Far-Infrared Spectroscopy

KARL DIETER MÖLLER
Professor of Physics
Fairleigh-Dickinson University
Teaneck, New Jersey

WALTER G. ROTHSCILD
Department of Chemistry
Scientific Research Staff, Ford Motor Company
Dearborn, Michigan

Physikalische Bibliothek
Fachbereich 5
Technische Hochschule Darmstadt
Hochschulstraße 2
D-6100 Darmstadt

I. Physikalisches Institut
der Technischen Hochschule
Darmstadt

WILEY-INTERSCIENCE
A DIVISION OF JOHN WILEY & SONS, INC.
Contents

1 Grating Spectrometers

A. Introduction 1

B. Optical Layout of Spectrometers 2
   a. General 2
   b. Littrow Mount 2
   c. Czerny-Turner Mount 4
   d. Ebert-Fastie Mount 6
   e. f-Number of the Monochromator 8

C. Gratings 8
   a. General 8
   b. Grating Formula and Intensity Distribution 9
   c. Spectral Slit Width 15

D. Energy Limitations on the Resolving Power 16

E. Filters 19
   a. Introduction 19
   b. Attenuation Requirements 20
   c. Elimination of Short-Wavelength Radiation 22
   d. Reflection Crystal Filters (Reststrahlen Filters) 24
   e. Transmission Crystal-Powder Filters 24
   f. Reflection Filter Gratings 30
   g. Transmission Filter Gratings 31
   h. Metal Mesh Reflection Filters 35
   j. Interference Filters 41

F. Checks for False Radiation 41
G. Polarization of Spectrometer Components  42
   a. Reflection Filter Gratings  43
   b. Diffraction Gratings  44
   c. Crystal Reflection Plates  44

H. Wavelength Calibration  44
   a. General  44
   b. Calibration with Water Vapor  46
   c. Calibration with Methyl Chloride and Other Compounds  49

References  52

2 COMMON PARTS OF GRATING SPECTROMETERS AND INTERFEROMETERS AND SOME ACCESSORIES

A. Sources  55

B. Detectors  57
   a. Detector Characterization  57
   b. Golay Detector  58
   c. Liquid-Helium Temperature Detectors  60
      1. Introduction and General Considerations  61
      2. Carbon Resistance and Doped Germanium Bolometers  61
      3. Indium-Antimonide Detector  64
      4. Doped Germanium Photoconducting Detectors  66
      5. Comparison of the Liquid-Helium Temperature Detectors and Problems of Their Use  67

C. Light-Pipes  68

D. Conical Light-Pipes (Channel Condensers)  72

E. Polarizers  75
   a. Linear Polarizers  75
      1. Pile-of-Plates Polarizer  75
      2. Wire-Grating Polarizer  76
      3. Pyrolytic Graphite Transmission Polarizer  78
   b. Circular and Elliptical Polarizers  79
      1. Soleil Compensator  79
      2. Polarizer Using a Magnetic Field  81

F. Multiple-Path Cells  82

G. Image Transformer  86

H. Vacuum System and Cryogenic Equipment  87

References  88
# 3 Fabry-Perot Interference Filters and Tunable Fabry-Perot Etalon

A. Fabry-Perot Interference Filters and Spectrometer 90
   a. General 90
   b. Airy Formula and Finesse 90

B. Reflectors for the Far-Infrared 92
   a. Metal Gratings in Empty Space 93
   b. Grating and Mesh in the Vicinity of a Dielectric Medium 96
   c. Metal Meshes and Their Equivalent Circuit Representation 97
   d. Phase Measurements 107
   e. Fabrication of Meshes 107

C. Interference Filters 109
   a. Theory of Two-Mesh Filters 109
   b. Formulas for the Calculation of the Transmittance of Multi-Mesh Filters 111
   c. Construction of Fabry-Perot Interference Filters 111
   d. Measurements on Interference Filters and Comparison with Theory 113
   e. Phase Measurements with Interference Filters 122

