Springer Theses

Recognizing Outstanding Ph.D. Research

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.

More information about this series at http://www.springer.com/series/8790

Akitoshi Shiotari

Reactivity of Nitric Oxide on Copper Surfaces

Elucidated by Direct Observation of Valence Orbitals

Doctoral Thesis accepted by
Kyoto University, Kyoto, Japan

Springer

Author
Dr. Akitoshi Shiotari
The University of Tokyo
Kashiwa
Japan

Supervisor
Prof. Hiroshi Okuyama
Kyoto University
Kyoto
Japan

ISSN 2190-5053 ISSN 2190-5061 (electronic)
Springer Theses
ISBN 978-981-10-4581-3 ISBN 978-981-10-4582-0 (eBook)
DOI 10.1007/978-981-10-4582-0

Library of Congress Control Number: 2017939899

Printed on acid-free paper

This Springer imprint is published by Springer Nature
The registered company is Springer Nature Singapore Pte Ltd.
The registered company address is: 152 Beach Road, #21-01/04 Gateway East, Singapore 189721, Singapore

Supervisor's Foreword

Scanning tunneling microscopy (STM) is currently routinely used in molecular science studies. In particular, its capability of imaging molecular orbitals has made it an invaluable tool for visualizing quantum chemistry in real space. However, the molecular orbitals are quite commonly hybridized with metallic bands of the substrate, which results in quenching of the localized orbital character. Therefore, a requisite for orbital imaging is that the orbital interaction with the substrate be sufficiently weak. A weaker interaction, however, might cause the molecule to diffuse across the template, making it difficult to image individual molecules. In this context, a copper substrate is ideal, where moderate interactions fix molecules to the surface while their orbitals remain localized on the molecule. A key factor for effective STM measurements is the position of the substrate d-band with respect to the Fermi level.

In his doctoral work, Akitoshi Shiotari imaged the $2\pi^*$ orbital of nitric oxide (NO) using STM. He used three kinds of low-index planes of copper as the substrates and showed that the orbital has either a degenerate (ring) or non-degenerate (dumbbell) character, depending on the structure of the templates. Most notably, in addition to imaging the orbital, the overlap between the molecules could also be controlled. Consequently, in this study, covalent bond formation could be visualized as a function of the intermolecular distance. Furthermore, by applying the full spectrum of STM techniques including scanning tunneling spectroscopy, inelastic electron tunneling spectroscopy, and "action" spectroscopy, he conducted a series of single-molecule chemical and physical surface studies of NO. From these studies, the intermolecular interactions, N–O bond dissociation, and electronic-vibrational coupling were elucidated. The local probe technique proved useful in disentangling the complex chemistry of NO on metal surfaces. This work provides a demonstration of the quantum properties of a molecule and is a useful reference for future single-molecule studies of NO on metal surfaces.

Kyoto, Japan
February 2017

Hiroshi Okuyama

Parts of this thesis have been published in the following journal articles:

- A. Shiotari, Y. Kitaguchi, H. Okuyama, S. Hatta, T. Aruga, "Imaging Covalent Bonding between Two NO Molecules on Cu(110)," *Physical Review Letters* **106**, 156104 (2011). Copyright 2011, American Physical Society. Reproduced with permission.
- A. Shiotari, S. Hatta, H. Okuyama, T. Aruga, "Role of hydrogen bonding in the catalytic reduction of nitric oxide," *Chemical Science* **5**, 922–926 (2014). Reproduced by permission of The Royal Society of Chemistry.
- A. Shiotari, T. Mitsui, H. Okuyama, S. Hatta, T. Aruga, T. Koitaya, J. Yoshinobu, "Configuration change of NO on Cu(110) as a function of temperature," *The Journal of Chemical Physics* **140**, 214706 (2014). Copyright 2014, American Institute Physics. Reproduced with permission.
- A. Shiotari, S. Hatta, H. Okuyama, T. Aruga, "Formation of unique trimer of nitric oxide on Cu(111)," *The Journal of Chemical Physics* **141**, 134705 (2014). Copyright 2014, American Institute Physics. Reproduced with permission.
- A. Shiotari, H. Okuyama, S. Hatta, T. Aruga, M. Alducin, T. Frederiksen, "Role of valence states of adsorbates in inelastic electron tunneling microscopy: A study of nitric oxide on Cu(110) and Cu(001)," *Phys. Rev. B* **94**, 075442 (2016). Copyright 2016, American Physical Society. Reproduced with permission.

Acknowledgements

First, I would like to express my deepest appreciation to my supervisor, Prof. Hiroshi Okuyama (Graduate School of Science, Kyoto University (KU), Japan) for giving me a wealth of insightful comments and suggestions. I also thank Prof. Tetsuya Aruga, Dr. Shinichiro Hatta, and other members of the surface chemistry laboratory at the Graduate School of Science, KU, for our many fruitful discussions.

I am grateful to Prof. Thomas Frederiksen and Dr. Maite Alducin (Donostia International Physics Center, Spain) for conducting theoretical calculations. I appreciate Prof. Jun Yoshinobu (Institute for Solid State Physics (ISSP), the University of Tokyo (UT), Japan) and Dr. Takanori Koitaya (Graduate School of Arts and Science, UT) for supporting my research when I was a visitor at the ISSP. I appreciate the support of Prof. Toshihiko Yokoyama (Institute for Molecular Science (IMS), Japan) and Prof. Takeshi Nakagawa (Kyushu University, Japan) during my research visit to the IMS. I am grateful to Mr. Takuya Mitsui (Nikon Corporation, Japan) for conducting experimental work with electron energy loss spectroscopy. I also would like to thank Prof. Yoshitada Morikawa, Prof. Ikutaro Hamada, and Dr. Yuji Hamamoto (Osaka University, Japan) for our fruitful discussions.

Dr. Takashi Kumagai (Fritz Haber Institute (FHI) of the Max Planck Society, Germany) provided me with an opportunity to research at the FHI, and I am deeply grateful to him because my six-month stay there, as a visiting student, was a precious and irreplaceable experience. I sincerely thank Prof. Martin Wolf for supervising my visiting research at the FHI. I also would like to acknowledge the support of Dr. Johannes Mielke, Dr. Janina Ladenthin, and the other researchers and staff at the FHI during my stay in Berlin.

I wish to thank Dr. Takashi Unuma (Tsu Local Meteorological Office, Japan) who has always encouraged me to maintain my motivation for research.

I thank Prof. Yoshiaki Sugimoto (Department of Advanced Materials Science, UT), Dr. Takashi Kumagai (FHI), and Mr. Hiroyuki Koshida (KU) for thier kind support during my thesis preparation.

I am grateful for the support given by the Japan Society for the Promotion of Science (JSPS KAKENHI Grant Number JP12J00219).

Finally, I am grateful to my family for their support.

Contents