Amplitude- and phase-resolved infrared nanoimaging and nanospectroscopy of polaritons in liquid environment

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Abstract: Polaritons allow for strong light-matter coupling and for highly sensitive analysis of (bio)chemical substances and processes. Nanoimaging of the polaritons' evanescent fields is critically important for experimental mode identification and field confinement studies. Here we describe two setups for polariton nanoimaging and spectroscopy in liquid. We first demonstrate the mapping of localized plasmon polaritons in metal antennas with a transflection infrared scattering-type scanning near-field optical microscope (s-SNOM), where the tip acts as a near-field scattering probe. We then demonstrate a total internal reflection (TIR) based setup, where the tip is both launching and probing ultra-confined polaritons in van der Waals materials (here phonon polaritons in hexagonal boron nitride flakes), laying the foundation for s-SNOM based polariton interferometry in liquid. Our results promise manifold applications, for example, in-situ studies of strong coupling between polaritons and molecular vibrations or chemical reactions at the bare or functionalized surfaces of polaritonic materials.

Keywords: scattering type scanning near-field optical microcopy (s-SNOM), nano-FTIR, liquid environment, polaritons, plasmonic antennas

Surface plasmon resonance (SPR) spectroscopy using metal surfaces is a widely used label-free technique for refractive index sensing, particularly for studying biomolecular interactions in their native environment, that is, in liquids[1–4]. Typically, SPR spectroscopy is performed in the visible spectral range. At infrared frequencies, where propagating plasmon polaritons are less confined, surface phonon polaritons could become an alternative[5]. On the other hand, localized plasmon resonances in metal antennas at infrared frequencies have recently boosted surface-enhanced infrared absorption spectroscopy (SEIRA) not only in air[6,7] but also in liquids[8–10], allowing for highly sensitive analysis of chemical composition and molecular conformations of minute amounts of a substance, offering new possibilities for plasmonic sensing in the infrared (IR) spectral range. More recently, ultra-confined infrared plasmon and phonon polaritons in van der Waals (vdW) materials such as graphene, hexagonal boron nitride (h-BN), and molybdenum trioxide (MoO_3) have attracted wide attention[11–15], as they promise ultra-compact and highly sensitive devices for molecular vibrational spectroscopy for (bio)chemical analysis[16–19]. The majority of these studies were performed in air. Considering that (bio)chemical processes often occur in liquid, it would be thus of great interest to explore the properties of ultra-confined vdW material polaritons in liquid environment, for future exploitation, for example, in mid-IR biosensing applications.

Graphene plasmons and phonon polaritons in polar vdW materials can be imaged in great detail by scattering-type scanning near-field optical microscopy (s-SNOM), photothermal expansion (PTE) microscopy and photo-induced force microscopy (PiFM). So far, polariton imaging in the aqueous phase has been demonstrated only by PTE[20] and PiFM[21], although the interferometric detection scheme of s-SNOM offers many advantages, including direct near-field phase measurements for retrieving phase and group velocities of polaritons[22], reconstruction of complex-valued dielectric functions[23,24], and tomographic sample reconstruction[25]. Further, s-SNOM allows for nanoimaging and nanospectroscopy in a broad spectral range from visible to sub-THz frequencies, using continuous wave (CW) and ultrafast lasers[26,27], synchrotrons[28,29], or free electron lasers[30]. For these reasons, first developments of mid-IR s-SNOM of samples in liquid environment have been initiated with graphene-based liquid cells, where the liquid is covered by graphene or a thin membrane and s-SNOM is operated in air[31–33]. More recently, both the near-field probe as well as the samples were immersed in liquid[34,35], following the basic concepts of well-established atomic force microscopy (AFM) in liquid. This technique may allow for imaging of even larger objects (such as whole cells) and for avoiding potential near-field interaction between the samples in the liquid and the membranes covering them. However, the reported techniques are not well established yet and challenged by various technical and scientific aspects, for example, complicated beam shapes were required when illuminating under normal incidence allowing nanoimaging but not spectroscopy[35], while TIR-based geometry was successfully used for nanospectroscopy but deemed challenging for nanoimaging due to effective beam path change during scanning[34]. Further, polariton imaging has not been demonstrated so far.

