

Ultrafast optical control of multivalley states in two-dimensional SnS

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We theoretically study the ultrafast optical control of multiple valley states in two-dimensional (2D) tin sulfide (SnS) monolayers, a member of the layered group-IV monochalcogenides, which is a promising class of materials for overcoming current challenges in valleytronics. By combining time-dependent density functional theory with Maxwell's equations, we simulate how both linearly and circularly polarized ultrashort laser pulses affect the electronic excitation dynamics and valley polarization in SnS. Our results reveal that the corrugated phosphorene-like crystal structure of SnS monolayers leads to the emergence of both linear and circular dichroism, allowing flexible manipulation of multivalley excitation by simply adjusting the light polarization. Moreover, the interplay between broken inversion symmetry and spin-orbit coupling gives rise to distinct Berry curvature effects and spin-valley coupling, thereby enabling circular dichroism. Furthermore, we propose that tuning the carrier-envelope phase of few-cycle femtosecond laser pulses can achieve subcycle, ultrafast switching among multiple valley states. These findings provide further insight into valley dynamics in 2D materials and may contribute to future developments in valleytronics applications.

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I. INTRODUCTION

The rise of two-dimensional (2D) materials, such as Graphene [1], transition metal dichalcogenides (TMDCs) [2], and h-BN [3] has opened new pathways for studying valleytronics phenomena [4,5]. These materials feature time-reversal-connected valleys in 2D hexagonal lattices, where two energy-degenerate but inequivalent K and K' points are distinguished by opposite spin angular momenta and Berry curvature [6]. To achieve valley polarization, which is crucial for valleytronics applications, time-reversal symmetry must be broken [7,8]. This can be achieved either by applying a magnetic field [5,9] or through dynamical processes like optical pumping with circularly polarized light [10,11]. In this context, valley-selective optical circular dichroism plays a pivotal role, as it enables the observation of the valley Hall effect, thus providing a pathway for the development of future valleytronics devices [12]. However, realizing practical

applications faces challenges due to stringent experimental requirements such as cryogenic temperatures and strong magnetic fields [9,11,13].

Recent studies highlight bulk group-IV monochalcogenides (MC), MX (where M = Sn, Ge and X = S, Se), as a promising class of materials for addressing the present challenges in valleytronics [14–19]. Bulk MCs have layered structures, where the layers are weakly bonded through van der Waals interactions. They feature D_{2h}^{16} space group with puckered layers akin to black phosphorus and exhibit high anisotropy between the armchair and zigzag directions [19–21]. Experimental findings have demonstrated valley-selective linear dichroism, revealing valley-specific optical transition rules [16,17]. Valleys along the Γ -X (V_X) and Γ -Y (V_Y) directions in reciprocal space can be selectively excited by x- and y-polarized light, respectively [14,16,17].

Interestingly, 2D layers of MC, consisting of mono- to a few layers, have also been synthesized experimentally [19,22,23]. Their anisotropic electronic and optical properties have been investigated theoretically within first-principles frameworks [20,21,24,25]. In particular, it is predicted that linearly polarized light can selectively excite paired valleys in MC monolayers, similar to their bulk counterparts. While previous studies have mainly focused on valley optical selection within the linear response [24–27], key questions remain unanswered regarding the nonlinear optical response. Specifically, will linear dichroism survive under strong laser fields, and what are the excitation dynamics? To fill these gaps,

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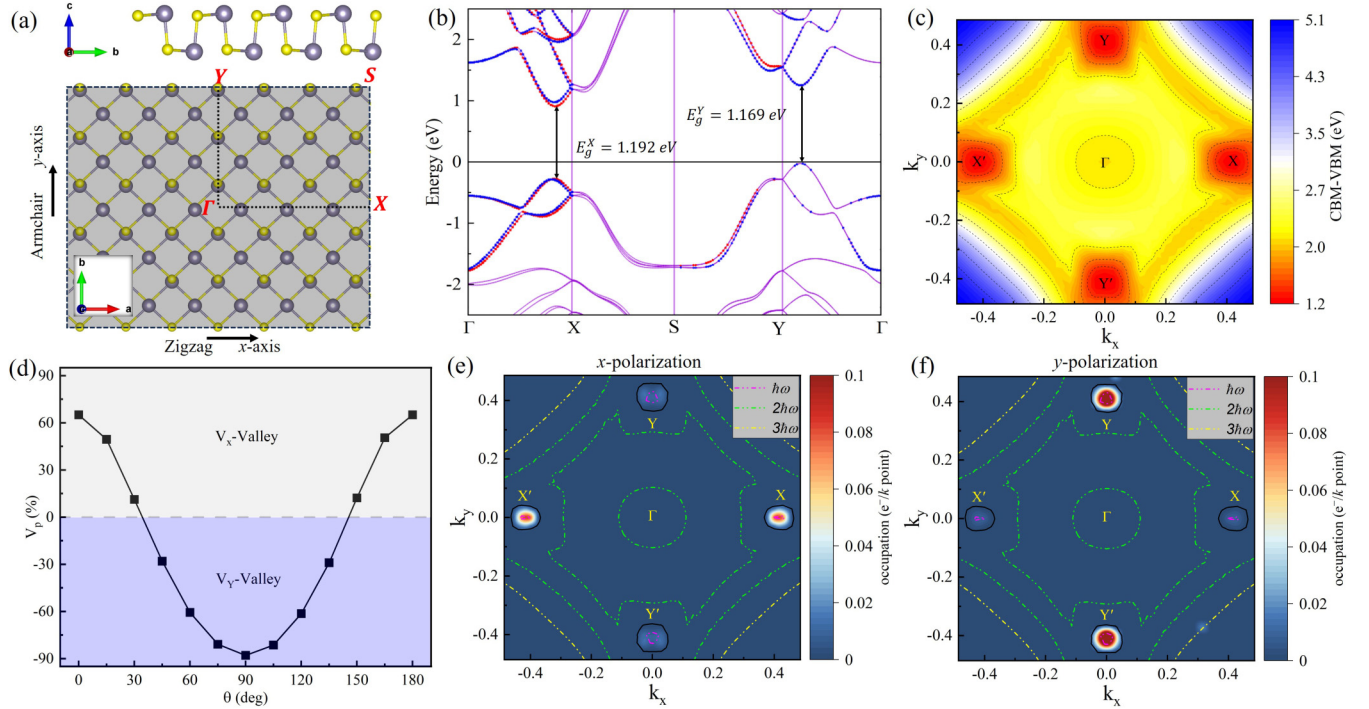


