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Over-coupled Helmholtz-like optical resonator for enhanced infrared spectroscopy of molecules

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Abstract. Electromagnetic Helmholtz resonators are able to strongly and homogeneously enhance an electric field in relatively large volumes, making them attractive for applications to surface enhanced infrared absorption spectroscopy of molecules. We show in this study that such a structure, designed in the over-coupling regime can demonstrate strong enhancement of molecular modes of the polymer poly(methyl methacrylate) and the explosive molecule 2,4-dinitrotoluene over a very wide wavelength range between 5 and 10 μm . Reflectivity contrast provides access to the analyte's absorption and quantitative information. Helmholtz-like resonators therefore offer a new platform for the creation of sensitive and versatile sensors.

1 Introduction

Metal-based optical resonators have been extensively studied for enhancing the infrared signature of various molecules, as they exhibit hot spots, i.e. small volumes where the electric field is strongly enhanced and electronic interactions increase the absorption of nearby molecules. This phenomenon is known as surface enhanced infrared absorption (SEIRA)[1]. Field enhancement logically became the figure of merit of resonators for SEIRA applications, drawing designs to converge towards reduced interaction volumes, like nanogaps in order to obtain the tightest field confinement [2]. The dominant strategy for SEIRA of a compound remains the tuning of the plasmonic resonance close to critical coupling condition ($R=0$ at resonance) to one or few vibrational modes of the molecules. The phenomenon is well described and absorption can be modelled with temporal coupled mode theory [3]. Nevertheless, it is possible to develop versatile structures capable of enhancing the entire fingerprint region (specific part of the molecule's spectrum in the mid-infrared), which can be achieved by using over-coupled structures [6]. Helmholtz-like optical resonators, offer relatively large interaction volume and their resonance wavelength as well as their coupling to free space is easily tuned thanks to four geometrical parameters [4, 5]. They demonstrate strong enhancement of molecular vibration modes in over-coupling configuration and over very large wavelength range between 5 μm and 10 μm . The same structure is used to enhance the infrared signatures of poly(methyl methacrylate (PMMA) and 2,4-dinitrotoluene

(DNT). It is possible to directly use the reflectivity contrast to recover the absorption of both molecules and retrieve quantitative information [6].

2 Over-coupled Helmholtz-like optical resonator

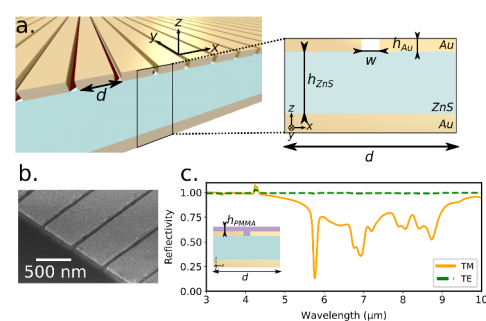


Figure 1. **a.** Structure of the Helmholtz-like optical resonator. **b.** Electron Beam Microscopy image of a resonator of dimensions $h_{\text{ZnS}} = 280$ nm, $h_{\text{Au}} = 45$ nm, $w = 50$ nm and $d = 600$ nm. **c.** Experimental spectra of the resonator covered with a 45 nm thick PMMA layer spin-coated on top of the ribbons and filling the slits in TM mode illumination (orange continuous line) and TE mode (dashed green line).

The Helmholtz-like optical resonator can be described as a LC resonator [5]. It consists of a dielectric layer over a gold substrate and covered with an array of gold ribbons, as presented in Fig.1.a that can be fabricated with electron

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beam lithography. In between the ribbons takes place the strong field enhancement at resonance [4]. Zinc Sulfide (ZnS) is chosen as a dielectric because of its transparency in the mid-infrared. The parameters h_{ZnS} the thickness of dielectric, h_{Au} the thickness of the gold ribbons, w the width of the gap between the ribbons and d the period are adjusted to tune the resonance wavelength and the coupling to free space, especially h_{ZnS} . One can fill the slit with an absorber, as a 45 nm thick layer of PMMA filling the slits and observe very strong enhancement of all the modes between 5 and 10 μm (Fig.1.c). Thanks to the low quality factor of the resonance, the reflectivity difference is less affected by the shift of the resonance due to the change of refractive index inside the slit (Surface Plasmon Resonance effect). Measurements are performed with a Fourier Transform Infrared spectrometer (FTIR) 70v by Bruker.

