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Aspect-ratio- and size-dependent emergence of the surface-plasmon resonance in gold nanorods – an *ab initio* TDDFT study†

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It is known that the surface-plasmon resonance (SPR) in small spherical Au nanoparticles of about 2 nm is strongly damped. We demonstrate that small Au nanorods with a high aspect ratio develop a strong longitudinal SPR, with intensity comparable to that in Ag rods, as soon as the resonance energy drops below the onset of the interband transitions due to the geometry. We present *ab initio* calculations of time-dependent density-functional theory of rods with lengths of up to 7 nm. By changing the length and width, not only the energy but also the character of the resonance in Au rods can be tuned. Moreover, the aspect ratio alone is not sufficient to predict the character of the spectrum; the absolute size matters.

Noble-metal nanoparticles (NPs) exhibit optical properties that open the pathway to a large number of interesting applications owing to the localized surface-plasmon resonance (SPR) that dominates their optical response in the visible and the ultraviolet regions. Applications include surface-enhanced Raman spectroscopy (SERS),¹ biomolecule sensing,² labeling of biomolecules,³ cancer therapy by rapid local heating,⁴ plasmonic enhancement of the absorption in solar cells⁵ and, importantly, nanophotonics.⁵ It is important to note that for such small nanoparticles, the classical description can no longer be expected to be valid; the quantum-mechanical nature of the nanoparticles has to be taken into account. This can be done using time-dependent density-functional theory (TDDFT) based

on either a jellium model of the nanostructures^{6,7} or using pseudopotentials⁸ or localized bases⁹ to describe the inhomogeneity on the atomistic level.

Gold and silver, despite their chemical similarity, show very different optical properties. In Ag NPs, the SPR is observed down to very small sizes (fewer than 20 atoms).¹⁰ By contrast, in spherical Au NPs, the resonance gets more and more damped with decreasing size due to the coupling with interband transitions from the d electrons, up to the point to disappear almost completely at about 2 nm.^{11–15} A good explicit description of the d electrons is, therefore, important for the description of small Au nanoparticles.

Moreover, the resonance energies are strongly dependent on the shape of the NPs. In particular, nanorods with high aspect ratios show a continuously decreasing resonance energy with increasing length, as it is well known for larger structures that can be described by classical Mie theory.^{16–18} In this case, the resonance energy depends only on the aspect ratio, not on the absolute size of the rods. The same redshift for increasing length has recently been shown quantum-mechanically using *ab initio* TDDFT for small pentagonal silver nanorods with up to 67 atoms¹⁹ and for larger rods using TDDFT based on a jellium model²⁰ as well as for even larger Au rods using the discrete dipole approximation.²¹

In the present communication, we show that small Au nanorods start to exhibit a strong longitudinal resonance as soon as the aspect-ratio-dependent red-shift is so large that the resonance energy falls below the onset of the interband transitions from the d electrons. We present *ab initio* TDDFT calculations of pentagonal Au and Ag rods with up to 145 atoms, corresponding to a length of 7 nm. For this number of atoms, spherical Au nanoparticles have a diameter of about 1.8 nm and do not show the resonance.⁸ The transition is geometry related and entirely different from the size-dependent appearance of the SPR in spherical particles. Comparison with thicker rods with up to 263 atoms and with linear Ag and Au chains shows that by changing the aspect ratio and absolute size, the resonance energy can be tuned in and out of the region where the

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† Electronic supplementary information (ESI) available: We show the density of states of the occupied states of the ground-state calculation for the gold rods. Furthermore, we show the complete set of spectra calculated for monatomic Au and Ag chains and the comparison of their peak energies and spectra with those of the nanorods. Moreover, the numerical details of the calculation are given along with a comparison with different exchange–correlation functionals as well as with a transition-based calculation. See DOI: 10.1039/c3cp53702a

coupling with the interband transitions leads to strong damping of the SPR, thus changing the character of the optical response decisively.

We study a family of pentagonal nanorods derived from the 13-atom decahedral cluster by stacking slabs of a fivefold ring and a central atom along the rotational axis. Pure-silver rods of this type have been investigated by Johnson and Aikens,¹⁹ bimetallic Ag–Au rods have been treated in a previous study.⁸ All spectra are shown for excitation in the direction parallel to the axis. Rods of larger width are obtained by adding one more shell of atoms compatible with the pentagonal symmetry, cf. Fig. 3 and 4.

