Frontiers of Surface-Enhanced Raman Scattering
Frontiers of Surface-Enhanced Raman Scattering

Single Nanoparticles and Single Cells

Edited by

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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.

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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 \(\omega\) and \(\omega'\) 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 \(A_v R/v_F\) 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-\(\zeta\) 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-\(\zeta\) 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
same as was used in earlier work [19], and is thought to represent a reasonable estimate of
the excited state dephasing lifetime.

1.3 Summary of Model Systems

The models discussed here are a few of many that could be imagined where ED and elec-
tronic structure calculations are coupled. The molecules are placed in close proximity (less
than 1 nm) to the metallic surface, as is common in SERS experiments. The methods used
here assume the plasmonic response of the metal nanoparticle considered in the ED calcu-
lations is negligibly perturbed by the presence of the molecule(s). This is reasonable in the
low concentration regime. Inclusion of a tetrahedral Ag_{20} cluster in the quantum mechan-
cal calculations allows us to add static CHEM enhancement effects to the results using
the method of Morton and Jensen [20]. Non-static CHEM contributions can be considered,
but caution must be taken due to the underestimation of charge transfer excitation energies
calculated with TDDFT [21].

The quantum mechanically treated cluster and larger metal particle are both incorporated
by making the particle and cluster surfaces coincident. We will call this an “overlay” struc-
ture, as previously described by Mullin et al. [16]. This structure for pyridine is shown
in Figure 1.1, where we contrast the overlay structure with that used for model G, where
the location of the molecule relative to the surface is not determined by a QM calculation.
This overlay structure is used in all the models we consider except for model G. Therefore,
model G will lack the static CHEM enhancement included in the other models, although
orientation and polarization averaging effects that would be associated with a molecule on
the nanoparticle surface are included. In model A, the static CHEM enhancement factor
(which varies with vibrational mode) is also included in the calculation, and we use the
molecule–surface distance from the electronic structure calculation to define the location
of the molecule for the EM calculation. We also note that calculating the response of the
quantum portion in the static limit will also avoid double counting of plasmon resonance
effects when the EM and CHEM enhancements are multiplied.

Models B, S, and V are all extensions of model A. Model B begins with model A and mul-
tiplies by the ratio of the Raman intensity for the isolated molecule at the frequency being
studied to the static Raman intensity. This model incorporates any frequency dependence

![Figure 1.1](image)

**Figure 1.1** Combined quantum mechanics/electrodynamics model systems (a) gas-phase quantum mechanically treated molecule and electrodynamics treated particle used in Model G and (b) molecule–Ag_{20} cluster treated quantum mechanically where the cluster surface is coincident (overlaid) with that of the particle treated with electrodynamics.
that the molecule polarizability might have, even resonance Raman enhancement, but that of the cluster is not included due to the problem with self-interaction errors. Model S allows the scattered frequency to differ from the incident frequency in the EM component of the enhancement. This model considers the Stokes shift, which takes into account the frequency dependence of the field enhancements caused by the metal particle(s). Model V expands upon model S by including a more complete surface averaging.

In the models involving the Ag_{20} cluster, the molecule orientation relative to the surface is fixed by the ground state structure of the molecule–cluster system. Spectra, which can be compared with experiment, are generated by fixing the position of the molecule relative to the particle surface. Then it is assumed that the azimuthal direction of the molecule relative to the polarization of the EM field is random. Therefore, an average of the intensity over azimuthal directions is used. This type of averaging was performed for Raman spectra for model G by Mullin and Schatz [16]. Expressions for the azimuthal averaging are presented later.

The use of Mie theory is not necessary for the general method used here and, as with any ED method, it comes with strengths and weaknesses. Mie theory provides an exact solution of Maxwell’s equations, and therefore can be used down to zero separation between molecule and metal. This provides an improvement over the FDTD method used in other work [16], as fields from FDTD become inaccurate close to the particle surface due to the finite difference approximation. A limitation of Mie theory, however, is it can only be used for single or assemblies of spherical particles. For more general particles, one is forced to use a numerical method.