Here, we introduce a normal-incidence mid-IR s-SNOM setup – operating with standard mid-IR Gaussian beams and the near-field probe being integrated into the liquid cell – for imaging the near-field distribution of plasmonic metal antennas in liquid. We also describe our total internal reflection setup, which allows for efficient coupling of standard mid-IR Gaussian beams to the near-field probe to perform both tip-enhanced infrared nanoimaging and nanospectroscopy. We apply this setup for amplitude- and phase-resolved imaging of ultra-confined propagating phonon polaritons (PhPs) on h-BN flakes, yielding not only the polariton dispersion but also the sign of the phase velocity, the latter not being directly accessible by PTE microscopy.

s-SNOM[36] is an AFM based technique where light is focused onto a metallized AFM tip. The tip acts as an antenna and concentrates the radiation to a highly confined and enhanced near-field spot at the tip apex. The near fields interact with the sample and modify the backscattered field depending on the sample's local dielectric properties. The backscattered field is recorded with a pseudo-heterodyne Michelson interferometer[37] as a function of the tip position yielding near-field amplitude (s) and phase (ϕ) images simultaneous to the sample topography. Background contributions are suppressed by higher harmonic demodulation of the backscattered field at $n\Omega$ for $n \geq 2$ where, Ω is the frequency at which the tip is oscillating normal to the sample surface (tapping mode AFM). In a typical s-SNOM experiment[38], the tip is illuminated in a side illumination scheme. However, such an illumination geometry is not suitable for operation in liquid and at infrared frequencies, owing to strong absorption and distortion of the infrared beam by the liquid (e.g., by H_2O).

We first describe our transflection s-SNOM setup for infrared antenna mapping (Figure 1a), which is based on a modified commercial s-SNOM (neaSNOM from Neaspec GmbH) setup. We illuminate a standard Pt-Ir coated AFM tip (NCPt arrow tip, Nanoworld) with a parabolic mirror ($f = 8\ \mathrm{mm}$) through the substrate and sample holder (CaF_2) at normal incidence with IR light from a tunable CO_2 laser (Access Laser Merit-G). Normal incidence is naturally an ideal geometry for antenna mapping, as it allows for efficient excitation of antennas while minimizing tip excitation (as the field polarization is perpendicular to the tip axis) and thus the distortion of the antenna fields[39,40]. To minimize the IR absorption by the water, we record the backscattered light through the substrate (in contrast to Ref. 40), employing the standard pseudo-heterodyne interferometer comprising an MCT detector (InfraRed Associates, Inc.) and higher harmonic signal demodulation (as described above). To operate the setup in water, we use an open liquid cell concept (Supporting Information S1), which is simply a droplet of water confined between the sample and a transparent window above the AFM cantilever (that allows for measuring cantilever deflection as part of AFM operation).

We demonstrate antenna mapping in liquid with a gold disk of $4\ \mu\mathrm{m}$ diameter on a CaF_2 substrate (Supporting Information S2), which exhibits a dipolar resonance at $10.5\ \mu\mathrm{m}$ wavelength. Simultaneous to the topography (Figure 1c, left), we observe two bright spots in the IR amplitude image (Figure 1c, middle). They are aligned along the polarization of the incident beam (indicated by double sided arrow in Figure 1b) and reveal the strongly enhanced fields of the in-plane oriented dipole. The phase (Figure 1c, right) at the position of the two bright spots is stable and nearly the same. Similar amplitude and phase images were obtained for the same disk imaged in air (Figure 1d), demonstrating that our setup allows for reliable amplitude- and phase-resolved imaging of infrared antenna modes without any distortion by the liquid (apart from a potential, small resonance shift due to the liquid, which does not affect the mode pattern). Compared with previous side-illumination s-SNOM experiments[41,42], the amplitude and phase pattern resemble the ones obtained with s-polarized illumination (where particularly the phase is the same for the two bright amplitude spots). This can be explained by a double scattering process[41,42], which is illustrated in Figure 1b. The near field of the antenna illuminates the tip and polarizes it. This additional tip-polarization can be approximated as an antenna-induced dipole in the tip. Due to its close proximity to the antenna, it radiates into the far field via the gold disk. Thus, the gold disk acts twice, first enhancing the tip-illumination and then enhancing the tip-scattering. For that reason, the amplitude image yields essentially the sum of the square of the in- and out-of-plane electric antenna near fields (weighted by the polarizability tensor of the tip) and a constant phase across the whole disk. A more detailed discussion goes beyond the scope of this paper, and we refer the interested reader to a detailed analysis provided in Ref. 41.

