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Combined Quantum Mechanics and Classical Electrodynamics Multiscale Approach for the Calculation of SERS Spectra

(A Brief Survey)

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Introduction (1)

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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**

Introduction (2)

- **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)**

Introduction (3)

- **Much progress has been achieved by accurate and efficient classical *electrodynamic* (ED) *simulations* of nanostructure optical properties**

- **Numerical methods such as f.i. *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!)**

Introduction (4)

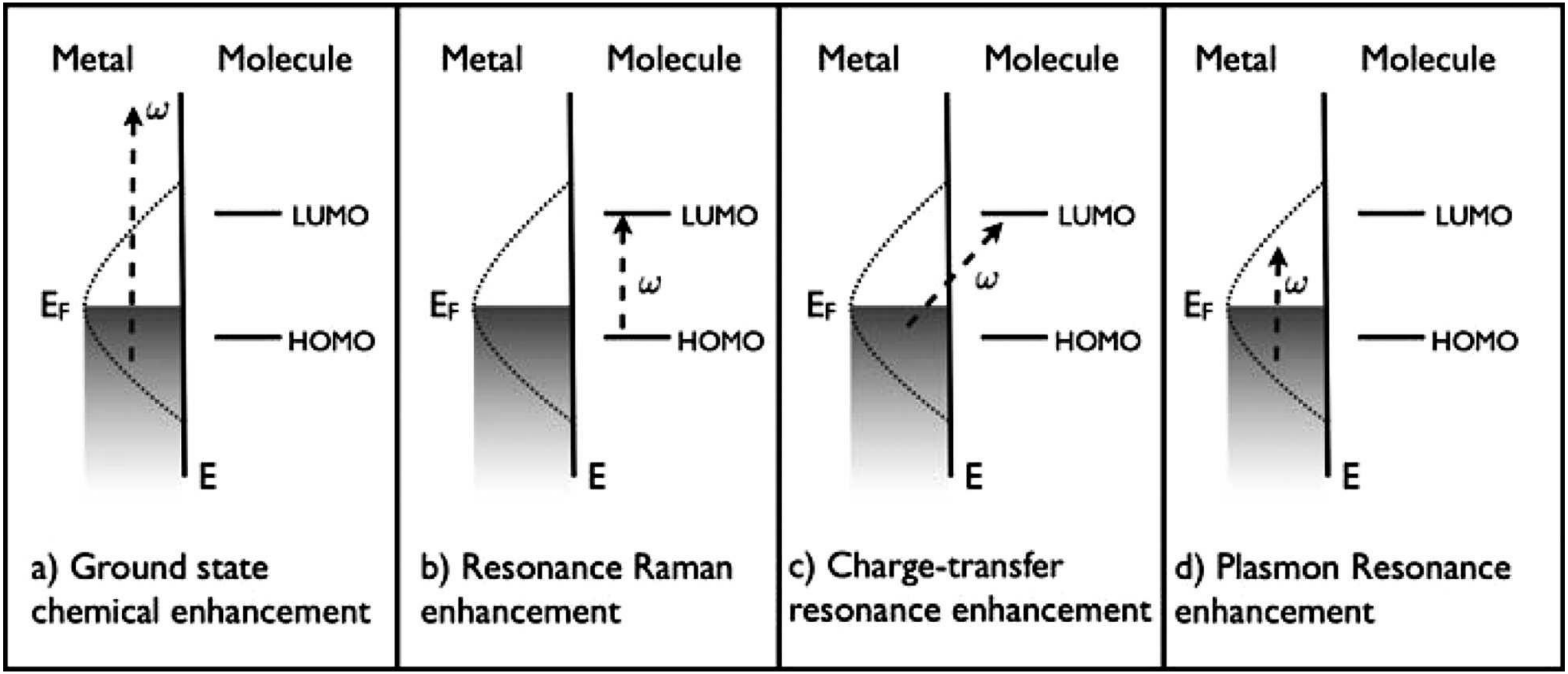
- ***Challenge*** **in building a theory for calculating SERS *optical response*, that includes both *quantum mechanics* (QM) and *classical electrodynamics* (ED):**
  - **Bridging the *length scales* needed for both approaches, which differ in *order of magnitude*!**
- ***Purely chemical*** **models of SERS based on QM are generally limited to *~1 nm* in size, *including* the metal particle/cluster**
- **EM field evalutations are usually based on *grids* or *finite elements*, that have *1 nm* dimensions at the *minimum***

Introduction (5)

- ***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



(QM) (QM) (QM) (ED+QM)

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

Enhancement mechanisms

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

b) ***Resonance Raman* (RR) enhancement with λ_{exc} being *resonant* with a *molecular electronic* transition**

c) ***Charge-transfer* (CT) resonance Raman enhancement with λ_{exc} being *resonant* to nanoparticle-adsorbant *CT-transitions***

d) **Enhancement due to a *very strong local field* (EM), when λ_{exc} is *resonant* with *the plasmon excitations* in the metal nanoparticle**

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

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

α_M : molecular polarizability
Q_M : a normal mode of the molecule

SERS (molecule adsorbed to nanoparticle/surface)

- **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:**

$$I^R = I_M^R \cdot \left| E^{loc} \right|^4$$

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*, $\varepsilon(\vec{r})$, and by a *magnetic permeability*, $\mu(\vec{r})$ (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, $\vec{E}(\vec{r},t)$,**
  - **the *magnetic* field, $\vec{B}(\vec{r},t)$, and**
  - **the *electric current density* $\vec{J}(\vec{r},t)$**

FDTD, Maxwell's equations (2)

