

Differential extinction of vibrational molecular overtone transitions with gold nanorods and its role in surface enhanced near-IR absorption (SENIRA)

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Abstract: Resonant coupling between plasmonic nanoantennas and molecular vibrational excitations is employed to amplify the weak overtone transitions that reside in the near-infrared. We explore for the first time the differential extinction of forbidden molecular overtone transitions coupled to the localized surface plasmons. We show a non-trivial interplay between the molecular absorption enhancement and suppression of plasmonic absorption in a coupled system. When the resonance conditions are met at 1.5 μm , two orders of magnitude enhancement of differential extinction as compared to the extinction of the same amount of free probe molecules is achieved. Our results pave a road toward a new class of surface enhanced near-infrared absorption-based sensors.

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1. Introduction

Near-infrared (NIR) spectroscopy focuses on interaction of near-infrared radiation with matter and is an important analytical technique for detection and recognition of chemical substances based on vibrational modes of their molecular constituents in pharmaceutical analysis, food quality determination, non-destructive analysis of biological materials to name a few [1–3]. However, molecular overtone bands lying in the NIR spectral region are forbidden in harmonic oscillator approximations. Such bands arise only from the anharmonicity of molecular vibrations which is rather weak leading to the overtone bands with the absorption cross-section of an order of magnitude smaller than the fundamental modes of the same degree of freedom [4]. Nevertheless, recent numerical and experimental results demonstrated that the overtone molecular vibration of aniline and N-methylaniline can be detected utilizing a silicon nanostrip rib waveguide [5].

Here we explore for the first time the mechanism of local field enhancement in molecular overtones. The local field enhancement can be realized with plasmonic materials by means of collective oscillations of free electrons in form of extended surface plasmon-polariton (SPP) in thin metal films [6–11] or localized surface plasmon resonance (LSPR) in plasmonic nanoantennas [12–15]. Meanwhile, we explored the influence of extended surface plasmon on absorption by molecular overtones, and showed that 100 times enhancement can be achieved [16]. This enhancement was observed when the absorption band of the molecular vibration N-H was detuned from the plasmonic resonance. It should be mentioned that enhancement and localization of electromagnetic fields in the close proximity of nanoantennas depend on their material, size, shape and the surrounding media [12]. Previously we found that the electronegative gold nanospheres are readily adsorbed on the tapered microfiber and electrostatically bonded to

amine-based molecules. Despite the non-resonant condition between the gold nanospheres and the amine-based molecules, we showed that the enhancement of the integrated overtone absorption in diffuse light propagation depends on the concentration of nanospheres [17]. Very interesting results were reported in [18]. The authors prepared porous gold nanodiscs that possess a broad plasmon resonance in the near-infrared range. When a random array of such nanodiscs is covered by a thin film of a material possessing absorption bands in the same spectral region, enhanced absorption of the composite material may be observed. Very large, up to four orders of magnitude, enhancement claimed in [18] is due to the use of analyte in the form of a self-assembled monolayer. In this case analyte presents exclusively in hot-spot regions. In general case, analyte occupies much larger volumes where the field enhancement is lower. Hence, the overall enhancement becomes lower as well. Despite this experimental observation of surface enhanced near-infrared absorption (SENIRA) of molecular overtones with plasmonic nanoantennas, this effect was not explored theoretically. The first work related to coupling of vibrational mode and plasmonic dipole oscillation of gold nanorods was theoretically implemented using a homogeneous weakly absorbing medium [19].

In this work we theoretically explore yet unclear possibility to enhance absorption by molecular overtone transitions in the near-field of plasmonic nanoantennas such as gold nanorods (GNRs) due to the combination of localized plasmon resonance and lightning rod effect [20]. Below we show that when the resonance conditions are met at $1.5\ \mu\text{m}$ the differential extinction due to the excitation of overtones of N-H and C-H stretching modes can be enhanced by two orders of magnitude as compared to the ordinary extinction of the same amount of molecules.

2. Theoretical model

Figure 1 shows the system we study. Weakly absorbing medium, described by the complex permittivity of N-Methylaniline molecule, encapsulates a gold nanorod and nanoellipsoid in a homogeneous shell-like manner. The incident beam is directed perpendicular to the gold nanoparticles as indicated by vector \mathbf{k} and polarized along the gold nanoparticles.

