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Vibrational overtones spectroscopy enabled by plasmonic nanoantennas

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ABSTRACT

Infrared spectroscopy is very powerful tool to analyze the chemicals based on their molecular signatures. The registration of the fundamental vibrational modes that lie in the far IR is extensively explored, however the excitation of derivatives namely high harmonics molecular vibrations overtones is still a mystery. Although the absorption cross-section of molecular transition overtones is order of magnitude smaller compared to their fundamental vibrations, the research of overtones is of high importance if just would be possible to detect them. In this work, we show that the challenge in detection of molecular overtones may be overcome with localized surface plasmon resonance effect in gold nanorods antennas. We use *N-Methylaniline* as a probe molecule since we confirmed the excitation its molecular transitions overtones in near-infrared around 1.5 μm . We calculate absorption cross-section of gold nanorods with fixed diameter of 10 nm and different lengths varying from 80 to 160 nm surrounded by a homogeneous medium with the optical properties of *N-Methylaniline*, using the finite element method (FEM). To single out the contribution of the overtone modes, computations were repeated with *N-Methylaniline* replaced by the dispersionless media mimicking only the mean value of *N-Methylaniline* refractive index, $n = 1.5712$, and eliminating absorption. We show, that the differential absorption in the spectral range of the first overtone of the $-NH$ vibration located at 1492 nm and the first overtone of the $-CH$ vibration located at 1676 nm have both positive and negative values due to the shifting of the gold nanorod plasmon resonance band.

Keywords: localized surface plasmon resonance, plasmonic nanoantenna, vibrational overtones spectroscopy, gold nanorods

1. INTRODUCTION

Plasmonic and nanophotonics is at the front of physics and optics science. Plasmonic nanoparticles localize the electromagnetic radiation and enhance peculiar optical phenomena such as extraordinary transmission^{1,2}, surface enhanced fluorescence³ and others^{4,5}. Here we explore the differential absorption as defined in ref.⁶ of by homogenous weakly absorbing medium in presence of surface plasmon oscillations.

Mid-infrared spectroscopy is very useful tool which allows to obtain the chemical information in the regard of the molecular overtones and series bands of the fundamental vibrational modes. Molecular overtone bands are bands observed in the vibrational spectrum of an anharmonic oscillator along with the fundamental band arising as a result of the transition $\Delta v = \pm 1$. The intensities of the overtones are small: they are approximately 1/10 and 1/100 of the intensity of the fundamental band for the 1st and 2nd overtones, respectively⁷.

Thus, it is more problematic to recognize the presence of chemical groups of molecules from their absorption spectra unlike from the “fingerprint” in the mid-infrared range due to the overlapping of absorption band of the overtones and other combinations. The molecular overtone and series bands are one to three orders of magnitude weaker than the fundamental transitions that correspond to the same degree of freedom. The study of enhancement of the absorption cross-section of the vibrational transitions overtones enabled by plasmon nanoparticles has a limited number of works and remains relevant up to now. This provides challenges for enhancement of the vibrational transitions overtones which can become an especially useful tool for sensing application.

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2. OBJECTS AND METHODS

In the present work the numerical simulation of optical properties was performed with Finite Element Methods (FEM) implemented in the commercial COMSOL Multiphysics 5.3 software in radio frequency (RF) module. Schematic of the model is depicted in the Figure 1.

Here, to calculate the absorption cross-section in near-infrared region we consider two cases: 1) when gold nanorod surrounded by a homogeneous medium with the optical properties of *N-Methylaniline* and, 2) by index matching oil with the constant refractive index 1.5712. The length of gold nanorods was varied from 80 to 160 nm while their diameters were kept constant at 10 nm. In the figure 1 we show the schematic of the simulation model. The thickness of the Perfectly Matched Layer (PML) equals to $\lambda/2$. The refractive index n and extinction coefficient k of gold was taken from ⁸.

