Combined Quantum Mechanics and Classical Electrodynamics Multiscale Approach for the Calculation of SERS Spectra (A Brief Survey)

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Key properties of metallic nanostructures: possibility of collective excitation of the conduction electrons by UV/Vis light

These surface plasmon excitations are responsible for remarkable size / shape / environment-dependent optical properties

Characterization of metallic nanoparticles in combination with detailed quantitative electromagnetic (EM) simulations enabled synthesis of particles with pre-determined spectral properties

This control of the optical properties of nanomaterials resulted in a wide range of applications in ultra-sensitive chemical and biological sensing
• Plasmon excitations lead to strongly enhanced EM fields near the nanoparticle’s surface

• This f.i. results in intense absorption, fluorescence and scattering characteristics of the nanoparticles,

• And is responsible for the EM contribution to the enhanced Raman signals (up to \(~10^{10}\), single molecule spectroscopy) observed in surface-enhanced Raman scattering (SERS)

• A complete picture of the various enhancement mechanisms (see below) is not available, due to the highly complicated experimental conditions (f.i. roughened surfaces, nanoparticle aggregates, chemical interactions of adsorbants to surfaces)
Much progress has been achieved by accurate and efficient classical *electrodynamics (ED) simulations* of nanostructure optical properties.

Numerical methods such as finite-difference time-domain (FDTD, see below) approaches were used to calculate the *plasmonic properties* of complex shapes and arrangements.

These *computational* procedures lead to detailed insight into the EM mechanism in SERS, but they do *not* provide any informations with respect to *chemical enhancement (CHEM)* (*molecules* are treated as *dipoles* or are *neglected* at all!)
• **Challenge** in building a theory for calculating SERS optical response, that includes both quantum mechanics (QM) and classical electrodynamics (ED):

  - Bridging the *length scales* needed for both approaches, which differ in *order of magnitude*!

• *Purely chemical* models of SERS based on QM are generally limited to ~1 nm in size, *including* the metal particle/cluster

• *EM field evaluations* are usually based on *grids* or *finite elements*, that have 1 nm dimensions at the *minimum*
For this reason, theoretical treatments of SERS often take one of two paths:

- One approach *neglects* the CHEM enhancement and *focuses* on the predominant EM enhancement.
- Other studies *only determine* the CHEM enhancement using *small atomic cluster* models of the nanoparticle.

Much of current research in this field focuses on *novel multiscale approaches* for analysis and understanding SERS *mechanisms* by

- Combination of *quantum mechanics* (e.g. RT-TDDFT, LR-TDDFT) and *classical electrodynamics* (f.i. FDTD, FEM, MMP) methods.
Enhancement mechanisms

(a) Ground state chemical enhancement
(b) Resonance Raman enhancement
(c) Charge-transfer resonance enhancement
(d) Plasmon Resonance enhancement

(According to G.C. Schatz et al., 2008)
Enhancement mechanisms

a) Enhancement due to ground state \textit{chemical interactions (CHEM)} between molecule (adsorbate) and nanoparticle/surface, not associated with any \textit{electronic excitations} of the nanoparticle-molecule system, $\lambda_{\text{exc}}$ arbitrarily chosen (UV/Vis, IR laser) (\textit{non-resonant})

b) \textit{Resonance Raman (RR)} enhancement with $\lambda_{\text{exc}}$ being \textit{resonant} with a \textit{molecular electronic} transition

c) \textit{Charge-transfer (CT)} resonance Raman enhancement with $\lambda_{\text{exc}}$ being \textit{resonant} to nanoparticle-adsorbant \textit{CT-transitions}

d) Enhancement due to a \textit{very strong local field (EM)}, when $\lambda_{\text{exc}}$ is \textit{resonant} with the \textit{plasmon excitations} in the metal nanoparticle
Normal Raman scattering (NRS, free molecule)

- **Raman scattering intensity** for the free molecule is given by:

\[ I_M^R \propto \left| \frac{\partial \alpha_M}{\partial Q_M} \right|^2 \]

\( \alpha_M \): molecular polarizability
\( Q_M \): a normal mode of the molecule
Raman scattering of the molecule is affected by EM interaction with a polarizable body (metallic particle) under radiation, located close to the molecule.

