Simulating Surface-Enhanced Raman Scattering with ADF

Lasse Jensen

Department of Chemistry
Pennsylvania State University
University Park

jensen@chem.psu.edu

PENNSTATE 1855

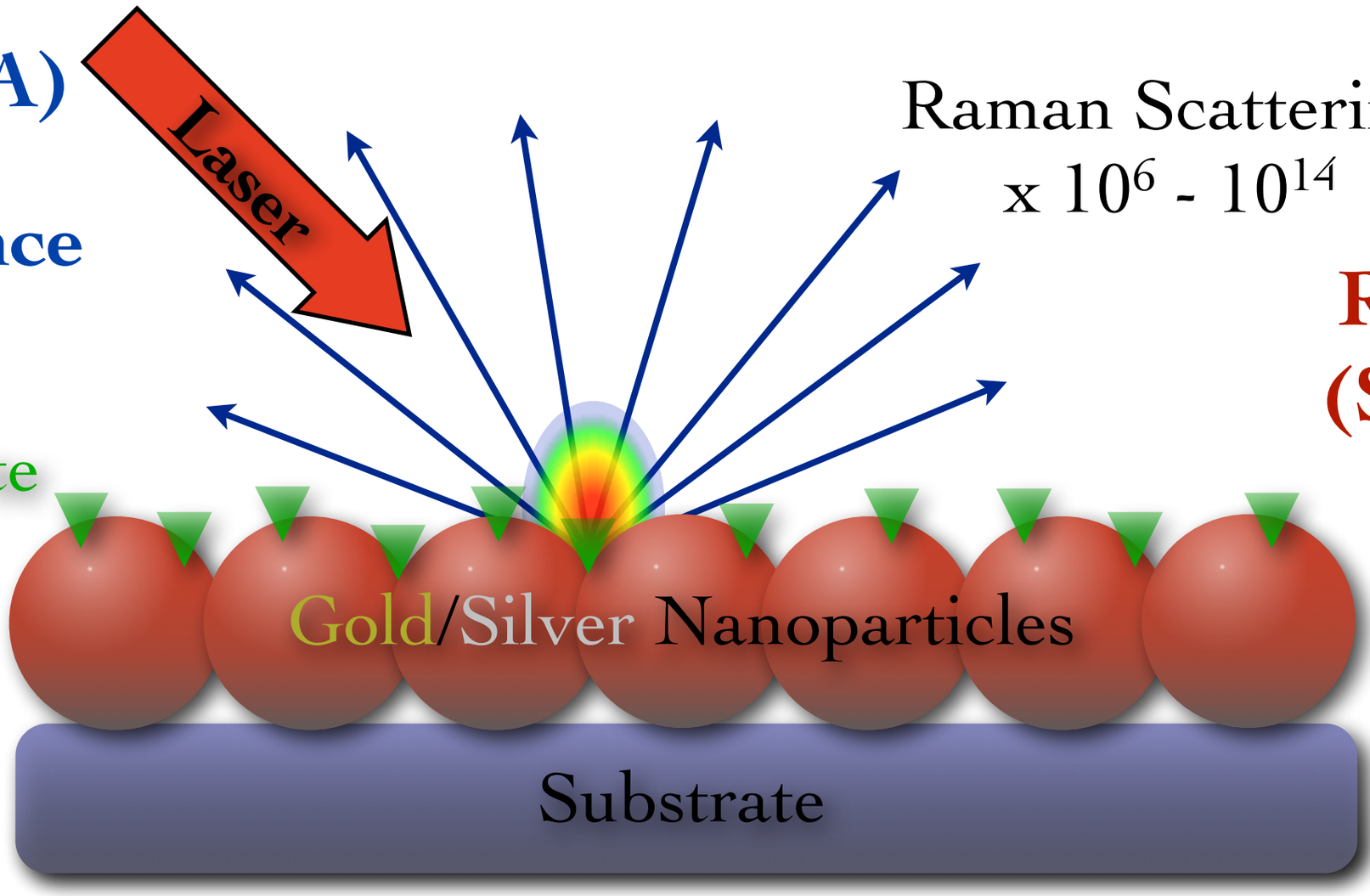
Surface-Enhanced Spectroscopy

Nanoparticles = Nano Amplifier

IR (SEIRA)

Fluorescence (SEF)

Raman Optical Activity (SEROA)



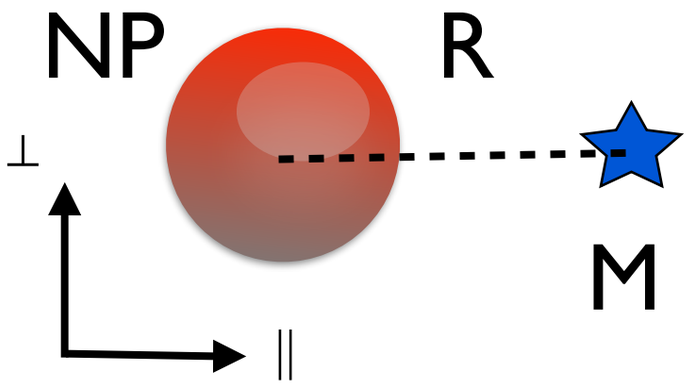
Raman Scattering
x 10^6 - 10^{14}

Raman (SERS)

hyper-Raman (SEHRS)

PENNSTATE 1855

SERS: The EM mechanism



Consider the molecule - nanoparticle systems as two interacting polarizable objects

$$\alpha_{\parallel} = \frac{\alpha_M + \alpha_{NP} + 4\alpha_M\alpha_{NP}/R^3}{1 - 4\alpha_M\alpha_{NP}/R^6}$$

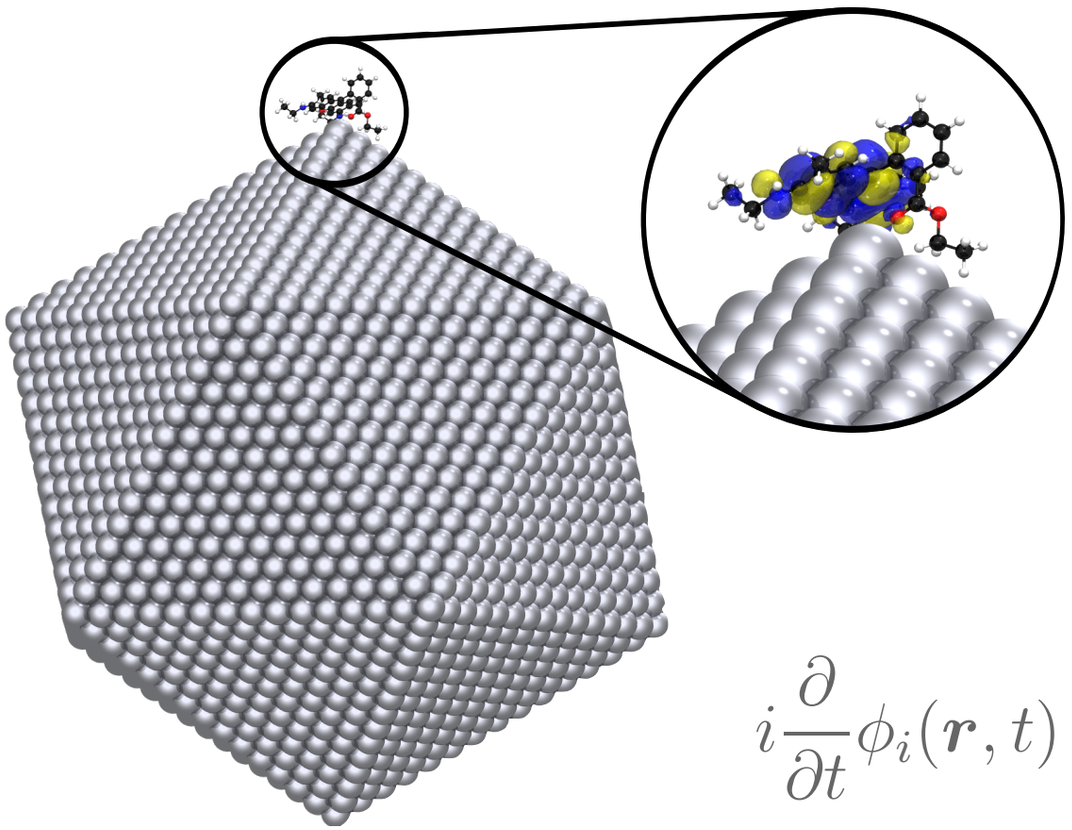
$$\alpha_{\perp} = \frac{\alpha_M + \alpha_{NP} - 2\alpha_M\alpha_{NP}/R^3}{1 - \alpha_M\alpha_{NP}/R^6}$$

Raman intensities given by change in polarizability as the molecule vibrates

$$I^R_{\parallel} \propto \left|\frac{\partial\alpha_{\parallel}}{\partial Q_M}\right|^2 = \left(\frac{\partial\alpha_M}{\partial Q_m}\right)^2 \times \frac{(1+2\alpha_{NP}/R^3)^4}{(1-4\alpha_{NP}\alpha_M/R^6)^4} = \left(\frac{\partial\alpha_M}{\partial Q_m}\right)^2 \times \left|E^{loc}_{\parallel}\right|^4$$

SERS depends on the local field to the fourth power.

