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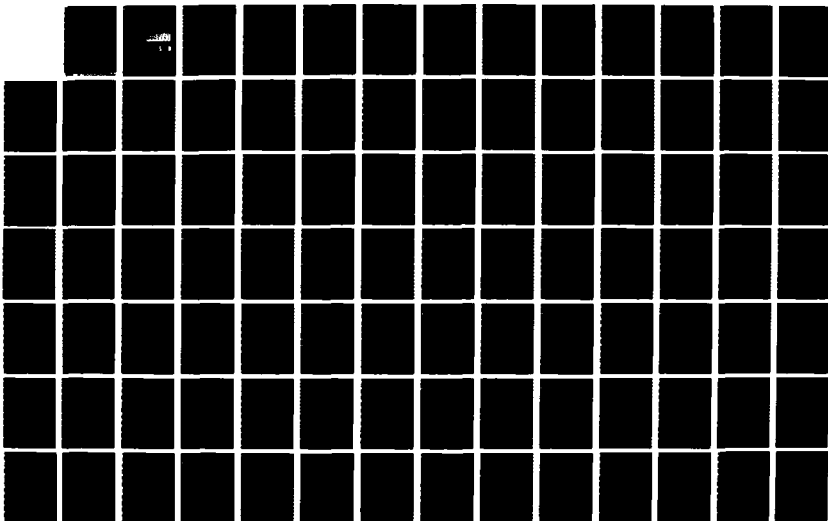
THE CONFERENCE ON THE DYNAMICS OF MOLECULAR COLLISIONS
HELD IN OGLEBAY PA (U) JOHNS HOPKINS UNIV BALTIMORE MD
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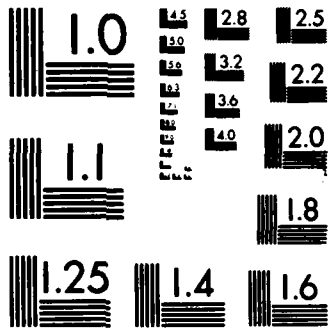
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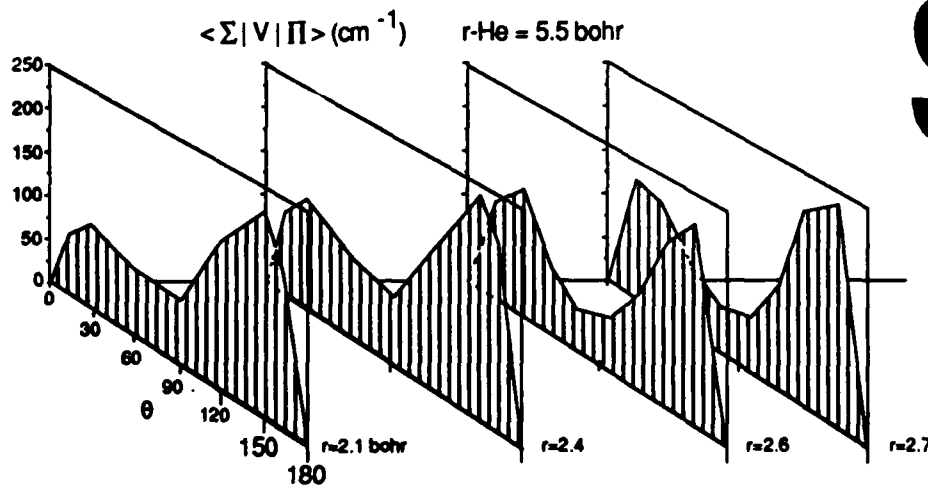
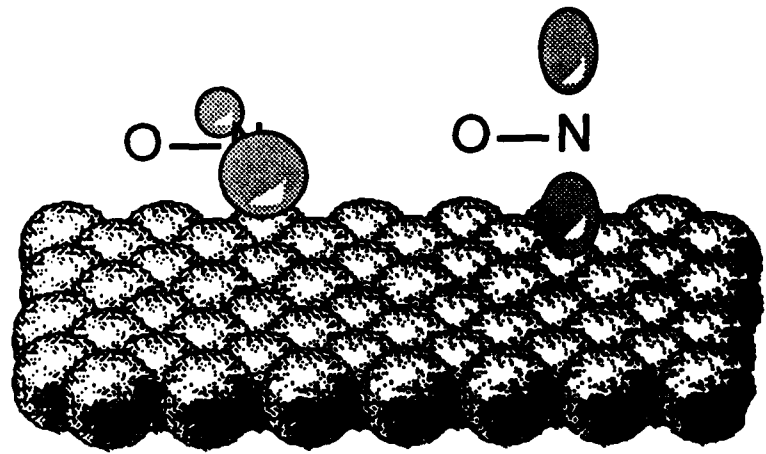
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1987 CONFERENCE ON THE DYNAMICS OF MOLECULAR COLLISIONS

July 12-17, 1987
Oglebay Park
Wheeling, West Virginia



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Cover Illustrations: (a) Upper figure. Representation of the two possible orientations of the singly-filled π^* orbital on the NO molecule with respect to the (111) plane of a Ag surface. Since the interaction with the surface will depend on the orientation of the π^* orbital, the scattering of NO from the surface cannot be described by a single potential energy surface. Quantum interference between collisions occurring on these two potential surfaces will result in unequal population of the two Λ -doublet levels in the scattered NO molecules.

(b) Lower figure. Nonadiabatic coupling matrix element between the $\text{CN}(X^2\Sigma^+)-\text{He}$ and $\text{CN}(A^2\Pi)-\text{He}$ diabatic states of A' symmetry as a function of the orientation angle θ and CN vibrational coordinate r , for a fixed $\text{CN}\cdots\text{He}$ distance of 5.5 bohr (from MCSCF calculations of H.-J. Werner and M. H. Alexander). It is this coupling which gives rise to collision-induced transitions between the A and X states of CN. The bimodal angular dependence of this matrix element illustrates its near homonuclear character. Figures provided by Millard Alexander.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The proceedings for the 1987 Conference on the Dynamics of Molecular Collisions, which was held in Oglebay Park, near Wheeling, WV, on July 12-17, is attached. There were formal sessions on both experimental and theoretical aspects of reactive collisions, inelastic energy transfer processes, and gas-surface interactions, as well as a special session on photodissociation and van der Waals molecules. There were 240 participants registered for the meetings, and 165 contributed papers were presented in several poster sessions.		

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Schedule of Presentations
1987 Conference on the Dynamics of Molecular Collisions
 Oglebay Park, Wheeling, WV, July 12-17, 1987
 Paul J. Dagdigan, Chairman; William H. Miller, Vice Chairman

Sunday, July 12

5:30 - 7:30 p.m. Registration and Reception

Monday, July 13

7:15 - 8:15 a.m.
 8:30 - 12:00 noon

Breakfast
 Session on Reactive Collisions (Experimental)
 Chairman/Discussion Leader: S. L. Anderson
 8:30 Announcements
 8:40 S. R. Leone, "Overview."
 9:30 Discussion
 9:50 Break
 10:10 Y. T. Lee, "Recent Crossed Molecular Beam
 Studies on Elementary Chemical Reactions."
 10:50 Discussion
 11:05 C. Y. Ng, "State-to-State Electron Transfer
 Reaction Dynamics."
 11:45 Discussion

12:15 - 1:15 p.m.
 6:00 - 7:00 p.m.
 7:20 - 10:10 p.m.

Lunch
 Dinner
 Session on Reactive Collisions (Theoretical)
 Chairman/Discussion Leader: J. M. Bowman
 7:20 D. G. Truhlar, "Overview."
 8:10 Discussion
 8:25 J. Manz, "Mode Selective Chemical
 Reactions."
 9:05 Discussion
 9:15 W. Meyer, "Theoretical Investigation of Electronic
 Structures and Reactive Collisions Involving
 Electronically Excited H₂."
 9:55 Discussion

Tuesday, July 14

7:15 - 8:15 a.m.
 8:30 - 11:55 a.m.

Breakfast
 Session on Inelastic Energy Transfer (Experimental)
 Chairman/Discussion Leader: C. A. Wight
 8:30 U. Buck, "Overview."
 9:20 Discussion
 9:40 Break
 10:05 K. Bergmann, "Rotational Rainbows in
 Electron-Molecule Scattering."
 10:45 Discussion
 11:00 G. W. Flynn, "Diode Laser Probing of Dynamic
 Energy Transfer Events."
 11:40 Discussion

12:15 - 1:15 p.m.
 2:00 - 2:30 p.m.
 6:00 - 7:00 p.m.
 7:30 - 10:00 p.m.

Lunch
 Conference Business Meeting
 Dinner
 Poster Session I

Wednesday, July 15

7:15 - 8:15 a.m.
 8:30 - 11:55 a.m.

Breakfast
 Session on Inelastic Energy Transfer (Theoretical)
 Chairman/Discussion Leader: F. R. McCourt
 8:30 R. Schinke, "Overview."
 9:20 Discussion

			9:40	Break
			10:05	D. J. Kouri, "Wavepacket Approach to Molecular Collisions."
			10:45	Discussion
			11:00	D. A. Micha, "Translational-to-Rovibrational Energy Transfer at Hyperthermal Velocities: Approaches Based on Collisional Time-Correlation Functions."
			11:40	Discussion
12:15	-	1:15		p.m. Lunch
6:00	-	7:00		p.m. Dinner
7:20	-	10:10		p.m. Session on Molecule-Surface Collisions (Experimental)
				Chairman/Discussion Leader: S. Bernasek
			7:20	S. J. Sibener, "Overview"
			8:10	Discussion
			8:25	M. Cardillo, "Hyperthermal Scattering from Surfaces: Electron Excitation, Ion Emission, and Rainbows."
			9:05	Discussion
			9:15	S. T. Ceyer, "Dynamics of Sticky Collisions with a Surface: Rotors, Splats, and Hammers."
			9:55	Discussion

Thursday, July 16

7:15	-	8:15		a.m. Breakfast
8:30	-	11:55		a.m. Session on Molecule-Surface Collisions (Theoretical)
				Chairman/Discussion Leader: J. W. Gadzuk
			8:30	J. C. Tully, "Overview."
			9:20	Discussion
			9:40	Break
			10:05	H. Metiu, "Time-Dependent Theory of Surface-Molecule Collisions: Gaussian Wave Packets and Fast Fourier Transform Methods."
			10:45	Discussion
			11:00	R. B. Gerber, "Atom Scattering from Surface Defects and from Disordered Surfaces."
			11:40	Discussion
12:15	-	1:15		p.m. Lunch
6:00	-	7:30		p.m. Banquet
8:00	-	10:00		p.m. Poster Session II

Friday, July 18

7:15	-	8:45		a.m. Breakfast
8:45	-	11:15		a.m. Session on Photodissociation/van der Waals Molecules
				Chairman/Discussion Leader: J. M. Lisy
			8:45	G. G. Ballint-Kurti, "Theory of Photodissociation Processes and Its Application to van der Waals Molecules."
			9:20	Discussion
			9:35	R. E. Miller, "The Structure and Photodissociation Dynamics of Binary and Tertiary van der Waals Complexes."
			10:10	Discussion
			10:25	D. Nesbitt, "Direct Absorption IR van der Waals Spectroscopy in Slit Supersonic Jets: Molecular Pinballs, Hinges, and Helicopters."
			11:00	Discussion
11:15	-	12:15		a.m. Lunch
12:30				p.m. Bus Departure for Greater Pittsburgh Airport

**ABSTRACTS
OF
PLENARY LECTURES**

AN OVERVIEW OF EXPERIMENTAL REACTION DYNAMICS

Stephen R. Leone
Joint Institute for Laboratory Astrophysics
Department of Chemistry and Biochemistry
National Bureau of Standards and University of Colorado
Boulder, Colorado 80309

In the past several years the field of reaction dynamics has enjoyed the continued ingenuity and enthusiasm of many experimentalists who quest for the ultimate in specificity and detail in an attempt to unmask the underlying features of reacting systems. Studies range from the most fundamental tests for theoretical comparison, for example $H + H_2$, to the most subtle aspects of finely split spin orbit states, the effects of quantum mechanical resonances, lambda doublet populations, and mode selected ion chemistry. There is tremendous interest in the reactions of species trapped within van der Waals clusters and the possibilities of fixing molecular geometries before reaction by condensing molecules in clusters or on surfaces. The search for a full elucidation of the transition state continues.

This presentation will also investigate some of the rapid progress and news in spin orbit reactivity, alignment and orientation effects, resonances, vector correlations, rotational rainbows, reactions of hot atoms, and vibrationally, rotationally, and electronically state specific systems. Some new achievements with advancing techniques such as position sensitive detectors, coincidence methods, and ever powerful laser and molecular beam methods will be reviewed.

RECENT CROSSED MOLECULAR BEAM STUDIES ON ELEMENTARY CHEMICAL REACTIONS

Yuan T. Lee

Materials and Molecular Research Division
Lawrence Berkeley Laboratory and
Department of Chemistry
University of California
Berkeley, California 94720 USA

This lecture will first briefly cover highlights of some of our recent investigations on the dynamics of elementary chemical reactions studied by the crossed molecular beams technique. The series of reactions which will be covered include endothermic substitution reactions involving bromine atoms and various chlorotoluene isomers, reaction of CH_3 with CF_3I and $(\text{CH}_3)_3\text{I}$ and the reaction of oxygen atom with C_2H_2 .

The main part of the lecture will focus on the reaction dynamics of electronically excited sodium atoms with simple molecules. Special attention will be paid to the reaction of $\text{Na}(4\text{D})$ with the NO_2 molecule. This reaction does not seem to proceed unless the relative kinetic energy exceeds 18 kcal/mol. Two distinct reaction channels with vastly different dynamics are observed in the measurements of product angular and velocity distributions. Although these products only appear at $m/e=23(\text{Na}^+)$ in mass spectrometric detection, they are likely to be NaO and NaO_2 . The alignment of the excited orbital of $\text{Na}(4\text{D})$ with respect to the relative velocity vector shows a dramatic effect on chemical reactivity. The rotation of the alignment of the $\text{Na}(4\text{D})$ orbital also shows a very different effect whether the orbital is rotated in the scattering plane which contains both molecular beams and the detector or out of the scattering plane. The implication of these observations will be discussed in great detail.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

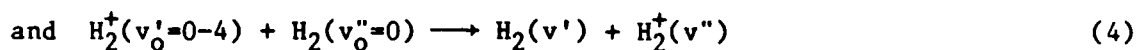
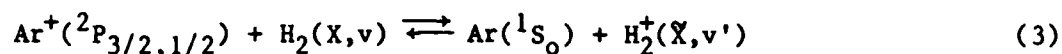
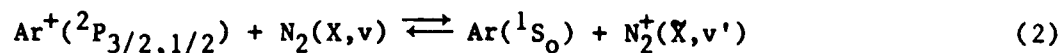
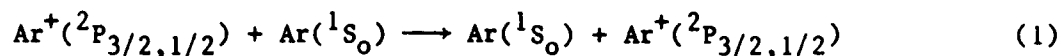
State-to-State Electron Transfer Reaction Dynamics

C. Y. Ng

Ames Laboratory-USDOE and Department of Chemistry
Iowa State University, Ames, Iowa 50011 USA

Abstract:

The development of two new ion-molecule reaction apparatus for the study of state-selected and state-to-state ion-molecule reaction dynamics will be described. Using these apparatus, state-to-state cross sectional data for the electron transfer reactions¹⁻⁴



have been obtained over wide kinetic energy ranges. These experiments provide detailed tests on the present theoretical understanding⁶⁻¹⁰ of electron transfer processes. Valuable insight into the roles of vibronic coupling and energy resonance in electron transfer has been gained from the examination of state-to-state cross sections of reactions (2) and (3) in the forward and backward directions.

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Abstract for 1987 Conference on the
Dynamics of Molecular Collisions,
Wheeling, WV, July 12-17, 1987

OVERVIEW LECTURE: THEORETICAL STUDIES
OF REACTIVE COLLISIONS

Donald G. Truhlar
Department of Chemistry and Supercomputer Institute,
University of Minnesota, Minneapolis, MN 55455

There are several new approaches to the quantum mechanical reactive scattering problem, and I will review these as a major part of the overview. Other topics covered will include semiclassical approximations, comparisons to experiment, and potential energy surfaces for reactive scattering.

Mode selective chemical reactions

Jörn Manz

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Germany

Mode selective chemical reactions allow efficient investment of energy in educts, as well as control of products' distributions. Various dynamical effects are demonstrated using experimental results as well as theoretical models and movies. The bimolecular examples include the Polanyi rules of vibrational versus translational mode selectivity in hydrogen atom plus dihalogenic molecule reactions, the relations of mode specific energy release in forward reactions versus mode selective energy consumption in back reactions as implied by microscopic reversibility and detailed balance, Bernstein-Levine-type information theoretic surprisal analyses of non-statistical effects, and Baer's rule of approximate conservation of translational energy as well as oscillatory reactivity and resonances in elementary hydrogen transfer reactions. The unimolecular examples cover mode selective dissociations of van-der-Waals complexes, small and large polyatomic molecules, with particular consideration of local versus hyperspherical mode selective resonance decay of vibrationally excited water and formaldehyde molecules.

THEORETICAL INVESTIGATION OF ELECTRONIC STRUCTURES AND
REACTIVE COLLISIONS INVOLVING ELECTRONICALLY EXCITED H₂.

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Fachbereich Chemie
Universität Kaiserslautern
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FED. REP. GERMANY

Problems encountered in the investigation of strongly changing electronic structures by advanced ab initio techniques will be discussed. They will be exemplified in particular by the small but nontrivial system H₂-H₂(B¹Σ_u⁺). The entrance channel interaction potential and possible pathways for reactive quenching will be characterized. The quenching cross section obtained from rather simple dynamical calculations is in excellent agreement with the measured ones. Comparison will be made with systems involving H₂^{*} and noble gases.

Inelastic Energy Transfer (Experimental)

U. Buck

Max-Planck-Institut für Strömungsforschung, D-3400 Göttingen,
Fed.Rep. of Germany

The study of rotational and vibrational energy transfer in molecular collisions is still a very active field of research. The interest comes from a range of applications in chemistry, spectroscopy and astrophysics as well as from the general aim to understand the underlying mechanism and the intermolecular potential. Accordingly, the measured quantity of interest is either a rate constant or a differential cross section both at a state resolved level of detail. While the measurement of state-to-state rate constants has reached a highly sophisticated level using excitation and detection with pulsed lasers, the measurement of angular dependent state selective cross sections in a crossed molecular beam experiment is not an easy task. Therefore often two other quantities are used to extract information on the interaction potential in which one of the strict requirements has been relaxed: state selective integral cross sections and the differential energy loss cross sections.

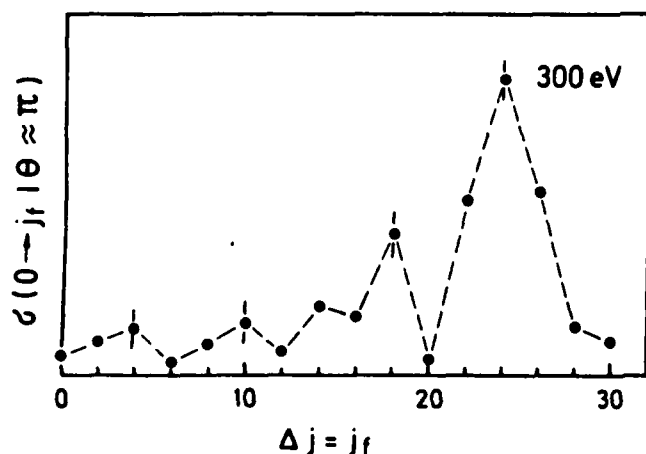
In the first part of this overview the experimental techniques for state preparation and state selection will be summarized and illustrated by typical examples both for cell experiments and molecular beam work. Then measured cross sections will be presented with particular emphasis on recent developments concerning diatomic open-shell molecules and vibrationally excited molecules as well as polyatomic molecules and small clusters. Finally the information content and the relation of the different measured quantities to the interaction potential will be discussed. This includes simple models for the interpretation of the data and the discussion of open questions in the field.

ROTATIONAL RAINBOWS IN ELECTRON-MOLECULE SCATTERING

K. Bergmann

Fachbereich Physik der Universität, Postfach 3049,
D-6750 Kaiserslautern, FRG

Rotational excitation of molecules in their electronic ground state by electron impact is one of the most important energy transfer processes in low temperature laboratory gas discharges and in low lying planetary ionospheric layers. Over the last few years, crossed beams experiments yielded total and differential cross sections and elucidated the mechanisms through which these processes proceed preferentially. No experimental nor theoretical investigations with state selection for other than hydrogen molecules or energies exceeding 100 eV have been reported. In particular, no experimental data are available for scattering in the backward direction. This angular range is not accessible in conventional electron scattering spectrometers. In this lecture state-to-state differential cross sections for scattering angles in the range $90^\circ < \Theta < 180^\circ$ for collision



energies of 150, 225 and 300 eV, using the well established state selection technique /1/, are presented /2/. We find rotational transitions as large as $\Delta j=28$ and pronounced rotational rainbow structures. This result is of fundamental importance because it is expected to be generally valid for high energy electron-molecule scattering.

Fig. 1: Rotational rainbow structure in Na_2 -e scattering.

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- 2 G. Ziegler, M. Rädle, O. Pütz, K. Jung, H. Ehrhardt, and K. Bergmann, to be published

George W. Flynn
Department of Chemistry
and Columbia Radiation Laboratory
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New York, NY 10027

DIODE LASER PROBING OF DYNAMIC ENERGY

TRANSFER EVENTS

Infrared diode lasers have been used to probe more than a dozen different carbon dioxide vibrational states and tens of rotational levels in each separate vibrational state produced as the result of collisions, photodissociation, and chemical reactions. Collisions between hot hydrogen or deuterium atoms (approximately 2eV translational energy) and cold CO₂ produce a wide distribution of excited vibrational and rotational states. Direct excitation of the CO₂ pure antisymmetric stretch levels 00⁰₁ and 00⁰₂ has been detected, and the rotational distribution produced in these vibrational states as a result of hot atom collisions is peaked at J=33. Relaxation of electronically-excited mercury atoms, NO₂ molecules, and azulene molecules due to collisions with a bath of room temperature CO₂ molecules has been studied. In these experiments, diodes are used to probe the energy of the vibrational modes of the CO₂ bath produced as a result of the relaxation of these electronically-excited donors. The low frequency CO₂ bending modes are produced more efficiently than the antisymmetric stretching modes for quenching of mercury atoms and azulene molecules, but the mechanism for relaxation of atoms, small and large molecules is clearly different in each case.

Inelastic Energy Transfer (Theoretical)

R. Schinke

Max-Planck-Institut für Strömungsforschung

D-3400 Göttingen, FRG

Recent developments of the theory of inelastic energy transfer will be reviewed. This includes new methods as well as applications to realistic systems. Of particular interest are rotational and vibrational excitation in atom-molecule and molecule-molecule collisions and the qualitative relation between the cross sections and the multi-dimensional potential energy surface. We will also consider electronic fine structure transitions in collisions with open shell molecules such as OH or NO. An appreciable amount of time will be allocated to direct photodissociation processes (half collisions) which are in many respects similar to atom-molecule collisions. The common features as well as significant differences will be discussed.

WAVEPACKET APPROACH TO MOLECULAR COLLISIONS

Donald J. Kouri
Department of Chemistry
University of Houston
Houston, TX 77004

The Schrödinger equation is a first-order linear partial differential equation and as a result, it is an initial value equation rather than a multipoint boundary value problem. This implies that one may obtain solutions corresponding to a single initial internal state when considering collision processes. An important consequence is that one may develop solution techniques which scale as the square of the number of quantum states involved in the collision. Further, most molecular beam experiments utilize a supersonic nozzle which leads to only a few initial internal states and therefore methods that only need calculate scattering for those may be very efficient. Time independent (close coupling) methods must calculate as many solutions to the scattering as there are coupled quantum states. As a result, they scale as the cube of the number of quantum states. Finally, wavepackets can contain components for many energies and thus the scattering information for all of the energies in the packet is obtained in a single wavepacket propagation. In this talk, the basic ideas of the wavepacket approach will be presented. The initial test calculations for the Lester-Bernstein model problem will be given to illustrate the method for gas phase collisions. These results include some obtained including 969 quantum states. In addition, sample applications to other scattering problems will be mentioned, including an exact quantum calculation done for N_2 scattered off a LiF model corrugated surface, which included 18,711 rotation-diffraction states. The extension of the approach to treat reactive gas phase collisions will also be indicated.

Abstract for the 1987 Conference on the
Dynamics of Molecular Collisions

TRANSLATIONAL-TO-ROVIBRATIONAL ENERGY TRANSFER AT HYPERTHERMAL
VELOCITIES: APPROACHES BASED ON COLLISIONAL TIME-CORRELATION
FUNCTIONS

David A. Micha
Departments of Chemistry and of Physics
University of Florida
Gainesville, Florida 32611

Methods based on collisional time-correlation functions can be used to describe mechanisms of energy transfer in collisions of pairs of molecules with hyperthermal kinetic energies, and to calculate double differential cross sections for energy and angular distributions. Impulsive scattering, semi-classical and operator algebraic methods have been applied to the scattering of atoms with free and adsorbed molecules to calculate cross sections for usual experimental conditions.[1-3]

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OVERVIEW: MOLECULE-SURFACE COLLISIONS (EXPERIMENTAL)

S. J. Sibener
Department of Chemistry
The University of Chicago
Chicago, IL 60637

Recent experimental advances made in the areas of gas-surface and laser-surface interactions will be reviewed. Subjects examined will include elastic, inelastic, and reactive scattering experiments, as well as laser and electron induced desorption processes. Information obtained on topics such as interaction potentials, surface structure, adsorbate and defect properties, state-to-state interactions, energy transfer, surface phonon dispersion, reaction dynamics, and laser desorption mechanisms will be highlighted.

"Hyperthermal Scattering from Surfaces: Electron
Excitation, Ion Emission, and Rainbows"

Mark J. Cardillo
AT&T Bell Laboratories
600 Mountain Ave.
Murray Hill, N.J.

ABSTRACT

Nonadiabatic excitation processes have been directly measured in the scattering of 2-15eV rare gas atoms from single crystal semiconductor surfaces. These include: electron-hole pair excitations, ejection of ionic substrate and adsorbate atoms (neutrals are also observed), and incident particle ionization.

In addition, sharp rainbow maxima are observed in the scattered angular distributions which are sensitive to the surface topography yet insensitive to the massive energy loss of the incident particle. The energy loss for all surfaces scales with the energy of local normal motion.

Simple models will be developed which provide good explanations of the principal observations, the critical aspects of which are confirmed by classical trajectory calculations.

Dynamics of Sticky Collisions with a Surface: Rotors, Splats and Hammers

S. T. CEYER
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, MA 02139

New and more direct evidence for the existence of a precursor molecule to molecular chemisorption will be discussed. We have found that there are two pathways through which CO chemisorbs on Ni(111): a pathway through which the CO molecule is initially adsorbed as a precursor to molecular chemisorption and a pathway through which adsorption into the molecular chemisorption state occurs directly from the gas phase. The precursor molecule is depicted as a tumbling rotor, still unhindered in its motion at 8K. These conclusions result from measurements of the effects of translational energy on chemisorption carried out in an apparatus combining molecular beam techniques with ultrahigh vacuum surface spectroscopies.

These techniques have also been used to show that there is a barrier to the dissociative chemisorption of CH₄ on Ni(111) and that the normal component of the translational energy of the incident CH₄ molecule is effective in surmounting it. The barrier arises from the energy necessary to deform the molecule to bring the carbon atom sufficiently close to the surface to form a Ni-C bond. Vibrational excitation of the incident CH₄ is similarly effective in promoting dissociative chemisorption. The large kinetic isotope effect and the exponential dependence of the dissociation probability on translational and vibrational energy indicate that tunneling also plays a role in the final C-H bond breaking step. The product of the dissociative chemisorption event is identified by high resolution electron energy loss spectroscopy as an adsorbed methyl radical and a hydrogen atom at a surface temperature of 130 K. The chemistry and stability of the methyl radicals are studied. The presence of this barrier presents a plausible explanation for an origin of the pressure gap in heterogeneous catalysis and provides a link between ultrahigh vacuum surface science and high pressure catalysis.

A new mechanism for dissociative chemisorption, collision-induced dissociation of adsorbates, will be discussed. We have shown that the dissociative chemisorption of CH₄, molecularly adsorbed on a Ni(111) surface at 46 K, is induced by the impact of incident Ar atoms. The probability for dissociative chemisorption is exponentially dependent on the normal component of the kinetic energy of the Ar atoms. The impact of the Ar atom deforms the molecularly adsorbed methane molecule into the configuration for the transition state that leads to dissociation. The implications of collision-induced dissociative chemisorption of adsorbates for high pressure catalysis are immense. No reaction mechanism for heterogeneous catalysis under high pressure conditions can now be considered complete without assessing the importance of collision-induced chemistry. Collision-induced dissociative chemisorption of adsorbates is likely another contributor to the origin of the pressure gap in heterogeneous catalysis.

This work is supported by the National Science Foundation (CHE-8508734) and the Synthetic Fuels Center of the Energy Lab at MIT.

Overview: Molecule-Surface Collisions (Theory)
John Tully, AT&T Bell Laboratories

Molecular collisions with surfaces have aspects in common with both gas-phase and liquid-phase dynamics. A gas-phase scattering picture is appropriate for initial and final states; i.e., questions concerning the efficacy of internal or translational energy in promoting reaction, the non-equilibrium disposal of energy in products, and the lifetime of the molecule-surface "collision complex" are relevant. During the time molecules are in close contact with the surface, however, the substrate plays a role similar to that of the solvent in solution chemistry. Interactions are mediated by the solvent, and frictional or stochastic elements are introduced. In addition, interesting dynamical effects emerge that, if not unique, are at least more prominent for gas-surface collisions. Among these are effects such as diffraction deriving from the crystal periodicity, continuous nesting of potential surfaces in metallic systems, and striking orientational effects imposed by the unique direction of the surface normal. Some current challenges in the theory of gas-surface interactions and recent progress toward surrounding these challenges will be summarized.

Time Dependent Theory of Surface-Molecule Collisions: Gaussian Wave Packets and Fast Fourier Transform Methods. Horia Metiu, Department of Chemistry, University of California, Santa Barbara, CA 93106.

We show results obtained by applying Gaussian wave packet and fast Fourier transform methods to study quantum processes occurring in molecule-surface collision problems. These cover He diffraction by a lattice in thermal motion, diffraction and rotational excitation of H_2 colliding with a surface and H_2 dissociation (in two dimensions!). If time permits we will discuss briefly simple model calculations pertinent to hydrogen diffusion on surfaces and adsorption-desorption processes in a system where desorption requires curve crossing.

Atom Scattering from Surface Defects and from Disordered Surfaces

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Abstract

Most recently, scattering of light atoms and molecules has emerged as a potentially powerful probe of imperfections on surfaces. Theoretical results are presented on the angular intensity distributions of atoms scattered from imperfect surfaces, which shed light on the relation between the measured intensity patterns and: The interaction between the defect and the scattered atom; Geometric parameters of the imperfection; The mutual (disordered) arrangement of the defects on the surface. Results are obtained also on the effects of defects on the diffractive scattering (from the crystalline part of the surface); Conditions for collapse of diffraction structure as disorder is increased; and new, non-Bragg intensity maxima due to scattering from the defects.

Calculations are presented for He scattering from vacancies on Pt(111), from CO adsorbates on Pt(111), and from mixtures of Xe and Ar in overlayers on Pt. Time-dependent quantum wavepacket techniques and the Sudden Approximation are used in different calculations. Specific findings include (1) Cross sections (measuring the attenuations of specular intensities) for scattering by adsorbates are sensitive to adsorbate location, but almost uninfluenced by interactions with the adsorbate image; (2) The energy and incidence angle dependence of the cross section suffice to determine an accurate He/defect potential; (3) New maxima in the scattering intensity are predicted associated with impurity-induced rainbows, and with impurity-induced selective adsorption; (4) Diffraction collapse in He scattering from mixed Xe + Ar overlayers is shown to occur as the "contamination" of the Xe by Ar is sufficiently increased.

It is argued that He scattering offers exciting possibilities for studying structural and dynamical properties of noncrystalline surfaces.

Theory of Photodissociation Processes
and its Application to van der Waals Molecules

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The theory of photodissociation and predissociation processes [1,2] is discussed and its application to van der Waals molecules reviewed. Results of applying the theory to the Ar-H₂ and Ar-HD van der Waals molecules are presented. The total integral photodissociation cross sections computed in the manner described correspond to the experimentally observed spectroscopic line shapes. Such line shapes for vibrational and rotational predissociation processes are presented and discussed [3]. Partial photodissociation cross sections, which tell us how the intermediate metastable predissociative complex decomposes into different fragment quantum states, are also given. For Ar-HD the results of the thermal averaging of many cross sections for individual elementary processes [4] to construct a simulated IR spectrum is presented [5]. New theoretical developments concerned with the application of multichannel quantum defect theory to such processes are discussed.

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THE STRUCTURE AND PHOTODISSOCIATION DYNAMICS OF BINARY AND
TERTIARY VAN DER WAALS MOLECULES

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Recent advances in the field of infrared laser-molecular beam spectroscopy have made possible the detailed study of both the structure and photochemistry of a wide range of van der Waals and hydrogen bonded molecules. In our laboratory, we have made use of the optothermal detection method to study a number of these systems. In several cases, we have been able to obtain excited state lifetimes (from the homogeneous broadening of the observed transitions) for more than one vibrational state of the molecule. These results indicate that there is a strong mode specificity for vibrational relaxation which can be understood in terms of simple geometrical factors. For example, in the T-shaped C_2H_2 -HF complex, excitation of the HF stretch, which is directly coupled to the van der Waals bond, gives rise to a shorter lifetime than that associated with the decoupled C-H stretch on the acetylene subgroup. This same effect has also been seen for the case of the "free" and "hydrogen bonded" C-H stretches of $(HCN)_2$ and F-H stretches of $(HF)_2$.

Recently, we have made considerable advances in the study of tertiary complexes such as $(CO_2)_3$ and $(HCN)_3$. In the case of the latter, both the linear and cyclic conformer have been observed. For the larger complexes, mode specific vibration relaxation is even more pronounced than in the dimers.

Direct Absorption IR van der Waals Spectroscopy in Slit Supersonic Jets:
Molecular Pinballs, Hinges and Helicopters

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Abstract:

The combination of high resolution cw tunable difference frequency generation, high sensitivity ($<10^{-6}/\sqrt{\text{Hz}}$) direct absorption methods and long path length (2.5cm) pulsed slit expansions provide a general method of spectroscopic investigation of weakly bound complexes in a cold molecular beam environment. The ability to probe both high frequency ("intramolecular") modes via fundamental absorptions as well as low frequency ("intermolecular") modes via hot band and combination band absorptions in these complexes permits investigation of the global features of the potential surface not sampled by rotational spectroscopic studies of the ground vibrational state. The floppy nature of the binding between the molecular constituents results in intramolecular dynamics (i.e. vibrationally averaged geometries, bond lengths, barriers to internal rotation, dissociation energies) that depend on internal quantum state. Since the intermolecular vibrational motion can occur on time scales comparable to end over end rotational motion, this results in a breakdown of traditional methods of spectroscopic analysis. These phenomena are discussed in the context of bimolecular complexes of HF with Ar, CO₂ and H₂ (D₂), in which large amplitude motion in stretch, bend and nearly free internal rotation are evidenced in the spectra and fully analyzed.

