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COMPLETED PROJECT SUMMARY

Title: Theoretical Studies of Homogeneous and Heterogeneous Reactions in Silicon Systems

Principal Investigators:

Lionel M. Raff
Regents Professor
Department of Chemistry
Oklahoma State U.
Stillwater, OK 74078
(405) 744-5939

Donald L. Thompson
Professor
Department of Chemistry
Oklahoma State U.
Stillwater, OK 74078
(405) 744-5174

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Senior Research Personnel:

Postdoctoral Research Associates and Faculty Associates:

Dr. David Martin: Dr. Martin is currently Associate Professor of Physics, Central State University, Edmond, Oklahoma.

Dr. Ronald Kay: Dr. Kay is currently Assistant Professor of Chemistry, Gordon College, MA.

Dr. Paras M. Agrawal: Dr. Agrawal is currently Associate Professor of Physics, Vikram University, Ujjain, India.

Dr. Harold W. Schranz: Dr. Schranz is currently a Research Fellow (Lecturer), Australian National University, Canberra, Australia.

Dr. James Peploski: Dr. Peploski is currently a postdoctoral research associate with our group.

Junior Research Personnel:

Dr. Michael Jezcerak, Ph.D., 1989: Dr. Jezcerak is currently an Assistant Professor of Chemistry, Central State University, Edmond, Oklahoma.

Dr. M. P. Sudhakaran, Ph. D., 1988: Dr. Sudhakaran is currently head of the Environmental Chemical Agency, Corpus Christi, Texas.

Publications

1. L. M. Raff, "Projection Methods for Obtaining Intramolecular Energy Transfer Rates from Classical Trajectory Results: Application to 1,2-difluoroethane", *J. Chem. Phys.* **89**, 5680 (1988).

2. M. Jezercak, P. M. Agrawal, D. L. Thompson, and L. M. Raff, "A Perturbation-Trajectory Method for the Study of Gas-Surface Collision Dynamics", *J. Chem. Phys.* **90**, 3363 (1989).

3. L. M. Raff, "Intramolecular Energy Transfer and Mode-Specific Effects in Unimolecular Reactions of 1,2-difluoroethane", *J. Chem. Phys.* **90**, 6313 (1989).

4. P. M. Agrawal, D. L. Thompson, and L. M. Raff, "Computational Studies of Heterogeneous Reactions of SiH_2 on Reconstructed Si(111)-(7x7) and Si(111)-(1x1) Surfaces", *J. Chem. Phys.* **91**, 5021 (1989).

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7. M. E. Riley, M. E. Coltrin, D. J. Diestler, M. Jezercak, P. M. Agrawal, D. L. Thompson, and L. M. Raff, "Comment on 'A Perturbation-Trajectory Method for the Study of Gas-Surface Collision Dynamics [*J. Chem. Phys.* **90**, 3363 (1989)]"
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9. D. L. Martin, L. M. Raff, and D. L. Thompson, "Silicon Dimer Formation by Three-Body Recombination", *J. Chem. Phys.* **92**, 5311 (1990).

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11. H. W. Schranz, L. M. Raff, and D. L. Thompson, "Correspondence of Canonical and Microcanonical Rate Constants using Phase Space Theory for Simple Bond Fissions", *Chem. Phys. Lett.*, **171**, 68 (1990).

12. H. W. Schranz, L. M. Raff, and D. L. Thompson, Statistical and Non-statistical Effects in Bond Fission Reactions of SiH_2 and Si_2H_6", *J. Chem. Phys.* **94**, 4219 (1991).

13. H. W. Schranz, L. M. Raff, and D. L. Thompson, "Non-statistical Effects in Bond Fission Reactions of 1,2-difluoroethane", *Chem. Phys. Lett.* , **182**, 455 (1991).

14. P. M. Agrawal, D. L. Thompson, and L. M. Raff, "Comparison of Silicon-atom Diffusion on the DAS and Binnig *et al.* Models of the Reconstructed Si(111)-(7x7) Surface", *J. Chem. Phys.* , **94**, 6243 (1991).

15. H. W. Schranz, L. M. Raff, and D. L. Thompson, "Intramolecular Energy Transfer and Mode-Specific Effects in Unimolecular Reactions of Disilane", J. Chem. Phys. **95**, 106 (1991).

Abstract of Objectives and Accomplishments:

The research investigations conducted with AFOSR support under Grant AFOSR-89-0085 includes the study of homogeneous and heterogeneous processes of particular importance in the chemical vapor deposition (CVD) of silicon from silane and disilane, the investigation of chemical processes occurring under conditions of close confinement, and the discovery and investigation of widespread non-statistical

dynamics and intramolecular energy transfer processes in larger polyatomic molecules.

The research program has involved primarily the theoretical study of the elementary reactions of importance in the chemical vapor deposition of silicon from silane and disilane. This includes the investigation of homogeneous unimolecular decomposition reactions of SiH_2, SiH_4, Si_2H_4, and Si_2H_6, a variety of nucleation reactions leading to silicon clusters such as Si_2, Si_3, and Si_4, and polymerization reactions leading to the higher silanes and silenes. Heterogeneous processes studied include sticking probabilities, scattering, and chemical reactions of H_2 and SiH_2 on Si(100), Si(111)-(1x1), and reconstructed Si(111)-(7x7) surfaces. Surface diffusion of hydrogen and silicon atoms on Si(111)-(1x1) and Si(111)-(7x7) have also received considerable attention.

In addition to the investigation of the dynamics of the above systems, we have also developed several new theoretical methods required to study such complex systems. These methods include: (1) methods for obtaining sufficiently accurate global potential-energy surfaces for use in trajectory calculations and in variational phase-space studies, (2) velocity reset procedures to simulate the effects of relaxation to bulk phonon modes of a surface, (3) perturbation methods that permit accurate gas-surface scattering studies to be carried out in a significantly reduced dimensional framework, (4) semi-empirical procedures for the computation of two-dimensional surface tunneling rates that take into account the effect of all of the surface phonon modes and possible tunneling paths, (5) highly efficient variational phase-space methods that incorporate exact evaluation of the integrals over momentum space and Efficient Microcanonical Sampling techniques, and (6) a new projection method for the computation of intramolecular energy transfer rates that obviates the necessity to arbitrarily define a "bond" or "mode energy". These methods have been tested by the silicon research, by studies of scattering of NO from Ag(111) surfaces, and by the investigation of the bimolecular reaction mechanism for $C_2H_4 + F_2$ and the unimolecular reaction of 1,2-difluoroethane. As a result of these investigations, we have discoved the presence of striking non-statistical effects in several gas-phase, unimolecular reactions that call into question the general use of statistical theories to treat such reactions. For example, we have found that simple bond-fission reactions of disilane and 1,2-difluoroethane are very poorly described by statistical theories of reaction rates. The underlying reasons for this are currently under investigation.

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6b. OFFICE SYMBOL *(If applicable)*

7a. NAME OF MONITORING ORGANIZATION
AFOSR/NC

ADDRESS *(City, State, and ZIP Code)*
Stillwater, Oklahoma 74078

7b. ADDRESS *(City, State, and ZIP Code)*
Building 410, Bolling AFB DC
20332-6448

NAME OF FUNDING / SPONSORING ORGANIZATION
AFOSR

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ADDRESS *(City, State, and ZIP Code)*
Building 410, Bolling AFB DC
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This Final Report for Grant AFOSR-89-0085 summarizes the results of research conducted under AFOSR support with particular emphasis on the investigations carried out during the three-year grant period for AFOSR-89-0085. The research reviewed includes homogeneous and heterogeneous processes of particular importance in the chemical vapor deposition (CVD) of silicon from silane and disilane, the study of chemical processes occurring under conditions of close confinement, non-statistical dynamics and intramolecular energy transfer processes. New methods for (1) obtaining potential energy surfaces for highly complex systems, (2) simulation of the effects of relaxation to the bulk in surface systems, (3) perturbation studies of gas-surface scattering, (4) computation of two-dimensional surface tunneling rates, (5) highly efficient variational phase space theory calculation of microconical unimolecular reaction rates, and (6) the computation of intramolecular vibrational relaxation rates are also described.

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2a. NAME OF RESPONSIBLE INDIVIDUAL
Professor Mark Gordon

22b. TELEPHONE *(Include Area Code)*
(202) 767-4963

22c. OFFICE SYMBOL
AFOSR/NC

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Final Report: Theoretical Studies of Homogeneous and Heterogeneous Reactions in Silicon Systems

Lionel M. Raff and Donald L. Thompson

Department of Chemistry
Oklahoma State University
Stillwater, Oklahoma 74078

Lionel M. Raff

Lionel M. Raff
Regents Professor
(405) 744-5939

Donald L. Thompson

Donald L. Thompson
Professor
(405) 744-5174

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Abstract:

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I. Introduction:

This report summarizes the research programs conducted with AFOSR support under Grant AFOSR-89-0085. For purposes of clarity, the research is discussed in the context of work completed under previous AFOSR support.

The program involves primarily the theoretical study of the elementary reactions of importance in the chemical vapor deposition of silicon from silane. This includes the investigation of homogeneous unimolecular decomposition reactions of SiH_2, SiH_4, Si_2H_4, and Si_2H_6, a variety of nucleation reactions leading to silicon clusters such as Si_2, Si_3, and Si_4, and polymerization reactions leading to the higher silanes and silenes. Heterogeneous processes under study include sticking probabilities, scattering, and chemical reactions of H_2 and SiH_2 on Si(100), Si(111)-(1x1), and reconstructed Si(111)-(7x7) surfaces. Surface diffusion of hydrogen and silicon atoms on Si(111)-(1x1) and Si(111)-(7x7) have also received considerable attention.

