

# Preface

Infrared (IR) spectroscopy strongly attracted the attention of theoretical physicists from the 1930s until the 1970s, and most of the important fundamentals were comprehensively organized in terms of molecular vibrations and rotations along with the rapid progress of quantum mechanics and chemistry. For experimental chemists, commercial IR spectrometers played a great role in the latter half of the twentieth century, and theoretical fundamentals were confirmed quantitatively by using a spectrometer. For example, the theoretical prediction of the Fermi resonance was experimentally recognized for many organic compounds.

At this early stage of IR spectroscopy, theoretical and experimental chemists made great efforts to establish fundamentals for analyzing IR spectra for chemistry. Some textbooks were devoted to summarizing IR bands characteristic of chemical groups in many organic and inorganic compounds in various chemical environments involving solvents and temperature. Correlations of some IR bands to hydrogen bonding, molecular conformation, and crystallinity were also studied, and IR spectroscopy was thus recognized as one of the most powerful analytical tools for discussing chemical compounds.

The accurate measurements of IR spectra were boosted by introducing the Fourier transform infrared (FT-IR) spectrometer, which guarantees both accuracy and precision in principle for both ordinate and abscissa axes thanks to the laser-based interferometer and stable digital electric circuits. Since FT-IR has great sensitivity, which can be used even for a monolayer analysis, many optical configurations were proposed, represented by the transmission, reflection-absorption (RA), attenuated total reflection (ATR), external reflection, and specular reflection techniques, so that the molecular orientation in an ultrathin film would be discussed by comparing it to the spectrum of a bulky sample. The great sensitivity of this “surface spectroscopy” is still outstanding in our current age. The power of molecular orientation analysis is also outstanding since it can be performed no matter how the crystallinity is in the film.

During the progress of FT-IR applications, another important theoretical framework was established in electrodynamics for surface spectroscopy. Since most of the analytical targets of FT-IR are condensed matter, electrodynamics

considering electric permittivity plays many crucial roles for revealing the surface selection rules of surface spectroscopies. The theoretical expressions of the surface spectrometry are particularly important for a strong absorbing matter represented by the carbonyl, nitrile, and perfluoroalkyl groups.

Unfortunately, education of electrodynamics in school is very far from popular in chemistry, and the aspect of “science of measurements” is not widespread even among vibrational spectroscopists. As a result, the overall picture of IR spectroscopy has long been oriented to quantum chemistry only, and surface spectroscopy has been forgotten except for some simple surface selection rules.

In recent years, nonlinear spectroscopic technique represented by the sum-frequency generation has rapidly been recognized even by a non-spectroscopist to be a powerful technique for discussing a detail of an interface. The problem is that such a user blindly relying on nonlinear spectroscopy *alone* is not aware of the intrinsic power of linear spectroscopy. The lack of an overall picture of IR spectroscopy is one of the reasons for the problem.

The goal of this book is, therefore, to summarize the overall picture of IR spectroscopy with respect to quantitative understanding of condensed matter. In particular, surface spectroscopy based on electrodynamics is described in detail in Chap. 3, so that a physical logic would not be omitted. In addition, the concept of convolution and the Kramers–Kronig relations are also described from a fundamental concept in Chap. 4. These concepts should not be introduced as formulae, since they comprise the essence of linear spectroscopy.

For a quantitative study using IR spectroscopy, in recent years multivariate analysis, i.e., chemometrics, is quite often employed. Therefore, the theoretical framework of chemometrics is presented in Chap. 5.

In Chap. 6, application studies of IR spectroscopy are presented. In particular, chemometrics and surface spectroscopy are merged to yield a new spectroscopic technique of p-polarized multiple-angle incidence resolution spectrometry (pMAIRS). This technique enables us to discuss the molecular orientation of each chemical group as well as the polymorph in a very thin film even with a surface roughness. As a good example to get beyond the analytical limit constrained by Maxwell equations, pMAIRS is introduced to provide an overall picture of IR spectroscopy.

In addition, quantitative discussion of IR spectra of perfluoroalkyl (Rf) compounds is added. An Rf compound has long been regarded as a compound similar to a normal hydrocarbon, and the particularity of an Rf compound in vibrational spectroscopy has been missed. As presented in detail in Chap. 6, the overall picture of IR spectroscopy works very powerfully to discuss an Rf compound. Moreover, the knowledge from factor group analysis based on quantum chemistry to surface spectroscopy in electrodynamics is necessary for fully discussing Rf compounds.

This book is a summary of my IR study with my colleagues, whom I thank greatly and appreciate deeply. In particular, the core part of Chap. 3 is the result of an invaluable contribution of a former student, Dr. Yuki Itoh.

I would be most happy if many scientists and engineers in the coming generations re-recognize the great intrinsic power of IR spectroscopy. Since FT-IR is widespread in laboratories, its power will help very much in studying material chemistry. What we need is only the overall picture of IR spectroscopy.

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