Raman Energy Density (RED) in the Context of Acousto-Plasmonics

José Luis Montaño-Priede,†,§ Adnen Mlayah,‡,¶ and Nicolas Large*,†

†Department of Physics and Astronomy, The University of Texas at San Antonio, San Antonio, Texas 78249, United States
‡Centre d’Elaboration de Matériaux et d’Etudes Structurales (CEMES), CNRS and Université Paul Sabatier - Toulouse III, 31055 Toulouse, France
¶Laboratoire d’Analyse et d’Architecture des Systèmes (LAAS), CNRS and Université Paul Sabatier - Toulouse III, 31031 Toulouse, France
§Current address: Department of Electricity and Electronics, FCT-ZTF, UPV-EHU, Bilbao, 48080, Spain

E-mail: nicolas.large@utsa.edu

Abstract

Interactions between elementary excitations such as plasmon-exciton and plasmon-phonon are of great interest from a fundamental point of view and for novel applications. While plasmon-exciton have been extensively studied both experimentally and theoretically, the interaction mechanisms between acoustic vibrations (phonons) and localized surface plasmons (LSPs) remain quite unexplored. In this work, we present a newly developed theoretical framework for the investigation of the interactions between confined acoustic vibrations and LSPs involved in resonant acoustic phonon Raman scattering. We express the Raman scattering process in the framework of the Fermi’s golden rule and introduce for the first time the concept of Raman energy density (RED). Similarly to the Raman-Brillouin electronic density (RBED) introduced...
for semiconductors, this new physical quantity is used as a theoretical tool for the interpretation of resonant Raman scattering mediated by LSPs in metallic nanoparticles. The RED represents the electromagnetic energy density excited by the Raman probe and modulated by the acoustic vibrations of the nanoparticle. We show that, similarly to the local density of optical states (LDOS) and the RBED, the RED can be mapped in the near-field region, which provides a clear picture of the interaction between LSPs and acoustic vibrations giving rise to inelastic scattering measurable in the far-field. Here, we use the newly introduced RED concept to investigate elastic (an)isotropy effects and extract the Raman selection rules of spherical nanoparticles embedded in a dielectric environment.

**Keywords**

Acousto-plasmonics, Raman scattering selection rules, Fermi’s golden rule, Raman energy density (RED), Localized surface plasmons (LSPs), Acoustic phonons

**Introduction**

It is widely known that the localized surface plasmon (LSP) properties of metallic nanostructures are governed by their size, composition, shape, environment, and interaction with neighboring nano-objects. Thanks to this, LSPs have proven to be very valuable for the realization of many applications, such as optoelectronic devices, sensors, detectors, communication devices, to name a few. In the past decade, a great deal of effort has been made to improve the performance of these plasmonic-based applications. One strategy has been to couple LSPs to other types of elementary excitations, including photonic modes, magnetic modes, and excitons. To date, this strategy has been very successful as it led to the emergence of new fundamental concepts and new technological applications.
Most of the studies focusing on metallic nanoparticles (NP), their plasmonic properties, and technological applications, consider them as static bodies at rest. However, LSPs can be temporarily modulated by acoustic vibrations, also known as acoustic phonons, naturally present in the nanomaterial and surrounding environment due to thermal effects. Very recently, there has been a renew of interest on the modulation effect of the localized surface plasmon resonances by (opto)mechanical modes and elastic waves. Such high frequency (GHz-THz) modulation can be used to increase detection and sensing accuracy of nanoscale objects such as molecules. For instance, these vibrating nanoparticles, acting as simple optomechanical nanoresonators, can be seen as nanoscale analogs to quartz crystal microbalances. Another work by Yoo et al. showed that epsilon-near-zero (ENZ) cavities can be used to achieve ultra-strong coupling between ENZ gap plasmon modes and optical phonons. Acoustic phonons Raman scattering has been shown to be a very effective, high precision, and non-invasive technique for nanometerology. It uses the acoustic vibrations, i.e., coherent movements of atoms, as local probes to determine sizes and distances at the nanoscale with very high accuracy. However, the effectiveness of this technique is directly related to the knowledge of the interaction mechanism between electrons (plasmons) and phonons (acoustic vibrations). Therefore, it is necessary to know what are the vibrational modes sustained by a given nanostructure (amplitude, frequency, symmetry) and know how they will interact with the LSPs to completely determine the Raman selection rules.

Here, we focus on the investigation of the dynamical properties of metallic nanoparticles by considering the interaction between acoustic vibrations and localized surface plasmons. The dynamical properties of LSPs are responsible for the transient optical absorption modulation, that can be observed in time-resolved transient absorption experiments, and for the acoustic SERS effect.

The study of the acousto-plasmonic properties gives unprecedented insight into the fundamental interactions between elementary excitations at the nanoscale and opens up new ways to probe the mechanical properties of nanoscale objects using optical spectroscopy.
Particularly, the acouto-plasmonic interaction in metallic nanoparticles has been studied in low-frequency Raman scattering experiments, in the 2 to 50 cm$^{-1}$ spectral region, where light is scattered by acoustic vibrations in the nanostructure. Acousto-plasmonic-driven Raman scattering can be described in three steps: i) incident photon absorption, ii) phonon emission or absorption by the lattice, and iii) scattered photon emission. The photon-phonon interaction is not direct, but rather occurs via the acousto-plasmonic coupling, i.e., photon-electron-phonon interaction. This interaction results in the direct modulation of the plasmon by the acoustic vibration, which we have previously theoretically studied. When the metal nanostructure is optically excited close to its LSP resonance, it leads to a strong acousto-plasmonic interaction. Similarly to the concept of near-electric-field hot spots in plasmonic nanostructures, the sites where acoustic vibrations produce large modulations of the plasmon-induced localized electric field at the nanostructure surface are called acousto-plasmonic hot spots.

In this work, the resonant Raman scattering process is described using a new approach based on a single direct acousto-plasmonic interaction process described by the Fermi’s golden rule. Within this framework, we introduce a new physical quantity, namely the Raman energy density (RED). Similarly to the Raman-Brillouin electronic density (RBED) introduced in semiconducting nanostructures, the RED allows us to study and monitor the acousto-plasmonic Raman scattering in the near-field. We modeled the acousto-plasmonic interaction by implementing vibration dynamics calculations (resonant ultrasound method, RUS) into electrodynamics calculations (discrete dipole approximation, DDA). We use this methodology to compute the acoustic phonons Raman spectra and investigate the interaction of the LSPs with isotropic and anisotropic acoustic vibrations, thus leading to the full determination of Raman selection rules. We show that the RED, which can be mapped in the near-field for each vibration mode, correlates the far-field Raman scattering to the local acousto-plasmonic hot-spots, provides a better understanding of the Raman scattering process including the Raman selection rules, and serves to study the plasmon-acoustic coupling
of complex nanostructures and plasmonic molecules.\textsuperscript{32,47,48}

\section*{Theoretical Formalism}

\subsection*{Raman Energy Density (RED)}

Fermi’s golden rule provides the rate at which atomic or electronic transitions take place between two states; the initial and final states are described by the wave functions $\varphi_{i(f)}$.\textsuperscript{49} Here, it provides the probability of transition per unit time associated with the Raman scattering process and is expressed as

\begin{equation}
\mathcal{R}_{fi}^{(1)} = \frac{2\pi}{\hbar} |\langle \varphi_f | H_{\text{int}}^0 | \varphi_i \rangle|^2 \delta(\omega_{fi} - \omega_{ex}),
\end{equation}

where $\omega_{fi} = \omega_f - \omega_i$ is the transition frequency between the initial and final plasmonic states \textit{(i.e., before and after the absorption/emission of the vibration)}, $\omega_{ex}$ is the incident optical wave frequency, $\delta(\omega_{fi} - \omega_{ex})$ is the density of final states, $\langle \varphi_f | H_{\text{int}}^0 | \varphi_i \rangle$ is the matrix element for the acousto-plasmonic interaction, and $H_{\text{int}}^0$ is the time-independent Hamiltonian.

