Tip-Enhanced Raman Scattering – a theoretical description accessing the chemical and electromagnetic contributions

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The excitation of collective electron dynamics inside the metallic nanoparticles induced by external light fields leads to strongly re-shaped electromagnetic nearfields with a complex spatial and temporal profile. The interaction of these modified and enhanced nearfields with systems located in close vicinity to the metallic nanoparticle is the origin of many astonishing physical and chemical phenomena, such as the formation of new quasi-particles, new mechanisms for chemical reactions or the ultra-high spatial resolution and selectivity in molecular detection.

For the theoretical description of such plasmonic hybrid systems in external light fields, it is necessary to describe both the electromagnetic interaction and the more chemical effects equally. In this talk, I will introduce our recent results on the theoretical description of these systems, with particular emphasis on spectroscopic applications, e.g., in the context of tip-enhanced Raman scattering spectroscopy and/or plasmon-induced catalysis [1-5]. Our calculations show pronounced changes of the Raman spectrum under non-resonant and resonant conditions and support the possibility of sub-nanometer spatial resolution.

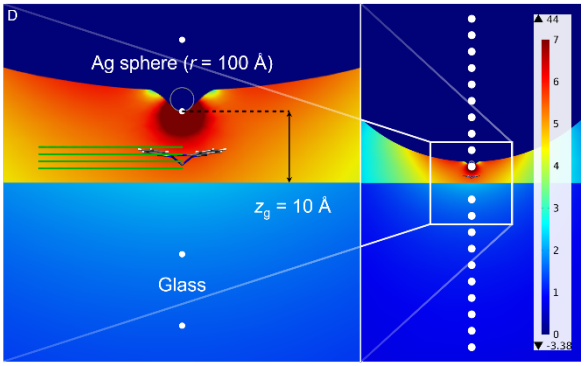

Figure 1: Schematic picture of modelling TERS: atomic-scale protrusions are included into the electromagnetic simulations. The resulting nearfield can be mimicked by parameterized point charges, which, in turn, can be included into quantum chemical calculations [2].

References

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