In addition to the investigation of the dynamics of the above systems, we have also developed several new theoretical methods required to study such complex systems. These methods include: (1) methods for obtaining sufficiently accurate global potential-energy surfaces for use in trajectory calculations and in variational phase-space studies, (2) velocity reset procedures to simulate the effects of relaxation to bulk phonon modes of a surface, (3) perturbation methods that permit accurate gas-surface scattering studies to be carried out in a significantly reduced dimensional framework, (4) semi-empirical procedures for the computation of two-dimensional surface tunneling rates that take into account the effect of all of the surface phonon modes and possible tunneling paths, (5) highly efficient variational phase-space methods that incorporate exact evaluation of the integrals over momentum space and Efficient Microcanonical Sampling techniques, and (6) a new projection method for the computation of intramolecular energy transfer rates that obviates the necessity to arbitrarily define a "bond" or "mode energy". These methods have been tested by the silicon research, by studies of scattering of NO from Ag(111) surfaces, and by the investigation of the bimolecular reaction mechanism for $C_2H_4 + F_2$ and the unimolecular reaction of 1,2-difluoroethane. As a result of these investigations, we have discoved the presence of striking non-statistical effects in several gas-phase, unimolecular reactions that call into question the general use of statistical theories to treat such reactions.

In Section II, we review the previous and current progress of our research program. The section concludes with a listing of all papers and presentations made under AFOSR sponsorship. The personnel associated with the program are described in Section III.

For the reader's convenience, we have concluded most sections and subsections with a brief summary. These summaries may be used to obtain a rapid overview of the entire proposal.

II. Review of Previous Work:

IIA. Overview

We have been conducting theoretical studies of the elementary homogeneous and heterogeneous processes involved in the chemical vapor deposition (CVD) of silicon from silane and disilane. The homogeneous gas-phase reactions investigated to date include the key unimolecular dissociation processes of Si_2H_6, Si_2H_4, SiH_4, and SiH_2. In each case, the calculations have treated all energetically accessible decomposition channels. Similar studies have also been carried out on 1,2-difluoroethane as part of a program designed to study reactions occurring under highly confined conditions. Bimolecular reactions that constitute important steps in polymerization processes leading to higher silanes have received considerable attention. Silicon clustering reactions that lead to the formation of Si_2, Si_3, and Si_4 aggregates have been examined and their relative importance in promoting silicon crystal growth in the CVD experiments determined.

The heterogeneous silicon surface processes that have been investigated to date include studies of sticking, dissociative chemisorption, energy transfer, surface diffusion, surface relaxation to bulk modes, chemical reactions, and tunneling effects of H, H_2, Si, Si_2, Si_3, Si_4, and SiH_2 species on Si(100), Si(111)-(1x1), and reconstructed Si(111)-(7x7) surfaces.

As mentioned above, we have initiated investigations of chemical processes that occur in very confined spaces. The study of such reactions has been listed as one of the key problems in silicon chemistry.[1] In order to determine the effects of close confinement upon the reactions in question, we have first conducted detailed dynamical studies of the corresponding gas-phase reactions to provide a basis for comparison with the results obtained when the reactions occur in a confined environment. The gas-phase dynamics predicted by these investigations have also provided us with a means of evaluating the accuracy of our methods for the development of global potential-energy surfaces.

As a result of our extensive investigations of microcanonical unimolecular decomposition reactions, we have recently discovered the existence of non-statistical effects that call into question the use of transition-state methods for the study of such reactions. To date, our investigations, coupled with some recently reported experimental results, suggest that these non-statistical effects may be widespread in reactions of polyatomic molecules. By comparing the detailed molecular and intramolecular energy transfer dynamics of the 2-chloroethyl radical (which behaves statistically) with those for 1,2-difluoroethane and disilane (which are nonstatistical), we have been able to formulate ome general principles that permit perdictions of nonstatistical dynamics to be made in advance of the experiments and/or calculations.

The chemistry involved in the above systems is, in many cases, very complex. Often several competing reaction channels must be considered. This has required the use of a wide variety of theoretical methods that include classical trajectories[2], variational phase-space theory methods such as those developed by Truhlar, Garrett, and coworkers[3] and by Voter and Doll[4], Monte Carlo methods with efficient microcanonical sampling procedures (EMS)[5-7], wavepacket calculations, perturbation methods[8,9], projection procedures[10] to follow intramolecular energy transfer processes, Langevin methods developed by Aldeman, Doll, and coworkers[11] and by Lucchese and Tully[12], and velocity reset methods such as those reported by Riley, Coltrin, and Diestler[13]. In addition, the need to obtain sufficiently accurate potential-energy surfaces has required the development of procedures that permit the results of *ab initio* SCF, CI, and Möller-Plesset fourth-order perturbation calculations (MP4) to be combined with pertinent experimental data to produce the required global potential-energy surfaces. In order to study surface tunneling effects, we have developed procedures that permit reaction-path methods to be coupled with variational phase-space theory[14].

The general thrust of our research has been to determine the extent to which existing methods are useful in the examination of complex chemical systems and, where necessary, to develop suitable extensions of existing methods or entirely new procedures. In this section, we review our accomplishments to date. The new methods developed and the principal results of each investigation are briefly summarized. At the end of the section, we give a complete listing of all papers published and oral presentations given.

II.B. Potential-Energy Hypersurfaces

The most crucial and difficult part of any dynamics study for a complex system is the development of a potential-energy hypersurface that is sufficiently close to the potential for the experimental system under investigation that the results of the dynamics calculations may be regarded as meaningful. Such surfaces must accurately represent all open reaction channels. Since it is obviously impossible to carry out converged, multi-referenced, complete configuration interaction calculations at a sufficiently large number of configuration points to completely characterize the hypersurface, the problem can never be "solved". However, our experience has shown that this level of accuracy is not necessary to obtain useful results. If certain key elements of the potential surface are accurately described and if the choice of functional forms used to the fit the available experimental and *ab initio* data is based on well-judged chemical and physical considerations, then the computed dynamics, rates, and mechanisms for the system are often in good to excellent accord with experiment even though many of the finer details of the surface may be incorrect.

The minimum data base required for the formulation of a global potential hypersurface contains data on the thermochemistry for all important reactant channels, fundamental vibrational frequencies and equilibrium geometric structures for all reactants and products, and potential-energy barriers for the reactions of importance. It is also very useful to have data concerning the structure and vibrational frequencies of the transition states. Much of this data is usually available from experimental measurement. Data related to the transition states and radical species can be obtained from electronic structure calculations.

Once the required data base is in-hand, a suitable analytical function for the system potential that can be accurately fitted to the data must be developed. In principle, the total potential may be written as a many-body expansion of the form

$$V = \sum V_i , \tag{1}$$

where the V_i are i-body terms and V includes the sum of all possible such terms. Murrell and co-workers[15] have made effective use of such an expansion for systems in which the number of atoms, N, is ≤ 4. For more complex systems, however, Eq.(1) becomes computationally intractable. In fact, even for the case $N = 4$, it is extremely difficult to use Eq.(1). For systems as complex as those of interest here, it is essentially impossible.

During the past three years, we have developed an approach to these problems that has proven itself to be very satisfactory. Basically, we employ many-body, parametrized functional forms suggested by chemical and physical considerations. This analytical potential is then fitted to the data base using an iterative scheme involving simultaneous parameter adjustment. Experience has shown that excellent fits can be achieved using such methods. Furthermore, we also find that the method often produces acceptable accuracy with regard to topographical features of the surface not directly addressed in the fitting process. Numerous direct comparisons of the results of dynamics calculations on potential surfaces obtained in this manner with experimental data have shown the extent of agreement to be generally good, and often excellent. Several examples of such agreement are given in the following sections. Although tedious and often difficult to implement, we believe that such a procedure is the only currently available route to ensure that the potential for the model system will be sufficiently close to that for the actual experimental system to permit meaningful dynamics calculations to be carried out.

We have previously applied the above method in the development of potential hypersurfaces for SiH_2[16], Si_3[17], Si_4[18], Si_2H_4[16], Si_2H_6[19], C_2H_4[20], and $H_2FC\text{-}CH_2F$[20,21]. In each case, these surfaces correctly predict a wide array of structural, energetic, and dynamical data for the system. The results discussed in the following sections serve as illustrations of the level of accuracy that we have been able to obtain using these methods.

Summary:

Global potential-energy hypersurfaces are obtained by employing many-body, parametrized functional forms suggested by chemical and physical considerations to fit a data base consisting of energies, structures, and potential surface curvatures for reactants, products, and transition states obtained from experimental measurements and the results of ab initio electronic structure calculations. The analytical potential is fitted to this data base using an iterative method involving simultaneous parameter adjustment. Using these methods, we have developed global potential surfaces for the SiH_2[16], Si_3[17], Si_4[18], Si_2H_4[16], Si_2H_6[19], C_2H_4[20], ***and*** $H_2FC\text{-}CH_2F$[20,21] ***systems. In each case, the global***

surfaces correctly predict a wide array of structural, energetic, and dynamical data for the system.

IIC. Silicon Chemistry

IIC.1. Homogeneous Reactions

Numerous homogeneous gas-phase reactions play a role in silicon crystal growth via CVD methods. Except at very low pressures[22], the initiating reactions in the silicon CVD process involve the unimolecular decomposition of the starting material. If this is silane, the principal reactions of interest are

(R1) $SiH_4 \text{ ---> } SiH_3 + H$,

(R2) $SiH_4 \text{ ---> } SiH_2 + H$, followed by

(R3) $SiH_2 \text{ ---> } SiH + H$, and

(R4) $SiH_2 \text{ ---> } Si + H_2$.

Once silicon atoms are formed via reaction R4, clustering processes are initiated. Silicon dimers may be formed directly by termolecular reactions such as

(R5) $Si + Si + M \text{ ---> } Si_2 + M$,

where M is any third body or via polymer decomposition pathways involving higher silanes:

(R6) $SiH_4 + SiH_2 \text{ ---> } Si_2H_6$,

(R7) $Si_2H_6 \text{ ---> } Si_2H_4 + H_2$,

(R8) $SiH_2 + SiH_2 \text{ ---> } Si_2H_4$, followed by

(R9) $Si_2H_4 \text{ ---> } Si_2H_2 + H_2$, and

(R10) $Si_2H_2 \text{ ---> } Si_2 + H_2$.

Once the Si_2 dimer is formed, higher silicon clusters may be formed via a series of monomer or dimer addition reactions of the form

(R11) $Si + Si_n \text{ ---> } Si_{n+1}$ and

(R12) $Si_2 + Si_n \text{ ---> } Si_{n+2}$,

provided the adducts, Si_{n+1} and Si_{n+2} , can be stabilized by collisions with a third body before they undergo unimolecular decomposition. Coltrin, Kee, and Miller[23] and Breiland, Coltrin, and Ho[24] have suggested that reactions R6-R10 are the major mechanistic pathways leading to silicon dimer formation.

