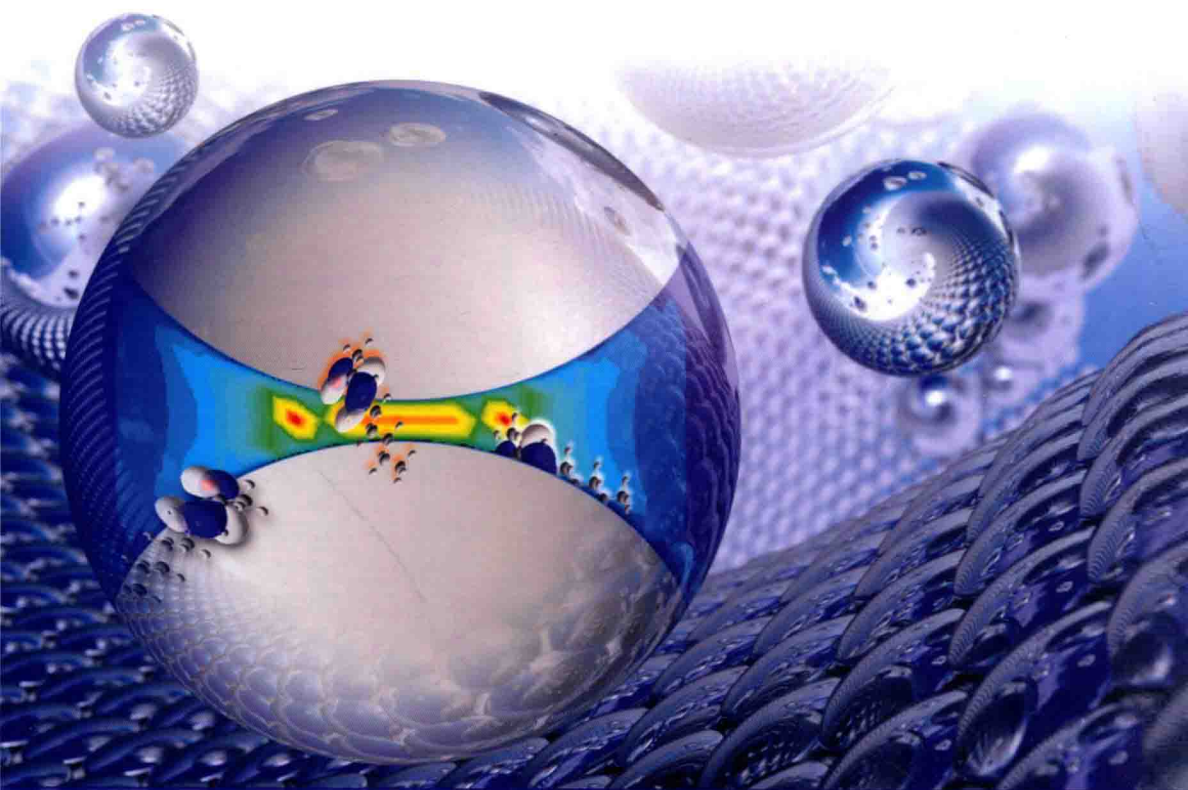


EDITORS

YUKIHIRO OZAKI | KATRIN KNEIPP | RICARDO AROCA

FRONTIERS OF SURFACE-ENHANCED RAMAN SCATTERING

SINGLE NANOPARTICLES AND SINGLE CELLS



WILEY

Frontiers of Surface-Enhanced Raman Scattering

Single Nanoparticles and Single Cells

Edited by

YUKIHIRO OZAKI

KATRIN KNEIPP

RICARDO ABOGA



WILEY

This edition first published 2014
© 2014 John Wiley & Sons Ltd

Registered office

John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, United Kingdom

For details of our global editorial offices, for customer services and for information about how to apply for permission to reuse the copyright material in this book please see our website at www.wiley.com.

The right of the author to be identified as the author of this work has been asserted in accordance with the Copyright, Designs and Patents Act 1988.

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, except as permitted by the UK Copyright, Designs and Patents Act 1988, without the prior permission of the publisher.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic books.

