Surface-enhanced Molecular Electron Energy Loss Spectroscopy

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Electron energy loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM) is becoming an important technique in spatially-resolved spectral characterization of optical and vibrational properties of matter at nanoscale. EELS has played a significant role in understanding localized polaritonic excitations in nanoantennas and also allows for studying molecular excitations in nanoconfined samples.

Here we theoretically describe the interaction of a localized electron beam with molecule-covered polaritonic nanoantennas, and propose the concept of surface-enhanced molecular EELS utilizing electromagnetic coupling between the nanoantenna and the molecular sample. Particularly, we study plasmonic and infrared phononic antennas covered by molecular layers, exhibiting either an excitonic or vibrational response. We demonstrate that EEL spectra of this molecule-antenna coupled system exhibit Fano-like or strong coupling features, similar to the ones observed in far-field optical and infrared spectroscopy. EELS offers the advantage to acquire spectral information with nanoscale spatial resolution, and importantly, to control the antenna-molecule coupling on demand.

Considering ongoing instrumental developments, EELS in STEM shows the potential to become a powerful tool for fundamental studies of molecules that are naturally or intentionally located on nanostructures supporting localized plasmon or phonon polaritons. Surface-enhanced EELS might also open the door to novel STEM-EELS applications such as remote- and thus damage-free- sensing of the excitonic and vibrational response of molecules, quantum dots or 2D materials.

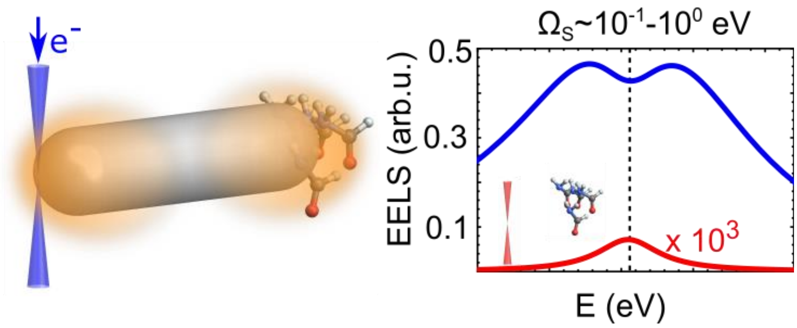

Figure: Schematic showing the proposed concept of remote sensing. The electron beam placed at apex of a silver nanorod excites a dipolar plasmon, which couples with molecules (exhibiting excitonic transition or vibrational excitation) attached to the opposite apex of the rod. The molecular signal transmitted via the plasmonic field appears as a Fano-like dip in blue spectrum. Excitation of the uncoupled molecular sample yields a small spectral peak, decaying rapidly with distance.

References

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