D. Tunable Fabry-Perot Interferometer 123

E. Fabry-Perot Interferometer in Higher Orders 125

F. Comparison of a Grating and a Fabry-Perot Spectrometer under Energy-Limited Conditions 125

References 127

# 4 Fourier Transform Spectroscopy

A. Introduction 128

B. Interferogram Function and Fourier Transformation 129

C. Finite Path Difference, Apodization, and Resolution 131

D. Sampling 136

E. Phase Error and Its Correction. Maladjustment 139

F. Advantages and Disadvantages of Fourier Transform Spectroscopy Compared to Grating Spectroscopy 144

G. Finite Aperture, Sensitivity, and Dynamic Range of the Recording System 145

H. Michelson Interferometer 146
I. Lamellar-Grating Interferometer 151
J. Interferometry in the Asymmetric Mode 156
   a. Introduction 156
   b. Theory and Experimental Results 157
References 160

5 LOW-FREQUENCY STRETCHING AND BENDING FUNDAMENTALS
A. Introduction 163
B. Disulfur Dichloride and Disulfur Dibromide 164
C. Carbon Suboxide and Carbon Subsulfide 167
D. 1,4-Dioxadiene 173
E. Molecules Containing Fluorine 174
   a. Xenon Difluoride 174
   b. Xenon Tetrafluoride 178
   c. Phosphorous Pentaffluoride and Arsenic Pentafluoride 179
F. Metal Carbonyls 183
G. Halogen Derivatives of Alkyl Compounds 186
   References 195

6 FAR-INFRARED SPECTRA OF HYDROGEN-BONDED SYSTEMS
A. Introduction 198
B. Self-Associated Phenols 200
C. Hydrogen Bonds between Phenols and Amines 207
D. Hydrogen Bonding in Carboxylic Acids 211
E. Solvent Effects on Hydrogen-Bond Frequencies 214
F. Concluding Remarks 217
   References 217

7 SKELETAL MODES OF STRAINED-RING SYSTEMS
A. Introduction 218
B. Theoretical Considerations 220
C. Symmetric Ring-Puckering Potential Functions 221
   a. Cyclobutane and Perfluorocyclobutane 221
   b. Trimethylene Oxide 222
Contents

8 Torsional Motions with Periodic Potential Barriers

A. Introduction 256

B. One-Top Molecules with Threefold Barriers 256
   a. Introduction 256
   b. Principal Axis Method (PAM) and the Hamiltonian of the Internal Rotation for a Symmetric-Top Molecule 257
   c. Hamiltonian in the Internal Axis Method (IAM) for a Symmetric-Top Molecule 260
   d. Potential Energy 262
   e. Asymmetric-Top Molecules without Structural Symmetry and the Principal Axis Method (PAM) 262
   f. Asymmetric-Top Molecules with a Plane of Symmetry and the Internal Axis Method (IAM) 263
   g. Far-Infrared Spectrum of Methyl Alcohol 264
   h. Far-Infrared Torsional Vibration Spectra of Various Molecules 269
   i. Selection Rules 273
   j. Spectra and Calculations of the Potential Function Constants 275
C. Two-Top Molecules of C\textsubscript{2v} and C\textsubscript{3v} Symmetry with Threefold Barriers 279
   a. Kinetic and Potential Energy 279
   b. Harmonic Oscillator Approximation 281
   c. Periodic Potential Model. Symmetry Properties, Energy Level Scheme, Selection Rules 283
   d. Spectra and the Calculation of the Potential Function Constants 285

D. Three-Top Molecules (C\textsubscript{3v}) With Threefold Barriers 288
   a. Theoretical Considerations 288
   b. Spectra and Potential Barriers 289

E. Twofold Barriers 291
   a. Hydrogen Peroxide and Deuterated Hydrogen Peroxide 291
   b. Twofold Barriers about a Carbon–Carbon Bond 298
   c. Meta- and Ortho-Substituted Benzaldehyde and Furan-2-aldehyde 300