We now consider dipolar transitions between LSP states. In the absence of any vibration \textit{(i.e., nanoparticle at rest)}, no transition can occur since the LSP states form a set of orthogonal eigenstates. When the nanoparticle vibrates, the LSP polarization vector is modulated, thus enabling transitions between LSP states.\textsuperscript{40} The interaction matrix elements between the confined acoustic vibrations and the LSP states, can be expressed as\textsuperscript{27}

\begin{equation}
\langle \varphi_f | H_{\text{int}}^0 | \varphi_i \rangle = - \int E_f(r) \cdot \delta_{\text{vib}} \mathbf{P}_i(r) dV,
\end{equation}

where $\mathbf{P}_i(r)$ is the polarization induced by the LSP excited by the Raman probe (initial LSP state) and modulated by confined acoustic vibrations ($\delta_{\text{vib}} \mathbf{P}_i$) and $E_f(r)$ is the local electric field associated with the final LSP state which gives rise to the scattered light experimentally.
detected. Using this interaction matrix element we can rewrite equation 1 as

\[ \mathcal{R}_{fi}^{(1)} = \frac{2\pi}{\hbar} \left| - \int \mathbf{E}_f(r) \cdot \delta_{\text{vib}} \mathbf{P}_i(r) dV \right|^2 \delta(\omega_{fi} - \omega_{\text{ex}}). \]  

(3)

We introduce and define the Raman energy density (RED) as \( \mathcal{U}_R(r, \omega_i, k_i, \omega_f, k_f) \equiv -\mathbf{E}_f(r) \cdot \delta_{\text{vib}} \mathbf{P}_i(r) \), which allows us to express the transition rate (equation 3) as

\[ \mathcal{R}_{fi}^{(1)} = \frac{2\pi}{\hbar} \left| \int \mathcal{U}_R(r, \omega_i, k_i, \omega_f, k_f) dV \right|^2 \delta(\omega_{fi} - \omega_{\text{ex}}), \]  

(4)

The RED is a complex local energy density that gives rise to the Raman scattering. It contains the excitation, interaction, and emission steps of the Raman scattering process and is expressed in J/m³. It is important to note that there are two fundamental differences between the RED introduced here and the RBED previously introduced for semiconducting nanostructures. First, the RED combines electric fields and polarizations into a product homogeneous to an energy density while the RBED considers electronic wavefunctions to give an effective electronic density. Second, contrary to its semiconductor analog, the RED includes the vibrational component through \( \delta_{\text{vib}} \mathbf{P}_i(r) \).

The RED can be divided into two different contributions and expressed as

\[ \mathcal{U}_R(r, \omega_i, k_i, \omega_f, k_f) = -\epsilon_0 \delta_{\text{vib}} \chi(r) \mathbf{E}_f(r) \cdot \mathbf{E}_i(r) - \epsilon_0 \chi(r) \mathbf{E}_f(r) \cdot \delta_{\text{vib}} \mathbf{E}_i(r), \]  

(5)

where \( \mathbf{E}_i(r) \) and \( \mathbf{E}_f(r) \) are the local electric fields associated to the LSP before and after the interaction with the acoustic vibrations, respectively. \( \chi \) is the electric susceptibility of the metallic nanoparticle and is defined here using the Drude model:

\[ \chi(\omega_{\text{ex}}, R) = \chi^{\text{ib}}(\omega_{\text{ex}}) - \frac{\omega_p^2}{\omega_{\text{ex}}^2 + i\omega_{\text{ex}} \gamma(\omega_{\text{ex}}, R)}, \]  

(6)

where \( \omega_p = \sqrt{n_e e^2/\varepsilon_0 m_e} \) is the bulk plasma frequency of the metal and \( \chi^{\text{ib}} \) is the interband electric susceptibility, which is size-independent. \( \chi \) is dependent on the nanoparticle radius,
$R$, through the size-corrected Drude damping $\gamma(\omega_{ex}, R) = \gamma_0 + g_S(\omega_{ex})v_F/R$, where $\gamma_0$ is the effective Drude damping, $g_S$ is obtained from a quantum treatment of the electron-surface interaction, and $v_F$ is the Fermi velocity.

**Volume Mechanism**

The first term in equation 5 is called the deformation potential coupling mechanism or volume mechanism. It describes the modulation of the electric susceptibility by the acoustic vibrations through $\delta_{\text{vib}}\chi(r)$. A change in a nanoparticle volume results in a change in the electronic band structure via the deformation potential. This particular mechanism has been the subject of a recent study by Saison-Francioso et al., which focused on the computational study of shape effect, electron density effect due to changes of the nanoparticle volume, and interband transition effects though the deformation potential mechanism. The effect of the electric susceptibility modulation on the intraband transitions is negligible in the visible range (where the LSP is located) because their excitations are in the infrared range. Whereas, the interband transition modulation contributes to the volume mechanism as they occur in the UV range, close to the LSP. The volume mechanism term is described as

$$
\mathcal{U}^{\text{VM}}_R(r) = -\epsilon_0\chi(r) \left[ \frac{V_{\text{DP}}}{\hbar\omega_{ex} - \hbar\omega_{\text{ib}}} \nabla \cdot \mathbf{u}(r) \right] \mathbf{E}_f(r) \cdot \mathbf{E}_i(r),
$$

where $\hbar\omega_{\text{ib}}$ is the interband transition threshold, $V_{\text{DP}}$ is the deformation potential, and $\nabla \cdot \mathbf{u}$ is the divergence of the displacement field $\mathbf{u}$ obtained from the elastodynamic calculations.

**Surface Mechanism**

The second term in equation 5 corresponds to the surface orientation coupling mechanism. Contrary to the volume mechanism, the surface mechanism is the dominant contribution to the Raman scattering process in metals. As it is well known, the LSP modes strongly depend on the shape of the nanoparticle. Therefore, the polarization induced by the LSP at the surface of the metallic nanoparticle experiences a modulation induced by the acoustic
vibrations, which are able to induce a change in the NP shape. A simple approximation to account for this surface orientation mechanism consists in a geometrical framework making use of the geometric factors (often called depolarization factors) in the nanoparticle polarizability tensor. However, in our work, we rigorously describe the surface mechanism in terms of the difference between the polarization vectors of the final and initial LSP states as

\[ U_{SM}^R(r) = -\varepsilon_0 \chi(r) E_f(r) \cdot [E_f(r) - E_i(r)] , \]

where we used \( P_{i(f)}(r) = \varepsilon_0 \chi(r) E_{i(f)}(r) \).

**Raman Scattering Spectrum**

The acoustic Raman scattering spectrum from a metallic nanoparticle, derived from Fermi’s golden rule for the acousto-plasmonic coupling (equation 4), is expressed as

\[ I_{Raman} = \sum_{vib} \frac{2\pi}{\hbar} \left| \int U_{R}^{vib}(r)dV \right|^2 \frac{\Gamma_{vib}}{(\hbar \omega_{ex} - \hbar \omega_{vib})^2 + (\Gamma_{vib}/2)^2} \cdot \frac{1}{e^{(\hbar \omega_{vib}/k_B T)} - 1} , \]

where the summation runs for all the acoustic vibration modes. \( U_{R}^{vib}, \Gamma_{vib}, \) and \( \omega_{vib} \) are the RED, spectral linewidth, and eigenfrequencies, respectively, of each acoustic vibration mode. The density of states \( \delta(\omega_{fi} - \omega_{ex}) \) is defined by an homogeneous peak broadening factor, described by a Lorentz distribution, and the Bose-Einstein population factor for the anti-Stokes process.

