Final Report: DE-FG02-98ER45704

Title: **Theoretical Studies of Energy and Momentum Exchange in Atomic and Molecular Scattering from Surfaces**

PI: **Joseph R. Manson**
Department of Physics and Astronomy
Clemson University
Clemson, South Carolina 29634

Table of Contents

I. Introduction

This final report covers the three-year granting period of DE-FG02-98ER45704 from July 1, 2001 to June 30, 2004 plus the one-year extension granted for the period July 1, 2004 to June 30, 2005. The total amount of this award was $180,000 ($150,000 for the period 1/7/01-30/6/04 plus $30,000 for the extension year). There were no unexpended funds at the end of the project on June 30, 2005.

The contributions that we have made during the grant period of DE-FG02-98ER45704 can be placed into six different categories: **(1)** advances in the **Theory of Molecule-Surface Scattering**, **(2)** advances in the **Theory of Atom-Surface Scattering**, **(3)** utilization of scattering theory to **Extract Physical Information about Surfaces**, **(4)** **Gas-Surface Interactions**, **(5)** **Ion Scattering** from surfaces and **(6) Scanning**

Tunneling Microscopy (STM). These six topics are discussed below as individual listings under the title "IV. **Detailed description of research accomplishments**".

These advances show that we have made significant progress on several scientific problems in atomic and molecular surface scattering during the course of this grant as well as contributions to other areas. It is also noted that this work, although fundamentally theoretical, is marked by its strong motivation to explain current experimental measurements. This was an important secondary goal in the proposed work. We have developed theory that is useful to experimentalists in the explanation and analysis of their experimental data, and this point is underscored by our collaborations with many experimental groups in both the U. S., Europe and Japan.

Since the beginning of this grant period in 2001 the research group of Manson at Clemson University has published 21 refereed journal articles with one additional paper currently submitted. These are listed below in the next section.

II. Publications

1. D. Farías, M. Patting, K.-H. Rieder and J. R. Manson, "Which Direction is Uphill?: Scattering of He Atom Grazing-Angle Diffraction Beams from Surface Steps", Surface Science **480**, L395 (2001).
2. Li Mubing, J. R. Manson and Andrew P. Graham, "An Experimental and Theoretical Analysis of the Multiphonon Excitation Probability for Einstein-like Modes in Atom-Surface Scattering", Phys. Rev. B **63**, 155410 (2001).
3. A. Muis and J. R. Manson, "Theory and Calculations of the Energy Accommodation Coefficient Using Classical Scattering Theory", Surface Science **486**, 82 (2001).
4. J. R. Manson and S. Miret-Artés, "Focused sticking of light mass particles in physisorption", Phys. Rev. B **63**, 121404 (2001).
5. Ileana Iftimia and J. R. Manson, "Theory of Molecule-Surface Scattering at Thermal and Hyperthermal Energies", Phys. Rev. Lett. **87**, 093201 (2001).
6. Li Mubing, J. R. Manson and Andrew P. Graham, "An Experimental and Theoretical Investigation of the Multiple Phonon Excitation of Monolayer Film Modes with Helium Atom Scattering: Kr/Pt(111)", Physical Review B **65**, 195404(2002).
7. A. Özer and J. R. Manson, "Comparison of One-Dimensional and Three-Dimensional Models for the Energy Accommodation Coefficient", Surface Science **502-503**, 352 (2002).
8. D. Farías, M. Patting, K.-H. Rieder and J. R. Manson, "Scattering of He Atoms from Surface Defects by Grazing-Angle Diffraction Beams", Physical Review B **65**, 165435 (2002).
9. Ileana Iftimia and J. R. Manson, "Theory of Mixed Classical-Quantum Scattering of Molecules from Surfaces", Phys. Rev. B**65**, 125401 (2002).
10. Ileana Iftimia and J. R. Manson, "Surface Scattering of Small Molecules: Theoretical Analysis of C_2H_2 Scattering from LiF(001)", Physical Review B **65**, 125412 (2002).
11. J. Dai and J. R. Manson, "Classical Theory for Scattering of Rigid Molecules from Surfaces", Nuclear Instruments and Methods in Physics B193, 497 (2002).
12. J. R. Manson, Andrew P. Graham and Mubing Li, "Multiple Quantum Excitation Probabilities of Einstein-Like Modes of Surface Adsorbates Induced by He Atom Scattering", Journal of Physics: Condens. Matter 14, 6233 (2002).
13. L.Bartels, S. W. Hla, A. Kühnle, G. Meyer, K.-H. Rieder and J. R. Manson, "STM observations of a one-dimensional electronic edge state at steps on Cu(111)", Physical Review B67, 205416 (2003).
14. Ileana Iftimia and J. R. Manson, "Theory of Molecule-Surface Scattering", Journal of

Electron Spectroscopy and Related Phenomena, **129**, 219 (2003).

