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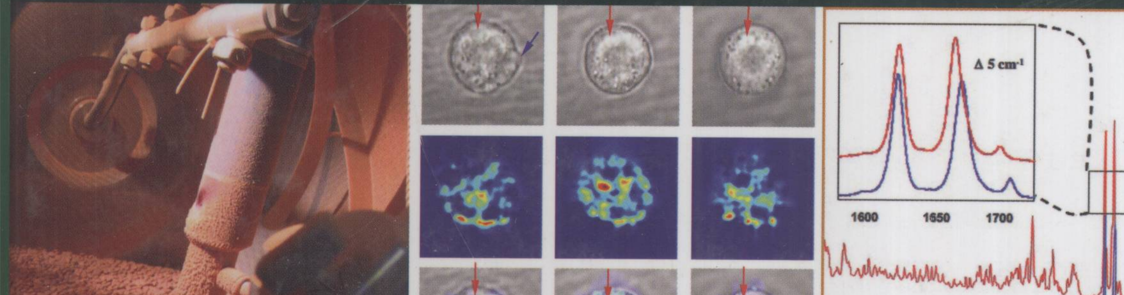

Edited by

SLOBODAN ŠAŠIĆ

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PREFACE

A review of the recent scientific literature persuasively demonstrates that Raman spectroscopy is becoming a viable industrial technique. This is best illustrated by the diverse and steadily increasing number of real-world Raman applications. Indeed, the number and quality of journal and conference publications that cover Raman spectroscopy applied to widely recognized targets highlights a strong trend towards Raman instruments becoming "standard kit." Hence, it is clear that this vibrational spectroscopy technique is no longer confined to academic laboratories and fundamental research, as has been the case for a long time, although significant advances are still being made in this area.

From the literature, a few books present a broad survey of the various aspects of industrial Raman, most notably "The Handbook of Vibrational Spectroscopy," by P. Griffiths and J. Chalmers, and "Analytical Applications of Raman Spectroscopy by M. Pelletier. However, the literature on Raman theory is far more diverse, with the excellent monograph by R. McCreery standing out as the text that most comprehensively covers all the elements of Raman spectroscopy as a technique. From the perspective of the pharmaceutical industry, there are a number of contributions that touch on the use of Raman spectroscopy in various parts of the business, but there is no single volume that collects and lists those efforts. The book in your hands is an attempt to gather and order the pharmaceutical applications of Raman in a single tome.

Regarding the pharmaceutical industry, near-infrared (NIR) spectroscopy is unquestionably the spectroscopic method of choice, as demonstrated by the number of NIR methods finding application in the pharmaceutical arena (and not only there: the food industry is an even more convincing example). The technique is well understood and employs instruments that are relatively inexpensive, easy to use and compliant with the standards of the industry. The one problem with NIR is that the spectra may appear to be too heavily overlapped and thus it is very demanding to extract useful information. The closest experimental techniques to NIR are infrared (IR) and Raman spectroscopies, the former of which will not be covered in this book. These techniques may be tested for applications on the same targets for which NIR is used. Although full comparison between the industrial positions of NIR and Raman is not really appropriate because of the much more industrially established position of NIR, it is prudent to consider Raman as an alternative. It is a technique that is progressing rapidly and is finding a role in solving real problems.

This book lists seven areas that are representative of where Raman spectroscopy can be employed in the pharmaceutical industry. Some of the applications are more developed while others are actually not far from making their initial steps into industrial laboratories. The readers will probably more easily familarize themselves with the quantitative or online applications rather than the somewhat more complex surface-enhanced Raman spectroscopy or Raman chemical imaging. The former applications are the most authoritative for the assessment of the industrial standing of Raman. The number of references and diversity of applications in these two fields best illustrate where and for what Raman spectroscopy is being used in the pharmaceutical context. The latter two methods are conceptually and mathematically more complex but are believed to carry some valuable advantages in comparison with other commonly used tools and, hence, they are making their way into pharmaceutical laboratories. The chapter on polymorphism describes the use of Raman spectroscopy in an area that is very specific and important for the formulation of the products in the pharmaceutical industry. Raman spectroscopy has actively been used in this area for some time now and is a recognized tool for use in polymorph screening. Finally, two chapters in this book address the biomedical perspectives of Raman in pharma. These chapters deal with the delivery/monitoring of active components through skin and the chemical imaging of cells. The results given there also hold clear the promise for Raman spectroscopy to become more amenable to everyday practice.