The formation of such clusters are a likely source of particulate formation in silicon CVD[23,25-27]. Calculations by Coltrin *et al.*[23] have predicted that Si_2 and Si_3 make the dominant contribution to the overall deposition rate in silicon CVD from silane at temperatures above 1150° C when the carrier gas is helium; these results for Si_2 in a silane CVD reactor have received qualitative experimental confirmation[24]. Consequently, our research group has devoted considerable attention to the study of the rates and mechanisms of such clustering reactions.

If silicon CVD is done using disilane as the starting material, then the initial homogeneous reactions are much more complex. Possible channels of importance include

(R13) $Si_2H_6 \dashrightarrow SiH_4 + SiH_2$,
(R14) $Si_2H_6 \dashrightarrow 2\,SiH_3$,
(R15) $Si_2H_6 \dashrightarrow Si_2H_5 + H$,
(R16) $Si_2H_6 \dashrightarrow H_3Si{=}SiH + H_2$,
(R17) $Si_2H_6 \dashrightarrow H_2Si{=}SiH_2 + H_2$,
(R18) $Si_2H_4 \dashrightarrow H_2Si{=}SiH + H$,
(R19) $Si_2H_4 \dashrightarrow H_2Si{=}Si + H_2$,
(R20) $Si_2H_4 \dashrightarrow HSi{=}SiH + H_2$, and
(R21) $Si_2H_4 \dashrightarrow 2\,SiH_2$.

To date, we have conducted theoretical studies of most of the above reactions. These investigations have employed quasiclassical trajectory techniques[2] and three classical variational phase-space methods. The first of the variational phase-space methods[28] uses an RRKM formalism but replaces the quantum-state counts with analogous classical sums over phase space. The calculated rate is then variationally minimized with respect to the location of the critical surface. This procedure is based upon the work of Farantos, Murrell, and Hajduk[29], Bhuiyan and Hase[30], and that of Noid, Koszykowski, Tabor, and Marcus[31] who have shown that there is often excellent agreement between the exact quantal sums and the classical phase-space integrals. The second variational method[32] (MCVPST) is an application of Doll's[4,33] generalization of Slater theory in which he has replaced the averaging over the normal mode vibrational phases with an average over the microcanonical ensemble. Doll used this method to examine the dissociation of four-atom clusters[33] and Adams[34] employed similar procedures to obtain vibrational predissociation rates for van der Waals clusters. Finally, we have adapted the Efficient

Microcanonical Sampling (EMS) methods developed by Hippler *et al.*[5] and Nyman *et al.*[6,7] to Doll's method[33] and coupled this with analytical evaluation of the integrals over the momentum space[35] to produce a highly efficient procedure for the study of unimolecular decomposition reactions in very complex molecular systems. We denote this procedure by EMS-TST.

We have also extended the MCVPST method to permit calculation of microcanonical unimolecular decomposition rates out of specified initial rotational states[36]. This method is a variant of that originally developed by Wardlaw and Marcus[37] who computed such rates using a transition-state procedure in which the "transitional" modes are treated with Monte Carlo methods while the quantum states for the remaining degrees of freedom are counted directly. Application of the rotational-state specific version of the MCVPST method to the decomposition of CH_4 on the *ab initio* potential surface developed by Duchovic, Hase, and Schlegel[38] gave results in accord with previous findings by Hase and Wolf[39] and by Miller and Brown[40] and showed that the method was more than an order of magnitude more computationally efficient than the corresponding classical trajectory calculations.

The dynamics of the silicon clustering reactions, R5, R11, and R12, leading to the formation of dimers, trimers, and tetramers have been examined using trajectory methods[17,18,41,42]. The potential-energy hypersurfaces for the Si_3 and Si_4 systems have been obtained using the methods described in Section II.B. The data bases required for the surface fitting were obtained from the *ab initio* results reported by Peyerimhoff and Buenker[43] for the Si_2 dimer and by Raghavachari[44,45] for the Si_3 and Si_4 clusters. The Si_2 calculations[43] were done at the CI level while Raghavachari[44,45] carried out both CI and MP4 calculations using (6s,5p,2d,1f) basis sets for the trimer and MP4 calculations with a 6-31G* basis set for the tetramer. The results provide data for several Si_3 and Si_4 electronic states having various geometries. In addition, we have incorporated the experimental data reported by Chatillon *et al.*[46] and Huber and Herzberg[47]. For the Si_3 system[17], the calculated rms deviation of the energies obtained from the global surface from the *ab initio* results[44] is 0.117 eV. Equilibrium geometries and energies are essentially in exact accord with the electronic structure calculations. The fundamental normal mode frequencies predicted by the global surface are within 37 cm^{-1} or less of those given by the MP4 calculations[44]. Results of similar quality are obtained for the tetramer[18]. In this case, the average difference between the predictions from the global surface and the *ab initio* data[45] for the internuclear distances for the minimum energy square, tetrahedron, and linear Si_4 structures is 0.166 a.u.; the error in any of these distances is less than 5%. The average deviation of the calculated fundamental frequencies for the ground-state Si_4 rhombus structure is 35.1 cm^{-1}.

The rates and dynamics for reaction R5 with M = Ar or Si have been investigated at temperatures of 800, 1000, and 1200 K[41,42]. The calculated rate coefficients for the [Ar,Si,Si] system all lie in the range of 1.34-1.46 x 10^{16} cm^6/mol^2-s. If rotationally trapped dimers are included, the results are in the range 2.51-2.68 x 10^{16} cm^6/mol^2-s. The weak temperature dependence is characterized by an activation energy of 1.2 kcal/mol. When Si is the third body, the rates are more than an order of magnitude larger. Four mechanistic pathways leading to recombination have been identified. These are (a) direct energy exchange, (b) direct atom exchange, (c) complex formation, and (d) metastable formation due to a rotational barrier. For the [Si,Si,Si] system, the relative contribution of these pathways are [(a)+ (b)] {66%}, (c) {6%}, and (d){28%}. Internal energy distributions for product Si_2 dimers have also been obtained for both systems.

Silicon clustering via reaction reaction R11 with n = 2 and 3 have also been examined[17,18]. Formation cross sections for the trimer are found to exhibit a near double exponential dependence upon relative translational energy. Calculated thermal rate coefficients are on the order of 10^{15} cm^3/mol-s and show a negative temperature dependence at temperatures below 200 K. Microcanonical rate coefficients at six different energies have been calculated. These results follow an RRK energy dependence with s = 2.67. The average Si_3 lifetimes are found to lie in the range 0.47 - 50.2 ps. The formation cross section for Si_4 peaks sharply near $E_t = 0$ and falls off in near linear fashion with energy. The thermal rate coefficients for tetramer formation lie in the range 6-8 x 10^{14} cm^3/mol-s for the temperature range 800-1500 K. Microcanonical rate coefficients are well-described by an RRK expression with s = 4.67. The average Si_4 lifetime is computed to be 413 ps at 800 K. This lifetime, as well as that for the trimer, are not sufficiently long to permit a stabilizing collision to occur at pressures characteristic of low-pressure CVD experiments. Consequently, we may conclude that if Si_3 and Si_4 play a role in silicon surface growth in CVD experiments, their formation must involve a pathway other than reaction R11. Some possible pathways are discussion in Section III.B.

The decomposition pathways and rates for silane, reactions R1-R4, have been investigated in the initial phases of the AFOSR project[28,32,48]. During the first two years of the current grant, we have directed our attention toward the study of the more complex Si_2H_4 and Si_2H_6 systems, reactions R13-R21[16,19,49].

The potential-energy surfaces for Si_2H_4 and Si_2H_6 were developed using the methods of Section II.B. The *ab initio* calculations reported by Ho, Coltrin, Binkley, and Melius[50,51], Gordon and co-workers[52,53], Binkley[54], and Peyerimhoff and Buenker[43] along with important experimental data obtained by Berkowitz *et al.*[55], Jasinski[56], and Inoue and Suzuki[57] make up the data base to which the global surfaces are fitted. These electronic structure calculations use CI and MP4 methods to obtain bond enthalpies, equilibrium geometries, fundamental vibrational frequencies, and transition-state enthalpies for SiH_n and Si_2H_n (n = 0-6) molecules. The experimental data provide Si-H bond energies and activation energies for some of the important decomposition channels. The resulting global surface for disilane contains 40 many-body terms with 88 parameters that describe the geometries, energies, and stretching, bending, and torsional motions for Si_2H_6, Si_2H_5, $H_3Si{=}SiH$, $H_2Si{=}SiH_2$, $H_2Si{=}SiH$, $H_2Si{=}Si$, $HSi{=}SiH$, H_2, SiH_2, and Si_2 species as well as the barrier heights and reaction profiles for all of the important reaction channels of the system described by reactions R13-R21. In general, the equilibrium bond lengths and angles given by this global surface are in agreement with the *ab initio* results to within 0.03 Å and 0.5°, respectively. The calculated heats of reaction for 24 different channels are in excellent agreement with the *ab initio* MP4 calculations[50-54] and with the experimental data[55-57]. The average error is 2.79 kcal/mol. The average deviation of the predicted fundamental frequencies for Si_2H_6, Si_2H_5, $H_3Si{=}SiH$, $H_2Si{=}SiH_2$, $H_2Si{=}SiH$, $H_2Si{=}Si$, and SiH_2 from the results reported by Ho *et al.*[50,51] is 55.7 cm^{-1}. The computed barrier heights are in accord with measured thermal activation energies[56,57].