The normal incidence transflection mode s-SNOM can be well applied when near fields are generated by an antenna and the tip has the exclusive role of being a scattering probe. However, for imaging ultra-confined polaritons in 2D materials, where the tip is often the polariton launcher, an efficient coupling of the incident light with the tip is necessary to generate concentrated near fields at the tip apex. This can be achieved by illuminating the tip via total internal reflection (TIR), as previously described by Ref. 34 for spectroscopic chemical imaging of biological samples. In the following, we demonstrate that this scheme can well be applied for both amplitude- and phase-resolved nanoimaging and nanospectroscopy of ultra-confined phonon polaritons (PhPs), specifically hyperbolic phonon polaritons in thin layers of h-BN.

The TIR s-SNOM setup is sketched in Figure 2a. An off-axis parabola ($f = 10\ \mathrm{mm}$) focuses the incident beam into a $2\ \mathrm{mm}$ thick ZnSe ($n = 2.4$) wedge at an angle of $50°$ relative to the tip axis. The ZnSe wedge was produced by polishing one of the faces of a ZnSe substrate at an angle of $30°$, in order to illuminate ZnSe/D_2O interface at an angle $\theta > \theta_c \approx 34°$ relative to the tip axis. This was done mostly due to space constraints in the current setup. The sample is placed onto the wedge that is placed on a CaF_2 window, and the same liquid cell concept as described in Figure 1a is applied (see Supporting Information S1). The tip is illuminated by the TIR-generated evanescent field at the sample-liquid interface, and the tip-scattered field is collected with the same parabolic mirror to perform either monochromatic nanoimaging or nanoscale resolved Fourier transform infrared (nano-FTIR) spectroscopy.

For nanoimaging (Figure 2a, top), the tip is illuminated with a frequency-tunable quantum cascade laser (QCL, Daylight Solutions Inc.). The backscattered field is recorded analogously to the transflection setup described above, yielding near-field amplitude (shown in Figure 2b) and phase images, s_n and ϕ_n, respectively. Note that scanning the ZnSe wedge in y-direction yields a phase gradient, which was subtracted from all phase images shown in this work (details in Supporting Information S3). For nano-FTIR spectroscopy (Figure 2a, bottom), the tip is illuminated with the broadband infrared radiation from a difference frequency generated laser supercontinuum (frequency range: $1200 - 1700\ \mathrm{cm}^{-1}$, average power: $500\mu\mathrm{W}$). The backscattered light is recorded with an asymmetric Fourier transform spectrometer, yielding amplitude (shown in Figure 2c) and phase spectra, $s_n(\omega)$ and $\phi_n(\omega)$, after normalization to corresponding reference spectra recorded on the bare substrate (ZnSe).

Figures 2d and 2e display typical approach curves recorded with the s-SNOM and nano-FTIR setup, respectively, showing the demodulated near-field amplitude signal s_n ($n \geq 2$) as a function of the tip-sample distance. A strong signal decay with increasing tip-sample distance can be seen, which is stronger for higher harmonic signals, analogous to what is well known from s-SNOM in air[43]. At large tip-sample distances, all curves decay towards the noise floor, verifying that background-free near-field signals are measured. The more rapid signal decay at higher harmonic signal demodulation in air is well known to significantly improve the surface sensitivity and spatial resolution of s-SNOM and nano-FTIR. Figures 2d and 2e thus show that higher harmonic demodulation may be exploited for increasing the spatial resolution and surface sensitivity in liquid as well.