In summary, the models used and the effects they account for are:

Model G: QM molecule, ED particle
Model A: QM molecule–cluster complex, ED particle
Model B: QM molecule–cluster complex, ED particle, molecular frequency dependence
Model S: QM molecule–cluster complex, ED particle, Stokes scattering
Model V: QM molecule–cluster complex, ED particle, Stokes scattering, surface averaging.

1.4 Azimuthal Averaging

A completely general expression for the Raman intensity is [16]:

$$I = Q^2 |E(\omega')\alpha'_m E(\omega)|^2 I_0 / E_0^4$$ (1.1)

Rotational degrees of freedom of the molecule may be considered by rotation of the polarizability tensor of the molecule in the previous expression. As a first approximation, if the molecule is allowed to rotate about the axis along which the molecule is bound to the particle, azimuthal averaging is being included. When the bound axis is the x-axis, the rotation matrices are included as shown:

$$E(\omega') \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos(\phi) & \sin(\phi) \\ 0 & -\sin(\phi) & \cos(\phi) \end{pmatrix} \alpha'_m \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos(\phi) & \sin(\phi) \\ 0 & -\sin(\phi) & \cos(\phi) \end{pmatrix} E(\omega)$$ (1.2)
The azimuthal angle $\phi$ is the angle between the lab-fixed $y$-axis and the rotating molecular $y'$-axis. Averaging over $\phi$ leads to the following expression for the azimuthal polarization averaged intensity (here taking the lab-fixed wavevector along $z$ so the polarization is along $x$ and $y$) [16]:

$$I(180^\circ) = \frac{d\sigma}{d\Omega}(180^\circ) = \frac{1}{2E_0^2} K_p \left[ \alpha_{m,xx}^2 \left( [E_x^1]^4 + [E_y^1]^4 \right) + \frac{1}{2} \left( \frac{1}{2} (\alpha_{m,yy} + \alpha_{m,zz})^2 + \alpha_{m,yz}^2 + \frac{1}{4} (\alpha_{m,yy} - \alpha_{m,zz})^2 \right) \right] \times \left( \{ [E_x^2]^2 + [E_y^2]^2 \}^2 + \{ [E_y^2]^2 + [E_z^2]^2 \}^2 \right)$$

$$+ 2 \left( \alpha_{m,yy}^2 + \alpha_{m,zz}^2 + \frac{1}{2} \alpha_{m,xy}^2 \alpha_{m,yz} + \frac{1}{2} \alpha_{m,xx}^2 \right) \times \left[ [E_x^3]^2 \left( [E_y^3]^2 + [E_z^3]^2 \right) + [E_y^3]^2 \left( [E_x^3]^2 + [E_z^3]^2 \right) \right]$$

(1.3)

Here $E_j^i$ refers to the $i$th component of the local field, with the initial polarization pointing in the $j$th direction.

### 1.5 SERS of Pyridine: Models G, A, B, S, and V

Experimental and theoretical studies of SERS of pyridine generally find around six peaks in the spectrum. The most intense peaks correspond to ring breathing modes at 983 and 1026 cm$^{-1}$ (normal modes will be referred to by their gas-phase DFT energies calculated at the level of theory outlined). Modestly intense ring stretching modes appear at 1208, 1472, and 1583 cm$^{-1}$, as well as a ring deformation mode at 598 cm$^{-1}$.