FIG. 1. (a) Schematic illustration of the SnS monolayer crystal structure. The upper panel shows the side view and the lower panel shows the top view, along with the respective BZ and high symmetry points. The gray (yellow) spheres represent Sn (S) atoms. (b) Electronic band structure with SOC along high symmetry points. The red and blue dots correspond to $S_z = \uparrow$ and $S_z = \downarrow$, respectively. (c) 2D map of the energy difference between the SnS CBM and VBM as a function of the wave vector $\mathbf{k}$ in the first BZ. (d) Polarization-dependent valley polarization. The positive values show the carrier density on the V_X valley while negative values show that carrier density is concentrated on V_Y -valley. $\mathbf{k}$ -resolved electron populations at the end of the pulse for (e) $\theta = 0^\circ$ and (f) $\theta = 90^\circ$ at weak intensity of 10^9 W cm^{-2} . The electron population is summed over the entire conduction band, and the dashed lines in (e) and (f) mark contours where the valence-conduction band gap matches $\hbar\omega$, $2\hbar\omega$, or $3\hbar\omega$, ($\hbar\omega = 1.1 \text{ eV}$) indicating resonant one-, two-, and three-photon absorption regions.

we will investigate how valley polarization evolves as the system transitions from linear to nonlinear optical regimes and how robust linear dichroism is under the strong field. Another significant aspect that has yet to be fully explored is the effect of transition from bulk to monolayer structures. This transition results in the loss of inversion symmetry, with monolayers belonging to the noncentrosymmetric C_{2v}^7 space group. In this symmetry-broken environment, spin-orbit coupling (SOC) generates an effective magnetic field that lifts the spin degeneracy. This raises the intriguing question: can monolayers of MCs exhibit spin(s)-valley(τ) coupling ($s \cdot \tau$) physics, similar to their TMDC counterparts, where the helicity of light controls both spin and valley characteristics, ultimately giving rise to circular dichroism?

Motivated by recent experimental demonstrations of sub-cycle control of valley dynamics [28,29], in this article, we investigate ultrafast electron dynamics driven by femtosecond laser pulses within the subpicosecond window before relaxation processes take effect. We focus on monolayer SnS, where the presence of heavy elements can result in significant SOC, making it suitable candidate to study the valleytronics and spintronics applications. Using the time-dependent density functional theory (TDDFT), we aim to explore the potential for SnS monolayer to exhibit multivalley states and identify the underlying mechanisms that govern such behavior. The outline of this paper is as follows. First, we revisit

the laser polarization-dependent valley polarization within the linear regime. We then explore the degree of inter- and intravalley polarization and robustness of the optical selection rule for the V_X and V_Y valleys in the nonlinear regime under the strong field. Next, we uncover a novel aspect of $s \cdot \tau$ coupling in monolayer SnS, driven by Berry curvature and the presence of time-reversal spin splitting. Lastly, we demonstrate the ultrafast optical control of multivalley selection on femtosecond timescales. Our study shows multivalley states and the coexistence of linear and circular dichroism in monolayer SnS, which can provide insight into valleytronics applications. The ultrafast valley polarization enables control of electron dynamics on subcycle timescales.

II. THEORETICAL FORMALISM

We consider a monolayer SnS, located in the xy plane [Fig. 1(a)] at $z = 0$, subject to a normally incident light pulse, and model their interaction by combining TDDFT and Maxwell's equations, referred to as the 2D Maxwell-TDDFT approach [30], using the open source package SALMON (Scalable *Ab-initio* Light-Matter simulator for Optics and Nanoscience) [31,32]. TDDFT offers a rigorous *ab initio* description of light-matter interactions, including the electronic and crystal structure together. This makes it a uniquely powerful approach for exploring ultrafast and nonlinear dy-

namics. The electronic response in SnS is calculated based on the TDDFT. The propagation of the incident light to the $+z$ direction, treated as macroscopic electromagnetic fields, is described by Maxwell's equations in terms of the vector potential $\mathbf{A}(z, t)$ with the x and y component,

$$\frac{1}{c^2} \frac{\partial^2 \mathbf{A}(z, t)}{\partial t^2} - \frac{\partial^2 \mathbf{A}(z, t)}{\partial z^2} = \frac{4\pi}{c} \mathbf{J}(z, t). \quad (1)$$