DIM/QM for Molecular Plasmonics



Developing new tools for describing optical properties of molecules near metal nanoparticles by combining Quantum Chemistry and Atomistic Electrodynamics Models

$$i\frac{\partial}{\partial t}\phi_i(\boldsymbol{r},t) = h_{\mathrm{KS}}[\rho(\boldsymbol{r},t)]\phi_i(\boldsymbol{r},t) \quad \rho(\boldsymbol{r},t) = \sum_{i=1}^{occ} n_i|\phi_i(\boldsymbol{r},t)|^2$$

$$h_{\mathrm{KS}}[\rho(\boldsymbol{r},t)] = -\frac{1}{2}\nabla^2 - \sum_m \frac{Z_m}{|\boldsymbol{r}-R_m|} + \int \frac{\rho(\boldsymbol{r},t)}{|\boldsymbol{r}-\boldsymbol{r}'|}dr' + \frac{\delta E^{XC}}{\delta\rho(\boldsymbol{r},t)} + \hat{V}^{\mathrm{DIM}}(\boldsymbol{r},t)$$

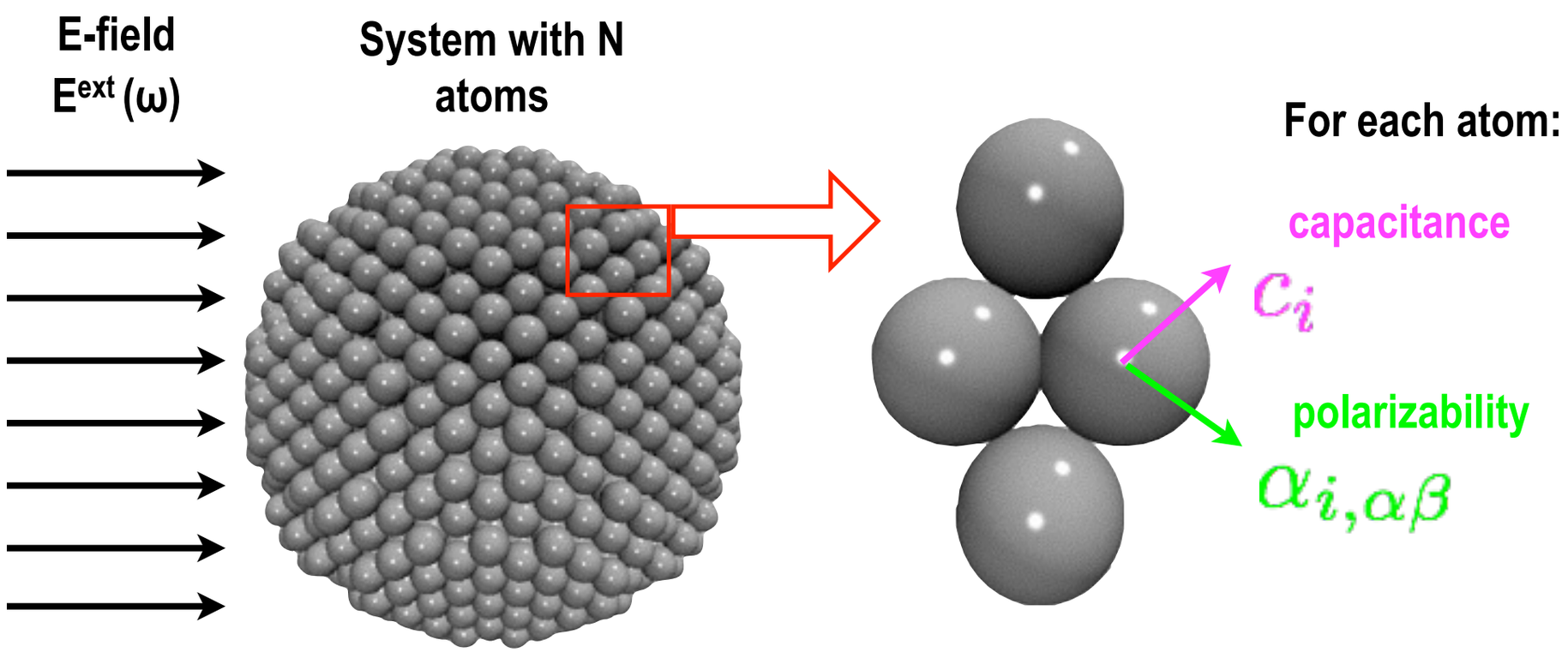
Applications

- Surface-enhanced Molecular Absorption
- Surface-enhanced Spectroscopy
- Metal-molecule Energy Transfer
- .....

PENNSTATE 1855

Atomistic model for Large Nanoparticles

Discrete Interaction Model



Self-consistent solution can be found by solving a set of linear equations

$$\begin{pmatrix} \boldsymbol{A}(\omega) & -\boldsymbol{M} & 0 \\ -\boldsymbol{M}^T & -\boldsymbol{C}(\omega) & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} \boldsymbol{\mu}^{\mathrm{ind}}(\omega) \\ \boldsymbol{q}^{\mathrm{ind}}(\omega) \\ \lambda \end{pmatrix} = \begin{pmatrix} \boldsymbol{E}^{\mathrm{SCF}}(\omega) \\ \boldsymbol{V}^{\mathrm{SCF}}(\omega) \\ q^{\mathrm{cluster}} \end{pmatrix}$$

Jensen, Jensen J. Phys. Chem. C, 2008, 112 ,15697,
J. Phys. Chem. C, 113, 15182, 2009

PENNSTATE 1855

DIM/QM Energy

DIM/QM Energy functional

$$U^{\mathrm{TOT}}[\rho] = U^{\mathrm{QM}}[\rho] + U^{\mathrm{DIM/QM}}[\rho] = U^{\mathrm{QM}}[\rho] + U^{\mathrm{POL}}[\rho] + U^{\mathrm{VDW}}$$

Polarization Energy

$$U^{\mathrm{POL}}[\rho] = -\frac{1}{2}\sum_{m}^{N} \mu_{m,\alpha}^{\mathrm{ind}} E_{m,\alpha}^{\mathrm{SCF}} + \frac{1}{2}\sum_{m}^{N} q_m^{\mathrm{ind}} V_m^{\mathrm{SCF}}$$

Variational minimization of total energy leads to effective Kohn-Sham equations

$$h_{\mathrm{KS}}[\rho(\boldsymbol{r}_j)] = -\frac{1}{2}\nabla^2 - \sum_J \frac{Z_J}{|\boldsymbol{r}_j - \boldsymbol{R}_J|} + \int \frac{\rho(\boldsymbol{r}_j)}{|\boldsymbol{r}_j - \boldsymbol{r}_i|} d\boldsymbol{r}_i + \frac{\delta E^{XC}}{\delta \rho(\boldsymbol{r}_j)} + \hat{V}^{\mathrm{DIM}}(\boldsymbol{r}_j)$$

Payton, Morton, Moore, Jensen, JCP , 136, 214103, 2012, ACR,47, 88-99, 2014

Coordination dependent VDW Energy

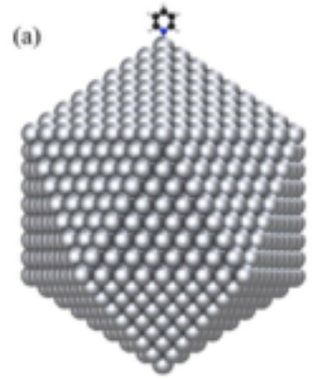
Standard AMBER LJ 6-12 potential

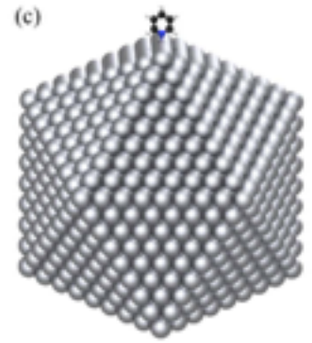
$$U^{\mathrm{VDW}} = \sum_{Jm} \varepsilon_{Jm} \left[\left(\frac{r_{e,Jm}}{|\boldsymbol{r}_{Jm}|} \right)^{12} - 2 \left(\frac{r_{e,Jm}}{|\boldsymbol{r}_{Jm}|} \right)^{6} \right]$$

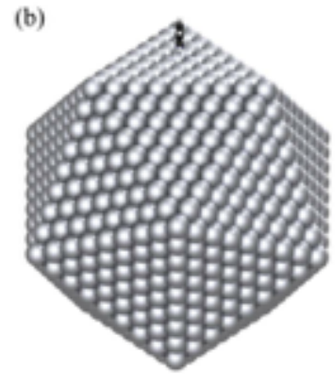
With coordination dependent parameters

$$r_{e,m} = r_{e,0} + (r_{e,1} - r_{e,0}) \frac{\mathrm{MIN}(CN_m, CN_{\max})}{CN_{\max}}$$

$$\varepsilon_m = \varepsilon_0 + (\varepsilon_1 - \varepsilon_0) \frac{\mathrm{MIN}(CN_m, CN_{\max})}{CN_{\max}}$$







