

Springer Theses

Recognizing Outstanding Ph.D. Research

For further volumes:
<http://www.springer.com/series/8790>

Aims and Scope

The series “Springer Theses” brings together a selection of the very best Ph.D. theses from around the world and across the physical sciences. Nominated and endorsed by two recognized specialists, each published volume has been selected for its scientific excellence and the high impact of its contents for the pertinent field of research. For greater accessibility to non-specialists, the published versions include an extended introduction, as well as a foreword by the student’s supervisor explaining the special relevance of the work for the field. As a whole, the series will provide a valuable resource both for newcomers to the research fields described, and for other scientists seeking detailed background information on special questions. Finally, it provides an accredited documentation of the valuable contributions made by today’s younger generation of scientists.

Theses are accepted into the series by invited nomination only and must fulfill all of the following criteria

- They must be written in good English.
- The topic should fall within the confines of Chemistry, Physics, Earth Sciences, Engineering and related interdisciplinary fields such as Materials, Nanoscience, Chemical Engineering, Complex Systems and Biophysics.
- The work reported in the thesis must represent a significant scientific advance.
- If the thesis includes previously published material, permission to reproduce this must be gained from the respective copyright holder.
- They must have been examined and passed during the 12 months prior to nomination.
- Each thesis should include a foreword by the supervisor outlining the significance of its content.
- The theses should have a clearly defined structure including an introduction accessible to scientists not expert in that particular field.

Barbara A. J. Lechner

Studying Complex Surface Dynamical Systems Using Helium-3 Spin-Echo Spectroscopy

Doctoral Thesis accepted by
the University of Cambridge, Cambridge, UK

 Springer

Author

Dr. Barbara A. J. Lechner
Materials Sciences Division
Lawrence Berkeley National Laboratory
Berkeley, CA
USA

Supervisor

Dr. John Ellis
Cavendish Laboratory
University of Cambridge
Cambridge
UK

ISSN 2190-5053

ISBN 978-3-319-01179-0

DOI 10.1007/978-3-319-01180-6

Springer Cham Heidelberg New York Dordrecht London

ISSN 2190-5061 (electronic)

ISBN 978-3-319-01180-6 (eBook)

Library of Congress Control Number: 2014935276

© Springer International Publishing Switzerland 2014

This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed. Exempted from this legal reservation are brief excerpts in connection with reviews or scholarly analysis or material supplied specifically for the purpose of being entered and executed on a computer system, for exclusive use by the purchaser of the work. Duplication of this publication or parts thereof is permitted only under the provisions of the Copyright Law of the Publisher's location, in its current version, and permission for use must always be obtained from Springer. Permissions for use may be obtained through RightsLink at the Copyright Clearance Center. Violations are liable to prosecution under the respective Copyright Law. The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

While the advice and information in this book are believed to be true and accurate at the date of publication, neither the authors nor the editors nor the publisher can accept any legal responsibility for any errors or omissions that may be made. The publisher makes no warranty, express or implied, with respect to the material contained herein.

Printed on acid-free paper

Springer is part of Springer Science+Business Media (www.springer.com)

Supervisor's Foreword

Helium Spin Echo (HeSE) is a novel technique, uniquely capable of studying surface motion on Ångström length and sub-pico- to nanosecond timescales. As such it can be used to “watch” atoms and molecules as they move around on a surface on the same time and length scales as the processes that control this motion—surface vibration, motion across a unit cell, and energy transfer to and from the heat bath supplied by the substrate—and yields a wealth of information inaccessible by other means.

The technique directly measures the ‘intermediate scattering function’ (ISF) which is the spatial Fourier transform of the van Hove pair correlation function $G(\mathbf{R}, t)$, which gives the probability that an atom or molecule will be at (\mathbf{R}, t) given there was an atom or molecule at $(\mathbf{R} = 0, t = 0)$. The information it supplies comes, therefore, in reciprocal space and correlation time, and as such the process of data interpretation is not a simple one.

Over the years the Cambridge Surface Physics group has developed a systematic approach to this complex process. Starting from simple systems involving the motion of single atoms and then small molecules such as CO, a library of characteristic “signatures” for different types of motion has been built up which can be used to determine the phenomenology of the process being studied—for example, is the diffusion proceeding by jumps, or is it ballistic in nature? Are there multiple jumps and in what directions are they occurring? Are there interactions between the diffusing species? Can the species move freely over the surface or are they confined to specific regions? What is the energy transfer rate between substrate and adsorbate? What is the activation energy for diffusion? For each new investigation the ISF is measured and quantified as a function of momentum transfer, direction, temperature, and coverage, and then the signature library is used to establish the basic processes that are occurring. Once this has been done, a system of molecular dynamics simulations coupled to simple scattering calculations is employed to confirm the phenomenological interpretation of the data and to put definite numbers on the parameters involved.