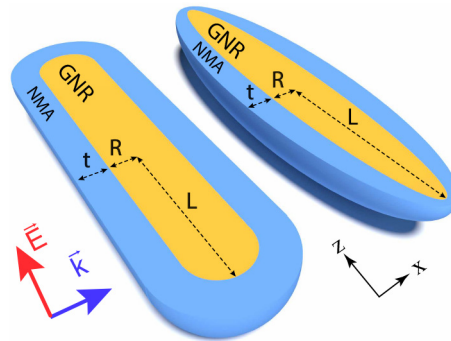


Fig. 1. Schematics of systems with gold nanorods (left) studied in numerical simulations and nanoellipsoids (right) used in the analytical model. The shells are made of N-Methylaniline (NMA). L and R are semi-major and semi-minor axes of gold nanoparticles respectively, while t is the thickness of molecular shells. The incident wave is polarized along the rod.

We study the contribution of GNR parameters in effect of SENIRA by molecular overtones. For this we built an analytical model of a confocal ellipsoidal core-shell nanoparticle. In the framework of quasi-static approximation, we express the absorption, scattering, and extinction

cross-sections through the particle polarizability [21,22]

$$\alpha = \frac{v \left((\epsilon_2 - \epsilon_m) \left[\epsilon_2 + (\epsilon_1 - \epsilon_2) (S^{(1)} - fS^{(2)}) \right] + f\epsilon_2 (\epsilon_1 - \epsilon_2) \right)}{\left(\left[\epsilon_2 + (\epsilon_1 - \epsilon_2) (S^{(1)} - fS^{(2)}) \right] \left[\epsilon_m + (\epsilon_2 - \epsilon_m) S^{(2)} \right] + fS^{(2)} \epsilon_2 (\epsilon_1 - \epsilon_2) \right)}, \quad (1)$$

$$\sigma_{ext} = \sigma_{abs} + \sigma_{sc} = 4\pi k \operatorname{Im}\{\alpha\} + \frac{8\pi}{3} k^4 |\alpha|^2, \quad (2)$$

where S^i ($i=1,2$) are the geometrical factors of the core and the shell in the direction of the polarization (Fig. 1); $\epsilon_1, \epsilon_2, \epsilon_m$ are the frequency-dependent dielectric permittivity function of the gold core, the molecular shell and surrounding media, correspondently; v is the full volume of the nanoparticle with the shell and f is the ratio of the inner core volume to v ; k is the wavenumber in the medium defined as $2\pi/\lambda$.

As the input parameters we consider the core and shell semi-axes and the frequency-dependent dielectric permittivities of the metal core, the shell and the surrounding medium, which was considered to be air.

To calculate the absorption, scattering and extinction cross-section spectra of complex systems comprising gold nanoparticles and molecular shells we used 3D full-wave computational models implemented in the commercial software COMSOL Multiphysics 5.4. In particular, the wave optics module for electromagnetic waves in the frequency domain was utilized. We included the perfectly matched layer (PML) in the form of a physical domain to absorb all scattered light. Gold nanorods were modeled as cylinders capped by hemispheres on both sides. Dimensions of all elements are given in the text and figure captions. The incident field oscillates in the z -direction with a k -vector pointing in the x -direction as shown in Fig. 1. The absorption cross-section (σ_{abs}) was calculated by integrating the power loss density over the particle volume. The scattering cross-section (σ_{sc}) was derived by integrating the Poynting vector over an imaginary sphere around the particle. Extinction cross section is the sum of both. The complex refractive index of the gold was obtained from the experimental work of Johnson and Christy [23].

The N-Methylaniline (NMA) was chosen as a representative probe-molecule example of an organic molecule that possesses overtone bands in the NIR spectral range [24–26]. The absorption bands at wavelengths of 1494 nm and 1676 nm are associated with the first overtones of N-H and C-H stretching modes. These bands are accompanied by the anomalous dispersion regions calculated based on a measured absorption spectra k as it follows from the Kramers-Kronig relations (presented in Figure 7(d) in [24]).

3. Results and discussion

First, we analyzed how the LSPR position depends on the analyte shell thickness, t . Since the enhanced near-field rapidly decays with the distance from the surface, effective interaction is possible here only at distances comparable to the nanoantenna dimensions. In addition, the aspect ratio of the nanoantenna should provide the resonant interaction between the longitudinal plasmon and an overtone excitation. Therefore, we choose the semi-minor axis of the gold nanoellipsoid as 5 nm, while varying the semi-major axis until the LSPR band overlaps with an overtone mode.

