Unveiling valley lifetimes of free charge carriers in monolayer WSe$_2$

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Two-dimensional transition metal dichalcogenides (TMDs) offer the possibility to address the electron’s valley degree of freedom making them interesting for valley-based electronics, so-called valleytronics\textsuperscript{1–3}. The device performance of potential valleytronic applications largely depends on the valley lifetimes of free charge carriers. Here, we report on nanosecond long, gate-dependent valley lifetimes of free charge carriers in WSe$_2$, unambiguously identified by the combination of time-resolved Kerr rotation (TRKR) and electrical transport measurements. While the valley polarization increases when tuning the Fermi level into the conduction or valence band, there is a strong decrease of the respective valley lifetime consistent with both electron-phonon and spin-orbit scattering. The longest lifetimes are seen for spin-polarized bound excitons in the band gap region. We explain our findings via two distinct, Fermi level-dependent scattering channels of optically excited, valley polarized bright trions either via dark or bound states. By electrostatic gating we demonstrate that WSe$_2$ can be tuned to be either an ideal host for long-lived localized spin states or allow for nanosecond valley lifetimes of free charge carriers ($>\text{10 ns}$) explaining the huge variation in previously reported lifetimes extracted from TRKR\textsuperscript{4–13}.

With band gaps in the optically visible energy range\textsuperscript{14–16} and spin-split valleys which allow the creation of valley- and spin-polarized excitons by circularly polarized light\textsuperscript{1,17}, monolayer (ML) TMDs are a very promising family of materials in the field of both spin- and valleytronics\textsuperscript{1,2,18}. However, the full potential of TMD-based devices for valleytronic applications critically depends on their valley lifetime of free charge carriers. So far, there is a huge variation in experimentally reported valley lifetimes, which range from the picosecond up to the microsecond timescale\textsuperscript{4–13}. Especially the longer lifetimes are not consistent with ab-initio studies that predict valley lifetimes in the picosecond range limited by electron-phonon coupling\textsuperscript{7,8}. This discrepancy is partly due to the ambiguous use of the term valley polarization, which can be explained in respect to two measurement techniques typically used for exploring spin and valley dynamics in ML TMDs: Time-resolved photoluminescence (TRPL) and time-resolved Kerr rotation (TRKR). Both techniques rely on the valley-selective optical excitation of excitons by circularly polarized laser pulses (see Fig. 1a, circles represent the photo-excited electron-hole pair, shaded areas represent the filling of the bands with free charge carriers). The situation in Fig. 1a is sometimes called a valley polarization as, e.g., the numbers of holes in the valence band differ between the K and K’ valleys. In this article we identify how such an exciton valley polarization can create a net valley polarization of free conduction and valence band states after the photo-excited charge carriers have recombined (see Fig. 1b) and determine the valley lifetimes of the respective free charge carrier valley polarization. Here, TRPL reaches its limitations as it is restricted to exciton lifetimes\textsuperscript{17} and is therefore not capable to determine a valley polarization of free charge carriers after exciton recombination. However, the probe pulse in TRKR can detect the temporal decay of the valley polarization from the Kerr rotation angle when tuned to the trion energy, as the creation of the trion depends on the availability of free charge carriers within each valley.

To identify the existence of a valley polarization of free charge carriers and determine its valley lifetimes, we combine TRKR, electrical transport measurements, and photoluminescence (PL) spectroscopy on ML WSe$_2$ protected by hexagonal boron nitride and contacted via graphite electrodes (see Method section and Supporting Information (SI) for details on device fabrication). The combination of electrical transport and PL measurements (Fig. 1c) allows to assign the position of the Fermi level to the corresponding back-gate voltage ($V_{BG}$)\textsuperscript{19}: Between $-80 \text{ V}$ and $-10 \text{ V}$ the Fermi-level is pinned within the band gap of the TMD due to mid-gap states, resulting in a very low conductance with a current of some tens of pA due to residual hopping transport\textsuperscript{20,21} and the dominance of bound exciton states ($X_{\text{bound}}$) in the PL spectrum\textsuperscript{17,22,23}. Between $-10 \text{ V}$ and $10 \text{ V}$ the current undergoes an exponential increase as the Fermi level moves through the tail states of the conduction band\textsuperscript{24,25}. Above $V_{BG} = 20 \text{ V}$ the Fermi level is tuned into the conduction band, resulting in a linear gate voltage dependence of the current in accordance to diffusive charge transport of free electrons and the complete disappearance of the neutral exciton ($X_0$) as enough free charge carriers are present for the formation of the energetically
favourable charged excitons (trions, $X_{\pm/0}$)\textsuperscript{17}. At even higher electron densities we observe the appearance of the $X'_-$ feature, which can either be attributed to the interaction of an exciton with the Fermi sea of free electrons or to the onset of filling the energetically higher, spin-split conduction band\textsuperscript{26–28}.

Fig. 1d shows TRKR traces for representative gate voltages measured with pump and probe energies in the trion regime at a temperature of $T = 40$ K, showing two exponentially decaying signals. Within the band gap ($V_{BG} = -40$ V, orange data points, dashed line represents the axis with the Kerr rotation angle $\theta_K$ being zero) a long-lived polarization with a lifetime exceeding the laser repetition interval of 12.5 ns can be observed together with a short-lived polarization of around 1 ns. In the transition regime between tail states and conduction band ($V_{BG} = 20$ V, green curve) the long-lived polarization starts to vanish, whereas the short-lived polarization first undergoes a sign reversal and then shows an increasing amplitude towards higher charge carrier densities at larger $V_{BG}$ values (compare green, blue, and violet curves within the first two ns). We fitted the data over the whole gate-voltage range by the sum of two exponential decays (solid lines) and plotted the extracted amplitudes and lifetimes in Figs. 1e and 1f, respectively.

The Kerr rotation amplitude $\theta_K$ of the long-lived polarization is almost constant over the whole gap regime and starts to disappear as soon as the Fermi level reaches the tail regime (red data points in Fig. 1e), demonstrating its connection to band gap states. On the other hand, the amplitude of the short-lived polarization (black data points) shows a linear increase with increasing charge carrier density between $V_{BG} = 10$ V and 50 V (see green line in Fig. 1e as a guide to the eye). As this increase goes...
hand in hand with the linear increase in current in this gate voltage range, it is clearly connected to the increasing number of free charge carriers in the conduction band and, hence, can be attributed to a valley polarization of these free charge carriers. This assignment is backed up by the fact that the amplitude reaches a maximum at around the same gate voltages where the X feature appears in the PL map of Fig. 1c. The decrease of $\theta_{BG}$ is expected at even larger $V_{BG}$ values as the filling of the upper, spin-inverted conduction band will reduce the overall net valley polarization of free charge carriers. Finally, the strong decrease in lifetime towards higher gate-voltages (see black data points in Fig. 1f) also supports our assignment of the measured valley polarization to the free band carriers, as such a decay is expected from both wave vector dependent electron-phonon and spin-orbit scattering mechanisms.

