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Probing Nanoparticle Substrate Interactions with Synchrotron Infrared Nanospectroscopy: Coupling Gold Nanorod Fabry-Pérot Resonances with SiO₂ and hBN Phonons

Joseph J. Liberko,¹ Jacob A. Busche,² Robyn Seils,³ Hans A. Bechtel,⁴

Philip D. Rack,^{3,5} David J. Masiello,^{2,*} and Jon P. Camden^{1,†}

¹*Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556, USA*

²*Department of Chemistry, University of Washington, Seattle, Washington 98195, USA*

³*Department of Materials Science and Engineering,*

University of Tennessee, Knoxville, Tennessee 37996, USA

⁴*Advanced Light Source Division, Lawrence Berkeley National Laboratory, Berkeley, 94720, California, USA*

⁵*Center for Nanophase Materials Science, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*

Spectroscopic interrogation of materials in the mid-infrared with nanometer spatial resolution is inherently difficult due to the long wavelengths involved, reduced detector efficiencies, and limited availability of spectrally bright, coherent light sources. Technological advances are driving techniques that overcome these challenges, enabling material characterization in this relatively unexplored spectral regime. Synchrotron infrared nanospectroscopy (SINS) is an imaging technique that provides local sample information of nanoscale target specimens in an experimental energy window between 330 and 5000 cm⁻¹. Using SINS, we analyzed a series of individual gold nanorods patterned on a SiO₂ substrate and on a flake of hexagonal boron nitride. The SINS spectra reveal interactions between the nanorod photonic Fabry-Pérot resonances and the surface phonon polaritons of each substrate which are characterized as avoided crossings. A coupled oscillator model of the hybrid system provides a deeper understanding of the coupling and provides a theoretical framework for future exploration.

I. INTRODUCTION

Advances in the design of nanoengineered materials endowed with tailorable mid-infrared (IR) responses have been accelerated by decades of prior research in plasmonics, photonics, and phononics. By leveraging knowledge gained from these communities, new strategies for creating tunable light-matter states that operate across the IR have emerged based on hybridizing electronic, optical, and vibrational degrees of freedom [1–3]. In such materials, their composite responses find origin in their bulk dielectric properties together with particle morphology and cluster geometry [4–9]. Characterizing these properties with simultaneously high spatial and spectral resolution is difficult but essential for the rational design of advanced materials with novel functionalities [10–14]. Today, a number of studies have made progress in this direction through a variety of near-field imaging and spectroscopy techniques [15–23], yet considerable work still lies ahead to better understand material design principles and characterization methods in the IR spectral

* masiello@uw.edu

† jon.camden@nd.edu

34 regime.

35 In this work, we investigate the nanoscale resonant coupling between the mid-IR Fabry-Pérot (F-P) modes of high-
 36 aspect ratio noble-metal nanorods [24–29] with the surface-phonon polaritons (SPhPs) [30, 31] of their supporting
 37 substrates. Due to their light like nature, we will refer to these surface plasmon polaritons as Fabry-Pérot (F-P) modes
 38 [24]. Previous work by Huck *et al.* [32] measured far-field extinction spectra from gold nanorods on SiO₂ substrates
 39 of various thicknesses and discovered an avoided crossing when the resonance positions of the nanorod series were
 40 plotted versus inverse nanorod length; however, these measurements did not probe the coupling in the near-field. More
 41 recently, Tizei *et al.* [33] explored strong coupling between SPhPs and the first F-P mode in long metal nanowires
 42 using electron energy-loss spectroscopy (EELS) performed in a scanning transmission electron microscope (STEM).
 43 In this study, silver nanorods were placed on thin hexagonal boron nitride (hBN) flakes with their ends suspended off
 44 the substrate. Probing the vacuum end of the nanorod minimized substrate losses and allowed the nanorod length to
 45 be systematically milled, via the electron beam, to tune the F-P response and produce an avoided crossing in the EEL
 46 spectrum. In general, the presence or absence of an avoided crossing depends on the specifics of the nanoparticle-
 47 substrate system and an avoided crossing is not expected when dealing with lossy modes or weak coupling [34]. The
 48 facile tunability of the nanorod F-P resonances employed here makes it an ideal system to study particle-substrate
 49 coupling.

50 Scattering-type scanning near-field optical microscopy (s-SNOM) utilizes light that is coupled into an atomic force
 51 microscope (AFM) to create a region of concentrated surface charges induced at its tip. The scattered field of these
 52 charges subsequently interacts with a target material, simultaneously gathering information about the spatial and
 53 spectral profiles of the target’s optical modes [35–40]. Since the scattered field contains both radiative and nonradiative
 54 components, the selection rules for s-SNOM are relaxed compared to far-field plane-wave illumination, as the actual
 55 collected signal in s-SNOM is the radiation from the coupled tip-sample region. Direct measurement of a nanoparticle’s
 56 dielectric response using such techniques provides: (1) a window into resonant energy transfer between nanostructured
 57 materials with their supporting substrates, (2) a method for analyzing irregularities of thin-film structures, and (3) an
 58 avenue for exploring quantum-size and surface-scattering effects [41–44]. Additionally, because the tip’s characteristic
 59 length scale is on the order of tens of nanometers, near-field effects allow s-SNOM to overcome Abbes diffraction limit
 60 [45].

61 By design, s-SNOM relies on a spectrally bright, collimated, and coherent light source because the tip focusing
 62 and scattering processes are inefficient. While this limitation has largely been overcome in the optical and ultraviolet
 63 spectral regions by advancements in laser technology, highly tunable IR sources remain limited [36]. Recently, Bechtel
 64 and co-workers [46] implemented an s-SNOM variant using the broadband and high-intensity IR radiation available
 65 from the synchrotron at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory called syn-
 66 chrotron infrared nanospectroscopy (SINS); see Fig. 1. The rich IR spectral contents of the ALS allows the response
 67 of a sample to be simultaneously collected at all IR frequencies to which available photon detectors are sensitive. The
 68 current ALS SINS instrument system is capable of ~ 0.5 meV spectral resolution that is considerably better than
 69 the ~ 5 meV resolution of STEM EELS such that, taken together with the 25 nm spatial resolution provided by the
 70 AFM tip, SINS is a uniquely powerful technique with which to probe nanostructures, especially those with narrow
 71 resonances, in the mid-IR region [47–56].