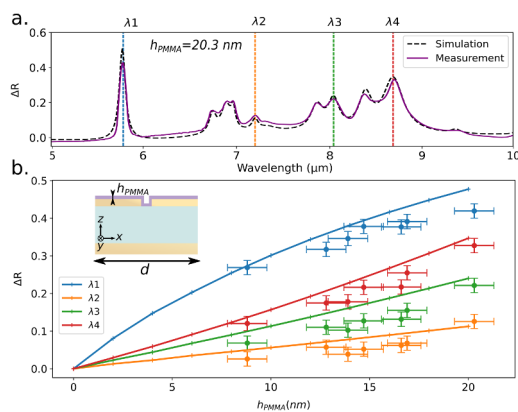


Figure 2. **a.** Calculated (dashed line) and experimental (continuous line) reflectivity difference spectra of a resonator with dimensions $h_{ZnS} = 530$ nm, $h_{Au} = 45$ nm, $w = 50$ nm and $d = 300$ nm covered with a 20.3 nm layer of PMMA. **b.** Calculated evolution of four absorption lines with the height of a perfect continuous layer of PMMA on top of a resonator. Experimental values are obtained with identical structures covered with layers of various thicknesses. Error bars are standard deviation.

Fig 2.a. shows the reflectivity difference spectrum $\Delta R = R_{withoutPMMA} - R_{withPMMA}$ for a structure resonating at 6.5 μm coupled to a 20 nm thick PMMA layer. Calculations are obtained with B-Splines Modal Method. Fig 2.b. presents the evolution of the reflectivity difference with the thickness of analyte film. The peak amplitude follows a quasi linear behavior that can be modeled by an analytical expression, establishing a link to the quantity of material in the resonator [6]. For experimental demonstration, eight identical structures were fabricated and spin-coated with PMMA solutions of various concentrations and at different speed in order to deposit films with thicknesses between 20.3 and 8.8 nm. For these extreme values, ΔR varies respectively from 0.5 to 0.25 for the 1730 cm^{-1} mode. Slight discrepancies with simulations can be attributed to the approximation of the PMMA layer by a continuous and perfectly flat layer.

3 SEIRA of 2,4-dinitrotoluene

Fig 3. presents the results of SEIRA spectroscopy using the previously introduced structure, this time coupled with

the explosive derivative 2,4-dinitrotoluene (DNT). A solution of 3.02 g/L of DNT in acetonitrile is deposited thanks to a microfluidic printer Microplotter II by Sonoplot. The 10 μm lateral resolution and the 20 μm wide aperture of the micropipette enable to cover a surface of $500 \times 500 \mu\text{m}^2$ with a volume of about 2 μL . The solvent evaporates in a few seconds and the sample spectrum is measured in five minutes. DNT being an organic volatile compound, it evaporates completely after this time limit. Nevertheless, after three minutes, the spectra (orange line) shows reflectivity difference over 0.5 for the 1536 cm^{-1} DNT mode and 0.2 after four minutes (green line). Measurements can be fitted with calculations considering a perfectly flat layer of DNT inside the slits of respectively 60 and 20 nm thickness. Both reflectivity difference spectra are compared to the theoretical absorption of the molecule, given by a Drude-Lorentz model from Fabas *et al.* [4].

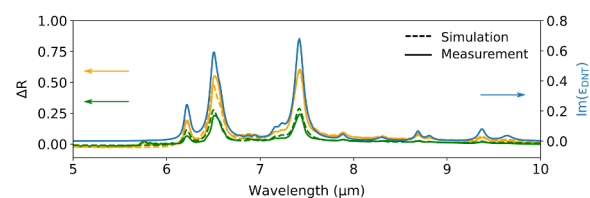


Figure 3. Reflectivity differences for both measurements taken three (orange line) and four (green line) minutes after deposition and imaginary part of the numerical Drude-Lorentz model of DNT [6].

4 Conclusion

Helmholtz-type optical resonators offer several advantages for device integration, such as high field enhancement in relatively large volumes, many degrees of freedom to adjust the resonant wavelength and free-space coupling, and high angular stability. The overcoupling regime provides broadband enhancement over a bandwidth of 5 microns, giving access to the analyte signature and amount of material with promising sensitivity performance.

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