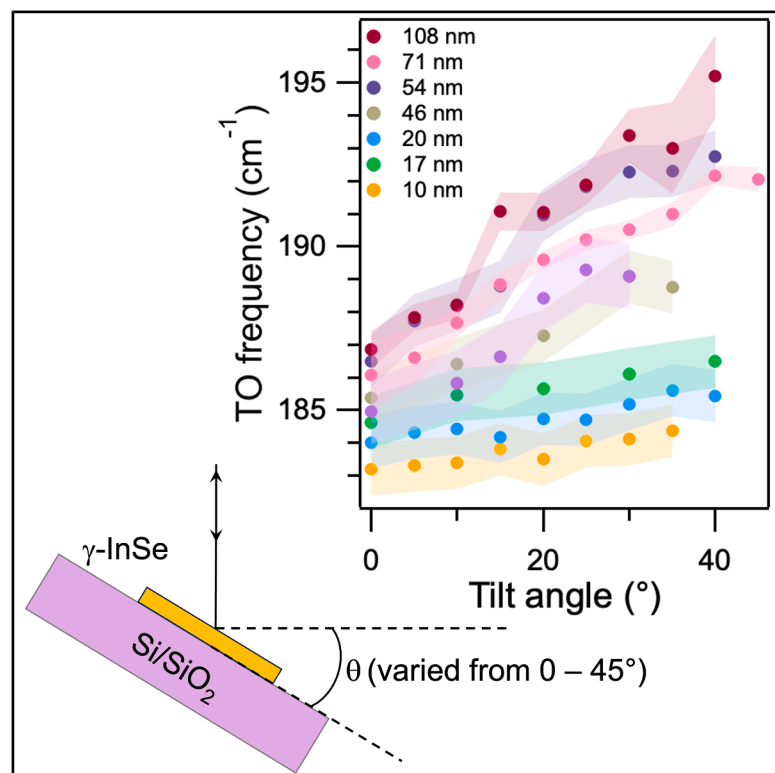


Thickness-dependent surface phonon polaritons in InSe

Graphical abstract



Authors

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In brief

Using Raman spectroscopy, we measured strong light-matter coupling in exfoliated indium selenide. Our measurements revealed a highly confined surface phonon polariton that exhibits the strongest coupling for 100-nm-thick flakes exfoliated onto silicon substrates. The strong light-matter coupling in this 2D material implies that indium selenide is a promising candidate for nanophotonics applications.

Highlights

- Thickness-dependent surface phonon polaritons observed in γ -InSe
- Polariton dispersion maximum for 100-nm-thick InSe
- The dispersion is strongly dependent on the dielectric substrate



Benchmark

First qualification/assessment of material properties and/or performance

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Article

Thickness-dependent surface phonon polaritons in InSe

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PROGRESS AND POTENTIAL Two-dimensional (2D) materials are the ideal platforms to investigate and manipulate polaritons, which arise from the coupling between light and quasiparticle excitations within the materials—phonons, magnons, plasmons, or excitons. Among these phonon polaritons (PhPs), which are hybridized modes formed through the interaction between photons and polar optical phonons, are particularly exciting because of their applications in subdiffractional optical sensing, infrared waveguides, modulators and detectors, optoelectronic and photonic circuit elements, nanoscale thermal management, and energy conversion. In this study, we investigate the thickness dependence of PhPs in an emerging 2D material, γ -InSe. We employ tilt angle-dependent resonant Raman spectroscopy to measure surface PhPs in mechanically exfoliated γ -InSe flakes with thicknesses ranging from 10 nm to 1.2 μ m, exfoliated onto SiO₂ and sapphire substrates. We observe a pronounced thickness-dependent dispersion of a polar transverse optical PhP mode, with a maximal slope near 100-nm thickness. Moreover, differences in the polariton dispersion on SiO₂ and sapphire show a distinct dependence on the dielectric environment. The polariton dispersions align with calculations that model the flakes as Fabry-Perot cavities supporting confined PhPs. Our findings advance our understanding of light-matter interactions in γ -InSe and highlight the potential for their use in nanophotonic devices.

SUMMARY

Two-dimensional (2D) materials are promising platforms for phonon polaritons (PhPs)—hybrid modes arising from photon-phonon interactions—that enable subwavelength light confinement and optoelectronic functionalities. γ -indium selenide (γ -InSe), an emerging 2D semiconductor with thickness-dependent optoelectronic properties, offers a unique system to explore confined surface phonon polaritons (SPhPs). Here, we employ tilt angle-dependent resonant Raman spectroscopy to measure SPhPs in γ -InSe flakes with thicknesses from 10 nm to 1.2 μ m, exfoliated on SiO₂ and sapphire substrates. We observe a pronounced thickness-dependent dispersion of the polar A₁(TO) phonon mode, with a maximal slope near 100-nm thickness, corresponding to the inverse absorption coefficient. Moreover, differences in the polariton dispersion on SiO₂ and sapphire show a dependence on the dielectric environment. The dispersions align with calculations modeling the flakes as Fabry-Perot cavities supporting confined SPhPs. These findings advance our understanding of light-matter interactions in γ -InSe and highlight the potential for their use in nanophotonic devices.

INTRODUCTION

Polaritons are quasiparticles formed through the interaction between light and polar solid-state excitations such as magnons, plasmons, excitons, or phonons.¹ Due to the strong light-matter coupling, they inherit properties from both matter and light, exhibiting both large optical non-linearities and fast propagation through the medium in which they are produced.² Plasmon and exciton polaritons have attracted significant attention owing to their potential applications in subdiffractional imaging, electro-optical modulation, lasing, and polaritonic computation.^{3–7} Nevertheless, plasmon polariton-based applications are limited by Ohmic losses, restricted confinement, lack of tunability, and limited compatibility with complementary metal-oxide-semiconductor (CMOS) integration, motivating the search for alternative polariton-based platforms.^{8,9}

One alternative is the phonon polariton (PhP), which is the hybridized mode formed through the interaction between the electromagnetic oscillation of photons and the atomic vibrations of a polar optical phonon.^{1,10–12} For most materials, these oscillations occur in the mid-infrared (IR) and terahertz wavelength region, enabling subdiffractional confinement of light. Additionally, PhPs can propagate over distances that are orders of magnitude longer than the typical mean free paths of phonons at the same frequency. The generation, manipulation, and detection of PhPs contribute to various technological applications such as subdiffractional optical sensing, IR waveguides, modulators and detectors, optoelectronic and photonic circuit elements, nanoscale thermal management, and energy conversion.^{8,13,14}

Recently, two-dimensional (2D) materials have garnered significant attention for hosting PhPs, as their strong anisotropy and atomically smooth surfaces can lead to confined, coherent hyperbolic PhPs with high momenta and directional propagation.^{15–19} Moreover, the properties of these materials can be controlled by external fields, tuned by varying thickness and environment (such as substrate choice and patterning), and further engineered by stacking different 2D materials in heterostructures for hybrid polaritonics.²⁰ The confinement of electromagnetic energy by PhPs is, therefore, highly promising for new forms of control over the dynamics of light-matter interactions, making 2D materials the ideal platforms to study these effects.^{8,16–18}

PhPs have been observed in 2D materials such as hBN, MoO₃, and their heterostructures, as well as in graphene/black phosphorus heterostructures.^{8,21–23} The reduced dimensionality in this class of materials often results in polar phonons that can interact strongly with IR excitation.^{4,5,24,25} In these systems, PhPs are typically measured using scanning near-field optical microscopy, where nanoscale optical near-field enhancement at the probe tips can excite the PhPs. Alternatively, PhPs can be launched into the material from patterned antennae or particles on the sample surface and imaged using the scanning probe.²⁶ While these methods provide unprecedented spatially resolved images of surface PhPs (SPhPs), they are complex and time-consuming measurements, often requiring specialized instrumentation and training.

