

# Extending the Reach of Phonon Polaritons to New Material Interactions

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## **EXECUTIVE SUMMARY**

This program demonstrated new types of materials and interactions for phonon polaritons. Under the right conditions, polar dielectric materials can have reststrahlen bands that support phonon polaritons, which we have investigated in prior NRL programs using semiconductor materials including silicon carbide, gallium nitride and boron nitride. Our key insight was that the requisite conditions regarding optical properties can also be satisfied by a wider range of materials, including inorganic and molecular crystals such as calcite. This opens new opportunities for expanding phonon polariton phenomena to more materials and an expanded spectral range. In this program, we demonstrated phonon polaritons in nanopillar arrays of calcite and expanded active tuning of phonon polaritons to new materials.

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# Extending the Reach of Phonon Polaritons to New Materials and Reaction Dynamics

## INTRODUCTION

Polar dielectric materials have reststrahlen bands, frequency ranges between the transverse and longitudinal optical (TO and LO) phonon bands in the mid infrared, where they behave optically like metals but with reduced optical loss. In this spectral region, they exhibit high reflectivity and support optical surface phonon-polariton (SPhPs) resonances, analogous to plasmon resonances in metals but with much narrower bands because they depend on vibrations. Researchers at NRL have led the field in mapping out the basic physics for high quality (Q) factor, narrow SPhP resonances and demonstrating their advantages for nanophotonic applications.[1-3] This includes demonstrating the ability to tune the resonances via the longitudinal optical plasmon coupling effect (LOPC) for both bulk reststrahlen band materials[4] and nanopillar arrays[5] of SiC. Nevertheless, at the beginning of this program, there had been almost no reports of exploiting SPhPs for chemical applications. The roadblock to such applications was (and remains) primarily the limited spectral coverage of semiconductor materials compared to the infrared spectrum of typical molecular targets of interest. In this program, our goal was to demonstrate new chemically relevant capabilities for these materials and phenomena by exploiting vibrational resonances in a wider range of materials and to show novel adsorbate surface effects that provide opportunities to understand and control surface processes and reactions.

SPhPs lead to sub-diffraction light confinement and enhanced matter light interactions like their surface plasmon counterparts, but with much higher quality factors (lower losses and narrower linewidths) because phonons have weaker interactions and longer lifetimes than electrons. SPhP band properties such as center frequency and width follow the same design rules and formalism as surface plasmon resonance bands;[6] they require a negative real part of the permittivity and depend on nanoparticle size and especially shape. However, their frequencies are limited to the reststrahlen band. Most of the work to date on SPhPs has been on polar dielectrics such as SiC, hexagonal boron nitride, and GaN with recent studies extending to MoO<sub>3</sub> and V<sub>2</sub>O<sub>5</sub>. [3,7-17] Our approach was to explore other types of materials using insulators and molecular crystals to extend reststrahlen effects and SPhPs to other spectral regions. Reststrahlen bands have been observed in many molecular crystals (e.g. calcite, CaCO<sub>3</sub>, ~1400 cm<sup>-1</sup>) but had not been exploited for generating phonon polaritons and enhanced surface optical or adsorbate interactions. One of the main goals of this program, demonstrating phonon polaritons in new materials, was achieved by observing phonon polaritons in nanostructures of calcite. In addition, several studies expanded on the ability to actively tune reststrahlen bands and phonon polaritons which are pertinent to developing new types of material-optical interactions and further extending the spectral coverage of SPhPs.

