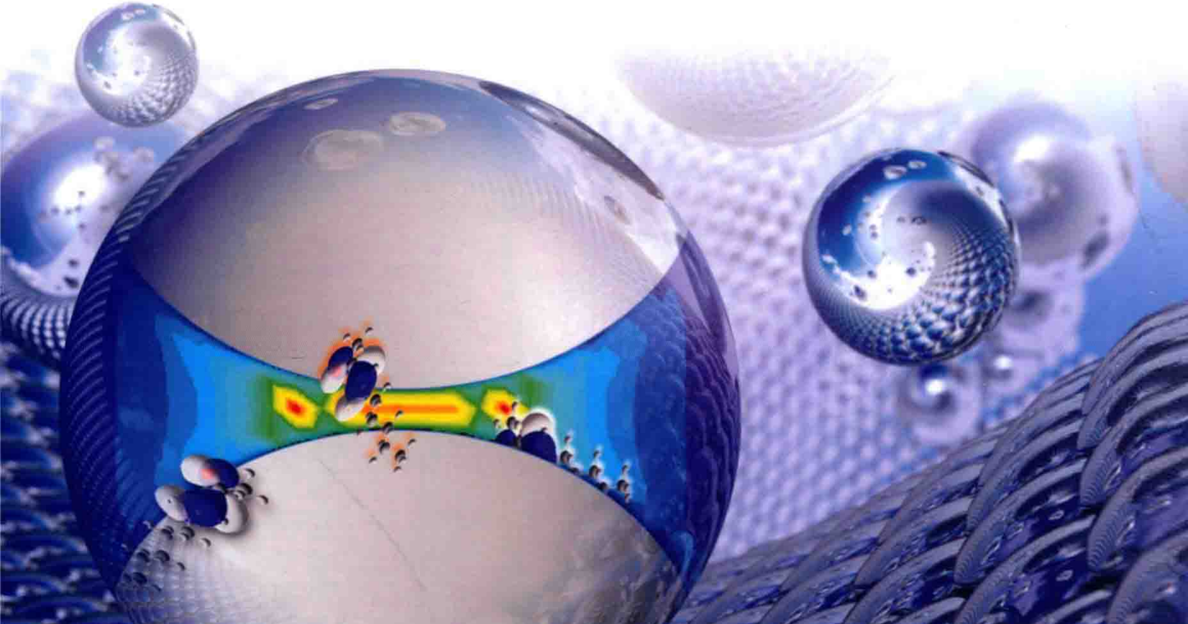
EDITORS

YUKIHIRO OZAKI | KATRIN KNEIPP | RICARDO AROCA

FRONTIERS OF SURFACE-ENHANCED RAMAN SCATTERING

SINGLE NANOPARTICLES AND SINGLE CELLS



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Frontiers of Surface-Enhanced Raman Scattering

Single Nanoparticles and Single Cells

Edited by

YUKIHIRO OZAKI
KATRIN KNEIPP
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List of Contributors

Aisha Alsaleh, Materials and Surface Science Group, University of Windsor, Canada

Ricardo Aroca, Materials and Surface Science Group, University of Windsor, Canada

Mohamad Banaee, School of Engineering and Applied Sciences, Harvard University, USA

Lev Chuntonov, Department of Chemical Physics, Weizmann Institute of Science, Israel; Department of Chemistry, University of Pennsylvania, USA

Ying Chen, Department of Chemistry and the Photonics Center, Boston University, USA

Yizhuo Chu, School of Engineering and Applied Sciences, Harvard University, USA

Carlos J. L. Constantino, Faculdade de Ciências e Tecnologia, UNESP Universidade Estadual Paulista, Brazil

Kenneth B. Crozier, School of Engineering and Applied Sciences, Harvard University, USA

Daniela Drescher, Department of Chemistry, Humboldt-Universität zu Berlin, Germany

Yoseph Gebregziabher, Department of Chemistry and the Photonics Center, Boston University, USA

