Inverted valley polarization in optically excited transition metal dichalcogenides

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Large spin–orbit coupling in combination with circular dichroism allows access to spin-polarized and valley-polarized states in a controlled way in transition metal dichalcogenides. The promising application in spin-valleytronics devices requires a thorough understanding of intervalley coupling mechanisms, which determine the lifetime of spin and valley polarizations. Here we present a joint theory–experiment study shedding light on the Dexter-like intervalley coupling. We reveal that this mechanism couples A and B excitonic states in different valleys, giving rise to an efficient intervalley transfer of coherent exciton populations. We demonstrate that the valley polarization vanishes and is even inverted for A excitons, when the B exciton is resonantly excited and vice versa. Our theoretical findings are supported by energy-resolved and valley-resolved pump-probe experiments and also provide an explanation for the recently measured up-conversion in photoluminescence. The gained insights might help to develop strategies to overcome the intrinsic limit for spin and valley polarizations.

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he promising implementation of monolayer transition metal dichalcogenides (TMDs) in spin-valleytronics is based on the spin-selective and valley-selective excitation of excitonic states. An important prerequisite for these applications is a profound understanding of the dynamics of optically excited spin and valley polarization. The challenge is to be able to control many-particle mechanisms by coupling and mixing excitonic states of different spin and valley. In previous theoretical and experimental studies, it has already been shown that in addition to relatively slow intervalley spin-flip scattering processes there is an efficient intervalley coupling mechanism via Coulomb exchange processes. This Coulomb-induced dipole–dipole interaction couples resonant excitonic states in K and K’ valleys, giving rise to a decay of valley polarization on a picosecond time scale. However, the coupling is relatively small and only occurs as a second-order process, since it requires a non-zero center-of-mass momentum that first has to be generated by exciton-disorder coupling, bie excitonic excitations, or exciton-phonon coupling.

In this work, we reveal a new intrinsic and direct Coulomb-driven intervalley coupling mechanism that is much more pronounced than the Coulomb exchange term and determines the optically accessible spin-valley polarizations in TMDs. We show that this interaction resembles the Dexter coupling between two optically accessible spin-valley polarizations in TMDs. We note that the distance between the valleys (Δk) enters the Coulomb potential, while it does not effect the excitonic wave functions. Furthermore, in the vicinity of the valleys, the coefficients are given by a phase, which cancels the geometric phase of the excitonic wave functions, cf. Methods section for details on the applied theory. We can estimate the coupling analytically by exploiting |Δk| >> |k - k’|, which allows us to evaluate the sums over the excitonic wave functions using two-dimensional 1 s excitonic functions. Assuming an exciton Bohr radius of 1 nm we find that the coupling strength to be in the range of 50 meV reflecting the high importance of the Dexter-like mechanism.

Before evaluating the full TMD Bloch equations (Eq. (3) in the Methods section), we first consider a simplified model to illustrate the efficiency of the initially off-resonant coupling. The Dexter interaction couples states with the same spin and in different valleys, i.e., A (B) excitons in the K valley couple to B’ (A’) excitons in the K’ valley, cf. Fig. 1. The nature of the Dexter coupling can be understood from a simple example: we assume two states with the eigenenergies E1 and E2 in different valleys. Valley 1 is optically excited with the Rabi frequency Ω1(t) giving rise to the microscopic polarization ps(t), which then interacts with the other valley via a coupling constant C12, inducing a polarization p2(t) in the unpumped valley 2. In Fourier space, the corresponding simplified Bloch equation can be solved analytically resulting in ps(ω) = Ω1(ω)H12(ω)/E2 - E1, inducing a polarization p2(ω) in the unpumped valley 2. In Fourier space, the corresponding simplified Bloch equation can be solved analytically resulting in ps(ω) = Ω1(ω)H12(ω)/E2 - E1, inducing a polarization p2(ω) in the unpumped valley 2.

