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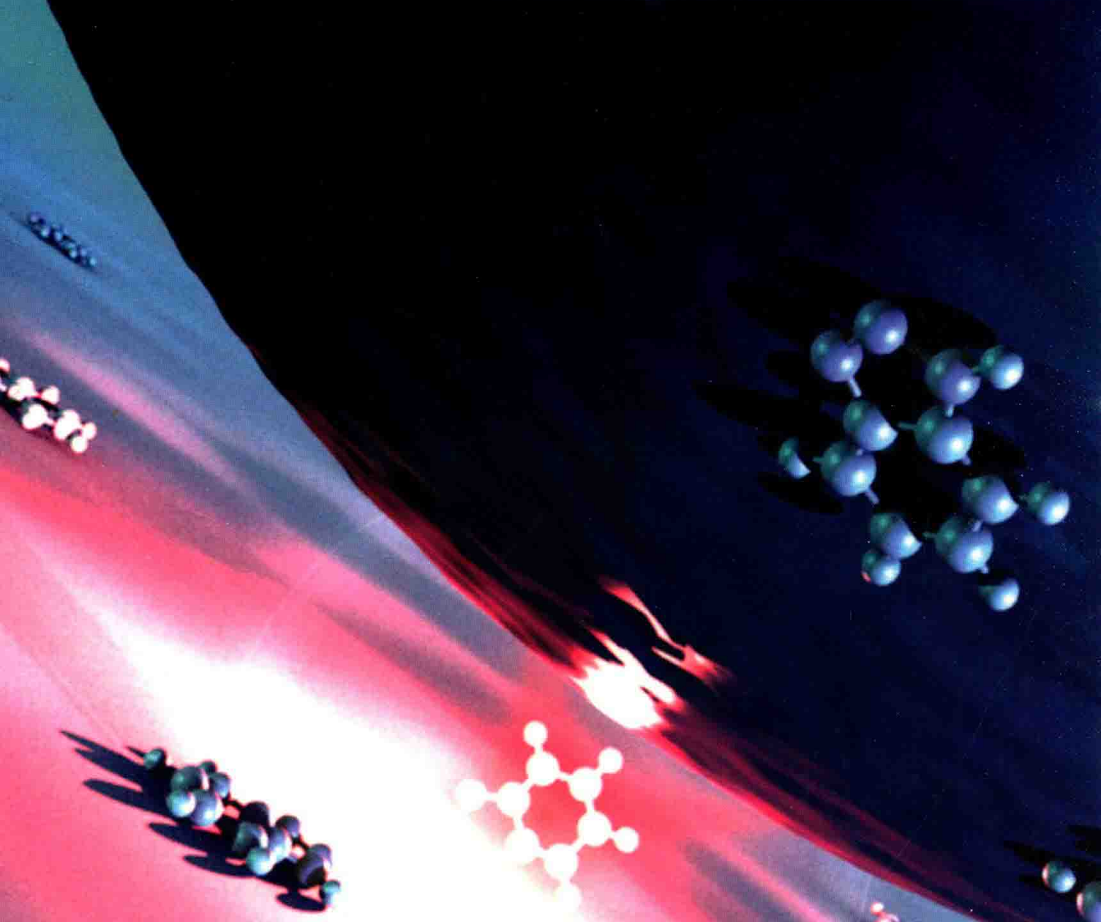
Principles of Surface-Enhanced Raman Spectroscopy

and related plasmonic effects



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Amsterdam • Boston • Heidelberg • London • New York • Oxford
Paris • San Diego • San Francisco • Singapore • Sydney • Tokyo

Elsevier
Radarweg 29, PO Box 211, 1000 AE Amsterdam, The Netherlands
Linacre House, Jordan Hill, Oxford OX2 8DP, UK

First edition 2009

British Library Cataloguing in Publication Data
A catalogue record for this book is available from the British Library

Library of Congress Cataloging-in-Publication Data
A catalog record for this book is available from the Library of Congress

ISBN: 978-0-444-52779-0

For information on all Elsevier publications visit our website at elsevierdirect.com

