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Letter

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Far Infrared Synchrotron Near-Field Nanoimaging and Nanospectroscopy

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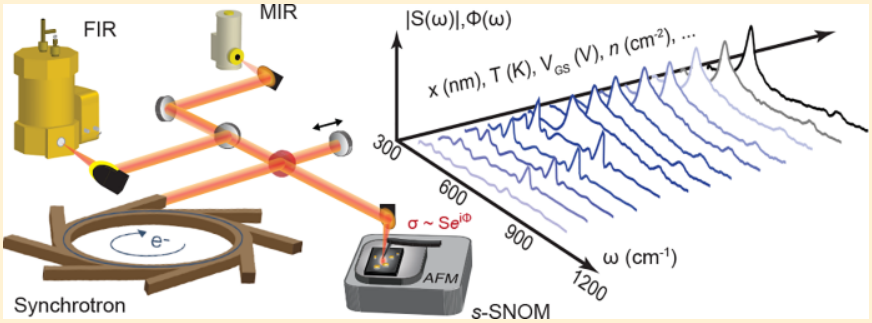
Supporting Information



ABSTRACT: Scattering scanning near-field optical microscopy (*s*-SNOM) has emerged as a powerful imaging and spectroscopic tool for investigating nanoscale heterogeneities in biology, quantum matter, and electronic and photonic devices. However, many materials are defined by a wide range of fundamental molecular and quantum states at far-infrared (FIR) resonant frequencies currently not accessible by *s*-SNOM. Here we show ultrabroadband FIR *s*-SNOM nanoimaging and spectroscopy by combining synchrotron infrared radiation with a novel fast and low-noise copper-doped germanium (Ge:Cu) photoconductive detector. This approach of FIR synchrotron infrared nanospectroscopy (SINS) extends the wavelength range of *s*-SNOM to 31 μm (320 cm^{-1}, 9.7 THz), exceeding conventional limits by an octave to lower energies. We demonstrate this new nanospectroscopic window by measuring elementary excitations of exemplary functional materials, including surface phonon polariton waves and optical phonons in oxides and layered ultrathin van der Waals materials, skeletal and conformational vibrations in molecular systems, and the highly tunable plasmonic response of graphene.

KEYWORDS: *far-infrared, near-field microscopy, s-SNOM, synchrotron infrared nanospectroscopy, graphene plasmonics, spatiospectral nanoimaging*

Near-field nanoscopy attracts increasing scientific attention, specifically in the implementation of infrared scattering type scanning near-field optical microscopy (IR *s*-SNOM).[1−4] It provides for nanoimaging and nanospectroscopy down to a few nanometer length scales, gaining insight into molecular orientation[5] and coupling,[6] catalytic activity,[7] heterogeneity in electron and lattice dynamics,[8,9] and plasmonic and polaritonic effects in quantum matter[10−13] with recent extension to the low temperature[9,14] and ultrafast regimes.[15−18] Despite these significant developments, *s*-SNOM has largely been limited to a narrow range of the electromagnetic spectrum of the near- to mid-IR at high frequencies, and the RF[19] and low THz[20] regime at low frequencies.

However, the far-infrared (FIR) and lower mid-infrared (MIR) spectral range (10−700 cm^{-1}, 14−1000 μm, 0.3−20 THz, 3−190 K) has yet remained largely unexplored in *s*-SNOM, despite the significance of its low-energy molecular and quantum state resonances that define material functions from condensed matter physics to biology and medicine. Many fundamental excitations and collective modes in solids have characteristic energies in the FIR, including the free carrier Drude response, crystal lattice vibrations, charge density waves, superconducting energy gaps, magnetic excitations, surface plasmon and phonon polaritons, and others (Figure 1a).[21] Similarly, in soft and biological molecular materials, the FIR provides spectral access to structurally specific ("fingerprint") vibrations and conformations via skeletal, torsional, and deformation modes, that allow for direct probing of, for example, the secondary structure of proteins.[22]

The extension of *s*-SNOM into the FIR range has largely been hampered by the lack of both suitable light sources and detectors. On the high frequency side, IR *s*-SNOM is performed with different femtosecond laser based super-

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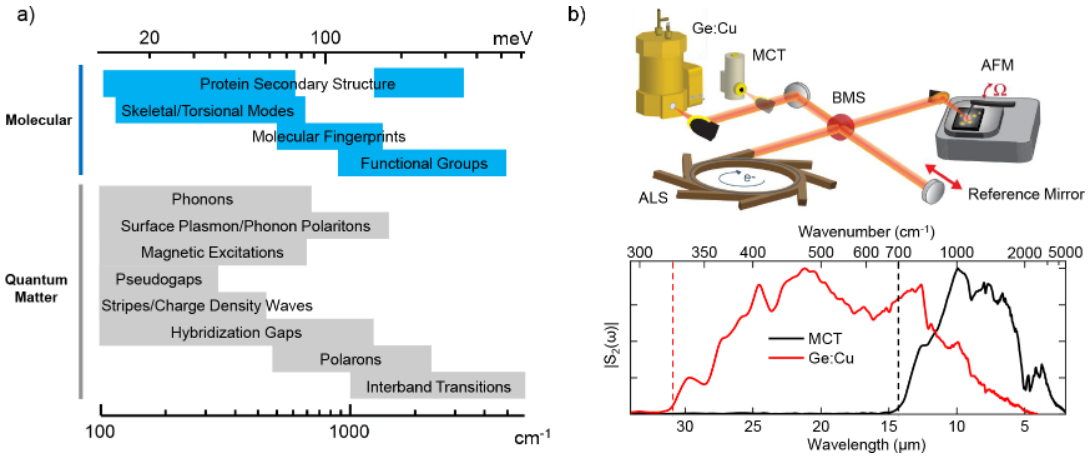

