The vibrations of gold nanowires and nanorods are investigated numerically in the framework of continuum elasticity using the Rayleigh-Ritz variational method. Special attention is paid to identify the vibrations relevant in Raman scattering experiments. A comprehensive description of the vibrations of nanorods is proposed by determining their symmetry, comparing with standing waves in the corresponding nanowires and estimating their Raman intensity. The role of experimentally relevant parameters such as the anisotropic cubic lattice structure, the presence of faceted lateral surfaces and the shape of the ends of the nanorods is evaluated. Elastic anisotropy is shown to play a significant role contrarily to the presence of facets. Localized vibrations are found for nanorods with flat ends. Their evolution as the shape of the ends is changed to half-spheres is discussed.

I. INTRODUCTION

Non-spherical gold nanoparticles have attracted considerable attention during the last few decades mainly because their optical properties are strongly shape-dependent. Gold nanorods (NRs) in particular have been the focus of many studies, some dedicated to understanding and controlling their synthesis while other focused on their properties. In this context, their acoustic vibrations have been investigated as a mean to measure the dimensions of the NRs, but also to study their acousto-plasmonic coupling with the localized surface plasmon resonance (LSPR). Transient absorption measurements are a tool of choice in this context in particular because single particle measurements are possible. It enables to observe totally symmetric vibrations, i.e., the extensional vibration which consists in an oscillation of the length of the NRs and the breathing vibration which is an oscillation of the radius. Low-frequency Raman scattering is also of interest as it obeys distinct selection rules. The same totally symmetric vibrations and others non-totally symmetric ones have been observed experimentally. A continuous-four-wave mixing approach has also been proposed recently. It was shown to be sensitive to some Raman active vibrations. Finally, another experimental technique known as extraordinary acoustic Raman spectroscopy was also proposed. It is a promising approach enabling single particle measurements which has not been applied to gold NRs yet.

Experimental measurements must be supported by calculations to understand the nature of the observed vibrations. Most often, continuum isotropic elasticity is assumed for NRs made of gold and other materials resulting in models based on analytic expressions in cylindrical coordinates. While this assumption is sometimes valid, it is also known to be a poor one in many cases. This is expected in particular for ultrathin gold nanowires (NW) and NRs which are single-crystalline. Gold is strongly anisotropic (Zener ratio: 2.9) which results for example in a large splitting of the quadrupolar vibrations of nanospheres (NS). Such a splitting must also exist for gold NRs but calculations of this splitting are lacking. In addition, anisotropic elasticity has also an impact on the other vibrations. It shifts the frequency of the extensional vibration significantly enough that taking into account elastic anisotropy is required. Anisotropy also results in the existence of several vibrations sharing the breathing character and therefore a broadening of the corresponding peak. This effect must be properly taken into account before discussing damping. Finally, the impact of non-circular cross-sections as observed in penta-twinned gold NRs or single-cristalline NRs must also be evaluated.

The purpose of this work is to investigate numerically the vibrations of gold NRs and in particular those which play a role in experiments. Vibrations of gold NWs are also calculated. The influence of elastic anisotropy, of the cross-section of the NWs and of the ends of the NRs are investigated. The frequencies of the NRs are also a tool of choice in this context in particular because single particle measurements are possible. It enables to observe totally symmetric vibrations, i.e., the extensional vibration which consists in an oscillation of the length of the NRs and the breathing vibration which is an oscillation of the radius. Low-frequency Raman scattering is also of interest as it obeys distinct selection rules. The same totally symmetric vibrations and others non-totally symmetric ones have been observed experimentally. A continuous-four-wave mixing approach has also been proposed recently. It was shown to be sensitive to some Raman active vibrations. Finally, another experimental technique known as extraordinary acoustic Raman spectroscopy was also proposed. It is a promising approach enabling single particle measurements which has not been applied to gold NRs yet.