CONTRIBUTED PAPERS

Tuesday Evening Session

Reactive Collisions - Theoretical (RT)

Reactive Collisions - Experimental (RE)

Molecule-Surface Collisions - Theoretical (ST)

Molecule-Surface Collisions - Experimental (SE)

Thursday Evening Session

Inelastic Energy Transfer - Theoretical (ET)

Inelastic Energy Transfer - Experimental (EE)

Photodissociation, Photoionization (P)

van der Waals Molecules (V)

Quantum Chemistry by Random Walk:
Application to the Potential Energy Surface for $F + H_2 \rightarrow HF + H$

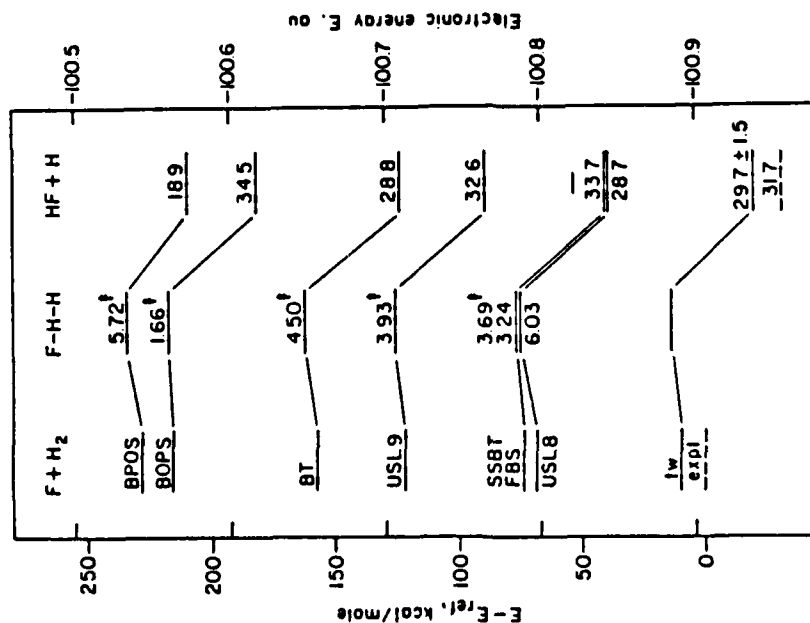
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We have applied the random walk method of solving the Schrodinger equation to determine energies of the following species: the fluorine atom F, the hydrogen fluoride molecule HF, and a number of F-H-H configurations of interest in determining the height and location of the saddle point for the reaction $F + H_2 \rightarrow HF + H$ and the characteristics of the potential energy surface in the region of the barrier. Several of the F-H-H configurations examined correspond to those suggested as saddle points in past variational calculations.

In what may be "Paradise Regained" we obtain electronic energies for these species which are approximately 65 kcal/mol below those of the lowest-energy variational calculations and for F and HF are only about 9 kcal/mol above the relativity-adjusted experimental values. Recovery of correlation energy is 96 percent complete. Since there is little room left for error, differences in energies among $F + H_2$, F-H-H, and HF + H are expected to be relatively free of error.

Thus far, we have obtained potential energies for F-H-H with statistical uncertainties of about 1 kcal/mol. We will reduce these for the most important configurations so that questions of saddle point height and location can be resolved.



N.B.: Incomplete list; †Theoretical saddle point, determined by search. Others at saddle points indicated by earlier studies.

QUANTUM MECHANICAL STUDY OF CHEMICAL REACTION AND CHARGE TRANSFER
PROCESSES IN THE $(\text{Ar}+\text{H}_2)^+$ SYSTEM

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Abstract

A quantum mechanical study within the Reactive Infinite Order Sudden Approximation for the ion-molecule system $(\text{Ar}^++\text{H}_2, \text{ArH}_2^+, \text{ArH}^++\text{H})$ is carried out.⁽¹⁾ All three arrangement channels for exchange and charge transfer were treated simultaneously. Steric factors, opacity functions, angular distributions and integral cross sections were calculated. The results whenever possible were compared with both, with experimental results⁽²⁾ and with trajectory surface hopping results.⁽³⁾ In general a reasonable agreement was obtained for both integral cross sections and differential cross sections. The main discrepancy is found for the integral cross section of the reaction $\text{Ar}+\text{H}_2^+(v_1=0) \rightarrow \text{ArH}^++\text{H}$ and a gratifying result is the nice fit between the experimental⁽⁴⁾ and quantum mechanical differential cross sections for the reaction $\text{Ar}^++\text{H}_2(v_1=0) \rightarrow \text{Ar}+\text{H}_2^+$. As mentioned, also steric factors were calculated and they seem to reveal the existence of a new mechanism not entirely understood.

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SOLUTION OF DISSOCIATIVE STATE IN SHIFTED CHEBYSHEV SERIES

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The solution in shifted Chebyshev series has been derived for the following dissociative state radial equation:

$$\frac{d^2R}{dr^2} + \frac{\Lambda^2 - N(N+1)}{r^2} R + [k^2 - U(r)] R = 0 \quad (1)$$

where $U(r) = B_1/r + B_2/r^2$. For $r \geq 1$, substitution of

$R(r) = (2s)^S \exp(ik/z + iplnz) F(z)$ into Eq.(1), where $z=1/r$,

$s = 1/2 + [1/4 + N(N+1) + B_2 - \Lambda^2]^{1/2}$ and $p = B_1/2k$, yields

the following confluent hypergeometric equation:

$$z^2 F''(z) + [(2 + 2ip)z - w] F'(z) + (s+ip)(1-s+ip) F(z) = 0 \quad (2)$$

where $w=2ik$. Substituting a shifted Chebyshev polynomial expansion^{1,2}, i.e. $F(z) = \sum_n G_n(w) T_n^*(z)$, into Eq.(2), and integrating Eq.(2) two times, we obtain a five-term recurrence relation as follows:

$$\begin{aligned} & \left[1 + \frac{(a_1-1)(a_2-1)}{n(n-1)} + \frac{a_1 + a_2 - 3}{n} \right] G_{n-2} \\ & + \left[4 + \frac{2(a_1 + a_2 - 3)}{n} + \frac{4w}{n} \right] G_{n-1} \\ & + \left[6 - \frac{2(a_1-1)(a_2-1)}{(n-1)(n+1)} \right] G_n + \left[4 - \frac{2(a_1 + a_2 - 3)}{n} - \frac{4w}{n} \right] G_{n+1} \\ & + \left[1 + \frac{(a_1-1)(a_2-1)}{n(n+1)} - \frac{a_1 + a_2 - 3}{n} \right] G_{n+2} = 0 \end{aligned} \quad (3)$$

Where $a_1 = s + ip$ and $a_2 = 1 - s + ip$. The expansion coefficients $G_n(w)$ can then be evaluated through the backward recursions.³ The above recurrence relation can be reduced to the four-term recurrence relation derived previously³. The new method developed here can be extended to solve the differential equations of different potential function $U(r)$.

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A New Approach for the Determination of Addition Rate Constants from the Analysis of Relaxation Measurements

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A variety of relaxation techniques has been applied to study the reaction rates of chemical processes in which extremely short-lived intermediate species play a fundamental role. E. B. Gordon, et al. [*Chem. Phys. Lett.* **35**, 79(1978)] have determined addition rate constants using a hydrogen maser to measure spin shifts and broadening in the hyperfine transition of atomic hydrogen. The technique of muonium spin relaxation, pioneered by the research group at TRIUMF [see D. G. Fleming, et al. *Muonium Chemistry--A Review*, in *Positronium and Muonium Chemistry*, H. J. Ache, ed., American Chemical Society, 1979], has been utilized to measure rate constants for a number of muonium addition and abstraction reactions in the presence of a buffer gas.

Previously, the results of relaxation experiments have been analyzed using an *abstraction* model. In this work we report the development of a new *addition* model which includes the competing processes of unimolecular decomposition and pressure stabilization. Both the unimolecular decomposition and the pressure stabilization rate constants included in the new model can be related directly to RRKM theory. The new model allows the determination of the high-pressure limit rate constant from data collected in relaxation experiments performed at *any* pressure.

This model is applied to a set of synthetic data (including a randomly generated noise component) designed to simulate the results of a muonium spin relaxation experiment. These calculations suggest that it is possible to extract both the high-pressure limit addition rate constant and the unimolecular decomposition rate constant, provided the noise component is well-controlled. Secondly, the new model is used to analyze actual data from a muonium spin relaxation experiment, permitting a comparison of the previous *abstraction* analysis with the current *addition* analysis.

ACKNOWLEDGEMENT: Work supported by the U. S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under contract W-31-109-ENG-38.

NUMERICAL INTEGRATION OF DIFFERENTIALLY COUPLED EQUATIONS:
APPLICATION TO THE STUDY OF NON-ADIABATIC INTERACTIONS IN MOLECULES

by

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ABSTRACT

It is shown that coupled differential equations involving derivative channel couplings, as arise in collision problems formulated in terms of adiabatic basis, can be solved numerically by a three points recurrence formula. This recurrence formula exhibits a structure similar to the well known Numerov formula for potential multiplicative coupled channels problems.

Introduction of differential couplings results in a lowering in the order of the integrator with respect to the step size 'h'. Nevertheless, this is expected to be compensated by the reduction in the number of coupled channels as a result of using an adiabatic basis. Indeed, it is known that non-adiabatic couplings of adiabatic states are generally more localized on the energy scale than the corresponding potential adiabatic couplings of equivalent diabatic states.

The above property is illustrated by results of the numerical integrations of coupled equations for the Hénon-Heiles hamiltonian in an adiabatic basis, using the present algorithm, and in the usual diabatic basis of zeroth order harmonic oscillator states, using the usual Numerov formula.

The Onset of Non-Rotating Wave Effects for
Reactive Collisions in a Laser Field

RT6

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A number of aspects of the breakdown of the rotating wave approximation (RWA) in laser modified reactive collision processes are examined. An analysis is presented into the factors which are responsible for the breakdown and our conclusions are similar to those in a recent article by Last, save with regard to the effect of varying laser field strength. We also consider ways in which one can correct for the onset of RWA breakdown. The schemes considered, all depend upon suppression (by matrix transformation) of low order couplings to the non-RWA channels. Application of the schemes and general investigation of non-RWA behavior is made for a simple model problem involving a single nuclear degree of freedom. We find that the results of the calculations lend support to our identified breakdown factors. Of the correction schemes, one is clearly to be preferred, although a second may also have merit. Finally, we discuss a number of complicating features of the theoretical description of laser modified collisions which may be expected to frequently accompany the appearance of non-RWA effects.

The Sensitivity Approach to the Analysis of
Parameter Dependencies in Reactive Collision Theory

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New working expressions are given for the first derivatives or elementary sensitivity coefficients of reactive and non-reactive scattering matrices with respect to an arbitrary input parameter. The expressions, as in our earlier work, are constructed for collinear reaction but within now a less restricted representation of the electronic-vibrational degrees of freedom. Application is made to two simple test problems. The first deals with the collision energy dependence of transmission and reflection on a one dimensional potential curve. We examine the relative convergence behavior of values and energy derivatives of the scattering elements with the steplength in our procedure for integrating the dynamical equations. The second test problem adds on a closed potential curve which is non-adiabatically coupled to the potential curve of the first (test problem). We examine the effectiveness of sensitivity and non-sensitivity calculations in describing how the scattering elements behave through the space of a parameter which centers the non-adiabatic coupling envelope. We find that for the single parameter variation, sensitivity and half-spaced non-sensitivity calculations using a common steplength, yield essentially equal quality descriptions of the parameter dependence. When this finding is projected into a multi-parametric context and we roughly estimate the relative work involved in the two approaches, a minimum order for the parameter space, i.e. 2, is identified such that the sensitivity approach may be expected to be the more efficient.

**Application of variational transition state theory
to the isomerization reaction $\text{HONO} \rightarrow \text{HNO}_2$ ***

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Unimolecular hydrogen migration reactions are important in gas-phase combustion processes. The isomerization of HONO is a prototypical example which is thought to be important in the combustion of nitro containing compounds. Although the HNO_2 species has not been seen directly under combustion or flame conditions, it has been postulated to explain experimental results. One possible route for production of HNO_2 is the isomerization of HONO, however, the barrier for this reaction is known to be high. One of the goals of this study is to obtain an estimate of the order of magnitude of the rate for this reaction.

High pressure thermal rate constants are computed for the $\text{HONO} \rightarrow \text{HNO}_2$ reaction using variational transition state theory with multidimensional transmission coefficients. The rates are computed using potential energy information obtained from *ab initio* electronic structure calculations. The potential energy and analytic first and second derivatives along the reaction path are calculated using the multiconfiguration self consistent field (MCSCF) method.

The barrier for this reaction is quite high (approximately 60 kcal/mol) which leads to very small computed rates when quantum mechanical tunneling effects are neglected. For temperatures from room temperature up to about 600K the reaction is dominated by tunneling; the tunneling correction factor varies over several orders of magnitude for this temperature range. Thus, although the barrier is very high, the reaction is facilitated by quantum mechanical tunneling. Preliminary results indicate that the reaction rate is appreciable for temperatures characteristic of combustion conditions.

A major concern in calculations based upon *ab initio* potential energy information is the effective use of the computed potential information. We examine the dependence of the computed rates on the amount of potential information available along the reaction path. The dependence of the rates on the level of accuracy of the *ab initio* potential energy information is also addressed.

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A new decomposition of the S-matrix for
multichannel resonant collisions^a

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The usual decomposition of a multichannel scattering matrix near an isolated, narrow resonance is given as a sum of a direct and resonant part. The direct part which describes the background scattering is regular and unitary. The resonant part features a pole at the complex resonance energy, and both its magnitude and phase change rapidly as the energy varies. Given the S-matrix, it is often a cumbersome task to extract resonance parameters from it. We propose a new decomposition that overcomes this difficulty, and derives from the standard one. The new resonant part is a complete analog of the single channel S-matrix. Its magnitude is constant, and its phase jumps by 2π as the energy increases. The resonant time-delays for each state-to-state transition are independent of the channel indices, and exhibit a Lorentzian shape from which the resonance energy and width are readily obtained. The square of the magnitude of the resonant S-matrix elements are the state-to-state transition probabilities of the resonant scattering, and are expressed in terms of the channel partial widths. The applicability of the proposed decomposition is demonstrated in a coupled-channel study of multichannel resonances and unimolecular decay in H-CO collisions using a global *ab initio* potential energy surface.

^aWork partly supported by the Department of Energy under Grant No. DE-FG05-86ER13568

Intramolecular Energy Transfer and Cis-Trans Isomerization of HONO

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Classical trajectories have been used to investigate intermolecular energy transfer and unimolecular reaction in nitrous acid. The influence of various initial normal mode excitations has been investigated. Power and coherence spectra are used to examine the intramolecular dynamics. The rate of cis-trans conversion is strongly dependent on site of initial excitation. The results show that the OH stretching mode is only weakly coupled to the other modes. Energy transfer out of excited states of the OH mode is slow and preferential partitioning of energy into that mode leads to reduced rate of isomerization.

Abstract of a paper for the Conference
on the Dynamics of Molecular
Collisions, Wheeling, WV, July 12-17,
1987

Ψ^2 Amplitude Density Method for
Atom-Molecule Rearrangement Collisions

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A new method has been developed for the quantum mechanical calculation of chemical reaction rates, and it is being applied to reactive collisions of H, D, O, F, Cl, and Br with H₂ in either the ground or first excited vibrational state. The method involves solving a set of coupled integral equations equivalent to the Schroedinger equation with scattering boundary conditions by expanding the amplitude density describing the chemical system in a square-integrable basis set. This method reduces the computational work involved in the problem to two steps: the numerical evaluation of multidimensional integrals and the solution of large sets of linear equations. Our program is designed for and run on a Cray-2 computer, and it takes advantage of its large memory and vector processing ability. The results obtained so far are very encouraging and have already helped to clarify disagreements between more approximate theoretical results and experimental results.

This work was supported in part by the National Science Foundation, the Minnesota Supercomputer Institute, and the Control Data Corporation.

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Monte Carlo simulation of RRKM unimolecular decomposition in molecular beam experiments.

Product OX angular and energy distributions from $O(^3P) + X_2$ ($X = Br, I$)

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Abstract

Statistical simulation was applied to the unimolecular decomposition of the collision complexes formed in the crossed beam experiments on $O(^3P) + Br_2$ [1] and $O(^3P) + I_2$ [2]. The simulation procedure [3-5] used the fundamentals of RRKM theory and included exact angular momentum conservation. The impact parameter distributions were varied to obtain the best fits. Good agreement with experimental laboratory angular distributions measured with O atoms seeded in both He and Ne was found for impact parameter distributions which were peaked at quite small values, in most cases between 2 and 3 Å. Product OX molecules were found to be rotationally excited and inverted with a mean rotational energy close to twice the value expected without angular momentum restrictions. The differences found between the calculated and the experimental angular distributions do not support any assumptions about osculating or shortlived complexes. The normal exoergicity ΔD_0 of 27 kJ/mol for the $O + I_2$ reaction agrees well with the experiments in Ref. [2].

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Dynamical tests of RRKM unimolecular decomposition on a simplified potential energy surface

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Abstract

The unimolecular decomposition of a model triatomic system similar to an excited water molecule was studied with the classical trajectory method. Energy term values for the different degrees of freedom were recorded for various product separation distances, using total angular momentum as a parameter, in the range 10–80 \hbar . Results for the same type of system were also found from our RRKM-type statistical algorithm which has previously been applied to the unimolecular decomposition of excited H_2O formed in crossed beams experiments [1] (experiments by Y.T. Lee et al. [2]), and in LIF experiments [3] (experiments by Luntz et al. [4]). The available energy is there distributed in an RRKM fashion between the degrees of freedom, observing strict conservation of total angular momentum. By comparing the two sets of results, a dynamical test of the fundamental assumptions in RRKM-type statistical theories is found. The comparison indicates good agreement between dynamical and statistical results for high but not for low values of total angular momentum. The main reason for this discrepancy appears to be dynamical effects close to the centrifugal barrier due to the asymmetry in the potential. These results will be used for further improving of the statistical simulation method for studies of unimolecular decomposition.

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ANHARMONIC VIBRATIONAL PARTITION FUNCTIONS FOR
POLYATOMIC MOLECULES AND TRANSITION STATES

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The calculation of accurate anharmonic vibrational energy levels for a given potential energy surface has recently become possible through the development of, e.g., vibrational SCF-CI programs. However, the application of such methods to the calculation of a sufficient number of vibrational levels for the evaluation of vibrational partition functions in polyatomic molecules is a major undertaking, and would be impractical for the calculation of partition functions for the bound vibrational modes of a reacting complex along a reaction path, as is needed in generalized transition state theory. One practical alternative in such cases is provided by second-order perturbation theory. While this approach is not in general as reliable for excited state energies as it is for the ground state, we have found in preliminary calculations that the individual excited state energies may not be very important in determining the partition function, as long as vibrational resonances are treated properly. In this talk, we will compare the results for partition functions computed from levels obtained by accurate methods and by perturbation theory for water and for the saddle point of the $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$ reaction. Further conclusions using perturbation theory for this reaction will also be discussed.

COMPLETE AB INITIO REACTION DYNAMICS STUDY FOR $\text{Ca} + \text{HF} \rightarrow \text{CaF} + \text{H}$

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ABSTRACT

A comprehensive first principles theoretical investigation has been carried out for the gas phase reaction $\text{Ca} + \text{HF} \rightarrow \text{CaF} + \text{H}$. The overall study involves three distinct elements: (a) generation of an accurate ab initio potential energy surface for the ground electronic state of the Ca-F-H system, (b) careful fitting of the computed surface to an analytical form suitable for three dimensional reactive scattering calculations, and (c) execution of classical trajectory calculations for Ca + HF collisions using the fitted potential surface.

The potential energy surface is dominated by a deep well corresponding to a stable linear H-Ca-F intermediate with an extremely small bending force constant. The preferred geometry for Ca attack on HF is markedly non-collinear with the saddle point for both the F atom exchange reaction and Ca atom insertion into the H-Ca-F well occurring for a Ca-F-H angle of 75° . The saddle point energy is 16.1 kcal/mol relative to Ca + HF (the barrier for the collinear reaction path is 30.0 kcal/mol). The analytical representation of the ab initio potential energy surface is based on a polynomial expansion in the three diatomic bond lengths and reproduces the values of the compute energies to within a root mean square deviation of 1.2 kcal/mol.

Classical trajectory calculations for $\text{Ca} + \text{HF}(v=1)$ utilizing the fitted surface establish the fact that the H-Ca-F potential well dominates the collision dynamics, thus qualifying Ca + HF as a bona fide example of a chemical insertion reaction. This finding is consistent with the interpretation of results from previous experimental studies on $\text{Ca} + \text{HF}(v=1)$. Due to the extensive sampling of the H-Ca-F well, many trajectories formed rather long-lived intermediate complexes before proceeding to diatomic end products. The results obtained support a number of generalizations relating to microscopic features of Ca + HF collisions. Among these are: (1) at fixed total collision energy, excitation of HF to $v=1$ is much more effective in promoting reaction than is placing the corresponding amount of energy in Ca, HF translation, (2) at fixed initial translational energy, reaction cross sections increase with increasing value of the HF rotational quantum number J, (3) for trajectories which enter the H-Ca-F well, escape to form products is favored by increasing initial HF J and escape back to reactants is favored by increasing initial relative translational energy, and (4) the CaF fractional product energy disposals are remarkably independent of initial collision conditions. These findings are compatible with the observation that significant intermode vibrational energy does not occur in the H-Ca-F intermediate on the collision time scale (1-2 ps).

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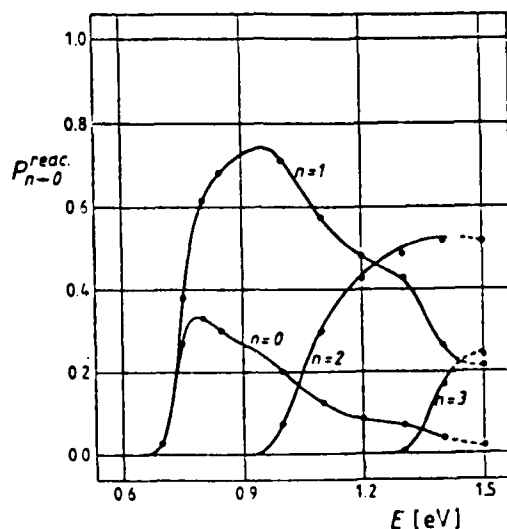
Abstract. We are investigating systematically the use of the finite element method (FEM) for solving the Schrödinger equation. The following work is devoted to the calculation of vibrational transition probabilities for the collinear reactive system A + BC (i.e. H + H₂ and their isotopes and F + H₂). The calculations are full two-dimensional as in the early work of Askar et al./1/ and the results are compared with the conventional basis set expansion methods using the R-matrix or S-matrix propagation.

We made extensive analysis of FEM on the vector-computer Cyber 205 and developed a vector code for the efficient use in two dimensions, so that in the near future applications even in three dimensions will be possible.

For the hydrogen isotope reactions we investigated the following combinations: a) H + H₂ b) H + DH, D + HD and H + μ H symmetric reaction c) D + HH, H + DD and $\mu \neq$ DD asymmetric reaction. We calculated the transition probability for five open vibrational channels and found excellent results compared to the known "exact" values.

The details of our FEM calculations are the following /2/: The symmetry of the potential surface was not used in case of a symmetric reaction in order to have a good comparison to the values of an asymmetric reaction. This results naturally into a larger number of grid points. The integration area was discretized into triangles where we defined quadratic polynomials for the local wavefunction. With this simple ansatz convergent results can be reached for most reactions with \approx 10000 grid points and in the case of F + H₂ with \approx 32000 grid points.

As an example in fig.1 we show our results for the reaction probability of $\mu + D_2$ ($n = 0,1,2,3$) \rightarrow μD ($n' = 0$) + D. The lines are results of Bondi et al. /3/ and the dots are the present results.



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TIME DEPENDENT SEMI-CLASSICAL REACTION DYNAMICS
VIA GAUSSIAN WAVEPACKETS

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A time dependent solution for a one dimensional atom-diatom exchange reaction is presented based upon a modification of Heller's semi-classical propagation of gaussian wavepackets (GWP's) scheme¹. The full scattering wavefunction, initialized as a product of an incoming plane wave times an internal oscillator state, is expanded in terms of GWP's in both translational and vibrational variables. We have found that a multiple GWP expansion in translations is crucial for providing an adequate final scattering wavefunction in both the reactant's and product's arrangement channels.

The time dependent quantum dynamics is treated within the interaction picture (IP) where the channel Moeller operators² are used explicitly. The propagation of the GWP's within the IP is a two step process: 1. all GWP's are propagated forward in time from t_0 using the full Hamiltonian until the translational center of each and every GWP resides in either the reactant's or product's channel asymptotically; 2. the forward propagation is then stopped (at t_{asp}) and all the GWP's are propagated backwards in time back to t_0 using the channel Hamiltonian appropriate for the asymptotic translational center of each GWP at t_{asp} .

The GWP's are propagated by solving the differential equations for the GWP parameters derived from the various Hamiltonians. Each GWP trajectory consists of the integration of Hamilton's equations of motion plus an accumulation of the classical action integral. Truncation of the Taylor expansion for the potential energy function at first order provides an analytic solution to the GWP width equation of motion. This analytic solution along with the IP propagation procedure provides a time dependent justification to the Frozen (width) Gaussian Approximation.

Scattering information is extracted by constructing wavefunction overlaps in each of the arrangement channels. Numerical results for the exchange reaction $H + H_2$ on the Porter-Karplus (II) potential energy surface³ are presented.

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ORIENTATION EFFECTS IN H REACTIVITY

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The study of reaction paths associated to collisions starting at a given value of the angle of attack is usually based on the analysis of exact and model classical trajectory results. A recent classical trajectory study of the $H + H_2$ system^{1/} has shown that reaction can occur either by exchange of the hydrogen atom with the nearest molecular end or (especially at higher collision energy) through its insertion into the hydrogen molecule. A tight correlation between the angle of attack of the incoming atom and the reactive outcome was found. According to these results, one can define a reaction cone inside which the large majority of trajectories react with the atom located on its apex.

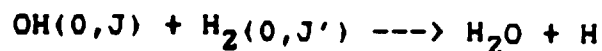
We are currently investigating the dynamics of $M + HY$ ($M = \text{alkali and alkaline earth, } Y = \text{halogen}$) and $H + XY$ ($X = \text{halogen}$) families of reactions. During our investigation we found that in the $Li HF$ reaction where the H atom is bound to a significantly heavier partner and the transition state has a bent geometry, reorientation mechanisms influence reactivity. In particular, it was found that especially when H is substituted by Mu attacks from the F side are scarcely or no reactive whereas attacks on the Mu side are highly reactive even if the final product is LiF . Such a reorientation effect disappears when H is substituted by heavier isotopes.

Orientational effects have been found to be important also for reaction of H with ICl . In fact, for H initially pointing toward I, 3.5% of events led to HCl . At the same time, 0.5% of collisions initially pointing toward Cl led to HI product. Reactive collisions ending with H bound to the atom towards which it was originally pointing are respectively 5.8% and 4.9% for I and Cl. A graphical study of these trajectories has evidenced the role played by migration of the impinging H atom around the target molecule for determining the final outcome.

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EFFECT OF REAGENT ROTATION ON THE REACTION



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Classical trajectory calculations on the reaction $\text{OH}(0, J) + \text{H}_2(0, J') \longrightarrow \text{H}_2\text{O} + \text{H}$ have been carried out for J up to 30 and J' up to 15 at several values of the collision energy. Both the Schatz-Elgersma¹ and Rashed-Brown² potential surfaces have been used.

Rotation in the H_2 bond shows reactivity trends similar to those seen in recent studies on $\text{H} + \text{H}_2$.³ Generally the reaction cross section increases as J' increases; however, near threshold this increase is preceded by a decrease for $J'=0-4$. Model calculations⁴ have succeeded in explaining the effect for $\text{H} + \text{H}_2$, and seem to be also useful for $\text{OH} + \text{H}_2$.

Rotation in OH produces different effects for different collision energy regimes. At high translational energy OH rotation tends to increase reaction cross sections, often after an initial decrease. At low translational energy, the reaction cross section increases up to a maximum near $J=20$, after which it decreases. Possible explanations for this behavior will be discussed.

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Quasiclassical and Semiclassical Approaches to
Molecular Collision Dynamics

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Research elucidating the details of molecular collision phenomena, especially reactive scattering and electronically nonadiabatic behavior, using one of several types of classical trajectory approach as the principal tool will be presented. These various "types" of classical trajectories range from the standard quasiclassical trajectory method, in which all degrees of freedom are treated classically after the imposition of a single quantum condition or constraint, to "quantum trajectories", which resemble classical trajectories only in form, but arise from an approximate solution to the time-dependent Schrödinger equation. The thrust of this research is two-fold: one aspect deals with developing concepts and methods, the other with their applications to chemical problems. The major "applications" project concerns the reaction of $O(^1D)$ with isotopes of H_2 . It and several "methods" projects will be summarized.

These "methods" projects include a fully three-dimensional application of a semiclassical (classical path) reactive scattering method employing hyperspherical coordinates. In this application, the "hyperradius" and the Euler angles specifying the overall orientation and rotation of the system are treated classically; the two "internal angles" that specify the arrangement of the system are treated using time-dependent quantum mechanics. No angular momentum decoupling approximations are made.

A "quantum trajectory" method which arises from a quantum mechanical treatment employing an approximate, separable time-dependent wavefunction of the form $X(x,t)Y(y,t)$, where x is the "relative" coordinate, y the "internal" coordinates, and $X(x,t)$ a Gaussian wavepacket that is constrained to remain Gaussian throughout the course of the collision, will also be discussed. An expression for "semiclassical T-matrix" elements in this theory and the sensitivity of computed transition probabilities to the initial values of the "free" parameters, which revealed a startling result, will be presented. In all cases in which the momentum transfer in the collision was "not too large", there appeared to be a unique value of the initial momentum for which wavepackets of all initial breadths gave exactly the same result. A formal explanation of this behavior, which follows from the basic assumptions of the theory, not only shows that such a "stationary point" should occur when the initial momentum is near the average of the initial and final asymptotic channel momenta for the transition in question, but also explains the shift in the value of the unique momentum away from the average of the asymptotic channel momenta, and why the theory breaks down for large magnitudes of momentum transfer in the "quantum trajectory".

EFFECTS OF DIATOMIC REAGENT ALIGNMENT ON THE A + BC REACTION

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ABSTRACT

Effects of diatomic reagent alignment on the prototype reaction $A + BC \rightarrow AB + C$ have been investigated by running classical trajectories on a modified version of the LEPS potential which permits the minimum energy path for reaction to be varied from collinear to broadside attack. Preliminary calculations on both exothermic (early barrier) and endothermic (late barrier) potentials have been performed for mass combinations of the class $H + H'L \rightarrow HH' + L$, where H and H' are heavy atoms and L is a light atom. Separate calculations have been performed for alignments in which the initial BC rotational angular momentum vector is either asymptotically parallel (or equivalently antiparallel) or asymptotically perpendicular to the direction of the A,BC initial relative velocity vector.

In all cases, initial BC rotational energies were chosen from a 300 K Boltzmann distribution and for each mass combination and potential surface utilized, BC(v=0) and BC(v=1) collisions have been studied at constant relative translational plus vibrational energies. Thus, for each case, the BC(v=0) and BC(v=1) average total collision energies were virtually identical.

For endothermic surfaces, a distinct reagent alignment effect [for both BC(v=0) and BC(v=1)] on the extent of product vibrational excitation is observed. Although the present studies are clearly model ones, the observed effect is in qualitative agreement with results obtained in alignment experiments on $Sr + HF(v=1)$. A similar but weaker effect is observed for BC(v=0) on exothermic surfaces, but is absent for BC(v=1).

Beyond product energy disposals, results obtained also demonstrate a marked effect, both for endothermic and exothermic potentials, of diatomic reagent alignment on reactive cross sections. Analysis of the observed trends suggests a possible underlying steric basis of the Polanyi rules which, for elementary bimolecular gas reactions, relate mode specific excitation to extent of reactivity. Results obtained are also suggestive of generalizations relating to the applicability of the Polanyi rules to reactions which favor non-collinear collisions.

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QUANTUM REACTIVE SCATTERING IN THREE DIMENSIONS
USING HYPERSPHERICAL (APH) COORDINATES.

TESTS ON $H+H_2$ AND $D+H_2$ *

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ABSTRACT

Accurate OC calculations of 3D quantum reactive scattering using hyperspherical (APH) coordinates are reported for both zero and nonzero total angular momentum J and for both symmetric ($H+H_2$) and unsymmetric ($D+H_2$) mass combinations. Accurate 3D reactive scattering calculations are now possible for heavier systems and higher energies than ever before.

*Work performed under the auspices of the U S Department of Energy.

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A calculation of the potential energy surface for HF-HF is reviewed.¹ The surface consists of 1,332 points computed with the GAUSSIAN 82 program² using a standard 6-311G** basis set. In addition to both molecules at equilibrium, several hundred points correspond to one molecule displaced from its equilibrium geometry. The MP4 data was fit to within 1 kcal/mole rms error using a modified London formula augmented by many-body polynomial terms³. A fit to a triple product of spherical functions was also investigated,⁴ and was found to be deficient at shorter internuclear separations, although satisfactory at separations larger than 6 a₀.

In this work the electron correlation energy is studied at several levels of perturbation theory in addition to the full MP4 level. The SCF, MP2, MP3 and MP4 levels are accurately fit and compared. It is shown that the most significant effect on the energy occurs at the MP2 level, with the next most significant change occurring at the full SDTQ-MP4 level. The global variation of the various surfaces is examined graphically to illustrate the effect of geometry on correlation energy.

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The Intel iPSC computer is composed of a number of independent processors operating asynchronously and communicating via message passing over a hypercube network.¹ In an n -cube configuration consisting of 2^n processors, each processor, or node, is connected to n other nodes and forms an n -dimensional hypercube, or binary n -cube. Rather than sharing a common memory, each node has its own local memory, and is a self contained computational unit running a Unix-like operating system called XENIX. For compute-intensive applications, using algorithms that adapt well to a concurrent architecture, such a machine offers the possibility of low cost supercomputer performance.

We report our experience in adapting two types of calculations to the hypercube, namely molecular dynamics simulation of a liquid, and quantum mechanical close-coupling calculations. Both types of calculation present a high degree of parallelism, and present the opportunity to investigate the efficiency of various algorithms. Since interprocess communication is the obvious bottleneck that must be overcome, some balance is needed between optimization of the numerical algorithms and the need to pass data between the nodes in an effective manner. The availability of vector boards that increase each processor's power a hundredfold for some applications makes this even more critical.

Since the nodes operate asynchronously, many novel applications can be envisioned, such as concurrent graphical analysis of a simulation, leading to new horizons in interactive modelling. Since several manufacturers are implementing the hypercube approach, it is worthy of study to anticipate some of the problems to be encountered in adapting our traditionally sequential algorithms to this highly parallel architecture.

* Work Supported by the National Science Foundation under Grant ISI-8661037.

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Combining Transition State Theory and Quasiclassical Trajectory Calculations for 3-Dimensional Reactive Collisions

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A major disadvantage of the conventional quasiclassical trajectory technique of investigating reactive collisions is its inefficiency. Often a very large proportion of the trajectories fail to react and are hence 'uninteresting'. This drawback can be overcome by starting the trajectories at the transition state so that almost all the trajectories reach the strong interaction region of the potential energy surface. Following earlier work¹ using purely classical methods and our own quasiclassical studies² of collinear systems, this paper reports the first 3-dimensional, quasiclassical calculations which combine transition state and trajectory techniques.

