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Article

Keywords: Exciton–phonon coupling (EXPC), MoSe₂, two-dimensional (2D) micro-spectroscopy

Posted Date: September 3rd, 2020

DOI: <https://doi.org/10.21203/rs.3.rs-68032/v1>

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Version of Record: A version of this preprint was published at Nature Communications on February 11th, 2021. See the published version at <https://doi.org/10.1038/s41467-021-20895-0>.

Exciton–phonon coupling strength in single-layer MoSe₂ at room temperature

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Single-layer transition metal dichalcogenides (1L-TMDs) are at the center of an ever increasing research effort both in terms of fundamental physics and applications. Exciton–phonon coupling (EXPC) plays a key role in determining the photonic and (opto)electronic properties of 1L-TMDs. However, the EXPC strength has not been measured at room temperature. Here, we develop two-dimensional (2D) micro-spectroscopy to determine EXPC of 1L-MoSe₂. We detect beating signals as a function of waiting time T , induced by

1 **the coupling between the A exciton and the A₁ optical phonon. Analysis of 2D beating**
2 **maps provides the EXPC with the help of simulations. The Huang–Rhys factor of ~1 is larger**
3 **than in most other inorganic semiconductor nanostructures. Our technique offers a unique**
4 **tool to measure EXPC also in other 1L-TMDs and heterogeneous semiconducting systems**
5 **with a spatial resolution ~260 nm, and will provide design-relevant parameters for the**
6 **development of novel optoelectronic devices.**

7 Layered materials (LMs)^{1–4}, such as single-layer (1L) transition metal dichalcogenides (1L-
8 TMDs)^{5–8}, are a promising platform for new photonic and optoelectronic devices. Bulk
9 semiconducting TMDs consist of covalently bound layers of the type MX₂, where M is a
10 metal (e.g., Mo, W) and X is a chalcogen atom (e.g., S, Se), held together by van der Waals
11 interactions³. When they are exfoliated or grown as 1L, quantum confinement induces an
12 indirect-to-direct bandgap transition^{5,6}. The reduced dimensionality is also responsible for
13 high exciton binding energies (hundreds of meV)^{7,8}, making 1L-TMDs excellent candidates
14 for optoelectronic devices at room temperature (RT)².

15 Exciton–phonon coupling (EXPC) plays a key role in determining the T-dependent
16 optoelectronic and transport properties of 1L-TMDs^{9–11}. It is responsible for, e.g., non-
17 radiative exciton decay^{9,10,12}, limiting the fluorescence quantum yield¹³, the formation of dark-
18 exciton phonon replicas¹⁴, and it mediates spin-flip processes, thus decreasing the lifetime of
19 spin/valley-polarized charge carriers¹⁵. For T<100 K, the interaction between excitons and
20 acoustic phonons induces linewidth broadening and dominates the excitonic resonance of 1L-
21 TMDs^{9,16,17}. While this interaction is well understood, the situation is different for higher T.
22 Ref. 18 suggested that the coupling between excitons and optical phonons induces sidebands
23 in the absorption spectrum of 1L-MoSe₂ at RT. Yet the spectral signature of this coupling is
24 obscured by inhomogeneous broadening¹⁸. The presence of EXPC was inferred from
25 resonance Raman scattering^{19,20} as well as time-resolved transmission measurements^{21,22},

1 where the A_1' optical phonon mode was observed to couple with the A excitonic resonance.
2 While the energetic position of excitons can be obtained from photoluminescence and the
3 energetic position of (ground-state) phonons from Raman measurements, this does not fully
4 characterize the system. For obtaining the complete Hamiltonian, one also requires the
5 displacement along the phonon coordinate of the exciton-state potential energy minimum
6 versus the ground state. This displacement is the EXPC strength, as further detailed below,
7 that determines how strongly phonons will be excited upon an optical transition to the exciton
8 state. To the best of our knowledge, the EXPC strength has never been determined for any
9 1L-TMD at room temperature, because overtone bands of the optical phonon mode were not
10 detectable^{19–22}, and thus the optical characterization of this (and similar) material(s) is
11 incomplete. We determine the missing quantity in the present work.

12 Optical four-wave-mixing experiments in semiconductors provide access to coherent
13 dynamics of excitons^{23–25,10}. In photon echo experiments the polarization state of incident
14 photons (circular or linear) allows one to uncover different mechanisms behind the signal
15 formation^{26,27}. Different level schemes can be distinguished by the polarization dependence²⁷.
16 Two-dimensional electronic spectroscopy (2DES) is a powerful tool to analyze light-induced
17 coherences in molecular systems^{28–31} and semiconductors^{32,33}. It is a generalized version of
18 transient absorption spectroscopy, providing frequency resolution not only for the probe step,
19 but also for the pump^{34–38}. Coherent broadband excitation of several quantum energy levels
20 leads to wave packets that may be detected as oscillations of specific peaks in the 2D maps as
21 a function of waiting time T ^{29,39}. Analysis of frequency, decay time, and the position of such
22 oscillations allows one to explore the underlying energy structure and the coupling
23 mechanism leading to level splittings^{29,39,40}.

24 It is challenging to apply 2DES on micro-scale samples or heterogeneous materials with
25 localized structural domains on a μm lateral scale, because the standard phase-matching
26 geometry requires the exciting beams to be non-collinear with respect to each other³⁶. This

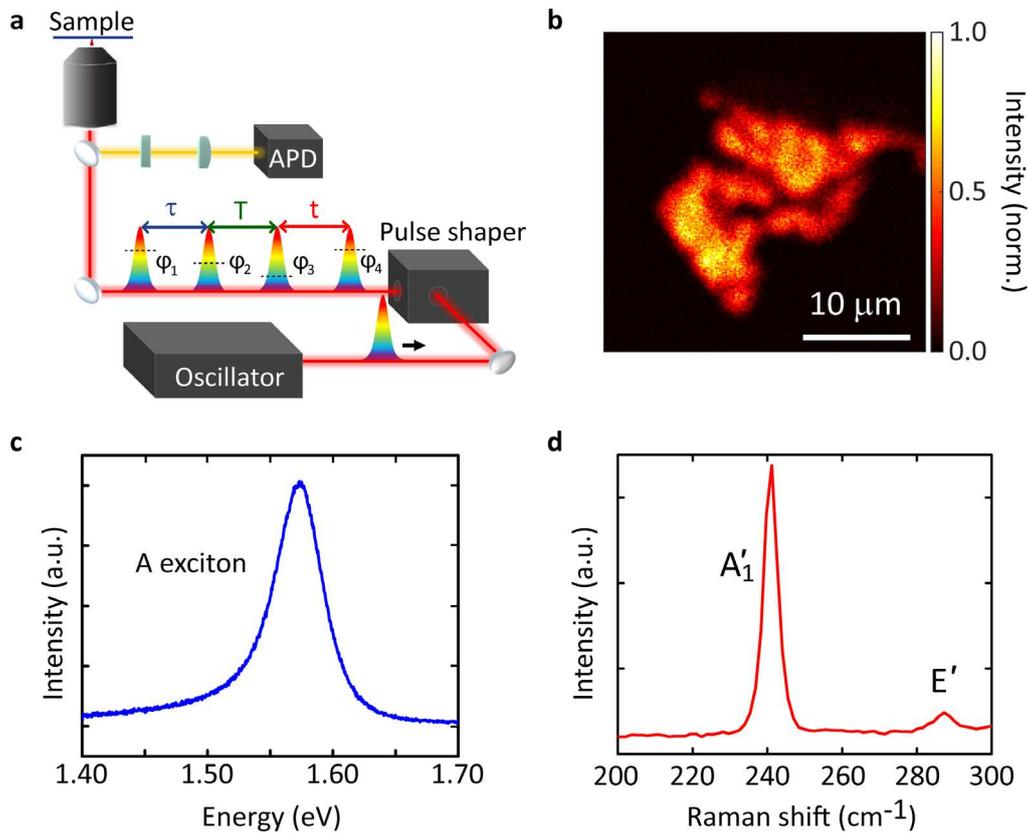
1 cannot be realized simultaneously when focusing with a high-numerical-aperture (high-NA)
2 objective, in which all incident light arrives from the same solid angle at the sample. As a
3 result, if one chooses to employ phase matching, this necessarily requires longer focal lengths,
4 leading to larger spot sizes and unwanted averaging over different spatial regions or crystal
5 orientations⁴¹. Instead, one can also select the signal by phase cycling^{42–44}, which relies on
6 detecting population-based signals as a function of inter-pulse phase combinations^{42,44,45}. The
7 collinear geometry accessible with phase cycling enables 2D micro-spectroscopy, i.e., the
8 combination of 2DES with fluorescence microscopy, to gain additional spatial resolution^{41,46}.