72 We begin by presenting SINS data to explore the transfer of energy between the low-energy multipolar F-P modes

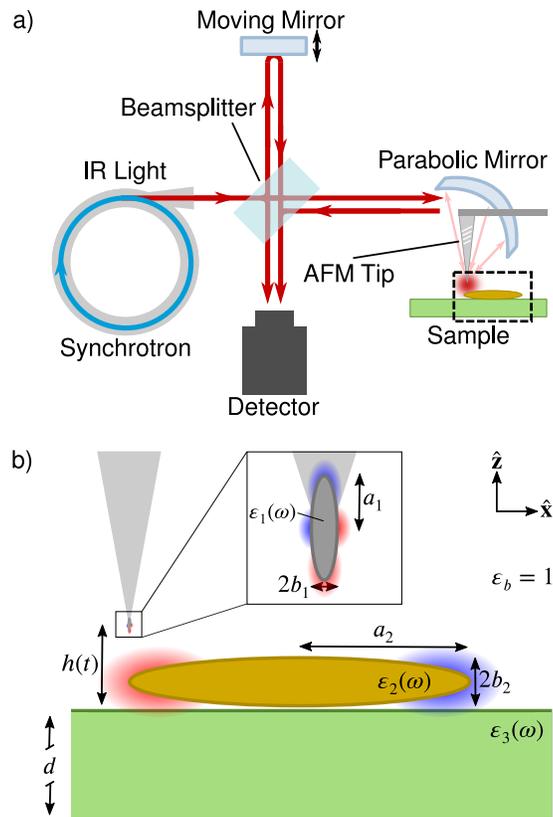


FIG. 1. (a) Schematic of the experimental SINS setup. The dashed box encloses the tip-sample interaction region. (b) Geometry of the idealized sample system and the model parameters used to build an analytical oscillator model of the tip-sample interaction (see text for details).

73 of individual gold nanowires and the IR SPhPs in a polar crystal substrate. Nanorod lengths are systematically
 74 fabricated and measured to evolve these F-P modes through the highest energy SPhP substrate mode of SiO_2 . Next,
 75 the substrate is exchanged for a van der Waals material to explore how the nanowire F-P modes interact with a
 76 different inherent set of IR SPhPs. To gain physical insight, we model the system analytically, deriving the SINS
 77 signal from the tip's effective polarizability and interpreting the spectral features contained therein with a simple
 78 oscillator model.

79 II. RESULTS AND DISCUSSION

80 A. Individual nanorod Analysis

81 The second harmonic SINS response of two nanorods ($1.13 \mu\text{m}$ and $2.18 \mu\text{m}$) on SiO_2 are shown in Fig. 2 as a
 82 function of scan distance along the centerline of each nanorod. SINS of the bare SiO_2 substrate (Fig. S1 of the
 83 Supplemental Material [SM], [57]) reveals a SPhP at 1219 cm^{-1} in the phase spectrum, and at 1126 cm^{-1} in the
 84 magnitude spectrum. Interestingly, this substrate feature is able to be detected through the 30 nm thick gold nanorod
 85 as seen in the SINS phase and magnitude spectra of the $1.13 \mu\text{m}$ nanorod along its full length. Lobes are observed
 86 at both nanorod ends around 2500 cm^{-1} in the SINS phase spectra and around 2200 cm^{-1} in the magnitude spectra

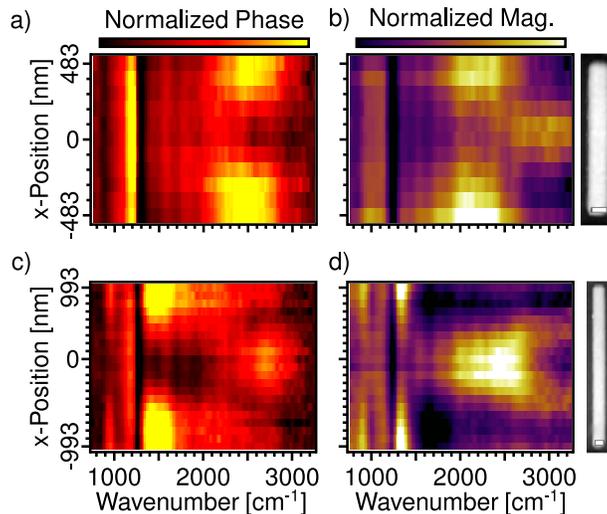


FIG. 2. SINS linescans showing the normalized phase (a and c) and normalized magnitude (b and d) for 1.13 (a and b) and 2.18 (c and d) μm long nanorods on an SiO_2 substrate as a function of distance from the nanorod center. AFM images of the nanorods scanned are included on the right, with each horizontal scale bar representing 100 nm. The unmixed $m = 1$ F-P mode is observed in the shorter nanorod whereas the longer nanorod shows the mixing of the $m = 1$ F-P mode with the substrate phonon and the emergence of the unmixed $m = 2$ F-P mode. To better highlight these behaviors, SINS intensity information is displayed over a given range (0.1 – 0.7 rad and 0.4 – 1.0 V) so that data outside of it saturates the image.

(Fig. 2ab) . The spatial distribution and energy range of this feature, together with previous studies [12, 24, 58], indicates that this is the first, $m = 1$, F-P mode. As the nanorod's first F-P mode and substrate's SPhP are separated by $\sim 1200 \text{ cm}^{-1}$, little mixing is expected.

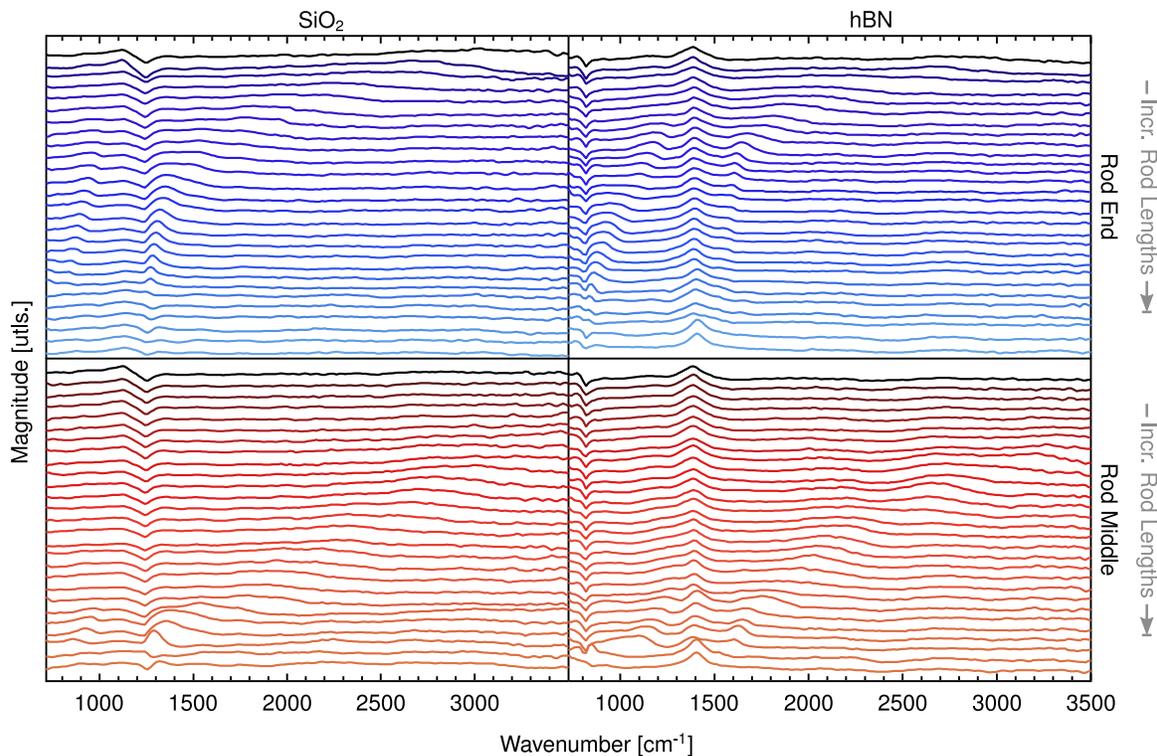
Increasing the nanorod length shifts the $m = 1$ F-P feature toward the lower energy SiO_2 SPhP [24], promoting interactions between the nanorod and substrate. SINS phase and magnitude linescan spectra of a 2.18 μm nanorod are shown in Fig. 2c and 2d, where the $m = 1$ F-P mode energy approaches the SPhP and a splitting is observed on either side of the SiO_2 phonon, with peaks at 950 cm^{-1} and 1450 cm^{-1} in both SINS phase and magnitude. Lengthening the nanorod also introduces a new feature in both spectra (around 2700 cm^{-1} in the phase spectra), which we attribute primarily to the second, $m = 2$, F-P mode based upon strong localization at the center of the nanorod. To further explore the peak splitting attributed to the first two F-P modes and SPhP mixing, we performed additional SINS characterization on more than two dozen nanorods of varying length on both SiO_2 and hBN substrates.