The free carrier valley polarization and the band gap polarization show distinctively different temperature dependencies of their respective lifetimes as depicted in Fig. 1g, where for $V_{BG} < 0$ V only the band gap polarization and for $V_{BG} > 0$ V only the valley polarization is plotted for simplicity (see dashed lines in Fig. 1f). The valley lifetime of the conduction band polarization strongly decreases from 20 ns at 10 K to below 200 ps at 70 K. Such a strong temperature dependence is expected if electron-phonon scattering limits the valley lifetimes. In contrast, the long-lived polarization in the band gap is far more robust against temperature and retains lifetimes of 10 ns at 70 K and can be well observed up to temperatures of around 100 K. This is the temperature at which the bound exciton emission in PL typically disappears, highlighting a possible connection between this long-lived polarization and bound excitons. This notion is backed up by comparing other publications showing either long-lived TRKR signals or bound exciton features in PL, respectively, showing that both signals often have similar temperature dependencies.

The mechanisms which explain both the formation of the free carrier valley polarization and the long-lived polarization in the gap region are depicted in Fig. 2. We start with the Fermi level tuned into the conduction band ($V_{BG} > 10$ V) at equilibrium conditions, i.e., an equal number of free charge carriers in both valleys (indicated by the shaded areas in the band structure). A circularly polarized laser pump pulse now excites valley-selectively electron-hole pairs (circles in Fig. 2a). By the interaction with the free conduction band carriers, the electron-hole pairs first create bright trions which, however, cannot directly be responsible for the TRKR signals in the ns range as their recombination times are typically in the ps range. The recombination of the photo-excited electron-hole pairs within the same valley can also not lead to a net valley polarization of resident charge carriers. In contrast, a net valley polarization can be formed only if one charge of the electron-hole pair scatters into the other valley. In case of WSe$_2$, this can easily happen by the intervalley transition of the electron into the energetically lower conduction band of the same spin-orientation in the K’-valley under the emission of an optical phonon (Fig. 2b). The subsequent recombination of the photo-excited holes with free electrons of the K-valley on the time-scale $\tau_{\text{obs}}$ (this process has a finite possibility as explained in the SI) will lead to a situation where the photo-excited electrons have increased the electron number in the K-valley. At the same time the K-valley is missing the same number of free electrons which recombined with the photo-excited holes (see Figs. 2c and 2d). This leads to a net valley polarization of conduction band electrons. We assign the Fermi level dependent valley lifetimes $\tau_{V}$ of the valley polarization created by this process to the black data points in Fig. 1f for $V_{BG} > 10$ V. Our model also explains the linear increase in Kerr rotation amplitude between $V_{BG} = 10$ V and 50 V in Fig. 1e, as with increasing free charge carrier density it becomes more likely that photo-excited holes can recombine with free charge carriers of the K-valley’s conduction band.

Next to the scattering via dark states, bright trions can also bind to localized states within the band gap caused e.g. by vacancies or dopant atoms. We identify these bound states as the origin of the long-lived polarization seen as the red data points in Fig. 1e and 1f. We note that this polarization is also measured with a laser probe pulse at the bright trion energy. When probing at the energetically lower bound exciton energies no Kerr rotation signal is observed. Therefore, we do not directly probe the polarization of the bound exciton states but rather have to consider a charge transfer process between bound excitons and the optically accessible conduction band states. This leads to a complication: On the one hand, the Fermi level has to be in the conduction band to have free carriers available both for the formation of the initially excited bright trions by the pump pulse and also for the creation of the final valley polarization. But at the same time, having the Fermi level in the conduction band also means that all band gap states are occupied by unpolarized charge carriers, preventing an interaction with bright trions.

In this context, it is important to consider the existence of charge puddles in the transition regions between gap and bands. Scanning tunneling spectroscopy studies revealed that monolayer TMDs can show conduction band minima (CBM) and valence band maxima (VBM) energies which can spatially vary by hundreds of meV over length-scales as small as 10 nm due to strain variations (see schematic in Fig. 2e). In this situation, charge puddles are formed as depicted by the shaded areas in Fig. 2e. While bright trions are easily formed with the charges in these puddles, their formation is diminished in nearby regions where the Fermi level is in the band gap. This picture accounts for the coexistence of both the exciton ($X_0$) and the trion feature ($X_+/−$) over a part of the gate voltage range in PL measurements as seen both in Fig. 1c and previous work. Our model for the long-lived polarization is now based on the assumption that a
photo-excited electron-hole pair can create a bound trion at a band gap state with an additional charge carrier taken from the conduction band (i.e. charges from the puddles) (Fig. 2f). The resulting imbalance of free charge carriers between K and K’ valley will relax to equilibrium conditions within the time-scale of the valley lifetime $\tau_v^{CB}$ (d). e, Due to strain variations, monolayer TMDs can show conduction band minima (CBM) and valence band maxima (VBM) energies which can spatially vary by hundreds of meV over length-scales as small as 10 nm$^{36}$, resulting in the appearance of charge puddles depicted as shaded areas. f to i, Scattering mechanism via bound states: The photo-excited electron-hole pair can create a long-lived bound trion at a band gap state with an additional charge carrier from the charge puddles (f), creating at the same time a valley polarization (g). During the bound trion’s recombination (h) the initially caught charge carrier can transfer back into its original valley and, hence, will again create a valley polarization (i).

The bound exciton lifetimes can reach up to the $\mu$s range$^{22,43}$, which is comparable to the longest reported lifetimes in TRKR measurements$^{5,6,8}$. Furthermore, it was demonstrated that these bound excitons show a certain degree of polarization in PL$^{22}$, indicating that a spin polarization of these bound excitons is not completely relaxed at the time of their recombination. Therefore, during the bound exciton’s recombination (Fig. 2h), we argue that the initially caught charge carrier will predominantly transfer back into the valley where it came from (the one with the same spin orientation) and, hence, will again create a valley polarization (Fig. 2i). As it is discussed in the SI in more detail, the measured long-lived TRKR signal mainly reflects the bound trion recombination time as $\tau_v^{CB} \ll \tau_v^{bound}$. The decrease in its amplitude (red data points in Fig. 1e) towards the conduction band can be well understood, as an increasing Fermi level will decrease the number of unoccupied localized states in the band gap at which a bright trion can be bound$^{22}$. An important aspect of our model is that it predicts a sign reversal of the net valley polarization for the two scattering mechanisms via dark and bound excitons (compare Figs. 2d and 2i where the net valley polarization is carried by K’ and by K states, respectively), which is indeed seen in the measurements (see black data points for positive and red data points for negative gate voltages in Fig. 1e).