Here we use c.g.s. units. By assuming that the monolayer is sufficiently thin, we can safely consider the vector potential is spatially uniform inside the thin layer. Thus, the electric current density $\mathbf{J}(z, t)$ in Eq. (1) can be approximated as

$$\mathbf{J}(z, t) \approx \delta(z) \mathbf{J}_{2D}(t), \quad (2)$$

where $\delta(z)$ denotes the Dirac delta function, and $\mathbf{J}_{2D}(t)$ the 2D current density inside the thin layer. We treat it as a boundary value problem among the incident $\mathbf{A}^{(i)}$, reflected $\mathbf{A}^{(r)}$, and transmitted fields $\mathbf{A}^{(t)}$ as follows. At the monolayer position ($z = 0$), $\mathbf{A}(z, t)$ is continuous, and its derivative fulfills

$$-\left. \frac{\partial \mathbf{A}(z, t)}{\partial z} \right|_{z=0+} + \left. \frac{\partial \mathbf{A}(z, t)}{\partial z} \right|_{z=0-} = \frac{4\pi}{c} \mathbf{J}(z, t). \quad (3)$$

The continuity condition reads

$$\mathbf{A}(z = 0, t) = \mathbf{A}^{(t)}(t) = \mathbf{A}^{(i)}(t) + \mathbf{A}^{(r)}(t). \quad (4)$$

From Eqs. (3) and (4), we obtain the fundamental equation of the 2D approximation method,

$$\frac{d\mathbf{A}^{(t)}}{dt} = \frac{d\mathbf{A}^{(i)}}{dt} + 2\pi \mathbf{J}_{2D}[\mathbf{A}^{(t)}](t), \quad (5)$$

where $\mathbf{J}_{2D}[\mathbf{A}^{(t)}](t)$ stresses that $\mathbf{J}_{2D}(t)$ is determined by the vector potential at $z = 0$ which is equal to $\mathbf{A}^{(t)}$.

The time evolution of electron Kohn-Sham orbitals in a unit cell driven by $\mathbf{A}^{(t)}$ is governed by the time-dependent Kohn-Sham (TDKS) equation. The TDKS for the Bloch orbital is expressed in the velocity gauge as

$$i\hbar \frac{\partial}{\partial t} u_{b,k}(\mathbf{r}, t) = \left[\frac{1}{2m_e} \left\{ -i\hbar \nabla + \hbar \mathbf{k} + \frac{e\mathbf{A}^{(t)}(t)}{c} \right\}^2 + \widehat{v}_{\text{ion}} + v_H(\mathbf{r}, t) + v_{xc}(\mathbf{r}, t) \right] u_{b,k}(\mathbf{r}, t), \quad (6)$$

where $u_{b,k}(\mathbf{r}, t)$ is the Bloch orbital with b being the band index and $\mathbf{k}$ the 2D crystal momentum of the thin layer. The $\widehat{v}_{\text{ion}}$, v_H , v_{xc} are ionic pseudopotential, Hartree potential, and the exchange-correlation potential, respectively. SOC is introduced through the j -dependent nonlocal potential [33]. The 2D current density in Eq. (4) is obtained from the Bloch orbitals $u_{b,k}(\mathbf{r}, t)$ as follows:

$$\mathbf{J}_{2D}(t) = -\frac{e}{m_e} \int dz \int_{\Omega} \frac{dx dy}{\Omega} \sum_{bk} u_{bk}^*(\mathbf{r}, t) \times \left\{ -i\hbar \nabla + \hbar \mathbf{k} + \frac{e\mathbf{A}^{(t)}(t)}{c} \right\} \times u_{b,k}(\mathbf{r}, t) + \mathbf{J}_{ps} \quad (7)$$

where Ω is the 2D unit-cell area of the 2D material and $\mathbf{J}_{ps}$ is a current contribution from the nonlocal pseudopotential.

The excited electron population is defined as

$$\rho_k(t) = \sum_{c,v} \left| \int_{\Omega} d^3\mathbf{r} u_{v,k}^* u_{c,k}^{GS} u_{\frac{e}{\hbar c} \mathbf{A}^{(t)}} \right|^2 \quad (8)$$

where v and c are the indices for the valence and conduction bands, respectively, and $u_{b,k}^{GS}(\mathbf{r}) = u_{b,k}(\mathbf{r}, t = 0)$ is the Bloch orbital in the ground state.

A. Computational details

The lattice constants along the zigzag and armchair directions of single-layer SnS are 4.08 and 4.28 Å. A vacuum layer of thickness 17 Å are attached to both sides of the layer. For electron-ion interaction, we employ the norm-conserving pseudopotential [34] for Sn and S atoms. The adiabatic local density approximation (LDA) with Perdew-Zunger functional [35] is used for the exchange and correlation. The SOC is implemented in a noncollinear mode [36,37]. We consider the linearly and circularly polarized laser field vector potential of the following wave form:

$$\mathbf{A}^{(i)}(t) = -\frac{cE_{\text{max}}}{\omega} f(t) \left[\cos \left\{ \omega \left(t - \frac{T_p}{2} \right) + \varphi \right\} \hat{\mathbf{x}} + \varepsilon \sin \left\{ \omega \left(t - \frac{T_p}{2} \right) + \varphi \right\} \hat{\mathbf{y}} \right], \quad (9)$$

where ω is the average frequency, E_{max} is the maximum amplitude of the electric field, φ is a carrier-envelope phase (CEP) and T_p is the foot-to-foot pulse duration, corresponding to $0.26T_p$ full width at half maximum pulse duration. The $\varepsilon = 0, 1$ and -1 describe the linear, right, and left polarization respectively.