B. Complete nanorod Series Analysis

A series of Au nanowires ($L = 0.7 - 10.0 \mu\text{m}$, details in Table SI of the SM) were lithographically patterned onto two different substrates: (1) 100 nm thick amorphous SiO_2 on a Si wafer and (2) 330 nm thick flake of exfoliated hBN on a Si wafer. Measurements were performed at the tip and center of each nanorod in the series to track the $m = 1$ and $m = 2$ F-P modes, respectively. The second harmonic SINS magnitude components are reported in Fig. 3 (phase is reported in Fig. S3 the SM), where the top of each waterfall plot begins with the shortest nanorod and ends at the bottom with the longest nanorod. For the SINS magnitude measurements obtained at the tip of the shortest nanorods

105 (top traces of Fig. 3) the SPhP feature is clearly isolated at 1126 and 1389 cm^{-1} for SiO_2 and hBN, respectively, with
 106 only the beginning of the red shoulder from the $m = 1$ F-P mode appearing in the high energy region. We confirm
 107 this as a SPhP feature by performing SINS on each substrate, in the absence of nanorods, to isolate and identify the
 108 substrate phonons (see Figs. S1 and S2 of SM). SINS performed at the center of the shortest nanorods (top red traces
 109 in Fig. 3) also exhibit an isolated SPhP feature.

110 Increasing the nanorod length allows the F-P modes [24] to mix with the SPhP, causing a secondary peak to emerge
 111 at 987 cm^{-1} in SiO_2 and at 1296 cm^{-1} in hBN. Interestingly, these secondary peaks emerge asymptotically, shifting to
 112 lower energies. While the secondary peaks on the SiO_2 substrate quickly diverge out of the observation window, the
 113 secondary peaks on hBN appear to converge towards 849 cm^{-1} . Concurrently, the F-P peak redshifts and asymptotes
 114 on the high energy side of the SPhP. This peak splitting around the isolated SPhP energy is indicative of an avoided
 115 crossing and further insight is provided by plotting the peak positions of both modes versus inverse nanorod length
 116 for each substrate (Fig. 4).



117

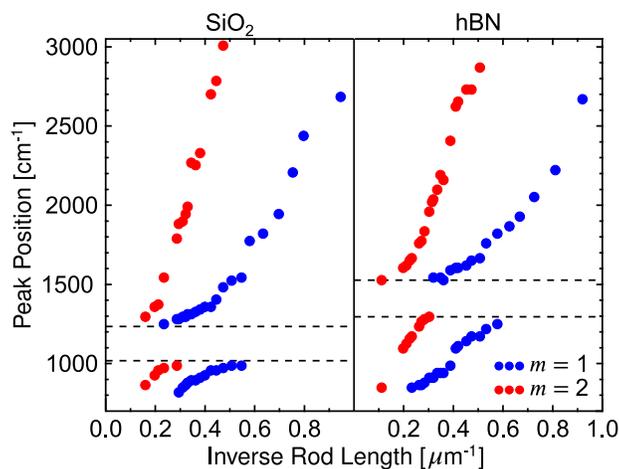
118 FIG. 3. SINS magnitude spectra from a series of nanorods ($L = 0.7 - 10.0 \mu\text{m}$) obtained at the end (blue tones) or middle (red
 119 tones) of the nanorod on SiO_2 (first column) and hBN (second column) substrates. The spectrum obtained from the shortest
 120 nanorod is plotted at the top in each panel with longer nanorod spectra vertically offset until the longest nanorod in each series
 121 is plotted at the bottom.

122

123 Fig. 4, displays the avoided crossings between the substrate SPhPs and the nanorod $m = 1$ (blue) and $m = 2$
 124 (red) F-P modes as measured in SINS magnitude (the associated avoided crossing in phase is presented in the SM
 125 as Fig. S3). In the SiO_2 avoided crossing, the asymptotic energies are 1248 cm^{-1} for the upper branch and 987

126 cm^{-1} for the lower branch. For the substrate thickness probed here, the upper branch of the avoided crossing is
 127 expected to align with the substrate's longitudinal optical phonon (LO) energy while the lower branch should align
 128 with the transverse optical phonon (TO) [32]. Our results are in good agreement with the previously reported LO
 129 and TO energies in amorphous SiO_2 (1248 cm^{-1} and 1064 cm^{-1} , respectively) [30], and are further consistent with
 130 the previously described far-field extinction measurements of a similar system [32].

131 Analyzing the nanorod evolution on hBN yields asymptotic energies of 1527 cm^{-1} for the upper branch and 1296
 132 cm^{-1} for the lower branch of the avoided crossing. The branch energies observed here are in good agreement with
 133 previous measurements of the LO and TO in hBN [59]. In a similar experiment, Ag nanorods on thinner flakes of
 134 hBN were investigated using EELS to reveal an avoided crossing [33], although the mixing of the $m = 2$ F-P mode
 135 with the SPhP was not fully observed. Nevertheless, the avoided crossing in Fig. 3 clearly indicates the mixing of
 136 the $m = 1$ and $m = 2$ F-P modes of Au nanorods with SPhPs in hBN. In addition, the upper branch of a second
 137 avoided crossing in hBN is evidenced by a concavity change around 1050 cm^{-1} in the lower $m = 1$ branch and energies
 138 asymptotically approaching 849 cm^{-1} for the lowest values of inverse nanorod length. The latter energy aligns well
 139 with the next highest LO present in hBN which has a recorded value of 828 cm^{-1} [59]. The forbidden region in the
 140 avoided crossings is the spectral range between the upper and lower branches and has a maximum value determined
 141 by the energy separation of a substrate's LO and TO values. Known as the Reststrahlen band, this spectral region
 142 is most often where $\text{Re}(\varepsilon)$ is negative [60]. In our experiments, we find branch separation energies of 261 cm^{-1} and
 143 231 cm^{-1} for the SiO_2 and hBN substrates, respectively. These results are in good agreement with the expected
 144 Reststrahlen bands calculated from their previously reported LO and TO values [30, 59]. Interestingly, these values
 145 correspond to roughly half of the minimum separation energies between the upper and lower peak position of both
 146 F-P nanorod resonances on each substrate; see Table S2 of SM.



