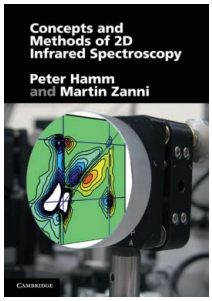
Journal of
Applied Crystallography
ISSN 0021-8898

book reviews

Works intended for this column should be sent direct to the Book-Review Editor, whose address appears in this issue. All reviews are also available from **Crystallography Journals Online**, supplemented where possible with direct links to the publisher's information.



Concepts and Methods of 2D Infrared Spectroscopy. By Peter Hamm and Martin Zanni. Pp. 296, 124 illustrations, 71 exercises. Cambridge University Press, 2011. Price (hardcover) 99.00 USD. ISBN 978-1-107-00005-6.

This book, written by Peter Hamm, Professor at the Institute of Physical Chemistry, University of Zurich, and Martin Zanni, Meloche-Bascom Professor in the Department of Chemistry, University of Wisconsin–Madison, introduces the essential concepts of two-dimensional (2D) IR spectroscopy. This is a cutting-edge experimental technique of vibrational time-resolved spectroscopy, which has been more and more widely applied in the past decade for investigations of structure and dynamics of molecules, molecular ensembles, and intra- and intermolecular energy transfer, from quite 'simple' water to complex biological systems. It fills the gap between the time scales of NMR and electronic UV–vis spectroscopies, providing bond-specific structural resolution, and can be applied in a 'snapshot' mode to study kinetics in many types of samples, including dilute solutions, solid-state systems or membranes.

The book is arranged in ten chapters, with an *Introduction* and five appendices. The *Introduction* gives a brief description of what 2D IR spectroscopy is and what can be done with this method. Chapter 2, *Designing multiple pulse experiments*, provides an overview of 2D IR spectroscopy, including a physical understanding of the experimental technique and interpretation of 2D IR experiments based on physical phenomena. It concludes with a Feynman diagrams approach, which is a useful tool for designing multiple pulse experiments. A short chapter 3, *Mukamelian or perturbative expansion of the density matrix*, derives the most essential equations used for quantitative description of these diagrams; this chapter is intended for those who want to understand the formalism of 2D IR spectroscopy in more detail. In chapter 4, *Basics of 2D IR spectroscopy*, the developed mathematical approach is applied to one- and two-dimensional IR spectra of some commonly studied systems. The chapter starts with the commonly used 'normal' IR spectroscopy and goes on to give a clear understanding of the new possibilities brought by the second dimension. The specifics of frequency domain and time domain spectroscopies are discussed. It is shown that 2D IR lineshape and cross-peak patterns depend upon the experimental setup chosen to measure the 2D IR spectra, and that some setups are better than others. Chapter 5, *Polarization control*, is concentrated on the role of polarization control in 2D IR spectroscopy. Polarization plays a central role in every method of vibrational spectroscopy. In standard pump–probe spectroscopies it has been used for many years to measure the rotational times of molecules or to eliminate rotational motion from dynamics measurements. The polarization dependence of 2D IR peaks provides the same capabilities, but polarization can do much more in two- and three-dimensional spectroscopies. Ordering of properly polarized pulses in a pulse sequence scales 2D IR peaks purposefully by altering their intensities and phases. By measuring these effects, the relative angles between transition dipoles can be measured, which provides an extremely insightful tool for monitoring the structures of molecules. Properly polarized pulse sequences can in some cases suppress or even completely eliminate the most intense peaks from the spectra, with better resolution of the fine structure of a 2D spectrum. Chapter 6, *Molecular couplings*, introduces a local mode description of molecular vibrations. This useful description of 2D IR spectra provides a conceptual framework for visualizing the molecular vibrations, especially of molecules built from repeating units, like proteins. In a three-dimensional structure, these local modes are coupled, forming delocalized states of vibrational excitons. The coupling between local modes depends on their relative distances and orientations, and thus is a probe of the three-dimensional structure, which is studied by 2D IR spectroscopy. Chapter 7, *2D IR lineshapes*, is devoted to lineshapes of 2D IR spectra. So far, dephasing of molecular vibrations has been considered just by phenomenological damping. Here a microscopic theory is developed that explains dephasing and relates it to the microscopic motion of the solvation shell or the molecule itself. The measurement of dephasing processes turns out to be a powerful tool for studying the dynamics of molecular systems in the solution phase. Chapter 8, *Dynamic cross peaks*, considers the effects of comparatively slow molecular dynamics in 2D IR spectra. In the previous chapter it was shown to affect infrared lineshapes; here dynamical processes of energy transfer between eigenstates are considered that alter the intensities of spectral peaks or create completely new peaks. Three types of energy relaxation occur, all of which have been observed experimentally: population relaxation, population transfer and coherence transfer. Only the simplest cases of relaxation processes are considered to avoid a rigorous treatment of relaxation processes in general. Chapter 9, *Experimental designs, data collection and processing*, is focused on practical aspects of implementing 2D IR spectroscopy in the laboratory and methods of processing the data. The field of 2D IR spectroscopy is still growing and evolving: new improvements and ideas appear continuously. Thus, some parts of this chapter may go out of date quickly,

but at this time there is no commercial 2D IR spectrometer available nor is there a consensus on the best way of collecting multidimensional spectra. Therefore experimenters are free to select the design of 2D IR spectrometer appropriate to their own taste and the task in hand. Some of the designs invented so far are discussed in detail, separated into three categories based on whether they can operate in the frequency domain only, in the time domain only, or in either domain. Chapter 10, *Simple simulation strategies*, outlines how computer simulations, like molecular dynamics, quantum chemistry, a combination of both or specially designed more sophisticated models, can be used to interpret experimental results of 2D IR spectroscopy. The molecular dynamics simulation package *Gromacs 3.3*, the quantum chemistry program *Gaussian09* for electronic structure calculations, and simple *Mathematica* or C codes are used. All the relevant computer programs in this chapter can be downloaded from the book web site (http://www.2d-ir-spectroscopy.com), so the reader has operational starting programs that can be modified further at will. The last chapter, *Pulse sequence design: some examples*, gives the basics to construct pulse sequences for 2D IR spectroscopy. Starting with the most traditional rephrasing and non-rephasing two-quantum sequences, it moves on to fifth-order two-quantum coherence, which also enables three-dimensional IR experiments. Currently, three-dimensional IR pulse sequences are largely unexplored, and this part illustrates basic concepts for more sophisticated experiments in the future. The book is finished with appendices, giving in a simple manner some mathematical formalism used in the text, and *Recommended reading*. Every chapter is concluded with exercises that help the reader to understand the subject in deeper detail. The answers can be downloaded from the book web site.

The general presentation of the text, equations and illustrations is quite clear and fluid, except for a few minor technical slip-ups: Fig. 2.5a and Fig. 7.1 are exact copies except for a little zooming, and the reference to Fig. 4.2c on page 65 goes to nowhere, as Fig. 4.2 includes parts a and b only (probably it should refer Fig. 4.2b).

The scientific level of the book, including its physical and mathematical treatment, is excellent. The authors are keen to expound quite complex matters in intuitive and physically apprehensible terms. Graduate students should easily be able to follow them, while scientists new to this field will be able to understand the potential, merits and possible problems of this innovative experimental method, enabling them to design their own spectrometers, invent their own pulse sequences and accurately interpret 2D IR spectra.

The reviewer would like to recommend this book to students, teaching staff and researchers alike, and hopes that they will enjoy and learn from the reading.

Alexander Vtyurin

Kirensky Institute of Physics, 660036 Krasnoyarsk, Russian Federation