Results

Theoretical model. The theoretical approach is based on the density matrix formalism, providing microscopic access to the time-resolved and energy-resolved dynamics of microscopic quantities, such as the microscopic polarization \( p^\delta = \left( a_i^\dagger a_i \right) \), which is a measure for the transition probability between the states i and j. We use the picture of second quantization introducing electron creation and annihilation operators \( a_i^\dagger \) and \( a_i \). The states are described by the compound indices i, j including the electronic momentum k, the spin-valley index \( \xi \) and \( \xi' \), denoting opposite valleys with the same spin, and the electronic band index \( \lambda = \nu, c \) standing for the valence and the conduction band. First, we define the many-particle Hamilton operator consisting of the interaction-free carrier contribution \( \hat{H}_0 \), the light–matter interaction \( \hat{H}_{1\nu} \) and the Coulomb interaction \( \hat{H}_C \). Then, we derive the TMD Bloch equation for the microscopic polarization \( p^\delta \) by exploiting the Heisenberg equation of motion. This quantity couples to incoherent carrier densities \( \left| p^\delta \right|^2 + \Delta \left| N^\delta \right|^2 \) including coherent \( \left| p^\delta \right|^2 \) and incoherent \( \left( \Delta \left| N^\delta \right|^2 \right) \) excitons. The microscopic polarization is directly excited via an external light source that introduces the coherent excitons, which then decay via phonons into incoherent excitons. In this work, we focus on the coherent exciton dynamics, where we include dephasing and the formation of incoherent excitons via phonon-scattering constants calculated on a microscopic footing. A microscopic description of the dissipation dynamics of incoherent excitons into dark states away from the light cone is beyond the scope of this analysis.
between the indirectly and directly driven valley as $v_{21}(\omega) = \frac{p_{s}([\omega] = C_{1s}}{E_{1s} - \hbar \omega}$. For resonant excitation to $E_{1} (\hbar \omega = 0)$, we find that the reduction of the valley polarization is determined by $\tilde{v}_{21} = v_{21}(\omega = 0) = C_{1s}}{E_{1s} - \hbar \omega}$, i.e., the ratio of the coupling constant and the energy separation of the states, e.g., analog to the spin–orbit coupling in TMDs. In contrast, for resonant excitation to $E_{2}$, we find that the valley polarization is completely inverted $r_{1}^{s}(\omega) \to -1$. This is a surprising result as the state $E_{2}$ is only indirectly driven. The intervalley coupling leads to an energy-dependent dominance of the indirectly driven polarization. For the investigated exemplary material tungsten disulphide (WS$_{2}$), $A_{1s}$ and $B_{1s}$ excitonic states are separated due to the spin–orbit coupling by $E_{1} - E_{2} \approx 400$ meV. Using the approximated value of 50 meV for the Dexter coupling, we obtain a scaling factor of $\tilde{v}_{21} \approx 0.125$. This estimation suggests that when resonantly pumping the $A_{1s}$ state, approximately $1/(1/\tilde{v}_{21} + 1) = 11\%$ of the light field is indirectly absorbed by the $B_{1s}$ state in the unpumped valley due to the Dexter coupling. This means that the induced valley polarization at the $A$ exciton is decreased by $11\%$ and inverted at the energy of the $B$ exciton, where the Dexter coupling leads to an intervalley up-conversion. In the case of MoS$_{2}$, where the energy separation of $A_{1s}$ and $B_{1s}$ is in the range of 150 meV, the same estimation predicts an indirect absorption of $30\%$ at the energy of $A_{1s}$ and $B_{1s}$ excitons in the unpumped valley suggesting a crucial role of Dexter coupling. c.f. Supplementary Note 4 for details on the estimation for different TMDs and substrates, portrayed in Supplementary Fig. 6. Note also that the discussed simple scaling model only takes into account the $1s$ states and therefore presents a lower limit for the Dexter coupling. Taking into account all possible coupling excitonic states as well as non-linear effects, Dexter coupling turns out to be even more efficient, as discussed below.