147

148 FIG. 4. Avoided crossing diagram derived from the SINS magnitude measurements for the complete nanorod series on both
 149 SiO_2 and hBN substrates. The $m = 1$ (blue) and $m = 2$ (red) F-P modes are plotted versus inverse nanorod length. Dotted
 150 black lines are the asymptotic energies.

C. Modeling and Discussion

1. Reconstruction of the SINS Observable

To augment the interpretation of the SINS signal, we present a reduced-order analytical model of the interactions between a F-P mode of the Au nanorod and a SPhP of the substrate. The model provides a simple and intuitive picture of the electromagnetic interactions within the sample and how each contributes to the observed spectra. As quantitative calculations involving the resonant surface modes of large particles are mathematically complicated and computationally expensive, we substitute these phenomena with simpler resonances that qualitatively reproduce the behavior of the system.

The $m = 1$ F-P mode of the target nanorod is modeled as the nonradiative long-axis dipolar mode of a prolate spheroid with long-axis radius a_2 and short-axis radius b_2 ; see Fig. 1. The long axis is taken to lie along the x -axis and the short axes lie in the yz -plane. The spectral properties of the dipolar mode are recovered from its polarizability, $\alpha_2(\omega)$, which encodes the contributions of both the nanorod's dielectric function $\varepsilon_2(\omega)$ and geometry and allows the dipolar mode to be approximated as a point dipole located at the spheroid's center [57, 61]. The dipole is defined as $\mathbf{p}_2(\omega) = \alpha_2(\omega)\mathcal{E}_{2x}(\mathbf{0}, \omega)$, wherein $\mathbf{p}_2(\omega)$ is the nanorod's long-axis dipole moment and $\mathcal{E}_{2x}(\mathbf{r}, \omega)$ is the x -component of the total electric field $\mathcal{E}_2(\mathbf{r}, \omega)$ that impinges on the nanorod.

The coupling between the nanorod and its surroundings is provided through this total field. It can be expanded as $\mathcal{E}_2(\mathbf{r}, \omega) = \mathbf{E}_0(\omega) + \mathbf{E}_1(\mathbf{r}, \omega) + \mathbf{E}_3(\mathbf{r}, \omega)$, where $\mathbf{E}_0(\omega)$ is the electric field provided by the synchrotron light source, assumed here to be spatially uniform within the tip-sample region and linearly polarized with components along both the x - and z -axes. Further, $\mathbf{E}_1(\mathbf{r}, \omega)$ is the field scattered from the AFM tip and $\mathbf{E}_3(\mathbf{r}, \omega)$ is the field scattered from the substrate. The last field can be modeled as the image response of the substrate to the excitation provided by the synchrotron, tip, and target, and is proportional to the surface response function $\beta(\omega) = [\varepsilon_3(\omega) - 1]/[\varepsilon_3(\omega) + 1]$, with $\varepsilon_3(\omega)$ representing the substrate's dielectric function.

The tip's scattered field is modeled as originating from a superposition of two dipoles, one oriented parallel to the surface of the substrate and the other normal, that lie at the centroid of the tip, \mathbf{r}_1 . The tip is taken to be a z -oriented prolate spheroid of long-axis radius a_1 , short-axis radius b_1 , and dielectric $\varepsilon_1(\omega)$ with a centroid raised a height $h > a_1$ above the substrate (see Fig. 1), such that the substrate-normal dipole is oriented along the tip's long axis, and the substrate-parallel dipole along the short axis. Similar to the treatment of the target nanorod, the tip's long (l) and short (s) axis dipole modes are given the polarizabilities of their spheroidal counterparts, $\mathbf{p}_1^{l,s}(\omega) = \alpha_1^{l,s}(\omega)\mathcal{E}_{1z,1x}(\mathbf{r}_1, \omega)$ (see Eq. (A16) of the SM), with $\mathcal{E}_{1i}(\mathbf{r}, \omega)$ the i^{th} component of the total electric field $\mathcal{E}_1(\mathbf{r}, \omega) = \mathbf{E}_0(\omega) + \mathbf{E}_2(\mathbf{r}, \omega) + \mathbf{E}_3(\mathbf{r}, \omega)$ acting on the tip. A more detailed discussion of these approximations is given further on.

The complete spectral response of the tip is especially useful, as it encodes the observable SINS spectrum. The most convenient way to describe this response is through the effective polarizabilities $\hat{\alpha}_1^{l,s}(\omega)$. These polarizabilities encapsulate the influence of all external sources on $\mathbf{p}_1^{l,s}(\omega)$, including sources which are in turn influenced by $\mathbf{p}_1^{l,s}(\omega)$ through coupling forces [62]. In this way, only a single force of the many that dictate the tip's polarization needs to be tracked, and the details of the rest of the system's motion follow from $\hat{\alpha}_1^{l,s}(\omega)$. In general, the only source of the tip's polarization that is experimentally characterizable is the synchrotron light, so it is singled out in the

188 implicit definition $\mathbf{p}_1^{l,s}(\omega) = \hat{\alpha}_1^{l,s}(\omega)\mathbf{E}_{0z,0x}(\omega)$, wherein $\mathbf{E}_{0i}(\omega)$ is the i^{th} -component of the synchrotron field. Thus,
 189 with knowledge of the explicit forms of the effective polarizabilities and the synchrotron field, the magnitude and
 190 phase of the tip's dipole moment and associated scattered fields can be recovered and converted, through oscillation
 191 of the tip and lock-in detection, into the SINS observable (see Eq. (3)).

192 The derivations of $\hat{\alpha}_1^{l,s}(\omega)$ are lengthy (see SM) but result in

$$\begin{aligned} \hat{\alpha}_1^l(\omega) &= \alpha_1^l(\omega) \frac{1 + \beta(\omega)}{1 - \alpha_1^l(\omega)\beta(\omega)/4h^3}, \\ \hat{\alpha}_1^s(\omega) &= \alpha_1^s(\omega) \frac{1 + 2\hat{\alpha}_2(\omega)/(a_2^2 + [h - b_2]^2)^{\frac{3}{2}}}{1 - \alpha_1^s(\omega)\beta(\omega)/8h^3 + 4\alpha_1^s(\omega)\hat{\alpha}_2(\omega)/(a_2^2 + [h - b_2]^2)^3}. \end{aligned} \quad (1)$$

194 For both tip dipoles, the effective polarizability is the product of its free-space polarizability $\alpha_1^{l,s}(\omega)$ and a frequency-
 195 dependent dressing factor. In the limit both $\hat{\alpha}_2(\omega)$ and $\beta(\omega)$ go to zero, either factor goes to one and the effective
 196 polarizabilities return to their free-space values. Further,

$$\hat{\alpha}_2(\omega) = \alpha_2(\omega) \frac{1}{1 - \alpha_2(\omega)\beta(\omega)/8b_2^3} \quad (2)$$

198 is the nanorod dipole's effective polarizability. Note that Eq. (2) does not depend on either polarizability $\alpha_1^{l,s}(\omega)$ of
 199 the tip, such that the nanorod's spectral response is assumed to be altered only by the substrate. This approximation
 200 is valid here because the tip's long-axis dipole cannot couple to the target nanorod's dipolar mode at all by symmetry
 201 and the tip's short-axis dipole (which can couple) is both far-detuned from the nanorod's response and many orders
 202 of magnitude weaker. More specifically, the detuning between the maxima of $\text{Im } \alpha_1^s(\omega)$ and $\text{Im } \alpha_2(\omega)$ is roughly $70\gamma_2$,
 203 with γ_2 the nanorod mode's FWHM, and the ratio of the maxima is $\sim 10^{-5}$.

