Supporting Information

Surface plasmon resonance in gold nanoparticles:

a review

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S1. Correction of Au optical constant for intrinsic size effects.

In general the optical properties of noble metals are determined by conduction electrons and d-band electrons.\(^1\),\(^2\) Therefore the dielectric constant in the UV–Vis–NIR regime is composed of two terms (Drude–Lorentz model):\(^3\)

\[
\varepsilon_{\text{bulk}}(\omega) = 1 + \chi_s(\omega) + \chi_d(\omega)
\]  
(S1.1)

where \(\chi_s(\omega)\) is the contribute of d-bands electrons and \(\chi_d(\omega)\) is that of s-band conduction electrons and can be expressed by a simple Drude–Sommerfeld model:

\[
\chi_s(\omega) = -\frac{\omega_p^2}{\omega^2 + (\Gamma_{\text{nr}})^2} + \frac{i \omega_p^2 \Gamma_{\text{bulk}}}{\omega^2 + (\Gamma_{\text{nr}})^2}
\]  
(S1.2)

On the assumption that only the free electron behaviour is affected by the size of nanoparticles, \(\varepsilon(\omega, L_{\text{eff}})\) can be expressed by replacing \(\Gamma_{\text{bulk}}^n\) with \(\Gamma_{\text{nr}}(L_{\text{eff}})\) in equation S1.2:

\[
\varepsilon(\omega, L_{\text{eff}}) = \varepsilon_{\text{bulk}}(\omega) + \frac{\omega_p^2}{\omega^2 + (\Gamma_{\text{nr}})^2} \left[ \frac{1}{\omega^2 + (\Gamma_{\text{nr}})^2} - \frac{1}{\omega^2 + (\Gamma_{\text{nr}}(L_{\text{eff}}))^2} \right] + i \frac{\omega_p^2}{\omega^2 + (\Gamma_{\text{nr}})^2} \left[ \frac{\Gamma_{\text{nr}}(L_{\text{eff}})}{\omega^2 + (\Gamma_{\text{nr}}(L_{\text{eff}}))^2} \right]
\]  
(S1.3)

As shown from equation S1.3, two terms can be isolated in the expression of the dielectric constant: the first term is equal to the bulk optical constant, while the second term accounts for the size effect on the dielectric response of nanometric objects. The \(\varepsilon_{\text{bulk}}(\omega)\) for Au is experimentally known with high precision (see paragraph 3.1 in the main article), hence correction of \(\varepsilon(\omega, L_{\text{eff}})\) for the size is straightforward.

Plasma frequency can be calculated according to eq. 9 in the main article and using the following parameters for bulk Au:\(^4\)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n_e)</td>
<td>(5.90 \times 10^{28} \text{ m}^{-3})</td>
</tr>
<tr>
<td>(m_{\text{eff}})</td>
<td>(1.00203 \times 10^{-30} \text{ kg})</td>
</tr>
<tr>
<td>(\Gamma_{\text{nr}}^{\text{bulk}})</td>
<td>(3.4014 \times 10^{13} \text{ Hz})</td>
</tr>
<tr>
<td>(v_f)</td>
<td>(1.40 \times 10^5 \text{ m/s})</td>
</tr>
</tbody>
</table>
S2. Analytical expression of the Mie model for spheres.

S2.1. Mie theory for compact spheres.

The extinction, scattering and absorption cross-sections of spherical nanoparticles ($\sigma_{\text{Ext}}$, $\sigma_{\text{Sca}}$ and $\sigma_{\text{Abs}}$) within the Mie model for compact spheres are:

$$\sigma_{\text{Ext}} = \frac{2\pi}{k^2} \sum_{L=1}^{\infty} (2L + 1) \text{Re}[a_L + b_L] \quad (S2.1)$$

$$\sigma_{\text{Sca}} = \frac{2\pi}{k^2} \sum_{L=1}^{\infty} (2L + 1) \left|a_L\right|^2 + \left|b_L\right|^2 \quad (S2.2)$$

