

Addressing chemical effects in light-matter interaction: From surface-enhanced Raman scattering to quantum technologies

Roberto A. Boto^{1,*}, Rubén Esteban², Bruno Candelas², Javier Aizpurua^{1,2} and David Casanova¹

¹Donostia International Physics Center DIPC, 20018, Donostia-San Sebastián, Spain

²Materials Physics Center, CSIC-UPV/EHU, 20018, Donostia-San Sebastián, Spain

*roberto.alvarez@ehu.es

Light-matter interactions are at the heart of strategic fields such as spectroscopy, sensing and quantum information. These interactions are enhanced when a molecule is located near a metallic particle able to sustain collective excitations of the electron density that induce extremely localized electromagnetic fields, and/or when the molecule possesses a significant response to electromagnetic fields. The molecular response strongly depends on the chemical structure of the molecule and on the chemical interaction between the molecule and the environment. In this work, we first address the chemical and electromagnetic interactions between the molecule and metallic particles in Surface-Enhanced Raman Scattering (SERS). We then study the effect of the molecular structure on the magnetic properties of boron-doped graphed nanoribbons with application in quantum computing.

SERS is a spectroscopic technique based on the enhancement of the Raman scattering of a molecule located near a metallic particle [1] as a result of two different mechanisms [2]: the chemical (CHEM) mechanism due to the chemical interaction between the metallic surface and the molecule, and the electromagnetic (EM) mechanism due to the extremely localised electromagnetic fields induced near the metallic particle. Here, we present an approach to differentiate the role of the CHEM and EM mechanisms in the total SERS enhancement obtained within DFT calculations. We apply this approach (which uses Time-Dependent Density Functional Theory (TDDFT) calculations of the optical response of metallic clusters [3]) to study the changes in the Raman spectrum of the molecule biphenyl-4,4'-dithiol (BPDT) (Fig. 1a) sandwiched between two gold clusters (Fig. 1b).

In the second part of this work, we address the design of boron-doped graphene nanoribbons (Fig. 1c) that host electron-spin qubits (two-level systems consisting in a superposition of electron-spin states) well-localized around the boron atoms, as shown by the spin density (Fig. 1d) [4]. Electron-spin qubits are manipulated by external magnetic fields, and thus the practical use of electron-spin qubits demands precise control of the magnetic properties that determine the coherence time of the qubits. We study the impact of the molecular structure on the coherence times within DFT for a selected number of boron-doped graphene nanoribbons.

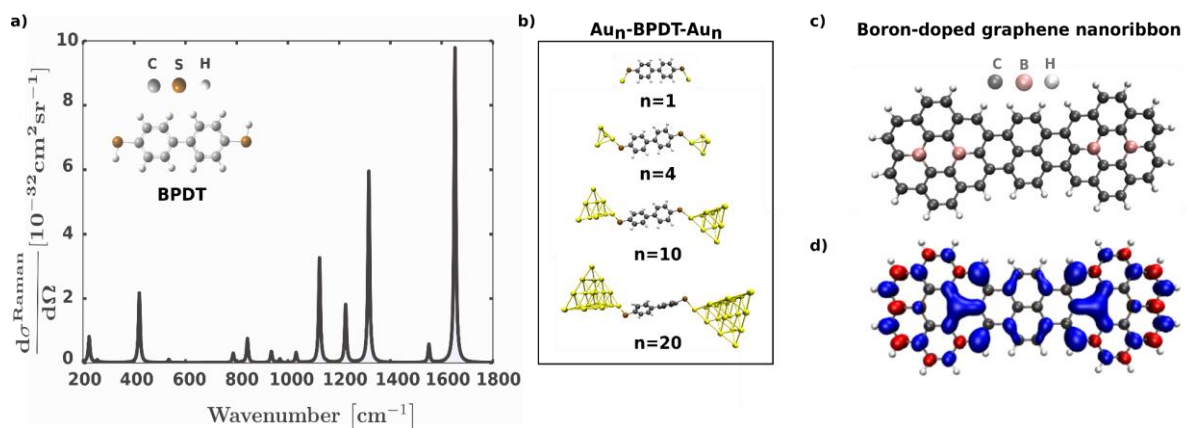


Figure 1. SERS enhancement factors of biphenyl-4,4'-dithiol (BPDT) sandwiched between two gold clusters and boron-doped graphene nanoribbons. Panel a): Raman spectrum of BPDT between 200 cm^{-1} and 1800 cm^{-1} . In the inset, we show a molecular model of the minimum energy structure of BPDT, where grey, white and brown

spheres represent carbon, hydrogen and sulfur atoms, respectively. **Panel b.** Molecular models of the minimum energy structures of BPDT sandwiched between two gold clusters of different size $\text{Au}_n\text{-BPDT-Au}_n$, $n=1, 4, 10$ and 20 , where yellow spheres represent gold atoms. **Panel c.** Molecular model of the minimum energy structure of a selected boron-doped graphene nanoribbon, where grey, white and pink spheres represent carbon, hydrogen and boron atoms, respectively. **Panel d.** 0.002 a.u. isosurface of the spin density of the nanoribbon shown in Panel c, where the blue and red volumes represent regions of excess of spin alpha and of spin beta density, respectively.

References

- [1] E. Le Ru, and P. Etchegoin., *Principles of Surface-Enhanced Raman Spectroscopy and related plasmonic effects* (Elsevier Science and Technology, United Kingdom, 2011).
- [2] S. M. Morton, D. W. Silverstein, *et al. Chemical reviews*, 2011, 111, 3692.
- [3] M. Urbieto, M. Barbry, *et al. ACS Nano*, 2018, 12, 585.
- [4] N. Friedrich, P. Brandimarte, *et al. Physical Review Letters*, 2020, 125, 146801.