

Helmholtz-like Nanoresonators Applied to Surface Enhanced Infrared Absorption

Alice Fabas, Hasnaa El Ouazzani, Jean-Paul Hugonin, Riad Haïdar, Jean-Jacques Greffet, Patrick Bouchon

▶ **To cite this version:**

Alice Fabas, Hasnaa El Ouazzani, Jean-Paul Hugonin, Riad Haïdar, Jean-Jacques Greffet, et al.. Helmholtz-like Nanoresonators Applied to Surface Enhanced Infrared Absorption. Metamaterials 2019, Sep 2019, ROME, Italy. hal-02409551

HAL Id: hal-02409551
https://hal.science/hal-02409551

Submitted on 13 Dec 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

13th International Congress on Artificial Materials for Novel Wave Phenomena - Metamaterials 2019
Rome, Italy, Sept. 16$^{\text{th}}$ - Sept. 21$^{\text{th}}$ 2019

Helmholtz-like Nanoresonators Applied to Surface Enhanced Infrared Absorption

A. Fabas[1], H. El Ouazzani[1], J.P. Hugonin[2], R. Haïdar[1,3], J.J. Greffet[2], and P. Bouchon[1]

[1]DOTA, ONERA, Université Paris-Saclay, 91123, Palaiseau, France
[2]Laboratoire Charles Fabry, Institut d'Optique Graduate School 91127, Palaiseau, France
[3]Ecole Polytechnique, Département de Physique, 91128, Palaiseau, France
alice.fabas@onera.fr

Abstract – **Nanostructures exhibiting high electric field enhancement are very appealing for infrared spectroscopic applications. The optical Helmholtz resonator presents very high enhancement factors within hot volumes. Nevertheless, its nanofabrication is rather challenging and has hindered its practical use. Here, we introduce and study, both theoretically and experimentally, a simplified nanostructure that supports an Helmholtz-like resonance with the expected high electric field enhancement. This resonator is then applied to the SEIRA detection of 2,4-dinitrotoluene, leading to reflectivity changes up to 15% at $\lambda = 6.6\,\mu\text{m}$.**

I. Introduction

Nanostructures based on surface plasmons know numerous applications such as infrared photodetection [1], improvement of solar cells [2] or thermal emission [3]. Plasmonics is also particularly flourishing when it comes to spectroscopy. Surface Enhanced Infrared Absorption (SEIRA) takes advantage of the high local electric field in the near field of nanostructures. Indeed, the vibrational absorptions of molecules in the infrared domain are enhanced by the high surface electric field, and thus, make the detection of a small quantity of matter possible [4]. As a consequence, many metallic antennas of various geometry have been developed in order to exhibit higher enhancement of the electric field [5, 6, 7]. The optical Helmholtz resonator was recently introduced, promising very high enhancement factors of the electric field. This perfect absorber, made from an analogy with the acoustic Helmholtz resonator, is a two-dimensional nanostructure made of a small slit above a metallic box. It presents a single resonance with no harmonics whose wavelength depends on its geometric parameters and the material filling its slit [8]. However, even if it was experimentally demonstrated [9], its fabrication remains challenging and limits its practical use.

Here, we present an alternative geometry for the optical Helmholtz resonator, widening the boxes of each individual resonator until they meet. This new approach makes nanofabrication way easier. We show that this resonator exhibits much of the properties of the initial optical Helmholtz resonators. In particular, the mass-spring system describing Helmholtz resonator is still valid and high electric field enhancement factor can be reached in a large volume. We experimentally demonstrate this Helmholtz-like resonance and applied it to the SEIRA detection of 2,4-Dinitrotoluene, thus confirming the ability of the Helmholtz resonances to concentrate the electric field in a small hot volume.

II. Helmholtz-like resonators description

The optical Helmholtz nanoresonator, shown on Fig. 1(a), whose enhancement factors are very high in large volume and not only in hot spots [10], was redesigned in order to make its fabrication easier. Therefore, the box of each individual resonator was widened until it meets its neighbors. As the width of the box is increased, the resonance is shifted towards higher wavelengths, which is in agreement with the model developed by Chevalier [8]. The maximum resonance wavelength is reached when the box width w_b is equal to the period d. The figure 1(d) shows the spectra of two resonators: the first one has the initial shape with a box width of $w_b = 600\,\text{nm}$ as the other one has reached the limit case $w_b = d = 1\,\mu\text{m}$. This new shape for which, boxes are not separated by metallic walls, is presented on Fig 1(b). It exhibits a large resonance that will be called Helmholtz-like resonance as the design of the structure is now equivalent to a Metal-insulator-metal grating structure.

The behavior of this resonance as an Helmholtz one must been confirmed by a study of the electromagnetic fields. The figures 1(c) and 1(e) show the maps of the magnetic and electric fields at the resonance for both Helmholtz and Helmholtz-like resonators. A clear separation between both fields can be seen: the magnetic one is almost homogeneous and only contained in the box volume while the electric one is limited to the slit. These distributions show clearly the respective inductive and capacitor behaviors of the box and the slit. The enhancement of the electric field inside the slit is constant and amounts to 10^4. This high enhancement is very appealing for sensing applications, and the use of the Helmholtz-like resonator for SEIRA is investigated in the following.