$$\sigma_{\text{Abs}} = \sigma_{\text{Ext}} - \sigma_{\text{Sca}} \quad (S2.3)$$

$$a_L = \frac{m \cdot \psi_L(mx) \cdot \psi_L'(x) - \psi_L'(mx) \cdot \psi_L(x)}{m \cdot \psi_L(mx) \cdot \eta_L'(x) - \psi_L'(mx) \cdot \eta_L(x)} \quad (S2.4)$$

$$b_L = \frac{\psi_L(mx) \cdot \psi_L'(x) - m \psi_L'(mx) \cdot \psi_L(x)}{\psi_L(mx) \cdot \eta_L'(x) - m \psi_L'(mx) \cdot \eta_L(x)} \quad (S2.5)$$

$$m = \frac{n(R)}{n_m} \quad (S2.6)$$

$$x = kR \quad (S2.7)$$

where $R$ is the sphere radius, $k$ is the modulus of the incident photon wavevector ($\vec{k}$) in the host matrix with refractive index $n_m$, $\psi_L$ and $\eta_L$ are the spherical Riccati-Bessel functions, and $n(R)$ is the complex refractive index of the sphere of radius $R$. In order to have an accurate evaluation of the cross-sections, the series must be truncated at a maximum value, $L_{\text{max}}$, that must ensure convergence and generally depends on the size parameter, $x$, of the particles. A widely used criterion proposed by Wiscombe is that: $L_{\text{max}} = x + 4x^{1/3} + 1$, for $x \leq 8$; $L_{\text{max}} = x + 4.05x^{1/3} + 2$, for $8 < x < 4200$; $L_{\text{max}} = x + 4x^{1/3} + 2$, for $x > 4200$.

The multipolar order ($L$) should be larger for larger sizes, and typically $L > 3$ for $R < 50$ nm and $L > 5$ of $R > 50$ nm.

S2.2. Mie theory for core-shell spheres.

The extinction, scattering and absorption cross-sections of core-shell spheres can be calculated using the generalization of the Mie model for multilayer spheres:

$$\sigma_{\text{Ext}} = \frac{2\pi}{k_h^2} \sum_{L=1}^{\infty} (2L + 1) \text{Re}[a_L + b_L] \quad (S2.8)$$

$$\sigma_{\text{Sca}} = \frac{2\pi}{k_h^2} \sum_{L=1}^{\infty} (2L + 1) \left|a_L\right|^2 + \left|b_L\right|^2 \quad (S2.9)$$

$$\sigma_{\text{Abs}} = \sigma_{\text{Ext}} - \sigma_{\text{Sca}} \quad (S2.10)$$
\[ a_L = \frac{m_r \cdot \psi_L(m, x_r) \cdot \left[ \psi_L'(x_r) + T_L \chi_L'(x_r) \right]}{m_r \cdot \eta_L(m, x_r) \cdot \left[ \psi_L'(x_r) + T_L \chi_L'(x_r) \right]} - \frac{\psi_L(m, x_r) \cdot \left[ \psi_L'(x_r) + T_L \chi_L'(x_r) \right]}{m_r \cdot \eta_L(m, x_r) \cdot \left[ \psi_L'(x_r) + T_L \chi_L'(x_r) \right]} \]  
\text{(S2.11)}

\[ b_L = \frac{m_r \cdot \psi_L(m, x_r) \cdot \left[ \psi_L'(x_r) + S_L \chi_L'(x_r) \right]}{m_r \cdot \eta_L(m, x_r) \cdot \left[ \psi_L'(x_r) + S_L \chi_L'(x_r) \right]} - \frac{\psi_L(m, x_r) \cdot \left[ \psi_L'(x_r) + S_L \chi_L'(x_r) \right]}{m_r \cdot \eta_L(m, x_r) \cdot \left[ \psi_L'(x_r) + S_L \chi_L'(x_r) \right]} \]  
\text{(S2.12)}