The unimolecular decomposition reactions of Si_2H_4 and Si_2H_6, reactions R13-R21, have been investigated on the above global potential-energy surfaces using trajectory[2,16,19,49] and variational EMS-TST methods[35,58]. In the latter calculations, the microcanonical rate coefficient, k(E), for unimolecular reactions is expressed as an average over the microcanonical ensemble[33]

(2) $k(E) = 0.5 \int d\Gamma\delta[H(\Gamma)-E]\,\delta[q_{RC} - q_C]\,|V_{RC}| \;/\; \int d\Gamma\delta[H(\Gamma)-E]$,

where Γ is the complete set of position and momentum coordinates [**q**, **p**], $H(\Gamma)$ is the Hamiltonian of the system excluding center-of-mass motion, $q_{RC} = q_{RC}(\mathbf{q})$ is the reaction coordinate, which may be a function of some or all of the coordinates **q**, q_C is the critical value required for reaction, and $|V_{RC}|$ is the absolute value of the velocity component perpendicular to the critical surface. The integrals over Γ in Eq.(2) are understood to be over the reactant portion of phase space. Equation (2) is equivalent to the microcanonical rate coefficient of generalized transition-state theory[59] for the special case that the critical surface separating reactant and product configurations is a function of coordinates only.

In the MCVPST[32] application of Eq.(2), the integrals are evaluated using Metropolis sampling over the entire 6N-dimensional phase space Γ. In addition, the delta function, $\delta[H(\Gamma)-E]$, is replaced with a prelimit form. While this procedure serves to increase the rate of convergence of the Monte Carlo sums that are used to approximate the integrals, it allows points lying off the energy shell to make unwanted contributions to the rate coefficient.

In the present calculations[35,58], we have introduced methods that obviate both of the above problems. By incorporation of the Efficient Microcanonical Sampling (EMS) procedure[5-7], we may eliminate the need to employ a prelimit form of the delta function and thereby remove any contribution to k(E) from phase-space points that lie off the energy shell. In addition, by exploiting the separability between potential and kinetic energy in the Hamiltonian, we may execute the integrations over the momentum coordinates in Eq.(2) analytically and thereby derive a closed-form expression for the average velocity perpendicular to the critical surface for the case of simple bond fission reactions[35]. When this is done, Eq.(2) becomes

(3) $k(E) = 0.5 \langle|V_{RC}|\rangle \int d\Gamma W(\mathbf{q})\delta[q_{RC} - q_C] \;/\; \int d\Gamma W(\mathbf{q})$,

where $W(\mathbf{q})$ is the appropriate EMS statistical weight that has been shown to be[5-7]

(4) $W(q) = [E-V(\mathbf{q})]^{(3N-5)/2}$.

For bond fission reactions, we have shown[35] $\langle|V_{RC}|\rangle$ to be given by

(5) $<|V_{RC}|> = [2K/\pi\mu_R]^{1/2} [(3N-5)/2!] / [(3N-4)/2]!$,

where μ_R is the reduced mass associated with the reaction coordinate and

(6) $K = E - V(q_C)$.

To increase the rate of convergence of Eq.(3), we have also included importance sampling to increase the probability that the Markov walk samples regions of higher potential[58]. To do this, we have employed an importance sampling weight, I(**q**), with the same form as W(**q**):

(7) $I(\mathbf{q}) = [E - V(\mathbf{q})]^a$,

which gives an effective weight function for the Markov walk of

(8) $W(\mathbf{q})/I(\mathbf{q}) = [E - V(\mathbf{q})]^{\{(3N-5)/2\} - a}$.

The exponent a is adjusted to provide a satisfactory Markov walk for accurate evaluation of both the numerator and denominator of Eq.(3).

The recombination of silylene molecules to form disilene,

(R22) $SiH_2 + SiH_2 \dashrightarrow Si_2H_4$,

has been examined using trajectory methods[16]. Cross sections and thermal rate coefficients have been determined over the range 300-1500 K. Thermally averaged formation cross sections vary from 66.3 to 28.7 $Å^2$ over this range. The corresponding thermal rate coefficients lie in the range 2-4 x 10^{14} cm^3/mol-s. We have found that the reaction exothermicity is primarily partitioned into the Si-Si stretch and the H-Si-H bending modes upon formation of Si_2H_4.

To date, there have been no measurements of the rate coefficients or cross sections for reaction R22. However, some photolysis data have been reported for the analogous reaction of SiH_3[60-62],

(R23) $SiH_3 + SiH_3 \dashrightarrow Si_2H_6$.

The reported rate coefficient for R23 was 0.5 x 10^{14} cm^3/mol-s at 373 K. This value is 1/4 the corresponding rate computed for reaction R22. Since the attractive interaction and Si-Si bond energy is greater for the recombination of SiH_2 than for SiH_3, and since we would expect more steric hindrance in the recombination process for SiH_3, our computed results seem to be in reasonable accord with the experimental data.

The dissociation dynamics of Si_2H_4 have been examined in great detail over the internal energy range $5.0 \leq E \leq 9.0$ eV[49]. In this range, the most important dissociation channel is three-center elimination of molecular hydrogen leading to $H_2Si=Si$, reaction R19. For energies below 7.0 eV, the other decomposition channels are, in order of importance, Si-Si bond rupture (R21), four-center H_2 elimination (R20), and Si-H bond rupture (R18). At or above 8.0 eV, four-center H_2 elimination replaces Si-Si bond rupture as the second most important dissociation channel. Microcanonical rate coefficients for all of these channels have been obtained. We find that three-center H_2 elimination involves a simultaneous rupture of both Si-H bonds whereas the four-center elimination channel is found to proceed by a hydrogen-atom transfer process followed by H_2 elimination. Except for a propensity to form H_2 with excess rotational energy, the energy partitioning among the products is nearly statistical.

The Si_2H_6 dissociation dynamics at seven internal energies ranging from 5.31 to 9.31 eV have been determined using both trajectory and EMS-TST methods[19,35,58]. At low internal energies, dissociation leading to $SiH_4 + SiH_2$, reaction R13, dominates the dynamics. For energies in the range $5.31 \leq E \leq 6.31$ eV, the various decomposition channels are, in order of importance, hydrogen-atom transfer leading to $SiH_4 + SiH_2$ (R13), Si-Si bond rupture (R14), three-center H_2 elimination (R16), Si-H bond rupture (R15), and four-center H_2 elimination (R17). At higher energies, entropy effects cause an inversion of this ordering such that Si-Si bond rupture becomes the major reaction channel followed by three-center H_2 elimination, $SiH_4 + SiH_2$ formation, Si-H bond rupture, and four-center H_2 elimination. Our results indicate that formation of disilene in silicon CVD experiments occurs predominately via the formation of $H_3Si=SiH$ from three-center H_2 elimination followed by a low-barrier hydrogen-atom transfer process. For all decomposition channels, most of the available energy is partitioned into vibrational modes of the products. To a large extent, product energy partitioning is found to be governed by statistical considerations. We find that while three-center H_2 elimination is a concerted reaction, it probably does not proceed via a symmetric pathway. Reaction R13 is found to concerted, but four-center H_2 elimination involves the rupture of one Si-H bond followed by a hydrogen transfer and a subsequent H_2 abstraction reaction to give the $H_2 + Si_2H_4$ products.

One of the most interesting, and perhaps important, findings of these studies is the fact that the EMS-TST calculations[58] of the microcanonical rate coefficients for Si-H and Si-Si bond rupture in Si_2H_6 demonstrate the existence of pronounced non-statistical effects in spite of the fact that the total internal energy content is well in excess of the dissociation thresholds. We have found evidence that such non-statistical effects may be widespread among polyatomic molecules. These results call into question the practice of using statistical methods, such as transition state theory, to investigate these reactions.

Summary:

We have employed trajectory and variational phase-space methods to examine the dynamics of silicon clustering reactions, silylene recombination, and unimolecular dissociation reactions of SiH_4, SiH_2, Si_2H_4, and Si_2H_6. Global potential-energy surfaces are developed for each of these systems using the results of electronic structure calculations and experimental measurements as the data base to which we fit many-body functional forms suggested by physical and chemical considerations. The global potentials are shown to give good to excellent results when compared to measured and/or calculated equilibrium geometries, energies, fundamental frequencies, and barrier heights. Dynamical results include cross sections, thermal and microcanonical rate coefficients, lifetimes, detailed mechanisms, and energy partitioning information for all open reaction channels. Striking non-statistical effects are found for the bond fission reactions of disilane.

IIC.2. Heterogeneous Reactions

The surface processes of interest in silicon CVD include inelastic surface scattering and sticking, dissociative chemisorption, surface diffusion, tunneling, and chemical reactions. To investigate these processes, we have employed MCVPST[32], trajectory[63], and master equation[64] methods to examine surface diffusion, and WKB semiclassical methods coupled with MCVPST calculations to study the effects of tunneling on hydrogen-atom diffusion[14]. Inelastic scattering events and sticking probabilities have been computed using semiclassical wavepacket[65], perturbation[8,9], and trajectory[66] methods. To date, the surface reactions investigated include the dissociative chemisorption of H_2 on Si(111) surfaces with and without partial hydrogen coverage[67,68], thermal desorption of molecular hydrogen from Si(111) surfaces[69,70], the chemisorption and subsequent decomposition of SiH_2 on Si(111)[71] and reconstructed Si(111)-(7x7) surfaces[72], and the chemisorption of silicon clusters, Si_n (n = 2,3,4), on Si(111)-(7x7) surfaces[73]. Of particular interest in these studies are the effects of surface temperature, surface orientation and reconstructions, surface dislocations and kinks, and surface coverage.

The problem of obtaining sufficiently accurate potential-energy surfaces is even more acute for heterogeneous systems than is the case for the gas-phase reactions discussed above. Except for a few cluster calculations for selected systems, along with some thermodynamic and spectroscopic data, there is usually very little information available on the topographical features of these potential surfaces. Consequently, we must content ourselves with the use of more empirical surfaces. Although we might expect such hypersurfaces to yield at most qualitative, or in some cases, semi-quantitative information, we have found that the results can be surprisingly good provided care is taken to fit the known energetics of the system as well as possible. Several examples taken from our recent studies are given below. In spite of some notable successes to the contrary, we generally regard our theoretical results in heterogeneous systems to be only indicators of the true system behavior, which is often unknown. Such "indicators" are useful in themselves and often point the way to new experiments or theoretical methods that will provide more accurate information.

