Anomalous spectral shift of near- and far-field plasmonic resonances in nano-gaps

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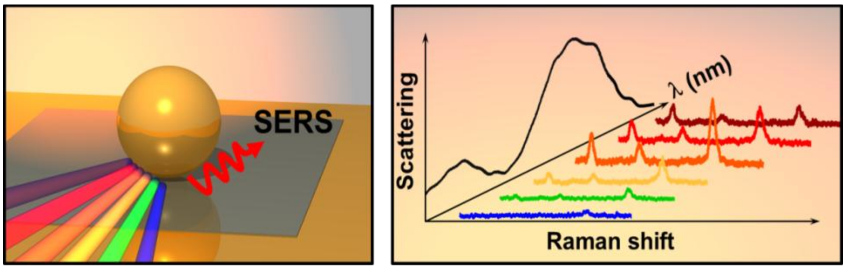
The control and tuning of near-field and far-field responses in plasmonic nanostructures represents a crucial aspect in the design of optimized platforms for field-enhanced spectroscopy. Due to the lack of methods that can directly compare and correlate both responses under similar environmental conditions, near- and far-field spectral behaviors have been often assumed to be identical.

We develop a widely tuneable optical technique to probe the near-field resonances within individual plasmonic structures and to directly compare it to the corresponding far-field response.

We investigate individual gold nanoparticles spaced 1nm above a gold mirror by a molecular monolayer [1]. We measure the near-field spectral resonance by devising a widely-tunable optical technique to track the SERS signals across the dark-field spectrum simultaneously measured on the same nanoparticle. For every nanostructure, we find the extracted near-field enhancement has a narrow Gaussian profile, always blueshifted (>40meV) with respect to the dark field scattering coupled mode. We find this agrees with theoretical predictions in such strongly coupled plasmonic systems. Using a transformation optics approach, we show the observed spectral shifts can be clearly ascribed to the different way that interference of plasmon gap modes operates in the near- and far-field. An additional benefit of our approach is to show that the ever-present SERS background, highly debated in the literature, does not come from the same spatial locations as the near-field controlled SERS peaks [2].



[1] Felix Benz et al., "Nano-optics of molecular-shunted plasmonic nanojunctions", *Nano Lett.* **15**, 669 (2015)
[2] Anna Lombardi et al. "Anomalous spectral shift of near- and far-field plasmonic resonances in nano-gaps", *ACS Photonics* **3**, 471 (2016)