Simulated gas-phase normal Raman spectra of pyridine using static and frequency-dependent polarizability derivatives are shown in Figure 1.2 along with experimental results from Golab et al. [22]. Differential cross-sections in both cases have been calculated assuming a wavelength of 357 nm, though only the frequency-dependent results include this wavelength in the response calculations. The specific wavelength chosen corresponds to the plasmon resonance frequency of the small silver particle in the QM/ED models later. Molecular resonance is not expected to occur at this wavelength as the electronic transitions of pyridine are at much higher energies. The calculated spectra are similar in appearance to experimental and other theoretical spectra [22, 23], and the only difference compared to our earlier work [16] is that the reference wavelength used previously was 514.5 nm rather than 357 nm. The strongest peaks are observed at 983 and 1026 cm$^{-1}$. Weak peaks appear at 598, 651, 1208, 1472, and 1583 cm$^{-1}$. The absolute intensity of the frequency-dependent spectrum is larger than that of the static spectrum, reflecting pre-resonance enhancement in pyridine. Frequency dependence effects constitute about a factor of 2 at 357 nm.

Previously, Mullin and Schatz have calculated SERS spectra using the QM/ED model G method with FDTD for Raman spectra [16]. Here, the model G approach is applied using Mie theory to describe the enhanced fields around a spherical silver nanoparticle. The spectrum resulting from a QM/ED (G) calculation, assuming a 0.25 nm molecule–metal sphere separation and an incident wavelength of 357 nm, is presented in...
Figure 1.2 Simulated normal Raman spectrum of pyridine using static and frequency-dependent polarizability derivatives. Differential cross-section is given in units of $10^{-30}$ cm$^2$ sr$^{-1}$ and is calculated assuming an incident wavelength of 357 nm. Peaks are broadened by a Lorentzian with a full width at half maximum of 10 cm$^{-1}$. Scale is for the broadened theoretical spectrum. Reproduced with permission from [23]. Copyright © 2007, American Chemical Society.

Figure 1.3. Only very minor changes in relative intensities are observed in comparison to the gas-phase spectrum. Raman intensities are enhanced by about $4 \times 10^3$, which corresponds to purely EM enhancement. The calculated enhancement factor is a factor of 2.5 lower than was found by Mullin and Schatz for a 1 nm separation. This is likely due to the inclusion of electron–surface scattering in the present ED calculations, which slightly dampens the plasmon excitation. Frequency dependence is also not included in the quantum calculations used in the present application, leading to weaker intensities compared to results in Mullin et al. [16].

CHEM enhancement effects can be added to the models by including a tetrahedral 20 atom silver cluster (Ag$_{20}$). This will be done for models A, B, S, and V in an application to pyridine. The geometry and Raman spectra of pyridine bound to this small cluster have been extensively studied in the literature [23, 24]. Calculations here only consider the “S-complex,” where the pyridine is bound to the central silver atom on the (111) face. Static CHEM enhancement in this arrangement contributes a factor of 2 to the intensity of the spectrum. Energies of vibrational modes, when bound to the silver cluster, do not change substantially in comparison to the gas phase. In the QM/ED models, the Ag$_{20}$ cluster is embedded in the 20 nm silver sphere, as shown in Figure 1.1b. The actual distance from the nanoparticle surface at which the field is evaluated is slightly larger than in previous work [16] leading to slightly lower enhancements overall.

Model A results are presented in Figure 1.4 along with an experimental SERS spectrum from Golab et al. [22]. Compared to the results for the gas-phase molecule and model G, relative intensities of modes at 983 and 1583 cm$^{-1}$ are increased. Better agreement with the
Figure 1.3  Simulated model G SERS spectrum of pyridine at a separation of 0.25 nm from a 10 nm radius silver sphere at an incident wavelength of 357 nm. Differential cross-section is given in units of $10^{-30}$ cm$^2$ sr$^{-1}$. Peaks are broadened by a Lorentzian with a full width at half maximum of 10 cm$^{-1}$.

Figure 1.4  Simulated model A SERS spectrum of pyridine using the static S-complex attached to a 20 nm diameter silver sphere for structure at an incident wavelength of 357 nm. Experimental SERS spectrum digitized from Ref. [23]. Differential cross-section is given in units of $10^{-30}$ cm$^2$ sr$^{-1}$. Peaks are broadened by a Lorentzian with a full width at half maximum of 10 cm$^{-1}$. Reproduced with permission from [23]. Copyright © 2007, American Chemical Society.
experimental SERS spectrum is seen with model A than with model G. Absolute intensities are nearly a factor of 4 larger than those obtained in model G, leading to overall enhancement of $1.5 \times 10^4$. A factor of $\sim 4 \times 10^3$ is due to EM enhancement, while the remaining factor of 3–4 is due to static CHEM enhancement.