Gilad Haran, Department of Chemical Physics, Weizmann Institute of Science, Rehovot, Israel

Tamitake Itoh, National Institute of Advanced Industrial Science and Technology (AIST), Japan

Satoshi Kawata, Department of Applied Physics, Osaka University, Japan

Yasutaka Kitahama, Department of Chemistry, School of Science and Technology, Kwansei Gakuin University, Japan

Harald Kneipp, Department of Physics, Technical University of Denmark, Denmark

Janina Kneipp, Department of Chemistry, Humboldt-Universität zu Berlin, Germany

Katrin Kneipp, Department of Physics, Technical University of Denmark, Denmark

Paul Lemler, Department of Chemistry and the Photonics Center, Boston University, USA

Jian-Feng Li, State Key Laboratory of Physical Chemistry of Solid Surfaces and College of Chemistry and Chemical Engineering, Xiamen University, China

Kei Murakoshi, Department of Chemistry, Hokkaido University, Japan

Hideki Nabika, Department of Chemistry, Hokkaido University, Japan

Fumika Nagasawa, Department of Chemistry, Hokkaido University, Japan

Yukihiro Ozaki, Department of Chemistry, School of Science and Technology, Kwansei Gakuin University, Japan

W. Ranjith Premasiri, Department of Chemistry and the Photonics Center, Boston University, USA

George C. Schatz, Chemistry Department, Northwestern University, USA

Mai Takase, Department of Chemistry, Hokkaido University, Japan

Zhong-Qun Tian, State Key Laboratory of Physical Chemistry of Solid Surfaces and College of Chemistry and Chemical Engineering, Xiamen University, China

Eric J. Titus, Department of Chemistry and Biochemistry, The University of Texas, USA

Nicholas A. Valley, Chemistry Department, Northwestern University, USA

Diogo Volpati, Faculdade de Ciências e Tecnologia, UNESP Universidade Estadual Paulista, Brazil

Dongxing Wang, School of Engineering and Applied Sciences, Harvard University, USA

Katherine A. Willets, Department of Chemistry and Biochemistry, The University of Texas, USA

Taka-aki Yano, Department of Electronic Chemistry, Tokyo Institute of Technology, Japan

Wenqi Zhu, School of Engineering and Applied Sciences, Harvard University, USA

Lawrence D. Ziegler, Department of Chemistry and the Photonics Center, Boston University, USA

Preface

The discovery of surface-enhanced Raman scattering (SERS) stretches back to the 1970s. It flourished for nearly four decades with a broad range of applications. Today, it is a vibrant quintessential embodiment of nanoscience and nanotechnology. SERS is a plasmon-based spectroscopy at the forefront of the developments in plasmonics, providing the fundamentals for theory and experiment.

SERS continues to grow with remarkable success. There are some major driving forces pushing forward new developments, among them it is worth mentioning three thriving areas. First is the success of single molecule detection by SERS; second the progress in the understanding of SERS fundamentals; and third, the development of nanoscience and nanotechnology. The level of understanding of SERS is currently so advanced that people are beginning to formulate strategies for exploiting SERS as a general platform for chemical and biological analysis with unprecedented routine levels of sensitivity, specificity and reproducibility.

This book is closely related to one of the symposia in Pacifichem 2010 "*Frontiers of Surface-Enhanced Raman Scattering: Single-Nanoparticles and Single Cells*". Thus, the collection is based on the Pacifichem SERS, and most of the contributors have been selected from invited speakers at the symposium. One of the most important purposes of the book is an attempt to convey to the scientific community the enthusiastic discussion on the state-of-the-art SERS during the symposium.

The symposium was, in essence, the first gathering so far convened to examine the "State of the new developments in SERS" with particular emphasis on single nanoparticles and single cells. With that in mind, in this book we have assembled the prime movers in the field worldwide, ensuring that we invited the seminal current contributors to SERS theory, substrate fabrication, applications of SERS to biosystems, chemical analysis, sensing, and of course fundamental innovation through experimentation.

