

VIBRATIONAL SPECTROSCOPY OF MOLECULES ON SURFACES

Edited by
JOHN T. YATES, Jr.
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Vibrational Spectroscopy of Molecules on Surfaces

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Vibrational Spectroscopy of Molecules on Surfaces

METHODS OF SURFACE CHARACTERIZATION

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Volume 1 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.

John T. Yates, Jr.
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Pittsburgh and Gaithersburg

Contents

1. Normal Modes at Surfaces	1
<i>N. V. Richardson and N. Sheppard</i>	
1. Introduction	1
2. The Vibrational Motions of Adsorbates at Surfaces	3
3. Spectroscopic Selection Rule	6
3.1. Infrared and Raman Spectroscopy	6
3.2. Vibrational Electron Energy Loss Spectroscopy (EELS)	7
3.3. Other Vibrational Spectroscopies	8
4. Site Symmetries of the Adsorbent	9
5. The Vibrational Modes of Isolated Surface Adsorption Complexes	14
5.1. Hydrogen on the (100) Face of a Cubic Metal	14
5.1.1. Site 1	15
5.1.2. Site 2	16
5.1.3. Site 4	16
5.2. CO Adsorbed Perpendicular to the (100) Face of a Cubic Metal ..	17
5.3. N ₂ Adsorbed Parallel to the Surface in the Bridge Site of a (100) Cubic Face	17
5.4. Ethylene on Bridge Sites of (100) or (111) Metal Faces	20
6. Two-Dimensional Adsorbate Arrays at Surfaces	21
7. The Vibrations of Adsorbate Arrays	24
7.1. $c(2 \times 2)$ Array of Adatoms in the Fourfold Hollow Site of the (100) Face of a Cubic Metal	29
7.2. Bridge Site Adatom Occupancy of the (100) Surface of a Cubic Metal	32
7.3. $c(4 \times 2)$ Structure for CO/Pt(111)	34
7.4. $c(4 \times 2)$ Structure for CO Adsorbed on Ni(111)	36
7.5. (2×1) Structure for CO Adsorbed on Ni(110) and Pd(110)	39
8. Adsorbent Surface Modes	39
8.1. $c(2 \times 2)$ Overlayers on Cu(100)	41
8.2. (1×2) Reconstruction of Ir(110), Pt(110), and Au(110)	43

9. Conclusion	45
<i>References</i>	46
2. Excitation Mechanisms in Vibrational Spectroscopy of Molecules on Surfaces	49
<i>J. W. Gadzuk</i>	
1. Introduction	49
1.1. Why Vibrational Spectroscopy?	50
1.2. Experimental Methods of Surface Vibrational Spectroscopy	52
1.2.1. Infrared-Absorption Spectroscopy	54
1.2.2. Surface-Enhanced Raman Spectroscopy	54
1.2.3. Electron Energy Loss Spectroscopy	56
1.2.4. Inelastic Tunneling Spectroscopy	57
1.2.5. Neutron Inelastic Scattering	57
1.2.6. Atomic Inelastic Scattering	58
1.3. Theoretical Strategies	58
2. Excitation Mechanisms	59
2.1. Harmonic Oscillator Mechanics	60
2.1.1. Free Oscillator	60
2.1.2. Forced Oscillator	60
2.2. Dynamic Dipoles	63
2.3. Radiative Excitation	65
2.4. Electronic Excitation	69
2.4.1. Dipole Scattering	69
2.4.2. Impact Scattering	72
2.5. Resonance Excitation	78
2.6. Neutron Excitation	83
3. Line-shape Information Content	86
3.1. Line-shape Generalities/Dephasing	87
3.2. Localized Oscillator–Continuum Systems	91
3.2.1. Electron–Hole Pairs	92
3.2.2. Phonons	93
3.2.3. Photons	95
3.2.4. Summary and Generalizations	95
3.3. Experimental Realization	96
<i>References</i>	99
3. Infrared Spectroscopy of High-Area Catalytic Surfaces	105
<i>A. T. Bell</i>	
1. Introduction	105
2. Techniques for the Acquisition of Spectra	106
2.1. Transmission Spectroscopy	106
2.2. Diffuse-Reflectance Spectroscopy	110
2.3. Photoacoustic Spectroscopy	112
3. Sample Preparation	114

4. Cell Designs	116
4.1. Transmission Spectroscopy	116
4.2. Diffuse-Reflectance and Photoacoustic Spectroscopies	122
5. Ancillary Equipment	124
6. Spectrometers	126
6.1. Dispersive Spectrometers	126
6.2. Fourier-Transform Spectrometers	128
6.3. Comparison of Fourier-Transform and Dispersive Spectrometers ..	130
6.3.1. Resolving Power	130
6.3.2. Signal-to-Noise Ratio	131
6.3.3. Data Acquisition, Storage, and Display	132
7. Concluding Remarks	133
<i>References</i>	133

4. Inelastic Electron Tunneling Spectroscopy 135

P. K. Hansma

1. Principles of the Method	135
1.1. A Water Analogy	135
1.2. Spectral Range, Sensitivity, Resolution, and Selection Rules	138
2. Description of Typical Apparatus	140
2.1. Apparatus for Sample Preparation	140
2.2. Apparatus for Measuring Spectra	143
3. Calibration, Artifacts, and Miscellaneous Problems	147
3.1. Calibration	147
3.2. Artifacts	148
3.3. Junction Geometry	149
3.4. Top Metal Electrode	150
3.5. Cryogenic Temperatures	153
4. Data Interpretation, Theory	154
4.1. Peak Position	154
4.2. Peak Widths	154
4.3. Peak Intensities	154
5. Examples of the Method's Use	158
5.1. Overview of Applications	158
5.2. The Study of Model Catalysts	161
5.3. The Study of Corrosion	168
6. Comparison with Other Techniques	170
7. Conclusions	175
<i>References</i>	176

