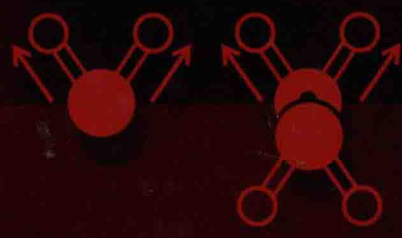
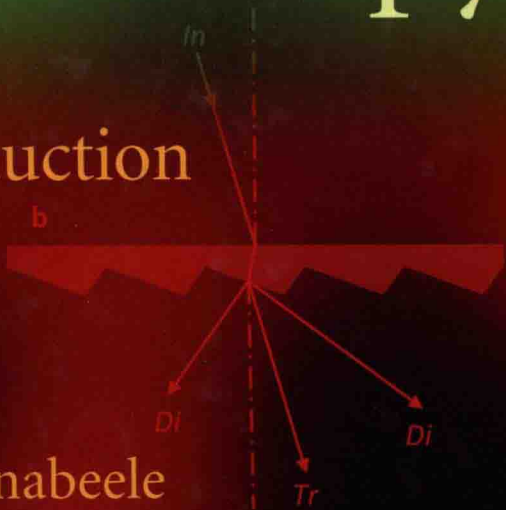
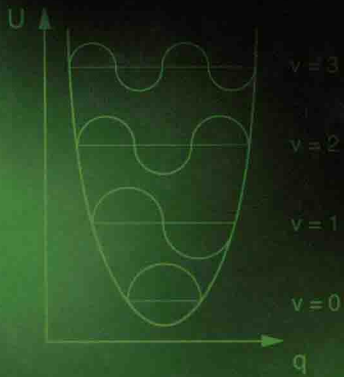




Practical Raman Spectroscopy

An Introduction

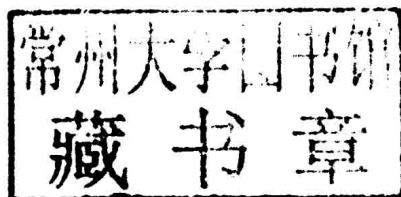
Peter Vandenberghe



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PRACTICAL RAMAN
SPECTROSCOPY –
AN INTRODUCTION

Peter Vandenabeele
Ghent University, Belgium



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**PRACTICAL RAMAN
SPECTROSCOPY –
AN INTRODUCTION**

*To my family – for all your support,
To my colleagues – that became friends,
To my students – who have never stopped inspiring me.*

About the Author

Peter Vandenaabeele obtained his masters' degree in chemistry at Ghent University, where he made his masters' thesis on thermal analysis of precursors for the synthesis of superconductors. His PhD research was carried out at the same university, but in the department of analytical chemistry, under the supervision of Prof. Dr. L. Moens. This research was on the optimisation of micro-Raman spectroscopy and total-reflection X-ray fluorescence for art analysis (2000). During his post-doctoral period Peter further worked on novel applications of Raman spectroscopy, in art analysis as well as in pharmaceuticals, microbiology and astrobiology. In 2007, the author was appointed as research professor in the department of archaeology of Ghent University, where he further can apply his analytical skills to study archaeological and artistic objects.

Peter Vandenaabeele has authored almost 100 research papers on Raman spectroscopy and in archaeometry. He has given many presentations on international conferences, of which several invited or plenary oral presentations. On many occasions he has written book chapters on Raman spectroscopy in archaeometrical research. As research professor, he has limited time to teach, but nevertheless, he enjoys introducing students in archaeometry as well as in Raman spectroscopy.

Preface

Raman spectroscopy is a very versatile molecular spectroscopic technique, with many different applications in a range of research fields. Whereas in its early days using this technique was very time-consuming and complex – and only applied in a few very specialised laboratories – today the technique is becoming increasingly popular in fundamental research as well as in applied science. Indeed, due to many instrumental evolutions, Raman spectroscopy has become increasingly more accessible and affordable. As a consequence, the technique has moved from the specialised laboratories towards more generally oriented laboratories. However, along with this broadening of applications, there is an increasing chance for misinterpretations and good training in Raman spectroscopy can help in avoiding these pitfalls.

This handbook starts with an introduction, where the history of Raman spectroscopy is sketched. In Chapter 1, the theoretical background of the technique is described. This theory is used to understand possible interferences (Chapter 2) and to study possible techniques to enhance the Raman intensity (Chapter 3). Chapter 4 focuses on the technical aspects of Raman spectroscopy: general aspects of Raman spectrometer construction and the properties of the different components. Together with these aspects, some considerations about noise in Raman spectra are discussed. The final chapter in this book (Chapter 5) describes aspects from

daily practices in a Raman spectroscopy laboratory. Common approaches are described, such as smoothing operations, baseline corrections, spectral searches, etc. This chapter tries to explain a little about what lies behind the buttons in your spectroscopy software package.

Throughout the book the readers are exposed to questions, where the answers are listed at the end of the book. We also provide discussion topics throughout the text, where the reader can evaluate whether he/she understood everything all right. In this book, we also provide some intermezzos – short texts illustrating or providing an illustration or background information on a topic that is discussed in the main text. In the end of the book we also give a short literature list for the interested reader.

I hope that this book can help people who are new in the field of Raman spectroscopy to understand the approach and to avoid some common pitfalls. May this encourage people to further explore and develop the broad range of possibilities that this technique offers!

