# Understanding Cantilever Transduction Efficiency and Spatial Resolution in Nanoscale Infrared Microscopy (AFM-IR)

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#### **ABSTRACT:**

Photothermal induced resonance (PTIR), also known as AFM-IR, enables nanoscale infrared (IR) imaging and spectroscopy by using the tip of an atomic force microscope to transduce the local photothermal expansion and contraction of a sample. The signal transduction efficiency and spatial resolution of PTIR depend on a multitude of sample, cantilever, and illumination source parameters in ways that are not yet well understood. Here, we elucidate and separate the effects of laser pulse length, pulse shape, sample thermalization time ( $\tau$ ), interfacial thermal conductance, and cantilever detection frequency by devising analytical and numerical models that link a sample's photothermal excitations to the cantilever dynamics over a broad bandwidth (10 MHz). The models indicate that shorter laser pulses excite probe oscillations over broader bandwidths and should be preferred for measuring samples with shorter thermalization times. Furthermore, we show that the spatial resolution critically depends on the interfacial thermal conductance between dissimilar materials and improves monotonically, but not linearly, with increasing cantilever detection frequencies. The resolution can be enhanced for samples that do not fully thermalize between pulses (i.e., laser repetition rates  $\gtrsim 1/3\tau$ ) as the probed depth becomes smaller than the film thickness. We believe that the insights presented here will accelerate the adoption and impact of PTIR analyses across a wide range of applications by informing experimental designs and measurement strategies as well as by guiding future technical advances.

SUBJECTS: Photothermal Induced Resonance, AFM-IR, Nanoscale Imaging, Thermal Transport, spatial resolution.

Photothermal induced resonance (PTIR),<sup>1-4</sup> also known as AFM-IR, measures infrared (IR) absorption spectra and maps with nanoscale resolution. This feat is achieved by using the probe of an atomic force microscope (AFM) to transduce the photothermal expansion of a sample illuminated by a pulsed, wavelength-tunable laser. Since the probe transduces only the sample expansion directly beneath its tip, the PTIR spatial resolution (about 10 nm to 20 nm)<sup>5–7</sup> greatly surpasses the resolutions of diffraction-limited, IR microscopy ( $\approx 40 \,\mu$ m, in practice)<sup>5,6,8</sup> and of thermal diffusion-limited AFM methods (roughly 500 nm to 1000 nm).<sup>9</sup> The PTIR signal is proportional to the local optical absorption coefficient of the sample and the spectra exhibit minimal distortions, even for strongly absorbing samples,<sup>10</sup> thereby enabling reliable identification of materials,<sup>8,11,12</sup> chemical groups,<sup>13,14</sup> and molecular conformations.<sup>15–18</sup> These capabilities, combined with the development of various PTIR measurement modalities,<sup>2,4</sup> have enabled analysis of a wide variety of samples in material science,<sup>14,19–21</sup> medicine,<sup>7,15,16</sup> optics,<sup>22–24</sup> optoelectronics,<sup>25</sup> geology,<sup>26,27</sup> and other fields, as discussed in recent reviews.<sup>1–4</sup>

The theory of PTIR signal transduction, tracing the flow of energy through the sample and cantilever, was proposed by Dazzi et al.<sup>28</sup> and later expanded theoretically<sup>10,29</sup> and validated experimentally.<sup>30,31</sup> Absorption of a laser pulse by the sample causes its temperature to rise and leads to its rapid thermal expansion. Afterward, the sample contracts as it cools and thermalizes with its surroundings. The fast expansion and contraction of the sample changes the instantaneous equilibrium position and imparts speed to the AFM probe, i.e., "kicking" it into oscillation. Both the sample expansion and the resulting cantilever oscillation amplitudes are proportional to the local absorption coefficient of the sample.<sup>11,30–33</sup> Direct measurement of the fast (1 ns to 2000 ns), minuscule (< 1 nm) sample expansion requires high sensitivity over a wide bandwidth, exceeding the capabilities of conventional AFM probes.<sup>31,34</sup> Instead, the PTIR signal is typically obtained by measuring the cantilever oscillations excited by the sample expansion and contraction. These oscillations (with quality factors, Q, typically between 25 and 250) are much longer lived than the sample expansion and are greatly amplified by the AFM optical lever detection scheme (see Figure 1a). After the absorption of a laser pulse (10 ns to 1000 ns long), the sample's expansion excites all the cantilever resonance modes at once. In the ringdown measurement modality (Figure 1b),<sup>35</sup> the laser repetition rate (e.g., 1 kHz) is much lower than the mechanical resonances of the cantilever and the PTIR signal is determined by the maximum amplitude of the oscillations at a resonance frequency selected with a narrowband filter. Alternatively, for the resonance-enhanced mode (Figure 1c),<sup>6</sup> the repetition rate of the pulsed laser is tuned to match a cantilever resonance, selectively amplifying its oscillations, and the PTIR signal, by  $Q/2\pi$  at that frequency.



**Figure 1:** (a) Photothermal induced resonance (PTIR) uses a pulsed infrared (IR) laser focused around an atomic force microscope probe tip in contact with the sample. The sample's photothermal expansion excites oscillations in the cantilever that are sensed via the deflection of a visible-light laser reflected from its backside. In ringdown operation (b), the 1 kHz laser pulse repetition rate ( $f_{pulse}$ ) is much lower than the cantilever resonance modes ( $f_{res}$ ), thereby exciting all the cantilever resonances at once. The relative amplitudes are to the frequency domain power spectrum of the sample expansion and contraction, as described in this work (see, e.g., Figure 2). By contrast, in resonance-enhanced operation (c),  $f_{pulse}$  matches the frequency of a selected cantilever mode, resonantly exciting it, thereby enhancing the PTIR signal proportional to the mode's quality factor.

Details of the sample expansion and contraction dynamics and of the cantilever's excited resonances (typically from  $\approx 70$  kHz to  $\approx 10$  MHz)<sup>4</sup> strongly affect the PTIR signal, spatial resolution, and the probed depth,<sup>3</sup> in ways that are not well understood. This knowledge gap stems from challenges in measuring the fast thermal expansion dynamics experimentally,<sup>31,34</sup> and from the incomplete theoretical understanding of the link between sample expansion and cantilever excitations dynamics.<sup>29</sup> One notable theoretical effort calculated the full dynamic thermo-elastic expansion of a sample composed of two polymers, separated by a sharp interface, for sinusoidal light illumination (1 kHz to 1 MHz).<sup>29</sup> However, the response to sinusoidal modulation is nearly single frequency and differs from the broadband response to short laser pulses.<sup>29</sup> Furthermore, the interfacial thermal conductance, which we show here critically determines the PTIR resolution, was neglected in those calculations<sup>29</sup> and in most other published studies.

Here, we suggest that estimating the characteristic time ( $\tau$ ) required by specific samples to thermalize with their surroundings and contract after absorbing a laser pulse provides valuable insights for configuring PTIR experiments to achieve desired spatial resolutions or signal-to-noise ratios. The sample thermalization time is typically beyond the experimenter's control and can vary widely between different samples ( $\approx 10$  ps to > 1000 ns), depending on the thermal properties of the sample and its interfaces, critically affecting the cantilever excitation. The interfacial thermal conductance (*G*) determines the heat flow at interfaces, and varies greatly based on the materials forming the interface and on defects, such as interfacial roughness, voids, etc.<sup>36</sup> Since *G* between the sample and the substrate (*G*<sub>Sample/Substrate</sub>) is often unknown, a lower limit of  $\tau$  can be estimated by assuming *G*<sub>Sample/Substrate</sub> =  $\infty$  according to:<sup>9,31,34</sup>

$$\tau = \frac{4}{\pi^2} \frac{\rho C z^2}{\eta},\tag{1}$$

where  $\eta$  is thermal conductivity,  $\rho$  is the density, and C the heat capacity of a sample with thickness z. When G is known, a more accurate estimate is given by the relationship<sup>34</sup>

$$z = \sqrt{\frac{\tau\eta}{\rho C}} \tan^{-1} \left( \frac{G_{\text{Sample/Substrate}}}{\eta} \sqrt{\frac{\tau\eta}{\rho C}} \right)$$
(2)