9 Here, we develop 2D micro-spectroscopy to resolve the spectral features of the phonon
10 sidebands in 1L-MoSe₂ at RT and determine the EXPC. We observe oscillations in 2D maps
11 that arise from the coupling between the A₁ optical phonon mode and the A exciton. From
12 comparison with simulated 2D beating maps, we deduce a Huang–Rhys factor, $S \sim 1$. This
13 implies a large EXPC strength for 1L-MoSe₂, when compared with other inorganic
14 semiconductor nanostructures, such as CdSe quantum dots⁴⁷ and rods⁴⁸, ZnSe quantum dots⁴⁹,
15 single-wall carbon nanotubes⁵⁰, etc., most of which fall in the range of 0–0.5 [51], providing
16 design-relevant information for the development of photonic devices based on 1L-MoSe₂. Our
17 method can be extended to other 1L-TMDs and materials and, additionally, also to other
18 important semiconducting systems, for which the ~ 260 -nm spatial resolution of the 2D micro-
19 spectroscopy is required, e.g., single-wall carbon nanotubes, van-der-Waals heterostructures
20 of layered materials, layered perovskites, bulk heterojunctions, or microcavities with
21 embedded semiconductors.

22 **Results and discussion**

23 The experimental setup is sketched in Fig. 1a. A Ti:sapphire oscillator emits 12-fs pulses
24 at 80 MHz repetition rate. A pulse shaper generates a collinear four-pulse sequence, focused
25 by a high-NA objective (NA = 1.4), so that a spatial resolution ~ 260 nm is achieved. To image

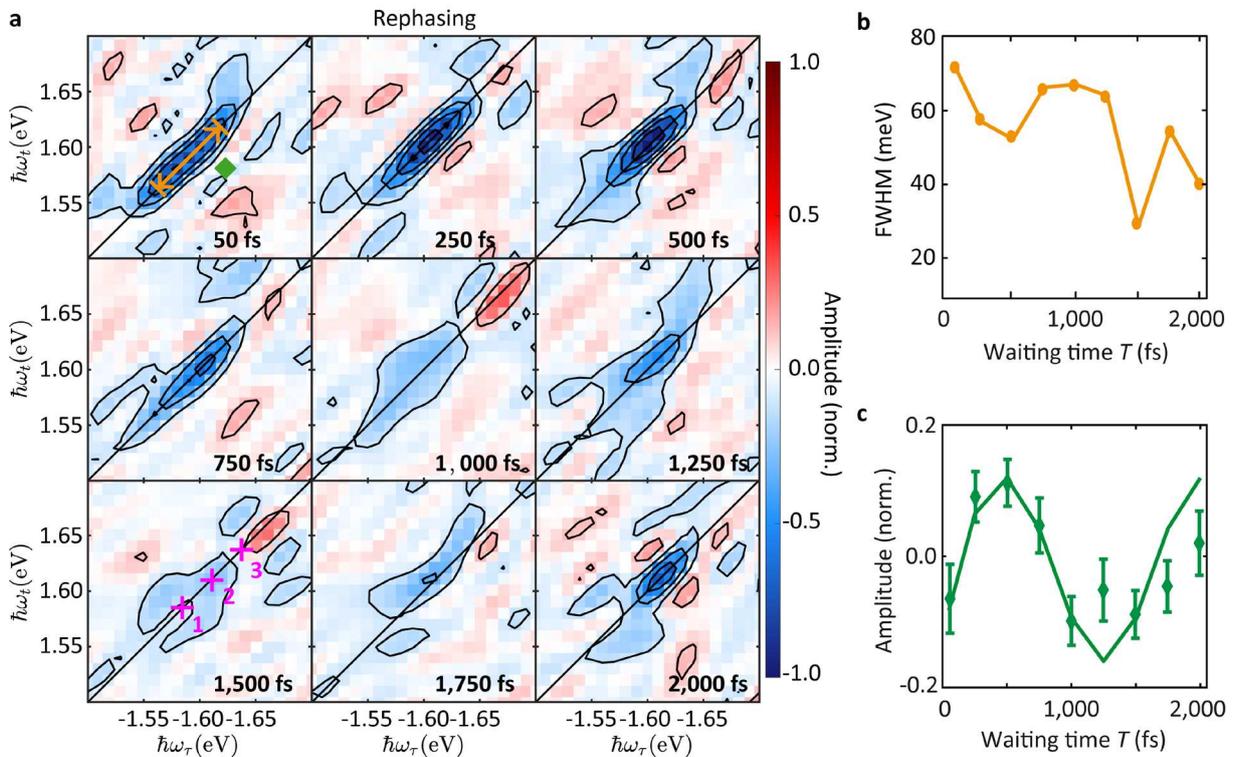
1 the sample, the laser focus is mapped by a piezo scanning stage, and the photoluminescence
 2 (PL) signal is detected by an avalanche photodiode (APD). For the 2D map, the PL intensity
 3 is detected while scanning a first coherence time τ (delay between the first two pulses), a
 4 waiting time T (delay between the second and the third pulses), and a second coherence time t
 5 (delay between the third and the fourth pulses, Fig. 1a). Fourier transformation over τ and t
 6 results in a 2D map for every T (see Methods for data acquisition details). Nonlinear signals
 7 are obtained by systematically scanning through a number of discrete phase steps for each
 8 pulse and for each pulse-delay combination, and rephasing and nonrephasing signals are
 9 retrieved as linear superpositions of differently phase-modulated data⁴⁴.



10

11 **Figure 1 | Overview of setup and the sample.** **a**, Fluorescence-detected 2D micro-spectroscopy setup.
 12 Four collinear laser pulses are generated by a pulse shaper with controllable inter-pulse time delays (τ , T , t)
 13 and phases (ϕ_i , $i = 1, 2, 3, 4$) and focused by a high-NA objective (Obj). The position of the sample is
 14 controlled by a piezo scanning stage (PSS). The PL signal is detected by an avalanche photodiode (APD). **b**,
 15 PL map obtained with the setup of panel **a**. **c**, PL and **d**, Raman spectrum for 514 nm excitation.

1 We investigate mechanically exfoliated 1L-MoSe₂ on a 200 μm fused silica substrate (see
 2 Methods for details). Figure 1b is a PL map, taken with the setup of Fig. 1a, for a
 3 representative sample. 1L-MoSe₂ has a direct bandgap at the K point of the Brillouin zone
 4 leading to two excitonic transitions A and B ~1.57 and 1.75 eV⁵². The PL spectrum (Fig. 1c)
 5 shows a single peak ~1.57 eV, due to the radiative recombination of A excitons⁵³. The Raman
 6 spectrum measured at 514 nm (Fig. 1d) shows the out-of-plane A₁ mode ~241 cm⁻¹ with full
 7 width at half maximum (FWHM) ~4 cm⁻¹, and the in-plane E' mode ~288 cm⁻¹ (FWHM ~6
 8 cm⁻¹). Both PL and Raman spectra confirm that the sample is 1L-MoSe₂^{53,19}.



9 **Figure 2 | Beating signal in the rephasing 2D maps. a**, Rephasing 2D maps at different T , normalized to
 10 the maximum absolute value of the real part of the map at $T = 500$ fs. **b**, Diagonal linewidth (indicated by
 11 the orange double arrow at $T = 50$ fs in panel a) versus T . **c**, Amplitude evolution (green diamonds) of one
 12 pixel (marked by the green diamond at $T = 50$ fs in panel a) and fit (solid green curve). The error bars are
 13 evaluated by calculating the fluctuations within a region containing background noise (Supplementary
 14 Note 4).
 15

1 The rephasing 2D maps in the region around the A exciton are shown in Fig. 2a for
2 various T , while the nonrephasing and absorptive 2D maps are in Supplementary Figs. 1 and 5,
3 respectively. The peak linewidth along the diagonal direction of the rephasing map (orange
4 double arrow in upper left panel) is plotted versus T in Fig. 2b. Closer analysis of the
5 systematic variation of this linewidth with T (Supplementary Note 2) indicates that there are 3
6 components along the diagonal, marked with purple crosses in the lower left panel of Fig. 2a,
7 whose amplitudes oscillate, but not in phase. Thus, when $T \sim 1,500$ fs, the amplitude of the
8 middle component is much higher than the other two, minimizing the effective diagonal
9 linewidth (minimum in Fig. 2b). The measured 2D maps capture the fourth-order nonlinear
10 optical response, as sixth-order contributions are negligible (Supplementary Note 3).

11 We then extract the amplitude evolution of an exemplary pixel (marked by the green
12 diamond in the 2D map at 50 fs) as a function of T (Fig. 2c). The number of points is
13 restricted due to the long measurement time (26 h for one point). A long-lived (>2 ps)
14 oscillation with amplitude above the noise level is observed. The reproducibility of the data is
15 confirmed by a second measurement for the same T in Supplementary Note 4.

16 We now analyze the origin of the oscillations in the 2D maps with the goal to deduce the
17 EXPC strength. Previous experiments reported that the trion signal in 1L-MoSe₂, located
18 ~ 0.03 eV below the neutral exciton peak⁵⁴, gradually dies out both in PL and absorption when
19 T increases from 15 to 295 K^{25,54}. The electronic coupling between excitons and trions,
20 observed at 20 K in Ref. 32, shows a dephasing time ~ 250 fs. Thus, wave packets involving
21 trions can be excluded as a source of the long-lived (>2 ps) RT oscillations in Fig. 2c.
22 Vibrational wave packets were reported at RT in Ref. 21,22, with a dephasing time ~ 4.5 ps
23 for 1L- and few-layer WSe₂²¹ and ~ 1.7 ps for 1L-MoS₂²². Therefore, EXPC can explain the
24 oscillations in our 2D maps. We extract the phonon energy from a fit (Fig. 2c, solid green
25 curve) and obtain, even for our undersampled (less than one data point for each oscillation

1 period as a result of a compromise arising from finite available data acquisition time) data, an
 2 oscillation period $\sim 136 \pm 2$ fs (see Supplementary Note 5 for the fitting procedure). This
 3 corresponds to an energy splitting between the participating states $\sim 30.4 \pm 0.4$ meV, matching
 4 the optical A'_1 phonon mode's energy ~ 29.9 meV, i.e., 241 cm^{-1} , as measured in the Raman
 5 spectrum of Fig. 1d.

