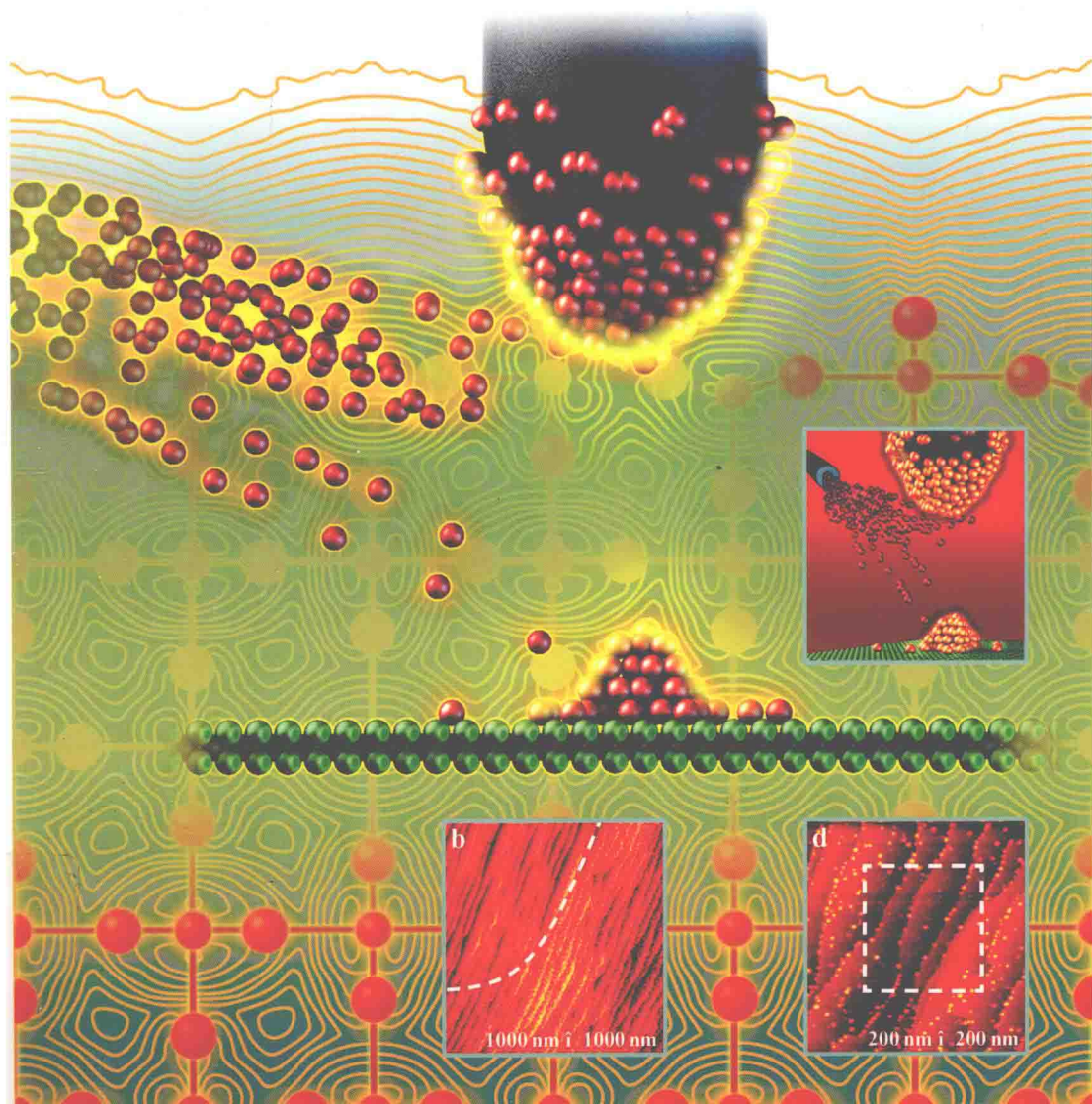


Edited by Michael Bowker and
Philip R. Davies

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Scanning Tunneling Microscopy in Surface Science, Nanoscience and Catalysis



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Michael Bowker and Philip R. Davies



WILEY-VCH Verlag GmbH & Co. KGaA

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Cover illustration

The STM images being past of the front cover picture have been kindly provided by the group of D. Wayne Goodman (authors of Chapter 3).