Payton, Morton, Moore, Jensen, JCP , 136, 214103, 2012, ACR, 47, 88-99, 2014

PENNSTATE 1855

The DIM/QM model

Time-dependent density functional theory

$$i\frac{\partial}{\partial t}\phi_i(\boldsymbol{r},t) = h_{\mathrm{KS}}[\rho(\boldsymbol{r},t)]\phi_i(\boldsymbol{r},t) \qquad \rho(\boldsymbol{r},t) = \sum_{i=1}^{occ} n_i|\phi_i(\boldsymbol{r},t)|^2$$

Effective Kohn-Sham operator

$$h_{\mathrm{KS}}[\rho(\boldsymbol{r},t)] = -\frac{1}{2}\nabla^2 - \sum_m \frac{Z_m}{|\boldsymbol{r}-R_m|} + \int \frac{\rho(\boldsymbol{r},t)}{|\boldsymbol{r}-\boldsymbol{r}'|}dr' + \frac{\delta E^{XC}}{\delta\rho(\boldsymbol{r},t)} + \hat{V}^{\mathrm{pert}}(\boldsymbol{r},t) + \hat{V}^{\mathrm{DIM}}(\boldsymbol{r},t)$$

Embedding Operator

$$\hat{V}^{\mathrm{DIM}}(\boldsymbol{r},\omega) = \sum_j \hat{V}^{\mathrm{el}}(r_j,\omega) + \sum_j \hat{V}^{\mathrm{pol}}(r_j,\omega),$$

Image Field

External perturbation

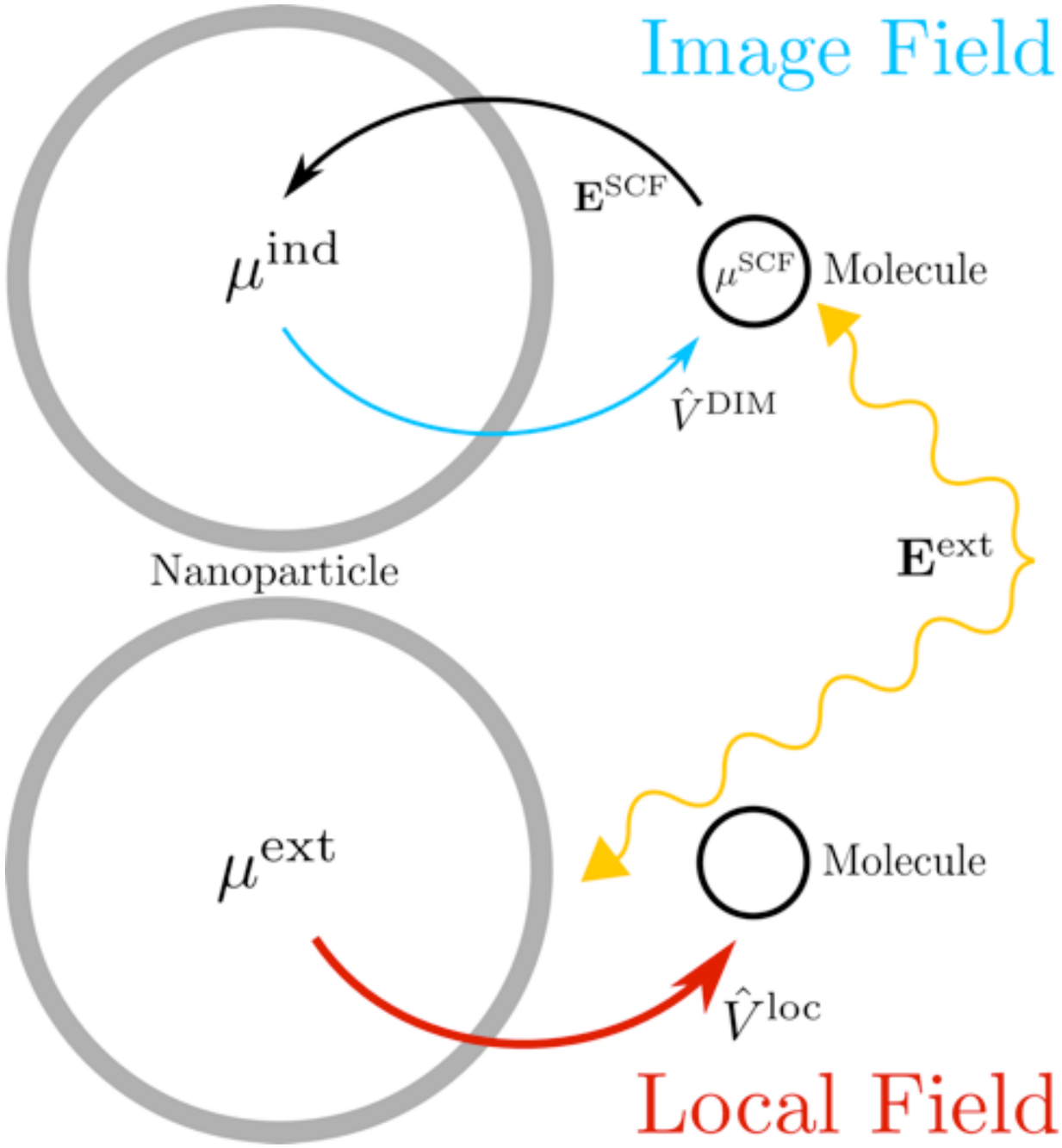
$$\hat{V}^{\mathrm{pert}}(\boldsymbol{r},\omega) = \sum_j \hat{V}^{\mathrm{ext}}(r_j,\omega) + \sum_j \hat{V}^{\mathrm{loc}}(r_j,\omega),$$

Local Field

Morton, Jensen, J. Chem. Phys., 135, 134103, 2011, J. Chem. Phys., 133, 074103, 2010

PENNSTATE 1855

DIM/QM - Polarizability



The total interacting polarizability can formally be written as

$$\alpha^{tot} = \alpha^{mol} + \alpha^{NP} + \alpha^{mol-NP} + \alpha^{NP-mol}$$

In DIM/QM all interactions between the molecule and the nanoparticle are included in the polarizability

$$\alpha^{DIM/QM} = \alpha^{mol} + \alpha^{mol-NP} + \alpha^{NP-mol}$$

All local field effects are contained in the polarizability!

Morton, Jensen, J. Chem. Phys., 135, 134103, 2011, J. Chem. Phys., 133, 074103, 2010

PENNSTATE 1855

DIM/QM - Damped response theory

First-order change in the density given by

$$\rho'(\boldsymbol{r},\omega) = \sum_{i,a} P'_{ia}(\omega)\phi_i(\boldsymbol{r})\phi_a^*(\boldsymbol{r}) + P'_{ai}(\omega)\phi_a(\boldsymbol{r})\phi_i^*(\boldsymbol{r}).$$

where the first-order density matrix is given by

$$P'_{st}(\omega) = \frac{\Delta n_{st}}{\omega - \omega_{st} + i\Gamma}\left[V'^{\mathrm{pert}}_{st}(\omega) + \sum_{u,v} K_{st,uv}P'_{uv}(\omega)\right].$$

$$\hat{V}^{\mathrm{pert}}(\boldsymbol{r},\omega) = \sum_j \hat{V}^{\mathrm{ext}}(r_j,\omega) + \sum_j \hat{V}^{\mathrm{loc}}(r_j,\omega),$$

the polarizability can then be obtained as

$$\alpha_{\alpha\beta}(\omega) = -\mathrm{Tr}[\boldsymbol{H}^{\alpha}(\omega)\boldsymbol{P}^{\beta}(\omega)]$$

where the matrix elements of the dipole operator is given by

$$H^{\alpha}_{st} = \langle s|\hat{\mu}_{\alpha}(\omega) + \hat{V}^{\mathrm{loc}}_{\alpha}(\omega)|t\rangle$$

Morton, Jensen, J. Chem. Phys., 135, 134103, 2011, J. Chem. Phys., 133, 074103, 2010

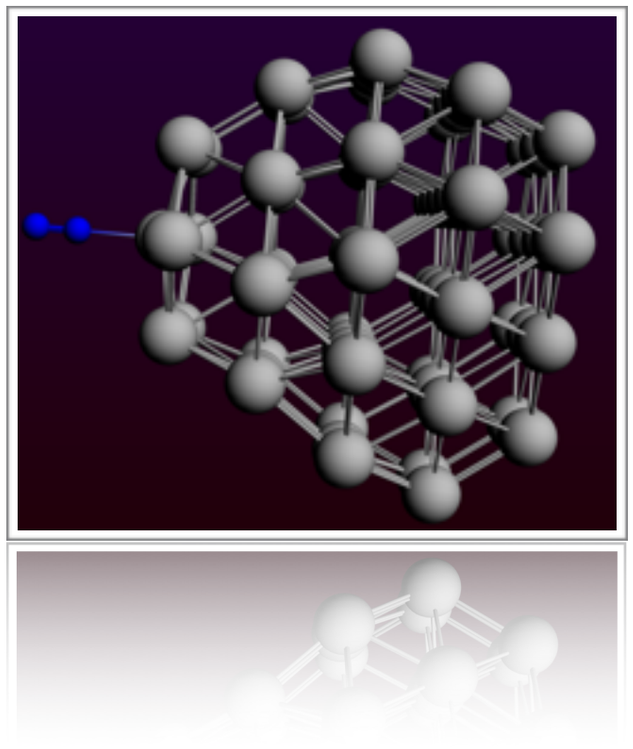
DIM/QM - Input setup

As an example we will consider N2 - Ag68

$ADFHOME/examples/adf/DIMQM_Raman

To run a DIM/QM Raman calculation three block keys needs to be set:

