. The Wigner Function and Transport Theory," Studies in Statistical Mechanics, Vol. I, ed. by J. deBoer and G. E. Uhlenbeck, North-Holland Publishing Co., Amsterdam, 1962, pp. 217-298. (With H. Mori and I. Oppenheim.)

16. "Note on Second-order W.K.B. Phase Shifts," Proc. Nat. Acad. of Sciences, 48, 803 (1962). (With S. Choi.)

17. "Study of the Reaction of K with HBr in Crossed Molecular Beams," J. Chem. Phys., 37, 2895 (1962). (With D. Beck and E. F. Greene.)

18. "The Study of Chemical Reactions in Crossed Molecular Beams," Proceedings of the XII Solvay Congress in Chemistry, Transfert d'Energie dans les Gas, Interscience Publishers, New York. (With E. F. Greene.)

* 19. "The Viscosity of Nitrogen, Helium, Neon and Argon from -78.5°C to 100°C below 200 Atmospheres," J. Chem. Phys., 38, 154 (1963). (With G. P. Flynn, R. V. Hanks, and N.A. Lemaire.)

20. "A Study of the Reaction of Potassium with CH_3Br in Crossed Molecular Beams," Ninth Symposium (International) on Combustion, Academic Press Inc., New York, 1963, p. 669. (With M. Ackerman, E. F. Greene, and A. L. Moursund.)

21. "On the Semiclassical Expansion of Scattering Phase Shifts," J. Chem. Phys., 40, 2151 (1964). (With S. Choi.)

* 22. "Composition Dependence of Nonequilibrium Effects in Gas-Phase Reactions," J. Chem. Phys., 40, 2572 (1964). (With C. W. Pyun.)

* 23. "Viscosity of Hydrogen, Deuterium, Methane, and Carbon Monoxide from -50° to 150°C below 200 Atmospheres," J. Chem. Phys., 41, 374 (1964). (With A. K. Barua, M. Afzal, and G. P. Flynn.)

24. "Elastic and Reactive Scattering of K by HCl and HI in Crossed Molecular Beams," J. Chem. Phys., 41, 1183 (1964). (With M. Ackerman, E. F. Greene and A. L. Moursund.)

25. "Proceedings of the International Seminar on the Transport Properties of Gases," organized by J. Kestin and J. Ross, Brown University, Providence, R.I. (1964).

*26. "The Viscosity of Moderately Dense Gases," J. Chem. Phys., 42, 263 (1965). (With S. K. Kim.)

27. "Semiclassical Theory of Rotational Excitation of a Diatomic Molecule by an Atom," J. Chem. Phys., 43, 2930 (1965). (With K. P. Lawley).

28. "Semiclassical Calculation of Rotational Excitation," J. Chem. Phys., 43, 2943 (1965). (With K. P. Lawley.)

29. "Teaching Physical Chemistry. Introduction to a Symposium," J. Chem. Ed., 42, 189 (1965).

*30. "Thermal Conductivity of Moderately Dense Gases," J. Chem. Phys., 43, 4166 (1965). (With S.K. Kim and G.P. Flynn.)

31. ADVANCES IN CHEMICAL PHYSICS, MOLECULAR BEAMS, Vol. 10, Edited by John Ross, John Wiley and Sons, New York, 1966.

32. "Elastic Scattering in Chemically Reactive Systems," in Advances in Chemical Physics, Molecular Beams, John Wiley and Sons, New York, 1966, p. 135. (With E. F. Greene and A. L. Moursund.)

33. "Calculation of Chemical Reaction Probabilities from Elastic Scattering Data," J. Chem. Phys., 44, 188 (1966). (With J. L. J. Rosenfeld.)

*34. "Nonequilibrium Effects in the Kinetics of Gas-Phase Reactions," J. Chem. Phys., 44, 1087 (1966). (With N. S. Snider.)

35. "The Current Brown University Experiment in Chemical Education," J. Chem. Education, 43, 112 (1966).

36. "Some Applications of the R-Matrix Theory to Reactive and Elastic Molecular Scattering," J. Chem. Phys., 44, 2467 (1966). (With B.C. Eu.)

37. "Comments on Two Derivations of a Transition State Theory of Chemical Reactions," J. Chem. Phys., 46, 411 (1967). (With B. C. Eu.)