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Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <http://dnb.d-nb.de>

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Printed in the Federal Republic of Germany
Printed on acid-free paper

Cover Design Formgeber, Eppelheim

Typesetting Thomson Digital, Noida, India

Printing Strauss GmbH, Mörlenbach

Bookbinding Litges & Dopf Buchbinderei GmbH, Heppenheim

ISBN: 978-3-527-31982-4

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and Catalysis**

Edited by
Michael Bowker and Philip R. Davies

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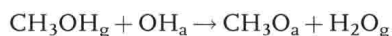
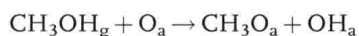
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Preface

The objective of this book is to highlight the important strides being made toward a molecular understanding of the processes that occur at surfaces through the unique information provided by the proximal scanning probe family of techniques: this principally involves scanning tunneling microscopy (STM) but some atomic force microscopy (AFM) experiments are also included.

The chapters in this book describe several *state-of-the-art* examples where an atomic understanding of surface processes is developing out of atomically resolved information provided by STM and AFM. The focus of much of the work is on understanding the fundamentals of catalysis, a reflection of the huge significance of heterogeneous catalysis in society today, but the discoveries being made in this field will undoubtedly have a much wider significance in the field of nanoscience/technology.

Reaction equations are derived from the results of global reaction measurements and considerations of stoichiometry. Until recently, the intermediates (and in particular the surface species) involved in the mechanism and their spatial location have remained largely theoretical. The advent of STM has, for the first time, allowed us the possibility of getting direct insight into this area. An example is the molecular identification of the sequence of reaction steps and of the species involved in the reaction of gas-phase methanol with oxygen on a copper surface. This produces methoxy groups as the first step, in which the slightly acidic hydrogen from the alcohol is stripped by surface oxygen leading to water desorption, as shown below, where the subscript "a" refers to an adsorbed species.



In this case, as in many others, STM has enabled us to identify the active sites at which reaction between methanol and adsorbed oxygen takes place, and has also allowed us to verify, at the atomic and the molecular scale, that the reaction does indeed occur in the way the above stoichiometric equations describe. This is invaluable information in the quest to understand and improve catalytic processes.

The principal advantage of the probe methods is their extraordinary spatial resolution (<0.1 nm) that does not, by necessity, require large areas of order. Their potential is further expanded by the ability to study surfaces under conditions that range from ultrahigh vacuum at cryogenic temperatures to industrially relevant pressures and temperatures to aggressive liquid phases. A major aim is to identify surface structures and intermediates present during operation *in situ* and *in operando*. There are three principal requirements to achieve these objectives: (i) high-pressure operation (already demonstrated by a number of individual groups in the field); (ii) the ability to image at high temperature while at high pressure (to some degree, this has been achieved, although there are limitations to the temperature range that can be studied, especially at above ambient pressure); (iii) fast scanning (of the order of 1–10 images per second) since catalytic turnover rates are often very high (e.g., 10 s^{-1}). This is also important for the ultimate aim of determining the statistics of the reaction (e.g., determining directly, *in situ*, the turnover number for the reaction). The authors believe that these aims will be realized in the next 10 years or so, but we are not quite there yet. There is plenty of room in the field for further developments.

It is fitting that this book should include a contribution from the laboratory of Somorjai, one of the principal exponents of the surface science approach to catalysis, who has developed a number of new approaches to the field and who, in recent years, has looked, in particular, at adsorption and surface reactions at high gas pressures. He reviews this work with some considerable and helpful focus on equipment developments. Similarly, Goodman has been a strong advocate of *in situ* high-pressure studies and has been at the forefront of developments in the field for some considerable time. He reviews the state of the art and generously acknowledges the contribution of colleagues in the field, some of whom have contributed to this volume.

Kolb and Simeone discuss the application of STM to samples in the liquid environment and deposition of metal from the STM tip itself, via reaction and neutralization of cations from solution, generating reproducible patterns at nanometer scales. The ability to control nanoparticle formation in terms of constant spacing, spatial arrangement, and monosized dispersion is a crucial one for future nanotechnology developments and Becker and Wandelt have also concerned themselves with the synthesis of reproducible patterns of particles at the nanoscale. They illustrate the potential of a bottom-up process, by gas-phase metal deposition, for generating model catalysts that can be studied both by spatially averaging techniques and by scanning tunneling microscopy.

Netzer and Surnev consider the problem of generating model catalyst systems for study using STM from a different direction. They examine the growth of thin oxide films on metal substrates, the “inverse” catalyst approach, and show the intrinsic beauty in the geometrical arrangements of thin-layer oxides that can be obtained when high-quality imaging is pursued. They also report the formation of new types of oxide structure in the 2D regime. Importantly, they give consideration to the particular problems of interpretation posed by STM images of thin oxide layers. Since STM images involve a convolution of the substrate, adsorbate, and STM tip

electronic states, interpretation of STM images is critical to all of the work presented in this book and the contribution by Hofer, Lin, and Teobaldi is particularly welcome since it provides a detailed review of the advances made in the theory of STM imaging, highlighting areas where theory now has a good grasp of the issues and where further development is needed.