6 We define the EXPC strength using the Franck–Condon coupling model⁵⁵, with the
 7 minimum number of states needed to describe the observed data (Fig. 3a). We consider an
 8 electronic (or excitonic) ground state $|g\rangle$ and an electronic (or excitonic) first excited state $|e\rangle$.
 9 Using a harmonic oscillator to approximate the dependence of potential energy on a
 10 vibrational (phonon) dimensionless coordinate q with the ground-state minimum at $q = 0$ [55]:

$$11 \quad V_g(q) = \frac{\hbar\omega}{2} q^2, \quad (1)$$

12 the potential curvature leads to a vibrational level spacing of $\hbar\omega$, where ω is the phonon
 13 angular frequency, creating sublevels $|g_i\rangle$, $i = 0, 1, 2, \dots$. For full information on the system,
 14 we also need to describe the excited-state potential⁵⁵,

$$15 \quad V_e(q) = \hbar\omega_{eg} + \frac{\hbar\omega}{2} (q + d)^2, \quad (2)$$

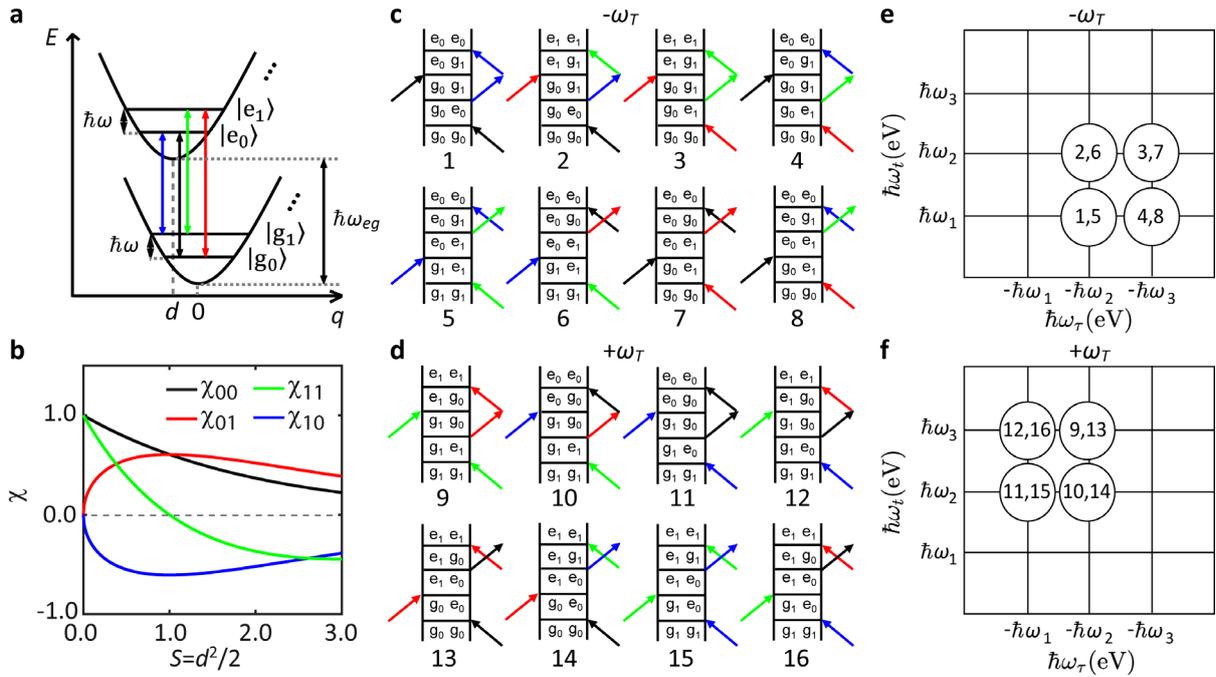
16 in which we assume, for simplicity, the same curvature, thus the same $\hbar\omega$ as in the ground
 17 state, a (vertical) energy difference $\hbar\omega_{eg}$, and a (horizontal) shift along the dimensionless
 18 phonon coordinate, d , between the two potential minima. This generates sublevels $|e_i\rangle$, $i = 0,$
 19 $1, 2, \dots$. Substituting Eq. 1 into Eq. 2 leads to:

$$20 \quad V_e = \hbar\omega_{eg} + V_g + \hbar\omega S + \hbar\omega q d, \quad (3)$$

21 where $\hbar\omega S$ is the reorganization energy.

22 The model of Fig. 3a delivers 3 transition energies, as observed experimentally (purple
 23 crosses in Fig. 2a): We assign component 1 (with the lowest energy $\hbar\omega_1$) to the transition

1 between $|g_1\rangle$ and $|e_0\rangle$ (blue color in Fig. 3), component 2 (with a higher energy $\hbar\omega_2$) to the
 2 two degenerate transitions between $|g_0\rangle$ and $|e_0\rangle$ and between $|g_1\rangle$ and $|e_1\rangle$ (black and green
 3 colors, respectively), and component 3 (with the highest energy $\hbar\omega_3$) to the transition
 4 between $|g_0\rangle$ and $|e_1\rangle$ (red color).



5
 6 **Figure 3 | Analysis of beating signals.** **a**, Schematic diagram of displaced harmonic oscillators (Franck–
 7 Condon coupling model⁵⁵) with two vibrational levels in the electronic ground state and two in the
 8 electronic excited state. **b**, Dependencies of Franck–Condon amplitudes χ_{ij} ($i, j = 0$ or 1) on S . **c,d**, Feynman
 9 pathways giving rise to the beating signals with (c) negative beating frequency $-\omega_T$ and (d) positive
 10 frequency $+\omega_T$. **e**, Beating-map locations of numbered Feynman pathways from panel c. **f**, Beating-map
 11 locations of numbered Feynman pathways from panel d. Transitions $|g_0\rangle\text{--}|e_0\rangle$, $|g_0\rangle\text{--}|e_1\rangle$, $|g_1\rangle\text{--}|e_0\rangle$, and
 12 $|g_1\rangle\text{--}|e_1\rangle$ are color-coded in black, red, blue, and green, respectively, for panels a–d.

13 Transitions between $|g_0\rangle$ and $|e_{i\geq 2}\rangle$ states are not observed in the 2D maps. This agrees
 14 with resonance Raman scattering^{19,20} and their time-domain analogues^{21,22}, where the A'_1
 15 overtone was not detected. This may imply an efficient nonradiative decay channel for the
 16 $|e_2\rangle$ state, which results in a fast dephasing time for the hot vibronic band transitions.
 17 Transitions between $|g_{i\geq 2}\rangle$ and $|e_0\rangle$ are also not observed in the 2D maps, which can be

1 explained as a negligible thermal population of $|g_{i \geq 2}\rangle$ due to a small Boltzmann factor at RT.
 2 The transition amplitudes between different vibronic sublevels (blue, black, green, and red
 3 arrows in Fig. 3a) are proportional to the overlap of the vibrational wave functions of initial
 4 and final state, i.e., the Franck–Condon amplitudes χ [56], plotted as a function of S in Fig. 3b.
 5 At $S = 0$, the red and blue curves are zero, indicating that it is not possible to excite $|e_1\rangle$
 6 starting from $|g_0\rangle$ or to reach $|g_1\rangle$ from $|e_0\rangle$, thus the electronic/excitonic excitation is
 7 decoupled from vibrations.

8 We now correlate S with the oscillatory signals. We perform an additional Fourier
 9 transformation of 2D maps with respect to T . This gives rise to a three-dimensional (3D)
 10 spectrum, which is a hypercube as a function of $\hbar\omega_\tau$, $\hbar\omega_T$ and $\hbar\omega_l$.