The Raman intensity can now be expressed as:

\[ I^R = I^R_M \cdot |E^{loc}|^4 \]

\( E^{loc} \): local field enhancement due to metal nanoparticle, get that from classical ED simulations, f.i. FDTD (!)
Finite-difference time-domain (FDTD) method (1)

- Light is assumed to **incident** on a system, that is **discretized** into **many small** buildings blocks.

- Each of them is characterized by a **dielectric permittivity**, $\varepsilon(\mathbf{r})$, and by a **magnetic permeability**, $\mu(\mathbf{r})$ (material's properties).

- Then **Maxwell's equations** (see below) are solved in the **real time domain** to obtain the **time evolution** of:
  - the **electric field**, $\mathbf{E}(\mathbf{r}, t)$,
  - the **magnetic field**, $\mathbf{B}(\mathbf{r}, t)$, and
  - the **electric current density**, $\mathbf{j}(\mathbf{r}, t)$.
### FDTD, Maxwell's equations (2)

<table>
<thead>
<tr>
<th>Name</th>
<th><strong>Integral</strong> equations</th>
<th><strong>Differential</strong> equations</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gauss's law</strong></td>
<td>$\iint_{\partial \Omega} \mathbf{E} \cdot d\mathbf{S} = \frac{1}{\varepsilon_0} \iint_{\Omega} \rho , dV$</td>
<td>$\nabla \cdot \mathbf{E} = \frac{\rho}{\varepsilon_0}$</td>
</tr>
<tr>
<td><strong>Gauss's law for magnetism</strong></td>
<td>$\iint_{\partial \Omega} \mathbf{B} \cdot d\mathbf{S} = 0$</td>
<td>$\nabla \cdot \mathbf{B} = 0$</td>
</tr>
<tr>
<td><strong>Maxwell–Faraday equation (Faraday's law of induction)</strong></td>
<td>$\oint_{\partial \Sigma} \mathbf{E} \cdot d\ell = -\frac{d}{dt} \iint_{\Sigma} \mathbf{B} \cdot d\mathbf{S}$</td>
<td>$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$</td>
</tr>
<tr>
<td><strong>Ampère's circuital law (with Maxwell's correction)</strong></td>
<td>$\oint_{\partial \Sigma} \mathbf{B} \cdot d\ell = \mu_0 \iint_{\Sigma} \left( \mathbf{J} + \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t} \right) \cdot d\mathbf{S}$</td>
<td>$\nabla \times \mathbf{B} = \mu_0 \left( \mathbf{J} + \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t} \right)$</td>
</tr>
</tbody>
</table>
FDTD, Maxwell's equations (in vacuo), wave equations (3)

\[ \nabla \cdot \mathbf{E} = 0 \quad \nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}, \]

\[ \nabla \cdot \mathbf{B} = 0 \quad \nabla \times \mathbf{B} = \frac{1}{c^2} \frac{\partial \mathbf{E}}{\partial t}. \]

\[ \frac{1}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} - \nabla^2 \mathbf{E} = 0, \quad \frac{1}{c^2} \frac{\partial^2 \mathbf{B}}{\partial t^2} - \nabla^2 \mathbf{B} = 0, \]

\[ c = \frac{1}{\sqrt{\mu_0 \varepsilon_0}} = 2.99792458 \times 10^8 \text{ m s}^{-1} \]

\[ c = \frac{1}{\sqrt{\mu_0 \mu_r \varepsilon_0 \varepsilon_r}} \quad \text{(Materials)} \]
The EM properties can also be determined in the frequency domain through Fourier transform.