Transferred to Digital Printing in 2009

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Preface

Surface-enhanced Raman scattering (SERS) was discovered in 1974 [1] and correctly interpreted in 1977 [2,3]. Since then, the field has grown enormously in breadth, depth, and understanding. One of the major characteristics of SERS is its *interdisciplinary nature*. SERS exists at the boundaries shared among physics, chemistry, colloid science, plasmonics, technology, engineering, and biology. There are several review articles in the field [4–6] for the advanced researcher together with a recent book dedicated to surface-enhanced vibrational spectroscopy by Ricardo Aroca [7]. Still, we put ourselves in the situation of a graduate student in physics, chemistry, physical chemistry, or chemical physics, undertaking a Ph.D. project in the area of SERS or related subjects and not having an in-depth understanding of Raman spectroscopy itself, the theory of plasmon resonances, or elements of colloid science. By their very nature, it is difficult to find a textbook that will summarize the principles of these rather dissimilar and disconnected topics. It is even less likely that this collection of topics was touched upon as a coherent unit during most undergraduate studies in physics or chemistry. A similar situation can arise for established researchers, either chemists or physicists, who are newcomers to the field but might not have a background in Raman spectroscopy or the physics of plasmons. Yet, a basic understanding of these topics is desirable to start a research project in SERS, and as a stepping stone to tackle the more specialized literature. This book finds its justification in that fact, and will hopefully fill (at least) a fraction of what we feel is an existing gap in the literature.

The content of the book covers most of the topics related to SERS and presents them as a coherent study program that can be tackled at different levels of complexity depending on the individual needs of the reader. For the most important subjects, we have attempted in our presentation to provide a *graded approach*: starting with a simple explanation of the most relevant concepts, which is then developed into a more rigorous exposition, including the more advanced aspects. In this way, we hope that this book will cater to a variety of readers with different skills and scientific backgrounds; an intrinsic characteristic of the general SERS and plasmonics community. To help the reader find his/her way through the various topics and the different level of complexities, a detailed overview of the content of the book and a few suggested reading plans are provided at the end of the introductory chapter.

This book is about *principles* and therefore does not attempt to replace the many excellent reviews in the field, which are concentrated mainly on the exposition of the latest research results and their interpretations. Review articles tend to be too specialized to spend time on basic aspects of, for example, molecular Raman spectroscopy or the physics of plasmon resonances in metals. This book therefore attempts to make emphasis on these underlying concepts. The selection of topics is *not* intended as a detailed collection of results of the current literature and the accompanying bibliography is far from being exhaustive. Such an extensive review of the older and current literature of SERS is, in fact, largely provided already in Ref. [7]. The most important examples of the current literature are used, of course, to stress concepts or to make the explanation of certain topics clearer, but it is by no means exhaustive. Moreover, we emphasize concepts and principles that *we* judge important as a general background to SERS, but it does not represent a complete (and unbiased) list of topics. Both authors are physicists by training (and at heart...), and there is a natural emphasis on physical aspects of the problem in the presentation. We have in fact deliberately tried to avoid too much overlap in the selection of topics with the recent book by Ricardo Aroca [7]. Not only that Aroca's insight into the field, from a more chemical point of view, is excellent but also, in this manner, we hope that the books will complement each other. One aspect we do particularly emphasize is the intricate link between SERS and the wider research field of *plasmonics*, i.e. the study and applications of the optical properties of metals. SERS can, in fact, be viewed as a subfield of plasmonics. The relation between SERS and related plasmonics effects is, we believe, symbiotic, and we attempt to emphasize this aspect repeatedly.

To conclude this preface, a tradition that we shall not attempt to escape is to thank the many people and institutions that made the book (directly or indirectly) possible. First of all, we would like to thank the continuous support of the MacDiarmid Institute for Advanced Materials and Nanotechnology in New Zealand, and by the same token, Victoria University of Wellington (where part of the Institute is hosted). In particular, we would like to thank its founding director (Prof. Paul T. Callaghan) who has been a continuous source of inspiration and support (economic and personal) during the last few years. Without the financial support of the MacDiarmid Institute and Victoria University of Wellington, this book would not have been possible. The Royal Society of New Zealand is also gratefully acknowledged for financial support during this period. In addition, we would like to thank our direct collaborators (past and present), and our students (in particular Robert C. Maher from Imperial College London, and Matthias Meyer, Evan Blackie, and Chris Galloway from Victoria University of Wellington) who paid (and are still paying) the high price of long hours in the lab studying the SERS effect. Special thanks are also given to Prof. Lesley F. Cohen of Imperial College London, who, many years ago, proposed for the first time the subject of SERS as a possible research topic to one of the authors (PGE). For the many scientific discussions and the longstanding collaboration we are very grateful.

Last but not least, we would like to thank our respective family members (Nancy and little Noah!, Sofía, and Julián) for their understanding and support during the long period while the writing was under way.

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Notations, units and other conventions

We have made our best efforts to use notations, conventions, and units that are consistent throughout the book. We summarize here (for reference) our specific choices.