Designations used by companies to distinguish their products are often claimed as trademarks. All brand names and product names used in this book are trade names, service marks, trademarks or registered trademarks of their respective owners. The publisher is not associated with any product or vendor mentioned in this book.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. It is sold on the understanding that the publisher is not engaged in rendering professional services and neither the publisher nor the author shall be liable for damages arising herefrom. If professional advice or other expert assistance is required, the services of a competent professional should be sought

The advice and strategies contained herein may not be suitable for every situation. In view of ongoing research, equipment modifications, changes in governmental regulations, and the constant flow of information relating to the use of experimental reagents, equipment, and devices, the reader is urged to review and evaluate the information provided in the package insert or instructions for each chemical, piece of equipment, reagent, or device for, among other things, any changes in the instructions or indication of usage and for added warnings and precautions. The fact that an organization or Website is referred to in this work as a citation and/or a potential source of further information does not mean that the author or the publisher endorses the information the organization or Website may provide or recommendations it may make. Further, readers should be aware that Internet Websites listed in this work may have changed or disappeared between when this work was written and when it is read. No warranty may be created or extended by any promotional statements for this work. Neither the publisher nor the author shall be liable for any damages arising herefrom.

Library of Congress Cataloging-in-Publication Data

Frontiers of surface-enhanced raman scattering : single-nanoparticles and single cells / edited by Yukihiro Ozaki, Katrin Kneipp, Ricardo Aroca.

pages cm

Includes index.

ISBN 978-1-118-35902-0 (cloth)

1. Raman effect, Surface enhanced. 2. Surfaces (Physics) 3. Raman spectroscopy. 4. Spectrum analysis. I. Ozaki, Y. (Yukihiro) editor of compilation. II. Kneipp, Katrin, editor of compilation. III. Aroca, Ricardo, editor of compilation.

QC454.R36F76 2014

543'.57 – dc23

2013037278

A catalogue record for this book is available from the British Library.

ISBN: 9781118359020 (Cloth)

Set in 10/12pt Times by Laserwords Private Limited, Chennai, India
Printed and bound in Singapore by Markono Print Media Pte Ltd

Frontiers of Surface-Enhanced Raman Scattering

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 Chuntanov, 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 Pacificchem 2010 “*Frontiers of Surface-Enhanced Raman Scattering: Single-Nanoparticles and Single Cells*”. Thus, the collection is based on the Pacificchem 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

<i>List of Contributors</i>	xi
<i>Preface</i>	xv
1. Calculation of Surface-Enhanced Raman Spectra Including Orientational and Stokes Effects Using TDDFT/Mie Theory QM/ED Method	1
<i>George C. Schatz and Nicholas A. Valley</i>	
1.1 Introduction: Combined Quantum Mechanics/ Electrodynamics Methods	1
1.2 Computational Details	3
1.3 Summary of Model Systems	4
1.4 Azimuthal Averaging	5
1.5 SERS of Pyridine: Models G, A, B, S, and V	6
1.6 Orientation Effects in SERS of Phthalocyanines	11
1.7 Two Particle QM/ED Calculations	13
1.8 Summary	15
Acknowledgment	16
References	16
2. Non-resonant SERS Using the Hottest Hot Spots of Plasmonic Nanoaggregates	19
<i>Katrin Kneipp and Harald Kneipp</i>	
2.1 Introduction	19
2.2 Aggregates of Silver and Gold Nanoparticles and Their Hot Spots	21
2.2.1 Evaluation of Plasmonic Nanoaggregates by Vibrational Pumping due to a Non-resonant SERS Process	21
2.2.2 Probing Plasmonic Nanoaggregates by Electron Energy Loss Spectroscopy	24
2.2.3 Probing Local Fields in Hot Spots by SERS and SEHRS	25
2.3 SERS Using Hot Silver Nanoaggregates and Non-resonant NIR Excitation	26
2.3.1 SERS Signal vs. Concentration of the Target Molecule	26
2.3.2 Spectroscopic Potential of Non-resonant SERS Using the Hottest Hot Spots	30
2.4 Summary and Conclusions	31
References	32