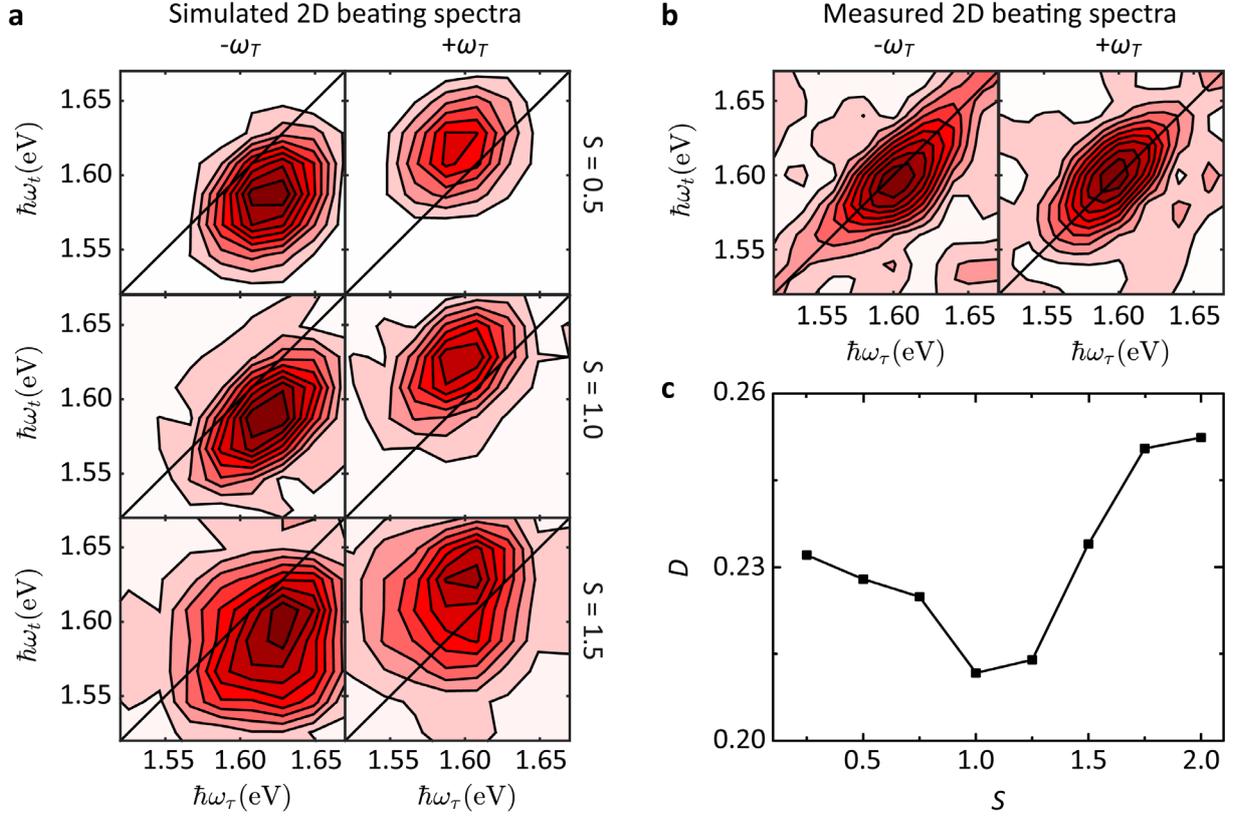
11 Figure 3c lists all possible rephasing Feynman pathways that can result in contributions at
 12 negative beating frequency $-\omega_T$. Their individual positions in the 2D beating maps are in Fig.
 13 3e. Figure 3d contains the contributions at positive ω_T , and Fig. 3f their positions in the 2D
 14 map. The peak position along the (horizontally displayed) $\hbar\omega_\tau$ excitation energy axis can be
 15 found by evaluating the energy difference between the states of the coherence created after
 16 the first light-field interaction. E.g., considering pathway 1, the first coherence created (and
 17 evolving with τ) is $|g_0\rangle\langle e_0|$. According to Fig. 3a (black arrow), this is located at the
 18 intermediate of the three possible transition energies for the excitation, i.e., at $\hbar\omega_2$, where the
 19 minus sign in Fig. 3e arises from the definition of sign of the frequency of a coherent state (a
 20 coherent state $|X\rangle\langle Y|$ has positive frequency when level $|X\rangle$ is higher in energy than level $|Y\rangle$
 21 and negative frequency if level $|X\rangle$ is lower than $|Y\rangle$, see Supplementary Note 1). Likewise,
 22 the coherence after the third interaction (and evolving with t) is $|e_0\rangle\langle g_1|$, at the lowest of the 3
 23 transition energies $\hbar\omega_1$ for the detection, according to the blue arrow in Fig. 3a with positive
 24 sign because $|e_0\rangle$ is higher than $|g_1\rangle$. All other peaks are assigned in a similar way, so that the
 25 displayed pattern emerges.

1 Adding all pathways, we expect the beating map to be located on the lower right of the
 2 diagonal for negative beating frequency (Fig. 3e), and on the upper left for positive (Fig. 3f).
 3 The precise shape of the overall beating map depends on the relative amplitudes of the
 4 individual Feynman pathways. Those depend on the initial populations of $|g_0\rangle$ and $|g_1\rangle$, hence
 5 on the sample temperature, and on the products of the Franck–Condon amplitudes of the 4
 6 involved transitions (colored arrows in Figs. 3c,d) that in turn depend on S (Fig. 3b). Thus,
 7 analyzing the shape of the beating maps allows us to estimate S .

8 For a quantitative evaluation, we simulate the 2D beating maps by numerically solving a
 9 Lindblad master equation⁵⁷ for a system described by the Franck–Condon model illustrated in
 10 Fig. 3a (see Methods for details). S is varied from 0.25 to 2 with a step size of 0.25. Fig. 4a
 11 plots the simulation for $S = 0.5, 1, \text{ and } 1.5$ from top to bottom. Data for other S are in
 12 Supplementary Fig. 13. We recognize the expected features of Figs. 3e,f. The pathway
 13 contributions overlap with each other, due to line broadening along the diagonal and anti-
 14 diagonal directions. For $S = 1.5$, the 4 underlying subpeaks create a square lineshape. For
 15 smaller S , the anti-diagonal linewidth changes strongly because of the varying relative
 16 contributions of the different Feynman pathways, leading to one asymmetric peak in each 2D
 17 beating map, whose center is located below (above) the diagonal line for negative (positive)
 18 beating frequency as predicted in Fig. 3e (Fig. 3f). The change in linewidth can be understood
 19 by considering that χ_{11} (Fig. 3b, solid green curve) crosses zero (the dashed gray line) for $S =$
 20 1, such that only Feynman pathways 1, 7, 11, 13, e.g., without $|g_1\rangle \rightarrow |e_1\rangle$ transition (green
 21 arrow in Figs. 3c,d), contribute. Therefore, the anti-diagonal linewidth reaches a minimum for
 22 $S = 1$.

23 Fig. 4b shows the experimental 2D beating maps at $-\omega_T$ (left) and $+\omega_T$ (right), obtained as
 24 cuts through the rephasing 3D spectrum at the same beating frequency as in the simulations,
 25 $\omega_T = 4.6 \times 10^{13} \text{ s}^{-1}$. The asymmetry with respect to the diagonal is visible, and the elliptical

- 1 shape [rather than roundish (small S) or squarish (large S)] points at an intermediate S by
- 2 comparison with simulations.



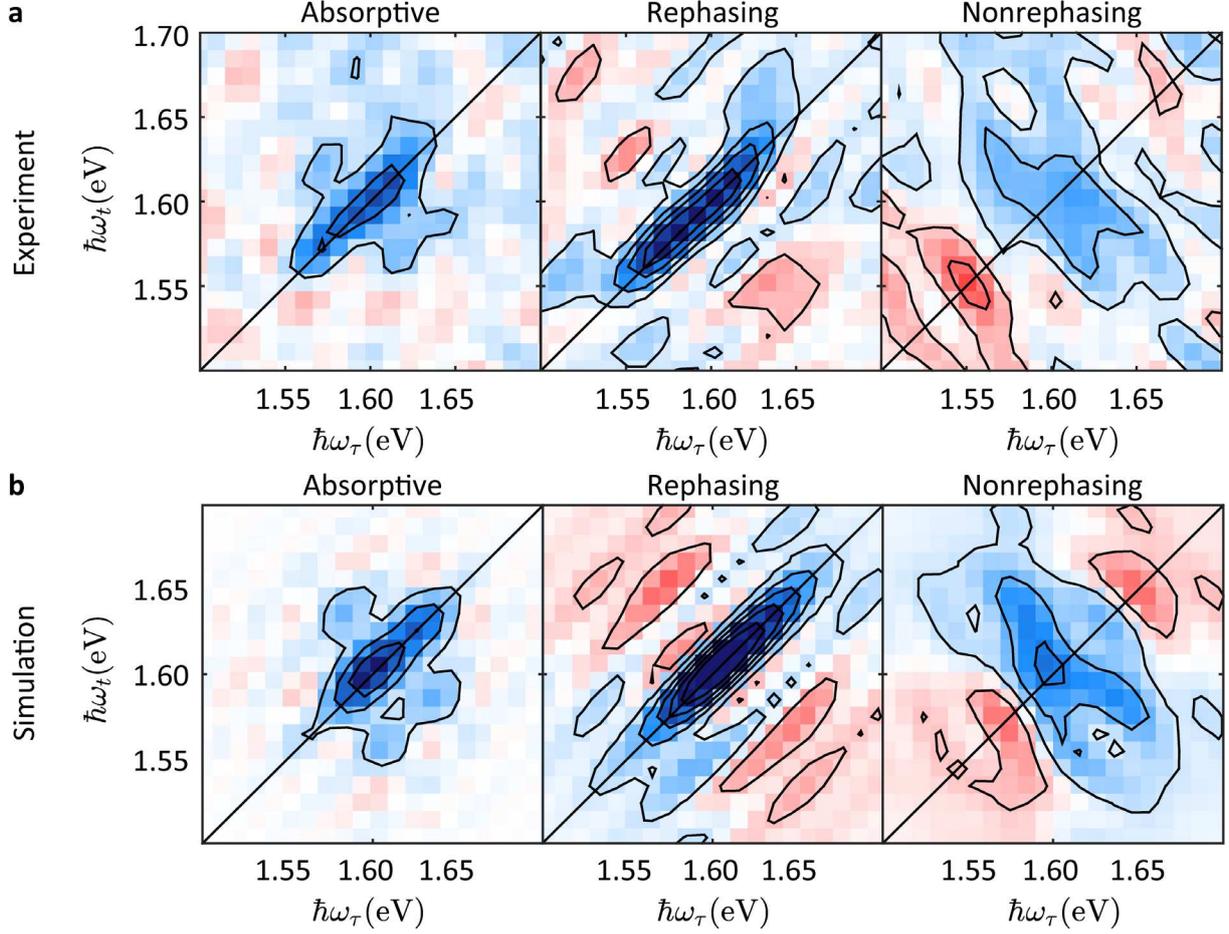
3
4 **Figure 4 | 2D beating maps.** **a**, Simulated 2D beating maps for $-\omega_T$ (left) and $+\omega_T$ (right) and $S = 0.5, 1, 1.5$
5 from top to bottom rows). **b**, Measured 2D beating maps with $-\omega_T$ (left) and $+\omega_T$ (right). **c**, The deviation,
6 D , between measured and simulated 2D beating maps versus S used in the simulation.