## PROGRESS AND RESULTS

Progress in the program includes a combination of theory, fabrication and experimental measurements to identify reststrahlen bands (RBs) and SPhP resonances in new materials. The accomplishments include growing or purchasing salt crystals and measuring infrared reflection spectra of them to determine if they have strong RBs that would support high quality (Q) SPhPs. Focused ion beam (FIB) fabrication was used to produce calcite nanopillar and nanohole arrays. The phonon resonances were measured for nanopillar arrays with different aspect ratios, the band properties were determined by fitting to yield center frequencies and linewidths and experimental



results were interpreted with the assistance of numerical simulations including field profiles of the modes.[18] Several time-resolved studies were performed to expand on our NRL-patented active tuning of phonon polaritons.[19] We had initially demonstrated tuning via the longitudinal optical plasmon coupling (LOPC) effect with nanosecond UV pump – IR probe studies on bulk SiC[4] as well as ultrafast measurements for SiC nanopillar array SPhPs.[5] That work also included the steady-state measurement of tuning of InP SPhPs at longer wavelengths. Published studies in this program include measuring the carrier dynamics of hexagonal boron nitride (hBN),[20] active tuning of the Berreman mode of GaN[21] and investigations of the effect of wavelength and penetration depth for active tuning of bulk RBs for GaN and SiC.[22] Other studies in progress include optical pumping of SiC gratings and GaN/AlN superlattices.

We identified ionic salts composed of molecular ions with strong absorption bands that are promising candidates for SPhP materials and grew crystals large enough for IR reflection and ellipsometry. Some materials were expected to have broad RBs based on previous reports in the literature (chlorate, nitrate, oxalate) while others were found to yield disappointingly narrow RBs, including sodium or potassium ferrocyanide ( $K_4Fe(CN)_6$ ), sodium nitroprusside ( $Na_2Fe(CN)_5NO$ ), ammonium thiocyanate ( $NH_4NCS$ ) and nickel sulfate ( $NaSO_4$ ). In addition, molecular crystals of tungsten hexacarbonyl ( $W(CO)_6$ ) were produced by recrystallization from organic solution. IR reflection measurements revealed a wide and structured RB in the region  $1920$ - $2040\text{ cm}^{-1}$  (as shown in Fig. 1). Spectra in Fig 1. show RBs for  $W(CO)_6$ ,  $KNO_3$ ,  $NaClO_3$  and a pressed pellet of  $NaNO_2$  power.