*38. "On the Determination of Potential Parameters from Transport Coefficients," J. Chem. Phys., 46, 818 (1967). (With S.K. Kim.)

39. "Non-reactive Scattering of K by HBr and DBr in Crossed Molecular Beams," J. Chem. Phys., 46, 3287 (1967). (With J. R. Airey, E.F. Greene, K. Kodera, and G.P. Reck.)

40. "Scattering of Potassium by a Series of Reactive and Non-reactive Compounds in Crossed Molecular Beams," J. Chem. Phys., 46, 3295 (1967). (With J. R. Airey, E.F. Greene, and G. P. Reck.)

41. "Evaluation of Scattering Cross Sections in the Optical Model by the Method of Stationary Phase," J. Chem. Phys., 46, 3306 (1967). (With H. Y. Sun.)

42. "Perturbed Stationary State Calculation of Collisions in a Reactive System," J. Chem. Phys., 47, 321 (1967). (With R. J. Suplinskas.)

*43. "Optical Potential for a Chemically Reactive System," Discussions of the Faraday Society (Toronto, September, 1967), 44, 39 (1967). (With B.C. Eu.)

44. "Molecular Beams and a Chemical Reaction, $K + CH_3I \rightarrow KI + CH_3$," Science 159, 587 (1968). (With E. F. Greene.)

45. "From Stoichiometry and Rate Law to Mechanism," J. Chem. Ed. 45, 381 (1968). (With J. O. Edwards and E. F. Greene.)

*46. "Interpretation of Elastic Scattering in Reactive Systems," J. Chem. Phys., 49, 843 (1968). (With Carl Nyeland.)

*47. "Solutions of Boltzmann Equation and Transport Processes," J. Chem. Phys., 49, 3754 (1968). (With R. C. Desai.)

48. "Small-Angle Scattering from Anisotropic Potentials," J. Chem. Phys., 50, 1038 (1969). (With R. Felton and R. J. Cross, Jr.)

49. "Reduction of the Effect of the Speed Distribution in the Cross Beam on Nonreactive Scattering Experiments," J. Chem. Phys., 50, 3122 (1969). (With E. F. Greene and M. H. Lau.)

*50. "Scattering of K and Cs by Several Compounds," J. Chem. Phys., 50, 3450 (1969). (With E. F. Greene, L.F. Hoffman, M.W. Lee and C.E. Young.)

*51. "Distorted-Wave Approximation in Faddeev's Theory of Reactive Scattering," J. Chem. Phys., 51, 159 (1969). (With B. C. Eu.)

*52. "Bimolecular Chemical Reaction Rates in Imperfect Gases," J. Chem. Phys., 51, 252 (1969). (With Michael R. Emptage.)

53. "Rate Coefficients, Reaction Cross Sections and Microscopic Reversibility" in Kinetic Processes in Gases and Plasmas, Academic Press, New York, 1969, pp. 281-320. (With J. C. Light and K. Shuler.)

*54. "Viscosity of Nitrogen, Helium, Hydrogen, and Argon from -100° to 25°C up to 150-250 Atmospheres," J. Chem. Phys., 51, 3856 (1969). (With J. A. Gracki and G. P. Flynn.)

*55. "Relaxation in a Dilute Binary Gas Mixture," J. Chem. Phys., 52, 1238 (1970). (With Raymond Kapral.)

*56. "Semiclassical Treatment of the Optical Model," J. Chem. Phys., 52, 1464 (1970). (With R. E. Roberts.)

*57. "Distorted Wave Born Series for Rotational Inelastic Scattering," J. Chem. Phys., 52, 5011 (1970). (With R. E. Roberts.)

58. "Pole Contributions in the Distorted Wave Born Series for Inelastic Scattering," J. Chem. Phys., 52, 6446 (1970). (With R. E. Roberts.)

59. "Elastic Scattering of Reactive Systems," Proceedings of the International School of Physics - Enrico Fermi - Course XLIV, in Molecular Beams and Reaction Kinetics, ed. by Ch. Schlier, Academic Press Inc., New York 1970, pp. 86-107 (With E. F. Greene.)