Units:

We use S.I. units throughout in all our expressions (except when discussing other units that are commonly used in the literature). These are, in our opinion, the more versatile choice for a subject spanning through such diverse areas of physics and chemistry. They are also more rigorous in many respects compared, for example, to Gaussian units.

We have also endeavored when possible to specify the units of the variables we define. This should help, we hope, in understanding the physical meaning of each variable. These are given in between brackets [...], using either:

- The basic S.I. units: kilogram [kg] for mass, meter [m] for length, second [s] for time, Ampere [A] for electric current, Kelvin [K] for temperature, and mole [mol] for amount of substance,
- Or commonly used *derived* S.I. units, such as Joule [J] = [m^2 kg s^{-2}] for energy, Watt [W] = [m^2 kg s^{-3}] = [J s^{-1}] for power, Coulomb [C] = [s A] for electric charge, or Volt [V] = [m^2 kg s^{-3} A^{-1}] for voltage.
- Or sometimes for simplicity in units of common physical constants, such as ϵ_0 [kg^{-1} m^{-3} s^4 A^2], the permittivity of vacuum. For example, polarizability is given in [ϵ_0 m^3] rather than the equivalent (but more cumbersome) S.I. expression [kg^{-1} s^4 A^2].
- Or common adimensional units to further clarify the meaning of the physical quantity. These include radians [rad] for angles or [rad s^{-1}] for angular frequency, and steradians [sr] for solid angles.

When relevant, we may also use "less rigorous", but "more conventional" units, such as electron-volt [eV] for energy, liter [L] for volume, or molar [M] = [mol L^{-1}] for concentration.

Mathematical notations:

Most mathematical notations we use are fairly standard. Variables are Greek or Roman letters in italics, such as a, A, or α. Vectors are represented by bold letters, such as $\mathbf{A}$. The unit vectors for a given coordinate frame are written as $\mathbf{e}_i$, where the subscript i refers to the corresponding axis. In Cartesian coordinates, where the vector position is $\mathbf{r} = (x, y, z)$, they are therefore $\mathbf{e}_x$, $\mathbf{e}_y$, $\mathbf{e}_z$. Spherical coordinates are denoted $\mathbf{r} = (r, \theta, \phi)$ and defined in Appendix H. The unit vectors are then $\mathbf{e}_r$, $\mathbf{e}_\theta$, $\mathbf{e}_\phi$ (and depend on position $\mathbf{r}$). Tensors are represented with a hat, such as $\hat{\alpha}$, or may be explicitly given as the tensorial product of two vectors, such as $\mathbf{e}_x \otimes \mathbf{e}_y$.

Variable names:

We have attempted to follow standard practices in terms of variable names, especially for common physical constants or quantities. All of them will be obvious within the context and in agreement with standard conventions in the literature.

Conventions:

We use a number of conventions that may differ from other treatments of the subject:

- A time dependence as $\exp(-i\omega t)$ is assumed for complex notations, which results in positive imaginary parts for response functions, such as the dielectric function ϵ or the polarizability α. This convention is commonly used in the *physics* literature, but is different from the convention normally used in *engineering*.
- Dielectric constants and dielectric functions are always *relative*. They are therefore adimensional quantities and should be multiplied by ϵ_0, the permittivity of vacuum, to obtain the absolute dielectric constant.

Moreover, as in many scientific publications, we make use of numerous acronyms, starting with SERS, the main subject of the book! These will be defined in the text as they are introduced, but in case of doubt, we have attempted to include them all in the index at the end of the book.

Computer codes:

Many of the most complicated equations given in this book are not given with the expectation that the reader will carry out further analytical studies from them. Rather, they are provided to be used for numerical calculations, thanks to which the reader may experiment at will, to understand the underlying physics or model problems adapted to his/her own specific needs.

To make this easier, we therefore also provide in some places a brief description of the actual numerical implementation (as Matlab scripts or functions). All the corresponding codes are available for download from the book's website: http://www.victoria.ac.nz/raman/book, and will be updated as required in the future. We have also included there (as examples) a number of Matlab scripts that can be used to reproduce (and adapt if necessary) many figures of the book. We hope that they will be easily usable by someone not familiar with the underlying mathematics or computer coding. A minimum knowledge of Matlab is, however, necessary and can be acquired quickly by browsing the Matlab help menu.

Book's website:

The book's website can be found at:

http://www.victoria.ac.nz/raman/book.

It contains an extensive section dedicated to Matlab computer codes relevant to SERS and plasmonics, many of which are based on the theory presented in the book and – in particular – on the material presented in the appendices. We will also attempt to update it regularly with various other information related to the book itself, and to SERS and plasmonics in general.

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