# Ultrafast Infrared Nano-Imaging of Strongly Coupled Phonon and Carrier Dynamics in Quantum Materials

by

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Thesis directed by Prof. Markus B. Raschke

Infrared (IR) vibrational scattering scanning near-field optical microscopy (s-SNOM) has advanced to become a powerful nano-imaging and -spectroscopy technique to probe molecular and lattice vibrations, low-energy electronic excitations and correlations, and related collective surface plasmon, phonon, or other polaritonic resonances. In combination with scanning probe microscopy, near-field infrared nano-spectroscopy and -imaging enables the study of complex heterogeneous materials with simultaneous nanoscale spatial resolution and quantum state spectroscopic specificity. IR s-SNOM has also been extended to studying dynamics in the time domain, where ultrafast vibrational and electronic spectroscopy unravels mechanisms underlying functionality in quantum materials. Femtosecond-to-picosecond dynamics are convolved with multiscale spatial heterogeneities, ranging from microscopic defects to the macroscopic domain level. This technique opens the door to elementary processes and interactions in functional materials with full spatio-temporal-spectral resolution.

In this thesis, I will describe my work in advancing *s*-SNOM through the design, testing, and implementation of ultrafast hyperspectral imaging modalities on both molecular and quantum systems.

Following the introduction, I will summarize the fundamentals of s-SNOM as advancements detailed here are based on these starting points. Then, I will detail three distinct method advancements made to improve the image quality, acquisition speed, and information content. By utilizing knowledge of the resonance being probed, the bandwidth of the excitation source, and the desired spectral resolution, I can transition from the stationary frame to the rotating frame to reduce the Nyquist maximum frequency cut-off. With the necessary maximum frequency reduced, fewer data points are needed along the reference arm axis compared to conventional hyperspectral imaging, enabling faster data acquisition of a higher resolution image over a higher field of view with automatic drift correction. I further have theoretically demonstrated that prior knowledge about the limited frequency range of the optical source in a nano-FTIR measurement and the fact that samples are typically composed of only a few different molecular constituents allows for faster detection algorithms. Specifically, compressive sensing and matrix completion techniques can be used to reduce the necessary data points from the Nyquist limit by a factor of 10. Further, this technique can be applied to active systems for adaptive algorithms that use previous measurements to inform future measurements during acquisition. Finally, I will detail advances made in ultrafast pump-probe nano-imaging and -spectroscopy, where pump modulation with selective interferometric detection isolates the difference between the excited and ground state. This advancement enables higher signal to noise ratios for low excited state contrast systems, especially necessary for the case of low repetition rate, far-from-equilibrium pump excitation parameter regimes.

Next, I will discuss my work performing spectroscopy with broad band infrared (IR) light sources, such as synchrotron radiation, fs broadband lasers, and ps narrowband lasers. This variety of light sources proved extremely useful for a variety of material systems. Synchrotron infrared nano-spectroscopy (SINS) has been used as a consistent diagnostic tool for molecular systems, like the self assembled monolayer 4-NTP, hydrocarbon and mineral systems, like oil filled pores in shale, and quantum systems, like strongly coupled heterostructures composed of multi-quantumwells and gold antennas. The advancements and discoveries here represent the successes of applying infrared spectroscopy to a variety of systems to discern inter-molecular coupling, spatially resolved hydrocarbon mapping, and phase resolved hybridization controlled weak to strong coupling.

Lastly, I will present ultrafast nano-FTIR on 2D transition metal dichalcogenide (TMD) systems, interfacial energy transfer, lattice expansion and phonon softening, and spatially inhomogeneous electron dynamics. Here, I performed visible pump, infrared probe nano-imaging spectrscopy, where I pumped the interband electronic state in WSe<sub>2</sub>, producing free carriers that thermalize through phonon emission within the TMD and then dissipate heat through the substrate. We perform ultrafast nano-FTIR on a phonon mode of the substrate as a means of monitoring local temperature. We find that the electron population in the TMD relaxation is also heterogeneous as an increase in carriers from a hot phonon bottleneck leads to an Auger recombination and stronger bright state population for faster excited state photo-relaxation.

I will close with a short summary of my work, and an outlook to future experimental efforts.

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# Chapter 1

#### Introduction

Infrared (IR) spectroscopy is routinely used for chemical identification and structural determination.<sup>1</sup> It is a minimally invasive and label-free technique that has applications in disciplines ranging from biology, chemistry, and condensed matter physics to space sciences. IR spectroscopy can be used to probe the Drude conductivity of metals and 2D quantum materials like graphene as well as low energy bandgaps, plasmons, and intersubband transitions.<sup>2–4</sup> In combination with conventional microscopy, infrared spectroscopy provides for chemical analysis and imaging at diffraction limited length scales.<sup>5,6</sup> The highest spatial resolution that IR microscopy has conventionally been able to achieve is ~2-20  $\mu$ m at 3-20  $\mu$ m wavelengths.<sup>7</sup>

Near-field scanning optical microscopy (NSOM) was first demonstrated in the 1980s, yet it had limited applicability, as the fiber throughput typically constrained sensitivity and minimum resolution to be  $\sim 100 \text{ nm.}^{8-10}$  The development of tip-enhanced scattering near-field microscopy increased the applicability of deep sub-diffraction limited imaging.

s-SNOM has enabled the study of fundamental interactions at the mesoscopic scale, but it lacked ultrafast temporal resolution until pump-probe spectroscopy was applied to the near-field. Two color time resolved measurements, where the signal from the pump alone can be removed with an optical filter, are now common and have been applied to quantum and molecular materials.<sup>11–13</sup> The combination of nm resolution with infrared frequencies at ultrafast time scales is a powerful technique to explore phenomena ranging from electron-electron interactions to vibrational strong coupling to surface plasmon polaritons (Figure 1.1).



Figure 1.1: Characteristic lengths and time scales for condensed matter phenomena | Condensed matter phenomena of fundamental particle interactions – caused by lattice or electronic degrees of freedom. Figure adapted from a design by O. Khatib.

In Chapter 2, I will introduce the fundamentals of *s*-SNOM. To begin, I summarize the basics of tapping mode AFM and the diffraction limit from a wave equation perspective. I then transition to discussing demodulation techniques and asymmetric heterodyne spectroscopy. Following this, I discuss light sources ranging from CW and fs pulsed lasers to synchrotron radiation. Finally, I conclude with a description of two tip-sample interaction models that serve as the basis for newly developed pump-probe modeling.

I then delve into near-field imaging and spectroscopy method advancements (Chapter 3). I have improved image acquisition speed by moving from the stationary frame into the rotating frame. Transforming frames lowers the Nyquist cut-off frequency, which reduces the necessary number of data points. I also discuss the collaborative effort of improving hyperspectral imaging by using prior knowledge for both compressive sensing and matrix completion techniques. I conclude with advancements made to ultrafast near-field spectroscopy and imaging, where pump-modulation together with heterodyne detection improves excited state contrast.

I then detail far-field spectroscopy, degenerate pump-probe dynamics, and near-field imaging and control of multi-quantum wells that are strongly coupled to infrared resonant antennas in Chapter 4. I utilized control through polarization, fluence, and tip localization to actively tune coupling strength.

Finally, I discuss transition metal dichalcogenides (TMDs) under far-from-equilibrium pump conditions. In Chapter 5, I use ultrafast heterodyne pump-probe spectroscopy to measure carrier behavior in WSe<sub>2</sub>. I build on this work by measuring the phonon softening in the SiO<sub>2</sub> substrate. I use this temperature dependent phonon mode both to measure thermal dissipation at the atomic interface and to measure spatial heterogeneity in substrate surface temperature. Thermal dissipation from WSe<sub>2</sub> to the substrate affects excited state electron dynamics through intra- and inter-valley coupling.

I conclude this thesis with a summary of the work conducted over the course of my PhD and an outlook for future directions in Chapter 6.

# Chapter 2

#### Scattering Scanning Near-Field Optical Microscopy

### 2.1 Introduction to near-field microscopy

In this chapter, I detail the background of near-field imaging. Specifically, I cover atomic force microscopes (AFMs) with their modes of operation and the tip-sample interactions. I follow this with the diffraction limit that conventionally obscures nanoscale heterogeneity. Then, I discuss optical sources for spectroscopy including continuous wave and pumped lasers as well as synchrotron radiation and near-field optical interaction models that are used to quantify nano-IR spectra. Finally, I conclude with signal isolation and artifact rejection for near-field data that are necessary for analyzing data.

# 2.2 Tapping Mode Atomic Force Microscopy

Atomic force microscopy serves as the basis for several specialized techniques, among them s-SNOM.<sup>14,15</sup> In 1985, Binnig and his coworkers built upon the STM by developing the AFM to study general samples, not just conductive ones.<sup>16</sup> Since then, the AFM has been refined and improved. A metallized silicon tip is used to probe the sample. The conductive tip acts as an optical antenna in the near-field region around the tip's apex.<sup>17</sup> The sample is scanned below the tip so that the tip remains in the focus of the IR light. AFM feedback is maintained through tapping amplitude. The tip is driven sinusoidally with a typical tapping amplitude between 40 and 80 nm.<sup>18</sup> The cantilever stiffness defines the resonant tapping frequency, which is between 200 and 300 kHz for the experiments described in this thesis. When the tip approaches the sample, the

resonant frequency red-shifts and tapping amplitude decreases. As the tip makes contact with the sample, the tapping amplitude sharply drops. To maintain good contact, the tapping amplitude is set to 80% of the free space value.

As an extension to tapping mode AFM, peak-force AFM can be used to extract mechanical properties about a sample's surface (Figure 2.1a). Previous studies<sup>19</sup> have correlated optical signals from a *s*-SNOM experiment (Figure 2.1b) with mechanical channels from an AFM (Figure 2.1c).



Figure 2.1: Combining optical and mechanical channels | **a.** Peak force mechanical channels as the tip approaches and withdraws from the sample surface. **b.** Asymmetric Michelson interferometer for *s*-SNOM measurements. **c.** Combining mechanical and optical channels for correlation and anti-correlation analysis. (Figure from<sup>19</sup>)

I also contributed to this multidimensional imaging by applying different light sources to s-SNOM measurements and correlating those results with mechanical properties from peak force AFM.<sup>20</sup>

# 2.3 Diffraction Limit

Conventionally, imaging systems have a minimal resolvable feature ultimately given by the wavelength of light. In order to study physical phenomena on their natural nm length scales, we need to first understand the limit to resolution. Historically, Ernst Abbe<sup>21</sup> was the first to describe the minimal distance d that two objects need to be away from each other to be resolvable

$$d = \frac{\lambda}{2 \,\mathrm{NA}},\tag{2.1}$$

where  $\lambda$  is the wavelength of the light and NA is the numerical aperture. When visible light and modern objective lenses are used, this separation distance is typically approximated as 250 nm, as 500 nm light is in the center of the visible spectrum and objectives with NA of ~1 are common.<sup>22</sup> While this is still too large of a sampling area to resolve nanoscopic fundamental phenomena, the situation is more than an order of magnitude worse for the infrared. Ignoring the limitations of IR objectives and assuming NA = 1, 10  $\mu$ m light can only be focused down to 5  $\mu$ m, which is clearly insufficient to study nanoscale phenomena at these optical frequencies.<sup>7</sup> Therefore, we must understand what gives rise to this limit.

To better understand and quantify the diffraction limit, we consider the case of imaging an object through a circular aperture, as this is a simple imaging system that can be used to understand the underlying physics. From time reversal symmetry, we can consider the projection of monochromatic light from an aperture to a screen as an analogous problem.<sup>23</sup> We use the Huygens-Fresnel principle to integrate over the aperture all light and propagate that light using the far-field traveling wave solutions to the wave equation,<sup>24</sup> such that

$$U \propto \int_{aperture} A(x', y') e^{-i\frac{2\pi}{\lambda z}(x'x+y'y)} dx' dy'$$
(2.2)

where U is the complex field amplitude, A is the complex amplitude of the aperture,  $\lambda$  is the wavelength of light, z is the propagation axis through the aperture, and x' and y' are the location

of the aperture. In polar coordinates, we make the substitution

$$\begin{aligned} x' &= \rho' \cos(\theta') \\ y' &= \rho' \sin(\theta') \\ x &= \rho \cos(\theta) \\ y &= \rho \sin(\theta), \end{aligned}$$
(2.3)

which transforms our previous equation to

$$U \propto \int_{aperture} A(\rho') e^{-i\frac{2\pi}{\lambda_z}\rho\rho'\cos(\theta-\theta')} \rho' d\rho' d\theta', \qquad (2.4)$$

where I have assumed angular symmetry of the aperture and used the cosine difference formula. Further, the integral equation for the zeroth order Bessel function can be substituted for

$$J_0(\frac{2\pi}{\lambda z}\rho\rho') = \int_0^{2\pi} e^{-i\frac{2\pi}{\lambda z}\rho\rho'\cos(\theta-\theta')}d\theta',$$
(2.5)

to compactify the complex field amplitude to

$$U \propto \int_{aperture} A(\rho') J_0(\frac{2\pi}{\lambda z} \rho \rho') \rho' d\rho'.$$
(2.6)

In the case of a circular aperture, the limits of integration for  $d\rho'$  are from 0 to the radius of the aperture. Using the recurrence property of Bessel functions and the fundamental theorem of calculus, we can evaluate this integral

$$U \propto J_1(\frac{\pi R\rho}{\lambda z}),$$
 (2.7)

which has its first zero at an argument of 3.8317. This combined with

$$\frac{\rho}{z} = \tan(\theta) \tag{2.8}$$

yields

$$\tan(\theta) = \frac{3.8317}{\pi} \frac{\lambda}{D},\tag{2.9}$$

which, upon the small angle approximation and simplifying constants, is the Rayleigh criterion for the diffraction limit.<sup>25</sup> While this is only one description for the resolution of an imaging system, the fundamental physical insight gained with this example generalizes to other, more complex systems. In order to elucidate the underlying resolution limitation, I give a practical example. A 1 cm diameter objective, with a focal length of 1 cm, will be able to resolve two objects if they are 610 nm apart. Near the diffraction limit,  $tan(\theta) \sim \theta = r/d$ , where r is the distance between two objects and d is the distance from the aperture to the objects. Typical high quality objectives will have an aperture to focal length ratio of ~2, which means objects can typically be resolved if they are separated by a distance larger than  $\lambda/2$ . Therefore, we need an imaging mechanism that can go beyond the diffraction limit.

One class of approaches to go beyond the diffraction limit is super resolution techniques. Specifically, stimulated emission depletion (STED) microscopy,<sup>26,27</sup> photo-activated localization microscopy (PALM),<sup>28</sup> and stochastic optical reconstruction microscopy (STORM)<sup>29</sup> have been used in biological systems to image large complex structures over wide fields of view. However, most super resolution techniques require chemical labeling, which is invasive and not generally applicable. Further, these techniques only image the system indirectly and do not offer access to fundamental physical phenomena on the nanoscale. Therefore, molecular vibrations, lattice phonons, and intersubband transitions, which all lie in the mid infrared (5  $\mu$ m - 20  $\mu$ m), are not accessible. With our example given above, and the r/d ratio of most good infrared objectives ( $r/d \sim 1$ ), resolution is conventionally limited to ~10  $\mu$ m, which is much larger than the natural length scale of mesoscopic physical phenomena.<sup>30-32</sup> Therefore, we seek to image in the near-field, where the diffraction limit does not apply.

#### 2.4 Optical Sources

In this section, I will briefly go over the different light sources used throughout the work presented in this thesis. The implementation of each of these light sources poses slight variations to the standard *s*-SNOM setup, and some imaging modalities are only possible through certain light sources.

#### 2.4.1 Continuous Wave Laser

I begin with continuous wave (CW) lasers, which are the simplest in this section. In CW operation, the laser is continuously pumped, and, for the applications listed below, a single resonant mode to be probed is selected. CW lasers in *s*-SNOM are used both for the IR probe and for visible guide lasers to aid in alignment. The IR probe is often either a CW quantum cascade laser (QCL) or gas laser. The visible guide lasers are typically either a gas laser (Helium Neon, He-Ne), or, more common recently, simple diode lasers.

- (1) Gas lasers used here utilize a gain medium that is electrically pumped inside a simple tube cavity, where one gaseous species (nitrogen in the case of a  $CO_2$  laser and Helium in the case of a He-Ne laser) is stimulated by the electrical pumping, decays, and transfers energy to another gaseous species  $CO_2$  for an appropriately named  $CO_2$  laser and Ne for the He-Ne laser.<sup>33</sup> This generates the necessary population inversion for lasing to occur. Because the lasing medium is a gas, the output light remains coherent over longer time frames than solid state lasers and therefore leads to exceptionally narrow linewidths. These light sources are exceptional for their stability and long coherence lengths but are limited as they are not able to be used for spectroscopy.<sup>34</sup>
- (2) Solid state lasers, like QCLs and diode lasers, are still CW yet exhibit notably shorter coherence lengths.<sup>35</sup> Diode lasers use electron hole recombination and the resulting photon emission to produce light with energy dependent on the bandgap, whereas QCLs operate in a qualitatively distinct manner. The tuning range of diode lasers is limited and is controllable only through temperature and doping levels, which alter the band diagram of the material. In contrast to this, QCLs string together a series of quantum wells, the size confinement of which modifies the band structure to produce subbands.<sup>36</sup> The energy difference between these subbands is considerably smaller than the bandgap. Therefore, QCLs are useful in producing IR light compared to the typical visible light in diode lasers.<sup>37</sup> The intersuband transitions used in QCLs occur within the conduction band as opposed

to between conduction and valence bands. A bias is then applied to the series of quantum wells so that the photon produced in one intersubband transition then stimulates a subsequent well. This process continues down the chip of quantum wells, producing highpowered output at relatively long wavelengths.<sup>38</sup> Again, similar to the slight adjustments possible to the bandgap energy in diode lasers with temperature, QCLs are tuned through lattice expansion and contraction through temperature variations. As the QCL expands, the quantum well widens and the bound states lower in energy. During contraction, the quantum well narrows and the bound states rise in energy. While this type of tuning is typically quite limited, broader tuning, which is common of modern QCLs, can be achieved through single wavelength stabilization. This approach uses an external cavity, where a grating (tunable through rotation) is used as the output coupler, selectively decreasing the gain threshold for a desired frequency.<sup>39</sup> The shorter coherence lengths of these CW lasers can make heterodyne techniques more difficult, but their ability to be tuned and their resulting applicability to spectroscopy makes them useful candidates for chemical imaging.

The CW nature of gas, diode, and quantum cascade lasers implies a very narrow linewidth and correspondingly, through its Fourier relationship, a long coherence time. The narrow line-width and single frequency nature means CW lasers application to *s*-SNOM is the easiest of the sources listed here and is primarily used for pre-characterization and quick measurements where spectral frequency mapping is not required. The most common implementation of a CW laser in *s*-SNOM is with a CO<sub>2</sub> laser at approximately 10.6  $\mu$ m for Drude mapping in 2D materials like, e.g., graphene.<sup>3</sup>

#### 2.4.2 Optical Parametric Amplification

I now discuss pulsed light sources, whose broad bandwidth enables Fourier transform spectroscopy. While more complex than single wavelength sources, optical parametric amplification, either in optical parametric amplifiers (OPAs) or optical parametric oscillators (OPOs), offers a wide tuning range through nonlinear phase matching pulsed output.<sup>40</sup> When a crystal lacks inversion symmetry, the crystal allows for a collection of non-linear processes to occur, namely frequency doubling, sum frequency generation (SFG), and difference frequency generation (DFG).<sup>41</sup> This  $\chi^{(2)}$ process (optical parametric amplification) uses a signal beam as a seed together with a higher frequency pump beam to convert photons of the pump into more photons of the signal beam. An idler beam is also generated and has energy equal to the difference in energy between the pump and seed.<sup>42</sup> This is most often carried out in the non-degenerate case, where the signal output is higher in energy than the idler. In the degenerate case, the seed is tuned to half the energy of the pump beam, and the resulting signal and idler pulses have equal energy. For efficient conversion to occur, the optical phases of the output waves must match the crystal structure. The crystal is rotated for phase matching until maximum output power is achieved.<sup>43</sup> The accessible bandwidth is limited by phase matching and typically, the thicker the nonlinear crystal, the more strongly the phase matching requirement is enforced, resulting in a narrow output spectrum. When the nonlinear process occurs in more material (since the crystal is thicker), higher powers are achievable.<sup>44</sup> OPAs and OPOs are primarily attractive because there is a lack of suitable ultrafast light sources in the near and mid IR.

The underlying process behind parametric amplification is an optical non-linear conversion. For the nonlinear process to occur, high peak strength electric fields must be employed, typically necessitating an ultrafast pulsed laser upstream of the amplification process.<sup>44</sup> Ultrafast mode-locked near-IR (Ytterbium based lasers, for example) or visible (titanium sapphire lasers, for example) pump lasers are split into two paths. One path is for the optical parametric amplification pump and the other is for white light generation in another non-linear crystal (YAG, for example). The resulting white light is then co-focused with the pump into a non-linear crystal, and phase matching is used to select the amplified portion of the white light spectrum.<sup>45</sup> OPAs and OPOs operate on the same underlying principle, but an OPO places the parametric amplification within a cavity for a higher output power at the expense of a slightly longer and spectrally narrower pulse.<sup>46</sup> With sufficient tuning and choice of non-linear crystal, the idler can be tuned to ~4-5  $\mu$ m and be directly used in *s*-SNOM. Difference frequency generation is used to get further into the IR.

## 2.4.3 Difference Frequency Generation

The tunability of both the signal and idler from parametric amplification can be used together with difference frequency generation to provide a tunable broadband infrared source. As mentioned above, crystals that lack inversion symmetry can also host difference frequency generation (DFG).<sup>41</sup> Here, two beams, focused into such a crystal, are converted into a third beam with energy equal to the difference of energies of the input beams. Again, as before, phase matching must be implemented for efficient difference frequency generation.<sup>47</sup> For *s*-SNOM, typical mid-IR broadband generation is performed by using a pump laser in the near-IR in an OPA or OPO. The resulting signal and idler beams are then mixed in DFG to produce mid- to far-IR light. For further IR generation, the OPA/OPO is simply tuned closer to degeneracy, such that the difference in energy between the signal and idler is smaller and the resulting light after DFG is lower in energy. The typical main limit to this process is optical absorption in the non-linear crystal. A common crystal choice is GaSe, which exhibits a strong absorption at 18  $\mu$ m, limiting the IR output through DFG to 550 cm<sup>-1.48</sup> DFG is therefore a key useful step in generating tunable broadband mid-IR light.

This concludes the section on pulses light sources for the mid infrared. Their broadband nature makes them ideal instruments for Fourier transform spectroscopy and their ultrafast pulses make them indispensable for ultrafast time resolved measurements.

#### 2.4.4 Synchrotron Radiation

The final light source of note for s-SNOM (or SINS) is the synchrotron. My experience with synchrotron infrared nanospectroscopy (SINS) is primarily at the advanced light source (ALS) in Berkeley, CA, so most of my discussion about synchrotrons will be focused on this example. Synchrotrons use the tangentially (to the path of motion) emitted electromagnetic radiation from relativistic electrons that traverse along curved trajectories (Figure 2.2A).

The etendue of the small diameter electron beam source makes the output light diffraction limited and spatially coherent with approximately 100-1000 times the spectral irradiance (Figure



Figure 2.2: Broadband light from a synchrotron source | **A.** Broadband synchrotron radiation is produced when relativistic electrons are accelerated by a constant magnetic field. **B.** Calculated spectral flux (red) and spectral irradiance (blue) for bend magnet radiation at the ALS, assuming a collection angle of 17 (V) mrad x 69 (H) mrad (solid line), which is standard for beamlines 2.4 and 5.4, and 80 (V) mrad x 69 (H) mrad (dotted lines), which enables the maximum extraction of the infrared light to 20 cm-1. The spectral flux was calculated with the SRW package using the accelerator parameters of the ALS and the spectral irradiance was calculated assuming a diffraction limited spot size for NA=0.4.<sup>49</sup>

2.2B) of an incoherent thermal source.<sup>50,51</sup> The electrons used in the synchrotron are packaged into bunches and have a repetition rate in the hundreds of MHz (500 MHz at the ALS), forming a total beam current of 0.5 A.<sup>49</sup> The resulting infrared radiation is dispersed in time, with a pulse length of, at the ALS, 60 ps. The large mass and careful beam pointing of synchrotrons provides for a stable light source. The high repetition rate further enables excellent near-field signal optimization and signal to noise ratios over long periods of time. Although previous synchrotron technology was limited to decay mode, where small losses over time lead to a reduction in beam current and resulting output radiation, modern advances have enabled top-off mode,<sup>52</sup> where additional electrons are continuously injected into the storage ring.<sup>53</sup> Near-field signal in decay mode would continuously vary with discrete jumps 2-3 times a day when the ring would be refilled. Top-off mode now enables stable near-field measurements over a period of hours and days, limited only by the stability of the AFM and the hold time of the detector.

This concludes the section on infrared light sources that can be used for IR s-SNOM. While this list is incomplete, it represents both the light sources used in the studies throughout the rest of the thesis as well as a good overview of common light sources for infrared spectroscopy.

#### 2.5 Near-field Optical Interaction

In this section, I will highlight the two most important models used to understand the tip sample interaction during s-SNOM. These two models are called out both for being analytical and for giving a simple intuitive understanding of the extracted quantitites and input parameters for understanding s-SNOM signals and spectra. Additional simulation and numerical models<sup>54</sup> have been developed but are only marginally more quantitatively accurate<sup>55</sup> at the expense of a simple physical understanding.

#### 2.5.1 Point Dipole Model

The simplest of the two analytical models is the point dipole model. In this model, the metalized AFM tip is reduced to a simple sphere with a known dielectric function  $\epsilon_{tip}(\omega)$ .<sup>17</sup> The dielectric function of metalized AFM tips is typically flat in the infrared, but, for quantitative modeling, known functions of gold, platinum-iridium, or platinum-silicide can be used. The polar-izability of the spherical tip is given by

$$\alpha_{tip} = 4\pi r^3 \epsilon_0 \frac{\epsilon_{tip} - 1}{\epsilon_{tip} + 2},\tag{2.10}$$

where r is the radius of the spherical tip,  $\epsilon_{tip}$  the dielectric function of the tip, and  $\epsilon_0$  the vacuum permittivity.



Figure 2.3: Coupling of probe dipole p and image dipole p' at small distances z = r - a; the applied electric field E is assumed **a**. perpendicular and **b**. parallel to the sample surface. (Figure from<sup>17</sup>)

 $\alpha_{tip}$  modifies the incident electric field, localizing it to interact with the sample.<sup>17</sup> The back scattered light is further affected by the interaction between the tip and sample. The light induces a dipole on the tip, which then forms an image dipole in the substrate  $p_{tip}^{im} = p_{tip}\beta$ , where  $\beta = \frac{\epsilon_{sam}(\omega)-1}{\epsilon_{sam}(\omega)+1}$ .  $\epsilon_{sam}$  is the desired outcome of the measurement (Figure 2.3). The combination of the tip polarizability and sample dielectric function combines in the point dipole model

$$\alpha_{eff}^{PDM} = \frac{\alpha_{tip}}{1 - \frac{\alpha_{tip\beta}}{16\pi\epsilon_0(r+z)^3}},\tag{2.11}$$

where z is the tip sample distance. Therefore, the near-field electric field is simply

$$E_{scat} = (1+r_P)^2 \,\alpha_{eff} \, E_0, \tag{2.12}$$

where  $r_P$ , comes from the far-field Fresnel reflection of the incident light. A key point that will be revisited later is that near-field imaging and spectroscopy will always contain artifacts and sample specific responses that can easily convolve sample morphology and composition with the desired near-field signal. For instance, even in this non-interfered near-field electric field, the far-field interaction with the sample is directly part of the measured near-field quantity. To understand this, imagine that a sample was coated in a monolayer with a metal carbonyl except for the area directly under the tip. The tip illumination path would still contain the metal carbonyl monolayer, effectively absorbing the incident light before it even reaches the tip. The squaring of the reflection coefficient term comes from the incident beam shaping and back-scatter beam shaping.<sup>56</sup> While s-polarized light should couple equally well to a spherical tip as p-polarized light, the true elongated nature of the tip preferentially selects for p-polarized light (Figure 2.3). This particular model is indeed quite simple and gives the correct physical intuition, yet it is quantitatively lacking.

## 2.5.2 Finite Dipole Model

To better address the quantitative tip sample interaction, the spherical tip approximation is perturbed to an elongated ellipsoid.



Figure 2.4: Comparison of a typical s-SNOM probe-sample configuration with the finite-dipole and the point-dipole model. **a.** The probing tip is typically an elongated structure illuminated by plain waves from the side. **b.** In the finite-dipole model the tip is approximated by a spheroid in a uniform electric field E0. **c.** In the point dipole model the tip is first reduced to a small sphere in an uniform electric field E0. The sphere is then further reduced to a point dipole located in its center. The scattered field is finally calculated from a dipolar near-field coupling with the sample. (Figure from<sup>56</sup>)

This ellipsoid is more similar to the tip's actual shape (Figure 2.4) and therefore models the effective polarizability

$$\alpha_{eff}^{FDM} = R^2 L \, \frac{\frac{2L}{R} + \ln\left(\frac{R}{4eL}\right)}{\ln\left(\frac{4L}{e^2}\right)} \left(2 + \frac{\beta \left(g - \frac{R+z}{L}\right) \ln\left(\frac{4L}{4z+3R}\right)}{\ln\left(\frac{4L}{R}\right) - \beta \left(g - \frac{3R+4z}{4L}\right) \ln\left(\frac{2L}{2z+R}\right)}\right)$$
(2.13)

much better.<sup>56,57</sup> Here, L and R are the half long (L = 600 nm is typical) and short axes (or radius of curvature) of the ellipsoid, respectively, and g is the constant ratio between a point charge and the charge on the tip with a value of  $g = \exp(i0.06)$  empirically used.<sup>57</sup>

The near-field interaction predicted by both the point dipole model (PDM) and the finite dipole model (FDM) causes an apparent red shift in center frequency compared to the far-field and natural energy of a resonant transition. This red shift scales with resonance strength, and therefore statistical correlations between resonance amplitude and center frequency can be complicated by this relationship. A similar effect occurs when the phase of a resonant complex optical response is analyzed, where the increased resonant strength blue shifts the resonance, broadens the linewidth, and turns an absorptive feature into a dispersive one. While phase is preferred for analysis, since it is entirely independent of artificial amplitude scaling within the amplitude response, using the imaginary component in its place addresses this issue.

Numerical models beyond the PDM or FDM have also been developed, especially for strongly resonant systems, like those of plasmonic particles. Specific modeling of a tip's exact shape, possible shadowing effects, far-field interference, sample morphology are also being developed.<sup>54, 58, 59</sup> Typically, these effects are ignored as it is assumed that self-referencing to a gold or other non-resonant substrate will normalize out these second order effects.

This concludes the section on near-field optical interaction models. We found that the PDM was sufficient for gaining a qualitative physical understanding of the tip-sample interaction. While the PDM is qualitatively useful, we also discussed the FDM, which is more quantitatively accurate at the expense of additional model complexity.

## 2.6 Signal Isolation and Artifact Rejection

In this section, I will discuss the sources and classification of artifacts. In order to avoid artifacts in *s*-SNOM data, or its interpretation, a fundamental understanding of near-field signals is needed.

## 2.6.1 Field Detection

To begin, I will discuss the detection, demodulation, and processing of near-field data starting with the detected electric fields. The current most common implementation of *s*-SNOM is with an asymmetric Michelson interferometer. Here, I will discuss the fields and detection involved in this general case and select subsets from this to address the different imaging modalities used in this thesis. A light source (narrowband or broadband) is sent into an asymmetric Michelson interferometer, and its beamsplitter divides the beam into a reference arm and a tip/sample arm (Fig. 2.5). Light from the beamsplitter in the sample arm is focused with an OAP onto the AFM



Figure 2.5: s-SNOM Experimental Setup | An s-SNOM experiment. A light source is directed to an AFM tip through an off axis parabolic, which collects the backscattered light and directs it to the detector. Interference with a reference arm enables spectral and phase resolution.

tip, which localizes the field and backscatters the near-field to the OAP, which collimates the light and directs it through the beamsplitter onto the detector OAP, which also focuses the light into the detector. In this process, there are three fields of interest, 1) the reference field  $E_{\rm ref}$ , 2) the nearfield  $E_{\rm NF}$ , and 3) the background field  $E_{\rm FF}$ , which overwhelms the near-field from the tip-sample area.<sup>60</sup>

Different detectors are used depending on the frequencies being studied. The most common detector for mid-infrared frequencies is a photovoltaic mercury cadmium telluride (MCT) detector. If additional bandwidth is needed, photoconductive detectors offer a wider detection tuning range and higher D<sup>\*</sup> at the expense of non-linearities in its power-to-signal conversion and increased noise. Near-IR experiments often require different detectors, as MCTs typically drop off in sensitivity starting at 5  $\mu$ m and are quite insensitive at less than 2  $\mu$ m. Detectors with other active elements, such as InGaAs, InSb, and PbSb, are used in place of MCTs. Far-IR measurements are typically performed with bolometers and doped Ge detectors.<sup>61–63</sup> Currently, the main limitation with these detectors is their speed, which slows down for detection further into the IR. The typical demodulation frequency in near-field measurements is  $\sim 500$  kHz, but this can be reduced to  $\sim 150$ kHz by using an AFM tip with a lower resonant frequency. At THz frequencies, electro optica sampling (EOS) is used, where the electric field (as opposed to the intensity) is directly detected using an ultrafast gating pulse.<sup>64,65</sup> However, the experimental complexity in performing EOS and the high signal-to-noise ratio (SNR) of MCTs usually restricts EOS to far-IR/THz measurements, where MCTs are not sensitive and alternative bandgap materials are not available. Since the work contained in this thesis uses an MCT, we will restrict the rest of the description to this detection modality.

I will now discuss near-field extraction. The MCT detects the intensity of light and is therefore referred to as a square law detector.<sup>60</sup> Therefore, the detected signal is

$$I_{Det}(x,t,\tilde{\nu}) = |E_{NF}(t,\tilde{\nu}) + E_{Bkg(t,\tilde{\nu})} + E_{Ref}(x,t,\tilde{\nu})|^{2}$$
  
$$= |E_{NF}(t,\tilde{\nu})|^{2} + |E_{Bkg}(t,\tilde{\nu})|^{2} + |E_{Ref}(x,t,\tilde{\nu})|^{2} + 2\operatorname{Re}\left(E_{Bkg}(t,\tilde{\nu})^{*}E_{Ref}(x,t,\tilde{\nu})\right)$$
  
$$+ 2\operatorname{Re}\left(E_{NF}(t,\tilde{\nu})^{*}E_{Bkg}(t,\tilde{\nu})\right) + 2\operatorname{Re}\left(E_{NF}(t,\tilde{\nu})^{*}E_{Ref}(x,t,\tilde{\nu})\right).$$
  
(2.14)

Here, the detected signal is dependent on the spectrum of the light  $(\tilde{\nu})$ , the tip position during its oscillation (t), and the relative optical path length between the tip arm and reference arm (x). In this expanded format, the background squared and reference-times-background terms serve no use and are simply far-field background terms. To isolate only the terms that contain the near-field signal, we use the time dependence of the near-field signal on the tip tapping motion to demodulate the detected intensity at the tapping frequency. The near-field signal depends nonlinearly on the tip sample distance, which is being modulated in a sinusoidal motion. The nonlinear dependence of the signal, based on a periodic function, means the Fourier transform of the near-field signal will contain signal at all of the harmonics of the tip tapping frequency. The first harmonic contains a significant far-field contribution, but the second harmonic is typically sufficient for near-field isolation.<sup>17,66-68</sup>

In order to demodulate the signal, a lock-in amplifier is used. The tip tapping frequency from from the AFM photodiode is analyzed within the lock-in amplifier to extract the tapping frequency, such that a synthetic waveform can be generated. For second harmonic near-field detection, the isolated frequency is doubled before the waveform is made. This waveform is then multiplied by the signal from the detector and the resulting product is integrated over the time constant, which sets the bandwidth of the detected signal in frequency space. Longer time constants have a narrower detected bandwidth about the demodulated frequency. This process then results in a detected intensity of

$$I_{Det}(x,t,\tilde{\nu}) = 2\operatorname{Re}(E_{NF}(t,\tilde{\nu})^* E_{Bkq}(t,\tilde{\nu}) + 2\operatorname{Re}(E_{NF}(t,\tilde{\nu})^* E_{Ref}(x,t,\tilde{\nu}),$$
(2.15)



Figure 2.6: Near-Field Signal | **A** The tip sinusoidally approaches and withdraws from the sample, which increases and decreases the near-field signal from electric field surface enhancement. The near-field signal is nonlinearly dependent on the tip sample distance and therefore yields a comb like Fourier transform. **B** The Fourier transform of the near-field signal, which shows the higher harmonics resulting from the nonlinear tip sample distance dependence.

where the  $E_{\rm NF}^2$  term was dropped as it is negligibly small. The first term is referred to as selfhomodyne and represents the signal that would be detected if the reference arm were blocked. While useful for alignment, the uncontrolled phase between the near-field and anything/everything in the focal area makes it effectively useless. The signal is not spectrally resolved, and constructive or destructive interference at certain wavelengths is dependent on the sample morphology and relative position of the tip to a scattering center. The second term enables spectral and phase resolution. Therefore, we wish to extract this heterodyne amplified near-field signal.

In order to isolate the near-field heterodyne signal, three common techniques are used. First, the reference arm is simply scanned across the zero phase difference, resulting in an interferogram. The DC offset of the interferogram is the unwanted self-homodyne term, but the AC component is extracted by subtracting a line of best fit (to account for slow drift) through the interferogram. This interferogram is asymmetric, resulting from the asymmetric (sample in one arm) nature of the interferometer. While symmetric interferometers use phase correction algorithms to improve the SNR of their spectra by imposing a zero phase response of the interferogram's Fourier transform, the asymmetric nature here enables full complex valued spectra to be obtained. The second technique is to modulate the reference arm with an optical chopper and detect at the chopper frequency sideband about the second harmonic of the tip tapping frequency. This was previously developed for single wavelength sources to perform chopper-demodulated two phase homodyne, but it has been extended for use in rotating frame s-SNOM. In the rotating frame, its implementation can be understood as chopper demodulated multi-step two phase homodyne, where spectral resolution from a Fourier transform can still be acquired. The final common technique is pseudoheterodyne, where the reference mirror is sinusoidally driven. Similar to chopper-demodulated two phase homodyne, sideband detection is performed. Here, instead of one sideband being detected at two different reference arm phases, two sidebands are detected (the first and second harmonics of the reference mirror frequency) to simultaneously acquire the in and out of phase signals (real and imaginary).<sup>60</sup> The division of imaginary and real components into the first and second sidebands respectively requires a specific amplitude for the driven mirror, which is wavelength dependent. Because of this, a broadband source is not generally compatible with pseudoheterodyne, as the real and imaginary components from frequencies outside of the center frequency mix between the two sidebands. For this reason, pseudoheterodyne is typically restricted to CW laser sources, spectrally focused lasers, or sufficiently filtered broadband light sources. Any of these three techniques extract the near-field heterodyne signal.

In this section, I have detailed how the near-field heterodyne signal can be extracted from a square law detector using a lock-in amplifier.

#### 2.6.2 Sideband and Tandem Demodulation

At this point, sideband detection has been mentioned in the context of heterodyne discrimination, but it is also used in the ultrafast studies mentioned later in this thesis. In this section, I will discuss different approaches to isolating signals from the combination of two distinct frequencies.