II. METHODS

In the following, the radius for the NSs and the circular NRs and NWs is kept constant at $R = 5\,\text{nm}$ and their main axis is along [001]. Octagonal NWs are also considered. Their surface is delimited by $\{7\bar{3}0\}$ planes as observed in elongated tetrahedral gold nanocrystals. The half-lengths along the $\langle100\rangle$ and $\langle110\rangle$ directions ($d_{100}/2 = 5.296\,\text{nm}$ and $d_{110}/2 = 5.243\,\text{nm}$) were chosen so that the surface area of the cross-section of all the NWs is the same. The results obtained for the dimensions given above can be used to determine the frequencies for different dimensions. The frequencies of the NSs scale as $1/R$. The same scaling applies to NRs provided the aspect ratio (length/diameter) is preserved. For NWs, both the frequencies and the wavevectors scale as $1/R$. The stiffness tensor for gold is defined by $C_{11} = 191\,\text{GPa}$.
$C_{12} = 162$ GPa and $C_{44} = 42.4$ GPa, and its mass density is $\rho = 19.283\frac{g}{cm^3}$. For the isotropic approximation of gold, the stiffness tensor obtained from the 3D averaged sound speeds is given by $C_{11} = 213.3$ GPa and $C_{12} = 152.6$ GPa.

Calculations for NWs are performed by taking into account the translational symmetry starting from the method proposed by Nishiguchi et al.\textsuperscript{21} for rectangular quantum wires. The calculations for circular NWs with isotropic elasticity are also checked with exact analytical expressions.\textsuperscript{22} Due to the translational symmetry, the vibrations of NWs are not discrete and form branches for varying wavevectors $q$. The vibrations of the NRs and NSs are obtained using the Rayleigh-Ritz variational method proposed by Nishiguchi et al.\textsuperscript{21} to take into account anisotropy due to the non-spherical shape or cubic elasticity. Similar calculations exist in the literature mostly for isotropic NRs.\textsuperscript{23,24} The present work improves on such previous works in several ways. All the vibrations are considered up to the first breathing-like mode. Totally symmetric and non-totally symmetric vibrations are investigated. The irreducible representations of the vibrations of the NRs and NSs are determined in order to distinguish them and also to bring out the vibrations of interest such as the Raman active ones.\textsuperscript{22} Similarly, the irreducible representation of the $q = 0$ phonons of the NWs are determined for the same point group as the one of the corresponding NRs, namely $D_{\text{sch}}$ for isotropic elasticity and circular cross-sections and $D_{\text{th}}$ otherwise, by taking into account a single symmetry plane perpendicular to the symmetry axis at $z = 0$. In addition, the variation of the volume of the NSs and NRs during the vibration is calculated to help identify breathing vibrations.\textsuperscript{22} For comparison, the variation of the surface area of the cross-section is also calculated for NWs. Calculations for NWs are then used to describe the vibrations of NWs in terms of confined vibrations (standing waves) when possible.

### III. RESULTS AND DISCUSSION

#### A. Nanowires

Fig. 1 presents the phonon branches for the circular NW with isotropic gold and the circular and octagonal NWs with cubic gold. For the Rayleigh-Ritz variational calculation, the displacements were expanded on the $x^l y^m z^n q^z$ basis with $l$ and $m$ being integers and $0 \leq l + m \leq 23$. For the octagonal NW, numerical issues with the Cholesky decomposition in the LAPACK ZHEGV routine\textsuperscript{25} restricted this range to $0 \leq l + m \leq 9$. We first note the excellent agreement for the isotropic circular NW with the exact analytic calculations.\textsuperscript{22} Only a few selected $q$ are shown in Fig. 1 (left) for the analytic method but the agreement is excellent over the 0-1 nm$^{-1}$ range ($\Delta \nu / \nu < 10^{-7}$).

The breathing and quadrupolar-like frequencies for NSs and NWs with isotropic and cubic elasticity are given in Table I. For the isotropic NS, only the spheroidal $\ell = 0$ (breathing) and $\ell = 2$ (quadrupolar) vibrations are Raman active. In the other cases, the modes were identified by checking the associated displacements. When changing the shape from a NS to a NW, the breathing frequency decreases much more ($\sim 70$ GHz) than the quadrupolar-like frequency ($\sim 10$ GHz).

Introducing elastic anisotropy\textsuperscript{26} results in a significant splitting of the quadrupolar-like modes as already reported for NSs.\textsuperscript{22} It confirms that elastic anisotropy must be taken into account for NWs too. As was discussed in a previous work for NSs,\textsuperscript{25} this splitting can be understood as transverse waves with sound speeds $\sqrt{\frac{C_{11}-C_{12}}{2\rho}}$ and $\sqrt{\frac{C_{44}}{\rho}}$ confined over the same distance (diameter).

