3

Department of Chemistry

Princeton University

Final Technical Report to

The Office of Naval Research

QUANTUM DYNAMICAL STUDIES OF THE DECOMPOSITION OF ENERGETIC MATERIALS CONTAINING DEFECT STRUCTURES

Grant No. N00014-91-J-1209

DTIC
S ELECTE D
MAR 0 7 1995
B

Covering the Period of

December 1, 1992 - November 30, 1994

DISTRIBUTION STATEMENT
Approved for public release;
Distribution Unlimited

DTIC QUALITY INSPECTED 4

Herschel Rabitz, Principal Investigator

19950227 166

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION U	1b RESTRICTIVE MARKINGS NA
2a. SECURITY CLASSIFICATION AUTHORITY NA	3. DISTRIBUTION/AVAILABILITY OF REPORT Distribution unlimited
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE NA	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) 130-6601-rpt-1	5. MONITORING ORGANIZATION REPORT NUMBER(S) NA

6a. NAME OF PERFORMING ORGANIZATION Princeton University	6b. OFFICE SYMBOL *(If applicable)*	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research
6c. ADDRESS *(City, State, and ZIP Code)* Princeton University Department of Chemistry Princeton, NJ 08544		7b. ADDRESS *(City, State, and ZIP Code)* 800 N. Quincy Street Arlington, VA 22217-5000
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL *(If applicable)* ONR	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-91-J-1209

8c. ADDRESS *(City, State, and ZIP Code)*
800 N. Quincy Street
Arlington, VA 22217-5000

10 SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO	PROJECT NO.	TASK NO	WORK UNIT ACCESSION NO.

11. TITLE *(Include Security Classification)*
Quantum Dynamical Studies of the Decomposition of Energetic Materials Containing Structure Defects

12. PERSONAL AUTHOR(S)
Herschel Rabitz

13a. TYPE OF REPORT	13b TIME COVERED	14. DATE OF REPORT *(Year, Month, Day)*	15 PAGE COUNT
Final Technical	FROM 12/1/92 TO 11/30/94	2/23/95	9

16 SUPPLEMENTARY NOTATION

17 COSATI CODES			18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*
FIELD	GROUP	SUB-GROUP	Molecular Energy Transfer, Gas-Solid Interactions, Energetic Materials

19 ABSTRACT *(Continue on reverse if necessary and identify by block number)*

During the period of this project, fundamental research was carried out in the area of chemical reactivity at the surface of solid materials. Emphasis was also placed on the underlying energetic transfer processes to the bulk material due to atomic and molecular fragment impacts at the interface. A fully quantum multiple collision theory approach was developed to study energetic materials reactivity, and a discrete-continuum hybrid theory for energy transfer was formulated. A series of model studies were executed with the theoretical formulations. The results revealed many of the basic principles of reactivity and energy transfer operative at interfaces or found in the propagating fronts of energetic materials. The specific research carried out under this grant is summarized in the report.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION U	
22a. NAME OF RESPONSIBLE INDIVIDUAL Donald H. Liebenberg	22b. TELEPHONE *(Include Area Code)* (703) 696-5383	22c. OFFICE SYMBOL ONR

DD Form 1473, JUN 86 *Previous editions are obsolete.* SECURITY CLASSIFICATION OF THIS PAGE

SUMMARY OF RESEARCH ACCOMPLISHMENTS

1. Quantum Dynamical Studies of the Decomposition of Energetic Materials.[1]

This research resulted in the development of a theoretical approach aimed at elucidating the microscopic dynamics of energetic materials fragmentation. Two interdependent components were combined to bridge the atomic and bulk realms. A hierarchy of quantal multiple scattering expansions were first introduced to decompose the complex reaction dynamics into coupled sequences of few-atom interactions, each of which was more amenable to calculation. This microscopic component was complemented by a continuum-mechanical process, to account for energy flow into the as yet unreacted bulk material. Such a dual approach allowed for the quantum mechanical treatment of coupled atomic-bulk dynamics in a self-consistent way that incorporated large thermal gradients. The analysis, in terms of coupled few-atom interactions, also yielded insight into the various pathways for reactivity and energy transfer.