In this work, we develop a discrete Fourier transform (DFT) theoretical framework linking the sample thermal expansion and contraction dynamics to cantilever excitations across a wide bandwidth (10 MHz). This analysis addresses PTIR experiments where the AFM cantilever operates in contact mode with ringdown<sup>35</sup> (Figure 1b) or resonanceenhanced (Figure 1c) excitations.<sup>6</sup> Our analysis considers isoenergetic pulses with practical values for laser pulse lengths (8 ns to 1000 ns), sample thermalization times (10 ns to 1000 ns), and cantilever frequencies (100 kHz to 10 MHz), based on commonly reported parameters. Results show that shorter laser pulses induce larger and faster sample expansions and should be preferred for measuring samples with shorter  $\tau$  (e.g., thin samples and samples with higher  $\eta$ ). In general, longer laser pulse lengths and samples with longer  $\tau$  preferentially excite lower frequency cantilever modes, while shorter pulses and samples with shorter  $\tau$  excite probe oscillations over broader bandwidths. We also use finitedifference time-domain simulations in combination with DFTs to analyze cantilever oscillations excited indirectly by non-absorbing media that expand through heat diffusion from an adjacent absorbing phase. This analysis shows that heat conduction across the interface between neighboring materials limits the PTIR lateral resolution, which improves monotonically (but not linearly) with increased cantilever detection frequency. For a 200 nm thick polymer heterostructure, the upper limit of the PTIR resolution is estimated to range from  $\approx 215$  nm at 100 kHz to  $\approx$  40 nm at 10 MHz. In general, differences in thermal expansion coefficient, density, specific heat, and stiffness of the neighboring materials can further enhance the resolution.<sup>9</sup> The resolution can also be enhanced for samples that do not fully thermalize between pulses (i.e., laser repetition rates  $\gtrsim 1/3_{\tau}$ ) in which case the probed depth becomes smaller than the film thickness. Importantly, we show that interfacial thermal conductance between adjacent materials critically determines the local PTIR signal contrast and spatial resolution. While higher frequency cantilever modes provide higher spatial resolution, they are characterized by larger modal stiffnesses and are typically harder to excite, leading to a compromise between signal-to-noise ratios and spatial resolution. This work helps to clarify PTIR signal transduction and guides the selection of suitable laser pulse lengths, cantilever modes, and measurements parameters, based on sample thermalization times that directly depend on its thickness and thermal conductivity.<sup>9,31</sup>

#### **METHODS**

In the following discussion, we present analytical and numerical models of a sample's photothermal expansion in response to laser pulses commonly used in PTIR experiments. The sample expansion ( $\Delta x$ ) due to the absorption of a laser pulse is proportional to its thermal expansion coefficient ( $\alpha_{exp}$ ) and to the local temperature change ( $\Delta T$ ), which varies in time (t) according to

$$\Delta x(t) \propto \alpha_{\exp} \Delta T(t) \tag{3}$$

The temperature change in the sample depends on the fraction of the incident light absorbed ( $\alpha_{abs}$ ) and is inversely proportional to the sample's heat capacity (*C*). The photothermally heated sample continuously dissipates heat to the (cooler) environment (e.g., the substrate and non-absorbing surroundings). The rate at which the sample loses heat is characterized by its thermalization time ( $\tau$ ),<sup>31</sup> which is the time for  $\Delta T$  to decay by a factor of 1/e after heating ceases. Accordingly, the rate of change in  $\Delta T$  can be described by the differential equation

$$\frac{d\Delta T(t)}{dt} = \frac{\alpha_{\rm abs}}{C} P(t) - \frac{1}{\tau} \Delta T(t)$$
<sup>(4)</sup>

where P(t) is the instantaneous laser power incident on the sample. Importantly, heat dissipation occurs whenever the temperature of the sample exceeds that of the environment, including while the laser pulse is heating the sample. The effects of heat dissipation during the laser pulse are more noticeable for longer pulses and for samples with shorter thermalization times, i.e., higher thermal conductivities and smaller thicknesses; see Eq. 1 and discussion below.

Lasers used in PTIR experiments emit light pulses with different durations, repetition rates, and power profiles, which can affect the measured PTIR signal strength and spatial resolution. For example, optical parametric oscillator (OPO) lasers typically emit short ( $\approx 10$  ns), high energy ( $\approx 10 \mu$ J) pulses at a fixed repetition rate ( $f_{pulse} = 1 \text{ kHz}$ ).<sup>5</sup> By contrast, quantum cascade lasers (QCLs) have longer, variable pulse lengths (40 ns to 1000 ns) and repetition rates (1 kHz to 3 MHz) but deliver smaller energies per pulse ( $\approx 10 \text{ nJ}$  to  $\approx 175 \text{ nJ}$ ).<sup>6</sup> Most QCLs used for PTIR experiments employ a maximum duty cycle of 10 %, therefore shorter pulses are associated with higher repetition rates and lower energies per pulse. Furthermore, the power profile of a laser pulse is not constant in time, effectively turning "on" and "off" over finite transition times (see Figure 2a). Here, we model symmetric rising and falling "edge" times ( $t_{edge}$ ), with linear changes in laser power, neighboring a period ( $t_{plateau}$ ) of constant "plateau" power ( $P_0$ ), as described by

$$P(t) = \begin{cases} P_0 \frac{t}{t_{edge}} , & \text{Rising edge} \\ P_0 & , & \text{Plateau} \\ P_0 \left( 1 - \frac{t - t_{edge} - t_{plateau}}{t_{edge}} \right), & \text{Falling edge} \\ 0 & , & \text{Thermalization} \end{cases}$$
(5)

for

Rising edge: $0 \le t \le t_{edge}$ Plateau: $t_{edge} \le t \le t_{plateau} + t_{edge}$ Falling edge: $t_{plateau} + t_{edge} \le t \le t_{plateau} + 2t_{edge}$ Thermalization: $t_{plateau} + 2t_{edge} \le t < f_{pulse}^{-1}$ 

(6)

Sufficiently long pulses (>  $2t_{edge}$ ) have trapezoidal power profiles, as illustrated in Figure 2a, whereas shorter pulse lengths result in triangular profiles (see, e.g., Figure S1a) comprised only of rising and falling edges ( $t_{\text{plateau}} = 0$ ). For ease of comparison, we use a consistent pulse energy (integrated over the entire power profile) for all pulses considered. Different laser types, and their respective pulse characteristics, lend themselves to different operational modes of PTIR. The fixed pulse repetition rates of OPO lasers are used for ringdown measurements (Figure 1b),<sup>5</sup> whereas QCLs that are capable of much higher, variable repetition rates are typically used in resonanceenhanced measurements (Figure 1c).<sup>6</sup> We focus our initial analysis on the cantilever deflection and oscillation induced by a single excitation-cooling cycle (i.e., a single absorbed laser pulse and subsequent thermalization time), over a period of 10 µs, thereby not directly considering the effects of resonant excitation, which would otherwise greatly enhance the measured PTIR signal at frequencies matching cantilever resonance modes. However, those effects can be easily accounted for in most samples when using laser pulse rates up to  $\approx 1$  MHz, and up to  $\approx 3$  MHz (limited by current QCL repetition rates) for samples with  $\tau < 100$  ns, as discussed below. For samples that do not fully thermalize before the arrival of the subsequent pulse (i.e., laser repetition rates  $\gtrsim 1/_{3\tau}$ ), multiple pulses should be simulated to account for the effect of heat accumulation, which results in probed depths smaller than the sample thickness (see below).

Due to the time-varying laser heating profile, the sample expansion can be divided piecewise into four phases; see Eq. 5 and Figure 2b. During the first two phases, encompassing the laser rising edge and plateau, ( $0 \le t \le t_{\text{plateau}} + 1t_{\text{edge}}$ ), the incident laser pulse heats the sample and causes it to expand. The sample start contracting towards the end of the falling edge and finally, after the pulse, the heated sample thermalizes with its environment. These rapid dimensional changes of the sample displace the probe from its equilibrium position and impart speed to it based on the rates of sample expansion and contraction, thereby exciting cantilever oscillations (see Figure 1b,c). This process typically occurs on timescales that are too fast to be measured directly by conventional AFM probes but has been recorded using ultra-fast optomechanical probes.<sup>31,34</sup> Solving Eq. 4, piecewise, for the laser heating profile described by Eq. 5, the change in the sample temperature is

$$\Delta T(t) = \begin{cases} \frac{a\tau}{t_{\rm edge}}(t-\tau) + c_1 e^{-\frac{t}{\tau}}, & \text{Rising edge} \\ a\tau + c_2 e^{-\frac{t'}{\tau}}, & \text{Plateau} \\ \frac{a\tau}{t_{\rm edge}}(t'' + \tau + t_{\rm edge}) + c_3 e^{-\frac{t''}{\tau}}, & \text{Falling edge} \\ c_4 e^{-\frac{t'''}{\tau}}, & \text{Thermalization} \end{cases}$$
(7)

where

$$a \equiv P_0 \frac{a_{abs}}{C}$$

$$t' \equiv t - t_{edge}$$

$$t'' \equiv t - t_{plateau} - t_{edge}$$

$$t''' \equiv t - t_{plateau} - 2t_{edge}$$
(8)

The constants  $c_i$  (i = 1 to 4) ensure that Eq. 7 satisfies the conditions that  $\Delta T(0) = 0$  (i.e., the sample is in equilibrium with its surroundings before the laser pulse) and that the temperature changes are continuous across the time boundaries described by Eq. 6 (e.g.,  $\Delta T_{\text{Rising edge}} = \Delta T_{\text{Plateau}}$  when  $t = t_{\text{edge}}$ ),

$$c_{1} = \frac{a\tau^{2}}{t_{edge}}$$

$$c_{2} = \frac{a\tau^{2}}{t_{edge}} \left( e^{-\frac{t_{edge}}{\tau}} - 1 \right)$$

$$c_{3} = \frac{a\tau^{2}}{t_{edge}} \left( e^{-\frac{t_{edge} + t_{plateau}}{\tau}} - e^{-\frac{t_{plateau}}{\tau}} - 1 \right)$$

$$c_{4} = \frac{a\tau^{2}}{t_{edge}} \left[ 1 + \left( e^{-\frac{t_{edge} + t_{plateau}}{\tau}} - e^{-\frac{t_{plateau}}{\tau}} - 1 \right) e^{-\frac{t_{edge}}{\tau}} \right]$$
(9)

In addition to the analytical model describing the photothermal expansion of a homogeneous sample, we use finite-difference time-domain methods (see Note S1 in the Supporting Information) to understand the PTIR signal and spatial resolution in the case of heterogeneous samples. Here, analysis of the heat flow through finite element models of polymer heterostructures composed by polymethyl methacrylate (PMMA) and SU-8<sup>a</sup>) resist on a ZnSe substrate provides insight into trends in the PTIR signal and spatial resolution near interfaces of dissimilar materials (absorbing, non-absorbing, and substrate).

a) The full description of the procedures used in this paper requires the identification of certain commercial products. The inclusion of such information should in no way be construed as indicating that such products are endorsed by NIST or are recommended by NIST or that they are necessarily the best materials for the purposes described.