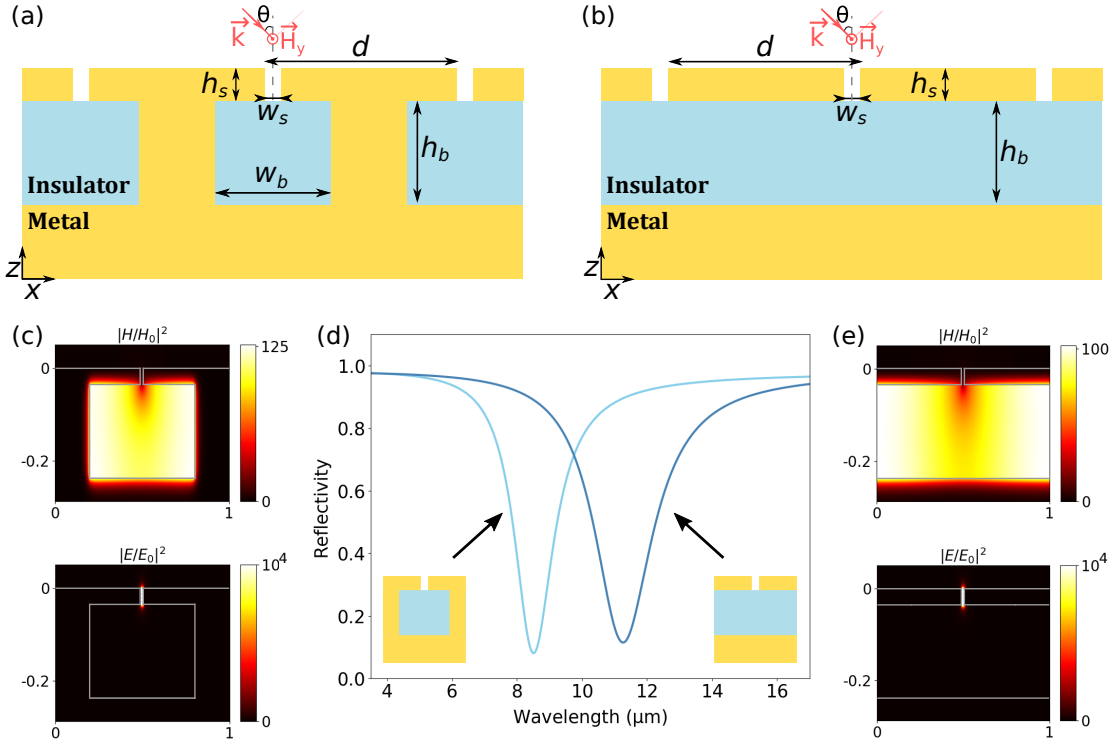


Fig. 1: (a) The optical Helmholtz resonator consists in a metallic slit-box structure. (b) The optical Helmholtz-like resonator is obtained in the asymptotic case where the boxes have their width w_b equals to the period d. (d) Comparison of infrared spectra in TM polarization of two resonators whose box widths are: $w_b = 600\,\mathrm{nm}$ and $w_b = 1\,\mu\mathrm{m}$. The other dimensions are identical: $d = 1\,\mu\mathrm{m}$, $h_b = 200\,\mathrm{nm}$, $h_s = 37\,\mathrm{nm}$ and $w_s = 12\,\mathrm{nm}$. For both resonators, the box is filled with a dielectric material of permittivity $\epsilon = 4.84$. (c) and (e) Maps of the magnetic and electric fields at the resonance, respectively for both resonators whose spectra are shown on (d).

III. Application to Surface Enhanced Infrared Absorption

Several Helmholtz-like resonators have been fabricated by stacking gold, silicon dioxide (SiO2) and nanostructured gold layers as represented on Fig. 2(a). Such structures have a high enhancement factor in the large volume of their slit as pointed out above and so, have been applied to SEIRA spectroscopy for 2,4-dinitrotoluene (2,4-DNT) molecules. DNT is a precursor of the well-known trinitrotoluene (TNT) explosive.

Solid 2,4-DNT was dissolved in acetonitrile with a concentration of $1.72\ \mathrm{mg/mL}$ and volumes of $5\mu\mathrm{L}$ were deposited on the Helmholtz-like resonators which surface is $16\ \mathrm{mm}^2$. Infrared spectra before and after deposit were measured thanks to a Fourier-transform Infrared Spectrometer, with incident beam as represented on Fig 2(a). Results are shown on Fig. 2(b). The resonator itself (blue line) exhibits a strong resonance around $6.4\,\mu\mathrm{m}$. When 2,4-DNT is added (red line), leaps of reflectivity are observed, at wavelengths matching the 2,4-DNT absorption peaks, with amplitudes up to 15%. A small shift of the resonance can also be observed due to a local modification of the refractive index in the slit. Such phenomenon is related to Surface Plasmon Resonance (SPR) spectroscopy [11]. Small peaks around $\lambda = 4.3\,\mu\mathrm{m}$ are absorptions of CO_2 molecules in the atmosphere.