We use a $\cos^4$ -type envelope function $f(t)$ given by

$$f(t) = \begin{cases} \cos^4 \left(\pi \frac{t - T_p/2}{T_p} \right), & 0 \leq t \leq T_p \\ 0, & \text{otherwise} \end{cases}, \quad (10)$$

We set the CEP $\varphi = 0$ unless otherwise stated (until Fig. 4). The spatial grid size and the number of k points in the 2D reciprocal space are optimized through examination of the convergence of the calculation results; the r grid is set to $26 \times 26 \times 120$, and the k -mesh 35×35 in the Brillouin zone (BZ). The time step size is set to 5×10^{-4} femtosecond.

III. RESULTS AND DISCUSSION

A. Dependence of valley polarization on laser polarization

SnS monolayer is isoelectronic and has a structure similar to corrugated phosphorene as shown in Fig. 1(a). However, the presence of two different atomic species lowers crystal symmetry. The relative displacement between tin and chalcogenide atoms breaks the mirror symmetry along the armchair direction (b axis) while preserving it along the zigzag direction (a axis). Figure 1(b) shows the electronic band structures at high-symmetry points, revealing the valence and conduction band exhibit two distinct maxima and minima along the Γ -X and Γ -Y sections of the BZ. Band profiles for the topmost valence (VBM) and the bottom conduction (CBM) bands were extracted from DFT, and the energy difference between CBM and VBM is illustrated in Fig. 1(c). These

profiles indicate the positions of potential direct transitions for electrons from the valence to the conduction band at locations $X(X')$ and $Y(Y')$, named V_X and V_Y valleys, respectively, with nearly identical band gaps whose values are indicated in Fig. 1(b). While our findings are in agreement with earlier LDA- and GGA-based studies [24,27,38], recent studies with the GW approximation or hybrid functionals (e.g., HSE) report larger bandgap for the SnS monolayer [20,21,26]. It is well known that standard LDA and GGA functionals usually underestimate the band gaps of semiconductors and that the hybrid functionals and the nonequilibrium Green's function can provide more accurate bandgap values. However, for time-evolution calculations, the hybrid functional involves an explosive increase in computational complexity, while nonequilibrium Green's function is computationally much more demanding in terms of both computation and memory, as they require storing the wave functions at each time step [39]. For this reason, LDA is commonly used within the TDDFT framework and provides valuable insights [40–48]. In addition, the central conclusions of this work are unaffected by the absolute value of the bandgap, as the valley-selective excitation dynamics under consideration are determined by the crystal symmetry and the resonance condition between the photon energy and the bandgap. Any quantitative shift in the bandgap can be compensated by selecting an appropriate excitation photon energy, ensuring that the physical mechanisms remain unchanged.

Let us begin by analyzing how the laser-induced valley polarization changes as we vary the polarization direction of linearly polarized pulses within the ab plane, or xy plane. The valley polarization is defined as

$$V_p = (\rho_X - \rho_Y)/(\rho_X + \rho_Y), \quad (11)$$

where, $\rho_{X(Y)}$ represents the electron densities obtained by integrating the conduction band electron population around the $X(Y)$ points inside the black dashed inner circle around $X(Y)$ in Fig. 1(c). We use a photon energy of 1.10 eV, which is close to the bandgaps at the valleys and corresponds to a wavelength of 1127 nm. The foot-to-foot pulse length is set to eight optical cycles, or 7.85 fs full width at half maximum (FWHM). Note that for all valley polarization calculations and the valley populations shown were evaluated immediately after the pulse ends, before any relaxation processes occur.

In this subsection, we consider the linear response, using a sufficiently weak intensity of 10^9 W cm^{-2} . Figure 1(d) shows that the maximum valley polarization is achieved along the $X\text{-}\Gamma\text{-}X'$ ($\theta = 0^\circ$, x polarization) and $Y\text{-}\Gamma\text{-}Y'$ ($\theta = 90^\circ$, y polarization) directions, indicating strong valley selectivity in high-symmetry directions. This observation confirms the valley-related optical selection rule that the valley polarization in the momentum space is maximized when the excitation polarization matches the corresponding crystal orientation in the real space. Although the central photon energy is $\hbar\omega = 1.10 \text{ eV}$, the applied pulse has an ultrashort duration (7.85 fs FWHM) which has a spectral width of $\sim 0.23 \text{ eV}$. As a result, its spectrum spans approximately 0.98–1.22 eV, overlapping X and Y valley band gaps, leading to single-photon absorption and a nonvanishing population in the linear regime. The magnitude of the valley polarization is larger in the V_Y valley ($\theta = 90^\circ$) than in the V_X valley ($\theta = 0^\circ$). This difference can

be attributed to the fact that an x -polarized light can populate both V_X and V_Y [Fig. 1(e)], though the V_X valleys are excited more strongly. On the other hand, a y -polarized light primarily excites the V_Y valleys and cannot excite the V_X valley [Fig. 1(f)], since there is no coupling between the valence and conduction band at V_X in the y direction [24].