Sideband demodulation requires two input frequencies and their chosen harmonics to deter-

mine where the signal will be demodulated in frequency space. Both cascaded or tandem demodulation and synchronized parallel demodulation can be used to detect sideband signals. Tandem demodulation occurs in two steps. First, the carrier signal (second harmonic of the tip tapping frequency for s-SNOM) is demodulated with a small time constant so that the center frequency and sidebands of interest are all contained within the output of this first stage. This process shifts the carrier frequency to 0. A second demodulation stage is used where the sideband signal is discriminated from the center frequency by demodulating at the modulated frequency (see Chapter 3). While tandem demodulation is intuitive, the repeated ADC and DAC add additional noise. Some lock-in amplifiers have an internal setting that enables the direct output of the demodulated signal for the second stage, avoiding this noise source. A further issue with tandem demodulation is the bandwidth passed after the first stage. If a sufficiently large enough bandwidth isn't used, the low pass filter during the first stage demodulation will partially reject the sideband signal, lowering the SNR. Tandem demodulation also has the drawback that if the two signals are out of phase with each other, no amplitude can be extracted, as the demodulation is symmetric about the new zero frequency. When the sidebands are in phase with each other and the amplitudes of each sideband are the same, then tandem demodulation is sufficient. On the other hand, synchronized parallel demodulation instead calculates the sideband frequencies and performs single stage demodulation on the signal directly. In this modality, the amplitudes and phases of the sidebands can be independently measured. The lock-in amplifiers typically used in commercial s-SNOM systems utilize synchronized parallel demodulation.

### 2.6.3 Fourier Transform Spectroscopy

In this section, I will discuss the relationship between the detected interferogram and spectrum. The reason why the Fourier transform of an interferogram yields the spectrum is not immediately obvious, so here we derive the relationship between the two bases.

The detector integrates the electric fields over times that are effectively infinite when compared to the optical cycle. Therefore, the intensity on the detector is

$$I(x) = \int \alpha(t) E_{inc}(t) E_{inc}^*\left(t - \frac{x}{c}\right) dt,$$
(2.16)

 $\operatorname{but}$ 

$$E_{inc}^*\left(t - \frac{x}{c}\right) = E_{inc}\left(\frac{x}{c} - t\right) = E_{inc}(t' - t)$$
(2.17)

with t' = x/c. Therefore,

$$I(t') = \int E_{NF}(t) E_{ref}(t'-t) dt.$$
 (2.18)

Taking the Fourier transform of both sides gives

$$\int I(t')e^{it'\omega}dt' = \int \int E_{NF}(t)E_{ref}(t'-t)e^{it'\omega}dtdt',$$
(2.19)

which can be simplified by adding a new variable s = t' - t, such that ds = dt' to

$$\int I(t')e^{it'\omega}dt' = \int \int E_{NF}(t)E_{ref}(s)e^{i\omega(s+t)}dtds.$$
(2.20)

We can then separate

$$\int I(t')e^{it'\omega}dt' = \int E_{NF}(t)e^{i\omega t}dt \int E_{ref}(s)e^{i\omega s}ds,$$
(2.21)

which is identified as

$$\int I(t')e^{it'\omega}dt' = E_{NF}(\omega)E_{ref}(\omega).$$
(2.22)

By taking the inverse Fourier transform

$$\int \int I(t')e^{it'\omega}e^{-it''\omega}dt'dt'' = \int E_{NF}(\omega)E_{ref}(\omega)e^{-it''\omega}dt''$$
(2.23)

with the identity
$$\int \int I(t')e^{it'\omega}e^{-it''\omega}dt'dt'' = \int I(t')\delta(t-t')dt' = I(t')$$
(2.24)

finally gives us

$$I(t') = \int E_{NF}(\omega) E_{ref}(\omega) e^{-it'\omega} dt', \qquad (2.25)$$

which gives us, with a couple of changes of units,

$$I(x) = \int E_{NF}(\tilde{\nu}) E_{ref}(\tilde{\nu}) e^{-i2\pi x \tilde{\nu}} d\tilde{\nu}.$$
(2.26)

It is now obvious that the detected interferogram I(x) is simply the Fourier transform of  $I(\tilde{\nu})$ 

$$I(x) = \int I(\tilde{\nu}) e^{-i2\pi x\tilde{\nu}} d\tilde{\nu}.$$
(2.27)

As previously alluded to, referencing the tip sample interaction to something that is spectrally flat is done in the frequency domain by division, such that

$$I(\widetilde{\nu}) = E_{NF}(\widetilde{\nu})E_{ref}(\widetilde{\nu}) \tag{2.28}$$

and so that

$$I(\widetilde{\nu}) = \frac{\alpha_{sample} E_{inc}(\widetilde{\nu}) E_{ref}(\widetilde{\nu})}{\alpha_{gold} E_{inc}(\widetilde{\nu}) E_{ref}(\widetilde{\nu})} = s_{NF}(\widetilde{\nu}) e^{i\phi_{NF}(\widetilde{\nu})}, \qquad (2.29)$$

where  $s_{NF}(\tilde{\nu})$  and  $\phi_{NF}(\tilde{\nu})$  are the amplitude and phase spectra, respectively.

## 2.6.4 Artifacts in *s*-SNOM

In this section, I will discuss the source and types of artifacts in s-SNOM. In addition to the artifacts mentioned above, I want to take a brief moment to discuss spectral and image interpretation. Spectrally, I have demonstrated how the uncontrolled phase between the tip scattered near-field and far-field background is a DC offset in interferogram space, which is subtracted before taking the Fourier transform to yield interpretable spectra. However, through the Fresnel coefficient in pump-modulated pump-probe spectroscopy, a Fano type interference can occur, where the self homodyne signal can still lead to artifacts spectrally.<sup>69</sup> This means that, in ground state measurements, care must be taken to observe heterogeneity on scales that are smaller than the wavelength of light, and broad spectral features resulting from preshaping interference should be ignored. Similar considerations for ultrafast spectroscopy must be taken and will be discussed in the ultrafast method section of this thesis (Chapter 3).

In addition to interference from the scattering type nature of s-SNOM, topographic features on a sample lead to artifacts in both spectra and images. Spectral artifacts result from the nonuniform near-field interaction based on a sample's morphology. Simply the strength of the nearfield interaction can vary spatially from either local topographic height changes, the gradient, or the second order topographic structure. For example, if the tip is on the back side (relative to the input light) of a tall sharp cliff, then no far-field light can couple to it, and the signal drops, causing the interpreted spectrum to be shifted as well. A more common example is when the tip is placed over a small indent on the surface. Here, the surface enhancement is typically increased and again shifts the spectrum. In terms of imaging, the changes in signal level will easily be manifest as well. My preferred approach to analyzing these sort of data is to look at the phase response. This is because it is the least sensitive to amplitude changes, as the real and imaginary components are the product of the amplitude with the respective trigonometric functions of phase. Therefore, care must be taken when comparing amplitudes of signals, especially on rough samples.

# 2.7 Conclusion

In this section, I have detailed how the core components of a s-SNOM measurement are operated and considerations in its typical use. I then discussed the diffraction limit and the fundamental physics leading to the constraint on measuring physical phenomena of interest at nanoscopic scales. I detailed the optical sources that will be used throughout the work addressed in the rest of this thesis and detailed the near-field optical interaction with two models that are frequently used to analyze *s*-SNOM data. I concluded with a fundamental discussion of the source of the near-field signal, its isolation, useful modalities, and spectral meaning and finished with sources of artifacts that must be considered when analyzing data.

## Chapter 3

### Method Development

## 3.1 Introduction

In this chapter, I will discuss different approaches to *s*-SNOM that I have developed during my PhD. The main advancements that I have made were in developing rotating frame, compressed sensing and matrix completion, and far from equilibrium excitation ultrafast pump-probe extensions to *s*-SNOM. The rotating frame was developed by me and this portion of the thesis is adapted from a publication.<sup>70</sup> The compressed sensing and matrix completion was work in collaboration with Simon Labouesse, where we combined my expertise in *s*-SNOM with his computer science expertise to apply techniques common in information theory to our specific collaboration and is also adapted from a previous publication.<sup>71</sup> The ultrafast method development, being the most involved project experimentally, involved input from a long line of students and post-docs from first demonstrations to a robust imaging tool and technique. This project was started by Omar Khatib and Sven Dönges, continued by Jun Nishida, who is the first author on the publication after which this section is adapted, and myself. All individuals were directly involved in the theory and development, with Nishida and myself performing experiments once the technique had been demonstrated.<sup>69</sup>

### **3.2** Rotating Frame

To begin, I will discuss imaging in the rotating frame, where data acquisition speed is increased by a factor of  $\sim 10$ .

While IR vibrational scattering scanning near-field optical microscopy (s-SNOM) has successfully been applied to applications ranging from biological to quantum materials, the acquisition of full spatiospectral image sets continue to be hindered by the sheer length of these higher dimensional data sets. As the technique continues to advance, additional data sets from time resolved measurements to tomography enabled by z dimension modulation and sensitivity will further exacerbate this problem. While non-Nyquist approaches have been proposed and will be discussed in detail in the following section, we demonstrate here a novel approach, where an increase in acquisition speed is achieved by changing basis from the stationary frame to the rotating frame at the lowest frequency in the IR carrier envelope. Specifically, we demonstrate here an increase in acquisition speed by a factor of 10 in a real direct comparative example. I stress the contrast of this example to theoretical proof of principle or post processing attempts by noting the actual experimental demonstration of this approach. To do this, we use prior knowledge about the light source and resonances that will be probed. The example demonstrated here is applying R-sSNOM (rotating-frame s-SNOM) to a mollusk shell, where we image ultrathin protein sheets within the prismatic layer. We achieve high voxel density in our hyperspectral image to resolve sparsely distributed molecules within a large field of view. While we applied this approach to a biological sample to perform molecular vibrational imaging, this approach is general and is beneficial for any system that has sparsely located features of interest and can further be applied to other higher dimensional nanoimaging modalities.

Chemical imaging in a wide range of molecular and quantum systems has been performed using IR *s*-SNOM.<sup>72–76</sup> Specific to biological systems, which host structural features from proteins at nanometer scales to cytoskeletons at multiple micron length scales, the active regions determining the biological function and utility are frequently sparsely distributed.<sup>77–81</sup> Here, we define sparsely distributed as being separated by distances far greater than the size of the feature of interest

$$\frac{l_{separation}}{l_{feature}} \gg 1. \tag{3.1}$$

Therefore, a hyperspectral imaging method with a high field of view and spatial resolution over a wide spectral range is desired. As data sets grow from dense (high resolution) voxels over large dimensions (field of view and spectral range), associated problems to the long data sets like drift of the sample, light source, and detector further compound as well.<sup>82</sup> During this time, if the biological system is still active, the sample being imaged can of course change as well. Beyond the simple annoyance of longer measurement times, these problems actively restrict future extensions for measurements. These constraints have limited *s*-SNOM's applicability, particularly for biomaterials.

Biological and chemical systems frequently need high pixel density imaging over wide fields of view on composite samples. As a representative example, Mollusk shells, with their extended shell structure, are largely composed of calcite and aragonite,<sup>83</sup> two different polymorphs of CaCO<sub>3</sub>, but have a small amount of organic material thought to direct the growth of the shell interspersed in the prismatic region. The organic material is typically less than 5% by weight and, in addition to growth control, modifies the crystal habit and type of polymorph that the CaCO<sub>3</sub> takes. The sparsity of its inclusion among the vast biomineral though has remained difficult to locate and study. Macroscopic ensemble average techniques measuring de-calcified shells has determined the organic fraction is at least partially made of proteins.<sup>84–87</sup> Proteins and polysaccharides have been extracted,<sup>88–91</sup> yet nano-scopic characterization in situ remains elusive.

In an effort to address these questions and similar challenges in other similarly complicated systems, compressive sensing has been applied to broadband *s*-SNOM through synchrotron based SINS.<sup>92</sup> In this approach, prior knowledge about the data, specifically in what basis the data is sparse (taken to be largely filled with zeroes), is used to reconstruct a sub-sampled data set. This approach enables sub-Nyquist sampling and achieves similar resolution and image fidelity to the fully sampled data set. Compressed sensing yields a probabilistic reconstruction to obtain a full data set from an incomplete one with far fewer actual measured data points. Similarly, nuclear magnetic resonance (NMR) has used rotating frame techniques where the spectroscopic carrier frequency is shifted out of the stationary frame, reducing the number of necessary data points to

collect a spectrum.<sup>93,94</sup> For a given desired spectroscopic resolution, faster detection is enabled by shifting the carrier frequency to zero and reducing the necessary Nyquist cut-off frequency. The rotating frame technique has been extended to time-domain optical spectroscopy in the far-field to improve acquisition speed and sensitivity.<sup>95–99</sup>

We have demonstrated rotating frame detection as an extension of *s*-SNOM in the application to chemically sensing and resolving proteins within the prismatic region of an oyster shell. The heterogeneous and sparse distribution of protein within the large field of view dominated by an extended calcite matrix was spectroscopically imaged by mapping the protein amide I IR response.

## **3.2.1** Rotating frame parameter space

Rotating frame is best applied in conjunction with an IR source of narrow bandwidth, so that the frequency shift is maximized. We choose to shift the zero-point frequency to the lowest energy of the laser spectrum. Mathematically, this can be understood as changing co-ordinates from  $\omega$ to  $\omega$ - $\omega_0$ , which allows for significantly shorter spectral acquisition times to achieve higher spatial data densities. Specifically, our direct comparison between R-*s*SNOM and conventional nano-FTIR indicates an imaging speed increase of a factor of 60. This faster imaging enables higher spatial resolution, limited by the radius of the AFM tip and near-field localization, over much wider fields of view conventionally accessible. For maximum speed enhancement, broad resonances (where the spectral resolution doesn't need to be high) and narrow bandwidth light sources should be used.

### 3.2.2 Experimental implementation

The experimental setup is only slightly perturbed from conventional nano-FTIR, where a chopper is included in the reference arm and a piezo mounted mirror is placed on a longer axis translation stage (Figure 3.1a). The light source used in our demonstration is the tunable output from difference frequency generation (DFG) between the signal and idler output beams from an optical parametric oscillator (Levante OPO, APE) using a AgGaS<sub>2</sub> crystal (Harmonixx DFG, APE) that is pumped with a Yb:KGW femtosecond laser (1034 nm, pulse duration 90 fs, 6 W, 75.7

MHz repetition rate, Flint, Light Conversion). While the output is tunable, we only use one center frequency for this experiment and direct 18 mW of 1680 cm<sup>-1</sup> into a s-SNOM instrument (nanoIR2s prototype, Anasys Instruments). An off axis parabolic mirror (OAP, NA=0.45, Reflected Focal Length= 25.4 mm) focuses the light to the apex of a gold coated AFM tip (160AC-GG OPUS,  $\mu$ mash). We use intermittent contact mode to modulate the near-field signal for lock-in extraction later. The back scattered light is collected with the same OAP and heterodyne amplified with reflected light from the reference arm to be detected by a HgCdTe (MCT KLD-0.5-J1/DC/11, Kolmar Technologies) detector. In conventional nano-FTIR, the Fourier transform of the resulting asymmetric interferogram yields the complex valued, phase resolved optical response of the tip sample interaction with spatial resolution given by field confinement and primarily the radius of the tip apex.

To extract the near-field, the MCT signal is demodulated at the second-harmonic of the tip tapping frequency  $\omega_{tip}$  using a lock-in amplifier (HF2LI, Zurich Instruments), as described above. When performing R-sSNOM, a chopper in the reference arm is used and the sideband  $2\omega_{tip} + \omega_{ref}$ of the near-field signal is collected to eliminate far-field background self homodyne, where  $\omega_{ref}$  is the chopping frequency. We follow established procedure by normalizing the spectrum to a gold reference, whose flat optical response leaves the particular focus, light source, and tip parameters available to be normalized out of the measurement. Since we are in the water absorption window, we eliminate artifacts from water vapor by purging the entire instrument with dry air. In addition to the reference mirror position being controllable with a piezo, the macroscopic longer range position was controlled with a linear direct drive translation stage (Aerotech, ANT95-50-L-MP).

## 3.2.3 Sample preparation

A widely studied model mollusk (*Crassostrea gigas*) has been characterized by its prismatic layer, which is a distinctive microstructure made of calcite columns that are closely packed and are more than 10s of microns tall.<sup>100</sup> In the cross plane (the dimension measured here), the columns are ~10  $\mu$ m across with ~1 $\mu$ m thick gaps made of thin polygonal sheaths of intercrystalline organic



Figure 3.1: Rotating Frame s-SNOM (R-sSNOM) |  $\mathbf{a}$ , Experimental design with broadband light source and asymmetric Michelson Interferometer with necessary modifications for rotating frame s-SNOM.  $\mathbf{b}$ , Schematic of the rotating frame reducing the frequency of the basis waveforms (red and orange) to generate new waveforms (blue and purple). The same information is encoded, but with the beat frequency between the rotation and basis.  $\mathbf{c}$ , Resonant IR feature within narrow laser spectral bandwidth.  $\mathbf{d}$ , Experimental interferogram (red) with a factor of 10 sub-sampled datapoints (blue).  $\mathbf{e}$ , Low frequency interferogram generated by rotating red experimental data by 1550 cm<sup>-1</sup> (red) and the similarly rotated sub-sampled points (blue).  $\mathbf{f}$ , Frequency comparison of stationary and rotating frame spectral response.<sup>70</sup>

material. The c-axis of these columns are homogeneously aligned to within 20 degrees and are perpendicular to the polished surface.<sup>101–103</sup> To prepare the samples for IR imaging, the polishing step was followed by a short  $\sim$ 3 second 0.1 M HCl etch, re-exposing the organic sheath.

### 3.2.4 Shifting frequencies

While a faster acquisition method, the rotating frame uses the lowered Nyquist cut-off frequency to reduce the number of data points necessary to resolve a spectral feature. The rotating frame approach is based on the linewidth  $\Gamma_{\rm vib}$ , center frequency  $\omega_{\rm vib}$  of the vibrational resonance to be probed (Fig. 3.1c), and rotation frequency  $\omega_{\rm rot}$  where  $\omega_{\rm rot}$  is less than  $\omega_{\rm vib}$  and is typically  $\omega_{\rm vib} - \Gamma_{\rm vib}$  or smaller. This concept is illustrated in Figure 3.1b, where the original basis vectors (red and orange) that span the rotation space are collected conventionally with the exception of larger reference arm step sizes (3.1a). The computational aspect of rotating frame can be thought of as a complex apodization of the acquired datasets (green spiral). The newly visualized (dark and light blue) have an apparently lower frequency but span the same space. This can also be thought of as spinning about a bloch sphere, where the vibrational resonance precesses with frequency  $\omega_{\rm vib}$ around the precession axis at the rotation frequency  $\omega_{\rm rot}$ . Going to the rotating frame subtracts off this rotation frequency  $\omega_{\rm vib}$ - $\omega_0$  so that the near-field signal interferogram only needs to be collected in steps of  $1/\Gamma_{\rm vib}$  up to the distance set by the desired spectral resolution. Typically, the necessary step size is based on the maximum frequency you want to be able to recover, but with the rotating frame, it now depends on  $\omega_{\rm vib} \Gamma_{\rm vib}$  and  $\omega_{\rm rot}$  while still being Nyquist limited. The example given here pushes these boundaries to the extreme to best illustrate the speed increase that can be achieved. Moving forward, to avoid aliasing and to ensure good quality spectra, a lower rotation frequency should be selected and a larger  $\Gamma$  should be assumed.

### **3.2.5** Proof of principle

To demonstrate the applicability of this technique, we simulate the process by sub-sampling a conventionally acquired nano-FTIR dataset. A standard nano-FTIR interferogram collected in the stationary frame is shown in figure 3.1d (red). A  $\sim$ 30x sub-sampled dataset is shown along in blue and in the stationary frame seems to not be a good representative of the full dataset, upon transitioning to the rotating frame, both interferograms are in clear close resemblance (Fig. 3.1e). Upon Fourier transformation and carrier frequency inverse shifting, we observe good spectral agreement between the R-*s*SNOM and Nqyist limited R-*s*SNOM spectra shown in 3.1f, red and blue respectively. In this specific example, chemical imaging is increased by 60 fold while maintaining voxel integration time so that the signal to noise ratio is the same between the two methods.

### 3.2.6 Imaging protein matrix

With the proof-of-concept pre-calculation achieved, R-sSNOM is demonstrated as a full hyperspectral imaging method to demonstrate the reduction in sampling needed when using the rotating frame. To put rotating frame into action, the full field of view is imaged at each reference arm delay point with spacing described above. To perform the rotation, we need two basis vectors (in and out of phase) to span the rotated space, which we achieve by performing chopper demodulated 2-phase homodyne imaging at each selected reference arm delay using previously described procedures.<sup>81</sup> To spectroscopically resolve voxels, we repeat the two-phase homodyne imaging at each reference arm, stack the images, correct for spatial drift, dropped pixels, and Fourier transform the interferogram collected by isolating single spatial positions within the hyperspectral data cube, and using the rotating frame algorithm described above. We use this technique to image 4000 voxels with 100 nm spatial resolution, 20 cm<sup>-1</sup> spectral resolution, and 200 cm<sup>-1</sup> bandwidth.

To directly compare conventional nano-FTIR to R-sSNOM imaging, we map the protein locations within an oyster shell to the prismatic region. The spatial distribution and extent of proteins within the prismatic region is unknown and the hierarchy of scales being imaged here is shown schematically in Figure 3.2a.

By centering the laser at the peak of the amide I response in this sample (determined by conventional nano-FTIR spectroscopy) at 1680 cm<sup>-1</sup>, we maximize signal overlap for the spectral response, while maintaining maximum rotation for the largest speed increase. A 4  $\mu$ m by 10  $\mu$ m field of view was selected as it covered two organic sheets. To image this region with 100 nm by 100 nm spatial resolution in R-sSNOM, we use 40 by 100 pixels (Fig. 3.2b). This is in contrast to the conventional stationary frame nano-FTIR experiment (Fig. 3.2c), where a much more conservative 10 by 30 pixel array was used to yield ~10 times fewer spatial points to match the same acquisition time (to maintain SNR comparability) with identical spectral resolution. Halfway through the conventional scan, an AFM image was collected in order to characterize sample drift. In the conventional image, the entirety of the ~1  $\mu$ m gap between calcite columns was mapped by only 3 voxels. The spectra in this measurement need to be locally referenced against a calcite (protein free) spectrum as the large spectral contribution of calcite interferes with the detection of the amide I response. The corresponding full spatio-spectral R-sSNOM phase data set is shown in figure 3.2d. A single example spectrum of the protein from the organic region is further shown in



Figure 3.2: Rotating frame R-sSNOM imaging  $| \mathbf{a} \rangle$ , The prismatic layer (middle schematic, thickness exaggerated) surrounded by organic sheaths (right). **b**, Near-field scattering amplitude heterodyne amplified at zero phase difference between tip and reference arms in the rotating frame and **c**, stationary frame. **d**, Spatio-spectral phase image of same region. **e**, Representative spectrum of location indicated in panel d showing typical amide I response of the organic sheath.<sup>70</sup>

figure 3.2e.

We now use the R-sSNOM amide I phase (Fig. 3.3b) with the AFM topography (Fig. 3.3a) to locate and map where the protein content is through correlation analysis and identifying 5 distinct regions based on the calcite and amide with the relative surface height (Fig. 3.3c). The etching process, which yields higher organic features relative to calcite, compares well the location of proteins in the prismatic region, yet R-sSNOM indicates that the extent of the protein is a smaller fraction of this relieved area. The distribution of amide phase and height data points can be seen as a correlation plot in figure 3.3d.



Figure 3.3: Comparison of Imaging Methods  $| \mathbf{a} \rangle$ , Topography from AFM. **b**, Strength of near-field phase response at 1680 cm<sup>-1</sup>. **c**, Correlation comparison of sample topography and amide phase response. Points of high value indicate high correlation, and points of low value indicate a deviation between topography and the local Amide population (see color-bar). **d**, Correlation plot of height and phase dependence between panels a and b (see color-bar).<sup>70</sup>

## 3.2.7 Drift and artifact compensation

The sample, in both R-sSNOM and conventional nano-FTIR, drifts during the acquisition of data. The magnitude of drift is given by the thermal instability of the AFM stage and is typically more than at least 1 nm/min. In conventional nano-FTIR, drift is typically accounted for by taking one or more reference images throughout the spectra collection process and using a fiducial marker on the sample as a tracking point to then correct for drift. However, because the data in R-sSNOM is collected through imaging with a stationary reference arm, rather than scanning the reference arm with a stationary sample, we simultaneously collect the height data channel. We then use this channel, with a cross correlation analysis in Fourier space, by using the first mirror step position as the reference point to then shift and stack the additional images on top. To calculate the shift, we search for the pixel with the highest cross correlation and generate a shift vector. We repeat this for every reference arm position and create a dictionary to stack the X and Y data channels as well as the larger translation stage steps. Once the images are shifted and stacked on top of each

other, we crop all of the images so that only the field of view contained within every page in the stack remains.

During the data collection process, occasional data points are lost based on the pixel quality for every mirror position resulting from instabilities in the laser output, chopper frequency, AFM tip frequency and their relations to each other during the demodulation process. Inevitably, occasional instabilities lead to a loss of reasonable value for at least a pixel, resulting in an unusually high value. The value typically skyrockets based on a step in the demodulation process losing lock on an input demodulation frequency, searching for the frequency at lower values, resulting in an increase in signal from 1/f noise. Fortunately, these errors are easy to catch and therefore are corrected by implementing a multistep algorithm. The implementation of 2 phase homodyne results in a duplicity of scans for each X and Y value as the AFM is raster scanned in a trace and retrace direction for both X and Y. Therefore, when a pixel is found to be lost in one channel, if the same spatial location exists in the Y channel, we substitute the redundant point. We perform this for both trace and retrace and average the resulting two images to increase our SNR. Next, if pixels remain where the value is still above a threshold, we interpolate the dropped pixel by averaging the surrounding 8 pixels. Finally, for the few remaining pixels that are clearly off by eye, a conservative threshold is imposed and capped with the maximum value. Finally, we repeat the scan for subsequent thresholds until the image converges.

While the data in conventional s-SNOM is collected in a different order (string wise versus page wise) than R-sSNOM, the interferograms are processed in the same way. First, the data vector is zero-padded to a length that is a power of 2, increasing the length of the data by almost a factor of 4, effectively interpolating the spectra with a sinc function. The interferogram is then apodized with a Blackman-Haris function to increase the SNR of the spectrum. The data is then shifted to put the center-burst in the middle and Fourier transformed with Matlab's FFT algorithm. The spectrum is normalized with a reference spectrum (calcite as mentioned above) by dividing the sample spectrum with the reference spectrum. The spectra are complex, so effectively, amplitude is divided and phase is subtracted.

To increase data fidelity (artifact rejection – see chapter 2 of this thesis), we modify the conventional s-SNOM setup by inserting a chopper into the reference arm, so that sideband demodulation can be used to directly isolate the heterodyne near-field signal. We give the chopper a frequency  $\Omega_{\text{REF}}$  and choose chopper blades so that the beam size is comparable to the blade size in an effort to best sinusoidally modulate the optical signal. Secondly, a piezo actuated mirror mount is added to the reference arm to have fast, reproducible, stable, and bidirectional accuracy of our mirror position at mesoscale distances to retrieve both the X and Y images to span the rotation basis. We use this in conjunction with the longer-range linear stage, which yields spectral resolution.

### 3.2.8 Robust imaging

We apply this concept to an image (Fig. 3.4) with many more voxels of data and map the surface position in the x and y dimensions and the height along the z dimension while coloring the surface with the relative strength of the phase response at 1680 cm<sup>-1</sup>, where the amide response is greatest. This image is in good agreement with the preferential etching performed to relatively raise the organic material.



Figure 3.4: Larger field of view R-sSNOM | Additional rotating frame data set acquired in the prismatic region of an Oyster shell showing a high protein concentration in a V-shaped region as determined by the Amide I response.<sup>70</sup>

## 3.2.9 Alternative chemical mapping approaches

Previous work has shown spectroscopy performed using tunable single-wavelength sources.<sup>32</sup> In these experiments, either self-homodyne or white light imaging can be performed. Unfortunately, the signal is still not background free, and the spectra obtained are difficult to normalize and interpret due to the frequency dependent power and stability of the light source. For proper hyperspectral imaging, a broadband source should be used in conjunction with a technique that allows for frequency dependent imaging to occur as well as a method for being background contamination free.



Figure 3.5: R-sSNOM and conventional nano-FTIR spatial resolution  $| \mathbf{a}$ , Rotating frame phase response at 1680 cm<sup>-1</sup>. **b**, Stationary frame phase response at 1680 cm<sup>-1</sup>. **c**, Feature edge comparison between rotating and stationary frame Amide I phase response at regions indicated in panels a and b.<sup>70</sup>

Most spectral mapping in s-SNOM has followed similar variants to conventional techniques.<sup>32,78</sup> The typical pattern goes as using the topographical channel to determine a region of interest, then a series of tip sample positions are identified where the tip is moved, reference arm swept, and spectra collected before moving onto the next point in the list. This creates the 3D data cube, where a spectrum is associated with each spatial position on the sample. While this is intuitive, there is quite a bit of "dead" time and does not scale to higher dimensions well. Further, as mentioned above, this method requires the AFM tip sample locations to be selected ahead of time and is assumed to remain valid at later times, an assumption often fraught with problems from thermal drift. Moving into the rotating frame, combined with techniques made for CW lasers,<sup>104</sup> the data collection is more targeted, improves with dimensional scaling, and automatically corrects for sample drift.

### 3.2.10 Spatial resolution

To directly compare the difference in achievable spatial resolution and how it is important for the demonstrated comparison to conventional *s*-SNOM, we show line-cuts of the amide slice images in figure 3.5 and see the slopes at the edge of a feature of interest are markedly different. This represents a non-trivial improvement on previous hyper-spectral imaging, where the fundamental resolution is given by the AFM tip radius, but is practicably limited by the acquisition time and associated problems.

#### **3.2.11** Spectral Artifacts

The spectrum shown above comparing R-*s*SNOM and conventional nano-FTIR are quite similar but do exhibit obvious differences, with the phase reconstruction showing larger discrepancies. This results from the inversion symmetry associated with the phase of the Fourier transform. Briefly, in the rotating frame collected at the Nyquist frequency cut-off limit, this symmetry necessitates a turning point near 1750 cm<sup>-1</sup>, which, because of how close this example is to the limit, contaminates the absolute spectral position and shape of the extracted amide I feature.

The spectral deviation between the conventional and rotating frame datasets is large here from the choice of measuring at the Nyquist limit – by choosing a larger effective bandwidth (decreasing step size) for the rotation, or choosing less broadband light sources and narrower resonances, this effect can be minimized. Here, the resonance is quite broad (comparable to the laser bandwidth) and our choice was sufficient for mapping the protein distribution. The shift of the apparent peak position by  $\sim 10 \text{ cm}^{-1}$  does not affect the identification and mapping in this system. Amide I peak positions also vary in center frequency and the variation within biological samples is frequently larger than the deviation observed here.

## 3.2.12 Theoretical formulation

We now consider the mathematical formulation for imaging in the rotating frame in direct comparison to conventional nano-FTIR. We then compare the two-phase homodyne implementation with a pseudoheterodyne approach. The near-field heterodyne amplified intensity in both the x and y demodulated channels in frequency space is given by equation 3.2

$$I_{\rm x}(k) = \sum_{n=0}^{N_{\rm STAT}-1} e^{\frac{-2\pi i}{N}k\tilde{x}_{\rm n}(t)} I_{\rm 2H}(\tilde{x}_{\rm n}(t))$$
(3.2)

Here,  $N_{STAT}$  is the number of data points collected along the interferogram, k is the output frequency of the transform,  $\tilde{x}$  is the position of the interferometer arm (where n is the sampling number — position index).<sup>70</sup> The complex valued response is normalized to a background reference signal and normalized via division. The Nyquist sampling theorem provides the smallest value that  $N_{STAT}$  can take, which, for our light source centered at the amide I resonance and a desired spectral resolution of 20 cm<sup>-1</sup>, is 181. In the rotating frame though, the relative optical frequency is the value of interest, and is shown in equation 3.3

$$I_{\rm x}(k-k_0) = \sum_{n=0}^{N_{\rm ROT}-1} e^{\frac{-2\pi i}{N}(k-k_0)(\tilde{x}_{\rm n}(t)+\tilde{\phi})} I_{2{\rm H}+\Omega}(\tilde{x}_{\rm n}(t)),$$
(3.3)

where we have included the subtracted frequency  $k_0$ , a mirror position offset  $\tilde{\phi}$  (controlled by the reference mirror piezo) and  $\Omega$  the chopper frequency. The minimum value of  $N_{ROT}$  is still given by the Nyquist sampling theorem, where  $\tilde{x}_n - \tilde{x}_{n-1}$  determines the maximum cut-off frequency, which we choose to be approximately  $3 * \Gamma_{vib}$ . Therefore, the minimum value  $N_{ROT}$  can take (for a resolution of 20 cm<sup>-1</sup>) is 21 - a reduction by almost an order of magnitude. While the minimum sampling number is lowered by approximately an order of magnitude. The typical implementation of *s*-SNOM though wouldn't be able to take advantage of this reduction as the reference arm mirror would still need to be scanned through the now redundant space. Therefore, the surface scanning technique for x and y extraction is borrowed from previously established two phase homodyne.

Because the implementation of rotating frame, for maximum acquisition speed enhancement, requires surface imaging at one reference arm mirror position, the standard DC subtraction (through line fitting mentioned in chapter 2) cannot be performed. In its place, we perform sideband detection off of the second harmonic near-field signal with the chopper frequency added to the reference arm. Two phase chopper demodulated homodyne has previously been used<sup>81</sup> for single wavelength sources, where the amplitude and phase could be extracted from the collected real and imaginary channels collected at the two phase positions. Image math then made the computation of amplitude and phase possible for imaging. We use this technique with a broadband light source by scanning the reference arm between image acquisition.

Figure 3.6a and b illustrates the possible experimental sideband detected data. The basis vectors behave normally (comparable to the standard *s*-SNOM approach) and slowly rotate to produce interferograms in the rotating frame. Pseudoheterodyne, while faster, is more difficult to implement with a broadband light source. The difficulty here is the normalization or amplitude drive condition that is necessary to set the real and imaginary components between the first and second sidebands. While technically possible, the real-life implementation of this approach is very sensitive to drift and not a practical way to implement R-sSNOM.<sup>105</sup> In pseudoheterodyne, the detected signal is given by



Figure 3.6: Method of Accessing Rotation Basis  $| \mathbf{a} \rangle$ , Experimental data of two typical interferograms as two basis vectors to span rotation space collected using the fine delay mirror control. **b**, Rotated interferograms of experimental data in panel b. **c**, Resonance-less model data generated by computing pseudo-heterodyne data collected by demodulating at the second harmonic of the cantilever frequency. **d**, Rotating frame applied to interferogram basis vectors acquired through pseudo-heterodyne.<sup>70</sup>

$$I(\omega) = \int_{-\infty}^{\infty} dt e^{-i\omega t} e^{\frac{-2\sigma^{2}\epsilon^{2}}{c^{2}}} \int_{\omega_{1}}^{\omega_{2}} d\omega_{0} e^{-i\omega_{0}t} \\ e^{\frac{-i2\omega_{0}\epsilon}{c}} e^{\frac{-2\sigma^{2}}{c^{2}}(\epsilon\xi sin(mt+\phi_{m})+\xi^{2}sin^{2}(mt+\phi_{m}))} \alpha_{\text{eff}}(\omega_{0},t) * \\ [J_{0}(2\omega_{0}\xi) + 2\sum_{n=1}^{\infty} (J_{2n}(2\omega_{0}\xi)cos(2n(mt+\phi_{m}))) + \\ iJ_{2n-1}(2\omega_{0}\xi)sin((2n-1)(mt+\phi_{m})))]$$
(3.4)

The nontrivial interplay between laser specification, specifically the center frequency  $\omega_0$  and importantly bandwidth  $\sigma$ , and detection parameters like oscillation amplitude  $\xi$  and phase offset  $\phi_{\rm m}$  has on the extracted near-field response  $\alpha_{\rm eff}$  makes teasing out the wavelength specific real and imaginary optical signals practicably impossible.

Specifically, the mirror DC position, center frequency of light source, and bandwidth cause the real and imaginary near-field response to mix as the mirror moves away from the ZPD. The sensitive behavior is shown in figure 3.6c. The high frequency oscillations of the signal in the rotating frame is not recoverable with larger mirror step sizes and we therefore implement multi-step chopperdemodulated two-phase homodyne for complex valued basis and self homodyne subtraction.

To eliminate the background term in pseudoheterodyne, and to simultaneously extract the real and imaginary optical response, sidebands are generated via the Jacobi-Anger expansion, where the argument of the electric field is linearly dependent on the sinusoidal motion of the reference mirror. These sidebands are symmetric about the second harmonic of the tip tapping frequency (or any higher order near-field harmonic) with signal strength dependent on the Jacobi-Anger expansion coefficients. In the particular case of a single wavelength source, pairs of neighboring sidebands (1 and 2, 3 and 4, etc), with appropriate drive strength, can be matched to have the same maximum amplitude, where signal in one channel is exchanged with the other through a phase offset. This is implemented experimentally by selecting a light source and oscillation frequency and tuning the drive strength, while adjusting phase, to the point where the maximum achievable values are the same for both sidebands.

We see that in addition to the difficulty of scaling the waveforms generated by pseudoheterodyne (and it being phase dependent — impossible to do in general for a broadband source), there is a complicated secondary envelope function for the two sidebands. Again, while it is theoretically possible to deconvolve this mixing, the experimental nature of crucially determining these parameters with stability on the few to 10s of hours timescale is simply not practical. Additionally, assuming the deconvolution could be done, the Jacobi-Anger expansion splits the near-field signal into an infinite series of sidebands, diluting the signal to channels that are discarded and decreasing the relative signal to noise compared to a method that creates sidebands of finite (or faster converging) order. From these considerations the choice for background free imaging between pseudo-heterodyne and chopper demodulation should clearly be the latter.<sup>70</sup>

### 3.2.13 Applying rotating frame for chemical imaging

The outer organic coating, periostracum, and inner chalky and foliated layers encapsulate the prismatic layer. The prismatic and inner layers are primarily made of calcite. Sampling portions of the shell was done with a rotary tool (Dremal) with a diamond-impregnated disc to create an oblique surface relative to the columns. To chemically map the protein distribution, the spatial resolution needs to be high as the protein deposits are nanoscopic, but the spectral resolution can be comparatively low. Here is the perfect application for R-sSNOM where these tradeoffs are leveraged.

In the rotating frame, the total scan length is set based on the desired spectral resolution and the step size is set based on the Nyquist cut-off frequency, which, to first order, is given by the bandwidth of the light source. The larger step sizes enabled by the reduced maximum necessary cut-off frequency enables faster data collection, which can be leveraged by the scanning method detailed above. This simultaneously, during the stacking process, enables passive drift compensation. Additionally, the static axis of the measurement is shifted from the sample to the reference arm, where the reference mirror only needs to be stable on the  $\sim \mu m$  scale instead of the  $\sim$ nm scale, enabling faster and more stable hyper-spectral chemical imaging.

Here, we use the same integration time per spatial point per reference mirror position and still see a speed increase by a factor of ~60 fold. To enable drift correction in a conventional *s*-SNOM experiment the sample must be imaged, conservatively, every 50 data points, which for a 100 by 100 pixel image (10,000 spatial positions), the re-imaging time alone (regardless of the time needed to actually collect spectra) is more than an order of magnitude more than the complete data acquisition time for R-*s*SNOM. Here, for the conventional approach, we select 20 cm<sup>-1</sup> spectral resolution and scan the reference mirror at 10  $\mu$ m/s, taking 25 seconds per spatial position. To complete 300 spectra, the total imaging time is 2.3 hours, whereas the same field of view is measured with R-*s*SNOM with the same spectral resolution, but 4,000 spatial positions in slightly less time. Therefore, R-*s*SNOM has more than an order of magnitude in improvement in the magnitude of acquired data points for the same scanning parameters, yielding a drift corrected and higher spatially resolved image to see more structural detail.