Due to challenges in measuring *G* for materials of low thermal conductivities, of the 3 interphases present in our model (PMMA/SU-8, PMMA/ZnSe, and SU-8/ZnSe), only the interfacial thermal conductance between SU-8 and ZnSe ( $G_{SU-8/ZnSe} = 3 \text{ MW} \cdot \text{K}^{-1} \cdot \text{m}^{-2}$ ) has been measured experimentally<sup>34</sup> and we are not aware of any work reporting the *G* between two polymers. Therefore, except where noted, we use  $G = 3 \text{ MW} \cdot \text{K}^{-1} \cdot \text{m}^{-2}$  at each of the three material interfaces in our simulations.

#### **RESULTS AND DISCUSSION**

Signal dependence on laser pulse length, pulse shape, and sample thermalization time. Based on the temperature dynamics described by Eq. 7, Figures 2b and S1–S3b show the timedomain expansion profiles of samples with different thermalization times for representative laser pulse lengths. Although all the excitation pulses (Figures 2a, S1–S3a) are isoenergetic, samples with shorter thermalization times (small z or high  $\eta$ , see Eq. 1) expand more slowly and do not reach the same maximum expansion since a greater fraction of the absorbed energy is lost to their surroundings during the heating phase. Accordingly, shorter pulse lengths induce larger and faster sample expansions than longer pulses of equal energy. For example, when illuminated by a laser pulse lasting 250 ns ( $t_{edge} = 20$  ns,  $t_{plateau} = 210$  ns; Figure 2b), the maximum expansion of a sample characterized by  $\tau = 1000$  ns is  $\approx 2.3 \times$  and  $\approx 20 \times$  greater than the expansions of samples with  $\tau = 100$  ns and 10 ns, respectively. Therefore, samples that thermalize quickly, such as gold<sup>9,37</sup> and other inorganic samples,<sup>38</sup> are generally harder to measure than samples that retain heat longer, such as polymers<sup>30</sup> and biological samples,<sup>16,17,39,40</sup> and should be probed with short laser pulses.<sup>11,19,35,41</sup>

The relative amplitudes of cantilever oscillation modes are linked to the power spectrum of the sample's photothermal dynamics. Intuitively, faster sample expansions and contractions (determined, in part, by the laser pulse and the sample thermalization time, respectively) excite more efficiently higher frequency modes than slower expansion dynamics. For example, an infinitely slow (quasistatic) sample expansion would produce no meaningful PTIR signal. To assess the relative cantilever excitation efficiency across a broad bandwidth, we compute excitation power spectra as the DFT of the time-domain sample expansion profiles that are directly proportional to Eq. 7. The DFT analysis presented here covers a broad range of frequencies relevant for both ringdown (all cantilever modes excited at once) and resonance-enhanced (a single, resonantly excited, mode) PTIR measurement modalities (see Figure 1b,c). Figures 2c and S1–S3c show that shorter thermalization times result in broader bandwidth excitations compared to samples that thermalize more slowly. Consequently, samples with longer  $\tau$  preferentially excite cantilever modes with lower frequencies. Since softer cantilevers (e.g.,  $k \approx 0.3$  N/m) generally have lower frequency bending modes compared with stiffer cantilevers, they will be more easily excited and should be preferred for measuring samples with longer  $\tau$ , including many polymers and biological samples.



**Figure 2:** (a) Trapezoidal laser pulse lasting 250 ns ( $t_{pulse}$ ), characterized by symmetric rising and falling edge times ( $t_{edge} = 20$  ns) and a constant-power plateau ( $t_{plateau} = 210$  ns). After the laser pulse, the sample thermalizes with its surroundings until the arrival of the next pulse, which is set by the pulse repetition frequency (here,  $f_{pulse} = 100$  kHz, i.e., 10 µs intervals). (b) The resulting time-domain expansion profiles of samples with different thermalization times ( $\tau = 10$  ns, 100 ns, 500 ns, and 1000 ns) when heated by the laser pulse in (a). (c) Magnitudes of the discrete Fourier transforms (DFTs) of the time-domain sample expansion profiles shown in (b); inset shows DFTs normalized to their values at 0 MHz.

The rate at which an incident laser pulse heats the sample affects the relative excitation efficiencies of different cantilever modes by changing the timescales over which the sample photothermally expands. Figure 3 compares the excitation power spectra of samples with different thermalization times (100 ns, 500 ns, 1000 ns) subjected to a wide range of laser heating profiles, from short (8 ns) pulses like those produced by OPO lasers, to longer pulses (up to 1000 ns) characteristic of QCLs. For the isoenergetic pulses considered here, peak powers vary significantly with pulse length, e.g.,  $P_0$  of an 8 ns triangular (OPO) pulse is nearly 250 × greater than that of a 1000 ns trapezoidal (QCL) pulse. Shorter pulses, which cause faster expansion of the sample, generally also have wider bandwidth excitation spectra with higher DFT magnitudes at frequencies corresponding to typical cantilever resonance modes (200 kHz to 1 MHz), compared to longer duration pulses. This trend is most evident in samples with shorter  $\tau$  since the overall contraction dynamics occur over correspondingly shorter timescales. The excitation efficiencies of lower cantilever resonances frequencies ( $\leq 100$  kHz) are the least affected by the laser pulse duration, but these are not typically used in practice due to the low-frequency pink (1/f) noise and because

of the lower spatial resolutions they provide. Intuitively, laser pulses with more abrupt raising and falling edges (e.g., rectangular pulses) should result in broader bandwidth cantilever excitations. However, given the range of cantilever oscillation periods ( $\approx 14 \ \mu s$  to 100 ns, for 70 kHz and 10 MHz, respectively), the timescales of typical laser pulse rise and fall times (around 4 ns to 20 ns) are fast enough to yield broad cantilever excitation spectra such that the effect of the laser pulse shape on the cantilever excitation power spectrum is typically small (see Figure S4).



**Figure 3:** (a) Time-domain photothermal expansion profiles induced by isoenergetic laser pulses with durations  $t_{pulse}$  and either triangular ( $t_{pulse} = 8$  ns and 40 ns) or trapezoidal ( $t_{pulse} = 250$  ns and 1000 ns) power profiles, as described by Eqs. 5 and 6, for samples with characteristic thermalization times ( $\tau = 100$  ns, 500 ns, and 1000 ns). (b) Magnitudes of the discrete Fourier transforms (DFTs) of the time-domain expansion profiles shown in (a). Note that the DFT magnitudes for pulse lengths of 8 ns and 40 ns in (b) are nearly overlapping, indicating that the much longer thermalization times ( $\tau \gg t_{pulse}$ ) influence the frequency response more strongly than the short pulse lengths.

**Spatial resolution dependence on cantilever frequency, laser pulse length, sample thermalization time, and interfacial thermal conductance.** In addition to the direct photothermal excitation of an optically absorbing phase, non-absorbing phases in the surrounding regions can be indirectly heated through thermal conduction. The thermal expansion caused by indirect heating can also generate a PTIR signal, though typically much weaker than on the absorbing phase. While this effect is commonly ignored, it partially determines the PTIR spatial resolution since it can blur the measured photothermal response across material boundaries. To understand this effect, we use finite-difference time-domain simulations (see details in Note S1)

to predict the thermal expansion of a non-absorbing photoresist polymer (SU-8) surrounding a strongly absorbing PMMA disk, on top of a ZnSe substrate commonly used for PTIR experiments; see Figure 4a.



