Proximity control of interlayer exciton-phonon hybridization in van der Waals heterostructures

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Van der Waals stacking has provided unprecedented flexibility in shaping many-body interactions by controlling electronic quantum confinement and orbital overlap. Theory has predicted that also electron-phonon coupling critically influences the quantum ground state of low-dimensional systems. Here we introduce proximity-controlled strong-coupling between Coulomb correlations and lattice dynamics in neighbouring van der Waals materials, creating new electrically neutral hybrid eigenmodes. Specifically, we explore how the internal orbital 1s-2p transition of Coulomb-bound electron-hole pairs in monolayer tungsten diselenide resonantly hybridizes with lattice vibrations of a polar capping layer of gypsum, giving rise to exciton-phonon mixed eigenmodes, called excitonic Lyman polarons. Tuning orbital exciton resonances across the vibrational resonances, we observe distinct anticrossing and polarons with adjustable exciton and phonon compositions. Such proximity-induced hybridization can be further controlled by quantum designing the spatial wavefunction overlap of excitons and phonons, providing a promising new strategy to engineer novel ground states of two-dimensional systems.

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Here, we use 2D WSe$_2$/gypsum (CaSO$_4$·2H$_2$O) heterostructures as model systems to demonstrate proximity-induced hybridization between phonons and electrically neutral excitons up to the strong-coupling regime. We tune a Coulomb-mediated quantization energy—the internal 1$s$–2$p$ Lyman transition of excitons in WSe$_2$—in resonance with polar phonon modes in a gypsum cover layer (Fig. 1a) to create new hybrid excitations called Lyman polarons, which we directly resolve with phase-locked few-cycle mid-infrared (MIR) probe pulses. Engineering the spatial shape of the exciton wavefunction at the atomic scale allows us to manipulate the remarkably strong exciton–phonon coupling and to induce a crosstalk between energetically remote electronic and phononic modes.

Results

Rydberg spectroscopy of Lyman polarons. We fabricated three classes of heterostructures—a WSe$_2$ ML, a 3R-stacked WSe$_2$ bilayer (BL), and a WSe$_2$/WS$_2$ (tungsten disulphide) heterobilayer (see Supplementary Note 1)—by mechanical exfoliation and all-dry viscoelastic stamping (see “Methods”). All samples were covered with a mechanically exfoliated gypsum layer and transferred onto diamond substrates. Figure 1b shows an exemplary optical micrograph of the WSe$_2$ ML/gypsum heterostructure, where strong photoluminescence can be observed from the WSe$_2$ ML, attesting to the radiative recombination of 1$s$ A excitons.
The internal resonance between the orbital $\Delta_1$ change of the real part of the optical conductivity, nonequilibrium system (see "Methods"). These modes are spectrally close to the internal resonance between the orbital $1s$ and $2p$ states of excitons in WSe$_2$, and are, thus, ideal for exploring the polaron physics that arises from the proximity-induced exciton–phonon coupling at the van der Waals interface. If the coupling strength exceeds the linewidth of both modes one may even expect exciton–phonon hybridization as the excitonic Lyman transition is resonantly dressed by the spatially nearby phonon field (Fig. 1a). In this proximity-induced strong-coupling scenario, Lyman polarons would emerge as new eigenstates of mixed electronic and structural character.

