Rice University

Density Matrix Calculation of Surface Enhanced Raman Scattering for Silver Nanoshells Coated with p-Mercaptoaniline

by

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A thesis submitted in partial fulfillment of the requirements for the degree Master of Science

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Abstract

The tremendous increase in Raman-scattered photons seen in Surface-Enhanced Raman Scattering (SERS) has led to its adoption as a common analytical laboratory tool in spite of lingering questions about the phenomenon. One recent example is the demonstration by Jackson, et al.,\textsuperscript{1,2} of SERS for silver nanoshells each consisting of an inner silica sphere encased in a silver shell. In concert with these experiments, the current investigation is directed at quantum mechanical calculation and modeling of the SERS signals to be expected for silver nanoshells coated by molecules based on \textit{ab initio} calculations on an AgPMA salt model with the thiol bonding to silver rather than an H atom as in the free PMA molecule. We take the information from these calculations and consider a density matrix formalism including the effects of the strong electromagnetic near fields around the metal surface,\textsuperscript{3} the molecules' orientation and energy, and the associated Raman spectra.
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1 Introduction

It has been known for decades that the vibration-specific scattered light in Raman spectroscopy could be enhanced by factors of up to $\sim 10^6$ for molecules on noble metal surfaces. With the recent push toward single-molecule SERS, it has been estimated that enhancement by factors $10^{12}$-$10^{14}$ are possible, though precise determination of enhancement factors is difficult experimentally. With increasing sophistication in nanoparticle/nanoarray design, new platforms for SERS are being made available, including investigation of p-mercaptoaniline (p-aminobenzenthiol, p-aminothiophenol) or PMA molecules adsorbed onto a silver nanoshell.

It is well known that SERS depends first and foremost on the strong electromagnetic near fields around the metal surface. This electromagnetic enhancement in SERS is not molecule-specific. However, for physisorbed or chemisorbed molecules, the total enhancement factors observed are still quite different from molecule to molecule and differences are observed in the relative intensities of vibrational features in SERS and unenhanced Raman spectra. These differences are ascribed to a "chemical effect" enhancement beyond, but smaller than, the better-understood electromagnetic enhancement. The chemical effect is frequently described by models involving transitions between neutral and ionic states of the molecule. In the charge transfer (CT) models of Persson, Ueba, and others, this interaction depends on overlaps between molecular and extended metal orbitals and the position of the Fermi energy of the metal particle.

Still within a purely local perspective, others have considered \textit{ab initio} calculations consisting of a molecule and a small metal complex. For example, Nakai and Nakatsuji have taken an approach for CO adsorbed on Ag that specifically considers molecular
distance from and orientation with respect to the metal surface. They focus on molecular orbitals (MO's) of Ag$_2$CO and Ag$_{10}$CO using time-dependent Hartree-Fock theory and the Placzek polarizability approximation to calculate SERS intensities. From this point of view, the interactions are interpreted as surface polarization interactions with molecular vibrations in an overall neutral complex, and the Raman spectroscopy is resonant when the laser frequency is close to transition energies of the complex. The more recent investigation of Ag$_2$-pyrazine by Arenas, et al.,$^{13}$ also takes this computational point of view with Hartree-Fock (HF) and Configuration-Interaction Singles (CIS) calculations, interpreting observed SERS vibrational features according to local symmetry. A similar situation occurs for calculations of pyridine on Cu, Ag and Au clusters.$^{14,15}$ These \textit{ab initio} methods with small attached metal clusters are increasingly able to elucidate aspects of the chemical effect in SERS on a molecule-by-molecule basis. To more fully characterize the SERS signal by quantum calculations, one needs more than simple local calculations. There is, for instance, significant variation in electronic levels as the size of the metal cluster increases. As in current-day calculations of the behavior of molecular electronic devices with metal cluster contacts,$^{16,17}$ one needs to grow the cluster significantly and then embed it in an appropriate many-body description of the mesoscopic nanoparticle. Furthermore, and most importantly, small cluster calculations alone are unable to capture the important interactions with the surface plasmons, which are collective oscillations of the substrate conduction electrons whose resonance properties depend sensitively on the geometry and morphology of the nanoparticle.

We here consider one or three metal atoms in our molecule metal complex., considering only qualitative features of the complex. From this model, our molecule is
evolved via the density matrix formalism in a manner similar to the recent work of Xu, et al.,\textsuperscript{18} and Johansson, et al.\textsuperscript{19} for two metallic nanospheres.

This treatment, which includes the important effects of population transfer and phase relaxation, readily generalizes to the case of a metal nanoshell and multiple vibrational modes. Here three dominant SERS-active vibrational modes identified by Jackson, et al., are simultaneously included.
2 SERS for Para-Mercaptoaniline Absorbed on Silver

With the density matrix calculation and subsequent spectral calculation as our final goal, we first consider an AgPMA or Ag₃PMA model with C₂ᵥ symmetry based on spectroscopies by Osawa et al. ²⁰ and Jackson et. al. ².

We first note the importance of symmetry in describing and assigning the vibrational modes. Since vibrational overtones and combination bands are rarely seen in SERS, it is only the lower-lying vibrations that are of concern and these are the ones best described in terms of normal modes. If we take \( Q = \{Q_1, Q_2, ..., Q_{39}\} \) as the normal modes of the ground electronic state, then the nuclear Hamiltonian for state \( n \) up to quadratic order in these coordinates is

\[
H_{\text{vib}}^n = -\frac{1}{2} \sum_i \frac{\partial^2}{\partial Q_i^2} + \sum_i f_{ni} Q_i + \frac{1}{2} \sum_i \sum_j f_{ni,j} Q_i Q_j
\]  

(1)

where the \( f_{ni} \) and \( f_{ni,j} \) are linear and quadratic force constants, respectively. In the planar C₂ᵥ geometry, the normal modes break into in-plane \( a_1 \) and \( b_2 \) and out-of-plane \( a_2 \) and \( b_1 \) subgroups. Invariance of the Hamiltonian under all symmetry operations of the group requires that only the \( a_1 \) \( f_{ni} \) components and only the \( a_1-a_1, b_2-b_2, a_2-a_2 \) and \( b_2-b_1 \) blocks of the \( f_{ni,j} \) matrix are nonzero. As a consequence, provided that the simple Taylor series expansion is valid over the spectrally-relevant excited-state geometries, only the \( a_1 \) modes are involved at the leading (linear) order. They thus dominate the ordinary Raman scattering spectra.

