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# Over-coupled Helmholtz-like optical resonator for broadband surface enhanced infrared absorption (SEIRA) spectroscopy

Laura Paggi<sup>a</sup>, Alice Fabas<sup>a</sup>, Hasnaa El Ouazzani<sup>a</sup>, Jean-Paul Hugonin<sup>b</sup>, Nathalie Bardou<sup>c</sup>,  
Christophe Dupuis<sup>c</sup>, Jean-Jacques Greffet<sup>b</sup>, and Patrick Bouchon<sup>a</sup>

<sup>a</sup>DOTA, ONERA, Université Paris Saclay, F-91123 Palaiseau, France

<sup>b</sup>Laboratoire Charles Fabry, Institut d'Optique Graduate School, CNRS, Université  
Paris-Saclay, 91127 Palaiseau, France

<sup>c</sup>Centre de Nanosciences et de Nanotechnologies (C2N), CNRS, Université Paris-Saclay, 10  
Boulevard Thomas Gobert, 91120 Palaiseau, France

## ABSTRACT

Many sub-wavelength structures have been used to enhance the infrared fingerprint of molecules in order to develop sensitive and versatile infrared spectroscopy molecular detection tools. Helmholtz-like optical resonators have the ability to strongly enhance electric fields in relatively large volumes and show good angular stability while their fabrication process is well mastered, what makes them interesting for an application to surface enhanced infrared absorption (SEIRA) spectroscopy. The overcoupled configuration shows new advantages compared to other coupling regimes: it can enhance the signature of vibrational modes of poly(methyl methacrylate (PMMA) up to 70% over 5  $\mu\text{m}$  wide wavelength range with a unique resonator. This study presents the behaviour of this promising structure compared to the original Helmholtz optical resonator and the application of different coupling regimes to SEIRA spectroscopy of PMMA, underlining the advantages of the overcoupling regime previously demonstrated.

**Keywords:** nanoresonator, surface enhanced infrared absorption, spectroscopy, detection

## 1. INTRODUCTION

Sub-wavelength metallic structures have kept on demonstrating potential for applications to Surface-Enhanced Infrared Absorption (SEIRA) spectroscopy.<sup>1</sup> These structures, able to strongly enhance electric fields can increase the absorption of chemical compounds placed in their vicinity. A majority of publications focus on developing optical resonators operating in reflection that are critically coupled to free space (*i.e.* reflectivity  $R$  is equal to zero at resonance) or undercoupled, with the highest enhancement of the field achievable.<sup>2-13</sup> Detection of very low quantity of material has been achieved.<sup>14,15</sup> A challenge remains in creating versatile and broadband enhancing devices. Strategies have been proposed like using multi-resonant structures,<sup>16-21</sup> epsilon near zero material,<sup>22</sup> but they stay limited or lack experimental demonstration. The inclusion of machine learning in data analysis and multiplexed antennas is a very promising approach, but it implies combining many resonators and probing different molecules.<sup>7</sup> Helmholtz-type optical resonators have the advantage of strongly enhancing the electric field homogeneously in a relatively large volume.<sup>11,23,24</sup> The overcoupled regime offer in this case many advantages: better enhancement, up to 70% and with only one resonator, it is possible to enhance all the vibration modes of the molecules over very large wavelength range.<sup>25</sup> In this work, we propose a parametric study of such a Helmholtz-type structure and explore the evolution of its spectral response according to geometry, as well as different coupling configurations and their enhancement of poly(methyl methacrylate (PMMA) infrared signature. A combination of few of these structures could enable to pave the fingerprint region to recover the specific signature of any molecule and create a versatile infrared spectroscopy detection platform.

Further author information: (Send correspondence to P.B.)