The optical absorption spectra are calculated by time-dependent density-functional theory using the real-space code octopus.^{22,23} Following a ground-state calculation, spectra are obtained using the time-evolution formalism.²⁴ We use the PBE exchange–correlation functional and norm-conserving Troullier–Martins pseudopotentials. The details of the calculations as well as a comparison with different exchange–correlation functionals are given in the ESI.†

Short gold rods exhibit multiple structures in the spectra and do not show a dominant resonance, as shown in Fig. 1. By contrast, already for 19 atoms, the Ag rods show a clear resonance that red-shifts with increasing length.¹⁹ Moreover, the absorption of Au is much less intense than that of the respective Ag rods.⁸ This is due to the strong coupling of the collective excitation with the interband transitions from the d band, which in Au is much closer to the Fermi energy than in Ag.²⁵ However, upon increase of the Au rod length, the response changes drastically: starting from 103 atoms (about 5 nm), a clear single resonance appears and dominates the spectrum,

as clearly shown in Fig. 1. Moreover, the intensity of the peak in the longest Au rod (Au₁₄₅, 7 nm) is comparable to that of its Ag counterpart.

This striking transition is due to the fact that the resonance starts to fall below possible interband transitions, which are responsible for the damping of the SPR in small Au nanoparticles. Photo-emission spectra of mass-selected Au_n[−] clusters show that the interband energy is slightly smaller than 2 eV in Au clusters between 21 and 200 atoms.²⁶ The density of states (DOS) from the ground-state DFT calculation of the Au₁₄₅ rod is included in Fig. 1 as a representative example, and a detailed comparison of the different rods is shown in Fig. S1 of the ESI.† The DOS of the occupied states of the longer rods with constant width does not change with length. Now interband transitions can take place from the d band into unoccupied states above the Fermi energy. Comparison with the rod spectra in Fig. 1 shows clearly that the longitudinal resonances become well-defined and strong once they fall below the energies of possible interband transitions. In this regime, the Au rods behave like silver rods, for which the resonance is below the interband threshold for all sizes.

Classically, the SPR is seen as a collective charge oscillation that can be excited by the electrical field of a light source.²⁷ In Fig. 2 we demonstrate that the excitation, calculated fully quantum-mechanically using TDDFT, corresponds indeed to the classical picture of the surface-plasmon. Following the perturbation at $t = 0$, the system evolves freely. The oscillation of the dipole moment of the rod is dominated by one single mode and is very stable over the time span of the calculation. We show four snapshots of the time-dependent density (shown is the difference to the ground-state density). The valence electrons show a strong coherent oscillation over the full size of the nanorod, the strong polarization shown in the first and the third snapshot corresponding to the maximum values of

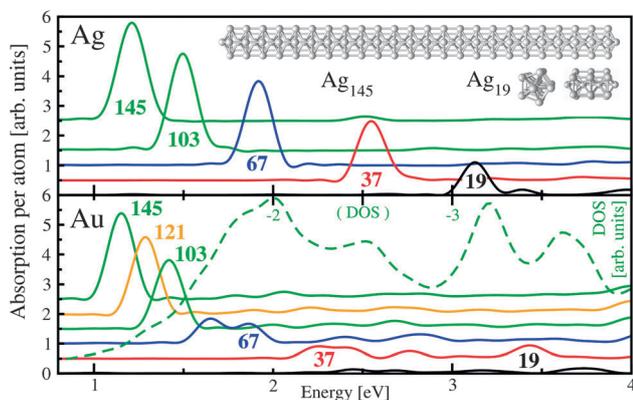


Fig. 1 Absorption spectra of pentagonal Au nanorods, shown along with their Ag counterparts for comparison, for excitation parallel to the axis. All spectra are normalized to the number of atoms so that intensities are directly comparable. Spectra are stacked for better visibility. The atomic structure is shown for the longest rod Ag₁₄₅, as well as for the shortest one, Ag₁₉, from two different perspectives. The respective Au rods have identical structures. Au_n denotes nanorods with n atoms, i.e., $(n - 1)/6 + 1$ center atoms along the rod axis, with $(n - 1)/6$ “slabs” consisting each of a five-fold ring and a center atom. In the lower panel, the density of states of the occupied states in the Au₁₄₅ nanorod is also shown (dashed line). The zero of its energy axis is the Fermi energy, and a broadening of 0.1 eV has been applied. Comparison with the DOS of the other rods is shown in the ESI.†