3-D vibrationally adiabatic transition states have been constructed using the adiabatic periodic reduction method.³ These transition states are sampled from a classical, thermal distribution over the bending, rotational and translational (i.e., reaction coordinate) motions. Trajectories are then run 'forwards' in time towards products or 'backwards' in time towards reagents. The forward trajectories give product state distributions, whilst the backward trajectories yield information about the extent of vibrational adiabaticity between reagents and transition state and the properties of the colliding reagents which lead to reaction. The trajectory procedure produces relative values for state-to-state rate constants. These are converted to absolute rate constants using adiabatic reactive sudden transition state theory.³

The method has been applied to $H + H_2(v)$ collisions occurring on the accurate LSTH potential energy surface⁴ with $0 \leq v \leq 9$. The results will be described and comparisons made with the results obtained in conventional trajectory calculations.⁵

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Abstract of a paper for the 1987
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Molecular Collisions, Wheeling,
WV, July 12-17, 1987

Completely Ψ^2 Golden Rule Method for
Resonance Energies, Widths and Branching Ratios

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Abstract. We have calculated resonance energies and widths for both one- and two-dimensional scattering resonances by a general method involving only Hamiltonian and overlap integrals in a single square-integrable basis set containing a scale parameter. We use a stabilization method with a compactness criterion to find the resonance energies and a generalization of the golden rule formalism to calculate the widths. For one-channel resonances we have found good agreement with accurate resonance energies and widths obtained by Breit-Wigner fits. Preliminary results on two-channel resonances indicate that we can calculate branching ratios to similar accuracy.

This work was supported in part by the National Science Foundation, by the Minnesota Supercomputer Institute, and by an NSF Graduate Fellowship to S.C.T.

**A COMPARISON OF LOCAL AND GLOBAL SINGLE
GAUSSIAN APPROXIMATIONS TO TIME DYNAMICS:
ONE DIMENSIONAL SYSTEMS**

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The detailed calculation of the dynamics of a chemical system is usually not considered due to the size and cost of the computation. It is thus useful to examine various approximation methods. Such methods first need to be tried out on simple systems, like one dimensional motion. Here two approaches to approximating the solutions of the Schrodinger and von Neumann equations by single time dependent Gaussians are explored and contrasted, explicitly for one dimensional barrier penetration. The first approach, in which no tunnelling occurs, is local in nature and characterized by an expansion of the equations of motion to second order about the average position of the Gaussian wavepacket or about the average position and momentum of the Gaussian Wigner function. This approach was first introduced by Heller [E.J. Heller, *J. Chem. Phys.* **62**, 1544 (1975)]. Here both Heller's approach and a more general truncation method are considered. Indeed tunnelling can be incorporated if second order terms in the quantal von Neumann equation are included. However, the resulting dynamics is unstable for kinetic energies where the exact wavepacket (and Wigner function) splits into non-negligible parts that represent reflection and transmission. In contrast, the second approach is a global method which is obtained by applying appropriate closure approximations to the equations of motion for the first and second order position and momentum expectation values. This method allows tunnelling and is stable at all kinetic energies. It is also possible to approximate the global equations in such a way that the local equations are obtained.

THE APPLICATION OF THE TIME DEPENDENT HARTREE FOCK METHOD
TO THE STUDY OF LOW-ENERGY, COLLINEAR ION-MOLECULE REACTIONS;
AN EXAMPLE: $H^+ + H_2 \rightarrow H_2 + H^+$

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Application of the Time Dependent Hartree Fock (TDHF) method to the problem of low energy ion-on-molecule scattering presents an opportunity to study non adiabatic processes dynamically (1). The electronic state is expressed as a single time dependent determinantal wave function with the motion of the nuclei evaluated classically. The electronic and nuclear motions and interactions are determined self consistently. A report of the application of this method to the highly reactive collinear collision of H^+ on H_2 is given. This collision is studied for two scattering energies, and for two different target H_2 vibrational levels. The resulting reaction and charge exchange probabilities are compared with two-state quantum mechanical calculations of Top and Baer (2). It is found that this method accurately predicts the reaction probability but gives charge exchange probabilities that agree only qualitatively with those calculated by Top and Baer.

Charge density contours of the H_3^+ system at selected time points during the collision are shown, as also are phase plane plots of the nuclear coordinates and the temporal progression of the net charge on the scattering proton. These plots show an interesting interplay between the electronic, vibrational, and translational energies during the collision.

A short description of the use of the TDHF method in reactive molecular scattering will be given including a discussion of the dynamic coupling terms that are implicitly included in this type of calculation. These dynamic terms are absent in the standard two-step approach of calculating the electronic potential energy surface and then calculating the classical trajectories on that surface.

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Comparison between Theory and Experiment for the Recombination



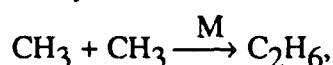
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The recombination of methyl radicals to ethane in the presence of a buffer gas M,



is of interest in combustion applications and in theoretical studies of loose transition state reactions. A microcanonical variational RRKM rate constant calculation, based on the flexible transition state theory of Wardlaw and Marcus (*J. Phys. Chem.* **1986**, *90*, 5383) and an adjustable empirical potential energy surface, is compared to recent measurements of this reaction in both Ar and He buffer gas. The calculations contain two adjustable parameters: a potential parameter α , which influences the tightness of the transition state and $\langle \Delta E \rangle_{\text{tot}}$, the total average energy change in metastable C_2H_6^* per collision with the buffer gas. For Ar buffer gas, the parameters are optimized to obtain the best agreement with the only directly measured high pressure limit (Hippler, et al. *Z. Phys. Chemie Neue Folge* **1984**, *142*, 1) and with pressure dependent measurements by Gutman, et al. or Pilling, et al. (*J. Phys. Chem.* **1985**, *89*, 2268) at 296, 474, 577, 700, 810, or 900 K. The resulting calculated rate constants have a 10.7% rms error with the measurements. The final value of $\langle \Delta E \rangle_{\text{tot}}$ is $-240 \pm 70 \text{ cm}^{-1}$ if temperature independent. However the data will permit a wide variety of temperature dependencies for $\langle \Delta E \rangle_{\text{tot}}$. The final value of α is $0.64 \pm 0.07 \text{ \AA}^{-1}$. With these two parameters fixed, additional calculated rate constants for Ar buffer gas at 407, 513, 539, and 1350 K are in good agreement with other measurements by either Pilling, et al., or Glanzer, et al. (*J. Comb. (Int.) Symp.* **1977**, *XVI*, 949). The calculated rate constants for Ar buffer gas have been extended up to 2000 K and accurately fit to a functional form recommended by Gilbert, et al. (*Ber Bunsenges. Phys. Chem.* **1983**, *87*, 169). This fit is an accurate representation of the calculations for the temperature range 300 - 2000 K and for all pressures where the rate constant is larger than $10^{-12} \text{ cc/molec-sec}$.

The calculations for He buffer gas can be compared to a small set of measurements by Gutman, et al. The agreement is good but not as good as with Ar buffer gas unless $\langle \Delta E \rangle_{\text{tot}}$ is made strongly temperature dependent. More extensive measurements are required before this result can be confirmed.

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Time Delay in a Chaotic Quantum Scattering System

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The quantum treatment of a two degree of freedom scattering system originally studied by Gutzwiller[†] is re-examined and new results for the time delay obtained. Although apparently not corresponding to any known physical system, this system is exceptional in that its scattering can be solved analytically yet its behaviour, as indicated by the role of the Riemann zeta function, is inherently chaotic. It is hoped that this simple, albeit somewhat abstract, system will provide insights into the nature and manifestations of quantum chaos in the scattering regime. In order to make the model more intuitive, we have recast the mathematical treatment, dropped Gutzwiller's curved space interpretation, and have explained the meaning of the phase shift and time delay in terms of plane waves and wave packets.

Plots of phase shifts (which are identical to Gutzwiller's) and time delays as a function of the "velocity" are presented. The chaos in the phase shift is evident. The chaotic contribution to the time delay fluctuates smoothly between positive and negative values, displaying fairly sharp positive peaks reminiscent of resonances in conventional scattering systems. At the time of writing an analysis of these "resonances" was underway; some results of this analysis will be included in the poster.

[†]M.C. Gutzwiller, *Physica* 7D, 341 (1985).

Ab Initio Potential Energy Surfaces of the Electronically
Excited Na atom with the O₂ and HCl molecules

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The potential energy surfaces of the reactive scattering processes between the Na(3S, 3P and 3D) atom with the O₂ and HCl molecules are investigated by ab initio configuration interaction (CI) calculations. The MRSD-CI method is applied with the DZP basis set. The effective core potential is used for the Na and Cl atoms. The mechanism of the Na atom quenching, the electronic state selectivity of reactions, and the internal energy distribution of the products are discussed based on the characteristics of the potential energy surfaces such as the barrier heights along reaction paths and of the surface crossing between several states.

Theoretical Studies of Nonadiabatic Processes
and Spin-Forbidden Radiative Processes

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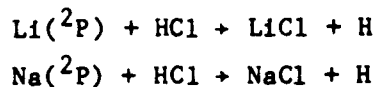
David R. Yarkony
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Nonadiabatic processes involve, in an adiabatic states approach, motion on two or more Born-Oppenheimer potential energy surfaces (PES's) which are coupled by terms including

$$g(J, I, R_\alpha, \underline{R}) = \langle \Psi_J(\underline{r}; \underline{R}) | \frac{\partial}{\partial R_\alpha} \Psi_I(\underline{r}; \underline{R}) \rangle_{\underline{r}}$$

where the $\Psi_J(\underline{r}; \underline{R})$ are the electronic wavefunctions for the adiabatic states. A recently developed method for determining $g(J, I, R_\alpha, \underline{R})$ for large scale MCSCF/CI wavefunctions¹ using analytic gradient techniques now permits efficient evaluation of these coupling matrix elements.

We will use this methodology to consider the nonadiabatic chemical quenching reactions^{2,3}



and (if results are available) the charge transfer reaction



For the $\text{Na}(^2\text{P}) + \text{HCl}$ reaction the $g(2^2\text{A}', 1^2\text{A}', R_\alpha, \underline{R})$ will be determined for three internal coordinates, R_α , in several regions of coordinate space, \underline{R} , including the vicinity of a saddle point on the $1^2\text{A}'$ PES and two minima on the $2^2\text{A}'$ PES in order to examine where the propensity for quenching might be significant and which degrees of freedom facilitate this process.

We will also discuss the radiative decay of the $a^1\Delta$ state of CH^- , i.e., the spin-forbidden dipole-allowed transition $a^1\Delta \rightarrow X^3\Sigma^-$. This transition is particularly difficult to treat theoretically since it derives its intensity by coupling to $^3\Pi$ and $^1\Pi$ states embedded in the $\text{CH} + e^-$ continuum. An approach will be presented which circumvents this difficulty.⁴

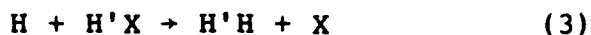
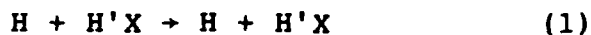
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Abstract for 1987 Dynamics of Molecular Collisions Poster

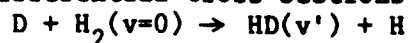
Energy Partitioning in the H + HX Reactions
at 1.6 eV Collision EnergyP.M. Aker, K.D. Tabor, G. Germann and J.J. Valentini
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Coherent anti-Stokes Raman Spectroscopy has been used to probe the initial vibrational and rotational distributions arising in the HX and H₂ products from reaction of translationally excited H-atoms with HX (where X = I, Br, Cl, F).



The conditions of the experiment are such that the distributions are probed after virtually only one collision of the fast H atom with the HX molecule. The use of isotopic labelling has allowed us to distinguish between inelastic energy transfer (1) and reactive exchange energy transfer (2). We also report the first measurements of the total vibrational and rotational distributions in the H₂ product of the H-atom abstraction reaction (3).

Pulsed Crossed Molecular Beam Measurements of Vibrationally
State-Resolved Differential Cross Sections for the Reaction



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By using pulsed molecular beam scattering methods coupled with laser photolysis we have measured, for the first time, vibrationally state-resolved differential cross sections for the hydrogen exchange reaction, $D + H_2 \rightarrow HD + H$.

Translationally hot D atoms (Etrans = 2.2 eV) are generated by ArF* (193 nm) laser photolysis of D₂S. A low pressure expansion of D₂S from a pulsed beam source is intersected by the mildly focused output of an excimer laser so that the D atoms are formed under nearly collisionless conditions. This results in the very narrow D atom velocity distribution ($\Delta v/v \approx 0.07$) necessary for this high resolution crossed beam experiment. The collimated D atom beam then intersects a skimmed pulsed supersonic beam of H₂. The reactively scattered HD product is ionized by electron impact in a differentially pumped ion source and detected by a quadrupole mass spectrometer followed by a particle counter. Internal state selectivity is achieved by time-of-flight (TOF) velocity analysis of the scattered product.

Results at a collision energy of 0.95 eV show clearly resolved peaks in the TOF spectrum for the slow laboratory HD products formed in $v=0$ and $v=1$ (scattering $\sim 180^\circ$ relative to the D atom center-of-mass direction). In addition, details concerning the rotational state distribution can be extracted from the shape of the TOF feature for each vibrational state. The translational energy dependence of the state-resolved differential cross sections has been investigated by varying the D,H₂ intersection angle. Under the current conditions, collision energies from about 0.8 eV to 1.1 eV are accessible. The results of these experiments and their implications concerning dynamical features of the reaction will be presented.

This research is supported by the Chemical Physics Program of the National Science Foundation, Grant No. CHE-8205769.

SPIN-ORBIT EFFECTS IN CHEMICAL REACTIONS:
Investigation of Ground State Products from Reactions of Ba(3D)

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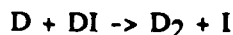
An optical-pumping state selection technique^{1,2} has been employed to determine the dependence of the cross sections for the production of ground-state barium halide products on incident spin-orbit state for the reaction of metastable Ba(6s5d 3D) with HX and CH₃X (X = Cl, Br). In addition, cross sections for the metastable 1D state were related to those of the 3D_J multiplet by optical pumping on an intercombination line. Ground-state products were detected by laser-induced fluorescence using the C - X transition. For the reactions studied, the spin-orbit dependence for the production of electronic ground-state barium halide molecules ($X^2\Sigma$) in which the product is highly vibrationally excited was substantial with the magnitude of the J-dependent cross sections having an ordering $J = 1 > J = 2 > J = 3$. This is an opposite ordering to that previously observed for the chemiluminescence channels in analogous reactions.² The magnitude of the spin-orbit effect depends upon both the halide reactant and product vibrational state monitored. However, for all the reactions in which the product was highly vibrationally excited, the lower energy $J = 1$ state was at least two times and up to four times more reactive than the $J = 3$ state. A significantly diminished variation of reactivity with incident J was observed for lower v in the hydrogen halides. Arguments will be presented which support that the variation of spin-orbit effect with product vibrational level is due to the dependence of the reaction dynamics on incident impact parameter.

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Deuterium Atom Abstraction Reactions

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Photolytic production of monoenergetic deuterium atoms via the excimer laser photolysis of deuterium iodide at 248 and 193 nm has given us information concerning the dynamics of the deuterium atom abstraction reaction:



at collision energies of 42 and 76 kcal/mole. A pulsed excimer laser was crossed with a continuous beam formed by the expansion of neat DI through a 0.5 mm nozzle at low pressures. Some of the deuterium atoms then react with unphotolyzed DI before they escape from the molecular beam and produce D_2 molecules whose translational energy distribution is then measured by the time of flight method.

The time of flight data obtained may be directly inverted to yield the translational energy distribution due to the skewed kinematics of the deuterium atom abstraction reactions. In general, the observed energy distributions indicate that the D_2 is produced in highly excited vibrational states. This shows that a large fraction of the energy available, which includes the 33 kcal/mole exothermicity, ends up in the internal energy of the D_2 molecule. Features are also observed which indicate that a momentum conserving spectator stripping mechanism may be important at these collision energies.

Moderation effects were observable at the highest target pressures, however, the data at the lowest pressures allows us to make these initial conclusions concerning the nascent translational energy distribution. Further experiments involving a polarized excimer laser and lower target densities will enable us to obtain a clearer picture of the dynamics of numerous isotopic hydrogen atom abstraction reactions in the near future.

ACKNOWLEDGEMENT

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC-03-7600098.

Absolute Rate Coefficient for $\text{NH}_2 + \text{NO}_2$ from 274 to 364 KDavid A. Dolson[†] and Robert D. StephensEnvironmental Science Department, General Motors Research
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The interest in reactions of amidogen radicals (NH_2) is largely due to the pivotal role that they play in the atmospheric chemistry of ammonia and in the reduction of NO in post-combustion gases. Although the reaction of amidogen with nitric oxide has received much attention recently, $\text{NH}_2 + \text{NO}_2$ may be of equal importance in the atmospheric chemistry of ammonia. Accurate measurements of rate constants and product yields are required for atmospheric modeling efforts and to aid the understanding of the reaction dynamics of the amidogen radical.

We report the results of an experimental measurement of the $\text{NH}_2 + \text{NO}_2$ reaction rate between 274 and 364 K using a laser photolysis - laser excited fluorescence technique. Our experimental results can be summarized by $k(T) = 5.7 \times 10^{-8} (T)^{-1.35} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over this temperature range. No pressure dependence of the reaction rate was detected with up to 40 Torr of helium. N_2O and H_2O were detected as stable reaction products with a modulated-beam mass spectrometer coupled to a fast flow tube reactor.

The many similarities between the reactions of NH_2 with NO_2 and with NO suggest that similar mechanisms may apply to both reactions. The experimental observations are consistent with the view that products are formed by rapid intramolecular rearrangements of an energetic collision complex (H_2NNO_2)[‡]. Further theoretical treatment of this reaction would improve our understanding of amidogen reaction dynamics.

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A Reinvestigation of the Laser-Initiated Cl₂/HBr Chain Reaction:
 Absolute Rate Constants and the v=2/v=1 Ratio from Cl + HBr → HCl(v) + Br

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 80309-0440

The Cl₂/HBr chain reaction has been reinvestigated using realtime state-selected observations of Δv = -1 chemiluminescence from the HCl(v) products following pulsed laser photolysis of Cl₂. These state-selected observations have been analyzed with a more complete kinetic treatment to obtain room temperature rate constants for the chain propagation steps and the vibrational deactivation of HCl(v=1,2) by HBr. The chain propagation rate constants are $k_{R1} = (1.02 \pm 0.15) \times 10^{-11}$ and $k_{R2} = (1.1 \pm 0.4) \times 10^{-15}$ cm³

molecule⁻¹ s⁻¹, respectively, for Cl + HBr $\xrightarrow{k_{R1}}$ HCl(v) + Br and Br + Cl₂ $\xrightarrow{k_{R2}}$ BrCl + Cl. Rate constants for vibrational deactivation of HCl(v=1) and HCl(v=2) by HBr are $k_{V1} = (1.06 \pm 0.16) \times 10^{-12}$ and $k_{V2} = (2.09 \pm 0.50) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹. Relative intensity measurements of the HCl v=2→1 and 1→0 vibrational fluorescence are used to obtain an HCl(v) product branching ratio, $N_{v=2}/N_{v=1} = 0.40 \pm 0.06$. The kinetic analysis indicates that broadband observations of infrared chemiluminescence may lead to erroneous rate constant determinations because of vibrational cascade, whereas the detection of individual vibrational states leads to correct results.

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Reactive Scattering from Double Minimum Potentials

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We present a crossed ion beam-molecular beam study of dehydration and dehydrohalogenation reactions of alcohols and alkyl halides with Li^+ at collision energies between 20 and 50 kcal mol⁻¹. The kinetic energy and angular distributions for the olefin- Li^+ and HX-Li^+ or $\text{H}_2\text{O-Li}^+$ products measured as a function of relative collision energy provide detailed information about the partitioning of energy in these complex reactions. As the relative collision energy increases, the intermediate complexes break up in a fraction of a rotational period, establishing the time scale for the reactive process as a few hundred femtoseconds. Like many low energy ion-molecule reactive processes, these systems are hypothesized to occur on a double minimum potential energy surface. The first well on the surface arises from the initial encounter complex formed by the approaching reagents, while a sizable barrier for isomerization to a second ionic complex prior to product formation plays a critical role in determining the overall rate and dynamics of the elimination process. This isomerization barrier lies below the asymptotic reactant or product energy levels, but serves as an entropic bottleneck to reaction. Encounter complexes formed as the reagents approach have a large probability for decaying back to reactants, with a very large transfer of initial translational energy to internal excitation of the neutral reagent. Direct observation of this non-reactive flux leads to an assessment of energy partitioning in both wells of the double-minimum potential energy surface. The energy dependent branching ratios for this non-reactive scattering relative to the reactive flux yield very precise (± 1 kcal mol⁻¹) estimates of the intermediate isomerization barriers. The experimental results provide tests of current double minimum potential models for ion-neutral reaction rates and their statistical foundations.

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Exchange Reactions of ^{18}OH with Various Oxygen Containing Molecules

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Cooperative Institute for Research in Environmental
Sciences, University of Colorado, Boulder, CO.

Oxygen atom exchange reactions of isotopically labeled ^{18}OH with various molecules of atmospheric importance were studied in a flow tube at room temperature. Laser magnetic resonance was used to measure the removal of the ^{18}OH and the appearance of the ^{16}OH product. Results showed that NO and NO_2 undergo rapid O-atom isotope exchange ($\approx 2 \times 10^{-11}$ and $\approx 1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively) No significant exchange was observed for CO, CO_2 , SO_2 , OCS, H_2O , O_2 , and N_2O . The experimental results will be discussed in terms of possible reaction mechanisms.

Why Radioactivity Must Be Used in Crossed Molecular Beam Reactive Scattering Experiments

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The study of reactive collisions in crossed molecular beams has reached a plateau in qualitatively new capabilities because for more than a decade the sensitivity of the general techniques presently in use has been only incrementally improved. Among the alternative techniques that have been explored, only one combines the possibility of wide generality with the orders-of-magnitude increase in sensitivity that is necessary to bring about further major advances: the use of reagent molecules that incorporate short-lived radioactive nuclides generated on-line at a nuclear accelerator¹. Many of the necessary techniques have already been developed for nuclear studies and for crossed-beam feasibility demonstration experiments using radioactive precursors in place of nuclear beams². Recently there has been a spectacular proliferation of small accelerators for use in analysis, materials processing, isotope production, nuclear medicine, etc., so the time is now right for their application to the study of reactive collisions between molecules.

A possible experimental program will be presented in sufficient detail to highlight the problems that can be foreseen. For specificity the study of the reaction $^{12}\text{NH}_3 + \text{Cl} \rightarrow ^{12}\text{NH}_2 + \text{HCl}$ is considered. Nitrogen-12, half life = 0.011 sec, is generated by the reaction $^{10}\text{B}(^3\text{He}, n)^{12}\text{N}$ using a multiple thin target and a 50- μA beam of 12.5-Mev ^3He ions from a minicyclotron (cost \sim \$250,000). The ^{12}N recoils from the target, is stopped in flowing gaseous helium, converted to $^{12}\text{NH}_3$ by reaction with hydrogen donors, and expanded from a nozzle to form a molecular beam of 10^7 molecules sec^{-1} . Each ^{12}N atom will disintegrate with the emission of a positron of median energy 8 Mev, which can be detected by known techniques with 100% efficiency and essentially zero background. The $^{12}\text{NH}_2$ can be very selectively detected in the presence of unreacted $^{12}\text{NH}_3$ with nearly unit efficiency via differential sticking coefficients or thermal chromatography. Pulsed nuclear beams from a post-acceleration storage ring plus detector timing techniques will allow the measurement of final state velocity distributions without sacrificing the nuclear beam intensity. Hodoscopic detector arrays will greatly increase overall data acquisition rates. In favorable systems doubly-differential cross sections as small as 10^{-4} A^2 per steradian per kcal mol^{-1} should be measurable.

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Crossed-Beam Reactive Scattering of $F_2 + C_6H_6$:
Heat of Formation of ipso- $C_6H_6F^\cdot$

RE10

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Angular distributions and relative total cross sections were measured for products of the collisions of F_2 with C_6H_6 at relative collision energies of 14 to 26 kcal mol⁻¹. For this work the Lee-design crossed beam scattering apparatus at the Institute for Molecular Science, Okazaki, Japan, was used. The most conspicuous product is the ipso-fluorocyclohexadienyl radical $\underline{1}$ - $C_6H_6F^\cdot$, which displays a rather narrow peak very near the laboratory center-of-mass angle at all collision energies studied. This suggests that the reaction $C_6H_6 + F_2 \rightarrow C_6H_6F^\cdot + F$ proceeds preferentially by a statistical or quasi-statistical mechanism. Product fluorobenzene, C_6H_5F , is masked at $M/e = 96$ by dissociative ionization of $C_6H_6F^\cdot$ near the center-of-mass angle but becomes clearly observable at smaller angles to which little or no $C_6H_6F^\cdot$ is scattered. This means that the reaction $C_6H_6 + F_2 \rightarrow C_6H_5F + HF$ occurs, and does so in such a way that the products acquire high translational energies. The dependence on collision energy of the total cross section for the production of $C_6H_6F^\cdot$ was measured, and displays a well-marked onset at 13.6 ± 0.4 kcal mol⁻¹. The mean final state translational energy as a function of collision energy was obtained from the angular distributions and also displays an apparent onset near 13-15 kcal mol⁻¹, meaning that the onset is most likely a true threshold. Improved measurements to confirm this observation are underway. The average final state translational energy asymptotically approaches 3.7 kcal mol⁻¹ as the collision energies are increased, which is so large that only a few vibrational modes of $C_6H_6F^\cdot$ can be involved in the energy partitioning. Therefore the reaction is not completely statistical. This conclusion is confirmed by the center-of-mass angular distribution, which favors backward scattering of product F atoms, but only by about 10-30%.

Our tentative value of the heat of formation of the ipso-fluorocyclohexadienyl radical is 14.6 ± 0.4 kcal mol⁻¹. This work shows that the crossed beam method can be used to make precision thermochemical measurements of polyatomic free radicals. It is also an outstanding example of a polyatomic-polyatomic reaction, for which type of reaction very few crossed beam reactive scattering studies have been reported.

J. R. G. supported in part by U. S. Department of Energy.

Properties and Reactivity of Thermalized, Mass-Selected
Aluminum and Boron Cluster Ions

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Aluminum and boron cluster ions produced by ion or laser sputtering are thermalized in multiple collisions with helium inside a radio frequency ion trap. The cooled boron clusters are then mass selected by a Wien filter and injected into a radio frequency ion guide. Interactions with a scattering gas inside this ion guide occur under single collision conditions at well defined collision energies. Collision induced dissociation with xenon yields quantitative dissociation energies and qualitative ionization potentials and structural information for the clusters. Clusters of aluminum have dissociation energies ranging from $0.85 \pm .40$ eV for Al_4^+ to $2.25 \pm .70$ eV for Al_7^+ . Reactions with O_2 are exoergic for both boron and aluminum clusters with the atomic ion being the main reaction product. The aluminum reactions with oxygen possess a small energy threshold (< 0.30 eV) which increases up to Al_7^+ and drops again at Al_8^+ . The boron clusters appear to have no threshold for reaction with oxygen. Reactions with D_2O and O_2 are also examined.

LASER-INITIATED HALF REACTION. VIBRATIONAL-ROTATIONAL STATE DISTRIBUTION OF NO PRODUCED FROM THE REACTANT PAIR, $O(^1D) \cdot N_2O$.

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Vibrational and rotational states distribution of NO produced from the reactant pair $O(^1D) \cdot N_2O$ was measured by the laser-induced fluorescence. The N_2O dimer was generated by the supersonic expansion of the mixture of N_2O in He or Ar through the pulse nozzle (0.4mm diam., 10 Hz), and it was converted to the reactant pair by the 193nm(ArF) laser irradiation. Frequency doubled tunable dye laser irradiated the jet with short delay behind the ArF laser to measure the laser-induced fluorescence of NO.

The formation of the N_2O dimer was confirmed by the quadrupole mass spectrometer. Intensities of the N_2O monomer, dimer, and trimer signals were measured as functions of the nozzle pressure and compared with the pressure dependence of the LIF signal of NO to identify the source of the NO product. The parallelism between the LIF signal and the dimer ion intensity was excellent and we concluded that the NO was produced from the N_2O dimer by the ArF laser irradiation.

The rotational distribution was measured for $v=0$ to 7 levels. At all vibrational levels, the distribution was almost Boltzmann-like with the temperature of 80-100 K.

The population of the vibrational levels were determined up to $v=7$. The distribution was bimodal, i.e. one maximum is $v=0$ and the other maximum is $v=3$ to 4. This distribution implies the formation of two kinds of NO. The Doppler widths of the LIF lines were measured for $v=0$ and $v=3$. The widths of $v=0$ lines are limited by the laser line width, i.e. narrower than 0.1 cm^{-1} , whereas those of $v=3$ lines are fairly broad, 0.2 cm^{-1} . These results indicate that two NO are formed by the reaction and one is vibrationally and translationally cool, and the other is hot.

The comparison will be made with the study of same reaction in the bulk condition and the details of the reaction mechanism will be discussed.

O(¹D₂) Reaction Dynamics Studies by Time-Resolved Fourier Transfer Spectroscopy.

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Since the presentation of our new algorithm for time-resolved Fourier transform spectroscopy at the Dynamics of Molecular Collisions meeting in Utah two years ago, the parameters of the experiment have been improved substantially and several new energy distribution studies have been carried out using low-pressure infrared emission spectroscopy. In its present form, the apparatus is capable of simultaneously recording up to 128 time-delayed spectra of an excitation event, spaced at a minimum of 10 nanoseconds with respect to each other and with subnanosecond time uncertainty. The minimum time delay is arbitrarily short and corrections for variable baseline and excitation amplitude are automatically included. The parameters of the system will be described, and several reaction dynamics studies carried out using the instrument will be reported.

The results to be reported will include studies of the dynamics of O(¹D₂) atom reactions with hydrogen halides and with several halogenated methanes. The energy partitioning into the diatomic products of these reactions (OH and HX, X a halogen atom) have been measured in experiments based on low-pressure infrared emission techniques; and in all cases, considerable vibrational excitation is found. It is generally believed that O(¹D₂) reactions proceed largely via insertion mechanisms involving the formation of a strongly-bound singlet intermediate species, hence the degree of product vibrational excitation created by these reactions is somewhat surprising. The dynamical features responsible for this result will be discussed in terms of the relevant potential energy surfaces. Where available, energy transfer information derived from the time-resolved measurements will be reported as well. In particular, state-specific rate data on processes of the kind OH(v) + HX(v=0) → OH(v-N) + HX(v') have been obtained.

Steric and Rotational Effects in the Reaction



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The effect of both the approach geometry and the initial reagent rotation on direct reactions is tightly related to the angular dependence of the potential energy of the system along the reactant valley as well as of the critical distance [1]. Experimental data on the influence of both types of reagent preparation provide direct qualitative evidence about these potential attributes and represent sensitive probes for theoretical predictions.

The title reaction has been investigated using the crossed molecular beam method. Preparation of the reagent molecules is achieved optically. For this purpose the beam of a colour center laser tuned to one of the R- or P-lines of the $v = 0 \rightarrow v = 1$ transition of HF is radiated perpendicularly through the HF beam and excites a fraction of the molecules ($\sim 3\%$ of the coupled ground state population at 10 mW laser power) to the desired $v = 1, j$ -state. As the laser light is linearly polarized the final state is aligned [2]. Depending on the angle between the polarization vector \vec{E} and the mean relative velocity \vec{v} the angle of attack is roughly 90° for $\vec{E} \perp \vec{v}$ while it is broadly distributed for $\vec{E} \parallel \vec{v}$.

Integral reaction cross sections $\sigma_r(j; E_{tr})$ have been measured for fixed E_{tr} as a function of j ($j = 0, 1, 2$ and 3) at collision energies $E_{tr} = 0.49, 0.75,$ and 1.21 eV. With rising j the cross section increases monotonously by 16% at $E_{tr} = 1.21$ eV while at $E_{tr} = 0.49$ eV it drops initially by 20% and reaches a flat minimum at $j = 2$. At $E_{tr} = 0.75$ eV it is constant till $j = 2$ and grows then by 12%. For $j = 2$ (R(1)-line) σ_r has been measured for the two approach geometries obtained with $\vec{E} \parallel \vec{v}$ (σ_{\parallel}) and $\vec{E} \perp \vec{v}$ (σ_{\perp}) at various E_{tr} ranging from 0.43 eV to 1.23 eV. The steric effect $(\sigma_{\parallel} - \sigma_{\perp})/\bar{\sigma}$ ($\bar{\sigma} = (\sigma_{\parallel} + \sigma_{\perp})/2$) amounts to 17% at $E_{tr} = 0.46$ eV; it decreases with rising E_{tr} and reaches zero near 1.2 eV.

All findings are consistent with the assumption that the potential energy surface features weak angular dependence within a wide range, insignificant steric hindrance and a collinear transition state.

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Vibrationally State-Selected Ion-Molecule Reactions with
Resonance Enhanced Multiphoton Ionization Generated Ions

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Due to the large number of ions produced and the possibility of a high degree of vibrational quantum state selectivity, resonance enhanced multiphoton ionization (REMPI) of a pulsed free jet can be an excellent source of ions for vibrationally state-selected ion-molecule reaction studies, as has recently been shown^{1,2}. In a new apparatus of beam-gas geometry, such a REMPI ion source will be used to investigate the the role of internal excitation in determining the rates and branching ratios of ion-molecule reactions, particularly those of astrophysical importance. Photoelectron energy spectroscopy and especially laser induced fluorescence of the nascent ions provide a means to follow the disposition of energy in the REMPI process.

Ions formed in the focus of the REMPI laser beam(s) are extracted, accelerated, injected into a 90 degree magnetic sector for mass analysis, and then decelerated by an exponential field lens down to the chosen collision energy before entering a differentially pumped scattering gas cell containing the neutral reagent. Products are collected by a quadrupole mass analyser mounted downstream. Collinear with the scattering chamber ion beam axis is another laser beam axis with fluorescence collection optics for diagnostic LIF of the ion beam. The separate 50 cm time-of-flight photoelectron spectrometer has triple mu-metal shielding and an all molybdenum enclosed flight path.

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Dynamics of the Reaction $O(^3P) + HBr \rightarrow OH(X^2\Pi) + Br$

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The nascent product state distribution of $OH(X^2\Pi)$, produced by hydrogen atom abstraction by $O(^3P)$ from HBr , with full resolution of v'' , N'' , spin-orbit and Λ -doublet sublevels was determined using LIF spectroscopy. The OH product was found to be highly internally excited with strongly inverted vibrational and rotational distributions. We observe no $OH(v''=0)$ and determine the vibrational branching ratio of $P(v''=1):P(v''=2)$ to be approximately 9:1. The rotational distributions for $OH(v''=1)$ and $OH(v''=2)$ show maxima at $N''\approx 12$ and $N''\approx 5$, respectively. The most highly excited states observed were $OH(v''=1, N''=16)$ and $OH(v''=2, N''=9)$, very close to the energetic limit imposed by the collision energy, internal excitation of reagents and exothermicity.

Independent quasiclassical trajectory studies on a LEPS¹ potential-energy surface have been carried out by Broida et al¹ for the $O(^3P) + HBr$ system. They were able to fit well the previous kinetic measurements on reaction rate as a function of temperature. Moreover, their calculations correctly predict the dominance of the $OH(v''=1)$ channel as well as high rotational excitation. We have performed further calculations using the same LEPS surface, allowing a quantitative comparison of results generated using initial conditions designed to match those of our experiment. We find that this LEPS surface is unable to reproduce the detailed internal state distribution.

Our observations are consistent with a $H + LH' \rightarrow HL + H'$ reaction which is dominated by kinematic effects. Similar behavior has been observed in hydrogen atom abstraction by halogen atoms where the product HX is found to be highly internally excited. This differs substantially from the dynamical behavior observed in hydrogen abstraction reactions of $O(^3P)$ from organic molecules, the only systems to have previously been studied, which exhibit very little rotational excitation. This has been argued to be the result of a very collinear reaction geometry. The dramatic dynamical differences in behavior of $O(^3P)$ abstraction of hydrogen from different classes of molecules will be discussed.