To confirm that our model indeed describes the underlying valley- and spin-dynamics consistently, we study a device made from ML MoSe$2$. In contrast to WSe$2$, in MoSe$2$ the formation of dark excitons is energetically not favorable due to its inverted conduction band spin ordering (see inset in Fig. 3a)$^{17,42}$. Hence, the scattering mechanism via dark excitons (Figs. 2b to 2d), which is responsible for the linear increase of the valley polarization with increasing charge carrier density, is not expected. In contrast, the scattering mechanism via bound excitons is still feasible in MoSe$2$ (Figs. 2f to 2i), but in that case the amplitude of the valley polarization is not limited by the...
amount of free charge carriers but rather by the number of bound excitons which can be created (see transition from Fig. 2f to 2g). And in fact, the TRKR data from the MoSe$_2$ sample shows both a long-lived and a short-lived polarization (see Figs. 3b and 3c) consistent to the scattering mechanism via bound states, but no increase of the Kerr rotation amplitude towards higher charge carrier densities, although the increase of the measured current by more than four orders of magnitude (Fig. 3a) clearly demonstrates that the Fermi level can be tuned into the conduction band of MoSe$_2$.

Finally, to confirm that our model also holds for the valence band we studied another WSe$_2$ sample in which we were able to tune the Fermi level all the way from the valence band into the conduction band. Figs. 4a and 4b show the Kerr rotation amplitude and the lifetime of the respective valley polarizations of both bands which got polarized by the scattering channel via dark trion states (Figs. 2b to 2d). Next to the conduction band, also the valence band shows the expected increase in the valley polarization and decrease in valley lifetimes with higher charge carrier densities. Interestingly, the valley lifetimes of the valence band states are a factor of 30 longer than the corresponding valley lifetimes of the conduction band states (see different y-axes).

Remarkably, the valley lifetimes in our samples are found to vary between 100 ps and tens of ns at 10 K, which is much longer than expected from ab-initio studies of pristine TMD monolayers that predict electron-phonon-limited valley lifetimes in the lower ps-range$^{7,8}$. Accordingly, to achieve such long-lived valley lifetimes the intervalley electron-phonon scattering has to be suppressed, which is most likely accomplished by fabrication-induced local strain variations in our samples. In this respect, it was shown that strain indeed has a significant impact on the band structure of TMDs$^{36,44}$, being able to suppress the electron-phonon coupling$^{32,45}$ and, hence, can e.g. lead to an increase in charge carrier mobilities$^{32,46}$.

Together with our model in Fig. 2 this possible strain-induced decrease in electron-phonon coupling can explain how an exciton valley polarization can create a nanosecond long valley polarization of free charge carriers. This valley polarization of free charge carriers can be clearly identified in our experiments, as 1.) its amplitude increases linearly with the gate-induced charge carrier density which goes hand in hand with a simultaneous increase in electrical conductance. 2.) its amplitude decreases as soon as the upper, spin-inverted conduction band starts to be filled, and 3.) its lifetime decreases towards higher charge carrier densities in accordance to theory about wave vector dependent electron-phonon and spin-orbit scattering mechanisms$^{7,29–33}$. Overall, we have
shown that by changing the Fermi level via gating, TMDs can be tuned to be either ideal hosts for long-lived localized spin states or allow valley lifetimes of conduction and valence band states exceeding 10 ns at 10 K, which are adequate timescales for both spin manipulation and valley transport.

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Methods: Measurement scheme to minimize photo-induced screening of the gate electric field — For optical measurements on 2-dimensional materials it is important to account for the screening of the gate electric field by photo-excited charged defects in the dielectric layer. We note that the true gate-dependent spin and valley dynamics can be masked when using a conventional measurement scheme, in which the time delay between pump and probe pulses is swept at a fixed gate voltage. Within this conventional measurement scheme a photo-induced temporal shift of the Fermi level on a laboratory timescale after setting a new gate voltage will lead to the fact that Kerr rotation signals within one time delay trace get recorded at effectively different charge carrier densities. We therefore developed a new measurement scheme in which we continuously sweep the gate voltage for fixed time delays between pump and probe pulses. In our new method each data point of a specific TRKR curve is recorded exactly the same amount of time after setting the corresponding gate voltage. All data points are thus recorded at the same charge carrier density. See the Supporting Information for a more detailed discussion on this matter.

Sample fabrication — Hexagonal boron nitride (hBN)/ML TMD half-stacks were transferred via a dry transfer method onto prepatterned electrodes fabricated on Si++/SiO2 (300 nm) wafers used as back gates. The fabrication of CVD WSe2 is described in Ref. 14. See SI for more details.

TRKR — We use two mode-locked Ti:sapphire lasers to independently tune the energies of both pump and probe laser pulses. The pump energy was kept \(\leq 1\) meV above the probe energy. Both energies were kept \(\leq 5\) meV near the peak position of the trion feature in PL. An electronic delay between both pulses covers the full laser repetition interval of 12.5 ns with a jitter of less than 1 ps. The pulse widths are 5 ps and the FWHM spot sizes are 8 \(\mu\)m. The power was kept between 200 – 600 \(\mu\)W. A detailed scheme of the experimental setup can be found in the SI.

PL — For excitation a diode cw-laser with an energy of 2.33 eV and a power of 1 \(\mu\)W was used. A lens with a numerical aperture of 0.66 focused the laser beam to a FWHM spot size of 6 \(\mu\)m and also collects the emitted PL light.
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Supporting Information: Unveiling valley lifetimes of free charge carriers in monolayer WSe$_2$

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This Supporting Information contains a description of the device fabrication in section I, a discussion on how to diminish the impact of the laser-induced screening of the gate electric field in section II, a discussion of the fitting method in section III, a discussion that the lifetime which we attribute to the valley polarization cannot be explained by a dark exciton lifetime in section IV, additional explanations to the figures shown in the main manuscript in section V, and a schematic of the used TRKR setup in section VI.