Therefore, integrating the local Raman energy density yields the far-field low-frequency Raman scattering spectrum from the plasmonic nanoparticle coupled to acoustic vibrations.
Computational Model and Methods

Computational Model

In order to demonstrate and illustrate the concept of RED, we have calculated the RED and computed the Raman spectrum of a free-standing Au spherical NP of radius $R = 2.5$ nm (Figure 1a), immersed in water (refractive index $n = 1.333$), and optically exited at its LSP resonance (LSPR, $\lambda_{ex} = 520$ nm, Figure 1). The incident optical excitation is a plane wave of unitary amplitude, polarized in $y$-direction, and traveling along the $x$-direction.

It is important to notice that, in our model, we neglect any mechanical interactions between the NP and the surrounding aqueous medium. However, note that for more rigid matrices, the mechanical coupling between the environment and the nanoparticle may need to be taken into consideration. Furthermore, the heat generated by the NP under optical excitation that could change the vibration frequencies and/or the LSPR have been found to be negligible and are, therefore, also neglected in our model.

Elastodynamics: Resonant Ultrasound Spectroscopy (RUS) Method

First, the displacement vector field $u(r)$ associated with each acoustic vibration mode is calculated assuming an elastic continuous medium and using the resonant ultrasound spectroscopy (RUS) method proposed by Visscher et al. to solve the Navier-Stokes hydrodynamic equations. RUS uses the longitudinal and transverse sound velocities in the metal and expands the displacement vectors onto a basis $\Phi_\zeta = x^i y^j z^k$, where $\zeta = (i, j, k)$ is the function label. Here, we used $0 \leq i + j + k \leq 20$ in order to achieve a good numerical convergence. All the eigenmodes obtained in RUS are orthonormalized. The values used for the Au density ($\rho$), longitudinal and transverse sound velocities ($v_L$ and $v_T$, respectively), and Poisson’s ratio ($\nu$) are provided in Table 1.
Figure 1: Absorption spectrum of a 5 nm Au NP in water calculated using DDA showing the dipolar LSPR located at 520 nm. Inset: 3D color map and cross-sectional plane (001) of the near electric field induced by the dipolar LSP at 520 nm.

**Electrodynamics: Discrete Dipole Approximation (DDA)**

Once the vibration modes have been calculated in RUS, we use the discrete dipole approximation (DDA; DDSCAT v7.3 package)\textsuperscript{46} to calculate the local electric field at the LSPR for the particle at rest (initial state) and the nanoparticle deformed by the different acoustic vibration modes (final states). In all the DDA simulations, we used an interdipole distance $d = 0.03$ nm to discretize the nanoparticle and obtain a good numerical convergence; the total number of dipoles within the nanoparticle volume ranges from $2.4 \times 10^6$ to $4.2 \times 10^6$. The physical parameters used for gold and used in equation \textsuperscript{6} are provided in Table 1.

Table 1: Gold parameters used for the RED and Raman spectrum calculations.
| Parameter   | Value       | Reference |
|-------------|-------------|-----------|
| $\chi^{ib}$ | J&C database | 54        |
| $\hbar\omega_p$ | 9.01 eV | 55        |
| $\gamma_0$  | 0.07 eV    | 55        |
| $g_S v_F$   | 0.915 eVnm | 55        |
| $V_{DP}$    | -0.8 eV    | 56        |
| $\hbar\omega^{ib}$ | 2.4 eV | 55        |

| Parameter   | Value       | Reference |
|-------------|-------------|-----------|
| $\rho$      | 19,700 kg/m$^3$ | 51        |
| $v_L$       | 3240 m/s   | 51        |
| $v_T$       | 1200 m/s   | 51        |
| $\nu$       | 0.42       | 51        |

Results and Discussions

Acoustic Vibrations

To compute the Raman scattering spectrum of a Au NP undergoing acoustic vibrations and the RED associated with each of these vibrations, we first calculate the surface displacements of a free-standing, homogeneous, isotropic, and elastic Au nanosphere induced by the acoustic vibration modes. In Lamb’s original paper, the acoustic vibration modes were classified into torsional and spheroidal modes.$^{57}$ Torsional modes do not induce any change in the materials density, which implies that the divergence of the displacement is $\nabla \cdot \mathbf{u} = 0$, thus leading to $U_{R}^{VM} = 0$. Moreover, because of the absence of shape change induced by such modes, we also have $U_{R}^{SM} = 0$. Therefore, because they do not contribute to either the surface or the volume mechanism, these torsional modes are Raman inactive and will thus be neglected in this work. On the other hand, spheroidal modes induce changes in the NP shape and/or volume. These modes are labeled $S_{n\ell m}$; where $n$, $\ell$, and $m$ denote the harmonic ($n = 1$ being the fundamental), the angular momentum number, and its $z$-component, respectively. The vibrational density of states is discrete and the mode eigenfrequencies are given by $\omega_{n\ell m}[\text{cm}^{-1}] = \xi_{n\ell m} v_L / 2R$, where $\xi_{n\ell m}$ is a mode-dependent coefficient.$^{51}$ Figures 2 and S1 show the surface displacements associated with the fundamental breathing mode ($S_{100}^1$; Figure 2b).
and the five-fold degenerated fundamental quadrupole modes ($S_{2m}^1$ with $m = 0, \pm 1, \pm 2$; Figure 2f-g).

Because gold exhibits a strong elastic anisotropy, we have also calculated the surface displacements associated with the six equivalent breathing and quadrupolar vibration modes from an anisotropic Au nanosphere. The irreducible representations of the anisotropic vibration modes have been determined based on the $O_h$ point group character table.$^{58}$ As a result of the elastic anisotropy, the spheroidal breathing modes transform into an $A_{1g}$ vibration (Figure 2h). Similarly, the anisotropy induces a partial degeneracy lift of the five-fold spheroidal quadrupolar mode which splits into two $E_g$ (Figure 2i-j) and three $T_{2g}$ (Figure 2k-m) degenerated vibrations; the latter can be projected onto spheroidal Lamb modes.$^{58}$

![Figure 2: (a) Au NP at rest. Top: NP deformed by the isotropic breathing $S_{00}^1$ ($d_0$) mode (b) and the five-fold degenerated quadrupole $S_{2m}^1$ ($d_1 - d_5$) vibration modes (c-g). Bottom: NP deformed by the anisotropic breathing $A_{1g}$ mode (h), the quadrupole $E_g$ ($E_{g(a)}$ and $E_{g(b)}$) modes (i-j), and the quadrupole $T_{2g}$ ($T_{2g(a)}$, $T_{2g(b)}$, and $T_{2g(c)}$) vibration modes (e-g).]
Table 2: Eigenfrequencies of the isotropic and anisotropic vibration modes calculated using RUS and compared to analytic results from Lamb theory.

| Mode | Frequency (cm⁻¹) | Mode | Frequency (cm⁻¹) | Mode | Frequency (cm⁻¹) |
|------|-----------------|------|-----------------|------|-----------------|
| $S_{00}^1$ | 20.8 | $d_0$ (Fig. 2b) | 20.8 | $A_{1g}$ (Fig. 2h) | 20.7 |
| $S_{20}^1$ | 7.1 | $d_1$ (Fig. 2c) | 7.1 | $E_g(a)$ (Fig. 2i) | 5.0 |
| $S_{2±1}^1$ | 7.1 | $d_2$ (Fig. 2d) | 7.1 | $E_g(b)$ (Fig. 2j) | 5.0 |
| $S_{2±1}^1$ | 7.1 | $d_3$ (Fig. 2e) | 7.1 | $T_{2g(a)}$ (Fig. 2k) | 8.0 |
| $S_{2±2}^1$ | 7.1 | $d_4$ (Fig. 2f) | 7.1 | $T_{2g(b)}$ (Fig. 2l) | 8.0 |
| $S_{2±2}^1$ | 7.1 | $d_5$ (Fig. 2g) | 7.1 | $T_{2g(c)}$ (Fig. 2m) | 8.0 |

The eigenfrequencies and the labels we use for each vibration are presented in Table 2. Because of the weak mechanical coupling between the nanoparticle and the surrounding aqueous environment, the nanoparticle can be considered as free and its acoustic vibration eigenfrequencies can be considered environment insensitive. Therefore, we also compare their eigenfrequencies obtained using RUS to analytical results from Lamb theory (Table 2).