Now, we model ultrafast pump-probe experiments by evaluating the Bloch equation (Eq. (3) in the methods section) for a non-linear excitation. We calculate the temporal evolution of the coherent and incoherent exciton densities in both valleys and for both spin systems, and evaluate the corresponding exciton population $N_{b}$ consisting of coherent and incoherent excitons for different delay times. Here $N_{b}$ describes the total exciton population in the valley $\xi$ and the excitonic state $n$. This allows us to compare the spin and valley polarization as a function of excitation energy, pump fluence, and delay time.

**Experimental methods.** To address the same quantities in experiments, we measure transient differential transmission of monolayer WS$_{2}$ with energy-resolved and valley-resolved femtosecond pump-probe experiments. A WS$_{2}$ monolayer on a borosilicate substrate is pumped by left circularly polarized laser pulses (200 fs), creating a population of excitons in a specific valley (K or K'). To probe the temporal and spectral dynamics of excitons we use linearly polarized pulses with a spectral bandwidth of 250 meV covering either the spectral range of A or B excitons. By analyzing the linearly polarized probe pulses transmitted through the monolayer for their circularly polarized components, we can simultaneously measure the dynamics in the pumped (“same circular polarization”, SCP) and unpumped valley (“opposite circular polarization”, OCP), cf. Supplementary Fig. 1. Observed changes of the spectral shapes at positive delay times are due to shifts of the exciton due to Coulomb renormalization, in particular biexcitons$^{15}$, and bleaching of the exciton absorption due to Pauli blocking$^{14}$. Integrating the spectra in the range of the exciton resonances (A or B) yields the dynamics proportional to the respective exciton densities in two valleys$^{14}$ and provides the valley polarization degree at different delay times and energies. Additional details of the experimental setup are given in Supplementary Note 1.
**Time-dependent valley polarization.** We first focus on the dynamics of the valley polarization (VP) $P_{n}^{\text{VP}}$ of A ($n = A$) and B excitons ($n = B$). The latter is defined as $P_{n}^{\text{VP}} = (N_{n}^{K} - N_{n}^{K'})/(N_{n}^{K} + N_{n}^{K'})$. Figure 2 illustrates the time-dependent exciton populations in A and B states after resonant excitation of the $A_{1s}$ exciton in the K valley with a temporally broad (200 fs) and spectrally narrow (20 meV) pump pulse. Simultaneously to the excitation of the A exciton (Fig. 2c), we find an increase in the B$'$ exciton population (Fig. 2a) resulting in an inversion of the VP (Fig. 2b). This VP follows the pump pulse in time, and it decays as soon as the pump pulse has vanished. The ultrafast dynamics of the VP clearly underlines the coherent nature of the observed process. This is consistently described via the coherent Dexter-like oscillation transfer between the valleys (Fig. 2b, d). The resonantly excited A exciton coherence drives the B$'$ exciton populations via the Dexter-like coupling. This induces an immediate formation of coherent B excitons in the unpumped valley, followed by a dephasing of the coherence via phonons. This dephasing induces incoherent excitons during the first 200 fs in both A and B$'$ states. The latter dissipate over the whole Brillouin zone, which leads to a decay of the valley polarization for B and A excitons, which has been characterized by a typical scattering constant $\gamma_{K-K'} = 1$ meV$^2$.[36]. Furthermore, we have extracted the lifetime of excitons from the experiments resulting in $\gamma_a = 50$ meV and $\gamma_b = 200$ meV for A and B excitons, respectively.

We find in both experiment and theory a strong inversion of the VP of B excitons in the range of $\approx 80\%$ when the $A_{1s}$ exciton is resonantly excited (Fig. 2b). However, the theoretical calculation predicts a VP of A excitons of 90%. This is qualitatively in line with the experimentally extracted A exciton time series for near-resonant experimental data in the SI. e, f Polarization dependent pump-probe measurement showing the OCP (opposite circular polarization) and SCP (same circular polarization) signal of the $A_{1s}$ and $B_{1s}$ excitons, for pumping the $A_{1s}$ exciton close to the resonance.