For this, we calculated extinction cross-sections of gold nanoellipsoids covered by thin shells of NMA in the form of confocal ellipsoids. Figure 2(a) shows the extinction cross-section of GNR as a function of the NMA shell thickness. The semi-major axis of the gold core is $L = 55.9$ nm that leads to the exact resonance with the first overtone of N-H mode when the shell thickness is $t = 20$ nm. Figure 2(b) shows the same dependence when the semi-major axis of the gold core is $L = 68.1$ nm that leads to the exact resonance with the first overtone of C-H mode when the shell thickness is $t = 20$ nm. The long wavelength shift of plasmon bands as a function

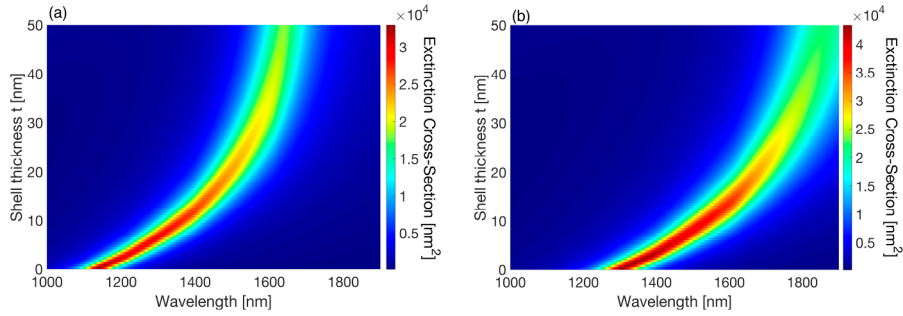


Fig. 2. Extinction cross-sections of gold nanoellipsoids with NMA shells of different thicknesses. (a) the semi-major axis of the gold core is $L = 55.9$ nm (b) the semi-major axis of the gold core is $L = 68.1$ nm. The semi-minor axis is $R = 5$ nm in both cases.

of the shell thickness t is rather strong at small shell thicknesses for $t < 40$ nm but saturates at shell thicknesses larger than $t > 40$ nm.

As proof-of-concept numerical simulations we built numerical model using COMSOL and show the tuning of the plasmon bands of GNR with the NMA overtone bands. Figure 3 shows calculated extinction (ECS), absorption (ACS) and scattering (SCS) cross-section of gold nanorods with NMA shell for $L = 49.9$ nm (Fig. 3(a)) and for $L = 60.6$ nm (Fig. 3(b)). The nanorod diameter is 10 nm. We choose the length of GNR such that it overlaps with the overtone bands of N-H located at 1494 nm and C-H located at 1676 nm. Considering the results presented in Fig. 3 one concludes that extinction is governed by absorption, while the scattering contribution is negligible.

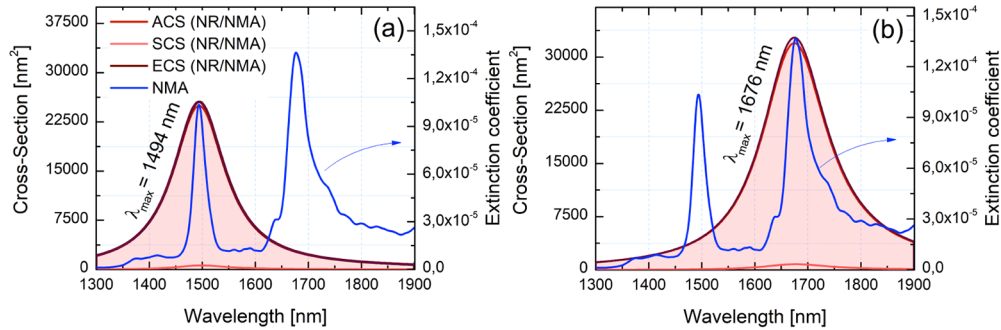


Fig. 3. Extinction (brown), absorption (red) and scattering (pink) cross-sections of gold nanorods with NMA shell. The nanorod diameter is set to 10 nm for (a) $L = 49.9$ nm, (b) $L = 60.6$ nm. The thickness of the NMA molecular shell is homogeneous and equals to $t = 20$ nm. Extinction coefficient of NMA (blue) is also shown for comparison.

The advantage of using GNR becomes evident when the concept of differential extinction is employed [16]. Experimentally, the differential absorption can be realized by comparing the extinction cross-section of a GNR surrounded by the analyte shell with that of a GNR surrounded by a shell of non-absorbing material that mimic only the mean value of the analyte's refractive index. Thus, the difference between cross-sections of absorbing and non-absorbing materials represents the influence of the analyte absorption and anomalous dispersion on the LSPR intensity and spectral position. On the other hand, it includes also the influence of the LSPR on the analyte absorption.