I. DETAILED INFORMATION ABOUT DEVICE FABRICATION

Fig. S1a shows an optical image and Fig. S1b the corresponding schematics of the WSe$_2$ sample used for the measurement presented in Fig. 1 of the main manuscript. It consists of a monolayer WSe$_2$ flake encapsulated by hBN and electrically contacted with graphitic leads. The sample is placed on a Si$^{++}$/SiO$_2$ substrate with an oxide thickness $d_{ox} \approx 300$ nm, which was used to apply a back-gate voltage. The ML WSe$_2$ flake was obtained by a standard exfoliation technique from a commercially available bulk crystal (HQ Graphene) onto a polydimethyloxane (PDMS) stamp. The ML was identified from optical contrast, Raman spectroscopy and in-situ PL response. Afterwards, the flake was covered with a top-hBN flake using a standard dry-transfer process. By means of reactive ion etching (RIE) we etched the flake into a rectangular shape. RIE was done with a gas mixture of O$_2$/CF$_4$ at a ratio of 1:4.

The subsequent fabrication steps, which are necessary to incorporate graphitic contacts, are depicted in Fig. S2. First, we built an hBN/graphite heterostructure on a Si$^{++}$/SiO$_2$ substrate. Then, the inverse image of the contact geometry was written by means of electron beam lithography into a spin-coated layer of polymethylmethacrylate (PMMA), which after development served as an etching mask for the following RIE step. We employed a selective RIE process using only O$_2$ that allows to etch graphite at a much higher rate than hBN. However, this process still is supposed to attack the hBN, resulting in a rougher surface inducing more strain than normally expected from an atomically flat hBN crystals.

In the next step, the WSe$_2$/hBN half-sandwich was picked up at 130°C with a PDMS/polycarbonate (PC) stamp and transferred onto the pre-patterned contact geometry by melting the PC membrane to the substrate. Finally, after dissolving the PC membrane with chloroform, leads to the graphitic contacts were patterned in a second electron beam lithography step before depositing Cr(5 nm)/Au(50 nm) contacts.

The MoSe$_2$ device used for the measurement discussed in Fig. 3 of the main manuscript, is a half-sandwiched ML MoSe$_2$ device contacted with graphitic leads used for transport measurements. Fig. S1c shows an optical image of this device before contacting one side of the transparent graphitic top-gate via a Cr/Au electrode. The MoSe$_2$ ML is highlighted by the orange dashed line and the top hBN flake by the green dashed line. The gate modulation in this device was achieved by a transparent graphitic top-gate (white dashed line). The MoSe$_2$ monolayer was exfoliated and covered with hBN in the same manner as described for the WSe$_2$ ML.

The fabrication steps for patterning the graphitic contacts are depicted in Fig. S3. The graphite was exfoliated onto a Si$^{++}$/SiO$_2$ substrate. Afterwards, the contact geometry was written by e-beam lithography as a positive image into a PMMA layer to define an aluminum hard mask. This hard mask was used for RIE etching with pure O$_2$. The aluminum mask was removed with tetramethylammoniumhydroxid (TMAH) and the MoSe$_2$/hBN half-sandwich was transferred onto the contacts. Finally, the graphitic top-gate and contacts were contacted by Cr/Au leads.

Fig. S1d shows an optical image of the CVD-grown WSe$_2$ device used for the measurements shown in Fig. 4 of the main manuscript. Directly after growth, an hBN flake was placed on the WSe$_2$ to protect it from degradation. Using the before-mentioned hot-pickup technique, the hBN/WSe$_2$ stack was transferred onto a Si$^{++}$/SiO$_2$(300 nm) substrate with prepatterned Cr/Au electrodes.

We note that all fabrication steps were down under ambient clean room conditions.
FIG. S1. a, Optical microscope image of the WSe$_2$ device used for the measurements in Fig. 1 of the main manuscript and b, schematic representation of the device structure. c, Optical microscope image of the MoSe$_2$ sample used for the measurement in Fig. 3 of the main manuscript. The image was taken before contacting the transparent graphitic top-gate via a Cr/Au electrode. c, Optical microscope image of the CVD-grown WSe$_2$ sample used for the measurements in Fig. 4 of the main manuscript.

FIG. S2. Fabrication process of the WSe$_2$ device used for the measurements shown in Fig. 1 of the main manuscript. a, Graphite/hBN stack on a Si$^{++}$/SiO$_2$ substrate. b, Reactive ion etching of the contact geometry as defined in an electron-beam lithography step. The PMMA layer serves as an etching mask. c, Device geometry after etching. The PMMA mask layer was removed with aceton. d, Transfer of the WSe$_2$/hBN half-sandwich onto the contact geometry. The half-sandwich was picked up with a hot pick-up method using a PDMS/PC stamp. e, Deposition of the half-sandwich by melting the transfer PC membrane to the substrate. Afterwards, the PC was dissolved in chloroform. f, Growth of Cr/Au for contacting the graphitic leads to finalize the device.
**II. HOW TO DIMINISH THE PHOTO-INDUCED SCREENING OF THE GATE-ELECTRIC FIELD**

To unveil the true gate-dependent spin and valley dynamics, the standard optical measurement techniques have to be modified to account for the screening of the gate electric field by photo-excited charged defects in the dielectric layer.\(^1\)\(^-\)\(^3\) We demonstrate that disregarding this procedure can lead to erroneous conclusions drawn from gate-dependent measurements.

Donor and acceptor like defect states in hBN and SiO\(_2\) (or defect states at the interface between these insulators and a 2D material) can be optically active for photons energies in the visible spectral range.\(^1\)\(^-\)\(^3\) In the presence of a gate electric field, which is applied across the dielectric layer, photo-excited charge carriers can either tunnel towards the 2D material or the gate electrode, leaving behind a charged defect state. This charged defect state will then screen the gate-electric field; which in turn will change the effective gate-induced charge carrier density in the 2D-material.\(^1\)\(^-\)\(^3\)

Furthermore, photo-induced changes in the properties of the TMD device can occur on significantly different time-scales.\(^4\)\(^-\)\(^6\) This complicates the optical measurement of the gate-dependent valley and spin dynamics: Once the gate-voltage is set to a certain value, the time-dependent photo-induced screening of the gate-electric field will lead to an unwanted change in gate-induced charge carrier densities and therefore a shift of the Fermi level over time. In particular, this is an issue in the "conventional" measurement technique where the gate-voltage is set to a fixed value and then the full TRKR curve gets recorded by varying the time delay \(\Delta t\) between pump and probe pulses over laboratory time. This is schematically depicted in Fig. S4a, where we assume that for each TRKR curve the Kerr rotation amplitude is measured at ten successive time delays before the next gate voltage is applied.