We hope this book will not only be useful but also enjoyable to read. We will be most gratified if the book can inspire readers to try novel and exciting SERS research.

Yukihiro Ozaki,
School of Science and Technology,
Kwansei Gakuin University

Katrin Kneipp,
Department of Physics,
Technical University of Denmark

Ricardo Aroca,
Materials and Surface Science Group,
University of Windsor

Contents

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Calculation of Surface-Enhanced Raman Spectra Including Orientational and Stokes Effects Using TDDFT/Mie Theory QM/ED Method

George C. Schatz and Nicholas A. Valley
Chemistry Department, Northwestern University, USA

New models combining a quantum mechanical description of a molecular system and an electrodynamics (ED) description of a metal nanoparticle to determine surface-enhanced Raman spectra are described. The models considered involve inclusion of frequency dependence, Stokes shifts, and the effects of surface averaging into previously developed models. Important changes in absolute intensities result from considering these effects while changes in the relative intensities are minor. In a study of metal phthalocyanine, strong variation in the spectrum with orientation of the molecule relative to the nanoparticle surface is noted, and only after orientation averaging is included is there agreement with experiment. We also present calculations with one of the models using a multi-nanoparticle system, and this is found to provide more experimentally realistic enhancements which slightly improve the spectra.

1.1 Introduction: Combined Quantum Mechanics/Electrodynamics Methods

The surface-enhanced Raman scattering (SERS) response spans multiple orders of magnitude, providing many important challenges to theoretical modeling. Theoretical

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and computational studies have approached this problem in a variety of ways [1–8]. Proper modeling of the full SERS effect must describe both the electromagnetic (EM) enhancement due to the plasmonic particle, and chemical (CHEM) enhancements involving response of the molecule that interacts chemically with the particle. EM enhancement results from oscillation of the conduction band electrons of the metallic structure, referred to as plasmon excitation, in response to an external field. The plasmon excitation enhances the local electric field at both the incident and scattered frequencies, greatly increasing the Raman cross-section of molecules close to the nanoparticle surface. CHEM enhancement is tied to charge transfer between molecule and metal particle, both in the ground and excited states, that results from orbital overlap. Generally, the EM enhancement is large compared to the CHEM enhancement [9], with up to a fourth-power dependence on the electric field (i.e., enhancement $\sim E^4$).

Theoretical modeling of SERS has historically taken one of two paths. One neglects CHEM effects, focusing only on the dominant EM enhancement as determined by the field induced at the position of the molecule by light interacting with the nanoparticle [3]. In the other, the focus can be placed on the CHEM enhancement by doing an electronic structure calculation for the molecule plus a small cluster of metal atoms [4]. To incorporate both mechanisms, it is necessary to combine ED and quantum mechanics (QM) calculations into the optical response, however, this idea has only recently been considered.

Previous work on combining QM and ED has considered the ED calculations for the particle in the absence of the analyte and then the plasmonic excitation is applied as a constant field to the molecule. Corni and Tomasi explicitly coupled electronic structure calculations for the analyte to an ED calculation for the particle in the frequency domain by including effective charges in the molecular Hamiltonian in the quasi-static approximation [10]. Lopata and Neuhauser developed a local, two-level random phase approximation model for density matrix evolution. This evaluated the molecular population transfer rate while the finite-difference time-domain (FDTD) method was used to describe the ED [11]. Masiello and Schatz applied a many body Greens function to evaluate plasmon-enhanced molecular absorption [12]. This enables a better treatment of the effect of the molecule–field interaction, but CHEM effects associated with charge transfer were not included in the applications. A discrete interaction model/QM method to explicitly model nanoparticle interaction has been described by Morton and Jensen [13, 14]. Here an atomistic representation of the nanoparticle (with atoms treated as polarizable dipoles) provides an explicit model for the optical properties of a molecule interacting with the nanoparticle surface. Recently, Chen and Schatz described a hybrid QM/ED method in the time domain using RT-TDDFT (real-time time-dependent density functional theory) in which fields from FDTD are used to provide a plasmon-enhanced driving field for the molecule [15]. More recently, a frequency domain linear response version of this theory has been developed by Mullin and Schatz [16] and applied to calculating SERS spectra for pyridine and Rhodamine 6G. In both studies TDDFT was used to determine frequency-dependent polarizability derivatives for the molecule, with the molecule taken to be in the gas-phase except with a restricted orientation that mimics the molecule on the surface. This approach for the coupling of QM with ED is denoted "model G".