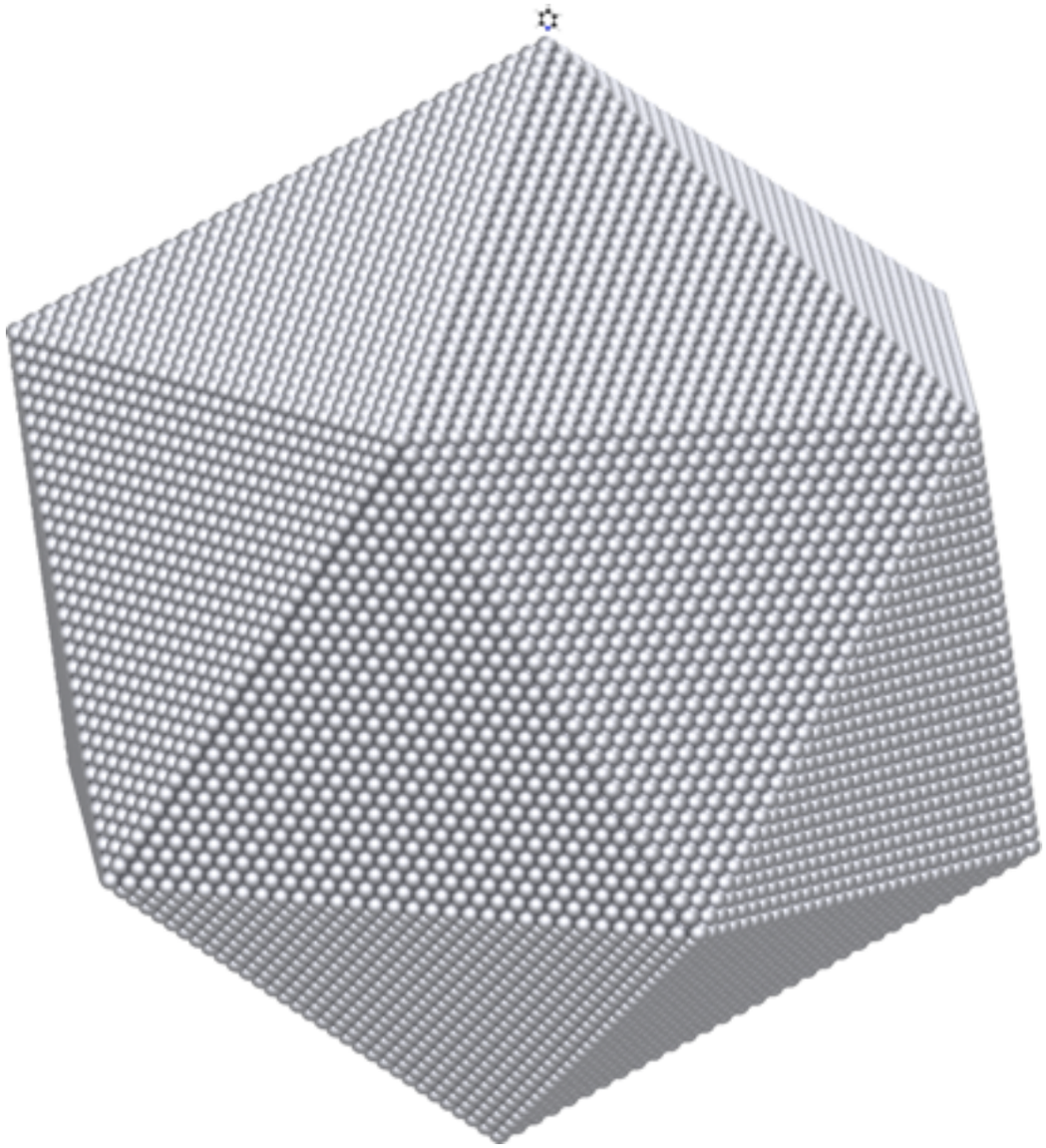
1. DIMQM
2. DIMPAR
3. AOREPONSE

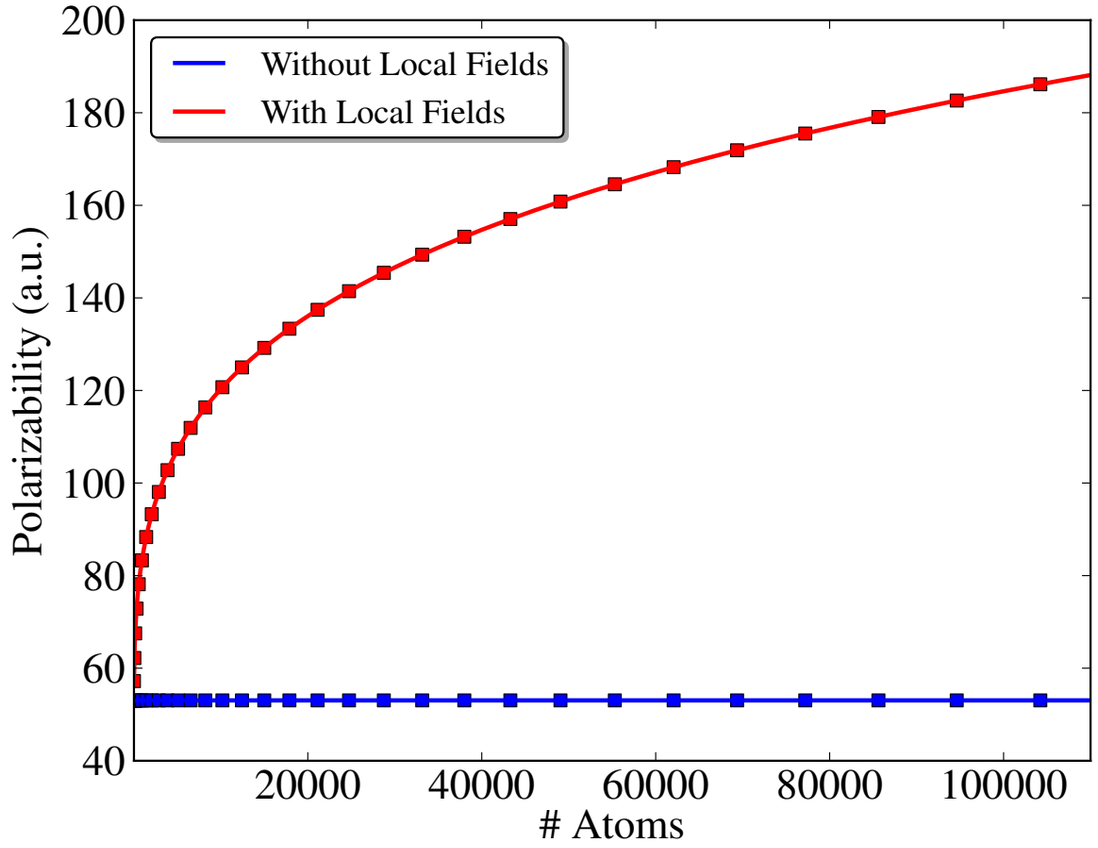


PENNSTATE 1855

Larger nanoparticles?

