

# Strong interaction of molecular vibrational overtones with near-guided surface plasmon polariton

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## ABSTRACT

Here, we report on the enhancement of molecular vibrational transitions overtones due to the excitation of surface plasmon polariton waves. We show that, assuming a modified Kretschmann-Reather configuration with ultra-thin dielectric over-layer, the effective absorption cross section of higher harmonics of molecular vibrations is boosted by at least two orders of magnitude. Based on the experimental observations reported by Karabchevsky and Kavokin [1] on photonic waveguides, we calculate the differential absorption which appears to exhibit a Fano-like line shape. This manifests the interaction between a narrow molecular resonance and a broad plasmonic mode. In fact, the interaction occurs due to the highest enhancement of the vibrational transitions overtones when the vibration mode and plasmonic mode are detuned. The enhancement factor reported in this study points on feasibility of vibrational overtones detection using conventional spectrometers. In addition, having high signal-to-noise ratio opens a new route for molecular detection and sensing.

**Keywords:** surface plasmon resonance, vibrational spectroscopy, molecular vibrations overtones, Fano resonances.

## INTRODUCTION

Mid-infrared (Mid-IR) spectroscopy is powerful technique for molecular detection. The absorption spectra of organic molecules, in this region, are characterized by a series of bands, directly linked to the vibrational modes. A fundamental vibrational transitions of organic molecules are typically in range of 3-20  $\mu\text{m}$  or in wavenumbers it is  $\sim 3300\text{--}500\text{ cm}^{-1}$ . Theoretically, spectroscopic transitions occur at sharp, well defined frequencies, leading to absorption lines with zero frequency width. However in practice, the mechanisms such as: 1) lifetime, 2) Doppler and 3) collisional broadenings endow measured absorption lines with finite widths and characteristic lineshape functions [2], directly related to the absorption coefficient and dielectric function of the molecule. Therefore, infrared absorption spectroscopy exhibits a great potential in sensing and molecular detection. For instance, it can be used for probing a subtle conformational changes of proteins to study the molecular basis for proteins functionality [3-4]. Despite their potential, the fundamental vibrations of organic molecules appear in mid-infrared region where bulky and expensive equipment is needed.

Molecular bonds signatures can be also deduced from the higher harmonics of vibrational transitions named overtones which appear in the near-infrared and recently has been efficiently detected on glass waveguides by Karabchevsky et. al. [1,5-6]. Because of its traditional usage for optics telecommunication, this region benefits from affordable powerful sources, optimized integrated photonic devices technology for light harnessing, low propagation losses, and high coupling efficiency compatible with silica fibers [5]. However, due to the inherent character of the ground state energy landscape, the cross section of vibrational transitions overtones are few orders of magnitude smaller than that of the fundamental transitions that correspond to the same degree of freedom. This makes vibrational transitions overtones less favorable for molecular detection. So far, no attempts were done to enhance the cross section of vibrational transitions overtones, in particular in the context of sensing and molecular detection.

One of the most widely used methods to increase the sensitivity of infrared absorption spectra is to enhance the electric field associated with the excitation of plasmonic resonances when light is incident on the nanoscale metallic films, traditionally, made of noble metals [4,7-10]. Considering the power absorbed by a material with a small imaginary part of its dielectric constant  $P_{Abs} = \frac{\omega}{2} \text{Im}(\varepsilon) |E|^2$  where  $E$  is the electric field in the material and  $\omega$  is the frequency, the

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absorption signal scales with the intensity  $|E|^2$ . The simple intuition of increasing signal with field enhancement is the basis for surface enhanced infrared absorption (SEIRA) spectroscopy. The field enhancement is normally achieved by exciting the localized surface plasmon resonances in the mid-infrared region of metallic particles having  $\sim 1\text{-}3\ \mu\text{m}$  length [4]. The possibility of exciting propagating surface plasmon polaritons on extended thin metallic films, on the other hand, still limited in SEIRA spectroscopy. This limitation stems from the fact that the dispersion of the surface plasmon at this spectral region asymptotically approaches the dispersion relation of the light in free space. Therefore, the plasmonic field becomes less confined to the surface. Composite plasmonic waveguide structures shown by Karabchevsky et al. [11] enable plasmonic field confinement to the metal film and we explore its potential for SEIRA spectroscopy.