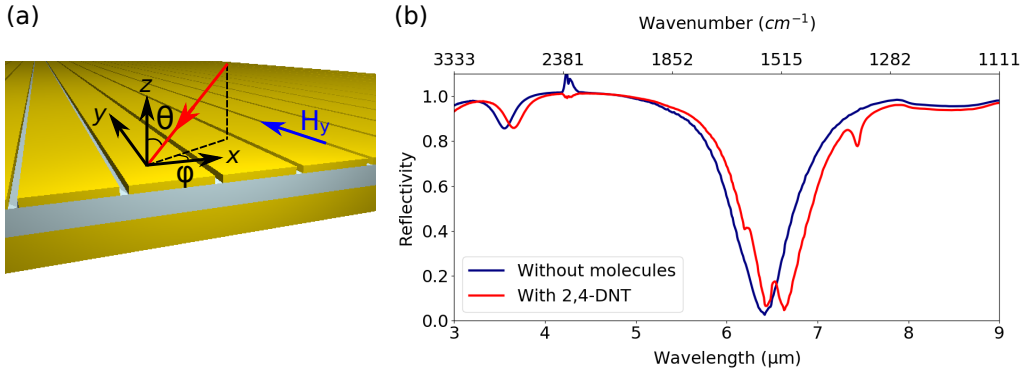


Fig. 2: (a) Three dimensional representation of an Helmholtz-like resonator with an incoming plane wave with the polar angle θ and the azimuthal angle ϕ. (b) Infrared reflection spectra of resonators, whose dimensions are $d = 3\,\mu\text{m}$, $w = 300\,\text{nm}$, $h_s = 100\,\text{nm}$ and $h_b = 50\,\text{nm}$, without (blue line) and with 2,4-DNT (red line).

These experimental results are paving the way to the design of a sensitive and specific sensor based on these Helmholtz-like resonators.

IV. Conclusion

A simplified geometry of the optical Helmholtz resonator has been put forward. It exhibits Helmholtz-like resonance in the infrared domain with similar properties to the initial optical Helmholtz resonator (high enhancement of the electric field in the whole volume of the slit, angular dependence, influence of the permittivity in the box). This resonator has been applied to the SEIRA detection of 2,4-dinitrotoluene, leading to reflectivity changes up to 15% at $\lambda = 6.6\,\mu\text{m}$.

Acknowledgement

This work is part of the HORUS project supported by the French National Research Agency (ANR, reference number ANR-16-CE39-0007).

References

[1] B.Y. Zheng, Y. Wang, P. Nordlander and N. J. Halas, "Color-Selective and CMOS-Compatible Photodetection Based on Aluminum Plasmonics," *Advanced Materials*, vol. 26, pp. 6318-6323, 2014.
[2] K.R. Catchpole and A. Polman, "Plasmonic solar cells," *Optics Express,* vol. 16, pp. 21793-21800, 2008.
[3] M. Makhsiyan, P. Bouchon, J. Jaeck, J.L. Pelouard, and R. Haïdar, "Shaping the spatial and spectral emissivity at the diffraction limit," *Applied Physics Letters,* vol. 107, p. 251103, 2015.
[4] M. Osawa, "Near-Field Optics and Surface Plasmon Polaritons," *Springer Berlin Heidelberg*, pp. 163-187, 2001.
[5] L. V. Brown, X. Yang, K. Zhao, B. Y. Zheng, P. Nordlander and N. J. Halas, "Fan-Shaped Gold Nanoantennas above Reflective Substrate for Surface-Enhanced Infrared Absorption (SEIRA)," *Nano Letters,* vol. 15, pp. 1272-1280, 2015.
[6] C. Huck, M. Tzschoppe, R. Semenyshyn, F. Neubrech and A. Pucci, "Chemical Identification of Single Ultrafine Particles Using Surface-Enhanced Infrared Absorption," *Physical Review Applied,* vol.11, p. 014036, 2019.
[7] T. G. Mayerhöfer and J. Popp, "Periodic array-based substrates for surface-enhanced infrared spectroscopy," *Nanophotonics,* vol. 7, pp. 39-79, 2018.
[8] P. Chevalier, P. Bouchon, R. Haïdar and F. Pardo, "Optical Helmholtz resonators ," *Applied Physics Letters,* vol. 105, p. 071110, 2014.
[9] P. Chevalier, P. Bouchon, M. Verdun, E. Steveler, N. Bardou, C. Dupuis, F. Pardo and R. Haïdar, "Experimental demonstration of the optical Helmholtz resonance," *Applied Physics Letters,* vol. 112, p. 171110, 2018.
[10] P. Chevalier, P. Bouchon, J.J. Greffet, J.L. Pelouard, R. Haïdar and F. Pardo, "Giant field enhancement in electromagnetic Helmholtz nanoantenna," *Physical Review B,* vol. 90, p. 195412, 2014.
[11] J. Homola, "Present and future of surface plasmon resonance biosensors," *Analytical and Bioanalytical Chemistry,* vol. 337, pp. 528-539, 2003.