3. Effect of Nanoparticle Symmetry on Plasmonic Fields: Implications for Single-Molecule Raman Scattering	37
<i>Lev Chuntanov and Gilad Haran</i>	
3.1 Introduction	37
3.2 Methodology	38
3.3 Plasmon Mode Structure of Nanoparticle Clusters	39
3.3.1 Dimers	39
3.3.2 Trimers	40
3.4 Effect of Plasmon Modes on SMSERS	47
3.4.1 Effect of the Spectral Lineshape	47
3.4.2 Effect of Multiple Normal Modes	49
3.5 Conclusions	54
Acknowledgment	54
References	54
4. Experimental Demonstration of Electromagnetic Mechanism of SERS and Quantitative Analysis of SERS Fluctuation Based on the Mechanism	59
<i>Tamitake Itoh</i>	
4.1 Experimental Demonstration of the EM Mechanism of SERS	59
4.1.1 Introduction	59
4.1.2 Observations of the EM Mechanism in SERS Spectral Variations	60
4.1.3 Observations of the EM Mechanism in the Refractive Index Dependence of SERS Spectra	62
4.1.4 Quantitative Evaluation of the EM Mechanism of SERS	64
4.1.5 Summary	72
4.2 Quantitative Analysis of SERS Fluctuation Based on the EM Mechanism	72
4.2.1 Introduction	72
4.2.2 Intensity and Spectral Fluctuation in SERS and SEF	73
4.2.3 Framework for Analysis of Fluctuation in SERS and SEF	73
4.2.4 Analysis of Intensity Fluctuation in SERS and SEF	76
4.2.5 Analysis of Spectral Fluctuation in SERS and SEF	78
4.2.6 Summary	82
4.3 Conclusion	82
Acknowledgments	83
References	83
5. Single-Molecule Surface-Enhanced Raman Scattering as a Probe for Adsorption Dynamics on Metal Surfaces	89
<i>Mai Takase, Fumika Nagasawa, Hideki Nabika and Kei Murakoshi</i>	
5.1 Introduction	89

5.2	Simultaneous Measurements of Conductance and SERS of a Single-Molecule Junction	90
5.3	SERS Observation Using Heterometallic Nanodimers at the Single-Molecule Level	96
5.4	Conclusion	101
	Acknowledgments	101
	References	101
6.	Analysis of Blinking SERS by a Power Law with an Exponential Function	107
	<i>Yasutaka Kitahama and Yukihiro Ozaki</i>	
6.1	Introduction	107
6.2	Materials and Methods	110
6.3	Power Law Analysis	110
6.4	Plasmon Resonance Wavelength Dependence	117
	6.4.1 Power Law Exponents for the Bright and Dark Events	117
	6.4.2 Truncation Time for the Dark Events	123
6.5	Energy Density Dependence	123
	6.5.1 Power Law Exponents for the Bright and Dark Events	123
	6.5.2 Truncation Time for the Dark Events	125
	6.5.3 Comparison with Other Analysis	126
6.6	Temperature Dependence	129
	6.6.1 Power Law Exponents for the Bright and Dark Events	129
	6.6.2 Truncation Time for the Dark Events	129
	6.6.3 Comparison with Other Analysis	130
6.7	Summary	132
	Acknowledgments	132
	References	133
7.	Tip-Enhanced Raman Spectroscopy (TERS) for Nanoscale Imaging and Analysis	139
	<i>Taka-aki Yano and Satoshi Kawata</i>	
7.1	Crucial Difference between TERS and SERS	139
7.2	TERS-Specific Spectral Change as a Function of Tip–Sample Distance	141
7.3	Mechanical Effect in TERS	143
7.4	Application to Analytical Nano-Imaging	144
7.5	Metallic Probe Tip: Design and Fabrication	149
7.6	Spatial Resolution	154
7.7	Real-Time and 3D Imaging: Perspectives	155
	References	156
8.	Shell-Isolated Nanoparticle-Enhanced Raman Spectroscopy (SHINERS)	163
	<i>Jian-Feng Li and Zhong-Qun Tian</i>	
8.1	Introduction	163
8.2	Synthesis of Various Shell-Isolated Nanoparticles (SHINs)	167