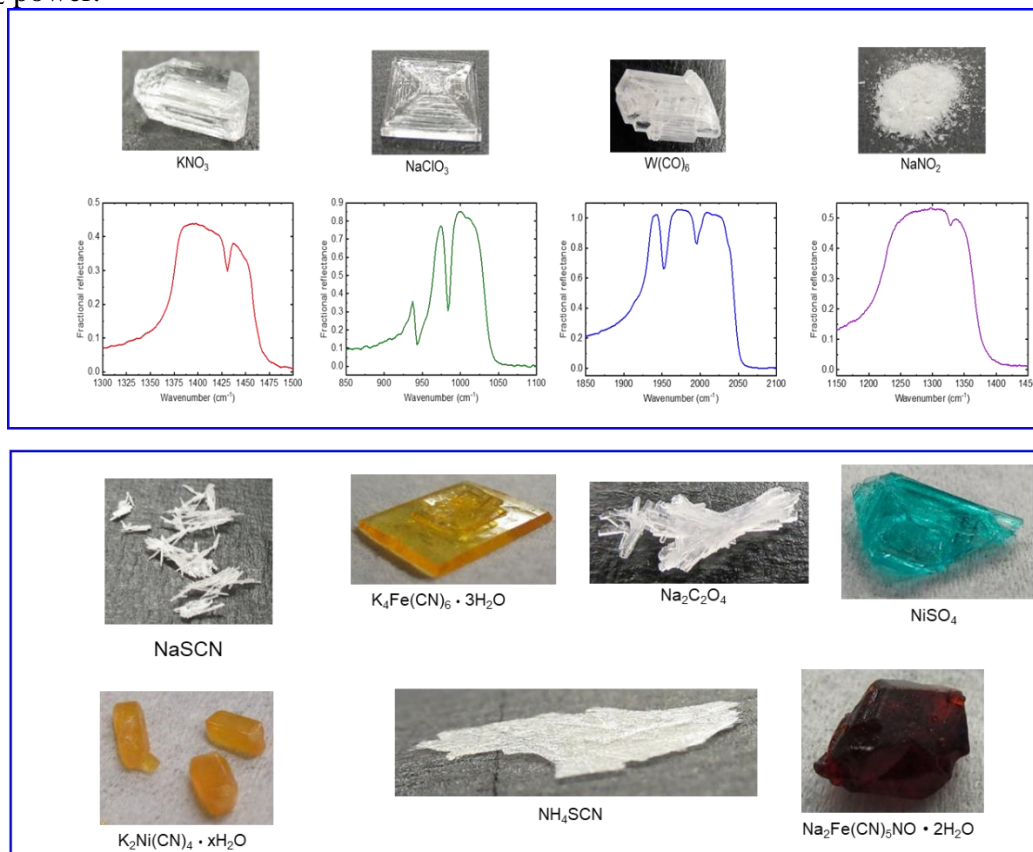


Fig. 1 — Images and measured IR reflectance spectra of materials exhibiting strong reststrahlen bands (top) and several crystals grown that exhibited weak or narrow reflection bands (bottom).

Hexagonal boron nitride (hBN) is a wide, indirect bandgap, 2D semiconductor that holds great promise for optoelectronic devices in the ultraviolet and mid-infrared spectral regimes. Studies at NRL and elsewhere have demonstrated that hBN is an intriguing SPhP material not only because it supports SPhPs at higher frequencies (up to  $1600\text{ cm}^{-1}$ ) than SiC (which is limited to frequencies lower than  $1000\text{ cm}^{-1}$ ) but also because it has the interesting and potentially advantageous property of being hyperbolic in the infrared.[23] This means it is highly optically anisotropic to such an extent that it is highly reflective and supports SPhP in two directions (along two optical axes) while being a simple dielectric in the third direction. This property affords an opportunity for novel nanophotonic applications such as hyperlensing and monolithic spectrally resolved devices. We performed visible pump – infrared probe studies to characterize the carrier dynamics of hBN which provides a basis for extending the concept of actively tuned SPhPs to this material.[20] Ultrafast transient transmission spectroscopy was used to characterize the carrier dynamics, which were found to be biexponential. At early delay times, the decay rate depends on pump fluence and was analyzed in terms of a bimolecular recombination mechanism. These results offer insight into the radiative recombination processes for deep ultraviolet optoelectronic devices and towards realizing active control of mid-IR nanophotonic responses.

We demonstrated active tuning of Berreman modes in thin films of GaN on a reflective silicon carbide substrate.[21] The Berreman effect in thin films of GaN gives rise to a strong, narrow resonance at  $737\text{ cm}^{-1}$ , occurring near the longitudinal optic (LO) phonon of the material. Taking advantage of the strong dependence on the LO phonon upon the free carrier density, we used the LOPC effect to actively tune this Berreman mode. Using time-resolved infrared reflectance spectroscopy while exciting free carriers in a thin film of GaN, we observed substantial shifts of the Berreman mode that are straightforward to analyze compared to other methods for evaluating LOPC-based polariton tuning. We demonstrated resonance shifts ( $\Delta\omega$ ) greater than the resonance width ( $\delta\omega$ ), realizing a respectable state-of-the-art tuning figure of merit  $\Delta\omega/\delta\omega \sim 0.7$ , and showed that the shift can be modulated on a sub-nanosecond timescale. These results illustrate the substantial promise for future photonic devices and for novel experimental designs for understanding SPhP-free-carrier interactions. One of the benefits of using Berreman modes is that they provide a way to create narrow phonon bands without having to fabricate nanostructures, which should facilitate planned demonstrations of surface enhanced infrared absorption of molecular species on these materials.