Similar to the issue of being right at the Nyquist limit mentioned above, the first few spectral datapoints following rotation can be affected by the dual of negative frequency components from frequency folding. We therefore choose to rotate this dataset at 1550 cm<sup>-1</sup>, which, with our selected step size, gives a maximum recoverable frequency of 1750 cm<sup>-1</sup>.

The capabilities of R-*s*SNOM are well matched to the needs of a nanometer convoluted organic-mineral interfaces sparsely distributed sample. The discrepancy between the feature length scale and the distribution length scale indicates the necessity of high-resolution large field of view imaging. In this example, we see a strong improvement in image quality, speed, and resolution with a generic approach that is ideally matched for chemical imaging in diffuse systems.

# 3.3 Compressed Sensing and Matrix Completion

I will now discuss compressed sensing (CS) and matrix completion (MC) as the next approach to improving data acquisition speed. While the rotating frame is Nyquist limited, CS and MS operate below the Nyquist limit. Similarly to the rotating frame, prior knowledge about the sample and light source is used in CS and MC to reduce the total number of data points. This work was performed in collaboration.<sup>71</sup>

#### 3.3.1 Conventional *s*-SNOM

While s-SNOM has been successful in providing for spectroscopic imaging of molecular and quantum materials with sub-diffraction imaging at the few nanometer scale, conventional data collection approaches are too slow to simultaneously capture highly resolved images over large fields of view. Weak resonances and light sources with limited spectral irradiance further exacerbate this issue as longer integration times are required per voxel within the multi-dimensional spatio-spectral dataset. As additional dimensions are added to s-SNOM imaging, like a delay axis for pump-probe ultrafast time resolved measurements, the time it takes to collect a complete dataset without sacrificing resolution along at least one axis is prohibitively long, requiring up to days. Sampling exactly at the Nyquist limit is only possible when the signal to noise ratio (SNR) is sufficiently high. However, an adaptive sampling method with compressed sampling and matrix completion enables a significant reduction in the necessary sampling rate, while maintaining data fidelity for chemical imaging and physical interpretation. We demonstrate this reduction in sampling rate through the use of complete datasets that were experimentally collected of a wide range of material systems, ranging from biological, to molecular, to quantum. We use these experimental datasets as the ground-truth and then apply deep under-sampling with recovery algorithms to reconstruct the full dataset. This approach demonstrated below is more than one order of magnitude faster compared to conventional *s*-SNOM and is 6 times smaller than the Nyquist limit, enabling a 30-fold reduction when compared to standard (300 nm stage sampling) methods. Compressed sensing and matrix completion with an adaptive sampling algorithm is fully generalizable and allows for high spatial resolution imaging over large fields of view.

Measuring vibrational and phonon resonances in molecular to quantum materials at the nanometer regime can be achieved with s-SNOM.<sup>14,15,106–109</sup> s-SNOM has been advanced to elucidate fundamental nanoscopic interactions that combine together, creating emergent phenomena at the meso- and macro-scopic scales. The combination of fundamental length scales together with the length scales where emergent phenomena occur require an imaging technique that simultaneously resolves nanometer features over micron distances. Conventional s-SNOM (I primarily mean nano-FTIR here, figure 3.7) is performed spatially across a sample (two dimensions: x,y) with spectral resolution, enabled by Fourier transform of an interferogram (one dimension: mirror position). While different imaging techniques exist to retrieve spectral information, the use of broadband IR light sources, like thermal sources, synchrotrons, and pulsed lasers, is ideal for measuring multiple vibrational modes, with the typical trade-off of brilliance for bandwidth. Low repetition lasers are further difficult to use as a sample's exposure to them can cause the sample to degrade or become damaged – reducing the total fluence available, which further limits SNR. The SNR ultimately limits the acquisition rate of s-SNOM, which is compounded for larger multidimensional datasets.

In order to simultaneously image multiple vibrational resonances throughout the mid-IR, the illumination source must be ultra-broad or broadly tunable from  $\sim 400 \text{ cm}^{-1}$  to  $\sim 5000 \text{ cm}^{-1}$ .<sup>110–114</sup> Hyper-spectral imaging time is inversely related to the near-field SNR and can ultimately be days to weeks long.

### 3.3.2 Methods for improving acquisition speed

As mentioned above, alternative methods, like rotating frame, have been introduced; yet, datasets acquired using those approaches continue to have redundancy in the collected data.<sup>70, 115</sup> Previous compressed sensing has shown nano-FTIR acquisition time reduction by  $\sim 70\%$ , where the standard spectral sparsity in the Fourier domain was utilized.<sup>116</sup> However, *s*-SNOM datasets also exhibit spatial redundancy, where additional previous work on spatio-spectral nano-FTIR datasets found reductions of 89 % possible.<sup>117</sup>

Image reduction techniques, while intensively used for other hyperspectral images, have seen limited application for s-SNOM.<sup>118–120</sup> Such examples of hyperspectral problems include the famous movie recommendation problem, system identification in control theory, and global positioning sensors.<sup>121–124</sup> In these approaches, matrix completion has relied on the small number of individual constituents present within a dataset.<sup>125,126</sup> We can apply this chemical species being measured in s-SNOM. We wish to reduce the necessary acquired data without losing physical relevance of the reconstructed data by using an adaptive sampling algorithm specific to the nature of s-SNOM measurements and by using matrix completion and compressed sensing with prior knowledge about, first, the light source, second, spectral sparsity in the Fourier domain, and third, the relatively small number of constituent chemical (or generally resonant) species.

We design a general reconstruction algorithm by optimizing both each penalty enforcing prior knowledge individually and the combination of optimization penalties on concert for each s-SNOM dataset. With these considerations, we are able to reconstruct s-SNOM hyperspectral images with only 3.4% of the original fully sampled data while maintaining data fidelity for physical interpretation. We combine this reconstruction algorithm with an adaptive sampling algorithm that selects mirror positions for each tip sample location. This extends random sampling, which is a universally accepted strategy for compressed sensing and matrix completion.<sup>127,128</sup> This sampling strategy uses an estimate of the normalized envelope of the interferogram center burst and free induction decay (FID) based on the reconstruction of measurements at previous tip-sample locations. This emphasis on the center burst and FID preferentially selects for the highest SNR data points and most relevant data points for Fourier analysis (figure 3.7B).

## 3.3.3 Spatio-spectral imaging

The fully sampled real experimental datasets that we use to study the performance of our smart s-SNOM approach are biological, quantum, and molecular materials.<sup>72</sup> We then sub-sample these ground truth measurements with adaptive sampling and apply the reconstruction algorithm to recover the rest of the data using prior knowledge about the sample and light source.

The high resolution over large field of view requirements for s-SNOM datasets are well suited to the strengths of compressed sampling (CS) and matrix completion (MC). In conventional nano-FITR, a series of AFM tip-sample locations are selected on a sample, typically in a regularly spaced rectangular grid. The sample is then moved under the AFM tip to the spatial position of interest and an interferogram is acquired by scanning a reference mirror. Each point in an interferogram is the data point from the optical interaction for one optical delay between the sample and reference arms. Experimentally, this is accomplished by scanning the reference arm at a constant speed with data points collected at regularly spaced delays with a trigger from the stage or reference arm position sensor.<sup>129</sup> Most of the data collected in an interferogram is redundant and therefore only a small fraction of the total interferogram datapoints are needed, enabling us to only use some of the mirror positions that are conventionally acquired. We use sample and light source prior knowledge to extract the rest of the datapoints.

Features of interest in infrared spectroscopy are generally categorized into two sets: resonant and non-resonant. Resonant features are typically thought of either single Lorentzian responses, or a Gaussian sum of Lorentzians. Non-resonant features of interest in the mid- to far-IR are typically



Figure 3.7: Smart s-SNOM schematic | (A) light source laser L or synchrotron S, beam splitter BS, scanning mirror M on reference arm. Sample on scanning stage under the tip T, point detector Mercury Cadmium Telluride or MCT. Hyperspectral images can be acquired by scanning the mirror and the sample. In case of a 2D grid scan or of a 1D line scan of the sample the final output is respectively a 3D or 2D hyperspectral image. If the sample is not moved but only the mirror is scanned the final output is a 1D spectrum. B) Diagram of smart s-SNOM. Our contribution: smart sampling system, provides a list of positions of the scanning mirrors for each sample point and reconstruction algorithm, to estimates the value of the missing data and hence recreates a fully sampled hyperspectral image X. At each new spatial position of the sample an intermediate reconstruction is calculated in order to evaluate an averaged envelope  $\overline{\mathcal{H}(X)}$  of the interferograms.  $\overline{\mathcal{H}(X)}$  is normalized and used as a random distribution to select the mirror positions for the next sample position.<sup>71</sup>

represented by the broad Drude response. Here, we restrict our analysis and application to spectrally significant resonant responses coming from either molecular vibrations or lattice phonons. In either case, the identity and environment dictate the frequency of the resonance. Each interferogram, taken at a selected tip-sample location, represents the optical response from a collection of species, which, upon Fourier transform, gives a sum of the vibrational spectra of the underlying species. Resonances in spectra are sparse, meaning only the spectral peak frequencies yield a non-zero signal. Their resonant nature further limits the bandwidth of non-zero values. Using the concepts of compressed sampling, the total number of necessary mirror positions in nano-FTIR can be reduced,<sup>116,117</sup> where established acquisition and reconstruction techniques are used.<sup>130–132</sup> The underlying principles of compressed sensing though requires 1) sparsity of the data in a domain distinct from the acquisition domain (how else could sampling be increased other than simply measuring where the signal is in the original domain) and 2) mathematical incoherence (each interferogram data point depends on the corresponding sparse domain data point differently) of the sensing matrix. The sensing matrix here is the combination of random sampling and the Fourier transform, which has previously been shown to be incoherent.<sup>133</sup> With these conditions satisfied, CS can be used on in the spectral (interferogram) dimension.

### 3.3.4 Compressive sensing and matrix completion

A further, and stronger for pulse laser sources, sparsity comes from the limited bandwidth of the light source relative to the entire domain of the Fourier transform. *s*-SNOM in the rotating frame has already demonstrated how this prior knowledge can be used to greatly reduce the number of necessary data points in the mirror dimension, but applied this knowledge in a fundamentally distinct way from CS.<sup>70</sup> At frequencies where the light source fluence is negligible, the spectrum values are effectively zero. Therefore, the spectrum can be truncated around the known frequency range of interest, increasing the compression factor and computation speed.

In addition to the sparsity that is used for CS, we know the number of individual elements giving rise to a resonant response is limited, which implies the measurement matrix will have a small rank. This assumption becomes stronger for larger data sets where more spatial points are collected. With a linear mixing model (where individual spectra add together with variable amplitudes), the rank of the measurement matrix is smaller than the number of chemical species contained within the sample at the measured locations. One caveat here though, is the spectral shifting that occurs from environmental effects, which effectively then are new chemical species, increasing the rank of the measurement matrix. The hyper-spectral image data collected with *s*-SNOM are consistent with a generative model, which are still approximately low rank.<sup>134</sup>

MC works by completing matrices with a penalty related to the low rank assumption.<sup>125,126</sup> To implement MC, the *s*-SNOM data set, which is 3 dimensional, is flattened into a 2 dimensional form, where the interferogram axis is along rows and each column is a tip-sample location. The data is sub-sampled here along rows, which correspond to the mirror positions and the remaining data can be used to recover the original data since the matrix has a low rank.

## 3.3.5 Adaptive sampling

The full field of view can be recovered from a smaller dataset by using redundancies intrinsic to the s-SNOM data. However, s-SNOM data has the most variation (and therefore least amount of sparseness) near the center-burst (maximum interference between sample and reference arms). This can additionally be used to improve the compression factor by weighting the probability of data sampling to the envelope of the interferogram, emphasizing the center-burst and FID. While the qualitative nature of the interferogram envelopes is consistent, depending on the light source and sample, the range of interferogram envelopes can be quite large. We therefore propose using a periodically updated envelope function that uses prior measurements to inform future measurements. To do this, the first tip-sample location uses a flat distribution so that random points along the interferogram axis are selected without bias. For this first spatial point, we use a conservative Nyquist number of randomly sampled points with the sparsity assumption (CS) to recover the full interferogram. We then move to the next tip-sample location and use the previously recovered interferogram to build the envelope function that will serve as the basis for the probability distribution for the next random sampling. We continue doing this for each next spatial point, where the average of the all previous interferograms and continually reduce the sampling rate so that the final compression factor is achieved.

This is implemented by moving the scanning mirror (figure 3.7) to the positions chosen by the smart s-SNOM and adaptive sampling algorithm. We apply this algorithm to the fully sampled data, simulating its implementation in practice. We then compare the recovered results with the ground truth through a mean square error calculation to determine the accuracy of the reconstruction. A more physically minded approach is to compare the resonant center frequencies of interest to determine data fidelity. We enforce a quadratic norm criterion that must be minimized while simultaneously adding a sparsity and low rank penalization. We therefore have a convex optimization criterion with two tunable parameters  $\lambda_1$  and  $\lambda_*$  based on sample type and light source. This criterion is minimized using a previously established algorithm.<sup>135</sup>

#### **3.3.6** Reconstruction algorithm

The generalized forward-backward algorithm that minimizes the quadratic norm, sparsity, and low rank penalizations enables the reduced number of necessary data points, while maintaining meaningful physical information. We represent the entire dataset in a sparse matrix form  $\tilde{X}$  by truncating an applied Fourier transform along the interferogram axis (rows). An optional wavelet transform along the columns can be used to enforce spatial sparsity.

$$X = W X F, (3.5)$$

where W and F are matrices performing a 2D wavelet transform and a truncated 1D Fourier transform respectively. This model is the Kronecker compressive sensing model.<sup>136</sup>  $\Phi$  is an n by n orthonormal matrix that represents the linear transform between the sparse domain and the measurement domain. The incoherence is measured by  $\mu = \sqrt{n} \max_{i,j} |\Phi_{ij}|$ .<sup>137</sup> The sparsity and incoherence conditions required by CS are thus satisfied here.<sup>136</sup>

We define the measured samples as y, such that

$$y = S \left( W^{\dagger} \otimes F \right) \quad \vec{wX} \tag{3.6}$$

with the Kronecker product  $\otimes$  and the sampling matrix S composed of 0 and a single 1 per line at the selected sample positions.

In general, s-SNOM is applied to a wide range of sample types, each with distinct spectral features that require independent tuning of our penalization parameters (figure 3.8). The sample types considered here are biological, molecular, and quantum. The light source used to measure each sample also affects the parameter tuning and we therefore use ultra-broadband synchrotron light (from the Advanced Light Source – ALS – in Berkeley) and broadband pulsed laser sources. The main contribution to the sampling strategy comes from the bandwidth of the light source, where the signal from broadband synchrotron light means the interferogram domain is already approximately sparse. Therefore, we naturally anticipate better compression performance on data collected with a pulsed laser.

# 3.3.7 Comparison to original measurements

We now define a reduction factor R as the ratio between the number of data points for the fully sampled dataset and the number of datapoints needed by smart s-SNOM in order to quantify the compression. While this is technically representative of the compression, ground truth measurements (normal conventional s-SNOM measurements) over-sample the maximum Nyquist cutoff frequency (smaller mirror steps) and also over-sample the spectral domain resolution (sample beyond optical interaction between sample and reference arm). Therefore, a more honest comparison is between the minimally sampled acquisition rate (Nyquist sampling) only over the range of optical interference and the smart s-SNOM sampling rate, which we define as the compression factor CF. While this is more honest, the experimental implementation of Nyquist sampling leads to a significant drop in the quality of the collected spectrum (which is why it isn't done in the first place), which is an unfair comparison to the smart s-SNOM results. The experimental measurements performed here are previously described for both synchrotron IR nano-spectroscopy (SINS) and laser based nano-FTIR.<sup>72</sup> For the most robust interpretation of the application of smart s-SNOM, we test against these two types of lights sources and 3 materials representing biological, molecular,

and quantum systems.

A SINS measurement on 400 nm thick  $\gamma$ -globulin, referenced to Si is shown in figure 3.8A.<sup>72</sup> The difficulty of measuring multiple resonant features with a low brilliance light source is highlighted with this example. Figure 3.8A shows the characteristic amide I,II, and III resonances of secondary protein structure present in  $\gamma$ -globulin. The entirety of this dataset is a single tip-sample location, meaning spatial redundancy and the low rank assumptions cannot be implemented. To compress this data, we use the sparsity of the spectrum and the known bandwidth of the light source, yet are unable to achieve a compression factor greater than 1, with a reduction factor of 17.

In contrast, figure 3.8B shows a nano-FTIR dataset measuring oriented PTFE with a Au reference. While the complex valued spectra are typically preferred to be viewed in terms of amplitude and phase, when the oscillator strength is appreciably strong, yielding a phase shift more than  $\sim 30$  %, real and imaginary spectra are preferred. The strong oscillators in PTFE, with phase amplitudes significantly over  $\sim 30$  % necessitate plotting real and imaginary values as the approximation between phase and imaginary through the small angle relation is no longer valid. This dataset, which includes multiple tip-sample locations, is compatible with the low rank prior, which is combined with the sparsity assumption to yield a compression factor of 4, indicating smart *s*-SNOM's capabilities for PTFE samples. The effect of compressed sensing and matrix completion individually are demonstrated in figure 3.9 and the extracted PTFE peak extraction under compression strength is shown in figure 3.10.

We now transition from strong molecular vibrations for chemical identification to a molecular vibration that is used to perform nano-crystallography through spectral analysis with the example of a metal carbonyl compound (2,3,7,8,12,13,17,18-Octaethyl-21H,23H-porphine ruthenium(II) carbonyl). The physical analysis performed on the spectra acquired with nano-FTIR is based on the splitting of  $\omega_0$  into  $\omega_-$  and  $\omega_+$  as the metal carbonyl crystalizes (figure 3.8C). The  $\omega_-$  and  $\omega_+$ resonances are close, complicating slight frequency differences in the full dataset that must be extracted from the sub-sampled dataset, yet a reduction factor of 4 is still achievable, indicating that smart s-SNOM faithfully reconstructs spectra for detailed analysis and can therefore be extended beyond simple chemical mapping.

The final example shown here represents a low brilliance light source again (ALS synchrotron radiation) to image an SiO<sub>2</sub> phonon mode. In contrast with the  $\gamma$ -globulin example described above, this dataset has multiple tip-sample locations in the form of a linescan. The spatial redundancy here enabled a much more significant reduction factor of 30 (compression factor of 6.5), even though the bandwidth of synchrotron radiation is extremely broad and the previous attempt at spectral sparsity did not yield significant results. The broad bandwidth, and therefore fast center-burst and FID highlights the importance of the adaptive sampling strategy, where we preferentially select data points where the interferogram has the most variation (figure 3.8D).

We now compare spectra in Fig. 3.8B the evenly sub-sampled and reconstructed dataset with the adaptive sub-sampled and reconstructed dataset, where we see an obvious improvement in the reconstruction fidelity. The broad range of material responses (with varying resonances) together with the light source used for each measurement in Fig. 3.8 shows how the envelope sampling strategy, while important, necessitates periodic updating to ensure the correct sampling distribution is implemented. The selected datapoints are shown in Fig. 3.8D (red crosses), where the majority are in the center-burst and FID regions. Seeing as the rest of the interferogram is flat (and therefore offers little in terms of non-redundant data), the selection is minimized. The single tip-sample location dataset used in Fig. 3.8A uses a flat distribution as previously discussed.

One metric for evaluation between the ground truth and reconstructed datasets is the relative mean square error (RMSE). The RMSE increases as the compression is increased and the example of PTFE with CF of 1, 10, 20, and 30, the RMSE is shown in Fig. 3.9. If only one spatial point is used, the RMSE is larger than if a full spatio-spectral dataset is used as additional redundancy from the spatial domain can be used to help reconstruct individual spectra. The RMSE for the PTFE dataset sub-selected to a single spatial point for the CF from Fig. 3.9 are 0.019, 0.0197, 0.440, and 0.794. As expected, the optimal parameter nuclear norm penalty is 0 as there is only one spatial point. Removing the  $\ell_1$  norm penalization results in an expected RMSE increase to 0.0185, 1.42, 1.53, 1.6 respectively. This improved reconstruction with agrees with previously reported



Figure 3.8: Application of smart s-SNOM to different materials systems (biological, molecular, and quantum), different light sources (Laser, ALS synchrotron) and different spatial scanning (single point, line and 2D scan) | Fully sampled datasets acquired experimentally (Blue curves). Mirror positions selected by our adaptive sampling strategy (Red crosses). Reconstructed spectrum in amplitude / phase or  $|A(\bar{\nu})|/\Phi(\bar{\nu})$  and real / imaginary part or  $Re(A(\bar{\nu}))/Im(A(\bar{\nu}))$  (Red and Black dotted curves respectively). For the PTFE sample, reconstruction from uniformly sampled measurements without the use of adaptive sampling (Green dotted curves). The reduction factor (R) is respectively 17, 30, 4, 30. The compression factor (CF) is respectively 1, 4, 1.6, 6.5. The regularization parameter called Nuc is respectively 0, 5, 0.75, 0.005. The regularization parameter  $\ell_1$  is respectively 0,  $10^{-6}$ , 0.01,  $4 * 10^{-5}$ .<sup>71</sup>

 $results.^{116,117}$ 

For the case when more than one tip-sample location is used though, the low rank assumption can be imposed, and MC can be effective. The crossover when enough tip-sample locations are used to make MC useful is when the number of distinct chemical species is fewer than the number of spatial locations. To emphasize this turning point, we compare the RMSE of reconstructions as a function of additional data points for a variety of CFs. The RMSE decreases with increasing spatial points (Fig. 3.9A). When used in combination with MC, we see that comparable RMSE can be achieved at higher CF from CS. The reconstruction of a series of linescans of different lengths and RF is shown in figure 3.9B, indicating MC's effectiveness with strong molecular oscillators. We further note that 6 spatial points is sufficient to demonstrate an advantage when using MC for PTFE, implying the number of distinct chemical species is quite small indeed (Fig. 3.9C).

In contrast to the holistic measure of RMSE, the extraction of physically relevant parameters for a resonance, like peak position, linewidth, and amplitude is sufficient. Quite often in nano-FTIR, one or a combination of these parameters is interpreted as physically meaningful to make conclusions about underlying physical phenomena at the 10s of nanometer scale, or less like in molecular rulers. Continuing with the PTFE example, the peak position of the symmetric (at  $w\nu_1 = 1168 cm^{-1}$ ) and antisymmetric (at  $w\nu_2 = 1241 cm^{-1}$ ) modes are of interest for coupling analysis. The ability to extract these values at different reduction factors is demonstrated in figure 3.10A, where the color map indicates the resonance parameter and the x and y dimensions are the location across the sample surface at increasing RF (1, 10, 30). Parameters extracted from the ground truth measurement are shown for comparison on top. The estimate of peak positions seems to be faithful at RF  $\leq 100$ , but the standard deviation increases dramatically with RF. R = 30yields reconstructions that are still sufficient for physically meaningful interpretation. A final effect of the algorithm employed here is a denoising effect, where noise is rejected by the algorithm based on redundancies within the data, as noise is evenly distributed in the Fourier domain, where the sparsity assumption is enforced. Further, noise is inherently not of low rank and is therefore further minimized by MC.

The choices made here in designing our algorithm for smart *s*-SNOM build on previous advances within the broad field of hyper-spectral image signal processing. Below, we motivate the choices made both in and out of favor as well as how our approach has its limitations.



Figure 3.9: Illustration of the effect of law rank assumption on the reconstruction error. | We use a PTFE 2D grid scan to emulate an acquisition of different sized line scans with 10, 20, and 40 pixels (see blue line corresponding to the image of panel B). A) Plots of relative mean square error as a function of the number of spatial points for different reduction factors. The largest quality improvement occurs between 1 and 6 spatial points. This can be different for other samples with a higher diversity of chemical species. B) For each number of points used, different reduction factors are emulated: 10, 20 and 30. The ground truth is plotted in blue and the reconstructions in red. At a given reduction factor the visual quality of the reconstruction improves with the number of spatial points sampled. C) Illustration of the principle of matrix completion. Each color red, green, and blue corresponds to one chemical species with a specific spectrum. Those images are separable in space (x, y) and frequency  $(\nu)$  and are therefore considered rank one images. In the case of a linear mixing model, the final hyper spectral image is a sum of a few (rank one) of these images if the number of chemical species is small in the sample. This explains the small rank assumption on hyperspectral images. (Taken from collaboration with<sup>71</sup>)


Figure 3.10: Extraction of physically relevant information from resonance peaks at different reduction factors. | A) Characterization of the two spectral peaks of the PTFE sample located at  $\nu_1 = 1168 \ cm^{-1}$  and  $\nu_2 = 1241 \ cm^{-1}$ ). Each stack corresponds to 3 images obtained from reconstruction at different reduction factors (from top to bottom respectively 1, 10 and 30). Each peak is characterized by its estimated position  $\nu'$ , amplitude  $|A(\bar{\nu}')|$ , phase  $\Phi(\bar{\nu}')$  and full width at half maximum FWHM. B) Plot of the relative mean square error between reconstruction and ground truth in red. Plot of the localization of the two peaks in blue as a function of the compression factor (top axis) and to the reduction factor, leading to potential physical misinterpretation of the reconstruction for high reduction or compression factors. (Taken from collaboration with<sup>71</sup>)

# 3.3.8 Further improvements

We start by considering the spatial redundancy within s-SNOM measurements, where most samples of interest are composed of chemical species organized in finite domains, rather than being randomly distributed. Finite domain images are known to be sparse in the wavelet<sup>138</sup> and 2D Curvelet domains with the additional constraint of smooth boundaries.<sup>139</sup> The addition of either of these transforms would naturally be implemented in the CS application of smart *s*-SNOM.<sup>140</sup> Combining CS in the spectral domain with these spatial transforms combines to be an example of CS referred to as Kronecker CS.<sup>136</sup> In a rare example of a sample with very sparsely located chemical species, imaging in the spatial domain (as is conventional), neither the wavelet nor curvelet transform would yield a sparse image as the source domain is already sparse. While the implementation of these additional transforms could, in principle, yield further CF and RF, the additional transform and reconstruction for each mirror position limits its applicability as both an additional assumption is made about the sample is made and the computational time cost grows substantially. We therefore only recommend this combination if the sample is known well enough and the computational power is sufficiently high.

A common assumption within the field of information theory and reconstruction algorithms is the positivity criterion. While the detected optical signal is necessarily positive, the total signal is demodulated at higher harmonics of the tip tapping frequency to isolate the near-field contribution based on the non-linear dependence of the near-field signal with tip-sample distance. Since each tip-sample location measurement comes from this demodulation, positivity can not be enforced.

The CF and RF presented here represent the amount of data that needs to be collected for comparison to the ground truth, but a practical implementation of how to scan the reference mirror quickly to these points, while maintaining SNR has thus far not been addressed. Specifically, a comparable tip-sample list with intermediate reference arm scanning can be used if the reference arm is selectively accelerated to minimize time between smart *s*-SNOM selected points of interest. An alternative is to optimize the total tip-sample-reference arm position list for maximum speed. While the practical implementation has not yet been demonstrated, the significant reduction in necessary data points shows promise for future implementation.

We next comment on the MC enforcement of low rank, where this prior knowledge or assumption reduces the number of necessary data points to complete missing entries in a matrix. The standard technique is to apply the nuclear norm  $\|\cdot\|_*$  penalization,<sup>128</sup> which is effectively the *l*1 norm of the matrix's singular values. We minimize the convex criterion to allow for both the CS and MS penalizations and use a convex criterion to minimize, enabling us easily to incorporate penalizations used in CS and MC:

$$J(wX) = F(wX) + G(wX)$$
(3.7)

$$F(wX) = || S \left( W^{\dagger} \otimes F \right) \operatorname{vect}(wX) - y ||^{2}$$
(3.8)

$$G(wX) = \lambda_1 \| wX \|_1 + \lambda_* \| wX \|_*$$
(3.9)

where we tune both  $\lambda_1, \lambda_*$  for the  $\|\cdot\|_1$  and l1 penalizations, similar to previous work.<sup>141</sup> The sparsity and low rank of the reconstructed dataset is enforced using the  $\ell_1$  and  $\ell_*$  norm, but other penalizations can be applied.



Figure 3.11: Error as a function of parameter settings for two different samples: PTFE and Amide. | Light sources are a laser and the synchrotron, respectively, to illustrate the estimator behavior for two different spectral sparsities. Colors represent reconstruction errors, spatial coordinates correspond to  $(\lambda_1, \lambda_*)$  parameter settings. Color saturates to pure yellow for error values bigger than the error obtained with  $\lambda_1 = 0$  and  $\lambda_* = 0$ . This way region where errors are reduced are more visible. The red circle indicates optimal settings, we observe that region around optimal settings gives similar errors. We observe that tuning the parameters is easy and does not necessarily need to be optimal to obtain relevant reconstructions. (Taken from collaboration with<sup>71</sup>)

However, introducing additional norms requires additional parameter tuning, which may or may not be helpful in overall CF/RF while maintaining data fidelity. For instance, in our example of 2 parameter tuning, we can balance the strength of sparsity and low rank through  $\lambda_1$  and  $\lambda_*$ . These effect of these parameters is shown though the RMSE in figure 3.11, with blue showing smaller reconstruction error than when no penalization is used.

### 3.3.9 Conclusion

We have demonstrated success in applying CS and MS to s-SNOM datasets. We implemented prior knowledge about the light source and sample characteristics along with an adaptive sampling strategy to reduce the number of necessary data points to be collected in a s-SNOM experiment. We have demonstrated impressive compression and reduction factors, improving on other advancements in improving s-SNOM data acquisition rates. We note that the performance demonstrated here improves with larger datasets, both in spatial extent (more spatial positions) and in spectral resolution (interferogram extent) as more redundancies are present. We further predict the addition of additional data axes, like time resolution for ultra-fast time resolved s-SNOM, likely dramatically further increases smart s-SNOM's performance. Smart s-SNOM therefore enables nanoscale measurements over large fields of view and can be extended to higher dimensional datasets.

# 3.4 Heterodyne Pump Probe *s*-SNOM

Finally, in this section, I will detail advancements made in near-field pump-probe ultrafast spectroscopy and imaging. Ultrafast carrier dynamics have been accessed through infrared nanoimaging in semiconductor, correlated-electron, and polaritonic materials. The contrast obtained in conventional approaches has remained too low for important weak and long-lived excitations when high repetition rate lasers are used for excitation in systems like, e.g., low-conductivity carriers, lattice phonons, and molecular vibrations. In an effort to improve the contrast, we demonstrate pump-modulated ultrafast excitation for infrared nano-imaging and -spectroscopy to fully and quantitatively characterize electron and vibration dynamics in space, time, and frequency. We use transient vibrational nano-FTIR to spatially resolve the excited-state polaron-cation coupling in lead halide perovskites to characterize the full dielectric response, on which the photovoltaic performance depends. This demonstrates the power of heterodyne pump-probe nano-imaging to image elementary processes in quantum and molecular materials. This work was performed in collaboration.<sup>69</sup>

# 3.4.1 Ultrafast phenomena

The unique optical and electronic properties of functional materials can be applied to applications including technologies based on quantum phase transitions in Mott transistors,<sup>142, 143</sup> photovoltaic carrier transport with polarons in lead halide perovskites,<sup>144, 145</sup> singlet fission driven by coherent phonons and vibrations,<sup>146–149</sup> and light-harvesting complexes based on electronic energy transfer.<sup>150</sup> The interplay of elementary electronic, vibrational, and phononic quantum states give rise to these emergent properties. Ultrafast spectroscopy is able to isolate the individual responses of mode-coupling and competing interactions by exciting the system through one degree of freedom and probing the dynamic response that is normally convolved in static spectroscopy.<sup>151–154</sup> New photoinduced quantum states are formed when the system is strongly perturbed and allow for the ultrafast control of polaronic, metallic, and superconductive charge carrier functionaliteis.<sup>155–157</sup> Extreme nonlinear optical phenomena from strong and ultra-short laser fields enable applications like high harmonic generation<sup>158, 159</sup> and light-field petahertz electronics.<sup>160, 161</sup>

Naturally, systems based on these sort of materials will exhibit spatial heterogeneity from lattice defects, grain boundaries, non-uniform doping, and strain.<sup>30, 162–166</sup> Therefore, a variety of time resolved nano-imaging techniques have been previously developed, like, e.g., ultrafast transmission microscopy (TEM),<sup>167, 168</sup> X-ray microscopy,<sup>169</sup> and electron emission microscopy (PEEM).<sup>170</sup> However, these approaches are not sensitive to the low-energy electron lattice coupling that dictate material and device behavior.

# 3.4.2 Ultrafast near-field

The recent implementation of ultrafast scattering scanning near-field optical microscopy (s-SNOM) contrasts with these more established techniques by probing the associated low-energy processes directly.<sup>11, 13, 105, 171–181</sup> Ultrafast nano-FTIR has,<sup>11, 173</sup> in particular, given access to carrier dynamics in a range of semiconducting,<sup>11, 175, 177</sup> polaritonic,<sup>174, 176</sup> and correlated-electron materials,<sup>171, 173</sup> together with electro-optic sampling (EOS),<sup>177</sup> to resolve spatial heterogeneity in the temporal dynamics and spectral differences and evolutions. To date, ultrafast infrared nano-imaging has only probed strong and short-lived collective excitations based on low-energy (high repetition rate > 10 MHz) laser sources, which naturally yield high SNRs. This of course though leaves out the ability to probe long-lived transient states and those that need a strong pump to, e.g., induce a phase transition or probe vibrational coupling in molecular materials. Resolving the full spatial, temporal, and spectral degrees of freedom has only recently<sup>175, 176</sup> been achieved with low-repetition excitation and therefore necessitates a generalized approach to enhance the contrast for these limited SNR applications.

Here, heterodyne visible pump infrared probe s-SNOM (HPP IR s-SNOM) has been demonstrated with a low repetition-rate laser to measure space, time, frequency, and phase degrees of freedom. In this approach, the system is excited with an optical pump and this transient excitedstate is probed with a low-energy pulse to determine the electronic and vibrational response. We use simultaneous sideband lock-in detection to isolate the induced third-order nano-localized polarization and extract interferograms in the time-domain to nano-image the ultrafast excited state for a variable excitation rate. The scheme of modulating the excitation in HPP IR s-SNOM directly resolves the transient response and is spectrally resolved such that quantitative modeling can extract the dielectric function of the material in its transient state. A combination of the finite dipole model and a four-layer reflection model is used.

As a representative example of soft molecular material transient nano-spectroscopy and imaging, we apply this technique to image the polaron-cation coupling in a triple cation perovskite that controls the photovoltaic response.<sup>182,183</sup> The low-repetition-rate excitation, together with high sensitivity detection, enables the study of long-lived vibrational responses in a soft molecular material. Therefore, the approach detailed here can be used to study elementary processes at the nanoscale that control the optical, photophysical, catalytic, and electronic properties of many functional materials.



#### 3.4.3 Experimental implementation

Figure 3.12: Heterodyne pump-probe nano-imaging | **A.** HPP IR *s*-SNOM, with the ~185 fs optical 1.2/2.4 eV (1030/515 nm) pump excitation, ~170 fs tunable mid-IR 0.12-0.25 eV (5 - 10  $\mu$ m) probe, and interferometric heterodyne near-field detection. AOM - acousto-optic modulator, DFG difference frequency generation, OAP - off-axis parabolic mirror, OPA - optical parametric amplifier, Osc. + RA - oscillator and regenerative amplifier laser system. **B.** Far-from-equilibrium excitation followed by mid-infrared probe of the transient low-energy vibrational and electronic response coupled to the excited state. **C.** The tip-localized time-domain signal of  $\Delta E_{\rm NF}(\bar{\nu})$ , from which the pump-induced change in the nano-localized complex dielectric function  $\Delta \tilde{\epsilon}_{\rm NF}(\bar{\nu})$  is retrieved with spatio-temporal-spectral resolution. **D.** Sideband-demodulated pump-probe interferogram  $\Delta I(t,T)$ for a Ge reference sample. **E.** *T*-dependent pump-probe transients from two different  $E_{\rm LO}$  phase values  $\Delta I(\phi = 0, T)$  and  $\Delta I(\phi = \pi, T)$ , the derived frequency-averaged heterodyne pump-probe amplitude relaxation  $R_{\rm HPP}(T)$ , and the self-homodyne pump-probe signal relaxation  $\Delta I_{\rm SHPP}(T)$ . Inset: tip-enhanced pump excitation in nano-localized probe volume, leading to faster relaxation from higher excited carrier density. (Taken from collaboration with<sup>69</sup>)

The schematics of HPP IR s-SNOM are shown in figure 3.12A-C. Here, a femtosecond Yb:KGW amplified laser ( $\sim$ 185 fs FWHM pulse at 1030 nm with a  $\sim$ 1 MHz repetition rate – Pharos, Light Conversion) pumps an optical parametric amplifier, producing, with difference frequency generation (DFG) between the signal and idler pulses, broadband infrared light. The shortest time intervals that can be resolved result from the cross correlation between the visible pump and infrared probe. The spatial resolution for nano-imaging and -spectroscopy is primarily given by the radius of the tip and is approximately 40 nm. Spectral resolution is achieved by following previously established techniques.<sup>73,112</sup> The atomic force microscope (AFM) used here (Innova AFM, Bruker) is placed in the sample arm of the asymmetric Michelson interferometer and is operated in intermittent, or tapping, mode, where the tip (ARROW-NCPt, NanoAndMore USA) is driven with a tip tapping frequency  $\omega_t$ . Time resolution T is achieved by spatially delaying the pump relative to the probe with a linear delay stage, which precedes and acousto-optic modulator (AOM) or mechanical chopper that modulates the pump excitation frequency  $\Omega_M$ . An off-axis parabolic mirror (NA = 0.45) focuses both the pump and probe light onto the tip apex. Figure 3.12B shows the detected excited-state absorption and corresponding ground state bleach by amplifying the near-field signal  $E_{\rm NF}$  with the reference field  $E_{\rm LO}$  detected with a mid-IR HgCdTe (MCT) detector. Lock-in (HF2LI, Zurich Instruments) demodulation is performed at  $n\omega_t$  (n = 1, 2, 3...) for near-field localization and background discrimination.<sup>73,112</sup>

The Yb:KGW amplified laser output (7  $\mu$ J) is split with ~6.5  $\mu$ J pumping the OPA, which generates signal and idler outputs that are then collinearly focused in a GaSe crystal, generating mid-infrared pulses via difference frequency generation that are tunable from 5-10  $\mu$ m with a typical pulse energy of ~ 40 nJ, which is used as the probe in our pump-probe near-field measurements. Simultaneously, 0.5  $\mu$ J is used either at its fundamental wavelength  $\lambda_{pump} = 1030$  nm or frequency doubled wavelength  $\lambda_{pump} = 515$  nm, which is generated by second-harmonic generation in a 2 mm-thick BBO crystal (CASTECH). The pulse duration of the pump is characterized by SHG auto-correlation (FROG) to 185 fs (FWHM intensity) with a 0.1 mm-thick BBO crystal (Figure 3.13A). The pump-probe cross correlation duration of 170 fs is determined by third-order SHG-DFG XFROG with a 0.3 mm-thick GaSe crystal (Figure 3.13B).