Name	Integral equations	Differential equations
Gauss's law	$\oint\!\!\oint_{\partial\Omega} \mathbf{E}\cdot\mathrm{d}\mathbf{S} = \frac{1}{\varepsilon_0}\iiint_{\Omega}\rho\,\mathrm{d}V$	$\nabla\cdot\mathbf{E} = \frac{\rho}{\varepsilon_0}$
Gauss's law for magnetism	$\oint\!\!\oint_{\partial\Omega} \mathbf{B}\cdot\mathrm{d}\mathbf{S} = 0$	$\nabla\cdot\mathbf{B} = 0$
Maxwell–Faraday equation (Faraday's law of induction)	$\oint_{\partial\Sigma} \mathbf{E}\cdot\mathrm{d}\boldsymbol{\ell} = -\frac{d}{dt}\iint_{\Sigma}\mathbf{B}\cdot\mathrm{d}\mathbf{S}$	$\nabla\times\mathbf{E} = -\frac{\partial\mathbf{B}}{\partial t}$
Ampère's circuital law (with Maxwell's correction)	$\oint_{\partial\Sigma} \mathbf{B}\cdot\mathrm{d}\boldsymbol{\ell} = \mu_0\iint_{\Sigma}\left(\mathbf{J}+\varepsilon_0\frac{\partial\mathbf{E}}{\partial t}\right)\cdot\mathrm{d}\mathbf{S}$	$\nabla\times\mathbf{B} = \mu_0\left(\mathbf{J}+\varepsilon_0\frac{\partial\mathbf{E}}{\partial t}\right)$

FDTD, Maxwell's equations (*in vacuo*), wave equations (3)

$$\nabla \cdot \mathbf{E} = 0 \qquad \nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t},$$

$$\nabla \cdot \mathbf{B} = 0 \qquad \nabla \times \mathbf{B} = \frac{1}{c^2}\frac{\partial \mathbf{E}}{\partial t}.$$

$$\frac{1}{c^2}\frac{\partial^2 \mathbf{E}}{\partial t^2} - \nabla^2 \mathbf{E} = 0\,, \qquad \frac{1}{c^2}\frac{\partial^2 \mathbf{B}}{\partial t^2} - \nabla^2 \mathbf{B} = 0\,,$$

$$c = \frac{1}{\sqrt{\mu_0 \varepsilon_0}} = 2.99792458 \times 10^8 \ \mathrm{m\ s^{-1}}$$

$$c = \frac{1}{\sqrt{\mu_0 \mu_r \varepsilon_0 \varepsilon_r}}$$

(Materials)

- **The *EM properties* can also be determined in the *frequency domain* through *Fourier transform***

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

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

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

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

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)**

Real-time time-dependent density functional theory (RT-TDDFT) (1)

- **For a molecule exposed to a *time-dependent external electric* Field, E_i, along axis i, the *dipole moment*, P_j, along axis j, in linear *first-order* approximation, is**

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

where P_{j0} is the *permanent* dipole moment and α_{ij} represents the linear *polarizability tensor*

- **In the *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 *induced* dipole moment, $P_j^{Ind}(t)$, is *defined* as

$$P_j^{Ind}(t) = P_j(t) - P_{j0}$$

- **In the *frequency* domain, we obtain**

$$P_j^{Ind}(\omega) = \alpha_{ij}(\omega) \cdot E_i(\omega) \ ,$$

where

$$\alpha_{ij}(\omega) = \frac{P_j^{Ind}(\omega)}{E_i(\omega)} = \frac{\int dt\ e^{+i\omega t} P_j^{Ind}(t) e^{-\Gamma t}}{\int dt\ \ e^{+i\omega t} E_i(t)}$$

- **This equation *relates* the *frequency-dependent polarizability tensor*, $\alpha_{ij}(\omega)$, to the *time evolution* of the molecule's *induced* dipole moment, $P_j^{Ind}(t)$, 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**

Real-time time-dependent density functional theory (RT-TDDFT) (3)

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- **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:**

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

- **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:**

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

- **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)