A different and much simpler technique for measuring the dispersion of PhPs is Raman spectroscopy.^{27,28} The

measurements can be conducted simply by tuning the angle of the incident and scattered light directions with respect to the sample, thus allowing the scattering momentum to vary along some crystallographic axis of interest. Specifically, the strong dispersion of SPhP energies along the sample surface can be measured by tilting the angle away from normal incidence in the typical backscattering measurement geometry. PhPs have been measured using Raman scattering for thin films and crystals of various polar materials like GaP, GaN, LiO₃, and GaAs.^{27–31} Despite the numerous studies of PhPs in polar semiconductors, relatively few measurements of PhPs in 2D semiconductors have been demonstrated.^{32–34} Furthermore, to our knowledge, the thickness dependence of the PhP dispersion across a wide range of thicknesses from the free space wavelength of light down to a few atomic layers in these 2D systems has not yet been fully explored.

Here, we focus on 2D γ -indium selenide (γ -InSe), which has attracted considerable interest for its potential in high-performance optical and electronic devices.³⁵ This interest is driven by its room temperature electron mobility exceeding silicon at equivalent thicknesses, a direct band gap persisting above few layer thicknesses, layer-tunable band structure, and remarkably strong optical responses.^{36–38} Investigations of optical excitations in thin films and heterostructures of InSe reveal intriguing physics such as flat bands,³⁹ ultrafast charge, and energy transfer.⁴⁰ Additionally, thickness-dependent optical responses have been observed in 10- to 1,000-nm-thick exfoliated flakes,⁴¹ which are outside the regime where quantum confinement induces significant changes in the electronic band structure.

In this work, we demonstrate the existence of highly confined, propagating SPhP modes in exfoliated γ -InSe flakes (with thicknesses ranging from 10 to 1,200 nm) through tilt angle-dependent, backscattered, resonant Raman spectroscopy. We observe a strong dispersion of a polar transverse optical A₁(TO) mode around 185 cm⁻¹, indicative of deep subwavelength confinement of light in InSe. The observed dispersion depends not only on the sample thickness but also on the dielectric environment, as shown by differences between InSe flakes exfoliated on SiO₂ and sapphire substrates. Furthermore, we develop a model that captures both the SPhP dispersion and the relative spectral weight of surface and volume PhP modes as a function of thickness in the backscattering geometry. This work expands the library of surface polariton host materials and paves the way for future Raman spectroscopic studies of polariton physics in a wide range of materials.

RESULTS

γ -InSe belongs to the R3m space group, with two chemical formulas per primitive rhombohedral unit cell.^{42,43} The normal vibrational modes at the Brillouin zone center are given by 4A₁ + 4E, out of which 1A₁ and 1E mode are acoustic modes and the other 3A₁ and 3E modes are both Raman- and IR-active optical modes.⁴³ Density functional theory (DFT) calculations reveal the atomic displacements of the 2 polar optical phonon modes, which are shown schematically in Figure 1A, and corresponding movies of the A₁(TO) vibration is provided in the supplemental information (Video S1). The calculated phonon

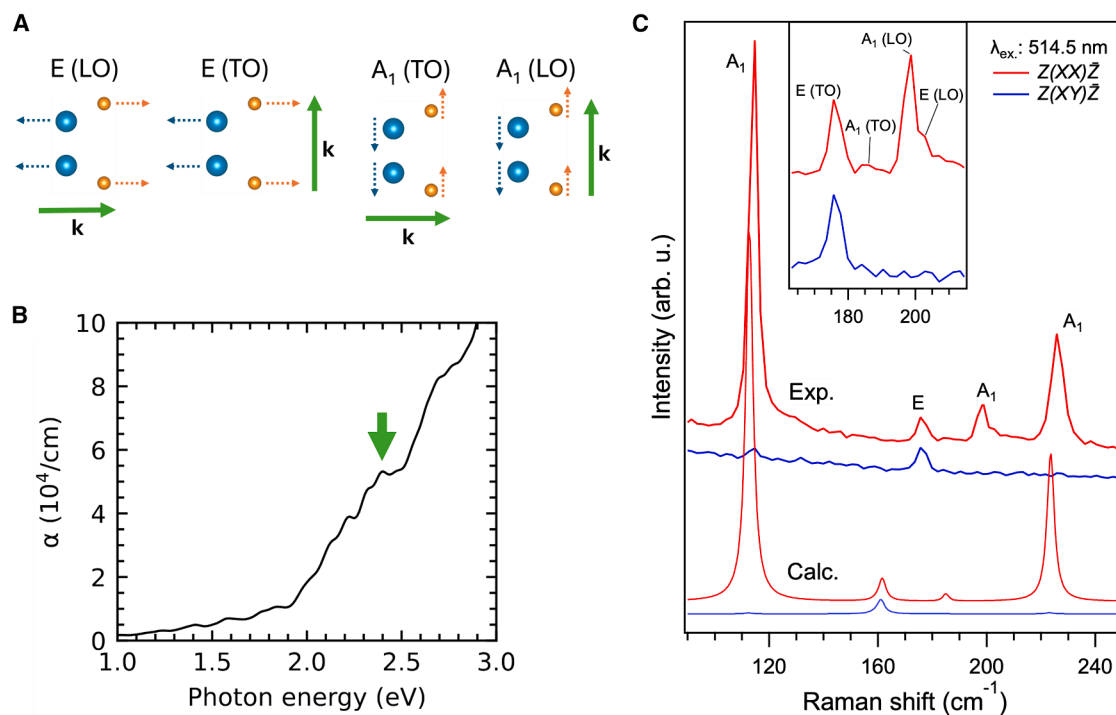


Figure 1. Optical characterization of bulk γ -InSe

(A) Atomic displacements of the A_1 and E optical phonon modes in γ -InSe, viewed along the a - b plane. The direction of propagation (green arrow) of the mode determines its LO or TO character.

(B) Calculated absorption coefficient α , with the arrow pointing to the laser excitation used at 514.5 nm or 2.41 eV.