15. Jinze Dai and J. R. Manson "Theoretical Analysis for the Determination of Surface Composition in Molten Ga-Bi Metal Alloys by Rare Gas Scattering", Journal of Chemical Physics **119**, 9842 (2003).
16. Iryna Moroz and J. R. Manson, "Calculations for methane scattering from LiF(001)", Phys. Rev. B **69**, 205406 (2004).
17. Iryna Moroz, Hailemariam Ambaye and J. R. Manson, "Molecule scattering from insulator and metal surfaces", Journal of Physics: Condens. Matter **16**, S2953 (2004).
18. Hailemariam Ambaye, J. R. Manson, Olaf Weiße, Claudia Wesenberg, Marcello Binetti and Eckart Hasselbrink, "Scattering of O_2 from Al(111)", J. Chem. Phys. **121**, 1901 (2004).
19. J. Powers, J. R. Manson, A. Lavery, C. Sosolik and J. Hampton, "Scattering of Low Energy K^+ Ions from Cu(001)", Phys. Rev. B **70**, 115413 (2004).
20. Iryna Moroz and J. R. Manson, "Methane scattering from Pt(111)", Physical Review B **71**, 113405 (2005).
21. Guoqing Fan and J. R. Manson, "Gas-surface scattering with multiple collisions in the physisorption potential well", Phys. Rev. B **72**, 085413 (2005).
22. Hailemariam Ambaye and J. R. Manson, "Calculations of Accommodation Coefficients for Diatomic Molecular Gases", submitted to the Physical Review E.

III. Research Papers at Scientific Meetings and Invited Presentations:

1. Manson, J. R. *"Scattering of Atoms and Molecules from Surfaces"*, Atomic, Molecular and Optical Physics at Surfaces, Harvard-Smithsonian Institute, Cambridge, MA (June 14-16, 2001), invited talk.

2. Manson, J. R. *"Theory of surface scattering of small molecules"*, and *"Theoretical analysis of the multiphonon excitation probability for Einstein-like modes in atom-surface scattering"*, Symposium on Surface Physics of the Japan Physical Society, Jan. 8-11, 2002, Furano, Japan, invited talks.

3. Iftimia, Ileana and Manson, J. R., *"Theory of Molecule-Surface Scattering"*, 22nd Werner Brandt Workshop, June 27-29, 2003, Namur, Belgium, prize for the best poster presented.

4. Iryna Moroz and J. R. Manson, *"Calculations of Methane Scattering from LiF(001)"*, Symposium on Surface Science, La Plagne, France, March 31-April 4, 2003.

5. J. R. Manson, *"Molecule-Surface Scattering"*, presented at the 23rd Werner Brandt Workshop, Berlin, Germnay, 12-14 July, 2004.

6. J. R. Manson, *"Scattering of Molecules by Surfaces"*, presented at the Donostia International Physics Center Workshop: Molecule-Surface Interactions: Elementary Reactive Processes, San Sebastian, Spain, September 7-11, 2004.

7. J. R. Manson, *"Scattering of Molecules from Surfaces"*, presented at the March Meeting of the American Physical Society, Montreal, Canada, March 22-26, 2004. This was an invited presentation in the Focus Session on Chemical Physics.

8. J. R. Manson, "Surface Scattering of Low-Energy Ions", 24th Brandt-Ritchie Workshop, University of Florida at Gainesville, April 10-12, 2005.

9. "Molecule-Surface Interactions", Freie Universität Berlin, Berlin, Germany, May 28, 2001.

10. "Theory of Scattering of Small Molecules from Surfaces", Humboldt Universität zu Berlin, Berlin, Germany, July 4, 2001.