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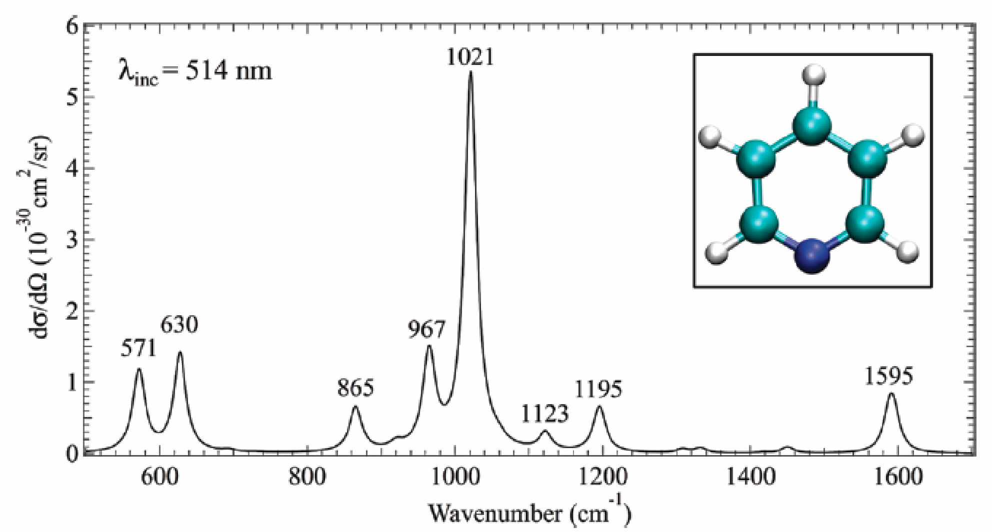
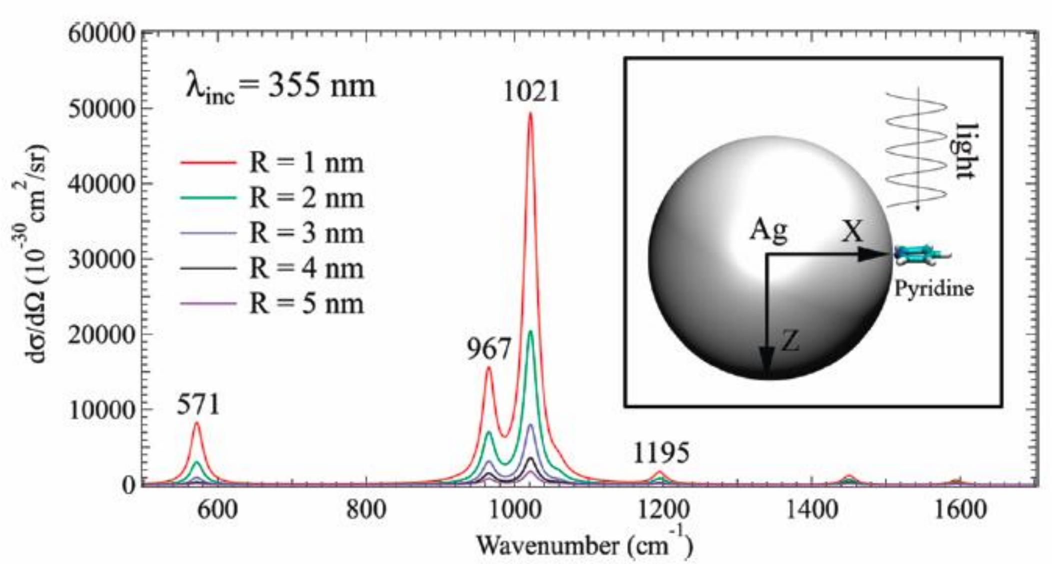
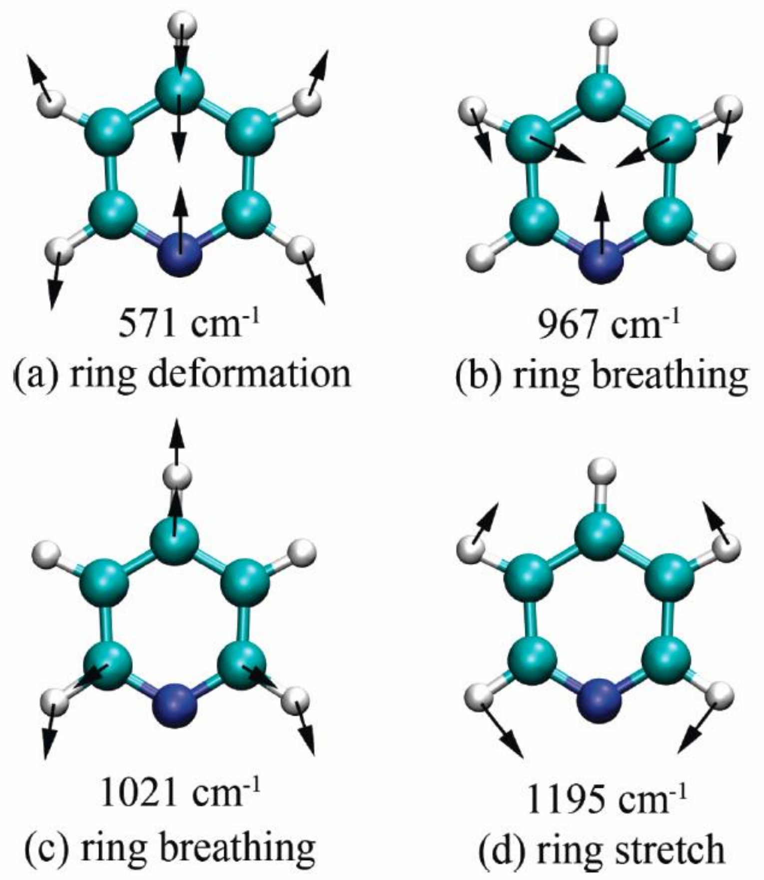




Standard example from the literature: Adsorption of pyridine on Silver (2)



Plasmon-enhanced **vibrational modes**

Standard example from the literature: Adsorption of pyridine on Silver (3)

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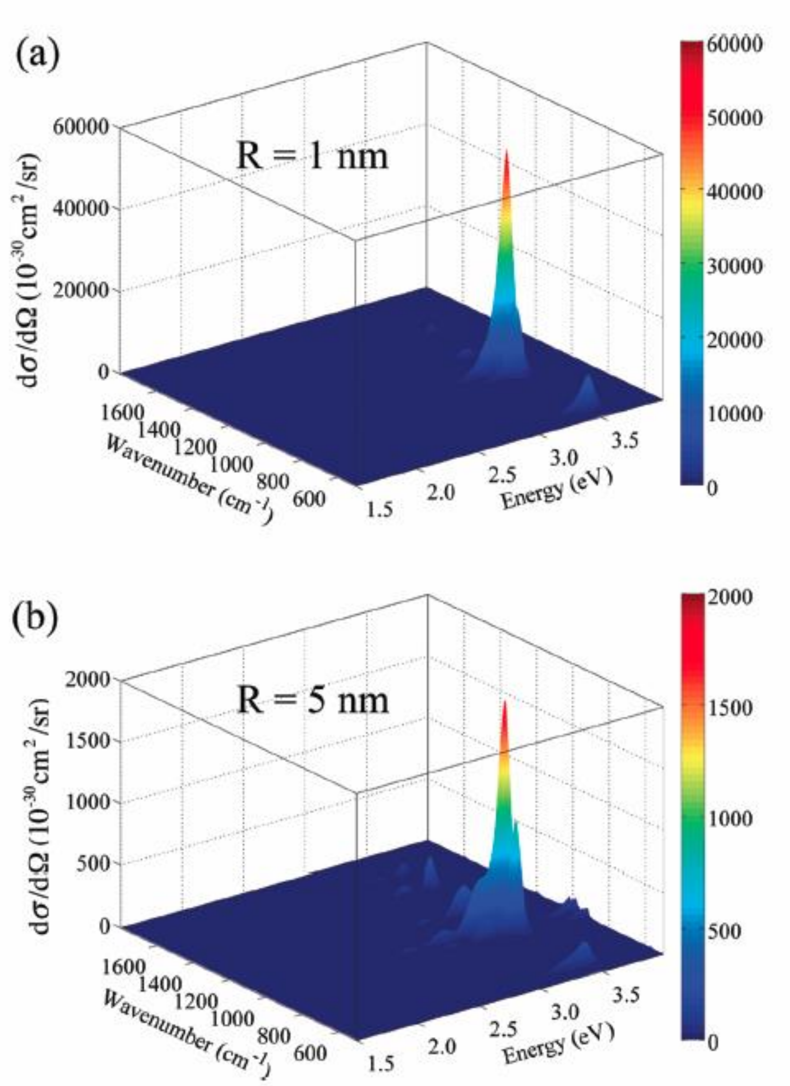