204 The substrate's modification of the nanorod's response is contained in the second term in the denominator of $\hat{\alpha}_2(\omega)$,
 205 which indicates coupling between the dipole and resonances in the substrate. In the case where $\alpha_2(\omega)$ and $\beta(\omega)$ each
 206 have a sufficiently strong single resonance, this term leads to mode splitting, as can be checked by comparison to the
 207 spectrum of two coupled oscillators [57].

208
 209 Each of the terms in the dressing factors of $\hat{\alpha}_1^{l,s}(\omega)$ are similarly responsible for encoding coupling effects into
 210 the tip's response. The numerator of either factor builds in additional driving forces on the tip that arise as the
 211 synchrotron directly excites the substrate (in $\hat{\alpha}_1^l$) or target (in $\hat{\alpha}_1^s$) and causes surface charges in either to push back
 212 on the tip. Meanwhile the denominators encode coupling effects: the terms that go like $\alpha_1^{l,s}(\omega)\beta(\omega)/h^3$ describe
 213 tip-substrate coupling and the term in $\hat{\alpha}_1^s$'s denominator proportional to $\alpha_1^s(\omega)\hat{\alpha}_2(\omega)$ builds tip-target coupling into
 214 the tip's response. From these terms, one can conclude that only the short-axis dipole of the tip can couple to $\mathbf{p}_2(\omega)$.
 215 The long-axis dipole can only couple to the substrate, such that the observables of $\mathbf{p}_1^l(\omega)$ serve only to obscure the
 216 features of $\hat{\alpha}_1^s(\omega)$.

217 Translation of the effective polarizabilities of the tip to a SINS signal is performed by allowing the tip-substrate
 218 separation to become time dependent, such that $h \rightarrow h(t) = h_0 + \Delta h \cos(\Omega_0 t)$, where h_0 is the time-average separation,
 219 Δh is the modulation depth, and $\Omega_0 \sim 100$ kHz is the tip's oscillation frequency. The resulting time-dependent

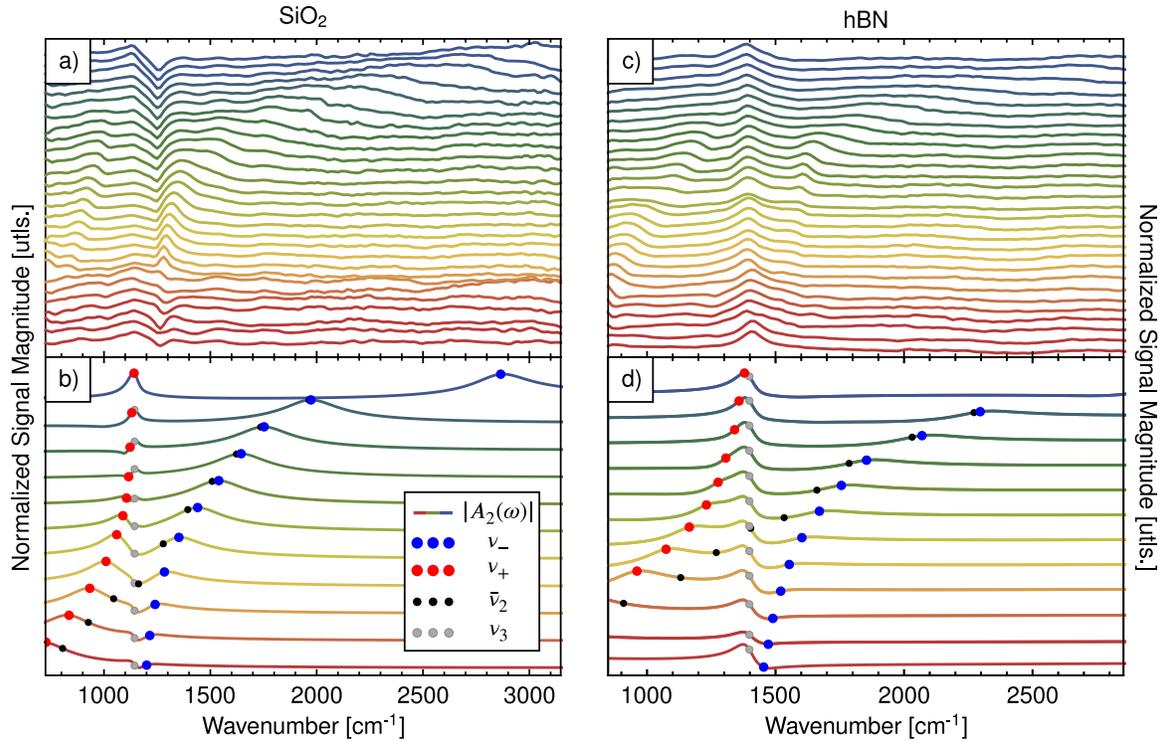


FIG. 5. Comparison of experimentally collected (a, c) and theoretically constructed (b, d) SINS magnitude spectra $|A_2(\omega)|$ of the $m = 1$ nanorod F-P mode. The experimental spectra were obtained from a series of target gold nanorods of lengths varying from $L = 0.7 - 10.0 \mu\text{m}$, while the theoretical spectra were generated using a target spheroid of long axis radius $a_2 = 9 \mu\text{m}$, short-axis radius $b_2 = 550 \text{ nm}$, plasma wavenumber $\omega_{p2}/2\pi c = 1633 \text{ cm}^{-1}$, scattering wavenumber $\gamma_2/2\pi c = 256.5 \text{ cm}^{-1}$, and variable Lorentz wavenumber $\omega_2/2\pi c = 805.5 - 2977 \text{ cm}^{-1}$. The nanorods were mounted on SiO_2 (a) and hBN (c) substrates, and these substrates were modeled theoretically (b, d) with plasma wavenumbers $\omega_{p3}/2\pi c = 362.9$ and 1169 cm^{-1} , damping wavenumbers $\gamma_3/2\pi c = 64.12$ and 92.75 cm^{-1} , Lorentz wavenumbers $\omega_3/2\pi c = 1147$ and 1398 cm^{-1} , and intraband dielectric constants $\epsilon_{\infty 3} = 1.2$ and 2.68 , respectively [63–65]. Additionally, the spectral locations of the uncoupled nanorod dipole ($\bar{\nu}_2$), uncoupled substrate SPhP (ν_3), and hybridized modes (ν_{\pm}) are superimposed on the spectra to demonstrate the effects of the nanorod-substrate coupling on the observable signal.

