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Mixed Quantum/Classical Approach to Surface-Enhanced Spectroscopies

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Abstract: We present a novel theoretical approach to calculate the optical response of molecular systems interacting with plasmonic substrates, either metallic or graphene-based.

Peculiar electromagnetic responses arise when a molecular system is adsorbed on plasmonic substrates under the effect of an external radiation. As an example, surface enhanced Raman scattering (SERS) has become a widely used analytical technique, taking advantage of the huge enhancement of the Raman signal when a target molecule is adsorbed on metal nanoaggregates [1]. This phenomenon can allow single molecule detection, thanks to enhancement factors as much as 10^{10} [1]. In this contribution, we present a novel theoretical approach to treat surface-enhanced spectroscopies, including SERS. The plasmonic structure is described by means of fully atomistic classical electromagnetic models, which have recently been developed by the present authors [2-5]. The adsorbed molecular system is treated at the quantum mechanical (QM) level. The approach can treat nanostructures of complex shape, and are general enough to describe both metal nanoparticles [2,3,5] and graphene-based materials [4,6] at the same level of accuracy. The approach has huge potential for large scale nanoplasmonic simulations (more than 1 million atoms), also for systems dominated by quantum effects, such as subnanometer junctions [2,5], or geometrical defects [6,7].

The robustness and reliability of the developed method is demonstrated for selected test cases and by the comparison with experimental spectra [8].

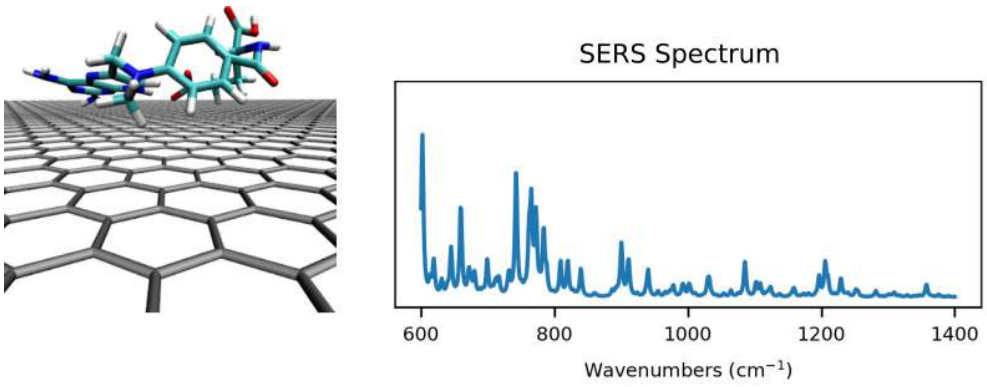

Fig. 1 Graphical depiction of methotrexate adsorbed on a graphene disk (left) and the corresponding calculated SERS spectrum (right).

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