In the experiment, we interrogate the actual spectrum of low-energy elementary excitations by a phase-locked MIR pulse. The transmitted waveform is electro-optically sampled at a variable delay time, $t_{pp}$, after resonant creation of $1s$ A excitons in the K valleys of WSe$_2$ by a $100$ fs near-infrared pump pulse (see "Methods"). A Fourier transform combined with a Fresnel analysis directly reveals the full dielectric response of the nonequilibrium system (see "Methods"). The pump-induced change of the real part of the optical conductivity, $\Delta\sigma_1$, and of the dielectric function, $\Delta\varepsilon_1$, describe the absorptive and inductive responses, respectively. The dielectric response of a photoexcited WSe$_2$ ML covered with hBN at $t_{pp} = 0$ ps (Fig. 2, gray spheres) is dominated by a maximum in $\Delta\sigma_1$ (Fig. 2a) and a corresponding zero crossing in $\Delta\varepsilon_1$ at a photon energy of $143$ meV (Fig. 2b). This resonance matches with the established internal $1s$–$2p$ Lyman transition in hBN-covered WSe$_2$ MLs and lies well below the $E_{1u}$ phonon mode in hBN ($\sim 172$ meV, see "Methods").

In marked contrast, $\Delta\sigma_1$ features a distinct mode splitting for the WSe$_2$/gypsum heterostructure (Fig. 2a, red spheres). The two peaks and corresponding dispersive sections in $\Delta\varepsilon_1$ (Fig. 2b, red spheres) are separated by $\sim 35$ meV and straddle the internal $1s$–$2p$ Lyman resonance of the WSe$_2$/hBN heterostructure. Interestingly, each peak is much narrower than the bare $1s$–$2p$ transition in the WSe$_2$/hBN heterostructure. Since the background dielectric constants (neglecting phonons) of gypsum and hBN are similar, the bare $1s$–$2p$ Lyman resonance in a gypsum-covered WSe$_2$ ML is expected to appear at an energy close to $143$ meV, which gives rise to only a small detuning ($\Delta E = 5$ meV) to the vibrational $\Delta_1$ mode in gypsum ($138$ meV). The prominent splitting of $\Delta\sigma_1$ of $\sim 35$ meV in the WSe$_2$/gypsum heterostructure clearly exceeds the detuning energy and, thus, implies that the two new resonances are indeed Lyman polarons caused by strong-coupling.

**Interlayer exciton–phonon hybridization.** Hybridization between the intra-excitonic resonance and a lattice phonon across the van der Waals interface should lead to a measurable anticrossing signature. To test this hypothesis, we perform similar experiments on the WSe$_2$ BL/gypsum heterostructure, where the intra-excitonic transition can be tuned through the phonon resonance. Strong interlayer orbital hybridization in the WSe$_2$ BL shifts the conduction band minimum from the K points to the $\Lambda$ points, leading to the formation of K–$\Lambda$ excitons ($\text{KX}^{-\Lambda}$) with wavefunctions delocalized over the top and bottom layer. Such interlayer orbital hybridization, which is also commonly observed in other 2D transition metal dichalcogenide (TMD) heterostructures, renders the internal $1s$–$2p$ Lyman transition more susceptible to many-body Coulomb renormalization than in a single ML. This offers a unique opportunity to tune the intra-excitonic resonance from $87$ to $69$ meV by merely increasing the excitation fluence from $5$ to $36$ $\mu$J $\text{cm}^{-2}$ (see Supplementary Note 2).

Figure 3a displays the MIR response of the WSe$_2$ BL/gypsum heterostructure at $t_{pp} = 3$ ps and various excitation densities. Strikingly, we observe a distinct anticrossing near the $1s$–$2p$ Lyman transition of K–$\Lambda$ excitons in the WSe$_2$ BL and the $\nu_4$ mode of gypsum upon increasing the excitation density. This is unequivocal evidence of hybridization of exciton and phonon modes across the atomic interface. In addition, the absorption for all excitation densities exhibits a discernible shoulder at a photon energy of $\sim 115$ meV (Fig. 3a, red arrow), which is very close to the $1s$–$2p$ resonance of K–K excitons ($\text{KX}^{-\Lambda}$). Such a transition is indeed expected to occur at short delay times $t_{pp} < 1$ ps, when the bound electron–hole pairs are prepared in the K valleys through direct interband excitation. However, the subtle interplay between 2D confinement and interlayer orbital overlap in the BL gives rise to a complex energy landscape, where the lowest-energy exciton state is given by K–$\Lambda$ species. Thus, subpicosecond thermalization of the electron to $\Lambda$ valleys via intervalley scattering should render the $1s$–$2p$ transition of K–K excitons weak. Yet, we clearly observe its spectral signature during the entire lifetime (see Supplementary Note 3). In addition, a new absorption band appears above the $\nu_5$ resonance of gypsum at an energy of $\sim 150$ meV (Fig. 3a, blue arrow). Its spectral position is nearly independent of the excitation density. We will show next that these surprising observations hallmark interlayer exciton–phonon hybridization involving as many as two phonon and two exciton resonances across the atomic interface, at once.