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REACTION OF BARIUM ATOMS WITH N₂O CLUSTERS

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The chemiluminescence of the reaction of barium atoms and N₂O molecules is observed in a crossed molecular beam experiment. The conditions of the molecular N₂O beam are varied so that this beam contains no or many large N₂O clusters. No additional chemiluminescence occurs when the cluster concentration is increased. The large difference in electronic structure between monomers and polymers, which has been shown by measurement of electron attachment, suggests that a different reaction channel yielding BaO solvated in a N₂O cluster could explain these results.

ABSTRACT

An experimental study of the dynamics of $H+H_2$ with total energy from 0.9 - 1.4 eV.

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Both $H+(\text{para})H_2$ and $H+(\text{normal})H_2$ with total energy from 0.9 - 1.4 eV were studied by time resolved CARS. Two resonance structures were observed which agreed with the theoretical prediction. With para H_2 we are able to distinguish the reactive scattering from the inelastic scattering. A surprisal parameter of 5 is found for the reactive scattering while 9 for the inelastic scattering. The resonances are more pronounced in $H+(\text{para})H_2$ than in the $H+(\text{normal})H_2$ indicated the parent molecule's rotational motion is coupled to the quasi-bound state.

The effect of reagent excitation on reactions of acetylene cations.

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Vibrationally and electronically state selected acetylene cations have been produced via multiphoton ionization and the electronic and vibrational identity of the resultant ions have been probed using photoelectron kinetic energy analysis. Ionization via good Rydberg states follow a strict $\Delta v=0$ propensity rule resulting in ions with > 90% vibrational purity. Ionization via mixed or valence states results in PES involving both stretching and bending modes. Excitation of bending vibrations in the excited state manifold has been found to generally lead to rapid non-radiative decay.

The reactions of the vibrationally 'pure' ions are being studied using radio frequency guided ion beam techniques. The effect of excitation of both the bending and stretching modes on the collision induced dissociation channels observed using various rare gas collision partners have been studied and the absolute cross sections for these channels are presented.

Chemiluminescent Reactions of Beams of Excited States of Cu and Ge with Halogens

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Studies of chemiluminescent (CL) reactions of Cu (2S) and Ge (3P) with F_2 ^{1,2} have been extended to include reactions of the lowest excited states, Cu (2D) and Ge (1D), with halogen molecules. These metastable states were generated in an electric discharge at the beam source orifice, and were monitored by fluorescence excited by a lamp or dye laser. Attenuation of the Ge beam by H_2 was used to attribute reaction to the 1D state rather than a higher metastable 1S state, as in a previous study of Sn.³ The effect of initial translational energy has been explored by a TOF beam-gas method for the total cross sections, and by using a crossed nozzle beam for some of the spectra. Cross sections for forming electronically excited metal fluorides are much larger relative to ground state reactions than predicted by statistical models, while the CL reactions with the heavier halogens are only allowed from the excited atomic states. After the first electron of the metal atom is largely transferred to the halogen molecule, the orbital symmetry of the other high-lying valence electron is thought to play a major role in determining the favored reaction pathways. In the case of Cu (2D) this electron is in a $4s$ orbital which is repelled from broadside approach to the halogen. For Ge (1D) the σ or π character of the $4p$ orbital determines whether the metal halide is in a Σ or π electronic state. In general, excited atom reactions studied appear to be direct, as evidenced by inverted vibrational populations. Some of the spectra have been successfully simulated using a least-squares fitting procedure, but for others (particularly CuI and GeCl) too little is known about the spectroscopic constants to achieve good fits.

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Energy Disposal in the Reaction of $\text{Mg}(^1\text{S}) + \text{Cl}_2 \rightarrow \text{MgCl}(^2\Sigma^+) + \text{Cl}$

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The reaction of $\text{Mg} + \text{Cl}_2$ yielding ground-state $\text{MgCl}(X^2\Sigma^+)$ product has been studied under single collision beam-gas conditions. The spectroscopy and internal state distribution of MgCl product were probed by laser induced fluorescence of the $\Delta v=0$ $X^2\Sigma^+-A^2\Pi$ band system. The form of the spectrum showed rotational population up to the exoergicity limit of 7500 cm^{-1} or $j=195$ for $v=0$; in contrast, the highest populated vibrational state ($v=9$, $f_v \approx .55$) was well below that permitted by the reaction exoergicity. Extension of the spectroscopic constants to the above limits for both the X and A state was accomplished by analysis of the spectrum obtained in this work in conjunction with reanalysis of the results of Morgan¹ and Barrow². An inversion procedure incorporating the extended set of spectroscopic constants was used to determine the internal energy disposal of the reaction. This yielded values of $.19 \pm .02$ for the average product vibrational energy, $\langle f_v \rangle$ and $.35 \pm .05$ for the average scaled rotational energy, $\langle g_{jv} \rangle$. The form of the extracted population distribution was consistent with a direct interaction mechanism in which repulsive energy release in the ionic complex $\text{Mg}^+ \cdots \text{Cl}^- \cdots \text{Cl}$ formed at the electron jump crossing radius of $\approx 3\text{\AA}$ determines product angular momentum and is thus uncoupled from attractive energy release in $\text{Mg}^+ \cdots \text{Cl}^-$ product formation.

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**Line Broadening as a Measure of the Extent of Laser-Assisted
Chemistry in the Reaction $\text{Mg } ({}^1\text{S}) + \text{CO}_2 \rightarrow \text{MgO } (\text{B } {}^1\Sigma^+) + \text{CO}$**

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Evidence of laser-assisted chemistry in the gas phase reaction of $\text{Mg } ({}^1\text{S})$ with carbon dioxide has been observed. In this experiment, energy to overcome the substantial reaction endoergicity ($\sim 35\,000\text{ cm}^{-1}$) for production of the excited $\text{B } {}^1\Sigma^+$ state of MgO is provided by a laser photon which is nonresonant with any reactant or product. The endoergicity nearly matches the energy of the ${}^1\text{P} \leftarrow {}^1\text{S}$ UV transition in atomic magnesium, through which the driving laser is tuned. Broadening of the atomic absorption line is observed, by resonance fluorescence, in the presence of small amounts of carbon dioxide, and production of excited MgO is detected by its visible fluorescence. Extended wing emission is observed in both the resonance and visible channels. Pressure broadening and other non-reactive effects have been ruled out.

Laser-assisted reactions have been considered in the context of a kinetic model which treats the absorbing species as a collisional "quasimolecule"¹. The model predicts that the cross section for absorption will depend on the energy defect between the driving photons, supplying the endoergicity of the reaction, and a resonance in a reactant. In our system, this energy defect is small. Additionally, the drive-energy dependence of the cross section should provide insight to the attractive nature of the intermolecular potential for this collision. This analysis, based on the quasi-static theory of line broadening as employed by Gallagher², is proceeding.

Support: Research Corporation.

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REACTIONS OF METHYL RADICALS WITH HALOALKANES

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We have carried out the first molecular beam reactive scattering studies of a radical with a polyatomic reagent. A supersonic beam of methyl radicals, generated by passing a dilute mixture of ditertiary butyl peroxide through a heated quartz nozzle, is crossed with a seeded haloalkane reagent beam. The nearly thermoneutral iodine abstraction reactions, $\text{CH}_3 + \text{RI} \rightarrow \text{CH}_3\text{I} + \text{R}$ for $\text{R} = \text{CF}_3$ and $(\text{CH}_3)_3\text{C}$, have been observed at collision energies around 14 kcal/mol. In both reactions, the CH_3I product is entirely backward scattered with respect to the incident CH_3 beam indicating that the radical must collide with the iodine atom within a narrow steric cone of acceptance in order for reaction to occur. The product angular distribution from $(\text{CH}_3)_3\text{CI}$ is somewhat narrower than that from CF_3I as a result of the larger number of vibrational modes in the t-butyl product. The cross section for bromine abstraction from CF_3Br is evidently much smaller since we detect no CH_3Br from the reaction $\text{CH}_3 + \text{CF}_3\text{Br} \rightarrow \text{CH}_3\text{Br} + \text{CF}_3$. This may result from both the smaller target area of the Br atom and a higher barrier to reaction. Other reactions are currently being investigated.

Reactive Scattering of $O(^3P)$ with Unsaturated Hydrocarbons

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We are currently investigating reactive scattering of ground state oxygen atoms with unsaturated hydrocarbons using the crossed molecular beam method with mass spectrometric detection.

In the reaction of $O(^3P)$ with ethylene most investigators have found evidence for $CH_3 + CHO$ as products¹. Experiments in our laboratory² have clearly shown that the formation of $C_2H_3O + H$ is an important channel. Today there is still a controversy about the relative cross-sections for those two channels. We are reinvestigating the reaction using ^{18}O in order to be able to distinguish between CHO product, at mass 31 and elastic scattering contributions from ethylene at mass 29. No determination of the relative cross sections has been done previously under true single collision conditions. This is important since this pathway can occur in a single step only if intersystem crossing to a singlet surface takes place or if the barrier for hydrogen migration in the triplet addition complex is lower than theoretical calculations³ indicate. Preliminary results indeed show no evidence for this channel under our experimental conditions.

For the reaction of $O(^3P)$ with cis- and trans-2-butene we are investigating the relative cross sections of the channels leading to $H + C_4H_7O$ and $CH_3 + C_3H_5O$, respectively, as well as the different reactivities of the two isomers.

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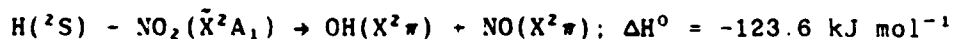
Acknowledgement:

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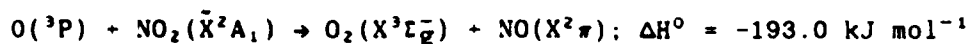
Product State Distributions from $H + NO_2 \rightarrow OH + NO$ Studied by Laser-Induced Fluorescence

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Bimolecular reactions between free radicals may proceed via a transitory collision complex, since the formation of a bond between the radicals can lead to a deep minimum on one of the potential energy surfaces which correlate with both the reagents and products. Such reactions proceed with essentially zero activation energy and measurements of the rovibrational product state distributions can indicate the extent to which the dynamics of reactive collisions are dominated by the formation of collision complexes. We are investigating several such reactions which produce NO and expect to report detailed results on the reaction:



and preliminary results on



and



The reactions take place in a low pressure chamber under 'arrested relaxation' conditions. The output of an excimer-pumped dye laser is Raman-shifted into the appropriate spectral range to induce fluorescence from NO (and OH) product molecules, and laser excitation spectra are recorded.

The $H - NO_2$ reaction is sufficiently exothermic to populate $v'' \leq 3$ in OH and $v'' \leq 3$ in NO. The OH product state distributions have been studied by other groups¹⁻³ and our results essentially confirm their data. The earlier work indicates that ca 25% of the energy released in the reaction should cause internal excitation of the NO. However, we detect no vibrational excitation of the NO ($[N_{v=1}/N_{v=0}] < 10^{-2}$). Experiments are now being performed at increasingly low total pressure in order to eliminate, as far as possible, any collisional relaxation. At the meeting we shall report the results of these measurements yielding spin-orbit, Λ -doublet and rotational state populations, as well as those for vibrational level populations.

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Investigations of Ion-Molecule and Electron-Molecule Dynamics
Using a New Laser Ionization Free Jet Flow Reactor

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ABSTRACT

A new kinetic technique has been developed to study mechanisms of intrabeam ion-molecule reactions in free jet expansions. Using multiple laser photoionization, it is possible to study reaction rates of state selected ions with a variety of neutral molecules at collisional temperatures in the 1 to 30⁰K regime. Results will be presented describing the kinetics of NO⁺ clustering reactions with NO and other small molecules. Using the same ionization technique, we demonstrate the ability to produce monoenergetic electrons with a distribution width of less than 3meV. The electron kinetic energy is continuously variable from 0 to 120 meV. The attachment dynamics of these electrons with cold beam molecules is investigated. Attachment to van der Waals clusters is found to proceed with extremely large cross sections and produces predominantly open shell parent anions of the parent monomer and its higher VDW homologs.

Direct Evidence for Multiple Entrance Channels in the Thermal Energy Ion-Molecule Reactions: $\text{Ne}^*(^3\text{P}_2) + \text{N}_2$ and $\text{Ar}^+ + \text{N}_2$ by Rotationally Resolved LIF

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Bimodal rotational distributions have been observed in the N_2^+ products of the Penning ionization reaction: $\text{Ne}^*(^3\text{P}_2) + \text{N}_2$ and in the charge transfer reaction: $\text{Ar}^+ + \text{N}_2$ at thermal energies. These results are interpreted as evidence for multiple entrance channels in both systems. In the Penning system, the rotational distributions are well fit by a bimodal Boltzmann distribution having a low temperature ranging from 45 to $60\text{K} \pm 10\text{K}$ and a high temperature varying between 200 and $500\text{K} \pm 50\text{K}$ depending on v level. In this system, the two major entrance channels arise from the relative orientation of the Ne^* core p orbital with respect to the relative velocity. The degree of rotational excitation can be modeled by "hard-sphere", inelastic collisions with an ellipsoidal potential of different ellipticity for each channel.

The rotational distributions for the charge transfer system can also be fit by a two component Boltzmann distribution. The two components have temperatures of $115 \pm 50\text{K}$ and $630 \pm 50\text{K}$ for $v = 0$ and $215\text{K} \pm 50\text{K}$ and $660\text{K} \pm 50\text{K}$ for $v = 1$. The two entrance channels in this case arise from an avoided crossing between the ground and excited surfaces of the system. Reactant flux that follows the adiabatic entrance channel misses the curve crossing on the incoming leg of the trajectory. This flux then samples a repulsive wall, and ultimately forms the rotationally cooler products by making the curve crossing to the charge-exchanged surface on the outgoing leg of the trajectory. In comparison, reactive flux that follows the diabatic entrance channel makes the curve crossing on the incoming leg and samples a potential well. A transient complex can then form with sufficient lifetime to permit partitioning of the available energy into the internal degrees of freedom. This channel, then, leads to the rotationally hotter products.

The observation of these rotational subtleties critically depends on quenching the initial rotation of the N_2 using a supersonic expansion.

" Spectroscopic Investigation of the Transition State: $K + NaCl \rightarrow KCl + Na$ "

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We are using photo-excitation to investigate the nature of transition states, i.e. states *in transition* between reagents and products. Specifically, we utilize a triple-beam configuration where effusive molecular beams of K and NaCl cross in the presence of a tunable dye laser. Previous work¹ involved laser wavelengths 735-590nm, which although not resonant with either reagent, nevertheless gave rise to excited Na* emission (589nm). We take this as evidence of photon absorption by the transition state. In order to preclude possible artifact processes involving the slight impurity K₂ (which can be resonant with our probe laser) we passed the atomic beam through an inhomogeneous magnetic field, which focussed the atom but not the dimer. Na* emission was found² to correlate with atomic K intensity, thus supporting our original interpretation of the photo-excitation spectrum.

However, the spectrum is featureless, obscuring conclusions about the fundamental forces involved with transition states. With an eye towards observing structure, we are reducing the number of initial states by seeding both molecular beams in rare gases. Concurrently, preliminary data suggests it is possible to excite the transition state with near infra-red frequencies and populate the first (bound) excited state of the quasi-molecule KClNa. This state can fluoresce back into a ground state well associated with certain nuclear geometries. This emission may exhibit structure, and toward that end we have developed a low light level f/2 spectrograph for multichannel data acquisition. This poster will present a summary of work to date on the project.

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LIF STUDY OF THE $F + I_2 \rightarrow IF + I$ REACTION

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The $I_2 + F \rightarrow IF + I$ reaction has been studied in a crossed beam experiment and the product IF is detected by laser induced fluorescence. The exoergicity of the reaction (1.23 eV) and the initial energy (kinetic collision energy ~ 0.1 eV, iodine internal energy, fluorine atom fine structure energy) make that the total energy available in the center of mass frame is between 1.33 and 1.45 eV. This is enough to populate IF (X, v) up to $v = 21$ if I is in the ground $^2P_{3/2}$ state or up to $v = 6$ if I is in the excited $^2P_{1/2}$ state.

With c.w. single frequency dye laser in the near infrared, we have detected about ten thousand lines of IF in the spectral ranges 700-790 and 836-873 nm. These lines have been identified and they give measurements of the relative population of the rovibrational levels of IF with $v = 9$ to 19 and $J = 0$ to 150. The population of about 1300 levels has been measured in this way :

- * For each vibrational level, the highest rotational level detected has an energy close to 1.40 eV, in agreement with the total available energy.
- * The rotational distribution presents, for most of the vibrational levels, a strong peak near highest values of the rotational quantum number J . This bimodal rotational distribution may be due to the existence of two types of trajectories, namely migratory and direct trajectories as observed in other $L + HH$ systems (e.g. $H + IC_2$ studied by J. Polanyi et al). Moreover migration was found important by Fletcher and Whitehead in their trajectory calculation of the $F + I_2$ reactive collision.
- * The vibrational distribution presents a broad peak around $v = 13$.

We have also detected the $v'' = 0$ level population with a c.w. single frequency dye laser in the blue (near 490 nm). Trickl and Wanner have detected a very intense population in this level ($P(v'' = 0) \sim 100 P(v'' = 13)$) and they interpreted this population as associated to the production of Iodine $^2P_{1/2}$ atoms, and this should have been the major branch of this reaction. However, direct detection of these excited Iodine atoms is in strong contradiction with this interpretation.

We have detected a considerably (50x) weaker population of the $v'' = 0$ level and we have shown by modulating the Fluorine beam that this population was not directly due to the reactive collisions in the beam. As a consequence, the production of low v'' levels and of excited iodine atoms appears to be a minor branch of the $F + I_2$ reaction.

FREE RADICAL CHAIN REACTIONS IN LOW-TEMPERATURE SOLIDS

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Photoinitiated reactions of chlorine with propane and cyclopropane have been studied in frozen thin films to investigate some of the effects of the solid state environment on the reaction mechanism. The experiments are conducted by depositing a pre-mixed sample of the halogen and hydrocarbon onto a CsI optical window at 10-77 K. Excimer laser photolysis of the thin films at 308 nm dissociates some of the chlorine molecules to initiate the reactions. Product yields and branching ratios are determined from transmission infrared spectra of the films recorded before and after photolysis.

In the propane system we find that radical-radical recombination dominates the reaction mechanism, resulting in very low product yields. Chlorine atoms may abstract H atoms at either primary or secondary sites in the propane molecule. The branching ratio between these two channels provides an interesting probe of hot atom effects in the solid.

Attack of chlorine atoms on cyclopropane occurs by addition and ring opening. This mechanism effectively separates radical pairs in the solid, inhibiting recombination. As a result, true chain reactions propagate through the solid and up to 30 product molecules are formed per UV photon absorbed by the sample. Interestingly, the sole product of the reaction is an unstable anti-anti conformer of 1,3-dichloropropane. Detection of specific conformers of reaction products is unique to solid-state studies and provides important clues to the details of the reaction mechanism on a molecular scale.

PRODUCTION AND LOSS OF $CF_2(^3B_1)$ IN THE $O + C_2F_4$ REACTION

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ABSTRACT

Low pressure fast flow measurements of the emission from $CF_2(^3B_1)$ generated in mixtures of O with C_2F_4 in Ar and similar measurements using the air afterglow to follow oxygen atoms were made. From measurements of the exponential decay of air afterglow emission, it is concluded that the reaction proceeds through a $C_2F_4O^*$ intermediary. From the intensity and time evolution of the $CF_2(^3B_1)$ emission it is found, contrary to existing belief, that the yield of $CF_2(^3B_1)$ is small (less than 1%) and its radiative lifetime is much shorter than 1s (~10 ns). The overall loss of O atoms at low C_2F_4 densities is characterized by rate constant of $1.2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$. Both NO and O_2 strongly quench the $CF_2(^3B_1)$, while quenching the precursor much less effectively. C_2F_4 quenches the precursor regenerating O, but does not quench $CF_2(^3B_1)$ significantly.

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The hydrodynamic behavior of flowing granular material is of considerable economic and scientific interest. An accurate representation of the stress tensor for granular material is central to successfully treating it as a continuum. Representations of such a stress tensor can be developed from either a continuum mechanics approach or a kinetic theory approach. Hopefully, these two approaches would yield similar forms for the stress tensor.

The continuum model approach considers the granular material to be isotropic and isothermal and postulates a linear stress tensor that depends on the void fraction, the gradient of the void fraction, the velocity, and the gradient of the velocity. Then by requiring the stress tensor to be frame indifferent, the stress tensor is restricted to depend on the void fraction, the gradient of the void fraction, and the symmetric part of the rate of deformation tensor. The resulting stress tensor is similar to that of a Navier-Stokes fluid except that an extra term appears, containing the dyadic formed from the gradient of the void fraction. This term is necessary because it predicts a stress in the direction normal to the plane of a one dimensional Couette flow of granular material as observed experimentally. In principle, the stress tensor for granular material derived by the continuum model approach is valid from extremely slow flows, in which the particles are in enduring contact, to very rapid flows in which the particles move chaotically and suffer only binary collisions. The major drawback to this approach is the large number of undetermined parameters which are introduced.

In this paper, an expression for the stress tensor for flowing granular material which contains no undetermined coefficients has been developed from Enskog's kinetic theory for dense gases. This approach supposes that the zeroth order approximation to the distribution of granule velocities is described by a Gaussian function, the variance of which is related to the degree of chaos in the movement of the granular particles. A granular temperature can be introduced analogous to the temperature of a gas. The stress tensor is determined by averaging the flux of momentum from the first order approximation to the velocity distribution, as given by Enskog's dense gas theory. This approximation is assumed to depend on the gradients of granular temperature, average velocity, and number density. The forms of the two terms in which the gradient of granular temperature and gradient of average velocity appear are determined by analogy with the Enskog approach as applied to gases. The third term, which describes the effect of the density gradient, does not appear in the Enskog development for gases. It appears in the development for granular material, because the particles suffer energy dissipating collisions. The importance of inelastic collisions is what distinguishes granular material from monatomic gases. In the past, this term was chosen in a manner that produced no dependence of the granular stress tensor on the dyadic of the density gradient. This is inconsistent with the form of the stress tensor as developed from continuum mechanics. Furthermore, the resulting stress tensor is limited to granular flows in which the granule velocities are chaotic enough to obey a Gaussian distribution and dilute enough so that only binary collisions occur. We propose an alternative choice which causes the granular stress tensor to be dependent on the dyadic of the density gradient. In so doing, the range of granular flows over which the stress tensor is applicable is increased, and the undetermined parameters which appear in the continuum model approach can be evaluated.

DYNAMICS OF MOLECULAR STEREOCHEMISTRY VIA ORIENTED MOLECULE
SCATTERING

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In a crossed molecular beam machine the steric dependence of the reaction $\text{Ba} + \text{N}_2\text{O} \rightarrow \text{BaO}^* + \text{N}_2$ has been investigated at variable translational energy, E_{tr} , as a function of the angle of attack of the N_2O -axis, which has been selected in the $(J_1, n_2, M) = (1, 1, 1)$ or $(2, 1, 2)$ state by means of a hexapole focuser. A strong orientational dependent reactive opacity function has been found and the alignment of the angular momentum of the BaO^* product molecule was found to depend on the orientation of the N_2O molecule. The implications of these observations for the dynamics of the chemical reaction will be discussed and compared with those obtained for the reaction $\text{Ca}(^1\text{D}) + \text{CH}_3\text{F}(1, 1, 1) \rightarrow \text{CaF}^*(\text{A or B}) + \text{CH}_3$.

Molecular Dynamics Study of the Diffusion Induced Rearrangement of the

Silicon {100} Surface, Donald W. Brenner^{*} and Barbara J. Garrison,

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Many semiconductor surfaces are known to exhibit large rearrangements of atoms in the surface region from the bulk configurations. The reconstruction of the silicon {100} surface, for example, involves the rebonding of surface atoms which would be second neighbors in the crystal into rows of dimers. In order to grow epitaxially on these surfaces, the reconstruction must somehow be rearranged so that surface atoms occupy bulk lattice sites. Molecular dynamics simulations of the silicon adatom induced rearrangement of the silicon {100} symmetric dimer reconstructed surface have been performed. A surface diffusion induced rearrangement of the reconstruction plays a critical role in the reordering of this surface which leads to good epitaxial growth. It will also be shown that diffusion plays much less of a role in the reordering induced by an amorphous overlayer. These results will be used to provide an atomic scale understanding of the high-energy ion channelling/blocking studies by Gossman and Feldman of the initial stages of silicon growth on this surface.¹

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**A VELOCITY-RESET METHOD FOR INCORPORATING A
THERMAL RESERVOIR INTO MOLECULAR DYNAMICS
SIMULATIONS OF LATTICE MOTION***

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The molecular dynamics simulation of gas-surface collisions or adspecies-lattice dynamics requires the partitioning of the solid into an active P zone (described by the equations of motion) and a reservoir. The approximation generated by this partitioning is improved if the damping and thermal motion caused by the reservoir are included in the P-zone dynamics. Here we present a new partial velocity reset method of accounting for damping and thermal agitation. The partial velocity reset method allows the simulation of dynamic processes in the systems of interest to us, namely, classical surface collisions and lattice dynamics. The partial velocity reset method becomes a robust computational procedure allowing for: (1) relaxation dynamics which are equivalent to the first-order damping theories, (2) inclusion of non-zero temperature effects on damping and dissipation, (3) rapid generation of initial states selected from a canonical ensemble, (4) preparation of individual collisions with the surface, and (4) approximate heat transport within the dynamic subset.

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THE CONFERENCE ON THE DYNAMICS OF MOLECULAR COLLISIONS
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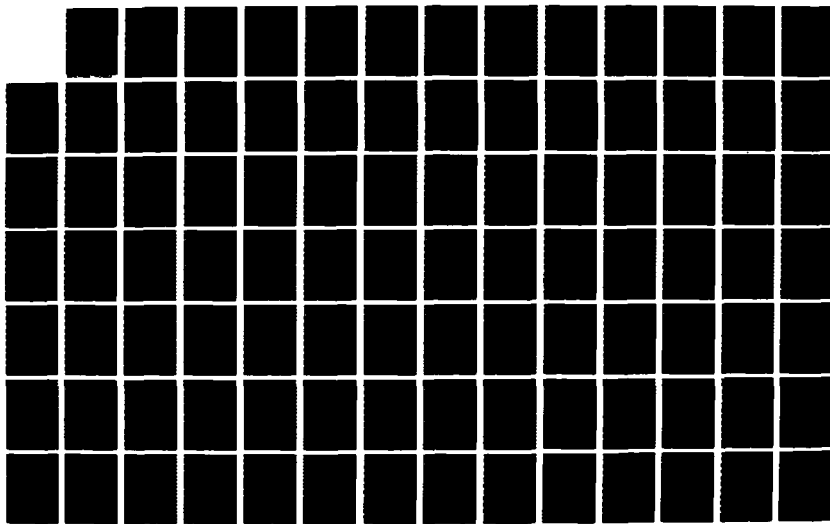
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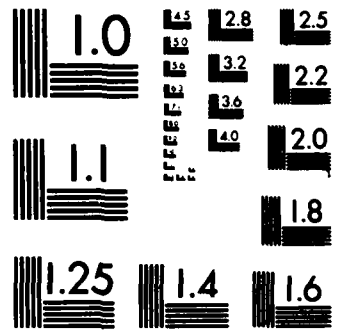
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Selectivity of Elementary Molecular
Processes in Molecule-Surface Collisions

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The theoretical basis for an experiment involving the scattering of polyatomic molecules from metal surfaces in which selective control of the fragmentation products is possible¹, will be presented. The current proposal is based on an adaptation of ideas put forth by Tannor and Rice² in which they "show that selectivity of reactivity is possible if an excited electronic state is used as an intermediary to assist chemistry on the ground electronic state surface". Selectivity can be attained by controlling the time structure of a coherent, two-photon process in which initial excitation to the excited state intermediary is followed by stimulated decay to the electronic ground state.

From the point of view of intra-molecular dynamics, a similar sequence of electronic transitions occurs in molecule-surface collisions involving charge transfer/harpooning^{3,4}. For an event in which a molecule picks up an electron on its incident trajectory and returns it to the surface on its outward leg, a temporary negative molecular ion is formed for the time duration between electron hops. This time scale is of the order of molecular vibrational times and can be controlled by varying the incident translational energy. While existing as a molecular ion, the polyatomic can distort into new geometrical configurations which, when returned to the electronic ground state potential surface, lead to fragmentation. The geometrical structure of the distortion, as controlled by the potential energy surface and the lifetime of the negative ion, determines the fragmentation distribution and hence selectivity in this elementary molecular process. Relative merits of the 2-photon versus surface collision mechanisms will be presented.

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Dynamics of diffusion and desorption processes of Cs on pyrolytic graphite basal surfaces: a new way to get into the bulk

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Abstract

Molecular beams have been used to study the interaction between Cs and graphite (or metal) surfaces. Using the so called field reversal, surface ionization kinetic method, a time resolution of 30 ns can be reached at present. Variations of this method have been applied to surface diffusion and desorption processes [1-3], as well as to the diffusion processes into, out from and through the bulk [4,5]. In the present study, an analytical diffusion model has been matched to the variation of the peak of the ion signal with the length of the retarding field period. Surface diffusion processes are observed, as well as the very rapid diffusion into the bulk. The new experiments give a barrier towards diffusion into the bulk of around 5.8 eV with a very large preexponential factor of the order of 10^{22} s^{-1} . This rapid process has been proposed [3] to be caused by very highly excited cesium atoms, presumably in the form of a Rydberg state. They are probably coupled to the existence of at least two separate binding states of Cs on the crystallite faces [3].

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Abstract

In the past few years, experimental investigations of NO scattering from various surfaces have yielded distributions of several quantities. In the present Monte Carlo trajectory study the aim has been to calculate angular and rotational distributions for NO/graphite surface scattering, simulating conditions used in experiments [1].

NO was modeled as a rigid rotor, each end interacting with a smooth vibrating surface through a Lennard-Jones 12-6 potential. In the model, the surface moved in one dimension under a linear restoring force. The same surface model has previously been successfully used for Br₂/graphite surface scattering [2]. We have also reported on the angular distributions for NO on graphite [3].

NO approached the graphite surface with a momentum large enough to require at least two hits from the carbon atoms before the NO molecule could leave the surface. Further, NO often made extended jumps on the surface before definitely leaving it, resulting in interaction times around or above 10^{-12} s.

In the experiments [1] on NO/graphite scattering it had been found that the rotational state population could be approximated by a Boltzmann distribution. The rotational temperature T_{rot} was found to equal the surface temperature T_s up to about 190 K, while at higher surface temperatures, T_{rot} approached a constant value of about 250 K. In the trajectory calculations, this behaviour was found using only the most populated rotational states. At higher energies, rotational rainbow structure was found, similar to the behaviour observed in experiments on NO/Ag(111) [3].

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TIME DEPENDENT THEORY OF GAS-SURFACE ENERGY TRANSFER

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Several time dependent studies have been made of gas-surface scattering in recent years, using both discrete^{2,3c,4} and Gaussian wave packet^{1,3a,3b} representations of the molecular wave function. All attempts to introduce finite surface temperature have involved a classical propagation of the surface atoms^{2,3a}, which is invalid for gas species of low mass or energy. We present a fully quantum mechanical theory of gas-surface energy transfer, which can be easily applied to any of these time dependent approaches. Using perturbation theory, the reduced density matrix for the gas atom/molecule is written in terms of three wave function-like objects, which obey Schrödinger-like equations of motion. Thus, the time evolution of the reduced density matrix requires only about three times the computational effort of the zero temperature calculation. The theory allows one to compute thermally averaged properties of the scattering molecular system at all times.

Results are presented for the scattering of He and Ne from various metal surfaces. The influence of coupling to bulk phonons and Raleigh modes is examined. Extensions to time dependent studies of dissociative adsorption^{3c} and rotationally inelastic diffraction^{3b,4} are considered.

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Classical Trajectory Method and Generalized Langevin Equation:
Atomic Motions on Solid Matrix

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Because of the wealth of details about the atomic motions provided by the classical trajectory simulation, i.e., the step by step variation in atomic momentum and position that make it possible to study the mechanism by which a process occurs. The classical trajectory method has obtained considerable development.

Using the newest program on the classical trajectory method (QCPE program No. 453), on the two-dimensional system up to 50 particles, we studied the vibrational relaxation of impurity molecules in solid matrices. However, we also did several preliminary studies on the reactions $C + CH_4$, $C + C_3H_8$ etc., in preparation for the above work. But we put emphasis on phase transition and atomic missing on 50 particles solid matrix to simulate some electron microscope-observed results recently (1). Some phase transition and atomic missing have been simulated.

However, comparing our results with the experimental data from electron microscopy, we found that there is a time scale problem between calculations and observations. By means of the generalized Langevin equation, it was concluded that the origin of this time scale difference is caused by the interaction of the system with the heat bath. Also we got some numeral comparison.

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DYNAMICS OF ADSORPTION/SCATTERING OF ATOMIC HYDROGEN ON PARTIALLY COVERED Si(111) SURFACES* ST8

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The adsorption and scattering of atomic hydrogen from a partially covered Si(111) surface has been investigated using classical trajectory methods.

The potential energy surface used in this study is expressed as the sum of a lattice potential, a lattice-atom interaction potential, and an atom-atom potential. The lattice interaction is Keating's potential [1] for the unreconstructed Si(111) lattice, as modified by Weber [2]. The atom-atom interaction is repulsive. There is experimental evidence that more than one binding site exists on the Si(111) surface for hydrogen interactions. There is no disagreement about the position of one of these sites, located directly above each surface silicon atom. The location of a second site is less well understood; however, several studies have suggested that this site is located in an interstitial position on the surface [3]. We have developed a lattice-atom interaction potential function with parameters fitted to available experimental data and theoretical information [4] for two types of binding sites for hydrogen on a Si(111) surface, a top binding site, and an interstitial or open binding site.

Adsorption of hydrogen has been studied as a function of hydrogen coverage on the Si(111) crystal face. Translational energy and scattered azimuthal angle distributions for scattering of a beam of hydrogen atoms will be presented. Sticking probabilities as a function of incident azimuthal angle, the mechanism of adsorption, and the effect of the heterogeneity of the binding sites on sticking and scattering will also be presented.

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Variable-step stochastic dynamics in gas-surface and condensed phase simulations*

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Two variable-step integration procedures are presented for solving the stochastic equations of motion describing the dynamics of chemical processes in condensed phases. The generalized Langevin equation (GLE) provides a convenient framework for studying explicitly the nuclear dynamics of a 'primary' or 'chemically-crucial' few-body region in which the effects of the heat bath are modeled by time-dependent memory and random force terms¹. Traditionally these equations of motion are solved using a low-order fixed-step integration scheme which requires small step sizes throughout a trajectory even though larger steps are acceptable for parts of the trajectory. A general variable-step integrator has not been previously developed for stochastic equations of motion because of the presence of the random force term which complicates the determination of the error in a given step of the integration which in turn is used to predict the next step size. We show how a variable-step integrator can be properly adapted for stochastic equations to yield an efficient yet reliable method.

The methods have been tested for a simple model of electronically inelastic collisions with an insulator surface in which the phonon manifold acts as a heat bath and the electronic states are localized. The semiclassical equations of motion are obtained from a formalism² based on the selfconsistent Eikonal method (SCEM) of treating the electronic inelasticities combined with the the GLE for the heat bath. The variable step algorithms are particularly well suited to the numerical task of following the much faster, and at the same time important, molecular electronic degrees of freedom along with the slower nuclear variables.