8.3	Characterizations of SHINs	169
8.3.1	Correlation of the SHINERS Intensity and Shell Thickness	169
8.3.2	Characterization of the Ultra-Thin Uniform Silica Shell	171
8.3.3	Influence of the SHINs on the Surface	172
8.4	Applications of SHINERS	173
8.4.1	Single-Crystal Electrode Surface	173
8.4.2	Non-Metallic Material Surfaces	175
8.4.3	Single Particle SHINERS	178
8.5	Different Strategies of SHINERS Compared to Previous SERS Works Using Core–Shell or Overlayer Structures	178
8.6	Advantages of Isolated Mode over Contact Mode	180
8.7	Concluding Discussion	184
8.8	Outlook	185
	Acknowledgments	186
	References	186
9.	Applying Super-Resolution Imaging Techniques to Problems in Single-Molecule SERS	193
	<i>Eric J. Titus and Katherine A. Willets</i>	
9.1	Introduction	193
9.1.1	Single-Molecule Surface-Enhanced Raman Scattering (SM-SERS)	193
9.1.2	Super-Resolution Imaging	194
9.2	Experimental Considerations for Super-Resolution SM-SERS	195
9.2.1	Sample Preparation	195
9.2.2	Instrument Set-up	196
9.2.3	Camera Pixels and Theoretical Uncertainties	197
9.2.4	Correlated Imaging and Spectroscopy in Super-Resolution SM-SERS	198
9.2.5	Correlated Optical and Structural Data	199
9.3	Super-Resolution SM-SERS Analysis	200
9.3.1	Mechanical Drift Correction	201
9.3.2	Analysis of Background Nanoparticle Luminescence	202
9.3.3	Calculating the SM-SERS Centroid Position	202
9.4	Super-Resolution SM-SERS Examples	204
9.4.1	Mapping SM-SERS Hot Spots	204
9.4.2	The Role of Plasmon-Enhanced Electromagnetic Fields: Structure Correlation Studies	206
9.4.3	The Role of the Molecule: Isotope-Edited Studies	210
9.5	Conclusions	214
	References	214

10. Lithographically-Fabricated SERS Substrates: Double Resonances, Nanogaps, and Beamed Emission	219
<i>Kenneth B. Crozier, Wenqi Zhu, Yizhuo Chu, Dongxing Wang and Mohamad Banaee</i>	
10.1 Introduction	219
10.2 Double Resonance SERS Substrates	220
10.3 Lithographically-Fabricated Nanogap Dimers	226
10.4 Beamed Raman Scattering	229
10.5 Conclusions	238
References	239
11. Plasmon-Enhanced Scattering and Fluorescence Used for Ultrasensitive Detection in Langmuir–Blodgett Monolayers	243
<i>Diogo Volpati, Aisha Alsaleh, Carlos J. L. Constantino and Ricardo F. Aroca</i>	
11.1 Introduction	243
11.2 Surface-Enhanced Resonance Raman Scattering of Tagged Phospholipids	245
11.2.1 Experimental Details	245
11.2.2 Langmuir and LB films	246
11.2.3 Electronic Absorption	247
11.2.4 Characteristic Vibrational Modes of the Tagged Phospholipid	248
11.2.5 Single Molecule Detection	250
11.3 Shell-Isolated Nanoparticle Enhanced Fluorescence (SHINEF)	251
11.3.1 Tuning the Enhancement Factor in SHINEF	251
11.3.2 SHINEF of Fluorescein-DHPE	253
11.4 Conclusions	254
Acknowledgments	255
References	255
12. SERS Analysis of Bacteria, Human Blood, and Cancer Cells: a Metabolomic and Diagnostic Tool	257
<i>W. Ranjith Premasiri, Paul Lemler, Ying Chen, Yoseph Gebregziabher and Lawrence D. Ziegler</i>	
12.1 Introduction	257
12.2 SERS of Bacterial Cells: Methodology and Diagnostics	258
12.3 Characteristics of SERS Spectra of Bacteria	261
12.4 PCA Barcode Analysis	263
12.5 Biological Origins of Bacterial SERS Signatures	265
12.6 SERS Bacterial Identification in Human Body Fluids: Bacteremia and UTI Diagnostics	266

12.7	Red Blood Cells and Hemoglobin: Blood Aging and Disease Detection	267
12.8	SERS of Whole Blood	269
12.9	SERS of RBCs	271
12.10	Malaria Detection	273
12.11	Cancer Cell Detection: Metabolic Profiling by SERS	273
12.12	Conclusions	276
	Acknowledgment	277
	References	277
13.	SERS in Cells: from Concepts to Practical Applications	285
	<i>Janina Kneipp and Daniela Drescher</i>	
13.1	Introduction	285
13.2	SERS Labels and SERS Nanoprobes: Different Approaches to Obtain Different Information	286
	13.2.1 Highlighting Cellular Substructures with SERS Labels	286
	13.2.2 Probing Intrinsic Cellular Biochemistry with SERS Nanoprobes	288
13.3	Consequences of Endocytotic Uptake and Processing for Intrinsic SERS Probing in Cells	289
13.4	Quantification of Metal Nanoparticles in Cells	292
13.5	Toxicity Considerations	295
13.6	Applications	298
	13.6.1 pH Nanosensors for Studies in Live Cells	298
	13.6.2 Following Cell Division with SERS	299
	Acknowledgment	301
	References	301
	Index	309

1

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

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