This is consistent with resonant experiments from Osawa, et. al., who looked at SERS and Surface Enhanced Infrared Absorption (SEIRA) measurements of PMA on silver island films and roughened silver electrodes. Osawa, et al., assigned PMA with C₂ᵥ
symmetry and found that SEIRA spectra were dominated by $a_1$ modes, indicating that each molecule is on average standing up with the in-plane symmetry axis normal to the metal surface. Also, the absence of an S-H stretching mode in any of the surface spectroscopies confirms that an Ag-S chemical bond is formed. Thus, the thiol-linked PMA molecule was inferred to be "standing up" with a linear Ag-S-C configuration and to have $C_{2v}$ symmetry beyond just the local symmetry of the benzene ring. The SERS measurements at 514.5 nm and surrounding excitation wavelengths also found strong $b_2$ activity. This, however, was identified within the model of Lombardi, et al.,\textsuperscript{11} as a resonance phenomenon between the metal Fermi energy and a charge transfer excited state occurring at $\sim$4.1 eV (300 nm) above the ground state for the free PMA molecule. In a recent analogous example of phthalimide attached to silver colloids and island via hydrogen atom extraction, the SERS spectra were shown to be much more similar to the ordinary Raman spectra of the free silver salt of phthalimide than those of the parent molecule.\textsuperscript{15} Ultimately, then, the natural model for use here is an AgPMA molecule with Ag-S binding in planar $C_{2v}$ symmetry (see Figure 1).
FIGURE 1. AgPMA salt mode considered in *ab initio* calculations where the hydrogen in free PMA has been replaced with a silver atom. An Ag,PMA model is also considered but not shown.

In more recent off-resonant experiments, Jackson, et al.,\(^1\text{,}^2\) have measured SERS response of PMA-coated nanoshells under carefully controlled conditions with 782 nm (1.6 eV) excitation. While several weak modes are observed in some of the nanoshell experiments, there are always three strong modes seen around 390, 1077 and 1590 cm\(^{-1}\), as well as usually weaker modes at 1180 and 1003 cm\(^{-1}\). In C\(_2\)\(_v\) geometry, these are expected to be of a\(_1\) symmetry since the resonant mechanism investigated by Osawa, et al., should not be activated at this longer wavelength. The b\(_2\) modes will therefore not play a role in the current investigation.

A partial summary of experimental and theoretical results is presented in Table 1, with the details of the Density Functional Theory (DFT) calculations explained below. Table 1 also excludes a 390 cm\(^{-1}\) mode seen by Jackson, et.al., which plays an important role in understanding further details of the molecular geometry. This mode will be described later.
<table>
<thead>
<tr>
<th>Assignment</th>
<th>Osawa, et al.²⁰</th>
<th>Jackson, et al.²</th>
<th>DFT Calc</th>
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<tr>
<td></td>
<td>SERS</td>
<td>SEIRA</td>
<td>SERS</td>
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<td>18&lt;sub&gt;a&lt;/sub&gt; (a&lt;sub&gt;1&lt;/sub&gt;)</td>
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<td>1280</td>
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<tr>
<td>7a'&lt;sub&gt;a&lt;/sub&gt; (a&lt;sub&gt;1&lt;/sub&gt;)</td>
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<td>1629</td>
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</table>
3 Ab Initio Calculations

3.1 Calculation basis and results

The ab initio calculations undertaken were of silver salts of PMA using either 1 or 3 Ag atoms, both of which cases allow the simplification of closed shell calculations. Both self-consistent field (SCF) and density functional theory (DFT) calculations were run using the Guassian program G03,\textsuperscript{21} initially keeping optimizations restricted to \(C_{2v}\) geometry to assist in vibrational assignments. For Ag\textsubscript{3}PMA, the additional Ag atoms are also kept in plane and find as a stationary geometry an isosceles triangle for which their separation is less than the distance of either to the first Ag atom. There are of course imaginary frequencies in \(C_{2v}\) geometry even with 1 Ag atom since the Ag atom prefers to bend out of plane. Nevertheless we are primarily concerned with the ring vibrations, which are mostly insensitive to the Ag orientation. Furthermore, other influences not included in our calculations can promote the straight-up geometry inferred by Osawa, et al.\textsuperscript{20} In particular, the actual situation for fully PMA coated nanoshells (estimated packing density of 0.3 nm\textsuperscript{2} per molecule\textsuperscript{22}) is that there are other nearby PMA molecules and, in some cases, solvent molecules.\textsuperscript{23} With ab initio calculations for silver salts of PMA, it is possible to investigate the sensitivity of the vibrational assignments to the addition of more Ag atoms.

To include some of the relativistic effects important for Ag atoms, we use the LANL2DZ basis and associated Effective Core Potential (ECP) available in Gaussian. This has been shown to be an appropriate basis for DFT in small molecules containing Cu, Ag or Au,\textsuperscript{24} and has also recently been used for similar SERS investigations in Ag\textsubscript{27}-pyrazine.\textsuperscript{13} For main-group elements, the LANL2DZ option uses the contracted D95 basis,
so further extended calculations were run using the 6-31g* basis set for non-silver atoms to make a comparison.

Our results are labeled SCFx and DFTx in Table 2. Table 2 shows the calculated modes falling in the primary ring-mode range starting from just under 1000 cm\(^{-1}\) in each of the methods. The frequencies are ordered numerically, so that there is some variation in mode placement between the different columns. The SCF and SCFx columns are generally expected to overestimate the vibrational frequencies by several percent, but it can be seen, for instance, that they fail to yield an \(a_1\) mode less than 100 cm\(^{-1}\) above the \(\nu_{18a}\) mode seen around 1000 cm\(^{-1}\) by Osawa, et al., and Jackson. For all DFT calculations - either LANL2DZ or extended basis, either 1 or 3 Ag atoms -- the vibrational mode is found within the range of 1015-1022 cm\(^{-1}\). As seen in Table 1, for our assignments, we expect for DFT calculations to overestimate by 2-4%. In terms of the usual vibrational scaling factors to be applied to calculated frequencies, then, factors in the range 0.96-0.98 will be obtained.
### TABLE 2: Calculated Vibrational Frequencies for Agₙ-PMA

<table>
<thead>
<tr>
<th></th>
<th>AgSφNH₂ (C₇₀)</th>
<th></th>
<th>Ag₃SφNH₃ (C₃v)</th>
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<tr>
<td>SCF</td>
<td>SCFx</td>
<td>DFT</td>
<td>DFTx</td>
<td>SCF</td>
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<tr>
<td>b₁</td>
<td>953</td>
<td>b₁ 920</td>
<td>a₂ 988</td>
<td>b₁ 943</td>
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<tr>
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</tr>
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<td>b₂ 1035</td>
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<tr>
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<td>Basis Set/Method</td>
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<td>SCF- Self Consistent Field method with LANL2DZ basis</td>
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<tr>
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<td>DFT- B3LYP Density Functional Theory with LANL2DZ basis</td>
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<td>DFTx- Density Functional Theory with LANL2DZ6-31g* basis</td>
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</table>