We demonstrate the imaging of hyperbolic phonon polaritons (PhPs) in liquid with exfoliated h-BN flakes which were transferred directly onto the top surface of the ZnSe wedge (Supporting Information S4). As liquid we used D_2O instead of H_2O, as its absorption within the frequency range of the broadband laser emission ($1200 - 1700\ \mathrm{cm}^{-1}$; required for h-BN polariton mapping) is lower than for H_2O [44,45]. Stronger absorption leads to a faster evaporation of the liquid, causing increased instabilities in the AFM operation. The topography image in Figure 3a clearly shows the smooth surface of the $110\ \mathrm{nm}$ thick h-BN flake with little noise, indicating a stable tapping-mode AFM operation in liquid. In the simultaneously recorded amplitude s_3 and phase ϕ_3 images at $1486\ \mathrm{cm}^{-1}$ (Figures 3c,d) we observe fringes on the h-BN surface, which are parallel to the h-BN edge, similar to s-SNOM observations of h-BN PhPs in air[13,46]. The fringes can be explained by the interference of PhPs, as illustrated in Figure 3b. Typically, the interference of edge and tip launched PhPs forms standing wave patterns, leading to a fringe spacing of either $\lambda_\mathrm{P}/2$ or λ_P, respectively, where λ_P is the wavelength of the phonon polaritons. Importantly, and in contrast to PTE measurements of phonon polaritons in liquid, amplitude and phase mapping enabled by s-SNOM allows us to directly determine the phase velocity of PhPs in liquid. To that end, we extract amplitude and phase line profiles (Figure 3e) from the images and plot them in the complex plane (phasor diagram, Figure 3f). An anticlockwise rotation is observed, corresponding to positive phase velocity with increasing the tip-edge distance x. For comparison, we imaged the same flake at the same IR frequency in air (Figure 3g-l). The images look similar, but the fringe spacing in the infrared images recorded in air is slightly larger than in the images recorded in liquid. This is expected, as D_2O has a higher permittivity compared to air, thus acting as a dielectric load[20]. Dielectric materials are well known and understood to reduce the polariton wavelength with increasing permittivity[47,48].

For a quantitative analysis and comparison of the phonon polariton properties in liquid and air, we imaged the h-BN flake at different frequencies (Figure 4a,c shows amplitude images, corresponding phase images are shown in Supporting Information S5). To measure the polariton momentum $q = 2\pi/\lambda_\mathrm{P}$ at each frequency, we extracted line profiles perpendicular to the h-BN edge and Fourier transformed them. The corresponding PhP momenta are plotted in Figure 4b (symbols), clearly showing the systematic shift of the experimental dispersion to higher wavevectors when the h-BN is imaged in liquid. Between $1500\ \mathrm{cm}^{-1}$ and $1600\ \mathrm{cm}^{-1}$ we did not observe fringes, which we attribute to the low signal-to-noise (S/N) ratio at these frequencies and to the increasing confinement of the PhPs. The latter does not allow for observing polaritons at $1600\ \mathrm{cm}^{-1}$, despite reasonable S/N ratio. We confirm our observations by calculating (see Supporting Information S6 and S7) the dispersion of the fundamental PhP mode (in literature often denoted M0) of an h-BN flake on ZnSe in either D_2O or air (blue and red curves in Figure 4b). The experimental data (symbols) and the calculated dispersion (lines) are in good agreement with each other for an h-BN thickness of $90\ \mathrm{nm}$, which is smaller than the experimental h-BN thickness, which we attribute to uncertainties in height measurements and dielectric data for the permittivities of h-BN and ZnSe. To further quantify the shift of the polariton momentum, respectively wavelength, we calculated λ_P as a function of the dielectric permittivity of the surrounding media, ϵ_m, at $1480\ \mathrm{cm}^{-1}$ (see Supporting Information S6 and S7). We observe a significant decrease of λ_P with increasing ϵ_m (Figure 5a). A change from air ($\epsilon_\mathrm{m} = 1$) to a liquid of $\epsilon_\mathrm{m} = 3$ yields a polariton wavelength compression of about $236\ \mathrm{nm}$, corresponding to about 23% and a sensitivity of $\Delta\lambda_\mathrm{P}/\Delta n_\mathrm{m} = 323\ \mathrm{nm/RIU}$, where $\Delta\lambda_\mathrm{P}$ is the wavelength change upon a refractive index change of Δn_m. Such fluid-control of the polariton wavelength in 2D materials could find interesting application potential for the development of reconfigurable polariton devices. s-SNOM operating in liquid – as demonstrated in this work – in the future can be applied for fundamental studies and for verification of corresponding device concepts.

