SERS Simulator (v. 1.0) - User Guide

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This tool allows you to dress the molecule's polarizabilities with the local electric fields and gradients from model spheres, dimers, and flat surfaces in order to generate the surface-enhanced Raman spectrum. The tool also allow you to change the molecule's orientation with respect to the surface in order to see how the spectrum changes. [D.V. Chulhai and L. Jensen *J. Phys. Chem. C* **2013**, *117*, 19622–19631]

Input

Rotation

Figure 1: Rotation input tab

- The **Molecule Euler Rotation Angles** section describes the rotation angles (in degrees) about the x, y and z axes of the molecule. These values can range between $-180°$ and $180°$.
- The **Incident Light Polarization** section describes the polarization of the incident light. Since we assume the quasistatic limit, the k vector of the incident radiation is irrelevant.

- **Orientational averaging** accounts for the possible orientational changes when going from the molecule-nanoparticle frame (the molecule is still considered fixed with respect to the nanoparticle) to the lab frame. If the molecule-nanoparticle system remains fixed with respect to the lab frame, this option should be turned off.
- **Field gradient** turns on/off the field gradient effect. Note that the molecule must be described by an A-tensor and C-tensor in the "Molecule" tab to use this option.

Molecule

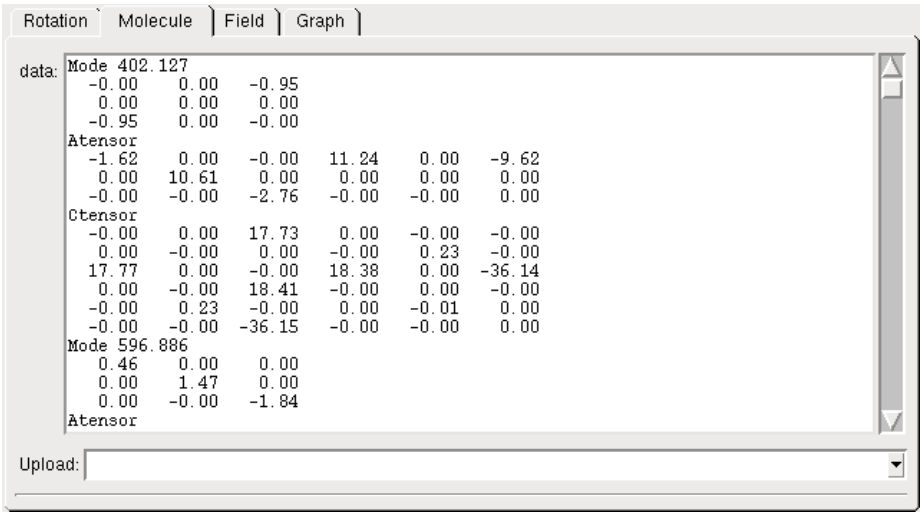

Figure 2: Molecule input tab

- **data** This describes the transition polarizabilities of the molecule. It is formatted as follows (do not include empty lines):
  - The keyword **Mode** (not case sensitive) followed by the mode frequency (in wave numbers) tells the tool that the data following this line all relate to this mode.
  - The three lines following **Mode** describes the transition polarizability for this mode. The different components of the polarizability are separated by spaces and are formatted as follows: `xxx.xxx` for real numbers and `xxx.xxx±xxx.xxxj` for complex numbers. This number format also applies to the A- and C- tensors (below). The polarizability is read in the following format:

    ```
    xx xy xz
    yx yy yz
    zx zy zz
    ```

  - The keyword **Atensor** (optional and not case sensitive) tells the tool that the following 3 lines describe the transition A-tensor, read in the following format:

```
x,xx x,xy x,xz x,yy x,yz x,zz
y,xx y,xy y,xz y,yy y,yz y,zz
z,xx z,xy z,xz z,yy z,yz z,zz
```

– The keyword **Ctensor** (optional and not case sensitive) tells the tool that the following 6 lines describe the transition C-tensor, read in the following format:

```
xx,xx xx,xy xx,xz xx,yy xx,yz xx,zz
xy,xx xy,xy xy,xz xy,yy xy,yz xy,zz
xz,xx xz,xy xz,xz xz,yy xz,yz xz,zz
yy,xx yy,xy yy,xz yy,yy yy,yz yy,zz
yz,xx yz,xy yz,xz yz,yy yz,yz yz,zz
zz,xx zz,xy zz,xz zz,yy zz,yz zz,zz
```

- **Upload** lets the user upload an already formatted standard text (**.txt*) file for the *data* field.