References 301

9 Pure Rotational Spectra of Vapors: Water

A. Introduction 303

B. Observed Spectra of Atmospheric Water Vapor 304
   a. Spectral Region 300 to 150 cm\textsuperscript{-1} 304
   b. Spectral Region 150 to 100 cm\textsuperscript{-1} 304
   c. Spectral Region 111 to 72 cm\textsuperscript{-1} 308
   d. Spectral Region 80 to 60 cm\textsuperscript{-1} 308
   e. Spectral Region 64 to 50 cm\textsuperscript{-1} 309
   f. Spectral Region 53 to 32 cm\textsuperscript{-1} 309
   g. Spectral Region 30 to 10 cm\textsuperscript{-1} 310

C. Computation and Tabulation of Pure Rotational Transitions of Water Vapor 313

D. Tabulation of Pure Rotational Water Vapor Transitions between 12 and 305 cm\textsuperscript{-1} 317

References 324

10 Collision-Induced Spectra at Long Wavelengths

A. Introduction 325
B. Theory of Induced Absorption 330
   a. Absorption Coefficients, Cluster Functions, and Induced Vibrational-Rotational Transitions 330
   b. Induced Pure Rotational Transitions 342
   c. Induced Pure Translational and Translational-Rotational Absorption 343

C. Experimental Observations 348
   a. Pure Translational Absorption. Helium-Argon and Neon-Argon Mixtures 348
   b. Rotational-Translational Absorption 358
      1. Hydrogen 358
      2. Nitrogen, Oxygen 359
   c. Pressure-Induced Quadrupole Spectra. Hydrogen Chloride and Hydrogen Bromide 362
   d. Induced Rotation-Translation Spectra in Liquids. Solutions of H_2, D_2, and HD in Liquid Ar 367

References 371

11 ROTATIONAL-TRANSLATIONAL MOTION IN CONDENSED PHASES

A. Introduction 373
B. The Heisenberg Picture 375
C. Rotational Motion from the Band Shapes of Vibrational Transitions 380
   a. Introduction 380
   b. Rotational Motion of Methylene Chloride (CH_2Cl_2) in Polystyrene 382
   c. Rotational Motion in Liquid Methyl Iodide 386
D. Rotational Motion from the Band Shapes of Rotational Spectra 389
   a. Introduction 389
   b. Individual Molecules. The Hydrogen Halides, Water, and Ammonia 394
   c. Rotational Motion of a Distortion in Liquid Carbon Tetrachloride 399
   d. Molecular Complexes and Clusters in Liquid Phases 403

References 411

12 FAR-INFRARED SPECTRA OF DIATOMIC CUBIC CRYSTALS

A. Introduction 412
B. Classical Description of Crystal Spectra 413
   a. Dielectric Constant, Refractive Index, and Extinction Coefficient 413
   b. Dispersion Formulas 416
   c. Kramers-Kronig Relations 419
   d. Dispersion Measurements on Alkali Halides 420
C. Effects of Periodicity 440
   a. Lattice Modes of Cubic Crystals 440
   b. Effects of Sample Geometry 447
   c. Selection Rules and General Appearance of the Spectra 451
D. Temperature Dependence of Phonon Interactions 460
   a. Occupation Number 460
   b. Frequency and Temperature Dependence of the Damping Constant 461
E. Structure Faults and Phonon Processes 465
   a. Supertransparency 465
   b. Diatomic Linear Chain with Symmetrically Placed Lattice Faults 465
References 470

13 FAR-INFRARED SPECTRA OF POLYATOMIC CRYSTALS

A. Introduction 472
B. Lattice Vibration Spectra of NiF₂, CoF₂, and FeF₂ 475
   a. Factor Group Analysis. General Principles 475
   b. Derivation of the Symmetry Species of the Fundamentals 480
   c. Experimental Results 490
C. Lattice Vibrations of KNiF₃ 492
D. Lattice Vibration in Crystalline Polyethylene 494
E. Spectra of Crystalline Nitrogen and Carbon Monoxide 497
F. Crystal Spectra of Complexes 500
   a. Silver Halide Complexes of the Types RAₓₓ₋ₓ, RAₓX₂, and R₂AₓX₃ 500
   b. Metal-Ligand Force Constants of Acetylacetonates 505
G. Temperature and Pressure Dependence of Lattice Modes 511
H. Vibrational Spectra of Orientationally Disordered Crystals. Translational Lattice Vibrations of Ice Ic and Ih 516
References 522
APPENDIX I  IMPURITY-INDUCED LATTICE ABSORPTION IN THE FAR-INFRARED, by A. J. Sievers