In the following we discuss, as an application example, the use of s-SNOM in liquid for studying vibrational strong coupling (VSC) between molecules and polaritons. Generally, VSC leads to new hybrid polariton modes, whose coherent exchange of energy is faster than the decay rate of the original modes[49,50], and can modify chemical reactions[51,52]. Recently, molecular vibrational strong coupling involving h-BN phonon polaritons was observed by s-SNOM polariton interferometry[53], analogous to Figure 4, but only in air. In Figure 5b we show by calculations how a liquid environment modifies VSC. The inset of Figure 5b shows the calculated dispersion (Supporting Information S6 and S7) of the fundamental phonon polariton mode (red dashed lines, $\epsilon_\mathrm{m} = 1$) when a $30\ \mathrm{nm}$ thick layer of CBP ($4,4'$-bis(*N*-carbazolyl)- $1,1'$-biphenyl) molecules is placed on top of a $30\ \mathrm{nm}$ thick h-BN layer. It reveals VSC by a splitting of the phonon polariton mode into an upper and lower polariton branch (red solid lines)[53] at the molecular vibrational frequency ($1450\ \mathrm{cm}^{-1}$, marked by horizontal dashed line, associated with the C-H deformation bond of CBP[54]). By adding liquid above the molecular layer, we find that VSC is maintained and even enhanced (blue and green curves in Fig. 5b), as the mode splitting (minimum distance between upper and lower polariton branch) and the coupling strength $g \approx \Omega/2$ increases with increasing permittivity ϵ_m of the liquid. This finding can be explained by the increased polariton momentum in liquid (see Figure 4b), which is accompanied by an increased field confinement near the h-BN surface. This, in turn, yields to a stronger overlap between the phonon polariton mode volume and the molecule layer, enhancing the light-matter coupling. As generally, chemical reactions and dynamics often require liquid environment, polariton imaging by s-SNOM in liquid opens up new possibilities for studying VSC involving ultra-confined polaritons.

We finally demonstrate experimentally nano-FTIR spectroscopic imaging in liquid. To that end, we recorded a line scan perpendicular to the edge of the h-BN flake. Figure 4d shows the normalized nano-FTIR amplitude spectra as a function of tip position x. We clearly see a horizontal bright feature centered at $1395\ \mathrm{cm}^{-1}$, which corresponds to the h-BN phonon resonance. More interestingly, we observe fringes, which we attribute to a PhP interference pattern, as the fringe spacing $\lambda_\mathrm{P}/2$ decreases continuously with increasing frequency. We find a good qualitative agreement to similar datasets recorded in air[13]. Figure 4d clearly demonstrates that hyperspectral nano-FTIR imaging of ultra-confined polaritons in liquid is possible. However, we refrain form a quantitative analysis of this data set, as the required long data acquisition time (1 hour and 20 minutes) and significant sample heating led to strong sample drift during nano-FTIR recording. In future developments and applications, this challenge of sample drift can be tackled by improving thermal stability of our setup and employing drift correction strategies[55]. Furthermore, the heating of the liquid could be reduced by employing heat sinks or implementing flow cells instead of the simple liquid droplet used in the presented work. We finally note that dielectric (materials) contrasts (e.g., between h-BN and ZnSe) obtained with our setup in liquid differ from those in air. Future studies are required to explore this phenomenon, which could be caused by illumination of the tip by both propagating and evanescent fields due to a non-optimal prism geometry (due to space restrictions in our current setup) or enhanced higher mechanical harmonic generation in liquid.