It is clear from Figure 2 that the directions of maximum deformation are mode-dependent. The isotropic breathing mode ($d_0$) is isotropically deformed in all directions due to its pure radial nature, thus preserving a spherical symmetry throughout the vibration period (Figure 2b). On the other hand, the anisotropic breathing mode ($A_{1g}$) has maximum deformations in the [100] directions, i.e., along the x-, y-, and z-directions, thus resulting in a breaking of the spherical symmetry (Figure 2h). For the sake of presentation, we have chosen a cross-sectional plane of the NP associated to each vibration mode which contains the direction of maximum deformation. Figure S1 in the Supporting Information shows the aforementioned cross-sectional planes of the surface displacements of a Au NP for each isotropic (blue line) and anisotropic (red line) vibration modes relative to the NP at rest (black line). These planes of maximum deformation are also chosen to contain the polarization direction (y-direction) of the optical excitation used in the electrodynamic calculations. Although more pronounced for the breathing modes (Figure S1a, Supporting Information),
the difference on the surface deformations between isotropic and anisotropic vibration modes are clearly visible in Figure S1.

**Plasmonic Near-Field**

In order to compute the RED, we have calculated the near electric field (NEF) of the Au NP at rest excited at its LSPR with a plane wave propagating in the $x$-direction and polarized in the $y$-direction ($i.e.$, initial state). The inset in Figure 1 shows the NEF spatial distribution at the surface of the NP and in the (001) plane ($xy$-plane); it clearly shows the dipolar nature of the LSP and a maximum electric field enhancement, $|E/E_0|$, of approximately 5.

Figure 3 shows the NEF spatial distributions on the surface of the NPs deformed by each acoustic vibration mode as well as in the cross-sectional planes of maximum deformation. As we discussed earlier, this figure shows how the near electric field is distinctively and spatially modulated by each individual vibration mode. However, it is important to notice that the amplitude of the modulation depends on the mode. This, will ultimately reflect on the intensity of the mode in the Raman spectrum as we will discuss further. Dynamic NEF modulations for all these acoustic vibration modes are shown in NEF-ISO.avi and NEF-ANISO.avi, Supporting Information.

The NEF distribution of the Au NP deformed by the isotropic breathing mode (Figure 3b) does not appear to change in comparison with the NEF of the NP at rest (Figure 3h). This absence of modulation from the isotropic breathing mode is due to (i) the conservation of the spherical symmetry and (ii) the size change smaller than the applied wavelength leading to negligible retardation effects. Therefore, the surface mechanism contribution to the RED will be negligible according to equation 8. On the other hand, the anisotropic breathing mode (Figure 3a) appears to have the largest electric field enhancement between the analyzed modes due to the highest localization of surfaces charges at the NP poles (along the $y$-direction). The same occurs for the $d_1$ and $E_{g(a)}$ vibration modes (Figure 3c,i) where the deformation of the NP is also along the applied electric field yielding a little
Figure 3: 2D and 3D spatial distributions of the near electric field induced by the dipolar localized surface plasmon and modulated by the isotropic (top) and anisotropic (bottom) vibration modes. The cross-sections are taken where the maximum deformation is located; the corresponding \((xyz)\) planes are indicated in each panel. (a) NP at rest, (b) isotropic breathing \(S^{1}_{00}\) \((d_{0})\) mode, (c-g) five-fold degenerated isotropic quadrupoles \(S^{1}_{2m}\) \((d_{1}-d_{5})\), (h) anisotropic breathing \(A_{1g}\) mode, (i,j) anisotropic quadrupole \(E_{g}\) \((E_{g(a)}\) and \(E_{g(b)}\)\) modes, and (k-l) anisotropic quadrupole \(T_{2g}\) \((T_{2g(a)}, T_{2g(b)}, \text{and } T_{2g(c)})\) modes.
more enhancement compared to the NP at rest. For the other modes, the electric field enhancement is imperceptibly changed because the surface displacements of the vibrating NP occur in directions other than that of the applied electric field polarization. Figure S2 in the Supporting Information also shows the NEF enhancement spatial distributions in the planes of maximum deformation, where the Δ-axis refers to the dimension of the specific plane (for example, Δ-axis is equivalent to x-axis for the (001) plane).

**Raman Energy Density (RED)**

We have calculated the partial RED associated with the surface and volume mechanisms as well as the total Raman energy density (in neV/nm³) for each isotropic and anisotropic vibration modes using equations 8, 7, and 5, respectively. It should be noted that the spatial region between the nanoparticle at rest and deformed surface was not considered and set to zero due to the lack of physical realism. Indeed, the surface location cannot be defined with a precision better than the inter-dipole spacing in the DDA simulations.

Figure 4 displays the spatial distribution maps of the real part of $U_{SM}^R$, $U_{VM}^R$, and $U_R$ for the isotropic (Figure 4a-c) and anisotropic (Figure 4d-f) breathing modes. These maps show the extent of the coupling between the acoustic vibrations and the dipolar localized surface plasmon yielding inelastic light scattering in and around the NP. These maps represent the acousto-plasmonic local source of the Raman scattering measured in the far-field. The partial RED associated with deformation of the NP surface ($U_{SM}^R$) of the $d_0$ mode is localized only on the NP surface, there is no acousto-plasmonic coupling inside the NP. When anisotropy is included (A$_1g$ mode) the $U_{SM}^R$ not only is enhanced due to the localization of the plasmon mode at the deformed surface, but also due to the acousto-plasmonic coupling occurring inside the NP. On the other hand, $U_{VM}^R$ shows a radially increasing acousto-plasmonic coupling from the surface to the center of the NP mainly induced by the larger expansion (or compression) inside the NP than under the surface in both isotropic and anisotropic cases (see Figure S3, Supporting Information). This result is also in agreement with the local
volume variations of the dielectric permittivity produced by the NP vibration modes, which has been recently predicted by Saison-Francioso et al.\textsuperscript{21}

Figure 4: Real part of the surface $U_R^{SM}$ (a,d), volume $U_R^{VM}$ (b,e), surface+volume $U_R$ (c,f) components of the RED associated with the isotropic (a-c) and the anisotropic (d-f) breathing modes.

When looking at the total RED ($U_R$, Figure 4c,f), it is clear that it is more spatially localized in the case of $A_{1g}$ than for $d_0$. These RED hot-spots correspond to regions where the NP exhibits simultaneously a strong surface deformation (from the vibration) and a strong induced local electric field (from the LSP). Nevertheless, it is important to notice that the Raman activity of each acoustic vibration mode is obtained by spatial integrating the RED (see equation 9). As a result of this spatial integration, the positive and negative quantities will cancel each other out, thus leading to a decrease or complete cancellation of the Raman response, even if some RED hot spots are present. Based on this observation, the $d_0$ mode is expected to lead to larger Raman efficiency than the $A_{1g}$ mode because there is no negative contribution to the RED for the former mode.