The total electric field, $\vec{E}_{\text{total}}(\vec{r}, \omega)$, at a given observation point, is then a combination of the scattered field, $\vec{E}_{\text{sca}}(\vec{r}, \omega)$, and of the incident field, $\vec{E}_0(\vec{r}, \omega)$:

$$\vec{E}_{\text{total}}(\vec{r}, \omega) = \vec{E}_{\text{sca}}(\vec{r}, \omega) + \vec{E}_0(\vec{r}, \omega)$$

A scattering response function, $\lambda(\vec{r}, \omega)$, which is defined as

$$\lambda(\vec{r}, \omega) \sim \frac{\vec{E}_{\text{sca}}(\vec{r}, \omega)}{\vec{E}_0(\vec{r}, \omega)}$$

provides a measure of the local field enhancement.
Dynamic (frequency-dependent) polarizabilities

- Dynamic (frequency-dependent) polarizabilities are necessary for e.g.
  - Calculation of Resonance Raman Spectra (RRS) or
  - Hybrid Quantum Mechanics / Classical Electrodynamics simulations (QM/ED)

- May be quantumchemically obtained by f.i.
  - Real-time time-dependent density functional theory (RT-TDDFT)
    (e.g. Octopus, NWChem)
  - "Excited state gradient" (EG) or "Short-time approximation" (STA)
    (f.i. Gaussian, TURBOMOLE, etc.)
  - Time-dependent density functional theory (TDDFT, linear response)
    or "Polarizability method" (PM)
    (e.g. ADF, Gaussian, NWChem)
For a molecule exposed to a \textit{time-dependent external electric} Field, $E_i$, along axis $i$, the \textit{dipole moment}, $P_j$, along axis $j$, in linear \textit{first-order} approximation, is

$$P_j = P_{j0} + \alpha_{ij} \cdot E_i,$$

where $P_{j0}$ is the \textit{permanent} dipole moment and $\alpha_{ij}$ represents the linear \textit{polarizability tensor}.

In the \textit{time} domain, one may then write

$$P_j(t) = P_{j0} + \int \frac{d\omega}{2\pi} e^{-i\omega t} \alpha_{ij}(\omega) \cdot E_i(\omega),$$

and the \textit{induced} dipole moment, $P_{j\text{Ind}}(t)$, is \textit{defined} as

$$P_{j\text{Ind}}(t) = P_j(t) - P_{j0}$$
Real-time time-dependent density functional theory
(RT-TDDFT) (2)

- In the *frequency* domain, we obtain

\[ P_{j}^{\text{Ind}}(\omega) = \alpha_{ij}(\omega) \cdot E_{i}(\omega) , \]

where

\[ \alpha_{ij}(\omega) = \frac{P_{j}^{\text{Ind}}(\omega)}{E_{i}(\omega)} = \frac{\int dt \ e^{+i\omega t} P_{j}^{\text{Ind}}(t) e^{-\Gamma t}}{\int dt \ e^{+i\omega t} E_{i}(t)} \]

- This equation relates the *frequency-dependent polarizability tensor*, \( \alpha_{ij}(\omega) \), to the *time evolution* of the molecule's induced dipole moment, \( P_{j}^{\text{Ind}}(t) \), under a *time-dependent* external electric field, \( E_{i}(t) \).

- This procedure allows *incorporation* of the effect of *coupling* to the *metal particle* on the *excited state dynamics* of the molecule.
Within the framework of DFT, the time-dependent dipole moment, $\vec{P}(t)$, can be calculated from the perturbed electron density, which arises, when the system is subjected to an applied electric field, $\vec{E}_0(t)$.