11. *"Theory of molecule-surface scattering"*, Max Planck Institut für Strömungsforschung, Göettingen, Germany, May 28, 2002.

12. *"Atomic and Molecular Scattering from Surfaces"*, University of Magdeburg, Germany, August 5, 2001

13. *"Gas-surface interactions"*, Ohio University, October 10, 2002.

14. *"Detection of Surface Defects by Grazing-Angle Diffraction"*, Freie Universität Berlin, Germany, June, 2002.

15. *"Atomic and Molecular Scattering from Surfaces"*, Department of Physics, University of Magdeburg, Germany, August 5, 2002.

16. *"Scattering of Molecules from Surfaces: The Case of)2/LiF(001)"*, Departments of Chemistry and Physics, University of Essen, Germany, July 17, 2003.

17. *"Atomic and Molecular Interactions with Surfaces"*, colloquium presented at the Department of Chemistry, Technical University of Munich, Germany, June 24, 2004.

18. *"Translational, Rotational and Internal Mode Energy Exchange in Molecule-Surface Interactions"*, colloquium presented at the Department of Physics, Cavendish Laboratory, Cambridge University, Cambridge, UK, July 28, 2004.

19. *"Interactions of Atoms and Molecules with Surfaces"*, seminar presented at the Department of Physics, Freie Universitaet Berlin, Berlin, Germany, June 2, 2004.

20. *"Atom-Surface and Molecule-Surface Scattering Theory"*, colloquium presented at the Department of Physics, University of Wisconsin, Madison, Wisconsin, November 18, 2004.

21. "Scattering of Atoms from Amorphous Surfaces", colloquium presented at the Laboratoire: Surface duVerre et Interfaces, Centre Natonale de Recherche Scientifique, Saint-Gobain-UMR 125, Paris, France.

22. "Low-Energy Ion Scattering from Surfaces", colloquium presented at the Department of Physics, the Humboldt Universität zu Berlin, Germany, June 29, 2005.

IV. Description of research accomplishments:

(1) Theory of Molecule-Surface Scattering. The most important advance achieved during this grant period is our development of the theory of molecule scattering from surfaces under conditions in which the translational and rotational motions of the molecule are treated classically (which is valid for almost all molecules except hydrogen) while treating the internal vibrational modes of the molecule with quantum semiclassical theory [5,9,10,11,14]. Thus, the theory includes the three major modes of energy and momentum exchange with the surface, i.e, phonon excitation (surface vibrations), rotational excitation of the molecules, and excitation of internal mode vibrations of the molecule. This work was initiated with postdoc Ileana Iftimia and our first results were reported in Physical Review Letters [5]. This was quickly followed by two longer papers in the Physical Review B [9,10], one mainly devoted to the theory and the second giving

4

detailed comparisons of our calculations with the experiments of Roger Miller of UNC for the scattering of acetylene from LiF(001). Measured angular distributions of acetylene scattered from the LiF surface were well explained by our theory, the measured final intensities as functions of the final rotational energy were explained, and the final rotational temperatures of the scattered particles were also calculated to be in agreement with measurements. Predictions were calculated for excitation probabilities of the internal molecular vibrational modes. Only the C_2H_2 bending modes are appreciably excited, and excitation probabilities were calculated in the range of 3% to 5%. (The internal stretch modes have energies too large to be significantly excited.) Symmetry effects were found to be important and isotopic substitutions of deuterium in the C_2H_2 projectiles are predicted to cause significant changes in excitation, in particular large increases in excitation probability for the ν_4 bending mode which has an energy of 76 meV for the C_2H_2 isomer.

After Iftimia's departure for Harvard University (she is currently at Tufts University), this program of research was taken over by the postdoc, Iryna Moroz. She further developed the theory and carried out calculations for the scattering of the more complicated molecule, methane, from alkali halide and metal surfaces [16,20]. Her initial results agreed very nicely with the somewhat limited methane scattering data available from the UNC group of Miller. However, the group of S. Yamamoto of Tsukuba University in Japan has recently begun a new program in molecular beam scattering from surfaces and has already generated extensive results for the scattering of methane from LiF(001), clean Pt(111) and well characterized adsorbate coverages on Pt(111) substrates. This new data from the Japanese group includes both angular distributions and energy-resolved time-of-flight data which provide an excellent test of our theory. Moroz's calculations agree well with the CH_4/LiF(001) data and correctly predict the energy, angular and surface temperature dependence of the angular distributions and time-of-flight spectra. These comparisons show that the attractive physisorption well of this system must be somewhat larger than 65 meV and that the repulsive part of the potential plays the dominant role in the scattering process. This work has been published in the Physical Review B [16]. A subsequent work, published also in the Physical Review B, examines the scattering of CH_4 from the metal surface Pt(111) [20]. Even better agreement was obtained than for the LiF data and the results indicate that the methane-Pt physisorption potential well must be at least 50 meV in depth.