The same analysis applies for the other isotropic and anisotropic modes. Figure 5 shows the total RED, $U_R$, calculated for each isotropic and anisotropic mode. The two RED components $U_R^{SM}$ and $U_R^{VM}$ of the same modes are presented in Figure S4 in the Supporting
Information. For most of the five-fold degenerated quadrupolar modes, the contribution of the $U_{SM}^R$ in the total RED is bigger than $U_{NM}^R$ for both isotropic and anisotropic cases. Nevertheless, as discussed above, cancellation of the negative and positive contribution to the RED lead to lower Raman efficiency for the $A_{1g}$ displacement. As for example, it could be expected that the contribution of the $d_3$, $d_4$, and $d_5$ modes (see Figure 5d-f) to the Raman spectrum will be low, also for $T_{2g}$ modes (see Figure 5j-l). On the other hand, it is also expected that the contribution of the $d_1$ and $E_{g(a)}$ modes will be large due to their high RED intensity inside the NP (most for the $U_{SM}^R$ contribution, see the center panels in Supporting Information Figure S4b). Although $d_2$ and $E_{g(b)}$ modes have positive values (Figure 5c and 5i, respectively), their contribution to their Raman spectrum is expected to be low due to their weak RED values.

**Acoustic Raman Spectra**

Figure 6a-c shows the components to the Raman spectrum associated with each isotropic vibration mode and considering the surface and volume mechanisms as well as the sum of the two mechanisms, respectively. We can see that the $d_1$ mode gives the strongest Raman response because its maximum displacement is parallel to the incident electric field polarization. On the other hand, $d_0$ and $d_2$ have very weak contributions through the surface mechanism because the former leads only to small changes of the NP shape and the latter exhibits the maximum deformation in the direction perpendicular to the incident electric field polarization. The only mode that leads to a strong contribution though the volume mechanism, and consequently to the Raman efficiency, is the $d_0$ mode. When the NP undergoes a $d_0$ mode, it experiences a global expansion (or compression) unlike the other modes, which on the contrary experience simultaneous compression and expansion at different locations on the NP surface (see center panel Figure S4, Supporting Information), and thus resulting in the destruction of the Raman signal.

On the other hand, the components to the Raman spectrum associated with each anisotropic
vibration mode and considering the surface and volume mechanisms as well as the sum of the two mechanisms are presented in Figure 6d-f, respectively. Similarly to the isotropic case, the quadrupolar modes produce a strong Raman signal through the surface mechanism while the breathing mode contribute through the volume mechanism. However, a few differences can be noticed: the $T_{2g}$ modes Raman peaks are shifted to higher energy and less intense than the isotropic counterparts $d_3$, $d_4$, and $d_6$ due to the difference between their sound velocities.

As a consequence, the Raman spectrum of an isotropic Au NP has principally two peaks, which correspond to the acousto-plasmonic coupling of the 5-fold degenerated quadrupolar vibration modes via surface mechanism and of the breathing mode via the volume mecha-
Figure 6: Raman spectra calculated using equation $9$ for the surface (a,d), volume (b,e), and both (c,f) mechanisms of the isotropic (a-c) and anisotropic (d-f) vibration modes.

The Raman spectrum of an anisotropic Au NP has three peaks. The two lower energy peaks are due to the quadrupolar $E_g$ and $T_{2g}$ modes coupled to the localized surface plasmon via the surface mechanism while the higher energy peak is due to the breathing $A_{1g}$ mode which is Raman active via the volume coupling mechanism (see Figure 7 red spectrum). As previously discussed, the positive and negative contributions of the RED associated with the anisotropic breathing mode cancel each other out, thus leading to a decrease the Raman intensity. This results in a more intense $d_0$ mode as compared to the $A_{1g}$ mode. As for the quadrupolar modes, it is important to note that we do recover the intensity relationship between the isotropic and anisotropic modes. Indeed, the sum of the intensities of the isotropic quadrupolar modes (i.e., $\sum_{k=1}^{5} d_k$) is equal to the sum of the intensities of the anisotropic quadrupolar modes (i.e., $\sum_{k=a}^{c} E_{g(k)} + T_{2g(k)}$), with a relative error of $1.5 \times 10^{-3}$. In both the isotropic and anisotropic cases, the quadrupolar $d_1$ and $E_{g(a)}$ modes are the most intense as previously discussed. These results are in excellent quanti-
Figure 7: Total Raman spectra calculated using equation 9 for the isotropic and anisotropic modes.

...tative agreement with several experiments performed by on small Au nanoparticles. In particular, they observed a lower intensity of the \( T_{2g} \) modes as compared to the \( E_g \) modes, which is what our theoretical approach predicts (Figure 7 red spectrum). Once again, the difference in intensity between these two anisotropic quadrupolar mode symmetries is found in the RED components. As it can be seen in Figure 5 the real parts of the RED associated with the \( T_{2g} \) modes (panels j-l) exhibit both positive and negative contributions, which will tend to cancel each other’s in equation 4. On the other hand, the real parts of the RED associated with the \( E_g \) modes (panels h-i) exhibit predominantly one either a positive or a negative contribution.

**Raman Selection Rules**

Finally, we compute the Raman spectra using equation 9 for various polarization configurations to determine the Raman selection rules. We demonstrate the contribution of each mode in the situation where an analyzer (polarization filter) parallel or perpendicular to...
Figure 8: Raman spectra calculated using equation 9 for the parallel (a,c) and cross (b,d) configurations of the isotropic (a,b) and anisotropic (c,d) modes.

The incident electric field is used before the Raman detector (Figure 8). We can see that all mode signals have slightly decreased in intensity when a parallel analyzer is used in both the isotropic and anisotropic cases. Nevertheless, when using a perpendicular analyzer (cross configuration), the breathing mode contribution becomes negligible and only a few quadrupolar contributions persist. It is well known from experiments that the breathing mode of a spherical nanoparticle is totally polarized, whereas the quadrupolar modes are only partially polarized. This can easily be understood when looking at the various RED components (Figure S4). Due to its spherical symmetry, the modulation produced by the isotropic breathing mode, through the surface mechanism, has no component perpendicular to the incident polarization (Figure S4a, top panel). However, it is important to notice that the breathing mode does not completely vanish, due to the weaker, yet contributing, volume component of the RED (Figure S4a, center panel). Conversely, the quadrupolar modes do
induce a RED with components along the incident field direction (Figure S4b-f, top). Their individual symmetries, which is given by relative orientation of the major deformation axis with respect to the incident polarization, dictates their relative Raman intensities (Figures S8 and S4). These observations are in excellent agreement with the theoretical work by Duval, which showed that for the Raman transition that excites a spherical breathing mode, the polarization of incident and scattered fields are parallel only, while they can be parallel or perpendicular for the quadrupolar modes. Our theoretical approach also explains the selections rules observed experimental by Tripathy et al. in the framework of acoustic SERS. Interestingly, we can notice that the experiments conducted by Tripathy et al. revealed a large number of harmonics for the various modes. While we limited our work to the fundamental modes ($n=1$) only, our approach can easily include harmonics as well to describe the experimental observations. With these harmonics, two important factors will impact the Raman intensity. First, the inner deformation associated with the presence of displacement nodes within the volume will directly impact the volume component of the RED. Second, the lower surface displacement amplitudes of these harmonics will be result in weaker modulation of the near electric field at the nanoparticle surface, thus directly impacting the surface component of the RED. Both of these effects lead to a decrease of the Raman scattering efficiency with increasing overtones, making them challenging to observe. While an atomistic description of the nanoparticle vibration eigenmodes is traditionally required, our RED Framework provides a new route to fully describe such high order harmonics in the acoustic Raman spectra.