Surface plots of *differential Raman scattering cross section* as a function of incident light and vibrational mode wavenumber

Adsorption of MBT on gold (1)
(MBT = 2-Mercaptobenzothiazole)

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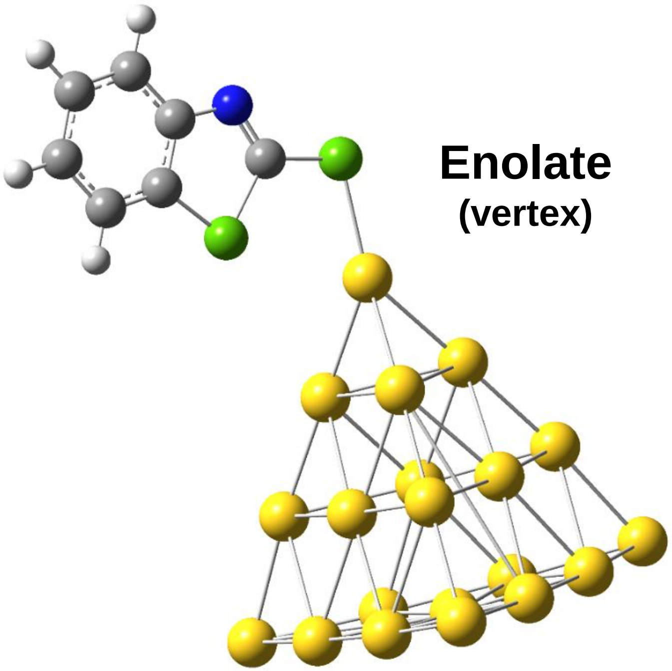
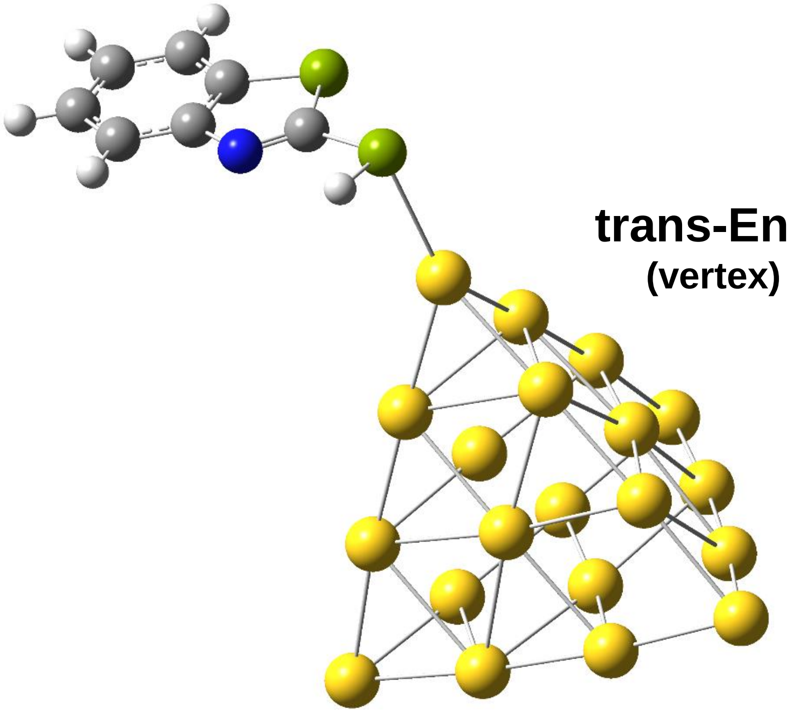
- **Computational model: MBT(*enolate/enol*) adsorbed on *tetrahedral* Au_{20}**



Enolate
(vertex)



trans-Enol
(vertex)

Different adsorption geometries!

Calculated relative stabilities for MBT(Enolate/Enol)-Au_{20} (2)

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

	Stabilization energies [kcal/mol]	
	Enolate (vertex) ("ad-atom" adsorption)	Enol (vertex) ("ad-atom" adsorption)
PBE/LanL2DZ (QZVP)	-53.2 (-56.8)	-9.2
B3LYP/LanL2DZ (QZVP)	-47.4 (-50.6)	-5.9
HCTH/LanL2DZ (QZVP)	-43.5 (-48.8)	-4.1
TPSS/LanL2DZ (QZVP)	-50.8 (-54.6)	-7.9
	"Chemisorption"	"Physisorption"

