Dynamics of Molecules and Clusters at Surfaces

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Preface

This thesis describes work carried out at the Cavendish Laboratory, Cambridge, from October 1991 to August 1995. This dissertation is a result of my own work and, except where specific reference is made, contains nothing which is the outcome of work done in collaboration with others.

I would like to begin by thanking my supervisor, Professor Richard Palmer, for his constant flow of ideas and encouragement throughout this project.

I would also like to express my gratitude to the various technicians at the Cavendish Laboratory, without whose fine work this project would not have been possible. I would particularly like to thank Rob Barrett, who built the condensation chamber of the cluster source, Terry Stubbings, for all his advice and help in the construction of so many parts of the cluster source, Dave Powell for his expert tuition and help in the use of the machines of the student workshop, and Howard Thompson, who constructed much of the electronics that powered the source. I would also like to thank Rik Balsod and Alan Campbell (of Birmingham University) for their expert craftsmanship in machining some of the more exacting components for the source, and Roger Beadle for so willingly sharing his store of knowledge on pumping, magnet cooling, fittings, flanges and filaments, crucibles and evaporation.

The SEM work in this thesis was carried out with the Hitachi S900 microscope of the Microelectronics Group, Cavendish Laboratory, and I am very grateful to Professor H. Ahmed and Dr. J. Cleaver for granting me permission to use it.

I am greatly indebted to Linda Kidder of the Department of Chemistry, John Hopkins University, Baltimore, USA for her invaluable advice in the design of the ion source, and other matters relating to the supersonic expansion of the beam.

Without having the other members of the group to go and annoy when the cluster source failed to perform yet again, I would not have survived the course. Special thanks go to Peter Durston and Kobus Kuipers who helped me to unwind after many a frustrating day, as we locked in mortal combat armed with two PCs and a serial cable. Thanks are also due to Peter Laitenberger, who was above such things, but always willing to listen and make useful suggestions. Thank you also to Bill Allison, Larry Silva, and Kobus Kuipers for those brain-storming sessions. Thanks too to Mek Nielsen for rescuing my thesis when the server crashed.

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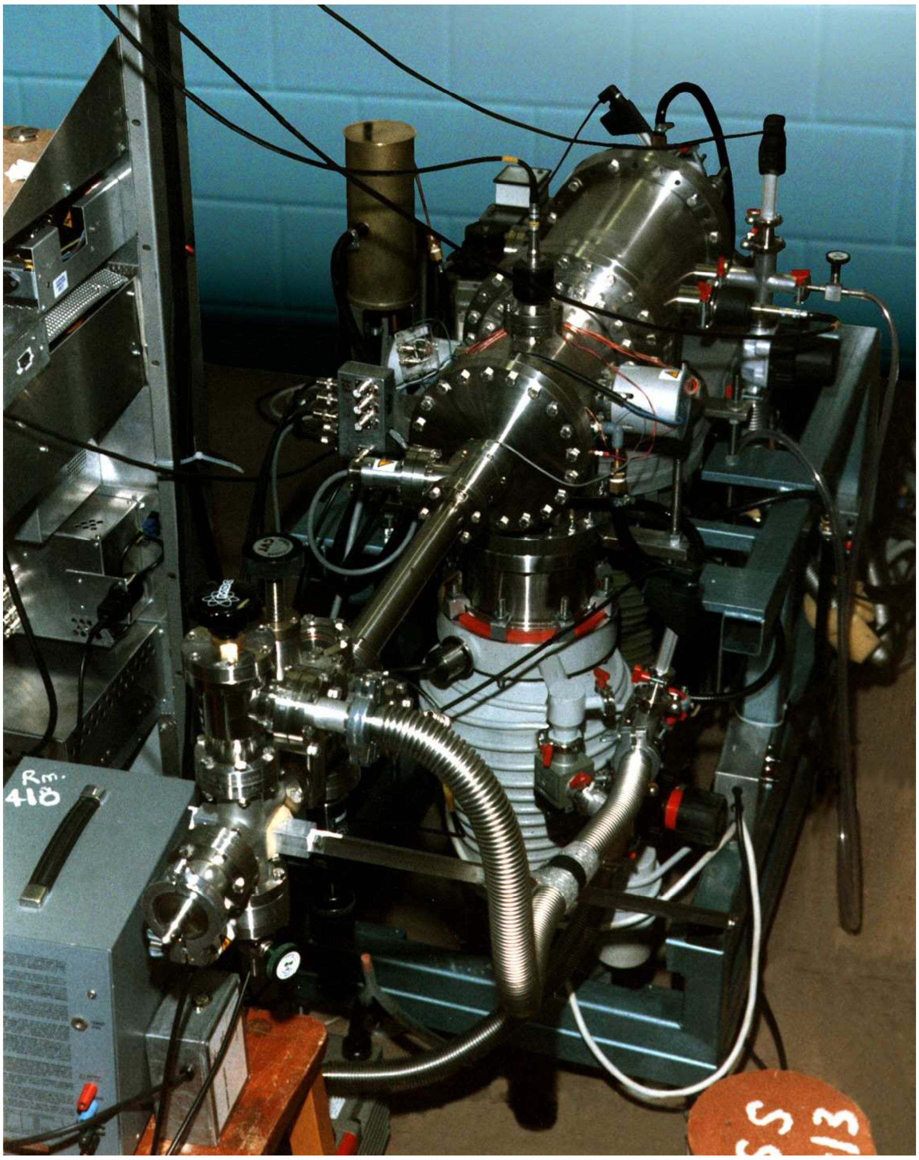
Finally, to my parents, I would like to say a very special thank you, for all the support, love, and encouragement that you have given to me.