The ability of STM to image at the atomic scale is particularly exemplified by the two other chapters in the book. Thornton and Pang discuss the identification of point defects at TiO_2 surfaces, a material that has played an important role in model catalyst studies to date. Point defects have been suggested to be responsible for much of the activity at oxide surfaces and the ability to identify these features and track their reactions with such species as oxygen and water represents a major advance in our ability to explore surface reactions. Meanwhile, Baddeley and Richardson concentrate on the effects of chirality at surfaces, and on the important field of surface chirality and its effects on adsorption, in a chapter that touches on one of the fundamental questions in the whole of science – the origins of life itself!

In recent years, studies using STM have expanded from the use of the atomically flat metal single crystals that have been the mainstay of surface science since the mid-1960s to complex oxide surfaces and to 3D nanoparticles, often grown on representative catalyst supports. The improvement in the technology and interpretation of imaging, and the increasing complexity of the surfaces being studied, ensures a pivotal role in the future for surface science, particularly in the context of the increasing practical importance of nanoscience in technological development.

Cardiff University,
December 2009

Michael Bowker and Philip R. Davies

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1

Chirality at Metal Surfaces

Chris J. Baddeley and Neville V. Richardson

1.1

Introduction

Since the mid-1990s, the number of surface science investigations of chirality at surfaces has increased exponentially. Advances in the technique of scanning tunneling microscopy (STM) have been crucial in enabling the visualization of single chiral molecules, clusters, and extended arrays. As such, STM has facilitated dramatic advances in the fundamental understanding of the interactions of chiral molecules with surfaces and the phenomena of chiral amplification and chiral recognition. These issues are of considerable technological importance, for example, in the development of heterogeneous catalysts for the production of chiral pharmaceuticals and in the design of biosensors. In addition, the understanding of chirality at surfaces may be a key to unraveling the complexities of the origin of life.

1.1.1

Definition of Chirality

The word chirality is derived from the Greek *kheir* meaning “hand.” It is the geometric property of an object that distinguishes a right hand from a left hand. Lord Kelvin provided a definition of chirality in his 1884 Baltimore Lectures, “I call any geometrical figure or group of points ‘chiral’ and say it has ‘chirality’, if its image in a plane mirror, ideally realized, cannot be brought into coincidence with itself.” For an isolated object, for example, a molecule, the above statement can be interpreted as being equivalent to requiring that the object possesses neither a mirror plane of symmetry nor a point of symmetry (center of inversion). If a molecule possesses either one of these symmetry elements, it can be superimposed on its mirror image and is therefore *achiral*. A chiral molecule and its mirror image are referred to as being a pair of *enantiomers*. Many organic molecules possess the property of chirality. Chiral centers are most commonly associated with the tetrahedral coordination of four different substituents. However, there are many examples of other rigid

structures that have chiral properties where a significant barrier exists to conformational change within the molecule.

1.1.2

Nomenclature of Chirality: The (*R*),(*S*) Convention

Most of the physical properties (e.g., boiling and melting point, density, refractive index, etc.) of two enantiomers are identical. Importantly, however, the two enantiomers interact differently with polarized light. When plane polarized light interacts with a sample of chiral molecules, there is a measurable net rotation of the plane of polarization. Such molecules are said to be optically active. If the chiral compound causes the plane of polarization to rotate in a clockwise (positive) direction as viewed by an observer facing the beam, the compound is said to be dextrorotatory. An anticlockwise (negative) rotation is caused by a levorotatory compound. Dextrorotatory chiral compounds are often given the label *D* or (+) while levorotatory compounds are denoted by *L* or (−).

In this chapter, we will use an alternative convention that labels chiral molecules according to their absolute stereochemistry. The (*R*),(*S*) convention or Cahn–Ingold–Prelog system was first introduced by Robert S. Cahn and Sir Christopher K. Ingold (University College, London) in 1951 and later modified by Vlado Prelog (Swiss Federal Institute of Technology) [1]. Essentially, the four atomic substituents at a stereocenter are identified and assigned a priority (1 (highest), 2, 3, 4 (lowest)) by atomic mass. If two atomic substituents are the same, their priority is defined by working outward along the chain of atoms until a point of difference is reached. Using the same considerations of atomic mass, the priority is then assigned at the first point of difference. For example, a $-\text{CH}_2-\text{CH}_3$ substituent has a higher priority than a $-\text{CH}_3$ substituent. Once the priority has been assigned around the stereocenter, the tetrahedral arrangement is viewed along the bond between the central atom and the lowest priority (4) substituent (often a C–H bond) from the opposite side to the substituent (Figure 1.1). If the three other substituents are arranged such that the path from 1 to 2 to 3 involves a clockwise rotation, the stereocenter is labeled (*R*) (Latin *rectus* for right). By contrast, if the path involves an anticlockwise rotation, the stereocenter is labeled (*S*) (Latin *sinister* for left). It is important to note that the absolute stereochemistry cannot be predicted from the *L* or *D* labels and vice versa.