To summarize, we demonstrated two methods enabling infrared s-SNOM imaging of polaritons in liquid. We first demonstrated a normal incidence transflection s-SNOM for background-free amplitude- and phase-resolved infrared nanoimaging of the near-field distribution of resonant plasmonic antennas in liquid. By tuning the plasmonic resonances to match the molecular vibrations, such a system could be used in the future for in-situ s-SNOM studies of (bio)chemical substances with enhanced sensitivity[56], vibrational strong coupling experiments[57], or plasmon-induced chemical modifications. We also demonstrated a TIR-based s-SNOM for nanoimaging and spectroscopy of ultra-confined h-BN phonon polaritons in liquid, showing that the presence of a liquid shifts the PhP dispersion to higher momenta. In the future, one could exploit polariton interferometry in liquid (pure solutions or buffer solutions containing specific molecules) for studying chemical interactions at the interface between the bare or functionalized polaritonic materials. We further envision in-situ studies of vibrational strong coupling between ultra-confined polaritons and molecular vibrations. Finally, we note that the TIR setup could be further optimized for standard s-SNOM and nano-FTIR based chemical mapping and identification of samples that are fully immersed in a liquid. The physical and chemical properties of the liquid should allow for stable AFM operation, and the liquids' infrared absorption should not obscure the near-field response of the sample. Apart from using water-based buffer solutions for biochemical studies, low-viscosity ionic liquids could be used for gating 2D materials and for studying phase transitions induced by ionic substitution.

Figure Captions

Figure 1. Normal incidence tansflection s-SNOM for mapping mid-IR plasmonic antennas. a) Schematic of the setup. PM, parabolic mirror; Ω, tip oscillation frequency. b) Illustration of near-field scattering process. The incident field E_{inc} illuminates the antenna (A). The antenna fields illuminate and polarizes the tip (T), which scatters the near fields via the antenna into the far field where it is detected interferometrically (not shown here). c,d) Topography, amplitude and phase (from left to right, respectively) images of the dipolar antenna mode of a gold disk (c) in H_2O and (d) in air. Mid-IR imaging wavelength is $10.5\ \mu\mathrm{m}$.

Figure 2. TIR based s-SNOM and nano-FTIR setup for imaging and spectroscopy in liquid a) Schematic of the setup for nanoimaging (s-SNOM) and nanospectroscopy (nano-FTIR). For s-SNOM, the tip is illuminated with a frequency-tunable QCL. The backscattered light is demodulated at tip frequency $n\Omega$ and recorded with a pseudo-heterodyne Michelson interferometer (top). BS, beamsplitter; PZ1, piezo actuated vibrating mirror. For nano-FTIR, the tip is illuminated with an infrared supercontinuum (IRSC) broadband laser. The backscattered light is analyzed using an asymmetric Fourier transform spectrometer (bottom). PZ2, piezo actuated translating mirror; FM, flip mirror. b) Example of an s-SNOM amplitude image s_3. Scalebar: $500\ \mathrm{nm}$. c) Example of a nano-FTIR amplitude spectrum. d) Approach curves showing the decay of s-SNOM amplitude signals s_n in liquid with increasing tip-sample distance (i.e., the minimum distance between the tip apex and the sample during an oscillation cycle of the tip as typically done in a tapping mode AFM) recorded at $1600\ \mathrm{cm}^{-1}$.Tapping amplitude (TA)$\sim 60\ \mathrm{nm}$. e) Approach curves for nano-FTIR signal (at white light position) in liquid. TA $\sim 120\ \mathrm{nm}$.