To enhance the vibrational transitions overtones in near-infrared, one can easily utilize the propagating surface plasmons (PSPR) since their spectral modes can be tailored in the near-infrared. This possibility may open the door for new vibrational spectroscopy tools for bio-sensing, molecular detection and diagnosis. In this proceeding, we explore the possibility of using PSPR to enhance vibrational transitions overtones in the near-infrared. Using classical models, we show that the absorption due to overtones of organic molecules can be enhanced and therefore easily detected.

## 2. Theory

### 2.1 The single-bounce element

Single bounce element, prism, was used to match the momentum of photon with that of surface plasmon in Kretschmann-Reather configuration. A thin metallic layer is deposited on the high-refractive index prism. The enhanced electric field on the metal interface due to the surface plasmon excitation boosts the sensitivity of the structure to probe minute changes in the refractive index of the adjacent dielectric medium. Although surface plasmon based sensors exhibit the highest sensitivity among the sensors based on the evanescent waves, an effort has been made to improve their sensitivity and detection limit over the last two decades [12]. We have shown that adding a thin dielectric film on top of the metallic layer significantly enhances the sensitivity and figure of merit of the sensor [13]. When the thickness of the over-layer is below the cut-off thickness of the  $\text{TM}_0$  guided mode, the spectral dip associated with the surface plasmon resonance becomes very narrow which improves the resolution of the measurement. Following Lahav *et al.* [15] we call this configuration near guided wave surface plasmon (NGWSPR). The basic structure that we interrogate here is composed of an SF11-made prism which is coated by a silver layer with 10 nm Si resulting in NGWSPR as shown in Fig. 1a. The thickness of the silver film is optimized to maximize the efficiency of the excited surface plasmon wave with the required wavelength. When this efficiency is maximized, a zero in the reflection spectrum of the Kretschmann-Reather configuration is obtained.

### 2.2 Molecular model

To assess the potential of NGWSPR for vibrational overtones enhancement, we use as a probe molecule the aromatic N-Methylaniline (NMA). This molecule constitutes a crucial component of many drugs, pesticides and explosive. Here, we use N-Methylaniline in hexane mixture, ratio of 2:3, having a background refractive index of 1.464769. It was shown in [1], that the probability of the transitions could be significantly enhanced due to the molecular aggregation effect on photonic waveguides, revealing a new mechanism of effective absorption enhancement in the near-infrared region. This effect resembles, ostensibly, the unusual increase of the transition dipole moment in molecular J- aggregates where individual monomers undergo dipole-dipole coupling to form delocalized state accompanied by huge oscillator strength [15].

The measured transmission spectrum of the mixture in a 1 mm thick cuvette, Fig. 1(d), was used to retrieve the refractive index. To estimate the real absorption of the target molecule, the dielectric function is presented by the Lorenz model with multiple resonances in the relevant spectral range was assumed as follows [16]:

$$\varepsilon(k) = \varepsilon_B - \sum_{j=1}^N \frac{f_j}{k^2 - k_{0j}^2 + ik\Gamma_j} \quad (1)$$

With,  $\epsilon_B$ ,  $f_j$ ,  $k_{0j}$ , and  $\Gamma_j$  the background dielectric contribution, oscillator strength, resonance wave vector, and the phenomenological damping constant of vibrational band  $j$  respectively. The absorption intensity of the band is determined by both  $f_j$  and  $\Gamma_j$  whereas the full width at half maximum is solely governed by  $\Gamma_j$ . In our fit procedure, all these parameters together with the thin film thickness were varied to obtain the best fit with the experimental measurements. The best-fit parameters are given in Table 1 and the dispersion properties of the NMA in Hex mixture are presented in Fig. 1c. The targeted mode to be enhanced is the first overtone of the N-H stretching mode, which appears around 1490 nm ( $6711\text{ cm}^{-1}$ ).