2. Multiquantum Vibrational Energy Transfer into Adsorbates on Solid Surfaces by Atomic Collisions: A Semiclassical Treatment Based on Dynamical Correlations.[2]

In this research, a semiclassical treatment for vibrational excitation of adsorbates on surfaces by atomic collisions in the superthermal energy regime ($0.5 \gtrsim E \gtrsim 5$ eV), previously introduced in one dimension [Vilallonga and Rabitz, *J. Chem. Phys.* **85**, 2300 (1986)], was extended to three dimensions. The projectile motion was represented in the limit of short de Broglie wavelengths (i.e., by classical trajectories and their associated phases), whereas adsorbate-surface vibrations were treated quantum mechanically. Using the Feynman-path integral representation of the transition operator, this limit was approached in a flexible way that did not require *a priori* assumptions about the gas-surface potential, and allowed for strong surface corrugation (e.g., due to molecules adsorbed at low surface coverage). Distributions of transferred energies were approximated nonperturbatively, by algebraic

☑
☐
☐
y Codes
Dist | Avail and/or Special
A-1

methods, using time-correlation functions of the semiclassical transition operator. A large number of energetically open states were thus incorporated, as well as the thermal average over initial of adsorbate modes and lattice phonons. The differential (in final angles and energy) scattered intensity was given in a form that was convenient for numerical calculations, since it required integration of Hamilton equations for the projectile, plus a straightforward sequence of fast Fourier transforms. This result was analyzed further in terms of adsorbate-localized vibrations and lattice phonons, in order to investigate how adsorbates can influence the structure of collisional energy-loss spectra. Particular attention was paid to the role of surface temperature, which can lead to different distributions for the energies going into adsorbates and phonons. Comparisons were made with Born-type approximations and impulsive treatments.

3. Multiquantum Vibrational Energy Transfer into Surface Rayleigh, Bulk Shear and Pressure Waves by Atom-Solid Surface Collisions.[3]

In this research, a discrete-hybrid continuum was developed for energy transfer into solid-state vibrations by atomic collisions. Surface vibrations were described in terms of the displacement field of a three-dimensional elastic continuum with a stress-free boundary. The displacement field was evaluated discretely at the surface lattice sites, and it was quantized by the standard methods for harmonic vibrations. This hybrid approach extended classical Debye models, to incorporate surface corrugation, lattice structure, and the Bose-Einstein statistics of phonons. The treatment was illustrated on He scattering from Pt(111) at superthermal collision energies (e.g., $E = 0.5$ eV) to probe the repulsive cores of the gas-surface potential. Accordingly, the projectile motion was approximated by classical trajectories, whereas all vibrational modes were treated quantum mechanically. The differential (in final angles and transferred energy) scattered intensity was obtained from time-correlation functions of the semiclassical transition operator, which incorporated numerous vibrational states, as well as surface temperature. A computational procedure was described for efficiently calculating multi-quantum transitions of very high order, using fast Fourier transforms. The distributions of transferred energies were analyzed in terms of the continuum vibrational modes, which included surface Rayleigh, shear-horizontal (SH), and coupled pressure/shear-vertical (PSV) waves. The mode-specific distributions were found to vary in distinct ways, as one changes collisional angles. On average, surface Rayleigh waves absorbed approximately one-half of the transferred energy, and the remainder was shared in comparable amounts by bulk SH and PSV waves.