Figure 3. Amplitude- and phase-resolved imaging of h-BN PhPs in liquid (a-f) and air (g-l). a) AFM topography of a $110\ \mathrm{nm}$ thick h-BN flake recorded in D_2O. b) Schematic of s-SNOM in liquid. c,d) Near-field amplitude and phase images recorded at $1486\ \mathrm{cm}^{-1}$ in D_2O, revealing a standing wave pattern caused by the PhP interference. e) Amplitude and phase line profiles extracted perpendicular to the h-BN edge (averaged over 50 lines), revealing a fringe spacing of $\lambda_{\mathrm{P}}/2$. f) Phasor diagram of the complex-valued near-field signal $\sigma_3 = s_3\ e^{i\phi_3}$, indicating a positive phase velocity of h-BN PhPs launched in D_2O. g-l) Same as a-f, but probing was done in air.

Figure 4. Dispersion of h-BN PhPs in liquid and air and nano-FTIR spectral line scan of h-BN in liquid. a) Near-field amplitude images s_3 of an h-BN flake in air. b) Dispersion of h-BN PhPs, symbols show PhP momenta obtained from line profiles taken from the images shown in panel a and c. The color plot indicates the calculated imaginary part of the momentum- and frequency-dependent Fresnel reflection coefficient, $\mathrm{Im}[r_{\mathrm{p}}]$, of a $90\ \mathrm{nm}$ thick h-BN flake on ZnSe in air (red) and D_2O (blue). c) Near-field amplitude images s_3 of an h-BN flake in liquid. d) Nano-FTIR line scan perpendicular to h-BN edge (indicated by the dashed vertical line), showing near-field amplitude signal as a function of frequency ω and distance x between the tip and the h-BN edge, $\mathrm{s}_2(\mathrm{x}, \omega)$. Black dashed lines are guides to the eye, tracing the interference fringes. Spectral resolution: $14\ \mathrm{cm}^{-1}$; Total acquisition time $\sim 1\mathrm{hr}20\mathrm{min}$.

Figure 5. Fluid control of PhP wavelength and vibrational strong coupling (VSC). a) PhP wavelength λ_{P} as a function of the dielectric permittivity of the surrounding medium ϵ_{m}, calculated for a $90\ \mathrm{nm}$ thick h-BN slab on a ZnSe substrate at $1480\ \mathrm{cm}^{-1}$. Inset shows sample sketch. Symbols indicate various liquids (for references see Supporting Information S7). b) Calculated dispersion of the fundamental hybrid polariton mode of a $30\ \mathrm{nm}$ thick h-BN slab covered with a $30\ \mathrm{nm}$ thick layer of CBP molecules, which is covered by liquids of different dielectric permittivities: $\epsilon_{\mathrm{m}} = 1$ (air, red curves), $\epsilon_{\mathrm{m}} = 1.82$ (D_2O, blue curves) and $\epsilon_{\mathrm{m}} = 3$ (green curves). Upper left inset: Comparison of the hybrid polariton mode in air (red solid curves) with the fundamental phonon polariton mode of an h-BN slab in air without molecules (red dashed curve). Lower right inset: Sketch of the sample. Gray horizontal dashed lines mark the molecular vibrational frequency $\omega_{\mathrm{C-H}}$. Vertical arrows indicate the mode splitting Ω.

Associated content

The Supporting Information is available free of charge via the internet at http://pubs.acs.org.

Schematic of the liquid cell used for s-SNOM imaging and nano-FTIR shown in this work. Antenna fabrication. Phase gradient correction applied to the s-SNOM phase images shown in this work (corresponding to Figure 3). h-BN exfoliation and transfer. Additional s-SNOM images of h-BN PhPs (corresponding to Figure 4). Polariton dispersion and wavelength calculation shown in Figure 4b and Figure 5. Dielectric function of materials used for calculations shown in Figure 4b and Figure 5.

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Competing interests

R.H. is a co-founder of Neaspec GmbH, a company producing scattering-type scanning near-field optical microscope systems, such as the one used in this study. The remaining authors declare no competing interests.

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