(C) Experimental polarized resonance Raman spectra from bulk γ -InSe and calculated spectra for parallel and crossed polarizations, $z(xx)\bar{z}$ (red) and $z(xy)\bar{z}$ (blue), respectively. Here, z is perpendicular to the layer stacking axis. The inset shows the selection rule-forbidden $A_1(\text{TO})$ and $E(\text{LO})$ modes that appear only due to resonant Raman scattering.

dispersion of bulk γ -InSe is plotted in Figure S1. Both DFT calculations and group theory reveal that the A_1 mode oscillates along the c axis, while the E mode oscillates in the ab plane (Figure 1A). By definition, the longitudinal optical [$A_1(\text{LO})$] phonons can be launched only by matching the scattering momentum k , parallel to their oscillation direction along the ab plane. On the other hand, with the scattering momentum parallel to the c axis, we expect to measure only E(TO) phonons.^{43–45}

The calculated optical absorption coefficient is presented in Figure 1B. While the band gap of bulk γ -InSe is around 1.25 eV (located at the Γ point), resonance Raman spectra can be obtained by using a laser excitation matching the higher energy E'_1 excitonic transition around 2.4 eV, indicated by the arrow in Figure 1B.^{44,46,47} This is also shown in the calculated electronic band structure and the density of states (Figure S2) where a saddle point in the valence band results in a van Hove singularity in the density of states.⁴⁸ The resonant excitation enables the measurement of all four E and A_1 symmetry LO and TO modes. This can be seen in the resonance Raman spectrum (Figure 1C), which shows linearly polarized Raman spectra collected at room temperature with 2.41 eV (514.5 nm) excitation from a bulk γ -InSe single crystal. The E and A_1 symmetries of the LO and TO modes are revealed in the co- and cross-polarized spectra, denoted in Porto notation as $z(xx)\bar{z}$ and $z(xy)\bar{z}$, respectively. Here, x, y and z are the Cartesian axes in the laboratory

frame. z and $\bar{z}$ are the directions of the incident and scattered light perpendicular to the layer stacking axis, respectively, and the laser polarization is in-plane along the x and y directions. We focus on the frequency region between 170 and 220 cm^{-1} where the 4 observed peaks correspond to the E and A_1 LO and TO modes (inset in Figure 1C). We note that even with the 2.41 eV resonance excitation, two of the peaks exhibit weak intensities. However, based on the comparison with previously published data,^{44,45,49,50} we assign the 4 polar Raman modes in bulk γ -InSe at 176, 186, 199, and 203 cm^{-1} as E(TO), $A_1(\text{TO})$, $A_1(\text{LO})$, and E(LO), respectively. As mentioned above, the $A_1(\text{TO})$ and E(LO) are forbidden by the typical selection rules in the backscattering geometry, ($k \parallel c$). However, they can be observed under resonant excitation.⁴⁴ Plotted in Figure 1C are the DFT-calculated spectra, which overall reproduce the shape of the experimentally measured spectra. The slight difference between the experimental and calculated frequencies can be attributed to the selected pseudopotential in DFT, which often leads to optical phonon frequency differences of up to 20 cm^{-1} between DFT calculations and experimental value.⁵¹

Considering that the scattering momenta of the LO and TO modes are either parallel or perpendicular to the c axis, the dispersions of the modes away from the Brillouin zone center can be measured by changing the incidence angle of the excitation laser. Conversely, the same can be achieved by tilting the sample with

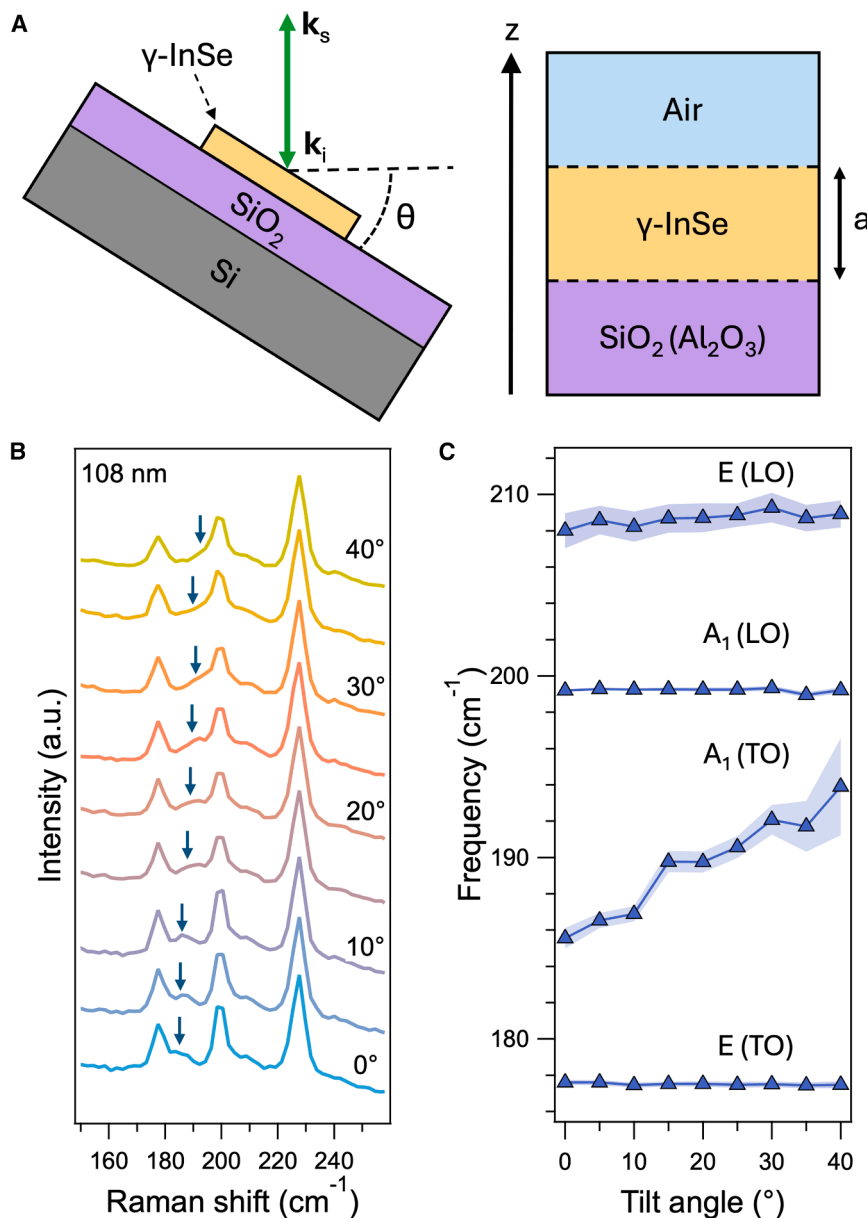


Figure 2. Tilt angle-dependent Raman spectra

(A) Left: View of the cross-section at the sample, showing two interfaces surrounding a γ -InSe flake with thickness a .

Right: Schematic of Raman backscattering experiment with sample tilt angle θ .

(B) Resonance Raman spectra collected at various angles between 0° and 40° from a 108-nm-thick InSe flake. The arrows indicate the SPhP.

(C) Frequencies of the 4 polar modes as a function of tilt angle. The standard deviations obtained from curve fitting are shown by the shaded areas. The $A_1(\text{TO})$ mode frequency exhibits a clear dispersion with increasing tilt angle.

vector is approximately 1/100 of the size of the Brillouin zone of γ -InSe, approximately at the Γ point ($k = 0$),⁵² as well as much greater than the wavevector of a photon at the phonon frequency ($\sim 10^3 \text{ cm}^{-1}$).²⁷ Thus, we expect bulk phonon modes to show negligible dispersion as a function of tilt angle.