The dominant anticrossing feature in Fig. 3a occurs at an energy close to the $\nu_4$ mode of gypsum ($78$ meV) and the $1s$–$2p$ resonance of K–$\Lambda$ excitons in WSe$_2$ ($69$–$87$ meV, depending on the excitation fluence), while additional optical transitions emerge at energies close to the $\nu_5$ mode ($138$ meV) and the $1s$–$2p$ resonance of K–K excitons ($115$ meV). Therefore, we consider how the $1s$–$2p$ transition of K–$\Lambda$ and K–K excitons (see Supplementary Note 4) hybridize with $\nu_4$ and $\nu_5$ phonons in gypsum. The electron–phonon interaction is commonly described by the Fröhlich Hamiltonian, which is linear in the phonon creation and annihilation operators and couples only states
Fig. 3 Anticrossing in interlayer exciton-phonon quantum hybridization. a Experimentally observed pump-induced changes of $\Delta n_0$ ($\tau_{pp} = 3$ ps, $T = 260$ K) of a 3R-stacked WSe$_2$ bilayer covered with few-layer gypsum, for different excitation fluences $\Phi$ indicated on the right. When $\Phi$ is increased from 5 to 36 $\mu$J cm$^{-2}$ (from bottom to top), many-body renormalization shifts the intra-excitonic resonance $E_{1s-2p}$ from above to below the $\nu_4$ phonon resonance, unveiling exciton-phonon anticrossing. The red dashed lines are guides to the eyes for the peak position of $|\Psi_1\rangle$ and $|\Psi_2\rangle$. The excellent agreement between theoretical simulation (black dashed lines) and experimental data (solid spheres) across all $E_{1s-2p}$ confirms the interlayer exciton-phonon hybridization. b Two-dimensional plot of the simulated $\Delta n_0$ spectra based on the Hamiltonian shown in Eq. (1) as a function of $E_{1s-2p}$. The color scale, vertical axis, and horizontal axis represent $\Delta n_0$, $E_{1s-2p}$, and the probe photon energy, respectively. Dashed white lines indicate the energies of Lyman polaron eigenstates ($|\Psi_n\rangle$, $n = 1, 2, 3, 4$). c Illustration of the effective coupling between different excitonic states (black lines) and phonon states (gray lines). When the zero-phonon 1s-2p transition energy of the K–A exciton state $|2p^{\K-A}, 0\nu_4, 1s^{\K-A}, 0\nu_3\rangle$ is tuned across the $\nu_4$ state $|1s^{\K-A}, 1\nu_4, 1s^{\K-K}, 0\nu_3\rangle$ (denoted by the thick red arrow) anticrossing occurs. d, e Solid lines show the calculated energies of the Lyman polaron eigenstates (d) and projection ($P_n$) of the eigenstates to the bare $|2p^{\K-A}, 0\nu_4, 1s^{\K-K}, 0\nu_3\rangle$ state (e) as a function of $E_{1s-2p}$. The dashed lines in d show the energies of $|1s^{\K-A}, 0\nu_4, 2p^{\K-K}, 0\nu_3\rangle$ (115 meV), $|1s^{\K-A}, 1\nu_4, 1s^{\K-K}, 0\nu_3\rangle$ (78 meV) and $|1s^{\K-A}, 0\nu_4, 1s^{\K-K}, 1\nu_3\rangle$ (138 meV). The symbols in d, e correspond to $|\Psi_n\rangle$ and were obtained from fits to the measured $\Delta n_0$ spectra.