**Figure 4:** (a) Top-down and radial schematic depictions of a sample composed of a polymethyl methacrylate (PMMA; blue) disk that homogeneously absorbs infrared (IR) light surrounded by a ring of non-absorbing photoresist polymer (SU-8; cyan), deposited on a non-absorbing substrate (ZnSe; gray). Here, we model a sample with dimensions  $R_{\text{disk}} = 0.5 \,\mu\text{m}$ ,  $R_{\text{ring}} = 1 \,\mu\text{m}$ ,  $h_{\text{sample}} = 200 \,\text{nm}$ , and  $h_{\text{substrate}} = 2 \,\text{mm}$ , with adiabatic boundaries around all outer edges and an interfacial thermal conductance of 3 MW·K<sup>-1</sup>·m<sup>-2</sup> at the PMMA/SU-8, PMMA/ZnSe and SU-8/ZnSe interfaces (see Note S1 for additional details). Direct absorption of IR light by PMMA produces a strong photothermal induced resonance (PTIR) signal. However, heat flowing from the warmer PMMA to the cooler SU-8 can also generate a weak PTIR signal, limiting the spatial resolution. (b–d) Spatiotemporal maps of the sample in response to an incident laser pulse with trapezoidal power profiles and total pulse lengths ( $t_{\text{pulse}}$ ) of (b) 60 ns, (c) 250 ns, and (d) 1000 ns. The maps show the time evolution (vertical axis) and radial distribution (horizontal axis) of the thickness-averaged sample temperature change ( $\Delta T_{\text{avg}}$ ), which is proportional to the PTIR signal.

Here, changes in the polymers' temperature, averaged through their thicknesses ( $\Delta T_{avg}$ ), are computed at discrete positions across the sample at different times during and after laser illumination. For isoenergetic trapezoidal pulses lasting 60 ns to 1000 ns (Figure 4b–d), as expected,  $\Delta T_{avg}$  is largest in the central (absorbing) PMMA disk and increases for shorter pulse lengths; see also Figures S6 and S7 for other pulse lengths and profiles. However, despite no direct photothermal heating, a modest temperature rise is also predicted in the SU-8 ring due to heat conduction across the PMMA/SU-8 interface, which limits the PTIR spatial resolution.

Next, we estimate the relative frequency-domain cantilever excitation efficiencies of such a heterogeneous sample by examining the DFTs of the time-domain  $\Delta T_{avg}$  profiles at different radial positions and for different laser pulse lengths. Expectedly, these excitation power spectra (Figure 5a) have the greatest magnitudes over the absorbing PMMA phase, where  $\Delta T_{avg}$  is the largest and occurs most quickly. An abrupt change in DFT magnitude occurs across the PMMA/SU-8 interface over a length scale that depends on the cantilever frequency due to the finite interfacial thermal conductance ( $G_{PMMA/SU-8}$ , see below). Nevertheless, the heat flowing across this interface leads to a greatly attenuated (but non-zero) PTIR excitation in the non-absorbing SU-8 phase, which is larger near the boundary. Figures 5b, S8, S9 show the normalized excitation power spectra across the interface as a function of the cantilever frequency, indicative of PTIR signal contrast, for different laser pulse lengths. The predicted PTIR signal varies relatively smoothly for cantilever frequencies  $\leq 1$  MHz and become sharper above  $\geq 5$  MHz. Interestingly, at a given frequency in the considered range, the effect of the laser pulse length on the PTIR resolution is negligible see Figure S10.



**Figure 5:** (a) Magnitudes of the discrete Fourier transforms (DFTs) of the average temperature changes on a heterogeneous PMMA/SU-8 sample (Figure 4a) excited by laser pulses with trapezoidal power profiles and lengths ( $t_{pulse}$ ) of 60 ns, 250 ns, and 1000 ns. These values are related to the relative cantilever excitation efficiencies at different frequencies across the sample. (b) Radial profiles (horizontal slices) of the DFT magnitudes shown in (a) at different frequencies, normalized with respect to the DFT magnitudes at the center of the disk (0 nm). The effect of the PMMA/SU-8 interfacial thermal conductance (3 MW·K<sup>-1</sup>·m<sup>-2</sup>) is evident in the abrupt change observed around 500 nm.



**Figure 6:** (a) Estimates of the PTIR spatial resolution as a function of the cantilever detection frequency for the sample described in Figure 4a (IR-absorbing PMMA disk surrounded by a non-absorbing SU-8 ring on a ZnSe substrate) in the case of 60 ns long trapezoidal power profile excitation (solid black line) and a sinusoidally modulated illumination source (dashed red line). Here, the spatial resolution is defined as the lateral distance over which the calculated DFT magnitudes vary between 80 % and 20 % of their maximum value, which is limited by the heat conduction through the PMMA/SU-8 interface. (b) Change in the normalized DFT magnitudes, occurring within 2 nm of the PMMA/SU-8 interface (between 499 nm, at the outer edge of PMMA, and 501 nm, near the inner edge of SU-8) for different interfacial thermal conductances and at cantilever frequencies. In these simulations, an 80 ns long laser pulse with a trapezoidal power profile directly heats the absorbing PMMA disk while accounting for thermal conduction into the outer SU-8 ring (see also Note S1 for additional details).

Here, we define the PTIR spatial resolution as the distance over which  $\Delta T_{avg}$  varies from 80 % to 20 % of its maximum value across a material interface. Using this definition, the spatial resolutions across the PMMA/SU-8 interface (Figure 6a) range from  $\approx 215$  nm at 100 kHz to  $\approx 40$  nm near 10 MHz. These results confirm that the PTIR resolution improves monotonically, but not linearly, as a function of the cantilever oscillation frequency. For the sample modelled here, at low frequencies ( $\leq 600$  kHz), a range that typically contains the first 3 cantilever resonance modes (e.g., approximately 70 kHz, 200 kHz, and 530 kHz) of soft (0.4 N/m) commercial silicon cantilevers, the improvement of the spatial resolution with frequency is relatively modest ( $< 1.1 \times$ ). However, with respect to 100 kHz measurements, the resolution improves by a factor of  $\approx 1.65 \times$  at 2 MHz, and  $\approx 5.5 \times$  at 10 MHz. We note that such predicted resolution improvements are linked exclusively to the cantilever detection frequency and do not account for the effects of heat accumulation that can occur in samples that do not fully thermalize before the arrival of subsequent pulses (i.e., for laser repetition rates  $\gtrsim 1/3\tau$ ) that could further boost the spatial resolution as the probed depths become smaller than the film thickness (see below discussion). Such conditions could occur for thick samples and for samples with low thermal conductivities, such as polymers.

Given the typical duty cycle and repetition rate limitations of QCLs (10 %, 3 MHz respectively), such effects should be negligible for samples with  $\tau \le 110$  ns. For the 200 nm thick PMMA studied here,  $\tau \approx 245$  ns, and therefore we expect that the measured spatial resolution to improve in resonance enhanced experiments with repetition rates  $\gtrsim 1.4$  MHz, with respect the resolutions computed here for a single excitation pulse. These results suggest that the effect of the cantilever frequency on the PTIR spatial resolution should be typically dominant with respect the effect of the laser pulse length and duty cycle up to 1 MHz, in agreement with experimental observations on a 150 nm thick PMMA sample (estimated  $\tau \approx 160$  ns) analyzed in the 60 kHz to 1 MHz range.<sup>42</sup>

Since QCLs have limited duty cycles (typically < 10 %), the effects of heat accumulation at high frequencies are more evident using sinusoidal modulation, which was recently implemented for AFM-IR (PTIR) experiments using a continuous, broadband synchrotron source.<sup>43,44</sup> For such sinusoidal excitations, after some initial transient dynamics, the photothermal expansion and contraction of the sample also varies sinusoidally at the same frequency (see Figure S11a) and exhibits a near monochromatic power spectrum (DFT). Figure S11b shows the PTIR signal across the heterogenous PMMA/SU-8 sample for sinusoidal modulation frequencies ranging from 100 kHz to 10 MHz. Like the trends seen in Figure 5b, the change in the peak DFT magnitude across the PMMA/SU-8 interface becomes progressively more abrupt as the modulation frequency increases (Figure S11b). This trend is reflected in the estimated spatial resolution (Figure 6a), which improves from  $\approx$  230 nm at 100 kHz to  $\approx$  35 nm at 10 MHz (over 6  $\times$ improvement). These estimates include the effect of the cantilever detection frequency and, implicitly at high frequencies, the effect of the laser modulation frequency for cases in which heat accumulation can lead to probed depths smaller than the sample thickness. The finite value of  $G_{\text{PMMA/ZnSe}}$  (<  $\infty$ , in contrast to the underlying assumption of Eq. 1) has the effect of slowing the sample thermalization, which can be described using an effective thermal conductivity ( $\eta_{eff}$ ) via Eq. 2.<sup>34</sup> For a 200 nm thick film of PMMA on ZnSe, with interfacial thermal conductance  $G_{\text{PMMA/ZnSe}} = 3 \text{ MW} \cdot \text{K}^{-1} \cdot \text{m}^{-2}$ ,  $\eta_{\text{eff}}$  (PMMA)  $\approx 0.137 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ . Therefore, we can estimate the probed depth ( $L_d$ ) due to sinusoidal modulation at frequency  $f_{mod}$  as:

$$L_{\rm d} = \sqrt{\frac{\eta_{\rm eff}}{\pi \rho C f_{\rm mod}}} \tag{10}$$

For a 200 nm thick PMMA film, the effects of heat accumulation in the sample are expected to occur at sinusoidal modulation frequencies > 670 kHz. To date, synchrotron experiments have relied to modulation frequencies of  $\approx$  70 kHz, near the lowest end of our considered range, with current efforts to reach  $\approx$  200 kHz.<sup>44</sup> Accordingly, we expect further improvements in the spatial resolution if even higher light modulation frequencies are used