From a symmetry perspective, the crystal structure of monolayer SnS exhibits mirror symmetry along the zigzag direction, which leads to a sign reversal of the single-particle transition dipole under x polarization, while it remains unchanged under y polarization. Thus, the transitions under x polarization typically occur between states with opposite parity, whereas those under y polarization connect states with the same parity [26]. The valence and conduction bands, along with the p_x orbital, belong to the same irreducible representation and this symmetry condition leads to a finite transition dipole moment, enabling optical excitation at the V_X valley under x -polarized light [24]. In contrast, under y -polarized light the states involved have different representations highlighting the valley selective excitations and linear dichroism in SnS monolayer under x - and y -polarized light. Our observation is consistent with preceding works based on the dipole matrix elements [24,27,38].

B. Linear dichroism under strong field

Let us next investigate how the valley polarization is affected if we increase the laser intensity to the nonlinear regime. To explore this, we apply laser pulses linearly polarized along the $\Gamma\text{-}X$ ($\theta = 0^\circ$) and $\Gamma\text{-}Y$ ($\theta = 90^\circ$) directions, with the same parameters as in the previous subsection, except for intensity. Figure 2 shows the k -resolved excited electron population distribution after the pulse, highlighting the valley selection V_X and V_Y through distinct electric field polarization (left and middle columns for x and y polarization, respectively). The dashed lines indicate resonance conditions where the energy difference between the valence and conduction band equals $n\hbar\omega$ ($\hbar\omega = 1.1 \text{ eV}$ with $n = 1, 2, 3$). These lines mark the onset of single and multiphoton absorption in the Brillouin zone. The time evolution of the energy-resolved electron-hole distribution for y polarization is also presented in the right column. The behavior is similar for x polarization. At an intensity of $10^{10} \text{ W cm}^{-2}$, x/y -polarized light primarily excites the corresponding V_X/V_Y valley [Fig. 2(a)]. The excited carriers are located precisely where the interband energy difference is $\hbar\omega$, indicating direct single-photon excitation from VBM to CBM at the X and Y points. The energy-resolved electron-hole distribution also shows the dominance of single-photon absorption over the entire pulse duration. As the intensity increases to $5 \times 10^{10} \text{ W cm}^{-2}$ [Fig. 2(b)], x/y -polarized light excites not only the V_X/V_Y valley but also the V_Y/V_X valley, involving both single- and two-photon ionization. In addition, the regions between the valleys are slightly excited along the two-photon absorption lines, indicated by green dash-double-dotted lines. The single-photon absorption peak remains prominent up to $\sim 20 \text{ fs}$ and exhibits oscillations. These oscillations align with the field maxima and correspond to the applied field frequency, suggesting they may arise from virtual excitations. A subsequent decline in the peak is observed by the end of the pulse, attributed to Rabi