differing by one optical phonon$^{26}$. The energetically lowest excited states of the uncoupled system, in which only one of the two exciton species or one of the two phonons is excited, can be denoted as $|2p^{\K-A}, 0\nu_4, 1s^{\K-K}, 0\nu_3\rangle$, $|1s^{\K-A}, 1\nu_4, 1s^{\K-K}, 0\nu_3\rangle$, $|1s^{\K-A}, 0\nu_4, 2p^{\K-K}, 0\nu_3\rangle$, $|1s^{\K-A}, 0\nu_4, 1s^{\K-K}, 1\nu_3\rangle$. The coupling between different states is illustrated in Fig. 3c. Using these basis vectors, we derive an effective Hamiltonian

$$H_{el} = \begin{pmatrix} E_{1s-2p}^{K-A} & V_1 & 0 & V_2 \\ V_1 & E_{ph}^{4} & V_3 & 0 \\ 0 & V_3 & E_{1s-2p}^{n} & V_4 \\ V_2 & 0 & V_4 & E_{ph}^{4} \end{pmatrix}.$$  

Here, $E_{1s-2p}^{K-A}$ ($E_{1s-2p}^{n}$) and $E_{ph}^{4}$ ($E_{ph}^{n}$) denote the 1s-2p resonance energy of K–A (K–K) excitons and the energy of the $\nu_4$ ($\nu_3$) mode, respectively, whereas $V_1$, $V_2$, $V_3$, and $V_4$ describe the exciton–phonon coupling constants (Fig. 3c, red arrows). At exciton densities for which $E_{1s-2p}^{n}$ is tuned through $E_{ph}^{4}$, the Hamiltonian shows that the resonant exciton–phonon hybridization leads to an avoided crossing. Quantitative comparison between experiment and theory can be achieved by directly solving the effective Hamiltonian and yields four new hybrid states ($|\Psi_n\rangle$, $n = 1, 2, 3, 4$) that consist of a superposition of the basis modes.

Figure 3b displays a 2D map of the simulated optical conductivity of the new polaron eigenstates $|\Psi_n\rangle$ as a function of the probe energy ($\hbar\omega$) and the position of $E_{1s-2p}^{K-A}$. Since the excitons in WSe$_2$ are largely thermalized as K–A species on a sub-picosecond scale, the oscillator strength of the resulting polarons observed therefor depends on their projection $P_n = \langle\Psi_n|2p^{\K-A}, 0\nu_4, 1s^{\K-K}, 0\nu_3\rangle$ onto the bare zero-phonon K–A exciton (see Supplementary Note 3). To validate our model, we fit the simulated optical conductivity to the experimental data (Fig. 3a). Again, we set $E_{ph}^{4} = 78$ meV and $E_{ph}^{n} = 138$ meV (see Fig. 1d), and $E_{1s-2p}^{K-K} = 115 \pm 5$ meV (ref. 22), while $E_{1s-2p}^{K-A}$ and the oscillator strength of the 1s–2p transition of the K–A exciton serve as fit parameters. For oscillator strengths similar to published values in ref. 22, the numerical adaption yields excellent agreement between theory and experiment and reproduces all optical transitions (Fig. 3a) and the prominent anticrossing (Fig. 3d).