P.B.: patrick.bouchon@onera.fr, Telephone: +33 (0)1 80 38 63 67

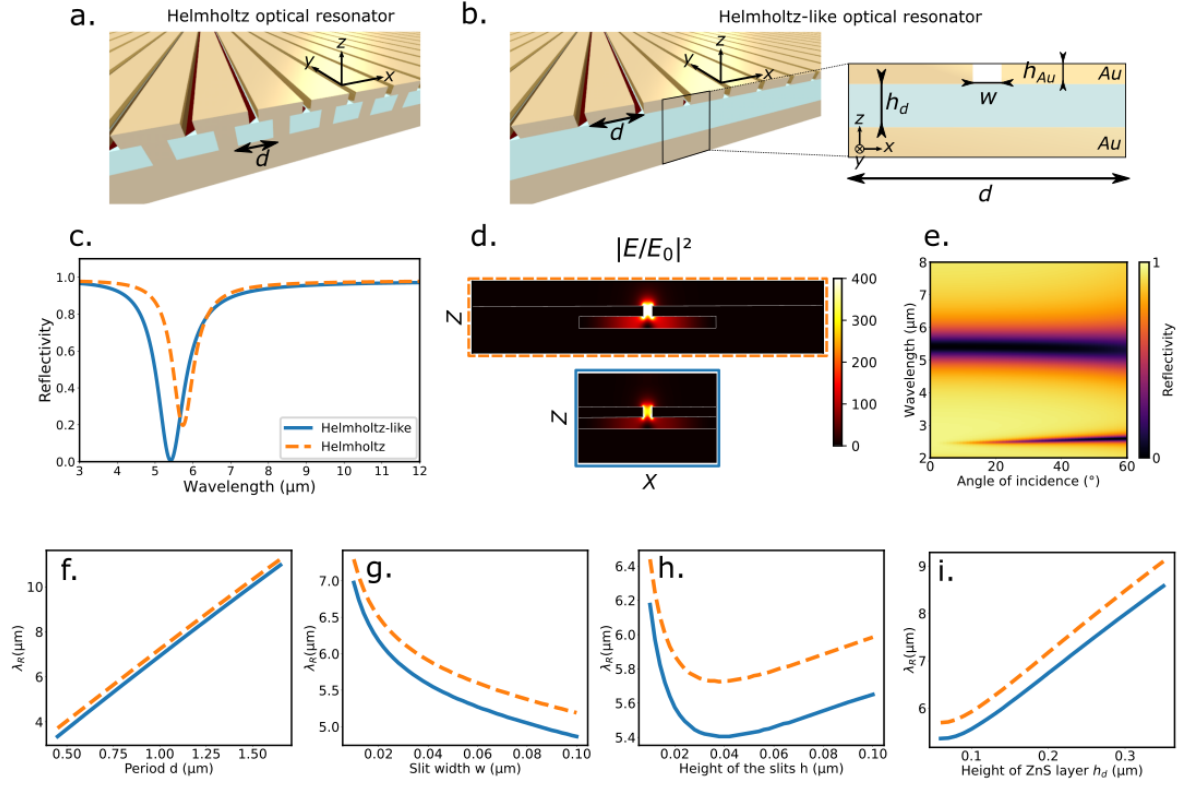


Figure 1. Structure of a. the Helmholtz optical resonator, b. the Helmholtz-like resonator, c. Calculated spectra and d. normalized electric field maps of the original Helmholtz resonator (orange dashed line) and the simplified version (continuous blue line), e. angular dependence of the Helmholtz-like resonator, f. to i. evolution of the resonance wavelength  $\lambda_R$  with the geometrical parameters  $d$ ,  $w$ ,  $h_{Au}$  and  $h_d$ .

## 2. HELMHOLTZ-LIKE RESONATOR

The optical Helmholtz resonator is a structure inspired from acoustics.<sup>23</sup> The Helmholtz-like resonator is likely constituted of a dielectric layer, on a gold substrate and surmounted by a gold layer nanostructured to form an array of ribbons. Compared to original Helmholtz optical resonator, the cavity walls have been suppressed in order to simplify the structure and its fabrication process. The valuable properties of the structure are nonetheless maintained: in between the ribbons, the field is concentrated at resonance. The resonance wavelength is tuned thanks to the geometrical parameters as the thickness of the dielectric layer  $h_d$ , the thickness of the ribbons  $h_{Au}$ , the width of the slits between the ribbons  $w$  and the period  $d$ . In this case the width of the box and the period are identical. Calculations are obtained using a B-Splines Modal Method.<sup>26</sup> For the following figures, we chose the following geometrical parameters:  $h_d = 50nm$ ,  $h_{Au} = 45nm$ ,  $w = 50nm$  and  $d = 765nm$ . For the closed cavity, the period is  $2\mu m$ . The dielectric layer is modeled with a model corresponding to zinc sulfide (ZnS)<sup>27</sup> and gold layers by a Drude model. Fig.1 shows the Helmholtz-type structures with both continuous and closed cavity along with a spectrum and normalized electric field distribution maps. At resonance, the field is highly confined inside the slit. The simplified structure keeps a strong angular tolerance, which is advantageous for device integration, in addition to the simpler fabrication process. The evolution of the resonance wavelength  $\lambda_R$  with the different geometrical parameters  $h_d$ ,  $h_{Au}$ ,  $w$  and  $d$  for both continuous and closed cavity are presented in Fig.1. The geometrical parameters influence the coupling of the system to free space by changing the system's