The direct detection of the excited minus ground state response is enabled by excitation modulation and simultaneous sideband detection at  $n\omega_t \pm \Omega_M$ , which builds on previous pump un-modulated schemes<sup>11,177</sup> that measure the sum of both the ground and excited state responses. The extraction of the time resolved response in this previous implementation is only possible for



Figure 3.13: Ultrafast pulse characterization | **A.** SHG intensity auto-correlation (FROG) of the 1030-nm pump pulse. **B.** Third-order SHG-DFG cross-correlation (XFROG) between the 1030-nm pump pulse and the 6000-nm probe pulse. Insets, left - nonlinear optical pathway for each signal. Insets, right - frequency-resolved optical gating (FROG) trace.<sup>69</sup>

systems that have a large excited state contrast. The SNR of this detection scheme is significantly improved and the spectra that are fit with an appropriate sample and tip interaction model are now quantitatively accurate, enabling spatial, temporal, and spectral resolution to fully characterize the full 4D transient material response.

We control the pump-probe delay by directing the pump beam to a 20 cm translation stage (SLLA42, SmarACT) fitted with a retroreflector (UBBR2.5-1S, Newport). As previously mentioned, a mechanical chopper (MC2000B, Thorlabs) or acousto-optic modulator (AOMO 3110-120 442-633 NM, Gooch & Housgo) operating at  $\Omega_{\rm M} \sim 3$  kHz ( $\lambda_{\rm pump} = 1030$  nm) and  $\Omega_{\rm M} \sim 50$  kHz ( $\lambda_{\rm pump} = 515$  nm) respectively. We then collinearly combine the pump with the mid-IR probe and steer them into an asymmetric Michelson interferometer. One arm is a reference arm containing mesh filter attenuators and scannable precision translation stage (ANT95-50-L-MP, Aerotech; or SLC1760, SmarACT) fitted with a reference mirror, generating TTL pulses every 300 nm of motion to trigger lock-in amplification sampling. The other interferometer arm contains the AFM (Innova, Bruker) and sample, where *p*-polarized pulses are focused with an off-axis parabolic mirror (NA = 0.45) onto the apex of a PtIr-coated metallic tip (ARROW-NCPt, NanoAndMore USA). The tip tapping frequency of  $\omega_{\rm t} \sim 250$  kHz with amplitude  $z_{\rm A} = 60 - 70$  nm periodically enhances the near-field signal, which then scatters and combines with the reference arm light to be focused into a HgCdTe detector (KLD-0.1-J1, Kolmar Technologies) after going through a germanium long pass filter to block pump scattered light.

The voltage signal from the MCT is fed into a lock-in amplifier and is demodulated at  $n\omega_t$ with the reference frequency coming from the tip feedback laser quad photo diode. To improve SNR, we demodulate at  $n\omega_t + \Omega_M$  and  $n\omega_t - \Omega_M$ , which corresponds to the near-field pump-probe excited state minus the near-field ground state. We simultaneously collect the conventional second harmonic signal as well so that ground state properties can simultaneously be compared to the transient response.

Specifically, germanium is often used as a reference sample, where we pump above the bandgap and probe the photocarriers produced by taking an interferogram  $\Delta I_{\text{HPP}}(t,T)$  at a selected pump-probe timing. The overall spectrally integrated time domain response is determined by scanning the pump probe delay at the zero phase difference (ZPD) reference arm position and at the  $\pi$  phase difference position and subtracting the resulting time traces, yielding the ultrafast heterodyne amplified temporally resolved decay (figure 3.12E). In germanium the ultrafast spectral response is dominated by the Drude response of the free carriers injected upon pump excitation.<sup>184</sup> The extremely broad nature of the Drude response in comparison to the probe bandwidth (~100 cm<sup>-1</sup> FWHM) implies the heterodyne transient response can be approximated by the two phase locations of the reference arm.

The recombination of photoinduced carriers that lead to the HPP signal decay  $R_{\text{HPP}}(T)$  (red) is clearly different than the self-homodyne decay (blue) where there is no interference. Specifically, the self-homodyne decay shows a previously far-field observed initial rise and slow decay,<sup>184</sup> whereas the heterodyne  $R_{\text{HPP}}(T)$  decay shows a clearly faster recovery. The convolution of the timedependent far-field phase unresolved background  $\Delta I_{\text{SHPP}}(T)$  causes this difference.<sup>105</sup> The nearfield enhanced pump leads to a higher carrier density generation at the tip location compared to the far-field background (Figure 3.12E inset). Since  $R_{\text{HPP}}(T)$  is background free, the faster relaxation reflects the faster recombination and scattering associated with the higher carrier density. Clearly, interferometric heterodyne detection with pump-modulation and sideband amplification is needed to quantitatively resolve transient dynamics in the high fluence regime and when the dynamics are pump fluence sensitive.

The spectrally integrated relaxation  $R_{\text{HPP}}(T)$  is estimated by recording the dynamic relaxation with reference arm at two phase values, specifically  $\phi = 0$  and  $\phi = \pi$ , which works well for broadband, instantaneous responses, like the Drude response in, e.g., semiconductors. The timing for the  $\phi = 0$  (constructive interference near the zero-path difference) is independent of frequency, but, technically, the  $\pi$  phase offset is frequency dependent. However, the narrow linewidth of the laser source used yields a  $\pi$  phase shift very close for the lowest and highest frequency components compared to the center frequency for the first half optical cycle near the ZPD. The error for this phase offset is only ~6 % or 0.6 fs in a 10 fs half optical cycle. This discrepancy is below the accuracy of the stage positioning and is therefore negligible. Thus, the two phase reference arm offset is sufficient for extracting the near-field spectrally integrated amplitude.

## **3.4.4** Theoretical framework

The pump-induced change in the complex dielectric function of a material is related to the spectrally resolved near-field response that has been evaluated with the point dipole model<sup>177</sup> and lightning rod model.<sup>175</sup> In order to directly model the experimental observable related to our new sideband-demodulated detection scheme for interferogram  $\Delta I_{\text{HPP}}(t)$  based on the underlying transient dielectric response  $\Delta \tilde{\epsilon}_{\text{NF}}(\bar{\nu})$ , a simple theoretical extension to the finite dipole model<sup>57</sup> and multi layered model (four in this case) is employed (figure 3.14).

To illustrate the application of a vibrational response coupled to photo injected carriers,<sup>183</sup> we study a thin 600 nm film on a thick substrate. Here, ground-state and excited-state dielectric functions  $\tilde{\epsilon}^{(0)}(\bar{\nu})$  and  $\Delta \tilde{\epsilon}_{\rm NF}(\bar{\nu})$  are assumed. Vibrational resonances at  $\bar{\nu}_{\rm gs}$  and  $\bar{\nu}_{\rm ex}$  are indicated in figure 3.14B, where the top layer  $d_1 = 100$  of the sample is excited by the pump and the remaining  $d_2 = 500$  nm is in the ground state. As previously established, the near-field scatter is calculated with and without pump excitation for a sinusoidally modulated tip-sample distance, demodulated



Figure 3.14: Retrieval of transient nanoscale response function | **A.** Theoretical framework to quantitatively relate the measured pump-induced near-field signal change  $\Delta E_{\rm NF}$  to the transient complex dielectric function  $\Delta \tilde{\epsilon}_{\rm NF}$ . **B.** Example ground-state complex dielectric function  $\tilde{\epsilon}^{(0)}(\bar{\nu})$  and its pump-induced change  $\Delta \tilde{\epsilon}_{\rm NF}(\bar{\nu})$  for a model vibrational response, with the ground-state resonance at  $\bar{\nu}_{\rm gs}$  and the frequency-shifted excited-state resonance at  $\bar{\nu}_{\rm ex}$ . **C.** Simulated heterodyne IR *s*-SNOM interferograms for the ground state  $I_{\rm NF}(t)$  and its pump-induced change  $\Delta I_{\rm HPP}(t)$ . **D.**  $E_{\rm NF}(\bar{\nu})$  and  $\Delta E_{\rm NF}(\bar{\nu})$  in frequency-domain, obtained from Fourier transform and  $E_{\rm LO}(\bar{\nu})$  deconvolution of the time-domain interferograms in C. (Taken from collaboration with<sup>69</sup>)

at the second harmonic of the tip tapping frequency. The ground state is then subtracted from the excited state to give the pump-modulated sideband detected result.

The calculated ground-state s-SNOM interferogram is shown in figure 3.14C ( $I_{\rm NF}(t)$  in black). a broadband carrier response and transient vibrational resonance compose the pump-induced response  $\Delta \tilde{\epsilon}_{\rm NF}(\bar{\nu})$ , giving rise to the measured pump-probe interferogram  $\Delta I_{\rm HPP}(t)$  (red). The broadband non-resonant term leads to an instantaneous centerburst, only limited by the probe pulse duration. This is followed by the vibrational free-induction decay (FID)<sup>73</sup> with  $\Delta I_{\rm HPP}(t)$ phase-shifted by the complex nature of the Drude response. We extend the established finite dipole model<sup>57</sup> with a four-layer model (figure 3.15A). Here, the four layers have a frequency dependent complex valued dielectric function, indexed by layer number  $\epsilon_i(\bar{\nu})$  (i = 0, 1, 2, 3). Specifically, the top and bottom layers are given by the dielectric response of air and substrate respectively. Layers 2 and 3 are the sample of interest, with layer 2 in the excited state, with depth given by the pump penetration depth and layer 3 remaining in the ground state. The far-field penetration depth is larger than the near-field localization, so the tip-sample optical interaction is assumed to be only with the excited state. The far-field reflection coefficient contains both ground and excited state optical signals.



Figure 3.15: Modeling parameters | **A.** Parameters defined for modeling the near-field scattering coefficient  $\sigma_{\rm NF}$ , in the ground and excited states, based on the finite dipole and four-layer model. **B**, **C.** Parametrization for computing the ground-state (B,  $\sigma_{\rm NF}^{(0)}$ ) and excited-state (C,  $\sigma_{\rm NF}^{(e)}$ ) near-field scattering coefficients. (Taken from collaboration with<sup>69</sup>)

Here,  $\sigma_{\rm NF}$  as a function of z (tip sample distance) is given by

$$\sigma_{\rm NF}(\overline{\nu}, z) = \alpha_{\rm eff}\{\tilde{\epsilon}_1(\overline{\nu}), z\} \cdot [1 + r_p(\overline{\nu})]^2, \qquad (3.10)$$

where the effective polarizability  $\alpha_{\text{eff}}\{\tilde{\epsilon}_1(\bar{\nu}), z\}$  is calculated with the FDM<sup>57</sup> and  $r_p(\bar{\nu})$  with the four-layer model, which is derived from the matrix transfer method<sup>185</sup>

$$r_p = \frac{r_{01}e^{-i\delta_1}[e^{-i\delta_2} + r_{12}r_{23}e^{i\delta_2}] + e^{i\delta_1}[r_{12}e^{-i\delta_2} + r_{23}e^{i\delta_2}]}{e^{-i\delta_1}[e^{-i\delta_2} + r_{12}r_{23}e^{i\delta_2}] + r_{01}e^{i\delta_1}[r_{12}e^{-i\delta_2} + r_{23}e^{i\delta_2}]},$$
(3.11)

where

$$k_{i} = \frac{2\pi}{\lambda} \sqrt{\epsilon_{i} - \sin^{2} \theta_{0}}$$
  

$$\delta_{i} = k_{i} d_{i}$$
  

$$r_{ij} = \frac{k_{i} \epsilon_{j} / \epsilon_{i} - k_{j}}{k_{i} \epsilon_{j} / \epsilon_{i} + k_{j}}.$$
  
(3.12)

We use  $\theta_0 = 60^\circ$  for the incident angle and  $\sigma_{\rm NF}(\overline{\nu}, z)$  is calculated as the second harmonic of the sinusoidally modulated tip sample distance.

To calculate the sideband HPP signal, the ground-state near-field signal

$$E_{\rm NF}(\overline{\nu}) = \sigma_{\rm NF, \ 2H}^{(0)}(\overline{\nu}) E_{\rm probe}(\overline{\nu})$$
(3.13)

is subtracted from the excited-state near-field signal

$$E_{\rm NF}(\overline{\nu}) + \Delta E_{\rm NF}(\overline{\nu}) = \sigma_{\rm NF, \ 2H}^{\rm (e)}(\overline{\nu}) E_{\rm probe}(\overline{\nu}). \tag{3.14}$$

After deconvolution with  $E_{\rm LO}(\bar{\nu})$ , the Fourier transform of  $\Delta I_{\rm HPP}(t)$  yield the spectral profiles of the photoinduced change  $\Delta E_{\rm NF}(\bar{\nu})$  (figure 3.14D red). The ground-state complex dielectric function  $\tilde{\epsilon}^{(0)}(\bar{\nu})$  is approximated by  $E_{\rm NF}(\bar{\nu})$ , as previously noted.<sup>57,73</sup> But, the complex convolution of the ground and excited state with compounded Fano-type interference between the excited-state carrier and vibrational responses compose  $\Delta E_{\rm NF}(\bar{\nu})$ . We use a Lorentz-Drude model for the vibrational resonance and broadband carrier response<sup>57</sup> to quantitatively retrieve the desired complex dielectric function  $\Delta \tilde{\epsilon}_{\rm NF}(\bar{\nu})$ . Therefore, the fundamental electronic and vibrational dynamics is described by  $\Delta \tilde{\epsilon}_{\rm NF}(\bar{\nu})$ . Fano interference can in general lead to complicated lineshapes in  $\Delta E_{\rm NF}$ , especially when narrow and broadband responses interfere. The theoretical framework developed here are universally applicable for HPP *s*-SNOM.

To isolate the pure ground-state response, we subtract the sideband interferogram from the conventional interferogram. Both the ground-state and excited minus ground-state interferograms are averaged, Fourier transformed, and referenced. We use phase line correction to determine the ZPD and use the same correction on the pump-probe interferogram so that the phase offset between ground state and pump-probe interferograms can be determined, yielding phase-locked spectroscopy that is critical for spectral analysis and fitting.

#### 3.4.5 Ultrafast nano-imaging and -spectroscopy of Perovskite

We applied HPP IR *s*-SNOM to a molecular material exemplified by a lead halide perovskite that can be seen in figure 3.16. Here, the useful optoelectronic response of lead halide perovskites is characterized by the spontaneous formation of long-lived free carriers and their significant diffusion lengths.<sup>186,187</sup> This unique performance has been speculated to be from the formation of polarons, where the charge-lattice coupling through electron phonon interactions across many unit cells that enable long diffusion lengths and coherent carrier transport from the coupling stabilization.<sup>144,145</sup>



Figure 3.16: Polaron-cation coupling in hybrid organic-inorganic perovskite FAMACs | **A.** Polaroncation coupling and associated blue-shift of molecular vibration. **B.** Far-field transmission visiblepump (2.4 eV) IR-probe spectrum at T = 0.5 ps (top), the ground-state (GS) vibrational absorbance  $A_{\rm vib}$  and transient absorbance  $\Delta A_{\rm vib}$  (bottom). (Taken from collaboration with<sup>69</sup>)

Previous work have investigated ground state heterogeneity in lead halide perovskites,<sup>188, 189</sup> yet the underlying polaronic heterogeneity and the non-uniform optoelectronic response that leads to photoluminescence intensity, carrier lifetime, open circuit voltage<sup>164, 188–190</sup> across multiple length scales remains an unexplained relationship. Previous ultrafast infrared vibrational spectroscopy has elucidated the cation polaron coupling in perovskites, yet was unable to resolve and explain spatial heterogeneity<sup>182, 191, 192</sup> (Figure 3.16A). Here though, we aim to address this nanoscale heterogeneity through HPP IR *s*-SNOM (figure 3.17). We first establish the ground- and excited-state vibrational responses of a thin film of triple cation perovskite FAMACs with far-field visible

pump infrared probe in a transmission geometry (figure 3.17b). Here, conventional far-field pumpprobe spectroscopy uses a collinearly propagating pump and probe beams that are focused with a f = 10 cm silver-coated off-axis parabolic mirror onto the sample surface. We collect and collimate the transmitted IR probe with an identical OAP and direct it into an interfermoter for spectral characterization upon detection and isolation with a HgCdTe detector and lock-in amplifier representively. We demodulate he photoinduced change  $\Delta T$  at the pump modulation frequency  $\Omega_{\rm M} \sim 10$  kHz and use a pump fluence of  $\sim 50 \ \mu J/{\rm cm}^2$ . This sample's chemical composition is  $[(FA_{0.83}MA_{0.17})_{0.95}Cs_{0.05}]Pb(I_{0.83}Br_{0.17})_3$ . Based on the pump fluence, focal spot size, and absorption coefficient, we estimate a peak carrier density of  $10^{19}$  cm<sup>-3</sup>, resulting in a broad background as the carriers couple to the lattice and forms a polaron,<sup>183</sup> which couples to the anti-symmetric vibrational stretch mode from the CN group in the formamidinium (FA) cation.<sup>191</sup> Figure 3.17b (bottom) shows the excited-state absorption that is blue shifted and stronger compared to the ground-state. The stronger absorption results from an enhanced transition dipole moment that agrees with previous measurements on similar perovskites,<sup>182,191</sup> which together with the blue shift indicates vibrational coupling to the polaron absorption at a lower resonance frequency, hybridizing the polaron-vibrational state (Figure 3.17A). Quantitatively, the polaron for this type of perovskite has previously been observed at  $1100 - 1200 \text{ cm}^{-1}$ , <sup>183, 192</sup> which with the  $\sim 5 \text{ cm}^{-1}$  blueshift, implies

 $a \sim 50 \text{ cm}^{-1}$  coupling strength.

This blue shift is attributed to coupling with a polaron absorption, previously observed near  $1200 \text{ cm}^{-1183,192}$  and describe the coupling with a simple phenomenological Hamiltonian

$$\hat{H} = \begin{pmatrix} \tilde{\nu}_{\text{pol.}} & J \\ & \\ J & \tilde{\nu}_{\text{vib.}} \end{pmatrix}, \qquad (3.15)$$

where  $\tilde{\nu}_{\text{pol.}} \sim 1200 \text{ cm}^{-1}$  and  $\tilde{\nu}_{\text{vib.}} = 1715 \text{ cm}^{-1}$  are the uncoupled polaron absorption and the molecular vibrational energies, respectively, and J is the coupling constant. Diagonalizing yields

$$\tilde{\nu}_{\pm} = \frac{\tilde{\nu}_{\text{pol.}} + \tilde{\nu}_{\text{vib.}} \pm \sqrt{4J^2 + (\tilde{\nu}_{\text{pol.}} - \tilde{\nu}_{\text{vib.}})^2}}{2}.$$
(3.16)



Figure 3.17: Transient vibrational nano-spectroscopy of FAMACs perovskite | **A.** Ground-state IR s-SNOM Re[ $E_{\rm NF}$ ] imaging (top; AFM topography, bottom). **B.** HPP IR s-SNOM interferogram  $\Delta I_{\rm NF}(t)$  acquired at T = 2 ps with instantaneous polaron absorption and long-lived transient vibrational coherence. **C.** Phase- and frequency-resolved nano-localized pump-probe  $\Delta E_{\rm NF}(\bar{\nu})$  and ground-state response  $E_{\rm NF}(\bar{\nu})$ . **D.** Decomposition of  $\rm Im}[\Delta E_{\rm NF}(\bar{\nu})]$  into the transient vibrational (Im $[\Delta E_{\rm NF, vib}(\bar{\nu})]$ ) and carrier (Im $[\Delta E_{\rm NF, car}(\bar{\nu})]$ ) contributions with a minor feature from Fanotype interference. **E.** The nano-localized transient vibrational signal Im $[\Delta E_{\rm NF, vib}(\bar{\nu})]$  at different sample locations shows nanoscale spatial heterogeneity in the polaron-cation coupling. (Taken from collaboration with<sup>69</sup>)

Here,  $\tilde{\nu}_+$  corresponds to the transient vibrational frequency. Figure 3.18 plots the transient peak shift  $\Delta = \tilde{\nu}_+ - \tilde{\nu}_{\text{vib.}}$  with respect to the varying coupling constant J. The observed peak shift of 5 - 8 cm<sup>-1</sup> in the near-field pump-probe measurement corresponds to a polaron-cation coupling constant of 50 - 70 cm<sup>-1</sup>.

The conventional pump-unmodulated detection and pump-modulated detection is compared in figure 3.19, where the conventional technique exhibits low-frequency noise that obscures the fast dynamics, which are easily seen in the sideband demodulated approach. Further, the conventional



Figure 3.18: Relationship between polaron-cation coupling constant and transient vibrational peak shift | The shift in the vibrational peak position observed in the excited state, induced by the coupling between the polaron absorption and molecular vibration as described in Eq. 3.16 for various coupling constant J. (Taken from collaboration with<sup>69</sup>)



Figure 3.19: Comparison of the excitation modulated and unmodulated detection | **A.** The *T*-dependent near-field pump-probe signal  $\Delta I$  demodulated at  $2\omega_t$  (pump unmodulated) and  $2\omega_t \pm \Omega_M$  (pump-modulated) channels. B. The spectrally resolved near-field pump-probe signal observed at T = 2 ps. While the  $2\omega_t$  channel is dominated by noise, in  $2\omega_t \pm \Omega_M$  channel the peak associated with the transient vibrational resonance is evident.<sup>69</sup>

pump probe spectrum is dominated by noise, whereas the transient vibrational response is easily seen with the sideband technique.

The spatial nanoscale heterogeneity of polaron-cation coupling in perovskite explored here

with HPP IR s-SNOMis summarized in figure 3.17A, where the instantaneous polaron absorption for the interferogram collected with T = 2 ps delay arises from the instantaneous carrier (polaron) response<sup>183</sup> and the long lived narrow resonance results from the coupled transient vibrational mode. We then Fourier transform this interferogram and recover the pump-induced transient vibrational peak at  $\bar{\nu}_{ex}$  in Im[ $\Delta E_{NF}(\bar{\nu})$ ], which is blue-shifted from the ground-state peak position  $\bar{\nu}_{gs}$  in Im[ $E_{NF}(\bar{\nu})$ ] by ~ 5 cm<sup>-1</sup>. This agrees with the far-field observed polaron-cation coupling.

Experimentally, we similarly (to the far-field experiment) collinearize the pump and probe beams, which we then focus to the apex of an AFM tip, located in an enclosure that is purged with nitrogen gas (< 1% O<sub>2</sub>) to suppress photoinduced degradation. We select a 15 by 15  $\mu$ m area to investigate polaron-cation coupling strength heterogeneity by spacing measurements 5  $\mu$ m apart so that each new location has not been dosed with pump to ensure measurements are independent of each other. We perform conventional heterodyne and sideband nano-FTIR at pump-probe delays of T = 2 with ~ 15 cm<sup>-1</sup> spectral resolution. We repeat this 30 times and average to improve SNR. Measurement stability is demonstrated by figure 3.20.



Figure 3.20: Transient vibrational nano-spectroscopy of a lead halide perovskite | **A.** Single  $I_{\rm NF}$  interferograms demodulated at  $2\omega_{\rm t}$  at the beginning and end of 10 minutes of data collection, acquired under constant illumination of the visible pump pulse with pump-probe timing delay T = 2 ps. Both interferograms are not normalized or offset, indicating no sign of sample photo-degradation. **B.** Retrieved nano-localized ground (black) and pump-induced (blue) complex dielectric functions from  $E_{\rm NF}(\bar{\nu})$  and  $\Delta E_{\rm NF}(\bar{\nu})$  in Figure 5C based on model fitting. (Taken from collaboration with<sup>69</sup>)

We take the ground state dielectric response and pump penetration depth (100 nm; based on

the absorption coefficient of the perovskite film characterized by UV-Vis absorption spectroscopy) with the substrate dielectric constant ( $\epsilon_{sub} \sim 1.69$ ) to determine  $\Delta E_{NF}$  by varying  $\Delta \epsilon_{NF}(\overline{\nu})$  with broadband responses and narrowband resonances to retrieve the dielectric function  $\Delta \epsilon_{NF}(\overline{\nu})$ .

In order to retrieve the transient complex dielectric function  $\Delta \tilde{\epsilon}_{\rm NF}(\bar{\nu})$ , we apply and fit this near-field spectra to the multi-layer finite dipole model described above (figure 3.14). Specifically, the background carrier response  $\Delta \tilde{\epsilon}_{\rm NF} \sim -0.1 + 0.3i$ , which agrees with  $\Delta E_{\rm NF}(\bar{\nu})$ , results from the polaron absorption. Here, the small carrier background does not give rise to a significant Fanotype interference (Figure 3.17D), meaning the nano-localized transient vibrational response can be recovered by simply subtracting the broad carrier background from  ${\rm Im}[\Delta E_{\rm NF}(\bar{\nu})]$ .

The narrow-band resonance in  $\Delta E_{\rm NF}(\bar{\nu})$  results from both the transient vibrational response and Fano-type interference. Here, to assess the effect a pure Fano-type interference has on the dielectric function, we model the ground-state as having a narrow-band resonance and the photoinduced  $\Delta \tilde{\epsilon}_{\rm NF, \ car}(\bar{\nu})$  results from a broad Drude response (Figure 3.21). The resonant feature can be seen near the ground-state resonance  $\bar{\nu}_{\rm gs}$ .



Figure 3.21: Fano-type interference induced by carrier background | **A.** Model input dielectric functions identical to Figure 2B but without the transient vibrational response. **B.**  $E_{\rm NF}(\bar{\nu})$  and  $\Delta E_{\rm NF, car}(\bar{\nu})$  calculated based on the input dielectric functions, with  $\Delta E_{\rm NF, car}(\bar{\nu})$  exhibiting Fanotype interference between the vibrational resonance and carrier background. **C.** The separated carrier and transient vibrational contributions to  $\rm Im}[\Delta E_{\rm NF}(\bar{\nu})]$  in Figure 2D, main text. (Taken from collaboration with<sup>69</sup>)

We obtain the vibrational near-field pump-probe signal  $\text{Im}[\Delta E_{\text{NF, vib}}(\bar{\nu})]$  by simply subtract-

ing out  $\text{Im}[\Delta E_{\text{NF, car}}(\bar{\nu})]$ . This results in a spectrum with good agreement to the transient dielectric function  $\text{Im}[\Delta \tilde{\epsilon}_{\text{NF}}]$  – therefore, we take the Fano-type interference to be at least approximately additive in  $\Delta E_{\text{NF}}$ . Technically though, the individual contributions can be teased out by careful fitting of the two independent contributions.

We now perform spectroscopy at different sample locations and observe a varying degree of vibrational peak shifts, ranging from 5 to 8 cm<sup>-1</sup>, indicating spatial heterogeneity in the coupling strength between the polaron and cation between 50 and 70 cm<sup>-1</sup> (figure 3.17E). This heterogeneity is not resolvable in the far-field and such coupling likely depends on the nanoscale heterogeneity in lattice elasticity.

Nanoscale heterogeneity in the local chemical composition that results in disorder of the lattice and strain has previously been experimentally observed and theoretically predicted.<sup>188–190, 193</sup> Here though, the ultrafast transient dynamics explored with HPP IR *s*-SNOM, the polaron formation, lifetime, and transport that defines the photovoltaic device performance is explored.

A mixture of three different A-site cations of formamidinium, methylammonium and cesium are used here in a composition of  $[(FA_{0.83}MA_{0.17})_{0.95}Cs_{0.05}]Pb$   $(I_{0.83}Br_{0.17})_3$ . A thin film is spincoated on a glass substrate as previously established.<sup>189,194</sup> As we see from this example, excitation modulation and sideband lock-in detection significantly increase sensitivity to the near-field pumpprobe signal of interest.

## **3.4.6** Comparison to other approaches

While many studies have recently been using un-modulated pump excitation to probe a range of low-energy phenomena in 2D, semiconductor, and other quantum materials,<sup>11,13,105,171–177,179</sup> this conventional approach has limited applicability to detecting strong carrier and plasmon responses, where the high contrast between the excited- and ground-state allows for low sensitivity detection approaches. Systems with lower excited state contrast have not yet been able to be studied, including dilute carrier, low-conductivity carrier, vibrational, and phonon systems that are important to many quantum and soft materials. Far-field methods have historically used pump modulation and lock-in or gated detection to discriminate the pump-induced response from the typically dominating ground-state response.<sup>195,196</sup> Here, we isolate the excited-state response from the ground state response by borrowing from these advances to extract the pure transient nano-localized spectrally resolved response. With this development, HPP IR *s*-SNOM is now universally applicable to resolve weak and strong perturbations and excitations and is, in general, compatible with ultra-violet to THz frequencies with appropriate optics and detection choices.<sup>197</sup> We have applied this new technique here to study the transient vibrational response in a lead halide perovskite to retrieve the phase and spectrally resolved vibrational response that we use as a quantitative marker for polaron-cation coupling strength. This coupling gives rise to the photovoltaic response in perovskites and is therefore of high importance. The nano-localized contrast and heterogeneity shown here, together with previous nano-localized measurements, indicate nanoscale lattice strain differences give rise to the fundamental carrier properties in perovskite solar cells.

From a condensed matter perspective, where electron-phonon coupling is of modern importance and study, nanoscale electronic excitation and vibrational probing is ideal for the study of 2D materials,<sup>198–200</sup> hybrid photovoltaics,<sup>145, 149, 183</sup> and nanoscale thermal transport.<sup>201</sup> Therefore, our new technique is an important step in mapping the inherent disorder in electron-phonon interactions and controlling nanoscale quantum technologies.<sup>164, 176, 202</sup>

### 3.4.7 Outlook

Following the same path as far-field advancements, HPP IR *s*-SNOM can be further extended to ultrafast spectroscopy techniques currently available in the far-field like pump re-pump probe spectroscopy as is performed in 2DIR to probe coherent population transfer at the nanoscale.<sup>150, 203, 204</sup> Adding interferometric detection to adiabatic plasmonic nano-focusing for four-wave mixing would enable 2D electronic spectroscopy at the nanoscale, characterizing free and bound carrier dynamics in quantum materials.<sup>205–207</sup> Therefore, we can use HPP *s*-SNOM to fully resolve the spatio-spectral evolution of fundamental interactions in functional materials that define the wide range of applications and properties. We have successfully applied the benefits of far-field ultrafast spectroscopy to probe local dynamics at the nanoscale.

# Chapter 4

# Strongly Coupled Multi-Quantum-Well Antenna Heterostructures

# 4.1 Introduction

In this chapter, I will discuss a polaritonic system based on an intersubband transition in a multi quantum well that strongly couples to an infrared resonant gold antenna. The sample was prepared by Nishant Nookala, the far-field theory was performed by Sander Mann, and the experiments and near-field theory were performed by me. This project is divided into two parts, starting with the far-field, where a reflection spectroscopy measurement was extended into the time domain with degenerate pump-probe spectroscopy and ending with the near-field, where the strongly coupled field profile is mapped out, demonstrating phase and coupling strength control.<sup>4</sup>

# 4.2 Strongly coupled polaritonic systems

The operation of all-optical photonic devices critically depends on the third-order nonlinear optical response, like power limiters, saturable absorbers, and switches for signal processing and computation. Significant changes in the properties of such materials are needed when high light intensities are not feasible for the typically limited nonlinear response of optical materials, even conventional non-linear crystals, where their IR performance is lacking. However, synthetically fabricated devices like metasurfaces demonstrate a giant third-order nonlinear response on the order of  $3.4 \cdot 10^{-13}$ , which can be used with an infrared subwavelength plasmonic nanocavity to control the coupling rate optically faster than 2 ps.

An intersubband polaritonic metasurface could be used as an all-optical modulated and controlled highly-nonlinear saturable absorber and optical power limiter. Further, a large coupling constant could be applied to cavity quantum electrodynamic (cQED) phenomena and related applications like quantum information systems, such as a controlled phase flip gate where the phase of light reflected from a cavity depends critically on the state that a strongly coupled emitter is in.<sup>208</sup>

Metasurfaces with highly nonlinear optical coefficients are desired as a wide range of applications call for them, like phase-matching, four wave mixing, beam switching and steering, optical limiting, and phase conjugation.<sup>209,210</sup> Achieving large both  $\chi^{(2)}$  and  $\chi^{(3)}$  has previously been attempted, where intrinsic metal and dielectric nonlinearities were explored.<sup>211–217</sup> Special materials, like epsilon-near-zero and J-aggregates, have also been studied for their nonlinear behavior.<sup>218–223</sup> To date though, the best approach for maximizing  $\chi^{(2)}$  is the combination of an intersubband transition from a multi-quantum well (MQW) strongly coupled to a plasmonic resonator, like a patch antenna or nanowire, forming an intersubband polaritonic metasurface.<sup>224,225</sup> The electronic states within the MQW are engineered to have a large nonlinear response when combined with the photonic field profiles of the resonant antenna.<sup>226</sup> These heterostructures give the, to date, largest non-linear response in any bulk material. The photonic engineering of the field profiles provide for a strong electric field that is highly confined and overlapped in the near-field with the MQW transition dipole moment that hosts the nonlinearity. Previous demonstrations of tailored nonlinear responses in meta surfaces have been performed from the near- to far-infrared, a spectral region typically devoid of (or weak) nonlinearities in naturally occurring materials.

### 4.2.1 Device design and fabrication

We have tailored the device's design to be temporally fast, highly nonlinear, compact and spectrally tunable based on fabrication and optical control. Specifically, the samples measured here are grown with molecular beam epitaxy on an InP substrate. 10 nm Ti and 20 nm Pt wetting layers for wafer metallization were formed with e-beam evaporation. 200 nm of Au was subsequently deposited. and thermocompressively bonded to another similarly metalized InP substrate, forming a metal backplane. Washing, polishing, and etching was performed to remove the original substrate. A 300 nm SiNx hard mask layer was deposited on top of 10 nm of Ti and 100 nm of Au. Antennas were mapped with e-beam lithography and formed by dry etching. The structure is fabricated by patterning down the InGaAs/AlInAs MQW before adding a thin gold strip, which is the plasmonic antenna that couples to the quantum well (figure 4.1a,b).<sup>227–231</sup> The hard mask was then removed, yielding the final product. A variety of antenna lengths were fabricated to account for material specific losses, ensuring at least one antenna length is suitable for near degenerate resonance.



Figure 4.1: Ultrafast, highly nonlinear metasurface with saturable absorption and optical power limiting functionalities  $| \mathbf{a} \rangle$  At low intensities, a nanoantenna is strongly coupled to an intersubband transition in the underlying MQW substrate (shown in green). As a result, polariton splitting is observed at the central frequency and the incident radiation is fully reflected. **b**) At high intensities, the intersubband transition is saturated, and the antenna resonance is not strongly coupled to it. The incident pulse is now largely absorbed, leading to a limiting response. **c**) The low intensity spectrum shows a clear signature of mode splitting due to strong coupling, while at high intensity only the antenna resonance is observed due to saturation of the intersubband transition (see Eq. 4.1). **d**) Change in metasurface absorption between low and high intensity illumination, highlighting saturable absorption (pink shading) and reverse-saturable absorption (green shading). (Taken from collaboration with<sup>4</sup>)

The heterostructure is imaged with a scanning electron microscope (SEM) and shown in figure 4.2a. Figure 4.2b shows the InGaAs/AlInAs MQW band diagram of a single "unit cell" that repeats 26 times over 400 nm. First principle modeling and absorption measurements confirm the transition between the ground state and first excited state is  $\nu_{12} = 40$  THz, whereas the transition from the first to second excited state is  $\nu_{23} = 25$  THz. This significant difference points to the potential being quite anharmonic, as is expected for an approximately square well potential from the nature of the barriers and wells.



Figure 4.2: Linear response of the polaritonic metasurface  $| \mathbf{a} \rangle$ , SEM image of the nonlinear metasurface under consideration, with patch antenna size  $l_x = 0.35 \ \mu m$  and  $l_y = 1.75 \ \mu m$  and unit cell size  $L_x = 2.1 \ \mu m$  and  $L_y = 3.15 \ \mu m$ . **b**, Band structure of the asymmetric multi-quantum well, highlighting the 1-2 and 2-3 transition, which is purposefully detuned from the 1-2 transition. **c**, Absorption spectrum measured with Fourier-transform infrared spectroscopy (FTIR) varying the antenna length  $l_y$ . A clear avoided crossing with the intersubband transition is observed. The dashed line indicates the transition frequency as obtained from bulk measurements. The color scale is shown in d. **d**, Absorption as calculated from Eq. 4.2 at low intensity, where the plasmon frequency  $\nu_p$  is varied rather than the antenna length. (Taken from collaboration with<sup>4</sup>)

We tune the antenna length within each patch by varying its length to find the antenna closest to degeneracy between the local surface plasmon resonance (LSPR) and the MQW intersubband transition (figure 4.2c). We perform a linear absorption measurement with far-field FTIR, where the strongly coupled system (two resonant peaks) shifts with antenna length. Here, we plot the frequency response of the absorption measurement on the y-axis, antenna length on the x-axis and the absorption ( $A = \frac{I_{in} - I_{reflect}}{I_{in}}$ , I<sub>in</sub> is the incident intensity and I<sub>reflect</sub> is the reflected intensity). The anticrossing behavior that can be read off in figure 4.2c is highlighted in figure 4.2d, where the dark mode at the intersection of the antenna and MQW resonances of fixed frequency is observed. The MQW transition dipole moment is out of plane and cannot be driven by the far-field incident radiation directly and is only driven through its coupling to the plasmonic antenna that does appreciably couple to the far-field.<sup>232-234</sup> Bulk absorption measurements of the MQW resonance give the expected resonance frequency, which is shown in figure 4.2d (dashed white line).

### 4.2.2 Nonlinear optical switching

The ultimate limit of the nonlinear conversion efficiency onsets upon saturation in intersubband polaritonic metasurfaces. Specifically, the population in the ground state of the MQW decreases to half, which lowers the absorption coefficient of the driving field.<sup>235</sup> We use this to our advantage here though, where extreme nonlinearity that exceeds perturbative responses reduces the effective coupling rate between the antenna and MQW (figure 4.1a,b)<sup>236,237</sup>

$$\Omega^2 = \Omega^2_{\rm R} (n_{\rm g} - n_{\rm e}) \tag{4.1}$$

where  $n_g$  and  $n_e$  are the ground and excited state occupancies in the MQW and  $\Omega^2_R$  is the vacuum Rabi frequency.

Being able to tune the coupling coefficient allows for all-optical control, where in one limit, the low fluence regime, significant energy transfer between the antenna and MQW occurs, whereas, in the high fluence regime, only the antenna is able to be driven further. This can be seen spectrally, where the low fluence regime is characterized by two distinct resonances formed by the strong coupling, forming upper and lower polaritonic branches. This is contrasted with the high fluence regime, where the saturation of the MQW no longer allows for absorption of radiation and therefore coupling to the antenna, yielding a single spectral resonance (figure 4.1c,d). Using this scheme of switching between strong and weak coupling as a nonlinear transition has previously been demonstrated in microcavities and plasmonic arrays coupled to molecules.<sup>209, 220, 223, 237</sup>

The strong coupling regime is defined as the coupling rate or splitting exceeding the individual resonance decoherence or linewidths respectively. This is contrasted though with the desire for an ultrafast response, which necessitates reasonably large linewidths and associated high loss rates. Simultaneously matching both of these conditions requires the coupling frequency to approach the frequency of resonances, the ultrastrong coupling regime, which has also been previously demonstrated.<sup>232,233,238,239</sup> We leverage the strong dipole moment of the MQW transition and large linewidth of a plasmonic resonator, from its native Drude damping, to achieve nonlinear switching at low intensities to be a sensitive saturable absorber at low intensities.