220 polarizabilities $\hat{\alpha}_1^{l,s}(\omega)$ can be expanded into a Fourier series with complex coefficients

$$221 \quad A_n^{l,s}(\omega) = \frac{\Omega_0}{2\pi} \int_{-\frac{\pi}{\Omega_0}}^{\frac{\pi}{\Omega_0}} \hat{\alpha}_1^{l,s}(\omega, t) e^{ni\Omega_0 t} dt \quad (3)$$

222 which are known to reproduce both the magnitude and phase of the SINS signal up to a scaling factor [38]. The
 223 synchrotron's light is assumed to be polarized at 45 degrees to the x -axis, such that both the long- and short-axis
 224 dipole modes of the tip are driven equally. The second-order Fourier coefficient of the total field flux at the location
 225 of the detector is then proportional to the average of the coefficients of the fields from each tip dipole, and can be
 226 modeled up to a constant scale factor by $A_2(\omega) = [A_2^l(\omega) + A_2^s(\omega)]/2$.

227 Fig. 5 shows the absolute magnitude $|A_2(\omega)|$. The tip is made of PtSi, which in the range of energies considered in
 228 Fig. 5 is well-modeled by a Drude-model dielectric $\epsilon_1(\omega) = 1 - \omega_{p1}^2/(\omega^2 + i\omega\gamma_1)$ with plasma wavenumber $\omega_{p1}/2\pi c =$
 229 $2.98 \times 10^4 \text{ cm}^{-1}$ and damping wavenumber $\gamma_1/2\pi c = 645 \text{ cm}^{-1}$ [66]. The metallic motion of the tip's electrons as well
 230 as its micron-scale length and conical geometry likely impart on it an optical response dominated by a continuous

spectrum of propagating surface plasmon modes. While the existence and properties of these modes have not yet been experimentally explored in PtSi tips, they have recently been investigated in similarly conductive gold tips [67–69]. We take from these earlier studies two conclusions, namely that the electric response of the tip does not contain resonances in the mid-IR when driven by sources near its apex and that the field profiles of its low-energy response are dipolar at each driving frequency ω just below its apex.

Building on previous successes modeling AFM tips using point dipoles and/or spheroidal particles, we model the tip’s apex as a pair of point-dipoles $\mathbf{p}_1^{l,s}$ with spheroidal polarizabilities that reproduce the apex’s featureless low-energy spectral response and field profile [37, 38, 70]. Both properties are achieved naturally. The spheroid model assumes the tip’s response is dominated by a pair of localized surface plasmon dipoles, both of which resonate at energies far higher than the resonance frequencies of the target nanorod dipoles and substrate SPhPs due to the relatively large value of ω_{p1} . Thus, the low-energy tails of the resonances provide the tip a flat spectral response below 4000 cm^{-1} (see Fig. S6) that minimally modifies the responses of the nanorod and substrate. The dipolar field profile of the tip immediately emerges from the dipole model.

The target nanorod is given a Lorentz-model dielectric function $\varepsilon_2(\omega) = 1 + \omega_{p2}^2/(\omega_2^2 - \omega^2 - i\omega\gamma_2)$ which provides \mathbf{p}_2 a singly-peaked resonant spectrum. Although the experiment uses a Au nanorod that is better modeled with a Drude dielectric function, we choose a Lorentz-model to easily tune the nanorod’s resonance frequency Ω_2 and mimic the hitherto ignored red-shift brought on by radiation damping [57]. Explicitly, $\Omega_2 = \sqrt{\omega_2^2 + \omega_{p2}^2 A_{10}(X_2)/[A_{10}(X_2) - B_{10}(X_2)]}$ such that ω_2 can be altered to tune the nanorod’s resonance; a Drude model with $\omega_2 \rightarrow 0$ is not flexible enough to recreate the magnitude of the radiation-induced shifts. Further, adjustments to the oscillator strength ω_{p2}^2 and damping rate γ_2 allow us to account for the related resonance suppression and linewidth modifications that appear in a fully-retarded treatment [24]. Each of the parameters of $\varepsilon_2(\omega)$ was fit to the experimental data and corroborated with gold nanorod data collected from Refs. [24, 58].

The substrate’s dielectric is simplified, in both Fig. 5 b and d, to a Lorentz dielectric with a single phonon mode at the LO phonon frequency ω_3 with oscillator strength ω_{p3}^2 , damping rate γ_3 , and static contribution $\varepsilon_{\infty 3}$ such that $\varepsilon_3(\omega) = \varepsilon_{\infty 3} + \omega_{p3}^2/(\omega_3^2 - \omega^2 - i\omega\gamma_3)$. This simplification allows for a clear depiction of mixing between the dipole’s resonance at Ω_2 and the substrate’s lone SPhP at $\Omega_3 = \sqrt{\omega_3^2 + \omega_{p3}^2/(\varepsilon_{\infty 3} + 1)}$ at the expense of neglecting the width of the Reststrahlen band of either substrate, within which many SPhPs exist and clear identification of individual hybrid modes is very difficult [30, 57, 59, 60].

The only significant error brought on by this approximation appears near the extremes of the nanorod series, where one pair of hybrid mode energies asymptotes to the edges of the Reststrahlen band in the experiment (Fig. 4) and to Ω_3 in the theoretical reproduction. Because the Reststrahlen band of either substrate is narrower than the linewidth of the nanorod’s dipolar mode and largely obscured by a strong peak in each collected spectrum, the vast majority of the observable features in the experimental signal lie outside this region and are well-modeled by the single-phonon approximation.

In particular, with an hBN substrate (Fig. 5c,d) the single-phonon approximation reproduces the spectral shifts and avoided crossing of the two peaks observed clearly in the experimental data on either side of the SPhP energy. It also reveals that the observed peaks reach a minimum separation at $|\Omega_2^2 - \Omega_3^2| = 0$, as expected from hybridization theory, and that the dipole’s linewidth is reduced due to its mixing with the narrower SPhP.

2. Oscillator Model of the Nanorod and Substrate Resonances

In the case of the SiO₂ substrate this behavior is not so clear. The ever-present feature at the SPhP energy, caused by coupling between $\mathbf{p}_1^l(\omega)$ and the SPhP, is altered at many values of Ω_2 . This is contrary to the behavior of hBN and produces asymmetries in the line shapes of the hybridized modes. While the effective polarizability model reproduces this behavior and reveals its cause to be the relatively weak phonon oscillator strength of SiO₂, it alone cannot help us to extract the resonance positions of the two hybrid modes from the atypical spectrum with significantly greater certainty than the approximations used to generate Fig. 4 already provide. Instead, the hybridized modes can be extracted with the aid of an oscillator model of the system because it provides analytical expressions for the hybrid resonance frequencies Ω_{\pm} via standard mode-mixing techniques. We begin with the definition of a coordinate $x(\omega) = \mathbf{p}_2(\omega) \cdot \hat{\mathbf{x}}/e$, which represents the complex magnitude of $\mathbf{p}_2(\omega)$ and is

$$x(\omega) = \frac{F(\omega)}{m_2} \frac{1}{\Omega_2^2 - \omega^2 - i\omega\gamma_2}. \quad (4)$$

Here, $F(\omega) = e\mathcal{E}_{2x}(\mathbf{0}, \omega)$ is the external force acting on the oscillator (assumed to be located at the origin, $\mathbf{r} = \mathbf{0}$) and $m_2 = 3e^2(A_{10} - B_{10})/c_2^3\omega_{p2}^2$ is the oscillator's mass.

