Preface

Raman spectroscopy has now become one of the key analytical tools for an extremely diverse range of applications. Although initially limited to research applications, it is now increasingly used for routine testing and quality control as well as process control applications. As the technology reaches such a level of maturity, it is an interesting exercise to look back and retrace the history that led to what is now one of the fastest growing molecular spectroscopy techniques.

In 1928, Sir C.V. Raman was awarded the Nobel Prize for discovering what will then be known as the Raman effect which relies on the fact that when light interacts with matter, the incoming wavelength is shifted as vibrational transitions are excited.

For the following 20 years, Raman scattering was used, in conjunction with infrared spectroscopy (IR), as a means to confirm the molecular configuration of a sample. For instance, the controversy about the structure of benzene was solved by Raman and IR spectroscopies. If the bonds between the carbon atoms in the ring alternated between single and double bonds, then the molecule would have D_{3h} symmetry, but not a center of symmetry. Without a center of symmetry, no vibration could be both Raman and IR active. If the single and double bonds resonate, then the molecule has D_{6h} which does have a center of symmetry and the "mutual exclusion selection rule" holds. Looking at the IR and Raman spectra overlaid, one will find that there are no overlapping bands. Therefore, benzene has a center of symmetry, meaning that it has the D_{6h} configuration. The complementary nature of Raman to infrared spectroscopy continues to lead to strong demand from many of the same end-users in industries such as pharmaceuticals, polymers and chemicals.

During this early period, it was easier to do Raman spectroscopy than IR because the IR sources and detectors could not provide high sensitivity levels. That all changed in the 1960's when the commercial Fourier Transform IR systems were developed with better detectors. The FTIR systems were quite sensitive and easy to use. The laser, also introduced during this period, was believed to provide a better source for Raman which would improve its sensitivity to study "real world" samples. Unfortunately, that did not happen because of the fluorescence interference from the samples. Curiously, during the early years, when spectroscopy was used to determine structure, samples had been extensively purified which meant that fluorescence from impurities was not seen as an interference. When studying real world samples, one does not usually have the option to purify the samples. The laser that was used during this period was an argon laser, with lines between 514 and 457 nm. As it happens, these lines are also ideal for exciting impurity fluorescence. As a consequence, Raman was a disappointment for many industrial applications.

Since then, tremendous progress was made in the instruments design to circumvent the two main limitations of this technique, namely: low sensitivity and fluorescence. The Raman effect tends to be a rather inefficient one, producing signals typically million times weaker than the exciting beam. Concurrently, fluorescence is a much more efficient effect, which can interfere with the measurement, often to the point where it would mask the Raman spectrum when it occurs. Successive implementation of more powerful and more diversified laser sources, together with more sensitive detectors have made Raman spectrometers commercially available and ready for industrial applications. This technique would then allow molecular analysis on a great variety of samples, non-destructively, with no sample preparation, and at ambient pressure and temperature. Raman spectra represent chemical fingerprints of samples under study, allowing the operator to easily identify unknown components, distinguish between several polymorphs and crystalline structures of a given compound, trace the production and consumption of chemical species in chemical reactions, etc.

Another significant step in the history of Raman spectroscopy is the coupling of a Raman spectrograph to an optical microscope. This seminal work was accomplished in 1974 by Professor Michel Delhaye at the Technical University of Lille in northern France[1] with the development of the MOLE^{TM}. The method involved bathing the sample in laser light over a large area and then transferring an image of the sample onto a camera after a Raman wavelength was selected with the spectrograph. It was recognized that the Raman microscope would complement the elemental information from the electron microprobe by providing information on molecular bonding between atoms. For example, if there was an organic impurity on an integrated circuit, the electron microprobe would tell you that there was carbon in the impurity. Whether that carbon was in the form of carbon black, graphite, polymer, photoresist, or any other of the possible organic molecules that might be in the circuit's environment, the electron microscope could not tell you. But a Raman spectrum could provide this critical information. Further developments made during the following decades led to better integrated instruments with higher spatial resolution thanks to the confocal design, greater versatility with more lasers wavelengths available and faster measurement speeds thanks to higher power laser sources, more efficient designs and more sensitive detectors. Its ability to localize and identify impurities at the micron scale has finally made it a workhorse analytical tool for both Research and routines QC/QA laboratories alike.

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[1] M Delhaye; P Dhamelincourt; *J Raman Spectrosc*. **1975** 3, 33–43.

It is then no wonder that Raman imaging has found an incredibly wide array of applications, from semiconductors to the pharmaceuticals, from art conservation to security, from biology to geology. Raman imaging provides a way to represent a sample in two or even three dimensions with information-rich content: chemical nature, molecular orientation, crystallinity ratios and polymorph content, strain and stress, all being accessible from the Raman spectra available for each pixel of the Raman image.

The first challenge in editing this book was to set its scope by drawing a perimeter in a wide field of applications while reflecting such diversity. The second challenge was to give a good picture of the state of the art for benchtop laboratory Raman instruments and common methods of so-called classical Raman imaging, while allowing the reader to get a grip on the most innovative developments being made at the research level. Choice was then made to also include work from some of the most prominent researchers from the technological frontier where stand near-field Raman imaging, coherent anti-Stokes Raman spectroscopy (CARS) and stimulated Raman spectroscopy (SRS).

The intended result is a book that is addressed to students, researcher and end-users alike, whether they are focused on one specific subject or working in a central laboratory brushing on very diverse applications. The goal is to give an overview of this powerful technique with concrete 'real world' examples directly from experts in the field and with a strong inclination towards application. We hope that this book will convey part of their experience and dispense some methodology and analytical recipes that are not always available from textbooks.

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