Two approaches are considered, one based upon the molecular timescale GLE (MTGLE)³ which is applicable to arbitrary memory kernels, and one based upon the Brownian harmonic-oscillator (BHO) form for the memory kernel⁴. In the MTGLE approach the heat bath is model as a white noise source and the white noise random force is sampled randomly leading to complications in use of high-order predictor-corrector algorithms. With the BHO form the random force is sampled from an exact conditional probability function which tends to smooth out the random fluctuations and make the approach amenable to the use of a high-order predictor-corrector algorithm. A new method which combines the BHO form for the memory function with the MTGLE equivalent chain representation permits modeling of arbitrary memory kernels and provides for a more justifiable implementation of the variable step method.

Applications of these methods will be presented for electronic excitation and quenching of atoms at insulator surfaces (such as oxygen atoms colliding with silica) and for the quenching of electronically excited species in condensed phases (such as metastable helium atoms in a rare gas condensed phase). In applications to the gas-surface collisions the variable step integration provides up to an order of magnitude increase in efficiency over fixed-step integration methods.

* Work supported by NASA under contract NAS2-12356 and the Air Force Rocket Propulsion Laboratory under contract F04611-86-C-0068.

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The Influence of Condensed Phase on Electronically Excited Metastables

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Excited He^* atoms in normal liquid ^4He (1^1S) environment exist¹ inside "bubbles" that have sizes and shapes characteristic of the electronic state of He^* as well as the thermodynamic state (pressure, temperature etc.) of the liquid. The bubbles are stabilized by the repulsive interaction of the Rydberg-like excited electron with bath He atoms.

In a large classical [room temperature with high pressure (gigapascals)] regime, where classical computer simulation methods (Monte Carlo, and Molecular Dynamics) can be employed to characterize these "bubble states", we assess the influence of the liquid in affecting the metastability of the He^* (2^3S) species. Due to the large size of the bubble (of diameter 5-10 angstroms), the trapped excited species undergo almost gas-surface-like collisions with the inner surface of the bubble, that are responsible for nonradiative quenching. Computer simulations provide the data (frequency moments of the heatbath spectral density) necessary to parameterize a Generalized Langevin Equation (GLE) model² of the condensed phase dynamics involved in the quenching process and the electronic inelasticity is described by the Self-Consistent Eikonal Method (SCEM)³ in a merged semiclassical formal framework^{4,5}.

The He^* along with the He atoms on the bubble's inner surface behave like a single-shell solventberg at lower pressures, whereas, a two-shell structure emerges in the high pressure regime. The simulated bubble radius varies between 5-3 angstroms in the pressure range, 1-15 GPa. The heatbath parameters are found to be very sensitive to pressure and temperature since these variables change the bubble radius and hence the solvent effect.

This work was supported by the
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Eikonal Treatment of Electronically Inelastic Processes in the Condensed Phase

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A practical route towards the dynamical description of localized electronic inelasticity in a condensed phase environment (gas-surface collisions, reactions in liquids etc.) is achieved by merging two powerful formulations. (1) the Self Consistent Eikonal Method (SCEM)¹ and (2) the Generalized Langevin Equation (GLE)² formalism.

Within the SCEM, electronic amplitudes are selfconsistently coupled to nuclear trajectories by employing an Ehrenfest effective potential and the short-wavelength approximation. The GLE framework provides effective few-body representation of many-body dynamics from heatbath-like influence of the condensed phase. Since the SCEM framework leads to Hamilton's equations, the GLE framework readily mixes with it to allow inclusion of nuclear variables such as the phonon manifold from a solid. The GLE is particularly well suited because it provides an accurate short-time description of many-body dynamics - exactly the feature sought in identifying condensed phase dynamical features that couple strongly to fast-varying electronic variables.

The combined formalism is quite versatile and computationally tractable. It is particularly efficient when implemented by adapting a variable step integration scheme³. Applications being pursued or already achieved include atom-insulator electronic quenching studies and electronic quenching in liquid Helium bubbles⁴. The resultant electronically inelastic stochastic dynamics formalism may be extended and employed for a variety of new applications such as laser-induced gas-surface chemistry and the influence of electron-hole pair creations in a metallic condensed phase.

This work was supported by NASA under contract NAS2-12356 and the Air Force Rocket Propulsion Laboratory under contract F04611-86-C-0068

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⁴ P. K. Swaminathan and C. S. Murthy, see abstract for contributed papers in this volume

DYNAMICS OF CLUSTER SCATTERING FROM SURFACES. Guo-Qin Xu, R.J. Holland, J. Levkoff, A. Robertson, Steven L. Bernasek, Department of Chemistry, Princeton University, Princeton, New Jersey 08544 and John C. Tully, AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974

We have studied nitrogen cluster beam scattering from Fe(111), Fe(110) and Ag(111) surfaces. The angular distributions and rotational energies of scattered species were measured by the electron beam induced fluorescence technique. The angular distributions show that the maximum density of the scattered fragments is near the surface tangent, essentially independent of the incident angles. The rotational energy measurements show that the fragments scattered near the surface normal direction have a higher rotational temperature than those near the surface tangent. This is the reverse of what is seen for diatomic molecules scattering from crystal surfaces.

In order to interpret these experimental results, theoretical calculations of argon cluster scattering from Pt(111) have been carried out by using the stochastic trajectory method. The results of this study show that the angular distributions of the fragments depend on the size of incident cluster, Ar_n . When $n_1 = 26$, the angular distributions have only one peak which is near the surface tangent angle for both $\theta_i = 30^\circ$ and 60° . It is found that the average energy of the scattered monomers increases with the scattered angle, which is the reverse of the trend for atoms scattering from surfaces. It is very interesting to note that cluster-surface collisions tremendously enhanced the trapping probability and the mobility of the trapped species in comparison to the atomic-surface collisions. A binary collision model is suggested to explain these results.

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QUASICLASSICAL TRAJECTORY STUDY OF ROTATIONAL
AND VIBRATIONAL ENERGY TRANSFER
IN NH₃ / GOLD GAS-SURFACE SCATTERING*

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Quasiclassical trajectories are used to study rotational energy transfer in the collision of a rigid-rotor NH₃ molecule with a flat, rigid gold surface. The anisotropic dipole-image dipole term in the long-range attractive potential causes the NH₃ to preferentially reorient with its dipole moment normal to the surface plane as it approaches surface. This reorientation decreases the rotational energy transfer and gives rise to a sharp rotational rainbow at zero rotational energy. The molecule preferentially scatters into low K rotational states (tumbling) rather than the $J = K$ states (spinning), in qualitative agreement with recent molecular beam/surface scattering experiments. These calculations have been extended to include the "umbrella" vibrational mode of the ammonia molecule to explain the high degree of vibrational energy transfer observed experimentally. Up to three quanta of excitation is transferred into this vibrational mode. The model predicts the threshold for the onset of vibrational excitation and the average final vibrational energy as a function of the incident normal translational energy in good agreement with experiment. These results indicate that a simple "mechanical" collision excitation mechanism can account for the facile vibrational excitation seen experimentally.

*This work was performed at Sandia National Laboratories, supported by the U.S. Department of Energy, under contract No.DE-AC04-76DP00789.

ROTATIONALLY AND VIBRATIONALLY INELASTIC SCATTERING
OF NH₃ FROM Au(111)*

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Employing molecular beam scattering and multiphoton laser ionization spectroscopy we have measured the rotational, vibrational, velocity, and angular distributions of NH₃ scattered from a Au(111) single crystal surface. The scattering is characterized by markedly non-equilibrium rotational, vibrational, and velocity distributions indicating a direct inelastic scattering mechanism. The rotational state distributions indicate that the NH₃ is preferentially scattered into the lowest K rotational states; these are states in which the molecule is tumbling normal to its symmetry axis as opposed to spinning about it. This is the first observation of a dynamical propensity in rotationally inelastic gas-surface scattering. In addition to the anomalous rotational distributions we observe up to three quanta of vibrational excitation in the NH₃ "umbrella" mode. Both the rotational and vibrational inelasticity scale linearly with incident normal kinetic energy and are insensitive to surface temperature. The detailed results and their implications will be presented.

*This work was performed at Sandia National Laboratories, supported by the U.S. Department of Energy, under contract No.DE-AC04-76DP00789.

A Comparison of Rotational Energy Accommodation
in Catalytically Produced OD and OH Radicals
Desorbing from a Smooth Pt(111) Single Crystal

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Abstract

Rotational energy distributions of OD and OH radical reaction products desorbing from a smooth Pt(111) single crystal have been measured by using the laser-induced fluorescence technique in conjunction with an UHV apparatus. The measured distributions are Boltzmann-like and the rotational temperatures scale with the surface temperatures over the temperature ranges studied. For OD, the average rotational to surface temperature ratio, T_r/T_s , is 0.95 ± 0.06 over the temperature range 1230-1440K. For OH, the average T_r/T_s ratio is somewhat lower, at 0.87 ± 0.05 , over the temperature range 1200-1470K.

For both OD and OH the rotational energy distributions over both the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ spin-orbit states have been measured by using Q, P, and R branch transitions. We have found the spin-orbit temperature to be the same as the rotational temperature in each of the OD and OH systems. The lack of preference for the P and R branch transitions over the Q branch transitions indicates a lack of preference for any lambda-doublet state and suggests that no rotational angular momentum polarization was present in our experiments.

This work examines the effect of the rotational constant on rotational energy accommodation under the influence of the same interaction potential between the surface and the two species. A rationalization will be given on the observed rotational energy accommodation for OD and OH.

FINAL STATE DISTRIBUTIONS IN MOLECULES SPUTTERED FROM SOLIDS.

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To understand the dynamics of molecule production during the physical erosion of surfaces by fast particles requires knowledge of the energy partitioning among the possible final states of the system. Laser-induced fluorescence of sputtered molecules is a sensitive means of obtaining these data and has been employed in the present experiment to provide high angular resolution final state distributions of sodium dimers formed by ion bombardment of metallic sodium surfaces. The results from this new experiment will be presented and discussed in terms of various possible models of the erosion process and how the results might be used to choose among them. In addition, preliminary efforts on chemical erosion studies will be presented.

Plated Graphite

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We have recently observed the first ordered monolayers of polar molecules (CH₃F, CH₃Cl) on single crystal surfaces (C(0001), Xe(111)/C(0001)), and have studied their structural characteristics using He atom diffraction.

When a CH₃F monolayer is deposited on graphite, the unit cell is $\sqrt{3} \times \sqrt{3}$ R30° with respect to the graphite substrate, with real space lattice parameters of 4.26 Å. The diffraction intensities suggest that the corrugation of this layer is approximately 0.6 Å. When this monolayer of CH₃F is physically separated from the graphite by an adsorbed spacer layer of xenon, (~4 Å), it is seen that the centre-of-mass positions of the CH₃F molecules are exactly those described above. The unit cell, however, is now $\sqrt{3} \times 2\sqrt{3}$ R30°, and corresponds to a striped arrangement of oriented dipoles, such that the repeat distance across the stripes is now twice the CH₃F-CH₃F nearest neighbour distance. This orientational order is apparently made possible by decreasing the array of dipoles' interactions with the polarizability of the graphite substrate.

Monolayers of CH₃Cl on C(0001) and on Xe(111)/C(0001) both show a rectangular unit cell which is uniaxially incommensurate, with real space lattice parameters of 4.26 Å and 6.38 Å. We believe that the increased polarizability of chlorine (with respect to fluorine) increases the lateral interactions within the layer such that the dipole-graphite interactions are not dominant; this is consistent with the unit cell of the CH₃Cl layer being smaller than the unit cell of the CH₃F layer, despite the larger volume of the CH₃Cl molecule.

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There has been considerable past interest in the dynamics of electronically inelastic collisions involving excited states of small molecules and radicals. Recently Dagdigian has used optical-optical double resonance (OODR) to investigate transitions between individual rotational and fine-structure levels of the $A^2\Pi$ and $X^2\Sigma^+$ states of CN. In these experiments initial CN A state levels were prepared by excitation in the A-X band system, while collisionally populated levels in the initial A state vibrational level and the nearly isoenergetic X state vibrational manifold were interrogated by detection of B-X fluorescence upon B-A and B-X probe laser excitation, respectively. Last year, Alexander and Corey developed the exact, fully quantum treatment of collision induced transitions between a Π and a Σ^+ electronic state.

Electronically inelastic collisions result from a mixing between the Π and Σ electronic states of the isolated molecule which is provoked by the approach of the collision partner. To describe this effect, qualitatively as well as quantitatively, it is necessary to understand the dependence on geometry of the matrix elements of this electrostatic potential in a diabatic (isolated molecule) basis. In order to transform to this diabatic basis, one must determine the non-adiabatic coupling matrix elements $\langle\Pi/(\partial/\partial q)/\Sigma\rangle$, where q designates the internal coordinates of the triatomic (molecule + perturber) system.

We shall report progress on state-averaged multiconfiguration self-consistent-field (SA-MCSCF) and multireference configuration-interaction (MCSCF-CI) calculations of the interaction of CN in both the excited $A^2\Pi$ and ground $X^2\Sigma^+$ states with He. The three adiabatic potential energy surfaces have been calculated for several values of the CN bond distance. A fit to this surface has then been used in Coupled-States calculations of the cross sections for inelastic collisions *within* the $A^2\Pi$ state. These results will be compared with the experimental cross sections, for collisions with Ar, obtained in Dagdigian's laboratory. In addition we have begun the calculation of the electronically nonadiabatic (first derivative) coupling matrix elements which are responsible for the $A\rightarrow X$ electronically *inelastic* transitions.

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THE EXPANSION OF ANGULAR-ENERGY PROBABILITY DISTRIBUTIONS FROM
TRAJECTORY CALCULATIONS IN 2-D FOURIER SERIES*

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Angular and energy distributions from classical trajectory calculations were expanded in one and two dimensional Fourier series. The method gives smooth, continuous "maps" of the product angle-energy distribution, $P(x,y)$. To test the method we calculated 9,200 $F+H_2$ trajectories at an initial energy of 3.0 kcal/mol using the Muckerman² potential energy surface. (1) Of these trajectories, 2,471 were reactive. The figure shows the 2-D product distribution for scattering angle ϕ versus vibrational energy of product HF.

$$x = E_{\text{vib}}/ET$$

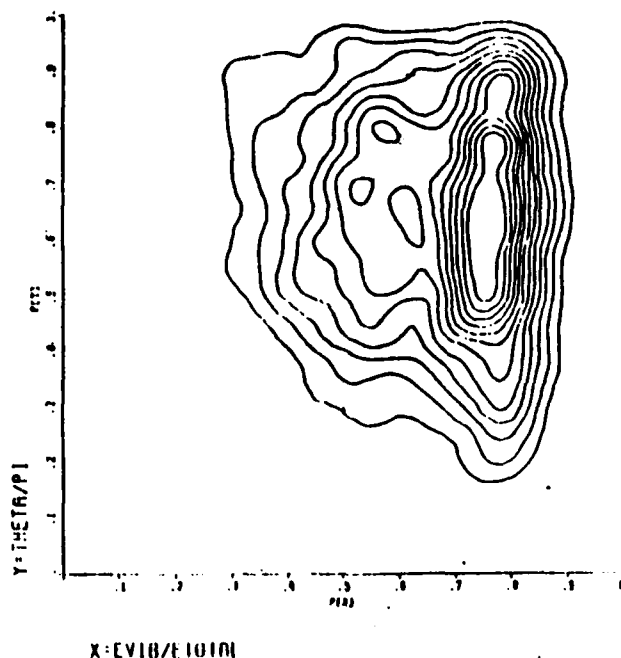
$$y = \phi/\pi$$

$$P(x,y) = \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} A_{nm} \sin(n\pi x) \sin(m\pi y) \exp[-(k^2 n^2 + l^2 m^2)]$$

Here ET is the total energy available to products, A_{nm} are Fourier coefficients calculated analogously to those for one dimensional series (2), and k and l are smoothing parameters determined from the statistics of the trajectory calculation. Countours indicate relative probability and are normalized such that integration over x and y gives unity. Countour intervals are 0.5.

Various angle-energy and energy-energy contour maps will be displayed. We believe this method provides the optimal way to display the results of such trajectory calculations.

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H+NO TRANSLATION-TO-VIBRATION/ROTATION ENERGY TRANSFER:

A CLASSICAL TRAJECTORY STUDY*

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In 1983 and 1985 Wight, Donaldson and Leone (1) published two papers describing the results of experiments in which translation-to-vibration/rotation energy distributions were measured. After publication of the initial experimental study we began a classical trajectory study of the H+NO scattering process using only the 'A' surface. In 1985 Colton and Schatz (2) published a classical trajectory study in which trajectories were run over all four surfaces that correlate with ground state H+NO. We here present the results of our trajectory calculations over the single 'A' surface. They compliment in several interesting ways the study of Colton and Schatz.

The semiempirical surface of Carter, Mills and Murrell (3) was used. The initial vibration energy was set to the zero point energy of NO. The initial translation energy was 3.0 kcal/mol and the initial rotation energy was set to zero. 2000 trajectories were run over this surface of which 886 gave excitation to the $v=1$ or higher state. Since the initial rotation energy was zero we were able to use the orientation of the initial N-NO velocity vector to distinguish H--NO from H--ON collisions. Some results are tabulated below. (All theoretical results are for the 'A' surface only.)

energy level	vibrational distributions			fraction of exciting col. at O or N side of mol.		
	v	traj. calc. this work	traj. calc. ref. 2.	experiment ref. 1.	H--ON	H--NO
1		0.38	0.36	0.55	0.41	0.59
2		0.22	0.19	0.24	0.45	0.55
3		0.15	0.19	0.07	0.47	0.53
4		0.09	0.13	0.05	0.58	0.42
5		0.07	0.05	0.04	0.92	0.08
6		0.04	0.04	0.03	0.92	0.08

We also added features to record the number of "nearly direct hits" and "complex formation." We will discuss the dynamics of rotational and vibrational excitation in relation to features of the potential energy surface.

* Supported by the National Science Council of the ROC.

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VIBRONIC SYMMETRY CORRELATION THEORY FOR THE PROTON SCATTERING FROM
HYDROCARBONS WITH DEGENERATE VALENCE ORBITALS

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A vibronic symmetry correlation theory¹ is proposed for the unusual results of proton-energy loss spectroscopy of J. Peter Toennies, M. Noll, G. Niedner and B. Friedrich.² The theory is based on protonated complex formation and charge transfer. Methane and acetylene are chosen as examples, both have degenerate highest occupied molecular orbitals. While the CH_5^+ complex may assume different configurations, it is shown that vibronic interaction promotes a conical-type intersection. This guides the proton to a path of lower potential in which the proton interacts mainly with one of the degenerate orbitals and minimally with the rest of orbitals that are orthogonal to this one, e.g. attack along the center of one tetrahedral edge results mainly in proton interaction with one of the t_2 component of T_d and yields a trigonal bipyramid complex $\text{CH}_5^+(D_{3h})$. In this, the second-order Jahn-Teller effect between the ground 1A_1 state and the excited $^1E'$ state promotes ν_6, γ (E') vibrations. The latter modes can correlate to the ν_4 (E) mode of the CH_4 - a mode that is observed² but is not accountable by the usual I.R. excitation. These E' vibrations are precisely those causing the Berry pseudorotation. In case of acetylene, the complex may assume the non-classical structure $\text{H}-\text{C} \equiv \text{C}-\text{H}$ or the classical vinyl cation structure $\text{H}_2\text{C}=\text{C}^+-\text{H}$. It is shown that the attack of proton along one of the π_u - orbital will promote $\nu_2^+(\Sigma_u^+)$ and $\nu_4^-(\pi_g)$ vibrations which may start the three protons off in a merry-go-round motion that interconverts the two isomeric forms in a two-dimensional planar elliptical 'orbit'. This is in lieu of a three-dimensional ellipsoidal orbit, even though acetylene initially has "cylindrical" symmetry. We consider such preferential interaction with one degenerate orbital to be a chemical reactional Jahn-Teller effect. We believe it to be especially prominent when charge transfer takes place resulting in degenerate cations with Renner-Teller³ or Jahn-Teller effect. The symmetry of the H^+ and $(\text{H}_2(T_d, ^1A_1))$ reactants may be different from that of the charge-transfer product $\text{H}(^2S)$ and $(\text{H}_2^+(T_d, ^2T_2))$ and the potential curves will cross. But, a preferential approach will give rise to a conical-intersection and result in an avoided intersection and charge-transfer. The center of tetrahedral edge attack resulting in $\nu_4^-(E')$ vibration of CH_4 also promotes the Jahn-Teller distortion from a 2T_2 state in T_d geometry to a 2B_2 state in D_{2d} geometry. The non-rigid molecular aspects of scattering and isomerization will be discussed in terms of complete nuclear permutation inversion group theory⁴⁻⁶.

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CALCULATION OF ROVIBRATIONAL SPECTRA OF WATER USING AN
ADIABATIC SEPARATION OF STRETCHING AND BENDING MOTIONS.

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We use an adiabatic separation of fast stretching modes from bending and overall rotational modes to calculate the spectrum of the water molecule^{1,2}. The potential used was that of Sorbie and Murrell³ as modified by Lawton and Child⁴. After freezing the bending angle, the stretching modes were solved by two different ways, 1) expanding the two-dimensional wavefunctions in a basis formed by products of harmonic oscillator eigenfunctions, and 2) using the numerical solutions of the OH bond. Both representations yield similar frequencies to those previously reported⁴, at least for excitations $\nu_1, \nu_2 \leq 8$. However, large differences were found from the values obtained in an one-dimensional calculation⁵. In order to get the necessary effective potentials for the bending motion, the stretching calculations were carried out a) at each bending angle, and b) extending in a perturbative way the quantities at the equilibrium angle. Finally, a body-fixed frame with one OH bond as the Z-axis was used to obtain the spectrum. In Table I, a few frequencies (in cm^{-1}) for JTOT=0 and low excitations are compared with "exact" theoretical values^{5,6} and also experimental data⁷.

Table I

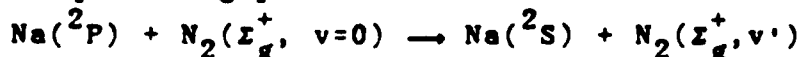
ν_1	ν_2	ν_3	Exp	Ref. 5	Ref. 6	This work
1	0	0	3657.054	3662.7	3671.73	3654.7
0	0	1	3755.930	3764.9	3764.11	3752.5
1	1	0	5234.977	5225.5	5226.59	5167.6
0	1	1	5331.269	5329.2	5325.35	5269.9
1	2	0	6775.094	6756.3	6734.34	6657.3
0	2	1	6871.522	6861.2	6841.42	6762.3

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ELECTRONIC QUENCHING OF Na(²P) BY COLLISION WITH
N₂ (Σ_g⁺, v=0) IN THE PERPENDICULAR CONFIGURATION

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We apply a close-coupling approach to study the
electronic quenching process



assuming a perpendicular configuration. The potential energy
surfaces used were those reported by Archirel et al¹. Instead
of the interelectronic coupling previously employed², we have
taken a gaussian expression

$$U_{\text{PS}}(R, r) = B \exp\{-\beta[R - R_c(r)]^2\}$$

where R is the atom-diatom distance r is the diatomic bond
length, R(r) is the crossing curve between both diabatic
electronic surfaces and B, β are adjustable parameters. This
coupling is able to reproduce the main features of the
collision, i.e., the inversion of the final diatomic
vibrational population and the high efficiency of the
quenching process. For thermal energies only one channel in
the initial state and eight in the final one are open. In
Table I we present the partial quenching probabilities at a
collision energy E=810 cm⁻¹. They were calculated taking into
account 9 channels in the final state and 2,4,...etc in the
initial state, using the values B=0.002 and β=8 (atomic
units). Convergence was achieved in a 9x10 calculation.

Table I

	P _{0→0}	P _{0→1}	P _{0→2}	P _{0→3}	P _{0→4}	P _{0→5}
9 x 2	6.41(-1)	6.30(-2)	4.09(-2)	3.57(-1)	5.22(-4)	5.05(-6)
9 x 4	7.07(-4)	1.99(-2)	3.77(-1)	7.76(-2)	1.44(-3)	1.93(-5)
9 x 6	4.88(-2)	2.33(-1)	1.76(-1)	4.67(-2)	7.06(-3)	2.24(-4)
9 x 8	4.87(-2)	2.91(-1)	1.46(-1)	3.61(-2)	5.56(-3)	9.98(-3)
9 x 9	4.25(-2)	3.05(-1)	1.14(-1)	2.02(-2)	1.49(-2)	6.26(-2)
9 x 10	5.72(-2)	2.70(-1)	6.47(-2)	9.51(-3)	2.52(-2)	6.28(-2)
9 x 11	5.95(-2)	2.64(-1)	6.66(-2)	1.20(-2)	2.38(-2)	6.32(-2)

Finally, partial quenching probabilities averaged by a
Boltzmann distribution of the temperature are presented in
Table II. The inversion of the final diatomic vibrational
population, in this temperature range, can be seen from
inspection of this table.

Table II

T(°k)	P̄ _{0→0}	P̄ _{0→1}	P̄ _{0→2}	P̄ _{0→3}	P̄ _{0→4}
200	1.50(-3)	1.04(-2)	5.20(-2)	1.48(-2)	4.58(-4)
400	3.16(-3)	1.67(-2)	4.61(-2)	1.36(-2)	5.20(-4)
600	4.95(-3)	2.20(-2)	4.09(-2)	1.22(-2)	6.05(-4)
800	6.48(-3)	2.61(-2)	3.68(-2)	1.12(-2)	6.69(-4)
1000	7.65(-3)	2.90(-2)	3.39(-2)	1.03(-2)	7.17(-4)

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Collision Complex Model Predictions for Electronic Transitions
in a Diatomic Molecule

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While much work has been done on collision-induced rotational and vibrational energy transfer, electronic transitions in molecules due to atomic collisions remains a relatively new topic. Alexander and Corey¹ have recently developed a quantum formulation which they applied to $2\Pi-2\Sigma$ transitions in a diatomic molecule that yield good qualitative results when compared to experiment. Previously, we applied this model to our QODR data² for the specific transitions $A^2\Pi_u(v=4)-X^2\Sigma_g^+(v=7,J)$ in N_2^+ due to collisions with helium atoms. We now extend this theoretical model by inserting an explicit interaction potential into Alexander and Corey's expression for the transition matrix, thereby removing the dependence on quantities they define as the base cross sections, σ_0 . Based on our previous work demonstrating the importance of the attractive force, we assume the N_2^+ and He form a metastable collision complex which predissociates, resulting in E→T energy transfer. By using a phenomenological potential to generate initial and final wavefunctions for the atom-molecule system, we are able to make predictions for relative cross sections precluding previous knowledge of the data.

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Nonadiabatic Reaction Dynamics Studies of
Li, Na (2P) + H₂, D₂ Quenching

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We have constructed diatomics-in-molecules (DIM) potential energy surfaces which have been optimized to agree with ab initio surfaces for Li, Na (2P) + H₂, D₂ quenching reactions. On the Na + H₂ surfaces we have used two different nonadiabatic classical trajectory methods to predict surface hopping: (1) transformation of the multidimensional surface intersection to a local one-dimensional curve crossing and calculation of the Landau-Zener transition probability (Muckerman-Stine method), and (2) integration of the coefficients of the adiabatic electronic states to determine transition probability (Blais-Truhlar method). For Na + H₂ we have compared nonadiabatic coupling terms calculated by DIM to ab initio values and find them to be in good agreement.

We report the results of over 5000 trajectories run at a variety of initial conditions using the two methods to describe surface hopping. We find method 2 in all cases gave significantly larger quenching cross sections than method 1. We find that the magnitudes of the quenching cross sections to be very sensitive to the details of the interacting potential energy surfaces.

Theoretical State-to-State Charge Transfer Cross Sections
for $\text{Ar}^+ + \text{N}_2$ and $\text{Ar}^+ + \text{CO}$ Collisions

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Theoretical state-to-state cross sections have been calculated for charge transfer in collisions of $\text{Ar}^+ ({}^2P_J) + \text{N}_2$ and $\text{Ar}^+ ({}^2P_J) + \text{CO}$. Our semiclassical theoretical method¹ computes the classical trajectory for each collision and solves the time-dependent Schrodinger equation along the trajectory for the vibronic states of the system. The potential energy surfaces and couplings have been calculated using the procedure of Archirel and Levy.²

Although N_2 and CO are isoelectronic, the ionization potentials of the two molecules differ by 1.6 eV. As a consequence, the charge transfer cross sections with Ar^+ are quite different. At $E_{\text{cm}} = 2$ eV, the total cross section for $\text{Ar}^+ + \text{N}_2$ is large, and the product states nearest in energy to the reactant state are primarily populated, even when this violates the Franck-Condon principle.³ For $\text{Ar}^+ + \text{CO}$ the reactant state is nearly resonant with $\text{Ar} + \text{CO}^+ (n' = 7)$, but the Franck-Condon factor for the transition $\text{CO} (n = 0) \rightarrow \text{CO}^+ (n' = 7)$ is zero. As a consequence, the total charge transfer cross section is small. The product state populations appear to represent a compromise between energy resonance and Franck-Condon factors. The calculations show that the $\text{CO}^+ (\text{A})$ state plays an important role in this system, even at low collision energies. We shall discuss these results in our poster.

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Low-Energy Collision-Induced Vibrational Energy Transfer in the HeI₂ System

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An investigation¹ is made of vibrational energy transfer in low-energy collisions between He and vibrationally excited I₂(B).² Taking into account the open-channel as well as closed-channel (Feshbach-type) resonances and the coupling between the rotational and the vibrational motions, it is shown that the dynamics is not sensitive to the resonance position,³ and that the enhancement of the vibrational relaxation cross section at low collision energies is due to resonances (both closed- and open-channel), the anharmonicity of the I₂ molecule, and the long-range attractive force of the intermolecular potential.⁴

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FULLY QUANTUM STUDIES OF COLLISIONS OF $\text{Li}_2(\text{B}^1\Pi_u)$ WITH He and Ne¹Didier Lemoine, Gregory C. Corey², and Millard H. Alexander

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More than a decade ago several experimental groups began the investigation of inelastic collisions within the excited $\text{B}^1\Pi_u$ electronic states of the alkali dimers. In these open-shell systems the relative motion of the collision partners can couple not only with the rotational motion of the molecule but also with the orbital motion of the electron in the singly filled π orbital of the alkali dimer. Motivated by this work a number of authors developed general frameworks for the treatment of the collisions of molecules in $^1\Pi$ electronic states. In several early treatments the interaction of the Π state molecule with a perturber atom was described in terms of a *single* potential energy surface which depended explicitly on the orientation of the singly filled π orbital. A less confusing description invokes the *two* potential energy surfaces which arise when the electronic degeneracy of a $^1\Pi$ electronic state is lifted by the approach of a collision partner. Much of the early experimental work, and the interpretation thereof, was devoted to the observed inequalities in the cross sections for *upward* ($J \rightarrow J + \Delta J$), as compared to *downward* ($J \rightarrow J - \Delta J$) transitions.

We report close-coupled (CC), coupled-states (CS), and infinite-order-sudden (IOS) cross sections for collisions of $\text{Li}_2(\text{B}^1\Pi_u)$ with He and Ne, a system currently under experimental study. Two choices were made for the relevant potential energy surfaces, both based on functional forms introduced by Poppe. Since these surfaces are simplistic, our goal will not be the determination of quantitative cross sections to compare with experiment. Rather we shall concentrate on exploring the range of validity of the CS and IOS approximations and investigating and interpreting quantum interference effects in the integral cross sections. These interference effects are clearly manifested, for example, in the variation with initial Λ -doublet level of the cross sections for $J \rightarrow J + \Delta J$ transitions.

¹ Research supported in part by the National Science Foundation under grant CHE85-506502.

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ABSTRACT FOR CONFERENCE ON
DYNAMICS OF MOLECULAR COLLISIONS

A Calculation of the Second Virial Coefficient
of Equilibrium and Normal Hydrogen

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Niblett and Takayanagi set up a formalism to solve coupled Schrodinger equations for hydrogen which they considered a mixture of J=0 and J=1 molecules where the J=0 molecules are spherical and the J=1 molecules are eleptical. We have used this formalism to calculate phase shifts and amplitudes in an energy grid from 1 to 1000 K. The J=0, J=0 interaction was determined from the HFD potential function of McConville and the phase shifts were found from a single Schrodinger equation. The angular part of the J1 interaction was taken as an additional P₂ (cosθ) repulsive term and a 1/r⁵ quadrupolar attractive term. The J=0, J=1 interaction leads to three coupled equations for J-j=0, ±1 and the J=1, J=1 interaction leads the nine coupled equations for J-j=0, ±1, ±2. The Takayanagi selection rules allow the latter set to be broken into four sets of 4, 2, 2 and 1 equations which are coupled in each set. The code uses the deVogelaere scheme for simultaneous numerical integration of the coupled equations. Then the R rotation done to satisfy the asymptotic boundary condition is accomplished by a matrix inversion in complex notation. The resultant phases and amplitudes are then stored according to E, J, J-j, and μ. The second virical and viscosity can be obtained from combinations of the phases and amplitudes. The second virial was found from an average of the amplitudes of the form

$$(2j+1) \delta \ln^2 \delta_j = \frac{1}{n} \sum_{\mu} \sum_J (E_{J\mu}^j)^2$$

where n = 3 fo, J=0, J=1 and n=5 for J=1, J=1.

The calculation for equilibrium hydrogen was obtained from B₀₀ and that for normal hydrogen from .06 B₀₀ + .375 B₁₀ + .56 B₁₁ agrees quite well with the experimental values tabulated in Dymond and Smith.

[†]Work was in collaboration with American Institute of Physics Summer Interns: Stephen Allegero, Michael Cavagnero, Joseph Dimarco, and Jonathan Luke.

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Higher-order adiabatic approximations for coupled systems,
by T. Tung Nguyen-Dang, Département de chimie, Université de Sherbrooke,
Sherbrooke, Québec, Canada, J1K 2R1.

It is shown that a higher-order adiabatic representation for any interacting system may be constructed via a proper unitary transformation of the system's hamiltonian. This transformation physically corresponds to a phase shift describing a retardation in the fast subsystem's response to the slow subsystem's motions. In this higher-order representation, the two subsystems are still adiabatically separated, even though first-order non-adiabatic interactions had been implicitly resummed, yielding residual second-order non-adiabatic couplings. The systematic search for the above phase-shift transformation is illustrated for simple two-body systems, ranging from dressed and free hydrogen atoms, to the Hénon-Heiles anharmonically coupled oscillator system. For this last non-integrable system, it is shown that the dynamics of the system appears, in the new adiabatic representation, to mimic closely the dynamics of the integrable anti-Hénon-Heiles system.

Spectroscopy and Dynamics of Alkali-Halide Charge Transfer States

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Near the dissociation threshold in a given isolated diatomic charge-transfer state, we can expect a dramatic change in the properties of the vibrational levels. The usual $^1\Sigma^+$ electronic state, with total angular momentum J , is well represented, in atomic units, by a Rittner-type potential [1,2]

$$V(R) = A \exp(-aR) - C/R^6 - \alpha/2R^4 + J(J+1)/2mR^2 - Z/R$$

Except for being rather anharmonic due to the skewness introduced by the soft $-Z/R$ term, we expect the spacings of the lowest vibrational levels to be reasonably normal. However, since the large amplitude vibrational levels just below the dissociation limit predominantly experience this coulombic interaction, we expect an infinite number of rotational-vibrational levels to be supported by the Rittner potential, with vibrational spacings given by the typical perturbed Rydberg expression

$$E_{J,v} = -Z^2 m/2(v+J+1-\mu_J)^2,$$

where m is the reduced mass of the diatomic molecule. The vibrational quantum number, v , measures the number of nodes in the given vibrational state and simply replaces the radial quantum number n we normally associate with electronic Rydberg states. We have used accurate numerical algorithms, based on the Milne's quantum number function [3], to evaluate the vibrational quantum defect $\mu_J(m)$. The exact transition from harmonic-like to Rydberg-like behavior depends in detail on the rotational angular momentum J and mass m , but typically for vibrational quantum numbers $v \geq \text{Order}(10^3)$ we achieve a reasonably exact Rydberg limit, with $\mu_J(m)$ approaching a constant, independent of v .