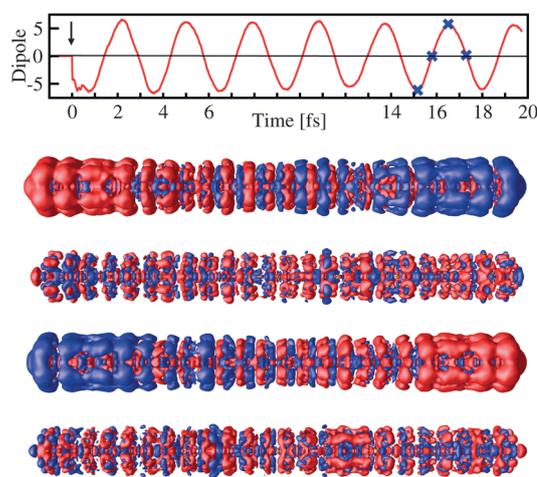


Fig. 2 Snapshots of the time-dependent electron density of the Au₁₄₅ rod. Red and blue correspond to equal positive and negative values of the difference to the ground state density. After the perturbation at $t = 0$, indicated by the arrow, the system evolves freely. The four snapshots correspond to one period of the oscillation of the dipole moment shown at the top, where the crosses show the times corresponding to the snapshots.

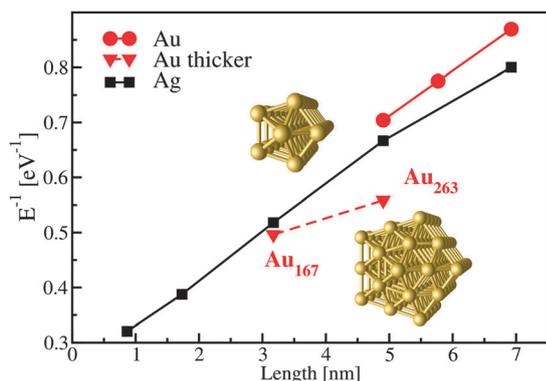


Fig. 3 Peak energy of the longitudinal excitation for pentagonal Au and Ag rods. A comparison with monatomic Au and Ag chains is shown in the ESI.†

the dipole moment. By contrast, at the points of zero overall dipole moment, the overall deviation from the ground-state density is small and limited to local fluctuations.

Having established the similarity of the long gold rods to silver rods, we compare the peak energies as a function of rod length in Fig. 3. The inverse peak energies of the gold rods with 103, 121, and 145 atoms (between 5 and 7 nm in length) show a linear behavior in complete analogy with that of the Ag rods of all lengths shown. The behavior of the silver rods is in agreement with the results of Johnson *et al.*¹⁹ Only the absolute value of the peak energies of Au is smaller due to the stronger polarizability of the d electrons in Au, compared to Ag.

In order to distinguish the effects of changing the aspect ratio and absolute size, we consider pentagonal rods to which another shell of atoms has been added, leading to the double-shell sizes of Au₈₇, Au₁₆₇, and Au₂₆₃ shown in Fig. 3 and 4, which correspond in length to the single-shell rods Au₃₇ (1.7 nm), Au₆₇ (3.2 nm), and Au₁₀₃ (4.9 nm). The 4.9 nm Au₁₀₃ rod is the shortest Au rod that shows the strong, clear-cut resonance (Fig. 1). As the aspect ratio is lowered by adding the additional shell but keeping the length unchanged, the resonance is blue-shifted, potentially back into the region where the coupling with

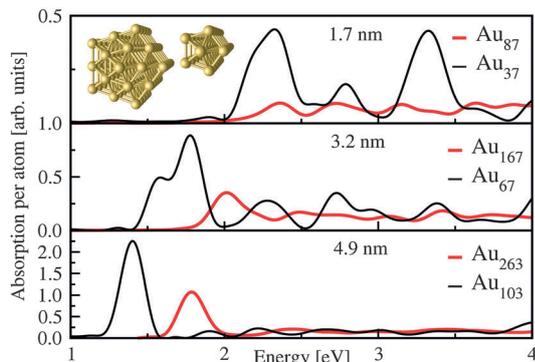


Fig. 4 Absorption spectra for three different lengths of gold nanorods of different thickness as indicated. (Red: double-shell rods; black: single-shell rods.) A comparison with the spectra of monatomic chains is shown in the ESI.†

the interband transitions attenuates the SPR. However, the spectrum of the double-shell rod Au₂₆₃, shown in Fig. 4, does show a clear, dominant resonance.