**Fig. 2** Exciton population and valley polarization. Temporal evolution of the exciton population and the resulting valley polarization (VP) of B excitons (a, b theory–experiment comparison) and A excitons (c, d theoretical calculation) after resonant excitation of $A_{1s}$ exciton in the K valley. The optically driven coherent A excitons couple via Dexter interaction to the B$'$ excitons in the unpumped K$'$ valley (see also Fig. 1). This coupling dominates the B exciton dynamics and instantaneously induces B$'$ exciton populations (a) and as a result a negative valley polarization (b) which decays within 0.5 picoseconds. c During the pump pulse (red-shaded area), A excitons are generated, which induce A$'$ excitons via electron-hole exchange interaction. d The corresponding optically induced valley polarization of A excitons (near-resonant experimental data in the SI). e, f Polarization dependent pump-probe measurement showing the OCP (opposite circular polarization) and SCP (same circular polarization) signal of the $A_{1s}$ and $B_{1s}$ excitons, for pumping the $A_{1s}$ exciton close to the resonance.
A1s. This shows that the VP for the off-resonant B exciton is inverted with respect to the resonantly pumped A exciton. In addition, in Supplementary Fig. 5 (cf. Supplementary Note 3) we have portrayed the time-dependent polarization of pumped and unpumped valleys. To underline these findings we analyze the population dynamics of the A1s and B1s excitons.

**Pump-dependent valley polarization.** After having revealed the time-resolved exciton population and valley polarization, we now present the impact of Dexter-like coupling when varying the pump energy and the pump fluence at time \( t = 0 \) fs. First, we analyze the energy dependence of the valley polarization shown in Fig. 3a, b. Here we calculate the generated exciton populations for different pump energies, from 20 meV below \( A_{1s} \) up to 50 meV above \( B_{1s} \). In the experiments, we tune the excitation energy from 2.1 to 2.48 eV while the pump fluence is fixed at \( 6 \mu \text{J cm}^{-2} \). Figure 3a, b show a direct comparison between the experimental estimated (dots) and theoretical (lines) VP for different pump energies of A and B excitons, respectively. The numerical calculations are in line with analytically estimated intervalley transfer of \( \sim 10\% \) for WS2, e.g., the VP is close to +90\% for resonant excitation and inverted in the off-resonant case.

Though the theoretical model can reproduce well the trend of the experiment, it does not capture all aspects of the VP dependence for different pump energies. While the theory shows a minor inversion of the A exciton VP, the experiment only indicates a clear reduction, it does not reach the inversion.

In Fig. 3a, both experiment and theory exhibit a pronounced decrease in the VP of A excitons for pump energies in the vicinity of the \( B_{1s} \) exciton. We find the inversion only in the case shown in Fig. 3b. Here experiment and theory yield an inverted valley polarization for the \( B_{1s} \) excitons for pump energies resonant and close to \( A_{1s} \), confirming the crucial role of the Dexter-induced intervalley exciton transfer. Though the theoretical model can reproduce well the trend of the experiment, it does not capture all aspects of the VP dependence for different pump energies. The quantitative discrepancy to the experiment might be due to the fact that the B exciton is in close proximity to a number of higher excitonic A states. This allows additional excitations and coupling processes including phonon-induced scattering and Coulomb exchange coupling. Another difference lies in the experimentally broader absorption spectrum, which can be ascribed to inhomogeneous dephasing and defect-induced absorption, which can reduce the valley polarization.