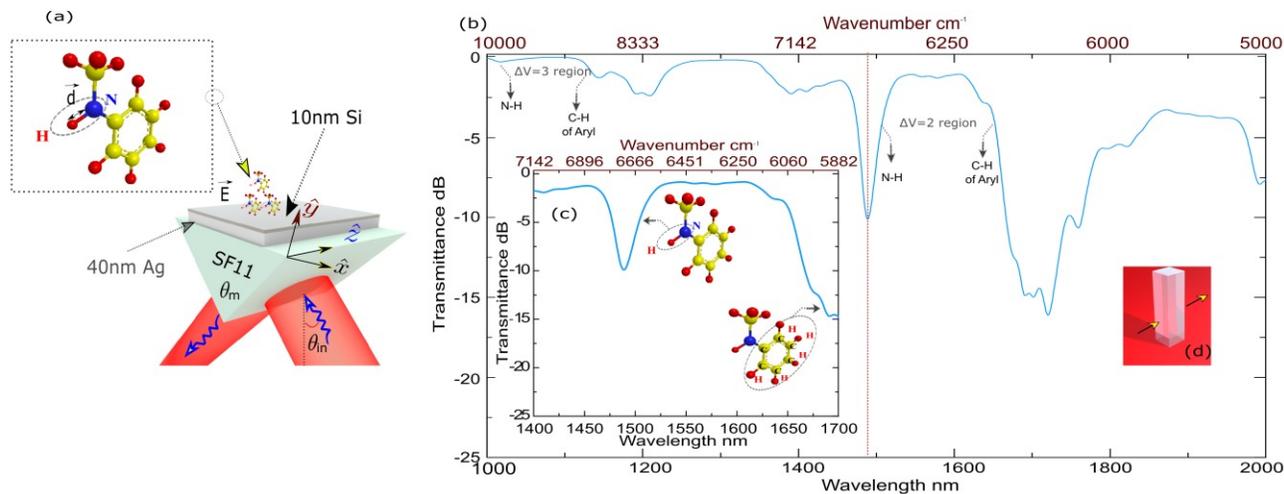


Figure 1. (a) Artistic impression of the molecules evanescently probed using single-bounce element in Kretschmann-Raether configuration. (b) Experimentally measured transmittance spectra of N-Methylaniline in hexane mixture. (c) zoomed transmittance at the overtone absorption of amine and C-H of Aryl bands. At (b)-(c) the molecule was excited at normal incidence using 1 mm thick cuvette.

Table 1 - Mixture dispersion parameters, ( $\epsilon_B = 1.464769^2$ ,  $d = 1\text{mm}$ ).

Oscillator No.	Oscillator strength	Resonance wavenumber	Damping constant
$j$	$f_j$	$k_j(\text{cm}^{-1})$	$\Gamma_j(\text{cm}^{-1})$
1	$10^2$	5680	120
2	$1.3 \times 10^2$	5807	100
3	$0.3 \times 10^2$	5875	80
4	$0.45 \times 10^2$	5921	80
5	$1.1 \times 10^2$	5972	130
6	$1.2 \times 10^2$	6716	120
7	$0.2 \times 10^2$	8764	90

## RESULTS

First, the surface plasmon is tuned to resonate at the vibration frequency of the first overtone of the amine band around 1490 nm. This was achieved by tuning the Ag layer thickness to 40 nm and the incident angle  $\theta_m$  (inside the prism) to 59.50 degrees. Inset of Fig. 2a shows that the electric field is significantly enhanced on the interface metal-dielectric which is now assumed to have the background index of the NMA in Hex mixture [17-18]. In addition, the linewidth of

the plasmonic dip is approximately one order of magnitude larger than that of the molecular band at the same wavelength (Fig. 2a). To quantify the absorption of the vibrational transition overtone due to the interaction with the plasmonic field we calculated the differential absorption  $\Delta A \equiv A_{mol} / A_{BG}$ . Here  $A_{mol}$  is the absorption when the molecule is present on top of the structure as a semi-infinite medium. Whereas  $A_{BG}$  is the absorption of the mixture considering only the background refractive index. Strictly speaking,  $A_{BG}$  is the absorption caused only by the plasmonic field when the vibrational transitions of the molecule are deactivated. Although one can easily recognize the absorption feature of the interrogated band at 1489 nm, it does not show a perfect Lorentzian shape as expected. The differential absorption signal  $\Delta A$  in Fig. 2b exhibits a Fano line shape due to the interference of the spectrally broad plasmon oscillations with the spectrally narrow molecular vibration. This behavior implies that the interaction between the plasmonic field and the vibrational overtone transition dipole moment is not straightforward. The microscopic origin of the Fano resonance arises from the constructive and destructive interference of a narrow discrete resonance with a broad spectral line or continuum [19, 20]. Sarraz et al. have shown [20] that the asymmetric profiles of this effect in agreement with the Fano formula. Fano resonances have also been observed in the frustrated total internal reflection spectra of prism-coupled square micro pillars and in the interactions of narrow Bragg resonances with broad Mie or Fabry-Perot bands in photonic crystals [21-22].