\[ T_L = -\frac{m_r \cdot \psi_L(m, x_r) \cdot \left[ \psi_L'(x_r) + T_L^{-1} \chi_L'(x_r) \right]}{m_r \cdot \chi_L(m, x_r) \cdot \left[ \psi_L'(x_r) + T_L^{-1} \chi_L'(x_r) \right]} + \frac{\psi_L(m, x_r) \cdot \chi_L(m, x_r) \cdot \left[ \psi_L'(x_r) + T_L^{-1} \chi_L'(x_r) \right]}{m_r \cdot \chi_L(m, x_r) \cdot \left[ \psi_L'(x_r) + T_L^{-1} \chi_L'(x_r) \right]} \]  
\text{(S2.13)}

\[ T_L' = -\frac{m_r \cdot \psi_L(m, x_r) \cdot \psi_L'(x_r) - \psi_L(m, x_r) \cdot \psi_L'(x_r)}{m_r \cdot \chi_L(m, x_r) \cdot \psi_L'(x_r) - \chi_L(m, x_r) \cdot \psi_L'(x_r)} \]  
\text{(S2.14)}

\[ S_L = -\frac{\psi_L(m, x_r) \cdot \left[ \psi_L'(x_r) + S_L^{-1} \chi_L'(x_r) \right]}{\chi_L(m, x_r) \cdot \left[ \psi_L'(x_r) + S_L^{-1} \chi_L'(x_r) \right]} + m_r \cdot \psi_L(m, x_r) \cdot \left[ \psi_L'(x_r) + S_L^{-1} \chi_L'(x_r) \right] \]  
\text{(S2.15)}

\[ S_L' = -\frac{\psi_L(m, x_r) \cdot \psi_L'(x_r) - m_r \cdot \psi_L(m, x_r) \cdot \psi_L'(x_r)}{\chi_L(m, x_r) \cdot \psi_L'(x_r) - m_r \cdot \chi_L(m, x_r) \cdot \psi_L'(x_r)} \]  
\text{(S2.16)}

\[ m_s = \frac{n_{s+1}}{n_s} \]  
\text{(S2.17)}

\[ x_r = k_h r_s \]  
\text{(S2.18)}

where \( \chi(x) \) is a spherical Riccati–Bessel function, \( k_h \) is the wavenumber of the incident photons calculated in the host matrix, and \( s \) is the layer number, ranging from 1 (the core) to \( r + 1 \) (the surrounding matrix with refractive index \( n_m \)), with \( r \) total number of layers. The considerations about the multipolar order \( (L) \) in compact spheres are valid for the core-shell sphere.

### S3. Gans and Fuchs models.


The Gans model is used to calculate the \( \sigma_{\text{Ext}} \) of ellipsoids in the quasistatic regime, that in case of Au means having the longer axis smaller than about 50 nm. For a spheroid (i.e. \( a > b = c \)) with random orientation \( \sigma_{\text{Ext}} \) is:

\[ \sigma_{\text{Ext}} = \frac{2\pi e m}{3\lambda} \sum_i \frac{1 \cdot P_i^2 \cdot \epsilon_i(\omega, R)}{\left[ \epsilon_i(\omega, R) + \frac{1 - P_j}{P_j} \cdot e_m \right]^2 + \left[ \epsilon_j(\omega, R) \right]^2} \]  
\text{(S3.1)}

\[ P_a = \frac{1 - e^2}{e^2} \left[ \frac{1}{2e} \ln \left( \frac{1 + e}{1 - e} \right) - 1 \right] \]  
\text{(S3.2)}

\[ P_b = P_c = \frac{1 - P_a}{2} \]  
\text{(S3.3)}
\[ e = \sqrt{1 - \left(\frac{b}{a}\right)^2} = \sqrt{1 - \left(\frac{1}{D}\right)^2} \]  

(S3.4)

where \( e \) is the eccentricity, that depends on the aspect ratio the spheroid \( D = a/b \). As expected for a metal particle with lower symmetry, a spheroid with two different axis has two SPRs.

S3.2. Analytical expression of the Fuchs model for cubic particles.