60. "Nonequilibrium Effects in Chemical Kinetics," Proceedings of the International School of Physics - Enrico Fermi, Course XLIV, in Molecular Beams and Reaction Kinetics, ed. by Ch. Schlier, Academic Press Inc. New York, 1970, pp. 249-257.

61. "Quantum Theory of Reactive Scattering," Proceedings of the International School of Physics, Enrico Fermi, Course XLIV, in Molecular Beams and Reaction Kinetics, ed. by Ch. Schlier, Academic Press Inc., New York, 1970, pp. 392-406.

62. "Potential Inversion for the Semiclassical Optical Model," J. Chem. Phys. 53, 2126 (1970). (With R. E. Roberts.)

*63. "Nonequilibrium Kinetics: Explicit Time-Dependence of Perturbed Distribution Functions and Autocorrelation Expressions," J. Chem. Phys. 53, 4387 (1970). (With Raymond Kapral and Suzanne Hudson.)

*64. "Estimate of Potential Surface for K-Cl-Cl," J. Chem. Phys. 54, 1665 (1971). (With Carl Nyeland)

*65. "Direct Interaction Theory of Reactive Molecular Collisions: K + Br_2 System," Can. J. Phys. 49, 966 (1971). (With B. C. Eu and J. H. Huntington)

*66. "Kinetic Energies of Ionization Products from Collisions of Ar-Ar, He-He Below 220 eV c.m. Energy," J. Chem. Phys. 55, 3506 (1971). (With R. H. Hammond, J. M. S. Henis and E. F. Greene).

*67. "Analysis of Symmetry in Chemical Reactions," J. Chem. Phys. 55, 3851 (1971). (With Thomas F. George.)

*68. "Instabilities in Coupled Chemical Reactions with Pressure-Dependent Rate Coefficients," J. Chem. Phys. 55, 4378 (1971). (With Peter J. Ortoleva.)

*69. "Penetration of Boundary Perturbations in Unstable Chemical Systems," J. Chem. Phys. 56, 287 (1972). (With Peter J. Ortoleva.)

*70. "Response of Unstable Chemical Systems to External Perturbations," J. Chem. Phys. 56, 293 (1972). (With Peter J. Ortoleva.)

*71. "Local Structures in Chemical Reactions with Heterogeneous Catalysis," J. Chem. Phys., 56, 4397 (1972). (With Peter Ortoleva).

*72. "Quasistatistical Complexes in Chemical Reactions," J. Chem. Phys. 56, 5786 (1972). (With Thomas F. George).

*73. "Molecular Beam Study of Polyatomic Free Radical Reactions. $CH_3 + Cl_2$ and Br_2." J. Chem. Phys. 57, 1351 (1972). (With D. L. McFadden, E. A. McCullough, Jr., F. Kalos, W. R. Gentry)

*74. "Optical Model for Vibrational Relaxation in Reactive Systems." J. Chem. Phys. 57, 1592 (1972). (With Lise Lotte Poulsen and Jeffrey I. Steinfeld.)

*75. "Interaction of Sound with Gas Phase Reactions," J. Chem. Phys. 57, 2672 (1972). (With Robert G. Gilbert, Hong-sup Hahn and Peter Ortoleva).

*76. "Dependence of Reactivity on Internal and Translational Energy in K + SF_6, CCl_4, and $SnCl_4$." J. Chem. Phys. 57, 2745 (1972). (With Thompson M. Sloane and S. Y. Tang).

*77. "Light Scattering from Systems with Chemical Oscillations and Dissipative Structures," J. Chem. Phys. 57, 4327 (1972). (With J. M. Deutch, S. Hudson and P. J. Ortoleva).

*78. "Total Cross Sections for Formation of Ions from CsBr by Collision with Ar, Xe, and NaBr(Ar)", J. Chem. Phys. 57, 4742 (1972). (With L. G. Piper, L. Hellemans, and J. Sloan).

*79. "Non-equilibrium Relaxation Methods. Acoustic Effects in Transient Chemical Reactions," J. Chem. Phys. 58, 3625 (1973). (With R. Gilbert and P. Ortoleva).

80. "Phase Waves in Oscillatory Chemical Reactions," J. Chem. Phys. 58, 5673 (1973). (With P. J. Ortoleva).