When Barbara commenced her thesis work, the need was to extend the signature library from those of single atomic species and simple molecules to more complex systems. To do this, Barbara undertook a systematic study of motion of a series of five-membered ring species, cyclopentadienyl, pyrrole, and thiophene, on

Cu(111). These adsorbates demonstrate bonding to the surface that ranges from ionic, through van-der Waals, to covalent and show the full range of dynamic phenomena—vibration, vibrational dephasing (seen as ‘intracell’ diffusion), lateral diffusion, rotational diffusion, and change of orientation with respect to the surface plane which manifests itself as confined motion perpendicular to the surface. The lateral adsorbate/substrate energy landscapes so-derived are compared with DFT calculations performed by collaborators—showing the significance of the zero point energy of the internal modes. Extremely high friction is found for lateral motion, which is shown to be due to coupling to the internal modes of the diffusing species, and the lateral interactions between molecules are studied via the correlated motion it induces.

We are fortunate that this work was undertaken by someone who is such a careful researcher and who could also describe her work so lucidly. While her published papers give the headline results, the thesis shows how the analysis is actually done. Barbara exploits and extends every aspect of the ‘library’ of signatures developed to this point in time and her thesis is a must for anyone who wishes to understand how to use the HeSE technique.

Cambridge, February 2014

Dr. John Ellis

Abstract

The aim of the present thesis is to extend the range of application of the helium-3 spin-echo (HeSE) technique to complex surface dynamical systems. A twofold approach is presented: the development of improved experimental equipment and the investigation of a series of prototypical aromatic adsorbate systems. [Chapter 1](#) discusses the motivation for this work and compares HeSE with other techniques probing surface motion. Subsequently, an introduction to the HeSE method is given in [Chap. 2](#), explaining the theoretical background and describing the main components of the Cambridge spectrometer as well as the principle data acquisition and interpretation methods.

[Chapters 3](#) and [4](#) describe the development and testing of two new pieces of equipment. MiniScat, a compact helium atom scattering apparatus, has been designed as a sample preparation facility to enable structural studies and increase the experimental throughput. A new supersonic helium beam source improves the resolution of the HeSE spectrometer by a factor of 5.5 and extends accessible timescales into the nanosecond range.

The dynamics of cyclopentadienyl (Cp) on Cu(111) are presented in [Chap. 5](#). The ionically bound Cp is remarkably mobile, moving in single jumps between adjacent hollow sites over an energy barrier of 41 ± 1 meV. The data exhibit multicomponent lineshapes that allow the determination of the energy difference between fcc and hcp sites of 10.6 ± 1.7 meV in a Bayesian method probing the probability space of all data combined. Molecular dynamics (MD) simulations provide a friction coefficient of 2.5 ± 0.5 ps⁻¹.

[Chapter 6](#) shows that a physisorbed pyrrole hops between bridge sites on Cu(111). Strong lateral interactions alter the lineshapes from a predicted double exponential toward an apparent single exponential decay. First principles density functional theory calculations reveal that a large contribution to the experimentally determined apparent activation energy of 53 ± 4 meV arises from a site-dependence in the zero point energies, primarily of the vibrational C–H and N–H out-of-plane bending and ring torsion modes which are not directly involved in the diffusion process.

The surface dynamics of thiophene/Cu(111) are investigated in [Chap. 7](#). Thiophene adsorbs on top sites and forms a covalent S–Cu bond. Two competing activated processes manifest themselves in a kink in the Arrhenius plot: jump diffusion between adjacent top sites over a barrier of 59–62 meV and rotation

around the S–Cu anchor point over a barrier of 17 ± 2 meV. In addition, flapping between different tilt angles is observed. MD simulations of the diffusive motion reveal an exceptionally high friction of 5 ± 2 ps⁻¹.

Acknowledgments

I would like to express my sincere gratitude to my supervisor Dr. John Ellis for his guidance, advice, and encouragement. His seemingly limitless enthusiasm for scientific matters was a great source of motivation throughout my time in this group. Likewise, I am indebted to Dr. Bill Allison who always took the time to support and advise me in my endeavours.