Even in the simplest $^1\Sigma^+$ alkali-halide charge-transfer system, M^+X^- , the Rittner potential is crossed by the potential curves originating from neutral, ground state $M(^2S)+X(^2P)$ collisions. This induces predissociation of the coulombic vibrational levels [1]. In previous studies of the charge-transfer dynamics only the diabatic coupling between the neutral and charge-transfer $^1\Sigma^+$ electronic states were included [2]. In our close-coupled calculations of the predissociation, we also include a coupling to the neutral $^3\Pi_0^+$ state. Using these three pure case(c) molecular states, with appropriate radial, rotational and spin-orbit couplings, we can evaluate the partial widths for predissociation into the specific $j=1/2$ and $j=3/2$ fine-structure states of the $X(^2P)$. Utilizing a rigorous analytic multichannel quantum defect representation of the resonance scattering [4], we attempt to isolate the effect of varying fine-structure splitting on the charge-transfer spectra for different alkali-halogen systems.

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Half Collision Matrix Methods Applied to Multichannel Curve Crossings

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We present methods of solving multichannel close-coupled equations by propagating a set of first-order equations for a specially designed Half Collision Matrix $X(r)$. The methods are predicated on choosing a reference potential and defining a pair of reference radial functions for each channel [1]. Although the choice is completely at our disposal, the propagation of the exact half collision equations is expedited by tailoring the potentials to the exact interaction matrix at each radial distance r .

An approximate Classical Half Collision Matrix $Z(r)$ can be defined by neglecting rapidly oscillating terms in the propagation of $X(r)$. This random phase approximation is valid in classically accessible regions of space, and can be viewed as a refinement of the semiclassical or impact parameter methods often used in scattering theory [2]. The resultant first order equations insure that the amplitude Z remains unitary throughout all space. This property can be used to justify the usual neglect of multichannel couplings when calculating Franck-Condon factors involving continuum transitions [1].

Because of linear dependences, the Half Collision Matrix methods can only be used in classically open regions, and must be preceded by some stable propagation of the coupled equations in non-classical regions. Using the exact expressions for dX/dr , we derive a stable algorithm for a Full Collision Matrix, $\Sigma(r) = X(X^*)^{-1}$, which is always unitary, and can always be propagated with numerical confidence even in non-classical regions.

The three methods, involving the propagation of the exact amplitudes $X(r)$ and $\Sigma(r)$, and the approximate amplitude $Z(r)$, are demonstrated by application to a multichannel curve crossing in atom-diatom vibrational energy transfer collisions. The resultant transition probabilities obtained from $X(\infty)$ and $\Sigma(\infty)$ for 10-channel couplings agree completely with those obtained from well-tested renormalized Numerov codes, independent of the choice of reference potentials. The classical half collision matrix $Z(\infty)$ also yields excellent results, but only when physically reasonable adiabatic or diabatic reference potentials are employed in the calculations.

The full collision amplitude $\Sigma(\infty)$ is directly related to the scattering matrix for a complete collision and the methods developed here can be used to calculate any close-coupling problem. However, the methods are especially well designed to study true half collision phenomena which require explicit knowledge of the half collision amplitude $X(\infty)$ [1]. Such phenomena include photodissociation, predissociation, pressure-broadened lineshapes and final state interactions which are approximated by frame transformation theory.

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COLLISIONAL ENERGY TRANSFER IN POLYATOMICS.
VIBRATIONAL EFFECTIVE HAMILTONIAN FOR CO₂-Ar

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In the processes of collision induced energy transfers between translation, rotation and vibration, the perturbations seen by the different vibration modes frequently vary adiabatically. The use of an adiabatic formulation enables to reduce considerably the coupling strengths while opening indirect transition paths. Then a perturbative approach, even at the first order, can give reliable results. The major difficulties occur in the construction of the adiabatic basis and non adiabatic coupling terms. We propose a new approach in the framework of the effective Hamiltonian for the CO₂-Ar system.

The Hamiltonian can be written as :

$$\mathcal{H} = \frac{1}{2} \mu (\dot{\vec{R}})^2 + \frac{1}{2} m (\dot{\vec{r}})^2 + \mathcal{H}_0^{\text{vib}} + V_1 + V(R, \cos\gamma, q) + \Delta \mathcal{H}$$

$\mathcal{H}_0^{\text{vib}}$ is the zero order vibrational Hamiltonian. V_1 is the anharmonic part of the vibrational Hamiltonian (limited to the fourth order). $V(R, \cos\gamma, q)$ is the interaction potential used in ref 1. $\Delta \mathcal{H}$ represents the rovibrational couplings limited to the first order, i.e. Coriolis and centrifugal terms.

The static part of the vibrational Hamiltonian

$$\mathcal{H}_{\text{sta}} = \mathcal{H}_0^{\text{vib}} + V_1 + V(R, \cos\gamma, q)$$

is bloc diagonalized using intermediate representations^{2, 3}. The basis set of 70 vibrational states is partitionned in 7 blocs of 1,2,4,6,1,9,47 states respectively. The procedure is repeated in about a hundred coordinates points, nodes of elliptical coordinates.

The dynamical equations are then expressed. The part corresponding to the adiabatic dynamics between quasi degenerated states-blocs and that corresponding to the internal dynamics in each bloc are clearly separated.

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Cis-Trans Isomerization of Methyl Nitrite*

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The unimolecular dynamics of methyl nitrite has been investigated by using quasiclassical trajectory methods. The rates of intramolecular cis-trans conversion have been calculated as a function of various initial excitations of CH bonds and selected normal modes. Also, the energy flow from CH overtones has been examined. Mode specificity of the internal conversion will be discussed.

* Work supported by the U.S. Army Research Office.

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THEORETICAL STUDY OF ENERGY TRANSFER IN COLLISIONS OF ALIGNED $\text{Ca}(4s5p^1P)$
ATOMS WITH NOBLE GASES¹

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The investigation of alignment effects in atomic and molecular collisions is presently emerging as a field of considerable interest. The present study was motivated by the recent experiment of Bussert, Neuschäfer and Leone where polarized laser excitation in a crossed beam was used to investigate the dependence on orbital alignment of the cross section for the $\text{Ca}(4s5p^1P) \rightarrow \text{Ca}(4s5p^3P)$ spin-changing transition. With He, Ne and Ar, the observed cross sections were larger when the Ca 5p orbital is aligned initially *perpendicular* to the direction of the relative velocity of the two partners. However, with Xe as the collision partner, the opposite result is found: the $^1P \rightarrow ^3P$ cross section is larger for *parallel* excitation. Lastly, in the case of Kr, no preferential alignment effect is observed.

In the full quantum theory of this process the $^1P \rightarrow ^3P$ spin changing transition occurs by means of the spin-orbit mixing between the 1P and $^3P_{j=1}$ states of the Ca atom. It is, furthermore, facilitated by the crossing between the $^1\Pi$ and $^3\Sigma$ potential curves which at long range correlate respectively, to the 1P and 3P states of the Ca atom.

As an extension of previous work on $\text{Ca}^+ \text{-He}$ collisions [B. Pouilly and M. H. Alexander, J. Chem. Phys. **86**, xxxx (1987)], we shall present the results of close-coupled calculations for the collision of $\text{Ca}(4s5p^1P)$ with the other noble gases (Ne, Ar, Kr, Xe). In addition we have studied the polarization dependence of the *reverse* ($^3P \rightarrow ^1P$) process, for which some experimental cross sections have also been obtained. Since the electrostatic potential curves for the relevant highly excited states of the Ca+rare gas systems are unknown, we modelled these curves using a flexible Morse-Spline-Van der Waals function. We have paid particular attention to the influence of the shape of the electrostatic curves on the polarization dependence of the cross sections.

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Energy Transfer and Reaction in Collisions
of Fast H Atoms with CO₂

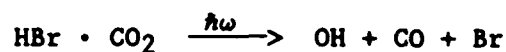
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In this paper we present the results of a state resolved quasiclassical trajectory study of the H + CO₂ collision system using a potential surface that we have developed by fitting ab initio calculations for all the HCO₂ minima and saddle points. Both reactive and nonreactive collisions are studied, with the nonreactive results being compared with recent measurements due to Flynn, Weston and coworkers, and the reactive results compared with measurements due to Kleinermanns and Wolfrum. Sensitivity of the results to features of the potential surface is considered, and it appears that rather tight bounds on the addition barrier to form HOCO can be inferred from the data.

We will also present results of a trajectory simulation of the photoinduced reaction



Comparisons with measurements due to Wittig and coworkers will be made, along with an analysis of the orientation dependence of the OH product state distributions.

DISSOCIATION OF H_2^+ BY He

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The collision induced dissociation CID process $H_2^+ + He \rightarrow He + H^+ + H$ has been studied over a wide range of kinetic energies and once more very recently (1) at low energies. Gislason and Guyon (2) discussed these experimental results and went deeper into the study of the mechanism of C.I.D. :

There are two potential energy surfaces which are relevant to the system HeH_2^+ . The ground surface is correlated to two diatomic bounds fragments $H_2^+ \Sigma_g^+ + He$ and $HeH^+ + H$, the excited surface to dissociative fragments $H_2^+ \Sigma_u^+ + He$ and $HeH + H^+$. Among these asymptotes, one can distinguish, first $H_2^+ \Sigma_g^+$ and Σ_u^+ where the one electron is shared equally between the two nuclei, $HeH^+ + H$, where it is located on the proton which is farther from the He atom, $HeH + H^+$ where it is on the proton the nearest the He. So the position of the proton relative to the atom (or its velocity) can be used to distinguish the two states which are nearly degenerate when all three nuclei are far apart. We are interested into the distribution of CID products between these two states.

To study the dynamics of the reaction, the adiabatic energies of the system were expressed in terms of diabatic terms relevant to the two electronic configurations $H_A^+ - H_B - He$ and $H_A - H_B^+ - He$: in C_{2v} the two 2A_1 diabatic states can cross and a Landau-Zener transition is possible but the transitions are in majority Demkov transitions.

The trajectories were carried out on adiabatic potential energy surfaces given by Whitton and Kuntz (3) and the surface hop was treated as localized Demkov and Landau-Zener transitions. The initial vibrational state of H_2^+ v , is varied between 0 and 10 and the relative kinetic energy, E_{rel} , between 3. and 1000 eV. The preliminary results show that the dissociation cross section on the excited surface is in the order of 7 % of the dissociation cross section on the ground surface

if ($v=0$ $E_{rel}=3eV$), 10% if ($v=10$ $E_{rel}=3eV$), 70% if ($v=0$ $E_{rel}=1000eV$). More detailed results will be presented at the Conference.

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Secondary Encounters in Collinear, Dissociative Atom-Diatom Collisions

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Classical trajectory simulations of dissociative collisions between a diatomic molecule A_2 and an atom M have shown that the correction κ_3 for recrossing of an appropriately chosen phase space dividing surface is independent of temperature T when collisions are dominated by $A-M$ repulsion. Recrossing in this case is thought to be due to secondary $A-M$ encounters in the course of a collision, but the physical basis of the T -independence of κ_3 has been unclear. As a first step toward providing such a basis, collinear classical trajectories were run for several of the same three body potentials and mass ratios that had been studied in the three dimensional simulations. Recrossing corrections derived from the collinear trajectories show a T behavior similar to that of κ_3 . The collinear results can be interpreted in terms of the single encounter impulsive collision model with a simple modification to account for secondary encounters.

Breakdown of the Phenomenological Rate Law
for the Dissociation of Diatomic Molecules

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We have solved the master equation describing the rates of change of vibrational level populations during the steady dissociation of a diatomic gas, AB, in mixtures of finite composition. V-T energy transfer processes among neighbouring levels as well as collision induced dissociation from the top-most level are considered. This simple model presents most of the features of real systems. Although more detailed models have been treated in the past and their corresponding rate equations solved numerically, none of those studies give the insight which the present analytical treatment affords and at the same time make predictions concerning the validity of the so-called linear mixture rule (LMR) for specific examples. This rule states that if k_{AB} is the rate coefficient for $AB + AB \rightarrow AB + A + B$ and k_M is the rate coefficient for $M + AB \rightarrow M + A + B$ (M is inert), then the overall rate coefficient, k , for the effective process $AB \rightarrow A + B$ is

$$k = k_{AB} x_{AB} + k_M x_M \quad (1)$$

It is well known that the LMR is not generally valid when non-equilibrium vibrational population distributions persist. This has been shown for unimolecular dissociation of polyatomic molecules [1], and theorems have been developed for the maximum size and direction of the deviation from the LMR [2]. In previous theoretical and experimental work we have shown that deviations can be severe for the vibrational relaxation of diatomic molecules [3] and of polyatomic molecules [4,5].

Eq. (1) implies the validity of the phenomenological rate law.

$$-\frac{d[AB]}{dt} = k[AB]([AB] + [M]), \quad (2)$$

with k independent of concentration. Because of the fundamental importance and universal use of eq. (2) we investigate the conditions for validity of eq. (1) as applied to the dissociation of diatomic molecules. We find that deviations can indeed be very serious. The deviations are most serious when (1) the relative AB:M efficiency for collisional induced dissociation differs most from the relative AB:M efficiency for collisional de-excitation, and (2) when the temperature is high. Deviations manifest themselves at low mole fractions of the least efficient collision partner.

We identify previously unrecognized examples of the phenomena from published research.

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ROTATIONAL ENERGY TRANSFER WITHIN THE $B^3\Pi_g$ $v=3$ MANIFOLD OF MOLECULAR NITROGEN

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An optical-optical double resonance experiment has been carried out to study rotationally inelastic collisions of N_2 $B^3\Pi_g$ $v=3$ by argon with initial and final rotational state resolution. This experiment is similar to that recently performed by Katayama,¹ but with higher spectral resolution here. Nitrogen molecules in the metastable A state are generated by collisional excitation transfer from metastable argon atoms. Specific B state rotational levels are prepared in a flow system by pulsed pump laser excitation of isolated rotational lines in the $B^3\Pi_g - A^3\Sigma^+$ (3,0) band near 688 nm. After a short delay (ca. 20 nsec), a probe laser interrogates the rotational populations in the B state by fluorescence excitation in the $C^3\Pi_u - B^3\Pi_g$ (0,3) band near 406 nm. Collisional transfer from incident levels in all 3 spin-orbit manifolds of the B state was investigated. For molecules initially in the F_1 ($\Omega=0$) manifold, a preference for conservation of fine-structure label with even ΔJ changes was observed. This propensity is very pronounced for the $J=0$ level but is considerably relaxed by $J=6$. By contrast, inelastic collisions involving the F_2 ($\Omega=1$) and F_3 ($\Omega=2$) manifolds do not exhibit a significant propensity to conserve fine-structure label. A slight residual preference for even ΔJ changes is observed in collisional transitions within the F_2 manifold. These experimental results will be compared to the propensity rules derived for homonuclear $^3\Pi$ rotationally inelastic collisions, both in the case (a)² and case (b) limits. The reduction of the predicted propensities by the transition to intermediate case coupling and "orbital-correlated" scattering will be discussed. The latter term refers to the difference potential for the N_2 -Ar interaction where the N_2 unfilled π orbital is in or perpendicular to the triatomic plane.

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A NEW CROSSED BEAM EXPERIMENT FOR STUDY OF VIBRATIONALLY INELASTIC SCATTERING WITH NEUTRAL POLYATOMICS. GLYOXAL.

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The laser pump-dispersed $S_1 \rightarrow S_0$ fluorescence probe method commonly used in bulb studies of rotational and vibrational energy transfer has been adapted to crossed molecular beams. These new experiments extend the state-resolved energy transfer studies to conditions of low rotational temperatures and controlled collision energies. We intend to use the method primarily with large polyatomics.

Our first polyatomic study involves collisions between S_1 glyoxal and each of several partners (H_2 , He, Ar, Kr and cyclohexane). Data are now available from five initial S_1 glyoxal vibrational levels ($v_{7b} = 0$ to about 700 cm^{-1}). The experiments prove quite feasible with respect to signal-to-noise levels, even when rotational resolution is imposed on the inelastic scattering observations.

Features reminiscent of bulb studies as well as very new aspects of energy transfer have emerged. For example H_2 scattering from the 0^0 glyoxal level excites only the lowest fundamental (the CHO-CHO torsion $v_7 \approx 233\text{ cm}^{-1}$) even though four other levels lie within the 600 cm^{-1} collision energy range. Thus the high state selectivity seen in many bulb experiments (and also S_0 beam experiments) appears once again. Scattering from other initial glyoxal levels behaves similarly. Single-collision rotationally inelastic scattering can be followed with resolution of the ΔK angular momentum change and the total rotational energy change. These data have been transformed into relative cross sections for scattering from 0^0 glyoxal initially with $J < 10$ and $K = 0$. When we compare the total cross section for rotational excitation to the total cross section for rovibrational excitation, we obtain results that are familiar from many other studies. Rotational excitation is about an order of magnitude more likely than rovibrational excitation. If, however, we plot the cross section as a function of energy transferred, we observe a completely different picture of the competition. Rotational and vibrational cross sections both fall off exponentially. The important point, however, is that the fall-off curves merge when placed on the same plot. In other words, for sufficiently large energy transfers (i.e., large enough to excite mode 7), equal probability exists for excitation of the torsional vibration mode and molecular rotations. In this case, there is no molecular distinction what-so-ever between rotational and vibrational excitation.

SPECTROSCOPY AND DYNAMICS OF HIGHLY VIBRATIONALLY EXCITED ACETYLENE

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A new technique enables the collisional relaxation of a highly vibrationally excited polyatomic molecule to be studied in previously unattainable detail. Direct overtone excitation of $3\nu_{\text{CH}}$ prepares acetylene in an initial state with $\sim 9600 \text{ cm}^{-1}$ excitation energy. Time resolved laser induced fluorescence (LIF) detection via excitation to the \tilde{A}^1A_u electronic state provides a monitor of the collisional relaxation pathways with rovibrational state resolution. The technique is also a potentially powerful spectroscopic tool. It accesses high-lying vibrational states whose symmetry and Franck-Condon overlap with the upper electronic surface can differ from thermally populated levels. Therefore, the technique provides new spectroscopic information about both collisionally accessed levels and the rovibrational structure of the excited electronic state.

Preliminary results demonstrate the value of this technique as a probe of collisional relaxation and as a spectroscopic tool. Temporal data show rapid collisional population of several rovibrational states followed by relaxation at a rate similar to gas kinetic. The symmetry of the overtone state allows \tilde{A} state vibrational levels of B_u symmetry to be reached in the LIF probe step. The initially prepared state is monitored via excitation to ν_6 (asymmetric in-plane bend) and to ν_5 (asymmetric C-H stretch), a previously unobserved vibration in the \tilde{A} state. Analysis of the spectrum indicates that the previous ν_4 and ν_6 vibrational assignments in the \tilde{A} state are reversed and must be reassigned. Weak couplings between vibrational states on the ground electronic surface are also evident in these experiments.

HIGH RESOLUTION CROSSED MOLECULAR BEAM STUDIES OF SPHERICAL AND
NON-SPHERICAL INTERMOLECULAR FORCES

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Much experimental and theoretical interest is currently being shown in the study of intermolecular potential energy surfaces (PES) for non-spherical interactions.¹ Once the PES is known to a sufficient accuracy, all the necessary data on rotational energy transfer can be calculated.

In our laboratory we have recently exploited the very detailed information content of diffraction scattering for the determination of interaction potentials for both spherical (atom-atom)^{2,3} and non-spherical (atom-molecule)^{3,4} systems. While for spherical systems the determination is very accurate and conclusive², for non-spherical systems its validity remains confined within the limits of the approximate scheme of analysis employed⁴, since it is still impracticable to perform exact quantum scattering calculations for potential fitting purposes.

We will report on high resolution elastic differential cross section (DCS) measurements for Ne-Ne, Ar, Kr and Xe, in which the diffraction quantum oscillations superimposed on the rainbow structure are for the first time clearly resolved at collision energies corresponding to room temperature beams.^{2,3,5} These new high quality data have allowed us to refine or assess, with high precision (better than 1%), the interatomic potentials for these systems, whose knowledge is considered⁶ to be the less accurate among the like and unlike rare gas pairs.

We will also report on precise measurements of total DCS for some simple atom-molecule systems (He-N₂, O₂ and NO,⁴ Ne-N₂, O₂ and NO,⁷ and He-CO₂⁸) in which an accurate evaluation of the phase and amplitude of the diffraction structure has brought to rather reliable potential energy surfaces within a multiproperty analysis in the infinite-order-sudden approximation. For instance, for the prototype (beyond the rare gas atom-H₂ cases) He-N₂ system a potential surface which predicts correctly a wide variety of scattering and bulk data and whose spherical part has an accuracy ($\leq 1\%$ on R_m and $< 5\%$ on ϵ) comparable to that achieved for the corresponding isotropic He-Ar system was recently derived.⁴

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MOLECULAR BEAM STUDIES OF THE INTERACTION OF OXYGEN ATOMS WITH RARE GASES AND METHANE

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To study intermolecular potential energies we measure integral cross sections as a function of the collision velocity. The apparatus used for the present experiments is that operating in our laboratory since a number of years and already described in several papers.^{1,2,3}

The main problems in these experiments are the production of an intense and stable oxygen atom beam and the control of the electron states and of the relative population of the involved magnetic sublevels. An inhomogeneous magnetic field is used to defocus from the beam direction those atoms which show a non zero effective magnetic moment, characterizing the electronic state and varying the relative population of magnetic sublevels. For the analysis of the present scattering data, we were guided by the consideration about angular momentum coupling schemes described in refs. 4,5,6. For the O-He system, for which a comparison is possible with accurate quantum chemical calculations of open shell interactions, it is found that van der Waals forces are still underestimated by theory.⁷

In addition we have performed experiments, using the same apparatus, to obtain integral cross sections for rare gas-methane systems.⁸ The presence of fully developed glory oscillations indicates that the anisotropy of methane plays only a minor role. Therefore these data can be treated in terms of a central field assumption. The substantially isotropic behaviour of methane under the present experimental conditions allows a significant understanding of integral cross sections measurement involving O atoms, where, then, anisotropy effects originate only from the non zero angular momentum of the atoms.

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STATE-TO-STATE ENERGY TRANSFER MEASUREMENTS
OF
VIBRATIONALLY EXCITED DIATOMIC MOLECULES WITH THERMAL COLLISION PARTNERS

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We present recent results on the state-to-state energy transfer rate measurements of vibrationally excited diatomic molecules. The technique of stimulated Raman scattering is used to prepare a single rotational level of the first vibrational level of a diatomic molecule, in this case HD, H₂, or HCl. State-selective multiphoton ionization is used to monitor populations in a specific ro-vibrational state in order to monitor the collisional transfer of energy from the initially prepared state to other states. By controlling the time delay between the Raman lasers and the Multiphoton Ionization laser, as well as the pressure, the collisional energy transfer rates are determined. This is done at sufficiently low pressures that the shape of the energy transfer function is directly determined. Rotational energy transfer has been studied in the systems of HD and HCL. In the H₂ system, in addition to rotational energy transfer, direct observation of vibration-vibration energy transfer between ortho and para hydrogen is measured.

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^{*} Summer Faculty Fellow (DHP) at the Combustion Research Facility during the period of work

STATE SELECTIVE STUDIES OF T + R,V ENERGY TRANSFER:
THE H + CO SYSTEM

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Energy transfer in inelastic H + CO collisions is investigated by measuring the quantum state distributions of the scattered, rovibrationally excited CO product.

The experiment is performed using a 1:10 coexpansion of a hydrogen atom precursor, such as H₂S, and CO in a pulsed supersonic beam. Pulsed laser photolysis of H₂S at $\lambda=222\text{nm}$ is the technique used to generate fast, monoenergetic hydrogen atoms with $E_{\text{trans}}=1.6\text{eV}$. The hydrogen atoms, thus produced, participate in a nominally single collision event with beam-cooled CO($v_i=0, J_i=2$). The resulting CO(v_f, J_f) distribution is determined from VUV laser induced fluorescence excitation spectra, recorded using the CO $\Lambda^1\Pi + X^1\Sigma^+$ band system.

The qualitative features of the observed CO $v_f=0$ and $v_f=1$ rotational distributions appear to be consistent within the framework of a classical, sudden collision occurring on a sharply repulsive potential surface. Comparisons are made with the predictions of an hard ellipse scattering model¹ as well as with the quasiclassical trajectory calculations of Schatz² on an *ab-initio* HCO ground state potential surface.

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ROTATIONAL LEVEL VARIATION OF VIBRATIONAL ENERGY TRANSFER
IN OH($A^2\Sigma^+$, $v' = 1$)

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Rate constants for the collisional removal of $v' = 1$ vibrational level of the $A^2\Sigma^+$ first excited electronic state of OH have been measured for specific rotational levels N' of the radical and a variety of collision partners. In these experiments, the output of a frequency-doubled excimer-pumped dye laser excites the molecules to an individual rotational level in $v' = 1$, and a transient digitizer and boxcar integrator record the time and wavelength dependence of the fluorescence. The excited OH radical can be removed from the initially excited level via reaction, quenching to $X^2\Pi_1$, vibrational energy transfer to $v' = 0$, rotational energy transfer within $v' = 1$, or spontaneous emission. We observe a significant decrease of the total collisional removal rate from $v' = 1$ (the sum of reaction, quenching, and vibrational energy transfer) with increasing rotational quantum number. For N_2 , CO_2 , CF_4 , and SF_6 the total removal rate is about a factor of two slower in $N' = 4$ compared to $N' = 0$. The electronic quenching for all but CO_2 is extremely slow and this difference in $v' = 1$ removal must be attributed to a decrease in vibrational energy transfer with rotational level.¹ This rotational level effect is similar to that observed for the total collisional removal rates of OH($A^2\Sigma^+$, $v' = 0$)² and NH($A^3\Pi_1$, $v' = 0$)³ indicating that similar processes may be operating in both kinds of collisions.

From the wavelength dependence of the fluorescence we also obtain the relative amounts of vibrational energy transfer versus electronic removal for several colliders. The species studied fall into three categories. In the first there are two molecules, H_2O and NH_3 , which remove the electronic state rapidly but cause little vibrational energy transfer. Both of these have large dipole moments; perhaps this causes rapid Σ - Π state mixing, leading to quenching and not transfer as the outcome of the collisional encounter. In the second are molecules for whom the removal and vibrational transfer are of similar magnitude: CO_2 , N_2O , and CH_4 . In the third are the poor quenchers, CF_4 , SF_6 , and N_2 . They cause relatively rapid vibrational transfer although they quench each vibrational state quite slowly. This indicates that they interact at long range but do not mix the excited and ground states well during the collision lifetime. How this is related to the electronic structure remains a mystery.

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ELECTRONIC QUENCHING AND FLUORESCENCE LIFETIME
OF THE TRIATOMIC RADICAL $\text{NCN}(A^3\Pi_u)$ Gregory P. Smith, Richard A. Copeland, and David R. Crosley
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Laser-induced fluorescence of NCN has been detected for the first time via the $A^3\Pi_u-X^3\Sigma_g^-$ electronic transition near 329 nm. The NCN radical was detected downstream of a 1.5 Torr He discharge containing about 10 mTorr of CF_4 and less than 5 mTorr of N_2 . From the time dependence of the fluorescence, we find a zero pressure fluorescence lifetime for the 0,0,0 and 0,1,0 vibrational levels of 183 ± 6 ns ($2-\sigma$). In addition to the strong 0,0,0 - 0,0,0 vibrational band, excitation spectra, fluorescence spectra, and lifetimes were also obtained for several previously unobserved, weak off-diagonal bands. The spectroscopic identification of some features is currently uncertain. Quenching cross sections were measured for the vibrationless level of the A-state for 13 different gases at 300 K. Values range over more than two orders of magnitude, from $< 0.1 \text{ \AA}^2$ for He and N_2 to values $> 50 \text{ \AA}^2$ for NO, Xe, and CCl_4 . The variation of the quenching cross section with collider cannot be correlated with the attractive part of the potential as was relatively successful for $\text{OH}(A^2\Sigma^+)$ quenching.¹ For example, the isoelectronic species N_2O and CO_2 show significantly different cross sections with N_2O quenching NCN about seven times faster than CO_2 . Possible explanations for the large variation in the magnitude of the quenching with collision partner will be presented.

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CARS Studies of Nonadiabatic Collision Processes:**"Vibrational Energy Distribution of H₂ after Red Wing Excitation of the Na(3p)-H₂-Collision Pair"**

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ABSTRACT:

Nonadiabatic collisions between atoms and molecules have drawn a large amount of attention in theoretical and experimental studies. In particular, the transfer of electronic energy of an atom to the vibrational, rotational and translational energy of a diatomic molecule (also called electronic quenching) can be considered an important fundamental process of this type and is thus extensively investigated. /1/

We study Na + H₂ as a model collision system for experimental and theoretical reasons. Ab initio potential surfaces are currently available, enabling comparison of experimental results with theoretical calculations. /2/

We apply a new experimental technique in the field of nonadiabatic processes to obtain a more detailed understanding of these energy transfer processes. We use Coherent Anti-Stokes Raman Spectroscopy (CARS) to measure directly the internal energy distribution of H₂ molecules produced by quenching of Na in the first excited state (3 P_{1/2}).

Furthermore, we analysed the internal state distribution of H₂ after nonresonant, red wing excitation of the Na(3p)-H₂ collision pair dependant on excitation wavelength. The detuning range was 600 cm⁻¹ to the red starting with excitation at 589 nm. /3/ We observed a marked change in the H₂ vibrational distribution compared to resonant excitation of sodium. To interpret this behaviour one needs detailed knowledge about potential energy surface crossings with scattering dynamical calculations.

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Isotope Effects in Excitation of CO₂ 00⁰₁ by Hot Atoms

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Tunable diode laser spectroscopy has been used to probe the internal state distribution of CO₂ after collision with H and D atoms produced by excimer laser photolysis of H₂S and D₂S, respectively. Time-resolved infrared absorption signals of carbon dioxide spectral lines provided nascent rovibrational distributions before collisional relaxation. H atoms are roughly twice as efficient as D atoms at exciting CO₂ to the 00⁰₁ asymmetric stretch vibrational level, in qualitative agreement with Landau-Teller arguments. Measurement of the rotational distribution of the 00⁰₁ state shows a peak in the distributions at about J=33 for both H and D atoms. Deuterium, however, shows a small but distinct preference for higher rotational excitation as compared to hydrogen, as revealed by a decreasing H* / D* excitation ratio as J increases. This result can be explained by angular momentum considerations. The D and H atoms are formed with nearly the same energy (2.16 eV for D, 2.30 eV for H), so for a collision of fixed impact parameter, deuterium will have more angular momentum by a factor of roughly 1.4, causing more rotational excitation.

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ISOTOPE EFFECTS IN THE HOT ATOM COLLISIONAL EXCITATION OF ISOENERGETIC STATES OF CO₂

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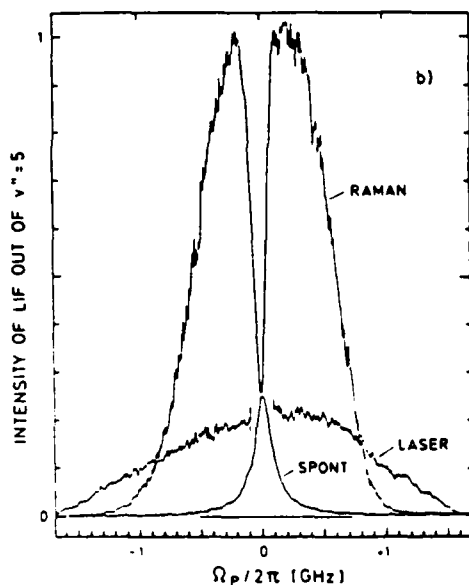
High resolution diode laser spectroscopy is used to probe specific rovibrational states of CO₂ molecules which are collisionally excited by translationally hot hydrogen or deuterium atoms. Time-resolved changes in the transmitted IR intensity are detected while monitoring the antisymmetric stretch $00^01 \rightarrow 00^02$ P(13) and ground state $00^00 \rightarrow 00^01$ P(78) isoenergetic transitions in CO₂ after UV photolysis of H₂S or D₂S. The low pressures ($P_{\text{tot}} = 25$ mtorr) employed permit direct measurement of nascent rotational populations. The measurements show that whereas the excitation of CO₂ 00^01 P(13) by hot H atoms is approximately 2.5 times as efficient as excitation by hot D atoms, the hot D atoms are about twice as efficient as hot H atoms in exciting CO₂ 00^00 P(78). These differences in excitation probabilities are accounted for by the different trajectories required to excite a stretch versus a highly rotationally excited ground state. In order to excite a pure stretch the collision must be end-on, whereas hot atoms may approach from almost any angle to collisionally excite high rotational levels of the ground state.

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EFFICIENT AND SELECTIVE POPULATION OF HIGH VIBRATIONAL LEVELS
BY STIMULATED NEAR RESONANCE RAMAN SCATTERING

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We report the successful application of an optically pumped molecular beam laser for efficient and selective population transfer from $v''=0$ to high lying vibrational levels of Na_2 in the electronic ground state [1]. The molecular beam itself acts as an active medium in an optically pumped laser, the gain of which is dominated by near resonance stimulated Raman scattering [2,3]. More than 50% of the molecules in a thermally populated rotational level of $v''=0$ can be transferred to a state $v_f \gg 1$. The level v_f is chosen by



appropriate adjustment of an intracavity tuning element (birefringent filter). With sufficiently intense pump lasers dynamic Stark splitting occurs and the maximum population transfer is observed for off resonant tuning of the pump laser (see Fig.1). Consequently spontaneous emission is significantly reduced. This ensures a high selectivity of the transfer.

Typically $>75\%$ of the molecules are found in the level v_f while $<25\%$ are distributed over other vibrational levels. The applicability of this technique for the study of collision processes involving vibrationally highly excited states is demonstrated. This technique is expected to be particularly valuable for the investigation of electronic and reactive processes.

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Collision Dynamics of the SiCl Radical in the B'²Δ State

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Collisions with rare gases rapidly deactivate SiCl radicals in the B'²Δ electronic state via a significant near-resonant electronic-to-electronic energy transfer pathway to the B²Σ⁺ state. Either the v' = 0 or 1 vibrational level of the B'²Δ is excited with tunable laser light; in the presence of rare gas quenchers fluorescence from the B²Σ⁺ is observed in the wavelength resolved data. The nascent vibrational distribution in B²Σ⁺ depends dramatically upon the rare gas collider, He, Ne, and Ar, and also varies with the initial vibrational level v' in B'²Δ. For v' = 0 the final state distribution from He collisions includes v = 0-2 and peaks in v = 1 of B²Σ⁺, whereas for Ne collisions only the v = 2 final state is observed. The fluorescence lifetime of the B-state is < 25 ns, significantly faster than the B' fluorescence lifetime of near 1 μs. When B²Σ⁺ is directly excited, no vibrational relaxation of the B-state is observed under the conditions used. Thus after exciting the B'²Δ, the collision induced fluorescence from the B²Σ⁺ provides the nascent vibrational distribution of the B²Σ⁺ resulting from the electronic-to-electronic energy transfer. Analysis of the branching ratio to these and other dark channels is currently underway.