The molecule-surface work is currently being continued by graduate student Haile Ambaye who has shown that the theory can explain several experiments that have looked at the excitation probabilities for rotational motion, and additionally he has obtained very promising agreement with the small amount of data available for the excitation of internal molecular vibrational modes upon collision with a surface [17,18]. In particular, Ambaye has obtained good agreement with the excitation probabilities as functions of final rotational energy for the cases of (1) NO/Ge(111), data from the group of G. Ertl at the MPI in Berlin, (2) NO/Ag(111), data from the group of D. Auerbach and C. Rettner of IBM San Jose, (3) NO/Cu(111), data from the group of G. Sitz of the University of Texas, and (4) N_2/Ru(0001), data from the group of A. Luntz of the University of Odense, Denmark. In all of these cases the theory does a good job of explaining the measured scattered intensity spectra as functions of final rotational energy, initial translational energy and surface temperature.

Ambaye's work on rotational excitation of diatomic molecules has explained the nature of the so-called "low energy rainbow" feature in the measured intensity versus rotational energy plots. This "low energy rainbow" consists of a steep decrease in the intensity as a function of final rotational energy and then a leveling off of the intensity at slightly higher energies, the whole extent of the feature usually occurring for rotational energies less than about 20 meV. What Ambaye has shown is that this feature is not at all due to any type of rainbow mechanism, instead it is a consequence of the very low rotational excitation of molecular jet beams. In general, for molecular jet beams of translational energy even as large as room temperature or higher, the rotational energy is decoupled from the translational energy and the rotational spectrum of the molecular beam will usually be approximately Maxwellian with a temperature of around 30-50 K. In the experiments cited above, the translational energy ranged from 100 meV up to about 1 eV, thus the incident molecular beam had a translational energy much larger than its rotational energy. Under such circumstances, rotational excitation is highly predominant and there is very little rotational de-excitation. This rotational excitation energy comes from the translational energy and from the surface vibrations (i.e., the surface vibrational energy, estimated at k_BT is, at room temperature, about 30 meV which is larger than the incident rotational energy of about 3-5 meV). Ambaye's calculations show that the feature is simply due to a very large probability of low energy rotational excitation for an incident beam that has a very low average rotational quantum number. Further calculations show that the "low energy rainbow" feature will disappear for an incident beam with higher rotational energy. A manuscript presenting our results on rotational excitations in surface collisions is in preparation.

(2) Theory of Atom-Surface Scattering. The scattering of atoms from surfaces is a major method for obtaining specific information about the physical properties of the surfaces of materials. In order to extract this information, however, it is necessary to have a theoretical interpretation of how various surface properties affect the scattered beam intensities. We have made contributions to the theory of sticking and trapping of atomic particles from surfaces, from which one can obtain information about the attractive forces near surfaces. These attractive forces are the same ones that cause the sticking of adsorbates or impurities at surfaces.

We have advanced the theory of focusing of incident beams of atoms into trapped states on the surface [4]. This is an effect in which beams incident on a surface at certain energies and angles will be focused and channeled very efficiently into the bound or trapped states. Previously, Manson and Miret-Artés have published on several such effects in diffraction and inelastic scattering and have described their usefulness in the interpretation of scattering spectra. In this new work, the authors found a channel in which incoming beams of He atoms under certain incident conditions can be focused into particular bound states in the attractive adsorption well of the interaction potential. This work shows that the effect may be important in the processes of trapping or sticking of incoming gas projectiles impinging on surface.