## 4.2.3 Strong coupling theory

The interaction between the MQW and antenna is described by coupled-mode theory and Maxwell-Bloch model in the rotating wave approximation, where the MQW is simplified to N two-level systems with coupling rate given by  $g.^{240-243}$ 

$$\dot{a} = (i\omega_{\rm c} - \gamma_{\rm r} - \gamma_{\rm a} - \gamma_{\rm s}(w+1))a + iNgq + \sqrt{2\gamma_{\rm r}s_+}$$

$$\tag{4.2}$$

$$\dot{q} = (i\omega_{\rm q} - \gamma_2)q - igaw \tag{4.3}$$

$$\dot{w} = 4g \operatorname{Im}\{qa^*\} - \gamma_1(w+1) \tag{4.4}$$

where  $\dot{a}$  describes the complex plasmon amplitude (normalized to the stored number of photons),  $\dot{q}$ off-diagonal elements of the MQW transition, and  $\dot{w}$  inversion of the population.<sup>243</sup> The plasmon resonance is described by its center frequency  $\omega_c$  and loss rates  $\gamma_r$  and  $\gamma_a$ , which are the radiation and absorption losses respectively. The MQW resonance on the other hand has its center frequency given by  $\omega_q$  and its loss rates summarized by  $\gamma_1$  and  $\gamma_2$ , which are the population decay and total decoherence respectively. The underlying physics is understood as the amplitude operator is externally pumped ( $s_+$  term), internally coupled (Ng term), and intrinsic restoring force (a term). The operator for the MQW is similarly structured without the external driving field, because the transition dipole moment forbids far-field excitation directly of the MQW. Therefore, we only drive the system with  $s_+$  (normalized for the number of photons/second). The inversion of the system is captured by w, which includes the antenna energy transfer as well as the MQW relaxation.

We add an intensity dependent decay rate  $\gamma_s$  to account for the additional MQW level beyond

the simple two level approximation, which comes into play at higher intensities and excited state populations. At sufficiently high enough intensities, the electrons are excited into the continuum and aren't bound by the wells within the MQW. However, at sufficiently low enough intensities, the system of equations reduces to coupled simple harmonic oscillators, with damping given by  $\gamma$ . We extract relevant parameters through low fluence measurements in the linear absorption regime and apply the relevant (fluence independent) parameters to measurements performed in the non-linear case (high fluence).

The MQW is best described as N two level systems indexed by  $|1\rangle$  and  $|2\rangle$ . The interaction of the plasmonic cavity with a single 2 level system is described by the dipole transition between the ground and first excited states though the coupling of the optical electric field from the plasmonic antenna cavity. The coupling strength and rate is described by the Rabi coupling rate  $\Omega$ . We combine creation and anihilation operators to describe the excitation  $\sigma_{12} = |2\rangle \langle 1|$  and decay  $\sigma_{21} = |1\rangle \langle 2|$  of carriers within the MQW.

If we restrict the MQW response to be summarized by a single 2 level system (N = 1), the Hamiltonian is

$$H = H_0 + H_{\rm int} + H_{\rm pump} \tag{4.5}$$

where the free evolution is given by  $H_0$ , the driving of the system is given by  $H_{pump}$ , and the interaction between the two level system and the plasmonic antenna is given by  $H_{int}$ . Specifically,

$$H_0 = \hbar \omega_c \hat{a}^{\dagger} \hat{a} + \sum_{i=1}^2 \hbar \omega_i \hat{\sigma}_{ii}$$
(4.6)

$$H_{\text{pump}} = d_{\text{c}} E_{+} \hat{\sigma} + h.c. \tag{4.7}$$

where we have used the cavity resonance  $\omega_c$  and the MQW electron energies  $\hbar \omega_{i=1,2}$  to describe the energy sum of the plasmonic cavity mode and the carriers in the MQW with the standard number operator. The number operator counts with creation and annihilation operators. The particle number is not conserved with pump as expected since we are supplying energy through the far-field driving. We now discuss the interaction Hamiltion, which is responsible for the coupling of the MQW to the antenna and is given by:

$$H_{\rm int} = \hbar g(\sigma_{12}\hat{a^{\dagger}} + h.c.) \tag{4.8}$$

with coupling rate g and creation operator  $\hat{a^{\dagger}}$  and 1-2 coupling via  $\sigma_{12}$ .

Approximating the expectation value of the product of two operators by taking the product of the expectation values gives the semiclassical approximation for the cavity field, polarization of the 1-2 transition and the occupation probabilities of the first and second excited states. These are given by

$$\dot{a} = (i\omega_{\rm c} - \gamma_{\rm r} - \gamma_{\rm a} - \gamma_{\rm s})a + igq + id_{\rm c}E(t) \tag{4.9}$$

$$\dot{q} = (i\omega_{12} - \frac{\gamma_1}{2} - \gamma_{dp,1} - \gamma_{dp,2})q - ig(\sigma_{22} - \sigma_{11})a$$
(4.10)

$$\sigma_{11}^{\cdot} = \gamma_{12}\sigma_{22} - 2q \operatorname{Im}\{qa^*\}$$
(4.11)

$$\sigma_{22}^{\cdot} = -\gamma_{12}\sigma_{22} + 2q \operatorname{Im}\{qa^*\}, \qquad (4.12)$$

where we recognize  $(\gamma_{dp,1} + \gamma_{dp,2})q$  in equation 4.10 as  $\gamma_2^*$ , the pure dephasing rate, which, when combined with  $\frac{\gamma_1}{2}$ , is the total decoherence rate  $\gamma_2$ . As mentioned above, we track the inversion by defining  $w = \sigma_{22} - \sigma_{11}$ . With the appropriate choice of normalization, we define the normalized quantity  $\sigma_{11} + \sigma_{22} = 1$ . We further connect our newly defined  $\frac{idc E(t)}{\hbar}$  as  $\sqrt{2\gamma_r s_+}$  that we defined above with normalization of  $s_+^* s_+$  as the number of photons per second. Upon inserting normalization conditions and recognized equalities, we nearly recover equations 4.2,4.3, and 4.4.

We now extend the single MQW picture to N MQW systems. To do this, we combine multiple MQW resonances through non-coupled interaction (with each other) to the cavity (where they do couple). To do this, we generalize our system of equations above and cast into matrix form, where the diagonal terms are the non-coupled free evolution terms and the first column and first row are the couplings between the cavity mode a and the MQW resonance. The other off diagonal terms are set to 0 under the assumption that they do not couple with each other. In principle, each MQW mode can have a slightly different coupling to the cavity, which we will label by indexing  $g_j$ , with j being the index of MQW two level system up to N such systems.

$$\begin{bmatrix} \dot{a} \\ \dot{q}_{1} \\ \dot{q}_{2} \\ \vdots \\ \dot{q}_{N} \end{bmatrix} = \begin{pmatrix} i\omega_{c} - \gamma_{c} & ig_{1} & ig_{2} & \cdots & ig_{N} \\ i\omega g_{1} & i\omega_{21} - \gamma_{2} & 0 & \cdots & 0 \\ i\omega g_{1} & 0 & i\omega_{21} - \gamma_{2} & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \cdots \\ i\omega g_{N} & 0 & 0 & \cdots & i\omega_{21} - \gamma_{2} \end{pmatrix} \begin{bmatrix} a \\ q_{1} \\ q_{2} \\ \vdots \\ q_{N} \end{bmatrix} + \begin{bmatrix} \sqrt{2\gamma_{r}}s_{+} \\ 0 \\ 0 \\ \vdots \\ q_{N} \end{bmatrix} , \quad (4.13)$$

In contrast to equation 4.4, we must keep track of each two level system inversion given by  $w_j$  and obeying

$$\dot{w}_{j} = 4g \operatorname{Im}(q_{j}a^{*}) - \gamma_{1}(w_{j} + 1).$$
(4.14)

If we assume that all MQWs equally couple to the antenna, we may assign all  $g_j$  to simply an effective g – doing so reduces our system of 2N + 1 equations to an effective 3 equation model where

$$\dot{a} = (i\omega_{\rm c} - \gamma_{\rm r} - \gamma_{\rm a})a + iNgq + \sqrt{2\gamma_{\rm r}s_+}$$
(4.15)

$$\dot{q} = (i\omega_{\rm q} - \gamma_2)q - igaw \tag{4.16}$$

$$\dot{w} = 4g \operatorname{Im}\{qa^*\} - \gamma_1(w+1), \qquad (4.17)$$

which looks like the familiar derivation prior to extending to N two level systems with the inclusion of N in the equation for  $\dot{a}$  and g taking on the new meaning of an effective coupling constant. In the low intensity approximation, we can read off the observed mode splitting as  $2\Omega_R = 2\sqrt{Ng}$ .

Now we will consider the case where the MQW is not simply a two level system. In reality, the MQW has 3 bound levels and a continuum. At sufficiently high enough intensities, where there is an apprecible pumping of electrons into the continuum, the electrons will experience a Drude damping from scattering off other electrons. This Drude damping can be added by the term  $\gamma_s(w + 1)$ , where the total loss rate is related to the inversion, which approximately tracks the number (upon scaling) of continuum electrons. With this insertion, we finally recover the full system of equations that describes the antenna MQW heterostructure

$$\dot{a} = (i\omega_{\rm c} - \gamma_{\rm r} - \gamma_{\rm a} - \gamma_{\rm s}(w+1))a + iNgq + \sqrt{2\gamma_{\rm r}s_+}$$

$$\tag{4.18}$$

$$\dot{q} = (i\omega_{\rm q} - \gamma_2)q - igaw \tag{4.19}$$

$$\dot{w} = 4g \operatorname{Im}\{qa^*\} - \gamma_1(w+1). \tag{4.20}$$

At low intensities, the Drude damping of the continuum MQW electrons can be neglected and we are left with

$$\dot{a} = (i\omega_{\rm c} - \gamma_{\rm r} - \gamma_{\rm a})a + iNgq + \sqrt{2\gamma_{\rm r}s_+}$$
(4.21)

$$\dot{q} = (i\omega_{\rm q} - \gamma_2)q - iga, \tag{4.22}$$

which upon using

$$s_{-} = s_{+} - \sqrt{2\gamma_r}a \tag{4.23}$$

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and

$$r = \frac{s_{-}}{s_{+}},\tag{4.24}$$

we calculate

$$r = 1 + \frac{2\gamma_r(i\Delta_q - \gamma_2)}{Ng^2 + (i\Delta_c - \gamma_r - \gamma_a)(i\Delta_q - \gamma_2)}$$

$$(4.25)$$

$$\Delta_q = \omega_{21} - \omega \tag{4.26}$$

$$\Delta_c = \omega_c - \omega. \tag{4.27}$$

The final assumption that I would like to address is the rotating wave approximation, which assumes only the linear terms from the semiclassical derivation above. This is valid in the weak and strong coupling regimes, but must be considered when the coupling strength reaches the ultrastrong coupling regime. This is defined as the coupling frequency being one tenth or more of the resonant transition frequency  $\Omega_R \geq 0.1\omega_0$ . In the experiment performed here, the coupling strength is approximately 0.13 of the resonant transition frequency, edging on the transition between strong and ultrastrong coupling. With some accuracy loss of absolute parameters, we choose to continue employing the rotating wave approximation as the physics are well described, with "effective" parameters rather than true parameters. The effect of the rotating wave approximation included versus without it can be summarized by analyzing the polariton branches as a function of coupling strength for both cases with and without the rotating wave approximation. In this comparison, the two photon cavity mode coupling that occurs near 80 THz is included in its coupling to the MQW.

## 4.2.4 MQW device characterization

We then apply the theory derived in the previous section to fit the FTIR spectra collected for various antenna lengths figure 4.4.

Both the unit cell size of the antenna MQW heterostructures and the widths of each antenna are kept constant. The MQW resonant frequency  $\omega_{21}$ , total dephasing rate  $\gamma_2$ , and coupling



Figure 4.3: Effect of ultrastrong coupling | In the model we apply the rotating wave approximation, which ignores quadratic and antiresonant terms. It is known that for very high Rabi frequencies these terms affect the splitting, as shown here by tracking the resonance frequencies. Here we show the effect of the antiresonant term. In the experiment described in the main text,  $\Omega_R/\omega = 0.13$ , and the resulting differences in splitting may safely be ignored. (Taken from collaboration with<sup>4</sup>)

strength  $\Omega$  are kept constant across all antenna lengths, whereas the antenna resonant frequency  $\omega_c$ , radiative damping  $\gamma_r$ , and absorption damping  $\gamma_a$  are fitting parameters for each array.

Figure 4.5 shows the extracted parameters for each antenna length and the frequency crossing between the MQW and antenna resonant frequency is clear. The antenna lengths for which the resonant frequencies are closest are those used in the experiments shown here. We use the parameters extracted in this experiment to inform our fitting.

# 4.3 Nonlinear reflectivity ensemble demonstration

We now proceed to the measurements that characterize the novel functional operating regimes for the metasurface for, e.g., optical switching and power limiting through saturable absorption. To begin, we perform spectroscopy of the MQW metasurface by an absorption measurement at two different fluences, medium peak intensity ( $\sim$ 70 kW/cm<sup>2</sup>) and high peak intensity ( $\sim$ 700 kW/cm<sup>2</sup>). We use a tunable ps laser (Carmina, APE) with a 15-20 cm<sup>-1</sup> bandwidth generated by spectral



Figure 4.4: Maxwell-Bloch model fits to FTIR spectra | FTIR spectra (blue) from six different arrays with the same unit cell size and antenna width, but different antenna length (mentioned as inset in each graph), were fit using the low-intensity Maxwell-Bloch model (red). The array under consideration in the main text is the bottom left one. The resulting parameters are shown in figure 4.5. (Taken from collaboration with<sup>4</sup>)

focusing of the difference frequency generation between the signal and idler pulse.

Here, a ps optical parametric oscillator (OPO) followed by difference frequency generation (DFG) generates mid-IR light with ~1.6 ps (intensity FWHM) pulses at a 40 MHz repetition rate. We focus this light onto a single array of antenna MQW heterostructures with a BaF<sub>2</sub> lens and control the fluence by tuning a wire-grid polarizer pair to adjust input power by turning the first polarizer relative to the second, maintaining final output polarization. We simultaneously measure the input and reflected power with 2 mercury-cadmium-telluride (MCT) detectors by using a ZnSe beam-splitter before the focusing lens. We use this geometry with simultaneous detection to normalize power fluctuations and we normalize our reflectance results to a Au reference as the mid-IR reflectance of Au is spectrally flat.

At the lower power used here, the system is not saturated, meaning the coupling strength is


Figure 4.5: Model parameters from the fitting procedure | To reduce degrees of freedom, the total coupling strength  $\sqrt{N\Omega}$ , the MQW 1 - 2 transition frequency  $\omega_q$  and linewidth  $\gamma_2$  were global fitting parameters. The other parameters were considered free per each metasurface. (Taken from collaboration with<sup>4</sup>)

still significant and splitting between the two hybridized modes can be observed. However, as the power is increased 10 fold, the MQW effectively saturates, turns transparent and no longer couples to the plasmonic antenna cavity, causing the polaritonic splitting to vanish, giving a single peak from the bare antenna resonance. While infinitely high power would be required to completely saturate the MQW (as there is no population inversion in this system), the high power used here is sufficient to take the system out of the strong coupling regime and into the weak coupling regime where only one mode is resolvable. Figure 4.6 shows the experimental data compared to the Maxwell-Bloch model with an effective coupling constant g that incorporates the contribution of N two-level systems (see above).



Figure 4.6: Experimental nonlinear tuning of the coupling coefficient  $| \mathbf{a} \rangle$ , Absorption spectra at low (~70  $kW/cm^2$ , blue) and high (~700  $kW/cm^2$ , red) peak intensities, demonstrating the transition from strong to weak coupling of the polaritonic metasurface. We also show the FTIR absorption spectrum for comparison. **b**, Absorption at 35.5 THz (left shaded region in a) as a function of peak intensity, demonstrating very large nonlinear absorption at low intensity. Experimental data is shown by circles, the predicted response from the model is shown with the solid line. **c**, Same as in panel b, but at 38 THz (middle shaded region in a). In this case we observe reversed saturable absorption (optical limiting) as the normal mode passes by. **d**, Power dependence at 40 THz (right shaded region in a). Here we observe maximal optical limiting for this sample. The black line shows the slope at low intensity, used to estimate the effective  $\text{Im}(\chi_{(eff)}^{(3)})$ .<sup>4</sup>

While the spectrum changes between the strong and weak coupling regime for two distinct powers, the total absorption at a single frequency non-linearly depends on the input intensity. To observe this, we tune to three frequencies as indicated in figure 4.6a. The fluence dependent response at these frequencies is summarized by figure 4.6b,c,d for 35.5 THz, 38 THz, and 40 THz respectively. We choose these frequencies as they represent the ultra-strongly coupled lower polariton branch, the strongly coupled lower polariton branch (at higher fluences), and the bare antenna resonant frequency, where absorption is maximized at yet higher fluences. When tuned to the ultra-strongly coupled polariton branch, increasing the fluence results in a reduction of the mode splitting (as the MQW begins to saturate), which causes the absorption to decrease as the lower polariton branch is swept (via power) to higher frequencies. At the intermediate tuning frequency, the absorption increases slightly with intensity as the mode splitting reduces with increasing fluence. Finally, when tuned to the bare antenna resonance, the absorption strongly increases as the MQW saturates and the bare antenna resonance is recovered, where we are effectively only driving the antenna LSPR. I would like to note though that when the MQW saturates the individual absorption rate decreases (trivially from saturation), yet the combined absorption increases at this frequency as the system is no longer significantly coupled.

As an additional consideration for the fitting performed here, we incorporate the effect a Gaussian laser source has on the measurements, where the intensity is not constant across the focal spot and therefore the response is heterogeneously averaged. We take the Gaussian beam profile to be

$$I(x,y) = I_0 e^{\frac{x^2 + y^2}{w_0^2}},$$
(4.28)

where  $w_0$  is the spot size  $(1/e^2)$  and  $I_0$  is the un-normalized total intensity. To model the intensity dependent absorption, we must average over each antenna in the array

$$A(I_0) = \frac{\sum_{x,y} A(I(x,y))I(x,y)}{\sum_{x,y} I(x,y)}$$
(4.29)

To compare the nonlinearity of this metasurface, we treat the sample as homogeneous and characterized by  $\chi^{(3)}$  as the change in absorption from low to high intensities. We define  $\beta = \frac{\Delta A}{2d}$ where  $\Delta A$  is the change in absorption between the two intensity regimes and d is the single pass distance, which is 500 nm for this sample. We therefore find  $\beta = 1.6 \cdot 10^7 \ cm GW^{-1}$  which implies  $\text{Im} \chi^{(3)} = 3.4 \cdot 10^{-13} \ m^2 V^{-2}$ , where we have used the relationship

$$\operatorname{Im} \chi^{(3)} = \frac{2\epsilon_0 n^2 c^2 \beta}{3\omega}.$$
(4.30)

To date, this is the highest third order nonlinearity by 2-3 orders of magnitude.<sup>218,219</sup>

#### 4.3.1 Ultrafast optical switching

These results have thus far been from the interaction of a single pulse with the metasurface, but the saturation can be started with a separate pump pulse as is the case for degenerate pumpprobe measurements performed here. We direct the pump pulse along a separate path and focus it onto the sample surface with an incidence angle of 30 degrees to normal. We use a high intensity pulse to pump the MQW into saturation and use a low fluence ( $\leq 50 kW cm^{-2}$ ) pulse to probe the system and not repump the MQW back to saturation at normal incidence.



Figure 4.7: Transient all-optical control of metasurface reflection | **a**, Schematic showing the alloptical control experiment. A pump pulse excites the metasurface at an oblique angle, while a weaker pulse probes the metasurface response under normal incidence with time difference t. **b**, A degenerate pump-probe measurement at 35.5 THz, demonstrating how the reflectivity can be increased all-optically at ultrafast timescales. The measurements are in excellent agreement with theoretical predictions, shown in red (with a peak intensity of 12.5  $kW/cm^2$ ). Shaded areas show measurement uncertainty. **c**, A similar measurement performed at a different frequency to demonstrate optical limiting (40 THz), showing that reflectivity can also be all-optically reduced, highlighting the versatility of the metasurface operation. The red line again shows theoretical predictions, now for a peak intensity of 30  $kW/cm^2$ .<sup>4</sup>

We use the same ps OPO/DFG system described above for the ground state measurement, but split the output mid-IR generated light into a strong pump and weak probe beam and direct them along different paths. The pump beam is focused onto the sample at an angle, whereas the probe beam is under normal incidence, just as it was for the ground state measurement. We move the pump beam focusing lens to optimize spatial overlap between the pump and probe at the sample surface. We again monitor the probe pulse, modulated at the pump and probe frequencies (to discriminate against the dominating ground state response) with two MCT detectors placed similarly on either side of a ZnSe beam-splitter. We simultaneously monitor the pump modulation frequency plus probe modulation frequency as a function of relative pump-probe delay to retrieve the time dependent reflectivity. Figure 4.7 shows the frequency dependent pump probe absorption traces. In figure 4.7a, the laser is tuned to 35.5 THz, the ultra-strongly coupled lower polariton branch. As expected from the power dependent results in figure 4.6, we observe a decrease in absorption immediately after pumping as the pump saturates the MQW and reduces the mode splitting, reducing the absorption at the lower polariton branch. We then tune the laser to 40 THz (figure 4.7b) and observe the opposite behavior, as expected. The time dependent Maxwell-Bloch model agrees well with the inclusion of finite pulse length (1.6 ps). We extract the population decay rate ( $T_1 = 1.73ps$ ) that is combined into the total dephasing rate for the time independent measurements in figure 4.6. The "rise time" (the time it takes to pump the MQW) is limited by the pulse length, which is limited by the bandwidth of the laser, which means the nonlinearity onset dynamics are on the 100s fs or less time scale. This enables the ultrafast control of the metasurface optical response and perfomance in applications like ultrafast optical switching and power limiting through saturable absorption.

#### 4.3.2 Performance limitations

We now look to find the fundamental limit of reflection contrast with our polaritonic metasurface. The ideal case is the optical limiter fully absorbing when the MQW is saturated and fully reflecting when the MQW is entirely in its ground state. The losses from Drude damping in the plasmonic antenna and the MQW is the fundamental limit of minimum reflection. The maximum reflection is limited by the critical coupling, when the metasurface is perfectly absorbing. To begin, we recall our previous definition of  $s_{-}$ 

$$s_{-} = 1 - \sqrt{2\gamma_r a} \tag{4.31}$$

and the definition of absorbance

$$A = 1 - |r|^2 = 1 - \frac{s_-^2}{s_+^2}, \tag{4.32}$$

which, in combination with the definition of absorbed (damped) power yields

$$A = \frac{P_{abs}}{P_{inc}} = \frac{2(\gamma_a |a|^2 + \gamma_2 |q|^2)}{|s_-|^2}$$
(4.33)

at high intensities w = 0 and a low intensities w = -1. Therefore, upon degeneracy  $\omega = \omega_0$ ,

$$A_{low} = \frac{4\gamma_2\gamma_r(\gamma_2\gamma_a + \Omega_R^2)}{(\gamma_2(\gamma_a + \gamma_r) + \Omega_R^2)^2}$$
(4.34)

$$A_{high} = \frac{4\gamma_r(\gamma_a + \gamma_s)}{(\gamma_r + \gamma_a + \gamma_s)^2},\tag{4.35}$$

but for the case  $\gamma_r = \gamma_a + \gamma_s$ ,  $A_{high} = 1$  and critical coupling is achieved. This condition applied to  $A_{low}$  though implies

$$A_{low}(\gamma_r = \gamma_a + \gamma_s) = \frac{(\Omega_R^2 - \gamma_2 \gamma_s)^2}{(\gamma_2 (2\gamma_a + \gamma_s) + \Omega_R^2)^2}.$$
(4.36)

We define the low intensity dephasing loss as  $\Gamma_2 = \Omega_R^2/\gamma_2$ , the relative plasmonic antenna absorption to losses in the MQW as  $\eta = \gamma_a/(\gamma_a + \Gamma_2)$ , and the fraction of Drude losses in the high intensity limit to the low intensity dephasing losses as  $f_s = \gamma_s/\Gamma_2$ , we can write a simple expression for the absolute contrast defined as  $|\Delta A| = |A_{high} - A_{low}|$  as

$$|\Delta A| = \frac{(1 - f_s)^2}{(\frac{1 + \eta}{1 - \eta} + f_s)^2}.$$
(4.37)

This gives the fundamental limit from the intrinsic losses in the MQW and plasmonic antenna.

We can explore the non-degenerate frequency as well, where we seek to maximize the absorption difference between the strongly coupled system (low fluence) and the weakly coupled system (high fluence) as defined by  $A_{low} - A_{high}$ , where we naturally will look to the peak position of either the lower or upper polariton branch. We refer to this as resonantly enhanced saturable absorption. The absorption contrast here is given by

$$|\Delta A| = \frac{\tilde{\gamma}_s(\tilde{\gamma}_s - 2\tilde{\gamma}_2) + 1}{(2\tilde{\gamma}_a + \tilde{\gamma}_s)^2 + 2\tilde{\gamma}_m(2\tilde{\gamma}_a + \tilde{\gamma}_s) + 1}$$
(4.38)

$$\tilde{\gamma}_2 = \gamma_2 / \Omega_R \tag{4.39}$$

$$\tilde{\gamma_a} = \gamma_a / \Omega_R \tag{4.40}$$

$$\tilde{\gamma_s} = \gamma_s / \Omega_R \tag{4.41}$$

$$\tilde{\gamma_m} = \gamma_m / \Omega_R. \tag{4.42}$$

Optical limiting at this critical coupling is shown in Figure 4.8. The first example (figure 4.8a) shows the metasurface with low absorption at low intensities at the critically coupled frequency at high intensities. The optical contrast here is  $|\Delta A| = 0.65$  for input parameters  $\eta = 0.031$  and  $f_s = 0.08$  (white circle figure 4.8a contour plot). As can be read off from the contour plot, minimizing both  $\eta$  and  $f_s$  will maximize absorption contrast and represents photonic and material engineering respectively. For example, using different materials with less Drude damping for the antenna and designing a MQW with longer total decoherence times would improve performance at the expense of ultrafast response times.

At the other end of the spectrum (contrast, not frequency), maximizing saturable absorption can be done in two ways. The first is to use a critically coupled system at low intensities (still using the same plasmonic antenna resonance) that then loses its critical coupling condition at high intensities. This behavior is symmetrically the same as what was demonstrated in figure 4.6. The second is to shift to either the lower or upper polaritonic branch, where the contrast now depends on  $\tilde{\gamma}_s$ ,  $\tilde{\gamma}_a$ , and  $\tilde{\gamma}_2$ . We highlight small  $\tilde{\gamma}_2$  in figure 4.8b and large  $\tilde{\gamma}_2$  in figure 4.8c, where they are 0.1 and 0.75 respectively. Again, as expected, maximum performance requires minimizing  $\gamma_a$  and  $\gamma_s$  and, ideally,  $\gamma_2$  – similarly looking to reduce the total decoherence rate of the MQW.



Figure 4.8: Limits to metasurface absorption contrast  $| \mathbf{a} \rangle$ , Saturable and reverse saturable absorption when aligned with the bare resonance frequencies. The top part shows an example of reverse saturable absorption with critical coupling at high intensity. The bottom part shows the absorption contrast achieved for combinations of  $\eta$  and  $f_s$ , where the circle corresponds to the parameters in the top subplot. **b**, Similar to a, but now for saturable absorption when aligned with a critically coupled normal mode at low intensity, when  $\gamma_2/\Omega = 0.1$ . **c**, Saturable absorption when aligned with a critically coupled normal mode at low intensity, when  $\gamma_2/\Omega = 0.75$ . (Taken from collaboration with<sup>4</sup>)

So far, we've determined that the design of our MQW antenna heterostructure yields an optical contrast of  $|\Delta A| = 0.2$  ( $\eta = 0.09$  and  $f_s = 0.32$ ). This deviates from the observed experimental results, where a maximum contrast of  $|\Delta A| = 0.3$  is observed. This results in our system not being critically coupled from  $\gamma_2$  being smaller than designed, which lowers the absorption at low fluences, increasing the observed optical contrast. We note that the greatest avenue for improved optical limiting contrast in the future will result from improved MQW designs where high intensity Drude damping is reduced and improved nanocavity antennas, where losses are similarly minimized.

#### 4.3.3 Ensemble performance summary

Ultrafast optical control of the coupling constant between a plasmonic antenna MQW heterostructure has been demonstrated in the mid-infrared with complete control between the ultrastrong, strong, and weak coupling regimes. This represents the highest nonlinear coefficient to date in the mid infrared spectral regime, where modest optical powers influence large spectral changes. Performance of next generation systems will critically depend on the damping rates of the plasmonic antenna and MQWs used in the heterostructures. To further study the cavity quantum electrodynamics phenomena associated with these heterstructures, we extend far-field measurements to the near-field, where the optical driving phase and coupling strength can both be simultaneously controlled with the use of a metalized atomic force microscope tip.<sup>239</sup>

### 4.4 Near-field quantum phase and hybridization control

While the results demonstrated above impressively show macroscopic ultrafast power limiting and optical switching behavior, resolving and controlling the phase and coupling strength for single antennas remains elusive. Near-field spectroscopy, with its deep sub-wavelength diffraction unlimited spatial resolution and complex response sensitivity, enables quantum state phase and hybridization control through tip sample positioning.

With applications from biological to quantum materials, infrared vibrational scattering scanning near-field optical microscopy (s-SNOM) has advanced to become a powerful nano-imaging and -spectroscopy technique and has previously been demonstrated in its application to infrared vibrational strong coupling.<sup>244</sup> Infrared polaritonic heterostructures based on a multi-quantumwell intersubband transition that are coupled to a gold antenna similarly exhibit novel hybrid state phenomena, including record-high nonlinear optical responses and optical power limiting behavior. However, the collective response of an ensemble of these structures are limited to static passive performance depending on fabrication parameters.<sup>4</sup> Here, we extend our demonstration of ultrafast optical switching to broadband and ultrafast infrared nano-probe imaging and spectroscopy of single antenna quantum well heterostructures to actively tune quantum-well saturation, coupling strength, and quantum path interference (figure 4.9) – the tip controls the interference pathways and relative coupling strength through manipulation of the nano-cavity mode volume.

Optical control is enabled through controlling the saturation level of the MQW, i.e. higher peak powers saturate the MQW and the coupling strength to the antenna decreases.<sup>239</sup> Midinfrared light was produced by narrowband mode difference frequency generation (DFG) between



Figure 4.9: Comparison of 2 versus 3 oscillator coupling | **left**, Far-field (previous section) strong coupling model, where mid-IR resonant antenna strongly couples to MQW. **right** Near-field strong coupling model where the tip position controls phase response through far-field driving.

the signal and idler of a 40 MHz 1032 nm pumped optical parametric oscillator (OPO), which produces light with a bandwidth of approximately 15 cm<sup>-1</sup> and a pulse duration of 1 ps. In farfield ultrafast degenerate pump-probe measurements, a Mach-Zehnder interferometer with one arm of variable delay length was used to generate the pump and probe pulses. Reflectivity measurements were detected in a balanced detection scheme to compensate for small drifts in the laser power. The ps pulse duration of the narrowband mode enabled bridging the gap between low and high peak intensities in order to observe both strong coupling in the low peak intensity limit and weak coupling in the high peak intensity limit.

However, full optical control demonstrated in the near-field (schematic figure 4.10) requires a variety of light sources were used, including low peak intensities provided by a synchrotron like the Advanced Light Source (ALS), which has a pulse duration of 60 ps, a repetition rate of 500 MHz, and a maximum power of 1 mW and the high peak intensities provided by the broadband mode of the same OPO/DFG combination that has 4 times or more shorter pulse lengths and used in a geometry with 5 times smaller focus spot size. The near-field measurements used these varying light sources to demonstrate the full optical tuning for hybridized states, phase resolved frequency imaging, and peak position power dependence.



Figure 4.10: Near-field Michelson interferometer for nano-FTIR and pseudo-heterodyne | Light source (synchrotron or ps laser) excites tip and antenna that couple to MQW, whose backscattered light is interferometrically detected with MCT.

Figure 4.11 shows the near-field spectral phase evolution down the antenna. Starting on the near side of the antenna relative to the incident beam and equivalently the back side of the surface plot, shows a similar spectrum to what was observed in the far-field measurements in the previous section. We observe two peaks notably different in magnitude, but through extensive measurements, this was determined to be dependent on the particular antenna being measured. The far-field equal weighting between lower and upper polariton branches resulting from ensemble averaging. As the tip is scanned along the antenna, the spectral peaks begin to shift into dispersive lineshapes by the middle of the antenna and finally turn into two distinct dips on the far end.

Through coupled oscillator modeling, this is understood as a difference in the driving phase of the MQW through the tip and antenna respectively. Specifically, as the sample is moved under the tip, the tip oscillation phase (and resulting near-field driving phase) obviously remains unchanged. The antenna that is being moved under the tip though, to first order within the beam spot of the light source focus also does not change phase. However, the antenna nature of the plasmonic resonance implies the phase of the oscillation in the near-field will be  $\sim 180^{\circ}$  out of phase from one end of the antenna to the other. This results in the MQW, which is driven both by the tip and the antenna, to experience drastically different driving fields as the sample is scanned below the tip,



Figure 4.11: Phase resolved single antenna strong coupling | Near-field phase spectrum in linescan along wire, starting (back) with tip at laser incident side, when both tip and antenna are in phase, ending (front) with tip at opposite side, where tip and antenna are  $180^{\circ}$  out of phase.

resulting in the evolution of the shape of the near-field phase spectrum.

We then proceed on to measurements using the same light source as the far-field, the ps OPO/DFG output from the APE Carmina. These ps pulses can be tuned through fluence with a wire-grid polarizer pair to drive the MQW from the low excited state population through saturation. At low fluences (figure 4.12a), we observe, through frequency resolved pseudo-heterodyne imaging, strong coupling at the frequencies observed with the ALS synchrotron. We monitor the coupling strength by plotting the difference in phase from one end of the antenna to the other, with resonant frequencies showing stronger phase differences, owing to the antenna like behavior in the hybridized state (figure 4.12c). We note here again that the asymmetry of peak amplitude is consistent for the same antenna measured using synchrotron radiation. However, as we increase the input fluence, we observe a transition of strong coupling to weak, interestingly, only at one end of the antenna (figure 4.12b). We again plot the antenna strength as a function of laser frequency and only observe one very broad peak (figure 4.12d).



Figure 4.12: Phase resolved single frequency imaging between strong and weak coupling regimes  $| \mathbf{a} \rangle$ , low peak power (strong coupling) pseudo-heterodyne imaging at tuned frequencies (z axis) – color scale is near-field phase response. **b**, medium peak power (weak coupling) pseudo-heterodyne imaging at tuned frequencies (z axis) – color scale is near-field phase response. **c** Phase difference (antenna strength) across wire as function of driving frequency, showing peak splitting, indicating strong coupling. **d** Phase difference along wire, showing no peak splitting, indicating weak coupling.

We attribute this asymmetry in peak splitting to the relative driving strength at one end of the antenna relative to the other. FTDT simulations similarly predict higher field concentrations at the near-side (relative to driving field) compared to the far side. We expect this as the tip effectively shadows the antenna when positioned at the near-side. This relative signal strength and driving field strength has also been reproducibly observed both in these samples and other antenna molecule samples.<sup>244</sup> We then plot the spectrum along the wire (similar to the synchrotron dataset, with less spectral resolution given the psuedo-heterodyne nature of the measurement – figure 4.13). This emphasizes the effect of the increased field strength on the near side of the antenna, where the MQW is driven more strongly (top, red), begins to saturate, causing the coupling strength to decrease. As the tip is moved down the antenna and the driving strength decreases, the MQW and antenna remain strongly coupled (bottom, blue).



Figure 4.13: Single fluence coupling strength tuning through tip positioning | Near-field phase spectra along the wire, starting on laser incidence side (top), ending on opposite side (bottom), where the transition from weak to strong coupling is observed.

We have shown how the nano-optical tip acts as a coupled antenna resonator and how the tip-sample nano-cavity enhances far-field coupling to control photon emission, electric field orientation, and nanoscopic field heterogeneity. We further extend the picosecond laser far-field optical power limiting and pump-probe characterization to probe and control the ultrafast near-field optical response, where the positioning of the tip, polarization of the incident light, and sample orientation can be tuned to give quantum state hybridization control and to perform qubit phase rotation operations.

# Chapter 5

### Ultrafast visible pump infrared probe of WSe<sub>2</sub> on SiO<sub>2</sub>

#### 5.1 Introduction

In this chapter, I will discuss the application of pump modulated pump-probe ultrafast imaging that I developed in chapter 3 to image heterogeneity in carrier dynamics in WSe<sub>2</sub> and local temperatures as a measure of thermal boundary conductance. This work was primarily designed, performed, and analyzed by me. Theoretical calculations were performed by collaborator Shiqian Hu under the guidance of Baowen Li.

# 5.2 Transition metal dichalcogenides

Transition-metal dichalcogenides (TMDs) have attracted significant attention due to their unique optical properties that depend on the symmetry and dimensionality for applications ranging from spintronics to atomically thin photodetectors and field effect transistors. The ultrafast dynamics that govern the excited state populations, spin polarization, and coherence are characterized by fast decaying intravalley bright excitons and long lived dark excitons in W centered TMDs.

In WSe<sub>2</sub>, the valence band and conduction band are split by strong Ising spin-orbit coupling that is hundreds of meV in the valence band, yet only few meV in the conduction band. The split in the valence band gives rise to so called A and B excitons with A being the lower energy of the two – for the energies used below, we will ignore contributions from the B band. The splitting of the conduction band though, for monolayer and few layer samples, gives rise to a k-valley opening from the broken inversion symmetry. This k-valley opening is what makes TMDs attractive for spintronic applications as the two bands are spin polarized. In W centered TMDs, an electron populating the thermal minimum state and a hole populating the A band valence band is called a dark exciton as the optical transition is spin forbidden and therefore slow  $\sim 300$  ps. In contrast, populating the higher conduction band state instead yields the bright exciton as the optical transition is extremely fast  $\sim 2$  ps.

The spin polarization for the k valley, with time reversal symmetry, determines the spin polarization for the k' valley. Here, the minimum energy state still forms the dark exciton with the k' A exciton valence band, but also couples to the k valley, forming a third coupled state, the intervalley bright exciton (bright here as the spin polarization flips between the k and k' valleys). In order to observe the dark exciton, different experimental approaches have been taken to either suppress the bright exciton (which normally dominates any dark exciton signal), or to enhance the dark exciton transition rate. One such method is to perform spectroscopic measurements at ultracold temperatures. The bright exciton is only populated during above resonance excitation relaxation and from thermal excitations from the dark exciton – by going to lower temperatures, this excitation channel can effectively be removed.

In a previously demonstrated cryogenic ultracold measurement, the decay of the dark exciton was found to have 2 time constants fit by a bi-exponential decay, with the additional decay constant came from coupling to the intervalley bright exciton. The time constants were  $\sim 30$  ps and  $\sim 300$ ps. Whenever a dark exciton is thermally populated to the bright exciton state, it rapidly decays through the spin allowed optical transition, and this time constant can then be ignored for these time scales. The coupled state equations are given as

$$\frac{dN_X(t)}{dt} = -(\gamma_X + \gamma_{X-D} + \gamma_{X-X_K})N_X(t) + \gamma_{X-D}N_D(t) + \gamma_{X-X_K}N_{X_K}(t)$$
(5.1)

$$\frac{dN_D(t)}{dt} = \gamma_{X-D}N_X(t) - (\gamma_D + \gamma_{X-D})N_D(t) + \gamma_{2D-2X_K}(N_{X_K}^2(t) - N_D^2(t))$$
(5.2)

$$\frac{dN_{X_K}(t)}{dt} = \gamma_{X-X_K} N_X(t) - (\gamma_{X_K} + \gamma_{X-X_K}) N_{X_K}(t) + \gamma_{2D-2X_K} (N_D^2(t) - N_{X_K}^2(t)),$$
(5.3)

where N is the population of the subscripted state,  $\gamma$  is the transition rate of the subscripted state, and t is time. Here, the subscripted states are X for the intravalley bright exciton, D for the intravalley dark exciton, and  $X_K$  for the intervalley bright exciton. Note the dependence on the square of the population in the equations for  $N_D$  and  $N_{X_K}$ , where the bimolecular process dominates. The coupling rates  $\gamma$  are in principle temperature dependent, but the above bandgap excitation and resulting carrier cooling emits phonons that contribute thermal excitations to populate the bright state, which is often neglected in cryogenic measurements. We keep this in mind as we investigate heterogeneity at the nanoscale in carrier generation and decay. We also make a final comment that going to cyrogenic temperatures, or turning on and off decay pathways is only necessary in the visible, where the names dark and bright exciton originate. Here, we choose to sidestep this problem and use an infrared probe as the entire carrier population can be directly assessed, regardless of its spin states.