At the inception of the program we recognized calcite as a promising SPhP material because it has a strong reststrahlen band, indicated by the relatively large splitting between the LO and TO bands, and favorable infrared optical constants in the  $1400\text{-}1550\text{ cm}^{-1}$  region of the mid-infrared.[24] It has also been recognized that calcite is hyperbolic like hBN.[24-26] Reflection spectra on different surfaces (commercially available cuts along 100 and 001 orientations) yield near total reflection in one case (001 as shown in Fig. 2) but only  $\sim 50\%$  in the other. We used focused ion beam (FIB) fabrication in commercially available calcite to produce several nanopillar arrays and observed SPhP resonances by IR reflection spectroscopy.[18] Initial fabrication attempts used a helium ion microscope but better results were obtained with the FIB combined with post processing etching. These are the first experimental observations of hyperbolic phonon polariton (HP) resonances in calcite nanopillars. We found that the HP modes redshift with increasing aspect ratio (AR= 0.5 to 1.1) and observed a new, possibly higher order mode as the pitch is reduced. The experimental results were interpreted with the assistance of both numerical simulations and an analytical model in which modes were assigned similar to those in studies of hBN nanocones.[23]. This is very exciting because it accomplishes one of the main objectives of

the program, to demonstrate SPhP in a new class of material. This work shows that a wide variety of polar dielectric materials can support phonon polaritons by demonstrating HPs in a new material, which is an important first step towards creating a library of materials with the appropriate phonon properties to extend phonon polariton applications throughout the infrared. This initial success was achieved with structures produced by FIB, but other methods, especially those that might scale up more readily, are currently being pursued including approaches to thin film growth, nanosphere lithography and solution nanoparticle fabrication.

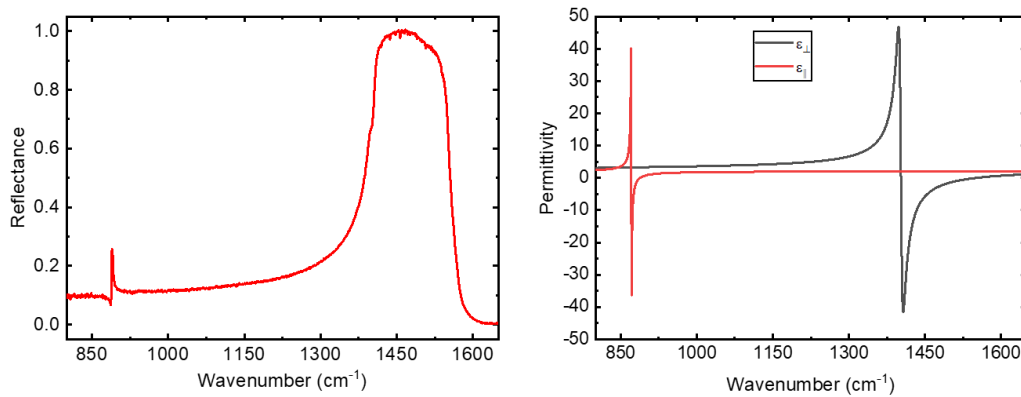


Fig. 2 — Calcite reflection spectra and optical constants.

The studies on nanopillars arrays were followed by analogous studies of nanohole arrays. Hyperbolic phonon polariton (HP) modes were observed in nanohole arrays fabricated in calcite.[27] We have also developed a qualitative understanding of the nature of the HP modes in nanohole arrays, in which the modes are most likely confined to the constrictions between adjacent holes. In such a model, changing the pitch and/or the diameter of the holes changes the dimensions of the constrictions and result in changing the HP resonance frequency in a predictable way. For example, for a fixed hole diameter and depth, decreasing the pitch between holes results in a slight shift of the HP mode to higher frequencies as shown in the measured spectra in Fig. 3 for holes that are 500  $\mu\text{m}$  diameter, 2  $\mu\text{m}$  deep for a range of pitches. In addition, if the distance between holes is small enough then multiple HP modes are observed, which is easier to see in the simulation as shown in Fig. 4. The ability to theoretically describe HPs in calcite is a first step towards understanding the nature of these modes in a variety of materials in order to expand the range of phonon polariton materials available for mid-IR nanophotonic applications.