In our initial studies, we have investigated inelastic scattering, sticking, and/or dissociative chemisorption of Si, H, H_2, and SiH_2 incident on unreconstructed Si(100) and Si(111) surfaces and partially-to-fully covered (with H atoms) Si(111) surfaces[65-68,71,72]. The lattice models used in these calculations have 9 to 60 atoms in the primary reaction zone (P-zone) and 70 or more in the secondary Q-zone[74]. Both Weber's parametrization[75] of Keating's[76] potential and a dissociative potential developed by Brenner and Garrison[77] were used to represent the lattice interactions. To incorporate the effects of relaxation of the P-zone atoms to the bulk phonon modes, we developed a velocity reset method[68] using concepts analogous to those employed by Riley, Coltrin, and Diestler[13]. In this method[68], the velocities of the peripheral atoms of the P-zone are reset at periodic intervals according to a prescription based on the local temperature and the temperature of the bulk. Berendsen *et al.*[78] have shown that this method is equivalent to a Langevin procedure under conditions that all frictional coefficients are equal and there is no Gaussian white noise term. In our more recent studies, we have utilized the Riley *et al.*[13] procedure to incorporate bulk relaxation effects.

The principal results obtained from the above studies are as follows: (1) Sticking coefficients for Si atoms and SiH_2 molecules are near unity at all surface temperatures. (2) The major processes observed in collisions of hydrogen atoms with partially covered Si(111) surfaces are direct scattering, exchange scattering, direct chemisorption, and chemisorption with exchange. (3) For the case of H-atom adsorption on partially-covered Si(111) surfaces, the extent of surface coverage is found to have only a small effect upon the calculated sticking probabilities. (4) Energy transfer to the bulk phonon modes is found to be a first-order process in which energy is transferred mainly from stretching motions of the adsorbate to the bending modes of the silicon surface. Rate coefficients for this transfer decrease with increasing surface temperature and are on the order of $1\text{-}2 \times 10^{12}\ s^{-1}$. (5) The nature of H_2 dissociative chemisorption on Si(111) surfaces is qualitatively similar to that observed by Wolken and co-workers[79-82] for the H_2-W(100) system and by Lee and DePristo[83,84] for H_2-Ni systems. The quantitative differences are mainly due to the increased exothermicity of H_2 chemisorption on Si(111) surfaces. H_2 adsorption in this system is always accompanied by dissociation and the sticking probabilities are virtually independent of surface relaxation, the size of the lattice model, and the nature of the lattice potential. Si-H vibrational energy transfer rates to the lattice are increased and surface mobilities are decreased by the inclusion of relaxation to bulk modes but the magnitude of these effects is less than a factor of two.

During the grant period for AFOSR-89-0085, we have directed our attention toward studies of the chemisorption and subsequent reaction of SiH_2[72], Si_2, Si_3, and Si_4 clusters, and silicon-atom diffusion rates[85,86] on reconstructed Si(111)-(7x7) surfaces. We have also developed perturbation methods that significantly reduce the computational requirements for the study of surface processes[8,9].

The dynamics of chemisorption and decomposition of SiH_2 on Si(111)-(7x7) surfaces have been investigated using trajectory methods[72]. The Binnig *et al.*[87] model is employed to represent the (7x7) reconstruction. The lattice model in these studies consists of the 12 silicon adatoms found by Binnig *et al.*[87] in the topmost layer of the surface, 81 silicon atoms in layer B, 99 in layer C, and 99 in layer D for a total of 291 atoms. In some calculations, we have employed the Keating lattice potential[76] with the force constants modified to yield the lattice strain energy predicted by the Brenner-Garrison potential[77]. In other studies, this lattice potential has been replaced with one suggested by Bolding and Andersen[88] to describe silicon clusters, crystals, and surfaces. This potential is a generalization of the bonding formulation used by Tersoff[89] in which the total potential is represented by a sum of two-body terms each of which contains an environment-dependent "interference" function. The SiH_2-surface interaction potential is fitted to calculated bond energies, structures, measured and/or calculated vibrational frequencies, and to *ab initio* calculations of the repulsive interactions between SiH_2 and the closed-shell lattice atoms using methods similar to those described in Section II.B.

Our results predict SiH_2 sticking probabilities to be near unity on the reconstructed surface. Subsequent to chemisorption the major mode of SiH_2 decomposition is found to be direct release of molecular hydrogen into the gas phase:

(R23) $\quad {}^*\text{-}SiH_2 \text{ ---> } {}^*\text{-}Si + H_2$,

where * represents a surface binding site. Hydrogen-atom dissociation to adjacent lattice sites is found to be the secondary decomposition channel:

(R24) $\quad {}^*\text{-}SiH_2 + {}^* \text{ ---> } {}^*\text{-}SiH + {}^*\text{-}H$.

The calculated rate coefficients are 3.4×10^{10} and 0.8×10^{10} s^{-1} for reactions R23 and R24, respectively.

At the time of publication of the above results, the only experimental data related to the surface decomposition of SiH_2 was that obtained by Farnaam and Olander[90] from their molecular beam studies of silane decomposition on Si(111)-(7x7) surfaces. They proposed that SiH_4 chemisorption occurs via the reaction

(R25) $\quad SiH_4 + {}^* + {}^*\text{-}{}^* \text{ ---> } {}^*\text{-}SiH_2 + H\text{-}{}^*\text{-}H + {}^*$.

Subsequent to chemisorption, these investigators observed only a single decomposition channel for chemisorbed SiH_2,, the concerted release of molecular hydrogen, reaction R23. The measured thermal rate coefficient for R23 at 1000 K is 5.9×10^2 s^{-1} or less[90]. The fact that experiments involving simultaneous surface reaction of SiH_4 and SiD_4 led only to the formation of H_2 and D_2 with no HD being produced, led Farnaam and Olander[90] to suggest that decomposition via hydrogen-atom transfer to adjacent lattice sites, reaction R24, does not occur.

In order to compare our computed rates for reaction R23 with the molecular beam data[90], we must extrapolate to the thermal regime. In the Farnaam-Olander experiments, *-SiH$_2$ is formed via reaction R25 which is probably nearly thermochemically neutral. Consequently, the measured rates for H_2 release will correspond to thermal rates. In contrast, in our calculations, *-SiH$_2$ is formed via chemisorption of $SiH_{2(g)}$ which is highly exothermic. As a result, the computed decomposition rates correspond to that for highly excited *-SiH$_2$. If we assume that these rate coefficients represent the high-temperature limiting values, we may estimate the corresponding thermal rates using the calculated barrier height for reaction R4 for the activation energy. The result of this calculation is a thermal rate coefficient of 9.4×10^{2} s^{-1} at 1000 K, which is in satisfactory agreement with the Farnaam-Olander[90] result considering the uncertainties inherent in the required extrapolation.

The major source of disagreement between our model studies and the molecular beam data[90] involves the *-SiH$_2$ decomposition mechanism. Farnaam and Olander find no evidence for the occurrence of reaction R24 whereas our calculations predict that it should be a secondary, but easily observable, channel. These predictions have recently been confirmed by Gates *et al.*[91] using static secondary ion mass spectrometry to observe the silicon hydride species formed by silane adsorption on clean, single Si(111)-(7x7) crystals. Their data show that *-SiH$_2$ is the only species formed on the surface by silane deposition. Subsequent to chemisorption, the mass spectral peaks show the presence of SiH_2 and SiH on the surface. Consequently, reaction R24 does occur as predicted by our calculations.

Most recently, we have initiated studies of the chemisorption and surface reaction dynamics of silicon clusters, Si_n ($n = 2,3,4$), on Si(111)-(7x7) surfaces[73]. These model studies utilize the Binnig *et al.*[87] surface described above with the Bolding-Anderson[88] lattice potential. The velocity reset method developed by Riley *et al.*[13] is employed to model relaxation to bulk phonon modes. To date, we have calculated sticking probabilities for each of the clusters and determined the various modes of chemisorption. For example, Figs. 1 and 2 illustrate the two most important species formed upon chemisorption of Si_4 clusters. In the gas phase, Si_4 is a planar rhombus. Figure 1 shows that many chemisorption events lead to the Si_4 cluster being bound by a single Si-Si bond with the rhomboidal plane of the cluster intact and nearly perpendicular to the surface plane. A second chemisorption mode is

[PAGE FOR FIGURES 1 AND 2]

shown in Fig. 2. Here, the symmetry of the cluster is distorted sufficiently to permit the formation of two Si-Si bonds.

The diffusion rates of silicon atoms on Si(111)-(7x7) surfaces are crucial factors in determining the nature and rate of silicon crystal growth. We have therefore computed such diffusion rates on both the Binnig *et al.*[87] and the dimer-adatom-stacking fault (DAS) model introduced by Takayanagai *et al.*[92]. The jump frequencies for site-to-site diffusion are computed using a canonical MCVPST[32] method. That is, Eq.(2) is cast into the form

$$(9) \quad F(T) = g \int P_{out}\, \rho\, \mathbf{v}\cdot d\mathbf{S} \,/ \int \rho\, d\Gamma ,$$

where F(T) is the classical flux across the critical surface at temperature T, ρ is the phase-space density of points, **S** is the critical surface, **v** is a generalized velocity vector, g is a correction factor for surface recrossing, and

$$(10) \quad P_{out} = +1 \text{ for } \mathbf{v}\cdot d\mathbf{S} > 0 \text{ and } P_{out} = 0 \text{ otherwise.}$$

For a system in thermal equilibrium, we have

$$(11) \quad \rho = \rho_o \exp[-\beta H].$$

Finally, in order to increase the convergence rate in the Monte Carlo evaluation of the phase-space integrals in Eq.(9), we incorporate importance sampling. Let V_a be the interaction between the lattice and the Si adatom. We define

$$(12) \quad H' = H - V_a .$$

Substitution of Eqs.(11) and (12) into (9) yields

$$(13) \quad F(T) = g \int P_{out} \exp[-\beta V_a] \exp[-\beta H']\, \mathbf{v}\cdot d\mathbf{S} \,/ \int \exp[-\beta V_a] \exp[-\beta H']\, d\Gamma .$$

In practice, the integrals in Eq.(13) are evaluated using a Markov walk governed by the distribution function $\exp[-\beta H']$.

The flux F(T) will be an upper limit to the true classical rate as long as the system is statistical. We have therefore obtained close upper bounds for the jump frequencies by minimization of F(T) with respect to the parameters of the critical surface. The correction factor for recrossing, g, is computed by the calculation of trajectories starting at the critical surface[93]. Once the site-to-site jump frequencies are in-hand, diffusion coefficients are obtained by solution of the appropriate master equation to obtain the average square displacements as a function of time which are, in turn, linearly related to the diffusion coefficient[64].