### 5.3 Nano-imaging dark excitons

To begin, we located WSe<sub>2</sub> flakes on a Au substrate and on an SiO<sub>2</sub> substrate. We then found smooth regions in the interior of the flake and performed a time trace on bulk WSe<sub>2</sub> on both Au and SiO<sub>2</sub> and on monolayer WSe<sub>2</sub> on SiO<sub>2</sub>. The pump modulated near-field signal (pump probe amplitude) was greatest on the Au, indicating optical enhancement from the substrate. We then collected time traces at different fluences as shown in figure 5.1a and fit the curves to bi-exponential fits (dashed).

We note that the fast time constant for each of the biexponential fits was fluence independent, indicating the process is intrinsic to the sample itself and does not result from sample heating or Auger like process. The second time constant though is fluence dependent and the relationship is shown in figure 5.1b, where we see to good agreement, a linear relationship between  $T_c$  and fluence.



Figure 5.1: Ultrafast heterodyne pump-probe dynamics on Au | **a**. Time traces at varying fluences of near-field amplitude signal decay. **b**. Bi-exponential fit slow time constant value as a function of fluence

We repeat this measurement for the bulk (figure 5.2) and monolayer (figure 5.3)  $WSe_2$  on  $SiO_2$ .



Figure 5.2: Ultrafast heterodyne pump-probe dynamics of bulk  $WSe_2$  on  $SiO_2 \mid a$ . Time traces at varying fluences of near-field amplitude signal decay. **b.** Bi-exponential fit slow time constant value as a function of fluence

We first note the higher pump fluence that we are able to use on the SiO<sub>2</sub> sample as the substrate enhancement is not as strong compared to the Au. We also note that the 0nJ energy y-intercept is remarkably similar between the Au and the SiO<sub>2</sub>, indicating a limit for bulk WSe<sub>2</sub>. The main difference between bulk WSe<sub>2</sub> on Au versus on SiO<sub>2</sub> is the proportionality constant between time constant and pump energy.

However, the monolayer case clearly shows different dynamics, where again, the fast time constant is independent of fluence, but the second time constant again is linearly related to fluence.



Figure 5.3: Ultrafast heterodyne pump-probe dynamics of monolayer  $WSe_2$  on  $SiO_2 \mid \mathbf{a}$ . Time traces at varying fluences of near-field amplitude signal decay. **b.** Bi-exponential fit slow time constant value as a function of fluence

The 0 energy y-intercept is lower than the bulk case. This sample has the least sensitivity to pump fluence and could be the result of optical saturation at the fluences experimentally available. To better observe the spatially dependent dynamics, we take an ultrafast nano-movie by collecting images (or frames) at varying time delays as shown in figure 5.4.



Figure 5.4: Ultrafast heterodyne pump-probe imaging bulk and monolayer WSe<sub>2</sub> on SiO<sub>2</sub> | Pump probe amplitude R(T,  $\tilde{\nu}_{int}$ ) at varying pump-probe delays.

From this movie, we observe the spatial extent and heterogeneity of what we previously saw from simple point time traces shown in figures 5.1a 5.2a 5.3a. Specifically, we observe the monolayer section decaying faster than the bulk, but also observe a significant edge enhancement.

Using the prior knowledge of cryogenic experiments where the dark state is known to couple to the intervalley bright state, generating a bi-exponential decay, and the knowledge that the majority of the carriers will be in the thermal minimum state, the dark exciton, we can use the Drude mapping from figure 5.4 as a nano-map of the population and dynamics of the dark exciton in WSe<sub>2</sub>. However, we note that the dark exciton dynamics are dictated by 2 time constants – 1 independent of fluence and 1 dependent. Therefore, to determine if this heterogeneity is simply an artifact of the pump fluence and whose dynamics are controlled by the local temperature or if results from edge effects that affect the carrier density in a more intrinsic nature to the  $WSe_2$  itself, we need to determine the thermal timescales. If the fluence dependent time constant is on the same order as the thermal decay time constant, we know the difference in long term dynamics results from simple Boltzmann excitations. However, if they differ, then the dark exciton within the WSe<sub>2</sub> flake is indeed intrinsically heterogeneous.

## 5.4 Nano-thermometry

Thermal transport across interfaces is of high technological relevance in, e.g., semiconducting nanoelectronics, 2D material nanocomposites, and energy transmission and converting devices. For materials with little phonon spectral overlap, like semiconductors on silicon with a thermal oxide, at length scales smaller than the phonon mean free path, the energy transfer resistance is dominated by the interface. However, the specifics of these interfacial processes are yet poorly understood as conventional spectroscopic techniques are limited in spatial resolution, interfacial sensitivity, or are too slow to resolve the ultrafast dynamics during cooling and associated relaxation processes. Here, ultrafast s-SNOM is implemented, with its evanescent signal spatially confined to the nanoscale to selectively resolve ultrafast dynamics at the interface and discriminated from the conventionally bulk dominated response. At the example for a monolayer to bulk transition metal dichalcogenide (TMD) on SiO<sub>2</sub>, pump modulated pump-probe nano-spectroscopy and -imaging is performed to measure interfacial thermal transport on few ps timescales through substrate phonon softening. Combined with molecular dynamic simulations, the relationships between maximum temperature. TMD layer number, and thermal boundary conductance (TBC) is quantified. The smaller TBC value of 46.7  $MW/m^2K$  for the monolayer  $WSe_2/SiO_2$  compared to the larger TBC value of 66.7  $MW/m^2K$  for the bulk  $WSe_2/SiO_2$  results from finite size effects of monolayer  $WSe_2$  compared to the phonon mean free path. The interfacial phonon scattering associated with higher temperatures further limits its thermal conductivity compared to bulk WSe<sub>2</sub>. The application of this approach allows for optimizing interfacial thermal management.

Higher temperatures from poor thermal transport across interfaces reduces the lifespan and

performance for a range of technological applications, namely semiconducting nano-electronics,<sup>245–247</sup> 2D material nanocomposites,<sup>248–250</sup> and energy transmission and conservation devices. Heat dissipation in these applications are governed by phonon emission and phonon transport.<sup>251–253</sup> The dynamics of phonon emission depend on non-radiative electronic relaxation and their dissipation depends on thermal transport. This is exacerbated between materials with little phonon spectral overlap, like semiconductors on silicon with a thermal oxide, at scales smaller than the phonon mean free path, where heat dissipation is primarily limited by the Kapitza resistance.<sup>254–256</sup>

One approach to address thermal management in devices is to model the effects of substrate engineering for increased thermal management by including additional dissipation pathways,<sup>248,250,257</sup> engineering surface roughness<sup>258,259</sup>), or by nanostructuring the interface to match the phonon mean free path.<sup>255,260</sup> Atomically thin field effect transistors, based on a transition metal dichalcogenide (TMD) gate,<sup>261,262</sup> can bridge the divide between modern semiconducting nano-electronics and 2D material nanocomposites. Here, fundamental exciton and carrier dynamics are governed by interfacial thermal transport between the TMD and the substrate through thermal excitations that couple bright and dark states.<sup>263–265</sup> Understanding interfacial thermal transport, informed by direct ultrafast interfacial measurements, would thus illuminate charge carrier dynamics and coupling in 2D semiconductors.

Understanding phonon and carrier dynamics and interactions and technological innovation for better thermal management design has previously been explored through explicit temperature mapping but has remained complicated by the nanoscale spatial dimensions involved,<sup>266,267</sup> the effect of the measurement on the system itself,<sup>268</sup> the thermal contact between the sensor and device,<sup>269</sup> and the optical properties of the device.<sup>270</sup>

Many experimental techniques have been developed in an attempt to address these short comings. Thermal conductivity, diffusivity, and specific heat in low dimensional systems can be investigated with the  $3\omega$  technique.<sup>271</sup> However, the signal is still convolved with bulk contributions and further lack nanoscale spatial resolution. Recently developed techniques, like Raman thermometry-based approaches, which have demonstrated success<sup>272–274</sup> over a wide temperature range and like conventional thermoreflectance (TDTR), which through sophisticated modeling and analysis can extract interfacial resistance, still lack the necessary spatial and temporal resolution necessary to study ultrafast thermal dynamics at the nanoscale.

Luminescent thermometers, applied in atomic, molecular, and semiconducting systems, utilize temperature dependent emission lines to spectrally resolve the thermometers temperature, but are unable to spatially resolve nanoscale heterogeneity and lack thermal contact to the region of interest. Point contact thermoelectric cantilever probes are too slow and require complex modeling of the impact the thermocouple/thermistor has on the local temperature by opening an additional dissipation pathway and the thermal contact to the device in question. While ultrafast thermoreflectance in principle offers a mechanism to study thermal dynamics of devices, it remains insensitive to nanoscale heterogeneity. No technique offers simultaneous interfacial to bulk context with nanometer and ultrafast spatio-temporal resolution.

Here, we implement ultrafast heterodyne pump-probe *s*-SNOM in a new pump-modulated modality to image ultrafast interfacial transport dynamics.<sup>69</sup> The near-field spatial confinement provides the desired few-nm spatial localization necessary to discriminate the interfacial response from the bulk. At the example of a monolayer to bulk TMD, we pump the interband electronic state of WSe<sub>2</sub> and quantitatively explore extreme temperatures in excess of 2000 K at ps timescales by measuring the SiO<sub>2</sub> substrate phonon mode that softens with temperature to measure interfacial thermal transport. These measurements, combined with molecular dynamics (MD) simulations, determine the monolayer WSe<sub>2</sub>/SiO<sub>2</sub> TBC 47 MW/m<sup>2</sup>KW/K and the bulk WSe<sub>2</sub>/SiO<sub>2</sub> TBC 67 MW/m<sup>2</sup>K. The results show that interfacial phonon scattering associated with the higher temperatures in monolayer WSe<sub>2</sub> and its finite size effects both limit its thermal conductivity compared to bulk WSe<sub>2</sub>. Therefore, the effect of thermal excitation coupling between electronic states in semiconductors increases as dimension is reduced.

Samples of  $WSe_2/SiO_2$  were prepared by exfoliation as previously established.<sup>275</sup> Briefly, bulk  $WSe_2$  (2D Semiconductors) was transferred to Si with a 300 nm oxide layer (MTI Corporation) with adhesive tape (ProTapes Nitto SPV224 PVC Vinyl Surface Protection Specialty Tape from Ama-

zon). The samples were pre-characterized by far-field micro-photoluminescence (PL) spectroscopy with a HeNe (10  $\mu$ W) focused onto the sample with a homemade microscope and the scattered light was focused into a spectrometer (f = 500 mm, SpectraPro 500i, Princeton Instruments) with a thermoelectrically cooled, electron-multiplied, charge-coupled device (CCD, ProEM+: 1600 eXcelon3, Princeton Instruments).

Ground state near-field optical amplitude R(T,  $\tilde{\nu}$ ) and phase  $\phi(T, \tilde{\nu})$  response of SiO<sub>2</sub> and WSe<sub>2</sub> are measured using a customized near-field *s*-SNOM nano-scope (Anasys Instruments/Bruker, nanoIR2-s prototype) (Fig. 5.5a). Femtosecond mid-IR light is generated by difference frequency generation (DFG) between the signal of one OPA (Light Conversion, Orpheus-1) and the idler of a second OPA (Light Conversion, Orpheus-F) that are both pumped by a 220 fs 1 MHz 1030 nm pump (Light conversion, Carbide-40). The 1200 cm<sup>-1</sup> output pulses are directed into an asymmetric Michelson interferometer with one arm focusing the IR light with an off axis parabolic mirror (OAP) onto a metalized atomic force microscope (AFM) tip (ARROW-NCPt, NanoAndMore USA) apex (Fig. 5.5b). The back scattered near-field is then heterodyne amplified and collected with a mercury cadmium telluride (MCT) detector (Kolmar, KLD-0.1), whose signal is lock-in amplified (HF2LI, Zurich Instruments) at the second harmonic of the tip tapping frequency for near-field isolation as previously established.<sup>69,173,258</sup>

We then apply ultrafast broadband nano-imaging and -spectroscopy to measure the ps dynamics of the SiO<sub>2</sub> phonon shift, following previously established procedures for far-from-equilibrium pump excitations.<sup>69</sup> Here, we use the 670 nm 180 fs signal output from one OPA (Light Conversion Orpheus-F) as the pump and delay it relative to the probe pulse with a retroreflector on a linear delay stage (SLLA42-270-S, SmarAct). To isolate the ultrafast response, we employ pump modulation with a chopper (500 Hz, Thorlabs) and near-field sideband detection ( $n\omega t + \Omega_p$ ). As illustrated in figure 5.5c, the photo-excited WSe<sub>2</sub> emits phonons through its thermalization, which then interfacially couples to the SiO<sub>2</sub> substrate, rapidly heating the lattice and causing the SiO<sub>2</sub> phonon to soften. These softened phonons are experimentally observed through pump-probe near-field phase spectra showing the characteristic phonon dip red-shifting.



Figure 5.5: Ultrafast heterodyne pump-probe nano-imaging lattice dynamics | **a.** HPP IR s-SNOM, with the 180 fs pump pulse (670 nm), 220 fs probe pulse (8.33  $\mu$ m), and interferometric near-field detection. DFG – difference frequency generation, BS – beam splitter, OAP – off axis parabolic, MCT – mercury cadmium telluride detector. **b.** Tip localization of pump pulse, which excites electrons in the WSe<sub>2</sub>, and the probe pulse, which measuring the Drude response in the WSe<sub>2</sub> and excited state phonon absorption in SiO<sub>2</sub>. **c.** Top: Ground state WSe<sub>2</sub>, with room temperature lattice spacing and corresponding phonon resonance. Bottom: far-from-equilibrium excitation and associated electron-lattice thermalization through phonon emission, heating the SiO<sub>2</sub> substrate, expanding the lattice and red-shifting the corresponding phonon overlap at low frequencies and not at the probed SiO<sub>2</sub>mid-IR resonance.

The density of states (DOS) is calculated by taking the Fourier-transform of the normalized

velocity auto-correlation functions (Cor(t)). The Cor(t) is given as

$$Cor(t) = \frac{\left\langle \sum_{i=1}^{n} m_i \boldsymbol{v}_i(t) \cdot \boldsymbol{v}_i(t) \right\rangle}{\left\langle \sum_{i=1}^{n} m_i \boldsymbol{v}_i(0) \cdot \boldsymbol{v}_i(0) \right\rangle},$$
(5.4)

where t is the correlation time, n is the number of atoms, m is the atomic mass, v is the velocity vector of the atom, and the brackets indicate the ensemble average. Here, the thermal effect on the DOS is achieved by changing the simulated temperature (affecting the velocity of the atoms) in molecular dynamics (Fig. 5.5d).

We perform the non-equilibrium molecular dynamics (NEMD) simulation to study the thermal boundary conductance at the interface between SiO<sub>2</sub> and multi-layers WSe<sub>2</sub>. The thermal boundary conductance G is calculated as,  $G = J/\Delta T$ , where  $\Delta T$  and J are the temperature difference and the heat flux across the interface, respectively.

We first measure multilayer WSe<sub>2</sub> on SiO<sub>2</sub> by pumping the interband electronic transition in WSe<sub>2</sub>, followed by infrared (IR) probe on the SiO<sub>2</sub> phonon at variable pump fluences. Figure 5.6a (blue) shows the near-field spectral phase response  $\phi(T=3 \text{ ps}, \bar{\nu})$  of the SiO<sub>2</sub> phonon with peak at  $\nu_0=1175 \text{ cm}^{-1}$  under pump fluence 50 W/cm<sup>2</sup>. Then phonon resonance frequency is red-shifted from its ground state value  $\nu_0=1203 \text{ cm}^{-1}$ . As the fluence is increased (Fig. 5.6a dark red = 180 W/cm<sup>2</sup>, red = 240 W/cm<sup>2</sup>), the phonon frequency continues to red-shift (Fig. 5.6a dark red:  $\nu_0=$ 1162 cm<sup>-1</sup>, red:  $\nu_0 = 1159 \text{ cm}^{-1}$ ). The spectra were fit with Lorentzian resonances in a 4-layer finite dipole model (FDM), where the 4 layers are air, WSe<sub>2</sub>, interfacially excited substrate, and ground-state substrate. The WSe<sub>2</sub> layer exhibits a broad, non-resonant Drude response that, to first order at these fluence values and sample parameters, inverts the spectral phase of the SiO<sub>2</sub> phonon absorption.<sup>69</sup> The substrate phonon resonance exhibits a red shifted SiO<sub>2</sub> phonon absorption from lattice expansion and a ground state bleach. Figure 5.6b shows the extracted center frequency as a function of fluence. The linear relationship between fluence and phonon shift (Fig. 5.6b) matches well with the linear trend expected from theoretical molecular dynamics simulation (Fig. 5.6b) inset). (For additional fluence dependent data, see SL) At the fluence of 240 W/cm<sup>2</sup>, we measure a local temperature of 1200 K.



Figure 5.6: SiO<sub>2</sub> phonon resonance shift as ultrafast temperature sensor | **a.** Power dependent ultrafast spectra (T = 3 ps) showing characteristic phonon absorption center frequency red-shift with increasing fluence. **b.** Model extracted center frequency as function of fluence. Inset: Lorentzian line shape fit to modeled density of states for varying temperatures (Fig. 5.8c), indicating good linear agreement with experimental power dependence. **c.** Time dependent spectra at identical fluences (120 W/cm<sup>2</sup>), indicating a blue shift with increasing time as the system cools back to room temperature (center frequency 1200 cm<sup>-1</sup>). **d.** Center frequencies of SiO<sub>2</sub> phonon extracted through HPP *s*-SNOM model indicating the asymptotic approach from maximally red-shifted to 1200 cm<sup>-1</sup>. Green trace: cross correlation between pump and probe. Gray dashed line: room temperature  $\nu_0$ . Inset: propagating thermally excited SiO<sub>2</sub> within the nearfield.

In order to address the cooling dynamics, we measure the spectro-temporal evolution of the phase  $\phi(\tilde{\nu})$  for a pump fluence of 120 W/cm<sup>2</sup> (Figure 5.6c red). The cooling dynamics indicate

a continuous SiO<sub>2</sub> phonon blue-shift from initial pump-induced resonant frequency of  $\nu_0 = 1166$  cm<sup>-1</sup>as shown in figure 5.6d (visible-IR cross correlation Fig. 5.6d green) at varying pump-probe delays. (Additional spectra were collected at varying pump-probe delays; see SI for details.<sup>69</sup>) We observe a mono-exponential exponential decay with time constant  $\tau = 13$  ps (Fig. 5.6d black dashed line) that asymptotes back to the ground state center frequency (Fig. 5.6d grey dashed line).

In order to observe local temperature differences across the sample, an image of the maximum near-field amplitude  $R(T = 3 \text{ ps}, \tilde{\nu}_{integrated})$  from the Drude response of the system was collected and is shown in Figure 5.7a (top). Here, the Drude response is a good measure for the relative carrier density that is spatially varying across the sample surface. We identify a strained monolayer region next to the bulk WSe<sub>2</sub> through AFM scanning (Fig. 5.7a bottom) combined with microphotoluminescence spectroscopy (Fig. 5.7b,  $\lambda_0 = 770$  nm, black dashed line) at location 2 (dark blue) in Figure 5.7a (unstrained ML WSe<sub>2</sub> center frequency Fig. 5.7b gray dashed line). The image of  $R(T = 3 \text{ ps}, \tilde{\nu}_{integrated})$  shows a homogeneously high carrier density in the center of both the ML and bulk WSe<sub>2</sub>, with a slightly decreased carrier density at their boundary. The boundary between the WSe<sub>2</sub> and the bare SiO<sub>2</sub> substrate shows a significant increase in carrier density compared to the center regions. To understand the higher carrier density, we perform nano-FTIR for the same pump-probe delay of 3 ps as shown in Figure 5.7c.

Spectra were collected at different sample positions of 1) center of the bulk  $WSe_2$  (Fig. 5.7c (1) blue), 2) the center of the ML  $WSe_2$  (Fig. 5.7c (2) dark blue), 3) the edge of the bulk  $WSe_2$ (Fig. 5.7c (3) dark red), and 4) the edge of the ML  $WSe_2$  (Fig. 5.7c (4) red). From the degree of red-shift at each location, we observe both that the center of the ML  $WSe_2$  reaches higher temperatures than the center of the bulk  $WSe_2$  and that the edge of both the ML and bulk  $WSe_2$  reaches higher temperatures than the center of either region. This can be intuitively understood as fewer dissipation pathways are available for the  $WSe_2$  to cool in plane and therefore heat builds up at the edge as illustrated in figure 5.7d. This also explains the increased carrier density observed in the Drude response (Fig. 5.7a). The increased local temperature, corresponding to a higher excited



Figure 5.7: Local variations in temperature and thermal boundary conductance | **a**. Top: Pump demodulated integrated near-field amplitude. Bottom: Topographic image of bulk WSe<sub>2</sub>, monolayer WSe<sub>2</sub> (dashed green) and substrate SiO<sub>2</sub>(dashed white). **b**. Far-field photoluminescence indicating strained monolayer in A. Gray dashed line: unstrained ML center frequency. Black dashed line: strained ML center Frequency. **c**. Ultrafast (T = 3 ps) SiO<sub>2</sub> phonon absorptions at different locations in the sample (indicated in A). In increasing temperature, center of bulk WSe<sub>2</sub>, center of monolayer WSe<sub>2</sub>, edge of bulk WSe<sub>2</sub>, and edge of monolayer WSe<sub>2</sub>. **d**. Schematic comparison of thermal dissipation at the center of a sample vs. the edge of the sample indicating the intralayer thermal transport in WSe<sub>2</sub> strongly affects local dissipation. **e**. Molecular dynamic simulation of thermal boundary conductance as a function of WSe<sub>2</sub> layer number, indicating phonon reflection and saturation once the mean free path is significantly smaller than the WSe<sub>2</sub> layer thickness.

phonon density, acting as a hot phonon bottleneck, restricting the carrier's ability to thermalize through phonon emission, thus causing an increase in carrier density at this pump-probe delay. We further observe that the ML WSe<sub>2</sub> red-shifts more and therefore reaches higher temperatures than the bulk WSe<sub>2</sub>. The difference in ML versus bulk WSe<sub>2</sub> temperature is a result of Beer's law with the mass of the system increasing faster than the absorbed energy. Molecular dynamic simulations predict a sharp increase in TBC for ML compared to bulk (Fig. 5.7e) as a finite size effect until the WSe<sub>2</sub> layer thickness exceeds the phonon mean free path.

To better understand these experimental results, we perform molecular dynamic simulations to model this system. The relationship between temperature and thermal boundary conductance is shown in figure 5.8a. We observe an inverse linear dependence on the TBC with temperature. Figure 5.8b shows the effect this has on the cooling dynamics, where hotter systems recover more slowly than their cooler counterparts. While the higher energy SiO<sub>2</sub> phonon shifts with temperature (Figure 5.8c), the low energy phonon modes participating in heat transfer are not temperature dependent, indicating the modification of the density of states overlap is not responsible for the difference in the TBC. While our ultrafast nano-thermometry method is sensitive to the surface volume, we don't directly measure just the surface layer of SiO<sub>2</sub> atoms. The relative temperature and depth dependent dynamics are shown in Figure 5.8d. Here, we note the trivial observation that the surface reaches higher temperatures faster than deeper locations in the SiO<sub>2</sub>, but specifically call out the sensitivity of the rise time on depth, where the top 2 nm reaches the maximum temperature in ~1 ps and the SiO<sub>2</sub> 16 nm from the surface takes ~50 ps (Figure 5.8d inset).

In the following, we discuss the mechanism behind the temperature dependent TBC. Simple Newtonian cooling predicts faster heat transfer at higher  $WSe_2$  temperatures. However, increased phonon densities at higher temperatures lead to phonon-phonon scattering. We quantified this relationship with molecular dynamic simulations, finding the intrinsic Umklapp phonon scattering, which has been observed at the GaN/SiC interface,<sup>276</sup> determines the TBC temperature relationship. This is directly observed in the cooling traces simulated for different starting temperatures. However, the location studied here exhibited a layer dependence as well, where we see both higher temperatures and thinner WSe<sub>2</sub> in the monolayer lead to slower cooling compared to the bulk.

We next discuss the processes that occur within the  $WSe_2$  that upon pumping generate the



Figure 5.8: Molecular dynamics modeling of  $SiO_2$  phonon | **a.** Molecular dynamic simulation of thermal boundary conductance between WSe<sub>2</sub> and SiO<sub>2</sub> for different interfacial temperatures indicating monotonically decreasing relationship with temperature. **b.** Molecular dynamics simulation of SiO<sub>2</sub> cooling over time for different starting WSe<sub>2</sub> temperatures. Inset: zoom in on first 50 ps rise and fall of temperature. **c.** Molecular dynamic simulation of density of states for SiO<sub>2</sub> at varying temperatures. Increasing temperature corresponds with red-shift of density of states peak. **d.** Molecular dynamics of temperature change in SiO<sub>2</sub> at increasing depths, spaced by 2 nm starting at the WSe<sub>2</sub>/SiO<sub>2</sub> interface (red). Inset: zoom in on the first 50 ps rise in temperature.

thermal load to be dissipated by the SiO<sub>2</sub>. The non-resonant, above bandgap excitation initially produces a population of hot electrons that then rapidly thermalize into excitons and carriers. This thermalization rapidly heats the WSe<sub>2</sub> lattice through phonon emission. The electron dynamics in WSe<sub>2</sub> are then dominated by continued thermalization and radiative emission of bright excitons, followed by the long lived electronic dark excitonic state.<sup>277</sup> The hot WSe<sub>2</sub> lattice then thermally interfacially heats the substrate, with temperature increase on the order of ps to 10s of ps depending on the distance from the surface, with the surface layer reaching maximum temperature the fastest. In the case of WSe<sub>2</sub> on SiO<sub>2</sub>, the higher energy phonons from the large bandgap of SiO<sub>2</sub> limits the interfacial energy transfer to primarily occur at the lowest phonon frequency modes as that is where the DOS overlap is greatest. While the higher energy SiO<sub>2</sub> phonons are temperature dependent, this change in the density of states doesn't affect the TBC as these modes don't participate in interfacial energy transfer.

The observed 10s of ps decay time constant and simultaneous lack of rise time observation together with the theoretical depth dependent result indicate extreme surface sensitivity. As previously mentioned, photoinjected carriers screen the substrate phonon mode, limiting our temporal resolution to dynamics that occur 3 ps after excitation. This screening further limits the evanescent near-field propagation from the tip, enhancing our surface specificity. Our pump modulated detection scheme is most sensitive to the largest deviation from the ground state. Therefore, the surface, whose temperature deviates the most from the ground state and therefore has the largest phonon shift, dominates the weaker signals from the bulk of the substrate, further localizing our near-field signal to the near surface region. The depth dependent molecular dynamic simulations further predict a gradient in the rise time of the substrate temperature along the surface normal axis within the first 10s of nm. However, the Drude screening in the first 3 ps completely obscures the substrate phonon temperature rise and the following dynamics are exclusively cooling, indicating our surface technique is specific to the first 1 nm and is largely insensitive to even the top 10 nm of the SiO<sub>2</sub> substrate.

Previous techniques have demonstrated great success in the wide temperature ranges accessible with Raman thermometry and the surface sensitive time domain thermoreflectance, but the lack of intrinsic surface sensitivity (rather than simply sample selection) limits their applicability to a wider class of material systems. Specifically, other work also looking at TMD to SiO<sub>2</sub> to Si systems, performing Raman thermometry, modeled a similar system, yet were insensitive to the TMD SiO<sub>2</sub> interface and instead used indirect measurements of the underlying Si.<sup>278,279</sup> Differences

in the extracted TBC value increasing with increasing temperature are explained as a positive correlation between temperature and phonon specific heat together with neglecting the temperature dependent absorption of  $MoS_2$ . However, our modeling and dynamics illustrate the importance of phonon-phonon scattering at the interface. The higher temperatures explored here further suggest that Umklapp scattering continues to dominate the interfacial thermal resistance at few nm length and thousands K temperature scales.

Alternative previous approaches, using thermocouple cantilever probes similarly probe nanoscopic volumes, but required complex numerical simulations of the tip sample interaction and lacked temporal resolution. Here, we directly observe the substrate phonon frequency shift as a measure of temperature and therefore interfacial thermal transport. Similarly, ultrafast thermo-reflectance spectroscopy has been used to measure the ultrafast response of molecular systems, but lacks spatial resolution. Our technique uses the combination of nano-probes for signal localization and ultrafast spectroscopy to resolve the ultrafast nanoscopic thermalization and interfacial thermal transport. Our approach is generalizable to other substrate systems whose phonons exhibit a temperature dependence. In the example of WSe<sub>2</sub> on SiO<sub>2</sub>, we've imaged heterogeneity in the spatial distribution of temperature, which will affect the dark exciton state lifetimes. The decay of these long lived states are dominated by coupling between the intravalley dark and bright excitons.<sup>280</sup> Therefore, the electronic relaxation is also expected to be spatially heterogeneous.

In conclusion, ultrafast s-SNOM has been implemented to selectively resolve ultrafast dynamics at the interface of WSe<sub>2</sub> and SiO<sub>2</sub>. Pump modulated pump-probe nano-spectroscopy and -imaging has been performed to measure interfacial thermal transport on the few ps timescale through substrate phonon softening. This has been combined with molecular dynamic simulations to quantify the relationships between maximum temperature, TMD layer number, and thermal boundary conductance (TBC). The lower TBC of the monolayer results from finite size effects of monolayer WSe<sub>2</sub> compared to the phonon mean free path. The interfacial phonon scattering associated with higher temperatures further limited its thermal conductivity compared to bulk WSe<sub>2</sub>.

# Chapter 6

# **Conclusion and Outlook**

# 6.1 Summary

In summary, this thesis covered the two main branches of research I performed. The first is method development of scanning optical microscopy and the second is its application to the study of electron dynamics in quantum materials. In this final chapter, I will take a look to the future to assess possible extensions, developments, and new applications.

### 6.1.1 Multi quantum well strong coupling

In summary, my studies (Chapter 4) on MQWs first demonstrated the macroscopic optical power limiting and switching behavior enabled by multi-quantum wells (MQWs) that are strongly coupled to plasmonic antennas. I noted the strong non-linearity of the reflection coefficient upon incident peak fluence through the saturation of the MQW and resulting decreased coupling strength in the heterostructure. This reduced coupling strength collapsed the hybridized states to the bare antenna resonance, which behaved classically under high fluences. I then extended this work to the near-field, where I demonstrated tip-sample nano-cavity enhancement. I used tip-sample positioning to control both the hybridized state phase and coupling strength through near-field illumination. This new avenue of control could enable qubit phase rotation operations in future quantum information technology applications.

#### 6.1.2 Tungsten diselenide

I demonstrated the power of nanoscale ultrafast spectroscopy (Chapter 5. Previous to this measurement, temperatures and dynamics were expected to be lower and slower. However, the 2000 K measured temperature and 10s of ps dynamics clearly show the interfacial thermal transport, at least directly at the interface, is faster with higher temperatures than previously estimated. I used a temperature decay time constant to calculate a TBC of 50 MW/m<sup>2</sup>K. I further qualitatively explored the relationship between the maximum temperature, TMD layer number, and TBC. I noted that higher temperatures lead to lower TBC from phonon-phonon scattering and that finite size effects of monolayer WSe<sub>2</sub> limit the interfacial thermal transport. Future applications with atomically thin two dimensional materials will require sophisticated substrate engineering for thermal management.

#### 6.2 Outlook

#### 6.2.1 Method Development

The state of the art s-SNOM has significantly advanced within just my time in the field from simple self-homodyne imaging, to ultrafast pump-probe, variable temperature, variable voltage, photochemistry, THz spectroscopy, and in liquid techniques becoming available and more consistently implemented. However, the increased complexity of these extended measurement techniques is rapidly lengthening measurement times to the point where a "full" dataset can not even be acquired as the dimensionality is simply too high. Below, I will address these issues individually.

<u>Errors in measurements and interpretation</u> On the most basic level, errors in measurements can easily result from improper isolation of the near-field signal as discussed in depth in Chapter 2. Self-homodyne imaging and topographic artifacts from simple near-field enhancement (where the tip-sample interaction is not as simple as a tip above a perfectly planar surface) confound measurement interpretation. Demodulation techniques can be used to improve heterodyne

near-field signal extraction (Chapter 3).

**Data acquisition rate** I see dimensionality of complicated datasets as a major limitation in the continued advancement of s-SNOM. Computational approaches like compressed sensing and matrix completion will become increasingly necessary for lengthy experiments, like, e.g., cavity mapping (z), temperature dependent (T), spectroscopy (t), ultrafast pump-probe spectroscopy (T), on a gated (V) quantum well (I) coupled (g) to a resonant antenna. In this experiment, which is a scientifically reasonable desired direction, the dimensionality of the total dataset is nine. For reference, the largest dataset shown in this thesis is four and took six months to complete. One further concern about large datasets is not simply the acquisition time, but is rather the analysis. Careful spectral analysis is important in the physical interpretation of s-SNOM datasets, but is notoriously difficult to generalize sufficiently for computer automatization.

# 6.2.2 Scientific progress on quantum materials

The two projects that I wish to discuss a possible future of are strongly coupled multiquantum-wells and transition metal dichalcogenide (TMD) projects. Both of these systems involve carrier coupling to a resonance, either strongly coupled to a gold antenna, or interfacially thermally coupled to an SiO<sub>2</sub> substrate.

**mid-IR strong coupling** Strong coupling has frequently been studied in both molecular and quantum systems both in the far-field and near-field. However, showing all optical coupling strength control, phase resolved and excitation interference through tip positioning has yet to be demonstrated (before the work presented in this thesis). Far-field time resolved measurements using degenerate pump probe measurements showed ultrafast optical control, but the implementation of this technique in the near-field is significantly more complicated. To measure the ultrafast  $t_1$ MQW decay in the near-field, we need to develop degenerate pump-probe nano-FTIR. Changing the interferometer scheme to, e.g., a modified Mach-Zehnder interferometer with one arm responsible
for the pump-probe near-field interaction and the other for spectroscopy could work. This scheme is still asymmetric such that phase information can be extracted, but also is background free from the heterodyne process.

**Transition metal dichacogenide electron dynamcis** The work presented here in this thesis covered the ultrafast interfacial thermal transport between photo-excited WSe<sub>2</sub> and an SiO<sub>2</sub> substrate. However in the process of measuring the resonant feature from the substrate (SiO<sub>2</sub> phonon), we also measured the Drude response from the electron gas within the WSe<sub>2</sub> itself. What is challenging when using visible spectroscopy (dark states are dark in the visible for a reason) is easily measured in the infrared (the sum of carrier populated states). Future measurements looking for the spatial evolution of bound exciton wavefunctions through 1s-2p absorption measurements in MoS<sub>2</sub> are planned. The exciton 2p wavefunction is predicted to extend by ~10 nm and should therefore be quite sensitive to defects, boundaries, and edges.

## 6.3 Final thoughts

s-SNOM has shown itself, through its applications to studying quantum and molecular materials, to be a power technique, giving rise to many high impact publications. I have demonstrated significant method advancements, imaging electron dynamics in quantum materials at nanoscopic volumes. Further, I give an outlook of possible future measurements and the field as a whole to study novel meso-scopic physical phenomena.

## Bibliography

- <sup>1</sup> Gerhard Herzberg and John William Tranter Spinks. *Molecular spectra and molecular structure:* Infrared and Raman spectra of polyatomic molecules. Van Nostrand Reinhold, (1945).
- <sup>2</sup> F Hitzel, A Hangleiter, S Bader, H.-J. Lugauer, and V Härle. Correlation of Defects and Local Bandgap Variations in GaInN/GaN/AlGaN LEDs. <u>physica status solidi (b)</u>, **228**(2):407–410, (2001).
- <sup>3</sup> J A Gerber, S Berweger, B T O'Callahan, and M B Raschke. *Phase-Resolved Surface Plasmon Interferometry of Graphene*. Physical Review Letters, **113**:55502, (2014).
- <sup>4</sup> Sander A Mann, Nishant Nookala, Samuel C Johnson, Michele Cotrufo, Ahmed Mekawy, John F Klem, Igal Brener, Markus B Raschke, Andrea Alù, and Mikhail A Belkin. Ultrafast optical switching and power limiting in intersubband polaritonic metasurfaces. <u>Optica</u>, 8(5):606–613, (2021).
- <sup>5</sup> Robert G Messerschmidt and Matthew A Harthcock. *Infrared microspectroscopy. Theory and applications*. Marcel Dekker, New York, NY, (1988).
- <sup>6</sup> Ira W Levin and Rohit Bhargava. Fourier Transform Infrared Vibrational Spectroscopic Imaging: Integrating Microscopy and Molecular Recognition. Annu. Rev. Phys. Chem, **56**:429–474, (2005).
- <sup>7</sup> M MINSKY. *Microscopy apparatus*, (1961).
- <sup>8</sup> A Lewis, M Isaacson, A Harootunian, and A Muray. Development of a 500 Å spatial resolution light microscope: I. light is efficiently transmitted through λ/16 diameter apertures. Ultramicroscopy, **13**(3):227–231, (1984).
- <sup>9</sup> D W Pohl, W Denk, and M Lanz. Optical stethoscopy: Image recording with resolution  $\lambda/20$ . Applied Physics Letters, 44(7):651–653, (1984).
- <sup>10</sup> E Betzig, J K Trautman, T D Harris, J S Weiner, and R L Kostelak. Breaking the diffraction barrier: Optical microscopy on a nanometric scale. Science, **251**(5000):1468–1470, (1991).
- <sup>11</sup> Martin Wagner, Alexander S McLeod, Scott J Maddox, Zhe Fei, Mengkun Liu, Richard D Averitt, Michael M Fogler, Seth R Bank, Fritz Keilmann, and D N Basov. Ultrafast dynamics of surface plasmons in InAs by time-resolved infrared nanospectroscopy. <u>Nano Lett.</u>, 14(8):4529–4534, (2014).