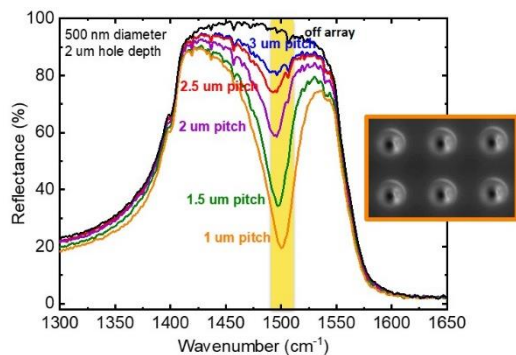


Figure 3 — IR reflectance spectra of several nanohole arrays in calcite. Hole diameter and depth are fixed at 500 nm and 2  $\mu\text{m}$ , respectively, for each array, and the pitch varies from 1–3  $\mu\text{m}$ .

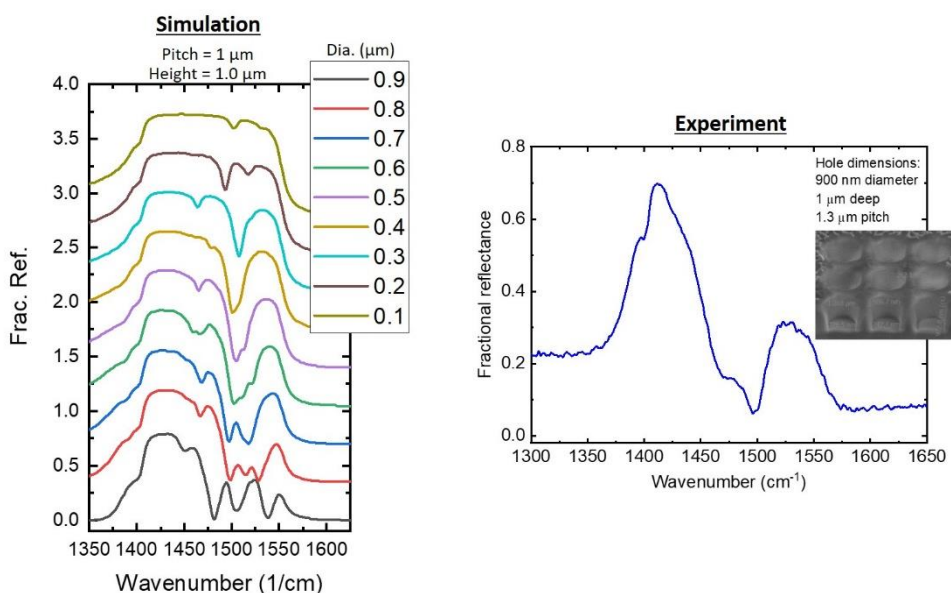


Figure 4 — Simulated and experimental IR reflection spectra of calcite nanohole arrays in which multiple HP resonances are observed when decreasing the distance between holes by increasing the hole diameter.

Regarding progress in theoretical efforts, density functional theory (DFT) methods were used to calculate the phonon spectrum of calcite and achieve excellent reproduction of the experimental reflection spectra as well as simulation of the orientation dependence of optical properties responsible for its hyperbolic nature.[28] The vibrational motions appear to involve little or no movement of the metal (Ca) atoms suggesting that other carbonates should have similar phonon properties and reflection spectra. The results also include simulations of nanopillar SPhPs which show good agreement with experimental studies published elsewhere.

Another series of first principles calculations were carried out using Quantum Espresso to calculate LO/TO phonon splittings for several materials. The calculations were successful for beryllium oxide (BeO), different polymorphs of  $\text{CaCO}_3$  (i.e., calcite, aragonite and vaterite), as well as  $\text{MgCO}_3$ , but did not provide good predictions for sodium chlorate ( $\text{NaClO}_3$ , for which we observed an RB in the region 980–1020  $\text{cm}^{-1}$ ),  $\text{NaNO}_2$  (which we observed as described below), or sodium oxalate ( $\text{NaC}_2\text{O}_4$ ).