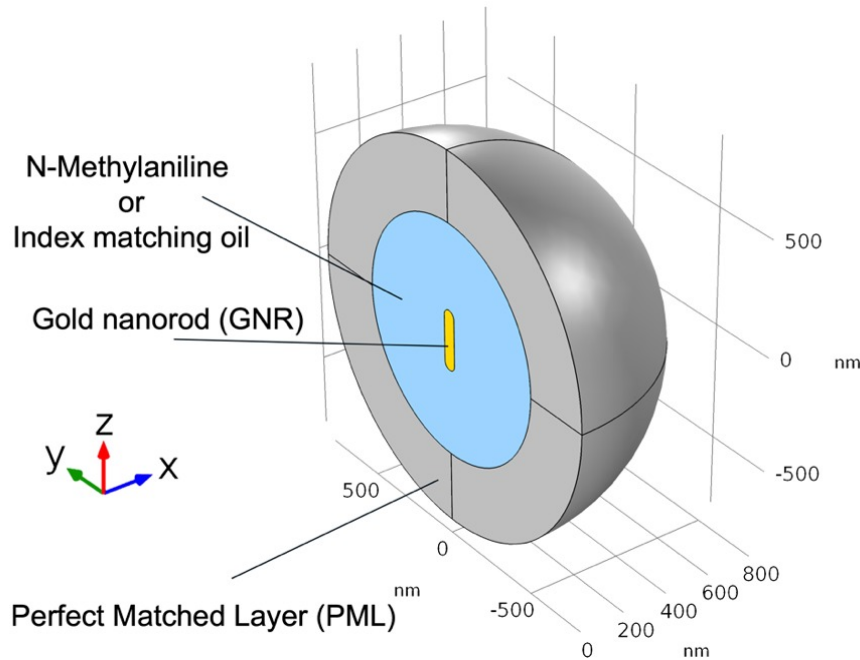


Figure 1. Schematic 3D simulation model of single gold nanorod surrounded by weakly absorbing homogeneous medium.

Extinction coefficient k and refractive index n of *N-Methylaniline* and their wavelength dependence were obtained by the measurement of the absorption spectrum. The measurements were carried out in a quartz cuvette with a path length of 1 mm. The optical constants were calculated in MATLAB[®] environment using the Kramers-Kronig relations as defined in ⁹

$$n(\omega) - 1 = \frac{2}{\pi} \cdot P \int_0^{\infty} \frac{\omega' k(\omega')}{(\omega'^2 - \omega^2)} d\omega' \quad (1)$$

The figure 2 shows the dispersion of pure *N-Methylaniline* calculated using equation 1. The red curve related to the extinction coefficient has two pronounced peaks. The peak at the wavelength of 1492 nm corresponds to the *-NH* first overtone band. The peak at the wavelength of 1676 nm corresponds to the *aryl -CH* first overtone band. This results is confirmed by the experimental work ¹⁰.

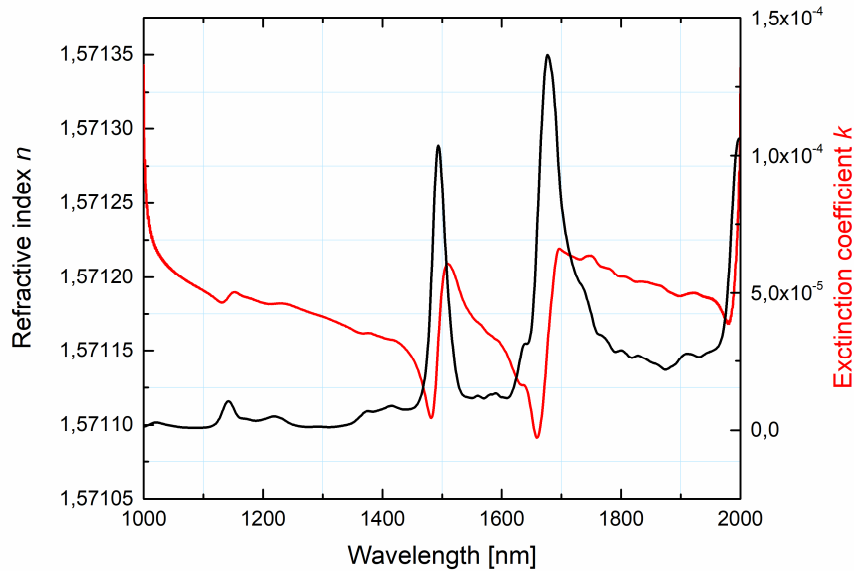


Figure 2. Dispersion characteristic of *N-Methylaniline* molecules as a function of the wavelength in near-infrared.