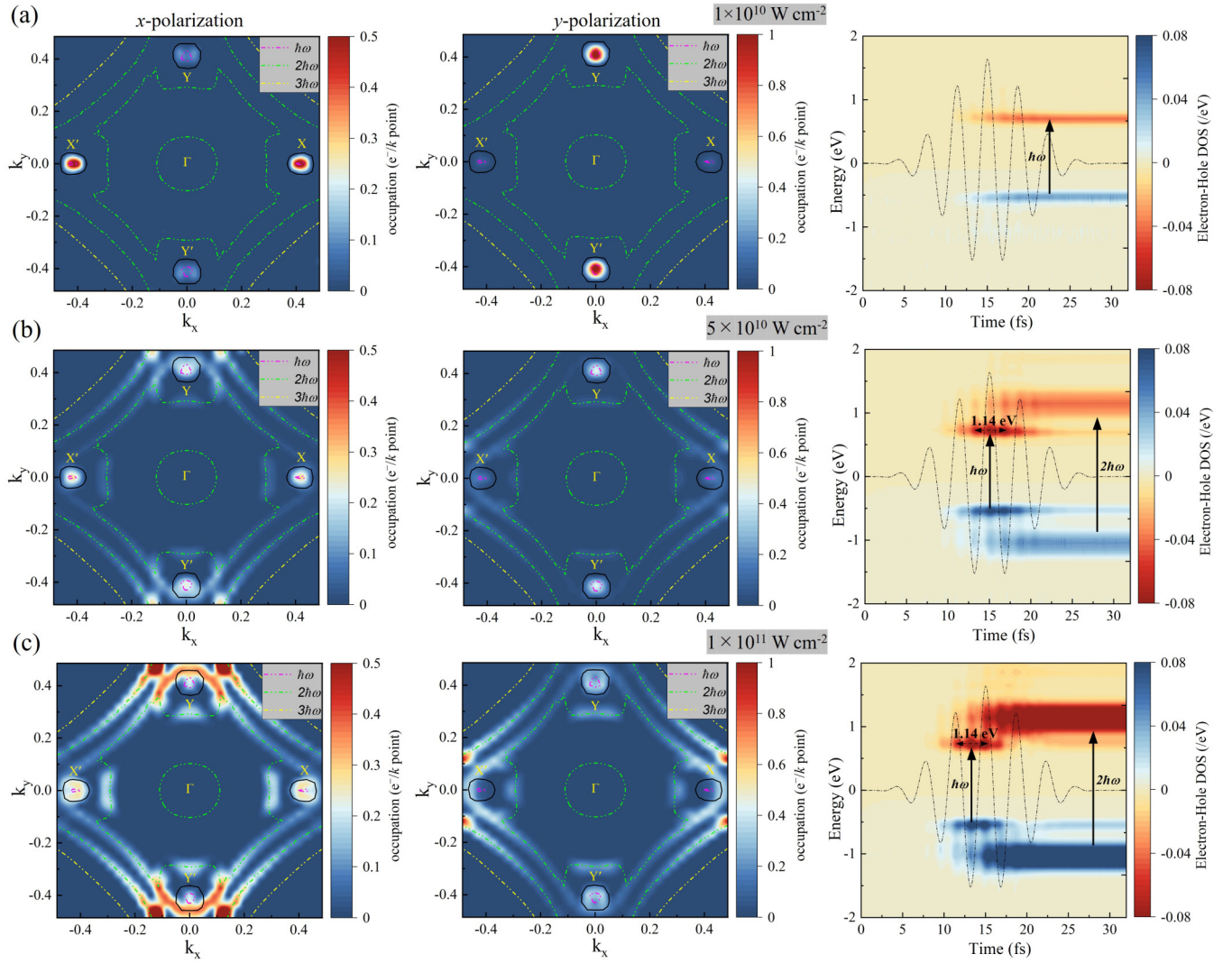


FIG. 2. Valley selective excitation by linearly polarized light in the first BZ at the end of the pulse for Γ -X (x polarization) and Γ -Y (y polarization) directions and the time-dependent evolution of the energy-resolved electron-hole distribution, projected onto ground state Kohn-Sham orbitals (far right panels) for (a) $1 \times 10^{10} \text{ W cm}^{-2}$ and (b) $5 \times 10^{10} \text{ W cm}^{-2}$ and (c) $1 \times 10^{11} \text{ W cm}^{-2}$. The contour lines indicate resonance conditions where the energy difference between the valence and conduction band equals $n\hbar\omega$ ($\hbar\omega = 1.1 \text{ eV}$, $n = 1, 2, 3$). The term occupation refers to the change in electron and hole occupation over time. The black dashed line shows the applied electric field.

oscillations. Our calculation of the ponderomotive energy ($\sim 11 \text{ meV}$) shows it is too small to close the one-photon channel, further supporting that the reduction is purely due to Rabi oscillations. At an even higher intensity of $10^{11} \text{ W cm}^{-2}$, we see substantial excitation in broader regions, particularly, with increased excitation along the X-Y direction [Fig. 2(c)]. Notably, x/y -polarized light excites electron around the V_Y/V_X valley more strongly than around the V_X/V_Y valley, in striking contrast to the low intensity cases. Indeed, the momentum matrix elements for the VBM to CBM transition are around the perpendicular valleys than around the parallel valleys, although they have significantly lower occurrence rate for lower intensities since these correspond to allowed indirect transitions [38]. One can see that as we increase the field strength, one-photon absorption reduces progressively. In the high-intensity case considered here, two-photon absorption takes the lead in the electron-hole distribution over time, and

higher-energy states become more important (not shown in the figure).

C. Inter- and intravalley polarization and electron dynamics

As we have seen above, x/y -polarized light does not only excite the V_X/V_Y valley but also the V_Y/V_X valley, especially in the nonlinear regime. In order to analyze the relation between laser polarization and valley excitation in more detail, let us define intervalley and intravalley polarization.

Intervalley polarization is defined as

$$P_{\text{inter}}^x = \frac{\rho_x^X - \rho_x^Y}{\rho_x^X + \rho_x^Y}, \quad P_{\text{inter}}^y = \frac{\rho_y^Y - \rho_y^X}{\rho_y^Y + \rho_y^X}, \quad (12)$$

where ρ_i^V (where $i = x, y$ and $V = X, Y$) represents the electron densities in the V valley under the i -polarized excitation pulse. P_{inter}^x and P_{inter}^y are the valley polarization [Eq. (11)] for

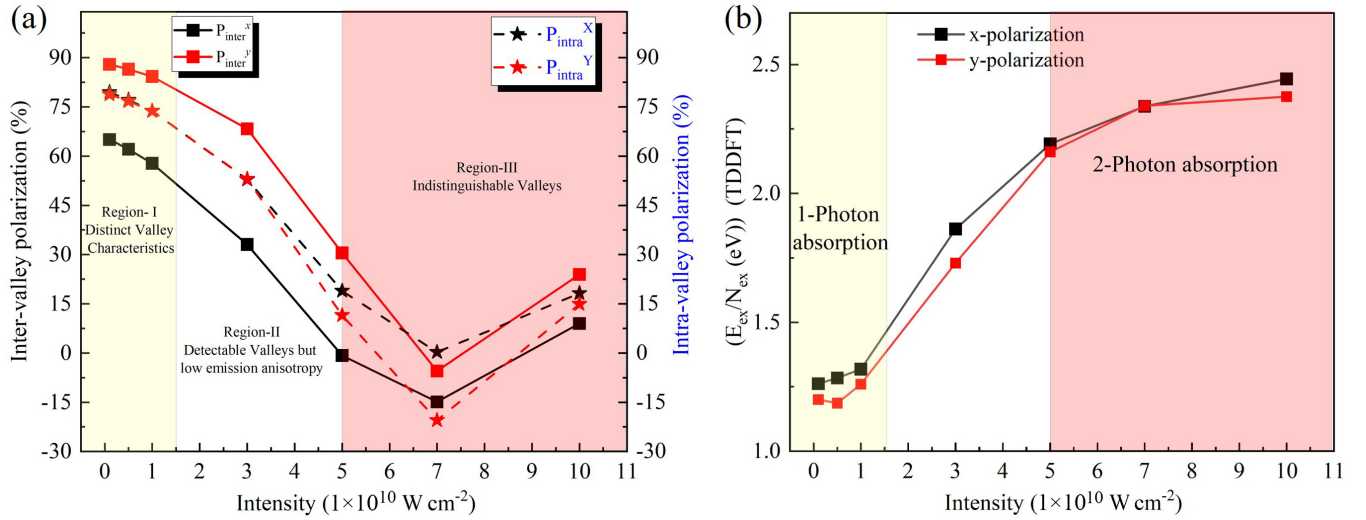


FIG. 3. (a) Inter- and intravalley polarization vs. laser intensity, illustrating three regions from strong valley polarization to suppressed valley polarization. (b) Change in photon excitation energy ($E_{\text{ex}}/N_{\text{ex}}$).