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

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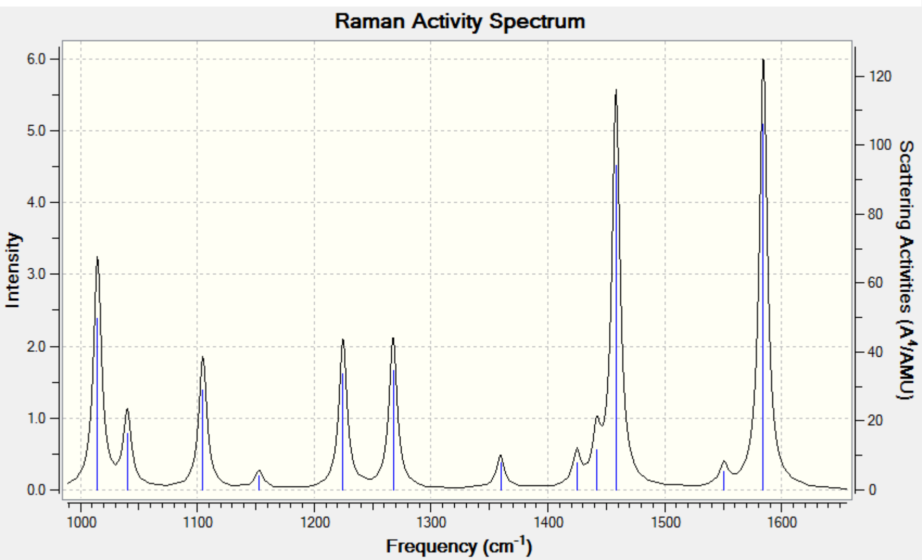
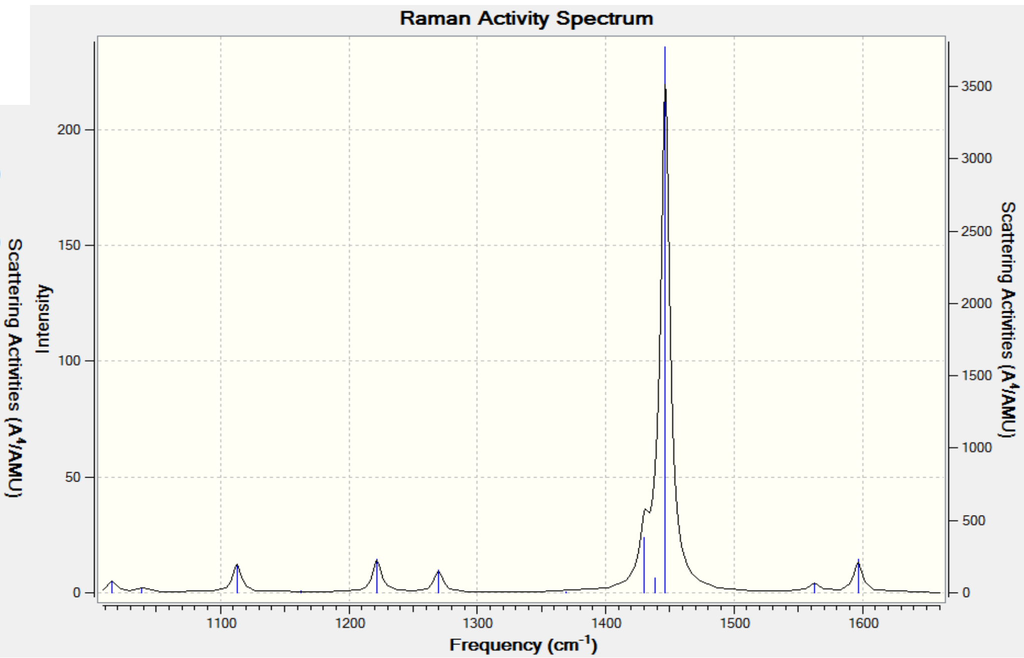
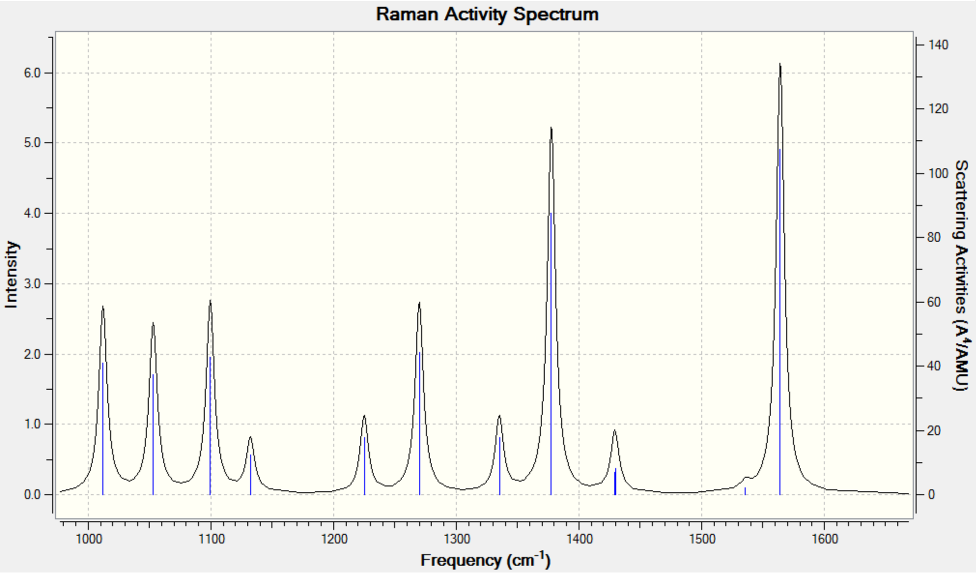


Free MBT molecule (Enolate)

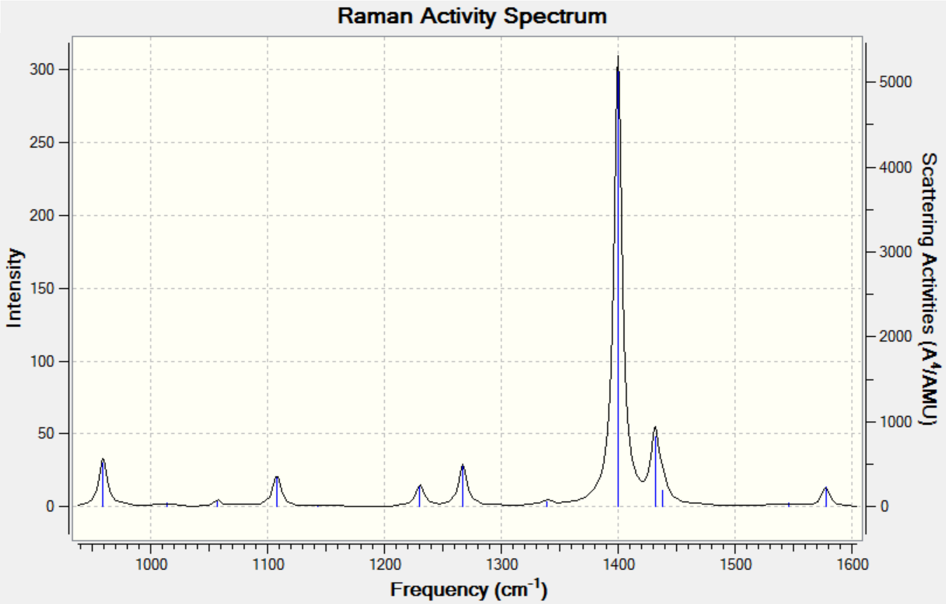


MBT(Enolate) on Au_{20}

Calculated Raman spectra: "PBE/QZVP" (4)