Special thanks go to Dr. Andrew Jardine for his help and advice on the design and construction of MiniScat and the new source, as well as to Dr. Holly Hedgeland who instructed and supported me during my first attempts at measuring and analysing data. Furthermore, I would like to thank my second supervisor Dr. Jacqui Cole for her encouragement.

Outside the group, I am indebted to Prof. Jane Hinch—initiator of the study of the dynamics of five-membered molecules—for her help, advice and many illuminating discussions. I am also grateful to collaborators Dr. Stephen Jenkins and Dr. Marco Sacchi for complementing my experimental work with their DFT calculations.

I wish to thank all previous and current students of the Surface Physics Group, in particular Dr. David Ward and Dr. Andrew Alderwick for generously sharing their computer knowledge and Dr. Pepijn Kole and Dr. David Chisnall for lending me a hand in the lab on numerous occasions in the process of constructing MiniScat and the source. Together with Dr. Fay Tuddenham, Dr. Suzanne Paterson, Dr. Eliza McIntosh, Kelsey Stoerzinger, and Jianding Zhu they made our lab an enjoyable and exciting place to work at. I am also thankful to the members of the Cavendish workshops, in particular Nigel Palfrey, Rik Balsod, Gavin Ross, and Peter Norman, for their help.

My special thanks go to Gonville and Caius College, its graduate community and Caius Boat Club for giving me a life outside the lab.

I am extremely grateful to my family and Florian for their support and encouragement throughout my studies.

Finally, I would like to thank the Austrian Academy of Sciences, the Austrian Exchange Service and the EPSRC for financial support.

Contents

1	Introduction	1
	References	4
2	The Helium-3 Spin-Echo Experiment	5
2.1	Helium Atom Scattering	5
2.1.1	Diffraction Measurements	6
2.1.2	Adsorption and Desorption Studies	7
2.1.3	Measuring Surface Dynamics	8
2.2	Helium-3 Spin-Echo Spectroscopy	10
2.3	The Cambridge Helium-3 Spin-Echo Spectrometer	11
2.4	Interpreting Helium-3 Spin-Echo Data	15
2.4.1	Jump Diffusion	17
2.4.2	Lateral Interactions: De Gennes Narrowing	24
2.4.3	Molecular Dynamics Simulations	29
	References	31
3	A New Helium Atom Scattering Apparatus	33
3.1	Motivation	33
3.2	Design and Experimental Setup	35
3.2.1	Vacuum System	35
3.2.2	Power Distribution and Computer Control	38
3.2.3	Beam Source	40
3.2.4	Scattering Chamber and Sample Preparation Facilities	40
3.2.5	Detector	42
3.2.6	Two Different Instrument Configurations	43
3.3	Characterisation	43
3.3.1	Uptake Measurements	44
3.3.2	Diffraction Studies	45
3.3.3	Thermal Desorption Spectroscopy	47
3.4	Conclusions	48
	References	49

4	An Improved High Intensity Supersonic Helium Beam Source . . .	51
4.1	Introduction	52
4.2	A New Low Temperature Nozzle Assembly	53
4.2.1	Design	54
4.2.2	Characterisation	56
4.3	Effects of Size and Shape of the Skimmer and Its Mount.	61
4.3.1	Design	61
4.3.2	Performance	63
4.3.3	Discussion and Future Work	65
4.4	Conclusions	68
	References	68
5	The Dynamics of Cyclopentadienyl on Cu(111)	71
5.1	Literature Background	72
5.1.1	The Structure of Cp	72
5.1.2	Cp Adsorption on Copper Surfaces	72
5.1.3	Cp Adsorption on Other Metal Surfaces	73
5.1.4	Metallocene Adsorption	74
5.2	Experimental Methods	75
5.3	Adsorption Behaviour	76
5.4	Measuring the Surface Dynamics	78
5.4.1	Multi-component Lineshapes	78
5.4.2	Jump Diffusion Curves	81
5.4.3	An Activation Energy from Temperature Dependence	83
5.5	First Principles Density Functional Theory Calculations.	85
5.6	Molecular Dynamics Simulations	87
5.6.1	Creating a Potential Energy Surface	87
5.6.2	Modelling Diffusion on a Lattice of fcc and hcp Sites.	89
5.6.3	Microscopic Aspects of the Friction	91
5.7	Weak Lateral Interactions.	93
5.8	Determining the Energy Difference Between fcc and hcp Hollow Sites	94
5.9	Intracell Diffusion as a Handle on Friction and Spring Constant.	98
5.10	Conclusions	101
	References	102
6	Quantum Influences in the Diffusive Motion of Pyrrole on Cu(111).	105
6.1	Literature Background	106
6.1.1	The Structure of Pyrrole	106
6.1.2	Pyrrole Adsorption on Copper Surfaces	107
6.1.3	Pyrrole Adsorption on Other Transition Metal Surfaces	108