### 3.2 Evidence for bent geometry

There is another important mode falling at around 390 cm⁻¹ which was observed by Jackson, et. al. We identify this lowest-frequency mode as having a significant S-Ag bond-stretching component and a consequent sensitivity to deviations of the Ag atom from the plane of the benzene ring. Such deformations lower the frequency of the mode, bringing it into better agreement with experiment. Table 3 shows the candidate modes falling in a 300-500 cm⁻¹ range.
<table>
<thead>
<tr>
<th>AgSφNH₂ (C₂ᵥ)</th>
<th>Ag₃SφNH₂ (C₂ᵥ)</th>
</tr>
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<tbody>
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<td>SCF</td>
<td>SCFx</td>
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<tr>
<td>b₂424</td>
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<tr>
<td>a₂466</td>
<td>a₂459</td>
</tr>
<tr>
<td>a₁469</td>
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**Basis Set/Method**
- SCF - Self Consistent Field method with LANL2DZ basis
- SCFx - Self-Consistent Field method with LANL2DZ-31g* basis
- DFT - B3LYP Density Functional Theory with LANL2DZ basis
- DFTx - Density Functional Theory with LANL2DZ-31g* basis

There is a persistent b₂ mode in the SCF, SCFx, DFT and DFTx calculations that is principally an in-plane wagging of the NH₂ moiety accompanied by slight torsional counter-movement by the aromatic ring. While this mode is close to the 390 cm⁻¹ feature seen by Jackson, et al., it is difficult to rationalize a reasonably strong SERS contribution by a solitary b₂ mode, especially at long wavelength excitation. The more likely candidate is the a₁ mode in Table 3 with a DFT/DTFx range of 436-455 cm⁻¹. This is certainly well outside of the 2-4% accuracy found for the other observed modes. This discrepancy is attributed primarily to a change in the Ag-S-C bond angle from 180°. Full geometry optimization for AgPMA provides an equilibrium value for this angle close to 105°, i.e., a tetrahedral angle. At this geometry, the a₁ mode has the much lower energy of 370 cm⁻¹, which is below the experimentally observed value. In view of the SEIRA results and the other environmental influences mentioned above but not included in the *ab initio* calculations, it is to be expected that the PMA molecules are in actuality slightly tilted from the straight-up configuration with the benzene plane leaning toward the surface face-on. Figure 4 shows our assembled assignments of vibrational motions in the limiting C₂ᵥ geometry to the features observed by Jackson, et al.
FIGURE 2. Mode assignments for the 5 dominant modes observed by Jackson et. al.

3.3 Results for excited electronic states

This bent geometry is expected to be important with regard to the energies of the excited electronic states. The symmetry group corresponding to the bent geometry is $C_s$ which can be decomposed into $A'$ and $A''$ irreducible representations (irreps). The $A'$ irrep is totally symmetric and dominates the excited states. This is shown in Figure 3 where the CIS/SCF energies above the ground state are plotted for the first 10 excited states of $\text{AgPMA}$ and $\text{Ag}_2\text{PMA}$ as a function of $\text{Ag-C-S}$ bend angle. For each fixed angle, all other orientational degrees of freedom are optimized in the ground state. The dot radius on each of the lines is proportional to the oscillator strength of the transition from the ground state in order to provide an indication of the expected importance (within the silver salt model) to optical transitions. An important common feature in the two molecules is the $A'$ LUMO falling less than 3 eV above the ground state. While this state has very weak oscillator strength for the linear configurations, it is nonzero and clearly increases with decreasing bond angle. It is seen, though, that the strongest transitions are at quite high energy relative to the laser energy of 1.6 eV when the $\text{Ag-S-C}$ angle is 180°. This is, at this
point, to be regarded as only a propensity since it would be important to include further
Ag atoms in the cluster to mimic the nanoshell surface for strongly bent geometries.
Given the SEIRA evidence of Osawa, et al., it is still to be concluded that the Ag-S-C
bond angle is not too different from the linear configuration, and that 782 nm excitation is
indeed off-resonant with respect to electronic transitions in the silver salts of PMA. For
these off-resonant transitions, multiple excited states will play a role, though for this
investigation we consider only one.

FIGURE 3. Energy correlation diagrams versus changes in the Ag-S-C bond angle
for the first 10 excited states of AgPMA and Ag₃PMA respectively. Dot radius
is proportional to oscillator strength.
3.4 Molecular Orbital in SERS

Finally, Gaussian allows us to consider the molecular orbitals (MO’s) involved in the optical transitions from the ground state to the nearest excited states and the associated transition dipole moments. For off-resonant SERS, the most significant transition is expected to be that from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). Within CIS, this is represented as a mixture of single-electron excitations between the HOMO and LUMO wave functions. The most important of these contributions is shown in Figure 4 for two geometries, one with an Ag-S-C bond angle of 140°, and one with an angle of 180°. For both angles, the one-electron orbital from the HOMO is a pi orbital exhibiting a strong density around the sulfur atom and a weak density around the silver atom. The orbitals from the LUMO exhibit strong density around the silver atom with little anywhere else. This transition in both cases can be identified as a charge transfer excitation. It appears in our calculations as a density change from the molecule to the metal, though the transitions probed at higher laser energies have been assigned as metal to molecule.²⁰
FIGURE 4. Dominant single electron orbital transitions between HOMO and LUMO for AgPMA. The pair on the left are for an Ag-S-C bond angle of 140° and the pair on the right are for an Ag-S-C bond angle of 180°.

By symmetry, the dipole moment associated with this transition lies along the line connecting the silver, sulfur, and carbon atoms. We note, however, that if the molecule is slightly bent, the dipole will also have a non-zero component normal to the benzene ring. If electronic contributions from states with other symmetries are considered, there can be allowed transition dipole components in all directions. The dipole moment is the key parameter in coupling light to matter and will serve an important role in formulating a Hamiltonian characterizing light matter interactions.

4 Hamiltonian for Light and Matter Interaction

4.1 Introduction

In the next sections, we will define the light-matter Hamiltonian, discuss the evolution of the density matrix, and extract from the density matrix the combined Raman and fluorescence spectra from two time dipole-dipole correlation functions. The \textit{ab initio}
calculations described above are used for guidance in model calculations. While the formulation is general, the numerical aspects of the calculations in this first density matrix treatment of PMA/nanoshell SERS will focus on the straight-up geometrical limit.

To begin, the Hamiltonian for a single molecule is

\[ H = H_0 + H' \]  \hspace{1cm} (2)

where \( H_0 \) is the electronic and vibrational Hamiltonian of the molecule and \( H' \) is the interaction Hamiltonian of the molecule with electromagnetic fields (the latter treated classically). The molecule is taken as AgPMA, i.e., one Ag atom is treated as part of the molecule rather than part of the nanoshell. Within the Born-Oppenheimer approximation, the field-free molecular eigenfunctions are

\[ \Psi_{n,v}(q,Q) = \psi_{n}^{el}(q,Q) \psi_{n,v}^{vib}(Q) \]  \hspace{1cm} (3)

where \( n \) and \( v \) are collective quantum numbers for electronic and vibrational motion, and \( q \) and \( Q \) their respective collective coordinates. The electronic wave functions depend parametrically on the nuclear coordinate geometry and, for a given electronic state \( n \), the vibrational wave functions are eigenfunctions of the nuclear Hamiltonian \( H_n^{vib} \). All vibrational modes except for the three Raman-active modes specifically identified by Jackson, et al., are regarded as spectator modes and not considered further.