4. Mechanisms of Collision-Induced Desorption of a Physisorbed Atom at Superthermal Energy: A Multiple Scattering Study.[4]

A Faddeev-Watson multiple scattering approach to gas-surface collision-induced desorption was developed in this study. The computational procedure was practical, yet allowed a fully quantum-mechanical treatment of gas-solid reactive scattering problems. The single plus double collision terms of the multiple collision series were included in the calculation, which provided a detailed description of the collision dynamics. The study focused on a simple model collision system: a heavy adsorbate on a rigid surface is ejected by a sufficiently energetic light projectile. Large differential cross sections were found when the amount of kinetic energy transferred from the projectile to the adsorbate coincided with that of a classical head-on elastic collision between two particles of the corresponding masses. In addition, when this energy transfer was a little over the binding energy of the bound state, double collisions analogous to classical off-center collisions, contributed significantly to the differential cross sections. The results also showed that qualitatively, the differential cross sections reached their maxima when the incident energy was about twice the binding energy of the adsorbate, then stayed approximately the same when the incident energy increased even further. In this study, the role of the form factor, which was the bound state wavefunction in momentum space, was also investigated. It was found that the angular distributions of the scattered projectile and the ejected adsorbate were very sensitive to the adsorbate form factor. Finally, a detailed comparison among the contributions to the differential cross sections from each of the collision terms provided information about the relative importance of various collision-induced desorption mechanisms.

5. Numerical Study of the Multiple-Scattering Series for Gas-Solid Dynamics Including Single- through Triple-Collision Terms.[5]

In this research, the multiple-scattering series for the transition amplitude in gas-surface collisions was examined, using elastic atom-surface diffraction as a test bed. Performing numerical calculations for various scattering angles and incident energies, the role of double and triple successive collisions between the projectile and the surface atoms was assessed. For rigid lattices, double- and triple-collision terms were found to be significant in the thermal energy regime, and even in the higher-energy regime, if the surface was highly corrugated. However, at superthermal incident energies ($E \gtrsim 0.2$ eV), the single-collision terms gave a good approximation to the overall scattering intensities, provided that the ranges of the atom-pair potentials did not overlap; nevertheless, multiple collisions were still important in elastic scattering with large parallel momentum transfers. These results indicated that single-collision approximations should be employed with care for elastic diffraction.

6. Atomic Collisions with Inhomogeneous Solid Surfaces: Multiple Scattering from Surface Defects and Mixed Overlayers.[6]

This study employed the multiple-scattering expansion of the transition operator to evaluate the role of multiple collisions in elastic scattering of atoms from adsorbates, on solid surfaces at superthermal temperatures ($E \gtrsim 0.1$ eV). The adsorbate-surface system was treated as a rigid body model in this study. Mixed-species periodic overlayers were considered, as well as two-layer systems simultaneously involving periodic and non-periodic configurations. The calculated scattering patterns showed rich structure due to the interference between waves scattered from different adsorbates. The enhanced sensitivity provided by wavevectors $k \gtrsim 10$ Å^{-1} could be exploited for surface characterization by scattering experiments. It was found that the single-collision approximation qualitatively reproduced the trends of the intensity, with respect to final angles. Double-collision terms were evaluated with the pole approximation, and were found to play an important role in large transfers of parallel momentum.

7. A Discrete-Continuum Hybrid Model for Vibrational Energy Transfer at the Gas-Solid Interface. II. The Quantal Evolution of Coupled Localized-Collective Motion.[7]

This study analyzed a new approach to the vibration of inhomogeneous surfaces, whereby surface defects and their surroundings were properly treated as discrete atoms while the remainder of the solid was represented by an elastic continuum of equivalent mass density and elasticity, with quantized vibrational waves. Such a hybrid treatment was aimed at describing defect-local motion, while fully coupled to collective vibrational waved in a quantum-mechanical fashion appropriate to inelastic gas-surface scattering. The study assessed how the hybrid model reproduced the response of the surface, by following the quantum-statistical moments of vibrational displacements, as the collision progressed. The results suggested that the discrete-continuum approach provides a powerful tool for describing collisional excitation of defect-laden surfaces, within a fully quantal treatment of surface motion.