A rough estimation of the \( \sigma_{\text{Ext}} \) in cubic metal nanoparticles in the quasistatic regime is provided by the Fuchs model.\(^5\)\(^-\)\(^26\) The presence of edge and corners prevents uniform polarization in a metal cube and originates several plasmon resonances. The resulting Fuchs polarization \( \alpha \) of a cube is:

\[ \alpha = \varepsilon_0 V \sum_{j=1}^{N} C_j \left[ \varepsilon(\omega, R) - \varepsilon_m \right] \left[ \varepsilon(\omega, R) - \varepsilon_m \right] + \varepsilon_m \]  

(S3.5)

\[ \sigma_{\text{Ext}} = \frac{4\pi\omega}{3c\varepsilon_0 \sqrt{\varepsilon_m}} \text{Im}[\alpha] \]  

(S3.6)

where \( C_j \) are the oscillator strengths and \( L_j \) are geometry factors due to depolarization. Plasmon resonances for a cube are 9, but only 6 have significant intensity, therefore \( N = 6 \).\(^26\)

S4. Additional details about DDA.

In the DDA it is assumed that the object is interacting with a monochromatic plane wave incident from infinity.\(^8\)\(^-\)\(^10\) The structure of interest, called “target”, is replaced by \( N \) polarizable points (i.e. \( N \) cubic dipoles) arranged in a cubic lattice with same geometry and permittivity of the original object.\(^8\)\(^-\)\(^11\) Calculations of the extinction cross section are accurate provided that the target adimensional “size parameter” \( x = 2\pi a_{\text{eff}} / \lambda < 25 \),\(^8\)\(^-\)\(^10\) where \( \lambda \) is the wavelength of the incident photons and \( a_{\text{eff}} \) is connected to target volume \( V \) by

\[ V = \frac{4}{3} \pi a_{\text{eff}}^3 \]  

(S4.1)

The basis of the DDA is that the polarization \( P_j \) induced on each dipole \( j \) of position \( r_j \) and polarizability \( p_j \) is given by

\[ \hat{P}_j = p_j \hat{E}_{\text{Loc}}(\hat{r}_j) \]  

(S4.2)

where \( \hat{E}_{\text{Loc}} \) is the electric field originated by the incident radiation of amplitude \( E_0 \), and includes the contribution of all other dipoles:

\[ \hat{E}_{\text{Loc}}(\hat{r}_j) = \hat{E}_0 \exp(i\hat{k} \cdot \hat{r}_j + i\omega t) - \sum_{l \neq j} \hat{A}_{lj} \hat{P}_l \]  

(S4.3)

where \( \hat{A}_{lj} \) is the interaction matrix and \( \hat{E}_{\text{inc}}(\hat{r}_j) = \hat{E}_0 \exp(i\hat{k} \cdot \hat{r}_j + i\omega t) \) is the incident monochromatic plane wave with frequency \( \omega \) and wavevector \( \hat{k} \).\(^8\)\(^-\)\(^10\)
The full expression of $\hat{A}_j \vec{P}_j$ (in c.g.s. units) is:

$$
\hat{A}_j \vec{P}_j = \frac{\exp\left(ik \cdot \vec{r}_j\right)}{r_{jj}^3} \left\{ k^2 \vec{r}_{jj} \times (\vec{r}_{jj} \times \vec{P}_j) + \frac{\left(1 - ik \cdot \vec{r}_{jj}\right)}{r_{jj}^2} \left[x_j^2 \vec{P}_j - 3 \vec{r}_{jj} \vec{r}_{jj} \cdot \vec{P}_j \right] \right\},
$$

(S4.4)

where $\vec{r}_{jj} = \vec{r}_j - \vec{r}_i$, $r_{jj} = |r_j - r_i|$.