The tilt angle-dependent (from 0° to 40°) resonance Raman spectra in the frequency range $150\text{--}260 \text{ cm}^{-1}$ from a 108 nm-thick mechanically exfoliated γ -InSe flake are shown in Figure 2B. Of the 4 polar phonon modes, the $A_1(\text{TO})$ mode at 184 cm^{-1} (indicated by the arrows in Figure 2B) exhibits a clear blueshift by $\sim 10 \text{ cm}^{-1}$ in frequency with increasing tilt angle up to 40° . However, the $E(\text{TO})$, $A_1(\text{LO})$ and $E(\text{LO})$ modes around 178, 199 and 208 cm^{-1} , respectively, exhibit negligible change in frequency with the increasing tilt angle. The blueshift of the $A_1(\text{TO})$ can be seen more clearly in Figure 2C, in which the frequencies (obtained by Lorentzian peak fitting) of the 4 polar modes are plotted as a function of tilt angle.

We note that our observation of tilt angle-dependent Raman peak frequency in InSe is similar to previous observations of highly dispersing PhPs in GaSe.^{32,33} The invariance of the $E(\text{TO})$ and $A_1(\text{LO})$ mode frequencies with increasing tilt angle is consistent with bulk or volume optical phonon modes, where the frequencies are approximately constant due to the parabolic dispersion near the Γ point. Meanwhile, the forbidden mode with a propagation direction along the layer surface [$A_1(\text{TO})$] shows a strong dispersion with increasing tilt angle, indicating that it is a SPhP.

To investigate the thickness dependence of the PhPs in γ -InSe, we measured resonance Raman spectra as a function of tilt angle from 14 mechanically exfoliated flakes with thicknesses ranging from 10 to 1,200 nm. Figure S3 shows a

respect to the incident laser excitation (normal in a backscattering geometry). To perform these measurements, we fabricated a fixture to manually tilt samples up to 45° from normal incidence. Figure 2A shows the schematic of our measurement configuration. The momentum transfer equation for light scattering is given by $q = k_i - k_s$, where q is the scattered phonon wavevector, and k_i and k_s are the wavevectors of the incident and scattered photons, respectively. For a backscattering configuration, $q_{\text{max}} \approx 2k_i$. By tilting the sample, the component of q along the sample surface is $q_{\parallel} = q_{\text{max}} \sin \theta$. It is through this component of the momentum transfer that we are able to probe SPhPs propagating along the InSe layers. Given the momentum of the 514.5 nm photon and the maximum tilt angle in our experiment of 45° , we get $q_{\text{max}} \sim 1 \times 10^5 \text{ cm}^{-1}$. At this momentum transfer, the measured wave-

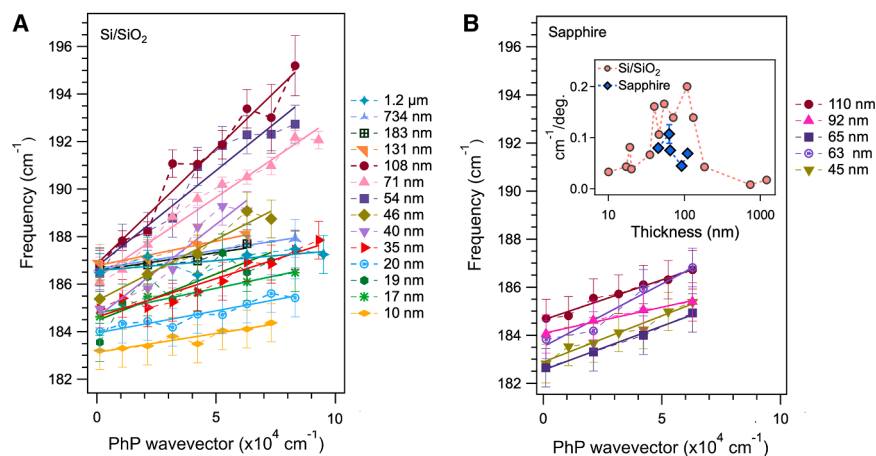


Figure 3. Phonon polariton dispersions on two substrates

(A and B) Dispersion of the PhP as a function of tilt angle θ for mechanically exfoliated γ -InSe flakes with varying thicknesses on (A) Si/SiO₂ and (B) sapphire. Inset: the log-linear plot shows the slopes of the PhP dispersions on Si/SiO₂ (red) as well as sapphire (blue) as a function of flake thickness. The frequency error bars represent one standard deviation, from the least squares fitting of the raw Raman spectra. We estimate the wavevector error to be approximately $0.5 \times 10^4 \text{ cm}^{-1}$, derived from an input beam 1 mm in diameter, and an objective free working distance of 8.2 mm.

representative atomic force microscope (AFM) image and the corresponding height profile of a 46 nm-thick exfoliated flake. All flakes exhibit dispersions of the PhP [$A_1(\text{TO})$ mode] with respect to the tilt angle, which are plotted in Figure 3A for exfoliated flakes on Si/SiO₂ (300-nm-thick oxide). The figure shows that the dispersion (slope of the PhP frequency vs. tilt angle) increases with thickness from 10 nm up to a maximum value for 108 nm-thick InSe. Beyond 108 nm, the dispersion again decreases for thicker flakes up to the highest measured thickness (1,200 nm). The thickness dependence of the PhP dispersion is shown in the inset in Figure 3B, going up from $0.03 \text{ cm}^{-1}/\text{degree}$ for 10 nm-thick InSe to $0.2 \text{ cm}^{-1}/\text{degree}$ for the 108-nm-thick flake. This results in a blueshift of $\sim 10 \text{ cm}^{-1}$ at the highest wavevector (tilt angle) measured.

Considering that an exfoliated InSe flake forms an optical cavity with two different boundaries (air and substrate), we decided to measure tilt angle-dependent Raman spectra from exfoliated flakes on a different substrate, effectively changing one of the boundary conditions. For these measurements, we chose single-side polished single-crystal C-plane sapphire and collected a limited set of data from 5 exfoliated γ -InSe flakes with thicknesses ranging from 45 to 110 nm. Similar to the flakes on Si/SiO₂, we observed evidence for a PhP involving the $A_1(\text{TO})$ mode. However, the dispersions of the PhPs are weaker than those observed for flakes with similar thicknesses on Si/SiO₂. This can be seen clearly in Figure 3B where the dispersions are very similar and do not exhibit a strong thickness dependence. Moreover, the lower slopes of the PhP dispersions for the flakes on sapphire compared to Si/SiO₂ can be seen in the inset in Figure 3B (blue data points). This observation indicates the strong dependency of the PhP on the boundaries of the γ -InSe cavity, further pointing to the surface nature of this PhP.

