

Preface

Everything is vague to a degree you do not realize till you have tried to make it precise.

Bertrand Russell

British author, mathematician, and philosopher (1872–1970)

Surface-enhanced Raman scattering (SERS) is a moving target. Every time you look at it, it mutates, and new speculations are suddenly on the horizon. This elusiveness seems to defy our ability to predict the outcome of each new SERS experiment. The uncertainty is even more challenging when one approaches the single molecule regime (single molecule detection – SMD), since the attempt at experimental measurement of SERS may actually affect the molecule, or the nanostructures interacting with the molecular system, or both. However, one should not be surprised by this lack of determinism. While it is often taken for granted in the analytical spectroscopy of ensemble averages, it is particularly significant in ultrasensitive chemical analysis where one is dealing with only a few quantum systems (molecules) and nanostructures, with pronounced quantum effects. The difficulty is compounded by the fact that the enhanced signal is the result of several contributions, and their separation into well-defined components is virtually impossible. Observed SERS spectra are the final result of multiple factors, and the contribution of these factors is case specific. It is therefore of the utmost importance to examine and analyze closely the set of variables that may play a role in producing observed SERS spectra.

In this book, SERS is narrowly defined as surface *plasmon-assisted enhancement* of Raman scattering. Therefore, the term SERS is used for molecules located on, or close to, nanostructures that can support surface plasmons leading to an electromagnetic (EM) field enhancement

of the Raman signal. This definition excludes smooth surfaces with only nonradiative plasmons and small atomic clusters where surface plasmons are not realized. There is consensus on the electromagnetic origin and fundamental properties of the signal enhancement of SERS, as assisted by surface plasmon excitation on certain nanostructures. Thus, the presence of this component in the observed enhanced intensity will define the observed spectrum as a SERS spectrum.

Defining SERS in terms of one of the components of the observed enhanced intensity may, at first, seem limited and narrow. However, this definition provides the basis for a full discussion of the observations, and also a guide for the experimentalist to tune experimental conditions according to the ultimate goal of their research project. The definition does not necessarily imply that the plasmon assisted contribution ought to be the largest; other resonances may contribute and, in some cases, produce dominant contributions. However, it is the presence of the plasmon resonance that will define the observed spectral intensities as a SERS spectrum. In addition to this binding definition, the main thrust of the book is to discuss only two of the many enhanced optical phenomena in surface-enhanced spectroscopy: surface-enhanced Raman scattering (SERS) and surface-enhanced infrared absorption (SEIRA). SERS and SEIRA form a new branch of vibrational spectroscopy, which we now call *surface-enhanced vibrational spectroscopy (SEVS)*, and it serves as the title for the book. SEVS deals with the enhanced spectra of molecules on specially fabricated nanostructures with the ability to support surface plasmons and to enhance optical signals. Stable molecular electronic states are characterized by their vibrational structure [1–3], and the great advantage of vibrational spectroscopy, which can provide the fingerprint of any molecular system, is in the vast body of vibrational assignment data for gas, liquid, solid and, most relevant to SEVS, surface complex systems. SEVS is an extremely powerful addition to surface-sensitive and single molecule spectroscopies (SMS). From the analytical perspective, a concentrated sample of an analyte (the adsorbed molecule to be assessed) should form complete monolayer coverage on the surface plasmon supporting nanostructure. However, SERS and SEIRA are not limited to the first monolayer and, indeed, the EM enhancement is a long-range phenomenon that decays more slowly than the field dipole. That being said, the first layer will dominate the SEVS spectrum, and it is the spectrum of this layer that could be used for the compilation of a database. Ultra-sensitive analysis in SERS will start at monolayer coverage and move in the direction of submonolayer coverage, to achieve the ultimate single molecule–nanostructure limit. Selection rules derived for infrared and

Raman spectra [2] also apply to adsorbed species, with some additional qualifications. For highly reflecting surfaces in the infrared region, only those vibrational modes with a component of the dynamic dipole perpendicular to the surface are observed. These stringent ‘surface-selection rules’ could severely limit the relative intensities in the recorded infrared spectrum. At the same time, this new spectrum provides information on the molecular orientation and molecule–surface interaction. The surface-selection rules that apply to infrared and Raman spectroscopy are extended to SEVS with yet additional qualifications imposed by the nature of the local field and/or the roughness of the surface used for SEVS.

The definition and the main components are illustrated in the cartoon shown in Figure 1, where single particles and clusters of particles supporting surface plasmons are interacting with a molecular probe.