A. Introduction 525
B. Impurity-Induced Absorption 531
C. Local Modes 534
D. Gap Modes 539
   a. Monatomic Impurities 539
   b. Molecular Impurities 544
E. Resonant Modes 544
   a. Model 544
   b. Observations 548
   c. Stress Effects 551
   d. Temperature Effects 553
F. Summary 554
References 554

APPENDIX II  DIELECTRIC PROPERTIES AND OPTICAL PHONONS IN PARA- AND FERRO-ELECTRIC PEROVSKITES, by C. H. Perry

A. Introduction 557
B. Lattice Modes Based on the Shell Model 560
C. Crystal Symmetry and Species of the Vibrational Modes 567
D. Infrared Reflection Measurements 568
E. Analysis of Reflection Spectra by Means of a Kramers-Kronig Relation or a Fit with a Classical Dispersion Formula 574
   a. Kramers-Kronig Analysis 574
   b. Classical Dispersion Analysis 577
F. The Dielectric Response Function 582
G. Paraelectric Crystals 586
H. Ferroelectric Crystals 586
I. Conclusions 589
References 590

APPENDIX III  MAGNETIC PHENOMENA IN THE FAR-INFRARED, by Isaac F. Silvera

A. Introduction 592
B. Cryostates 594
C. Antiferromagnetic Insulators 595
D. Spin Wave Excitation Spectra 597
E. Single-Magnon Absorption 600
F. Two-Magnon Absorption 603
G. Crystalline Electric Field Effects 605

References 610

APPENDIX IV FAR-INFRARED SPECTROSCOPIC STUDIES OF SEMICONDUCTORS, by R. Kaplan

A. Optical Lattice Vibrations and Free Carrier Effects 612
   a. Transmission and Reflection Measurements 612
   b. Measurement of Emission 616
B. Impurity Absorption and Photoconductivity 619
   a. Energy States of Impurity Atoms in Germanium and Silicon 620
   b. Hydrogenic Impurity States in Indium Antimonide 625
   c. Far-Infrared Resonant Absorption due to Donor Impurity Pairs in Silicon 630
C. Cyclotron Resonance Investigations 630
   a. Cyclotron Resonance Studies Using Mixed Microwave-Optical Techniques 631
   b. Cyclotron Resonance Studies Using Purely Optical Techniques 635
D. Coupled Phonon—Free Carrier Modes 640
   a. Polaron Modes 641
   b. Coupled Collective Plasma Cyclotron—Longitudinal Optical Phonon Modes 643

References 645

APPENDIX V SUPERCONDUCTIVITY, by Gerhart K. Gaulé

A. Introduction 647
   a. Far-Infrared Radiation and Superconductivity as Low-Energy Phenomena 647
   c. Cooling Requirements for Superconductors 650
B. Homogeneous Superconductors in Weak Fields  652
   a. The Two-Fluid Model. Resistive Bolometers  653
   b. The Energy Gap and Its Optical Significance  656
C. Homogeneous Superconductors in Strong Fields  665
D. Composite and Weakly Coupled Superconductors  666
E. Superconductivity in Conjunction with Other Solid State
   Effects. Parametric Thermometer  669
References  670

APPENDIX VI  RAPID-SCAN FOURIER SPECTROSCOPY, by Ernest V. Loewenstein
   A. Introduction  672
   B. Order-Sorting and Interference Modulation  675
   C. Rapid-Scan Fourier Spectroscopy  676
   D. Summary  677
      References  678

APPENDIX VII  A FAR-INFRARED BIBLIOGRAPHY, by E. D. Palik  679

AUTHOR INDEX TO BIBLIOGRAPHY  761

INDEX  777