The LO-TO frequencies of a phonon span the Reststrahlen band, characterized as a region of spectral range in which the real part of the dielectric function is negative.¹⁹ It is within this region that we can find polaritons confined to a planar surface. To understand the thickness dependence of the SPhPs in γ -InSe flakes on different dielectric substrates, we solved Maxwell's equation for polariton modes of a finite-thickness slab, surrounded by air and a dielectric (details of the calculations are

included in Note S1). The result of our calculation for a 108 nm-thick γ -InSe flake on 300 nm SiO₂ is shown in Figure 4A. The finite boundaries of the InSe flake form a Fabry-Perot cavity, quantizing the PhP modes into several transverse magnetic (TM) branches. Our calculations show that the electromagnetic field distribution in the transverse electric (TE) polariton modes leads to much lower excitation efficiency than in the TM mode. Plotting the electric field intensity of the polariton states near $4 \times 10^4 \text{ cm}^{-1}$ in Figures 4B and 4C (indicated by the dashed arrows in Figure 4A), the most dispersive branch is shown to have a highly localized electric field profile at the interface between γ -InSe and the dielectric substrate ($\epsilon > 1$), thus confirming the PhP measured in our study as a SPhP.

We find that for increasing thicknesses, the most dispersive branch corresponding to the $A_1(\text{TO})$ SPhP has an increasing effective slope (Figure 4D). In other words, the TM PhP mode in question has a remarkably high velocity along the surface in the bulk limit, closer to the light line. As the thickness decreases, the confinement effect can be seen by the substantially lower velocity. That is, for a fixed energy, the SPhP excited in InSe has a lower group velocity and smaller wavelengths for thinner films, more tightly confining the field in all three dimensions. As large confinement factors are beneficial for enhancing electro- and acousto-optical transduction, γ -InSe may be a promising material for applications including next-generation communication, sensing, and subdiffractional imaging. Furthermore, we expect that these trends should continue to lower thicknesses; however, InSe is known to undergo gradual band structure changes due to quantum confinement at ultralow thicknesses ($< 10 \text{ nm}$).³⁶ The thickness-dependent band structure may then change the resonance condition, obscuring the observation of SPhPs in InSe flakes below 10 nm, using a 514.5-nm laser excitation.

Our calculations are also consistent with the experimental observations presented in Figure 3C, where the dispersion of the $A_1(\text{TO})$ mode (approximated by a linear slope) increases with film thickness; however, this trend continues only until the dispersion seems to peak just above 100 nm. The discrepancy can be understood qualitatively by noting that the absorption coefficient of InSe for 514.5-nm excitation is $\sim 5.4 \times 10^4 \text{ cm}^{-1}$

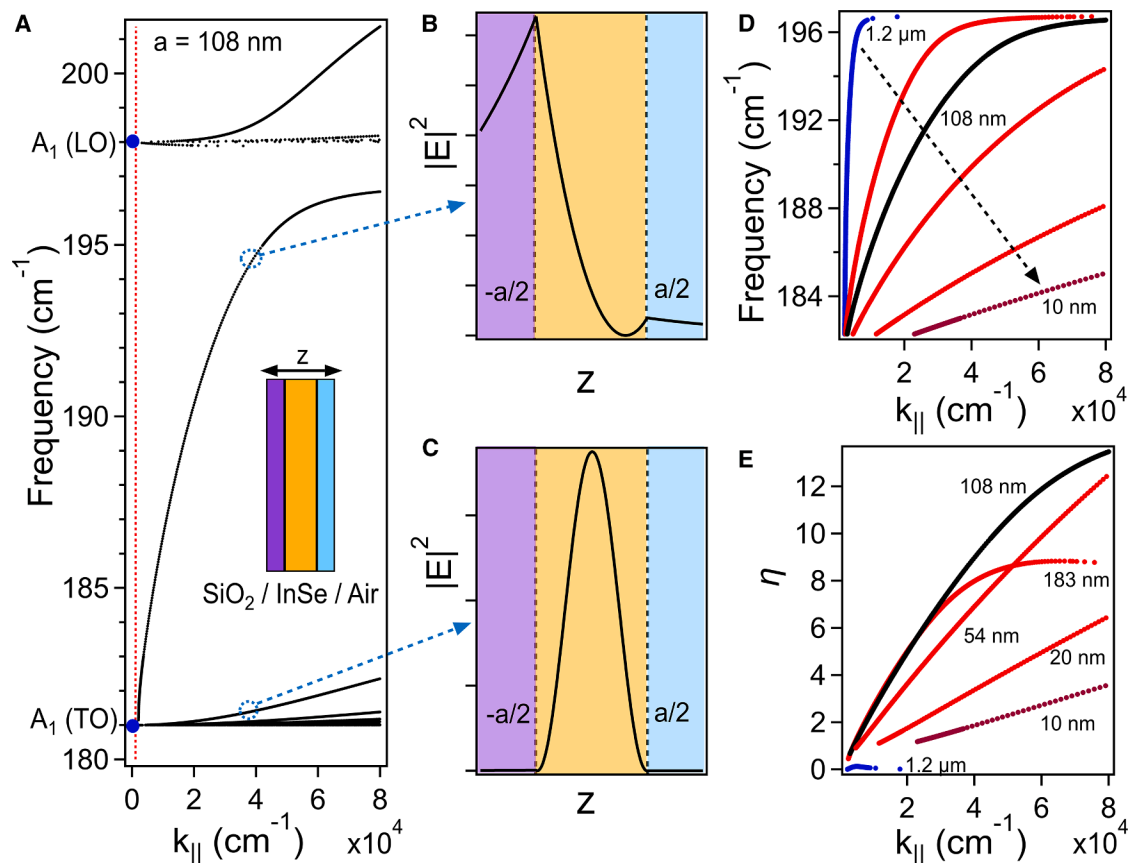


Figure 4. Calculated phonon polariton dispersions of γ -InSe flakes on SiO_2

(A) The calculated PhP dispersion as a function of propagating wavevector parallel to the layers, $k_{||}$, for a γ -InSe flake of thickness $a = 108$ nm on SiO_2 , with $\epsilon = 3.9$. The LO and TO frequencies from a previous bulk measurement are marked by solid blue dots.⁴⁵ (B and C) The electric field strength as a function of position along the thickness of the 108 nm flake for two different dispersive TM modes at $k_{||} \approx 4 \times 10^4 \text{ cm}^{-1}$. The three distinct regions from left to right are SiO_2 , γ -InSe, and air. (D) The strongest dispersing TM PhP (first branch) for several thicknesses (1200, 183, 108, 54, 20, and 10 nm) is shown. The dashed arrow indicates the decrease in dispersion with confinement (decreasing thickness). (E) The corresponding scattering efficiency, η , for the same flakes for the first branch shown in (D).

according to our calculations (Figure 1B). This implies that the laser penetration depth ($1/\alpha$) is ≈ 185 nm according to our single-particle DFT calculations. Therefore, backscattering from flakes with thicknesses greater than $1/\alpha$ should not allow the excitation of the highly dispersive polariton located primarily at the γ -InSe- SiO_2 interface. We introduce a coupling efficiency parameter between the SPhP mode and the incident laser to model this effect. Such a parameter, η , is proportional to the Raman scattering intensity and defined as:

$$\eta = \frac{\int_{-a}^a e^{(z-a)/l} |F_y(z)|^2 dz}{\int_{-\infty}^{\infty} |F_y(z)|^2 dz}, \quad (\text{Equation 1})$$

where F is the strength of the electromagnetic field (see supplemental information), and $2a$ is the thickness of InSe. A penetration length $l = 125$ nm was chosen to match the slope change at the critical thickness, as shown in the inset of Figure 3B. Note that excitonic effects are expected to increase the absorption coefficient α calculated within the single-particle

picture. Moreover, the incident light does not excite a polariton directly; instead, through the Raman scattering process, the laser-excited electronic state decays into another intermediate state by exciting a polariton. The excited and intermediate states are real in our resonance Raman experiment. These states are near the E'_1 excitonic transition ~ 2.41 eV and play a major role in allowing the observation of the SPhPs. The contribution of the E'_1 exciton to the Raman cross-section of the measured SPhP (i.e., exciton-phonon coupling) is still unexplored, and is beyond the scope of this work.