The ratio of these sound speeds is the square root of the Zener anisotropy ratio ($1.7105$ for cubic gold). In this simple approach, it is equal to the frequency ratio after splitting. Indeed, the ratio of the $q = 0$ B$_{2g}$ and B$_{1g}$ frequencies is 1.7044. Therefore, the square of this ratio as measured for example from Raman spectra is expected to be an accurate estimate of the Zener anisotropy ratio.

The difference between the octagonal and circular NWs is very small. Again, the same conclusion was reached for nanocrystals having similar shapes (sphere, cuboctahedron and truncated cuboctahedron) provided the volume was the same.\textsuperscript{12} For this reason, only circular NWs and NRs are considered in the following. The phonon branches starting with the NWs vibrations listed in Table I are highlighted in Fig. 1. The branch starting from the $q = 0$ breathing vibration is not highlighted in the same way because it couples with other branches making its dispersion interesting up to the first anti-crossing feature only. Instead, a dashed thick blue curve is plotted as a guide for the eye. It was obtained by following the modes having the largest surface area variation during vibration. It was determined for the anisotropic circular NW and fitted to $\omega_{\text{breathing}} = 230 + 782q^2 - 1207q^4 + 945q^6$ where $\omega$ is in GHz and $q$ in nm$^{-1}$. The same curve is plotted for the three NWs. The breathing modes are very similar for the three NWs except for the position of the anti-crossing patterns.

|          | breathing          | quadrupolar         |
|----------|--------------------|---------------------|
|          | isotropic          | cubic               | isotropic          | cubic               |
| NS       | $310.93$           | $310.12$            | $106.20$           | $E_g$               | $74.62$             |
| $\ell = 0$ | $A_{1g}$           | $235.97$            | $B_{1g}$           | $64.99$             |
| circular NW | $241.06$           | $235.63$            | $93.94$           | $B_{1g}$           | $110.77$           |
| $q = 0$ | $A_{1g}$           | $A_{1g}$            | $B_{2g}$           | $94.11$           | $110.88$           |
| octagonal NW | $240.50$           | $235.97$            | $93.80$           | $B_{1g}$           | $64.93$           |

**TABLE I.** Breathing(-like) and quadrupolar(-like) frequencies for NSs, circular and octagonal NWs with isotropic and cubic elasticity. The irreducible representations are given (D$_{\text{th}}$ point group), $\ell$ is given for the spherical symmetry (isotropic NS) and $m$ for the cylindrical one (isotropic circular NW).
FIG. 1. Top: phonon dispersion for the isotropic circular NW (left) and the anisotropic circular (center) and octagonal (right) NWs. Analytical calculations for the isotropic circular NW are shown with circles (left) for a few selected \( q \). Zone center \( A_{1g} \) modes are shown with blue arrows, \( B_{1g} \) with red arrows and \( B_{2g} \) with black arrows. The dilatational branch is colored in blue, the branch starting from the lowest frequency \( B_{1g} \) mode is colored in red and the \( B_{2g} \) one in black. The isotropic \( E_{2g} \) modes are shown with both red and black arrows and the branch starting from the lowest frequency \( E_{2g} \) mode is dashed in red and black (left). The same dashed thick blue curve is plotted as a guide for the eye for a breathing branch without anti-crossing patterns.

Bottom: displacement in the \( xy \) plane of the lowest frequency \( q = 0 \) phonons of the anisotropic circular cylinder. For the \( E_{g} \) vibrations, the displacements are along \( z \) and the black and white areas move in opposite directions.

B. Nanorods

Let us start by considering the extensional modes of the NRs. They correspond to dilatational phonons of the NWs (blue curves in Fig. 1) confined along the length of the NR. Their frequencies can be derived assuming free boundary conditions at both ends. For a NR with flat ends and considering first the totally symmetric modes which are Raman active, \( q = (2n + 1) \frac{\pi}{L} \) with \( n = 0, 1, \ldots \). We compare the frequencies of the lowest \( A_{1g} \) vibrations with this expression in Fig. 2 (top left). The agreement is remarkable for the first few overtones. A very good agreement is also obtained for the lowest frequency \( A_{2u} \) vibrations (Raman inactive) which are their anti-symmetric analogues corresponding to \( q = 2n \frac{\pi}{L} \).