While the connection between $\mathbf{p}_2(\omega)$ and $x(\omega)$ is straightforward, the connection between the substrate's SPhP and an oscillator coordinate is not. Leaving the details for the SM, the substrate's scattered field at the origin can be defined as

$$\mathbf{E}_3(\mathbf{0}, \omega) = -\frac{e}{\sqrt{8L^3b_2^3}}([Q_{01}(\omega) + Y_{01}(\omega)]\hat{\mathbf{x}} + [Q_{00}(\omega) + Y_{00}(\omega)]\hat{\mathbf{z}}). \quad (5)$$

Here, the coordinates $Q_{pm}(\omega)$ represent independent SPhPs with azimuthal node structure $m = \{0, 1, \dots\}$ and reflection parity about the x -axis (p even or odd). Their resonant behavior is similar to that of $x(\omega)$, with

$$Q_{pm}(\omega) = \frac{\mathcal{F}_{pm}(\omega)}{M_m} \frac{1}{\Omega_3^2 - \omega^2 - i\omega\gamma_3}, \quad (6)$$

wherein $M_m = (2 - \delta_{m0})e^2(\varepsilon_{\infty 3} + 1)^2/\omega_{p3}^2d^3$ are the mode masses. Due to the substrate's infinite extent, a characteristic length factor, d , is used, akin to the quantization lengths often used in quantum optical theories. As is true in box quantization, the observables of the system are independent of d , and it serves only to provide sensible units and an overall scale to the oscillator picture.

From the forms of Eqs. (5) and (6), it is clear why both dipoles of the tip can couple to an SPhP resonance at Ω_3 in the substrate without indirectly coupling to each other. Because the SPhP responses $1/(\Omega_3^2 - \omega^2 - i\omega\gamma_3)$ are the same for all (p, m) and the tip-substrate couplings are $-\mathbf{p}_1^l(\omega) \cdot \mathbf{E}_{3z}(\mathbf{0}, \omega) \propto x(\omega)Q_{00}(\omega)$ and $-\mathbf{p}_1^s(\omega) \cdot \mathbf{E}_{3x}(\mathbf{0}, \omega) \propto x(\omega)Q_{01}(\omega)$, the dipoles interact with independent SPhP modes $Q_{pm}(\omega)$ of different symmetry but identical spectral behavior.

The coordinates $Y_{pm}(\omega)$ describe the excitation of independent substrate modes that respond instantaneously to stimuli and do not oscillate. From their definition $Y_{pm}(\omega) = L^3\beta_{\infty}\mathcal{F}_{pm}(\omega)/(2 - \delta_{m0})e^2$, one can see that as $\varepsilon_{\infty 3} \rightarrow 1$ the factor $\beta_{\infty} = (\varepsilon_{\infty 3} - 1)/(\varepsilon_{\infty 3} + 1) \rightarrow 0$. Thus, the static coordinates do not contribute to the scattered field unless $\varepsilon_{\infty 3} > 1$.

The functional forms of the forces $\mathcal{F}_{pm}(\omega)$ on the SPhPs are complicated. Derivations of the forces are left for the SM, where their dependence upon the charge distribution of the nanorod and the nanorod coordinate are made

303 explicit. Further, since the force $F(\omega)$ acting on the nanorod dipole contains a term $e\mathbf{E}_3(\mathbf{0}, \omega) \cdot \hat{\mathbf{x}}$, we note that
 304 $F(\omega) \propto Q_{01}(\omega)$. In this way, the forces on either oscillator mediate their coupling, and the forces' explicit forms lead
 305 to the coupled equations of motion

$$\begin{aligned} x(\omega) (\bar{\Omega}_2^2 - \omega^2 - i\omega\gamma_2) - \frac{g}{m_2} Q_{01}(\omega) &= \frac{F_0(\omega)}{m_2}, \\ Q_{01}(\omega) (\Omega_3^2 - \omega^2 - i\omega\gamma_3) - \frac{g}{m_3} x(\omega) &= 0. \end{aligned} \quad (7)$$

307 Here, $m_3 = M_1$ is the mass of the lone SPhP mode $Q_{01}(\omega)$ that can couple to the target nanorod's resonance
 308 and $F_0(\omega) = eE_{0x}(\omega)$ is the force applied on the nanorod by the synchrotron light. The lowered frequency $\bar{\Omega}_2 =$
 309 $\sqrt{\Omega_2^2 - \beta_\infty e^2 / 8b_2^3 m_2}$ encapsulates the contribution of $Y_{01}(\omega)$ on the nanorod's spectrum: the substrate's static re-
 310 sponse induces a redshift on the nanorod's dipole that is small for $\varepsilon_{\infty 3} \sim 1$ and large as $\varepsilon_{\infty 3} \gg 1$. The static
 311 coordinates are thus not explicitly represented in Eq. (7).

312 It is convenient to decouple the equations of motion using standard techniques that produce normal modes x_\pm and
 313 normal mode frequencies $\Omega_\pm^2 = \bar{\Omega}_2^2 S_\pm^2(\theta) + \Omega_3^2 S_\mp^2(\theta) \pm g \sin(2\theta) / \sqrt{m_2 m_3}$, where $S_+(\theta) = \cos \theta$, $S_-(\theta) = \sin \theta$, and
 314 $\theta = (1/2) \tan^{-1}(2g / \sqrt{m_2 m_3} [\bar{\Omega}_2^2 - \Omega_3^2])$ is the mixing angle that determines the degree of hybridization between $x(\omega)$
 315 and $Q_{01}(\omega)$. Here $g = -e^2 / \sqrt{8d^3 b_2^3}$ is a constant coupling strength that, along with the masses m_2 and m_3 , sets the
 316 scale of mixing in the system, while the variable detuning $\bar{\Omega}_2^2 - \Omega_3^2$ between the modes' natural frequencies allows the
 317 system to transition through the point of maximal mixing where θ flips from $\pi/4$ to $-\pi/4$.

318 To visualize this transition, normal mode frequencies are superimposed on the spectra of Fig. 5 as the wavenumbers
 319 $\nu_\pm = \Omega_\pm / 2\pi c$ with $d = 1$ cm and $|g| = 2.0 \times 10^{-13}$ g/s². They demonstrate that the observable peaks of $|A_2(\omega)|$ are
 320 indeed located near the normal modes of the system even when the peaks have strange lineshapes. Additionally, in
 321 cases where one peak is difficult to discern, the hybridization model shows that one of the normal mode wavenumbers
 322 ν_\pm has approached $\nu_3 = \Omega_3 / hc$ such that the resonant lineshape of the associated mode $x_\pm(\omega)$ has become buried by
 323 the parasitic signal from the substrate mode $Q_{00}(\omega)$ that couples directly with the tip.