In addition to this state-specific electronic-to-electronic energy transfer, total collisional removal rates from the v' = 0 and 1 levels of the B'²Δ are measured. Laser-induced fluorescence of the SiCl radical is observed in the afterglow of a microwave discharge in rare gas with a trace of added SiCl₄. The initial excitation to the B'²Δ state uses light from a frequency doubled, excimer pumped, dye laser tuned to the Q₁₁ band head of either the (0,0) or (1,0) vibrational bands of the B'²Δ - X²Π electronic transition. The resulting fluorescence is time resolved at various rare gas concentrations to obtain collisional removal rate constants; preliminary results are given in Table 1.

This work is supported by internal research and development funds of SRI International.

Table 1. Total Removal Cross Sections ($\sigma = k/\langle v \rangle$, Å²) for B'²Δ SiCl.

	He	Ne	Ar
v' = 0	4.3	5.7	16
v' = 1	5.0	1.4	8.4

Quenching of Infra-Red Fluorescence in NO₂*

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The first excited electronic state (²B₂) of NO₂ is strongly mixed with high vibrational levels of the ground state. NO₂ was promoted to this state by irradiation with 505 nm light from an excimer-pumped dye laser. The rise and subsequent decay of infrared fluorescence involving single quantum changes in the ν₁, ν₂, ν₃ and ν₁ + ν₃ vibrational modes was monitored, using appropriate filters and solid state detectors. The pressure ranged from 0.1 to 40 torr.

The fluorescence at the asymmetric stretch (ν₃) frequency shows markedly slower rise and decay times than the other modes. The combination ν₁ + ν₃ band is very intense and does not appear to be in equilibrium with ν₁ or ν₃.

Our results so far indicate the following approximate rate constants.

Mode	Rise Rate Constant (x 10 ⁻¹¹ cm ³ sec ⁻¹)	Decay Rate Constant (x 10 ⁻¹¹ cm ³ sec ⁻¹)
ν ₁	3.0 ± 1.2	3.0 ± 1.2
ν ₂	> 10.	3.0 ± 1.5
ν ₃	1.1 ± 0.1	0.2 ± 0.2
ν ₁ + ν ₃	> 10.	0.6 ± 0.2

A second, slower decay component of order 10⁻¹³ cm³ sec⁻¹ is clearly apparent for ν₁ and ν₂ at higher pressures (> 12 torr).

Work is still in progress on the interpretation of these results and further experiments are planned.

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DISSOCIATIVE RECOMBINATION IN ARGON

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Inert gases are characterized by two important features which make them attractive candidates for the development of high energy laser systems, either directly as VUV laser devices or as energy storage media. These two features are 1) a large fraction of the energy lost by an energetic particle interacting with the inert gas, such as a high energy electron, leads to ionization and 2) upon neutralization a large fraction of the electron-ion recombination energy is channeled into the excitation of only a few atomic levels. The reaction governing the ion neutralization process has long been recognized to be the dissociative recombination reaction



where X^* is an excited atomic energy level of the inert gas, X . In the present work dissociative recombination of argon was studied over the pressure range 20 to 200 kPa at a temperature of 291 K. Reaction (1) has been investigated by several workers for all the inert gases at low pressures. Because all high power inert gas laser systems operate at pressures of 100's kPa it is important to be able to predict the influence of pressure on Reaction (1) and to explore the effect of 3 body processes on electron-ion recombination. In the present work pulse radiolysis and laser photoionization were combined to measure α , the dissociative recombination rate constant, in pure Ar. A pulse of 1 MeV electrons was used to create a small concentration of $Ar_2(^3\Sigma_u^+)$ excimer. After a selected delay time from the initial electron beam pulse, $Ar_2(^3\Sigma_u^+)$ was photoionized by a pulse of 308 nm laser radiation thus creating a small excess of Ar_2^+ ions directly. The dissociative recombination of Ar_2^+ was followed by monitoring emission from $Ar(3p^54p)$ atomic states, created directly in Reaction (1), or by monitoring the time dependence of $Ar(3p^54s)$ atomic states by absorption spectrophotometry.

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Ro-Vibrational State Mixing in the C-H Stretch Region of Norbornadiene

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Infrared laser induced fluorescence has been used to probe the extent of state mixing, as well as its rotational dependence, in the C-H stretch region of norbornadiene in the electronic ground state. Both total and dispersed IR fluorescence were collected from molecules, cooled and isolated in a molecular beam, after excitation with an infrared optical parametric oscillator. The *dilution factor*, which is inversely related to the number of coupled states, has been measured for four C-H stretch bands, and in addition, the rotational dependence of the dilution factor has been investigated by exciting different positions, or average J values, within a single ro-vibrational band. The relative energy contents of various vibrational modes, whose fluorescence was observed, have also been determined. An approximate average coupling width of 0.1 cm^{-1} can be derived from the dilution factors and the calculated state density of the ro-vibrational bath states $|l_i\rangle$ that are permitted by symmetry and angular momentum to couple to the zero order optically active ro-vibrational state $|s\rangle$. The rotational dependence of the dilution factor shows that the number of mixed states is proportional to $2J + 1$, where J is the total angular momentum quantum number for the $|s\rangle$ state. Allowing for both Coriolis and Fermi type couplings within a width of 0.1 cm^{-1} , we can adequately predict the distribution of the excitation energy among the modes of the molecule by using a straightforward statistical model, which assumes equal coupling between all the zero order ro-vibrational states that have the correct energy, symmetry, and J to couple. This study of norbornadiene and other recent work in our laboratory on a variety of molecules illustrate the strong correlation between the extent of state mixing and ro-vibrational state density regardless of molecular structure.

LASER DOUBLE RESONANCE MEASUREMENTS OF THE VIBRATIONAL
ENERGY TRANSFER RATES AND MECHANISMS OF DEUTERIUM
FLUORIDE ($v = 1,2,3$)

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Overtone vibration-laser double resonance measurements determine the self-relaxation rate constants for DF($v=1,2$) to be $k_1 = (0.37 \pm 0.03) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_2 = (22.0 \pm 0.6) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Preliminary work demonstrates a total relaxation rate of DF($v=3$) that is slower than that for DF($v=2$). These experiments show that DF($v=2$) relaxes solely by vibration-to-vibration (V-V) energy transfer; in contrast, the fraction of HF($v=2$) molecules that relax by V-V energy transfer is 59%.

The results demonstrate that the magnitude of the energy defects for the available pathways plays a significant role in determining the energy transfer mechanism for the relaxation of DF($v \geq 2$) and HF($v \geq 2$). A comparison of the $v=1$ rate constants for DF and HF indicates that rotational degrees of freedom are the primary receptor modes for the vibration-to-translation, rotation energy transfer process.

Vibrationally resolved Charge Transfer in $H^+ + H_2$, CO_2 , and N_2O at $E_{\text{coll}} = 30\text{eV}$

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Little is known about vibrational excitation in charge transfer collisions involving molecules, since in most previous scattering experiments individual vibrational states could not be resolved. Recently we were able to resolve the vibrational state distributions for the exoergic charge transfer reaction of H^+ with O_2 in a crossed beam experiment at an energy of 23eV in the angular range of $0^\circ \leq \Theta \leq 10^\circ$ [1].

In the present work the same apparatus has been used to study the charge transfer reactions of H^+ with H_2 ($\Delta E=1.83\text{eV}$), CO_2 ($\Delta E=0.19\text{eV}$), and N_2O ($\Delta E=-0.71\text{eV}$). Angular distributions as well as energy loss spectra have been measured for both the (in)elastically scattered protons and the charge transfer product H-atoms at a laboratory energy of 30eV and scattering angles up to 12° . For both endoergic systems (H_2 , CO_2) the results give clear evidence for a two step mechanism, in which the neutral target molecule is vibrationally excited by the strong interaction with the proton in the first part of the collision followed by charge transfer to the near-resonant vibrational states of the molecular ion in the second part. Nevertheless, an important difference should be pointed out between H_2 and CO_2 . The charge transfer process in $H^+ + H_2$ takes place by conversion of the vibrational excitation into electronic energy to overcome the large endoergicity. In contrast, in the only slightly endoergic $H^+ + CO_2$ system we observe a conservation of vibrational distributions, which for both CO_2 and CO_2^+ consists of predominant excitation of the asymmetric stretch mode ν_3 . The more exoergic $H^+ + N_2O$ charge transfer looks similar to CO_2 but there is some evidence that charge transfer may also occur in the incoming part of the collision.

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ROTATIONAL EXCITATION OF AMMONIA COLLIDING
WITH H₂ AND He.

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I) We have studied the ammonia absorption profile in the near infrared (6 μ m and 3 μ m) and far infrared using laser spectroscopy (diode and colour center lasers) and a FT spectrometer. We are interested by NH₃-H₂ and NH₃-He collisions with two aims :

- The study of interference effects in the infrared.
- The access to new experimental results at room and at low temperatures because there are relatively few measurements of lines broadening in the ν_4 band and the ν_3 band. More these systems have an astrophysical interest.

In the case of NH₃-He, the cross relaxation rates are found to be negligible. These results are different from NH₃-H₂. In this case the cross relaxation rates are larger. More we have put in evidence a vibrational effect (the results in the ν_3 band are different from the ν_4 band).

We have compared our experimental results to the calculation done by G. Billing. He has done extensive calculations of cross sections and the rate coefficients for rotational excitation of ammonia colliding with helium on ab initio potential energy surfaces. He has used a semi classical collision model. Our results are in a good agreement with his calculations.

The first results with the parahydrogen show that these cross-sections are 30% smaller from the normal hydrogen and are completely different from He. These results tremendous change the theoretical hypothesis. Indeed it has been currently admitted that the collisions with helium are the same than collisions with the parahydrogen.

II) We have undertaken time resolved infrared infrared double resonance using two tunable infrared laser. The pump laser is a high pressure CO₂ laser and the probe laser is a diode laser. Preliminary results are discussed here.

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State-to-State Vibrational Relaxation in ${}^1B_{2u}$ Benzene- d_6 Induced by Low Energy Collisions with He, H_2 , N_2 and Ar.

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Time-resolved dispersed fluorescence spectroscopy has been used to study very-low-energy collision-induced vibrational relaxation in ${}^1B_{2u}$ benzene- d_6 expanded in a supersonic free jet. Several expansion gases have been used to enable the rate coefficients for vibrational relaxation to be obtained as a function of collision partner in the very low energy collision regime. Benzene- d_6 is found to undergo vibrational deactivation with each of the chosen collision partners He, H_2 , N_2 and Ar. This study focuses on measuring state-to-state relaxation rates and branching ratios for vibrational relaxation from the S_1 vibrational level 6^1 ($\epsilon_{\text{vib}} = 498 \text{ cm}^{-1}$) to all energetically accessible S_1 vibrational levels, namely 10^1 ($\epsilon_{\text{vib}} = 454 \text{ cm}^{-1}$), 16^2 ($\epsilon_{\text{vib}} = 414 \text{ cm}^{-1}$), 11^1 ($\epsilon_{\text{vib}} = 382 \text{ cm}^{-1}$), 16^1 ($\epsilon_{\text{vib}} = 208 \text{ cm}^{-1}$) and 0^0 ($\epsilon_{\text{vib}} = 0 \text{ cm}^{-1}$) as well as two as yet unidentified channels. Argon and nitrogen are found to be most efficient collision partners ($\sigma_{\text{obs}}/\sigma_{\text{hs}} \sim 1-2$) in inducing relaxation, whereas hydrogen and helium are found to be an order of magnitude less efficient. The relaxation channels $6^1 \rightarrow 10^1$ and $6^1 \rightarrow 11^1$ are the dominant deactivation pathways for all the gases studied. The relative importance of other relaxation pathways changes with collision partner. There appears to be a light or small collision partner effect, whereby the propensity of transfer for the channel $6^1 \rightarrow 10^1$ ($\Delta\epsilon_{\text{vib}} = 44 \text{ cm}^{-1}$) seems to be redistributed among other channels, involving a greater energy or momentum gap, as the collision partner becomes lighter.

Scattering of High Vibrationally Excited Molecules: $\text{Li}_2(v \leq 21) + \text{Na}$

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A beam of vibrationally hot Li_2 -molecules with a vibrational state distribution with $v \leq 21$ has been generated via Franck-Condon pumping by use of an actively stabilized CW ring dye laser. After scattering from a secondary beam of Na atoms the remaining intensity in the forward direction in a specific vibrational state has been measured by laser induced fluorescence with a second ring dye laser. In this way it is possible to measure the integral total cross section as a function of the vibrational state. Since the collision time is longer than the vibrational period we are justified in assuming vibrationally adiabatic collisions in which the internuclear distance is given by the vibrational expectation value. The measured cross sections show a dramatic increase of the total state selective integral cross section of about 110% as the mean internuclear distance of Li_2 increases from 2.7 Å to 3.6 Å. This is to be compared with only 15% in analogous experiments on He and Kr [1]. The large difference in Na collisions is attributed to a transition from a weakly attractive van der Waals potential at small v to covalent Li-Na potential at high v . The use of linearly polarized light from the probe laser has made it possible to observe a large increase in the anisotropy of highly vibrationally excited molecules compared to the ground state molecules.

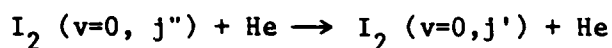
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State-to-State Rotational Excitation of I_2 in Collisions with He

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Our work has focused on the behavior of the state-to-state integral cross sections for the rotationally inelastic process:



where the initial distribution spans $j'' = 0-5$.

The apparatus incorporates two pulsed molecular beams, which cross at a variable intersection angle,^{1,2} and a laser-induced fluorescence detector. An intracavity etalon in the dye laser provides resolution sufficient to observe discrete I_2 rotational states.

We obtain data in two complementary experiments. First, the excitation probability for a final rotational state is $j' = 30, 52, \text{ and } 53$ over a collision energy range 25-225 meV. In addition, cross sections are determined as a function of the angular momentum transfer j , at a fixed collision energy E_0 . We show results for $E_0 = 75$ meV and $E_0 = 87$ meV.

Comparison of the data to a simple, classical rigid ellipsoid model allows for the extraction of an anisotropy of the repulsive character of the scattering potential energy surface.³ The anisotropy parameter, defined as the difference between the major and minor axes of the ellipsoid, has been determined to be 1.6 angstroms.

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RESTRICTED PHASE SPACE MODELS APPLIED
TO THE ENERGY DEPENDENCE OF ISOTOPE
BRANCHING IN $\text{He}^*(2^1\text{S}, 2^3\text{S}) + \text{HD}$ IONIZATION

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The usual phase space theory (PST) gives equal weight to all possible angular momentum vectorial combinations consistent with the conservation laws, while it is well known, for example, from the trajectory studies of Polanyi and coworkers that on a repulsive potential energy surface, combinations of L' (orbital) and J' (rotational) product angular momenta with L' antiparallel to J' are favored. We suggest that this represents one side of a coin whose reverse is the case of an attractive, angle-dependent surface that favors $L' \parallel J'$. Thus we can partition angular phase space into "attractive" and "repulsive" halves for which, if we take $m_{l'} > 0$, then $m_{j'} > 0$ and $m_{j'} < 0$, respectively. We refer to the attractive coupling as a slingshot model, in which the pebble (ejected atom) and slingshooter (remaining molecule) spin in the same direction. We apply full PST and both forms of restricted PST (RPST), in combination with a modified turning point model to predict the energy dependence of $\text{HeD}^+/\text{HeH}^+$ isotope branching in the ionization of HD by $\text{He}^*(2^1\text{S}, 2^3\text{S})$. Attractive RPST, the slingshot model, is found to give the best agreement with experiment, as suggested by the features of the HeH_2^+ potential energy surface.

NEAR RESONANT CHARGE EXCHANGE OF FAST MOLECULAR IONS WITH CESIUM: AN EXPERIMENTAL STUDY.

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In near resonant charge exchange (NRCE) collisions between keV molecular ions with Cesium atoms highly excited molecular states (I.P.= 3.8 eV) are formed. Using translational spectroscopy, as developed by De Bruijn and Los (1) we are able to study in detail all dissociative processes following the CE process. The kinetic energy release spectra have high resolution for ion optical standards and reveal information on the spectroscopy (position of the levels) and the dynamics (decay mode, lifetimes).

We will present data on the H_2^+/Cs system and the HeH^+/Cs and Mg systems and their isotopes. In NRCE of H_2^+ with Cesium vapor the $c^3\Pi_u$ state is one of the dominantly populated states. The $c^3\Pi_u^+$ (2) state decays via an allowed predissociation to the repulsive $b^3\Sigma_u^+$ state coupled by rotational coupling. The $c^3\Pi_u^-$ state is metastable and undetected in our experiments. We measured and calculated (within a pure precession model for the electronic coupling) the lifetimes of the first $c^3\Pi_u^+$ levels for H_2 (3), HD and D_2 . The lifetimes strongly increase with increasing mass.

In collisions of HeH^+ with Cesium Rydberg states of HeH converging to the stable HeH^+ ion are formed ($A^2\Sigma^+$, $B^2\Pi$ and to a less extent $C^2\Sigma^+$) (4). Coupling with the repulsive ground state of the (excimer) HeH molecule is the fate of all formed molecules. The experiments show the decay route of the populated levels to be predissociation for the A-, radiation for the B-state. The C-state decays via radiation for 3HeD and via predissociation for 4HeH . Calculations have been made using SCF-HF electronic wavefunctions and the Fermi Golden rule. These confirm the experimental results (5).

The NRCE collisions of HeH^+/Mg favors population of the repulsive ground state which enables a study of anisotropy in the HeH^+-Mg potential (He versus H forward). The results of these experiments will be shown on the conference.

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MAGNETIC DEFLECTION ANALYSIS
OF EXCITED ATOM BEAMS

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Spatially resolved Stern-Gerlach deflection patterns have been obtained for electronically excited, supersonic metastable beams of $\text{He}^*(2^3\text{S})$, $\text{Ne}^*(3s^3\text{P}_2)$, $\text{Ar}^*(4s^3\text{P}_2)$, $\text{Kr}^*(5s^3\text{P}_2)$ and $\text{Xe}^*(6s^3\text{P}_2)$. Electron impact excitation energy was varied between 100 and 400 eV, the magnet used was of the classic two-wire-field geometry,¹ and the detector was a cold Ta wire surrounded by a grounded shield and a pair of positively biased collector plates to remove stray surface Penning electrons. Mounted on a commercial motorized translation stage, the detector could be scanned ± 12 mm from beam center. For Ne^* through Xe^* , fine structure population ratios $^3\text{P}_2/^3\text{P}_0$ using three independent means of evaluating the deflection data were obtained as a function of electron energy. At 400 eV electron energy, the ratios are: $\text{Ne}^* - 3.35 \pm 0.2$; $\text{Ar}^* - 2.97 \pm 0.2$; $\text{Kr}^* - 6.05 \pm 0.8$; and $\text{Xe}^* - 2.75 \pm 0.2$. For all the metastables, the ratio declines by 20-40% as the electron energy is increased from 100 to 400 eV. The results are useful for analysis of non-state-selected scattering experiments and estimation of absolute laser-state-selection efficiencies, and the method shows promise for both state-selection and aligned-angular-momentum studies of metastable quenching collisions.

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INELASTIC AND REACTIVE SCATTERING OF EXCITED ALKALI ATOMS WITH O₂.

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Collisions of excited alkali atoms with O₂ have been studied both experimentally and theoretically.

On the experimental side, the cross section of the Na(4D+5S) collisional transfer has been measured in absolute values as a function of the collision energy using a crossed beam apparatus. Experimental results are also available on reactions of Na(4D) with O₂ giving NaO as product [1].

On the theoretical side, both inelastic and reactive channels have been included into a single model based on multiple crossings between curves describing the Na(n,l)-O₂, Na⁺-O₂⁻(X²Πg) and Na⁺-O₂⁻(A²Πu) system. Additionally, estimation of the excited ion pair surface Na⁺-O₂⁻(A²Πu) is provided.

Regarding the inelastic process, quantitative agreement is observed between the calculations and the experimental results for both the absolute value of the cross-section and its energy dependence. Similar agreement is found for another colliding system (Rb(7S+→5D)/O₂). This suggests that in spite of its approximations, the calculation model gives fairly reliable predictions for inelastic processes involving 4 eV electronic excited states [2].

The reactive cross section has been calculated as a function of several parameters: collision energy, impact parameters and approach geometry of the Na-O₂ system. The results have been sorted according to the reactive intermediate Na⁺-O₂⁻(X²Πg) and Na⁺-O₂⁻(A²Πu). Reaction via Na⁺-O₂⁻(X²Πg) has a very small cross-section and do not contribute efficiently to the reaction. The competition of the inelastic processes Na(4D)→n,l with the reaction via Na⁺-O₂⁻(X²Πg) is the essential reason for this channel to make such a small contribution to the reaction. Reaction via Na⁺-O₂⁻(A²Πu) seems to account for the experimental observations. This includes a high threshold energy for the reaction, and backward scattering of the NaO product with respect to the incoming Na atoms.

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 To appear in J. Chem. Phys.

QUANTUM-MECHANICAL STUDY OF FINE-STRUCTURE TRANSITIONS
IN COLLISIONS OF Rb(5^2P_j) WITH H₂ AND D₂

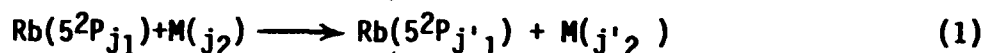
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Three-dimensional close-coupling quantum-mechanical calculations have been carried out for the processes



in which M is H₂ or D₂ in the $^1\Sigma_g^+$ ($v=0$) ground state and in a rotational level j_2 . The method treats M as a rigid-rotator /1/ and is a generalization of that developed for processes (1) when M is a structureless rare gas atom /2/. In this method, the three-body interaction describing the Rb-M system is expanded in a limited number of spherical harmonics if only the 5^2P configuration of Rb and a few rotational levels j_2 are considered. The expansion coefficients are determined from pseudopotential molecular-structure calculations /3/, leading to realistic adiabatic potential surfaces and the evaluation of the main nonadiabatic coupling terms involved during the collision. A space-fixed formulation of the scattering theory is used and the close-coupling calculations include the rotational levels $j_2=0, 2, 4$ and $j_2=1, 3$. The total cross sections for the level-to-level transitions (1) are determined in the energy range from thresholds up to about 0.3 eV. Good agreement between experiment /4/ and theory has been obtained /5/ for the $5^2P_{1/2} \rightarrow 5^2P_{3/2}$ transition in Rb.

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T_1 Barrier Height, $S_1 - T_1$ Intersystem Crossing Rate, and the
 S_0 Radical Channel Threshold of Formaldehyde

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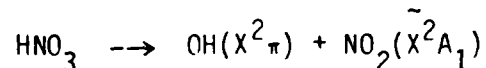
Vacuum UV Laser-induced fluorescence has been used to detect the atomic products in the photofragmentations of H_2CO , D_2CO , and $HDCO$. For the first time, the T_1 exit barrier height and the $S_1 - T_1$ intersystem crossing rate near the T_1 barrier top have been determined from sharp increases in the H/D branching ratio as well as the Doppler widths of the atomic transitions. The exit barrier height lies between 3.0 - 6.0 kcal/mol, and the intersystem crossing rate equals $4 \times 10^7 \text{ s}^{-1}$.

From the energy where the atomic fragment disappears, the threshold for the radical dissociation channel on the S_0 surface has also been measured with an unprecedented accuracy. For H_2CO the threshold energy is 86.42 ± 0.14 kcal/mol. The best values for the heat of formation and the C-H bond enthalpy of HCO radical derived from the threshold energies are 9.84 ± 0.18 kcal/mol and 15.84 ± 0.15 kcal/mol, respectively.

The highest level of ab initio calculation so far could not match the measured threshold energy within the uncertainties of either the experiment or the calculation.

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The photodissociation of nitric acid has been extensively studied. the quantum yield for the process



has been measured to be close to one.¹

Laser induced fluorescence measurements show that the OH(X²_π) is formed in the ground vibrational state with a peak in the rotational distribution around K=6.² Although the formation of OH(A²_Σ⁺) is thermodynamically allowed at this wavelength the threshold for this channel was found to be 147.5nm.³

Emission from electronically excited NO₂ was measured and found to extend down to 398nm, its dissociation limit. However this channel is believed to have a quantum yield of less than 0.5%⁴ The same authors observed the formation of electronically excited OH(A²_Σ⁺) via a two photon process in which the second step is postulated to be the secondary photodissociation of a low-lying triplet state of HONO.⁵

The crossed laser-molecular beam technique has been applied to the photodissociation of HNO₃ at 193 nm. The time-of-flight spectra of masses 17 (OH⁺) and 30 (NO⁺) reveal at least three different primary photodissociation channels. In addition the anisotropy parameter β will be determined.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under contract No. DE-AC-0376SF00098

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A TIME-RESOLVED FTIR EMISSION STUDY OF THE LASER PHOTOLYSIS OF CH_2CFCl at 193nm.

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The technique of time-resolved FTIR photofragment emission spectroscopy has been used to study the photodissociation of 1,1 chlorofluoroethylene at 193nm. Time-resolved interferograms are obtained by slaving a high repetition rate excimer laser to the moving mirror of the interferometer. This allows each point of the interferogram to be collected at the same fixed delay time relative to the pulsing of the laser. The time resolution is limited by the risetime of the infrared detector in use, typically between 3 - 20 microseconds. The sensitivity of the technique is sufficient to allow use of precursor pressures low enough to observe product rovibrational state distributions under collisionless conditions.

We have examined in detail the HF elimination pathway of the title photodecomposition. Nascent HF rotational and vibrational energy distributions have been obtained. The vibrational energy distribution in the first four excited levels of product HF are $V = 1/2/3/4 = 0.36/0.31/0.23/0.11$. The observed HF rotational distributions exhibit marked dynamical effects, with HF observed up to $J = 14$ and rotational temperatures in the range of 3000 K. A comparison of the rotational distributions in different vibrational levels indicates that a larger fraction of the remaining energy is partitioned into HF rotation in the higher vibrational levels. This result suggests that the rotational energy in the HF product is determined by the relative motions of the hydrogen and fluorine atoms at the time of HF bond formation.

Future experiments will consider the HCl elimination product and the branching fractions into other energetically allowed fragmentation pathways.

Product State Distribution and Spectroscopy of Half Collision Processes Studied by Vector Correlations.

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Vector correlations open a new area to study the dynamics of half collisions. Furthermore, the excited transition state just before the dissociation process can be characterized (e.g., geometry, symmetry), as well as the contribution of different dissociative states to the product state distribution.

Hydrogen peroxide has been optically excited at different wavelengths and the OH photofragment completely characterized by Doppler and polarization spectroscopy. The entire internal state distribution, translational energy, angular distribution, rotational alignment, and vector correlations between rotational (\vec{J}) and translational (\vec{v}) motions of OH products are measured. The (\vec{v}, \vec{J}) correlation was determined quantitatively from experimental data. In addition, the expectation values $\langle J_x^2 \rangle$, $\langle J_y^2 \rangle$, and $\langle J_z^2 \rangle$ were obtained, giving information about the origin of the product rotation.

The symmetry, geometry and lifetime of the excited H_2O_2 parent were determined. When hydrogen peroxide is excited at 193 nm the two electronic excited states, \tilde{A}^1A and \tilde{B}^1B , are involved in the dissociation process with a contribution of 60% and 40%, respectively. Information about microscopic reaction probabilities of coincident pairs is also obtained. This correlation between the rotational angular momentum of the two molecular fragments is obtained by high resolved Doppler profiles.

CN-fragment orientation produced in the photodissociation of ICN with circularly polarized light*

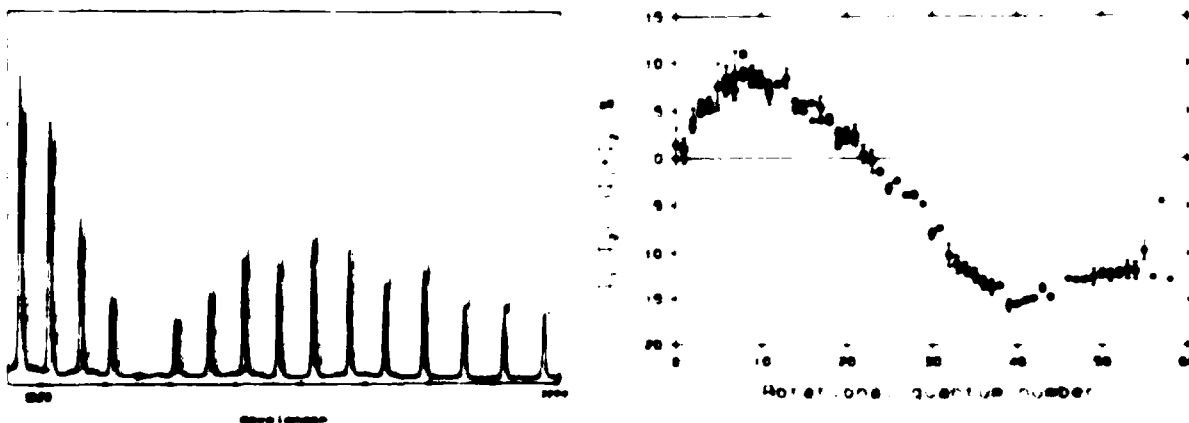
P5

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Using polarized light, detailed insights into the nature of photodissociation processes are achievable. In many studies linearly polarized light has been used to deduce the alignment of the photofragments and thereby the nature of the electronic states involved.

Using *circularly* polarized light even more information about the dynamics of the photodissociation process might be obtainable. We have performed an experiment whereby excimer laser light is circularly polarized and used to photodissociate ICN at 249 nm. The resulting $CN(X^2\Sigma^+)$ -fragment is detected using a pulsed dye laser which is also circularly polarized. The lasers are counterpropagating and define thereby a common quantization axis. A photomultiplier in a direction perpendicular to this axis observes the fluorescence. By changing the probe laser polarization from left- to right-hand circularity we obtain a pair of signals whose difference measures the orientation of the rotational angular momentum of the CN-fragment.

We see strong effects and remarkable variation with the rotational state. Particularly, low rotational states show an orientation in the opposite direction to that of the high states. This difference may well be related to the finding that low rotational quantum numbers are formed with excited $k(2P_{1/2})$, whereas high rotational states correlate with $l(2P_{3/2})$. For the fine-structure states in $v=2$ we find opposite orientation of these states. We conclude that our method promises new insights into the angular momentum recoupling which controls the branching between these exit channels.



Left Fig. $CN(X^2\Sigma^+, v=0)$ -spectrum around the band origin, showing the obtained signal for both circular probe polarizations. P- versus R-lines are showing opposite effects

Right Fig. Normalized signal differences for probing with left- or right-hand circular polarized light as function of the rotational quantum number. Diamonds: R-lines, open circles: P-lines (sign inverted).

* We wish to thank the National Science Foundation for support of this work under NSF-PHY 85-06668. E. H. thanks the Deutsche Forschungsgemeinschaft for support.

Rotationally and Vibrationally Resolved Final State Distributions in CO₂ Photofragments formed in the UV Photolysis of Pyruvic Acid

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Time domain absorption spectroscopy using a tunable infrared diode laser has been used to measure rotational and vibrational product state distributions in the 193 nm photofragmentation of pyruvic acid. Nascent vibrational population distributions have been obtained for ten vibrational levels in CO₂ (00⁰0), (01¹0), (02²0), (03³0), (04⁴0), (00⁰1), (00⁰2), (00⁰3), (01¹1), and (02²1). Approximately 97% of the CO₂ photofragments are formed directly in the vibrational ground state. The remaining CO₂ molecules are found to have with a significant degree of vibrational excitation, having mode temperatures of $T(v_2)=1800\pm 150$ K, $T(v_3)=3700\pm 1000$ K, and $T(v_2+v_3)=2000\pm 400$ K. These results suggest that the 193 nm photolysis proceeds through more than one dissociation channel and involves a number of different photofragments. Preliminary results at 248 nm show a similar partitioning of vibrational energy between the excited bending (v_2) and antisymmetric stretching (v_3) modes. We have also obtained rotationally resolved state distributions of the CO₂ photoproduct in the (00⁰0), (01¹0), and (02²0) vibrational levels. These results indicate substantial rotational excitation of CO₂, with broad distributions having peaks near $J=30$ (as compared with $J=17$ for CO₂ at 298 K) and significant rotational excitation beyond $J=60$. Preliminary results also indicate that rovibrationally excited CO photofragments are formed immediately following the 193 nm laser pulse.

Vibrationally Mediated Photodissociation of Hydrogen Peroxide

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Vibrationally mediated photodissociation is a means of studying the spectroscopy of bound vibrational overtone states and of probing the photodissociation dynamics of highly vibrationally excited molecules.¹ Highly vibrationally excited hydrogen peroxide molecules are prepared by initial excitation in the region of the third ($4\nu_{\text{OH}}$) or fourth ($5\nu_{\text{OH}}$) overtone of the OH stretching vibration. A second photon dissociates the initially prepared molecule and yields vibrational overtone excitation spectra of bound states. The rotational-vibrational states of the OH fragments are probed with laser induced fluorescence. The excitation spectra and product state distributions obtained provide information on the nature of the bound intermediate state and on the influence of the vibrational excitation on the dissociation dynamics. The coarse vibrational structure of the excitation spectra agree with a spectroscopic model that includes the torsional vibration.² For dissociation through the $4\nu_{\text{OH}}$ transition, 10% of the OH fragments are vibrationally excited, in contrast to direct ultraviolet photodissociation experiments that find no vibrationally excited OH. While only states having significant OO stretching character are efficiently dissociated by the second photon, the dissociation preserves some of the initial OH stretching vibration.

Vibrationally mediated photodissociation of hydrogen peroxide molecules cooled in a supersonic expansion³ allows study of vibrational states below the dissociation barrier without complications from thermal congestion.

¹T.M. Ticich, H.-R. Dubal, M.D. Likar, L.J. Butler, and F.F. Crim, *J. Chem. Phys.* (1987), submitted for publication

²H.-R. Dubal and F.F. Crim, *J. Chem. Phys.* **83** 3863 (1985)

³L.J. Butler, T.M. Ticich, M.D. Likar, and F.F. Crim, *J. Chem. Phys.* **85** 2331 (1986); 6251 (1986)

METASTABLE DECAY OF PHOTOIONIZED NIOBIUM CLUSTERS*

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The metastable decay of photoionized niobium clusters (Nb_n^+) has been observed in a newly constructed cluster beam machine. The decay manifests itself in the time-of-flight (TOF) mass spectrum as an asymmetric broadening of daughter ion peaks at the photoionizing laser photon energy from 3.5 to 5.6 eV. At 6.4 eV photon energy the asymmetric broadening is diminishingly small. Furthermore, the broadening is specific in the daughter ion cluster size in that it is very pronounced for some clusters but not as much for others. Several new experimental techniques have been developed to unravel the decay mechanism and its kinetics. The electron TOF spectrum consists of a single narrow peak (FWHM < 30 ns), eliminating the possibility of any delayed ionization process. The pulse ion extraction method has been developed to measure the decay rate constants and to establish the mechanisms of the fragmentation, evaporation and/or fission of the photoionized clusters. For example, at 5 eV photon energy it is found that within the experimental time window evaporation dominates for the smaller clusters ($n < 15$), whereas fission fragmentation becomes facile for $15 < n < 30$. The decay constants obtained all fall within $0.5 - 2.0 \times 10^6 \text{ sec}^{-1}$. By using the two-color, multiphoton technique the existence of long-lived intermediate states in the metal clusters ($n > 4$) has been clearly demonstrated for the first time. This result is in sharp contrast with general conjectures based upon the "vibronic soup" picture in describing the metal clusters. The details of the experimental results and their implications will be presented.

*Work supported by the U. S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under Contract W-31-109-Eng-38.

ENERGY-SELECTIVE ELECTRON-IMPACT IONIZATION IN A
MOLECULAR BEAM: APPLICATIONS TO VIBRATIONAL OVERTONE
SPECTROSCOPY AND UV PHOTODISSOCIATION STUDIES

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We have developed new techniques to study vibrational overtone spectroscopy and ultraviolet photodissociation processes in molecular beams using energy-selective electron-impact ionization. We will describe our versatile molecular beam apparatus which incorporates a pulsed, low-energy electron gun and a time-of-flight mass spectrometer.