This first successful comparison demonstrates that determining the phonon frequencies of the NW as a function of \( q \) (in this case for the dilatational branch) can be
sufficient to calculate the frequency of some vibrations of the NRs with flat ends (in this case the extensional ones) for arbitrary diameters and lengths. The agreement is very good including above 40 GHz where the NW dilatational phonon frequency is no longer proportional to \( q \). This frequency range is relevant for short NRs and for overtones.

In Fig. 2 (top right), the same approach is used for NRs with half-sphere ends. The agreement is not as good as before, but the simple calculation using the NW dilatational branch still provides a rather good approximation of the frequency. The agreement is improved for large \( L \) by using \( q \) determined from the equivalent length \( L_{eq} = L - \frac{2}{3} R \) which corresponds to the length of a NR with flat ends having the same volume.

2. Torsional modes

A similar treatment can be applied to torsional vibrations which consist in rotations around the symmetry axis of the NRs. These vibrations are of course associated to the NW torsion phonon branch whose frequency is proportional to \( q \) (linear variation in Fig. 1). Odd torsional vibrations of the NRs correspond to the \( A_{2g} \) irreducible representation and even vibrations correspond to \( A_{1u} \). The confinement along \( L \) results in \( q = n \frac{\pi}{L} \) with odd values of \( n \) for \( A_{1u} \) and even values for \( A_{2g} \). Fig. 2 (bottom) shows the resulting frequencies for both kinds of NRs. As before, the agreement for NRs with straight ends is remarkable. However, the deviation observed for NRs with half-sphere ends is larger.

3. Bending modes

The third NW phonon branch with a vanishing frequency at \( q = 0 \) is for flexural phonons. It is related to the bending vibrations of the NR with irreducible representations \( E_u \) and \( E_g \). These vibrations can be modeled analytically using the Euler-Bernoulli or Timoshenko beam theory. The resulting frequencies vary as \( 1/L^2 \). This variation is reproduced at large \( L \) by considering confined modes at \( q = n \frac{\pi}{L} \) because the slope of the NW flexural phonon branch vanishes at \( q = 0 \). However, the frequencies are significantly different (not shown). This is because this trivial approach does not reproduce the displacements obtained in the framework of the Timoshenko beam theory which contain hyperbolic functions of spatial coordinates (sinh and cosh). Therefore, a given NR bending vibration can not be easily matched to a NW flexural phonon with \( e^{iqz} \) dependence and real \( q \). To check the \( 1/L^2 \) variation, all the lowest frequency branches of the NRs are plotted in Fig. 3 (bottom). Logarithmic scales are used in order to distinguish between different behaviors at large \( L \). Branches whose frequency does not depend on \( L \) have a constant frequency (slope 0). This is the case for phonons confined along a direction perpendicular to the axis of the NRs. Some of them will be discussed later. Modes whose frequency vary as \( 1/L \) have slope -1. This is the case for vibrations confined along the length of the NRs. These branches are the extensional and torsional vibrations discussed above. The remaining branches whose slopes tend to -2 at large \( L \) are the \( E_u \) and \( E_g \) bending vibrations.

4. Quadrupolar-like modes

Let us now consider vibrations of the NRs whose frequency does not tend to zero as \( L \) increases and how they relate or not to phonon branches of the NWs whose frequency does not vanish at \( q = 0 \). Vibrations similar to the quadrupolar vibrations of the NSs are of course of interest since they correspond to the most intense low-frequency Raman peak for NSs. As presented in Table 1, the branches of interest for the NRs are the \( B_{1g} \) and \( B_{2g} \) ones. They are plotted in Fig. 4. The \( B_{1g} \) vibrations correspond to out of phase elongations along both \( \langle 100 \rangle \) directions perpendicular to the symmetry axis of the NRs. For the \( B_{2g} \) vibrations, the elongations are along the \( \langle 110 \rangle \) directions. See Fig. 4 (bottom).

The first notable feature is the existence of isolated low-frequency \( B_{1g} \) and \( B_{2g} \) modes for NRs with flat ends.
branches of the NWs as a function of their length $L$. The NWs ends are flat (left) or half-spheres (right). The $E_g$ branches are plotted with full circles and a continuous line (blue online) and the $E_u$ branches with empty circles and a dashed line (red online). All the other modes are plotted with black circles and a continuous line. Three slopes 0, -1 and -2 are plotted for comparison.