8. Sensitivity Analysis of the Potential for Elastic Gas-Solid Scattering from Surface Defects.[8]

The role of surface defects in elastic gas-solid collisions was investigated in this research, by means of a recently developed numerical procedure based on the Møller operator and wavepackets. Since the procedure explicitly evaluated the scattering wavefunction, it yielded the probabilities for scattering from the given initial state into all possible final states, as well as the sensitivity of the probabilities, with respect to variations in the gas-surface potential. Probabilities and their functional sensitivities were calculated for a simulated Pt surface exhibiting various configurations of vacancies: isolated sites, "interacting" di-vacancies, and closely-packed tri-vacancies. The functional sensitivities indicated which regions of the gas-defect-solid potential were most relevant to the scattering dynamics. The resultant physical insight should be ultimately helpful for inverting experimental data, to obtain the interaction potential.

9. Gas-Surface Dynamics (A Thematic Issue of *Computer Physics Communications*).[9]

During the past two decades, the subject of atomic and molecular interactions with solid surfaces has expanded rapidly, and has become an important sub-field of surface science. This is partly due to the development of beam-scattering techniques into quantitative probes of surface structure and dynamics. On the other hand, rigorous, i.e., quantum mechanical, calculations present a difficult computational challenge, due to the large number of quantal states that may be accessible during the collision and that, often, are not known precisely. Solid surfaces under realistic conditions exhibit a variety of defect structures and disorder, for which numerical evaluation of the required statistical averages would be prohibitive. A number of treatments have been developed to enable practical calculations of gas-surface dynamics. This thematic issue brought together some of the most recent developments in this field. We served as Editors of this volume, which contained articles from 11 authors.

ONR-SUPPORTED PUBLICATIONS RESULTING FROM THIS RESEARCH

1. Quantum Dynamical Studies of the Decomposition of Energetic Materials, H. Rabitz and E. Vilallonga, in *Structure and Properties of Energetic Materials*, Vol. 296, p. 281, edited by R.W. Armstrong and J.J. Gilman, (Materials Research Society, Pittsburgh, 1993).
2. Multiquantum Vibrational Energy Transfer into Adsorbates on Solid Surfaces by Atomic Collisions: A Semiclassical Treatment Based on Dynamical Correlations, E. Vilallonga and H. Rabitz, *J. Chem. Phys.*, **97**, 1562 (1992).
3. Multiquantum Vibrational Energy Transfer into Surface Rayleigh, Bulk Shear and Pressure Waves by Atom-Solid Surface Collisions: A Discrete Continuum Hybrid Treatment with Applications to He-Pt(111), E. Vilallonga and H. Rabitz, *J. Chem. Phys.*, **97**, 1576 (1992).
4. Mechanisms of collision-induced desorption of a physisorbed atom at superthermal energy: A multiple scattering study, K. Yang, H. Cheng, E. Vilallonga, and H. Rabitz, *Surf. Sci.*, submitted.
5. Numerical study of the multiple-scattering series for gas-solid dynamics including single- through triple-collision terms, H. Cheng, K. Yang, E. Vilallonga, and H. Rabitz, *Phys. Rev. A*, **49**, 1096 (1994).
6. Atomic Collisions with Inhomogeneous Solid Surfaces: Multiple Scattering from Surface Defects and Mixed Overlayers, H. Cheng, K. Yang, E. Vilallonga, and H. Rabitz, *Surf. Sci.*, **304**, 168 (1994).
7. A discrete-continuum hybrid model for vibrational energy transfer at the gas-solid interface. II. The quantal evolution of coupled localized-collective motion, E. Vilallonga and H. Rabitz, *J. Chem. Phys.*, **100**, 8506 (1994).
8. Sensitivity analysis of the potential for elastic gas-solid scattering from surface defects, R. Viswanathan, S. Shi, E. Vilallonga, and H. Rabitz, *Surf. Sci.*, **271**, 217 (1992).
9. *Gas-Surface Dynamics* (A Thematic Issue of *Computer Physics Communications)*, edited by E. Vilallonga, and H. Rabitz, **80** (Elsevier, Amsterdam, 1994).