*81. "Molecular Beam Study of Polyatomic Free Radical Reactions. Angular Distributions," J. Chem. Phys. 59, 121 (1973). (With D. L. McFadden, E. A. McCullough, Jr. and F. Kalos).

*82. "Oscillations, Multiple Steady States, and Instabilities in Illuminated Systems," J. Chem. Phys. 59, 241 (1973). (With Abraham Nitzan).

*83. "Quantum Dynamical Theory of Molecular Collisions," Ann. Rev. Phys. Chem. 24, (1973). (With Thomas F. George).

84. "Physical Chemistry in Cambridge, Massachusetts," Ann. Rev. Phys. Chem. 24 (1973). (With E. Bright Wilson).

85. "Chemical Oscillations and Multiple Steady States Due to Variable Boundary Permeability," J. Theor. Biol. 41, 503 (1973). (with Hong-sup Hahn and P. J. Ortoleva).

86. "Transport Phenomena - 1973," Foreword, J. Kestin and J. Ross, AIP Conf. Proceedings No. 11, 1973, p. VII.

87. "A Theory of Asymmetric Cell Division (Differentiation)," Developmental Biology 34, f-19 (1973). (With Peter J. Ortoleva).

88. "A Chemical Instability Mechanism for Asymmetric Cell Differentiation," Biophys. Chem. 1, 87 (1973). With Peter Ortoleva).

*89. "Far-from-equilibrium phenomena at local sites of reaction", J. Chem. Phys. 60, 3124 (1974). (With K. Bimbong-Bota and P. Ortoleva).

*90. "Symmetry breaking instabilities in illuminated systems," J. Chem. Phys. 60, 3134 (1974). (With A. Nitzan and P. Ortoleva).

*91. "Mechanism of chemical instability for periodic precipitation phenomena," J. Chem. Phys. 60, 3458 (1974). (With Michele Flicker).

92. "Studies in Dissipative Phenomena with Biological Applications," Proceedings of the Solvay Conference on Membranes, Dissipative Structures and Evolution, Brussels, "Advances in Chemical Physics (1974). (With P. Ortoleva).

*93. "On a Variety of Wave Phenomena in Chemical Reactions," J. Chem. Phys. 60, 5090 (1974) (With P. Ortoleva).

*94. "A Comment on Fluctuation Around Nonequilibrium Steady States," J. Stat. Phys. 10, 379 (1974) (With A. Nitzan).

*95. "Fluctuations and Transitions at Chemical Instabilities: the Analogy to Phase Transitions," J. Chem. Phys. 61, 1056 (1974) (With A. Nitzan, P. Ortoleva and John Deutch).

*96. "On symmetry properties of reaction coordinates," J. Chem. Phys. 61, 3200 (1974) (with H. Metiu, R. Silbey and T.F. George).

97. "Threshold Excitations, Relaxation Oscillations, and Effect of Noise in an Enzyme Reaction," Proc. Nat. Acad. Sci. 71, 4067 (1974). (With H-S Hahn, A. Nitzan, P. Ortoleva).

*98. "On the Theory of Time Resolved Near-Resonance Light Scattering," J. Chem. Phys. 63, 1289 (1975) (With H. Metiu and A. Nitzan).

99. "Nucleation in Systems with Multiple Stationary States," Faraday Symposium 9-R.I. London - Physical Chemistry of Oscillatory Phenomena (1974) (With A. Nitzan and P. Ortoleva.

*100. "A stochastic theory of cluster growth in homogeneous nucleation," J. Chem. Phys. 63, 3156 (1975). With Kazuo Kitahara and Horia Metiu.

*101. "Theory of propagation of discontinuities in kinetic systems with multiple time scales: Fronts, fron multiplicity, and pulses," J. Chem. Phys. 63, 3398 (1975) (with Peter Ortoleva)

102. "Concentration enhancement in laser induced mass separation," J. Chem. Phys. 63, 4556 (1975). (with Fritz S. Klein)

*103. "Derivation of stochastic equations for nonequilibrium Ising mean field model," J. Chem. Phys. 63, 5116 (1975). (with K. Kitahara and H. Metiu).

*104. "Symmetry rules for nonconcerted reactions," Chem. Phys. 11, 259 (1975). (with H. Metiu and T. George).