New multiscale models have recently been developed for the combination of QM and classical ED for describing surface-enhanced Raman and hyper-Raman spectra including CHEM and EM enhancement mechanisms for both [16]. In these models, TDDFT (in the frequency domain) is used for the QM calculation, and Mie theory (restricted to spherical particles) is used for the ED calculations. A new feature, however, is that the surface of a metal cluster treated quantum mechanically is overlaid with the surface of the metal particle to combine the two calculations. In model A, the electric field from plasmon excitation of the metal particle is combined with the CHEM enhancement associated with a static treatment of the molecule-metal structure to determine overall spectra. In model B, the frequency dependence of the Raman spectrum of the isolated molecule is combined with the enhancements determined using model A to refine the enhancement estimate and include resonance Raman effects in the molecule.

Models A, B, and G all neglect the Stokes shifting of the scattered light and use a three point approximation to determine the average over positions of the molecule on the surface. To more faithfully describe Raman scattering, in this paper we present improved models that couple QM calculations and ED calculations to include both EM and CHEM mechanisms, and which remove the previous limitations. In particular, model A has been modified to include Stokes shifting in the EM enhancement, replacing $|E(\omega)|^4$ by $|E(\omega)E(\omega')|^2$ where ω and ω' are the incident and Stokes shifted frequencies, respectively. This leads to model S, and we show how this effect changes both the magnitude and the shape of the Raman spectrum for pyridine. Further modifications to model S to include more extensive surface averaging leads to model V. Comparisons with experiment for metal phthalocyanines and for pyridine demonstrate important improvements in the predictions of these models compared to earlier work. We also show how the EM mechanism can be evaluated for our models for nanoparticle dimers, using Mie theory, leading to much higher enhancement values.

1.2 Computational Details

The calculation of the field for spheres is performed with a locally developed Mie theory code. The silver dielectric parameters used are those from Johnson and Christy [17]. For small particles, electron scattering from the nanoparticle surface becomes an important source of electron dephasing. A factor Av_F/R in the Drude expression for the plasmon width, where v_F is the Fermi velocity, R is the particle radius, and A is an empirical parameter, is included to correct for this. A value of 0.1 for A will be used here.

Quantum mechanical calculations have been performed using the Amsterdam Density Functional (ADF) program package [18]. For systems including pyridine, full geometry optimization and frequency calculations were completed using the Perdew–Wang (PW91) XC-potential and a triple-ζ polarized Slater type (TZP) basis set. All calculations for phthalocyanines were performed with a Becke–Perdew (BP86) XC-potential and a TZP basis set.

Polarizabilities for pyridine were calculated with the AOResponse module, and the asymptotically correct statistical average of orbital potential (SAOP) model XC-potential. The SAOP model potential has been designed to give accurate excited state properties, allowing accurate calculation of response properties. An even-tempered quadruple-ζ plus triple polarization (ET-QZ3P) polar basis set was used for C, H, and N, while a TZP basis set was used for Ag. Scalar relativistic effects for the Ag atoms were accounted for with the zeroth order regular approximation (ZORA). Frequency-dependent polarizabilities were calculated using a global damping parameter of $\Gamma = 0.004$ au (0.1 eV); this is the