Figure 4E shows the corresponding η of the first (most dispersive) polariton branch for different thicknesses. Even though the thickest sample can host the highest dispersive SPhP mode, its coupling to the laser excitation effectively drops to zero due to the lower absorption coefficient of γ -InSe at 514.5 nm at that thickness. Simulations demonstrate a crossover of around 108 nm, a value similar to the absorption penetration length l , such that η drops significantly at thicknesses larger than l . Our simulation result enables us to explain the sharp change of the

slope shown in Figure 3B—because another TM polariton branch with nearly flat dispersion starts to dominate the Raman scattering signal as the corresponding η value for the flat band is an order of magnitude larger (Figure S4).

To conclude, we measured resonance Raman spectra from mechanically exfoliated flakes of γ -InSe on Si/SiO₂ and sapphire substrates. By tilting the samples with respect to the normally incident Raman laser in the backscattering configuration, we probed the dispersion of a SPhP mode up to a wavevector of $9.3 \times 10^4 \text{ cm}^{-1}$. This dispersion occurs due to the formation of surface-confined PhPs within the double Reststrahlen bands of an E(LO) and A₁(TO) phonon mode. The magnitude of the dispersion strongly depends on the flake thickness, as well as the dielectric constant of the substrate. We modeled the polariton dispersion, which showed that the SPhPs are tightly confined within the InSe layers, bound on either side by the dielectric substrate and air. Furthermore, we introduced a parameter that captures the coupling efficiency of the SPhP mode, which showed that the coupling efficiency is maximized for a thickness of γ -InSe around 100 nm, in agreement with our experimental observations. Overall, our study shows the presence of thickness-dependent confined SPhPs in γ -InSe and expands the range of potential applications in this exciting technologically relevant 2D material.

METHODS

Single crystal growth and exfoliation

γ -InSe single crystals were grown by the vertical Bridgman method, using a polycrystalline charge of 1.04:0.96 In:Se stoichiometry. Structural characterization and detailed growth parameters of the crystals are reported elsewhere.³⁷ For Raman measurements, InSe flakes were mechanically exfoliated onto SiO₂/Si (with a 280 nm thermal oxide) and sapphire substrates.

Raman scattering measurements

Room temperature Raman spectra were collected with a Renishaw inVia Raman microscope. The spectra were collected in the backscattering configuration by exciting bulk and exfoliated γ -InSe flakes on Si/SiO₂ and sapphire substrates. Near-resonance (non-resonance) Raman spectra were collected with 514.5 (633) nm excitation by focusing the laser through a 50 $\times$ objective lens onto the exfoliated flakes. For all measurements, the laser power was kept at under 1 mW to avoid heating from the laser, and typical spectral collection times were 3–5 min, with 10–30 s exposure times and multiple acquisitions. The tilt angle-dependent measurements were collected with the help of a custom fixture fabricated by attaching the substrate on to a manual rotation mount (Thorlabs Inc.). Spectra were collected by manually tilting the substrate with respect to the laser every 5° up to 45°.

First-principles calculations

The electronic structures and phonon dispersion of bulk γ -InSe were calculated using DFT and density functional perturbation theory (DFPT) with the Quantum ESPRESSO package,^{53,54} respectively. The unit cell of γ -InSe has a layered rhombohedral crystal structure (space group of R3m) that consists of three

Se-In-In-Se layers in ABC stacking order. For optimizing structure, all atomic positions and lattice vectors were optimized by using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) method⁵¹ with convergence criteria for force and stress set to 1.0×10^{-4} Ry/a.u. and 0.005 GPa, respectively. The optimized lattice constants are $a = b = 4.014 \text{ \AA}$ and $c = 25.204 \text{ \AA}$, which are consistent with experimental data ($a = b = 4.002 \text{ \AA}$ and $c = 24.961 \text{ \AA}$).⁵⁵ A cut-off energy of 120 Ry (1.63 keV) was selected for the plane-wave basis. Here, we adopted In.pz-hgh.UPF and Se.pz-hgh.UPF⁵⁶ for the pseudopotential files of the In and Se atoms, respectively. The **k**-grid of $8 \times 8 \times 2$ and **q**-grid of $4 \times 4 \times 2$ were used for the electronic structure and phonon dispersion calculations, respectively.

To calculate the optical absorption coefficient of γ -InSe, the epsilon.x code in Quantum ESPRESSO was used with independent particle approximation,⁵¹ in which a large **k**-grid of $30 \times 30 \times 8$ was used to calculate the non-self-consistent field to achieve convergence in the absorption coefficient.

To calculate the first-order resonance Raman spectra, we used the QERaman code.⁵⁷ In the QERaman code, the first-order resonance Raman spectra were calculated by the third-order time-dependent perturbation theory,⁵⁸ in which a dense **k**-grid of $20 \times 20 \times 4$ was used to evaluate the electron-photon and electron-phonon matrix elements based on the convergence test. The broadening factor of the resonance condition, which is related to lifetime of the photoexcited carrier, was selected to be 0.02 eV based on the fitting data from the experimental spectra.

RESOURCE AVAILABILITY

Lead contact

Requests for further information and resources should be directed to and will be fulfilled by the lead contact, Rahul Rao (rahul.rao.2@us.af.mil).

Materials availability

This study did not generate new materials.

Data and code availability

Any additional information required to reanalyze the data reported in this paper is available from the lead contact upon request.

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AUTHOR CONTRIBUTIONS

Conceptualization, R.R.; methodology and investigation, T.T.M., M.A.A., V.L., S.K., A.D., M.A.S., N.T.H., J.H., D.J., M.S., R.S., V.P., N.R.G., and R.R.; writing – original draft, R.R. and T.T.M.; writing – review & editing, M.A.A., S.K., A.D., M.A.S., N.T.H., J.H., D.J., M.S., R.S., and V.P.

DECLARATION OF INTERESTS

The authors declare no competing interests.