Free MBT molecule (Enolate)



MBT(Enolate) on Au_{20}

Calculated Raman spectra: "PBE/LanL2DZ" (5)

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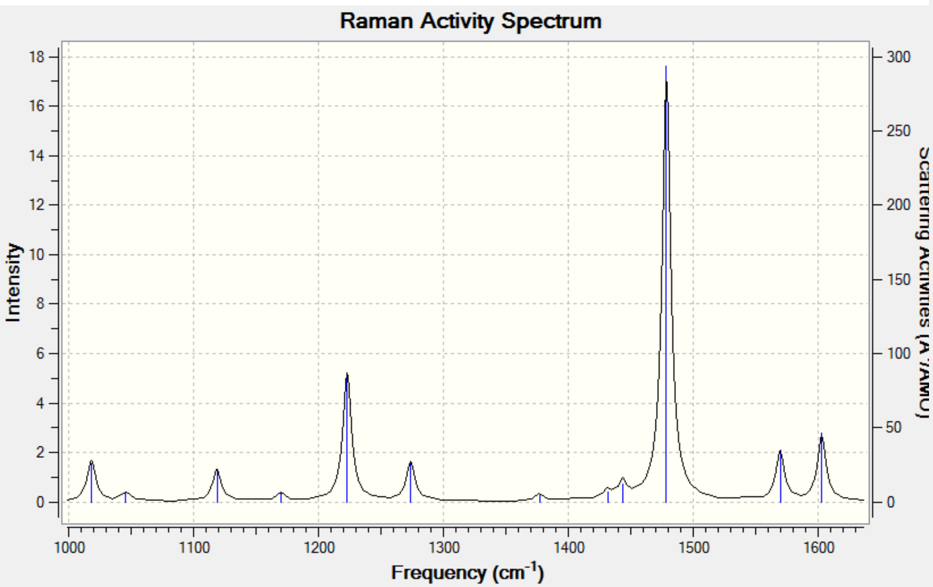

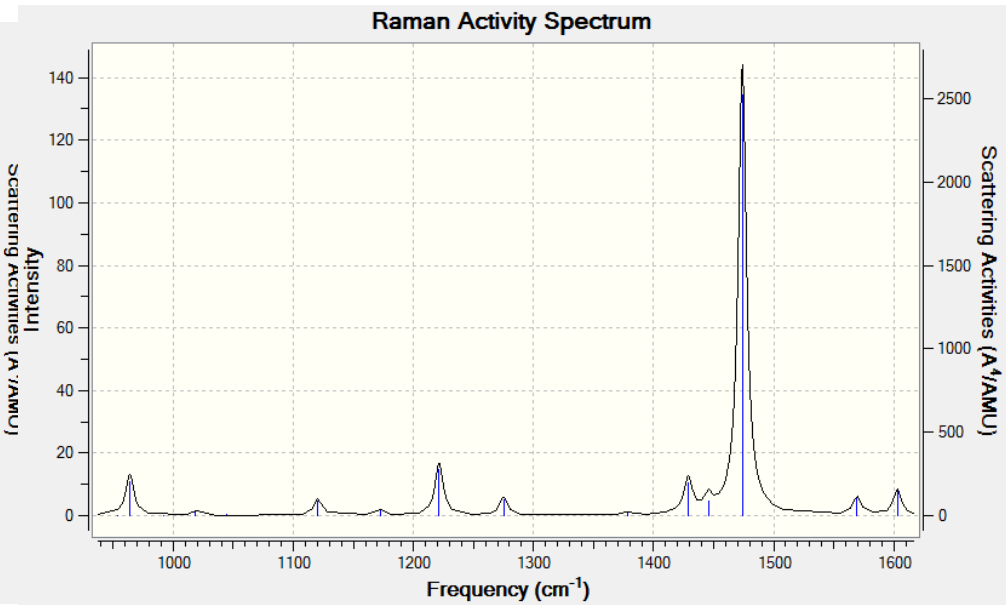

Free MBT molecule (trans-Enol)

MBT(trans-Enol) on Au_{20}

Experiment: SERS spectra of MBT on Gold (6)