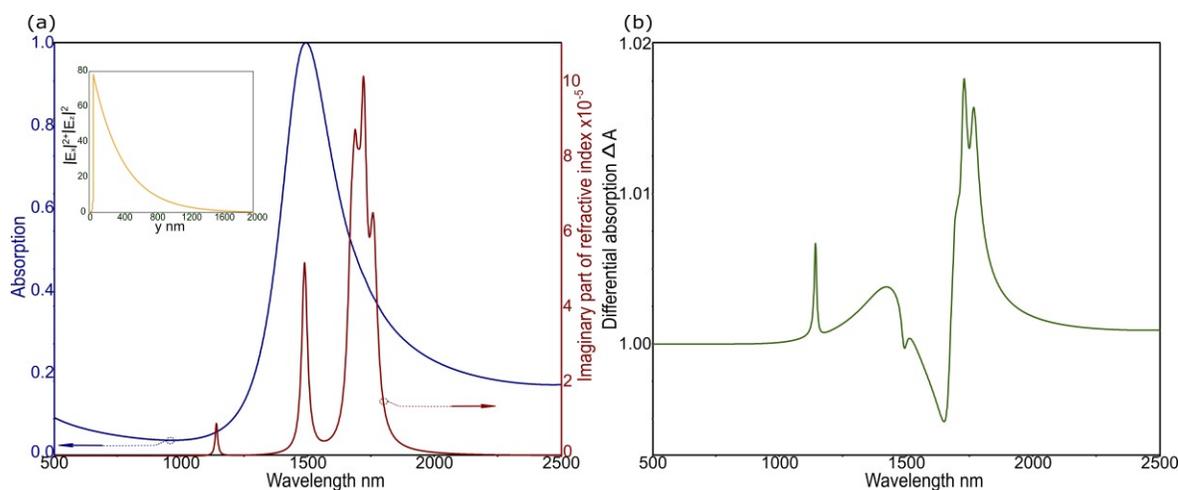


Figure 2. (a) Absorption spectrum of the SPR overlapped with the imaginary part of refractive index of the mixture under consideration. (b) Differential absorption when the SPR is tuned to be in resonance with the absorption band of the molecule.

We explore further the overtone-SPR interaction, and shift the plasmonic resonance across the vibrational band by tuning the incident angle of the broad-band incident light. When the plasmon mode shifts toward the higher wavelengths, the resonance becomes broader and consequently its lifetime becomes shorter [10]. The incidence angles and the Ag film thickness were tuned to sweep the SPR from 1000 nm to 2000 nm as can be seen in Fig. 3. The well-pronounced broadening that is obtained when the SPR reaches 2000 nm is due to the overlap with another SPR mode that is caused by the prism dispersion as was shown by Shalabney et al. [23]. Here, we focus on using the SPR excited at shorter wavelength. The other mode should be observed in longer wavelengths and they approach each other when the incident angle decreased.

$\Delta A$  of the N-H overtone at 1489 changes versus its location with respect to the plasmonic dip. When the molecular absorption band falls on the right shoulder of the SPR dip, it shows a small signal which gradually increases when the molecular band moves to regions where the SPR has larger slopes as can be seen in Fig 3a and Fig 3b when the vibrational mode matches the SPR wavelength as shown in Fig. 3c,  $\Delta A$  is almost completely depressed. The detected signal appears to get significantly enhanced when it is located on the left shoulder of the SPR where the plasmonic mode is steeper.  $\Delta A$  reaches  $\sim 4\%$  when the molecular band is on the steepest region of the SPR mode as can be seen in Fig. 3d- Fig. 3f. Here we stress, that this signal can be easily detected by conventional spectrometers having a reasonable signal-to-noise ratio.

When comparing the enhanced absorption in Fig. 3f with the absorption of the molecule inside the cuvette, Fig. 1a-b, we found that the effective absorption cross section of the molecule is enhanced by at least 100 times when it is detected by the NGWSPR configuration.

