Probing low-energy hyperbolic polaritons in van der Waals crystals with an electron microscope

A. Govyadinov[1], A. Konečná[1,2], A. Chuvilin[1,3], S. Vélez[1], I. Dolado[1], A. Y. Nikitin[1,3], S. Lopatin[4], F. Casanova[1,3], L. E. Hueso[1,3], J. Aizpurua[2,5], R. Hillenbrand[1,3]*

[1] CIC NanoGUNE, Donostia-San Sebastián, Spain
[2] Materials Physics Center CFM, CSIC-UPV/EHU, Donostia-San Sebastián, Spain
[3] IKERBASQUE, Basque Foundation for Science, Bilbao, Spain
[4] KAUST, Thuwal, Saudi Arabia
[5] Donostia International Physics Center DIPC, Donostia-San Sebastián, Spain
**email: agovyadinov@nanogune.eu*

Van der Waals (vdW) materials exhibit intriguing structural, electronic, and photonic properties. Much of these properties result from the large anisotropy in the bonding strength of atoms within the atomic layers and across them, and, therefore, are often intimately connected with the corresponding phonons. The investigation of vdW materials thus often requires probing low mid-IR energies. Electron energy loss spectroscopy within scanning transmission electron microscopy (STEM-EELS) allows for spatially resolved mapping of a variety of excitations in condensed matter and can provide unprecedented structural information about the sample for correlative studies. However, its detection is typically limited to energy losses in the eV range – too large for probing phonons or mid-infrared plasmons.

Here, we enabled conventional STEM-EELS to probe energy loss down to 100 meV (~12 μm), which allowed us to probe phononic excitations in the upper Reststrahlen band (169–200 meV) of hexagonal boron nitride (h-BN), a representative van der Waals material. Interestingly, the h-BN spectra from an exfoliated flake show dependence on the flake thickness and on the distance of the electron beam to the flake edges [1]. To explain these observations, we developed a classical response theory that describes the interaction of fast electrons with (anisotropic) van der Waals slabs, revealing that the electron energy loss is dominated not by the excitation of bulk phonons (as often regarded), but by hyperbolic phonon polaritons – volume-propagating polaritons with hyperbolic dispersion [2]. We further show evidence that the electron beam excites hyperbolic surface phonon-polaritons [3] at the edges of h-BN flake, which is important for STEM-EELS studies of vdW nanostructures.

The dominance of hyperbolic polaritons in EELS spectra of vdW materials makes STEM-EELS suitable for the investigation of their optical/polaritonic properties, with our work serving as a foundation for such investigations.

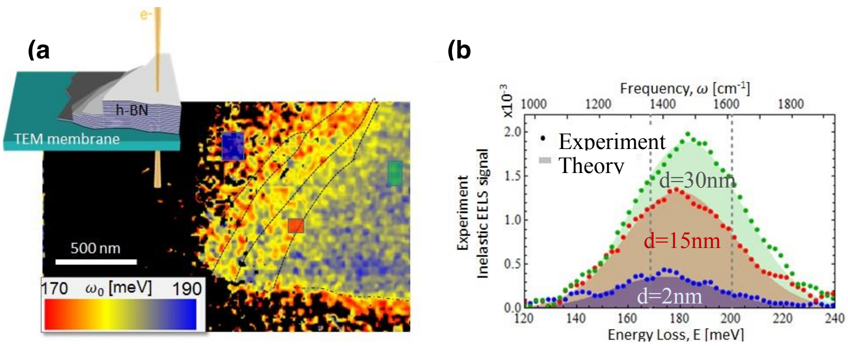

Figure 1. (a) EELS map of phononic excitations in an h-BN flake (sample geometry is displayed in the inset showing the variation of thickness from a few monolayers to 30 nm). (b) Our theory (filled curves) fully reproduces thickness-dependent shifts observed in the experimental spectra (dots) and relates them to the excitation of hyperbolic phonon-polaritons.

[1] A. Govyadinov, A. Conečná, A. Chuvilin et al. *Nature Comms*. **8**, 95 (2017)
[2] D. Basov, M. Fogler and F.J. Garcia de Abajo, *Science* **354**, aag1992 (2016)
[3] P. Li, I. Dolado, F.J. Alfaro-Mozaz et al. *Nano Lett*. **17**, 228 (2017)