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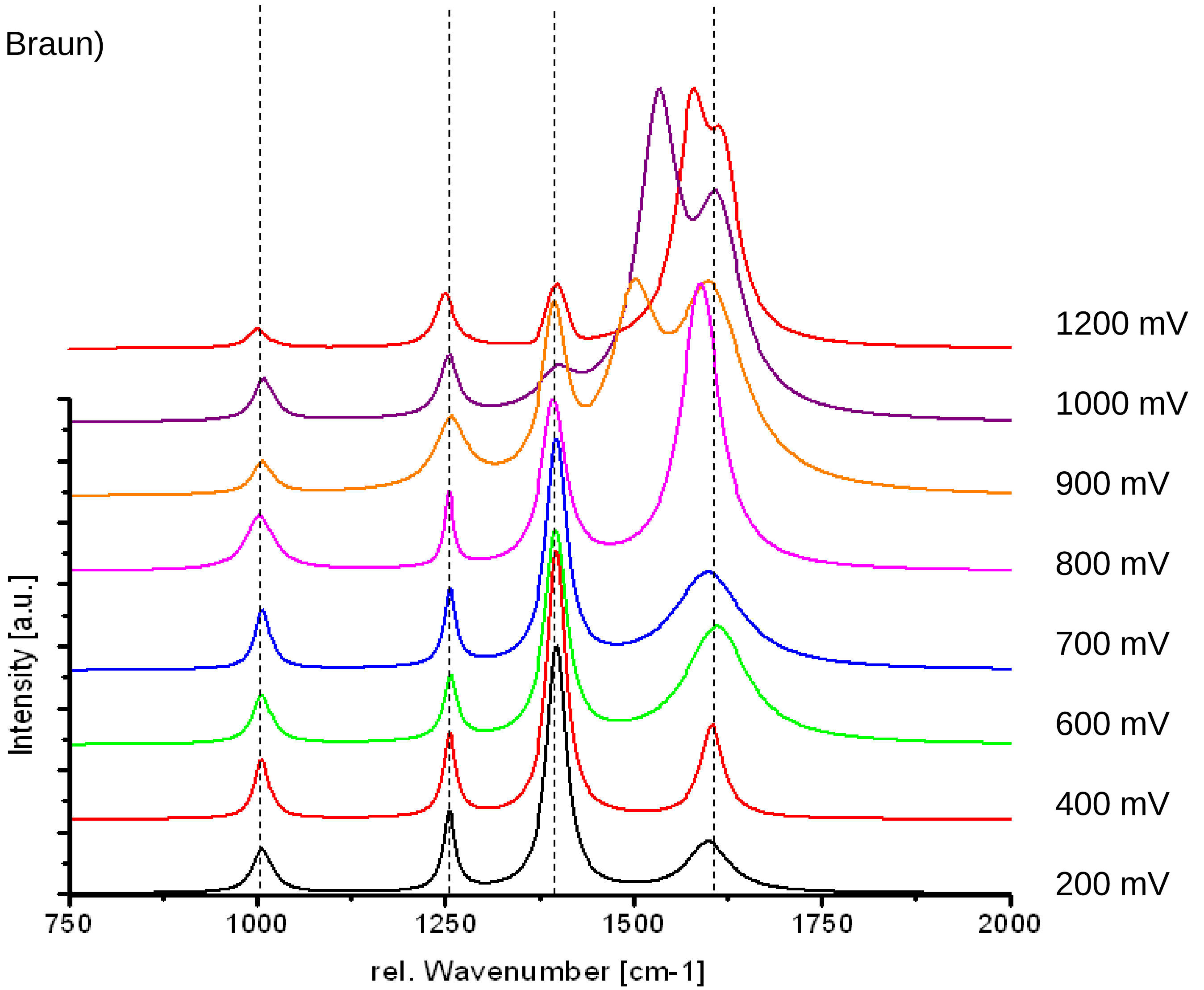
(D. Zhang, K. Braun)



Experiment vs. Theory ("PBE/LanL2DZ") (7)

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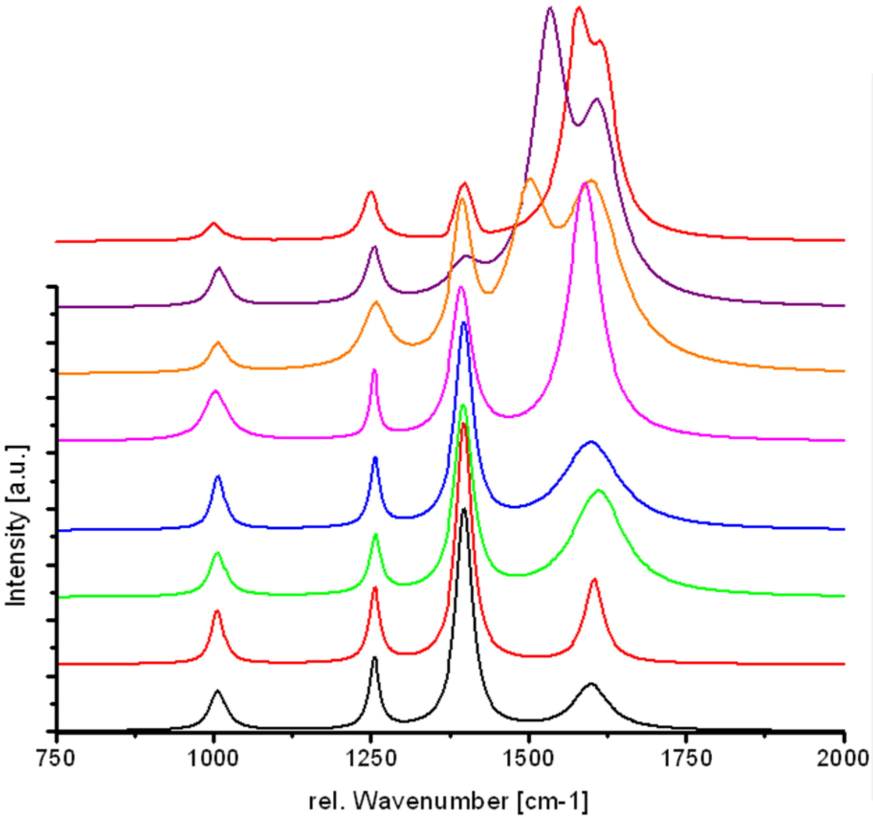

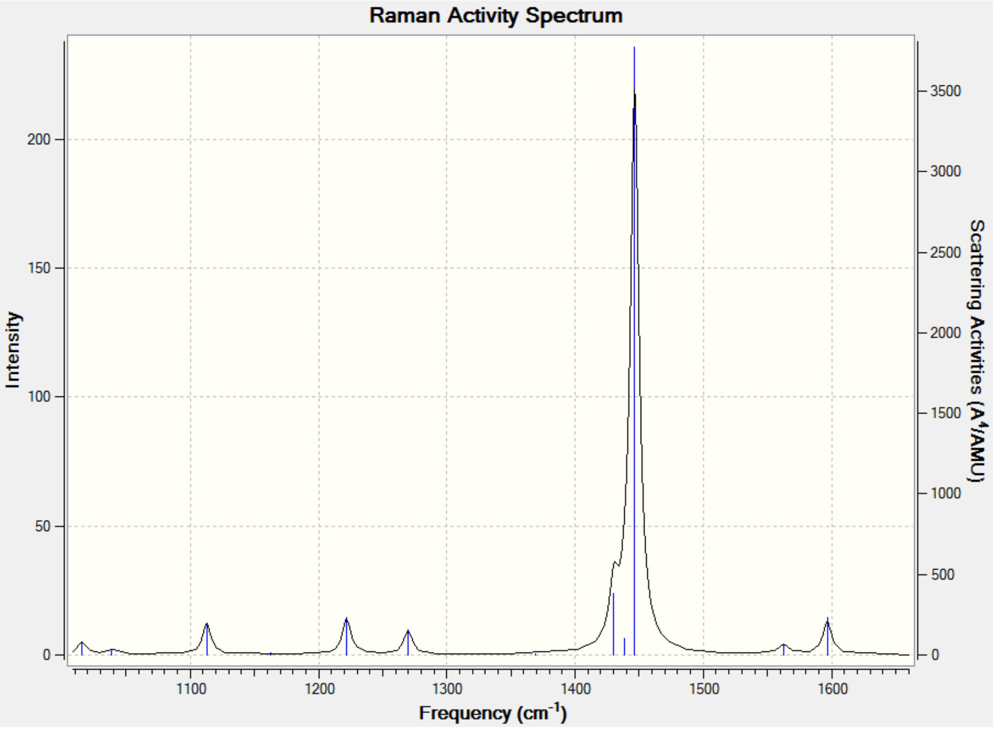

MBT(Enolate) on Au_{20}

Experiment vs. Theory ("PBE/LanL2DZ") (8)