3. RESULTS AND DISCUSSION

The absorption cross-section spectra of the single gold nanorod surrounded by a medium with 500 nm layer thickness are shown in the Figure 3. First, we calculated the absorption cross-section of the gold nanorod in a lossless medium with the wavelength-independent refractive index $n=1.5712$. In accordance with the well-known results of the quasi-static theory the plasmon bands in the longer gold nanorods experience a red-shift.

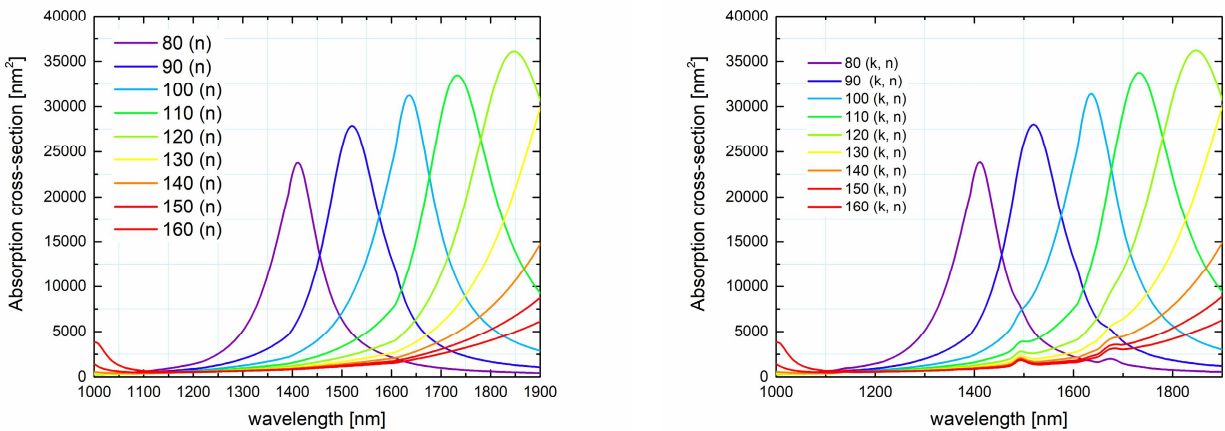


Figure 3. The absorption cross-section as function of the wavelength. The single gold nanorod surrounded by: (left) the media with the refractive index of 1.5712 and (right) in presence of weakly absorbing homogenous medium associated with *N – Methylaniline* molecular absorption.

In the presence of *N – Methylaniline* molecular absorption cross-section of gold nanorods undergoes complex changes in the spectral range of absorption and anomalous dispersion of *N – Methylaniline*. To better explore these changes, we

calculated the differential absorption shown in Figure 4. The differential absorption takes both positive and negative values in the spectral range of *N-Methylaniline* absorption band. The positive values of the differential absorption spectra are interpreted as the absorption of the *N-Methylaniline* molecules enhanced in the near field of the plasmons excited in the gold nanorods. Negative peaks of the differential spectra, however, are due to the fast variation of refractive index in weakly absorbing medium that leads to the shift of the plasmon band. The reasons for the enhanced sensitivity of the differential spectra to the presence of the molecules in the gold nanorod environment becomes clear if one consider the field distribution presented in Figure 5. Large concentration of the field in the immediate proximity of the gold nanorods leads to the both effects: enhanced absorption of the nearby molecules and enhanced sensitivity of plasmon band position to the optical properties of the environment.