We have also developed the theory of scattering of grazing-exit angle diffraction beams from defects and impurities on the surface [1,8]. It was recently shown by D. Farias, M. Patting and K.-H. Rieder that diffraction beams produced when a monoenergetic He atom beam scatters from an ordered metal surface can be observed at

large scattering angles, and even under conditions when the diffraction beams exit parallel to the surface. Under such grazing-exit conditions, a very large intensity diffuse scattering peak was observed. Working together with the above authors, Manson proposed that this large anomalous intensity is due to scattering of He atoms out of the grazing-angle diffraction beam by impurities such as steps on the surface. A theoretical analysis based on scattering of the grazing-angle beams from steps showed that the calculated scattered intensity matched well with the observed experimental anomalous intensities for double steps, i.e., for steps that were exactly twice the height of the expected value for single steps on the surface. Single steps appear unobservable for the particular Rh(113) surface investigated because their very broad scattering signal cannot be distinguished from the background. One important result of this work is that measurement of the anomalous signal immediately distinguishes the miscut direction of the crystal. When metal crystals are cut and polished, there is always an inevitable miscut that results in step defects on the surface. These steps are perpendicular to the direction of the miscut, with more steps in the "uphill" direction (at 0^0 azimuthal angle) and fewer steps in the "downhill" direction (the opposite direction with azimuthal angle 180^0). In the uphill direction, where there are many more steps encountered by a grazing-angle diffraction beam, the anomalous signal is very large. However, in the downhill direction, the anomalous signal is such smaller since fewer step faces are encountered. Thus, a simple measurement in the two directions suffices to distinguish the azimuthal direction of the crystal miscut. Another interesting prediction of this work is that grazing-angle He atom diffraction scattering may be a new way to look at other surface defects, especially inelastic scattering from such defects. This work was published in Surface Science and the Physical Review B [1,8].

In work based on the experimental data measured in the group of Gilbert Nathanson of the Department of Chemistry at the University of Wisconsin, we have shown that relatively simple measurements of the temperature and energy dependence of atom-surface scattering measurements can give the mean-square corrugation height of the surface interaction potential for heavy atoms scattered by surfaces [15]. Heavy atoms at energies even as small as thermal energies exhibit essentially no quantum features such as diffraction or single-phonon events, and consequently can be treated with classical theory. Other work, stimulated by the experimental measurements of the Nathanson group, has been to demonstrate that the surface segregation of liquid metal alloys can be accurately predicted and measured using heavy rare gas scattering [15]. In particular, we have shown that the surface segregation of Bi in Ga-Bi alloys with a weak concentration of Bi can be very accurately measured as a function of surface temperature using the time-of-flight resolved scattering of Ar beams.

A very interesting area of current research is a theory that can calculate the trapping of an incident beam of atoms by the physisorption well, and can further calculate the motion of the adsorbed atoms until they are eventually desorbed [21]. In this way we are able to calculate the distributions of directly scattered atoms and to separately calculate the trapped-desorbed fraction. This problem is of interest because of the very old, but still generally accepted, assumption of James Clerk Maxwell that the trapped-desorbed fraction will be an equilibrium distribution. Among an number of new results coming from this current research is the fact that we can directly show that this trapped-desorbed fraction is not always in equilibrium with the surface, and in some cases can be

very much in a non-equilibrium state. This problem is discussed in more detail below in Sec. 4 on Gas-Surface Interactions.

(3) Extracting Important Physical Information about Surfaces. Our theoretical results have been used in several major efforts to characterize the physical properties of surfaces. The first of these was a study, with Dr. A. Graham of the Max Planck Institute at Goettingen Germany and graduate student Mubing Li, on energy exchange between an incident beam of He atoms and adsorbate covered surfaces [2,6]. The other was with graduate student Jinze Dai on the scattering of Ar atoms from liquid metal alloys in order to determine the fraction of surface segregation of each of the alloy components [16].

In the work on adsorbed layers, we studied energy exchange to the very low energy vibrational states of CO impurities on a Cu(001) surface, and for a monolayer of Kr adsorbed on a Pt(111) surface. In both cases the excitation energy for one vibrational quantum is close to 4 meV. We showed that in both cases, the intensity spectrum of scattered He atoms was well described by a theory in which the energy was exchanged via mechanical excitation of the adsorbate vibrations. The experimentally measured spectra consist of multiple quantum excitation peaks of the Einstein mode, and our theoretical analysis correctly predicts both the number of such peaks as well as their relative intensity. Such a study enables both determination of the vibrational energies of the adsorbate modes as well as the polarizations (or vibrational directions) of the modes. This information is important because it enables characterization of how adsorbates interact with projectiles hitting the surface, and in particular, one of the major mechanisms for energy exchange between a surface in contact with a gas is through excitation of these low energy vibrational modes.