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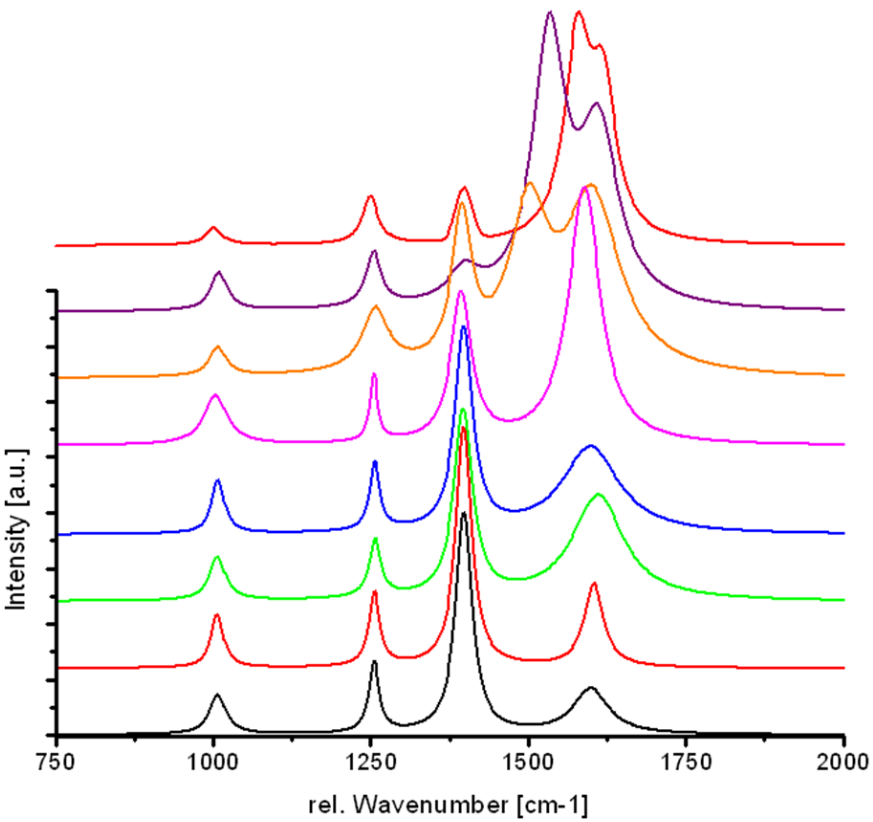

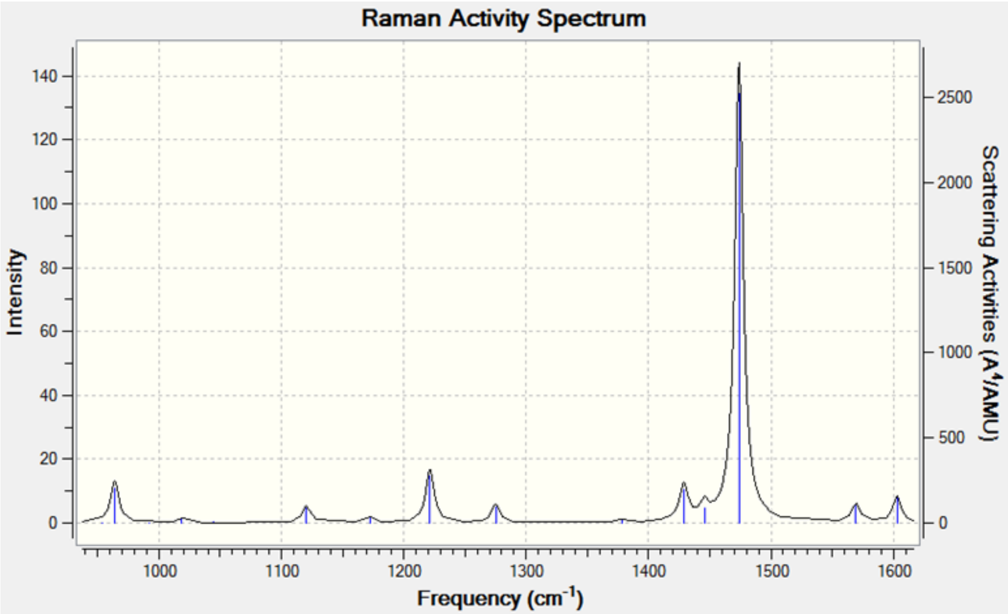

MBT(trans-Enol) on Au_{20}

Literature

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- Lasse Jensen, Christine M. Aikens and George C. Schatz:
  "Electronic structure methods for studying surface-enhanced Raman scattering"
  Chem. Soc. Rev., 2008, **37**, 1061–1073.

- Hanning Chen, Jeffrey M. McMahon, Mark A. Ratner and George C. Schatz:
  "Classical electrodynamics coupled to quantum mechanics for calculation of molecular optical properties: a RT-TDDFT/FDTD approach"
  J. Chem. Phys. C, 2010, **114**, 14384–14392.

- Jonathan Mullin and George C. Schatz:
  "Combined linear response quantum mechanics andclassical electrodynamics (QM/ED) method for the calculation of surface-enhanced Raman spectra"
  J. Phys. Chem. A, 2012, **116**, 1931–1938.