To reduce the role of defects, we study the resonant excitation of the A exciton while probing the B exciton states for different pump fluences. Under these conditions the major part of the coherence is generated in resonance to the intrinsic states, which reduces the relative amount of defect-assisted absorption. Furthermore, we can control the excitation density in experiment and theory in a comparable way. In Fig. 3c, d, we show the enhanced excitation of the B exciton as the pump fluence of the excitation pulse (resonant to the A exciton) increases. Due to the larger excitation density we observe in both experiment and in theory an increase of the excitation of B excitons in both valleys. The purple line shows the off-resonantly excited B excitons in the pumped valley, the blue line that B excitons induced via Dexter coupling in the other valley. The latter becomes more efficient for stronger excitation. As a result, we find a higher increase of the population of B excitons in the unpumped valley than in the pumped valley. Note that this is in full analogy to the findings of ref. 19, where an increased signal of the B excitons was observed for larger pump fluences.
in both valleys. Here the off-resonantly excited B excitons in the pumped valley (purple line) and the B excitons induced via Dexter coupling in the unpumped valley (blue line) are compared. The latter becomes more efficient for stronger excitation, where the phase-space filling induces an asymmetry between the directly excited A exciton and the indirectly (weaker) excited B′ exciton. As a result, the oscillation transfer from the A exciton to B′ is more efficient than the back-coupling process. Therefore, stronger excitation leads to a higher relative increase of indirectly excited B excitons. As a result, we find a higher increase of the population of B excitons in the unpumped valley. Note that this result is in analogy to the findings of ref. 19, where an increased signal of the B excitons was observed for larger CW pump fluences. The inversion of the VP is also evident in the experiment, when pumping the A exciton and probing the B exciton. Here theory and experiment show an inversion of up to −80%.

Photoluminescence. To further demonstrate the importance of Dexter-like intervalley coupling, we calculate the valley polarization in the case of continuously pumped WSe₂, aiming at the explanation of the recently observed up-conversion in ref. 19. Here we selectively excite A₁s excitons with cw σ⁺ polarized light. We expect the Dexter coupling to be even more pronounced due to the static excitation leading to ultralong lifetimes of the coupling microscopic polarizations. Evaluating the Bloch equation, we have access to coherent exciton populations \( |p_{\nu}^{\pm}|^2 \) that determine the coherent contributions to the photoluminescence

\[
I_{p\pm}(\omega) \propto \text{Im} \left( \sum_{\nu} \frac{|p_{\nu}^{\pm}|^2}{E_\nu - \hbar \omega - i\gamma} \right).
\]

Here we assume a small dephasing of \( \gamma = 2 \text{ meV} \), which is in agreement to the measured excitonic linewidth at low temperatures in ref. 19. We observe a strong photoluminescence from higher energetic states despite the initial excitation at the A₁ exciton corresponding to the experimentally measured up-conversion in ref. 19. In particular, we find a considerable PL signal from the A₂s and the B₁s state (Fig. 4), which arises from the non-linear coupling terms in the TMD Bloch equation (second line in Eq. (3) in the Methods section). They enable coupling of excitonic states with different quantum numbers \( n,m \) giving rise to an increasing up-conversion to higher excitonic states at higher pump intensities (cf. orange arrows in Fig. 1a). As a result, we find a two orders of magnitude stronger up-conversion from the A₁ to the A₂s state compared to the case without coupling (cf. dashed lines in Fig. 4). Furthermore, we calculate the PL signal for σ⁺ and σ⁻ polarized light. Without the Dexter coupling (dashed lines), only σ⁻ is emitted. Switching on the Dexter coupling, we also observe a considerable contribution of σ⁺ light. The VP for the A₁ exciton is reduced to 28%, which is in good agreement with the experimentally estimated value of ~20%38. Similarly to the pump-probe experiments, we observe a Dexter-induced inversion of the VP of the B exciton. Here the contribution of the σ⁻ light is even higher and exceeds the value for σ⁺ light—again in excellent agreement with the experiment19.

The Dexter-like intervalley coupling can explain the surprising valley inversion during and shortly after the optical excitation on the sub-picosecond time scale, as well as for CW excitation on longer time scales. For the latter case, it may be an additional process, since one cannot rule out higher-order relaxation mechanisms occurring on a picosecond or a nanosecond time scale. An alternative explanation for the observed up-conversion and inversion of the VP is given in ref. 19, where the inversion is attributed to two-photon absorption followed by a relaxation mechanism under the influence of attractive boson interactions. While this process may be relevant in the CW experiment situation, it can be ruled out in the presented ultrafast pump-probe experiment, where the formation of excitons and the formation of the inverted VP take place on the same time scale (<200 fs)22,39,40 (cf. Fig. 2).