The following time-dependent Schrödinger equation (TDSE), for this reason, is used:

$$i \frac{\partial}{\partial t} \varphi(r, t) = \left[-\frac{1}{2} \nabla^2 + \int dr' \frac{\rho(r', t)}{|r - r'|} + \frac{\delta E_{xc}[\rho(r, t)]}{\delta \rho(r, t)} - \vec{E}_0(t) \cdot \vec{r}\right] \varphi(r, t)$$

The coupling Hamiltonian between the external electric field and the molecule is given by:

$$- \int \varphi^*(r) \vec{E}_0(t) \cdot \vec{r} \varphi(r) dr = -\vec{E}_0(t) \cdot \int \varphi^*(r) \vec{r} \varphi(r) dr = -\vec{E}_0(t) \cdot \vec{P}(r)$$
• Under the assumption of a uniform scattered electric field, $\vec{E}_{sca}(\vec{r}, t)$, the Hamiltonian of the adsorbate molecule in the presence of an incident field, $\vec{E}_0(\vec{r}, t)$, at the RT-TDDFT level of theory, can be written as:

$$\hat{H}(t) = -\frac{1}{2} \nabla^2 + \int d\vec{r}' \frac{\rho(\vec{r}', t)}{|\vec{r} - \vec{r}'|} + \frac{\delta E_{xc}[\rho(\vec{r}, t)]}{\delta \rho(\vec{r}, t)} - \vec{E}_0(t) \cdot \vec{r} - \vec{E}_{sca}(t) \cdot \vec{r}$$

• The scattered field, imposed by the polarized nanoparticle, can be obtained via the above scattering response function $\lambda(\vec{r}, \omega)$
Standard example from the literature: Adsorption of pyridine on Silver (1)
Standard example from the literature: Adsorption of pyridine on Silver (2)

Plasmon-enhanced vibrational modes
Standard example from the literature: Adsorption of pyridine on Silver (3)

Surface plots of *differential Raman scattering cross section* as a function of incident light and vibrational mode wavenumber.

- **R = 1 nm**
- **R = 5 nm**

Image of 3D plots showing differential Raman scattering cross section as a function of wavenumber and energy.
Adsorption of MBT on gold (1)
(MBT = 2-Mercaptobenzothiazole)

- Computational model: $\text{MBT}(\text{enolate/enol})$ adsorbed on tetrahedral $\text{Au}_{20}$

Different adsorption geometries!
Calculated relative stabilities for MBT(Enolate/Enol)-Au$_{20}$ (2)

- **Gaussian09**: Optimized geometries, Raman and IR vibrational frequencies and intensities, all structures considered represent minima on the respective BO energy hypersurface, no BSSE corrections applied for interaction energies

<table>
<thead>
<tr>
<th>Method</th>
<th>Enolate (vertex) (&quot;ad-atom&quot; adsorption)</th>
<th>Enol (vertex) (&quot;ad-atom&quot; adsorption)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBE/LanL2DZ (QZVP)</td>
<td>-53.2 (-56.8)</td>
<td>-9.2</td>
</tr>
<tr>
<td>B3LYP/LanL2DZ (QZVP)</td>
<td>-47.4 (-50.6)</td>
<td>-5.9</td>
</tr>
<tr>
<td>HCTH/LanL2DZ (QZVP)</td>
<td>-43.5 (-48.8)</td>
<td>-4.1</td>
</tr>
<tr>
<td>TPSS/LanL2DZ (QZVP)</td>
<td>-50.8 (-54.6)</td>
<td>-7.9</td>
</tr>
</tbody>
</table>

"Chemisorption" "Physisorption"
Calculated Raman spectra: "PBE/LanL2DZ " (3)

Free MBT molecule (Enolate)

MBT(Enolate) on Au$_{20}$
Calculated Raman spectra: "PBE/QZVP" (4)

Free MBT molecule (Enolate)  

MBT(Enolate) on Au_{20}
Calculated Raman spectra: "PBE/LanL2DZ" (5)

Free MBT molecule (trans-Enol)  MBT(trans-Enol) on Au$_{20}$
Experiment: SERS spectra of MBT on Gold (6)

(D. Zhang, K. Braun)
Experiment vs. Theory ("PBE/LanL2DZ") (7)
Experiment vs. Theory ("PBE/LanL2DZ") (8)
Literature