Considering the vibrational Hamiltonian in Eq (1), the Raman spectra are expected to be most sensitive to the linear terms (displacements of equilibrium positions) in the potential.\(^{25}\) Vibrational overtones and combination bands are rarely seen in SERS,\(^{26}\) so that there is little experimental information with which to determine higher-order force constants in any case. Consequently, it is reasonable to ignore the differences between
ground and excited state quadratic terms as a first approximation. The resulting vibrational Hamiltonian

\[
H_n^{\text{vib}} = \sum_i \hbar \omega_i \left[ -\frac{1}{2} \frac{\partial^2}{\partial Q_i^2} + \frac{1}{2} \left( Q_i - d_Q_{ni} \right)^2 \right] + \Delta_n. \tag{4}
\]

is separable in the normal modes (Parallel Modes Approximation\textsuperscript{25}). Each single-mode Hamiltonian is that of a displaced oscillator. The constant \( \Delta_n \) is the adiabatic electronic energy shift above the ground state minimum, while the vertical shift is given by \( \Delta_n + \sum_i \hbar \omega_i d_Q_{ni}^2 \). This model is the simplest for which the excited state potential slopes at the equilibrium geometry are the structural parameters influencing the SERS spectra, but is easily generalized as needed.

For the interaction Hamiltonian in the Multipolar Gauge (see Yang, et al.,\textsuperscript{27} and references therein) and the Electric Dipole Approximation, we have

\[
H' = \mathbf{d} \cdot \mathbf{E}_{\text{tot}}(\mathbf{r}, t) \tag{5}
\]

where \( \mathbf{d} \) is the dipole operator of the molecule and \( \mathbf{E}_{\text{tot}}(\mathbf{r}, t) \) is the cw electric field of frequency \( \omega \) at the molecular position \( \mathbf{r} = (r, \theta, \phi) \)

\[
\mathbf{E}_{\text{tot}}(\mathbf{r}, t) = \frac{1}{2} \left[ E_\omega(\mathbf{r}) e^{-i\omega t} + E_\omega^*(\mathbf{r}) e^{i\omega t} \right]. \tag{6}
\]

This field is the sum of the incident laser field \( \mathbf{E}_I(\mathbf{r}, t) \) and the corresponding field \( \mathbf{E}_{sp}(\mathbf{r}, t) \) generated by scattering from the surface plasmon oscillations of the nanoshell. This description thus combines the essential elements of the electromagnetic local field enhancement (due to \( \mathbf{E}_{sp} \)) with certain elements of the chemical effect (considering the silver salt AgPMA).
4.2 Vector spherical harmonics (Mie theory)

The incident and scattered fields can be found through expansion in vector spherical harmonics and solution of electromagnetic boundary conditions. Aden and Kerker derived this solution for the shell case in 1951\textsuperscript{28}. They considered the electric and magnetic fields in a source-free homogenous medium that satisfies a vector wave equation

$$\nabla \times \nabla \times \mathbf{A} - k^2 \mathbf{A} = 0. \quad (7)$$

Independent solutions are constructed according to

$$\mathbf{M}_{lm}(r, \theta, \phi) = \nabla u_{lm}(r, \theta, \phi) \times \mathbf{r}$$

$$\mathbf{N}_{lm}(r, \theta, \phi) = \frac{1}{k} \nabla \times \nabla u_{lm}(r, \theta, \phi) \times \mathbf{r}. \quad (8)$$

These fields are divergenceless, and the potentials $u_{lm}$ are a complete set of functions satisfying the scalar wave equation

$$\nabla^2 u + k^2 u = 0. \quad (9)$$

For the shell problem, Aden and Kerker used spherical coordinates, for which

$$u_{mn}(R, \theta, \phi) \propto z_n(kR) P_n^m(\cos(\theta)) \exp(\mathrm{i}m\phi). \quad (10)$$

Here $z_n(kR)$ is either the spherical Bessel function of the first kind, $j_n(kR)$, used for a region of space including the origin, or the spherical Hankel function of the first kind, $h_n(kR)$, used for a region of space at large distances from the origin. This potential provides the vector expansion for the field

$$\mathbf{E}(r) = E_0 \sum_{l=1}^{\infty} \sum_{m=-l}^{l} \left[ a_{lm} \mathbf{M}_{lm}^z(kr) + b_{lm} \mathbf{N}_{lm}^z(kr) \right]. \quad (11)$$

The explicit forms of these functions are given, for example, by Sarkar and Halas,\textsuperscript{29} who use associated Legendre functions $P_l^m(\cos \theta)$ with the Condon and Shortley choice of
phase. The implied time dependence of the field component is $e^{-i\omega t}$, and the subscript $\omega$ is henceforth dropped.

We consider an incident field propagating along the $z$-axis and polarized along the $x$-axis, and use the following transformations to simplify the vector expansion,

$$ F_{elm} = \frac{1}{2} \left( F_{lm} + F_{lm}^* \right) $$
$$ F_{olm} = \frac{1}{2i} \left( F_{lm} - F_{lm}^* \right) $$

(12)

where $F_{lm}$ stands for either the $M_{lm}^z(kr)$ or $N_{lm}^z(kr)$ basis function. The new basis is similarly defined, except for the replacement of $e^{im\phi}$ by $\cos m\phi$ (subscript $e$) or $\sin m\phi$ (subscript $o$). From Sarkar and Halas,[ref] one also has that

$$ M_{-lm} = (-1)^l \frac{(l-m)!}{(l+m)!} M_{lm}^* $$
$$ N_{-lm} = (-1)^l \frac{(l-m)!}{(l+m)!} N_{lm}^* $$

(13)

These relations yield for the $e^{-i\omega t}$ component of the incident wave, the expansion

$$ E_i(r) = E_0 \times e^{ikz} $$
$$ = E_0 \sum_{l=1}^{\infty} i^{l+2} \frac{2l+1}{l(l+1)} \left[ M_{ol1}^j(kr) - i N_{el1}^j(kr) \right] $$

(14)

and the corresponding scattered field expansion from the surface plasmon

$$ E_{sp}(r) = E_0 \sum_{l=1}^{\infty} i^{l+2} \frac{2l+1}{l(l+1)} \left[ a_l M_{ol1}^h(kr) - i b_l N_{el1}^h(kr) \right], $$