The calculated silicon-atom diffusion coefficients on the Binnig *et al.*[87] surface are $D = 2.15 \times 10^{-3} \exp[-1.51 \text{ eV}/kT] \text{ cm}^2/\text{s}$. The calculated activation energy of 1.51 eV is in excellent accord with the results obtained by Farrow[95] from molecular-beam pyrolysis data on SiH_4 deposition. In contrast, diffusion on the DAS surface[92] is predicted to be much slower due to the larger spacing between dangling bonds on this model of the (7x7) reconstruction[94]. The calculated ratio D[Binnig *et al.*]/D[DAS] is 32 at 1000 K and 2.5×10^9 at 300 K. In addition, we find that preferential directions of diffusion exist on the Binnig *et al.* surface. These directions correspond to "gateways" at three of the four corners of the (7x7) unit cell. In contrast, diffusion on the DAS surface is predicted to be isotropic. Consequently, the extreme differences in rates and directions of flow for diffusion on the two models of the reconstruction suggest that careful measurement of such quantities may provide an additional experimental method for differentiating the two proposed models of the surface.

To conclude this section on heterogeneous processes, we briefly describe a new perturbation method that we have developed during the current grant period for the simplified treatment of gas-surface interactions[8,9]. Our method utilizes the usual separation of the system Hamiltonian into zones. The primary (P) zone generally includes those atoms directly involved in the process under consideration plus an arbitrary number of atoms occupying nearby sites. The secondary or Q-zone usually includes a larger number of atoms further removed from the site at which the process of interest is occurring. These atoms are assumed to affect the process only indirectly through the transfer of energy in and out of the P-zone. In some models, a stationary boundary zone (B-zone) is also included to reduce edge effects. The system Hamiltonian is then written

$$(14) \quad H = T_P + T_Q + V_P + V_{PQ} + V_Q + V_{PB} ,$$

where T_P and T_Q are the kinetic energy terms for the P- and Q-zones, respectively. V_P and V_Q contain the potential for the P and Q-zone atoms alone. The interactions between P-zone and Q-zone atoms and between P-zone and boundary atoms are represented by V_{PQ} and V_{PB}, respectively.

The various approximate methods that have been suggested to date differ primarily in the procedures used to treat the above Hamiltonian. For example, Riley, Coltrin, and Diestler[13] replace the T_Q, V_Q, V_{PQ}, and V_{PB} terms with a prescription that resets the velocities of the P-zone atoms that border the Q-zone at specified time intervals. The most commonly used method involves the use of a generalized Langevin equation in place of the Q-zone terms[11,12]. In this procedure, the T_Q, V_Q, V_{PQ}, and V_{PB} terms in Eq.(14) are all replaced by a set of Langevin-type equations that operate on the peripheral atoms of the P-zone. The net result of this replacement is an energy fluctuation of the P-zone atoms that represents the effect of the "heat bath" or Q-zone atoms.

In the perturbation method we have developed, the effects of the Q-zone atoms are incorporated using the unforced solutions for these atoms. The method assumes that the Q-zone motion is relatively unperturbed by collision events in the P-zone. The correct form of the P-zone-Q-zone interaction V_{PQ} is retained and the motion of all P-zone atoms is treated exactly.

Let the N-atom system be partitioned such that there are N_P, N_Q, and N_B atoms in the P, Q, and B zones, respectively. In general, we will have $N_P = N_A + M$, where N_A is the number of atoms in the colliding molecule, A, and M is an arbitrarily chosen number of atoms in the lattice. Let u_i ($i = 1,2,\ldots,3N_A$), x_i ($i = 1,2,\ldots,3M$), y_i ($i = 1,2,\ldots,3N_Q$), and z_i ($i = 1,2,\ldots,3N_B$) denote the atomic coordinates for the atoms in the incident molecule, the P-zone lattice atoms, and the Q and B zones, respectively. In this notation, we may write Eq.(14) as

$$(15)\quad H = T_A(u_i) + T_M(x_i) + T_Q(y_i) + V_P{}^A(u_i,x_i) + V_P{}^L(x_i) + V_Q(y_i) + V_{PQ}{}^L(x_i,y_i) + V_{PQ}{}^A(u_i,y_i) + V_{PB}(u_i,x_i;z_i)\ ,$$

where the V_{PB} term depends only parametrically upon the z_i. In Eq.(15), the P-Q interaction has been written as the sum of a lattice-lattice interaction, $V_{PQ}{}^L(x_i,y_i)$, and an interaction between the incident molecule and the Q-zone, $V_{PQ}{}^A(u_i,y_i)$. The P-zone potential is likewise separated into the sum of a lattice-lattice interaction, $V_P{}^L(x_i)$, and a lattice-A interaction, $V_P{}^A(u_i,x_i)$.

It is now explicitly assumed that the lattice Q-zone motion is unperturbed by the collision of molecule A with the surface. That is, we assume that the effect of $V_{PQ}{}^A(u_i,y_i)$ on the y_i is negligibly small and that the effect of the lattice-lattice interaction term, $V_{PQ}{}^L(x_i,y_i)$, upon the Q-zone motion is unaffected by the collision of A with the surface. Under these conditions, the Q-zone motion may be obtained by direct solution of Hamilton's equations using the lattice Hamiltonian

$$(16)\quad H_L = T_M(x_i) + T_Q(y_i) + V_P{}^L(x_i) + V_Q(y_i) + V_{PQ}{}^L(x_i,y_i)\ .$$

The results of such a solution yield the Q-zone atomic coordinates as functions of time. Direct substitution of these functions into Eq.(15) gives a P-zone Hamiltonian of the form

$$(17)\quad H_P = T_A(u_i) + T_M(x_i) + V_P{}^A(u_i,x_i) + V_P{}^L(x_i) + V_{PQ}{}^L[x_i,y_i(t)] + V_{PQ}{}^A[u_i,y_i(t)] + V_{PB}(u_i,x_i;z_i)\ .$$

It is assumed that the P-zone dynamics may be obtained by solution of Hamilton's equations using H_P as the Hamiltonian. If the collision event exerts only a negligibly small perturbation upon the Q-zone motion, the results obtained using Eq.(17) will approach those resulting from a full solution of the complete problem using Eq.(15).

We have applied the above method to the inelastic scattering of NO from Ag(111) surfaces and to chemisorption and surface reaction of SiH_2 on Si(111) surfaces[8,9]. For the NO system, the translational and rotational energy distributions of scattered NO molecules, the differential cross sections, and the NO sticking probabilities as a function of incident translational energy obtained from the perturbation calculations with $N_P = 2$ are in almost exact agreement with results obtained from a full treatment of the dynamics. That is, the perturbation method permits a near exact determination of the system dynamics from the results of two-body trajectories. Equally good results are obtained for the SiH_2/Si(111) system if the size of the P-zone is increased to $N_P = 9$.

In general, the accuracy of the perturbation method increases as the incident-to-lattice atom mass ratio decreases. A decrease in the strength of the interaction between the incident molecule and the Q-zone, the incident translational energy, or the lattice temperature also improves the accuracy of the perturbation treatment. The method is therefore best suited to the study of inelastic, light-molecule collisions with heavy-atom surfaces at low temperatures. For such cases, near exact results can be obtained with very small values of N_P. For strong interactions or for interactions of long duration, the method will, of course, fail[9].

Summary:

During the first two years of the current grant period, we have determined the reaction dynamics of SiH_2 chemisorption and subsequent surface reaction on reconstructed Si(111)-(7x7) surfaces[72]. The scattering and chemisorption of Si_2, Si_3, and Si_4 clusters[73] and the rates and patterns of silicon-atom surface diffusion on these reconstructed surfaces have also been investigated using both the Binnig et al.[87] and the DAS[92] models of the (7x7) surface[93,94]. The SiH_2 surface decomposition mechanism has been found to involve two major channels, (a) direct molecular elimination of H_2 and (b) the dissociation of hydrogen atoms to adjacent lattice sites to yield -SiH and -H surface species. Rate coefficients computed for each of these channels shows the first to be the more important. These predictions, although at odds with older experimental data[90], have recently been confirmed by new SIMS measurements[91]. Sticking coefficients and chemisorption modes for each of the silicon clusters have been determined. Diffusion rates and activation energies for silicon-atom diffusion on Si(111)-(7x7) have been obtained. Diffusion is predicted to be non-isotropic on the Binnig et al[87] model of the (7x7) surface but isotropic on the DAS[92] surface. In addition, we predict very different diffusion rates on the two surfaces. It is suggested that these differences may provide an additional means of experimentally differentiating between the models. Finally, we have developed a new perturbation method for treating gas-surface interactions that significantly reduces the computational effort required[8,9]. The method is shown to give nearly exact results in favorable cases.

II.D. $C_2H_4 + F_2$ and the 1,2-Difluoroethane Systems:

We have carried out several investigations involving the reactions of F_2 with ethylene and the unimolecular decomposition dynamics of 1,2-difluoroethane. The motivation for these studies arises from two considerations.

First, there are very few experimental studies that provide detailed dynamical information about the gas-phase silicon reactions. Consequently, it is difficult to assess the accuracy of our theoretical results for these systems. In contrast, there exists a wealth of experimental data related to the above systems that provide excellent benchmarks that may be used to assess the accuracy of our methods. Secondly, in Section III.D., we propose to conduct a study of chemical processes that occur under conditions of close confinement. We intend to use fluorine reactions in cryogenic matrices as prototypes of such reactions since there exists a large body of experimental data on such systems. The gas-phase calculations will therefore serve as a basis for the determination of the effects of close confinement upon these systems.

The principal reactions of interest for the ethylene + F_2 system are

(R26) $C_2H_4 + F_2 \dashrightarrow [H_2FC\text{-}CFH_2]^*$,

(R27) $C_2H_4 + F_2 \dashrightarrow H_2C\text{-}CH_2F + F$, and

(R28) $C_2H_4 + F_2 \dashrightarrow H_2C{=}CHF + HF$.