We note that the interfacial thermal conductance between the sample and the substrate is often unknown but it is an important parameter that affects the thermalization times of thin films; see Eq. 2.<sup>34</sup> For example, for SU-8 on ZnSe,  $G_{SU-8/ZnSe}$  is the dominant factor determining  $\tau$  for thicknesses up to  $\approx 150$  nm, while  $\eta$  becomes the dominant factor for thicker samples.<sup>34</sup> While the attainable spatial resolution improves at higher frequencies,<sup>3,8,42</sup> higher cantilever frequencies are characterized by larger modal stiffnesses and are typically harder to excite, especially for longer

duration laser pulses and for samples with longer thermalization times, as noted previously (see, e.g., Figures 3 and 5). Although such a tradeoff is unavoidable with conventional AFM probes, recently developed optomechanical probes with nanosized cantilevers,<sup>34</sup> engineered to have both low modal stiffnesses ( $\approx 1$  N/m) and high resonant frequencies ( $\approx 10$  MHz), have the potential to improve the spatial resolution without sacrificing the signal-to-noise ratios thanks to low displacement noise across a large bandwidth.

The nominal spatial resolutions computed for the heterogeneous PMMA/SU-8 sample (see above) exceed the typical resolutions that can be obtained experimentally with PTIR (as small as  $\approx 20$  nm) in contact mode.<sup>5,6</sup> In practice, the PTIR signal intensity also depends on the thermal expansion coefficients,<sup>9</sup> density, specific heat, stiffness,<sup>7</sup> and damping coefficient<sup>45</sup> of the sample directly under the probe tip. Therefore, the PTIR contrast and spatial resolution at the interface between dissimilar materials can be enhanced by disparities in thermal and mechanical properties.<sup>9</sup> The simulations presented here, which compute temperature changes in the sample over time, account for differences in the heat capacity and density between PMMA and SU-8 but, without loss of generality, they neglect differences in the thermal expansion coefficients, stiffness, and mechanical damping (see Note S1 for details). Consequently, the estimated spatial resolutions should be considered an upper limit.

The rate of heat conduction across the interface that determines the PTIR signal contrast and spatial resolution critically depends on the interfacial thermal conductance. Figure S12 reports the normalized DFT magnitudes across the PMMA/SU-8 interface for different  $G_{\text{PMMA/SU-8}}$  and cantilever detection frequencies. Clearly, the PTIR signal contrast and resolution improve with both increasing detection frequency and decreasing values of  $G_{\text{PMMA/SU-8}}$ . Figure 6b summarizes those trends, showing the variation of the DFT magnitude within a 2 nm span across the PMMA/SU-8 interface. At 200 kHz, that change in DFT magnitude (PTIR signal contrast), increases from  $\approx 3$  % for  $G_{\text{SU-8/ZnSe}} = 30$  MW·K<sup>-1</sup>·m<sup>-2</sup> to  $\approx 68$  % for  $G_{\text{SU-8/ZnSe}} = 0.3$  MW·K<sup>-1</sup>·m<sup>-2</sup>. At 10 MHz, the DFT magnitude change varies from  $\approx 7$  % to  $\approx 90$  % over the same range of  $G_{\text{SU-8/ZnSe}}$ .

#### CONCLUSIONS

In summary, we developed a theoretical framework to understand PTIR signal intensity and spatial resolution by linking the fast photothermal sample expansion and contraction dynamics due to isoenergetic laser pulses with the resulting cantilever excitations across a wide bandwidth (10 MHz). With this analysis, we explored the effects of the laser pulse length (8 ns to 1000 ns), modulation frequency (100 kHz to 10 MHz), cantilever contact resonance frequencies (1 kHz to 10 MHz), sample thermalization time (10 ns to 1000 ns), and interfacial thermal conductance between adjacent phases ( $0.3 \text{ MW} \cdot \text{K}^{-1} \cdot \text{m}^{-2}$ ). Our results rationalize experimental observations at the sparse, discrete frequencies corresponding to the mechanical modes of commercially available AFM cantilevers and enable analysis over a broad continuous bandwidth (10 MHz). Notably, our approach enables distinction between the effects of cantilever detection frequency and laser

repetition rate, two parameters that are neither continuously nor independently varied in the experiments, on the PTIR spatial resolution.

Sample thermalization times play a crucial role in PTIR signal transduction and in the application of our analysis. Accordingly, estimation of  $\tau$  based on a sample's thermal properties can serve as an initial step towards optimization of PTIR signal and spatial resolution. Overall, longer laser pulses and samples characterized by longer  $\tau$  preferentially excite lower frequency cantilever modes, while shorter duration pulses and samples with shorter  $\tau$  excite probe oscillations over broader bandwidths. Therefore, shorter laser pulses are expected to yield higher signal-to-noise ratios, and should be preferred, for measuring samples with shorter  $\tau$  (e.g., thin samples and samples with higher  $\eta$ ). We show that the PTIR spatial resolution is limited by indirect heating due to heat conduction across the boundaries of dissimilar materials and that it critically depends on the interfacial thermal conductance of the boundaries. We show that for 200 nm thick PMMA/SU-8 lateral heterostructures on ZnSe, representative of commonly studied PTIR samples, the estimated PTIR resolution improves monotonically (but not linearly) with increasing cantilever detection frequency, from  $\approx 215$  nm at 100 kHz to  $\approx 40$  nm at 10 MHz. Differences of thermo-mechanical properties between neighboring materials can further enhance the PTIR resolution.<sup>9</sup> The PTIR resolution is also expected to improve when the laser repetition rates  $\geq 1/3\tau$  in which case the sample does not fully thermalize between pulses as the probed depths is expected to become smaller than the film thickness. We believe that this effect underpins the recently introduced AFM-IR surface sensitivity mode,<sup>3</sup> and that it contributes to the lateral spatial resolution of tapping mode AFM-IR (down to  $\approx$  5 nm),<sup>8</sup> two measurement modalities that leverage laser pulses with high (> 1.5 MHz) repetition rates.

Although cantilever modes with higher frequencies provide higher spatial resolution, these modes are typically stiffer, leading to a lower PTIR signal-to-noise ratios, thereby forcing the PTIR operator to adopt a compromise between these desirable, but anticorrelated, properties. The recent development of soft ( $\approx 1$  N/m), high-frequency ( $\approx 10$  MHz) AFM cantilevers<sup>31,34</sup> provides excellent characteristics for PTIR transduction, overcoming such tradeoffs and promises to improve the PTIR resolution limit further.

By rationalizing the PTIR transduction efficiency and spatial resolution with respect to the sample thermalization time, this work provides insights for measurement optimization and for the development of novel PTIR measurement modalities, laser sources, and suitable AFM cantilevers. We believe that the insights presented here will guide the development of best practices in PTIR experiments as well as further the application of PTIR across many disciplines.

# ASSOCIATED CONTENT

# **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/\_\_\_\_\_.

Supporting analysis of analytical model with different laser pulses, polymer heterostructure model details and boundary conditions, supporting analysis of polymer heterostructure model, supporting analysis of sinusoidally modulated excitation, excitation power spectra across sample with different interfacial thermal conductances. (PDF)

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# **Author Contributions**

This project was initiated by A.C. and developed by A.C. and J.J.S. Analytical modeling and analysis was accomplished by J.J.S and finite-difference time domain simulations were run by G.P. and analyzed by J.J.S. The manuscript was written by J.J.S. and A.C., with figures made by J.J.S.

## Notes

The authors declare no competing financial interest.