The work on scattering of argon atoms from liquid metal surfaces was initiated in response to an important new experiment developed by the group of Gilbert Nathanson at the University of Wisconsin as mentioned briefly in section (1) above. Several years ago, they measured scattering distributions of several rare gases (He, Ne, Ar and Xe) scattering from the liquid metals Ga, Bi and In. We developed our classical mechanical theories for these cases, and were able to explain their results rather well. We have now used extensions of these theories to analyze recent data from that group on Ar scattering from liquid metal alloys of small amounts of Bi in Ga. In particular, it was desired to know the extent of surface segregation of the Bi as a function of temperature. Nathanson *et al.* measured the surface segregation independently by Auger spectroscopy, a very difficult measurement. However, the combination of their Ar scattering measurements compared to theory appears, as a result of our analysis, to be a more accurate and easier method of determining the surface segregation.

The work on the scattering of grazing-angle atomic diffraction beams by surface defects, published with Farias, Rieder and Patting in the Physical Review B and discussed above in Sec. (2), has shown that defects on the surface can be clearly detected in the diffuse incoherent scattering under grazing exiting diffraction conditions, and clearly delineates the possibility of gaining information on the size, shape and vibrational characteristics of surface defects [1,8].

As explained in (2) above, we have shown how simple measurements of the temperature and energy dependence of the atom-surface scattering spectra, even in the

case of classical scattering conditions, can reveal information on the roughness of a surface.

(4) Gas-Surface Interactions. An important part of our work is applying currently available theoretical methods to problems of the exchange of energy and momentum at the interface between a gas and a surface. We have carried out calculations of the energy accommodation coefficient, which is a measure of the energy exchange at the interface between a gas and a surface [3]. These calculations used, for the first time, a realistic and fully three-dimensional scattering model. After the initial study we made a comparison of one-dimensional with three-dimensional models which was published in Surface Science [7]. This study of 1-D models was expected to show that they were inadequate to describe the energy accommodation coefficient, and as one consequence of this work we clearly delineated the shortcomings of 1-D models. However, since 1-D models are much easier to work with, e.g., a fully 3-D model of the accommodation coefficient requires at least a six-dimensional integral while the 1-D model requires only a double integral, a very important secondary reason for carrying out this work was to see if 1-D models retained enough physical reality to be useful for evaluating higher order processes and multiple scattering. Our conclusion is that 1-D models are not adequate for providing quantitative results, but are capable of giving very dependable qualitative behavior of the accommodation coefficients on all of the experimentally controllable parameters.

We have now extended this initial accommodation coefficient work to molecular gases. Graduate student Haile Ambaye has submitted to the Physical Review E a report of his work extending this to calculations of energy as well as momentum accommodation coefficients at the interfaces of molecular gases with surfaces. In this manuscript he has shown that our molecule-surface scattering theories predict quite well recently measured accommodation coefficients of oxygen molecules on amorphous SiO_2 surfaces [22]. This work represents the first time that a realistic theory of molecular scattering has been able to accurately predict accommodation coefficients for molecular gases.

Our program of gas-surface dynamics has been taken over by graduate student Guoqing Fan, and the results that he has obtained are some of the most exciting developments we have to report. Guoqing has developed a multiple scattering theory which allows him to calculate both the scattering and the trapping inside the adsorption well after the initial collision of the gas with the surface [21]. Then, by a cleverly designed iterative process, he can follow the motions of the trapped particles as they move back and forth in the well while continuing to have multiple collisions with the surface. Throughout the process the calculation produces the energy distribution function of both the remaining trapped particles and those that have escaped into the continuum and leave the surface. Fan's initial results indicate that, under certain conditions, the desorbed gas particles leave the surface in an equilibrium Boltzmann distribution just as suggested in the mid-1800s by James Clerk Maxwell when he initially proposed the concept of an energy accommodation coefficient. To our knowledge, this is the first calculation using a scattering model that is sufficiently realistic to test the Maxwell hypothesis. However, under some circumstances the calculations demonstrate that the trapped-desorbed particles escape the surface with an energy distribution that is quite