The extinction cross section ($\sigma_{\text{ext}}$) of the target is then given by

$$
\sigma_{\text{ext}} = \frac{4\pi k}{E_0^2} \sum_{j=1}^{N} \left(\vec{E}_{\text{inc}}^* \cdot \vec{P}_j\right)
$$

(S4.5)

where $\vec{E}_{\text{inc}}^*$ is the complex conjugate of the incident electric field.$^8$-$^{10}$

A crucial point of the DDA is the use of an appropriate expression for $p_j$. When calculations are performed with the DDSCAT software,$^9$ $p_j$ is typically expressed according to the lattice dispersion relation (LDR) developed by Draine and Goodman,$^8$, $^9$, $^{11}$ i.e. as a correction of the Clausius-Mossotti polarizability by a series expansion of $k \cdot d$ and $\varepsilon_m$, with $d$ the interdipole spacing and $\varepsilon_m$ the matrix dielectric constant:

$$
p_{\text{LD}}^j = \frac{p_{\text{CM}}^j}{1 + p_{\text{CM}}^j \left[b_1 + b_2 \varepsilon_j + b_3 S \varepsilon_j \left(\frac{k^2}{d}\right)\right]},
$$

(S4.6)

where $\varepsilon_j$ is the dipole permittivity, $b_1$, $b_2$, $b_3$ and $S$ are coefficients of the expansions, and $p_{\text{CM}}^j$ is the Clausius-Mossotti polarizability

$$
p_{\text{CM}}^j = \left(\frac{d}{3}\right)^2 \frac{\varepsilon_j - 1}{\varepsilon_j + 2}
$$

(S4.7)

The expression for $p_j$ developed by Draine and Goodman is valid only for interdipole spacing $d \ll \lambda$.$^8$-$^{10}$

**S5. Additional details about the T-matrix method.**

Here we explain the basics of the T-matrix method, also known as extended boundary condition method. A comprehensive review of the method can be found in Borghese, Denti, and Saija (2007)$^{12}$ and in Mishchenko, Lacis, and Travis (2002),$^{13}$ while a comprehensive review of the applications of the T-matrix method in plasmonics is given in Khlebtsov (2013).$^{14}$

The method is based on the multipole expansions of the electromagnetic fields, so mainly the same framework in which the Lorenz-Mie theory develops. It assumes that the particle is embedded into an homogeneous, isotropic, non magnetic, indefinite medium of real refractive index $n$. The
incident field is the polarized plane wave described in terms of its complex amplitude of the time-
harmonic field (phasor):
\[ \mathbf{E}_{\text{inc}} = E_0 \hat{e}_{\text{inc}} \exp(i \mathbf{k}_{\text{inc}} \cdot \mathbf{r}), \]
with amplitude \( E_0 \), unit polarization vector \( \hat{e}_{\text{inc}} \), and propagation vector \( \mathbf{k}_{\text{inc}} = k \hat{k}_{\text{inc}} \), where \( k = n \omega / c \), with light frequency \( \omega \). The origin of the reference frame is assumed to lie within the particle.

The starting point of the method is the field expansion in terms of spherical multipole fields, i.e., the vector solutions of the Maxwell equations in a homogeneous medium that are simultaneous eigenfunctions of the square and of the \( z \)-component of the angular momentum, as well as of the parity operator.

The expansion of the incident field is:\textsuperscript{12,15}
\[ \mathbf{E}_{\text{inc}} = E_0 \sum_{\ell m} J^{(p)}_{\ell m}(r, k) W^{(p)}_{\ell m}(\hat{e}_{\text{inc}}, \hat{k}_{\text{inc}}) \]
where \( J^{(p)}_{\ell m} \) are defined as
\[ J^{(1)}_{\ell m} = j_{\ell}(kr)X_{\ell m} \]
\[ J^{(2)}_{\ell m} = \frac{1}{k} \nabla \times J^{(1)}_{\ell m} \]
where the superscripts 1 and 2 are the values of the parity index \( p \) distinguishing the magnetic multipole fields \( (p = 1) \) from the electric ones \( (p = 2) \), \( j_{\ell} \) are spherical Bessel functions, and \( X_{\ell m} \) are vector spherical harmonics.\textsuperscript{16} The amplitudes \( W^{(p)}_{\ell m} \) for a plane wave are known.\textsuperscript{12}