7 To determine the EXPC strength quantitatively, we calculate the deviation D between
8 measured and simulated 2D beating maps:

$$9 \quad D = \sqrt{\frac{1}{N^2} \sum_{i=1}^N \sum_{j=1}^N (A_{ij} - \tilde{A}_{ij})^2}, \quad (4)$$

10 where N is the pixel number in each dimension of the 2D beating maps, A_{ij} (\tilde{A}_{ij}) is the
11 amplitude of the pixel in column i and row j of the simulated (experimental) 2D beating map.
12 Figure 4c plots D versus S . We find the best agreement for $S = 1$. We then compare the
13 experimental regular absorptive, rephasing, and nonrephasing 2D maps for $T = 50$ fs (Fig. 5a)

1 with the simulation using the optimal S (Fig. 5b) and find good agreement, confirming the
 2 reliability of our Franck–Condon model.



3
 4 **Figure 5 | Absorptive (left), rephasing (middle), and nonrephasing (right) real-valued 2D maps at $T = 50$**
 5 **fs. a, Experiment. b, Simulation using the deduced optimal $S = 1$.**

6 Conclusion

7 We carried out spatially resolved, fluorescence-detected 2D micro-spectroscopy on 1L-
 8 MoSe₂. We identified phonon sidebands upon excitation of the A exciton, due to coupling to
 9 the optical phonon mode A₁'. While the phonon is not resolved in linear absorption or PL
 10 spectra at room temperature, analysis of the 2D beating frequency as a function of waiting
 11 time allowed us to assign the phonon mode via comparison with Raman data. We determined
 12 the exciton–phonon coupling strength, i.e., the displacement along the phonon coordinate of
 13 the excited-exciton oscillator potential with respect to the ground state, and found a Huang–

1 Rhys factor, $S \sim 1$, by comparison with simulations of 2D beating maps. The measured $S \sim 1$ is
2 larger than most reported values ($S \sim 0-0.5$) of other inorganic semiconductor nanostructures⁵¹,
3 such as CdSe quantum dots⁴⁷ and rods⁴⁸, ZnSe quantum dots⁴⁹, single-wall carbon
4 nanotubes⁵⁰, etc., indicating a strong EXPC. This finding may benefit, among others, the
5 development of TMD-based polariton devices⁵⁸, in which the polariton-relaxation process
6 strongly depends on the EXPC strength⁵⁹.

7 Our space-, time-, and excitation/detection-frequency-resolved spectroscopy provides a
8 unique tool to measure EXPC strength also in other layered TMDs, and can be extended to
9 other semiconducting systems for which phonon-induced subbands are expected in the
10 excitonic lineshape, such as single-wall carbon nanotubes⁶⁰, layered perovskites⁶¹, bulk
11 heterojunctions⁶², or other organic crystals. Because of the high spatial resolution of ~ 260 nm,
12 our technique can also be used to study excitonic coupling in layered materials
13 heterostructures or microcavities with embedded semiconductors. The determination of EXPC
14 will provide design-relevant parameters for the development of photonic and optoelectronic
15 devices based on these semiconducting systems.

16 **Methods**

17 **Samples fabrication.** The samples are prepared by micromechanical cleavage⁶³ of bulk
18 MoSe₂ from HQ Graphene. Micromechanical cleavage is performed with
19 polydimethylsiloxane (PDMS) and, after inspection under an optical microscope, 1L-MoSe₂
20 is dry transferred in ambient conditions to a 200 μm fused silica substrate⁶⁴. After transfer, the
21 samples are characterized by Raman and PL with a Renishaw Invia spectrometer at 514 nm
22 and with a 50 \times objective. Metallic frames (Cr/Au) are fabricated around selected 1L-MoSe₂
23 flakes on fused silica by laser-writer lithography to facilitate the identification of the samples'
24 position.

1 **Data acquisition.** A femtosecond oscillator (Venteon Laser Technologies GmbH, Pulse One
2 PE) provides a laser spectrum ranging from 650 to 950 nm, confined by a hard aperture in the
3 Fourier plane of a $4f$ -based pulse shaper in front of the liquid-crystal display (LCD, Jenoptik
4 Optical Systems GmbH, SLM-S640d). The aperture acts as a short-pass filter at 808 nm, so
5 that the longer-wavelength PL can be detected without scattering from the pump light. A
6 Schott KG5 color filter further modulates the spectrum into a smooth shape, which ensures
7 the absence of pronounced side peaks and other irregularities in the temporal pulse profile.
8 The laser focus in the microscope is mapped by a piezo scanning stage (P-517.3CL, PI,
9 Germany). Excitation occurs through a focusing objective (Nikon Plan Apo, $100\times/1.40$). PL is
10 collected through the same objective, transmitted through a dichroic beam splitter (DBS, AHF
11 Analysentechnik, F48-810) and an additional emission filter (EF, AHF Analysentechnik, F76-
12 810), and detected by an APD (Perkin Elmer, SPCM-CD 2801).

13 Linearly polarized light, acting as a superposition of left- and right-hand circularly
14 polarized light, is used to simultaneously excite both the transitions in the K and K' valleys.
15 According to the relative band alignment, in Mo-based TMDs the intra-valley scattering
16 processes are dominant over the inter-valley scatterings⁹. This allows us to model our system
17 accounting just for the K valley, since the energy structures of the K and K' valleys are
18 identical⁶⁵. The pump fluence is $\sim 2 \mu\text{J}/\text{cm}^2$.

19 We obtain the 2D maps by scanning τ and t in steps of 3 fs each from 0 to 99 fs, for $T =$
20 50, 250, 500, 750, 1000, 1250, 1500, 1750, 2000 fs, using the spectral modulation function⁶⁶:

$$21 \quad M(\omega) = \exp[i(\omega - \omega_0(1 - \gamma))(-\tau - T)] + \exp[i(\omega - \omega_0(1 - \gamma))(-T) + i\phi_{12}] +$$

$$22 \quad \exp[i\phi_{13}] + \exp[i(\omega - \omega_0(1 - \gamma))t + i\phi_{14}], \quad (5)$$

23 at a center frequency $\omega_0 = 2.5 \times 10^{15} \text{s}^{-1}$. We avoid undersampling with time steps of 3 fs by
24 employing a partially rotating frame with $\gamma = 0.2$. The third pulse is fixed at time 0, so that

1 when 2D maps are measured at a certain T , only the first and fourth pulses are delayed. By
2 setting the phase of the first pulse to 0, three relative phases, i.e., ϕ_{12} , ϕ_{13} , and ϕ_{14} , are
3 scanned in a 27-step phase-cycling scheme, where each relative phase takes values of 0, $\frac{2\pi}{3}$,
4 and $\frac{4\pi}{3}$. This allows us to select rephasing and nonrephasing contributions individually from
5 the complete raw data^{67,46}. We obtain absorptive 2D maps by summing the real parts of the
6 rephasing and nonrephasing 2D maps, cancelling dispersion terms, leaving a pure absorptive
7 lineshape³⁸. Due to the finite response time of the liquid crystals of our pulse shaper, we wait
8 ~ 500 ms after changing the phase mask before taking data. PL is averaged over ~ 1 ms for
9 each APD acquisition period. Including additional averaging (1000 times for each pulse
10 shape), the total measurement time for one 2D map is ~ 26 h. The group delay dispersion at the
11 sample position is compensated by adding an additional phase to the modulation function⁴⁶.