100k atoms ~ 20 nm diameter



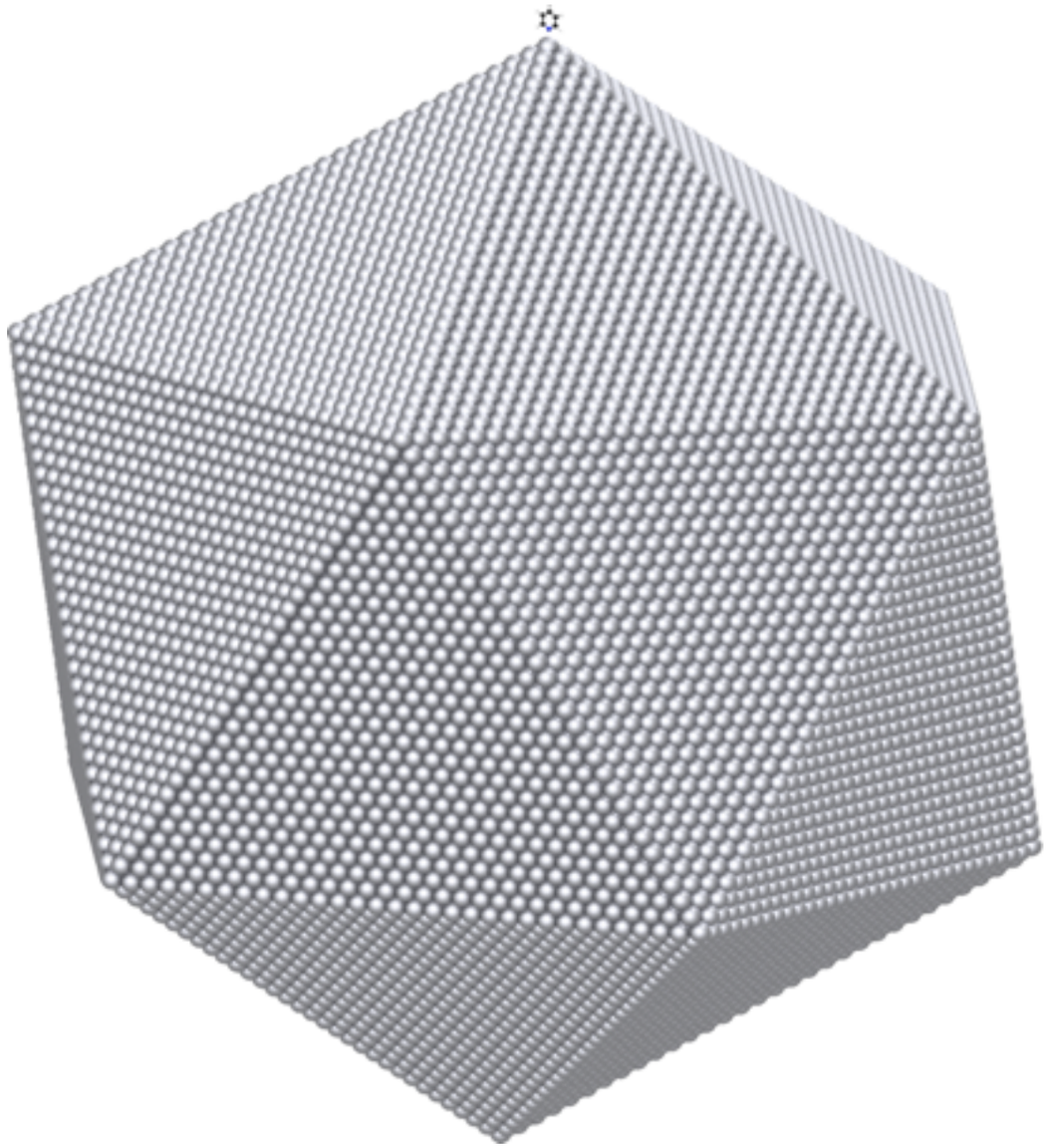


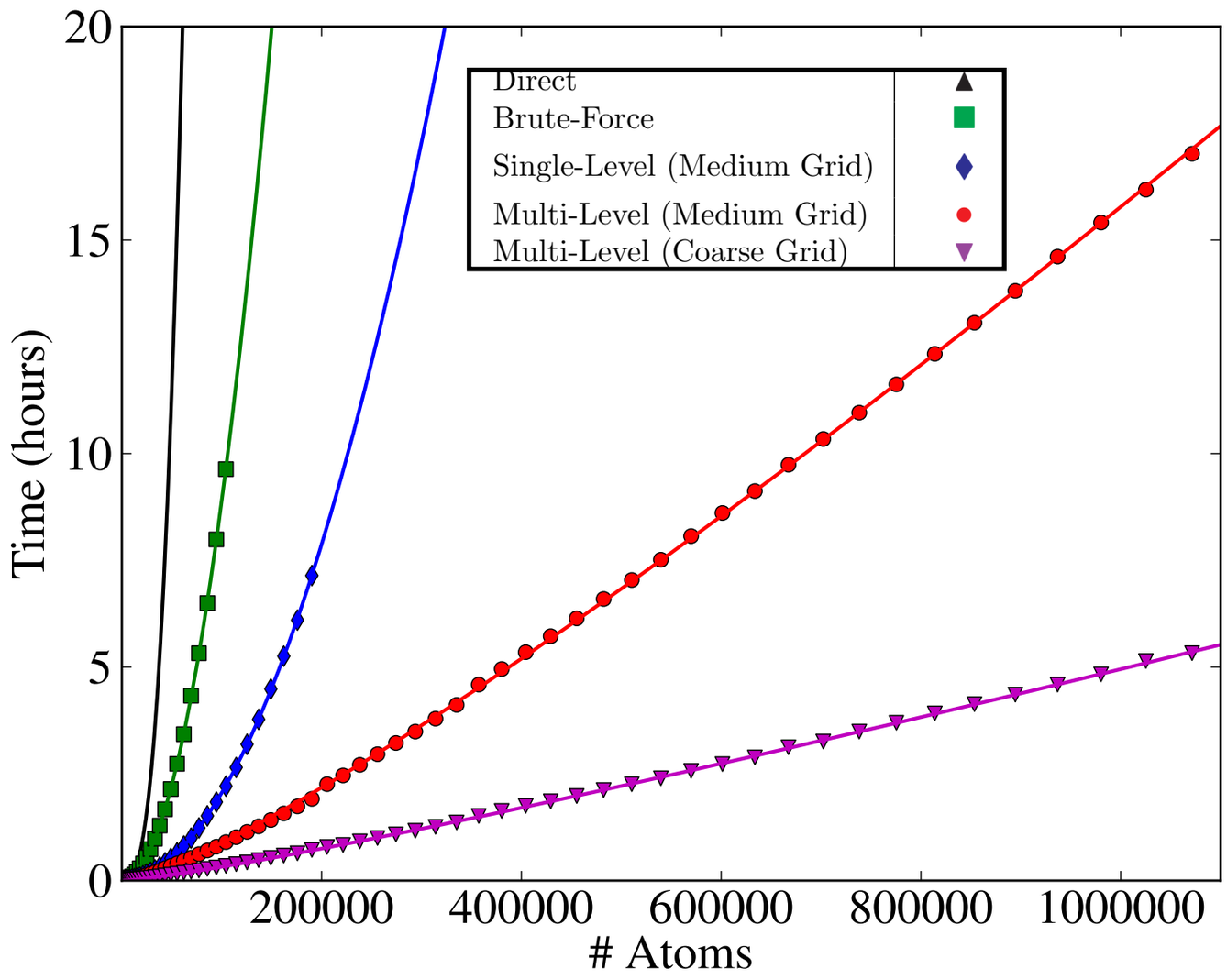
Need to do a multiple nanoparticles of size 10-100nm!