(15)

where the coefficients $a_l$ and $b_l$ are obtained by field continuity conditions at the inner and outer shell surfaces.\cite{28} These coefficients depend on the incident frequency and the dielectric functions of the core, shell and outside medium.
Each of the terms in the expansion over $l$ of the scattered field corresponds to a different surface plasmon multipole mode. For shell radii much smaller than the incident wavelength, the series converges very quickly and is dominated by dipole ($l = 1$) and sometimes quadrupole ($l = 2$) contributions. All of the differences from the case of solid spheres reside in the coefficients $a_l$ and $b_l$, which depend on the core/shell aspect ratio $a/b$, the incident field frequency, and the dielectric functions of the core, shell and surrounding medium. These plasmons are broadened by radiative damping on time scales of ca. 10 fs$^{30-32}$ as well as nonradiative damping (e.g., coupling to electron-hole continua and electron scattering). Prodan, et al.$^{33,34}$ have shown that the nanoshell surface plasmons may usefully be regarded as hybridizations of those for a sphere and a cavity, and that this interpretation generalizes to the addition of more layers. This is in strong analogy to hybridization of atomic orbitals to form molecular orbitals in molecular quantum mechanics and provides a new approach for the design of nanophotonic devices. For the simple nanoshell, there are two hybridized surface plasmons for each $l$ with frequencies $\omega_{l\pm}$. For the dipole case, the lower-frequency $\omega_{1-}$ is the optically active mode relevant to the SERS process.

We consider the case of a 57 nm radius silver nanoshell around a 39 nm radius silica core with dielectric constant 2.04. the resonance energy of the optically-active lower-energy dipole surface plasmon is $\omega_{1-}\sim 3.6$ eV, with higher multipoles falling progressively to higher energies. The illuminating field for a wavelength of 782 nm (1.6 eV) is strongly off-resonant with the surface plasmon, so only mild local field enhancements are to be expected in this case. Using the complex index of refraction data of Johnson and Christie,$^{35}$ the $\hat{r}$, $\hat{\Theta}$, $\hat{\phi}$, $\hat{x}$, $\hat{y}$ and $\hat{z}$ scattered field components just outside
the outer radius are mapped on the nanoshell surface in Fig. 5. It is seen that $E_{sp}$ is primarily radial in character and focused along the initial polarization axis, but is neither a spherical nor a plane wave.

\[
\begin{array}{ccc}
E_{r} & E_{\theta} & E_{\phi} \\
E_{x} & E_{y} & E_{z}
\end{array}
\]

FIGURE 5. Magnitudes of spherical and Cartesian components of scattered field $E_{sp}$ just outside a 39/57 nm Ag nanoshell. The incident field is a unit-magnitude plane wave field propagating in +z direction and polarized in +x direction with wavelength 782 nm. The components are mapped as functions of angular position around the nanoshell.

4.3 Matrix elements of interaction hamiltonian

With the fields well in hand, we return to the dipole-operator matrix elements of $H'$ between molecular wave functions. These vanish if $n' = n$, but are otherwise

\[
\langle n', \nu' | H' | n, \nu \rangle = \frac{1}{2} \left\{ \int \psi^{vib}_{n', \nu'}(Q) \mu_{n' n}(Q) \cdot \mathbf{E}(r) e^{-i \omega t} \psi^{vib}_{n, \nu}(Q) dQ \right\} n' > n
\]

\[
\left\{ \int \psi^{vib}_{n', \nu'}(Q) \mu_{n' n}(Q) \cdot \mathbf{E}(r) e^{i \omega t} \psi^{vib}_{n, \nu}(Q) dQ \right\} n' < n
\]

(16)

where the transition dipole functions are electronic matrix elements.
\[ \mu_{n'n}(Q) = \int \psi_{n'}^e(q; Q) d\psi_{n}^e(q; Q) \, dq \]  
\((17)\)

In the Condon Approximation, the coordinate dependence of these functions is neglected, i.e., \( \mu_{n'n}(Q) \sim \mu_{n'n} \), and therefore

\[ \langle n', \nu'|H'|n, \nu \rangle = \frac{1}{2} F_{n'n'\nu n n \nu} \mu_{n'n} \cdot \begin{cases} E(r)e^{-i\omega t} & n' > n \\ E^*(r)e^{i\omega t} & n' < n \end{cases} \]  
\((18)\)

Within the Parallel Modes Approximation, the Franck-Condon factors reduce to a product of 1D factors,

\[ F_{n'n'\nu n \nu} = \int \psi_{n'n'}^{vib}(Q) \psi_{n, \nu}^{vib}(Q) \, dQ \]

\[ = \prod_i \int \psi_{n'i \nu_i}^{vib}(Q_i) \psi_{n, \nu_i}^{vib}(Q_i) \, dQ_i, \]  
\((19)\)

which are trivially calculated.
5 Density Matrix Evolution

5.1 Equation of motion

Given the above Hamiltonian, we can find the density matrix at different times. The density matrix describes the populations and coherences of the different states. In the simplest case in the Schrödinger picture, it is a direct product of time dependent states

$$\rho(t) = \langle \psi(t) | \psi(t) \rangle$$  \hspace{1cm} (20)

Using the Schrödinger wave equation

$$i\hbar \frac{d}{dt} \langle \psi(t) \rangle = H(t) |\psi(t)\rangle$$

$$-i\hbar \frac{d}{dt} \langle \psi(t) | = \langle \psi | H(t)$$  \hspace{1cm} (21)

we find the evolution of the density matrix $\rho(t)$ under the Hamiltonian in Eq. (2) is given by

$$\frac{d}{dt} \langle \psi(t) | \psi(t) \rangle = \left( \frac{d}{dt} |\psi(t)\rangle \right) \langle \psi(t) | + |\psi(t)\rangle \left( \frac{d}{dt} \langle \psi(t) | \right)$$

$$= \frac{1}{i\hbar} \{ H(t) |\psi(t)\rangle \langle \psi(t) | - |\psi(t)\rangle \langle \psi(t) | H(t) \}$$

$$= \frac{1}{i\hbar} [H(t), \rho(t)]$$  \hspace{1cm} (22)

5.2 Population decay

To include relaxation and decay, let us briefly consider a Hamiltonian with quantized fields,

$$H = H_{mol} + \mathbf{d} \cdot \mathbf{E}_{tot}(r, t) + H_R.$$  \hspace{1cm} (23)

Here $H_R$ is the energy of the radiation field included as a reservoir into which photons emitted by the molecule can decay. The corresponding density matrix
\[ \chi(t) = \langle \psi(t), R(t) \rangle \langle \psi(t), R(t) \rangle \]  
(24)

must then also be included to reflect the infinite number of reservoir states \( R(t) \) as well as the states for the system under consideration. This more general density matrix can then be averaged over the states of the reservoir to provide a reduced density matrix for the molecular system, \( \rho(t) = Tr_R \{ \chi(t) \} \). This yields a density matrix similar to the previous one, though with a different equation of motion \(^{36}\)

\[ \frac{d}{dt} \rho(t) = \frac{1}{i\hbar} [H(t), \rho(t)] + L_1 \rho(t) \]  
(25)

with terms corresponding to population decay of the excited molecular states. The population decay components of the Liouville equation reside in the superoperator \( L_1 \), which is taken to be a sum of Lindblad forms,\(^ {37,38} \)

\[ L_1 \rho = \frac{1}{2} \sum_{j,k} \Gamma_{k,j} \left( 2\sigma_{k,j} \rho \sigma_{j,k} - \sigma_{j,k} \sigma_{k,j} \rho - \rho \sigma_{j,k} \sigma_{k,j} \right) \]  
(26)

in order to maintain positivity of probabilities extracted from the dynamically evolving density matrix. (There are, however, constraints on \( N \)-level quantum systems.\(^ {39}\)) The \( j \) and \( k \) indices run over the entire set of included vibronic levels \( n \) and \( v \). Each \( \sigma_{j,k} \) matrix has a \((j, k)\) element unity and all the rest zero, and the constant \( \Gamma_{k,j} \) corresponds to the rate of population decays from state \( j \) to state \( k \).