Discussion

In summary, we have presented a joint theory–experiment study on the decay of optically accessible valley polarization in TMDs. On the basis of a microscopic approach and high-resolution two-color pump-probe experiments, we reveal the crucial importance of the Coulomb-induced Dexter-like intervalley coupling mechanism. We find an efficient coupling of A and B excitonic states in different valleys giving rise to an intervalley transfer of coherent exciton populations. As a result, the valley polarization breaks down and is quasi-instantaneously inverted for B excitons when the A excitonic state is resonantly excited, and vice versa. We show that the upper limit for the achievable valley polarization is given by the ratio of the Dexter coupling strength and the energy difference between A and B excitons that is determined by the spin–orbit coupling. The theoretical prediction is confirmed in spectrally and valley-resolved pump-probe experiments.

Methods

Theoretical formalism. On the basis of the density matrix formalism, we derive the TMD Bloch equation for the microscopic polarization \( \mathbf{P}^{\nu} \) within the coherent limit10,11,41. To account for the crucial importance of excitons, we project the solution for the microscopic polarization into an excitonic basis using the transformation \( \mathbf{P}^{\nu} = \sum_{\kappa} \mathbf{P}^{\kappa} \mathbb{P}^{\kappa}_{\nu} \). The appearing excitonic wave functions \( \mathbb{P}^{\kappa}_{\nu} \) are calculated by solving the Wannier equation, an eigenvalue equation for excitons that also provides the excitonic energies \( E^{\nu}_{\kappa} \) of the state \( \nu \). The TMD Bloch equation reads in the excitonic basis for the microscopic polarization:

\[
\dot{\mathbf{P}}^{\kappa}_{\nu} = \mathbf{B}^{\kappa}_{\nu} \mathbf{P}^{\kappa}_{\nu} - \mathbf{P}^{\nu} - \sum_{\kappa} \left( \mathbb{D}^{\nu}_{\kappa} \mathbf{P}^{\kappa}_{\nu} + \Delta_{\kappa} \mathbf{P}^{\nu}_{\kappa} + \Delta_{\kappa} \mathbf{P}^{\nu}_{\kappa} \right) + \sum_{\kappa} \mathbb{I}^{\nu}_{\kappa} \left( \mathbf{P}^{\kappa}_{\nu} \mathbf{P}^{\kappa}_{\nu} + \Delta_{\kappa} \mathbf{P}^{\nu}_{\kappa} + \Delta_{\kappa} \mathbf{P}^{\nu}_{\kappa} \right) + \sum_{\kappa} \mathbb{Y}^{\nu}_{\kappa} \left( \mathbf{P}^{\kappa}_{\nu} \mathbf{P}^{\kappa}_{\nu} + \Delta_{\kappa} \mathbf{P}^{\nu}_{\kappa} + \Delta_{\kappa} \mathbf{P}^{\nu}_{\kappa} \right) + \sum_{\kappa} \mathbb{N}^{\nu}_{\kappa} \left( \mathbf{P}^{\kappa}_{\nu} \mathbf{P}^{\kappa}_{\nu} + \Delta_{\kappa} \mathbf{P}^{\nu}_{\kappa} + \Delta_{\kappa} \mathbf{P}^{\nu}_{\kappa} \right) + \sum_{\kappa} \mathbb{M}^{\nu}_{\kappa} \left( \mathbf{P}^{\kappa}_{\nu} \mathbf{P}^{\kappa}_{\nu} + \Delta_{\kappa} \mathbf{P}^{\nu}_{\kappa} + \Delta_{\kappa} \mathbf{P}^{\nu}_{\kappa} \right) + \sum_{\kappa} \mathbb{N}^{\nu}_{\kappa} \left( \mathbf{P}^{\kappa}_{\nu} \mathbf{P}^{\kappa}_{\nu} + \Delta_{\kappa} \mathbf{P}^{\nu}_{\kappa} + \Delta_{\kappa} \mathbf{P}^{\nu}_{\kappa} \right)
\]

inducing incoherent exciton densities via phonon scattering,

\[
\dot{\mathbf{P}}^{\nu} = 2 \gamma_{\nu} \mathbf{P}^{\nu} + \mathbf{P}^{\nu} - \gamma_{\nu} \mathbf{P}^{\nu} - \gamma_{\nu} \Delta_{\nu} \mathbf{P}^{\nu} - \gamma_{\nu} \Delta_{\nu} \mathbf{P}^{\nu}
\]