PENNSTATE 1855

DIM/QM for large nanoparticles

Fast Solver using Cartesian Cell Multipole Method

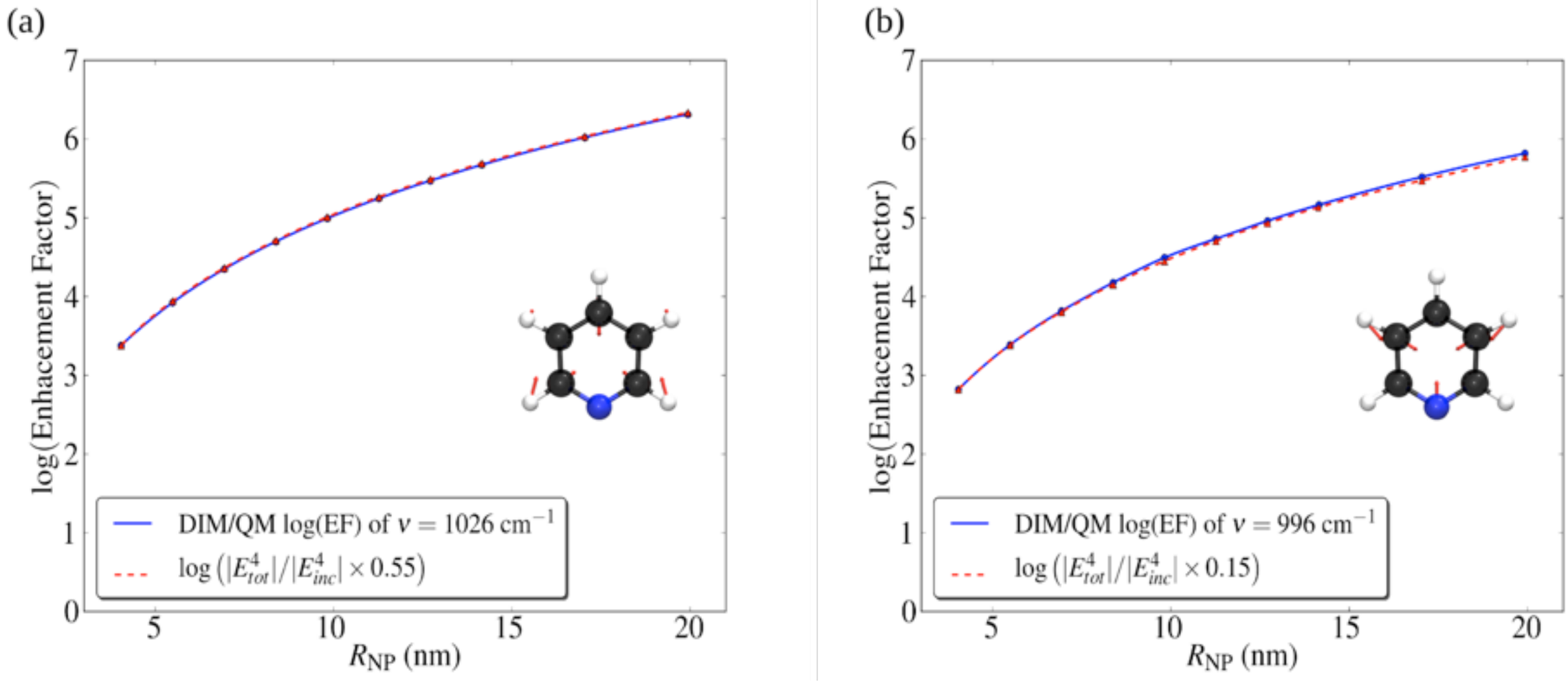




PENNSTATE
1855

Larger nanoparticles

Fast Solver using Cartesian Cell Multipole Method



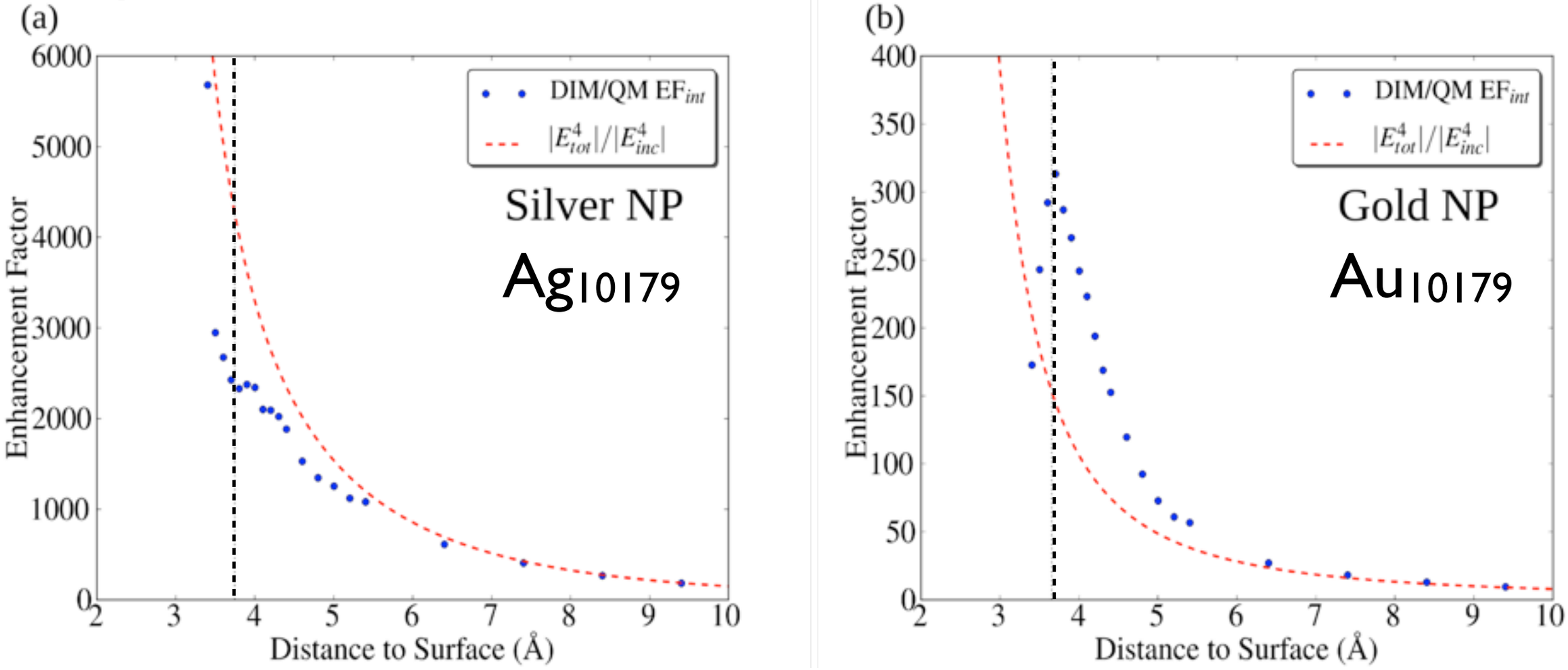
R = 20 nm ~ one million atoms!

Payton, Morton, Moore, Jensen, ACR, 47, 88-99, 2014

PENNSTATE 1855

Distance Effect in SERS

Pyridine on the vertex of a 8 nm icosahedron @ 3.6 eV



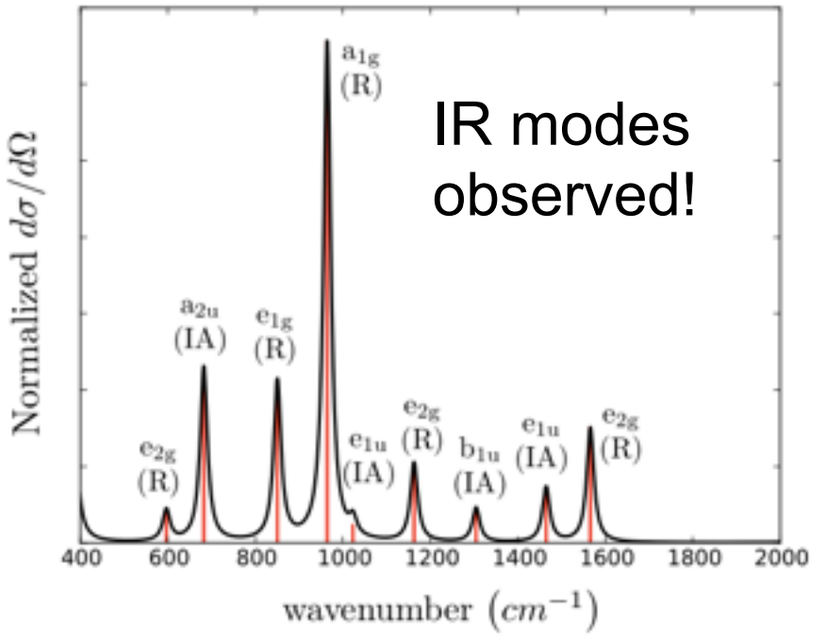
Enhancement reduced at the surface due to overlapping charge-distributions of the molecule and the metal

Payton, Morton, Moore, Jensen, ACR, 47, 88-99, 2014

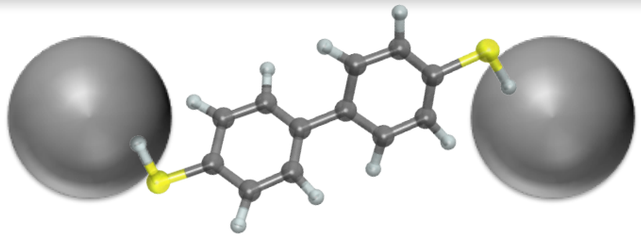
PENNSTATE 1855

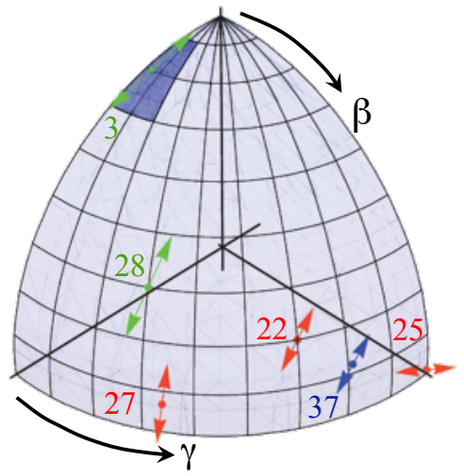
Inhomogeneous Electric Fields in SERS

Benzene on rough silver surface

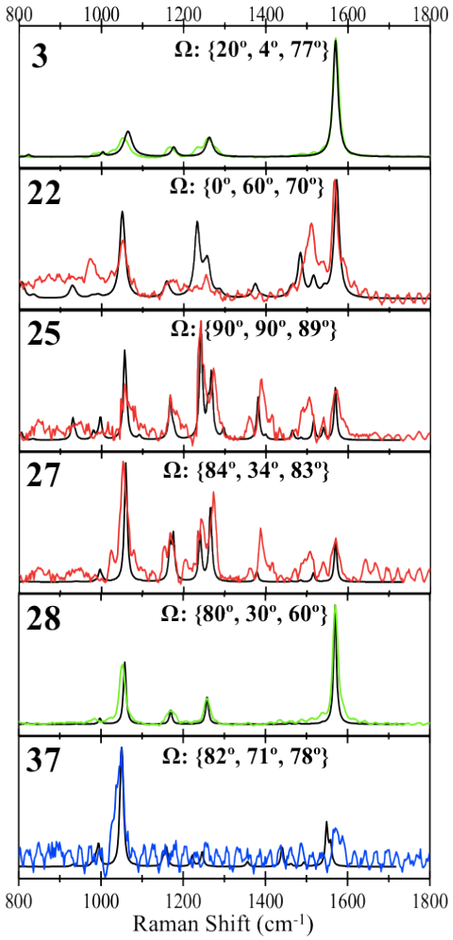


Moskovits et al. *J. Chem. Phys.*, **1980**, *73*, 6068





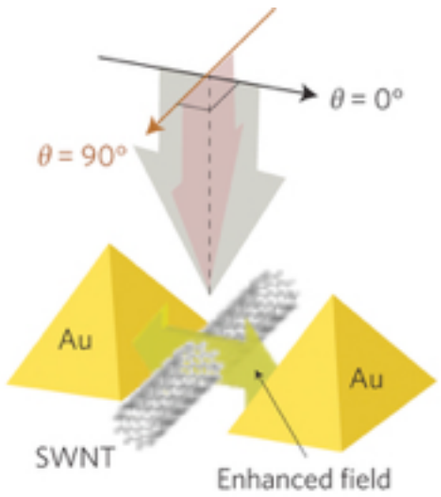
"A molecule GPS"