Field

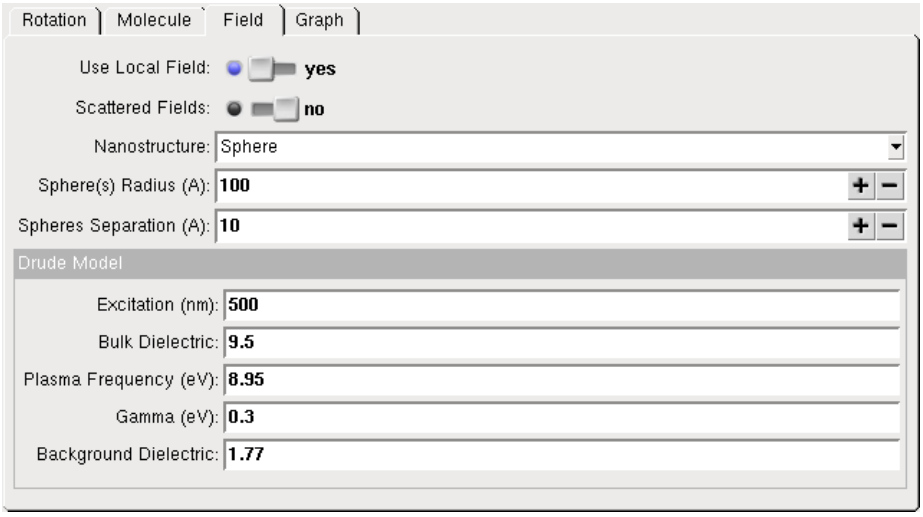

Figure 3: Field input tab

- **Use Local Field** switches between surface-enhanced Raman (on) and normal Raman (off). For normal Raman scattering, the "Orientational averaging" option should always be on.

- The **Scattered Fields** option uses different enhancement for the incident and scattered fields. Field enhancements are calculated for every $\omega_I + \omega_\nu$, where ω_I is the incident frequency, and ω_ν is the vibrational frequency.

- **Nanostructure** lets the user chose between three types of model fields: *Sphere*; *Dimer*; and *Flat Surface*. Further options include:

- **Sphere(s) Radius (A)** defines the radius of the sphere in Ångstroms (or both spheres in the case of the dimer system). This parameter determines the polarizability of the spheres or the flat surface. Since the molecule is always on the surface or the sphere, the field magnitudes remain the same for all radii. The radius then determines the relative magnitudes of the fields and gradients (smaller radii results in larger field gradient to field ratios).
- **Spheres Separation (A)** is used only for the *Dimer* nanostructure, and determines the separation of the two point-dipole spheres. The molecule in this case is placed in the center of the two spheres, for which case the field gradients are always (in the parallel axis) zero.

• **Drude Model** determines the Drude parameters for the generation of the fields.

- **Excitation (nm)** determines the incident laser excitation wavelength (ω_I) in nanometers.
- **Bulk Dielectric** is the bulk dielectric constant of the material (default is for silver).
- **Plasma Frequency (eV)** is the plasma resonance frequency in electron volts (default is for silver).
- **Gamma (eV)** is the plasma resonance damping parameter in electron volts.
- **Background Dielectric** is the dielectric constant for the background media (default is for water).

Graph

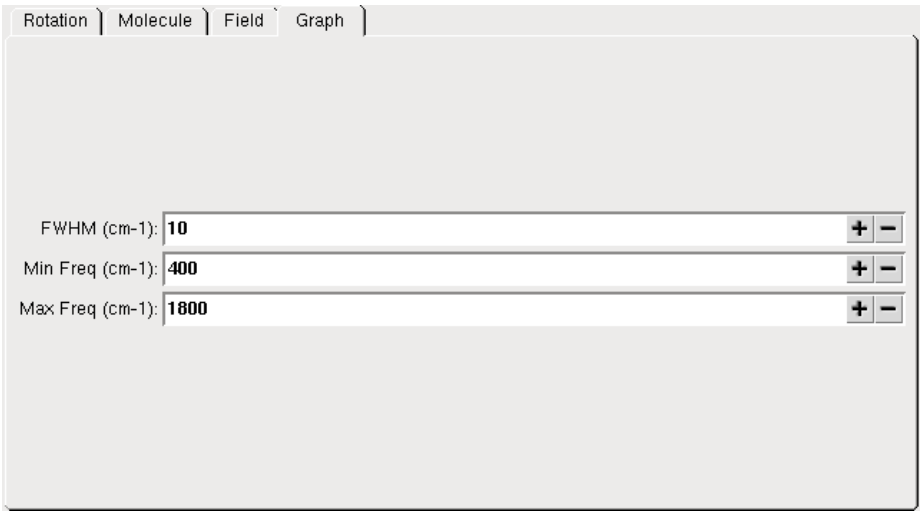

Figure 4: Graph input tab

- **FWHM (cm-1)** determines the full-width at half-maximum used in the Lorenztian broadening (in wave numbers) of the surface-enhanced Raman spectra.
- **Min Freq (cm-1)** specifies the minimum frequency (in wave numbers) to display on the graph.
- **Max Freq (cm-1)** specifies the maximum frequency (in wave numbers) to display on the graph.