The field within the particle can be written as
\[ \mathbf{E}_{\text{np}} = E_0 \sum_{\ell m} C^{(p)}_{\ell m} J^{(p)}_{\ell m}(r, n_k) \]

The expansion of the scattered field is
\[ \mathbf{E}_{\text{sca}} = E_0 \sum_{\ell m} A^{(p)}_{\ell m} \mathbf{H}^{(p)}_{\ell m}(r, nk) \]
where \( \mathbf{H}^{(p)}_{\ell m} \) indicates multipole fields satisfying the radiation condition at infinity. They are identical to the \( J^{(p)}_{\ell m} \) multipole fields except for the substitution of the spherical Hankel functions of the first kind, \( h_{\ell m} \), in place of the spherical Bessel function \( j_{\ell} \). The amplitudes \( A^{(p)}_{\ell m} \) of the scattered field can be calculated imposing the boundary condition across the surface of the particle.

From a formal point of view, the scattering process can be described by a linear operator \( S \) defined by the equation
\[ \mathbf{E}_{\text{sca}} = S \mathbf{E}_{\text{inc}} \]
The operator $S$, called transition operator, can be introduced thanks to the linearity of the Maxwell equations and of the equations expressing the boundary conditions across the surface of the particle. The elements of the T-matrix contain all the information about the scattering process, but are independent on the state of polarization of the incident field.

The T-matrix approach has proved to be very suitable to solve the light scattering problem by aggregates of spherical particles. The first progress in devising a technique to calculate the optical properties of linear chains of spherical particles is due to Bruning and Lo.\textsuperscript{17} Peterson and Strom extended the description to general aggregation geometry,\textsuperscript{18} and finally Borghese et al. gave a relevant contribution thanks to the introduction of an addition theorem for multipole fields.\textsuperscript{12,19,20} In the years computational methods were gradually improved to consider increased number of monomers with increasing size.\textsuperscript{21}

**S6. Analytical expressions for EMTs.**

**S6.1. Maxwell-Garnett dielectric function.** Maxwell-Garnett model is obtained by inserting the multipolar polarizability in the electrostatic limit, into the the Clausius–Mossotti formula, that links the polarizability of the NPs to their effective dielectric function $\varepsilon_{\text{eff}}$:\textsuperscript{3}

$$\varepsilon_{\text{eff}} = \frac{\varepsilon_{\text{m}}(l + 2f) + 2\varepsilon_{\text{m}}(l - f)}{\varepsilon_{\text{m}}(l - f) + \varepsilon_{\text{m}}(2 + f)}$$  \hspace{1cm} (S6.1)

where $f$ is the filling fraction (i.e. the volume fraction of NPs over the total in a nanocomposite), and $\varepsilon_{\text{m}}$ is the medium optical constant.

Since the Clausius-Mossotti formula accounts only for dipolar interactions, the Maxwell-Garnett model works well only with relatively dilute samples ($f \sim 3$), for which only dipolar interactions are important.\textsuperscript{22}

**S6.2. Bruggeman dielectric function.**

In the Bruggeman description,\textsuperscript{23} the effective dielectric function is given as:\textsuperscript{21,24,25}

$$\varepsilon_{\text{eff}} = \varepsilon_B \pm \sqrt{\varepsilon_B^2 + \frac{\varepsilon_{\text{Au}}\varepsilon_{\text{M}}}{2}}$$  \hspace{1cm} (S6.2)

where

$$\varepsilon_B = \frac{\varepsilon_{\text{M}}(2 - 3f) - \varepsilon_{\text{Au}}(1 - 3f)}{4}$$  \hspace{1cm} (S6.3)

When the imaginary part of the effective dielectric function becomes negative, the negative square root has to be used.\textsuperscript{25}
S7. Additional details about resonant SERS (SERRS).