**Conclusions**

We have introduced the Raman energy density (RED) as a new theoretical tool for the interpretation of resonant Raman scattering mediated by LSPs in metallic nanostructures. Analogous to the LDOS, it represents the electromagnetic energy density, in neV/nm$^3$, which
is excited by the Raman probe and modulated by acoustic vibrations of the nanostructure. It is a local quantity that can be mapped in the near-field region, thus providing a clear picture of the acousto-plasmonic interaction which gives rise to the inelastic scattering measurable in the far-field. It allowed us to calculate for the first time the Raman selection rules taking into account a surrounding medium and the modulation of the polarization in this medium. We have shown that it can predict the Raman active modes as well as the vibration modes forbidden by the Raman selection rules for both isotropic and anisotropic acoustic vibration modes; in excellent quantitative agreement with other theoretical frameworks and experiments. This new physical quantity provides significant insight about the origin of the plasmon-vibration coupling (volume vs. surface mechanisms).

It is worth noting that the framework proposed here goes well beyond plasmonic nanoparticles and is very general as it can be applied to all type of nanomaterials including semiconductors and dielectrics. For instance, dielectric nanoparticles sustain Mie resonances, which give rise to local induced electric fields. In such case, similar electrodynamic simulations can be performed and coupled to the elastodynamic calculations to compute the resulting acoustic Raman scattering spectra and associated RED. Lastly, semiconductor quantum dots can also be described using this approach. While the local electric field induced by excitons will be much weaker, leading to a small surface contribution, the volume deformation is expected to strongly modulate the electronic density of state of the quantum dot; thus leading to a strong volume contribution. Other aspects which can also be integrated into this framework is the mechanical properties of the surrounding medium, which affect the vibrational properties of the nanoparticles embedded in it. Our approach can capture, and provide insight into the mechanical and electromagnetic coupling through the RED and computed Raman spectra.

The RED constitutes a novel, unique tool for the exploration of physical effects such as acoustic SERS, vibrational transfer, vibrational hybridization, vibrational sensing, nanoscale photothermal effects and heat dissipation, and other optomechanical phenom-
ena between neighboring NPs, substrates, and surrounding medium. It constitutes a step towards the realization of nanophononic platforms capable of probing simultaneously electronic, thermal, and phononic states.

**Associated Content**

**Supporting Information**

The Supporting Information is available free of charge.

-[PDF]: (S1) Surface deformations for each vibration mode. (S2) Local electric field enhancements for each vibration mode. (S3) Divergence of the displacement for the breathing modes. (S4) Surface and volume components of the RED for each vibration mode. (S5) Mode decomposition of the Raman spectra. (S6) Mode decomposition and selection rules.

-[GIF]: Dynamic near-field modulation by the isotropic and anisotropic modes.

**Author Information**

**Corresponding author**

*Email: Nicolas.Large@utsa.edu*

**Author Contributions**

A.M. and N.L. developed the theoretical framework, J.L.M.P. and N.L. developed the computational codes and performed the computational simulations. All authors have discussed and interpreted the results, contributed to writing and editing the manuscript, and have given approval to the final version.
Notes

The authors declare no competing financial interests.

Acknowledgement

This work received financial support from the Army Research Office (ARO) under Grant Number W911NF-18-1-0439, the Office of Naval Research (ONR) under Grant Number N00014-21-1-2729, and the NanoX Grant ANR-17-EURE-0009 in the framework of the "Programme des Investissements d'Avenir". It received computational support from UTSA’s HPC cluster Shamu, operated by the Office of Information Technology. We thank Dr. Lucien Saviot from the Laboratoire Interdisciplinaire Carnot de Bourgogne at the Université de Bourgogne for the valuable and constructive discussions and for providing the RUS codes used for the calculation of the acoustic vibrations.

References

(1) Link, S.; Mohamed, M. B.; El-Sayed, M. A. Simulation of the Optical Absorption Spectra of Gold Nanorods as a Function of Their Aspect Ratio and the Effect of the Medium Dielectric Constant. J. Phys. Chem. B 1999, 103, 3073–3077.

(2) Kelly, K. L.; Coronado, E.; Zhao, L. L.; Schatz, G. C. The Optical Properties of Metal Nanoparticles: The Influence of Size, Shape, and Dielectric Environment. J. Phys. Chem. B 2003, 107, 668–677.

(3) Grady, N. K.; Halas, N. J.; Nordlander, P. Influence of Dielectric Function Properties on the Optical Response of Plasmon Resonant Metallic Nanoparticles. Chem. Phys. Lett. 2004, 399, 167–171.

(4) González, A. L.; Noguez, C. Influence of Morphology on the Optical Properties of Metal Nanoparticles. J. Comput. Theor. Nanosci. 2007, 4, 231–238.
(5) Montaño Priede, L.; Peña Rodríguez, O.; Rivera, A.; Guerrero-Martínez, A.; Pal, U. Optimizing the Electric Field Around Solid and Core–Shell Alloy Nanostructures for Near-Field Applications. *Nanoscale* 2016, 8, 14836–14845.

(6) Martinsson, E.; Shahjamali, M. M.; Large, N.; Zaraee, N.; Zhou, Y.; Schatz, G. C.; Mirkin, C. A.; Aili, D. Influence of Surfactant Bilayers on the Refractive Index Sensitivity and Catalytic Properties of Anisotropic Gold Nanoparticles. *Small* 2016, 12, 330–342.

(7) Large, N.; Abb, M.; Aizpurua, J.; Muskens, O. Photoconducively Loaded Plasmonic Nanoantenna as Building Block for Ultracompact Optical Switches. *Nano Lett.* 2010, 10, 1741–1746, Citations: 2.

(8) Doiron, B.; Mota, M.; Wells, M. P.; Bower, R.; Mihai, A.; Li, Y.; Cohen, L. F.; Alford, N. M.; Petrov, P. K.; Oulton, R. F.; Maier, S. A. Quantifying Figures of Merit for Localized Surface Plasmon Resonance Applications: A Materials Survey. *ACS Photonics* 2019, 6, 240–259.

(9) Ozbay, E. Plasmonics: Merging Photonics and Electronics at Nanoscale Dimensions. *Science* 2006, 311, 189–193.

(10) Park, D. J.; Zhang, C.; Ku, J. C.; Zhou, Y.; Schatz, G. C.; Mirkin, C. A. Plasmonic Photonic Crystals Realized Through DNA-Programmable Assembly. *PNAS* 2015, 112, 977–981.

(11) Wang, D.; Yang, A.; Hryn, A. J.; Schatz, G. C.; Odom, T. W. Superlattice Plasmons in Hierarchical Au Nanoparticle Arrays. *ACS Photonics* 2015, 2, 1789–1794.

(12) Sachan, R.; Malasi, A.; Ge, J.; Yadavali, S.; Krishna, H.; Gangopadhyay, A.; Garcia, H.; Duscher, G.; Kalyanaraman, R. Ferroplasmons: Intense Localized Surface Plasmons in Metal-Ferromagnetic Nanoparticles. *ACS Nano* 2014, 8, 9790–9798.
(13) Ge, J.; Malasi, A.; Passarelli, N.; Pérez, L. A.; Coronado, E. A.; Sachan, R.; Kalyanaraman, R. Ferroplasmons: Novel plasmons in metal-ferromagnetic bimetallic nanostructures. *Microsc. Microanal.* **2015**, *21*, 2381–2382.