The frequency dependence of the polarizability derivatives at 357 nm is taken into account in model B. Figure 1.5 presents the spectrum resulting from model B. In comparison with model A, the relative intensities of modes at 983 and 1026 cm$^{-1}$ are increased. Again, the spectrum agrees well with the experimental SERS spectrum. Both model A and model B strongly underestimate the peak at 1208 cm$^{-1}$. The absolute intensity of the model B spectrum is about twice what is seen for model A. This is due to the inclusion of the frequency dependence.

While models G, A, and B result in reasonable results in comparison to experimental SERS spectra, they make unnecessary approximations. They first assume the incident and scattered light have the same frequency in the ED calculations. This leads to an overestimation of the EM enhancement as all the fields are assumed to be at the plasmon resonance frequency where the greatest field enhancement will occur. If the frequency of the scattered light is allowed to be different than the incident frequency, they will no longer experience optimal enhancement, which leads to a weaker signal. This will also lead to modes being enhanced to different degrees, depending on their vibrational energies. Modes with low energies will have smaller Stokes shifts and be nearer the plasmon resonance if the incident frequency is at or near the plasmon resonance. This can change the relative intensities of the peaks in the spectrum and will be dependent on the incident frequency and the frequency dependence of the fields of the specific nanoparticle system.

**Figure 1.5** Simulated model B SERS spectrum of pyridine using the static S-complex attached to a 20 nm diameter silver sphere for structure at an incident wavelength of 357 nm. Differential cross-section is given in units of $10^{-30}$ cm$^2$ sr$^{-1}$. Peaks are broadened by a Lorentzian with a full width at half maximum of 10 cm$^{-1}$. 
Another approximation involves the limited amount of field information used from the ED calculations. Models G, A, and B only take into account field enhancements at three points (i.e., along the x-, y-, and z-axes) on the spherical particle. Since the incident k-vector is along z, and the polarizations are along x or y, these points are also special points where the field enhancement is the maximum for a specific Cartesian direction in the molecular frame. It will be shown that this results in an overestimation of the enhancement as well. Models S and V expand upon model A to correct the errors introduced by each of these approximations. Model S uses different field enhancements for the scattered light by performing the ED calculations at the incident frequency and each of the Stokes shifted frequencies. Model V expands on model S by numerically averaging spectra obtained at each point in a grid over the surface of the nanoparticle(s). For each of these models, two incident frequencies will be compared, one (357 nm) corresponding to the plasmon resonance and another (347 nm) that, along with the Stokes shifted 1583 cm\(^{-1}\) peak (367 nm), straddles the plasmon resonance peak.

Results using model S with an incident wavelength of 347 and 357 nm are displayed in Figure 1.6. For the system studied, the different incident light energies lead to peaks with roughly the same relative intensities. The absolute intensities are about 50% larger when the incident light is at the plasmon resonance than when the incident and scattered light straddle the plasmon resonance. Better agreement with experimental SERS spectra is obtained with model S than the previous models, as the mode at 598 cm\(^{-1}\) increases in intensity relative to the peak at 1583 cm\(^{-1}\). Inclusion of the Stokes shift results in a factor of 3 decrease in the calculated EM enhancement factor, making it $\sim 1 \times 10^3$.