The coupling constants retrieved from fitting the model to the experimental data amount to $V_1 \approx V_2 = 20 \pm 2$ meV and $V_4 \approx V_3 = 31 \pm 2$ meV (see Supplementary Note 3), even exceeding values reported in quantum dots$^{22}$. This result is remarkable given that in our experiments strong-coupling is only achieved by proximity across the van der Waals interface. The ratio $V_2 / V_3 \approx V_1 / V_4 \approx \sqrt{2}$ qualitatively reflects the relative dipole moments of the $\nu_4$ and $\nu_3$ modes (see Supplementary Note 3). Our analysis also allows us to assign the high-frequency features in Fig. 3a to $|\Psi_1\rangle$ and $|\Psi_4\rangle$. Even when the K–K excitons are weakly populated at $\tau_{pp} = 3$ ps and the $\nu_3$ phonon resonance is far-detuned from the 1s–2p transition of K–A excitons, the strong-coupling scenario allows for these Lyman polarons to emerge. In addition, by increasing the excitation density, many-body Coulomb...
thereby modify the Lyman composition of \( \Delta \) (blue) heterostructure at 
\[ \Psi \]
Gray dotted lines indicate the spectral positions of ν compared to the WSe2 BL/gypsum heterostructure. a) Comparison to the WSe2 BL/gypsum heterostructure. For example, for WSe2 and WS2 depletes the Lyman resonance of Xintra, while between WSe2 and WS2 depletes the Lyman resonance of Xintra, while 
\[ \Psi, \]
Spatial distribution of the excitons in the WSe2/WS2/gypsum (left) and the spatial distribution of the excitons in the WSe2/WS2/gypsum (left) and 
\[ \Psi, \]
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Discussion
Our results reveal that even charge-neutral quasiparticles can interact with phonons across a van der Waals interface in the strong-coupling limit. Controlling excitonic wavefunctions at the atomic length scale can modify the coupling strength. We expect important implications for the study of polaron physics with charged and neutral excitations in a wide range of atomically thin strongly correlated electronic systems. In particular, polarons are known to play a crucial role in the formation of charge-density waves in Mott insulators and Cooper pairs in superconductors. Moreover, excitons in TMD heterostructures embody important properties arising from the valley degree of freedom and can be engineered from topologically protected edge states of moiré superlattices. In the future, it might, thus, even become possible to transfer fascinating aspects of chirality and nontrivial topology to polaron transport.

Methods
Sample preparation. All heterostructure compounds were exfoliated mechanically from a bulk single crystal using the viscoelastic transfer method. We used gypsum and hBN as dielectric cover layers. The vibrational νs and νp modes of the SO4 tetrahedral groups are close to the internal 1s–2p transition of excitons in WSe2. In contrast, the prominent 1s–2p mode in hBN at 172 meV is far-detuned from the internal 1s–2p exciton transition in the WSe2 layer. The exfoliated gypsum, hBN, and TMD layers were inspected under an optical microscope and subsequently stacked on top of each other on a diamond substrate with a micro-positioning stage. To remove any adsorbates, the samples were annealed at a temperature of 150 °C and a pressure of 1 × 10⁻5 mbar for 5 h. The twist angle of the WSe2 BL was ensured by the tear and stack method: Starting from an extremely large exfoliated monolayer, only half of it is transferred onto the substrate. Consequently, transferring the remaining part of the ML onto the diamond substrate yields a perfectly aligned WSe2 BL.

Ultrafast pump-probe spectroscopy. Supplementary Figure 6a depicts a schematic of the experimental setup. A home-built Ti:sapphire laser amplifier with a repetition rate of 400 kHz delivers ultrashort 12-fs NIR pulses. The output of the beam is divided into three branches. A first part of the laser output is filtered by a bandpass filter with a center wavelength closed to the longwave 1s A exciton transition in the WSe2 layer, and a bandwidth of 9 nm, resulting in 100-fs pulses. Another part of the laser pulse generates single-cycle MIR probe pulses via optical rectification in a GaSe or an LGS crystal (NOX1). The probe pulse propagates through the sample after a variable delay time \( t_{fp} \). The electric field waveform of the MIR transient and any changes induced by the nonequilibrium polarization of the sample are fully resolved by electro-optic sampling utilizing a second nonlinear material. The electric field waveform of the MIR probe transient as a function of the electro-optic sampling time \( t_{eo} \). The MIR probe pulse is centered at a frequency of 32 THz with a full-width at half-maximum of 18 THz (Supplementary Figure 6c, black curve) and a spectral phase that is nearly flat (Supplementary Figure 6c, blue curve). Using serial lock-in detection, we simultaneously record the pump-induced change \( \Delta E(\omega) \) and a reference \( E(\omega) \) of the MIR electric field as a function of \( t_{eo} \).