the x - and y -polarized pulses, respectively. On the other hand, intravalley is defined as

$$P_{\text{intra}}^x = \frac{\rho_x^x - \rho_y^x}{\rho_x^x + \rho_y^x}, \quad P_{\text{intra}}^y = \frac{\rho_y^y - \rho_x^y}{\rho_y^y + \rho_x^y} \quad (13)$$

The intervalley polarization measures $P_{\text{inter}}^x = \frac{\rho_x^x - \rho_y^y}{\rho_x^x + \rho_y^y}$, $P_{\text{inter}}^y = \frac{\rho_y^y - \rho_x^x}{\rho_y^y + \rho_x^x}$, the difference in excitation between the two valleys (V_X and V_Y) for a given laser polarization, which corresponds to comparing experimental photoluminescence (PL) intensities between the valleys. The intravalley polarization quantifies the effect of laser polarization direction on the excitation of each valley, corresponding to comparing PL intensities under parallel and cross-polarization. In other words, the former evaluates the anisotropy between V_X and V_Y , while the latter determines the emission characteristics and anisotropy within each valley.

The analysis of intervalley and intravalley polarizations reveals that P_{inter}^y is consistently higher than P_{inter}^x over the entire intensity range examined, while P_{intra}^x and P_{intra}^y have similar values. In addition, we can identify three distinct intensity regions [Fig. 3(a)] as follows:

Region I. At weak field strengths ($1 \times 10^9 - 1 \times 10^{10} \text{ W cm}^{-2}$), both inter- and intravalley polarization exhibit high values, indicating strong valley selectivity and efficient linear dichroism, though they slightly decrease with increasing intensity.

Region II. At intermediate field strengths ($3 \times 10^{10} - 5 \times 10^{10} \text{ W cm}^{-2}$), intervalley polarization decreases significantly, and linear dichroism weakens, as intensity increases. In this intensity region, this occurs as the pulse excites both valleys comparably, reducing asymmetry. The intervalley polarization at the V_X valley almost vanishes at $5 \times 10^{10} \text{ W cm}^{-2}$, while it remains positive ($\sim 30\%$) at V_Y ; there is still a noticeable difference between the V_X and V_Y valleys.

Region III. At strong field strengths ($> 5 \times 10^{10} \text{ W cm}^{-2}$), the valley optical selection rules break down. Both the

inter- and intravalley polarization become even negative at $7 \times 10^{10} \text{ W cm}^{-2}$, which indicates that the V_Y and V_X valleys are excited more by orthogonal polarization than by parallel polarization. Interestingly, valley polarization reincreases and becomes positive again with further increase in intensity. However, as we have seen in Fig. 2(c), the excitation areas around the V_X and V_Y valleys expand and are no longer completely isolated rendering valleys indistinguishable.

To further elucidate the reduction in valley polarization and linear dichroism, we plot the absorbed energy, evaluated as work done by laser field, per excited electron vs. laser intensity in Fig. 3(b). At low field strength (Region I), the absorbed energy per electron is approximately $1.2 \sim 1.3 \text{ eV}$, close to the photon energy (1.10 eV), signifying that single-photon absorption dominates the photoexcitation process. Single-photon absorption highlights the optical transitions expected at the direct bandgaps located at the X and Y points of the BZ, preserving linear dichroism, since the transition probabilities are directly related to the polarization of the light. The absorbed energy per electron increases in the intermediate region (Region II), which suggests the onset of two-photon absorption, leading to a reduction of valley polarization. At higher field strengths (Region III), two-photon absorption is the main excitation path, as we have seen in Fig. 2. This detailed analysis shows that the key factor driving the change in valley polarization is the transition from single-photon to two-photon absorption. Two-photon absorption follows selection rules distinct from those for single-photon absorption, resulting in increased electron populations in the valleys on the transverse axis, thereby rendering valley selection irrelevant. Our findings suggest that linear dichroism only prevails under linear response and is suppressed by two-photon excitation.

D. Berry curvature and spin-valley coupling

Berry curvature [50–53] is an essential physical property in valleytronics, capturing the geometric aspects of wave

