METHODS OF SURFACE CHARACTERIZATION • VOLUME 1

VIBRATIONAL SPECTROSCOPY OF MOLECULES ON SURFACES

Edited by
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and
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Vibrational Spectroscopy of Molecules on Surfaces

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Preface to the Series

A large variety of techniques are now being used to characterize many different surface properties. While many of these techniques are relatively simple in concept, their successful utilization involves rather complex instrumentation, avoiding many problems, discerning artifacts, and careful analysis of the data. Different methods are required for handling, preparing, and processing different types of specimen materials. Many scientists develop surface characterization methods, and there are extensive developments in techniques reported each year.

We have designed this series to assist newcomers to the field of surface characterization, although we hope that the series will also be of value to more experienced workers. The approach is pedagogical or tutorial. Our main objective is to describe the principles, techniques, and methods that are considered important for surface characterization, with emphasis on how important surface characterization measurements are made and how to ensure that the measurements and interpretations are satisfactory, to the greatest extent possible. At this time, we have planned four volumes, but others may follow.

This first volume brings together a description of methods for vibrational spectroscopy of molecules on surfaces. Most of the techniques are currently under active development; commercial instrumentation is not yet available for some techniques, but this situation could change in the next few years. The current state of the art of each technique is described, as are its relative capabilities. An important component of this volume is the summary of the relevant theory.

Two volumes are in preparation which will contain descriptions of the techniques and methods of electron and ion spectroscopies which are in widespread use for surface analysis. These volumes are largely concerned with techniques for which commercial instrumentation is available. The books will fill the gap between a manufacturer's handbook and review articles which highlight the latest scientific developments.

A fourth volume will give descriptions of techniques for specimen handling and depth profiling. It will provide a compilation of methods that have proven useful for specimen handling and treatment, and it will also address the common artifacts and problems associated with the bombardment of solid surfaces by electrons and ions. Finally, a description will be given of methods for depth profiling.

Surface characterization measurements are being used increasingly in diverse areas of science and technology. We hope that this series will be useful in ensuring that these measurements can be made as efficiently and reliably as possible. Comments on the series are welcomed, as are suggestions for volumes on additional topics.

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Preface

The observation of the vibrational spectra of adsorbed species provides one of the most incisive methods for understanding chemical and physical phenomena on surfaces. At the present time, many approaches may be applied to studies of molecular vibrations on surfaces. Some of these are used on high-area solids of technological importance (e.g., heterogeneous catalysts) while others are applied to single-crystal substrates to gain better understanding under conditions of controlled surface structure.

This book has attempted to bring together in one place a discussion of the major methods used to measure vibrational spectra of surface species. The emphasis is on *basic concepts* and *experimental methods* rather than a current survey of the extensive literature in this field.

Two introductory chapters describe the basic theoretical aspects of vibrational spectroscopy on surfaces, dealing with normal modes and excitation mechanisms in vibrational spectroscopy. The remaining seven chapters deal with various methods employed to observe surface vibrations. These are arranged in an order that first treats the use of various methods on surfaces that are not of the single-crystal type. It is in this area that the field first got started in the late 1940s with pioneering work by Terenin and others in the Soviet Union, and by Eischens and others in the United States in the 1950s. The last four chapters deal with relatively recent methods that permit vibrational studies to be made on single-crystal substrates.

The basic philosophy of *Vibrational Spectroscopy of Molecules on Surfaces* has been to present information of a fundamental and practical type that can be used by students just beginning to enter the field. In addition, the authors have often included rather recent developments to lend a timely quality to each of the chapters.

The editors wish to extend their thanks to all of the authors whose work made this book possible.

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Normal Modes at Surfaces

N. V. Richardson and N. Sheppard

1. Introduction

Vibrational spectroscopic techniques have played a major role in extending our understanding of structure, bonding, and reactivity in all phases of matter. Only relatively recently has it become feasible to apply these powerful experimental methods to the study of surfaces and species adsorbed at those surfaces. Vibrational spectroscopy has the great advantage over many other surface-sensitive spectroscopies that one has available a vast body of data, already collected and understood, for gas phase, liquid phase, and solid systems. The concept of group frequency is of great importance. Similarly, our knowledge of spectroscopic activity in the gas phase and in three-dimensional crystalline arrays is well developed and amenable to the powerful methods of group theory in its interpretation.

An explosion of interest has occurred in the application of vibrational techniques to the surface environment. Understandably, the greatest body of data comes from adsorption on finely divided solids, using transmission infrared absorption spectroscopy or the inelastic scattering of thermal neutrons.[1–4] More recently Raman, reflection-absorption infrared, and electron energy loss (EEL) spectroscopies have been applied to adsorption on single-crystal surfaces.[5–10] These investigations can be supported by low-energy electron diffraction (LEED)

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measurements, which can identify ordered arrays of adsorbed species.[11] The latter, in turn, puts greater emphasis on the symmetry properties, both of isolated complexes, which might occur at low adsorbate coverages, and of regular arrays occurring at well-defined coverages. Application of spectroscopic selection rules, based on the symmetry properties of the system under investigation, allows a more rigorous and penetrating analysis of the spectroscopic data. This chapter seeks, therefore, to provide a timely systematic discussion of the symmetry properties of surfaces and surface-absorbed species and then to build on this a description of the vibrational properties of the system. The discussion is supplemented and clarified by inclusion of some examples for which the existing literature exhibits a number of misunderstandings.

Some of this work has previously appeared in an article by Sheppard and Erkelens.[12] In addition, Smith and Eckstrom[13] had previously discussed some particular cases of singly adsorbed molecules and ordered arrays. Nichols and Hexter have discussed, in group theoretical terms, some spectroscopic selection rules in relation to site symmetries of adsorbed molecules and overall symmetries of the combined adsorbate/adsorbent lattices.[14,15] Richardson and Sass[16] and Hexter with Albrecht[17] and with Nichols[18] had earlier discussed the more strictly specified Raman activity of vibrations of individual adsorbed molecules on metal single-crystal surfaces. In these cases, the screening of charges by metal surfaces must be taken into account. This is also true for ir and EELS leading to the "metal-surface selection rules." An introduction to some aspects of the symmetry properties of surfaces and their influence on experimental observations has been given by Richardson and Bradshaw.[19] A very good background to many of the topics covered in this chapter can be found in the textbook on EELS by Ibach and Mills.[9]

In Section 2, we discuss the connection between gas phase degrees of freedom and the vibrational degrees of freedom for the corresponding absorbed species, together with the mixing of adsorbate- and adsorbent-derived vibrations. In Section 3, we briefly review the selection rules governing the various spectroscopic techniques available for surface investigations but concentrate on those for EELS, ir, and Raman.

Section 4 introduces the symmetry consequences of an interface. We examine the symmetry properties of clean surfaces and of particular sites on those surfaces. Finally, in this section, we consider the symmetry reductions experienced by species on adsorption and the combined symmetry of adsorbate and adsorbent site. Section 4 is supported by specific examples covered in Section 5.

Sections 6 and 7 present a similar assessment of the behavior of ordered arrays of adsorbates, including a discussion of the delocalized