105. "Stochastic theory of the kinetics of phase transitions," J. Chem. Phys. 64, 292 (1976). (with H. Metiu and K. Kitahara)

106. "Molecular beam studies of methyl radical reactions with halogen molecules: product angular and velocity distributions." J. Chem. Phys. 64, 1804 (1976). (with J. Makowski, C. Mims and G. W. Stewart).

107. "Photodissociation of NO_2 in the region 458 to 630 nm," J. Chem. Phys. 64, 3560 (1976) (with C. L. Creel).

108. "A derivation and comparison of two equations (Landau-Ginzburg and Cahn) for the kinetics of phase transitions," J. Chem. Phys. 65, 393 (1976). (with Horia Metiu and Kazuo Kitahara).

109. "Nonequilibrium Kinetics: Exact and Approximate Solutions," J. Stat. Phys. 14, 469 (1976). (with S. Hudson).

110. "Dynamical theory of migration of an adsorbed atom on solid surfaces," J. Chem. Phys. 65, 2871 (1976) (with K. Kitahara, H. Metiu and R. Silbey).

111. "Superradiance and Energy Transfer Within a System of Atoms," Physica 84A, 1 (1976) (with J. P. Stone and A. Nitzan).

112. "Multiple Stationary States and Hysteresis in a Chemical Reaction," J. Chem. Phys. 65, 3779 (1976). (with C. L. Creel).

113. "Coherent and Diffusional Motion of a Chemisorbed Atom," Chem. Phys. Letters 43, 189 (1976), (with H. Metiu, K. Kitahara and R. Silbey)

*114. "Temporal and Spatial Structures in Chemical Instabilities" Ber. Bunsenges. 80, 1112 (1976) John Ross.

115. "Franck-Condon factors in studies of dynamics of chemical reactions. I. General theory, application to collinear atom-diatom reactions" J. Chem. Phys. 66, 1021(1977). (With George C. Schatz)

116. "Franck-Condon factors in studies of dynamics of chemical reactions. II. Vibration-rotation distributions in atom-diatom reactions" J. Chem. Phys. 66, 1037 (1977). (With George C. Schatz)

117. "Franck-Condon factors in studies of the dynamics of chemical reactions. III. Analysis of information theory for vibration-rotation distributions and isotopic branching ratios." J. Chem. Phys. 66, 2943 (1977). (With George C. Schatz)

118. "On stochastic reductions in molecular collision theory: Projection operator formalism; application to classical and quantum forced oscillator model." J. Chem. Phys. 66, 3609 (1977) (with George C. Schatz and Frank J. McLafferty).

119. "Cooperative instability phenomena in arrays of catalytic sites" J. Chem. Phys. 66, 3650 (1977) (With E. K. Bimpong-Bota, A. Nitzan, and P. Ortoleva.

120. "On the quasiadiabatic description of the dynamics of electronically adiabatic chemical reactions" J. Chem. Phys. 66, 3759 (1977) (With Shaul Mukamel).

121. "Formation of ensembles with constraints of coherence" J. Chem. Phys. 66, 5064 (1977) (With Itamar Procaccia and Shaul Mukamel)

122. "Comment on non-statistical behavior in laser chemistry and chemical activation" J. Chem. Phys. 66, 5235 (1977). (With Shaul Mukamel)

123. "Aperiodic and Periodic Oscillations in Fluorescence Intensity from Irradiated Chlorocarbon Solutions of Anthracene and 9, 10-Dimethylanthracene." J. Am. Chem. Soc. 99, 6119 (1977) (with Robert L. Bose and Mark S. Wrighton).

124. "Stochastic reduction for dynamics of reactions with complex formation". J. Chem. Phys. 67, 2007 (1977) (with David J. Zvijac and Shaul Mukamel).

125. "The 1977 Nobel Prize in Chemistry," Science 198, 716 (1977) (with Itamar Procaccia).

126. "Stability and Relative Stability in Reactive Systems Far from Equilibrium. I. Thermodynamic Analysis," J. Chem. Phys. 67, 5558 (1977) (with Itamar Procaccia).