Output

Spectrum

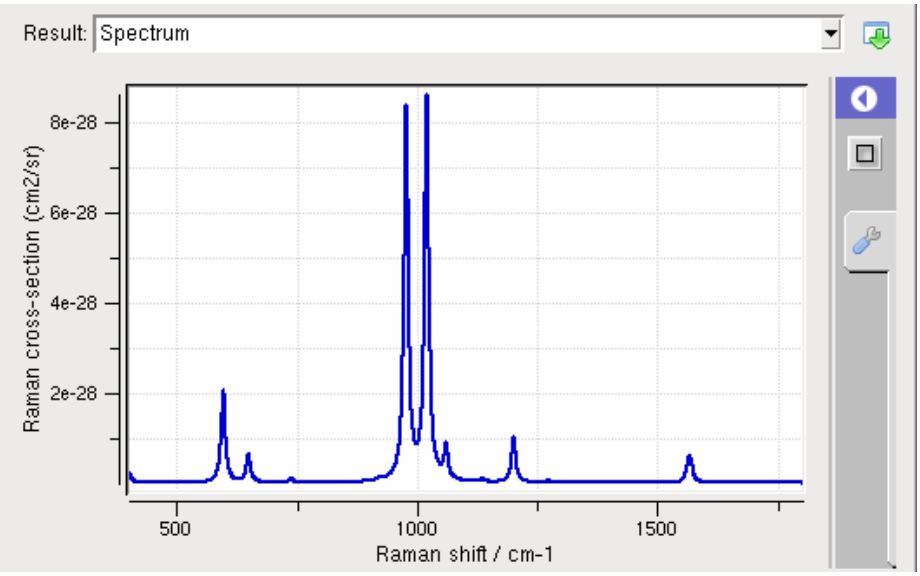

Figure 5: Output surface-enhanced Raman spectrum

Shows the simulated surface-enhanced Raman spectrum. Cross-section is in units of cm^2/sr.

Plasmon

Shows the simulated plasmon resonance based on the parameters in the *Field* input tab.

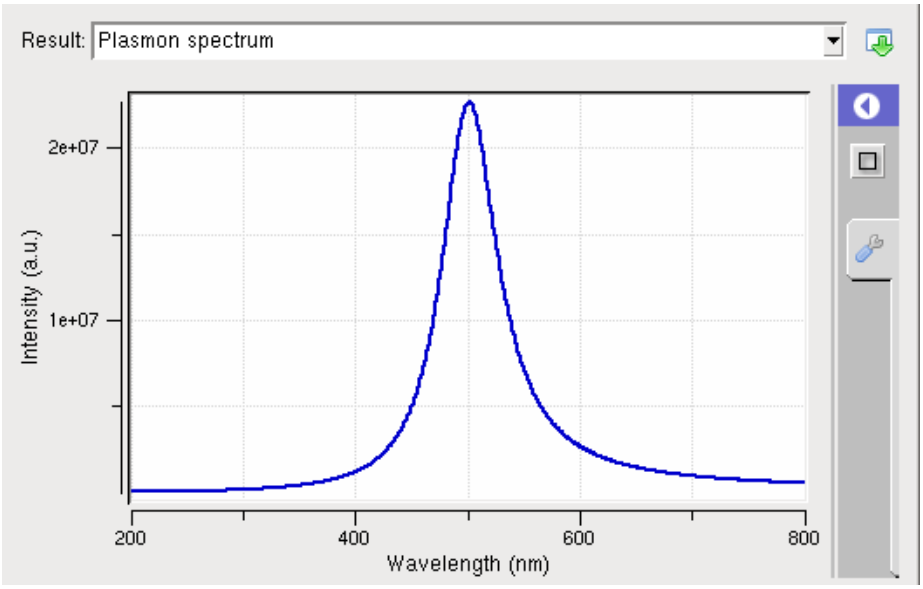

Figure 6: Output Plasmon resonance