SUPPLEMENTAL INFORMATION

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REFERENCES

- Basov, D.N., Asenjo-Garcia, A., Schuck, P.J., Zhu, X., and Rubio, A. (2020). Polariton panorama. *Nanophotonics* **10**, 549–577.
- Xu, D., Mandal, A., Baxter, J.M., Cheng, S.-W., Lee, I., Su, H., Liu, S., Reichman, D.R., and Delor, M. (2023). Ultrafast imaging of polariton propagation and interactions. *Nat. Commun.* **14**, 3881.
- Caldwell, J.D., Glembocki, O.J., Francescato, Y., Sharac, N., Giannini, V., Bezares, F.J., Long, J.P., Owrutsky, J.C., Vurgaftman, I., Tischler, J.G., et al. (2013). Low-loss, extreme subdiffraction photon confinement via silicon carbide localized surface phonon polariton resonators. *Nano Lett.* **13**, 3690–3697.
- Caldwell, J.D., Kretinin, A.V., Chen, Y., Giannini, V., Fogler, M.M., Francescato, Y., Ellis, C.T., Tischler, J.G., Woods, C.R., Giles, A.J., et al. (2014). Sub-diffractive volume-confined polaritons in the natural hyperbolic material hexagonal boron nitride. *Nat. Commun.* **5**, 5221.
- Dai, S., Fei, Z., Ma, Q., Rodin, A.S., Wagner, M., McLeod, A.S., Liu, M.K., Gannett, W., Regan, W., Watanabe, K., et al. (2014). Tunable phonon polaritons in atomically thin van der Waals crystals of boron nitride. *Science* **343**, 1125–1129.
- Chen, D.-Z.A., Narayanaswamy, A., and Chen, G. (2005). Surface phonon-polariton mediated thermal conductivity enhancement of amorphous thin films. *Phys. Rev. B* **72**, 155435.
- Pan, Z., Lu, G., Li, X., McBride, J.R., Juneja, R., Long, M., Lindsay, L., Caldwell, J.D., and Li, D. (2023). Remarkable heat conduction mediated by non-equilibrium phonon polaritons. *Nature* **623**, 307–312.
- Hu, G., Shen, J., Qiu, C.-W., Alù, A., and Dai, S. (2020). Phonon polaritons and hyperbolic response in van der Waals materials. *Adv. Opt. Mater.* **8**, 1901393.
- Yan, H., Low, T., Zhu, W., Wu, Y., Freitag, M., Li, X., Guinea, F., Avouris, P., and Xia, F. (2013). Damping pathways of mid-infrared plasmons in graphene nanostructures. *Nat. Photonics* **7**, 394–399.
- Huang, K. (1951). Lattice vibrations and optical waves in ionic crystals. *Nature* **167**, 779–780.
- Burstein, E., Ushioda, S., and Pinczuk, A. (1968). Raman scattering by polaritons. *Solid State Commun.* **6**, 407–411.
- Boardman, A.D. (1982). *Electromagnetic Surface Modes* (Wiley).
- Venkataram, P.S., Hermann, J., Tkatchenko, A., and Rodriguez, A.W. (2018). Phonon-polariton mediated thermal radiation and heat transfer among molecules and macroscopic bodies: nonlocal electromagnetic response at mesoscopic scales. *Phys. Rev. Lett.* **121**, 045901.
- Ma, Y., Zhong, G., Dai, Z., and Ou, Q. (2024). In-plane hyperbolic phonon polaritons: materials, properties, and nanophotonic devices. *npj Nanophotonics* **1**, 25.
- Mills, D.L. (1975). Attenuation of surface polaritons by surface roughness. *Phys. Rev. B* **12**, 4036–4046.
- Rivera, N., Christensen, T., and Narang, P. (2019). Phonon polaritonics in two-dimensional materials. *Nano Lett.* **19**, 2653–2660.
- Basov, D.N., Fogler, M.M., and García de Abajo, F.J. (2016). Polaritons in van der Waals materials. *Science* **354**, aag1992.
- Low, T., Chaves, A., Caldwell, J.D., Kumar, A., Fang, N.X., Avouris, P., Heinz, T.F., Guinea, F., Martin-Moreno, L., and Koppens, F. (2017). Polaritons in layered two-dimensional materials. *Nat. Mater.* **16**, 182–194.
- Wang, H., Kumar, A., Dai, S., Lin, X., Jacob, Z., Oh, S.-H., Menon, V., Narimanov, E., Kim, Y.D., Wang, J.-P., et al. (2024). Planar hyperbolic polaritons in 2D van der Waals materials. *Nat. Commun.* **15**, 69. <https://doi.org/10.1038/s41467-023-43992-8>.
- Guo, X., Lyu, W., Chen, T., Luo, Y., Wu, C., Yang, B., Sun, Z., García de Abajo, F.J., Yang, X., and Dai, Q. (2023). Polaritons in van der Waals heterostructures. *Adv. Mater.* **35**, 2201856.
- Chaudhary, K., Tamagnone, M., Rezaee, M., Bediako, D.K., Ambrosio, A., Kim, P., and Capasso, F. (2019). Engineering phonon polaritons in van der Waals heterostructures to enhance in-plane optical anisotropy. *Sci. Adv.* **5**, eaau7171.
- Tamagnone, M., Ambrosio, A., Chaudhary, K., Jauregui, L.A., Kim, P., Wilson, W.L., and Capasso, F. (2018). Ultra-confined mid-infrared resonant phonon polaritons in van der Waals nanostructures. *Sci. Adv.* **4**, eaat7189.
- Zheng, Z., Chen, J., Wang, Y., Wang, X., Chen, X., Liu, P., Xu, J., Xie, W., Chen, H., Deng, S., and Xu, N. (2018). Highly confined and tunable hyperbolic phonon polaritons in van der Waals semiconducting transition metal oxides. *Adv. Mater.* **30**, 1705318.
- Xu, X.G., Ghamsari, B.G., Jiang, J.-H., Gilburd, L., Andreev, G.O., Zhi, C., Bando, Y., Golberg, D., Berini, P., and Walker, G.C. (2014). One-dimensional surface phonon polaritons in boron nitride nanotubes. *Nat. Commun.* **5**, 4782–4786.
- Chen, M., Lin, X., Dinh, T.H., Zheng, Z., Shen, J., Ma, Q., Chen, H., Jarillo-Herrero, P., and Dai, S. (2020). Configurable phonon polaritons in twisted α -MoO₃. *Nat. Mater.* **19**, 1307–1311.
- Hillenbrand, R., Abate, Y., Liu, M., Chen, X., and Basov, D. (2025). Visible-to-thz near-field nanoscopy. *Nat. Rev. Mater.* **10**, 285.
- Henry, C.H., and Hopfield, J.J. (1965). Raman scattering by polaritons. *Phys. Rev. Lett.* **15**, 964–966.
- Mills, D.L., Chen, Y.J., and Burstein, E. (1976). Raman scattering of light by polaritons in thin films; surface polaritons and size effects. *Phys. Rev. B* **13**, 4419–4438.
- Irmer, G., Röder, C., Himcinschi, C., and Kortus, J. (2013). Phonon polaritons in uniaxial crystals: A Raman scattering study of polaritons in α -GaN. *Phys. Rev. B Condens. Matter* **88**, 104303.
- Otaguro, W., Wiener-Avnear, E., Arguello, C.A., and Porto, S.P.S. (1971). Phonons, polaritons, and oblique phonons in LiIO₃ by Raman scattering and infrared reflection. *Phys. Rev. B* **4**, 4542–4551.
- Evans, D.J., Ushioda, S., and McMullen, J.D. (1973). Raman scattering from surface polaritons in a GaAs film. *Phys. Rev. Lett.* **31**, 369–372.
- Sasaki, Y., and Ushioda, S. (1983). Guided-wave polaritons in thin films of the layered compound GaSe. *Phys. Rev. B* **27**, 1122–1135.
- Bergeron, A., Gradziel, C., Leonelli, R., and Francoeur, S. (2023). Probing hyperbolic and surface phonon-polaritons in 2D materials using Raman spectroscopy. *Nat. Commun.* **14**, 4098.
- Zhou, L., Wirth, K., Bui, M.N., Rani, R., Grützmacher, D., Taubner, T., and Kardynał, B.E. (2024). Resonant raman scattering of surface phonon polaritons mediated by excitons in WS₂ films. *ACS Photonics* **11**, 3079–3086.