Extracting the dielectric response function. To extract the pump-induced change of the dielectric function of our samples with ultrafast NIR pump-MIR probe spectroscopy, we use serial lock-in detection. Hereby, a first lock-in amplifier records the

Shaping the interlayer exciton–phonon coupling strength. The interlayer exciton–phonon hybridization can be custom-tailored by engineering the spatial overlap of exciton and phonon wavefunctions on the atomic scale. To demonstrate this possibility, we create spatially well-defined intra- (X^\text{intra}) and interlayer exciton (X^\text{inter}) phases by interfacing the WSe2 ML with a WS2 ML in a WSe2/WS2/gypsum heterostructure. Unlike in the WSe2 BL/gypsum heterostructure, the interlayer excitons in WSe2 are now spatially separated from gypsum by the WS2 ML (Fig. 4a). Ultrafast charge separation at the interface between WSe2 and WS2 depletes the Lyman resonance of X^\text{intra}, while the transition of X^\text{inter} emerges on the sub-picosecond timescale. Figure 4b shows Δ\( \Psi \)_\( s \) of the WSe2/WS2/gypsum heterostructure at \( t_{fp} = 1 \) and 10 ps. The MIR response arising from exciton–phonon coupling is qualitatively similar to that observed in the WSe2 BL/gypsum heterostructure. This is partly because both the \( E_{\text{intra}}^{1s-2p} = 69 \) meV and interlayer \( E_{\text{intra}}^{1s-2p} = 114 \) meV 1s–2p resonances in the WSe2/WS2 heterostructure are similar to \( E_{\text{intra}}^{1s-2p} = 69 \)–87 meV, depending on the excitation fluence, and \( E_{\text{intra}}^{1s-2p} = 115 \) meV in the WSe2 BL, respectively. However, a direct comparison between Δ\( \Psi \)_\( s \) of both systems reveals a strong enhancement of the oscillator strength of the \( |\Psi_4\rangle \) mode and larger splitting between \( |\Psi_1\rangle \) and \( |\Psi_2\rangle \) in the WSe2/WS2/gypsum heterostructure (Fig. 4c). By fitting the experimental data with our coupling model, we found that the large oscillator strength of \( |\Psi_4\rangle \) arises from enhanced phonon coupling to X^\text{inter} of \( V_1 = 22 ± 2 \) meV and \( V_2 = 36 ± 2 \) meV, which may be related to the dipolar nature of interlayer excitons. Meanwhile, the interlayer exciton–phonon coupling strength, which results directly from X^\text{inter} confined in the WSe2 layer, amounts to \( V_3 = 16 ± 2 \) meV and \( V_4 = 25 ± 2 \) meV (see Supplementary Note 5). The reduction of coupling strength, \( V_3 \) and \( V_4 \), by at least 20% compared to the WSe2 BL/gypsum case can be attributed to the atomically small spatial separation of the WSe2 ML from gypsum, which illustrates how exciton–phonon interaction could be fine-tuned in search for new phases of matter.