324 Finally, we note that strong coupling has been achieved in the experimental systems with both SiO₂ and hBN
 325 substrates. This can be observed directly from the marked separation between the coupled resonances of the hBN
 326 substrate and can be inferred from an analysis of the difference of the squared hybrid frequencies at maximal mixing,
 327 $\Omega_+^2(\pi/4) - \Omega_-^2(\pi/4) = 2g / \sqrt{m_2 m_3}$. With the uncoupled SPhP masses $m_3 = 1.194 \times 10^{-46}$ g and 3.219×10^{-47} g in the
 328 SiO₂ and hBN substrates, respectively, and the nanorod's dipole mode mass $m_2 = 2.686 \times 10^{-36}$ g, the characteristic
 329 splitting constant $\sqrt{2|g| / \sqrt{m_2 m_3}} / 2\pi c$ is equal to 793 cm⁻¹ (SiO₂) and 1100 cm⁻¹ (hBN), at least a factor of three
 330 larger than the linewidths $\gamma_3 / 2\pi c = 64.1$ cm⁻¹ (SiO₂), 92.6 cm⁻¹ (hBN), and $\gamma_2 / 2\pi c = 256$ cm⁻¹ of the system.

331 Using a more traditional metric, one can see from the theoretical model that the hybridized resonances of both
 332 the SiO₂ and hBN systems are always split by at least the average of the uncoupled mode linewidths, such that
 333 $R(\theta) = 2|\Omega_+(\theta) - \Omega_-(\theta)| / (\gamma_2 + \gamma_3) > 1$ is satisfied for all mixing angles [71–73]. At maximal mixing ($\theta = \pi/4$), R is
 334 minimized and equal to 1.71 and 2.51, respectively. Additionally, with $\bar{\Omega}_2 = \Omega_3 = \Omega_0$ at maximal mixing, the splitting
 335 can be simplified via a power series to $\Omega_+(\pi/4) - \Omega_-(\pi/4) \approx g / \Omega_0 \sqrt{m_2 m_3} = \sigma$, with σ the form of the coupling
 336 strength that appears in quantum-optical treatments of interacting cavities [74–76]. This simplification produces
 337 strong coupling ratios $R(\pi/4) \approx 2|\sigma| / (\gamma_2 + \gamma_3) = 1.71$ (SiO₂) and 2.48 (hBN), as well as values of 0.24 (SiO₂) and
 338 0.31 (hBN) for the ultrastrong coupling condition $|\sigma| / \Omega_0$.

339 Experimental approximations of the strong and ultrastrong coupling conditions can also be recovered directly from

340 the SINS data. However, as both substrates possess more than one SPhP that couples to the F-P mode of the rod
 341 and none of the SPhP linewidths can be directly extracted from the signal, the coupling ratio R must be replaced
 342 by a similar ratio R' that contains only measurable quantities and accounts for the width of the Reststrahlen band.
 343 The most convenient form of the new ratio is $R'(\theta) = 2[|\Omega'_+(\theta) - \Omega'_-(\theta)| - \Delta]/[\gamma'_+(\theta) + \gamma'_-(\theta)]$, where Ω'_\pm are the
 344 measured hybrid frequencies, γ'_\pm are the measured linewidths of the hybrid modes, and Δ is the Reststrahlen band
 345 width as reported in Fig. 4. At maximal mixing, $R'(\pi/4) = 1.35$ (SiO₂) and 2.10 (hBN), in good agreement with the
 346 theory. Finally, approximating the shared natural frequency of the SPhP and F-P mode at maximal mixing, Ω'_0 , to
 347 lie at the center of the Reststrahlen band, the ultrastrong coupling condition $|\sigma'|/\Omega'_0 \approx (\gamma_+ + \gamma_-)R'(\pi/4)/2\Omega'_0$ takes
 348 a value of 0.17 for either substrate material.

349 III. CONCLUSION

350 In conclusion, we report the observation of strong coupling between the $m = 1$ and 2 F-P modes of $L = 0.7 - 10.0 \mu\text{m}$
 351 long gold nanorods and the SPhP modes of a polar crystal (SiO₂) and a Van der Waals (hBN) substrate using SINS.
 352 The hybridization of the nanorod resonances with the substrate is made clear by the experiment, which leverages the
 353 unique IR sensitivity and spatial selectivity of SINS to characterize the anticrossing behavior of the hybrid F-P-SPhP
 354 mode pairs as the F-P modes are tuned in and out of resonance with the SPhPs. The coupling of the $m = 1$ mode
 355 is confirmed by a reduced-order model that describes in detail the individual interactions of the nanorod, substrate,
 356 and AFM tip to produce both a reconstruction of the SINS observable and a mechanical analogy that interprets the
 357 spectral features therein. Importantly, the theoretical model accounts for the interference of the substrate in the SINS
 358 signal and allows for the clear interpretation of SINS spectra that lack the clearly defined resonances observed in
 359 more familiar optical and electron-beam spectroscopies. This combined experimental and theoretical investigation of
 360 interacting IR resonances in a tunable nanoscopic system provides a blueprint for the design and fabrication of more
 361 tailored IR nanophotonic systems for use in future molecular sensing, cavity-controlled chemistry, and optical circuit
 362 applications.

363 IV. MATERIALS AND METHODS

364 **Apparatus.** The SINS setup consists of a synchrotron light source, KBr beamsplitter, rapid-scan FTIR system,
 365 atomic force microscope (AFM), and a mercury cadmium telluride (MCT) detector. The beamsplitter forms an
 366 asymmetric Michelson type interferometer with the rapid-scan FTIR as one arm and the AFM tip/sample as the
 367 other [46]. Light from the synchrotron, $3 - 13 \mu\text{m}$ wavelengths ($3333 - 769 \text{ cm}^{-1}$), is focused onto the sample and
 368 platinum silicide AFM tip with a gold, 0.4 NA, parabolic mirror. Over multiple visits to the ALS we find that
 369 replicate samples yield quantitatively similar results indicating good reproducibility in the sample preparation and
 370 AFM tip conditions (see SM Fig S5). The MCT detector records the recombined signal which is demodulated by a
 371 lock-in amplifier at the second harmonic. These interferograms are Fourier Transformed, turning them into broadband
 372 spectral responses. The entirety of these experiments were collected with a spectral resolution of 32 cm^{-1} . A single
 373 point spectrum, which is actually an average of 256 individual scans, takes 90 seconds to acquire at this resolution.
 374 Since the setup is operating in the near to mid IR, the entire system is purged with N₂ to minimize atmospheric H₂O

375 and CO₂ signatures.

376 **Sample Fabrication.** The Au nanorod lengths are designed to be 0.5 – 4.0 (0.1 μm increments) and 1 – 10 (1 μm
 377 increments) μm with a constant height of 30 nm, a width of 100 nm, and a 50 nm radius of curvature at their ends.
 378 We expect these to exhibit both $m = 1$ and $m = 2$ F-P mode resonances in the SINS energy range of 700 – 5000
 379 cm^{-1} [24]. Au nanorods were patterned using electron beam lithography on: 1) a 100 nm thermal SiO₂ film on a
 380 double side polished silicon wafer and 2) a 330 nm thick exfoliated flake of hexagonal boron nitride (hBN) on a double
 381 side polished silicon wafer. Additionally, a 10 $\mu\text{m} \times 10 \mu\text{m} \times 30$ nm Au structure was patterned, which provides
 382 a reference for the phase and magnitude information and serves to optimize the SINS MCT detector signal. The
 383 substrate is cut to approximately 10 mm x 10 mm and mounted on a customized AFM sample holder with super glue.

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