35. Song, S., Altvater, M., Lee, W., Shin, H.S., Glavin, N., and Jariwala, D. (2026). Indium selenides for next-generation low-power computing devices. *Nat. Rev. Electr. Eng.* **3**, 185–201.
36. Bandurin, D.A., Tyurnina, A.V., Yu, G.L., Mishchenko, A., Zólyomi, V., Morozov, S.V., Kumar, R.K., Gorbachev, R.V., Kudrynskiy, Z.R., Pezzini, S., et al. (2017). High electron mobility, quantum hall effect and anomalous optical response in atomically thin InSe. *Nat. Nanotechnol.* **12**, 223–227.
37. Pike, N.A., Pachter, R., Altvater, M.A., Stevens, C.E., Klein, M., Hendrickson, J.R., Zhang, H., Krylyuk, S., Davydov, A.V., and Glavin, N.R. (2024). Understanding the origin and implication of the indirect-to-direct bandgap transition in multilayer InSe. *J. Phys. Chem. C* **128**, 7957–7967.
38. Temel, T., Zhu, S., Chen, W., Wang, C., Duan, R., Wang, F., Hu, D.J.J., Yang, Y., Chae, S.H., Liu, Z., et al. (2025). Strong mid-infrared optical harmonic processes mediated by excitons in layered indium selenide. *Laser Photon. Rev.* **19**, 2402111. <https://doi.org/10.1002/lpor.202402111>.
39. Pasquale, G., Sun, Z., Čerpevičs, K.N., Perea-Causin, R., Tagarelli, F., Watanabe, K., Taniguchi, T., Malic, E., Yazyev, O.V., and Kis, A. (2022). Flat-band-induced many-body interactions and exciton complexes in a layered semiconductor. *Nano Lett.* **22**, 8883–8891.
40. Altvater, M.A., Stevens, C.E., Pike, N.A., Hendrickson, J.R., Rao, R., Krylyuk, S., Davydov, A.V., Jariwala, D., Pachter, R., Snure, M., and Glavin, N.R. (2025). Efficient energy transfer and photoluminescence enhancement in 2D MoS₂/bulk InSe van der Waals heterostructures. *npj 2D Mater. Appl.* **9**, 31.
41. Li, C., Zhao, L., Shang, Q., Wang, R., Bai, P., Zhang, J., Gao, Y., Cao, Q., Wei, Z., and Zhang, Q. (2022). Room-temperature near-infrared excitonic lasing from mechanically exfoliated InSe microflake. *ACS Nano* **16**, 1477–1485.
42. Likforman, A., Carré, D., Etienne, J., and Bachet, B. (1975). Structure cristalline du monoséléniure d'indium InSe. *Acta Crystallogr. B* **31**, 1252–1254. <https://doi.org/10.1107/S0567740875005006>.
43. Ikari, T., Shigetomi, S., and Hashimoto, K. (1982). Crystal structure and Raman spectra of InSe. *physica status solidi (b)* **111**, 477–481.
44. Kuroda, N., and Nishina, Y. (1978). Resonant Raman scattering at higher M₀ exciton edge in layer compound InSe. *Solid State Commun.* **28**, 439–443.
45. Gasanly, N.M., Yavdov, B.M., Tagirov, V.I., and Vinogradov, E.A. (1978). Infrared and Raman spectra of layer InSe single crystals. *Phys. Stat. Solid B* **89**, K43. <https://doi.org/10.1002/pssb.2220890155>.
46. Kuroda, N., Munakata, I., and Nishina, Y. (1980). Exciton transitions from spin-orbit split off valence bands in layer compound InSe. *Solid State Commun.* **33**, 687–691.
47. Ashokan, S., Jain, K., Balkanski, M., and Julien, C. (1991). Resonant Raman scattering in quasi-two-dimensional InSe near the M₀ and M₁ critical points. *Phys. Rev. B* **44**, 11133–11142.
48. Zólyomi, V., Drummond, N.D., and Fal'ko, V. (2014). Electrons and phonons in single layers of hexagonal indium chalcogenides from ab initio calculations. *Phys. Rev. B* **89**, 205416.
49. Kuroda, N., and Nishina, Y. (1979). Directional dispersion of extraordinary phonons in layer compound InSe. *Solid State Commun.* **30**, 95–98.
50. Jouanne, M., Julien, C., and Balkanski, M. (1987). Polarization studies of polar phonons of InSe. *Phys. Status Solidi* **144**, K147–K150.
51. Hung, N.T., Nugraha, A.R., and Saito, R. (2022). *Quantum ESPRESSO Course for Solid-State Physics* (Jenny Stanford Publishing).
52. Hayes, W., and Loudon, R. (2004). *Scattering of Light by Crystals*. Dover Books on Physics Courier Corporation. ISBN 0-486-43866-X.
53. Giannozzi, P., Baroni, S., Bonini, N., Calandra, M., Car, R., Cavazzoni, C., Ceresoli, D., Chiarotti, G.L., Cococcioni, M., Dabo, I., et al. (2009). QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. *J. Phys. Condens. Matter* **21**, 395502.
54. Baroni, S., De Gironcoli, S., Dal Corso, A., and Giannozzi, P. (2001). Phonons and related crystal properties from density-functional perturbation theory. *Rev. Mod. Phys.* **73**, 515–562.
55. Mudd, G.W., Svatek, S.A., Ren, T., Patané, A., Makarovskiy, O., Eaves, L., Beton, P.H., Kovalyuk, Z.D., Lashkarev, G.V., Kudrynskiy, Z.R., and Dmitriev, A.I. (2013). Tuning the bandgap of exfoliated InSe nanosheets by quantum confinement. *Adv. Mater.* **25**, 5714–5718.
56. Hartwigsen, C., Gedecker, S., and Hutter, J. (1998). Relativistic separable dual-space Gaussian pseudopotentials from H to Rn. *Phys. Rev. B* **58**, 3641–3662.
57. Hung, N.T., Huang, J., Tatsumi, Y., Yang, T., and Saito, R. (2024). QERaman: An open-source program for calculating resonance Raman spectra based on Quantum ESPRESSO. *Comput. Phys. Commun.* **295**, 108967.
58. Saito, R., Hung, N.T., Yang, T., Huang, J., Liu, H.-L., Gulo, D.P., Han, S., and Tong, L. (2025). Deep-ultraviolet and helicity-dependent Raman spectroscopy for carbon nanotubes and 2D materials. *Small* **21**, 2308558.