127. "Stability and Relative Stability in Reactive Systems Far from Equilibrium. II. Kinetic Analysis of Relative Stability of Multiple Stationary States," J. Chem. Phys. 67, 5565 (1977) (with Itamar Procaccia).

128. "Kinetics of Aerosol Formation in Irradiated Gaseous NO_2-SO_2 Mixtures," J. Chem. Phys. 68, 663 (1978) (with Kazutoshi Iwamoto and Nathan Presser).

129. "Consequences of size dependence of transition probabilities in stochastic equations," J. Chem. Phys. 68, 1205 (1978) (with Shaul Mukamel and Itamar Procaccia).

IN PRESS

"Chemical relaxation pulses and waves. Analysis of lowest order multiple time scale expansion," accepted J. Chem. Phys. (with Michael Collins.

"Statistical Reduction for Strongly Driven Simple Quantum Systems," accepted Physical Review (with S. Mukamel and I. Oppenheim).

"On the theory of unimolecular reactions: Application of mean first passage time to reaction rates," accepted J. Chem. Phys. (with Itamar Procaccia and Shaul Mukamel).

"A Basis for Orbital Symmetry Rules," accepted Angew. Chemie (with Horia Metiu and George M. Whitesides.

"Statistical Mechanical Theory of the Kinetics of Phase Transitions," accepted Adv. Stat. Mech. (with H. Metiu and K. Kitahara).

"Remarks on Chemical Instabilities," Proceedings of the XVIth Solvay Conference, to appear in Advances in Chemical Physics, Wiley-Interscience, N.Y.

"Instability and Far-from-equilibrium States of Chemically Reacting Systems," to appear in Advances in Chemical Physics, (with P. Hanusse and P. Ortoleva).

"Franck-Condon Factors in Studies of Dynamics of Chemical Reactions. IV. Non-adiabatic Collisions," accepted J. Chem. Phys. (with David J. Zvijac).

"On the efficiency of rate processes," submitted to J. Chem. Phys. (with Dina Gutkowicz-Krusin and Itamar Procaccia).

"Analytic Results for Asymmetric Random Walk with Exponential Transition Probabilities," submitted to J. Stat. Phys. (with Dina Gutkowicz-Krusin and Itamar Procaccia).

"Comment on 'Rate of Polymorphic Transformation Between Phase II and III of Hexachloroethane'," submitted to J. Chem. Soc. (with Horia Metiu)

"Kinetic Instabilities in First Order Phase Transitions," submitted to J. Chem. Phys. (with Ronald Lovett and Peter Ortoleva).

To be submitted:

"The reaction of photo-excited NO_2 with Cyclopropane," to be submitted to J. Chem. Phys. (with N. Presser, H. Petek and G. Eadens).

"Formation of spatial structures in illuminated systems," to be submitted to J. Chem. Phys. (with K. Iwamoto and N. Presser).

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER MIT-90-PU	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) EXPERIMENTAL AND THEORETICAL STUDIES OF CHEMICAL DYNAMIC AND INSTABILITIES IN IRREVERSIBLE PROCESSES		5. TYPE OF REPORT & PERIOD COVERED Final Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) John Ross		8. CONTRACT OR GRANT NUMBER(s) N00014-75-C-1143
9. PERFORMING ORGANIZATION NAME AND ADDRESS Chemistry Department, Massachusetts Institute of Technology, Cambridge, MA 02139		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR-098-038
11. CONTROLLING OFFICE NAME AND ADDRESS Project SQUID Headquaters, Chaffee Hall, Purdue University, West Lafayette, Indiana 47907		12. REPORT DATE August 1978
		13. NUMBER OF PAGES
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Office of Naval Research, Power Program, Code 473, Department of the Navy, 800 No. Quincy St., Arlington, VA 22217		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

This document has been approved for public release and sale; its distribution is unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

Same

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Experimental
Chemical Dynamics
Theoretical
Instabilities

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The final report summarizes the work accomplished under the subcontract. The overall objectives of the investigation were as follows: The determination of molecular properties of chemical dynamics for reactions of importance to combustion and propulsion. Molecular beam techniques were used for the experimental part of this work and were accompanied by theoretical studies in chemical dynamics. The second purpose was the study of the interaction of chemical reactions with transport processes and flows in gases in which instabilities may occur.

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)