ratio of radiative loss over non radiative loss  $\gamma_r/\gamma_{nr}$ .<sup>28</sup> The critical parameter is the thickness of the dielectric layer.

### 3. APPLICATION TO SEIRA

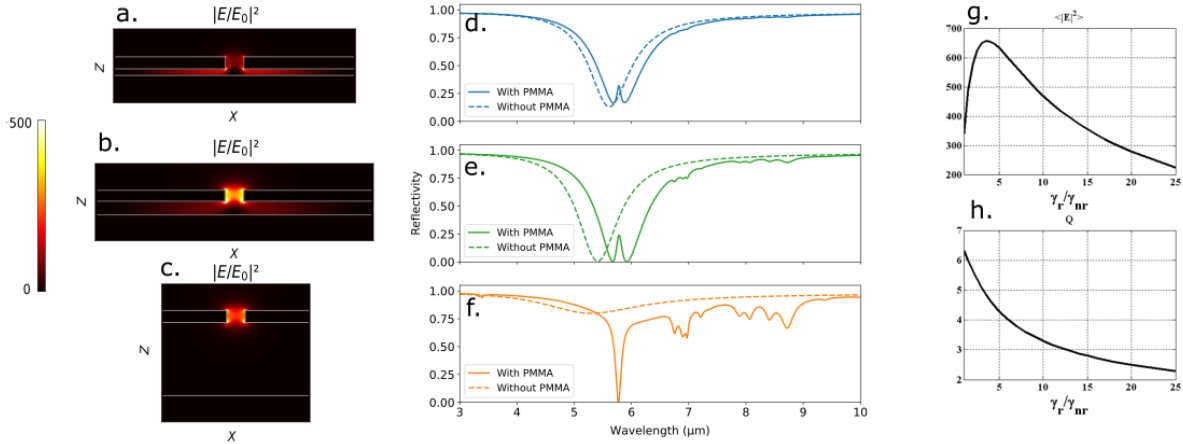


Figure 2. Normalized electric field maps and calculated spectra of Helmholtz-like resonators a,d. in undercoupling regime ( $hb = 20nm$ ), b,e. in critical coupling regime ( $hb = 50nm$ ) and c,f. in overcoupling regime ( $hb = 280nm$ ). For all geometries the slit is 45 nm high and 50 nm wide. Periods are adapted to match the 5.8  $\mu m$  mode of PMMA. g. Evolution of the field intensity as a function of the loss ratio, h. Evolution of the quality factor with the loss ratio.

One can demonstrate the SEIRA potential of the structure by adding an analyte in the slits, here chosen as a 45 nm PMMA layer described in the calculations by a dielectric permittivity given by a Drude-Lorentz model.<sup>25, 29</sup> The layer is placed on top of the ribbons and filling the slits. For all geometries, the slits dimensions are identical and the period has been adapted to tune the resonator with the strong vibration mode of PMMA at 5.8  $\mu m$ . If the thickness of the ZnS layer is decreased to 20 nm, the ratio of losses is inferior to 1 and the overall system shifts towards undercoupling. A typical SEIRA effect (peak of reflectivity) appears at 5.8  $\mu m$  testifying of the coupling between the Helmholtz resonance and PMMA mode. This phenomenon has been previously described in literature using Temporal Coupled Mode Theory.<sup>28</sup> In the contrast is limited theoretically, as it start from a lower absorption. The field enhancement is also low, as shown on Fig.2.a. In Fig 2.b. is showed the result starting from a resonator close to the critically coupled configuration ( $h_d = 50nm$ ), The reflectivity change is around 20 % and the field is better enhanced. Nevertheless, other vibrational modes are not significantly enhanced.