Quantitatively, *differential extinction*, DE, as [16,19]:

$$DE = \sigma_{ext}^{NR/NMA} - \sigma_{ext}^{NR/NMA^*}, \quad (3)$$

where the first term $\sigma_{ext}^{NR/NMA}$ represents the extinction cross-section of GNR with NMA shell, while the second term σ_{ext}^{NR/NMA^*} represents the same value with NMA replaced by a dummy medium of constant dielectric permittivity. Figure 4 shows the calculated DE in spectral ranges of the first overtones of the N-H and C-H stretching modes. Interestingly, the sign of the wavelength dependent DE alternates in both cases.

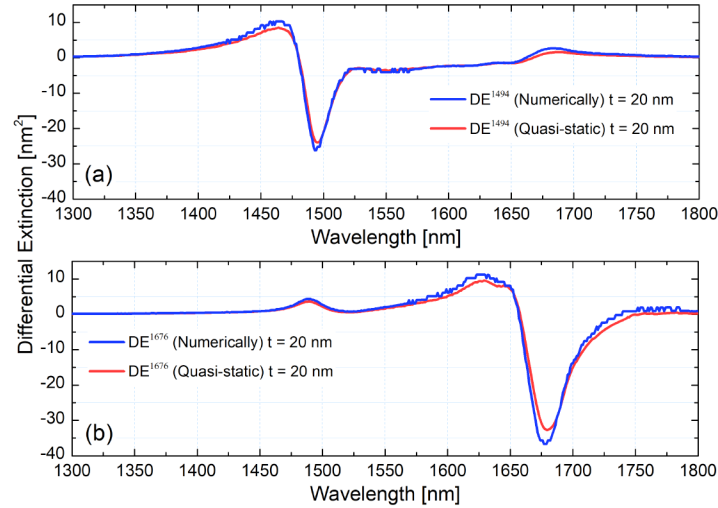


Fig. 4. Comparative analysis of differential extinction (DE) spectra of gold nanorod and nanoellipsoid with NMA shells: (a) with semi-major axes $L = 49.9$ (nanorod) and $L = 55.9$ nm (nanoellipsoid); (b) $L = 60.6$ (nanorod) and $L = 68.1$ nm (nanoellipsoid). Blue curves correspond to numerically calculated results (nanorod) while the red curves correspond to results obtained in the quasi-static approximation (nanoellipsoid)

Figure 4 shows the calculated DE in spectral ranges of the first overtones of the N-H and C-H stretching modes. Interestingly, the sign of wavelength dependent DE alternates in both cases.

We choose the aspect ratio of nanorods for the Fig. 4 as $L/R = 9.98$ and the aspect ratio of nanorods for the Fig. 4(b) as $L/R = 12.12$. Numerically calculated DEs (blue) are very well reproduced by the DEs obtained in the quasi-static approximation (red) (Eq.1) provided the aspect ratios of the GNRs are adjusted to match the plasmon resonance with the corresponding overtone ($L/R = 11.18$ Fig. 4(a) and $L/R = 13.62$ in Fig. 4(b)). It is important to note that in the case exact resonance between the plasmon in the GNR and the molecular overtone transition the sign of DE alternates. Contrary to that in the non-resonant case DE is strictly positive. It may be clearly seen in Fig. 4 for C-H overtone transition at 1676 nm when the plasmon in the nanorod is tuned on 1494 nm (Fig. 4(a)) and for N-H overtone transition at 1494 nm when the plasmon in the nanorod is tuned on 1676 nm.

To explore the role of GNRs in the detectivity enhancement of small amounts of NMA, extinction cross-sections of pure NMA shells (without GNR) were compared with the DE. Figure 5 shows the dependence of both values on the NMA shell thickness. When the resonance conditions are met, the DE values exceed the extinction cross-sections of the pure NMA shells by two orders of magnitude. In particular, the first overtone of N-H stretching mode located at 1494 nm is enhanced 114 times, while the first overtone of C-H stretching mode located at 1676 nm is enhanced 135 times. Figure 5(a) shows variations in cross-sections versus shell thickness

for $\lambda = 1494$ nm and the GNR semi-major axis is equal 49.9 nm. The resonance conditions for the plasmon excitation are met when the shell thickness is equal to 20 nm. Similarly, the optical properties in the form of ECS and ACS as function of the shell thickness are presented in Fig. 5(b) whereby $\lambda = 1676$ nm with GNR semi-major axis $L = 60.6$ nm.