Peter Vandenabeele
Ghent University, Belgium

Acknowledgements

It would not have been possible for me to perform and develop my research in Raman spectroscopy without continuous support from many colleagues and friends – too many to name them all so I'll just mention three: Professor Luc Moens gave me the opportunity, freedom and support to explore different aspects of this technique; Professor Bernard Gilbert always encouraged me to continue this research and patiently introduced me to many aspects of Raman spectroscopy; finally, Professor Howell Edwards has continued to inspire me in many discussions on all sorts of Raman spectroscopy applications.

Writing a book is a demanding job, that took much more time than initially expected. All people at John Wiley were, however, still supportive and understanding. Thanks to all, especially Jenny Cossham, Sarah Tilley, Zoë Mills, Jasmine Kao, Krupa Muthu and Martin Noble.

Finally, I would like to thank my wife Isabel and my daughters for their support and understanding, especially on the evenings when I was writing behind my computer.

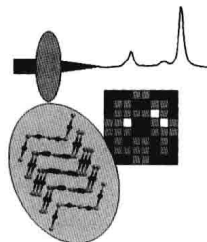
I hope that you, dear reader, enjoy reading through this book.

Acronyms, Abbreviations and Symbols

$\bar{\nu} = \frac{1}{\lambda}$	Absolute wavenumber
$\bar{\alpha}$	Average polarisability
%T	Percentage of the transmitted light
μ	Reduced mass of a molecule
c	The speed of light
CCD	Charge coupled device
E	Electrical field
F	Force
h	Planck's constant ($h = 6.6260755_{40} \cdot 10^{-34} \text{ J} \cdot \text{s}$)
I	Intensity
k	Boltzmann constant ($k = 1.380658_{12} \cdot 10^{-23} \text{ J} \cdot \text{K}^{-1}$)
n	Refractive index
N.A.	Numerical aperture
O.D.	Optical density
p	Dipole moment
p_0	Amplitude of the oscillating dipole moment
q	Displacement
Q_k, Q_l	Normal coordinates, corresponding with the k^{th} and l^{th} normal vibration
Q_{v0}	Amplitude of the normal vibration

SD	Standard deviation of the signal
t	Time
U	Potential energy
v	Vibrational quantum number
α	Polarisability
α_{aniso}	Anisotropic polarisability tensor
α_{iso}	Isotropic polarisability tensor
β	Hyperpolarisability
γ	2nd hyperpolarisability
γ	Anisotropy factor
δ	Bending vibration
ϵ_0	Permittivity of vacuum ($8.854187817 \cdot 10^{-12} \text{ C}^2 \cdot \text{N}^{-1} \cdot \text{m}^{-2}$)
κ	Force constant of a bond
ν	Stretching vibration
ρ	Degree of depolarisation
ρ	Rotation
σ	Noise
Φ	Electromagnetic flux
φ_v	Phase angle
Ω	Solid angle
ν_0	Frequency of incident radiation
ν_m	Frequency of measured radiation
ν_o	Vibrational frequency of the electromagnetic radiation
ν_v	Vibrational frequency of the molecule
ω	Raman wavenumber (in cm^{-1})
ψ_v	Vibrational wave function

Introduction to Raman Spectroscopy



*I'm picking up good vibrations
She's giving me the excitations
Good, (bop bop) good vibrations*

The Beach Boys, 'Good Vibrations', 1966

Learning Objectives

- To appreciate the historical background of Raman spectroscopy
- To understand how instrumental improvements opened the way to new Raman spectroscopic applications

It was on 28 February 1928 that Sir C.V. Raman and K.S. Krishnan for the first time succeeded in demonstrating the inelastic scattering of light by a fluid. For this work, in 1930, Raman was honoured with the Nobel Prize. At the time, they used filtered sunlight to excite the molecules and photographic plates were used to record the spectrum. It took about 24 hours to record a spectrum of a beaker with ca. 600 ml of pure liquid. Knowing this, it is clear that Raman spectroscopy for a long time was only limited to specialised

research laboratories and that the technique was considered as a curiosum. Today, Raman spectroscopy has moved out of the highly specialised laboratories and is available not only in many research institutions, but also as a reliable technique for quality control or even for sorting out plastics in the recycling industry.

Indeed, in today's research, Raman spectroscopy is appreciated for many different reasons. First, the technique is a relatively fast method and well-suited to investigating solids, liquids, solutions and even gases, depending on the experimental set-up used. For the analysis of solids often barely – if any – sample preparation is needed: just position it under the microscope and focus the laser beam. Liquids can be measured through glass vials and, as opposed to infrared spectroscopy, the presence of water does not hamper the measurements. Small portable spectrometers are now available and fibre optics probe heads allow us to record spectra from a distance, which is useful for analysis in harsh conditions or for the investigation of, for instance, explosives. Mobile analysis allows objects to be in situ and in a noninvasive way. Micro-Raman spectroscopy is one of the rare spectroscopic methods that enables us to obtain molecular information at the micrometer-scale. Chemometrics can be used during Raman spectroscopy studies, and molecules are easily interpreted by using automated algorithms for searching spectral libraries.

Current Raman spectroscopy research is very different from the approach adopted in the early days. Instrumentation has seriously evolved, and as a consequence sample sizes and measuring times are seriously reduced. Historically it has been seen that (r)evolutions in Raman spectroscopy research (e.g. new applications, access for a larger group of scientists, etc.) are often caused by the availability of new equipment or instrumental innovations. A first improvement since Raman's days was the introduction of mercury lamps as a source of excitation. However, measuring procedures and alignment remained quite complex and Raman spectroscopy was for a