

## Addressing Vibrational Excitations in Van der Waals Materials and Molecular Layers Within Electron Energy Loss Spectroscopy

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Only recently, specially designed instrumentation for spatially-resolved electron energy-loss spectroscopy (EELS) has been developed to increase the attainable spectral resolution and the operating spectral range [1]. This progress has dramatically broadened the potential for applications of EELS for probing low-loss vibrational excitations. Pioneering experiments have demonstrated the capability of the fast electrons in Scanning Transmission Electron Microscopy (STEM) to probe vibrational fingerprints in organic samples [2], ionic crystals [3], and also in van der Waals materials [4].

In our work [4], we theoretically and experimentally studied the very low-loss EELS of multilayer hexagonal boron nitride (h-BN), a representative van der Waals structure. The weak coupling between individual atomic layers results in extreme optical anisotropy, which gives rise to the existence of hyperbolic phonon polaritons (h-PhPs) in this material: coupled excitations of optical phonons and light with hyperbolic dispersion in the range of 90 – 200 meV [5]. h-PhPs might be key to many emerging photonic technologies relying on nanoscale light confinement and manipulation [5,6]. Thus, an efficient design and utilization of h-BN structures require spectroscopic studies with adequate spatial resolution, a target which can be provided by EELS utilizing fast electrons as localized electromagnetic probes.

To that end, we performed spatially-resolved EELS on a simple h-BN flake structure with an optimized STEM-EELS tool [7], which revealed the spectral dependence of the loss spectra on the h-BN thickness and on the proximity of the electron beam to the material edge (Fig. 1A). Such behavior is a consequence of the polaritonic nature of the induced phonon-polaritonic excitations. Indeed, with help of the classical dielectric response theory for EELS, applied to anisotropic slabs and edges, we demonstrate that the electron energy loss in h-BN is dominated by h-PhP excitation and not directly by bulk phonons as in preliminary interpretations [1]. This finding nicely describes and quantitatively match experimental observations (see an example of h-BN loss spectra in Fig. 1B). We thus suggest that EELS can be a technique complementary to scanning near-field optical microscopy [6] for characterization of low-energy phonon polaritons.

Furthermore, we foresee that EELS can be exploited to address important phenomena involving the electromagnetic coupling between different types of low-energy excitations. We thus theoretically propose the concept of "Surface-Enhanced Molecular EELS" where we show that an electron beam can address the electromagnetic near-field coupling between antenna polaritons and molecular vibrations and excitons. We demonstrate this concept by studying the interaction of a localized electron beam with a coupled system composed of polaritonic nanoantenna particles covered by molecules. We show that EEL spectra of the coupled system exhibits Fano-like or even stronger coupling features, similar to the

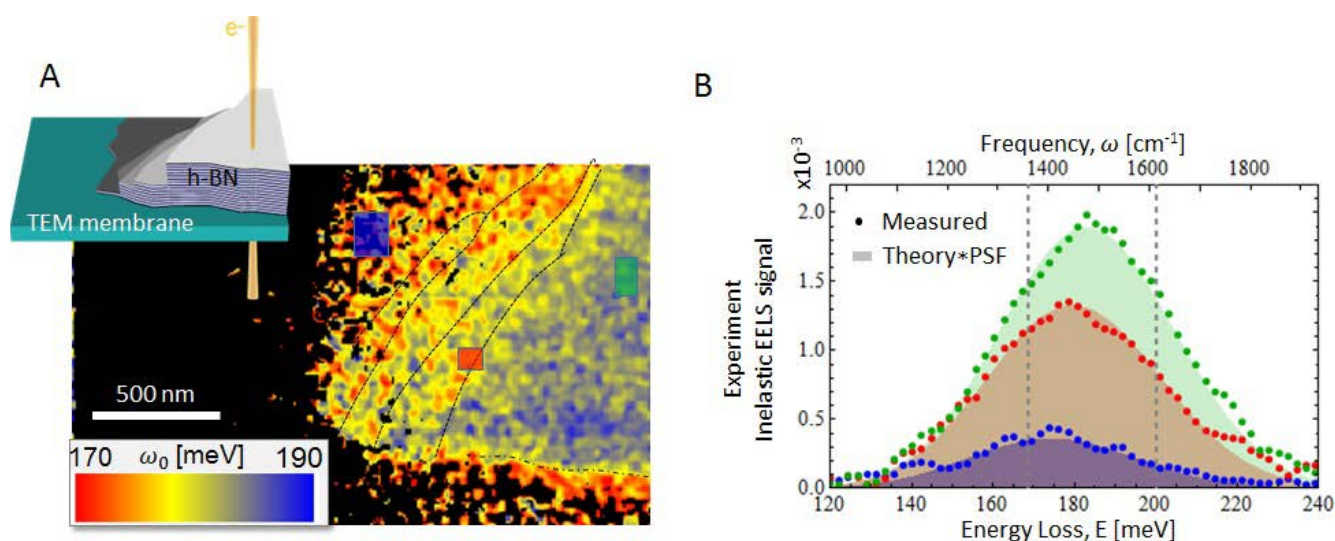
ones observed in far-field surface-enhanced optical and infrared spectroscopy. In our situation, however, the localized electron beam enables to control the antenna-molecule coupling on demand at the nanoscale.

Considering the ongoing instrumental developments of the last years, EELS in STEM could become a powerful tool for fundamental spectroscopic studies of molecules that are naturally or intentionally located on nanostructures supporting localized plasmon or phonon polaritons. Surface-enhanced molecular EELS might substantially increase the sensitivity to otherwise weak molecular signals, avoiding at the same time radiation damage. The concept proposed here thus suggests a path to apply EELS in a variety of situations involving the interest for molecular information, *e.g.* for detecting vibrational fingerprints from ultrathin molecular layers at catalytic particles or for studying composition of cell membranes and their active sites.

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**Figure 1.** A) Contour plot addressing the energy loss peak position in an EELS map for the different electron beam positions on a h-BN flake (sample geometry is displayed in the inset showing the variation of thickness from a few monolayers to 30 nm). B) Experimental EELS spectra from different sample areas, as marked on the map in A are in excellent agreement with convolved theoretical spectra calculated for the corresponding h-BN thicknesses.