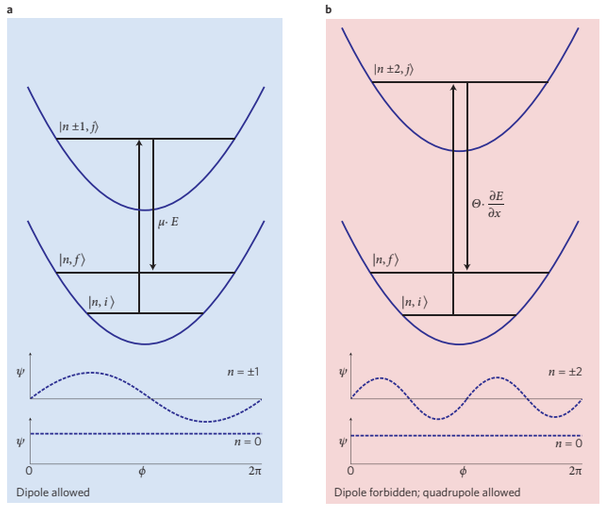


Electric dipole, quadrupole, and magnetic dipole scattering observed

Apkarian et al., ACS Nano, 2012

Plasmon-Induced Electronic Excitation





Murakoshi et al. Nature Photonics, 2013

Inhomogeneous electric fields lead to breakdown of dipole selection rules

Lasse Jensen - ADF webinar - February -2014

PENNSTATE 1855

Inhomogeneous fields in SERS: Theory

The induced dipole moment in an inhomogeneous field is given by

$$\mu_\alpha = \alpha_{\alpha\beta} E_\beta + \frac{1}{3} A_{\alpha\beta\gamma} E_{\beta\gamma} + G_{\alpha\beta} B_\beta + \cdots$$

Raman scattering in an inhomogeneous field

$$\alpha''_{\alpha\beta} = \left[\delta_{\alpha\gamma} + F^{\mathrm{loc},\alpha}_\gamma(\omega_S)\right] \alpha_{\gamma\delta} \left[\delta_{\beta\delta} + F^{\mathrm{loc},\beta}_\delta(\omega_L)\right] \text{ Electric dipole}$$

$$+ \frac{1}{3} \left[\delta_{\alpha\gamma} + F^{\mathrm{loc},\alpha}_\gamma(\omega_S)\right] A_{\gamma\delta\epsilon} F^{\mathrm{loc},\beta}_{\delta\epsilon}(\omega_L) \qquad \text{Quadrupole}$$

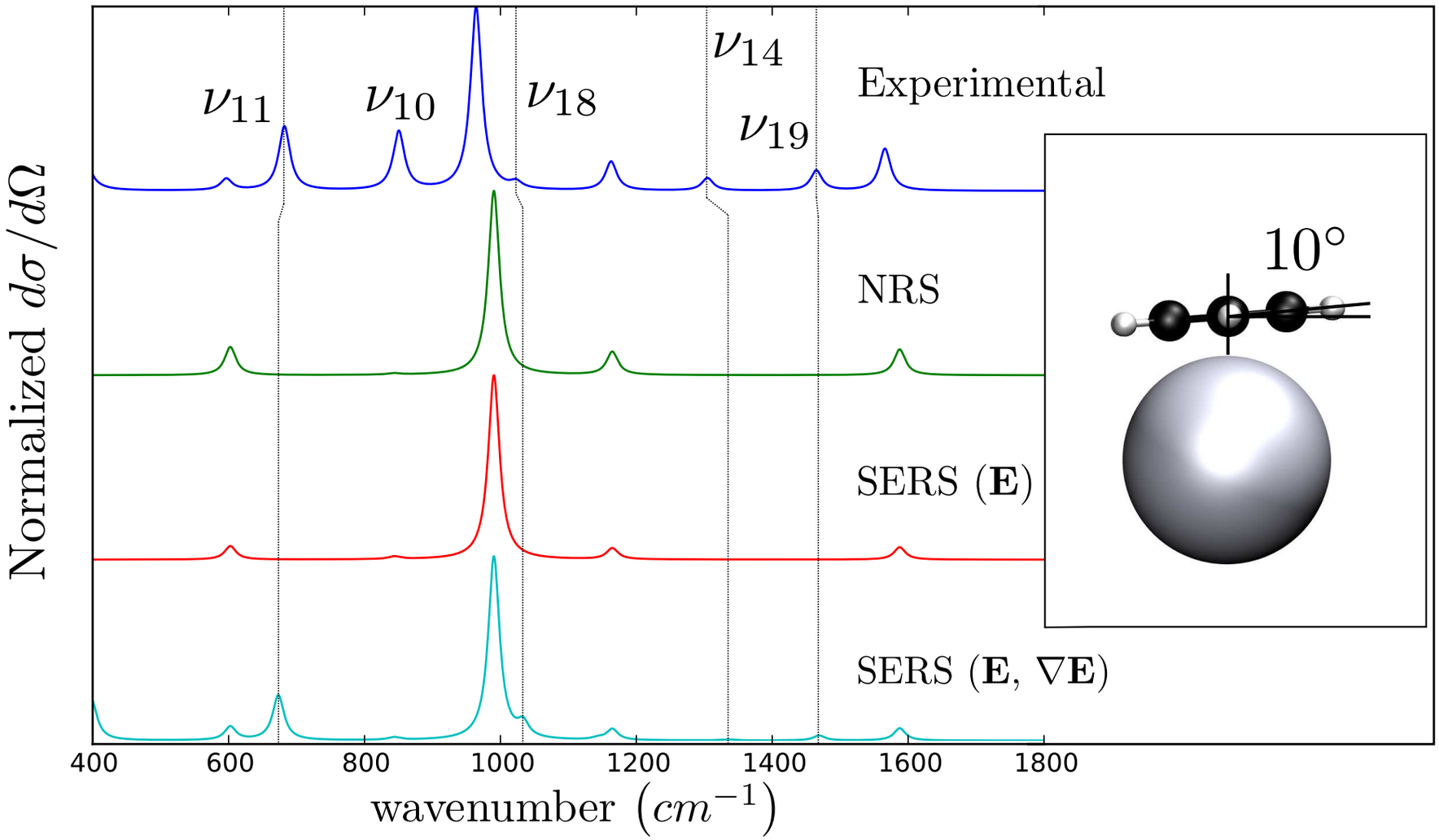
$$- \frac{i}{\omega} \left[\delta_{\alpha\gamma} + F^{\mathrm{loc},\alpha}_\gamma(\omega_S)\right] G_{\gamma\delta} \epsilon_{\delta\epsilon\zeta} F^{\mathrm{loc},\beta}_{\epsilon\zeta}(\omega_L) \text{ Magnetic dipole}$$

Dressed polarizability formalism - QM + ED

Chulahi, Jensen, J Phys. Chem. C. 117, 19622-19631 , 2013

Inhomogeneous fields in SERS: Benzene

EXP. Moskovits, M., DiLella, D.P., *J. Chem. Phys.*, **1980**, *73*, 6068-6075.

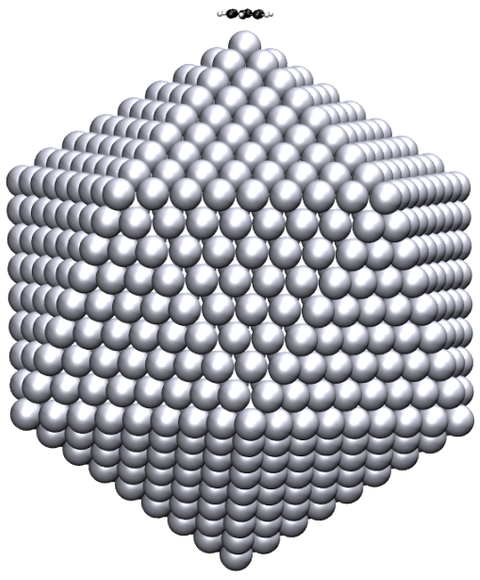


Experimental observed bands reproduced assuming "atomic roughness" and 10 degree angle