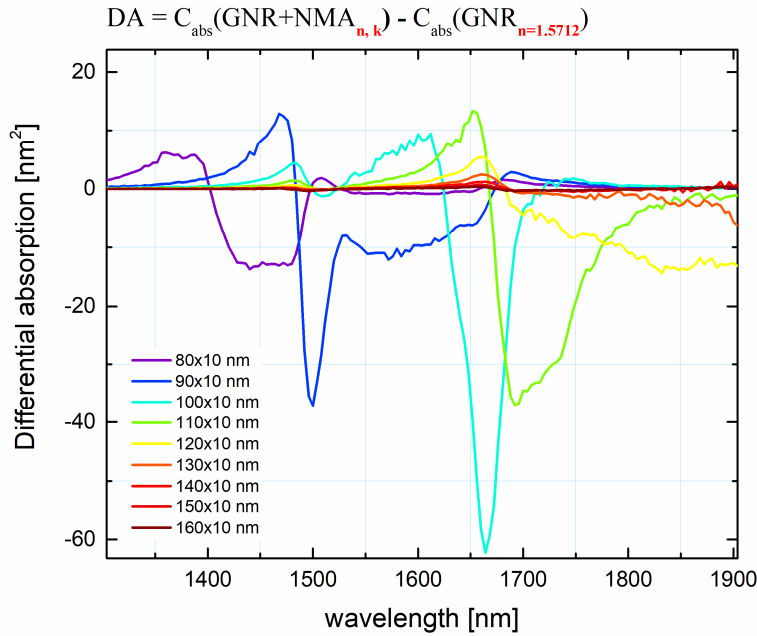


Figure 4. Differential absorption (DA) spectra as a function of the wavelength (C_{abs} is absorption cross-section, GNR is gold nanorod, NMA is *N-Methylaniline*).

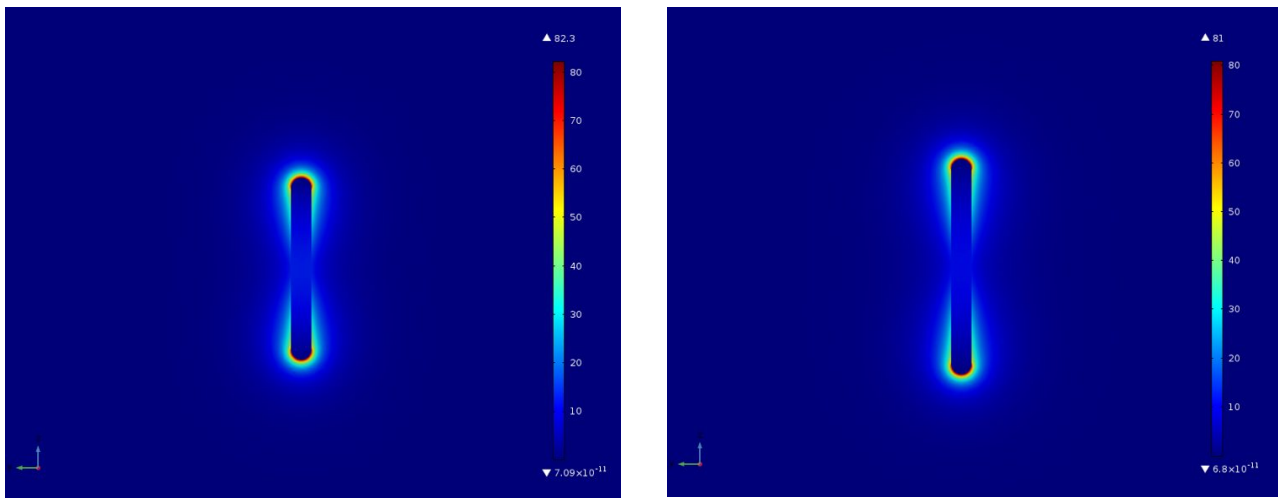


Figure 5. The normalized electric field distribution of the single gold nanorod: $88 \times 10 \text{ nm}$ (left) and $105 \times 10 \text{ nm}$ (right).

4. CONCLUSION

We explored the differential absorption cross-section of weakly absorbing homogenous medium associated with absorption of *N-Methylaniline* chemical in presence of gold nanorods. By the choice of the suitable aspect ratio of the gold nanorods their plasmon band may be brought in line with the expected position of the sought molecular vibration. Then, with the use of the differential absorption spectra the vibration frequency and the presence of the molecules may be determined. We believe that our work may pave the road to overtone spectroscopy tools in near-infrared enhanced with nanoantennas.

5. ACKNOWLEDGMENT

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