The dynamics of the excitonic polarization \( \mathbf{P}^{\nu} \) is driven by an external optical field denoted by the Rabi frequency \( \Omega^{\nu} \left( t \right) \) including the...
vector potential $A(t)$ and the optical matrix element $M_{\Omega k}^{\Omega k'}$ weighted by the excitonic wave function $\Psi^\Omega_k$. The optical matrix element is analytically obtained by using nearest-neighbor tight-binding wave functions. Non-linear phase-space filling effects have also been taken into account in $D^{\Omega \Omega'}_{N} (t) = \sum_k g_{\Omega k} g_{\Omega' k} V^{\Omega \Omega'}_{kk} e^{i Q_k (t)}$. Furthermore, the excitonic polarization oscillates with $\omega_0 = (E_0 + \gamma_{\text{homo}})$, where $\gamma_{\text{homo}}$ corresponds to the radiative decay rate determining the homogeneous dephasing of the polarization [cf. Supplementary Fig. 3].

The second and the third line in Eq. (3) describe the Coulomb-induced inter-excitonic coupling ($t$ term) and intervalley bandgap renormalization ($Y$ term). The first two states of the same spin within one valley (Fig. 1), while the latter leads to a red-shift of excitonic resonances in one valley due to the optically excited carrier occupations in the other valley [3]. The corresponding coupling elements read

$$
\gamma^{\Omega \Omega'}_{kk',kk} = \sum_{\lambda} g_{\Omega k} g_{\Omega' k'} \left( \frac{2 g_{\Omega k} g_{\Omega k'} V^{\Omega \Omega'}_{kk} e^{i q_a}}{\epsilon_0 \epsilon_r r_0} \right) \sum_{\lambda} g_{\lambda k} g_{\lambda k'} V^{\lambda \lambda}_{kk',kk},
$$

(5)

$$
\gamma^{\Omega \Omega'}_{kk',kk} = \sum_{\lambda} g_{\Omega k} g_{\Omega k'} \left( \frac{2 g_{\Omega k} g_{\Omega k'} V^{\Omega \Omega'}_{kk} e^{i q_a}}{\epsilon_0 \epsilon_r r_0} \right) \sum_{\lambda} g_{\lambda k} g_{\lambda k'} V^{\lambda \lambda}_{kk',kk},
$$

(6)

with the screened Coulomb matrix elements $\gamma^{\Omega \Omega'}_{kk',kk}$. Finally, the last line in Eq. (3) describes the intrinsic Coulomb-induced intervalley coupling of excitonic states in different valleys and has been discussed in the main text. Similarly to the Rabi frequency, we also consider non-linear phase-space filling effects scaling with $D^{\Omega \Omega'}_{N} (t) = \sum_k g_{\Omega k} g_{\Omega' k} V^{\Omega \Omega'}_{kk} e^{i Q_k (t)}$.

The appearing Coulomb matrix elements are taken from PBE-based DFT calculations. In WS$_2$ they correspond to the distance of the involved states located within one valley ($\Delta_{\Omega} = 0$) or in different valleys ($\Delta_{\Omega} = K - K$).

The values of the effective masses $m^*_i$ of the spin-degenerated parabolic bands around the K points are taken from PBE-based DFT calculations. In WS$_2$, they correspond to $m^*_3 = 0.36$, $m^*_2 = 0.27$ for the conduction band, and $m^*_1 = 0.36$, $m^*_0 = 0.50$ for the valence band.

Data availability

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

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**Author contributions**

G.B. and I.B.-V. have performed the theoretical calculations of the valley polarization. The experimental studies have been carried out by the coauthors from the University of Münster. All coauthors have contributed to the writing of the manuscript and the interpretation of results.

**Additional information**

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