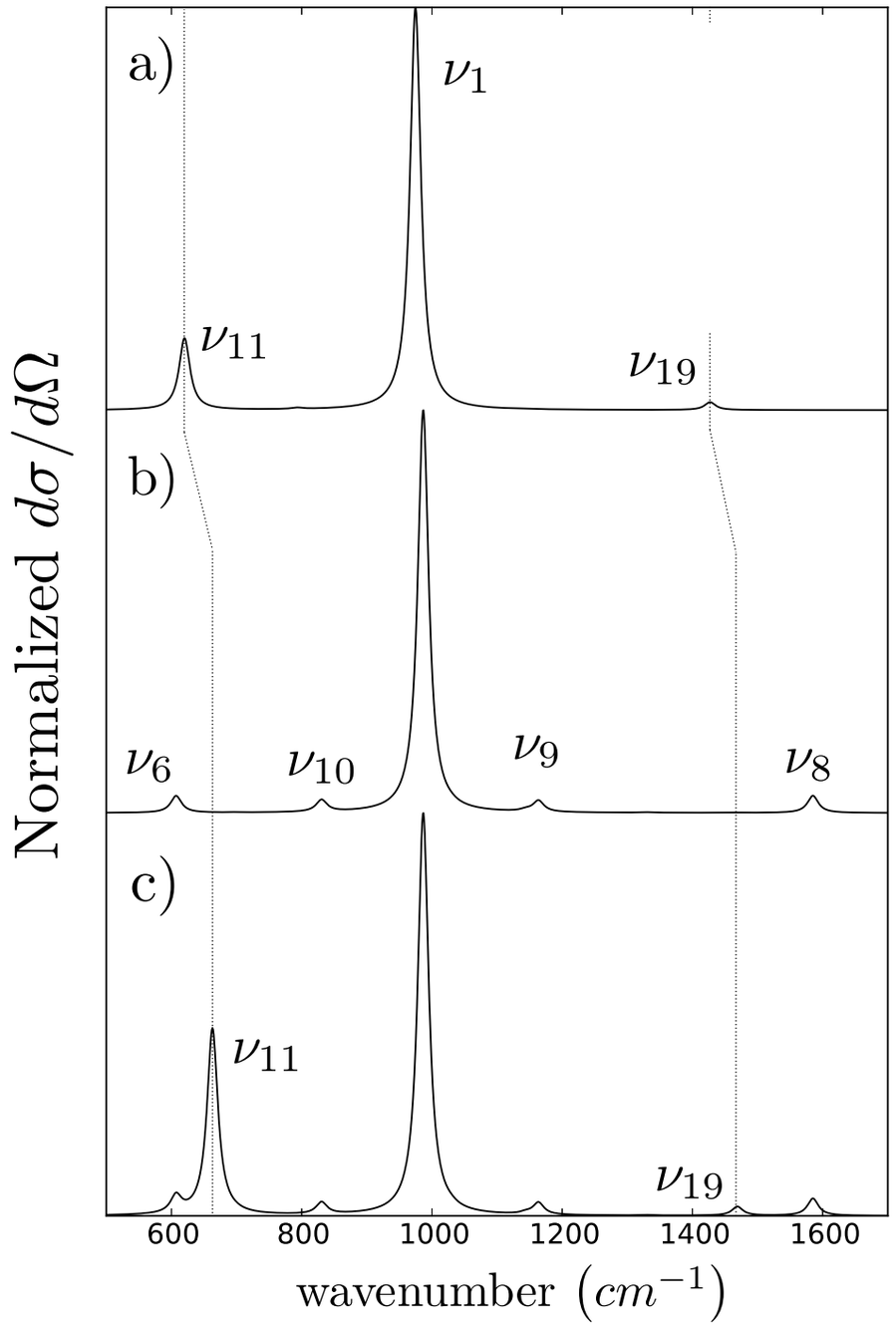
Chulahi, Jensen, J Phys. Chem. C. 117, 19622-19631 , 2013

PENNSTATE 1855

Inhomogeneous fields in SERS: DIM/QM



DIM/QM simulations contains the local field-gradient effects.



DIM/QM

SERS ($\boldsymbol{E}^{\mathrm{DIM}}$)

SERS ($\boldsymbol{E}^{\mathrm{DIM}}$, $\nabla \boldsymbol{E}^{\mathrm{DIM}}$)

Chulahi, Jensen, J Phys. Chem. C. 117, 19622-19631 , 2013

PENNSTATE 1855

Conclusions

- **Essential to describe the detailed atomistic structure of the nanoparticle and the specific orientation of the molecule relative to the nanoparticle**

- **SERS enhancements depend strongly on the adsorption site and molecular electronic and geometric structure**

- **$|E|^4$ approximation to SERS works well a little away from the surface but needs to be corrected at the surface of the nanoparticle**

- **Field gradient effects are important and can provide specific information about molecular orientations using SERS**

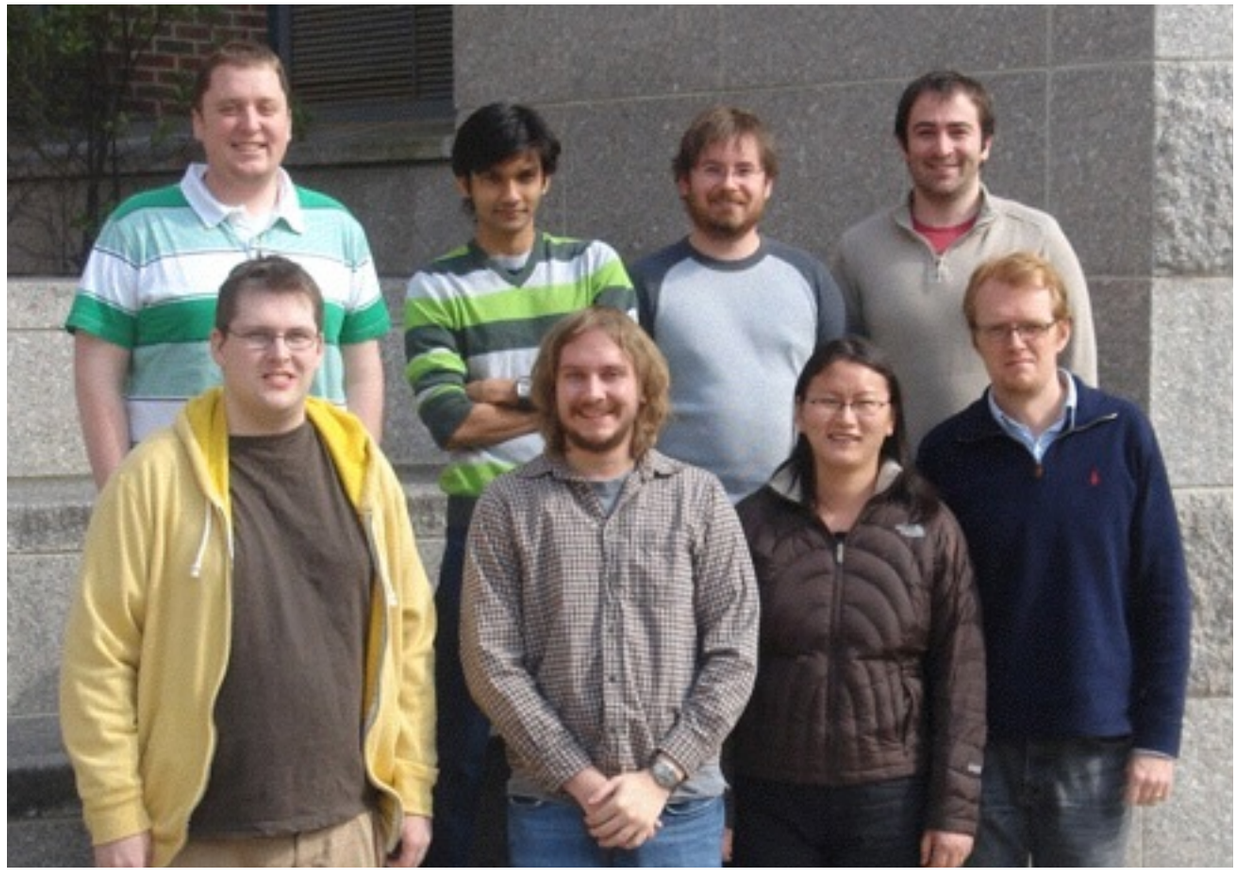
- **Hybrid methods like DIM/QM that combine electronic structure theory with electrodynamics simulations are promising avenues for obtaining detailed insights into plasmon-molecule coupling**

Acknowledgement

Current Group:
-Dr. Linlin Jensen
-Dr. Daniel Silverstein
-Justin Moore
-Phillip Weiss
-Dhabih Chulhai
-Zhongwei Hu

Past members
-Dr. John Payton
-Dr. Seth Morton (Ph.D '12)
-Dr. Bala K. Juluri (Ph.D. '11)
-Ebo Ewusi-Annan (M.S. '10)
-Krista A. Kane (M.S. '09)
-Shannon Fusina*
-Victoria Henderson*
-John Rinaldi*
-Ishita Trivedi*
-Phil Salant*

*undergraduate student



Collaborators:
- Tony Huang (PSU)
- Amar Flood (IU)
- Jon Camden (UT)
- Paul Weiss (UCLA)
- Niri Govind (PNNL)
- Ray Schaak (PSU)
- Ben Lear (PSU)
- Ayusman Sen (PSU)
- Scott Phillips (PSU)

CaSTL CENTER
Chemistry at the Space-Time Limit

Funding:
- Start-up funds Penn State
- MRSEC Penn State Center for Nanoscale Science
- NSF
- CaSTL, Chemistry at the Space-Time Limit

TeraGrid
EMSL
PENNSTATE
1855