Atomistic multiscale modeling of surface-enhanced IR absorption

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Abstract: We present a multiscale quantum mechanics (QM)/classical approach to model surface-enhanced IR absorption (SEIRA) spectra of molecules near plasmonic nanostructures. The frequency-dependent ωFQ and ωFQFμ models describe the plasmonic properties of graphene-based and noble metal nanostructures. Computed SEIRA spectra are compared to calculated SE Raman Scattering (SERS) signals and experimental data.

Surface-enhanced vibrational spectroscopies, including surface-enhanced infrared absorption (SEIRA) and surface-enhanced Raman scattering (SERS), selectively amplify molecular vibrational signals by exploiting the intense local electric field enhancement near plasmonic nanostructures.[1-3] Accurately modeling this enhancement is crucial for predicting and interpreting SEIRA and SERS signals.

Multiscale approaches enable the prediction of enhanced spectroscopic responses by coupling a quantum mechanical (QM) description of the molecule with classical electromagnetic models of the plasmonic substrate.[8] In this framework, the molecule is treated at the DFT level, while the plasmonic substrate is characterized using the ωFQ and ωFQFμ models. The ωFQ and ωFQFμ models are fully atomistic classical force fields based on a Drude-conduction mechanism, incorporating an ad hoc phenomenological correction to account for quantum tunneling effects, which can treat alkali metals[4], graphene-based materials[5], and noble metal nanostructures.[6] These models accurately describe local field enhancement by capturing atomic-scale features of the plasmonic substrate, such as edges, tips, defects, and junctions.[4,7] This approach allows for the simulation of large plasmonic systems comprising thousands of atoms and enables tuning of the plasmon resonance frequency, thereby enhancing the molecule's spectroscopic response.[8,9] Our group has recently introduced multiscale QM/classical approaches, such as QM/ωFQ and QM/ωFQFμ, for calculating SERS spectra.[9]

In this work, we extend the QM/ωFQ and QM/ωFQFμ approaches to predict the SEIRA spectra of molecules close to plasmonic nanostructures. As a first application, we use our novel approach to predict the SEIRA signals of adenine nucleobase (ADE) in proximity to gold nanostructures, investigating its spectral dependence on adsorption site (vertex vs. face) and molecular orientation. Figure 1 presents SEIRA spectra for ADE in six different molecular orientations adsorbed on the vertex of a gold nano-icosahedron (Au_{10179} Ih). The spectral shapes and enhancement factors for various binding configurations are analyzed and compared to QM/ωFQFμ SERS calculations and experimental data.[10]

We then explore the SEIRA spectra of ADE on graphene-based nanostructures, focusing on how their structural and electronic properties influence spectral patterns and enhancement. Graphene and its derivatives have gained significant attention as SEIRA substrates due to their tunable plasmonic response in the mid-IR range.[3,11] By adjusting the plasmon resonance frequency to match molecular vibrations, SEIRA absorption can be optimized. This tuning can be achieved through structural modifications, such as varying the size and geometry of graphene nanostructures, or by controlling their carrier density via electrical gating or chemical doping. The ωFQ model provides an effective framework for capturing these effects, enabling a fine-tuned description of the optical response of graphene substrates and their role in SEIRA enhancement. Accordingly, we systematically investigate how the SEIRA signals of adenine depend on the size and Fermi energy of graphene nanodisks, providing insights to optimize molecular detection on graphene-based plasmonic platforms.

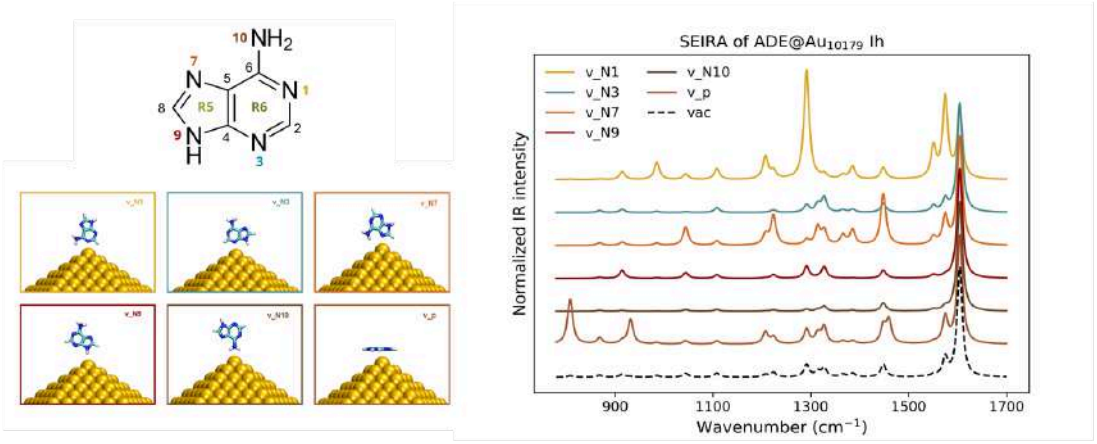

Figure 1: Normalized SEIRA spectra of ADE in the region 800-1700 cm^{-1} for the six configurations on the vertex of the gold nano-icosahedron (Au_{10179} Ih).

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