Top: $E_g$ branches in the frequency range of the $q = 0$ $E_g$ vibration of the NW. The continuous black curves are the confined vibrations calculated from the NW phonon branch at $q = n \frac{\pi}{L}$ with odd $n$.

(Fig. 4 (left)). Their frequencies at about 62 and 91 GHz hardly depend on $L$. This is at odd with most other branches which tend to stack up to form the phonon branches of the NWs as $L \to \infty$. These two isolated branches of the NRs can not be related to the NW phonon branches plotted in Fig. 1. Looking at the corresponding displacements reveals that the vibrations are localized at both ends of the NRs. Libov$^{[33]}$ reported the existence of such localized vibrations as $m = 2$ vibrations for isotropic NRs with flat ends. In the present case they split due to cubic anisotropy into $B_{1g}$ and $B_{2g}$.

No such isolated branch is observed for NRs with half-spheres at both ends (Fig. 4 (center)). Obviously, the frequency of vibrations localized at the ends depend on the shape of the ends. Figure 4 (right) presents the variation of the frequencies of the same vibrations for $L = 30$ nm as a function of the shape of both ends of the NRs. The shape is defined by a spheroid with two radii equal to $R$ and the other radius $R_c$ varying from 0 for flat ends to $R$ for half-sphere ends. The frequency of the localized vibrations increases with $R_c$ and the isolated branches couple and merge with the other branches. These localized vibrations can be related to vibrations of the NSs. By considering the associated displacements and the symmetry of the vibrations, they were shown to be equivalent to the torsional vibrations of an isotropic NS with $\ell = 3$ and $m = \pm 2$ whose frequency is 154.39 GHz which is larger than that of the $l = 2$ spheroidal mode at 106.20 GHz. They also split into $B_{1g}$ and $B_{2g}$ when elastic and shape anisotropies are taken into account. In all of these cases, the lowest frequency quadrupolar-like vibrations (see Table 1) have a frequency lower than that of the torsional-like vibrations coming from the $\ell = 3$ and $m = \pm 2$ vibrations. Therefore, for NRs with half-sphere ends, there are no separate localized vibrations branches but rather coupled localized and quadrupolar-like vibrations.

The frequency of confined quadrupolar-like $B_{1g}$ and $B_{2g}$ vibrations was determined from the corresponding NW phonon branch using $q = (2n + 1) \frac{\pi}{L}$. The corresponding branches are plotted in Fig. 4 (left and cen-
For NRs with flat ends, the agreement between the frequencies for the NRs and the ones determined from the NW phonon branches is good for the B_{1g} vibrations. The agreement is excellent for the B_{2g} vibrations above 110 GHz. The anti-symmetric vibrations of the same origin (B_{2g} for B_{1g} and B_{1a} for B_{2g}) are also plotted for completeness. The agreement is not so good for NRs with half-sphere ends. As discussed above, this is due to the coupling with the localized vibrations. This coupling manifests as complex anti-crossing patterns due to the fact that branches having the same irreducible representation do not cross. The same rule explains the complex frequency variations for B_{2g} vibrations between 105 and 110 GHz. Contrarily to the extensional and torsional vibrations discussed before, the frequency variations of the NW quadrupolar-like B_{1g} and B_{2g} phonon branches with q are not monotone. Their frequencies decrease slightly at small q and then increase. The decrease is more pronounced for B_{2g}. As a result, the branches for the different overtones of the calculated confined vibrations cross. This is hardly noticeable for B_{1g} but it is clearly visible for B_{2g}. This results in anti-crossing patterns which render the assignment of the B_{2g} vibrations to a specific overtone sometimes difficult in this frequency range. This also explains why the lowest B_{2g} frequency does not match with the frequency of the NW phonon branch at q = 0. It corresponds to the lowest frequency of the phonon branch which is at ≃ 105.7 GHz, i.e., about 5 GHz less than the q = 0 value. For B_{1g}, this difference is two orders of magnitude less (−0.07 GHz).