6.2	Experimental Methods	110
6.3	Adsorption Behaviour	111
6.4	Measuring the Surface Dynamics	116
6.4.1	Experimental Lineshapes	116
6.4.2	Hopping over an Energy Barrier	119
6.4.3	Momentum Transfer and Coverage Dependence of the Dynamics	119
6.5	First Principles Density Functional Theory Calculations.	124
6.6	Molecular Dynamics Simulations Investigate the Effect of Lateral Interactions	126
6.6.1	Creating a Potential Energy Surface	127
6.6.2	Modelling the Diffusion of Pyrrole/Cu(111).	128
6.6.3	Interaction Potential	133
6.6.4	Influences of Lateral Interactions on the Lineshapes	135
6.7	Lateral Changes in the Zero Point Energies of Vibrational Modes	138
6.8	Conclusions and Outlook	139
	References	140
7	The Atomic-Scale Motion of Thiophene on Cu(111).	143
7.1	Literature Background	144
7.1.1	The Structure of Thiophene	144
7.1.2	Thiophene Adsorption on Cu(111)	145
7.2	Experimental Methods	148
7.3	Adsorption Behaviour	148
7.4	Measuring the Surface Dynamics	152
7.4.1	Complex Lineshapes	152
7.4.2	Two Competing Activated Processes.	155
7.4.3	Jump Diffusion	156
7.4.4	Activated Rotation	158
7.4.5	Flapping of the Molecular Ring	159
7.5	First Principles Density Functional Theory Calculations.	162
7.6	Molecular Dynamics Simulations Reveal an Exceptionally High Friction	162
7.7	Conclusions	166
	References	167
8	Conclusions	169
8.1	Equipment Development	169
8.2	Dynamics Experiments.	170
	References	172

Publications Related to the Thesis

Results from the present thesis have been published in:

- F. E. Tuddenham, H. Hedgeland, A. P. Jardine, B. A. J. Lechner, B. J. Hinch and W. Allison, Lineshapes in quasi-elastic scattering from species hopping between non-equivalent surface sites, *Surf. Sci.*, 604, 1459–1475 (2010).
- H. Hedgeland, B. A. J. Lechner, F. E. Tuddenham, A. P. Jardine, W. Allison, J. Ellis, M. Sacchi, S. J. Jenkins and B. J. Hinch, Weak Intermolecular Interactions in an Ionically Bound Molecular Adsorbate: Cyclopentadienyl/Cu(111), *Phys. Rev. Lett.*, 106, 186101 (2011).
- B. A. J. Lechner, H. Hedgeland, J. Ellis, W. Allison, M. Sacchi, S. J. Jenkins and B. J. Hinch, Quantum Influences in the Diffusive Motion of Pyrrole/Cu(111), *Angew. Chem. Int. Ed.*, 52, 5085–5088 (2013).
- B. A. J. Lechner, M. Sacchi, A. P. Jardine, H. Hedgeland, W. Allison, J. Ellis, S. J. Jenkins P. C. Dastoor and B. J. Hinch, Jumping, Rotating and Flapping: The Atomic-Scale Motion of Thiophene on Cu(111), *J. Phys. Chem. Lett.*, 4, 1953–1958 (2013).
- B. A. J. Lechner, A. S. de Wijn, H. Hedgeland, A. P. Jardine, B. J. Hinch, W. Allison and J. Ellis, Atomic scale friction of molecular adsorbates during diffusion, *J. Chem. Phys.*, 138, 194710 (2013).
- B. A. J. Lechner, H. Hedgeland, W. Allison, J. Ellis, and A. P. Jardine, A new design for a low-temperature high-intensity helium beam source, *Rev. Sci. Instrum.*, 84, 026105 (2013).
- B. A. J. Lechner, P. R. Kole, H. Hedgeland, A. P. Jardine, W. Allison, B. J. Hinch and J. Ellis, Ultra-high precision determination of site energy differences using a Bayesian method, *Phys. Rev. B.*, 89, 121405(R) (2014).