Once 1,2-difluoroethane is formed, the mechanism and associated rates for its decomposition become the focus of attention. This decomposition reaction may proceed via several channels that include

(R29) $H_2FC\text{-}CH_2F \dashrightarrow H_2C{=}CHF + HF$,

(R30) $H_2FC\text{-}CH_2F \dashrightarrow H_2FC\text{-}CH_2 + F$,

(R31) $H_2FC\text{-}CH_2F \dashrightarrow H_2FC\text{-}CHF + H$, and

(R32) $H_2FC\text{-}CH_2F \dashrightarrow 2\ CH_2F$,

A global potential-energy surface for the $C_2H_4F_2$ system has been developed using the methods described in Section II.B.[20,21]. The predicted barrier heights for four-center F_2 addition across the ethylene double bond (R26), for HF elimination from 1,2-difluoroethane (R29), for hydrogen-atom abstraction by a fluorine atom, and for rotation about the C=C double bond are all in near exact agreement with experimental data[96-98]. Using this surface, we have investigated the gas-phase bimolecular reaction rates and mechanism for the reaction of F_2 with C_2H_4, reactions R26-R28[99], as well as rates for the unimolecular decomposition of 1,2-difluoroethane upon random internal excitation[100], and upon mode-specific excitation[101].

There are numerous benchmarks that illustrate the accuracy of our results. Our calculations on gas-phase $C_2H_4 + F_2$ reactions[99] predict that the reaction products are, in order of importance, fluoroethyl radicals + fluorine atoms and HF + fluoroethylene. This is in complete accord with the experimental results reported by Kapralova *et al.*[96] and with the crossed molecular beam data obtained by Grover *et al.*[102] on the analogous benzene + F_2 reaction. For unimolecular dissociation of 1,2-difluoroethane, the decomposition channels are, in order of importance, reactions R29, R32, and R31. The calculated microcanonical rate coefficient for HF elimination (R29) at 138 kcal/mol internal excitation is 2.5×10^{11} s^{-1}. The extrapolated experimental result reported by Chang *et al.*[103] is 4.0×10^{11} s-1. The calculations predict that 71-74% of the reaction exothermicity will remain in the olefin whenever reaction R29 occurs. This is in general agreement with several experimental studies[103-105]. Table I shows a comparison of the relative population densities of the different HF vibrational states predicted by the calculations[100,101] with very recent data reported by Arunan, Wategaonkar, and Setser[106] for the analogous reaction of CH_3-CF_3. The extent of agreement is clearly very good considering the fact that the molecules involved, although very similar, are not identical.

Table I

Comparison of relative population density of different vibrational states of HF after four-center elimination reaction

HF(v)	Cal. [CH_2F-CH_2F] (a)	Expt. [CH_3-CF_3] (b)
0	2.05	1.42
1	1.00	1.00
2	0.71	0.60
3	0.19	0.23
4	0.05	0.06
5	0.00	0.00

(a) Reference 100 (b) Reference 106

Summary:

A global potential-energy surface has been developed for the $C_2H_4F_2$ system[20,21] and reactions of F_2 with ethylene[99] and of the unimolecular decomposition of 1,2-difluoroethane[100,101] have been investigated to provide a means of assessing the accuracy of our computation methods for systems of this degree of complexity

and to provide the necessary background for determination of the effects of close confinement upon chemical reactions, which is to be investigated in future studies. Comparison of the results with a wide variety of data obtained from thermal, molecular beam, and chemical activation experiments shows the accuracy of the calculations to be sufficient to draw meaningful conclusions about the dynamics.

II.E. Intramolecular Energy Transfer Rates:

In many theoretical investigations, it is necessary to compute the rates and pathways of intramolecular energy flow. Such calculations have proven to be difficult, especially in highly coupled, polyatomic systems. In general, classical studies of intramolecular energy transfer involve the integration of the Hamiltonian equations of motion on some potential-energy surface. "Bond" or "mode energies" are then computed from the results. Intramolecular energy transfer pathways and rates are inferred from the calculated time variation of these quantities[107]. This procedure obviously involves an arbitrary definition of the "bond energy" which generally assumes a mode separability that does not exist. Consequently, all potential and kinetic coupling terms involving the mode coordinates are omitted from the definition. As a result, one can never be certain whether a variation in "bond energy" is due to actual energy transfer to or from other modes or merely to changes in the magnitudes of the omitted coupling terms. Nor is it possible to be certain that the results themselves are not dependent upon the arbitrary definition adopted for the "bond" or "mode energy".

We have recently reported a general method for analyzing the results of classical trajectory calculations to obtain the details of intramolecular energy transfer that obviates the need to arbitrarily define a "bond" or "mode energy"[10]. The method is based on the determination of the time dependence of the normal-mode velocities by projection of the instantaneous Cartesian velocities of the atoms onto the normal-mode vectors. The basic idea is as follows:

Let $\mathbf{L}_i$ ($i = 1,2,3,\ldots,3N$) represent a set of normalized ($3N \times 1$) transformation vectors that project the normal-mode vibrations ($1 \leq i \leq 3N-6$), the center-of-mass translations ($3N-5 \leq i \leq 3N-3$), and the rotations about the molecular center-of-mass ($3N-2 \leq i \leq 3N$) onto the Cartesian displacements, q_j ($j = 1,2,3,...,3N$). That is, at time t, the instantaneous Cartesian velocities may be written as linear combinations of the corresponding elements of the $\mathbf{L}_i$:

(18) $$\dot{q}_i(t) = \sum_j^{N} \dot{Q}_j(t) L_{ij} \quad \text{for } (i = 1,2,3,...,3N) .$$

Equation (18) may be written in matrix form as

(19) $$\dot{\mathbf{q}}(t) = \mathbf{L}\, \dot{\mathbf{Q}}(t) ,$$

where $\mathbf{L}$ is a ($3N \times 3N$) square matrix whose columns are the normalized projection vectors $\mathbf{L}_i$. $\dot{\mathbf{q}}(t)$ is a ($3N \times 1$) column vector whose elements are the Cartesian velocities and $\dot{\mathbf{Q}}(t)$ is a ($3N \times 1$) column vector whose elements are the normal mode, center-of-mass, and rotation velocities. The normal-mode velocities may therefore be obtained from

(20) $$\dot{\mathbf{Q}}(t) = \mathbf{L}^{-1}\, \dot{\mathbf{q}}(t) .$$

The kinetic energy, T, at time t is

(21) $$T(t) = 0.5 \sum m_i \dot{q}_i^2(t) .$$

Substitution of Eq.(18) yields

(22) $$T(t) = 0.5 \left[\sum_i m_i \sum_j \sum_k \dot{Q}_j(t)\, \dot{Q}_k(t)\, L_{ij} L_{ik} \right] = 0.5 \left[\sum_i m_i \sum_j \dot{Q}_j^2(t)\, L_{ij}^2 \right]$$

since the kinetic energy is diagonal when expressed in terms of the normal mode velocities. Consequently, the kinetic energy may be written as

(23) $$T(t) = \sum_k a_k \dot{Q}_k^2(t) ,$$

provided the mode constant a_k is defined to be

(24) $$a_k = 0.5 \sum_i m_i L_{ik}^2 .$$

Equation (23) shows that the total molecular kinetic energy is the uncoupled sum of the individual mode kinetic energies, $T_i(t)$, where

(25) $$T_i(t) = a_i \dot{Q}_i^2(t) .$$

Since the total energy associated with a given mode alternates between potential and kinetic energy with a frequency closely associated with the mode frequency, the flow of energy through the molecule may be conveniently and exactly monitored by examination of the envelope functions for plots of the time variation of the various $T_i(t)$. Thus, for the special case of an uncoupled harmonic potential where the normal modes energies are constants of the motion, we would expect to see $T_i(t)$ oscillate with a frequency characteristic of the mode frequency but with an amplitude that is independent of time. The envelope function would be a constant reflecting the constant energy in the mode. If, on the other hand, energy is rapidly leaving a particular mode, this will be reflected by an envelope function with a large negative slope. This will be the case independent of the nature of the potential-energy surface.

The average total energy associated with a given mode may be obtained from the results of the trajectory integration using Eqs.(20) and (25) in conjunction with the virial theorem which requires that the total energy, on the average, be equipartitioned between kinetic and potential energy. For a given potential, the results are exact within the framework of the classical approximation.

This method has been applied to the study of intramolecular energy flow in gas-phase 1,2-difluoroethane[10]. Decay rates and pathways of energy flow for initial excitation of each of the 18 vibrational modes have been determined. The results obtained from the time variation of the normal-mode velocities were used to extract the entire first-order mode-to-mode energy transfer rate coefficient matrix. Essentially, this provides a complete description of intramolecular energy flow in the molecule.

Summary:

We have developed an exact projection method that permits intramolecular energy transfer rates and pathways to be determined from the results of classical trajectory calculations without the necessity to arbitrarily define a "bond" or "mode energy". The method is based upon the calculation of the envelope functions of the mode kinetic energies in a coordinate system in which the kinetic energy is diagonal. The method has been applied to the determination of IVR rates and pathways in 1,2-difluoroethane[10].

II.F. Publications and Oral Presentations

Since 1982, a total of 47 papers have been published reporting the results of research done under AFOSR support. Fifteen (15) of these papers report results of research done during the the grant period for AFOSR-89-0085. A complete listing follows:

1. P. M. Agrawal and L. M. Raff, "A Semiclassical Wavepacket Model for the Investigation of Elastic and Inelastic Gas-Surface Scattering", *J. Chem. Phys.* **77**, 3946 (1982).

2. P. M. Agrawal, N. C. Agrawal, R. Viswanathan, and L. M. Raff, "Rate Calculations from Time-Dependent Wavepacket Methods: The Relationship of the Pure-State and Canonical Total Reaction Probability", *J. Chem. Phys.* **80**, 760, (1984).

3. R. Viswanathan, D. L. Thompson, and L. M. Raff, "Theoretical Investigations of Elementary Processes in the Chemical Vapor Deposition of Silicon from Silane: Unimolecular Decomposition of SiH_4", *J. Chem. Phys.* **80**, 4230 (1984).