### 5.3 Decoherence

Further terms govern loss of coherences between quantum levels beyond that automatically caused by population decay. This dephasing was identified by Xu, et al., and Johansson, et al., as important for the production of the extended continuum background frequently seen in SERS experiments on both the Stokes and Anti-Stokes side.
of the laser frequency. This term appears as a superoperator $L_2$ providing for the
dephasing of the transition dipoles between the ground and excited electronic states,

$$L_2 \rho = - \sum_{n>0} \sum_{j \in 0}^{k \in n} \Gamma_{0n}^{ph} \left( \sigma_{jk} \rho_{jk} + \sigma_{kj} \rho_{kj} \right)$$  \hspace{1cm} (27)$$

Coherences and populations can therefore decay on different time scales. We have in
summary for the equation of motion of the density matrix

$$\frac{d}{dt} \rho = \frac{1}{i\hbar} [H(t),\rho(t)] + L_1 \rho + L_2 \rho$$

$$= \frac{1}{i\hbar} [H(t),\rho(t)] + \frac{1}{2} \sum_{j,k} \Gamma_{kj} \left( 2\sigma_{kj} \rho \sigma_{jk} - \sigma_{jk} \sigma_{kj} \rho - \rho \sigma_{jk} \sigma_{kj} \right)$$  \hspace{1cm} (28)$$

$$- \sum_{n>0} \sum_{j \in 0}^{k \in n} \Gamma_{0n}^{ph} \left( \sigma_{jk} \rho_{jk} + \sigma_{kj} \rho_{kj} \right)$$

This is almost the equation of motion we will use for propagation of the density matrix.
However, we need to further consider the details of the $\Gamma_{kj}$ decay terms since they are
strongly modified in SERS compared to unenhanced Raman spectroscopy.

5.4 Spontaneous emission enhancement

Within unenhanced spectroscopies, the photon emission rates arising by electronic
decay from $n'$ to $n$ can be approximated by Fermi's Golden Rule are

$$\Gamma_{n' n}^{0} = \frac{\omega_{n' n}^{3}}{3 \pi \epsilon_0 c} \left| \mu_{n' n} \right|^{2} \left| F_{n' n} \right|^{2}$$  \hspace{1cm} (29)$$

where

$$\omega_{n' n} = \frac{\Delta_{n'} - \Delta_{n}}{\hbar} + \sum_{i} \omega_{i} (v_{i'} - v_{i})$$  \hspace{1cm} (30)$$

It is an important aspect of SERS that the rate of photon emission is strongly enhanced,$^{40}$
with the emission enhancement scaling roughly as the square of the local field evaluated at
the Raman-shifted frequency.\textsuperscript{41} This is in accord with the fact that emission rates can be modified by placing molecules in electromagnetic cavities,\textsuperscript{42-46} near metallic planes\textsuperscript{47-54}, dielectric and metallic nanobodies,\textsuperscript{40,55-61} and along photonic crystals.\textsuperscript{62} One may approach this problem \((i)\) using quantized electromagnetic fields, with rates calculated via Fermi’s Golden Rule and the local density of states of the field, or \((ii)\) using classical field calculations based on modification of the asymptotic energy flux for a radiating classical dipole near a dielectric or conducting surface. For atoms or molecules near dielectric slabs, both lossless\textsuperscript{50,51} and absorbing,\textsuperscript{63} it has been shown that equivalent results are obtained classically and quantum mechanically. For dielectric spheres, the quantum and classical results are equivalent at least through first order in time-dependent perturbation theory.\textsuperscript{50,51,58}

We accordingly consider the modification of emission rates around the core-shell nanoparticles from the perspective of purely classical fields. This may be accomplished in complete parallel to the treatments of Kerker, et al.,\textsuperscript{41} and Chew\textsuperscript{57} for solid spheres. In particular, we assume a point dipole \(\mathbf{p}\) at position \(\mathbf{r}\) near the nanoshell oscillating at the Raman shifted frequency \(\omega_{n',v',n,v}\) with electric field \(\mathbf{E}_d\) and use vector spherical harmonics to calculate the secondary scattered field \(\mathbf{E}_s\) in the presence of the nanoshell. One derives the radiative decay rate for the excited state by integrating the far-field Poynting vector \(\mathbf{S}\) over all angles

\[
R = \frac{e^2}{r^3} \int \mathbf{S} \cdot d\Omega = \frac{c}{8\pi} \frac{\varepsilon_{\text{med}}}{\mu_{\text{med}}} r^2 \int |\mathbf{E}_d + \mathbf{E}_s|^2 \, d\Omega \tag{31}
\]

as well as the radiated power \(R_0\) in the absence of the sphere \(R_0 = c k^4 \varepsilon_{\text{med}} \mu_{\text{med}}^2 / 3\varepsilon_{\text{med}}^2\).
At the end of the calculations, one has a radiative enhancement factor (relative to the dipole-only case)

\[
\frac{R}{R_0} = x_r = \frac{3}{2 p^2} \sum_{l=1}^{\infty} (2l+1) \left[ \frac{p_r^2}{p} [l(l+1)(k_3 r)]^{-2} \left| j_l(k_3 r') + b_l h_l^{(1)}(k_3 r') \right|^2 \right]
\]

\[
+ \frac{p_0^2 + p_\phi^2}{2} \left[ \left| j_l(k_3 r') + a_l h_l^{(1)}(k_3 r') \right|^2 + \left| \eta_l^l(k_3 r') + b_l \eta_l^h(k_3 r') \right|^2 \right],
\]

(32)

\[
\eta_l^l(x) = \frac{1}{x} \frac{d}{dx} x z_l(x).
\]

(33)