- <sup>12</sup> M Böhmler, A Huber, and M Eisele. THz nano-spectroscopy with 25 nm spatial and 10 fs time resolution. In <u>2016 41st International Conference on Infrared, Millimeter, and Terahertz waves</u> (IRMMW-THz), pages 1–2, (2016).
- <sup>13</sup> Sven A Dönges, Omar Khatib, Brian T O'Callahan, Joanna M Atkin, Jae Hyung Park, David Cobden, and Markus B Raschke. Ultrafast Nanoimaging of the Photoinduced Phase Transition Dynamics in VO2. Nano Letters, 16(5):3029–3035, (2016).
- <sup>14</sup> FYHK Zenhausern, Y Martin, and H K Wickramasinghe. Scanning interferometric apertureless microscopy: optical imaging at 10 angstrom resolution. Science, 269(5227):1083–1085, (1995).
- <sup>15</sup> Yasushi Inouye and Satoshi Kawata. Near-field scanning optical microscope with a metallic probe tip. Optics letters, **19**(3):159–161, (1994).
- <sup>16</sup> G Binnig, C F Quate, and C Gerber. *Atomic force microscope*. <u>Physical Review Letters</u>, **56**(9):930–933, (1986).
- <sup>17</sup> B Knoll and F Keilmann. Enhanced dielectric contrast in scattering-type scanning near-field optical microscopy. Optics Communications, 182(4):321–328, (2000).
- <sup>18</sup> Joanna M Atkin, Samuel Berweger, Andrew C Jones, and Markus B Raschke. Nano-optical imaging and spectroscopy of order, phases, and domains in complex solids. <u>Advances in Physics</u>, 61(6):745–842, (2012).
- <sup>19</sup> Benjamin Pollard and Markus B Raschke. Correlative infrared nanospectroscopic and nanomechanical imaging of block copolymer microdomains. Beilstein J. Nanotechnol, 7:605–612, (2016).
- <sup>20</sup> Rebekah E Simon, Samuel C Johnson, Omar Khatib, Markus B Raschke, and David A Budd. Correlative nano-spectroscopic imaging of heterogeneity in migrated petroleum in unconventional reservoir pores. Fuel, **300**:120836, (2021).
- <sup>21</sup> E Abbe. Beiträge zur Theorie des Mikroskops und der mikroskopischen Wahrnehmung: I. Die Construction von Mikroskopen auf Grund der Theorie. <u>Archiv für mikroskopische Anatomie</u>, 9(1):413–418, (1873).
- <sup>22</sup> Jeff Squier and Michiel Müller. High resolution nonlinear microscopy: A review of sources and methods for achieving optimal imaging. <u>Review of Scientific Instruments</u>, **72**(7):2855–2867, (2001).
- <sup>23</sup> J David Jackson. *Electrodynamics*. The Optics Encyclopedia, (1975).
- <sup>24</sup> F Depasse, M A Paesler, D Courjon, and J M Vigoureux. Huygens-Fresnel principle in the near field. Opt. Lett., **20**(3):234–236, (1995).
- <sup>25</sup> J W S Rayleigh. XXXI. Investigations in optics, with special reference to the spectroscope. The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science, 8(49):261-274, (1879).
- <sup>26</sup> S W Hell and J Wichmann. Breaking the diffraction resolution limit by stimulated emission: stimulated-emission-depletion fluorescence microscopy. Optics Letters, **19**(11):780, (1994).
- <sup>27</sup> T A Klar and S W Hell. Subdiffraction resolution in far-field fluorescence microscopy. Optics Letters, 24(14):954, (1999).

- <sup>28</sup> E Betzig, G H Patterson, R Sougrat, O W Lindwasser, S Olenych, J S Bonifacino, M W Davidson, J Lippincott-Schwartz, and H F Hess. *Imaging intracellular fluorescent proteins at nanometer resolution*. Science, **313**(5793):1642–1645, (2006).
- <sup>29</sup> M J Rust, M Bates, and X Zhuang. Sub-diffraction-limit imaging by stochastic optical reconstruction microscopy (STORM). Nature Methods, **3**(10):793-795, (2006).
- <sup>30</sup> Andrew C Jones, Samuel Berweger, Jiang Wei, David Cobden, and Markus B Raschke. Nanooptical investigations of the metal-insulator phase behavior of individual VO2 microcrystals. Nano Lett., **10**(5):1574–1581, (2010).
- <sup>31</sup> Eric A. Muller, Benjamin Pollard, Hans A. Bechtel, Peter van Blerkom, and Markus B. Raschke. Infrared vibrational nano-crystallography and nano-imaging. <u>Science Advances</u>, 2:1601006, (2016).
- <sup>32</sup> Benjamin Pollard, Eric A Muller, Karsten Hinrichs, and Markus B Raschke. Vibrational nanospectroscopic imaging correlating structure with intermolecular coupling and dynamics. <u>Nature</u> Communications, 5:3587, (2014).
- <sup>33</sup> W R Bennett. Inversion Mechanisms in Gas Lasers. Appl. Opt., 4(S1):3–22, (1965).
- <sup>34</sup> C K N Patel. CW HIGH POWER N2-CO2 LASER. Applied Physics Letters, 7(1):15-17, (1965).
- <sup>35</sup> Faist Jerome, Capasso Federico, Sivco Deborah L., Sirtori Carlo, Hutchinson Albert L., and Cho Alfred Y. Quantum Cascade Laser. Science, **264**(5158):553–556, (1994).
- <sup>36</sup> E Odoh and Augustine S Njapba. A Review of Semiconductor Quantum Well Devices. <u>Advances</u> in Physics Theories and Applications, **46**:26–32, (2015).
- <sup>37</sup> Beck Mattias, Hofstetter Daniel, Aellen Thierry, Faist Jérôme, Oesterle Ursula, Ilegems Marc, Gini Emilio, and Melchior Hans. Continuous Wave Operation of a Mid-Infrared Semiconductor Laser at Room Temperature. Science, **295**(5553):301–305, (2002).
- <sup>38</sup> Fernando Agulló-López, José Manuel Cabrera, and Fernando Agulló-Rueda. *Electrooptics: Phenomena, materials and applications*. Academic Press, New York, (1994).
- <sup>39</sup> Andreas Hugi, Romain Terazzi, Yargo Bonetti, Andreas Wittmann, Milan Fischer, Mattias Beck, Jérôme Faist, and Emilio Gini. *External cavity quantum cascade laser tunable from 7.6 to 11.4 micrometres.* Applied Physics Letters, **95**(6):61103, (2009).
- <sup>40</sup> J A Giordmaine and Robert C Miller. Tunable Coherent Parametric Oscillation in LiNbO<sub>3</sub> at Optical Frequencies. Phys. Rev. Lett., **14**(24):973–976, (1965).
- <sup>41</sup> S Akhmanov, A Kovrigin, Algis Piskarskas, V Fadeev, and R Khokhlov. Observation of Parametric Amplification in the Optical Range. Jetp Letters - JETP LETT-ENGL TR, 2, (1965).
- <sup>42</sup> R Baumgartner and R Byer. Optical parametric amplification. <u>IEEE Journal of Quantum</u> Electronics, **15**(6):432–444, (1979).
- <sup>43</sup> D N Schimpf, J Rothhardt, J Limpert, A Tünnermann, and D C Hanna. Theoretical analysis of the gain bandwidth for noncollinear parametric amplification of ultrafast pulses. J. Opt. Soc. Am. B, 24(11):2837–2846, (2007).

- <sup>44</sup> A Galvanauskas, A Hariharan, D Harter, M A Arbore, and M M Fejer. *High-energy femtosecond pulse amlification in a quasi-phase-matched parametric amplifier*. <u>Opt. Lett.</u>, **23**(3):210–212, (1998).
- <sup>45</sup> Giulio Cerullo and Sandro De Silvestri. Ultrafast optical parametric amplifiers. <u>Review of</u> Scientific Instruments, **74**(1):1–18, (2003).
- <sup>46</sup> Bruno E Schmidt, Nicolas Thiré, Maxime Boivin, Antoine Laramée, François Poitras, Guy Lebrun, Tsuneyuki Ozaki, Heide Ibrahim, and François Légaré. *Frequency domain optical parametric amplification*. Nature Communications, 5(1):3643, (2014).
- <sup>47</sup> M Bass, P A Franken, A E Hill, C W Peters, and G Weinreich. Optical Mixing. <u>Phys. Rev.</u> Lett., 8(1):18, (1962).
- <sup>48</sup> Wei Shi, Yujie J Ding, Xiaodong Mu, and Nils Fernelius. Tunable and coherent nanosecond radiation in the range of 2.7-28.7 μm based on difference-frequency generation in gallium selenide. Applied Physics Letters, 80(21):3889–3891, (2002).
- <sup>49</sup> Hans A. Bechtel, Samuel C. Johnson, Omar Khatib, Eric A. Muler, and Markus B. Raschke. Synchrotron infrared nano-spectroscopy and -imaging. Surface Science Reports, 75(3), (2020).
- <sup>50</sup> W D Duncan and Gwyn P Williams. Infrared synchrotron radiation from electron storage rings. Appl. Opt., **22**(18):2914–2923, (1983).
- <sup>51</sup> K D Möller, D P Siddons, C J Hirschmugl, D Scardino, P Petrone, D Carlson, and G P Williams. *Two-mirror wave-front-dividing interferometer for infraredsynchrotron radiation*. <u>Appl. Opt.</u>, **30**(30):4297–4301, (1991).
- <sup>52</sup> C Steier, B Bailey, K Baptiste, W Barry, A Biocca, W Byrne, P Casey, M Chin, R Donahue, R Duarte, M Fahmie, B Gath, S Jacobson, J Julian, J Y Jung, M Kritscher, S Kwiatkowski, S Marks, P McKean, R Mueller, H Nishimura, J ONeill, G Portmann, S Prestemon, D Robin, S Rossi, F Sannibale, T Scarvie, R Schlueter, D Shuman, A Smith-Baumann, G Stover, C Timossi, W Wan, T Warwick, R Wells, J Weber, and E Williams. *Successful Completion of the Top-off Upgrade of the Advanced Light Source*. <u>AIP Conference Proceedings</u>, **1234**(1):575–578, (2010).
- <sup>53</sup> C Steier, B Bailey, K Baptiste, W Barry, A Biocca, W Byrne, M Chin, R Donahue, R Duarte, M Fahmie, B Gath, S Jacobson, J Julian, J Y Jung, S Kwiatkowski, S Marks, R Mueller, H Nishimura, J ONeill, S Prestemon, D Robin, S Rossi, F Sannibale, T Scarvie, R Schlueter, D Shuman, G Stover, C Timossi, T Warwick, J Weber, and E Williams. *Status of the top-off upgrade of the ALS.* In <u>2007 IEEE Particle Accelerator Conference (PAC)</u>, pages 1197–1199, (2007).
- <sup>54</sup> F Mooshammer, M A Huber, F Sandner, M Plankl, M Zizlsperger, and R Huber. Quantifying Nanoscale Electromagnetic Fields in Near-Field Microscopy by Fourier Demodulation Analysis. ACS Photonics, 7(2):344–351, (2020).
- <sup>55</sup> Alexander S McLeod, P Kelly, M D Goldflam, Z Gainsforth, A J Westphal, Gerardo Dominguez, Mark H Thiemens, Michael M Fogler, and D N Basov. *Model for quantitative tip-enhanced spectroscopy and the extraction of nanoscale-resolved optical constants*. <u>Phys. Rev. B</u>, **90**(8):85136, (2014).

- <sup>56</sup> A Cvitkovic, N Ocelic, and R Hillenbrand. Analytical model for quantitative prediction of material contrasts in scattering-type near-field optical microscopy. <u>Optics Express</u>, **15**(14):8550–8565, (2007).
- <sup>57</sup> Alexander A Govyadinov, Iban Amenabar, Florian Huth, P Scott Carney, and Rainer Hillenbrand. Quantitative Measurement of Local Infrared Absorption and Dielectric Function with Tip-Enhanced Near-Field Microscopy. J. Phys. Chem. Lett., 4(9):1526–1531, (2013).
- <sup>58</sup> R Esteban, R Vogelgesang, and K Kern. *Tip-substrate interaction in optical near-field microscopy*. Physical Review B, **75**(19):195410, (2007).
- <sup>59</sup> X Chen, C F B Lo, W Zheng, H Hu, Q Dai, and M K Liu. Rigorous numerical modeling of scattering-type scanning near-field optical microscopy and spectroscopy. <u>Applied Physics Letters</u>, **111**(22):223110, (2017).
- <sup>60</sup> Nenad Ocelic, Andreas Huber, and Rainer Hillenbrand. Pseudoheterodyne detection for background-free near-field spectroscopy. Applied Physics Letters, 89:101124, (2006).
- <sup>61</sup> O Khatib, H A Bechtel, M C Martin, M B Raschke, and G L Carr. Far infrared synchrotron near-field nano-imaging and -spectroscopy. ACS Photonics, 5:2773–2779, (2018).
- <sup>62</sup> D Lang, J Döring, T Nörenberg, Á Butykai, I Kézsmárki, H Schneider, S Winnerl, M Helm, S C Kehr, and L M Eng. *Infrared nanoscopy down to liquid helium temperatures*. <u>Review of</u> Scientific Instruments, **89**(3):33702, (2018).
- <sup>63</sup> F Kuschewski, H.-G. G von Ribbeck, J Döring, S Winnerl, L M Eng, and S C Kehr. Narrowband near-field nanoscopy in the spectral range from 1.3 to 8.5 THz. <u>Applied Physics Letters</u>, 108(11):113102, (2016).
- <sup>64</sup> Q Wu, M Litz, and X C Zhang. Broadband detection capability of ZnTe electro-optic field detectors. Applied Physics Letters, 68(21):2924, (1996).
- <sup>65</sup> H T Chen, R Kersting, and G C Cho. *Terahertz imaging with nanometer resolution*. <u>Applied</u> Physics Letters, **83**(15):3009–3011, (2003).
- <sup>66</sup> Rainer Hillenbrand and Fritz Keilmann. Complex optical constants on a subwavelength scale. Physical Review Letters, 85(14):3029, (2000).
- <sup>67</sup> G Wurtz, R Bachelot, and P Royer. Imaging a GaAlAs laser diode in operation using apertureless scanning near-field optical microscopy. <u>European Physical Journal Applied: Physics</u>, 5(3):269– 275, (1999).
- <sup>68</sup> M Labardi, S Patanè, and M Allegrini. Artifact-free near-field optical imaging by apertureless microscopy. Applied Physics Letters, 77(5):621–623, (2000).
- <sup>69</sup> Jun Nishida, Samuel C. Johnson, Peter T. S. Chang, Dylan M. Wharton, Sven A. Doenges, Omar Khatib, and Markus B. Raschke. Ultrafast infrared nano-imaging of cooperative carrier and vibrational dynamics. In Preparation, (2021).
- <sup>70</sup> Samuel C. Johnson, Eric A. Muller, Omar Khatib, Elisa A. Bonnin, Alexander C. Gagnon, and Markus B. Raschke. *Infrared nanospectroscopic imaging in the rotating frame*. <u>Optica</u>, **6**(4):424–429, (2019).

- <sup>71</sup> Simon Labouesse, Samuel C. Johnson, Hans A. Bechtel, Markus B. Raschke, and Rafael Piestun. Smart scattering scanning near-field optical microscopy (smart s-SNOM). <u>Proceedings of the</u> National Academy of Sciences, (2020).
- <sup>72</sup> Hans A Bechtel, Eric A Muller, Robert L Olmon, Michael C Martin, and Markus B Raschke. Ultrabroadband infrared nanospectroscopic imaging. <u>Proceedings of the National Academy of</u> Sciences of the United States of America, **111**(20):7191–7196, (2014).
- <sup>73</sup> Eric A Muller, Benjamin Pollard, and Markus B Raschke. Infrared Chemical Nano-Imaging: Accessing Structure, Coupling, and Dynamics on Molecular Length Scales. <u>The Journal of</u> Physical Chemistry Letters, 6:1275–1284, (2015).
- <sup>74</sup> Omar Khatib, Hans A Bechtel, Michael C Martin, Markus B Raschke, and G Lawrence Carr. Far Infrared Synchrotron Near-Field Nanoimaging and Nanospectroscopy. <u>ACS Photonics</u>, 5(7):2773–2779, (2018).
- <sup>75</sup> Benjamin Pollard, Francisco C B Maia, Markus B Raschke, and Raul O Freitas. Infrared Vibrational Nanospectroscopy by Self-Referenced Interferometry. Nano Letters, 16:55–61, (2016).
- <sup>76</sup> Jianing Chen, Michela Badioli, Pablo Alonso-González, Sukosin Thongrattanasiri, Florian Huth, Johann Osmond, Marko Spasenović, Alba Centeno, Amaia Pesquera, Philippe Godignon, Amaia Zurutuza Elorza, Nicolas Camara, F Javier García de Abajo, Rainer Hillenbrand, and Frank H L Koppens. Optical nano-imaging of gate-tunable graphene plasmons. Nature, **487**:77, (2012).
- <sup>77</sup> Iban Amenabar, Simon Poly, Wiwat Nuansing, Elmar H Hubrich, Alexander A Govyadinov, Florian Huth, Roman Krutokhvostov, Lianbing Zhang, Mato Knez, Joachim Heberle, Alexander M Bittner, and Rainer Hillenbrand. *Structural analysis and mapping of individual protein complexes by infrared nanospectroscopy*. Nature Communications, 4:2890, (2013).
- <sup>78</sup> Iban Amenabar, Simon Poly, Monika Goikoetxea, Wiwat Nuansing, Peter Lasch, and Rainer Hillenbrand. Hyperspectral infrared nanoimaging of organic samples based on Fourier transform infrared nanospectroscopy. Nature Communications, 8:14402, (2017).
- <sup>79</sup> Antonio Cricenti, Renato Generosi, Marco Luce, Paolo Perfetti, Giorgio Margaritondo, David Talley, Jas S Sanghera, Ishwar D Aggarwal, Norman H Tolk, Agostina Congiu-Castellano, Mark A Rizzo, and David W Piston. *Chemically Resolved Imaging of Biological Cells and Thin Films by Infrared Scanning Near-Field Optical Microscopy*. <u>Biophysical Journal</u>, **85**:2705–2710, (2003).
- <sup>80</sup> Markus Brehm, Thomas Taubner, Rainer Hillenbrand, and Fritz Keilmann. Infrared Spectroscopic Mapping of Single Nanoparticles and Viruses at Nanoscale Resolution. <u>Nano Letters</u>, 6(7):1307–1310, (2006).
- <sup>81</sup>Samuel Berweger, Duc M Nguyen, Eric A Muller, Hans A Bechtel, Thomas T Perkins, and Markus B Raschke. Nano-Chemical Infrared Imaging of Membrane Proteins in Lipid Bilayers. Journal of the American Chemical Society, 135:18292–18295, (2013).
- <sup>82</sup> Masayuki Abe, Yoshiaki Sugimoto, Takashi Namikawa, Kenichi Morita, Noriaki Oyabu, and Seizo Morita. Drift-compensated data acquisition performed at room temperature with frequency modulation atomic force microscopy. <u>Appl. Phys. Lett. Applied Physics Letters</u>, **90**:203103, (2007).

- <sup>83</sup> Frederic Marin, Nathalie Le Roy, and Benjamin Marie. The formation and mineralization of mollusk shell. Frontiers in Bioscience, S4:1099–1125, (2012).
- <sup>84</sup> Yannicke Dauphin, Alexander D Ball, Hiram Castillo-Michel, Corinne Chevallard, Jean-Pierre Cuif, Bastien Farre, Stéphane Pouvreau, and Murielle Salomé. In situ distribution and characterization of the organic content of the oyster shell Crassostrea gigas (Mollusca, Bivalvia). Micron, 44:373–383, (2013).
- <sup>85</sup> Yannicke Dauphin, Jean-Pierre Cuif, Jean Doucet, Murielle Salom, Jean Susini, and C Terry Willams. In situ chemical speciation of sulfur in calcitic biominerals and the simple prism concept. Journal of Structural Biology, 142:272–280, (2003).
- <sup>86</sup> Bastien Farre, Alain Brunelle, Olivier Laprévote, Jean-Pierre Cuif, C Terry Williams, and Yannnicke Dauphin. Shell layers of the black-lip pearl oyster Pinctada margaritifera: Matching microstructure and composition. <u>Comparative Biochemistry and Physiology, Part B</u>, 159:131– 139, (2011).
- <sup>87</sup> Fre´de´ric Marin, Boaz Pokroy, Gilles Luquet, Pierre Layrolle, and Klaas De Groot. Protein mapping of calcium carbonate biominerals by immunogold. Biomaterials, 28:2368–2377, (2007).
- <sup>88</sup> Benjamin Marie, Isabelle Zanella-Cléon, Nathalie Guichard, Michel Becchi, and Frédéric Marin. Novel Proteins from the Calcifying Shell Matrix of the Pacific Oyster Crassostrea gigas. <u>Marine</u> Biotechnology, **13**(6):1159–1168, (2011).
- <sup>89</sup> Benjamin Marie, Caroline Joubert, Alexandre Tayalé, Isabelle Zanella-Cléon, Corinne Belliard, David Piquemal, Nathalie Cochennec-Laureau, Frédéric Marin, Yannick Gueguen, and Caroline Montagnani. Different secretory repertoires control the biomineralization processes of prism and nacre deposition of the pearl oyster shell. Proceedings of the National Academy of Sciences of the United States of America, **109**(51):20986–20991, (2012).
- <sup>90</sup> Yannicke Dauphin. Soluble Organic Matrices of the Calcitic Prismatic Shell Layers of Two Pteriomorphid Bivalves. The Journal of Biological Chemistry, 278(17):15168–15177, (2003).
- <sup>91</sup> Frédéric Marin, Gilles Luquet, Benjamin Marie, and Davorin Medakovic. Molluscan Shell Proteins: Primary Structure, Origin, and Evolution. <u>Current Topics in Developmental Biology</u>, 80:209–276, (2007).
- <sup>92</sup> Bernd Kästner, C. Magnus Johnson, Peter Hermann, Mattias Kruskopf, Klaus Pierz, Arne Hoehl, Andrea Hornemann, Georg Ulrich, Jakob Fehmel, Piotr Patoka, Eckart Rü, and Gerhard Ulm. *Infrared Nanospectroscopy of Phospholipid and Surfactin Monolayer Domains*. <u>ACS</u> Omega, **3**:4141–4147, (2018).
- <sup>93</sup> I.I. Rabi, N.F. Ramsey, and J. Schwinger. Use of Rotating Coordinates in Magnetic Resonance Problems. Reviews of Modern Physics, 26(2):167–171, (1954).
- <sup>94</sup> James Keeler. Understanding NMR Spectroscopy. Wiley, Cambridge, (2002).
- <sup>95</sup> Allison W Albrecht, John D Hybl, Sarah M Gallagher Faeder, and David M Jonas. Experimental distinction between phase shifts and time delays: Implications for femtosecond spectroscopy and coherent control of chemical reactions. Journal of Chemical Physics, 111(24):10934–10956, (1999).

- <sup>96</sup> Christoph Scheurer and Shaul Mukamel. Magnetic Resonance Analogies in Multidimensional Vibrational Spectroscopy. Bull. Chem. Soc. Jpn, 75:989–999, (2002).
- <sup>97</sup> Sang-Hee Shim and Martin T. Zanni. How to turn your pump-probe instrument into a multidimensional spectrometer: 2D IR and Vis spectroscopies via pulse shaping. <u>Physical Chemistry</u> Chemical Physics, **11**(5):737–884, (2009).
- <sup>98</sup> S K Karthick Kumar, A Tamimi, and M. D. Fayer. Comparisons of 2D IR measured spectral diffusion in rotating frames using pulse shaping and in the stationary frame using the standard method. The Journal of Chemical Physics, 137:184201, (2012).
- <sup>99</sup> Patrick L. Kramer, Chiara H. Giammanco, Amr Tamimi, David J. Hoffman, Kathleen P. Sokolowsky, and Michael D. Fayer. *Quasi-rotating frame: accurate line shape determination with increased efficiency in noncollinear 2D optical spectroscopy*. Journal of the Optical Society of America B, **33**(6):1143–1156, (2016).
- <sup>100</sup> G. J. CARTER. *Guide to bivalve shell microstructures*. <u>Skeletal growth of aquatic organisms</u>., pages 645–673, (1980).
- <sup>101</sup> Joanne Macdonald, Andy Freer, and Maggie Cusack. Alignment of Crystallographic c-Axis throughout the Four Distinct Microstructural Layers of the Oyster Crassostrea gigas. Crystal Growth and Design, 10:1243–1246, (2010).
- <sup>102</sup> Antonio Gerardo Checa, Alejandro B Rodri´guez-Navarro, and Fransico J Esteban-Delgado. The nature and formation of calcitic columnar prismatic shell layers in pteriomorphian bivalves. Biomaterials, 26:6404–6414, (2005).
- <sup>103</sup> Ian C Olson, Rebecca A Metzler, Nobumichi Tamura, Martin Kunz, Christopher E Killian, and Pupa U.P.A. Gilbert. *Crystal lattice tilting in prismatic calcite*. Journal of Structural Biology, 183:180–190, (2013).
- <sup>104</sup> Benjamin Pollard and Markus B Raschke. Correlative infrared nanospectroscopic and nanomechanical imaging of block copolymer microdomains. Beilstein J. Nanotechnol, **7**:605–612, (2016).
- <sup>105</sup> A J Sternbach, J Hinton, T Slusar, A S Mcleod, M K Liu, A Frenzel, M Wagner, R Iraheta, F Keilmann, A Leitenstorfer, M Fogler, H.-T Kim, R D Averitt, and D N Basov. Artifact free time resolved near-field spectroscopy. Optics Express, 25(23):28589–28611, (2017).
- <sup>106</sup> Samuel Berweger, Duc M Nguyen, Eric A Muller, Hans A Bechtel, Thomas T Perkins, and Markus B Raschke. Nano-chemical infrared imaging of membrane proteins in lipid bilayers. Journal of the American Chemical Society, **135**(49):18292–18295, (2013).
- <sup>107</sup> A J Huber, J Wittborn, and R Hillenbrand. Infrared spectroscopic near-field mapping of single nanotransistors. Nanotechnology, **21**(23):235702, (2010).
- <sup>108</sup> R Bachelot, P Gleyzes, and A C Boccara. Near-field optical microscope based on local perturbation of a diffraction spot. Optics letters, **20**(18):1924–1926, (1995).
- <sup>109</sup> Fritz Keilmann and Rainer Hillenbrand. Near-field microscopy by elastic light scattering from a tip. Phil. Trans. R. Soc. A., **362**:787–805, (2004).

- <sup>110</sup> Xiaoji G Xu, Mathias Rang, Ian M Craig, and Markus B Raschke. *Pushing the sample-size limit* of infrared vibrational nanospectroscopy: from monolayer toward single molecule sensitivity. <u>The</u> journal of physical chemistry letters, **3**(13):1836–1841, (2012).
- <sup>111</sup> S Amarie and F Keilmann. Broadband-infrared assessment of phonon resonance in scatteringtype near-field microscopy. Physical Review B, 83(4):45404, (2011).
- <sup>112</sup> Florian Huth, Alexander Govyadinov, Sergiu Amarie, Wiwat Nuansing, Fritz Keilmann, and Rainer Hillenbrand. Nano-FTIR Absorption Spectroscopy of Molecular Fingerprints at 20 nm Spatial Resolution. Nano Lett., **12**(8):3973–3978, (2012).
- <sup>113</sup> Rupert Huber, A Brodschelm, F Tauser, and A Leitenstorfer. Generation and field-resolved detection of femtosecond electromagnetic pulses tunable up to 41 THz. <u>Applied Physics Letters</u>, **76**(22):3191–3193, (2000).
- <sup>114</sup> Carmella Calabrese, Ashley M Stingel, Lei Shen, and Poul B Petersen. Ultrafast continuum mid-infrared spectroscopy: probing the entire vibrational spectrum in a single laser shot with femtosecond time resolution. Optics letters, **37**(12):2265–2267, (2012).
- <sup>115</sup> M Schnell, Paul Scott Carney, and R Hillenbrand. Synthetic optical holography for rapid nanoimaging. Nature communications, **5**:3499, (2014).
- <sup>116</sup> Ori Katz, Jonathan M Levitt, and Yaron Silberberg. Compressive Fourier Transform Spectroscopy. In <u>Frontiers in Optics 2010/Laser Science XXVI</u>, page FTuE3. Optical Society of America, (2010).
- <sup>117</sup> Bernd Kästner, Franko Schmähling, Andrea Hornemann, Georg Ulrich, Arne Hoehl, Mattias Kruskopf, Klaus Pierz, Markus B Raschke, Gerd Wübbeler, and Clemens Elster. *Compressed sensing FTIR nano-spectroscopy and nano-imaging*. Opt. Express, **26**(14):18115–18124, (2018).
- <sup>118</sup> Mohammad Golbabaee and Pierre Vandergheynst. Hyperspectral image compressed sensing via low-rank and joint-sparse matrix recovery. In <u>Acoustics, Speech and Signal Processing</u> (ICASSP), 2012 IEEE International Conference on, pages 2741–2744. Ieee, (2012).
- <sup>119</sup> Fernando Soldevila, Jonathan Dong, Enrique Tajahuerce, Sylvain Gigan, and Hilton B de Aguiar. Fast compressive Raman bio-imaging via matrix completion. <u>Optica</u>, 6(3):341–346, (2019).
- <sup>120</sup> Haonan Lin, Chien-Sheng Liao, Pu Wang, Nan Kong, and Ji-Xin Cheng. Spectroscopic stimulated Raman scattering imaging of highly dynamic specimens through matrix completion. <u>Light:</u> Science & Applications, 7(5):17179, (2018).
- <sup>121</sup> Jian-Feng Cai, Emmanuel J Candès, and Zuowei Shen. A singular value thresholding algorithm for matrix completion. SIAM Journal on Optimization, 20(4):1956–1982, (2010).
- <sup>122</sup> Zhang Liu and Lieven Vandenberghe. Interior-point method for nuclear norm approximation with application to system identification. <u>SIAM Journal on Matrix Analysis and Applications</u>, **31**(3):1235–1256, (2009).
- <sup>123</sup> Pratik Biswas, Tzu-Chen Lian, Ta-Chung Wang, and Yinyu Ye. Semidefinite programming based algorithms for sensor network localization. <u>ACM Transactions on Sensor Networks (TOSN)</u>, 2(2):188–220, (2006).

- <sup>124</sup> Amit Singer. A remark on global positioning from local distances. <u>Proceedings of the National</u> Academy of Sciences, **105**(28):9507–9511, (2008).
- <sup>125</sup> Emmanuel J Candès and Benjamin Recht. Exact matrix completion via convex optimization. Foundations of Computational mathematics, 9(6):717, (2009).
- <sup>126</sup> Emmanuel J Candes and Yaniv Plan. Matrix completion with noise. <u>Proceedings of the IEEE</u>, 98(6):925–936, (2010).
- <sup>127</sup> Emmanuel J Candes and Terence Tao. Near-optimal signal recovery from random projections: Universal encoding strategies? <u>IEEE transactions on information theory</u>, **52**(12):5406–5425, (2006).
- <sup>128</sup> Emmanuel J Candès and Terence Tao. *The power of convex relaxation: Near-optimal matrix completion*. IEEE Transactions on Information Theory, **56**(5):2053–2080, (2010).
- <sup>129</sup> C M Snively, S Katzenberger, G Oskarsdottir, and J Lauterbach. *Fourier-transform infrared imaging using a rapid-scan spectrometer*. Optics letters, **24**(24):1841–1843, (1999).
- <sup>130</sup> Emmanuel J Candès and Others. *Compressive sampling*. In <u>Proceedings of the international</u> congress of mathematicians, volume 3, pages 1433–1452. Madrid, Spain, (2006).
- <sup>131</sup> David L Donoho. Compressed sensing. <u>IEEE Transactions on information theory</u>, **52**(4):1289–1306, (2006).
- <sup>132</sup> Emmanuel J Candès and Michael B Wakin. An introduction to compressive sampling. <u>IEEE</u> signal processing magazine, **25**(2):21–30, (2008).
- <sup>133</sup> Candes Emmanuel, Justin Romberg, and Terence Tao. Robust uncertainty principles: Exact signal reconstruction from highly incomplete frequency information. <u>IEEE Transactions on</u> information theory, **52**(2):489–509, (2004).
- <sup>134</sup> Madeleine Udell and Alex Townsend. Why Are Big Data Matrices Approximately Low Rank? SIAM Journal on Mathematics of Data Science, 1(1):144–160, (2019).
- <sup>135</sup> Hugo Raguet, Jalal Fadili, and Gabriel Peyré. A generalized forward-backward splitting. <u>SIAM</u> Journal on Imaging Sciences, 6(3):1199–1226, (2013).
- <sup>136</sup> Marco F Duarte and Richard G Baraniuk. *Kronecker compressive sensing*. <u>IEEE Transactions</u> on Image Processing, **21**(2):494–504, (2012).
- <sup>137</sup> Emmanuel Candes and Justin Romberg. Sparsity and incoherence in compressive sampling. Inverse problems, **23**(3):969, (2007).
- <sup>138</sup> Marc Antonini, Michel Barlaud, Pierre Mathieu, and Ingrid Daubechies. Image coding using wavelet transform. IEEE Transactions on image processing, 1(2):205–220, (1992).
- <sup>139</sup> Emmanuel J Candes and David L Donoho. Curvelets: A surprisingly effective nonadaptive representation for objects with edges. Technical report, Stanford Univ Ca Dept of Statistics, (2000).
- <sup>140</sup> Yufan Luo and Sean B Andersson. A continuous sampling pattern design algorithm for atomic force microscopy images. Ultramicroscopy, **196**:167–179, (2019).

- <sup>141</sup> Anupriya Gogna, Ankita Shukla, H K Agarwal, and Angshul Majumdar. Split Bregman algorithms for sparse/joint-sparse and low-rank signal recovery: application in compressive hyperspectral imaging. In <u>Image Processing (ICIP)</u>, 2014 IEEE International Conference on, pages 1302–1306. IEEE, (2014).
- <sup>142</sup> D M Newns, J A Misewich, C C Tsuei, A Gupta, B A Scott, and A Schrott. Mott transition field effect transistor. Appl. Phys. Lett., 73(6):780–782, (1998).
- <sup>143</sup> M Nakano, K Shibuya, D Okuyama, T Hatano, S Ono, M Kawasaki, Y Iwasa, and Y Tokura. Collective bulk carrier delocalization driven by electrostatic surface charge accumulation. <u>Nature</u>, 487(7408):459–462, (2012).
- <sup>144</sup> X.-Y. Zhu and V Podzorov. Charge Carriers in Hybrid Organic-Inorganic Lead Halide Perovskites Might Be Protected as Large Polarons. J. Phys. Chem. Lett., **6**(23):4758–4761, (2015).
- <sup>145</sup> Kiyoshi Miyata, Timothy L Atallah, and X.-Y. Zhu. Lead halide perovskites: Crystal-liquid duality, phonon glass electron crystals, and large polaron formation. <u>Sci. Adv.</u>, 3(10):e1701469, (2017).
- <sup>146</sup> Kiyoshi Miyata, Yuki Kurashige, Kazuya Watanabe, Toshiki Sugimoto, Shota Takahashi, Shunsuke Tanaka, Jun Takeya, Takeshi Yanai, and Yoshiyasu Matsumoto. Coherent singlet fission activated by symmetry breaking. Nat. Chem., 9(10):983–989, (2017).
- <sup>147</sup> Kajari Bera, Christopher J Douglas, and Renee R Frontiera. Femtosecond Raman Microscopy Reveals Structural Dynamics Leading to Triplet Separation in Rubrene Singlet Fission. J. Phys. Chem. Lett., 8(23):5929–5934, (2017).
- <sup>148</sup> Christoph Schnedermann, Antonios M Alvertis, Torsten Wende, Steven Lukman, Jiaqi Feng, Florian A Y N Schröder, David H P Turban, Jishan Wu, Nicholas D M Hine, Neil C Greenham, Alex W Chin, Akshay Rao, Philipp Kukura, and Andrew J Musser. A molecular movie of ultrafast singlet fission. Nat. Commun., 10(1):1–11, (2019).
- <sup>149</sup> Hong Guang Duan, Ajay Jha, Xin Li, Vandana Tiwari, Hanyang Ye, Pabitra K Nayak, Xiao Lei Zhu, Zheng Li, Todd J Martinez, Michael Thorwart, and R J.Dwayne Miller. *Intermolecular vibrations mediate ultrafast singlet fission*. Sci. Adv., 6(38):52–70, (2020).
- <sup>150</sup> Gregory D Scholes, Graham R Fleming, Lin X Chen, Alán Aspuru-Guzik, Andreas Buchleitner, David F Coker, Gregory S Engel, Rienk Van Grondelle, Akihito Ishizaki, David M Jonas, Jeff S Lundeen, James K McCusker, Shaul Mukamel, Jennifer P Ogilvie, Alexandra Olaya-Castro, Mark A Ratner, Frank C Spano, K Birgitta Whaley, and Xiaoyang Zhu. Using coherence to enhance function in chemical and biophysical systems, (2017).
- <sup>151</sup> A Von Hoegen, R Mankowsky, M Fechner, M Först, and A Cavalleri. Probing the interatomic potential of solids with strong-field nonlinear phononics. <u>Nature</u>, **555**(7694):79–82, (2018).
- <sup>152</sup> Eugenio Cinquanta, Daniele Meggiolaro, Silvia G Motti, Marina Gandini, Marcelo J P Alcocer, Quinten A Akkerman, Caterina Vozzi, Liberato Manna, Filippo De Angelis, Annamaria Petrozza, and Salvatore Stagira. Ultrafast THz Probe of Photoinduced Polarons in Lead-Halide Perovskites. Phys. Rev. Lett., **122**(16):166601, (2019).

- <sup>153</sup> Randy D Mehlenbacher, Thomas J McDonough, Maksim Grechko, Meng Yin Wu, Michael S Arnold, and Martin T Zanni. Energy transfer pathways in semiconducting carbon nanotubes revealed using two-dimensional white-light spectroscopy. Nat. Commun., 6(1):1–7, (2015).
- <sup>154</sup> Hikaru Kuramochi, Genki Aoyama, Hajime Okajima, Akira Sakamoto, Shinji Kanegawa, Osamu Sato, Satoshi Takeuchi, and Tahei Tahara. *Femtosecond Polarization Switching in the Crystal of a [CrCo] Dinuclear Complex.* Angew. Chem. Int. Ed., **59**(37):anie.202004583, (2020).
- <sup>155</sup> Matteo Rini, Ra'anan Tobey, Nicky Dean, Jiro Itatani, Yasuhide Tomioka, Yoshinori Tokura, Robert W Schoenlein, and Andrea Cavalleri. Control of the electronic phase of a manganite by mode-selective vibrational excitation. Nature, 449(7158):72–74, (2007).
- <sup>156</sup> M Mitrano, A Cantaluppi, D Nicoletti, S Kaiser, A Perucchi, S Lupi, P Di Pietro, D Pontiroli, M Riccò, S R Clark, D Jaksch, and A Cavalleri. *Possible light-induced superconductivity in K3* C60 at high temperature. Nature, **530**(7591):461–464, (2016).
- <sup>157</sup> A X Gray, M C Hoffmann, J Jeong, N P Aetukuri, D Zhu, H Y Hwang, N C Brandt, H Wen, A J Sternbach, S Bonetti, A H Reid, R Kukreja, C Graves, T Wang, P Granitzka, Z Chen, D J Higley, T Chase, E Jal, E Abreu, M K Liu, T C Weng, D Sokaras, D Nordlund, M Chollet, R Alonso-Mori, H Lemke, J M Glownia, M Trigo, Y Zhu, H Ohldag, J W Freeland, M G Samant, J Berakdar, R D Averitt, K A Nelson, S S P Parkin, and H A Dürr. Ultrafast terahertz field control of electronic and structural interactions in vanadium dioxide. <u>Phys. Rev. B</u>, **98**(4):45104, (2018).
- <sup>158</sup> Naotaka Yoshikawa, Tomohiro Tamaya, and Koichiro Tanaka. Optics: High-harmonic generation in graphene enhanced by elliptically polarized light excitation. <u>Science</u>, **356**(6339):736–738, (2017).
- <sup>159</sup> Hassan A Hafez, Sergey Kovalev, Jan Christoph Deinert, Zoltán Mics, Bertram Green, Nilesh Awari, Min Chen, Semyon Germanskiy, Ulf Lehnert, Jochen Teichert, Zhe Wang, Klaas Jan Tielrooij, Zhaoyang Liu, Zongping Chen, Akimitsu Narita, Klaus Müllen, Mischa Bonn, Michael Gensch, and Dmitry Turchinovich. Extremely efficient terahertz high-harmonic generation in graphene by hot Dirac fermions. Nature, 561(7724):507–511, (2018).
- <sup>160</sup> Zheng Yang, Changhyun Ko, and Shriram Ramanathan. Oxide Electronics Utilizing Ultrafast Metal-Insulator Transitions. Annu. Rev. Mater. Res., 41(1):337–367, (2011).
- <sup>161</sup> F Schlaepfer, M Lucchini, S A Sato, M Volkov, L Kasmi, N Hartmann, A Rubio, L Gallmann, and U Keller. Attosecond optical-field-enhanced carrier injection into the gaas conduction band. Nat. Phys., 14(6):560–564, (2018).
- <sup>162</sup> M M Qazilbash, M Brehm, Byung Gyu Chae, P C Ho, G O Andreev, Bong Jun Kim, Sun Jin Yun, A V Balatsky, M B Maple, F Keilmann, Hyun Tak Kim, and D N Basov. *Mott transition in* VO2 revealed by infrared spectroscopy and nano-imaging. Science, **318**(5857):1750–1753, (2007).
- <sup>163</sup> Brian T O'Callahan, Andrew C Jones, Jae Hyung Park, David H Cobden, Joanna M Atkin, and Markus B Raschke. *Inhomogeneity of the ultrafast insulator-to-metal transition dynamics* of VO2. Nat. Commun., 6(1):1–8, (2015).
- <sup>164</sup> Elizabeth M Tennyson, Tiarnan A S Doherty, and Samuel D Stranks. *Heterogeneity at multiple length scales in halide perovskite semiconductors*. Nat. Rev. Mater., 4(9):573–587, (2019).