From both previous examples, as for many structures proposed in the literature, the reflectivity contrast is hard to recover, as the spectrum is shifted due to the effect of the change of refractive index. Post-processing strategies are usually required to obtain the information.

By increasing the thickness of the ZnS layer to 280 nm, one can obtain an overcoupled system: the resonator cannot absorb all the incident light, it saturates, and the resonance appears wide and has a weak amplitude. In this case, the field intensity is lower (Fig.2.c.), which is not always the case (Fig.2.g.<sup>25</sup>). With the addition of a PMMA layer as previously described, the overall system shifts towards critical coupling (maximum absorption) and the PMMA modes are enhanced as proven by dips in reflectivity due to exalted absorption.

In this case, the overcoupled regime shows a clear advantage over the previous configurations. The low quality factor of the resonance enables to use reflectivity difference values without and with the PMMA layer  $\Delta R = R_{without} - R_{with}$ . The reflectivity difference is thus 75% for the 5.8  $\mu m$  PMMA mode. The resonance shifts due to refractive index change has less influence, which makes the tuning less critical the information

about the analyte easier to recover. Other absorption peaks of the molecule are visible at higher wavelengths. By taking a resonator with a higher resonance wavelength, it is possible to obtain higher enhancement of all modes between 5 and 10  $\mu\text{m}$  as the field enhancement is maintained along the wide resonance.<sup>25</sup>

### 3.1 Experimental results

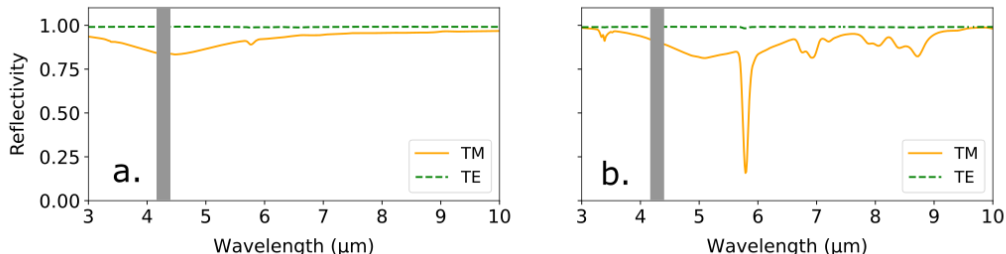


Figure 3. Measured spectra of a. the bare array and b. the array covered with a 45 nm PMMA layer, for TM (orange continuous line) and TE polarization (green dashed line). Grey areas cover the absorption of CO<sub>2</sub>. Dimensions  $h_{Au}= 45$  nm,  $h_d=280$  nm,  $w= 50$  nm and  $d= 400$  nm.

The simple stacked structure of the Helmholtz-type resonator has the advantage to be fabricated using well-known processes. A 280 nm thick ZnS layer is deposited on a gold substrate and the gold ribbons are then created with electron-beam lithography. The PMMA layer used as analyte is deposited by spin-coating in order to obtain a thin layer of about 50 nm filling the slit. Measurements are performed with Fourier Transform Infrared (FTIR) spectrometer. The reflectivity difference obtained is inferior to the theoretical value due to a slight detuning induced by the presence of traces of PMMA under the ribbons left after the lift-off process. Presence of traces of PMMA in the slits is also confirmed on the spectrum of the bare array (Fig.3.a.) by the little reflectivity dip at 5.8  $\mu\text{m}$ .

## 4. CONCLUSION

We presented the behavior of the Helmholtz-type optical resonator with different geometries as well as different coupling regimes. The simplified geometry enables to maintain the properties of the Helmholtz resonator that are attractive for device integration like homogeneous enhancement of the field in large volumes and strong angular tolerance while simplifying the system and fabrication process. The results show clear advantages of the overcoupled configuration, as previously described.<sup>25</sup> The structure gives larger reflectivity difference, is more robust to geometry fluctuations as the resonance is broad and less affected by the shift of the plasmon resonance, which make analysis of spectra easier. A combination of such structures could give access to the entire fingerprint of molecules and pave the way to the creation of versatile SEIRA sensors.

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