Model V is performed by using the Mie theory calculated field enhancements at points sampled around the entire surface of the spherical particle (i.e., uniformly in azimuthal

![Figure 1.6](image-url)  
*Figure 1.6* Simulated model S SERS spectra of pyridine using the static S-complex attached to a 20 nm diameter silver sphere for structure at an incident wavelength of 347 and 357 nm. Differential cross-section is given in units of $10^{-30}$ cm\(^2\) sr\(^{-1}\). Peaks are broadened by a Lorentzian with a full width at half maximum of 10 cm\(^{-1}\).
Figure 1.7  Simulated model V SERS spectra of pyridine using the static S-complex attached to a 20 nm diameter silver sphere for structure at an incident wavelength of 347 and 357 nm (red). Experimental spectrum from Ref. [23] is included. Differential cross-section is given in units of $10^{-30}$ cm$^2$ sr$^{-1}$. Peaks are broadened by a Lorentzian with a full width at half maximum of 10 cm$^{-1}$. Reproduced with permission from [23]. Copyright © 2007, American Chemical Society

angle and uniformly in $\cos(\theta)$ where $\theta$ is the polar angle). Specifically we choose 3 nm point spacing in the determination of the Raman spectra. Spectra obtained using Model V are shown in Figure 1.7 along with the experimental spectrum from Golab et al. [22]. Only minor changes in relative intensities are noted compared to the model S spectrum. A very minor peak corresponding to the 1208 cm$^{-1}$ mode can be seen. The surface averaging causes a decrease in absolute intensities by around a factor of 5. At 357 nm excitation the total enhancement is $1 \times 10^3$, which is reasonable for a single sphere. Excitation at the plasmon resonance still shows 50% stronger intensity than excitation at 347 nm.

1.6 Orientation Effects in SERS of Phthalocyanines

To test the utility of the QM/ED methods discussed, we use them to explain the existence of an extraneous peak in a calculated gas-phase spectrum of a metal phthalocyanine when compared to an experimental surface-enhanced spectrum. The comparison can be seen in Figure 1.8. Metal phthalocyanines have recently [25] been used as targets in tip-enhanced Raman spectroscopy (TERS) experiments and consist of a central metal atom and a surrounding porphyrin-like aromatic structure.

Metal phthalocyanines generally adopt a planar geometry with D$_{4h}$ point group symmetry. Calculated bond lengths and angles were found to be in agreement with previous DFT calculations by Basova et al. [26] (for copper phthalocyanine) and Murray et al. [27] (for zinc phthalocyanine) as well as crystallographic data [28]. Theoretical gas-phase calculations agree well with the experimental spectrum, except for a calculated peak that appears
near 1370 cm\(^{-1}\). Calculations including a metal cluster (model A) found CHEM effects to be weak and the extra peak persisted.

The QM/ED model G was employed to investigate the dependence of the spectrum on the orientation of the molecule with respect to the surface. Model G allows analysis of the effects of molecular orientation relative to the surface without the need for performing a new quantum mechanical calculation for each orientation. This is not the case for the models that include a metal cluster in the quantum mechanical calculations. Calculations were performed on the closed-shell ZnPc, while experimental results from Ref. [26] are obtained using CuPc. Currently, the available electronic structure codes do not have the ability to calculate resonance response for open shell species, so instead of performing calculations on the open-shell CuPc, calculations are performed on the closed-shell ZnPc. The ZnPc spectrum is very similar to the CuPc spectrum, and the same two peaks at about 1340 and 1370 cm\(^{-1}\) appear in the same location. As the angle between the plane of the phthalocyanine and the surface was decreased, only the intensity and not the shape of the spectrum was altered. Experimental evidence pointed to the phthalocyanine lying flat on the surface. When this geometry was studied, the spectrum in Figure 1.9 was the result.

When the molecule is flat on the surface, the peak near 1370 cm\(^{-1}\) that is not observed experimentally disappears in the theoretical spectrum. The spectrum as a whole, however, no longer resembles the experimental spectrum, and is much weaker in intensity. Since the plane of the molecule is strictly constrained to be parallel to the surface, only modes with out-of-plane character show up. Modes with only in-plane character, like the 1370 cm\(^{-1}\) mode, do not appear.