In this method, data point #1 is recorded right after setting the gate voltage, whereas the last data point of this curve (#10 in this example) may be recorded minutes later (this is the time we need to measure our actual TRKR curves, which consist of up to 200 data point measured at different time delays). But during this measurement time, the photo-doping effect will continuously shift the Fermi level. As a result, the data points within a single TRKR curves are recorded at different charge carrier densities.

To circumvent this problem, we adapted our measurement scheme by first setting a time delay and then record the Kerr rotation signal for a full gate voltage sweep (see numbering of data points in Fig. S4b). For maximum comparability, we use the same gate sweep direction and velocity for all TRKR, PL, and electrical measurements, which ensures the photo-doping effect impacts all measurements in the same way.

With this method, each data point of a specific TRKR...
FIG. S4. a, Schematic representation of the conventional TRKR measurement scheme where the time delay between pump and probe laser pulses is successively increased from $\Delta t = 0$ ns to 12 ns before the next TRKR trace gets recorded for the next gate voltage (see numbering of data points). Due to temporal changes in the screening of the gate-electric field on laboratory time scales, subsequent data point measured at the same gate-voltage might be recorded at a slightly different charge carrier densities. b, Schematic representation of our new TRKR measuring scheme, where a full gate-sweep is performed for each time delay (see numbering of data points). c, As the time delays in this new method are distributed randomly, a change of device properties over lab time can be identified by the same apparent “noise” signal for different gate voltages. d, to f, Direct comparison between the conventional and the new measurement method. Both gate-dependent TRKR measurements were conducted right after each other on the same day, but yield significantly different amplitudes, lifetimes and overall gate-dependent changes.

curve has the same "history", i.e., each data point is not only recorded exactly at the same time after setting the corresponding gate voltage, but also the temporal course of both setting and staying at previous gate voltages during the continuous illumination of the sample is exactly the same. Therefore, we can be certain that all data point of a specific TRKR curve are in fact recorded at the same charge carrier density.

In our new method we also randomize the sequence of the time delays (see numbering of data points in Fig. S4b). This is an important step for identifying changes of the device properties on laboratory time-scales, which are especially pronounced within the first few hours of each new cooling cycle. We suspect that this temporal change is due to an degassing of initially adsorbed molecules on top of the devices due to laser illumination. In this context, we note that one cooling cycle usually extends over five days before we have to change the liquid helium container. At this point, the device necessarily has to be warmed up to room temperature and residuals from gas permeation through the elastomer sealing gaskets, micro-leakages or other gas loads my absorb on the devices.

When using the conventional measurement scheme, the temporal change of the device properties due to the degassing of absorbed molecules over laboratory time may emerge in a TRKR measurement as an exponentially decaying signal and therefore can lead to a misinterpretation of the measurement. Instead, in our new method this change over laboratory time is randomly distributed over the whole range of measured delay times. Therefore, a change in device properties over lab time can easily be identified as an apparent, highly reproducible "noise" signal when comparing delay scans at different gate voltages. This is depicted in Fig. S4c where we show a gate-dependent TRKR measurements recorded right after cooling down the device from ambient conditions. The TRKR curves for the three gate voltages are vertically shifted for better visibility. It becomes obvious that the apparent noise of these curves is almost identical, showing that in fact the device slowly changes its properties over time and that the change in Kerr rotation amplitude due to photo-induced effects is more pronounced than the actual noise. Especially the first few measurements at time delays of xxx and xxx ns are clearly visible as peaks because the exponentially decreasing amplitude over laboratory time has its strongest impact. We discard...
measurements as shown in Fig. S4c and wait until the device properties have settled to such an extent that the random noise is visible between different traces.

A direct comparison between both methods is depicted in Figs. S4d to S4f, where we plot the Kerr rotation amplitude and lifetime of the Kerr rotation signal we assign to the valley polarization of free charge carriers. Both gate dependent TRKR measurements were taken directly one after the other on the first day of a new cooling cycle, first by the conventional method, then by the new method. For the former, the first TRKR curve was measured at a gate voltage close to 80 V and then the gate voltage was continuously decreased to 20 V. The extracted Kerr rotation amplitude almost decays exponential in the gate sweep direction (see Fig. S4d).

This is a clear indication of the exponentially decaying change in device properties due to the photo-induced effects. In contrast, with our new method we clearly observe the linear increase in polarization with increasing gate voltage (see green line in Fig. S4e) which is expected from a valley polarization of free charge carriers.

Next to the gate-dependent Kerr rotation amplitudes, also the extracted lifetimes differ significantly between both measurement methods as shown in Fig. S4f. The apparent lifetimes in case of the conventional method are much shorter than the ones obtained from the new method. This discrepancy is due to the fact that in case of the conventional method the exponentially decreasing change in device properties over laboratory time is projected onto the sweep velocity of the delay-time: A slow measurement of the time-delay trace would project the largest change in the exponentially decreasing change of device properties over laboratory time into the first few measured time delays, yielding an apparent short lifetime. A fast measurement of the time-delay trace would instead distribute the same change in device properties over a larger span of measured time-delays, therefore yielding a longer apparent lifetime.

Finally, we note that the photo-induced screening of the gate field leads to a minor complication in the comparison of gate-dependent PL and TRKR data. As stated before, we use the same gate sweep direction and velocity for all TRKR and PL measurements, which ensures the photo-induced effects impact all measurements in a similar way. The only difference stems from the laser excitation energy which was around 1.7 eV in case of TRKR and 2.33 eV in case of PL measurements. But a higher laser energy yields a stronger photo-doping effect as additional, energetically lower defect states can be excited. This explains why the three regions identified in both TRKR and PL data (the gap region, the tail region, and the conduction band region) seem to slightly differ by a few volts in the back gate voltage dependent measurements in Fig. 1 of the main manuscript.