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### REFERENCES

- (1) Centrone, A. Infrared Imaging and Spectroscopy Beyond the Diffraction Limit. *Annu. Rev. Anal. Chem.* **2015**, *8* (1), 101–126.
- (2) Kurouski, D.; Dazzi, A.; Zenobi, R.; Centrone, A. Infrared and Raman Chemical Imaging and Spectroscopy at the Nanoscale. *Chem. Soc. Rev.* **2020**, *49* (11), 3315–3347.
- (3) Mathurin, J.; Deniset-Besseau, A.; Bazin, D.; Dartois, E.; Wagner, M.; Dazzi, A. Photothermal AFM-IR Spectroscopy and Imaging: Status, Challenges, and Trends. *J. Appl. Phys.* **2022**, *131* (1), 010901.
- (4) Schwartz, J. J.; Jakob, D. S.; Centrone, A. A Guide to Nanoscale IR Spectroscopy: Resonance Enhanced Transduction in Contact and Tapping Mode AFM-IR. *Chem. Soc. Rev.* 2022.
- (5) Katzenmeyer, A. M.; Holland, G.; Kjoller, K.; Centrone, A. Absorption Spectroscopy and Imaging from the Visible through Mid-Infrared with 20 nm Resolution. *Anal. Chem.* **2015**, 87 (6), 3154–3159.
- (6) Lu, F.; Jin, M.; Belkin, M. A. Tip-Enhanced Infrared Nanospectroscopy via Molecular Expansion Force Detection. *Nat. Photon.* **2014**, *8* (4), 307–312.
- (7) Wieland, K.; Ramer, G.; Weiss, V. U.; Allmaier, G.; Lendl, B.; Centrone, A. Nanoscale Chemical Imaging of Individual Chemotherapeutic Cytarabine-Loaded Liposomal Nanocarriers. *Nano Res.* 2019, *12* (1), 197–203.
- (8) Ma, X.; Pavlidis, G.; Dillon, E.; Beltran, V.; Schwartz, J. J.; Thoury, M.; Borondics, F.; Sandt, C.; Kjoller, K.; Berrie, B. H.; Centrone, A. Micro to Nano: Multiscale IR Analyses Reveal Zinc Soap Heterogeneity in a 19th-Century Painting by Corot. *Anal. Chem.* 2022, 94 (7), 3103–3110.
- (9) Katzenmeyer, A. M.; Holland, G.; Chae, J.; Band, A.; Kjoller, K.; Centrone, A. Mid-Infrared Spectroscopy beyond the Diffraction Limit via Direct Measurement of the Photothermal Effect. *Nanoscale* **2015**, *7* (42), 17637–17641.
- (10) Ramer, G.; Aksyuk, V. A.; Centrone, A. Quantitative Chemical Analysis at the Nanoscale Using the Photothermal Induced Resonance Technique. *Anal. Chem.* 2017, 89 (24), 13524– 13531.
- (11) Tang, F.; Bao, P.; Su, Z. Analysis of Nanodomain Composition in High-Impact Polypropylene by Atomic Force Microscopy-Infrared. *Anal. Chem.* **2016**, *88* (9), 4926–4930.
- (12) Schwartz, J. J.; Chuang, H.-J.; Rosenberger, M. R.; Sivaram, S. V.; McCreary, K. M.; Jonker, B. T.; Centrone, A. Chemical Identification of Interlayer Contaminants within van der Waals Heterostructures. *ACS Appl. Mater. Interfaces* 2019, *11* (28), 25578–25585.
- (13) Liu, Z.; Nørgaard, K.; Overgaard, M. H.; Ceccato, M.; Mackenzie, D. M. A.; Stenger, N.; Stipp, S. L. S.; Hassenkam, T. Direct Observation of Oxygen Configuration on Individual Graphene Oxide Sheets. *Carbon* **2018**, *127*, 141–148.
- (14) Katzenmeyer, A. M.; Canivet, J.; Holland, G.; Farrusseng, D.; Centrone, A. Assessing Chemical Heterogeneity at the Nanoscale in Mixed-Ligand Metal–Organic Frameworks with the PTIR Technique. *Angew. Chem., Int. Ed.* **2014**, *53* (11), 2852–2856.
- (15) Ruggeri, F. S.; Habchi, J.; Chia, S.; Horne, R. I.; Vendruscolo, M.; Knowles, T. P. J. Infrared Nanospectroscopy Reveals the Molecular Interaction Fingerprint of an Aggregation Inhibitor with Single Aβ42 Oligomers. *Nat. Commun.* **2021**, *12* (1), 688.
- (16) Dou, T.; Li, Z.; Zhang, J.; Evilevitch, A.; Kurouski, D. Nanoscale Structural Characterization of Individual Viral Particles Using Atomic Force Microscopy Infrared Spectroscopy (AFM-IR) and Tip-Enhanced Raman Spectroscopy (TERS). *Anal. Chem.* **2020**, *92* (16), 11297– 11304.

- (17) Ramer, G.; Ruggeri, F. S.; Levin, A.; Knowles, T. P. J.; Centrone, A. Determination of Polypeptide Conformation with Nanoscale Resolution in Water. *ACS Nano* 2018, *12* (7), 6612–6619.
- (18) Giliberti, V.; Polito, R.; Ritter, E.; Broser, M.; Hegemann, P.; Puskar, L.; Schade, U.; Zanetti-Polzi, L.; Daidone, I.; Corni, S.; Rusconi, F.; Biagioni, P.; Baldassarre, L.; Ortolani, M. Tip-Enhanced Infrared Difference-Nanospectroscopy of the Proton Pump Activity of Bacteriorhodopsin in Single Purple Membrane Patches. *Nano Lett.* **2019**, *19* (5), 3104–3114.
- (19) Morsch, S.; Lyon, S.; Gibbon, S. R. The Degradation Mechanism of an Epoxy-Phenolic Can Coating. *Prog. Org. Coat.* **2017**, *102*, 37–43.
- (20) Strelcov, E.; Dong, Q.; Li, T.; Chae, J.; Shao, Y.; Deng, Y.; Gruverman, A.; Huang, J.; Centrone, A. CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> Perovskites: Ferroelasticity Revealed. *Sci. Adv. 3* (4), e1602165.
- (21) Delen, G.; Ristanović, Z.; Mandemaker, L. D. B.; Weckhuysen, B. M. Mechanistic Insights into Growth of Surface-Mounted Metal-Organic Framework Films Resolved by Infrared (Nano-) Spectroscopy. *Chem.: Eur. J.* 2018, 24 (1), 187–195.
- (22) Schwartz, J. J.; Le, S. T.; Krylyuk, S.; Richter, C. A.; Davydov, A. V.; Centrone, A. Substrate-Mediated Hyperbolic Phonon Polaritons in MoO3. *Nanophotonics* **2021**, *10* (5), 1517–1527.
- (23) Aksyuk, V.; Lahiri, B.; Holland, G.; Centrone, A. Near-Field Asymmetries in Plasmonic Resonators. *Nanoscale* **2015**, *7* (8), 3634–3644.
- (24) Gallacher, K.; Millar, R. W.; Paul, D. J.; Frigerio, J.; Ballabio, A.; Isella, G.; Rusconi, F.; Biagioni, P.; Giliberti, V.; Sorgi, A.; Sorgi, A.; Baldassarre, L.; Ortolani, M.; Ortolani, M. Characterization of Integrated Waveguides by Atomic-Force-Microscopy-Assisted Mid-Infrared Imaging and Spectroscopy. *Opt. Express* **2020**, *28* (15), 22186–22199.
- (25) Yuan, Y.; Chae, J.; Shao, Y.; Wang, Q.; Xiao, Z.; Centrone, A.; Huang, J. Photovoltaic Switching Mechanism in Lateral Structure Hybrid Perovskite Solar Cells. *Adv. Energy Mater.* 2015, 5 (15), 1500615.
- (26) Kebukawa, Y.; Kobayashi, H.; Urayama, N.; Baden, N.; Kondo, M.; Zolensky, M. E.; Kobayashi, K. Nanoscale Infrared Imaging Analysis of Carbonaceous Chondrites to Understand Organic-Mineral Interactions during Aqueous Alteration. *Proc. Natl. Acad. Sci.* U.S.A. 2019, 116 (3), 753–758.
- (27) Jubb, A. M.; Birdwell, J. E.; Hackley, P. C.; Hatcherian, J. J.; Qu, J. Nanoscale Molecular Composition of Solid Bitumen from the Eagle Ford Group across a Natural Thermal Maturity Gradient. *Energy Fuels* **2020**, *34* (7), 8167–8177.
- (28) Dazzi, A.; Glotin, F.; Carminati, R. Theory of Infrared Nanospectroscopy by Photothermal Induced Resonance. J. Appl. Phys. 2010, 107 (12), 124519.
- (29) Morozovska, A. N.; Eliseev, E. A.; Borodinov, N.; Ovchinnikova, O. S.; Morozovsky, N. V.; Kalinin, S. V. Photothermoelastic Contrast in Nanoscale Infrared Spectroscopy. *Appl. Phys. Lett.* 2018, *112* (3), 033105.
- (30) Lahiri, B.; Holland, G.; Centrone, A. Chemical Imaging Beyond the Diffraction Limit: Experimental Validation of the PTIR Technique. *Small* **2013**, *9* (3), 439–445.
- (31) Chae, J.; An, S.; Ramer, G.; Stavila, V.; Holland, G.; Yoon, Y.; Talin, A. A.; Allendorf, M.; Aksyuk, V. A.; Centrone, A. Nanophotonic Atomic Force Microscope Transducers Enable Chemical Composition and Thermal Conductivity Measurements at the Nanoscale. *Nano Lett.* 2017, *17* (9), 5587–5594.
- (32) Lahiri, B.; Holland, G.; Aksyuk, V.; Centrone, A. Nanoscale Imaging of Plasmonic Hot Spots and Dark Modes with the Photothermal-Induced Resonance Technique. *Nano Lett.* 2013, 13 (7), 3218–3224.