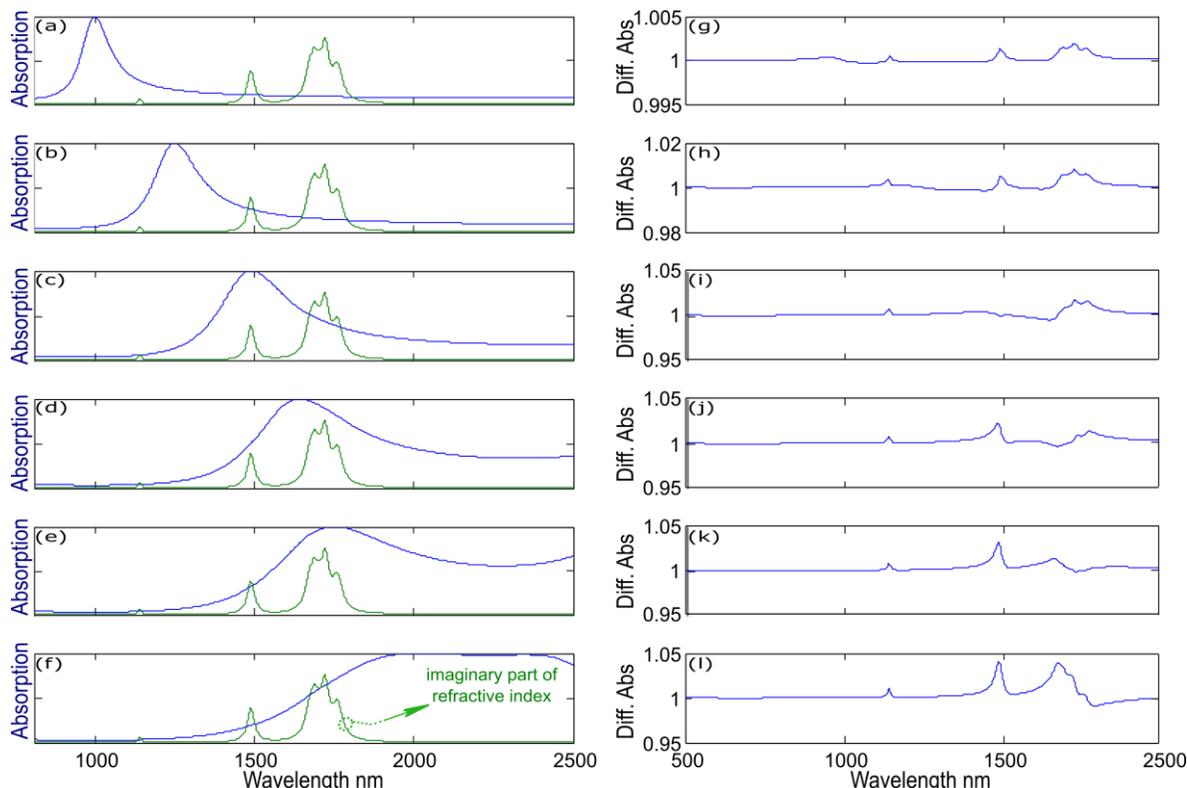


Figure 3. (a)–(f) evolution of the SPR mode for different incident angles overlapped with the spectrum of the imaginary part of refractive index of the mixture under consideration. (g)–(l) the corresponding differential absorption measured for the cases a-f.

## CONCLUSION

To conclude, the theoretical study of the interaction between molecular vibrational transitions overtones and surface plasmon waves is reported. We show that by enhancing the electromagnetic field in which the molecules are embedded, one can elevate the probability of molecular vibrations overtones for detection and sensing. The local field in the proposed configuration is boosted by exciting the surface plasmon polariton mode on the interface between a thin metallic film and the molecule to be sensed. By utilizing the near-guided wave surface plasmon resonance configuration, we enhance the effective absorption cross section of vibrational transitions overtones by more than two orders of magnitude. This enhancement enables the detection of overtones by standard spectrometers with high signal-to-noise ratio. We observed that the maximum enhancement does not occur when the vibrational mode is in resonance with the plasmonic oscillation. However, detuning between the SPR and the vibration is needed to enhance the differential absorption signal due to the Fano-like interaction between the two modes. Further works should be performed in order to understand more deeply the nature of this interaction.

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