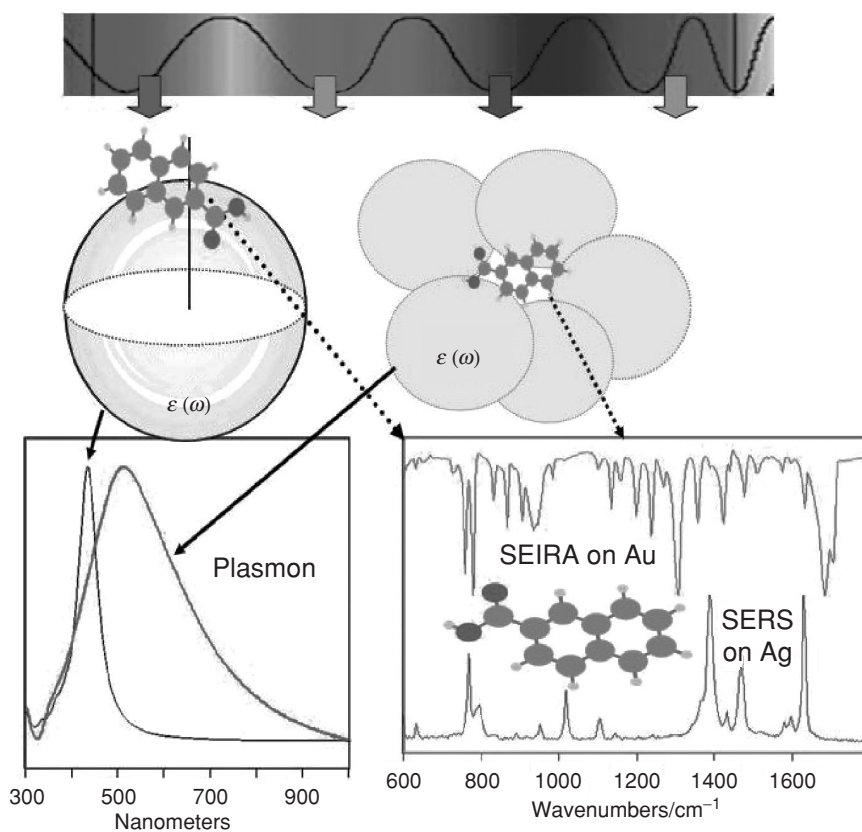


Figure 1 The three SEVS elements: the molecule, the electromagnetic radiation and the nanostructure, with the resulting plasmon and surface-enhanced spectra.

The study of vibrational energy levels, or vibrational spectroscopy, is carried out mainly with infrared absorption or inelastic scattering (Raman) [1–3] of electromagnetic radiation [4]. The quantum description of the vibrating molecule provides the energy levels, and that is followed by the study of the dynamics of the molecule–light interaction [5]. The information obtained from Raman scattering and that gathered from infrared absorption are complementary, to the point of being mutually exclusive for centrosymmetric molecules. SEVS spectra are the result of the molecule–light interaction when the molecule is near or attached to a nanostructure supporting surface plasmons. In the end, regardless of the mechanisms involved, the information, as in vibrational spectroscopy, is contained in a Raman or an infrared spectrum, and the challenge is in the interpretation of these spectra.

In vibrational spectroscopy, the molecular spectra are indeed ensemble-averaged spectra of many molecules. In SEVS, ensemble-averaged SERS and SEIRA spectra also form the bulk of the accumulated spectroscopic data. However, in the absence of the statistical average, the properties of the SERS spectrum of a single molecule would be unique, since it is a very sensitive probe of its environment. Hence it is profitable to make a distinction between ‘average SERS’ spectra and ‘single molecule’ spectra.

The presence of a nanostructure, most commonly a noble metal nanostructure, with the intrinsic property of enhancing optical signals, may leave its own footprints in the SEVS spectra. The nanostructure’s trail can be detected in a characteristic frequency due to the surface complex, a frequency shift, a peculiar bandwidth, a distinct relative intensity or a temporal behavior giving rise to fluctuations of the signal. Enhancing nanostructures can be fabricated as isolated particles, nanorods, nanowires or aggregates. However, in many applications of SEVS the nanostructures are fabricated on to a solid substrate, and thereby further spectral features may be observed due to reflections and refraction phenomena on the surface of the substrates. Inevitably, there exists the danger of drawing the line in the wrong place when discussing vibrational spectroscopy on surfaces and surface-enhanced vibrational spectroscopy. The definition of SEVS, used here, separates the results obtained on ‘flat’ or smooth reflecting metal surfaces from the SEVS results obtained on modified surfaces that contain enhancing nanostructures.