- <sup>165</sup> Dane W DeQuilettes, Sarthak Jariwala, Sven Burke, Mark E Ziffer, Jacob T.-W. Wang, Henry J Snaith, and David S Ginger. Tracking Photoexcited Carriers in Hybrid Perovskite Semiconductors: Trap-Dominated Spatial Heterogeneity and Diffusion. <u>ACS Nano</u>, **11**(11):11488–11496, (2017).
- <sup>166</sup> Andrew C Jones, Nicholas M Kearns, Jia Jung Ho, Jessica T Flach, and Martin T Zanni. Impact of non-equilibrium molecular packings on singlet fission in microcrystals observed using 2D white-light microscopy. Nat. Chem., **12**(1):40–47, (2020).
- <sup>167</sup> Vladimir A Lobastov, Ramesh Srinivasan, and Ahmed H Zewail. Four-dimensional ultrafast electron microscopy. Proc. Natl. Acad. Sci. U. S. A., **102**(20):7069–7073, (2005).
- <sup>168</sup> Armin Feist, Nora Bach, Nara Rubiano da Silva, Thomas Danz, Marcel Möller, Katharina E Priebe, Till Domröse, J Gregor Gatzmann, Stefan Rost, Jakob Schauss, Stefanie Strauch, Reiner Bormann, Murat Sivis, Sascha Schäfer, and Claus Ropers. Ultrafast transmission electron microscopy using a laser-driven field emitter: Femtosecond resolution with a high coherence electron beam. Ultramicroscopy, **176**:63–73, (2017).
- <sup>169</sup> Haidan Wen, Mathew J Cherukara, and Martin V Holt. Time-Resolved X-Ray Microscopy for Materials Science. Annu. Rev. Mater. Res., 49(1):389–415, (2019).
- <sup>170</sup> Maciej Dąbrowski, Yanan Dai, and Hrvoje Petek. Ultrafast Photoemission Electron Microscopy: Imaging Plasmons in Space and Time. Chem. Rev., **120**(13):6247–6287, (2020).
- <sup>171</sup> M A Huber, M Plankl, M Eisele, R E Marvel, F Sandner, T Korn, C Schüller, R F Haglund, R Huber, and T L Cocker. Ultrafast Mid-Infrared Nanoscopy of Strained Vanadium Dioxide Nanobeams. Nano Lett., 16(2):1421–1427, (2016).
- <sup>172</sup> Markus A Huber, Fabian Mooshammer, Markus Plankl, Leonardo Viti, Fabian Sandner, Lukas Z Kastner, Tobias Frank, Jaroslav Fabian, Miriam S Vitiello, Tyler L Cocker, and Rupert Huber. *Femtosecond photo-switching of interface polaritons in black phosphorus heterostructures*. <u>Nat.</u> Nanotechnol., **12**(3):207–211, (2017).
- <sup>173</sup> Martin Wagner, Zhe Fei, Alexander S McLeod, Aleksandr S Rodin, Wenzhong Bao, Eric G Iwinski, Zeng Zhao, Michael Goldflam, Mengkun Liu, Gerardo Dominguez, Mark Thiemens, Michael M Fogler, Antonio H Castro Neto, Chun Ning Lau, Sergiu Amarie, Fritz Keilmann, and D N Basov. Ultrafast and nanoscale plasmonic phenomena in exfoliated graphene revealed by infrared pump-probe nanoscopy. Nano Lett., 14(2):894–900, (2014).
- <sup>174</sup> G X Ni, L Wang, M D Goldflam, M Wagner, Z Fei, A S McLeod, M K Liu, F Keilmann, B Özyilmaz, A H Castro Neto, J Hone, M M Fogler, and D N Basov. Ultrafast optical switching of infrared plasmon polaritons in high-mobility graphene. Nat. Photonics, **10**(4):244–247, (2016).
- <sup>175</sup> A Charnukha, A Sternbach, H T Stinson, R Schlereth, C Brüne, L W Molenkamp, and D N Basov. Ultrafast nonlocal collective dynamics of Kane plasmon-polaritons in a narrow-gap semiconductor. Sci. Adv., 5(8):eaau9956, (2019).
- <sup>176</sup> A J Sternbach, S H Chae, S Latini, A A Rikhter, Y Shao, B Li, D Rhodes, B Kim, P J Schuck, X Xu, X Y Zhu, R D Averitt, J Hone, M M Fogler, A Rubio, and D N Basov. *Programmable hyperbolic polaritons in van der Waals semiconductors*. <u>Science</u>, **371**(6529):617–620, (2021).

- <sup>177</sup> M Eisele, T L Cocker, M A Huber, M Plankl, L Viti, D Ercolani, L Sorba, M S Vitiello, and R Huber. Ultrafast multi-terahertz nano-spectroscopy with sub-cycle temporal resolution. <u>Nat.</u> Photonics, 8(11):841–845, (2014).
- <sup>178</sup> Tyler L Cocker, Dominik Peller, Ping Yu, Jascha Repp, and Rupert Huber. *Tracking the ultrafast motion of a single molecule by femtosecond orbital imaging*. Nature, **539**(7628):263–267, (2016).
- <sup>179</sup> Ziheng Yao, Suheng Xu, Debo Hu, Xinzhong Chen, Qing Dai, and Mengkun Liu. Nanoimaging and Nanospectroscopy of Polaritons with Time Resolved s-SNOM. <u>Adv. Opt. Mater.</u>, 8(5):1–18, (2020).
- <sup>180</sup> Tao Jiang, Vasily Kravtsov, Mikhail Tokman, Alexey Belyanin, and Markus B Raschke. Ultrafast coherent nonlinear nanooptics and nanoimaging of graphene. <u>Nat. Nanotechnol.</u>, **14**(9):838–843, (2019).
- <sup>181</sup> Vasily Kravtsov, Ronald Ulbricht, Joanna M Atkin, and Markus B Raschke. *Plasmonic nanofo-cused four-wave mixing for femtosecond near-field imaging*. <u>Nat. Nanotechnol.</u>, **11**(5):459–464, (2016).
- <sup>182</sup> Kyle T Munson, Christopher Grieco, Eric R Kennehan, Robert J Stewart, and John B Asbury. *Time-Resolved Infrared Spectroscopy Directly Probes Free and Trapped Carriers in Organo-Halide Perovskites.* ACS Energy Lett., 2(3):651–658, (2017).
- <sup>183</sup> Kyle T Munson, Eric R Kennehan, Grayson S Doucette, and John B Asbury. Dynamic Disorder Dominates Delocalization, Transport, and Recombination in Halide Perovskites. <u>Chem</u>, 4(12):2826–2843, (2018).
- <sup>184</sup> Tien Tien Yeh, Hideto Shirai, Chien Ming Tu, Takao Fuji, Takayoshi Kobayashi, and Chih Wei Luo. Ultrafast carrier dynamics in Ge by ultra-broadband mid-infrared probe spectroscopy. <u>Sci.</u> Rep., 7(1):1–10, (2017).
- <sup>185</sup> Charalambos C Katsidis and Dimitrios I Siapkas. General transfer-matrix method for optical multilayer systems with coherent, partially coherent, and incoherent interference. <u>Appl. Opt.</u>, 41(19):3978, (2002).
- <sup>186</sup> Michael M Lee, Joël Teuscher, Tsutomu Miyasaka, Takurou N Murakami, and Henry J Snaith. *Efficient hybrid solar cells based on meso-superstructured organometal halide perovskites*. Science, **338**(6107):643–647, (2012).
- <sup>187</sup> Samuel D Stranks, Giles E Eperon, Giulia Grancini, Christopher Menelaou, Marcelo J P Alcocer, Tomas Leijtens, Laura M Herz, Annamaria Petrozza, and Henry J Snaith. *Electron-hole diffu*sion lengths exceeding 1 micrometer in an organometal trihalide perovskite absorber. <u>Science</u>, **342**(6156):341–344, (2013).
- <sup>188</sup> Timothy W Jones, Anna Osherov, Mejd Alsari, Melany Sponseller, Benjamin C Duck, Young-Kwang Jung, Charles Settens, Farnaz Niroui, Roberto Brenes, Camelia V Stan, Yao Li, Mojtaba Abdi-Jalebi, Nobumichi Tamura, J Emyr Macdonald, Manfred Burghammer, Richard H Friend, Vladimir Bulović, Aron Walsh, Gregory J Wilson, Samuele Lilliu, and Samuel D Stranks. Lattice strain causes non-radiative losses in halide perovskites. <u>Energy Environ. Sci.</u>, **12**(2):596–606, (2019).

- <sup>189</sup> Jun Nishida, Amani H. Alfaifi, Thomas P. Gray, Sean E. Shaheen, and Markus B. Raschke. *Heterogeneous cation-lattice interaction and dynamics in triple cation perovskites revealed by infrared vibrational nanoscopy*. Angew. Chem. Int. Ed., (2020).
- <sup>190</sup> Dominik J Kubicki, Daniel Prochowicz, Albert Hofstetter, Shaik M Zakeeruddin, Michael Grätzel, and Lyndon Emsley. Phase Segregation in Cs-, Rb- and K-Doped Mixed-Cation (MA)x(FA)1-xPbI3 Hybrid Perovskites from Solid-State NMR. J. Am. Chem. Soc., 139(40):14173-14180, (2017).
- <sup>191</sup> Victoria C A Taylor, Devendra Tiwari, Marta Duchi, Paul M Donaldson, Ian P Clark, David J Fermin, and Thomas A A Oliver. *Investigating the Role of the Organic Cation in Formamidinium Lead Iodide Perovskite Using Ultrafast Spectroscopy*. J. Phys. Chem. Lett., 9(4):895–901, (2018).
- <sup>192</sup> Kyle T Munson, John R Swartzfager, and John B Asbury. Lattice Anharmonicity: A Double-Edged Sword for 3D Perovskite-Based Optoelectronics. <u>ACS Energy Lett.</u>, 4(8):1888–1897, (2019).
- <sup>193</sup> Dibyajyoti Ghosh, Alexander R Smith, Alison B Walker, and M Saiful Islam. Mixed A-Cation Perovskites for Solar Cells: Atomic-Scale Insights Into Structural Distortion, Hydrogen Bonding, and Electronic Properties. Chem. Mater., **30**(15):5194–5204, (2018).
- <sup>194</sup> Michael Saliba, Taisuke Matsui, Ji Youn Seo, Konrad Domanski, Juan Pablo Correa-Baena, Mohammad Khaja Nazeeruddin, Shaik M Zakeeruddin, Wolfgang Tress, Antonio Abate, Anders Hagfeldt, and Michael Grätzel. *Cesium-containing triple cation perovskite solar cells: Improved stability, reproducibility and high efficiency.* Energy Environ. Sci., **9**(6):1989–1997, (2016).
- <sup>195</sup> J P Heritage, J G Bergman, A Pinczuk, and J M Worlock. Surface picosecond raman gain spectroscopy of a cyanide monolayer on silver. Chem. Phys. Lett., **67**(2-3):229–232, (1979).
- <sup>196</sup> Philippe Bado, Scott B Wilson, and Kent R Wilson. Multiple modulation for optical pump-probe spectroscopy. Rev. Sci. Instrum., 53(5):706–707, (1982).
- <sup>197</sup> M Plankl, P E Faria Junior, F Mooshammer, T Siday, M Zizlsperger, F Sandner, F Schiegl, S Maier, M A Huber, M Gmitra, J Fabian, J L Boland, T L Cocker, and R Huber. Subcycle contact-free nanoscopy of ultrafast interlayer transport in atomically thin heterostructures. <u>Nat.</u> Photonics, pages 1–7, (2021).
- <sup>198</sup> Jun Yan, Yuanbo Zhang, Philip Kim, and Aron Pinczuk. Electric field effect tuning of electronphonon coupling in graphene. Phys. Rev. Lett., **98**(16):166802, (2007).
- <sup>199</sup> Chenhao Jin, Jonghwan Kim, Joonki Suh, Zhiwen Shi, Bin Chen, Xi Fan, Matthew Kam, Kenji Watanabe, Takashi Taniguchi, Sefaattin Tongay, Alex Zettl, Junqiao Wu, and Feng Wang. Interlayer electron-phonon coupling in WSe 2/hBN heterostructures. <u>Nat. Phys.</u>, 13(2):127–131, (2017).
- <sup>200</sup> Yingchao Zhang, Xun Shi, Wenjing You, Zhensheng Tao, Yigui Zhong, Fairoja Cheenicode Kabeer, Pablo Maldonado, Peter M Oppeneer, Michael Bauer, Kai Rossnagel, Henry Kapteyn, and Margaret Murnane. *Coherent modulation of the electron temperature and electron-phonon couplings in a 2D material*. Proc. Natl. Acad. Sci. U. S. A., **117**(16):8788–8793, (2020).
- <sup>201</sup> Wei Wang and David G Cahill. Limits to thermal transport in nanoscale metal bilayers due to weak electron-phonon coupling in Au and Cu. Phys. Rev. Lett., **109**(17):175503, (2012).

- <sup>202</sup> Andreij C Gadelha, Douglas A A Ohlberg, Cassiano Rabelo, Eliel G S Neto, Thiago L Vasconcelos, João L Campos, Jessica S Lemos, Vinícius Ornelas, Daniel Miranda, Rafael Nadas, Fabiano C Santana, Kenji Watanabe, Takashi Taniguchi, Benoit van Troeye, Michael Lamparski, Vincent Meunier, Viet Hung Nguyen, Dawid Paszko, Jean Christophe Charlier, Leonardo C Campos, Luiz G Cançado, Gilberto Medeiros-Ribeiro, and Ado Jorio. Lattice dynamics localization in low-angle twisted bilayer graphene. Nature, **590**:405, (2021).
- <sup>203</sup> Thomas A A Oliver, Nicholas H C Lewis, and Graham R Fleming. Correlating the motion of electrons and nuclei with two-dimensional electronic-vibrational spectroscopy. <u>Proc. Natl. Acad.</u> Sci. U. S. A., **111**(28):10061–10066, (2014).
- <sup>204</sup> Peter Hamm and Martin T Zanni. Concepts and Methods of 2D Infrared Spectroscopy. Cambridge University Press, (2011).
- <sup>205</sup> Galan Moody, Chandriker Kavir Dass, Kai Hao, Chang Hsiao Chen, Lain Jong Li, Akshay Singh, Kha Tran, Genevieve Clark, Xiaodong Xu, Gunnar Berghäuser, Ermin Malic, Andreas Knorr, and Xiaoqin Li. Intrinsic homogeneous linewidth and broadening mechanisms of excitons in monolayer transition metal dichalcogenides. Nat. Commun., 6(1):1–6, (2015).
- <sup>206</sup> Tomasz Jakubczyk, Valentin Delmonte, MacIej Koperski, Karol Nogajewski, Clément Faugeras, Wolfgang Langbein, Marek Potemski, and Jacek Kasprzak. *Radiatively Limited Dephasing and Exciton Dynamics in MoSe2 Monolayers Revealed with Four-Wave Mixing Microscopy*. <u>Nano</u> Lett., **16**(9):5333–5339, (2016).
- <sup>207</sup> P Dey, J Paul, Z Wang, C E Stevens, C Liu, A H Romero, J Shan, D J Hilton, and D Karaiskaj. Optical Coherence in Atomic-Monolayer Transition-Metal Dichalcogenides Limited by Electron-Phonon Interactions. Phys. Rev. Lett., **116**(12):127402, (2016).
- <sup>208</sup> F Kimiaee Asadi, S C Wein, and C Simon. Cavity-assisted controlled phase-flip gates. <u>Phys.</u> Rev. A, **102**(1):13703, (2020).
- <sup>209</sup> Mykhailo Tymchenko, J Sebastian Gomez-Diaz, Jongwon Lee, Nishant Nookala, Mikhail A Belkin, and Andrea Alù. Gradient Nonlinear Pancharatnam-Berry Metasurfaces. <u>Physical</u> Review Letters, **115**(20):207403, (2015).
- <sup>210</sup> Nishant Nookala, Jongwon Lee, Mykhailo Tymchenko, J Sebastian Gomez-Diaz, Frederic Demmerle, Gerhard Boehm, Kueifu Lai, Gennady Shvets, Markus-Christian Amann, Andrea Alu, and Mikhail Belkin. Ultrathin gradient nonlinear metasurface with a giant nonlinear response. Optica, 3(3):283–288, (2016).
- <sup>211</sup> Martti Kauranen and Anatoly V Zayats. Nonlinear plasmonics. <u>Nature Photonics</u>, 6(11):737–748, (2012).
- <sup>212</sup> H Baida, D Mongin, D Christofilos, G Bachelier, A Crut, P Maioli, N Del Fatti, and F Vallée. Ultrafast Nonlinear Optical Response of a Single Gold Nanorod near Its Surface Plasmon Resonance. Physical Review Letters, **107**(5):57402, (2011).
- <sup>213</sup> Mengxin Ren, Baohua Jia, Jun-Yu Ou, Eric Plum, Jianfa Zhang, Kevin F MacDonald, Andrey E Nikolaenko, Jingjun Xu, Min Gu, and Nikolay I Zheludev. Nanostructured Plasmonic Medium for Terahertz Bandwidth All-Optical Switching. Advanced Materials, 23(46):5540–5544, (2011).

- <sup>214</sup> Yuanmu Yang, Wenyi Wang, Abdelaziz Boulesbaa, Ivan I Kravchenko, Dayrl P Briggs, Alexander Puretzky, David Geohegan, and Jason Valentine. Nonlinear Fano-Resonant Dielectric Metasurfaces. Nano Letters, **15**(11):7388–7393, (2015).
- <sup>215</sup> Maxim R Shcherbakov, Polina P Vabishchevich, Alexander S Shorokhov, Katie E Chong, Duk-Yong Choi, Isabelle Staude, Andrey E Miroshnichenko, Dragomir N Neshev, Andrey A Fedyanin, and Yuri S Kivshar. Ultrafast All-Optical Switching with Magnetic Resonances in Nonlinear Dielectric Nanostructures. Nano Letters, **15**(10):6985–6990, (2015).
- <sup>216</sup> Sheng Liu, Michael B Sinclair, Sina Saravi, Gordon A Keeler, Yuanmu Yang, John Reno, Gregory M Peake, Frank Setzpfandt, Isabelle Staude, Thomas Pertsch, and Igal Brener. *Resonantly Enhanced Second-Harmonic Generation Using III-V Semiconductor All-Dielectric Metasurfaces*. Nano Letters, **16**(9):5426–5432, (2016).
- <sup>217</sup> Varvara V Zubyuk, Polina P Vabishchevich, Maxim R Shcherbakov, Alexander S Shorokhov, Anna N Fedotova, Sheng Liu, Gordon Keeler, Tatyana V Dolgova, Isabelle Staude, Igal Brener, and Andrey A Fedyanin. Low-Power Absorption Saturation in Semiconductor Metasurfaces. ACS Photonics, 6(11):2797–2806, (2019).
- <sup>218</sup> L Caspani, R.P.M. Kaipurath, M Clerici, M Ferrera, T Roger, J Kim, N Kinsey, M Pietrzyk, A Di Falco, V.M. Shalaev, A Boltasseva, and D Faccio. *Enhanced Nonlinear Refractive Index* in ε-Near-Zero Materials. Physical Review Letters, **116**(23):233901, (2016).
- <sup>219</sup> M Zahirul Alam, Sebastian A Schulz, Jeremy Upham, Israel De Leon, and Robert W Boyd. Large optical nonlinearity of nanoantennas coupled to an epsilon-near-zero material. <u>Nature</u> Photonics, **12**(2):79–83, (2018).
- <sup>220</sup> M Zahirul Alam, Israel De Leon, and Robert W Boyd. Large optical nonlinearity of indium tin oxide in its epsilon-near-zero region. Science, **352**(6287):795–797, (2016).
- <sup>221</sup> Jing Yang, Javin Hatcherian, Paul C Hackley, and Andrew E Pomerantz. Nanoscale geochemical and geomechanical characterization of organic matter in shale. <u>Nature Communications</u>, 8(1):2179, (2017).
- <sup>222</sup> Yuanmu Yang, Jian Lu, Alejandro Manjavacas, Ting S Luk, Hanzhe Liu, Kyle Kelley, Jon-Paul Maria, Evan L Runnerstrom, Michael B Sinclair, Shambhu Ghimire, and Igal Brener. *High-harmonic generation from an epsilon-near-zero material*. <u>Nature Physics</u>, **15**(10):1022–1026, (2019).
- <sup>223</sup> P Vasa, R Pomraenke, G Cirmi, E De Re, W Wang, S Schwieger, D Leipold, E Runge, G Cerullo, and C Lienau. Ultrafast Manipulation of Strong Coupling in Metal-Molecular Aggregate Hybrid Nanostructures. ACS Nano, 4(12):7559–7565, (2010).
- <sup>224</sup> Parinda Vasa, Wei Wang, Robert Pomraenke, Melanie Lammers, Margherita Maiuri, Cristian Manzoni, Giulio Cerullo, and Christoph Lienau. *Real-time observation of ultrafast Rabi oscillations between excitons and plasmons in metal nanostructures with J-aggregates*. <u>Nature</u> Photonics, 7(2):128–132, (2013).
- <sup>225</sup> Nche T Fofang, Nathaniel K Grady, Zhiyuan Fan, Alexander O Govorov, and Naomi J Halas. Plexciton Dynamics: Exciton-Plasmon Coupling in a J-Aggregate-Au Nanoshell Complex Provides a Mechanism for Nonlinearity. Nano Letters, **11**(4):1556–1560, (2011).

- <sup>226</sup> A Manjavacas, F J García de Abajo, and P Nordlander. Quantum Plexcitonics: Strongly Interacting Plasmons and Excitons. Nano Letters, **11**(6):2318–2323, (2011).
- <sup>227</sup> R Butté, G Delalleau, A I Tartakovskii, M S Skolnick, V N Astratov, J J Baumberg, G Malpuech, A Di Carlo, A V Kavokin, and J S Roberts. *Transition from strong to weak coupling and the* onset of lasing in semiconductor microcavities. Physical Review B, **65**(20):205310, (2002).
- <sup>228</sup> A Benz, S Campione, S Liu, I Montaño, J F Klem, A Allerman, J R Wendt, M B Sinclair, F Capolino, and I Brener. Strong coupling in the sub-wavelength limit using metamaterial nanocavities. Nature Communications, 4(1):2882, (2013).
- <sup>229</sup> G Khitrova, H M Gibbs, F Jahnke, M Kira, and S W Koch. Nonlinear optics of normal-modecoupling semiconductor microcavities. Reviews of Modern Physics, **71**(5):1591–1639, (1999).
- <sup>230</sup> Simone Zanotto, Federica Bianco, Lucia Sorba, Giorgio Biasiol, and Alessandro Tredicucci. Saturation and bistability of defect-mode intersubband polaritons. <u>Physical Review B</u>, **91**(8):85308, (2015).
- <sup>231</sup> Y Todorov, A M Andrews, R Colombelli, S De Liberato, C Ciuti, P Klang, G Strasser, and C Sirtori. Ultrastrong Light-Matter Coupling Regime with Polariton Dots. <u>Physical Review</u> Letters, **105**(19):196402, (2010).
- <sup>232</sup> Yingnan Liu, Jongwon Lee, Stephen March, Nishant Nookala, Daniele Palaferri, John F Klem, Seth R Bank, Igal Brener, and Mikhail A Belkin. *Difference-Frequency Generation in Polaritonic Intersubband Nonlinear Metasurfaces*. Advanced Optical Materials, **6**(20):1800681, (2018).
- <sup>233</sup> J S Gomez-Diaz, M Tymchenko, J Lee, M A Belkin, and Andrea Alù. Nonlinear processes in multi-quantum-well plasmonic metasurfaces: Electromagnetic response, saturation effects, limits, and potentials. Physical Review B, 92(12):125429, (2015).
- <sup>234</sup> G Günter, A A Anappara, J Hees, A Sell, G Biasiol, L Sorba, S De Liberato, C Ciuti, A Tredicucci, A Leitenstorfer, and R Huber. Sub-cycle switch-on of ultrastrong light-matter interaction. Nature, 458(7235):178–181, (2009).
- <sup>235</sup> Carlo Sirtori, Federico Capasso, Deborah L Sivco, S N G Chu, and Alfred Y Cho. Observation of large second order susceptibility via intersubband transitions at λ~ 10 µm in asymmetric coupled AlInAs/GaInAs quantum wells. Applied Physics Letters, **59**(18):2302–2304, (1991).
- <sup>236</sup> F Capasso, C Sirtori, and A Y Cho. Coupled quantum well semiconductors with giant electric field tunable nonlinear optical properties in the infrared. <u>IEEE Journal of Quantum Electronics</u>, **30**(5):1313–1326, (1994).
- <sup>237</sup> E Rosencher, A Fiore, B Vinter, V Berger, Ph. Bois, and J Nagle. Quantum Engineering of Optical Nonlinearities. Science, **271**(5246):168–173, (1996).
- <sup>238</sup> Omri Wolf, Andrew A Allerman, Xuedan Ma, Joel R Wendt, Alex Y Song, Eric A Shaner, and Igal Brener. Enhanced optical nonlinearities in the near-infrared using III-nitride heterostructures coupled to metamaterials. Applied Physics Letters, **107**(15):151108, (2015).
- <sup>239</sup> Simone Zanotto, Riccardo Degl'Innocenti, Ji-Hua Xu, Lucia Sorba, Alessandro Tredicucci, and Giorgio Biasiol. Ultrafast optical bleaching of intersubband cavity polaritons. <u>Physical Review</u> B, 86(20):201302, (2012).

- <sup>240</sup> P Jouy, A Vasanelli, Y Todorov, A Delteil, G Biasiol, L Sorba, and C Sirtori. Transition from strong to ultrastrong coupling regime in mid-infrared metal-dielectric-metal cavities. <u>Applied</u> Physics Letters, **98**(23):231114, (2011).
- <sup>241</sup> Y Todorov, A M Andrews, I Sagnes, R Colombelli, P Klang, G Strasser, and C Sirtori. Strong Light-Matter Coupling in Subwavelength Metal-Dielectric Microcavities at Terahertz Frequencies. Physical Review Letters, **102**(18):186402, (2009).
- <sup>242</sup> Anton Frisk Kockum, Adam Miranowicz, Simone De Liberato, Salvatore Savasta, and Franco Nori. Ultrastrong coupling between light and matter. Nature Reviews Physics, 1(1):19–40, (2019).
- <sup>243</sup> Daniele Palaferri, Yanko Todorov, Alireza Mottaghizadeh, Giulia Frucci, Giorgio Biasiol, and Carlo Sirtori. Ultra-subwavelength resonators for high temperature high performance quantum detectors. New Journal of Physics, 18(11):113016, (2016).
- <sup>244</sup> Eric A. Muller, Benjamin Pollard, Hans A. Bechtel, Ronen Adato, Dordaneh Etezadi, Hatice Altug, and Markus B. Raschke. Nanoimaging and Control of Molecular Vibrations through Electromagnetically Induced Scattering Reaching the Strong Coupling Regime. <u>ACS Photonics</u>, 5:3594–3600, (2018).
- <sup>245</sup> J Schleeh, J Mateos, I Íñiguez-de-la Torre, N Wadefalk, P A Nilsson, J Grahn, and A J Minnich. *Phonon black-body radiation limit for heat dissipation in electronics*. <u>Nature Materials</u>, 14(2):187–192, (2015).
- <sup>246</sup> David G Cahill, Paul V Braun, Gang Chen, David R Clarke, Shanhui Fan, Kenneth E Goodson, Pawel Keblinski, William P King, Gerald D Mahan, Arun Majumdar, Humphrey J Maris, Simon R Phillpot, Eric Pop, and Li Shi. Nanoscale thermal transport. II. 2003–2012. <u>Applied</u> Physics Reviews, 1(1):11305, (2014).
- <sup>247</sup> Arden L Moore and Li Shi. Emerging challenges and materials for thermal management of electronics. <u>Materials Today</u>, **17**(4):163–174, (2014).
- <sup>248</sup> Michael Shtein, Roey Nadiv, Matat Buzaglo, Keren Kahil, and Oren Regev. Thermally Conductive Graphene-Polymer Composites: Size, Percolation, and Synergy Effects. <u>Chemistry of</u> Materials, **27**(6):2100–2106, (2015).
- <sup>249</sup> Muhammad Rubayat Bin Shahadat, Md. Ferdous Alam, Nur Alam Mandal, and Md. Mahasin Ali. Thermal Transportation Behaviour Prediction of Defective Graphene Sheet at Various Temperature: A Molecular Dynamics Study. <u>American Journal of Nanomaterials</u>, 6(1):34–40, (2018).
- <sup>250</sup> Jae Hun Seol, Insun Jo, Arden L Moore, Lucas Lindsay, Zachary H Aitken, Michael T Pettes, Xuesong Li, Zhen Yao, Rui Huang, David Broido, Natalio Mingo, Rodney S Ruoff, and Li Shi. *Two-Dimensional Phonon Transport in Supported Graphene*. <u>Science</u>, **328**(5975):213 LP —-216, (2010).
- <sup>251</sup> Tuong-Van Nguyen, Thomas Knudsen, Ulrik Larsen, and Fredrik Haglind. Thermodynamic evaluation of the Kalina split-cycle concepts for waste heat recovery applications. <u>Energy</u>, **71**:277– 288, (2014).

- <sup>252</sup> Sylvain Quoilin, Martijn Van Den Broek, Sébastien Declaye, Pierre Dewallef, and Vincent Lemort. *Techno-economic survey of Organic Rankine Cycle (ORC) systems*. <u>Renewable and Sustainable Energy Reviews</u>, **22**:168–186, (2013).
- <sup>253</sup> Bertrand F Tchanche, Gr. Lambrinos, A Frangoudakis, and G Papadakis. Low-grade heat conversion into power using organic Rankine cycles A review of various applications. <u>Renewable</u> and Sustainable Energy Reviews, **15**(8):3963–3979, (2011).
- <sup>254</sup> Y S Ju and K E Goodson. Phonon scattering in silicon films with thickness of order 100 nm. Applied Physics Letters, 74(20):3005–3007, (1999).
- <sup>255</sup> Meng Shen and Pawel Keblinski. Ballistic vs. diffusive heat transfer across nanoscopic films of layered crystals. Journal of Applied Physics, **115**(14):144310, (2014).
- <sup>256</sup> Zhi Liang, Kiran Sasikumar, and Pawel Keblinski. Thermal Transport across a Substrate-Thin-Film Interface: Effects of Film Thickness and Surface Roughness. <u>Physical Review Letters</u>, 113(6):65901, (2014).
- <sup>257</sup> Yang Hong, Lei Li, Xiao Cheng Zeng, and Jingchao Zhang. Tuning thermal contact conductance at graphene–copper interface via surface nanoengineering. Nanoscale, 7(14):6286–6294, (2015).
- <sup>258</sup> Sanghamitra Neogi, J Sebastian Reparaz, Luiz Felipe C Pereira, Bartlomiej Graczykowski, Markus R Wagner, Marianna Sledzinska, Andrey Shchepetov, Mika Prunnila, Jouni Ahopelto, Clivia M Sotomayor-Torres, and Davide Donadio. *Tuning Thermal Transport in Ultrathin Sili*con Membranes by Surface Nanoscale Engineering. ACS Nano, 9(4):3820–3828, (2015).
- <sup>259</sup> Yuping He, Davide Donadio, Joo-Hyoung Lee, Jeffrey C Grossman, and Giulia Galli. Thermal Transport in Nanoporous Silicon: Interplay between Disorder at Mesoscopic and Atomic Scales. ACS Nano, 5(3):1839–1844, (2011).
- <sup>260</sup> Soonshin Kwon, Matthew C Wingert, Jianlin Zheng, Jie Xiang, and Renkun Chen. Thermal transport in Si and Ge nanostructures in the 'confinement' regime. <u>Nanoscale</u>, 8(27):13155– 13167, (2016).
- <sup>261</sup> N R Pradhan, D Rhodes, S Memaran, J M Poumirol, D Smirnov, S Talapatra, S Feng, N Perea-Lopez, A L Elias, M Terrones, P M Ajayan, and L Balicas. *Hall and field-effect mobilities in few layered p-WSe2 field-effect transistors*. Scientific Reports, 5(1):8979, (2015).
- <sup>262</sup> Hui Fang, Steven Chuang, Ting Chia Chang, Kuniharu Takei, Toshitake Takahashi, and Ali Javey. *High-Performance Single Layered WSe2 p-FETs with Chemically Doped Contacts*. <u>Nano Letters</u>, **12**(7):3788–3792, (2012).
- <sup>263</sup> Samuel Brem, August Ekman, Dominik Christiansen, Florian Katsch, Malte Selig, Cedric Robert, Xavier Marie, Bernhard Urbaszek, Andreas Knorr, and Ermin Malic. *Phonon-Assisted Photoluminescence from Indirect Excitons in Monolayers of Transition-Metal Dichalcogenides*. Nano Letters, **20**(4):2849–2856, (2020).
- <sup>264</sup> Tsz Wing Lo, Qiang Zhang, Meng Qiu, Xuyun Guo, Yongjun Meng, Ye Zhu, Jun Jun Xiao, Wei Jin, Chi Wah Leung, and Dangyuan Lei. Thermal Redistribution of Exciton Population in Monolayer Transition Metal Dichalcogenides Probed with Plasmon-Exciton Coupling Spectroscopy. ACS Photonics, 6(2):411-421, (2019).

- <sup>265</sup> Zhipeng Li, Tianmeng Wang, Chenhao Jin, Zhengguang Lu, Zhen Lian, Yuze Meng, Mark Blei, Shiyuan Gao, Takashi Taniguchi, Kenji Watanabe, Tianhui Ren, Sefaattin Tongay, Li Yang, Dmitry Smirnov, Ting Cao, and Su-Fei Shi. *Emerging photoluminescence from the dark-exciton phonon replica in monolayer WSe2*. Nature Communications, **10**(1):2469, (2019).
- <sup>266</sup> Carolyn A Paddock and Gary L Eesley. Transient thermoreflectance from thin metal films. Journal of Applied Physics, **60**(1):285–290, (1986).
- <sup>267</sup> Scott Huxtable, David G Cahill, Vincent Fauconnier, Jeffrey O White, and Ji-Cheng Zhao. Thermal conductivity imaging at micrometre-scale resolution for combinatorial studies of materials. Nature Materials, 3(5):298–301, (2004).
- <sup>268</sup> Elika Saïdi, Benjamin Samson, Lionel Aigouy, Sebastian Volz, Peter Löw, Christian Bergaud, and Michel Mortier. Scanning thermal imaging by near-field fluorescence spectroscopy. Nanotechnology, **20**(11):115703, (2009).
- <sup>269</sup> Seid Sadat, Aaron Tan, Yi Jie Chua, and Pramod Reddy. Nanoscale Thermometry Using Point Contact Thermocouples. Nano Letters, **10**(7):2613–2617, (2010).
- <sup>270</sup> G Tessier, M Bardoux, C Boué, C Filloy, and D Fournier. Back side thermal imaging of integrated circuits at high spatial resolution. Applied Physics Letters, **90**(17):171112, (2007).
- <sup>271</sup> David G Cahill. Thermal conductivity measurement from 30 to 750 K: the  $3\omega$  method. Review of Scientific Instruments, **61**(2):802–808, (1990).
- <sup>272</sup> Alexander A Balandin, Suchismita Ghosh, Wenzhong Bao, Irene Calizo, Desalegne Teweldebrhan, Feng Miao, and Chun Ning Lau. Superior Thermal Conductivity of Single-Layer Graphene. Nano Letters, 8(3):902–907, (2008).
- <sup>273</sup> Satyaprakash Sahoo, Anand P S Gaur, Majid Ahmadi, Maxime J.-F. Guinel, and Ram S Katiyar. *Temperature-Dependent Raman Studies and Thermal Conductivity of Few-Layer MoS2*. <u>The</u> Journal of Physical Chemistry C, **117**(17):9042–9047, (2013).
- <sup>274</sup> Rusen Yan, Jeffrey R Simpson, Simone Bertolazzi, Jacopo Brivio, Michael Watson, Xufei Wu, Andras Kis, Tengfei Luo, Angela R Hight Walker, and Huili Grace Xing. *Thermal Conductivity of Monolayer Molybdenum Disulfide Obtained from Temperature-Dependent Raman Spectroscopy*. ACS Nano, 8(1):986–993, (2014).
- <sup>275</sup> Stacy Liang, Md N Hasan, and Jung-Hun Seo. Direct Observation of Raman Spectra in Black Phosphorus under Uniaxial Strain Conditions, (2019).
- <sup>276</sup> Andrei Sarua, Hangfeng Ji, K P Hilton, D J Wallis, Michael J Uren, T Martin, and Martin Kuball. Thermal Boundary Resistance Between GaN and Substrate in AlGaN/GaN Electronic Devices. IEEE Transactions on Electron Devices, 54(12):3152–3158, (2007).
- <sup>277</sup> Yanhao Tang, Kin Fai Mak, and Jie Shan. Long valley lifetime of dark excitons in single-layer WSe2. Nature Communications, **10**(1):4047, (2019).
- <sup>278</sup> Andrzej Taube, Jarosław Judek, Anna Łapińska, and Mariusz Zdrojek. Temperature-Dependent Thermal Properties of Supported MoS2 Monolayers. <u>ACS Applied Materials & Interfaces</u>, 7(9):5061–5065, (2015).

- <sup>279</sup> Eilam Yalon, Özgür Burak Aslan, Kirby K H Smithe, Connor J McClellan, Saurabh V Suryavanshi, Feng Xiong, Aditya Sood, Christopher M Neumann, Xiaoqing Xu, Kenneth E Goodson, Tony F Heinz, and Eric Pop. Temperature-Dependent Thermal Boundary Conductance of Monolayer MoS2 by Raman Thermometry. <u>ACS Applied Materials & Interfaces</u>, 9(49):43013–43020, (2017).
- <sup>280</sup> Shao-Yu Chen, Maciej Pieczarka, Matthias Wurdack, Eliezer Estrecho, Takashi Taniguchi, Kenji Watanabe, Jun Yan, Elena A. Ostrovskaya, and Michael S. Fuhrer. Long-lived populations of momentum- and spin-indirect excitons in monolayer WSe2. <u>arXiv preprint arXiv:2009.09602</u>, (2020).

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