This is of exactly the same form as for the solid sphere case,\textsuperscript{57,58} except that the coefficients \(a_l\) and \(b_l\) are the Mie coefficients for the nanoshell.\textsuperscript{28} (However, these coefficients and the wave vectors are evaluated here at the Raman-shifted frequency.) For complex dielectric functions, additional losses (Joule heating) will occur. The combined decay rate in this case can be expressed in terms of the dyadic Green function of the field (density of electromagnetic states).\textsuperscript{49,57,59} The total radiative and non-radiative decay rate enhancement is then given by

\[
X_{rrr} = 1 + \frac{3}{2} \frac{p_r^2}{p} \text{Re} \sum_{l=1}^{\infty} (2l+1) l(l+1)(k_3 r)^{-2} b_l^f \left[ h_l^{(1)}(k_3 r') \right]^2
\]

\[
+ \frac{3}{4} \frac{p_0^2 + p_\phi^2}{p} \text{Re} \sum_{l=1}^{\infty} (2l+1) \left[ a_l \left[ h_l^{(1)}(k_3 r') \right]^2 + b_l \left[ \eta_l^h(k_3 r') \right]^2 \right].
\]

(34)

As shown by Chew for spheres,\textsuperscript{57} these expansions are equivalent for the lossless case of purely real dielectric functions.
As discussed by Xu, et al.,\textsuperscript{18} and Johansson et. al.,\textsuperscript{19} further decay rate enhancement occurs from electron-hole pair creation due to non-local dielectric effects not covered in the Mie-type calculations. These effects become most significant as the molecule-nanoshell distance decreases. For the present calculations, we will only take these effects into account by introducing a phenomenological parameter \( X_{e_h} \). Thus, for excited state electronic decay, we take

\[
\Gamma_{n'n''n'V} = (X_{mr} + X_{eh}) \Gamma_{n'n''nV}^0,
\]

and the factor \( X_{mr} \) provides only a lower bound to the decay enhancement.

Since this work does not consider processes between different excited states, all elements of \( H' \) and \( L_1 \rho \) not connecting to the ground electronic state are neglected hereafter. These contributions can be included readily if needed.

For vibrational relaxation, \( n' = n \), molecular loss processes of a single vibrational quantum at a time are allowed as in the single-mode treatment.\textsuperscript{18,19} In the absence of further information about the distinct vibrational mode decays, the rates in a given electronic state \( n \) are taken to be governed by a single phenomenological constant \( \Gamma_n^{\text{vib}} \). For a decay from vibrational state \( v_i \) of mode \( i \) to state \( v_{i-1} \), the appropriate constant appearing in \( L_1 \rho \) is \( v_i \Gamma_n^{\text{vib}} \).

Thus we have a methodology for modifying the spontaneous emission of a molecule in the presence of our nanoshell. This modification along with the additional dephasing term will give spectra different than that for the free AgPMA molecule as discussed in the next section.
6 Emission Spectra for PMA Adsorbed onto Nanoshell

6.1 Two time correlation function

To find the emission spectra for PMA adsorbed onto our silver nanoshell, we must consider the degree of first order temporal coherence of the emitted light given by

\[ \left\langle E^*(r,t)E(r,t+\tau) \right\rangle, \]

where \( E \) is the electric field for a point dipole in free space

\[
E = d \frac{e^{i(kr - \omega t)}}{4\pi \varepsilon_0 c^2 r} \tag{36}
\]

In relation to the intensity of scattered light we have in MKS units

\[
I_{sc} = 2\varepsilon_0 c \left\langle E(r,t) E^*(r,t + \tau) \right\rangle. \tag{37}
\]

Where \( I_{sc} \) is the intensity of the scattered field. The Wiener-Khintchine theorem,\(^{64}\) connects this intensity to the spectral distribution of the radiation through

\[
I_{sc}(\omega) = \frac{1}{\pi} \text{Re} \left[ \int_0^\infty d\tau 2\varepsilon_0 c \left\langle E^*(r,t)E(r,t+\tau) \right\rangle e^{i\omega\tau} \right] \tag{38}
\]

we have for the above cross section

\[
\frac{d^2\sigma}{d\Omega d(\hbar\omega)} = \frac{\omega^4}{l_{inc} 8\pi^3 c^3 \varepsilon_0 \hbar} \text{Re} \int_0^\infty d\tau e^{i\omega\tau} \left\langle d^*(t) d(t + \tau) \right\rangle \tag{39}
\]

Now consider the dipoles as operators for a molecule at position \( r \). We can then expand the dipole operator in the molecular basis with the approximation that matrix elements between excited states are neglected (these are only involved in excited electronic state processes not considered here),
\[ \mathbf{d}(\mathbf{r}) = \sum_{n'v'} \sum_{v} \langle n'v'|\mathbf{d}(\mathbf{r})|0v\rangle|n'v\rangle\langle 0v| + \sum_{n'v'} \sum_{v} \langle 0v|\mathbf{d}(\mathbf{r})|n'v\rangle|0v\rangle\langle n'v' | \]

\[ = \mathbf{d}^{(+)}(\mathbf{r}) + \mathbf{d}^{(-)}(\mathbf{r}). \quad (40) \]

Here the plus and minus dipole moments are the operator analogs for the dipoles in the above cross section. Within a quantized field treatment, the spectra are obtained by Fourier transformation of the two-time dipole-dipole correlation functions, \[ \langle \mathbf{d}^{(-)}(\mathbf{r},t)\mathbf{d}^{(+)}(\mathbf{r},t + \tau) \rangle, \]
written here in dyadic form. Note that quantizing the fields is used here only to develop a form for calculating spectra and does not inhibit us from including classical fields in the Hamiltonian. The quantities \( \mathbf{d}^{(\pm)}(\mathbf{r},t) \) represent the time-evolved operators in the Heisenberg representation. With the initial density matrix in the form

\[ \rho(0) = \sum_{u} \sum_{u''} \rho_{0u0u''}(T)|0u\rangle\langle 0u''| \quad (41) \]

The time-dependent correlation functions may be approximately evaluated by use of the Quantum Regression Theorem,\(^{36,67}\) though with the caveat that not all of the required assumptions are strictly obeyed.\(^{19}\) So for the correlation function at two different times we have
\[ \langle \mathbf{d}^{(-)}(\mathbf{r},t) \mathbf{d}^{(+)}(\mathbf{r},t+\tau) \rangle = \langle \mathbf{d}^{(-)}(\mathbf{r},t) U_0(\tau) \mathbf{d}^{(+)}(\mathbf{r},t+\tau) U_0^\dagger(\tau) \rangle \]
\[ = Tr_\mathcal{RS}\left[ \rho(0) \mathbf{d}^{(-)}(\mathbf{r},t) \mathbf{d}^{(+)}(\mathbf{r},t+\tau) \right] \]
\[ = Tr_\mathcal{RS}\left[ e^{i\mathcal{H}t/\hbar} \rho(t) e^{-i\mathcal{H}t/\hbar} e^{i\mathcal{H}t/\hbar} e^{i\mathcal{H}(t+\tau)/\hbar} \mathbf{d}^{(-)}(\mathbf{r},0) e^{-i\mathcal{H}(t+\tau)/\hbar} \mathbf{d}^{(+)}(\mathbf{r},0) e^{-i\mathcal{H}(t+\tau)/\hbar} \right] \]
\[ = Tr_\mathcal{RS}\left[ e^{i\mathcal{H}t/\hbar} \rho(t) \mathbf{d}^{(-)}(\mathbf{r},t) e^{i\mathcal{H}(t+\tau)/\hbar} \mathbf{d}^{(+)}(\mathbf{r},t+\tau) e^{-i\mathcal{H}(t+\tau)/\hbar} \right] \]
\[ = Tr_\mathcal{RS}\left[ \mathbf{d}^{(+)}(\mathbf{r},t+\tau) e^{-i\mathcal{H}(t+\tau)/\hbar} \rho(t) \mathbf{d}^{(-)}(\mathbf{r},t) e^{i\mathcal{H}(t+\tau)/\hbar} \right] \]
\[ = Tr_\mathcal{RS}\left[ e^{-i\mathcal{H}(t+\tau)/\hbar} \rho(t) \mathbf{d}^{(-)}(\mathbf{r},t) e^{i\mathcal{H}(t+\tau)/\hbar} \right] \]
\[ (42) \]