III. FITTING METHOD AND RESULTS

The lifetimes $\tau_i$ (i = v for valley or i = b for bound exciton) and Kerr rotation amplitudes $\Theta_i$ in the main manuscript were acquired by fitting the TRKR curves by a two-exponential function of the form:

$$\Theta_K(t) = \Theta_v \cdot \exp \left( -\frac{t}{\tau_v} \right) + \Theta_b \cdot \exp \left( -\frac{t}{\tau_b} \right)$$

(1)

However, when fitting the TRKR curves, we have to consider that at low temperatures the long-lived bound exciton polarization is much longer than the laser repetition interval of $T_{\text{rep}} = 12.5$ ns. This leads to a non-zero Kerr rotation signal slightly before the next pump pulse reaches the sample at $\Delta t = 0$ ns (see e.g. orange curve in Fig. 1d or the schematic in Fig. S5(a)). Therefore, we now consider the influence of the subsequent pump pulse on an already existing exciton population stemming from previous pulses. For this, we assume that the pump pulse will have a negligible effect on the already existing excitons. Accordingly, the TRKR data can be fitted by a sum over several pulses and a bi-exponential decay of the form:

$$\Theta_K(t) = \Theta_v \cdot \exp \left( -\frac{t}{\tau_v} \right)$$

$$+ \sum_n \Theta'_b \cdot \exp \left( -\frac{t + nT_{\text{rep}}}{\tau_b} \right)$$

(2)

We note that equations 1 and 2 yield exactly the same lifetimes $\tau_i$ as the terms which depend on the time $t$ are mathematically identical. The fitting procedures only results in different Kerr rotation amplitudes of the bound exciton polarization. Factoring out the exponential term for the bound exciton signal in equation 2 yields the following relationship:

$$\Theta_b = \Theta'_b \sum_n \exp \left( -\frac{n \cdot T_{\text{rep}}}{\tau_b} \right)$$

(3)

The two amplitudes $\Theta_b$ and $\Theta'_b$ are schematically depicted in Fig. S5a. Here the solid black curve is the TRKR curve which is the sum of the 1 ns long signal stemming from the valley polarization (black dashed line) and the longer-lived signal originating from the polarized bound excitons (red dashed line). In the main manuscript we plot $\Theta_b$, i.e. the overall Kerr rotation amplitude of the bound exciton signal measured from $\Theta_K = 0$ as this amplitude is the most intuitive one when comparing the fitted values to the raw data. According to equation 3 the amplitude $\Theta_b$ not only considers the impact of the last pump pulse, but is the weighted sum over all previous pulses. Instead the amplitude $\Theta'_b$ is the actual increase in the long-lived TRKR signal created by each individual pulse (see green arrow in Fig. S5a).

Fig. S5b shows the same data as Fig. 1e of the main manuscript, which was obtained by using the fitting function of equation 1. Instead, Fig. S5c depicts results of the
FIG. S5. a, Schematic representation of the different Kerr rotation amplitudes obtained by the two fitting functions in equations 1 and 2, respectively. $\Theta_v'$ (green arrow) only depicts the increase in the long-lived signal induced by the current pump pulse, whereas $\Theta_b$ represents the total amplitude, which also includes leftover polarization from previous pump pulses. b, and c, Direct comparison of the results using the two fitting functions.

Next, we note that the amplitude of the valley polarization $\Theta_v$ is most likely underestimated in the band gap region by the used fitting model. To illustrate this, we simulate the data shown in Figs. 1e and 1f based on the model depicted in Fig. 2. We use a simplified three level system where the respective levels, $\tau_{\text{rec}}$ denoting the occupation numbers of the respective levels, $\tau_{\text{bound}}$ the recombination lifetime of the bound excitons, and $\tau_v$ the valley lifetime.

We solve this system of coupled rate equations by numerical integration. First, we focus on the process responsible for the creation of the valley polarization during the recombination of the bound excitons (illustrated in Figs. 2h to 2i). We therefore initialize the system by putting $10^5$ excitons in the $|B\rangle$ level and setting the occupation numbers of the other levels to zero (see Fig. S6a). The lifetime $\tau_{\text{bound}}$ of the bound exciton level is set to $24\,\text{ns}$ in accordance to the measurements in the band gap region of Fig. 1f. The resulting temporal occupation of $|V\rangle$ is simulated for different valley lifetimes $\tau_v$ (see Fig. S6b). We note that the occupation of the level $|V\rangle$ is most relevant for the Kerr rotation signal. This becomes obvious as a Kerr rotation can only be measured for probe pulse energies tuned into the bright trion regime. As explained in the main manuscript, this is due to the fact that the additional charge carrier, which is needed for the formation of the trion, has to come from the bands. Hence, the valley-selective excitation of trions can directly probe a valley polarization of free charge carriers. Consistent to this, no Kerr rotation signal is observed when probing at the energetically lower bound exciton energies. Hence, we only plot the occupation of the level $|V\rangle$ and not the one of $|B\rangle$.

The corresponding temporal evolution of the $|V\rangle$ occupations in Fig. S6b show three distinct regimes: As the level $|V\rangle$ is empty at $\Delta t = 0$, there is an initial increase in occupation number with the time constant of $\tau_v$. The occupation number then shows a maximum af-
FIG. S6. a, A three state model used to simulate the lifetime of the Kerr rotation originating from the bound exciton states. Bound excitons recombine with a lifetime of \( \tau_{\text{rec}}^{\text{bound}} \) and polarize the valleys during the recombination process (see Fig. 2h). The valley polarization then relaxes into the ground state via a rate of \( 1/\tau_v \). b, Results from numerical simulation for an initial configuration of \( N_V = 0 \) and \( N_B = 10^5 \) at \( t = 0 \) for different \( \tau_v \). c, Same data as in Fig. 1f. d, f, Results of the three state model by additionally assuming an initial occupation of the \( |V| \) state at \( t = 0 \). Further explanation see text.

ter approximately \( 3 \cdot \tau_v \). At this point the filling of this level through level \( |B\rangle \) and the time constant \( \tau_{\text{rec}}^{\text{bound}} \) are equal to its emptying to the ground state with the time constant \( \tau_v \). Afterwards, the occupation number of \( |V\rangle \) slowly decreases. We fit this decrease by an exponential function and confirm that for \( \tau_v \ll \tau_{\text{rec}}^{\text{bound}} \) the decay time is equal to the recombination time of bound excitons used for the simulation (\( \tau_{\text{rec}}^{\text{bound}} = 24 \text{ ns} \)). This is also expected, as under such conditions the number of particles in \( |V\rangle \) is only determined by the number of most recent transitions from \( |B\rangle \) to \( |V\rangle \) via the time \( \tau_{\text{rec}}^{\text{bound}} \). All other particles in \( |V\rangle \) have already decayed into the ground state. The fitted recombination time only deviates from the input value if \( \tau_v \) approaches \( \tau_{\text{rec}}^{\text{bound}} \) as the measured valley lifetime in Fig. 1f (\( \tau_v = 1 \text{ ns} \)) is one order of magnitude shorter than the long-lived bound exciton lifetimes (24 ns), we are confident that this long-lived Kerr rotation signal represents the bound exciton recombination time \( \tau_{\text{rec}}^{\text{bound}} \) (see green curve in Fig. S6b).