In nature, a remarkable, and so far unexplained, fact is that the amino acid building blocks of all proteins are exclusively left-handed and that the sugars contained within the double helix structure of DNA are exclusively right-handed. The consequences of the chirality of living organisms are far reaching. The human sense of smell, for example, is able to distinguish between pure (*R*)-limonene (smelling of oranges) and (*S*)-limonene (smelling of lemons). More significantly, two enantiomeric forms of an organic molecule can have different physiological effects on human body. In many cases, one enantiomer is the active component while the opposite enantiomer has no effect (e.g., ibuprofen where the (*S*)-enantiomer is active). However, often the two enantiomers have dramatically different effects. For example, (*S*)-methamphetamine

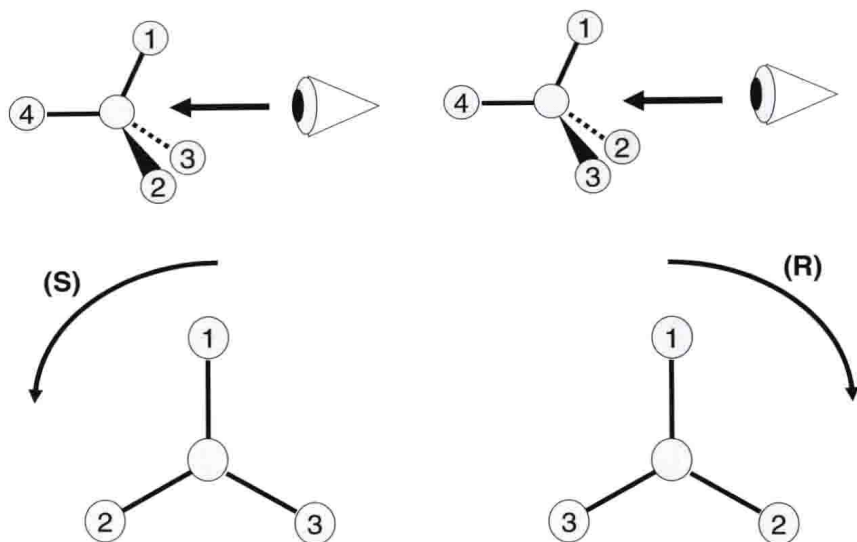


Figure 1.1 Schematic diagram explaining the Cahn-Ingold-Prelog convention for determining the absolute stereochemistry of a chiral molecule.

is a psychostimulant while (*R*)-methamphetamine is the active ingredient in many nasal decongestants (Figure 1.2).

In the pharmaceutical industry, about half of all of the new drugs being tested require the production of exclusively one enantiomeric product. Thermodynamically, this is a challenging problem since the two isolated enantiomers have identical Gibbs energies; the reaction from prochiral reagent to product should therefore result in a 50 : 50 (*racemic*) mixture at equilibrium. To skew the reaction pathway to form one product with close to 100% enantioselectivity is nontrivial. Knowles [2], Noyori [3], and Sharpless [4] were awarded the Nobel Prize in Chemistry in 2001 for developing enantioselective homogeneous catalysts capable of producing chiral molecules on an industrial scale. Typically, these catalysts consist of organometallic complexes with chiral ligands. Access to the metal center by the reagent is strongly sterically influenced by the chiral ligands resulting in preferential formation of one enantiomeric product. There are many potential advantages of using heterogeneous catalysts, not least the ease of separation of the catalyst from the products. However, despite extensive research over several decades, relatively few successful catalysts have been synthesized on a laboratory scale and the impact on industrial catalysis is essentially negligible. One of the primary motivations behind surface science studies of chirality at surfaces is to understand the surface chemistry underpinning chiral catalysis and to develop methodologies for the rational design of chiral catalysts. Similarly, those interested in issues related to the origin of life are investigating the possibility that surfaces were responsible for the initial seeding of the chiral building blocks of life and that, presumably via some chiral amplification effects, this led to the overwhelming dominance of left-handed amino acids and right-handed sugars in