As noted above, we now have several studies on free carrier photoinjection into polar semiconductors which can drastically modify the IR optical properties of the material via coupling of the longitudinal optical (LO) phonon to the free carrier plasma. Both the ability to modulate SPhPs, i.e., the shift or modulation depth, as well as its relaxation dynamics, depend on the carrier distribution, such that one of the primary loss mechanisms is diffusion of the carriers out of the pillars into the bulk substrate. We measured transients in the reststrahlen band region of bulk 4H-SiC and GaN for multiple excitation wavelengths and demonstrated how the IR response depends on the pump wavelength and resulting penetration depth of the excitation.[22]

Other active tuning studies included measuring transient UV (266 nm) pump – IR reflection probe for SiC gratings with different heights (0.5–1.2  $\mu\text{m}$ ), various widths (0.6–2  $\mu\text{m}$ ) and pitches (2–4.4  $\mu\text{m}$ ), which exhibit resonances in the 900–960  $\text{cm}^{-1}$  region, as shown in Fig. 5. These structures could provide an opportunity to gain insight into the diffusion processes that influence the modulation depth and lifetime for actively tuned SPhP resonances in SiC. Transient spectra of the absorbance changes following 266 nm excitation, reconstructed spectra for the pump (R) and unpumped ( $R_0$ ) reflection and a decay (at 947  $\text{cm}^{-1}$ ) are shown in Fig. 6 for a 1  $\mu\text{m}$  high, 1.4  $\mu\text{m}$  wide, 4.4  $\mu\text{m}$  pitch grating. The pumped resonance is blue shifted about 5  $\text{cm}^{-1}$  compared to the unpumped case. We were unable to identify any clear dependence of the decay time on the grating height, which might have indicated carrier lifetimes that are limited by diffusion.

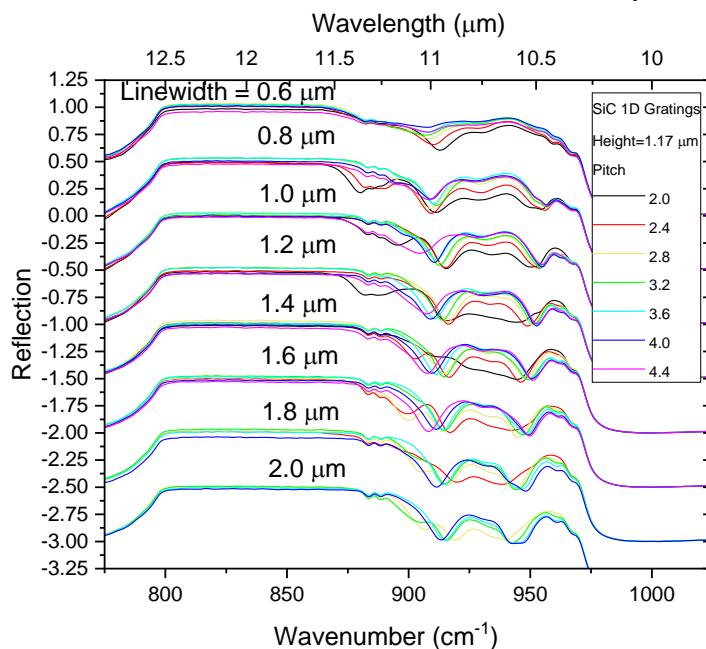


Fig. 5 — Steady-state reflection spectra of SiC gratings with various dimensions.