This conclusion is also important for the interpretation of gate-dependent lifetimes of the bound excitons (red data points in Fig. 1f and Fig. S6c), as the decrease in lifetimes starting in the tail region cannot be due to the decreasing valley lifetime. This is illustrated in Fig. S6c by the open triangular data points, for which we assume a gate-voltage independent bound exciton lifetime of 24 ns and simulated the impact of the decreasing valley lifetimes on the fitted values. As it is also depicted in Fig. S6b, a decreasing valley lifetime from 1 ns (green curve) to 50 ps (red curve) changes the fitted exciton lifetimes only marginally by a maximum of 0.1 ns. Accordingly, the actual bound exciton recombination time \( \tau_{\text{rec}}^{\text{bound}} \) has to decrease towards higher gate voltages (i.e. higher free charge carrier densities). This might be due to both screening and band gap renormalization effects.

Of course, we do not observe the increase in polarization seen in Fig. S6b in the raw data (see Fig. 1d). This is due to the fact that we have neglected that the creation of the bound trions also directly creates a valley polarization (see Fig. 2f and 2g). Hence, we extend our simulation by initializing both the \( |V\rangle \) and the \( |B\rangle \) states with the same initial occupation number (Fig. S6d) and assume a valley lifetime of 1 ns. The resulting time evolution of the \( |V\rangle \) state is depicted in Fig. S6e as a solid line and shows an exponential decrease as our TRKR data. For comparison, we also include the curve from Fig. S6f for the same valley
lifetime as a dashed line.

The simulated curve can be fitted perfectly by the bi-exponential function of equation 1 (see dashed red line in Fig. S6f). Most importantly, the fit yields exactly the two lifetimes put into the simulation, i.e. 1 ns for the valley lifetime and 24 ns for the bound exciton lifetime. This is not self-evident, as the fit function assumes an erroneous time-dependence of the long-lived signal (green dashed line in Fig. S6f) compared to the actual time dependent amplitude according to our model (solid green line). The most important impact of this analysis is that the Kerr rotation amplitude of the valley polarization at \( t = 0 \) gets underestimated: Instead of \( N_V^{\text{true}} \), we only determine the amplitude \( N_V^{\text{fit}} \). Hence, the real amplitude of the valley polarization \( \Theta_V \) is most likely larger than \( \Theta_V^{\text{fit}} \) in Fig. S5c.

IV. DARK EXCITONS

Dark excitons cannot couple to circularly polarized photons with E-field vectors parallel to the plane of the TMD layer. Nevertheless, in-plane symmetry dictates that spin-flip transitions such as the recombination process depicted in Fig. 2c are possible via the coupling to photons with a propagation direction in the plane of the TMD layer with out-of-plane linear polarization. Accordingly, PL emission from dark excitons can be seen in PL setups which are capable of detecting in-plane emissions.

We now discuss the TRKR signal, which we attribute to the valley polarization (Fig. 1d) cannot be assigned to dark excitons. Overall, there are three arguments against such an assignment:

1.) By far the most important argument is that gate dependent PL measurements show a decreasing amplitude of dark exciton emission for increasing charge carrier densities. This is in complete contradiction to the increase of the valley polarization with increasing charge carrier density as seen in Fig. 1e and 4a.

2.) Even at the lowest temperatures, gate-dependent dark exciton recombination times (at zero magnetic field) barely reach 1 ns. Instead, we measure lifetimes of up to 30 ns (see Fig. 1f and 4b) for the Kerr rotation signal we attribute to the valley polarization.

3.) A recent publication based on spin-noise measurements excluded dark excitons as a source of long-lived signals in TRKR measurements.

V. COMMENTS AND ADDITIONAL EXPLANATIONS TO THE FIGURES OF THE MAIN MANUSCRIPT

A. Fig. 1c

**Schottky barriers:** One main problem in contacting 2-dimensional semiconductors is the formation of Schottky barriers between the TMD flake and the contacts. Depending on the sign of the applied dc bias voltage, either the drain or the source contact is therefore reversed biased, whereas the other contact is forward biased. In this respect, our graphitic contacts are no different and we observe pronounced Schottky barrier characteristics in all of our devices. Therefore, the main drop of the applied 5 V bias voltage will occur over the reversed biased Schottky barrier and not across the TMD channel.

Furthermore, we note that the measured resistance at a constant bias voltage varies significantly between different contacts even on the same device. Unfortunately, the impedance of some contacts are too high to even use these contacts as voltage probes. This is the reason that no Hall-effect measurement could be conducted on the device shown in Fig. S1(a) to determine the free charge carrier density as a function of gate-voltage.

**X’ feature:** At high electron densities we observe the appearance of the so-called X’ feature in the PL data, whose physical origin has not fully been determined. One possible explanation of this PL feature is a different interaction of excitons with low and high charge carrier densities, respectively. It is argued that a trion can only be considered as a three-particle object at low enough charge carrier densities, whereas at higher charge carrier densities the interaction between excitons and a Fermi sea of free electrons leads to an exciton-polaron picture. However, we believe that this explanation is rather unlikely to explain the X’ feature in our measurements, as the transition between the three-particle and the exciton-polaron picture is argued to occur at quite low charge carrier densities (the Fermi level position \( E_F \) measured form the conduction band minimum has to be much smaller than the trion binding energy \( E_T \)). In contrast, we argue that the X’ feature is due to the onset of the upper spin-split conduction band.

To support this picture, we estimate the position of the Fermi level \( E_F \) for the gate voltage range of the X’ emission.

First, we model the ML TMD as a two-dimensional electron gas (2DEG). This assumption is justified as the electron’s Fermi wavelength \( \lambda_F \) is much larger than the thickness of the monolayer TMD. As long as \( E_F \) is close enough to the conduction band minimums at the \( K/K’ \) valleys the bands can be approximated to follow a nearly quadratic dispersion relation, giving rise to a well-defined effective mass \( m^* \). Under these circumstances the position of the Fermi level as a function of charge carrier density is given as:

\[
E_F = \frac{2\pi h^2 n}{m^* g_s g_v},
\]

with the spin degeneracy \( g_s \), the valley degeneracy \( g_v \), the effective mass \( m^* \) and the reduced Planck’s constant \( h \). To express the charge carrier density \( n \) as a function of gate voltage \( V_G \), we use the standard plate capacitor model. As soon as the Fermi level is within the conduction or valence band of the monolayer TMD, we consider all effects due to the band gap, mid-gap states, tail states,
and quantum capacitance by introducing the so-called
threshold voltage $V_{th}$ and write:\textsuperscript{23–25}

$$n = \frac{\varepsilon_0 \varepsilon_r}{d \cdot e} (V_G - V_{th}),$$ \hspace{1cm} (7)

with $\varepsilon_0$ being the vacuum permittivity, $\varepsilon_r$ the relative
permittivity of the dielectric, $e$ the elementary charge, and $d$
the dielectric thickness. For the device shown in Fig. 1, we estimate
the threshold voltage to be $V_{th} \approx 10$ V. This is the gate voltage
at which the current starts to increase linearly with increasing back gate voltage. Putting in all
values, we end up with a charge carrier density of around
$4 \cdot 10^{12} \text{ cm}^{-2}$ at a gate voltage of 80 V.