(14) Schlather, A. E.; Large, N.; Urban, A. S.; Nordlander, P.; Halas, N. J. Near-Field Mediated Plexcitonic Coupling and Giant Rabi Splitting in Individual Metallic Dimers. *Nano Lett.* **2013**, *13*, 3281–3286, PMID: 23746061.

(15) Abid, I.; Chen, W.; Yuan, J.; Najmaei, S.; nafiel, E. C. P.; Péchou, R.; Large, N.; Lou, J.; Mlayah, A. Surface Enhanced Resonant Raman Scattering in Hybrid MoSe2@Au Nanostructures. *Opt. Express* **2018**, *26*, 29411–29423.

(16) Fofang, N. T.; Park, T.-H.; Neumann, O.; Mirin, N. A.; Nordlander, P.; Halas, N. J. Plexcitonic Nanoparticles: Plasmon-Exciton Coupling in Nanoshell-J-Aggregate Complexes. *Nano Lett.* **2008**, *8*, 3481–3487.

(17) Zhou, W.; Dridi, M.; Suh, J. Y.; hul Hoon Kim,; Co, D. T.; Wasielewski, M. R.; Schatz, G. C.; Odom, T. W. Lasing Action in Strongly Coupled Plasmonic Nanocavity Arrays. *Nat. Nanotech.* **2013**, *8*, 506–506.

(18) Juodénas, M.; Peckus, D.; Tamulevičius, T.; Yamauchi, Y.; Tamulevičius, S.; Henzie, J. Effect of Ag Nanocube Optomechanical Modes on Plasmonic Surface Lattice Resonances. *ACS Photonics* **2020**, *7*, 3130–3140.

(19) Oumekloul, Z.; Moutaouekkil, M.; Lévêque, G.; Talbi, A.; Mir, A.; Akjouj, A. Nanomechanical modulation cavities of localized surface plasmon resonance with elastic whispering-gallery modes. *J. Appl. Phys.* **2020**, *127*, 023105.

(20) Cunha, J.; Guo, T.-L.; Della Valle, G.; Koya, A. N.; Proietti Zaccaria, R.; Alabastri, A. Controlling Light, Heat, and Vibrations in Plasmonics and Phononics. *Adv. Opt. Mater.* **2020**, *8*, 2001225.
(21) Saison-Francioso, O.; Lévêque, G.; Akjouj, A. Numerical Modeling of Acousto-Plasmonic Coupling in Metallic Nanoparticles. *J. Phys. Chem. C* 2020, 124, 12120–12133.

(22) Girard, A.; Saviot, L.; Pedetti, S.; Tessier, M. D.; Margueritat, J.; Gehan, H.; Mahler, B.; Dubertret, B.; Mermet, A. The Mass Load Effect on the Resonant Acoustic Frequencies of Colloidal Semiconductor Nanoplatelets. *Nanoscale* 2016, 8, 13251–13256.

(23) Yoo, D.; de León-Pérez, F.; Pelton, M.; Lee, I.-H.; Mohr, D. A.; Raschke, M. B.; Caldwell, J. D.; Martín-Moreno, L.; Oh, S.-H. Ultrastrong plasmon-phonon coupling via epsilon-near-zero nanocavities. *Nat. Photon.* 2021, 15, 125–130.

(24) Cazayous, M.; Groenen, J.; Huntzinger, J. R.; Mlayah, A.; Schmidt, O. G. Spatial Correlations and Raman Scattering Interferences in Self-Assembled Quantum Dot Multilayer. *Phys. Rev. B* 2001, 64, 33306–33306.

(25) Cazayous, M.; Groenen, J.; Huntzinger, J. R.; Mlayah, A.; Schmidt, O. G.; Eberl, K. A New Tool for Measuring Island Dimensions and Spatial Correlations in Quantum Dot Multilayer: Raman Scattering Interferences. *Mat. Sci. Engin. B* 2002, 88, 173–176.

(26) Duval, E. Far-Infrared and Raman Vibrational Transitions of a Solid Sphere: Selection Rules. *Phys. Rev. B* 1992, 46, 5795–5797.

(27) Large, N.; Saviot, L.; Margueritat, J.; Gonzalo, J.; Afonso, C. N.; Arbouet, A.; Langot, P.; Mlayah, A.; Aizpurua, J. Acousto-Plasmonic Hot Spots in Metallic Nano-Objects. *Nano Lett.* 2009, 9, 3732–3738.

(28) Marty, R.; Arbouet, A.; Girard, C.; Mlayah, A.; Paillard, V.; Lin, V. K.; Teo, S. L.; Tripathy, S. Damping of the Acoustic Vibrations of Individual Gold Nanoparticles. *Nano Lett.* 2011, 11, 3301–3306.
(29) O’Brien, K.; Lanzillotti-Kimura, N. D.; Rho, J.; Suchowski, H.; Yin, X.; Zhang, X. Ultrafast Acousto-Plasmonic Control and Sensing in Complex Nanostructures. Nat. Comm. 2014, 5, 4042–4042.

(30) Kirschner, M. S.; Lethiec, C. M.; Lin, X.-M.; Schatz, G. C.; Chen, L. X.; Schaller, R. D. Size-Dependent Coherent-Phonon Plasmon Modulation and Deformation Characterization in Gold Bipyramids and Nanojavelins. ACS Photonics 2016, 3, 758–763.

(31) Lethiec, C. M.; Madison, L. R.; Schatz, G. C. Dependence of Plasmon Energies on the Acoustic Normal Modes of Agn (n = 20, 84, and 120) Clusters. J. Phys. Chem. C 2016, 120, 20572–20578.

(32) Yi, C.; Dongare, P. D.; Su, M.-N.; Wang, W.; Chakraborty, D.; Wen, F.; Chang, W.-S.; Sader, J. E.; Nordlander, P.; Halas, N. J.; Link, S. Vibrational Coupling in Plasmonic Molecules. PNAS 2017, 114, 11621–11626.

(33) Ahmed, A.; Pelton, M.; Guest, J. R. Understanding How Acoustic Vibrations Modulate the Optical Response of Plasmonic Metal Nanoparticles. ACS Nano 2017, 11, 9360–9369.

(34) Ahmed, A.; Gelfand, R.; Storm, S. D.; Lee, A.; Klinkova, A.; Guest, J. R.; Pelton, M. Low-Frequency Oscillations in Optical Measurements of Metal-Nanoparticle Vibrations. Nano Lett. 2022, 0, null.

(35) Tripathy, S.; Marty, R.; Lin, V. K.; Teo, S. L.; Ye, E.; Arbouet, A.; Saviot, L.; Girard, C.; Han, M. Y.; Mlayah, A. Acousto-Plasmonic and Surface-Enhanced Raman Scattering Properties of Coupled Gold Nanospheres/Nanodisk Trimers. Nano Lett. 2011, 11, 431–437.

(36) Girard, A.; Gehan, H.; Crut, A.; Mermet, A.; Saviot, L.; Margueritat, J. Mechanical Coupling in Gold Nanoparticles Supermolecules Revealed by Plasmon-Enhanced Ultralow Frequency Raman Spectroscopy. Nano Lett. 2016, 16, 3843–3849.
(37) Girard, A.; Lermé, J.; Gehan, H.; Margueritat, J.; Mermet, A. Mechanisms of Resonant Low Frequency Raman Scattering from Metallic Nanoparticle Lamb Modes. *J. Chem. Phys.* **2017**, *146*, 194201.

(38) Apell, S. P.; Mukhopadhyay, G.; Antosiewicz, T. J.; Aizpurua, J. *Shape-sensitive inelastic scattering from metallic nanoparticles*; Advances in Quantum Chemistry; Academic Press, 2022.