- (33) Baldassarre, L.; Giliberti, V.; Rosa, A.; Ortolani, M.; Bonamore, A.; Baiocco, P.; Kjoller, K.; Calvani, P.; Nucara, A. Mapping the Amide I Absorption in Single Bacteria and Mammalian Cells with Resonant Infrared Nanospectroscopy. *Nanotechnology* **2016**, *27* (7), 075101.
- (34) Wang, M.; Ramer, G.; Perez-Morelo, D. J.; Pavlidis, G.; Schwartz, J. J.; Yu, L.; Ilic, R.; Aksyuk, V. A.; Centrone, A. High Throughput Nanoimaging of Thermal Conductivity and Interfacial Thermal Conductance. *Nano Lett.* **2022**.
- (35) Katzenmeyer, A. M.; Aksyuk, V.; Centrone, A. Nanoscale Infrared Spectroscopy: Improving the Spectral Range of the Photothermal Induced Resonance Technique. *Anal. Chem.* 2013, 85 (4), 1972–1979.
- (36) Hopkins, P. E. Thermal Transport across Solid Interfaces with Nanoscale Imperfections: Effects of Roughness, Disorder, Dislocations, and Bonding on Thermal Boundary Conductance. *ISRN Mech. Eng.* **2013**, *2013*, e682586.
- (37) Katzenmeyer, A. M.; Chae, J.; Kasica, R.; Holland, G.; Lahiri, B.; Centrone, A. Nanoscale Imaging and Spectroscopy of Plasmonic Modes with the PTIR Technique. *Adv. Opt. Mater.* 2014, 2 (8), 718–722.
- (38) Yoon, Y.; Chae, J.; Katzenmeyer, A. M.; Yoon, H. P.; Schumacher, J.; An, S.; Centrone, A.; Zhitenev, N. Nanoscale Imaging and Spectroscopy of Band Gap and Defects in Polycrystalline Photovoltaic Devices. *Nanoscale* **2017**, *9* (23), 7771–7780.
- (39) Kochan, K.; Perez-Guaita, D.; Pissang, J.; Jiang, J.-H.; Peleg, A. Y.; McNaughton, D.; Heraud, P.; Wood, B. R. In Vivo Atomic Force Microscopy–Infrared Spectroscopy of Bacteria. *J. Royal Soc. Interface* **2018**, *15* (140), 20180115.
- (40) Dazzi, A.; Prazeres, R.; Glotin, F.; Ortega, J. M.; Al-Sawaftah, M.; de Frutos, M. Chemical Mapping of the Distribution of Viruses into Infected Bacteria with a Photothermal Method. *Ultramicroscopy* 2008, 108 (7), 635–641.
- (41) Rickard, M. A.; Meyers, G. F.; Habersberger, B. M.; Reinhardt, C. W.; Stanley, J. J. Nanoscale Chemical Imaging of a Deuterium-Labeled Polyolefin Copolymer in a Polyolefin Blend by Atomic Force Microscopy-Infrared Spectroscopy. *Polymer* 2017, *129*, 247–251.
- (42) Quaroni, L. Understanding and Controlling Spatial Resolution, Sensitivity, and Surface Selectivity in Resonant-Mode Photothermal-Induced Resonance Spectroscopy. *Anal. Chem.* 2020, 92 (5), 3544–3554.
- (43) Donaldson, P. M.; Kelley, C. S.; Frogley, M. D.; Filik, J.; Wehbe, K.; Cinque, G. Broadband Near-Field Infrared Spectromicroscopy Using Photothermal Probes and Synchrotron Radiation. *Opt. Express* **2016**, *24* (3), 1852–1864.
- (44) Frogley, M. D.; Lekkas, I.; Kelley, C. S.; Cinque, G. Performances for Broadband Synchrotron Photothermal Infrared Nano-Spectroscopy at Diamond Light Source. *Infrared Phys. Technol.* **2020**, *105*, 103238.
- (45) Barlow, D. E.; Biffinger, J. C.; Cockrell-Zugell, A. L.; Lo, M.; Kjoller, K.; Cook, D.; Lee, W. K.; Pehrsson, P. E.; Crookes-Goodson, W. J.; Hung, C.-S.; Nadeau, L. J.; Russell, J. N. The Importance of Correcting for Variable Probe–Sample Interactions in AFM-IR Spectroscopy: AFM-IR of Dried Bacteria on a Polyurethane Film. *Analyst* 2016, *141* (16), 4848–4854.

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# Supporting Information:

# Understanding Cantilever Transduction Efficiency and Spatial Resolution in Nanoscale Infrared Microscopy (AFM-IR)

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- Excitation power spectra across sample with different interfacial thermal conductances: Figure S12

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**Figure S1:** (a) Triangular laser pulse lasting 8 ns ( $t_{pulse}$ ), characterized by symmetric rising and falling edge times ( $t_{edge} = 4$  ns). After the laser pulse, the sample thermalizes with its surroundings until the arrival of the next pulse, which is set by the pulse repetition frequency (here,  $f_{pulse} = 100$  kHz, i.e., 10 µs intervals). (b) The resulting time-domain expansion profiles of samples with different thermalization times ( $\tau = 10$  ns, 100 ns, 500 ns, and 1000 ns) when heated by the laser pulse in (a). (c) Magnitudes of the discrete Fourier transforms (DFTs) of the time-domain sample expansion profiles shown in (b); inset shows DFTs normalized to their values at 0 MHz.



**Figure S2:** (a) Triangular laser pulse lasting 40 ns ( $t_{pulse}$ ), characterized by symmetric rising and falling edge times ( $t_{edge} = 20$  ns). After the laser pulse, the sample thermalizes with its surroundings until the arrival of the next pulse, which is set by the pulse repetition frequency (here,  $f_{pulse} = 100$  kHz, i.e., 10 µs intervals). (b) The resulting time-domain expansion profiles of samples with different thermalization times ( $\tau = 10$  ns, 100 ns, 500 ns, and 1000 ns) when heated by the laser pulse in (a). (c) Magnitudes of the discrete Fourier transforms (DFTs) of the time-domain sample expansion profiles shown in (b); inset shows DFTs normalized to their values at 0 MHz.



**Figure S3:** (a) Trapezoidal laser pulse lasting 1000 ns ( $t_{pulse}$ ), characterized by symmetric rising and falling edge times ( $t_{edge} = 20$  ns) and a constant-power plateau ( $t_{plateau} = 960$  ns). After the laser pulse, the sample thermalizes with its surroundings until the arrival of the next pulse, which is set by the pulse repetition frequency (here,  $f_{pulse} = 100$  kHz, i.e., 10 µs intervals). (b) The resulting time-domain expansion profiles of samples with different thermalization times ( $\tau = 100$  ns, 500 ns, and 1000 ns) when heated by the laser pulse in (a). (c) Magnitudes of the discrete Fourier transforms (DFTs) of the time-domain sample expansion profiles shown in (b); inset shows DFTs normalized to their values at 0 MHz.



**Figure S4:** (a) Heating profiles generated by isoenergic triangular (dashed line) and square (solid line) infrared laser pulses with total duration,  $t_{pulse} = 40$  ns. The heating power of the triangular pulse increases linearly from the onset of the pulse at t = 0 ns until 20 ns, after which the power decreases linearly until the end of the pulse at 40 ns. The square pulse delivers a uniform power over the duration of the pulse. After the laser pulse, the sample thermalizes with its surroundings until the arrival of the next pulse, which is set by the pulse repetition frequency (here,  $f_{pulse} = 100$  kHz, i.e., 10 µs intervals). (b) Time-domain expansion profile of samples with different thermalization times ( $\tau = 10$  ns, 100 ns, 500 ns, and 1000 ns) when heated by the laser pulses in (a): triangular heating pulse plotted with dashed lines, square pulse with solid lines. (c) Magnitudes of the discrete Fourier transforms (DFTs) of the time-domain sample expansion profiles shown in (b); inset shows DFTs normalized to their values at 0 MHz. Triangular heating pulse plotted with dashed lines. Note that the square pulse and the resulting data are defined with time steps of 0.01 ns, with the corresponding DFT scaled down by a factor of 0.01 ×, compared to the triangular pulse data, which has time steps of 1 ns.

#### Note S1: Finite-Difference Modeling of Absorbing/Non-Absorbing Heterostructures

To understand photothermal induced resonance (PTIR) spatial resolution, commercially available software and finite-difference methods were used to model the heat transfer in absorbing/non-absorbing heterostructures. A two-dimensional, axisymmetric model with a 5 nm element quadrilateral mesh was developed to study the heating and cooling of a PMMA/SU-8 ring heterostructure on a ZnSe substrate in the PTIR experiments. The PMMA/SU-8 thickness was 200 nm, while the ZnSe substrate was 2 mm thick; see Figure 4a. The thermal boundary conditions for this structure are depicted in Figure S5. Adiabatic conditions were enforced at the outer boundaries (shown as a thick green line) since heat loss via conduction and convection through the surrounding air is assumed to much smaller than the conduction to the substrate.<sup>1</sup> Additionally, at the three solid interfaces (PMMA/ZnSe, SU-8/ZnSe, and PMMA/SU-8), the interfacial thermal conductances (*G*) were set to prescribed values. At the PMMA/SU-8 interface, *G*<sub>PMMA/SU-8</sub> was varied over the range of 0.3 MW·K<sup>-1</sup>·m<sup>-2</sup> to 30 MW·K<sup>-1</sup>·m<sup>-2</sup>. The properties used for each material are listed in Table S1. The PMMA region was heated at a rate of *P*(*t*) to simulate the laser photothermal heating during the incident laser pulse.