The writers of this book hope that the material presented will be of interest to those who practice Raman spectroscopy at various levels in the pharmaceutical industry, as well as to those who are beginners in the field or just pondering the possibilities of Raman. The variety of topics and level of detail explored is such that all the essential links between Raman spectroscopy and the pharmaceutical industry are covered. As a result, the authors anticipate that this publication will encourage readers from the industry to give greater consideration to Raman and that those readers from academia might gain a better understanding of the current industrial status and requirements of the technique.

Slobodan Šašić

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INTRODUCTION TO RAMAN SPECTROSCOPY

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Raman spectroscopy may have seemed too much of a burden in the past to handle. Until 20 years ago, one had to gain some experience before becoming capable of measuring satisfactory Raman spectra. Some even said that Raman spectroscopy was "patience-testing spectroscopy," or 'a romance of patience.' But this is changing now, rapidly. While unquestionably being used in basic research for quite a long time, Raman spectroscopy is nowadays steadily gaining on importance for online monitoring of chemical reactions, analysis of food, pharmaceuticals, and chemicals, and increasingly for many other real-world applications.

Similar to infrared (IR) spectroscopy, Raman spectroscopy yields detailed information about molecular vibrations. As molecular vibrations are very sensitive to strength and types of chemical bonds, vibrational spectroscopy techniques, such as IR and Raman spectroscopy, are useful not only in identifying molecules but also in shedding light on molecular structures. In addition, IR and Raman spectra also reflect changes in the surroundings of the molecules and are thus helpful in studying intra- and intermolecular interactions.

1.1 HISTORY OF RAMAN SPECTROSCOPY

Raman spectroscopy is based on the effect of radiation being scattered with a change of frequency and its history goes 80 years back. It was in 1928 that Indian scientists

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Raman and Krishnan [Raman 1928] discovered the scattering effect that is named after Raman and that earned him a Nobel Prize in 1930. Raman spectroscopy, however, developed relatively slowly for several reasons. First, Raman experiments were not easy to carry out because of the extremely weak intensity of the Raman scattered light (roughly below 10^{-10} of that of exciting light or even weaker). Raman spectroscopy gained momentum in 1970s owing to the lasers becoming more available to researchers and thus assuming the role of primary source of excitation light, replacing the mercury-based sources of radiation. Nevertheless, the difficulty of finely adjusting optical systems was still present. Second, fluorescence from the sample severely interfered with detection of Raman scattered photons. Excitation of Raman scattering with the light of a wavelength within the visible region may concomitantly excite fluorescence from the sample or impurities contained therein. When the intensity of fluorescence is strong, the Raman signal is barely visible on top of incomparably stronger, broad fluorescence signal. The third reason is decomposition and denaturation of the samples irradiated with relatively strong laser light for a long time due to inefficient detection of scattered radiation. Due to this, despite being by nature a nondestructive method of analysis, in some cases Raman spectroscopy ended up being considered a 'fatally' destructive method. These three problems, the difficulty of measurement, fluorescence, and decomposition seriously limited applications of Raman spectroscopy despite it being theoretically quite promising. Except for a few examples, Raman spectroscopy barely found any industrial or medical application.

This situation has greatly changed over the recent two decades. It is no exaggeration to claim that a new revolution in Raman spectroscopy occurred throughout the 1990s. While it was the dissemination of laser sources that drove the revolution in 1970s, this time a combination of multiple factors revolutionized applications of Raman spectroscopy: the sophistication of laser sources, the technological progress of detectors, the development of excellent optical filters, significant improvements in software, strong progress in application of data analysis methods, and so on. With regard to applications, the emergence of near-infrared (NIR) laser sources of excitation gave an entirely different perspective on applicability of Raman spectroscopy for tackling real-world issues (including both NIR FT-Raman spectroscopy and NIR multichannel Raman spectroscopy). The introduction of NIR lasers was noticeably important because the three above-mentioned problems were significantly alleviated; in particular, excitation with NIR light largely prevented occurrence of fluorescence and eliminated light-induced decomposition. In addition, FT-Raman spectrometers do not really require fine adjustment of optical systems.

Besides Raman spectrometers with NIR excitation, those equipped with ultraviolet (UV) laser sources are also being more frequently used for solving real-world problems. In addition, of particular significance is the recent rapid development of Raman microscopes and near-field Raman devices that can be easily coupled to automated microscope stages assembling thus Raman mapping/imaging instruments.

Today's Raman instruments are compact devices with very reasonably sized key components (almost miniaturized in comparison with large devices used before the 1990s) such as lasers, spectrometers, or detectors. These instruments are rather easy

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