12 **Simulations.** To simulate the 2D maps, we solve the Lindblad quantum master equation⁵⁷

$$13 \quad \frac{\partial}{\partial t'} \rho(t') = -\frac{i}{\hbar} [\mathcal{H}(t'), \rho(t')] + \sum_j \frac{1}{T_j} \left(\mathcal{L}_j \rho(t') \mathcal{L}_j^\dagger - \frac{1}{2} \mathcal{L}_j^\dagger \mathcal{L}_j \rho(t') - \frac{1}{2} \rho(t') \mathcal{L}_j \mathcal{L}_j^\dagger \right), \quad (6)$$

14 where the time evolution of the density matrix $\rho(t')$ of the quantum system under a
15 Hamiltonian $\mathcal{H}(t')$ is treated in the Liouville–von Neumann formalism, with the extension of
16 dissipative and pure dephasing effects, $\mathcal{H}(t')$ is expressed as the sum of a time-independent
17 Hamiltonian $\mathcal{H}_0 = \hbar\omega_m \sum_m |m\rangle\langle m|$ and an interaction Hamiltonian $\mathcal{H}_I(t') =$
18 $\gamma_{\text{ex}} E(t') \sum_{m \neq n} \mu_{m,n} (|m\rangle\langle n| + |n\rangle\langle m|)$, where $|m\rangle$ (or $|n\rangle$) are the unperturbed eigenstates
19 with eigenenergies $\hbar\omega_m$ (or $\hbar\omega_n$), γ_{ex} is the field coupling strength for excitation with the
20 external electric field $E(t')$, $\mu_{m,n}$ is the transition dipole moment between states $|m\rangle$ and $|n\rangle$,
21 T_j represents the time associated with a pure dephasing or population relaxation process, and
22 the Lindblad operators \mathcal{L}_j are defined as $\mathcal{L}_j = a_n^\dagger a_m$ for pure dephasing and $\mathcal{L}_j = a_m^\dagger a_n$ with
23 $m \neq n$ for a population relaxation process, where a_m^\dagger and a_n denote the creation and
24 annihilation operators, respectively.

1 We assume a four-level system, with two vibrational levels in the ground electronic state
2 ($|g_0\rangle$ and $|g_1\rangle$) and two vibronically excited states ($|e_0\rangle$ and $|e_1\rangle$), as in Fig. 3a. The splittings
3 within the subbands are taken to be identical, i.e., we use the same energy separations (30
4 meV^{21}) between $|g_0\rangle$ and $|g_1\rangle$ as well as between $|e_0\rangle$ and $|e_1\rangle$. The Franck–Condon
5 amplitudes between $|g_i\rangle$ and $|e_j\rangle$, i.e., χ_{ij} ($i, j = 0$ or 1) depend on S as for Fig. 3b. The initial
6 populations of $|g_0\rangle$ and $|g_1\rangle$ are determined by the temperature, according to the Boltzmann
7 distribution. In Supplementary Note 7 we estimate the heating through laser irradiation during
8 the experiment and find the sample to remain close to RT.

9 The excitation laser field is calculated from the experimentally utilized laser spectrum
10 assuming a flat phase and then adding the transfer function:

$$\begin{aligned}
11 \quad M(\omega) = & \exp[i(\omega - \omega_0(1 - \gamma))(T_{\text{off}})] + \exp[i(\omega - \omega_0(1 - \gamma))(T_{\text{off}} + \tau) + i\phi_{12}] + \\
12 \quad & \exp[i(\omega - \omega_0(1 - \gamma))(T_{\text{off}} + \tau + T) + i\phi_{13}] + \exp[i(\omega - \omega_0(1 - \gamma))(T_{\text{off}} + \tau + T + t) + \\
13 \quad & i\phi_{14}], \tag{7}
\end{aligned}$$

14 where T_{off} is an offset of the position of the first pulse in time domain, set at 100 fs to avoid
15 cutting off the first pulse at time zero. In the experimental modulation function of Eq. 5, time
16 zero is set at the maximum of the third pulse, leading to a different mathematical expression.
17 However, this difference does not affect the resulting 2D maps, since only relative time delays
18 between the pulses are relevant. τ and t in the simulation are scanned with the same
19 parameters as in the experiment, from 0 to 99 fs in steps of 3 fs with $\gamma = 0.2$, whereas T is
20 scanned from 0 to 200 fs in steps of 25 fs.

21 Inhomogeneous broadening due to a Gaussian distribution of excitonic transition
22 frequencies is taken into account by obtaining the inhomogeneously broadened response
23 function, $S_I(\tau, t)$, from the homogeneous response, $S(\tau, t)$. From solving Eq. 6, via:

$$24 \quad S_I(\tau, t) = S(\tau, t) \cdot \exp[-\Delta^2 \cdot (\tau \mp t)^2], \tag{8}$$

1 where Δ is a parameter linearly proportional to the inhomogeneous linewidth broadening, - is
2 applied for the rephasing signal, and + for the nonrephasing signal. Eq. 8 is used under two
3 assumptions. 1) Spectral diffusion can be ignored within the $T = 2$ ps window of the
4 measurements. Typically, spectral diffusion is caused by environmental fluctuations around
5 the transition dipoles, inducing a broadening along the anti-diagonal direction for the
6 absorptive 2D maps as T increases³⁸. This is not observed in our experiments (Supplementary
7 Figure 5), indicating a much slower than 2 ps modulation time constant of the environment,
8 justifying the use of Eq. 8. 2) The vibrational frequency does not change with the excitonic
9 transition energy, also assumed for the model of Fig. 3a and Eqs. 1–3. If this was not fulfilled,
10 a tilt of elongated peaks in the 2D beating maps relative to the diagonal would be observed⁴⁰,
11 unlike in our measurements (Fig. 4b).

12 **Data availability**

13 The data that support the findings of this study are available from the corresponding author
14 upon reasonable request.

15 **Acknowledgements**

16 We thank Pavel Malý for support with computations of 2D maps. We acknowledge funding
17 by the European Research Council (ERC) – Grants No. 614623, Hetero2D, GSYNCOR;
18 EPSRC Grants EP/K01711X/1, EP/K017144/1, EP/N010345/1, and EP/L016087/1; and the
19 EU Graphene and Quantum Flagships.

20 **Author contributions**

21 D.L., C.T., and M.N. performed spectroscopic measurements. D.L. analyzed the 2DES data
22 and conducted the 2DES simulations. S.D.C. supervised C.T.; T.B., G.C. and A.C.F. initiated
23 and supervised the project. G.S. and G.W. prepared and characterized the samples. All authors

1 discussed results. D.L., C.T., G.C., T.B. and A.C.F. wrote the paper with input from all
2 coauthors.

3 **Competing interests**

4 The authors declare no competing interests.

5 **Additional information**

6 **Supplementary information** is available for this paper.

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Figures

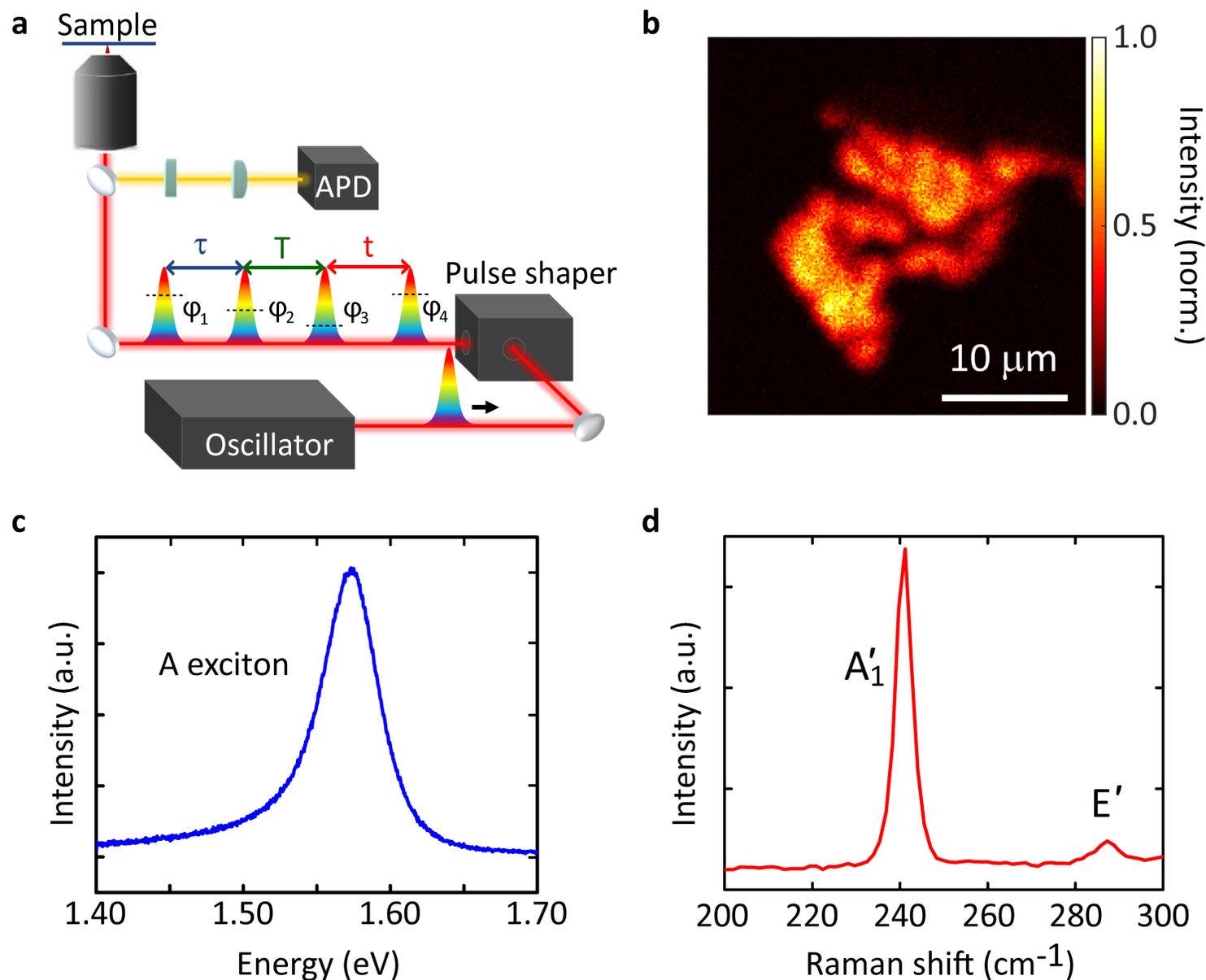


Figure 1

Overview of setup and the sample. **a**, Fluorescence-detected 2D micro-spectroscopy setup. Four collinear laser pulses are generated by a pulse shaper with controllable inter-pulse time delays (τ , T , t) and phases (ϕ_i , $i = 1, 2, 3, 4$) and focused by a high-NA objective (Obj). The position of the sample is controlled by a piezo scanning stage (PSS). The PL signal is detected by an avalanche photodiode (APD). **b**, PL map obtained with the setup of panel **a**. **c**, PL and **d**, Raman spectrum for 514 nm excitation.