Using this apparatus we have observed the (301)-(000) transition in water by energy-selective electron-impact ionization of the overtone-excited molecules. This demonstrates a new technique that may be generally applicable for detecting vibrationally excited molecules in molecular beams.

Energy-selective electron-impact ionization is also useful for detecting photodissociation products in the presence of large quantities of parent molecules. Our time-of-flight mass spectrometer allows us to identify primary photofragmentation pathways and measure translational energy distributions of the neutral photofragments. Results from the ultraviolet photodissociation of ethyl iodide illustrate this technique.

TWO COLOR VIBRATIONALLY MEDIATED PHOTODISSOCIATION
OF NITRIC ACID

P10

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The study of molecular photodissociation has recently attracted considerable interest from both experimentalists and theorists¹. Because photodissociation is a process in which the initial conditions are defined accurately, a thorough study of these "half" collisions offers excellent insight into more complicated collisional processes.

One important aspect of the photodissociation process that needs to be explored further is the effect of vibrational excitation. We present the first results on the photodissociation of highly vibrationally excited molecules using photons of two different wavelengths. In these two-color experiments, one photon excites a vibrational overtone transition and a second photon, of a different wavelength, promotes the vibrationally energized molecules to a dissociative electronic state. We have applied this two-color vibrationally mediated photodissociation scheme to nitric acid (HONO_2) by using the third overtone of the OH stretching vibration ($4\nu_{\text{OH}}$) to deposit the initial energy and a second photon (355 nm) to dissociate the energized molecule. A third laser monitors the dissociation process by laser induced fluorescence on the A-X transition of the OH photofragment. The present results on nitric acid² in conjunction with our earlier work on hydrogen peroxide² illustrate the potential generality of using vibrational overtone excitation as a preparative first step for investigating photodissociation of vibrationally excited molecules.

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Theory of Electronically Inelastic Infrared Multiphoton Processes

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We have implemented a generalization of an eikonal treatment of photodissociation¹ of polyatomics to treat polyatomic Infrared Multiphoton Excitation and Dissociation (IRMPE and IRMPD) processes. In the Self-Consistent Eikonal Method (SCEM)², a common eikonal wavefunction ansatz is employed leading to selfconsistent "electronic plus nuclear" dynamics in terms of Hamilton's equations in electronic amplitude as well as nuclear position and momentum variables.

The treatment of few photon IRMPE processes is best done by employing the electron-field representation, where the SCEM amplitude equations will directly yield time-dependent populations of specified IR frequency-dressed states, representing dynamical evolution of selective multiphoton absorption. Dissociative levels of excitation (IRMPD) involving several dozens of photons and incoherent absorption are readily modelled by employing a driving-field semiclassical representation of the radiation field that forces the SCEM electronically inelastic Hamiltonian dynamics. Trajectories of an electronically nonadiabatic driven field model system show dramatic effects when contrasted with the equivalent electronically adiabatic limiting case trajectories compiled earlier by Martin and Wyatt.³

This work was supported by NSF under grant number ISI-8560163

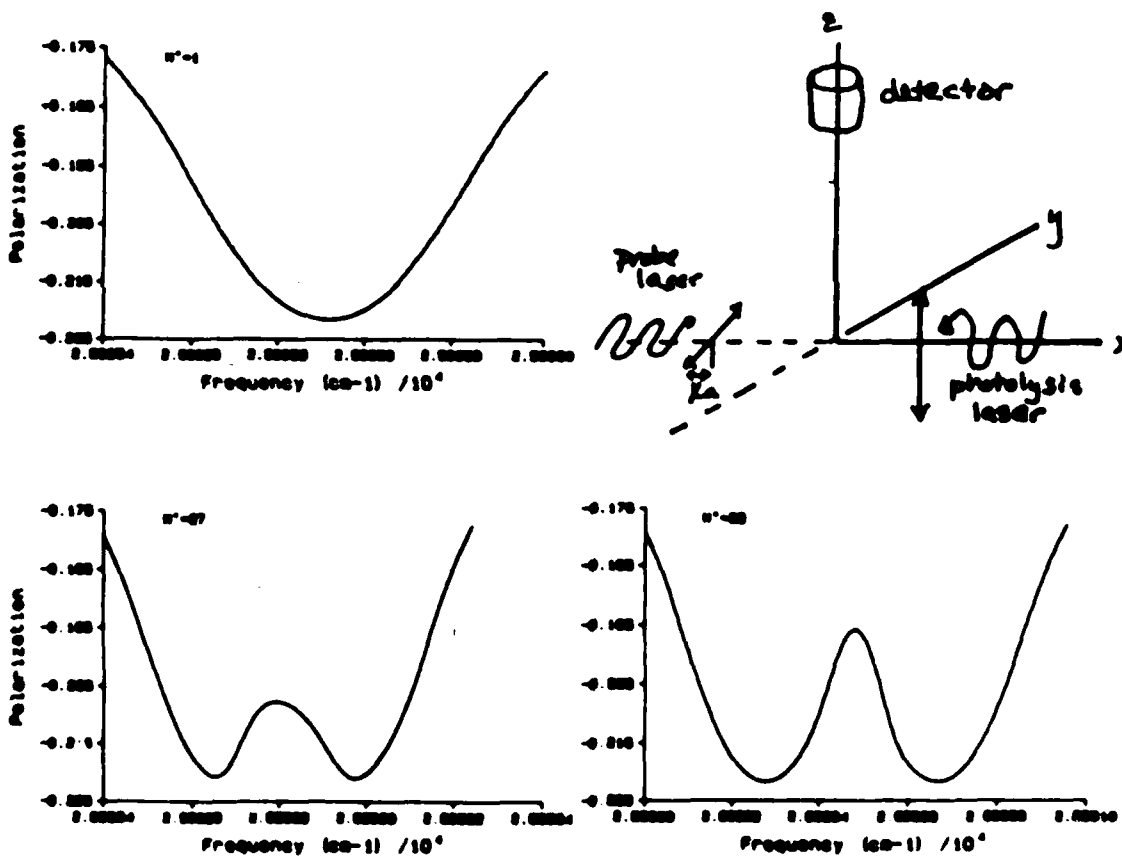
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Photodissociation of ICN at 249 nm : Correlation between \underline{v} and \underline{J} in the CN photofragment, *J.R.Waldeck, E.Hasselbrink and R.N.Zare, Stanford University--When dissociating a triatomic molecule, one expects the rotational angular momentum, \underline{N} , to be opposed to the orbital angular momentum (therefore perpendicular to \underline{v}) as the primary dissociative force (impulse between I and CN) is in the plane of the molecule. However, it seems that out-of-plane forces, are necessary to explain the fine-structure populations which are observed for the CN photofragment.¹ We investigate the correlation between \underline{v} and \underline{J} by measuring variation in polarization $\{P = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp})\}$ across Doppler-broadened CN rotational lines. Examining correlations such as those between \underline{v} and \underline{J} may help to elucidate the nature of angular momentum recoupling or the role or nonadiabatic effects during dissociation.

Shown below is the expected variation of polarization across the CN (X^2I^+) rotational line profile. The simulation is done assuming a parallel transition, \underline{v} perpendicular to \underline{J} , and the experimental geometry shown :



* We wish to thank the National Science Foundation for support of this work under NSF PHY 85-06668.

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PHOTOFRAGMENT SPECTROSCOPY OF IRON CARBONYL AT SEVERAL
PHOTOLYSIS WAVELENGTHS

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The photofragmentation dynamics of $\text{Fe}(\text{CO})_5$ has been studied under molecular beam conditions, using vacuum ultraviolet laser-induced fluorescence to detect the CO photofragments. Using this technique we have determined the detailed energy release (vibrational, rotational, and translational) for 193, 249, 266, and 351 nm photolysis wavelengths.

At all photolysis wavelengths, the product energy distributions are Boltzmann-like, with all degrees of freedom showing the same behaviour. These results can be described by a fully statistical model for the photofragmentation, in which the photolysis photon energy is completely randomized in the parent $\text{Fe}(\text{CO})_5$ molecule before any dissociation occurs. Fragmentation then occurs by sequential CO loss, with the energy release in each step being fully statistical. This mechanism is independent of photolysis wavelength.

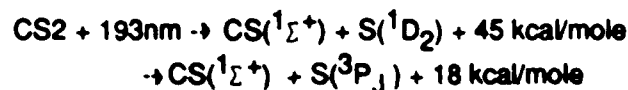
We have carried out calculations using a microcanonical statistical model based on the postulated mechanism. In these calculations literature values for bond energies and vibrational frequencies were used, without adjustment, and all modes were included. The agreement between the calculated and measured $\text{CO}(v,J,T)$ distributions was excellent at all wavelengths, which we interpret as being conclusive proof that our statistical model is correct.

In this poster, both experimental and theoretical results will be presented. A preliminary report of these results (for 193 nm only) has already been published [J Phys Chem **91**, 506 (1987)]

PHOTOFRAGMENT SPECTROSCOPY OF CS₂: DIRECT RESOLUTION OF SINGLET AND
TRIPLET DYNAMICS

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The photofragmentation dynamics of CS₂ at 193nm has been studied under supersonic molecular beam conditions, using vacuum ultraviolet laser-induced fluorescence spectroscopy (VUV LIF) to detect the atomic S photoproducts. We have used the VUV LIF method to study the photofragmentation of metal carbonyls¹, and it has been described previously^{1,2}. The 193nm photolysis of CS₂ yields the following:



where the first reaction is the singlet channel, and the second reaction is the triplet channel. By directly detecting the S atom products under collision free conditions, the branching between these two channels has been determined to be triplet/singlet = 2.8, thus resolving a long-standing controversy in the literature.

The high resolution of our VUV detection system enables us to measure the translational energy distribution and recoil velocity angular distribution by Doppler spectroscopy. As the S(³P_J) and S(¹D₂) products are detected separately, this method also unambiguously resolves the singlet and triplet dissociation dynamics. These results will be discussed in terms of the detailed photofragmentation mechanism for CS₂.

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PHOTOFRAGMENTATION DYNAMICS OF H₂S AT 193, 222 AND 248 nm: DIRECT
PROBING OF ROTATIONAL EXCITATION IN SH($\nu=0,1$)

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The nascent rotational distribution of the SH($X^2\Pi_{3/2}, v=0$) fragment following photodissociation of H₂S at 193, 222 and 248 nm has been measured by laser induced fluorescence (LIF). Additionally, the SH($X^2\Pi_{3/2}, v=1$) fragment has been directly probed for the first time by LIF following photodissociation of H₂S at 193 and 222 nm. In all cases, the rotational distributions can be characterized as Boltzmann, with only a small percentage of the the total available energy appearing as rotation in the SH photofragment. Previous experiments suggest that approximately 90% of the total exoergicity is partitioned into the translational degrees of freedom of the photofragments.^{1,2} In our experiments, the rotational lines arising from SH($X^2\Pi_{3/2}, v=0$) show Doppler broadening consistent with that observation. However, the rotational lines originating from SH($X^2\Pi_{3/2}, v=1$) are considerably narrower. The possibility of two distinct dissociation channels is discussed.

[†] NRC/NRL Postdoctoral Research Associate

W. G. Hawkins and P. L. Houston, *J. Chem. Phys.* **73**, 2481 (1976); **76**, 2487 (1982);
J. N. A. van Veen, K. A. M. Brion, G. J. Brode, and A. E. DeWitt, *J. Chem. Phys.* **74**, 1011 (1981).

PHOTOPHYSICS AND PHOTOCHEMISTRY OF H₂S AT 157 nm

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Irradiation of H₂S at 157 nm leads to three experimentally observed photophysical and photochemical processes. First, prompt emission in the wavelength region 320-360 nm is attributed to the direct photochemical production of SH(A²Σ). Second, structured vacuum ultraviolet (VUV) emission in the wavelength region 155-190 nm is most likely due to fluorescence from the lowest lying Rydberg state of H₂S, which is accessed by absorption of a 157 nm photon. The spacing between bands in the VUV emission is consistent with vibrational spacing of the bending mode (ν_2) of ground state H₂S, suggesting a quasi-linear geometry for the Rydberg state. Finally, SH(X²Π_{3/2,1/2}) produced by 157 nm photodissociation is probed by laser induced fluorescence (LIF). No SH(X²Π_{3/2,1/2}, v=0) is produced promptly, but is detected within 200 ns. The origin of this photoproduct is discussed.

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MULTIPHOTON DISSOCIATION OF ORGANOMETALLIC NITROSYLS

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Abstract

The mechanism of dissociation of organometallic nitrosyls is assessed by studying the state distributions of the NO photofragments. The nascent NO population is probed both in the 450-520 nm region by [2+2] MPI and in the 220-225 nm by [1+1] MPI. The fragment distributions are found to depend on the competition between multiphoton excitation and metal-ligand dissociation. In the visible, the first factor dominates resulting in a highly nonstatistical rotational distribution, which is very similar for all compounds studied. In the U.V., the experimentals can be performed at low laser power densities. In this case, intramolecular energy transfer is favored, and the fragment is characterized approximately by statistical state distribution. In all cases, high rotational excitation is observed, indicative of dissociation from a bent metal-nitrosyl potential surface.

THEORY OF DIATOMIC PHOTODISSOCIATION TO OPEN SHELL ATOMS IN THE PRESENCE OF AN EXTERNAL MAGNETIC FIELD

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The theory of diatomic photodissociation in the presence of a magnetic field is developed from the generalized theory of diatomic photodissociation of Singer et al.^{1,2} by incorporating the magnetic interactions and by decoupling the asymptotic Hund's case e states. The external magnetic field is predicted to produce several novel effects on the photodissociation of a heteronuclear diatomic molecule dissociating to open shell fragments, in part, because the magnetic field makes the total angular momentum J no longer a good quantum number and also because it lifts the asymptotic degeneracies of the fragment magnetic sublevels. Thus, the magnetic field may couple nearby resonances of different total J that are noninteracting in the absence of the field, while other resonances may be broadened by coupling to states of different total J in the continuum. The lifting of the fragment magnetic sublevel degeneracies imparts an orientation to the photofragments, which can be determined by kinematics and knowledge of the initial bound state. When only a single fragment magnetic channel is open asymptotically, it is shown that the near threshold photodissociation provides a means of producing polarized atomic beams. The effects of magnetic fields on resonances in the near threshold dissociation of CH^+ are studied to illustrate the theory and to show changes in the relative orientation of fragments in passing through resonances.

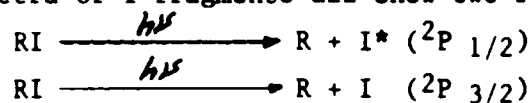
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PHOTOFRAGMENTATION OF ALKYL IODIDES — Photofragmentation
Channels and Energy Partitioning of the Fragments

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Xian Zhong, Yuhui Huang, Wanquan Fang and Xiaojun Wu

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Studies on the photofragmentation of CH_3I , $\text{C}_2\text{H}_5\text{I}$, $n\text{-C}_3\text{H}_7\text{I}$, $\text{iso-C}_3\text{H}_7\text{I}$ and $t\text{-C}_4\text{H}_9\text{I}$ have been carried out using our newly-built photofragment spectrometer with rotatable molecular beam source. The pulsed molecular beam is crossed with KrF (248nm) laser beam. TOF spectra of I fragments all show two reaction channels,



The obtained channel ratios I^*/I are 3.0, 2.4, 1.6, 1.0 and 1.3, respectively.

The bond dissociation energy $D_{\text{C-I}}$ for CH_3I and $\text{C}_2\text{H}_5\text{I}$ are determined to be 55.0 ± 0.5 and 55.3 ± 1.0 Kcal/mol, respectively, according to the highest translational energy release in I^* channels.

The internal excitation E_{int} of alkyl fragments R has been determined by energy balance. The fraction of available energy E_{avl} going into E_{int} of R, $E_{\text{int}}/E_{\text{avl}}$, are

Channel	CH_3I	$\text{C}_2\text{H}_5\text{I}$	$n\text{-C}_3\text{H}_7\text{I}$	$\text{iso-C}_3\text{H}_7\text{I}$	$t\text{-C}_4\text{H}_9\text{I}$
I^*	0.12	0.32	0.49	0.63	0.71
<u>I</u>	<u>0.17</u>	0.39	0.57	0.64	0.73

These values agree to direct impulsive model of unimolecular decomposition and most of them are close to the "soft" radical limit.

The underlined results are quite different from those given by other laboratories.

Discussions of the results have been also given.

THE PHOTODISSOCIATION OF HO₂
 AN INSIGHT BASED ON AB-INITIO ELECTRONIC STRUCTURE CALCULATIONS

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The photodissociation of the hydroperoxyl radical is discussed based on MRD-CI electronic structure calculations. A previous study⁽¹⁾ based on a cut of the potential energy surfaces along the O-OH coordinate is broadened by also considering cuts along OO-H and Θ which permit a wider and deeper insight into process.

The absorption of light is analyzed based on the calculated vertical excitation spectrum and oscillator strengths for transitions from the ground to the lowest excited states. This permits to pinpoint the photoexcited species. Its subsequent evolution is examined in light of the data provided by the curves, i.e., shape, interactions and correlations of the electronic states along the fragmentation pathways. This information enables one to visualize diverse fragmentation mechanisms. Further theoretical arguments together with experimental data are then used to establish feasibility criteria for the various possibilities.

The photodissociation of HO₂ in the range of excitation energies $5 < \Delta E < 6.4$ eV appears to proceed as follows: upon light absorption the system is promoted, via a Franck-Condon transition, to the ²A"(1a"→2a") excited state, the only species with a sizeable oscillator strength. Once on the excited state surface, HO₂^{*} (²A") may dissociate either into O + OH or O₂ + H, both instances being permitted from the energetical viewpoint; yet, ²A" is repulsive along O-O and bound along O-H, so the former is the viable dissociation channel. There remain two fragmentation possibilities OH(X²Π) + O(³P) and OH(X²Π) + O(¹D); according to the curves O(³P) is produced in the adiabatic process, whereas the non-adiabatic one yields O(¹D). Arguments are presented which indicate the dissociation proceeds diabatically on the surface of the initially populated ²A" state yielding O(¹D), so providing an explanation of the experimental findings.

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THE p-DIFLUOROBENZENE-Ar VAN DER WAALS COMPLEX. VIBRATIONAL PREDISSOCIATION AND IVR.

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The S_1 p-difluorobenzene-Ar (pDFB-Ar) complex has been characterized by fluorescence excitation spectra and by fluorescence spectra after pumping each of twelve S_1 vibrational levels ranging up to $\nu_{16} = 1250 \text{ cm}^{-1}$. The fluorescence spectra variously contain structure from the initially pumped complex level, other complex levels, and the pDFB monomer. In some cases, additional fluorescence spectra were obtained from pumping the Ar-ring stretch. Vibrational predissociation (VP) was probed by exciting the complex to the vibrational levels higher than the complex dissociation energy and observing the final states of pDFB monomer after dissociation. VP characterizes seven of the excited levels consisting of six different vibrational modes. In every case, VP is highly selective with respect to the "product" states in S_1 pDFB monomer. It appears that VP time scales are generally in the nsec range but vary modestly for different initial modes. IVR within the S_1 complex occurs from a few of the initial levels and is highly sensitive to the initial level identity.

Time- and State-Resolved Studies of Vibrational Predissociation
of Weakly Bound Molecular Clusters

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ABSTRACT

Experimental measurements of the complete product state distributions and predissociation lifetimes of vibrationally excited nitric oxide dimer are described. Single-quantum excitations of the symmetric (ν_1 , 1870 cm^{-1}) and antisymmetric (ν_4 , 1789 cm^{-1}) NO stretching fundamentals produce fragments which carry away most ($\sim 80\%$) of the available energy as kinetic energy. Interestingly, there is a significant difference in the fragment spin-orbit state distributions observed following excitation of these two modes. Picosecond laser pump-probe experiments reveal a dramatic mode-specific effect: excitation of the ν_4 mode leads to a 39ps predissociative lifetime, while excitation of the higher energy ν_1 mode initiates a much less efficient predissociation, with a lifetime of 880ps.

Predissociation dynamics of methyl iodide clusters

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We have measured the u.v. direct absorption spectra of jet-cooled methyl iodide in its valence (A) and Rydberg (B,C) states. The formation of methyl iodide dimers results in several changes to the observed spectra. A significant blue shift (500 cm^{-1}) is seen in the purely dissociative valence state upon when methyl iodide dimers are present in the jet. The Rydberg states are not significantly shifted with respect to the ground state upon dimer formation. However, we observe splittings in the origin bands, very different relative intensities in the main progression and "new" modes, not seen in the monomer spectrum. These observations are all explained by a solvent-induced shift in the position of the predissociative surface crossing of the A-state with B and C. This shift slows the predissociation, allowing vibronic states which are rapidly dissociating in the monomer to become visible in the dimer. Similar effects are observed in clusters of acetone.

Methyl iodide clusters higher than the dimer exhibit a strong continuum beneath the B-state and interferences between this continuum and the main progression. This effect is observed for methyl iodide clustered with itself and with rare gases (Ar, Kr, Xe). It may be due to an excitation of exciton-type states in the higher clusters.

State-to-State Measurements of the Vibrational
Predissociation Dynamics of HeCl_2

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Abstract

Well resolved state-to-state data are reported for the vibrational predissociation of specific rotational levels of $\text{HeCl}_2(\text{B})$ with 8 vibrational quanta in the Cl-Cl stretching mode. The state resolution is sufficient to clearly reveal the symmetry constraints on the dynamics. The product rotational state distribution has two distinct maxima separated by a node which implies the existence of either a rotational rainbow or quantum interference in the product channels. "Parity-selected" excitation spectra are obtained which reduce spectral congestion and aid in the assignment of individual rovibronic transitions.

Direct Measurement of the Vibrational Predissociation
Lifetime of NeBr_2 in the Ground Electronic State

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Abstract

The vibrational predissociation lifetime of NeBr_2 in the ground electronic state with one vibrational quantum in the halogen stretch was measured directly in a free jet expansion. $\text{NeBr}_2(X, v=1)$ was detected by optical-optical double resonance to monitor the population as a function of distance from the nozzle to the laser interaction region. The vibrational predissociation lifetime for $\text{NeBr}_2(X, v=1)$ was determined to be $8 \pm 3 \mu\text{s}$. The results are compared to previous studies of $\text{Br}_2(B)$ using the energy gap model.

STATE SELECTIVE PHOTOFRAGMENTATION OF ICl-Ne VAN DER WAALS
COMPLEXES

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The vibrational predissociation dynamics of ICl-Ne van der Waals complexes has been investigated for a series of vibrational levels in the $A(^3\Pi_1)$ state manifold. Visible laser excitation prepares the complexes in selected rovibrational levels in the A state. Coupling of the vibrational excitation, initially localized in the ICl bond, to the weak van der Waals bond results in predissociation of the complex. Fragmentation proceeds with the loss of one or two quanta of ICl vibrational energy. The nascent rotational/vibrational distribution is probed by excitation of the ICl A state photofragments to an ion pair state. The product state distribution reflects the dominant features of the reaction pathway and provides an important key to understanding the reaction mechanism.

By initially populating different vibrational levels in the complex, the energetics and lifetime of the predissociation can be selectively altered. Detailed product state distributions will be presented for dissociation of ICl-Ne from A state vibrational levels with predissociation lifetimes ranging from nanoseconds¹ to a few picoseconds. Analysis of results will be discussed in the context of statistical theories of photodissociation and inelastic scattering theories.

¹J.C. Drobits, J.M. Skene and M.I. Lester, *J. Chem. Phys.* **84**, 2896 (1986).

RESONANT PHOTOIONIZATION SPECTROSCOPY OF REFRACTORY METAL-
RARE GAS COMPLEXES

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The weakly attractive interatomic potential between a refractory metal and a rare gas atom is explored by direct spectroscopic access of rovibronic levels in the AlAr van der Waals complex. Mass-resolved resonance-enhanced multiphoton ionization is used to probe the spectral region about the Al $^2S_{1/2} - ^2P_{1/2}$ transition. A vibrational progression in the AlAr $^2\Sigma^+$ state is identified on the AlAr $^+$ mass channel. Lower limits for binding energies in the X $^2\Pi_{1/2}$ and B $^2\Sigma^+$ states are found to be 133 and 373 cm^{-1} , respectively. Results are compared to earlier work on NaAr.

PHOTODISSOCIATION DYNAMICS OF ICl-RARE GAS COMPLEXES IN THE B³Π₀₊ STATE

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The unimolecular dissociation dynamics of ICl-He and ICl-Ne van der Waals (vdW) complexes in the B ³Π₀₊ state is examined at the state-to-state level of detail through optical-optical double resonance methods. The vdW complex is prepared in the B state with 2 or 3 quanta of vibrational excitation in the ICl stretching mode. Vibrational predissociation is monitored by subsequent excitation of ICl photofragments on B(vg)-B(vg=1,2) transitions. The predissociation dynamics, evolve on a nanosecond timescale, yet result in highly peaked, nonstatistical ICl rotational product state distributions. The nascent rotational distributions are compared with statistical theories and models of inelastic scattering.

Production of $C_2H_4Cl^+$ by Photoionization of the
Weak Complex $C_2H_4:HCl$

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The photoionization efficiency (PIE) spectrum from 10 to 1200 Å for production of the ion $C_2H_4Cl^+$ from the products of room-temperature jet expansions of a 1:4 mixture of C_2H_4 and HCl was measured at several nozzle pressures. Careful analysis of the jet expansion products was then used to resolve the PIE spectrum for the process



from the spectra for the production of $C_2H_4Cl^+$ from trimers and larger clusters. The spectrum for rxn 1 is dominated by two peaks; at 15.2 eV, sharply cut off on the high-energy side and skewed to lower energies, and at 17.4 eV, broad. Facts significant to understanding the lower-energy peak are: (1) in free HCl there are two overlapping progressions of strong, autoionizing Rydberg lines in the region; (2) the abrupt drop-off that forms the high-energy side occurs very near the energy at which the Cl atom becomes unbound from product $C_2H_4Cl^+$ (15.1 eV). The first onset of $C_2H_4Cl^+$ occurs at 12.40 ± 0.15 eV, while the true threshold is at 11.17 eV. This substantial difference, 28 kcal mol⁻¹, is caused by the large change in geometry between the complex and the product. The complex has a perpendicular structure in which the chlorine atom is distant from the C_2H_4 plane with the H atom intervening, while the product has the Cl atom sigma-bonded to a carbon atom. The energy of the first onset is only a little lower than the ionization potential of free HCl (12.75 eV), and nearly the same as the photoionization threshold of the 1^2B_{2g} state of $C_2H_4^+$ from free C_2H_4 . On the other hand, the next higher obvious onset, at 14.2 eV, does not correspond to any state of HCl^+ , but is very close to the photoionization threshold of the 1^2A_g state of $C_2H_4^+$. Therefore, which moiety serves as chromophore depends sensitively on photon energy. Reaction 1 cannot be statistical as observed because the energies needed to dissociate $C_2H_4:HCl$ into $C_2H_4 + HCl$ and $C_2H_5Cl^+$ into $C_2H_4^+ + HCl$, ~ 3 and 5 kcal mol⁻¹ respectively, are very much smaller than the 4 eV needed to break a C-H or Cl-H bond. Consequently the latter process cannot compete detectably with the former in a statistical mechanism. The partitioning of energy between translation and excitation is not known, except that the excitation of product $C_2H_4Cl^+$ stable enough to be detected is unlikely to exceed 3.9 eV.

Work done at Brookhaven National Laboratory under contract DE-AC02-76CH00016 with the U. S. Dept. of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

Vibrational and rotational wave functions for He...Cl₂, Ne...Cl₂ and Ar...Cl₂
and

A three dimensional quantum mechanical study
of Ne...Cl₂ vibrational predissociation

by

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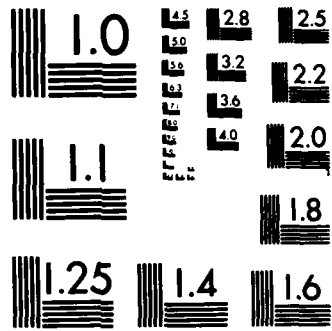
Abstract

We present calculations that form a basis for understanding the structure, spectroscopy and dynamics of the van der Waals molecules He...Cl₂, Ne...Cl₂ and Ar...Cl₂. Using realistic model intermolecular potentials, we have calculated vibrational wave functions for the modes associated with the van der Waals degrees of freedom. Pictorial representations of these wave functions show the excitations of the bending and the stretching motions of the weak bond. The energy levels obtained are used to check the validity of one dimensional model potentials for the stretching coordinate, while calculations for different total angular momentum allow comparison with rigid rotor models.

As for the dynamics, we present detailed three dimensional quantum mechanical calculations for vibrational predissociation of the Ne...Cl₂ van der Waals complex and compare the results with experiments. Two processes have been studied:

- i) Ne...Cl₂(X, v = 1) → Ne + Cl₂(X, v = 0), and
- ii) Ne...Cl₂(B, v = 11) → Ne + Cl₂(B, v = 10, 9),

where *v* denotes the vibrational quantum number of Cl₂ while X and B specify electronic states of Ne...Cl₂ which correlate with the X¹Σ₀⁺ and B³Π₀⁺ states of the free Cl₂ molecule respectively. The calculations provide lifetimes and final rotational state distributions of the Cl₂ fragments. The effects of exciting the van der Waals bending mode and the overall rotation of the complex have also been studied.



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

NEAR INFRARED LASER SPECTROSCOPY OF NITROUS OXIDE DIMER

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The optothermal detection method has been used to obtain a sub-Doppler resolution infrared spectrum of $(\text{N}_2\text{O})_2$. This spectrum has been assigned and fit to obtain an accurate set of rotational constants. Spin statistics associated with the centro-symmetric structure are easily discerned in the spectrum. Comparisons between the experimental structure and those predicted from an empirical potential surface for $(\text{N}_2\text{O})_2$ are given.

Poster Session

High Resolution 193nm Laser Photofragmentation Time of
Flight Mass Spectrometric Study of CS₂ and CS₂ Clusters

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Abstract:

High resolution time-of-flight (TOF) spectra for CS and S produced by the process $CS_2 + h\nu(193 \text{ nm}) \rightarrow CS(X,v) + S(^3P \text{ or } ^1D)$ have been measured using a rotating beam source laser photofragmentation TOF mass spectrometer. Structures corresponding to the formation of $CS(X,v=0-5) + S(^1D)$ are resolved. The production of S^+ from CS fragments by electron impact at electron energies $<50\text{eV}$ is found to be insignificant. The product kinetic energy distribution derived from the TOF spectra of CS and S are in agreement, indicating that the further dissociation of the CS fragment due to the absorption of a second photon within the laser pulse is not important. The product kinetic energy distribution is consistent with the conclusion of previous laser induced fluorescence experiments ^{1,2} (that the $^3P:^1D$ branching ratio is 2 and that the vibrational population of CS is peaked at $v=3$).

Time-of-flight spectra for photofragments originating from CS₂ clusters reveal that $(CS_2)_n$, $n>1$, formed in the process $(CS_2)_{n+1} + h\nu(193\text{nm}) \rightarrow CS + S + (CS_2)_n$, acquire only a small amount of kinetic energy.

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Dynamics of Collisional Energy Flow in Weakly Bound Complexes

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ABSTRACT

Collisional energy transfer dynamics in weakly bound complexes is studied at collision energies above and below the fragmentation threshold in classical mechanics. The collinear collision of a linear complex $C \cdots B-A$, where C is an atom or a diatomic molecule, with an incident atom is considered. For the collision energy range 0.01 - 10 eV, energy transfer to the complex is efficient, and essentially all of the energy transferred to the complex is localized in the bond. The energy initially stored in the molecular bond remains in it when the collision is over, and the bond gains essentially no energy from translation. The collision model is formulated such that the incident atom hits the outer atom A of the molecular unit $B-A$, so the efficient energy build-up in the weak bond indicates an easy flow of energy across the stiff molecular bond from the initial impact region. Energy flows from the molecular bond to the weak bond through a sequence of energy gain-loss steps on a subpicosecond time scale.

VIBRATIONAL PREDISSOCIATION OF THE He-I₂-Ne COMPLEX.
APPROXIMATE QUASICLASSICAL AND QUANTAL CALCULATIONS.

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We study the dynamics of vibrational predissociation of the He-I₂ (B, v=28)-Ne cluster. As it is well known, a full quantal treatment of the four-body system becomes prohibitively difficult. Hence, we simplify the problem by assuming a configuration in which the iodine molecule remains perpendicular to a plane containing the rare gas atoms, accounting for the iodine stretching, the He and Ne vibrations, and also the oscillation in the angle formed by both weak bonds. This is a realistic configuration since, for each isolated X-I₂ complex (X=He, Ne) the perpendicular situation is the more stable. Moreover, there is a large difference between the rotational constants of I₂, Ne-I₂ and He-I₂, 0.04, 0.05 and 0.30 cm⁻², respectively, on one hand, and the stretching frequency of He-Ne, 10 cm⁻¹, on the other hand.

Now, we apply a quasiclassical trajectory method (QCT) close to that previously used¹. According to a total energy equal to the iodine vibrational energy plus the quantal ground energies corresponding to He-Ne and perpendicular He-I₂ and Ne-I₂, the necessary initial conditions are randomly selected. The relevant Hamilton equations are then numerically integrated and the distribution of non-dissociated trajectories is fitted to an exponential law of decay providing us the total rate of dissociation of the complex.

Also, after using a diabatic approximation to describe the iodine vibrations, we solve the resulting effective tri-atomic problem within an adiabatic angular framework³, obtaining angular-dependent ground energies of the complex and associated rates⁴ that are finally averaged on the angular motion.

We present in Table I a comparison between quasiclassical and quantal results, showing the good agreement of these approximate treatments. Also, from the quantal partial rates, the lower stability of the stronger van der Waals bond in the complex may be noted.

Table I	ETOT	θ -range	Γ_{He}	Γ_{Ne}	Γ_{TOT}
=====	(cm ⁻¹)	(degrees)	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)
QCT	[-93.5, -94.7]	[40, 70]			0.55
Quant.	-93.97	[41, 65]	0.23	0.46	0.69

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VIBRATIONAL PREDISSOCIATION OF Ne-Cl₂: A CLOSE-
COUPLING INFINITE ORDER SUDDEN APPROXIMATION

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We apply a model closely related to the "infinite order sudden approximation" (IOSA) to study the vibrational predissociation of the Ne-Cl₂(v=11) van der Waals molecule. The stretching motions within the complex are exactly solved in the close-coupling formalism at each atom-diatomic molecule orientation, providing us angular-dependent energies and rates. The bending motion is then considered in an approximate way and three-dimensional energies together with averaged predissociation rates are obtained. The potential energy surface was that previously used by N. Halberstadt¹. Since the experiment² and also very recent full-quantal calculations³ show a strong dominance of the $\Delta v = -1$ predissociation channel, only the vibrational channels v=11 (closed) and v=10 (open) were taken into account.

A total angular momentum J=0 has been assumed along all the calculations, that have been carried out for twenty-five values of the orientation angle θ equally spaced over the range [0, $\pi/2$].

In Table I we present a few energies and linewidths, in cm⁻¹, calculated at collinear, $\pi/3$ and perpendicular configurations, together with averaged 3D values

	coll.	$\pi/3$	$\pi/2$	3D
E	-16.39	-30.40	-53.18	-46.90
Γ	0.0015	0.00011	0.0105	0.0081

Table I

The 3D energy and lifetime ($\tau = h/2\Gamma \approx 330$ ps) are in agreement with full quantal results³. However, the last quantity becomes three times bigger than the experimental value². This fact may be attributed to the potential energy surface employed.

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Smith, I. W. M.	RT25,RE25
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