With this result the position of the Fermi energy at this
gate voltage can now be calculated from equation 6. In
the case of a ML TMD the spin degeneracy is lifted ($g_s = 1$)
and only valley degeneracy has to be considered ($g_v = 2$).
We furthermore assume $m^* = 0.28 \cdot m_e$,\textsuperscript{26} which finally
yields a Fermi energy of about 40 meV. This energy is well
within the range of the assumed spin splitting between
lower and upper conduction band.\textsuperscript{26,27}

$$\text{B. Figs. 1d, 1e and 1f}$$

The reason for showing 40 K data: At 40 K the
lifetime of the valley polarization is significantly shorter
than the lifetime of the bound exciton signal over the
whole gate voltage range (see Fig. 1f). This is necessary
to reliable extract both lifetimes from a twofponential fit
to the raw data. However, at lower temperatures (see
Fig. 1g) the lifetime of the valley polarization approaches
the lifetime of the bound excitons especially at low charge
carrier densities (i.e. low gate voltages). Therefore, it
gets difficult to distinguish both signals in a TRKR curve and fitting gets challenging. We e.g. attribute the small decrease in the bound exciton lifetimes towards 0 V backgate voltage seen for 10 K and 20 K to this fitting issue. Instead, for all other temperatures, at which valley
and bound exciton lifetimes are far enough apart, the
bound exciton lifetimes are almost constant over the
depicted gate voltage range.

Blue data points: As seen in Fig. 1e, the Kerr rotation
signal which we attributed to the valley polarization
of free charge carriers undergoes a sign reversal. Because
of its small amplitude, the fitting gets very error-prone in
the region where it crosses the $\theta_K = 0$ axis. Nevertheless,
the fitting routine yields the smooth transition of the
Kerr rotation amplitude as seen in Fig. 1e, if the degree of
freedom for the fit is reduced. This was done by assuming
a fixed valley lifetime in this gate voltage regime (see
blue data points in Fig. 1f) which allows for a continuous
transition between the positive and negative gate voltages.

C. Fig. 3b,c

Additional TRKR signal in the lower ps range:
For the WSe\textsubscript{2} device in Fig. 1, we have focused on the
nanosecond time-scale to discuss the valley and bound
exciton dynamics. Nevertheless, when increasing the
temporal resolution of our measurement, we can also
observe a much shorter-lived Kerr rotation signal with a
lifetime in the lower ps-range. We attribute this initial
fast depolarization, which is shown in Fig. 3, to the
lifetime of bright excitons.

Consistent to the varying values of the bright exciton
lifetimes reported in literature,\textsuperscript{28–31} also the additional
short-lived TRKR signal shows strongly varying lifetimes
for different samples. In some samples, it is barely resolvable
as the effective temporal resolution of our TRKR setup is limited by the pulse widths of both pump and
probe lasers to 5 ps (we have chosen the energy-resolution
of a ps-laser over the temporal resolution of a fs-laser).
In other samples, the lifetime of this signal can reach up
to some tens of ps.

In this context, we now discuss the $\approx 200$ ps long Kerr
rotation signal shown in Fig. 3 of the main manuscript
for the monolayer MoSe\textsubscript{2} device, which we attribute
to the valley lifetime of this sample. Inconsistent to
this assignment is the fact that its lifetime does not decrease for higher charge carrier densities (i.e. higher positive gate voltages), which would be expected
from both electron-phonon and spin-orbit scattering
mechanisms.\textsuperscript{32–37} At the same time, the 200 ps lie within
the upper range of reported bright exciton lifetimes.\textsuperscript{28}
Therefore, we cannot exclude that this signal could also
result from relatively long recombination times of bright
excitons.

We note that the MoSe\textsubscript{2} flake is not fully encapsu-
lated by hBN, but instead is in contact with SiO$_2$ on the bottom side (see Fig. S3). In such a case, the variations in conduction band minima (CBM) and valence band maxima (VBM) energies as illustrated in Fig. 2e are especially pronounced.$^{38}$ We attribute this to be the reason for the much more pronounced overlap of the three different regimes (the gap region, the tail region, and the conduction band region) of this device compared to e.g. the device shown in Fig. 1 of the main manuscript.

VI. TIME-RESOLVED KERR ROTATION SETUP

Fig. S8 schematically depicts the setup used to conduct the TRKR experiments. Two wavelength tunable modelocked Ti:sapphire lasers (SPECTRA PHYSICS Tsunami) operating at 80 MHz repetition rate were used as pump and probe laser sources with typical pulse widths of about 5 ps. Both lasers can be synchronized via a lock-to-clock (LTCL) laser synchronization unit to set a variable time delay between pump and probe pulses ranging from 0 ns to 12.5 ns.$^{39}$ The polarization of the pump beam can be switched between $\sigma^+$, $\sigma^-$ and linear by applying a voltage to the liquid crystal variable retarder. The laser beams are focused onto the sample by a 15 mm focal length aspheric lens (0.66 NA). Typical spot diameters are 8 $\mu$m FWHM. In order to distinguish and filter the pump from the probe beam, the pump beam enters and leaves the lens in a distance of 5 mm with respect to the probe beam position passing the lens in its center. Therefore, the probe beam hits the sample perpendicularly and gets reflected into itself before being guided towards the detection arm. Here, a pin-hole of 150 $\mu$m diameter is placed to block any off-axis beam reflections that might disturb the signal. After passing another half-wave plate serving to equilibrate the detection diodes when the pump is blocked, finally the probe beam gets split into its perpendicularly polarized components which are detected by the diodes A and B, respectively.$^{40}$

For measuring the Kerr rotation angle we modulate the pump and probe beams with optical choppers driven at a fast modulation frequency of 7 kHz (pump) and a slower frequency of 340 Hz (probe). The pre-amplified A-B diode signal can then be demodulated using two lock-in-amplifier stages yielding the TRKR signal.
FIG. S8. Schematic of the experimental setup. Pump and probe laser pulses stem from two independently tunable Ti-sapphire ps lasers, which are synchronized and electronically delayed with a temporal jitter of less than 1 ps. The Kerr rotation signal is detected by a polarization bridge with balanced photodiodes. The Kerr signal is further analyzed using a spectrometer and an autocorrelator.
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