**Figure S5:** Boundary conditions used to model the photothermal heating and subsequent thermalization of a PMMA/SU-8 heterostructure on a ZnSe substrate (see also Figure 4a). The two-dimensional, axisymmetric model contains three different interfaces (thick lines with arrows depicting the direction of heat flow) with defined interfacial thermal conductances (*G*). The interfacial thermal conductances,  $G_{PMMA/ZnSe}$  and  $G_{SU-8/ZnSe}$  (orange), were set to 3 MW·K<sup>-1</sup>·m<sup>-2</sup> for all calculations, while  $G_{PMMA/SU-8}$  (magenta) varied between 0.3 MW·K<sup>-1</sup>·m<sup>-2</sup> and 30 MW·K<sup>-1</sup>·m<sup>-2</sup> for Figure 6b and set to 3 MW·K<sup>-1</sup>·m<sup>-2</sup> for all other calculations. The PMMA region was heated at a rate of P(t) during the incident laser pulse to simulate photothermal heating. Adiabatic outer boundary conditions were enforced to preventing heat flow through the exterior surfaces (green) of the sample and substrate. See Table S1 for material properties.

<b>Property</b> <sup>a</sup>	Material		
	PMMA <sup>b</sup>	<b>SU-8</b>	ZnSe <sup>S2</sup>
Thermal Conductivity, $k$ (W/m·K)	$0.178^{S1}$	$0.206^{S3}$	18
Heat Capacity, C <sub>p</sub> (J/kg·K)	1368 <sup>S4</sup>	1200 <sup>S5</sup>	339
Density, $\rho$ (kg/m <sup>3</sup> )	1190 <sup>S4</sup>	1219 <sup>S5</sup>	5270

Table S1: Properties of Materials Used in Finite-Difference Time-Domain Model.

<sup>*a*</sup>For the purposes of these simulations, these values are treated as exact numbers. We do not anticipate reasonable experimental uncertainties or minor deviations from these values to meaningfully impact the results presented here. <sup>*b*</sup>Polymethyl methacrylate.



**Figure S6:** Spatiotemporal maps of a heterogeneous PMMA/SU-8 sample (Figure 4a in the main text) in response to an incident laser pulse with trapezoidal power profiles and total pulse lengths  $(t_{pulse})$  of (a) 80 ns and (b) 100 ns. The maps show the time evolution (vertical axis) and radial distribution (horizontal axis) of the thickness-averaged sample temperature change ( $\Delta T_{avg}$ ), which is proportional to the PTIR signal (see Note S1 for additional details).



**Figure S7:** Spatiotemporal maps of a heterogeneous PMMA/SU-8 sample (Figure 4a in the main text) in response to an incident laser pulse with triangular power profiles and total pulse lengths  $(t_{pulse})$  of (a) 8 ns, (b) 20 ns and (c) 40 ns. The maps show the time evolution (vertical axis) and radial distribution (horizontal axis) of the thickness-averaged sample temperature change ( $\Delta T_{avg}$ ), which is proportional to the PTIR signal (see Note S1 for additional details)



**Figure S8:** (a) Magnitudes of the discrete Fourier transforms (DFTs) of the average temperature changes in a heterogeneous PMMA/SU-8 sample (Figure 4a in the main text) excited by laser pulses with trapezoidal power profiles and lengths ( $t_{pulse}$ ) of 80 ns, and 100 ns. These values are related to the relative cantilever excitation efficiencies at different frequencies across the sample. (b) Radial profiles (horizontal slices) of the DFT magnitudes shown in (a) at different frequencies, normalized with respect to the DFT magnitudes at the center of the disk (0 nm). (c) Frequency profiles (vertical slices) of the DFT magnitudes shown in (a) at different radial positions, normalized by the magnitudes at 0 MHz. The effect of the PMMA/SU-8 interfacial thermal conductance (3 MW·K<sup>-1</sup>·m<sup>-2</sup>) is evident in the abrupt change observed around 500 nm.



**Figure S9:** (a) Magnitudes of the discrete Fourier transforms (DFTs) of the average temperature changes in a heterogeneous PMMA/SU-8 sample (Figure 4a in the main text) excited by laser pulses with triangular power profiles and lengths ( $t_{pulse}$ ) of 8 ns, 20 ns and 40 ns. These values are related to the relative cantilever excitation efficiencies at different frequencies across the sample. (b) Radial profiles (horizontal slices) of the DFT magnitudes shown in (a) at different frequencies, normalized with respect to the DFT magnitudes at the center of the disk (0 nm). (c) Frequency profiles (vertical slices) of the DFT magnitudes shown in (a) at different radial positions, normalized by the magnitudes at 0 MHz. The effect of the PMMA/SU-8 interfacial thermal conductance (3 MW·K<sup>-1</sup>·m<sup>-2</sup>) is evident in the abrupt change observed around 500 nm.



**Figure S10:** Comparisons of the normalized magnitudes of the discrete Fourier transforms (DFTs) of the average temperature changes at different frequencies (0.2 MHz, 1 MHz, 5 MHz, and 10 MHz, as indicated), across a heterogeneous PMMA/SU-8 sample (Figure 4a); insets show magnified views around the PMMA/SU-8 interface at 500 nm. These power spectra are related to the relative cantilever excitation efficiencies at different frequencies across the sample. In these simulations, laser pulses with triangular (8 ns duration) or a trapezoidal (100 ns, 250 ns, 1000 ns durations) power profiles heat the absorbing PMMA disk while accounting for thermal conduction into the outer SU-8 ring (see also Note S1 for additional details). Dashed horizontal lines indicate 80 % and 20 % of maximum DFT magnitude, used here to determine the spatial resolution.



**Figure S11:** (a) Photothermally induced average temperature changes ( $\Delta T_{avg}$ ) over time at selected positions across a heterogeneous PMMA/SU-8 sample (Figure 4a) illuminated continuously by a sinusoidally modulated source (shown here at 100 kHz). (b) Comparisons of the normalized peak magnitudes of the discrete Fourier transforms (DFTs) of the temperature changes for different source modulation frequencies (0.1 MHz, 1 MHz, 2.5 MHz, 5 MHz, and 10 MHz), which are related to the relative cantilever excitation efficiencies. Dashed horizontal lines indicate 80 % and 20 % of maximum DFT magnitude, used here to determine the spatial resolution (see Figure 6a). In these simulations, a continuous, sinusoidally modulated illumination source heats the absorbing PMMA disk while accounting for thermal conduction into the outer SU-8 ring (see also Note S1 for additional details).



**Figure S12:** Comparisons of the normalized magnitudes of the discrete Fourier transforms (DFTs) of the average temperature changes at different frequencies (0.2 MHz, 1 MHz, 5 MHz, and 10 MHz, as indicated), across a heterogeneous PMMA/SU-8 sample (Figure 4a in the main text) with different interfacial thermal conductances; insets show magnified views around the PMMA/SU-8 interface at 500 nm. These power spectra are related to the relative cantilever excitation efficiencies at different frequencies across the sample.

#### **Supporting References**

- (S1) Chae, J.; An, S.; Ramer, G.; Stavila, V.; Holland, G.; Yoon, Y.; Talin, A. A.; Allendorf, M.; Aksyuk, V. A.; Centrone, A. Nanophotonic Atomic Force Microscope Transducers Enable Chemical Composition and Thermal Conductivity Measurements at the Nanoscale. *Nano Lett.* 2017, *17* (9), 5587–5594.
- (S2) Zinc Selenide (ZnSe) Optical Material. Zinc Selenide (ZnSe) Optical Material. https://www.crystran.co.uk/optical-materials/zinc-selenide-znse (accessed 2022-05-25).
- (S3) Wang, M.; Ramer, G.; Perez-Morelo, D. J.; Pavlidis, G.; Schwartz, J. J.; Yu, L.; Ilic, R.; Aksyuk, V. A.; Centrone, A. High Throughput Nanoimaging of Thermal Conductivity and Interfacial Thermal Conductance. *Nano Lett.* 2022.
- (S4) Gaur, U.; Lau, S.; Wunderlich, B. B.; Wunderlich, B. Heat Capacity and Other Thermodynamic Properties of Linear Macromolecules VI. Acrylic Polymers. J. Phys. Chem. Ref. Data 1982, 11 (4), 1065–1089.
- (S5) Lai, J.-L.; Liao, C.-J.; Su, G.-D. J. Using an SU-8 Photoresist Structure and Cytochrome C Thin Film Sensing Material for a Microbolometer. *Sensors* **2012**, *12* (12), 16390–16403.