**Fig. 4 MIR response of the WSe2/WS2/gypsum heterostructure and comparison to the WSe2 BL/gypsum heterostructure.** a) Schematic of the spatial distribution of the excitons in the WSe2/WS2/gypsum (left) and the WSe2 BL/gypsum (right) heterostructure. The relative distance of interlayer excitons (X^\text{intra} in the WSe2/WS2 heterostructure and X^\text{intra} in the WSe2 BL) to the vibrational modes in gypsum yields different coupling strength. b) Pump-induced change of the real part of the optical conductivity \( \Delta \sigma \) for different \( t_{fp} \) for a WSe2/WS2/gypsum heterostructure (\( T = 230 \) K). Green spheres: experimental data. Black dashed line: theoretical simulation. Gray dotted lines indicate the spectral positions of |\Psi_1\rangle. c) Comparison between \( \Delta \sigma \) of the WSe2/WS2/gypsum (green) and the WSe2 BL/gypsum (blue) heterostructure at \( t_{fp} = 10 \) ps. Spheres: experimental data. Shaded areas: theoretical simulation. Green and blue arrows indicate the positions of |\Psi_1\rangle and |\Psi_2\rangle.
electro-optic signal of our MIR probe field. Due to the modulation of the optical pump, the transmitted MIR probe field varies by the pump-induced change \( \Delta E_{\text{pp}}(t_\text{m}) \). This quantity is read out in a second lock-in amplifier at the modulation frequency of the pump. Simultaneously, the electro-optic signal is averaged in an analog low-pass to obtain a reference signal \( E_{\text{eos}}(t_\text{m}) = \frac{1}{2}(E_{\text{pp}}(t_\text{m}, t_\text{pp}) + E_{\text{pp}}(t_\text{m}, -t_\text{pp})) \), where \( E_{\text{eos}}(t_\text{m}) \) is the signal after transmission through the sample in thermal equilibrium and \( E_{\text{pp}}(t_\text{m}, t_\text{pp}) = E_{\text{pp}}(t_\text{m}) + \Delta E_{\text{pp}}(t_\text{m}, t_\text{pp}) \) is the signal after transmission through the excited sample at \( t_\text{pp} \). From these quantities \( E_{\text{eos}}(t_\text{m}) \) and \( E_{\text{pp}}(t_\text{m}) \) are directly extracted. Subsequently, a Fourier transform for a fixed \( t_\text{pp} \) yields \( E_{\text{eos}}(\omega, t_\text{pp}) \) and \( E_{\text{pp}}(\omega, t_\text{pp}) \), which in turn provides us with the complex-valued field transfer coefficient of our layered structure

\[
T_{\text{pp}}(\omega, t_\text{pp}) = T_{\text{eos}}(\omega, t_\text{pp}) T_{\text{pp}}(\omega) = \frac{E_{\text{eos}}(\omega, t_\text{pp})}{E_{\text{eos}}(\omega)} T_{\text{pp}}(\omega),
\]

where \( T_{\text{eos}}(\omega) \) is the equilibrium field transmission coefficient and \( T_{\text{pp}}(\omega, t_\text{pp}) \) denotes the pump-induced change thereof. These quantities are completely defined by the equilibrium dielectric function \( \varepsilon(\omega) \) and its pump-induced change \( \Delta \varepsilon(\omega, t_\text{pp}) \). By using the established optical transfer-matrix formalism\(^{14} \), we express the experimentally measured \( T_{\text{eos}}(\omega, t_\text{pp}) \) with the dielectric function. Finally, we insert the known equilibrium dielectric function and numerically invert the optical transfer-matrix formalism to extract the coveted quantity \( \Delta \varepsilon(\omega, t_\text{pp}) \) discussed in the main text. Owing to the extremely thin sample thickness, challenges associated with Fabry–Perot resonances are unproblematic here and the inversion algorithm is especially stable and quantitatively reliable.

Data availability

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request to give guidance to the interested party.

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Author contributions

The study was conceived by P.M., C.-K.Y., and R.H. and supervised by C.-K.Y., E.M., and I.H. The study was supervised by C.-K.Y. and R.H. and requests for materials should be addressed to C.-K.Y. or R.H.

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Competing interests

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