(39) Marty, R.; Mlayah, A.; Arbouet, A.; Girard, C.; Tripathy, S. Plasphonics: Local Hybridization of Plasmons and Phonons. *Opt. Express* **2013**, *21*, 4551–4559.

(40) Bachelier, G.; Mlayah, A. Surface Plasmon Mediated Raman Scattering in Metal Nanoparticles. *Phys. Rev. B* **2004**, *69*, 205408.

(41) Bachelier, G.; Margueritat, J.; Mlayah, A.; Gonzalo, J.; N. Afonso, C. Size Dispersion Effects on the Low-Frequency Raman Scattering of Quasispherical Silver Nanoparticles: Experiment and Theory. *Phys. Rev. B* **2007**, *76*.

(42) Huntzinger, J.-R.; Mlayah, A.; Paillard, V.; Wellner, A.; Combe, N.; Bonafos, C. Electron-Acoustic-Phonon Interaction and Resonant Raman Scattering in Ge Quantum Dots: Matrix and Quantum Confinement Effects. *Phys. Rev. B* **2006**, *74*, 115308.

(43) Mlayah, A.; Huntzinger, J.-R.; Large, N. Raman-Brillouin Light Scattering in Low-Dimensional Systems: Photoelastic Model Versus Quantum Model. *Phys. Rev. B* **2007**, *75*, 245303.

(44) Large, N.; Huntzinger, J.-R.; Aizpurua, J.; Jusserand, B.; Mlayah, A. Raman-Brillouin Electronic Density in Short Period Superlattices. *Phys. Rev. B* **2010**, *82*, 075310–075318.

(45) Visscher, W. M.; Migliori, A.; Bell, T. M.; Reinert, R. A. On the Normal Modes of
Free Vibration of Inhomogeneous and Anisotropic Elastic Objects. *J. Acoust. Soc. Am.* **1991**, *90*, 2154–2154.

(46) Draine, B.; Flatau, P. Discrete Dipole Approximation for Scattering Calculations. *J. Opt. Soc. Am. A* **1994**, *11*, 1491–1499.

(47) Temnov, V. V. Ultrafast Acousto-Magneto-Plasmonics. *Nat. Photon.* **2012**, *6*, 728–736.

(48) Mrabti, A.; Lévêque, G.; Akjouj, A.; Pennec, Y.; Djafari-Rouhani, B.; Nicolas, R.; Maurer, T.; Adam, P.-M. Elastoplasmonic Interaction in Metal-Insulator-Metal Localized Surface Plasmon Systems. *Phys. Rev. B* **2016**, *94*, 075405.

(49) Feldman, L.; Mayer, J. *Fundamentals of Surface and Thin Film Analysis*; North-Holland, 1986.

(50) Cottancin, E.; Celep, G.; Lermé, J.; Pellarin, M.; Huntzinger, J. R.; Vialle, J. L.; Broyer, M. Optical Properties of Noble Metal Clusters as a Function of the Size: Comparison between Experiments and a Semi-Quantal Theory. *Theor. Chem. Acc.* **2006**, *116*, 514–523.

(51) Voisin, C.; Christofilos, D.; Fatti, N. D.; Vallée, F. Environment Effect on the Acoustic Vibration of Metal Nanoparticles. *Physica B* **2002**, *316-317*, 89 – 94.

(52) Combe, N.; Saviot, L. Acoustic Modes in Metallic Nanoparticles: Atomistic versus Elasticity Modeling. *Phys. Rev. B* **2009**, *80*, 035411–035411.

(53) Murray, D. B.; Saviot, L. Phonons in an Inhomogeneous Continuum: Vibrations of an Embedded Nanoparticle. *Phys. Rev. B* **2004**, *69*, 094305–094305.

(54) Johnson, P. B.; Christy, R. W. Optical Constants of the Noble Metals. *Phys. Rev. B* **1972**, *6*, 4370–4379.
(55) Derkachova, A.; Kolwas, K.; Demchenko, I. Dielectric Function for Gold in Plasmonics Applications: Size Dependence of Plasmon Resonance Frequencies and Damping Rates for Nanospheres. *Plasmonics* **2016**, *11*, 941–951.

(56) Szczepanek, P.; Glosser, R. Piezo-Optical Constants of Gold. *Solid State Commun.* **1974**, *15*, 1425 – 1429.

(57) Lamb, H. On the Vibrations of an Elastic Sphere. *Proc. London Math. Soc.* **1881**, *s1-13*, 189–212.

(58) Saviot, L.; Murray, D. B. Acoustic Vibrations of Anisotropic Nanoparticles. *Phys. Rev. B* **2009**, *79*, 214101.

(59) Saviot, L.; Combe, N.; Mlayah, A. Number of observable features in the acoustic Raman spectra of nanocrystals. *Phys. Rev. B* **2012**, *85*, 075405.

(60) Girard, A.; Gehan, H.; Mermet, A.; Bonnet, C.; Lermé, J.; Berthelot, A.; Cottancin, E.; Crut, A.; Margueritat, J. Acoustic Mode Hybridization in a Single Dimer of Gold Nanoparticles. *Nano Lett.* **2018**, *18*, null, PMID: 29715427.
Supporting Information for Raman Energy Density (RED) in the Context of Acousto-Plasmonics

José Luis Montaño Priede$^{1,2}$, Adnen Mlayah$^{3,4}$, Nicolas Large$^{1,*}$

$^1$Department of Physics and Astronomy, The University of Texas at San Antonio, San Antonio, Texas 78249, United States

$^2$Current address: Department of Electricity and Electronics, FCT-ZTF, UPV-EHU, Bilbao, 48080, Spain

$^3$Centre d’Elaboration de Matériaux et d’Etudes Structurales (CEMES), CNRS and Université Paul Sabatier - Toulouse III, 31055 Toulouse, France

$^4$Laboratoire d’Analyse et d’Architecture des Systèmes (LAAS), CNRS and Université Paul Sabatier - Toulouse III, 31031 Toulouse, France

$^*$nicolas.large@utsa.edu

Figure S1: Comparison on the surface deformations between the NP at rest (black), isotropic vibration modes (blue), and the anisotropic vibration modes (red) in the plane of maximum deformation.
Figure S2: Near electric fields associated with the isotropic (top) and anisotropic (bottom) vibration modes in the plane of maximum deformation. $\Delta$ represents the horizontal axis and depends on the chosen plane. (a) Isotropic breathing $S_{100}^1$ ($d_0$) mode, (b-f) five-degenerated isotropic quadrupoles $S_{2m}^1$ ($d_1 - d_5$), (g) anisotropic breathing $A_{1g}$ mode, (h,i) anisotropic quadrupole $E_g$ ($E_{g(a)}$ and $E_{g(b)}$) modes, and (j-l) anisotropic quadrupole $T_{2g}$ ($T_{2g(a)}$, $T_{2g(b)}$, and $T_{2g(c)}$) modes.
Figure S3: Divergence of the displacement field of the $d_0$ (blue) and $A_{1g}$ (red) breathing modes along the $x$-direction ($y = z = 0$).
Figure S4: Real part of the surface (top), volume (center), and both (bottom) mechanism terms of the RED associated with the isotropic (left) and anisotropic (right) vibration modes. Within each panel (a) refers to the breathing mode and (b-f) refer to the quadrupolar modes.
Figure S5: Computed Raman spectra showing the Raman selection rules for each isotropic (upper panels) and anisotropic (lower panels) acoustic vibration mode. The Raman selection rules are obtained in parallel (purple) and cross (orange) configurations.
Figure S6: Computed Raman spectra showing the Raman selection rules for each isotropic (upper panels) and anisotropic (lower panels) acoustic vibration mode. The Raman selection rules are obtained in parallel and cross configurations.