The quadrupolar vibration of the isotropic sphere (spheroidal modes with ℓ = 2 and degeneracy 5) split into A_{1g} + B_{1g} + B_{2g} + E_g in D_{4h}. We have considered the A_{1g} (extensional) and B_{1g} and B_{2g} modes above. The frequencies of the E_g modes are plotted in Fig. 3. At low-frequency, they correspond to overtones of the bending modes as already discussed. Anti-crossing patterns appear at 86.9 GHz which is the frequency of the E_g modes (degeneracy 2, q = 0) of the corresponding NW. These are thickness-shear vibrations whose displacement is along the z axis of the NW. One mode corresponds to the x > 0 part of the NW moving along +z while the x < 0 part moves along −z. The other mode is obtained by replacing x by y. During such vibrations, the external shape of the NW remains unchanged. Therefore, a very small coupling with the surface plasmon resonance is expected for the NW. For NRs, the frequencies of the corresponding modes are plotted in Fig. 3 (top) using the same procedure as before. In that case, the shape of the NRs varies during the vibrations because they correspond to phonons propagating along z with a non-vanishing wavevector (q = nπ/2) and also because of the shape of the ends. Still, the intensity of the corresponding Raman peaks must tend to zero as the aspect ratio of the NRs increases to turn into a NW.

5. Breathing-like modes

Applying the same procedure to breathing-like vibrations is more challenging because of the convergence issues and also because of the mixing with other vibrations. Convergence is very good for the lowest frequency vibrations but it decreases as the vibration index increases. For L = 10 nm, the vibration index for the breathing-like vibrations is about 100. For L = 60 nm, it is about 350. This is due to vibrations whose frequency decreases as L → ∞ to form the NW phonon branches at lower frequency. Convergence issues render calculations for large L less reliable. In addition, several totally symmetric A_{1g} branches couple with the breathing-like vibrations. They come from the spheroidal vibrations of the isotropic NS with even ℓ and m = 0. This results in several anti-crossing patterns in the L range investigated in this work. As seen before, this renders the interpretation in terms of confined vibrations less reliable. Two modifications are introduced to overcome this issue. First, the breathing-like vibrations are identified by looking at the volume variations. This enables to weight the numerous A_{1g} vibrations according to their breathing-like character. The modes corresponding to the largest circles are those who are expected to add up to form the feature associated to “the” breathing mode in pump-probe or Raman experiments. In addition, the NW phonon branch used for the calculation of the confined vibrations is the one which was used as a guide for the eye in Fig. 1. This results in a simpler picture which is free of anti-crossing patterns. Fig. 5 displays the resulting branches and the confined vibrations calculated with q = (2n + 1)π/2. As expected, the calculated confined vibrations fail to capture all the details of the complex coupling between the numerous A_{1g} branches. But the first confined branch matches quantitatively the vibrations having the largest volume variation for both kinds of NRs. The following branch with the largest volume variation is also reproduced for L > 40 nm. A closer investigation of the anti-crossing patterns in Fig. 1 reveals that the breathing branch couples with two almost flat branches starting from the next two q = 0 A_{1g} phonons at 274 and 323 GHz. The A_{1g} vibrations of the NRs at about these two frequencies have larger volume variations. As a conclusion, while a main breathing-like feature definitively exists in Fig. 5 which is correctly described in terms of a fundamental confined vibration, other factors come into play which may manifest in experiments as close peaks or a broader peak.

C. Raman intensities

In order to illustrate the previous results, low-frequency Raman spectra have been calculated and are presented in Fig. 6. Similar calculations have been carried out until now only for isotropic spherical NPs using analytic expressions for the vibrations (Lamb modes) and the electric field inside the NPs (Mie solutions). Ana-
lytic expressions are not available for the anisotropic and non-spherical NPs considered in this work. To overcome this problem, the spectra in Fig. 6 were calculated according to the method described in Ref. 34 (equations 11 and 12), using the vibrations obtained previously and assuming a constant electric field inside the NPs. As a result, the calculation of the intensity comes down to evaluating the Brillouin scattering term of Ref. 35, i.e., a volume integral involving only the displacement field and the retardation effect ($e^{-i\mathbf{q} \cdot \mathbf{R}}$). By expanding this last term as $1 - i\mathbf{q} \cdot \mathbf{R} + \cdots$, the calculation only requires to evaluate volume integrals of $x^l y^m z^n$ functions for which analytical expressions exist as in the Rayleigh-Ritz approach presented before.