Figure 1. (a) Infrared energy scales and associated phenomena in molecular and quantum matter; (b) Top: ultrabroadband SINS experimental configuration with extension to far-infrared frequencies; bottom: SINS reference spectrum using MCT (black curve) and Ge:Cu (red curve) detectors, demonstrating extended near-field spectroscopic performance at frequencies down to 320 cm^{-1}.

continuum and parametric generation sources for broadband or broadly tunable mid-IR radiation, yet limited by suitable nonlinear optical crystals for frequency conversation to wavelengths <18 μm.[23] At low frequencies, THz *s*-SNOM nanoimaging is performed with continuous wave THz sources, such as gas lasers and QCLs at a limited number of fixed frequencies,[20,24] or with broadband THz light generated from photoconductive antennas, limited to <3 THz[25−27] and low power output.

To date, far-IR *s*-SNOM has only routinely been achieved using a free electron laser (FEL) that provides the necessary high intensity quasi-cw radiation as needed for *s*-SNOM.[28,29] Although in principle continuously tunable from 1.5−75 THz (50−2500 cm^{-1}, 4−200 μm), for *s*-SNOM nanospectroscopy, a broadband FIR light source with simultaneous high bandwidth and spectral irradiance across a broad spectral range would be most desirable. Not only does this enable signal multiplexing and self-referencing to eliminate noise and systematic errors, but it also allows for the simultaneous probing of multiple characteristic material resonances, as desirable in monitoring kinetics of phase transitions or chemical transformations on the nanoscale.

In addition to limitations in the availability of suitable light sources is a lack of far-infrared detectors with the necessary speed and sensitivity for FIR *s*-SNOM. Mid-IR detectors based on small bandgap semiconductor alloys, such as $Hg_{1-x}Cd_xTe$ (MCT), have a long-wavelength cutoff typically at 600 cm^{-1}, with extension to lower frequency at the expense of drastically reduced sensitivity and challenged by material limitations. On the other hand, conventional FIR detectors such as pyroelectric deuterated triglycine sulfate (DTGS) or liquid helium cooled Si bolometers only operate at < few kHz frequencies and have too slow response times. Extrinsic impurity photoconductors based on doped Si or Ge offer fast intrinsic response times (<100 ns) and small bandgaps in the FIR, yet in their usual implementation are plagued by excess thermal background and electronic noise, rendering them unsuitable for *s*-SNOM (see Supporting Information for extended discussion).

In this Letter, we demonstrate ultrabroadband near-field nanospectroscopy covering the qualitatively new regime of far-IR *s*-SNOM. We utilize synchrotron radiation, which provides a low-noise, broadband, and coherent light source with high spectral irradiance at frequencies spanning from THz to the extreme UV region.[30] To detect the tip-scattered near-field FIR signal we have developed a custom, MHz bandwidth Ge:Cu photoconductor with superior sensitivity for spectroscopic FIR *s*-SNOM nanoimaging. With this approach we are able to extend the wavelength range of *s*-SNOM by one octave, overcoming conventional limits, down to 31 μm (320 cm^{-1}).

To demonstrate the performance in this new spectral regime, we probe previously inaccessible types of excitations with far-IR *s*-SNOM. This includes low energy phonons in anisotropic bulk crystalline media, as well as layered van der Waals systems, of interest for potential nanophotonics applications as natural hyperbolic materials. Skeletal deformations and torsional modes in organic semiconductor films allow for the simultaneous nanoprobing of several vibrational degrees of freedom in molecular materials, which heavily influence the low energy electronic and transport properties of functional devices. We access the THz plasmonic regime in graphene, including plasmon−phonon substrate interactions, and demonstrate a high degree of gate tunability. Lastly, we provide a platform to extend to yet longer wavelengths by combining with other extrinsic Ge detectors.

Figure 1b displays a schematic of the ultrabroadband *s*-SNOM nanospectroscopy implementation, based on an atomic force microscope (AFM) using metal-coated tips, and interferometric detection as described previously.[30] IR synchrotron radiation is provided by the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory in two experimental configurations: Beamline 5.4, employing a specially modified AFM (Innova, Bruker) coupled to a commercial FTIR Spectrometer (Nicolet 6700, Thermo-Scientific), and Beamline 2.4 using a commercial nanoscope (neaSNOM, Neaspec GmbH), to measure the spectral near-field scattering amplitude and phase response $|S(\omega)|e^{i\Phi(\omega)}$. As a direct probe of the sample dielectric function, broadband *s*-SNOM amplitude and phase typically exhibit simple dispersive and absorptive lineshapes, respectively, for weaker oscillators, and a more complicated hybrid response for strongly resonant and collective excitations.[23,31] The customized LHe-cooled Ge:Cu detector for synchrotron infrared nanospectroscopy (SINS) provides a broadband response (2−31 μm) and suitable sensitivity ($D^* > 10^{10}$ cm·$\sqrt{\text{Hz}}$/W). The low energy cutoff of Ge:Cu of 31 μm (320 cm^{-1}), limited by impurity band

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