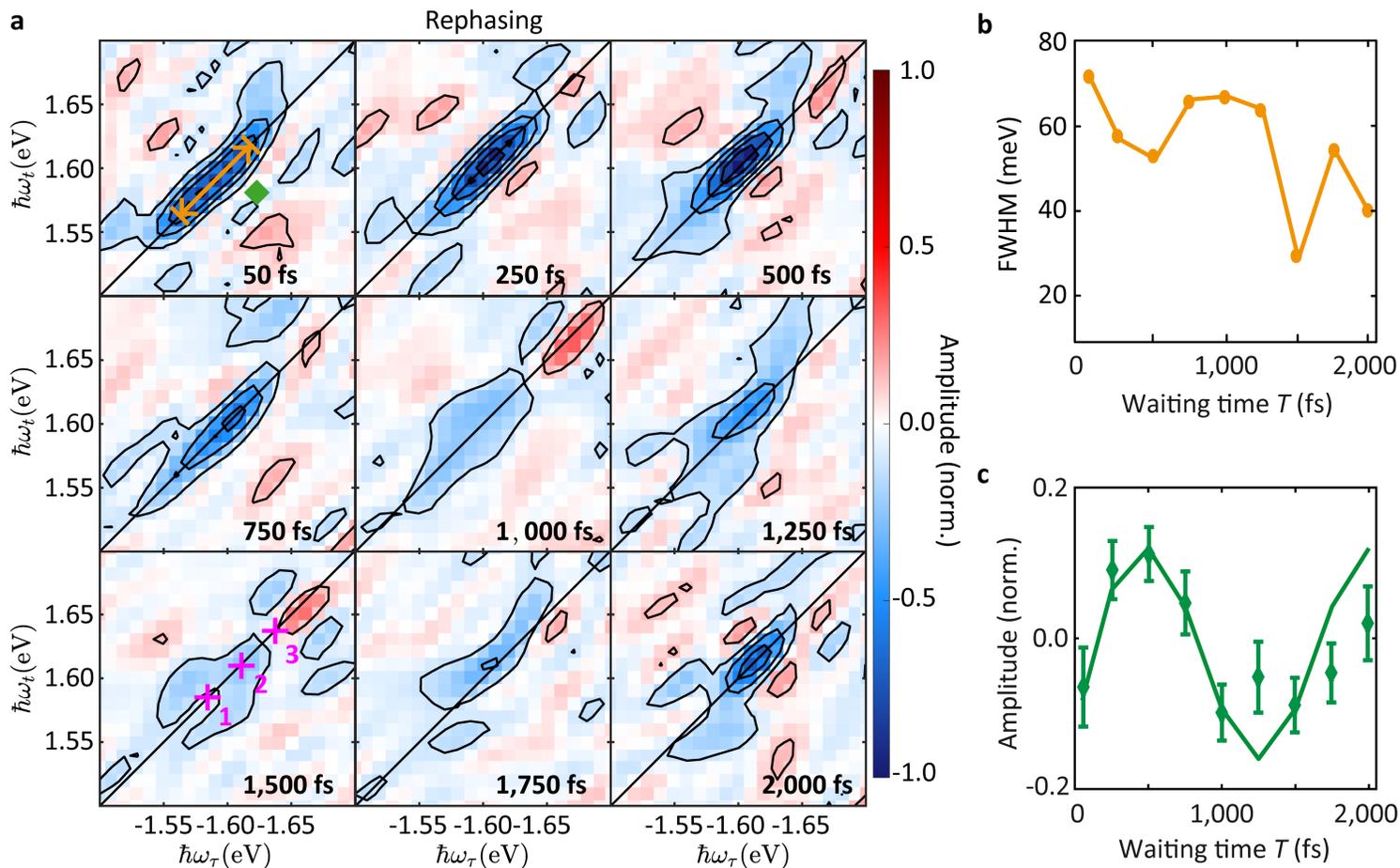


Figure 2

Beating signal in the rephasing 2D maps. a, Rephasing 2D maps at different T , normalized to the maximum absolute value of the real part of the map at $T = 500$ fs. b, Diagonal linewidth (indicated by the orange double arrow at $T = 50$ fs in panel a) versus T . c, Amplitude evolution (green diamonds) of one pixel (marked by the green diamond at $T = 50$ fs in panel a) and fit (solid green curve). The error bars are evaluated by calculating the fluctuations within a region containing background noise (Supplementary Note 4).

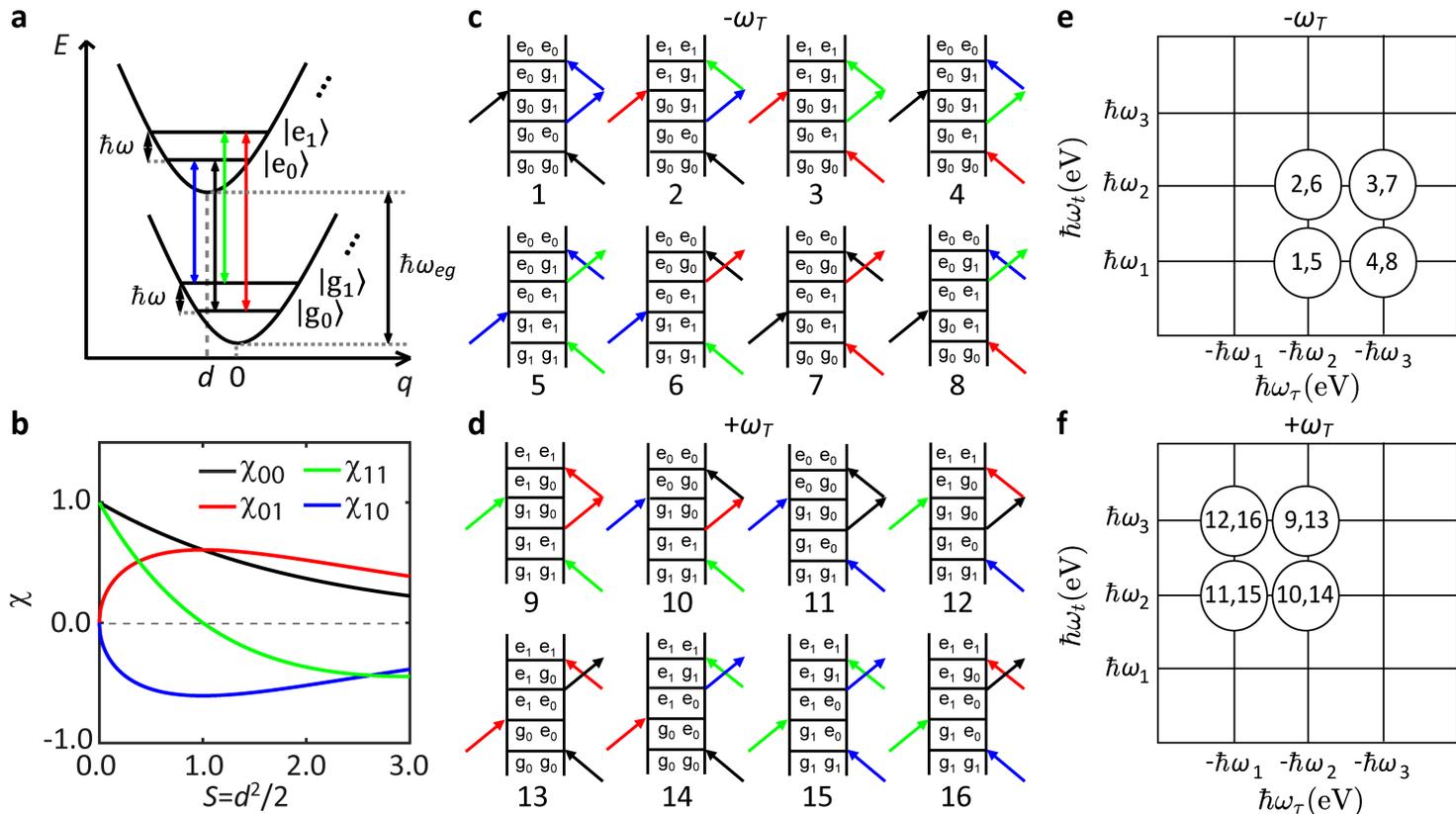


Figure 3

Analysis of beating signals. a, Schematic diagram of displaced harmonic oscillators (Franck–Condon coupling model⁵⁵) with two vibrational levels in the electronic ground state and two in the electronic excited state. b, Dependencies of Franck–Condon amplitudes χ_{ij} ($i, j = 0$ or 1) on S . c,d, Feynman pathways giving rise to the beating signals with (c) negative beating frequency $-\omega_T$ and (d) positive frequency $+\omega_T$. e, Beating-map locations of numbered Feynman pathways from panel c. f, Beating-map locations of numbered Feynman pathways from panel d. Transitions $|g_0\rangle \rightarrow |e_0\rangle$, $|g_0\rangle \rightarrow |e_1\rangle$, $|g_1\rangle \rightarrow |e_0\rangle$, and $|g_1\rangle \rightarrow |e_1\rangle$ are color-coded in black, red, blue, and green, respectively, for panels a–d.