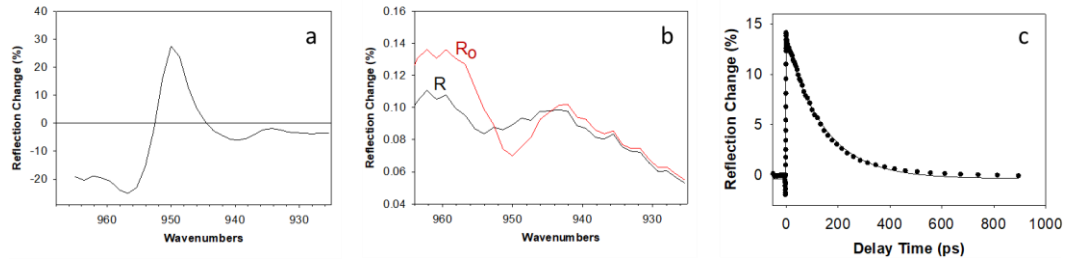


Fig. 6 — Transient a) reflection changes, b) pump and unpumped reflection spectra at 5 ps, and c) transient decay for UV pump / IR probe of SiC grating

Other photomodulation studies included measuring the UV pump, IR transient response for superlattices of GaN/AlN with  $\sim 1$  nm layers, a type of phonon hybrid.[2] The goal was to observe tuning of AlN LO from pumping the free carriers in GaN in what might be called heterogeneous LOPC tuning. The steady-state spectra were previously measured and analyzed by Ratchford et al.[29] Although we observed strong transient signals, including a response we attribute to perturbed free induction decay, there is little evidence of AlN LO tuning from pumping the carriers in GaN.

We have measured reflection spectra for pressed pellets of sodium nitrite ( $\text{NaNO}_2$ ) which show a high reflectivity reststrahlen band between  $1225$  and  $1365$   $\text{cm}^{-1}$ , making this a promising material for SPhPs (Fig. 1). In addition, the inherent damping of the material impacts the optical properties and influences how high of a quality factor (Q factor) might be achieved for an SPhP resonance. The intrinsic vibrational relaxation is one contribution to the damping, and we have measured steady-state IR spectra and IR pump – IR probe transients to determine spectral shifts and vibrational relaxation dynamics for the nitrite anion near  $1250$   $\text{cm}^{-1}$  in several solvents.[30] The IR band is very broad ( $\sim 75$   $\text{cm}^{-1}$  in  $\text{H}_2\text{O}$ ) and the relaxation times are very short (0.9, 0.5 and 2.1 ps in  $\text{H}_2\text{O}$ ,  $\text{D}_2\text{O}$  and dimethyl sulfoxide, respectively). From the perspective of anion solvation, it is atypical that the relaxation is faster in  $\text{D}_2\text{O}$  than  $\text{H}_2\text{O}$ , which could be due to  $\text{D}_2\text{O}$  solvent bands in the region, and it is probably the fastest relaxation observed for an anion in DMSO. The rapid relaxation suggests that the damping is also probably strong in the crystal and SPhPs from this material would probably have low Q factors.

Despite an early example (which has not been reproduced),[31] there have been very few reports of SEIRA with SPhPs. In one reported attempt, the interactions of molecular absorptions on SPhPs resulted in strong coupling, probably due to the similar widths of the molecular and SPhP bands.[32] We made several attempts to measure SIEIRA and evidence of the metal surface selection rule. In the metal surface selection rule,[33] vibrations with transition moments oriented parallel to the surface are weaker while those perpendicular are enhanced because of image charge effects. We investigated poly methyl methacrylate and terephthalic acid films ( $<100$  nm) on calcite nanopillar arrays and on unstructured surfaces of various materials with and without metallic-like reststrahlen bands in order to observe SEIRA or evidence of the metal surface selection rule effects without success.

## CONCLUSIONS

In this program, “Extending the Reach of Phonon Polaritons to New Materials and Reaction Dynamics” we attempted to build on the success of demonstrating SPhPs in semiconductor polar dielectrics to a broader range of materials and spectral ranges. We were able to demonstrate phonon polaritons in nanopillar arrays in calcite and more recently have been able to complement it with observing resonances in nanohole arrays. In addition we carried out several studies on active tuning of phonon polaritons, including in the Berreman mode of GaN.

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