Photograph of the inert gas condensation cluster deposition source, described in detail in chapter 3, and with which most of the experimental work in this thesis was performed.

This thesis was typeset with Microsoft Word 5.1a on an Apple Macintosh computer. Figures were prepared with ClarisDraw, Kaleidagraph from Abelbeck Software, and Adobe Photoshop. The scanning electron microscope micrographs were electronically analysed on a Macintosh Performa 630 computer using the public domain NIH Image program, developed at the U.S. National Institutes of Health and available from the Internet by anonymous FTP from zippy.nimh.nih.gov or on floppy disk from the National Technical Information Service, Springfield, Virginia, part number PB95-500195GEI. The MS-DOS public domain application SIMION was used for ion ray tracing simulations. SIMION is written by and available from D. A. Dahl and J. E. Delmore of the Idaho Engineering Laboratory, EG&G Idaho Inc, P. O. Box 1625, Idaho Falls, ID 83415. A few of the graphs in this thesis were replotted from published data, with the use of the Macintosh application DataThief, written by and copyright of Kees Huyser and Jan van der Laan of the Computer Systems Group of the Nuclear Physics Section at the National Institute for Nuclear Physics and High Energy Physics, Amsterdam. DataThief is available from any info-mac mirror FTP site.

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Summary

An understanding of the dynamical behaviour of adsorbates on surfaces is essential to the development of materials and devices with controlled structure on the nanometre scale. In this thesis I examine two systems. The major part of the work concerns the development of a source of size selected metallic clusters, and the deposition and diffusion of silver clusters on a highly oriented pyrolytic graphite (HOPG) surface. The final part of the thesis reports an investigation of electron stimulated desorption of ions from O_2 films on HOPG.

In chapter one, I review recent work in cluster physics, concentrating mainly on experiments with deposited clusters.

Chapter two is a review of techniques used to generate free cluster beams. This includes examination of the various technologies and techniques involved in cluster production, beam formation, and mass selection. This chapter also gives a detailed account of the principles of operation of a gas condensation cluster source. In chapter three, I present a detailed account of the design, characterisation and commissioning of a gas condensation cluster source.

Chapter four contains the results of a series of experiments on the deposition and diffusion of silver clusters on HOPG. The results of landing clusters with controlled kinetic energy (KE) show that silver clusters deposited with a KE of 400 eV or more become pinned to the surface, whereas clusters deposited with 200 eV or less diffuse across the surface after landing and aggregate into round particles with a 'universal' diameter of ~14 nm. This preferred diameter is attributed to the strain between the silver and graphite lattices. The deposition rate and the cluster impact angle are also shown to be important parameters, which strongly influence the morphology of the islands. Computer simulation results indicate that, to produce the observed island size distributions, the mobility of the particles must fall off rapidly as their size increases.

In chapter five, I present results from angular resolved electron stimulated desorption studies of O^-, O_2^- and O_3^- produced from ordered films of O_2 on HOPG. Resonances in the yields of all products as a function of electron impact energy are attributed to dissociative electron attachment, generating O^- ions, which can react with neighbouring O_2 molecules in the film. Characteristic differences in the ion yield profiles from one product to another are explained in terms of a binary collision model, which estimates the KE of the ion products, and thus the probability of escape from the polarisation potential induced in the O_2 film. The model is consistent with the measured angular distributions of desorbed ions.

Abbreviations and Acronyms

AFM	Atomic force microscope/microscopy
amu	Atomic mass units
BSE	Back-scattered electron
CRT	Cathode ray tube
DA	Dissociative attachment
DD	Dipolar dissociation
DLA	Diffusion-limited aggregation
E-T	Everhart-Thornley (electron detector)
EELS	Electron energy loss spectrometer/spectrometry
EC	Evaporation-condensation (mechanism of diffusion)
ESD	Electron stimulated desorption
HOPG	Highly oriented pyrolytic graphite
ICB	Ionised cluster beam
KE	Kinetic energy
LECBD	Low energy cluster beam deposition
LEED	Low energy electron diffraction
LMIS	Liquid metal ion source
ML	Monolayer
PACIS	Pulsed arc cluster ion source
PD	Periphery diffusion
SE	Secondary electron
SEM	Scanning electron microscope/microscopy
STM	Scanning tunnelling microscope/microscopy
UHV	Ultra-high vacuum
UPS	Ultra-violet photo-electron spectroscopy
VSP	Velocity slip parameter
XPS	X-ray photo-electron spectroscopy

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