In summary, SEVS is the vibrational spectroscopy of molecules that is realized on well-defined nanostructures. It is a new molecular spectroscopy that is highly dependent on the optical properties, size and shape of metallic nanostructures. SERS, in particular, permits giant amplification of the optical signal and single molecule detection. At the SMD level,

temporal phenomena or fluctuations may be used as a probe for surface dynamics. Observing and manipulating biomolecules in single molecule spectroscopy may directly reveal their dynamic behavior, knowing that to detect dynamic behavior of target molecules using ensemble-averaged measurements is almost impossible. Experimentally, near-field scanning optical microscopy (NSOM) has joined the common far-field Raman scattering, making it possible to analyze optical properties with a spatial resolution below the diffraction limit. In a parallel development, SEVS is becoming a viable technique for nanoparticle characterization.

This book begins by devoting a chapter to reviewing the vibrating molecule and the origin of infrared and Raman spectra. These are the fundamentals and they provide the reference needed for the interpretation of SEVS results. Chapter 2 contains brief discussions on the absorption and scattering of light by metallic nanoparticles (important for SERS interpretation), the fabrication of nanostructures [6] and the selection of the appropriate experimental conditions for SERS and SEIRA. Light absorption enhancement by nanoparticles and light scattering enhancement by nanoparticles supporting surface plasmon are, in themselves, an active field of research in physics and chemistry [7, 8]. The theory and detection of surface plasmons of isolated particles of different size and shape [9] have been advanced by several groups and the references can be found in Chapter 2. Furthermore, aggregates of nanoparticles can sustain localized and delocalized surface plasmons, and highly localized modes, or *hot spots*, allowing for the concentration of electromagnetic energy in small parts of the system [10]. Finally, a section on reflection spectroscopy with special attention to reflection-absorption infrared spectroscopy (RAIRS) is also included to explain the effect that reflecting surfaces have on the observed relative intensities of vibrational spectra.

Chapter 3 is dedicated to SERS as a surface plasmon-assisted spectroscopy. The most rudimentary models that provide guidance for the experimentalist are also included. Chapter 4 is an attempt to examine the chemical effects, or the role in the observed SERS spectra of contributions due to molecule-nanostructure interactions. Chapter 5 is dedicated to demonstrating that SERS is observed for any type of molecular system, and is, thereby, not molecular specific. A database is provided on the web for the thousands of references that were reviewed. These form a catalog of molecules studied by SERS or SERRS, organized according to the type of molecule system, and intended to help experimentalists who would like to use SERS as an analytical tool. This is not a comprehensive database, but the time has come for the creation of a collection of SERS spectra that will be useful for analytical applications. Chapter 6

is an overview of SERS applications. Chapter 7 describes SEIRA and its applications. Each chapter contains extensive citations to help the user and to make the book a useful reference. The book contains a glossary that is intended to be helpful given the multidisciplinary nature of SERS (chemistry, solid-state physics, optics and electrodynamics).

Thousands of publications, many excellent reviews and, in particular, the expanding analytical applications of SERS and SEIRA are of such importance that there is a need for a text on methods and interpretation of spectra. This book has been written with the intention of meeting, in part, that need. Since much of the material covered in this book is recent, it is not possible to feel as comfortable in the description and of the subject as in a more settled field of spectroscopy, and some users may find the effort premature. However, I believe that the subject dealt with here is important and should be part of the working knowledge of chemists, physicists and material scientists. An attempt to summarize the developments to date is worth the risk of criticism.

REFERENCES

- [1] G. Herzberg, *Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand, Princeton, NJ, 1945.
- [2] E.B. Wilson Jr, J.C. Decius and P.C. Cross, *Molecular Vibrations; The Theory of Infrared and Raman Vibrational Spectra*, McGraw-Hill, New York, 1955.
- [3] M.B. Bolkenshtein, L.A. Gribov, M.A. Eliashevich and B.I. Stepanov, *Molecular Vibrations*, Nauka, Moscow, 1972.
- [4] M. Born and E. Wolf, *Principles of Optics*, Pergamon Press, Oxford, 1975.
- [5] J.D. Macomber, *The Dynamics of Spectroscopic Transitions*, John Wiley & Sons, Inc., New York, 1976.
- [6] G.A. Ozin and A.C. Arsenault, *Nanochemistry. A Chemical Approach to Nanomaterials*, Royal Society of Chemistry, Cambridge, 2005.
- [7] D.L. Feldheim and C.A. Foss (eds), *Metal Nanoparticles. Synthesis, Characterization and Applications*, Marcel Dekker, New York, 2002.
- [8] G. Schmid (ed.), *Nanoparticles. From Theory to Applications*, Wiley-VCH, Weinheim, 2005.
- [9] E.A. Coronado and G.C. Schatz, *J. Chem. Phys.*, **119**, 2003, 3926–3934.
- [10] M.I. Stockman, S.V. Faleev and D.J. Bergman, *Phys. Rev. Lett.*, 2001, **87**, 167401/1–167401/4.