5. Incoherent Inelastic Neutron Scattering: Vibrational Spectroscopy of Adsorbed Molecules on Surfaces 183

R. R. Cavanagh, J. J. Rush, and R. D. Kelley

1. Introduction	183
2. Fundamental Physics of Neutron Scattering	185

3. Experimental	188
3.1 Modified Triple-Axis Spectrometer	189
3.2. Time-of-Flight Spectrometry	192
3.3. Sample Cells	193
3.4. Sample Preparation	197
3.5. Data Acquisition	198
4. Analysis of Data	199
4.1. Force Models and Vibrational Dynamics	199
4.2. Neutron Spectra	202
4.3. Diffusion and Reorientation	202
5. Examples	206
5.1. Hydrogen/Raney Nickel	206
5.2. Hydrogen + Carbon Monoxide/Raney Nickel	209
5.3. Hydrocarbons on Platinum Black	211
5.4. Hydrocarbons in Zeolites	213
5.5. Diffusive Motions	214
6. Summary	217
References	219
 6. Electron Energy Loss Spectroscopy	223
<i>N. R. Avery</i>	
1. Background	223
2. The Spectrometer	225
2.1. General Requirements	225
2.2. The Energy Selectors	226
2.3. The Electron Monochromator	231
2.3.1. Input and Output Electron Optics	231
2.3.2. Current Available from Electron Monochromator	236
2.3.3. The Electron Source	237
2.4. The Energy Analyzer	238
2.4.1. The Suppressor	238
2.4.2. Electron Detectors	239
3. Construction Materials and Methods	241
3.1. Materials	241
3.2. Fabrication Methods	242
3.3. Shielding	245
4. Monochromator and Analyzer Power Supplies	246
5. Operating an EEL Spectrometer	250
5.1. Tuning	251
5.1.1. Aligning the Beam	251
5.1.2. Optimizing of the Beam	253
5.2. Calibration	255
6. Application of EELS to Surface Chemistry	257
6.1. Experimental	257
6.2. Surface Reaction Intermediate and Kinetics; Time-Resolved	

EELS	261
<i>References</i>	264
7. Reflection Absorption Infrared Spectroscopy	267
<i>B. E. Hayden</i>	
1. Introduction	267
1.1. Historical Development	267
1.2. General Principles	269
1.3. A Comparison with Other Techniques	277
2. Experimental Considerations	279
2.1. Optical Configuration	282
2.2. Radiation Sources	284
2.3. Monochromators and Interferometers	288
2.4. Modulation	292
2.5. Signal Detection	296
3. Applications	298
3.1. Selection Rules and the Adsorbate Geometry	298
3.2. Vibrational Frequencies as Fingerprints	304
3.3. Coverage-Dependent Frequency Shifts	316
3.3.1. Dipole Coupling	317
3.3.2. The Static Shift	320
3.4. Natural Half-Widths and Line Shapes	326
3.5. Intensities	332
4. Outlook	337
4.1. High-Resolution Vibrational Studies	338
4.2. Catalysis on Single Crystals	339
<i>References</i>	340
8. Raman Spectroscopy	345
<i>A. Campion</i>	
1. Introduction	345
2. Theory	348
2.1. Classical: The Polarizability Tensor	348
2.2. Quantum Mechanical: Selection Rules and Intensities	354
3. Experimental Considerations	357
3.1. Sensitivity and Surface Selectivity	357
3.2. Single-Crystal Surfaces	360
3.2.1. Electromagnetic Fields at Surfaces	360
3.2.2. Angle-Resolved Measurements	369
3.2.3. Selection Rules	373
3.3. High Surface Area Materials	377
4. Instrumentation	378
4.1. Laser Sources	378
4.2. Sample Configurations	380
4.2.1. Single-Crystal Samples	380

4.2.2. High Surface Area Materials	382
4.3. Conventional Detection Systems	383
4.3.1. Scanning Monochromators	384
4.3.2. Photomultipliers	384
4.3.3. Counting electronics	385
4.4. Multichannel detection	386
4.4.1. Spectrographs	386
4.4.2. Detector Arrays	386
5. Examples and Applications	389
5.1. Adsorbates on Single-Crystal Surfaces	389
5.2. High Surface Area Materials	393
5.2.1. Supports, Catalyst Structure	393
5.2.2. Adsorbates	396
6. Surface-Enhanced Raman Scattering	399
6.1. Introduction	399
6.2. Electromagnetic Enhancement	401
6.3. Chemical Enhancement	405
6.4. Applications of SERS	408
7. Outlook	410
References	412
 9. Infrared Spectroscopy of Adsorbates on Metals: Direct Absorption and Emission	 417
<i>P. L. Richards and R. G. Tobin</i>	
1. Introduction	417
2. Status of Relevant Technology	421
2.1. Overview	421
2.2. Photon Noise	425
2.3. Detectors	429
2.4. Spectrometers	431
2.5. Conclusions for Surface Spectroscopy	432
3. Direct Absorption Spectroscopy	433
3.1. Techniques for Measurement of Absorbed Power	433
3.2. Sensitivity of Thermal Detection	433
3.3. The Direct Absorption Instrument	436
3.4. Experimental Results: CO on Ag	442
3.5. Surface Calorimetry	447
4. Infrared Emission Spectroscopy	449
4.1. The Emission Spectrometer	449
4.2. Experimental Results: CO on Ni(100)	455
4.3. Arrays and the Multichannel Advantage	457
4.4. Nonequilibrium Emission and Chemiluminescence	458
References	459
 Index	 465

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-adsorbed 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 adsorbed 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