The validity of this approach is dubious since the variation of the electric field inside the NPs is not taken into account. For example, it fails to reproduce the depolarized scattering by the quadrupolar-like modes. Still, the spectrum calculated for the isotropic spherical NP is similar to the one in Ref. 34. For this reason, the calculated spectra are expected to provide an insightful “first-order” approximation of actual Raman measurements.

The spectra in Fig. 6 were calculated using all the vibration modes confirming that only the Raman-active ones contribute to the spectra. All the Raman peaks were convoluted by a Lorentzian function (full width at half-maximum 2 GHz). The calculations were performed for the backscattering geometry along [1 0 0] (line) and [1 1 0] (dotted line) with the light polarization along [0 0 1]. They clearly confirm the previously discussed features, namely the presence of intense peaks for the quadrupolar-like A$_{1g}$ (extensional), B$_{1g}$ and B$_{2g}$ modes, no significant scattering from the localized vibrations (flat ends) and the E$_g$ modes, and small peaks for the breathing-like vibrations. Deviations from these calculations are expected because of the variations of the electric field inside the nanoparticles even for isotropic spheres. Larger deviations can also occur when NPs are close enough that the surface plasmons of neighbor NPs couple. In that case, new low-frequency Raman peaks may appear as recently observed in gold nanoparticles super-molecules.

IV. CONCLUSION

The vibrations of gold NRs have been investigated in order to point out the experimentally relevant ones and in particular those which are expected to have the largest Raman cross sections. To this end, gold NRs and NWs have been considered using the Rayleigh-Ritz variational method. The symmetry and the volume variation of the modes were determined. Raman spectra have also been calculated by considering only the Brillouin scattering mechanism. Elastic anisotropy is shown to play a major role for NWs made of single domain cubic gold.
The vibrations of NRs with flat ends have been compared with confined vibrations obtained as phonons of the NW at fixed wavevector \( q = \pi / n \). The frequencies of most vibrations of the NRs can be estimated quickly and rather accurately using only the dispersion curves of the NW and the length of the NRs. This simple picture enabled to understand quantitatively and often qualitatively the origin of the main Raman active vibrations including the totally symmetric ones which are of interest in time-domain measurements. Localized \( B_{1g} \) and \( B_{2g} \) vibrations have been identified. Their Raman scattering cross-sections are small because they are related to torsional vibrations of the NSs. However, the Raman intensities calculated in this work would have to be reconsidered in particular when surface enhanced Raman scattering conditions are met, for example when the ends of neighbor NRs are very close. This study also quantifies the influence of the shape of the ends of the NRs. Differences between flat and half-sphere ends are small as far as fundamental vibrations are concerned. Larger differences exist for overtones. Vibrations localized at the ends of the NRs are also strongly affected. However, observing these differences in experimental measurements is very challenging. On the opposite, the major role played by elastic anisotropy has been highlighted. The resulting splitting of the quadrupolar-like vibrations is expected to be a clear signature of the single domain cubic gold inner structure as already reported for NSs.\(^{11}\)