For our application, it is only required to solve the density matrix equations to a time \( t \) for which steady-state behavior is approximately obtained, post-multiply the result by the components of \( \mathbf{d}^{(-)}(\mathbf{r}) \), evolve the latter to time \( t+\tau \), and pre-multiply by the components of \( \mathbf{d}^{(+)}(\mathbf{r}) \). In the dipole operator’s most general form, we must consider the operator’s directional nature and evolve each of the \( \mathbf{d}^{(-)}(\mathbf{r}) \) components separately, following with the pre-multiplication of the \( \mathbf{d}^{(+)}(\mathbf{r}) \) components forming a dyadic. We consider, however, only the radial direction for this investigation. Following through with this recipe, we can find the Raman spectrum.
6.2 Results

An example spectrum for a frequency distribution of the dipole correlation function is given in Figure 6 for a molecule with two electronic levels separated by 2.65 eV corresponding to the lowest excited energy in an A' singlet state in our DFT calculations. The molecule is considered at a position of highest electric field on the nanoshell, and the 390 cm\(^{-1}\), 1080 cm\(^{-1}\) and 1590 cm\(^{-1}\) modes are included in both the ground and excited state. The incident electric fields correspond to scattered light with a wavelength of 782 nm from a nanoshell with a 79 nm silica core and a 9 nm silver shell. The largest peak corresponds to the electronic transition of the molecule, while the peaks to the red side correspond to the three Stokes-shifted frequencies included in the model. To the blue side, one can see the much weaker Anti-Stokes peaks, in this case only the 390 cm\(^{-1}\) mode since the others disappear into the background of the electronic transition peak.

The important model characteristics influencing the spectra include the electronic dephasing terms, the vibrational decay between levels within the same electronic state, and the energy between the ground and excited states. The geometry of the excited state potential is kept at small displacements relative to the ground state, and therefore, the resulting modifications to the Frank Condon factors do not change the frequency distribution of the correlation function significantly.
FIGURE 6. Spectral transform of the two-time correlation function. The incident laser frequency is 782 nm and the two AgPMA electronic states are separated by 2.65 eV.

Figure 7 (a) compares the frequency distribution for the two-time correlation function looking at the additional coherence decay introduced by Johanssen et. al. A decay term of $1 \times 10^{-15}$ 1/s corresponds to the red color and a decay term of $1 \times 10^{-4}$ 1/s corresponds to blue. As shown in the figure, the increased decay flattens the 390 cm$^{-1}$ mode on the Anti-Stokes side while also broadening the entire blue side of the electronic transition peak. On the Stokes side the increased decay decreases the intensity of the peaks but does not broaden the linewidth as much as the Anti Stokes side. Figure 7 (b) show the same model but with an electronic energy of 4.25 eV consistent with one of the energies of high oscillator strength given in Figure 3. In Figure 7 (b), the dephasing terms and the respective colors are consistent with Figure 7 (a). For this case, the molecule is further off resonant with the 782 nm laser, and the Anti-Stokes peak is actually higher than for the peak with much less dephasing (shown by the red line). The Stokes side peaks are again decreased in intensity, except with broader lineshapes.
FIGURE 7. Correlation function frequency distributions comparing dephasing terms with a gamma value of $1 \times 10^{-15}$ 1/s (red) and $1 \times 10^{-4}$ 1/s (blue) for an electronic energy spacing of 2.65 eV (a) and 4.25 eV (b).

Figure 8 shows the importance of the decay rates for vibrational levels of the same electronic state. Note that Fermi’s Golden Rule does not govern this decay rate. Figure 8 (a) plots the decay time of the correlation functions with an inter-electronic decay of $1 \times 10^{-7}$ 1/s for the dashed line and $1 \times 10^{-4}$ 1/s for the solid line. Figure 8 (b) shows the frequency distribution where red corresponds to the $1 \times 10^{-4}$ 1/s decay and blue corresponds to the $1 \times 10^{-7}$ 1/s decay. The increased decay obviously causes the decrease of all the peaks, broadening each feature.
FIGURE 8. Correlation function versus time (a) and its frequency distribution (b) comparing the vibrational decay for levels of the same electronic state for gamma values of $1 \times 10^{-4}$ 1/s (red) and $1 \times 10^{-7}$ 1/s (blue).

6.3 Conclusions

From these results, one can see that the dephasing terms are more important when the molecule is further off resonant, giving a higher anti-Stokes peak and background. The fluorescent background of the entire spectrum can also be attributed to this dephasing term. The frequency distribution, however, is dominated by the molecule’s response to the incident light characterized by the spacing between the two electronic energy levels, and while the presence of the nanoshell altered the correlation function, it certainly did not cause the intensity enhancement seen in SERS experiments.
With respect to the detection, the modification of the cross section by the enhanced fields given by Johnannsen et. al.

\[
\frac{d^2\sigma}{d\Omega d(\hbar\omega)} = \frac{\omega^4 |M(\omega)|^2}{l_m 8\pi^3 \epsilon_0^3 \epsilon_0^2} \text{Re} \int_0^\infty d\tau e^{i\omega\tau} \langle a^{(-)}(0)a^{(+)}(\tau) \rangle,
\]  

is much more important than the modification of the correlation function by the enhanced fields for off resonant molecules, although both modifications are important in the effects of the fluorescent background and increase of intensity of the Anti Stokes side.

Further, we remember the strength of interaction between molecule and incident field given by the Hamiltonian in Eq (2) is a small perturbation, and while the cross section is drastically effected by the nanoshell the correlation function itself is not drastically altered.

Finally, we further note that understanding the relaxation between vibrational states of the electronic state is shown to be very important. This relaxation has been characterized by a decay rate, yet because the rate is not governed by Fermi’s Golden rule, additional work must be done to understand appropriate values of this constant. Further work must also be done to consider higher electronic states as well as higher vibrational states including overtones and combination bands.
7 Bibliography

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