The reason for this is two-fold. First, it can be assumed that the Au₂₆₃ rod is already of the size where the SPR starts to be observed in small spherical nanoparticles, although the transition is aided by the red-shift of the resonance due to the rod geometry.

Second, inspection of the density of states shows that the onset of the d band in the double-shell rods is smoother than in the thin rods (see Fig. S2 of the ESI†), which certainly influences the interband transitions. This is particularly evident from the comparison of the double-shell Au₂₆₃ rod with the 3.2 nm Au₆₇ rod. The peak energy of Au₆₇ is equal or even slightly lower than that of Au₂₆₃, but there is a double-peak structure. However, these two rods, Au₆₇ (3.2 nm) and Au₂₆₃ (4.9 nm), have comparable aspect ratios. The comparison of their spectra is, therefore, highly interesting because it shows that the aspect ratio alone is *not* sufficient to determine the character of the spectra; in the size range that we consider, the absolute size of the rods is very important.

Finally, it is interesting to note that the same effects that are observed in the Ag and Au rods are already present in the optical response of monatomic Au and Ag chains, which have been studied recently by Guidez and Aikens.²⁸ They can be seen as the limiting case of nanorods of very small width. Spectra of Au chains are compared to the nanorod results in Fig. S5 of the ESI,† the complete set of spectra is shown in Fig. S3 of the ESI.† They are in good agreement with the spectra in ref. 28, although our energies are in general slightly lower due to differences in the calculation, particularly due to the use of different exchange-correlation functionals. As for the rods, Ag shows strong longitudinal resonances even for very short chains, while in Au the resonance of, *e.g.*, Au₆ is fragmented and the relatively strong peak at 1.2 eV is not the lowest excitation visible in the spectrum. Between 1.2 and 3.0 eV, interband transitions from the d band are visible that do not change strongly with length, again in agreement with the findings of Guidez *et al.*²⁸ As shown in the ESI,† Au chains show the same type of transition as the rods: the longitudinal resonance becomes strong once it is well separated from the latter transitions. In Fig. S4 of the ESI,† we compare the peak energies of the chains with those of the rods, finding a strong analogy between the two systems, in particular the linear dependence of $1/E$ on the length. The slope of the lines is larger because the aspect ratio, although difficult to define, increases more rapidly with the length than in the case of the rods.

In conclusion, we have explicitly shown the aspect-ratio-dependent transition of the longitudinal optical response of Au nanorods from the strongly damped case of short rods to the plasmonic regime of strong resonances, starting from about 5 nm in length. To this end, we have calculated the optical response of rods of up to 7 nm (145 atoms) using *ab initio* time-dependent density-functional theory. The strong longitudinal resonances in Au develop due to the general red-shift of the resonances with increasing rod length once their energy falls below the onset of the interband transitions from the d band.

Their intensity as well as their dependence on the rod length are very close to those of their Ag counterparts. The energies of the filled d states remain unchanged upon increase of the length, as evidenced by the unchanged density of states. Comparison with the longitudinal resonances of monatomic Au and Ag chains shows strong analogies to the case of the rods. Moreover, an increase of width leads to a blue-shift for constant length, shifting the SPR of the 4.9 nm Au₂₆₃ rod to an energy where the SPR of the narrower Au₆₇ is damped and fragmented. Due to the larger size and the resulting smoother onset of the d band, Au₂₆₃ retains the single well-defined resonance. The absolute size is decisive, the aspect ratio alone is not sufficient to predict the spectra. Our results hence show that the resonance in Au rods can be tuned in energy and character, by changing the aspect ratio and size.

Notes added in proof

Very recently, we became aware of a study by Guidez *et al.* of smaller pentagonal Au rods (up to 84 Au atoms) using the LB94 functional, with similar tendencies found but differences remaining [Guidez *et al.*, *J. Phys. Chem. C*, 2013, **117**, 12325–12336], and of a study by Piccini *et al.* of Au rods based on the fcc bulk structure [Piccini *et al.*, *J. Phys. Chem. C*, 2013, **117**, 17196–17204].

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