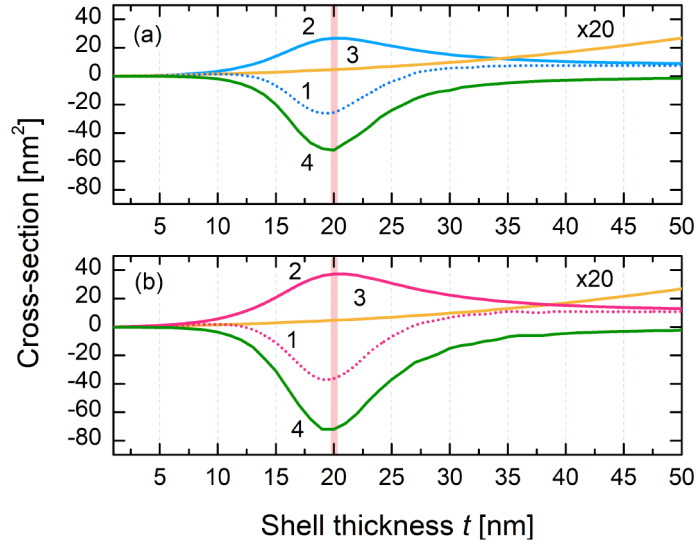


Fig. 5. (a) Optical cross-section as function of shell thickness of NMA: (1) differential extinction, (2) absorption cross-section of NMA shell encapsulating GNR, (3) extinction cross-section of the NMA shell without the GNR, and (4) the difference between ACSs of the GNR -with and -without the NMA shell GNR semi-major axis (a) L is 49.9 nm and the wavelength is set to 1494 nm. Absorption cross-section of the NMA shell when the GNR is absent is multiplied by 20. (b) same graphs as in subplot (a) for the case when the wavelength is set to 1676 nm, while L is 60.6 nm.

Enhanced absorption in the NMA shell due to the plasmon near-field is accompanied by reduced absorption in the GNR due to the screening effect [27]. As a matter of fact, neither enhanced absorption in the shell nor the reduced absorption in the core can be observed in the far-field separately. However, they combine favorably leading to very large DE values.

DE dependence on both: the NMA thickness and the incident radiation wavelength based on analytical model is presented in Fig. 6. In both plots the dark curve corresponds to the maxima of the LSPR. The vertical dashed lines mark the location of overtone bands, while the horizontal dashed lines correspond to NMA thickness of 20 nm that leads to coincidence of the LSPR in the chosen nanorod with the corresponding overtone band. Inspection of Fig. 6 to the conclusion that the main features of DE already noted in particular cases presented in Fig. 4 and Fig. 5 namely, that the largest absolute value of DE is obtained at the resonance and the sign of this largest DE value is negative are confirmed.

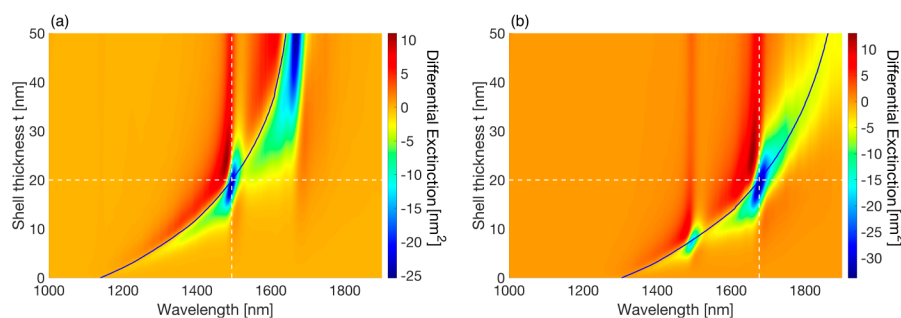


Fig. 6. (a) Differential extinction (DE) values are given as the functions of the NMA shell thickness and the incident radiation wavelength for GNR with semi-major axis of: $L = 55.9$ nm (a) and $L = 68.1$ nm (b), respectively. The vertical dashed lines show the position of two overtone bands, while the horizontal dashed lines mark the shell thickness ($t = 20$ nm) that leads to tuned plasmon resonance with the corresponding overtone band. The dark curve is drawn through the maxima of the plasmon resonances.

4. Conclusion

In conclusion, we explored for the first time the *differential extinction* of forbidden molecular overtone transitions coupled to the localized surface plasmons. We showed that the differential extinction provides the SENIRA with two orders of magnitude enhancement. The non-trivial consequence of the simulations is that the enhanced absorption in the analyte is accompanied by the reduced absorption in the gold nanorods that overruns the absorption enhancement of the analyte and forms the signal that may be readily sensed in the far-field. Hence, local field enhancement of nanoparticle can result in the considerable sensitivity improvements of overtone spectroscopy in the NIR spectral range.

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Disclosures

The authors declare that there are no conflicts of interest related to this article.

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