4. R. Turner, L. M. Raff, and D. L. Thompson, "Theoretical Studies of Tunneling Processes in Three-Body Exchange Reactions of van der Waals Rare Gas Dimers", *J. Chem. Phys.* **80**, 3189 (1984).

5. L. M. Raff, R. Viswanathan, and D. L. Thompson, "Unimolecular Dissociation of Methane: A Trajectory Study Using Metropolis Sampling", *J. Chem. Phys.* **80**, 6141 (1984).

6. R. Viswanathan, L. M. Raff, and D. L. Thompson, "Monte Carlo Random Walk Calculations of Unimolecular Dissociation of Methane", *J. Chem. Phys.* **81**, 3118 (1984).

7. R. Viswanathan, L. M. Raff, and D. L. Thompson, "Monte Carlo Transition-State Theory: XH_4 --> XH_3 + H (X=C,Si)", *J. Chem. Phys.* **81**, 828 (1984).

8. I. NoorBatcha, L. M. Raff, and D. L. Thompson, "Classical Trajectory Study of adsorption and Surface Diffusion of Si on Si(100)", *J. Chem. Phys.* **81**, 3715 (1984).

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11. R. Viswanathan, D. L. Thompson, and L. M. Raff, "A Valence-Bond Potential-Energy Surface for Silylene Dissociation", *J. Phys. Chem.* **89**, 1428 (1985).

12. R. Viswanathan, L. M. Raff, and D. L. Thompson, "Monte Carlo Transition State Study of Angular Momentum Effects on the Unimolecular Dissociation of CH_4 on the Duchovic-Hase-Schlegel *Ab Initio* Surface", *J. Chem. Phys.* **82**, 3083 (1985).

13, I. NoorBatcha, L. M. Raff, and D. L. Thompson, "Monte Carlo Random Walk Study of H_2 Recombination and Desorption on a Si(111) Surface", *J. Chem. Phys.* **83**, 1382 (1985).

14. C. B. Smith, P. M. Agrawal, and L. M. Raff, "Semiclassical Wavepacket Studies of Elastic and Inelastic Atom-Surface Scattering from a 3D Model Surface", *J. Chem. Phys.* **83**, 1411 (1985).

15. I. NoorBatcha, L. M. Raff, and D. L. Thompson, "Effect of Lattice Potential upon the Surface Diffusion of Si on Si(100)", *J. Chem. Phys.* **83**, 6009 (1985).

16. D. L. Martin, D. L. Thompson, and L. M. Raff, "Theoretical Studies of Termolecular Thermal Recombination of Silicon Atoms", *J. Chem. Phys.* **84**, 4426 (1986).

17. I. NoorBatcha, L. M. Raff, D. L. Thompson, and R. Viswanathan, "Dynamics of Unimolecular Dissociation of Silylene", *J. Chem. Phys.* **84**, 4341 (1986).

18. C. Arnold, N. S. Gettys, D. L. Thompson, and L. M. Raff, "Theoretical Studies of Vibrationally-Assisted Reactions of the O_3-NO van der Waals Complex", *J. Chem. Phys.* **84**, 3803 (1986).

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22. B. M. Rice, L. M. Raff, and D. L. Thompson, "The Dynamics of H_2 Scattering and Dissociative Chemisorption on a Si(111) Surface", *J. Chem. Phys.* **86**, 1608 (1987).

23. L. M. Raff and D. L. Thompson, "Reply to the 'Comment on Silane Pyrolysis and the Insertion of Silylene into Molecular Hydrogen' ", *J. Chem. Phys.* **86**, 3058 (1987).

24. H. Gai, D. L. Thompson, and L. M. Raff, "Trajectory Study of the Formation and Decay of Silicon Trimer Complexes in Monomer-Dimer Collisions", *J. Chem. Phys.* **88**, 156 (1988).

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27. P. M. Agrawal, D. L. Thompson, and L. M. Raff, "Computational Studies of Heterogeneous Reactions of SiH_2 on Si(111) Surfaces", *Surf. Sci.* **195**, 283 (1988).

28. P. M. Agrawal, D. L. Thompson, and L. M. Raff, "Computational Studies of SiH_2 + SiH_2 Recombination Reaction Dynamics on a Global Potential Surface Fitted to *Ab Initio* and Experimental Data", *J. Chem. Phys.* **88**, 5948 (1988).

29. B. M. Rice, L. M. Raff, and D. L. Thompson, "Dynamics of Chemisorption/ Scattering of Atomic Hydrogen on Partially Covered Si(111) Surfaces", *Surf. Sci.* **198**, 360 (1988).

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31. L. M. Raff and R. W. Graham, "Unimolecular Dissociation Dynamics of 1,2-difluoroethane and of the C_2H_4-F_2 van der Waals Complex", *J. Phys. Chem.* **92**, 5111 (1988).

32. P. M. Agrawal, D. L. Thompson, and L. M. Raff, "Trajectory Studies of Unimolecular Reactions of Si_2H_4 and SiH_2 on a Global Potential Surface Fitted to *Ab Initio* and Experimental Data", *J. Chem. Phys.* **89**, 741 (1988).

The following papers report the results of research completed during the three-year grant period for AFOSR-89-0085:

33. L. M. Raff, "Projection Methods for Obtaining Intramolecular Energy Transfer Rates from Classical Trajectory Results: Application to 1,2-difluoroethane", *J. Chem. Phys.* **89**, 5680 (1988).

34. M. Jezercak, P. M. Agrawal, D. L. Thompson, and L. M. Raff, "A Perturbation-Trajectory Method for the Study of Gas-Surface Collision Dynamics", *J. Chem. Phys.* **90**, 3363 (1989).

35. L. M. Raff, "Intramolecular Energy Transfer and Mode-Specific Effects in Unimolecular Reactions of 1,2-difluoroethane", *J. Chem. Phys.* **90**, 6313 (1989).

36. P. M. Agrawal, D. L. Thompson, and L. M. Raff, "Computational Studies of Heterogeneous Reactions of SiH_2 on Reconstructed Si(111)-(7x7) and Si(111)-(1x1) Surfaces", *J. Chem. Phys.* **91**, 5021 (1989).

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38. P. M. Agrawal, D. L. Thompson, and L. M. Raff, "Unimolecular Dissociation Dynamics of Disilane", *J. Chem. Phys.* **92**, 1069 (1990).

39. M. E. Riley, M. E. Coltrin, D. J. Diestler, M. Jezercak, P. M. Agrawal, D. L. Thompson, and L. M. Raff, "Comment on 'A Perturbation-Trajectory Method for the Study of Gas-Surface Collision Dynamics [*J. Chem. Phys.* **90**, 3363 (1989)]" *J. Chem. Phys.* **92**, 817 (1990).

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43. H. W. Schranz, L. M. Raff, and D. L. Thompson, "Correspondence of Canonical and Microcanonical Rate Constants using Phase Space Theory for Simple Bond Fissions", *Chem. Phys. Lett.*, **171**, 68 (1990).

44. H. W. Schranz, L. M. Raff, and D. L. Thompson, Statistical and Non-statistical Effects in Bond Fission Reactions of SiH_2 and Si_2H_6", *J. Chem. Phys.* **94**, 4219 (1991).

45. H. W. Schranz, L. M. Raff, and D. L. Thompson, "Non-statistical Effects in Bond Fission Reactions of 1,2-difluoroethane", *Chem. Phys. Lett.* , **182**, 455 (1991).

46. P. M. Agrawal, D. L. Thompson, and L. M. Raff, "Comparison of Silicon-atom Diffusion on the DAS and Binnig *et al.* Models of the Reconstructed Si(111)-(7x7) Surface", *J. Chem. Phys.* , **94**, 6243 (1991).

47. H. W. Schranz, L. M. Raff, and D. L. Thompson, "Intramolecular Energy Transfer and Mode-Specific Effects in Unimolecular Reactions of Disilane", J. Chem. Phys. **95**, 106 (1991).

The following papers and seminars related to the work supported by AFOSR-89-0085 have been presented:

1. L. M. Raff and D. L. Thompson, "Reactions on Reconstructed Silicon Surfaces", **Air Force Office of Scientific Research Contractor's Meeting,** Captiva Bay, Florida, October, 1989.

2. L. M. Raff, "Reactions and Diffusion on Reconstructed Si(111)-(7x7) Surfaces", **Symposium on Many-Body Dynamics at Surfaces,** National American Physical Society Meeting, Anaheim, California, March, 1990.

3. L. M. Raff and D. L. Thompson, "Theoretical Chemical Dynamics Studies of Elementary Processes Occurring on Silicon Surfaces", **Symposium on Key Problems in Silicon Chemistry**, University of Colorado, Boulder, Colorado, May 10-11, 1990.

4. H. W. Schranz, L. M. Raff, and D. L. Thompson, "Comparison of Variational Transition State Theory and Trajectory Calculations for the Simple Bond Fission of Microcanonically Highly Excited SiH_2 and Si_2H_6", **XIX Conference on Photochemistry**, University of Michigan, Ann Arbor, Michigan, June 24-29, 1990.

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on "The Chemistry of Matrix-Isolated Species", Plymouth, N. H. July, 1991.

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III. Personnel:

In addition to the Principal Investigators, Donald L. Thompson and Lionel M. Raff, the personnel who have received full or partial support under AFOSR-89-0085 include:

Graduate Students:

Dr. Michael Jezcerak, Ph.D., 1989: Dr. Jezcerak is currently an Assistant Professor of Chemistry, Central State University, Edmond, Oklahoma.

Dr. M. P. Sudhakaran, Ph. D., 1988: Dr. Sudhakaran is currently head of the Environmental Chemical Agency, Corpus Chrusti, Texas.

Postdoctoral Research Associates and Faculty Associates:

Dr. David Martin: Dr. Martin is currently Associate Professor of Physics, Central State University, Edmond, Oklahoma.

Dr. Ronald Kay: Dr. Kay is currently Assistant Professor of Chemistry, Gordon College, MA.

Dr. Paras M. Agrawal: Dr. Agrawal is currently Associate Professor of Physics, Vikram University, Ujjain, India.

Dr. Harold W. Schranz: Dr. Schranz is currently Assistant Professor of Chemistry, Australian National University, Canberra, Australia.

Dr. James Peploski: Dr. Peploski is currently a postdoctoral research associate with our group.

IV. References

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