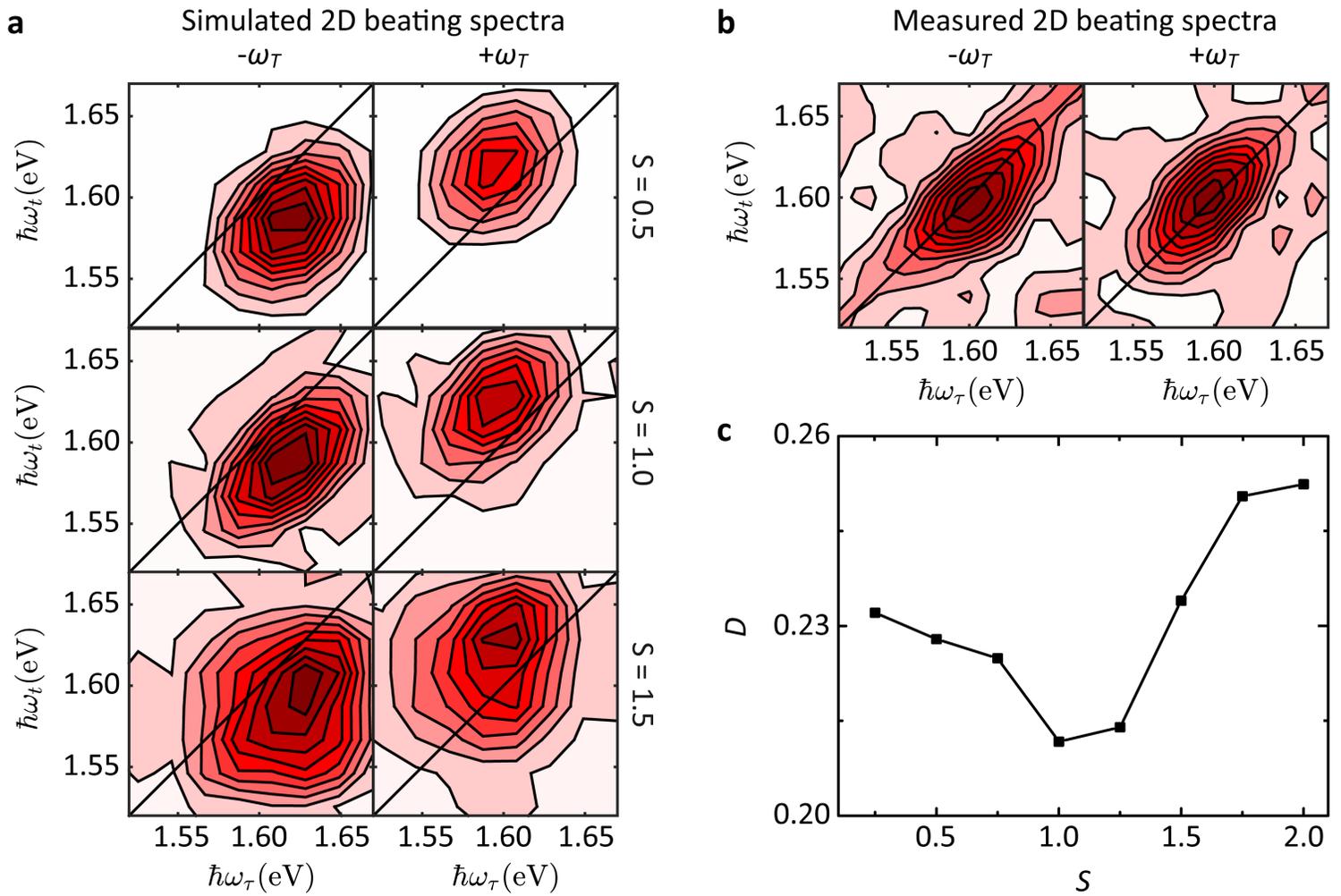


Figure 4

2D beating maps. a, Simulated 2D beating maps for $-\omega_T$ (left) and $+\omega_T$ (right) and $S = 0.5, 1, 1.5$ from top to bottom rows). b, Measured 2D beating maps with $-\omega_T$ (left) and $+\omega_T$ (right). c, The deviation, D , between measured and simulated 2D beating maps versus S used in the simulation.

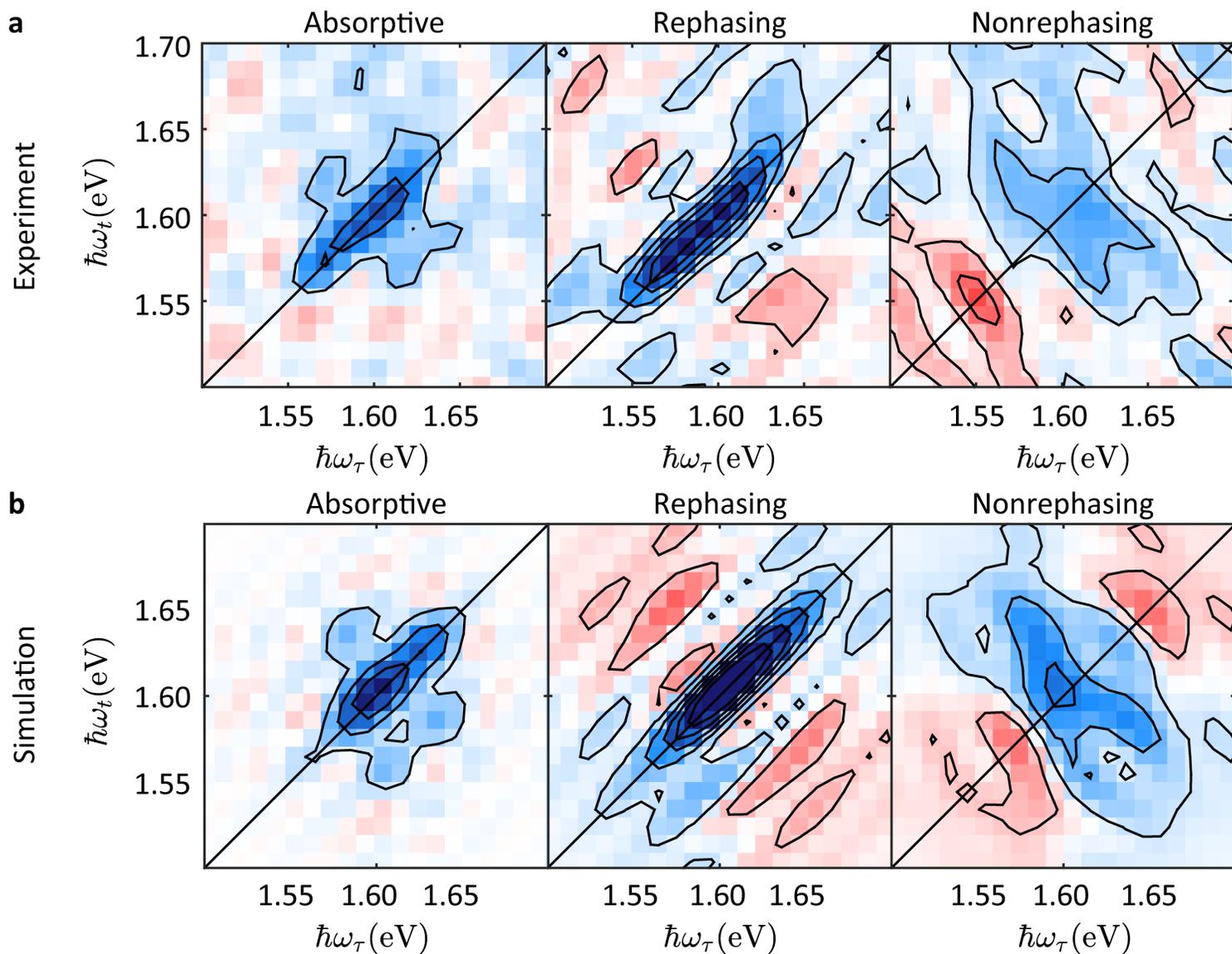


Figure 5

Absorptive (left), rephasing (middle), and nonrephasing (right) real-valued 2D maps at $T = 50$ fs. a, Experiment. b, Simulation using the deduced optimal $S = 1$.

Supplementary Files

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