The intensity of the Raman signal is related to the absolute differential Raman scattering cross section \(d\sigma_R/d\Omega\) of a single scattering object according to the following equation:\(^{26-28}\)

\[
I_R(\lambda_R) = \frac{d\sigma_R}{d\Omega} I_i(\lambda_i) \delta\Omega
\]

(S7.1)

where \(I_i(\lambda_i)\) is the incident laser power with wavelength \(\lambda_i\) and \(I_R(\lambda_R)\) is the intensity of the Raman radiation scattered at \(\lambda_R\) in the solid angle of collection \(\delta\Omega\).

In case of a series of analytes adsorbed on a SERS substrate, the signal intensity is given by the sum of the \(d\sigma_R/d\Omega\) of all the Raman active molecules hosted in the sample. For each molecule \(i\), the \(d\sigma_R/d\Omega\) can be expressed as:

\[
\left( \frac{d\sigma_R}{d\Omega} \right)_i = G_{SERS}^i F_R^i
\]

(S7.2)

where \(F_R^i\) is the term depending on the Raman scattering cross section of the Raman reporter \(i\) and \(G_{SERS}^i\) is the SERS enhancement factor due to the plasmonic substrate. Therefore \(G_{SERS}^i\) accounts for the actual local electric field \(E_{loc}\) probed by each molecule on the metal surface during the Raman measurement and depends on the structure of the nanoparticle and on the localization of the Raman reporter. From equation S7.2 it is clear that the Raman intensity can not be compared only by looking at the enhancement factor, but one must consider also the Raman scattering cross section of the single Raman reporters and the summation over all the Raman reporters hosted in the label.

The \(d\sigma_R/d\Omega\) of ordinary organic molecules in far-from-electronic-resonance conditions is of the order of \(10^{-32} - 10^{-30}\) \(\text{cm}^2/\text{sr}\), but it can be as high as \(10^{-24}\) \(\text{cm}^2/\text{sr}\) for some dyes in case of resonant Raman scattering.\(^{28}\) In close to resonance conditions the only relevant contributions are those corresponding to the transition from the ground to the excited electronic state. Therefore, for a vibrational mode with energy \(\omega_{FI}\), we can express \(F_R^i\) by the following simplified expression:\(^{29-32}\)

\[
F_R^i \approx K \left( \frac{\omega_c - \omega_{FI}}{\omega_{FI}} \right)^4 \left( \left| \frac{\langle F | v' \rangle \langle v' | I \rangle}{\langle F | v' \rangle \langle v' | I \rangle} \right|^2 \right) \left( \frac{\omega_c - \omega_e}{1 - \exp \left( -\frac{\hbar \omega_{FI}}{k_B T} \right)} \right)^4 \left( \frac{\omega_c - \omega_e}{1 - \exp \left( -\frac{\hbar \omega_{FI}}{k_B T} \right)} \right)^4 + \Gamma^2 \right)^2
\]

(S7.3)

where \(\omega_c\) is the frequency of the incoming excitation photons; \(\omega_{ge}\) is the frequency of the transition from the vibrational state \(I\) of the ground electronic state \(g\) to the vibrational state \(v'\) of the excited electronic state \(e\); \(F\) is the final vibrational state of the anelastic scattering process; \(\langle F | v' \rangle\) and \(\langle v' | I \rangle\) are the Franck-Condon overlap amplitudes; \(\Gamma\) is the damping term of the electronic transition; \(k_B\) is the Boltzmann constant; \(T\) is the temperature and \(K\) contains all the other constant terms. It is worth to point out that the second term of equation S7.3 is a lorentzian with a maximum where the
laser excitation wavelength equals the electronic resonance, and therefore it can be approximated as:

\[ F \approx K' \frac{l}{(\omega_{se} - \omega_h)^2 + \Gamma^2} \]  

(S7.4)

where \( \omega_h \) is the frequency of the incoming excitation photons, \( \omega_{se} \) is the frequency of the transition from the vibrational state \( I \) of the ground electronic state \( g \) to the vibrational state \( v' \) of the excited electronic state \( e \), \( \Gamma \) is the damping term of the electronic transition and \( K' \) is a factor accounting for the other quantum-mechanical terms characteristic of the molecule.

Bibliography.