---

1. S. E. Lohse and C. J. Murphy, *Chemistry of Materials* **25**, 1250 (2013)
2. N. Large, L. Saviot, J. Margueritat, J. Gonzalo, C. N. Afonso, A. Arbouet, P. Langot, A. Mlayah, and J. Aizpurua, *Nano Lett.* **9**, 3732 (2009)
3. A. Crut, P. Mäloli, N. D. Fatti, and F. Vallée, *Physics Reports* **549**, 1 (2015)
4. M. Hu, X. Wang, G. V. Hartland, P. Mulvaney, J. P. Juste, and J. E. Sader, *Journal of the American Chemical Society* **125**, 14925 (2003)
5. J. Margueritat, J. Gonzalo, C. N. Afonso, G. Bachelier, A. Mlayah, A. S. Laaraker, D. B. Murray, and L. Saviot, *Appl. Phys. A* **89**, 369 (2007)
6. J. Margueritat, J. Gonzalo, C. N. Afonso, A. Mlayah, D. B. Murray, and L. Saviot, *Nano Lett.* **6**, 2037 (2006)
7. J. Wu, D. Xiang, and R. Gordon, *Opt. Express* **24**, 12458 (2016)
8. S. Wheaton, R. M. Gelfand, and R. Gordon, *Nature Photonics* **9**, 68 (2015)
9. A. A. Balandin and V. A. Fonoberov, *Journal of Biomedical Nanotechnology* **1**, 90 (2005)
10. N. Pazos-Pérez, D. Baranov, S. Irser, M. Hilgendorff, L. M. Liz-Marzán, and M. Giersig, *Langmuir* **24**, 9855 (2008)
11. H. Portales, N. Goubet, L. Saviot, S. Adichtchev, D. B. Murray, A. Mermet, E. Duval, and M.-P. Pilien, *Proc. Natl. Acad. Sci. U.S.A* **105**, 14784 (2008).
12. L. Saviot and D. B. Murray, *Phys. Rev. B* **79**, 214101 (2009)
13. S. V. Goupalov, *Nano Letters* **14**, 1590 (2014)
14. S. V. Goupalov, *Nano Letters* **14**, 2232 (2014)
15. K. Yu, P. Zijlstra, J. E. Sader, Q.-H. Xu, and M. Orrit, *Nano Letters* **13**, 2710 (2013)
16. Y. Gan, Z. Sun, and Z. Chen, *Phys. Chem. Chem. Phys.* **18**, 22590 (2016)
17. L. Novotny, *Phys. Rev. Lett.* **98**, 266802 (2007)
18. G. W. Bryant, F. J. García de Abajo, and J. Aizpurua, *Nano Letters* **8**, 631 (2008)
19. R. Rajendra, P. K. Gangadharan, S. Tripathi, S. Kurungot, and N. Ballav, *Nanoscale* **8**, 19224 (2016)
20. R. F. S. Hearmon, in *The elastic constants of crystals and other anisotropic materials*, Landolt-Börnstein New-Series, Group III, Vol. 18, supplement to III/11, edited by K. H. Hellwege and A. M. Hellwege (Springer-Verlag, Berlin, 1984).
21. N. Nishiguchi, Y. Ando, and M. N. Wybourne, *Journal of Physics: Condensed Matter* **9**, 5751 (1997)
22. W. M. Visscher, A. Migliori, T. M. Bell, and R. A. Reiner, *J. Acoust. Soc. Am.* **90**, 2154 (1991)
23. J. Z. Jr., *The Journal of the Acoustical Society of America* **51**, 265 (1972)
24. V. T. Grinchenko and G. L. Komissarova, *Soviet Applied Mechanics* **16**, 1 (1980)
25. A. W. Leissa and J. So, *The Journal of the Acoustical Society of America* **98**, 2122 (1995)
26. P. R. Heyliger and W. L. Johnson, *The Journal of the Acoustical Society of America* **113**, 1812 (2003)
27. T. Jaglinski and R. S. Lakes, *Review of Scientific Instruments* **82**, 035105 (2011)
28. E. Anderson, Z. Bai, C. Bischof, S. Blackford, J. Demmel, J. Dongarra, J. Du Croz, A. Greenbaum, S. Hammarling, A. McKenney, and D. Sorensen, *LAPACK Users’ Guide*, 3rd ed. (Society for Industrial and Applied Mathematics, Philadelphia, PA, 1999).
29. The slope at \( q = 0 \) of the torsional and longitudinal branches are identical for anisotropic NWs in Fig. 1. This is an accidental coincidence for the \( C_{ij} \) chosen in this work.
30. B. Stephanidis, S. Adichtchev, S. Etienne, S. Migot, E. Duval, and A. Mermet, *Phys. Rev. B* **76**, 121404 (2007)
31. D. Libov, *Proceedings of Meetings on Acoustics* **19**, 065061 (2013)
32. A. C. Eringen and E. S. Suhubi, “Elastodynamics,” (Academic Press, New York, San Francisco, London, 1975) p. 791.
33. G. Bachelier and A. Mlayah, *Phys. Rev. B* **69**, 205408 (2004)
34. A. Girard, J. Lerné, H. Gehan, J. Margueritat, and A. Mermet, *The Journal of Chemical Physics* **146**, 194201 (2017)
35. M. Montagna, *Phys. Rev. B* **77**, 045418 (2008)
36. A. Girard, H. Gehan, A. Crut, A. Mermet, L. Saviot, and J. Margueritat, *Nano Lett.* **16**, 3843 (2016)