different from equilibrium, in violation of the Maxwell assumption. The conditions under which such non-equilibrium trapping-desorption occurs are for systems with high energy incident beams and small adsorption well depths. Fan's theory is able to calculate the average trapping time of an adsorbed particle, another important result. Even more promising, the numerical algorithm that Fan has used is very fast, taking only a few seconds of CPU time to calculate the complete desorption of all initially trapped particles for a typical system such as Ne or Ar accommodating at a tungsten surface. Because of the speed of the iteration algorithm, Fan has been able to extend his theory to fully realistic three-dimensional calculations of both scattering by well-defined incident beams and even for the much more time-consuming case of an equilibrium gas in contact with the surface. In the latter configuration, he has been able to calculate accommodation coefficients for the heavy rare gases in contact with metal surfaces and has achieved reasonable agreement with available experimental data. His one-dimensional calculations have already been published in the Physical Review B [21] and the three-dimensional results are being prepared in a manuscript.

(5) Ion Scattering. Undergraduate student Judson Powers completed a research project on the scattering of low energy, singly-charged potassium atoms from a Cu(001) surface that has now been published in the Physical Review B [19]. He analyzed data measured by Chad Sosolik and Jennifer Hampton of Cornell University, from the group of the late Barbara Cooper. Previously, another undergraduate student, Andre Muis, made a successful analysis of data for sodium ion scattering from Cu(001) by this same group, and for the current case of potassium ions the agreement between theory and experiment is even better. Since the major mechanism for energy exchange in our theory is exchange of phonons (i.e., thermal vibrations of the target metal crystal), the analysis allows a clear estimate of how important phonon interactions are compared to other possible modes of energy loss of the ions.

(6) Scanning Tunneling Microscopy. A new direction in research developed during the course of this grant is the investigation of the possibility of an edge electronic state associated with long, straight step edges on metal surfaces. This work was motivated by STM measurements carried out in the group of K.-H. Rieder of the Free University of Berlin (with whom we have had a long-standing collaboration in the area of He atom scattering). These measurements showed an unusual feature in the STM spectrum when the tip was in the vicinity of a step edge, i.e., the STM measurements indicated a "bump" in the local density of electronic states at the top of the step. After several discussions of this effect Manson proposed a theory based on the idea that there could be a bound state of the electron at the step edge [13]. This bound state is due to the electron self-energy, similar to the image state of an electron near a flat metal surface. At a step edge, the polarization of the surface charge density is even more pronounced than on a flat surface in the presence of a nearby charge, so such a self-trapped electron would have a lower energy than the surface image state and would be highly localized at the top of the step. The dipole force associated with Smoluchowski smoothing of the electron sea near a step also must be taken into consideration. Further measurements seemed to confirm these predictions, and indeed the "bump" in the local density of states is quite localized and is seen at potential biases below the onset of the surface image state, and all of these

observations are consistent with our model. This work was reported in the Physical Review B [13]. In the future we intend to carry out a full theoretical treatment to evaluate the potential energy of a charge near the top edge of a surface step, and then use this potential to solve the Schrödinger equation to determine the bound states that can exist in such a linear two-dimensional potential well. If the current interpretation survives further investigation this could be an important result because the edge state will be a variety of "quantum wire".

V. Education and Development

The primary education and development activities carried out during this grant period have been in the area of education of the graduate and undergraduate students working with this research group. Three Ph. D. graduate students were supported or partially supported by this grant, Hailemariam Ambaye, Wayne Hayes and Guoqing Fan. Two Masters degree students, Mubng Li and Jinze Dai, participated in this work. In addition, one undergraduate student, Judson Powers, was supported partly by this grant and mainly by a REU supplement to the PI's NSF grant. The postdoctoral research associates working with this program were Ileana Iftimia and Iryna Moroz. All of the above members of this group have advanced their scientific knowledge and education as a result of the opportunities provided by this grant. They have not only had opportunities to carry out original research, they have presented this research at the meetings and all have published papers in respected, refereed journals. They also have opportunities to communicate their results to colleagues here at Clemson through our weekly group seminars and our Solid State Seminar.