functions and acting like a magnetic field in the momentum space. Berry curvature is given by $B_n(\mathbf{k}) = \nabla \times \mathbf{W}_{nk}$, where $\mathbf{W}_{nk} = -iu_{nk}|\frac{\partial}{\partial \mathbf{k}}|u_{nk}$ and $|u_{nk}\rangle$ is a normalized Kohn-Sham orbital, and n the band index. Figure 4(a) shows the k -resolved Berry curvature $B_n(\mathbf{k})$, obtained by summing the contributions from all occupied (valence) bands at each $\mathbf{k}$ point in the 2D Brillouin zone. The nonvanishing $B_n(\mathbf{k})$ in the SnS monolayer arises from its noncentrosymmetric lattice structure. The $B_n(\mathbf{k})$ properties are directly tied to the symmetry of the orthorhombic SnS monolayer. The system preserves mirror symmetry along the x direction, i.e., $M_x: (x, y) \rightarrow (-x, y)$. Under this operation, $\mathbf{k} \rightarrow (-k_x, k_y)$, the Berry curvature transforms as $B_n(k_x, k_y) \rightarrow -B_n(-k_x, k_y)$. In the presence of time-reversal symmetry and a single mirror plane, $B_n(\mathbf{k})$ behaves as an odd function and an even function [54] of k_x and k_y respectively. Therefore, the Berry curvature is positive and negative at X and X' valley-points, respectively, similar to hexagonal 2D TMDC monolayers where the K and K' valleys exhibit opposite Berry curvature due to broken inversion symmetry [4,7]. In contrast, pristine graphene is centrosymmetric, but external perturbations can break this symmetry, inducing a finite bandgap and valley-contrasting Berry curvature [55]. In addition, the lack of inversion symmetry leads to spin splitting of 6 and 70 meV on VBM and CBM, respectively, [Fig. 1(b)] with opposite spin at the time-reversal points X and X' owing to SOC. In contrast, the Y and Y' points have vanishing Berry curvature and spin splitting, possibly due to the absence of mirror symmetry with respect to the x axis. The Zeeman-type spin splitting leads to the V_X valley splitting into the two degenerate but inequivalent valleys at X and X' points analogous to the K and K' valleys in monolayers of TMDCs [4]. As a result, the SnS monolayer exhibits $s \cdot \tau$ coupling with optical selectivity determined by the spin index [12,56], and valley selectivity can be achieved by the helicity of light. This selective excitation mechanism is used in TMDCs monolayers, where circularly polarized light enables valley-specific excitation [10,17]. In this approach, the two valleys (K and K') are selectively excited by photons with opposite helicity, a phenomenon known as circular dichroism [57].

E. Circular dichroism in 2D SnS

Let us consider circularly polarized pulses with the same wavelength and pulse duration as those employed for linearly polarized pulses. As mentioned above, the combination of broken inversion symmetry and time-reversal symmetry ensures that the energy of the spin-down state at X' is equal to the energy of the spin-up state at X, i.e., $E_{\downarrow}(X') = E_{\uparrow}(X)$, effectively linking spin-down and spin-up states across the X' and X points. Due to this selection rule, interband transitions at the X and X' valleys can be selectively excited by right-hand circularly (RHC) and left-hand circularly (LHC) polarized light, respectively, yielding equivalent magnitudes of circular valley polarization [Eq. (14)], albeit in opposite valleys. Figures 4(b)–4(d) illustrates the excited carrier population under the RHC and LHC light. When RHC is applied, mainly spin-up electrons are excited to the conduction band at X (left panel), while mainly spin-down electrons are excited at X' when LHC (right panel) is applied. This results in a robust circular dichroic effect in the excited state populations.

The circular dichroism is evaluated in terms of circular valley polarization, which is defined similarly to that in TMDCs as follows:

$$\sigma^{\text{RHC(LHC)}} = \frac{\rho_X - \rho_{X'}}{\rho_X + \rho_{X'}}, \quad (14)$$

where ρ_X and $\rho_{X'}$ are electron densities around the X and X' valley points, respectively. Note that, unlike TMDC where in an ideal case the $\sigma^{\text{LHC}}/\sigma^{\text{RHC}}$ gives $\sim 100\%$ circular dichroism [10,58,59], the SnS monolayer exhibits strong but not absolute circular dichroism. We observe a maximum circular valley polarization of 44% in the weak field limit [Fig. 4(e)]. The relatively moderate circular valley polarization compared to the linear polarization case [Fig. 3(a)] can be attributed to the small spin splitting of VBM and CBM at the X(X') valleys, which limits the degree of polarization. Figure 4(e) shows a trend that is strikingly similar to the trend we have seen for linear polarization [Fig. 3(a)]; Under weak field where the X and X' valleys are distinct, circular dichroism initially appears but decreases with increasing field intensity. At resonant frequencies, both linear and circular polarizations exhibit single-photon transitions, localizing carriers at the valley points. However, at intensities $\geq 5 \times 10^{10} \text{ W cm}^{-2}$, two-photon absorption becomes prominent, causing circular valley polarization to decrease as the population shifts toward regions adjacent to the valleys. At the highest field intensity region, the nonlinear interaction further spreads excited electrons beyond the X and X' points, similar to the behavior observed for linear polarization. The SnS monolayer has not only V_X and V_Y valleys but also X-X' valley states, each governed by distinct optical selection rules. This allows the formation of multivalley states, providing additional valley degrees of freedom within a single system. Moreover, these valleys can be selectively accessed via linear and circular dichroism, providing a way to control valley-specific excitations. The multivalley physics discussed here is expected to extend to other group-IV monochalcogenides with the α -phase structure, such as SnSe and GeSe, which feature multivalley points and exhibit anisotropic optical and electronic properties. However, material-specific band structure and SOC strength can affect the multivalley state. SnS exhibits relatively strong SOC, which facilitates circular dichroism and enhances the optical accessibility of multiple valley states. In materials with weaker SOC, optical pumping may be less effective. However, the presence of Berry curvature due to noncentrosymmetric structure allows the electric detection of $s \cdot \tau$ polarization through an anomalous velocity perpendicular to the applied electric field [$\sim \mathbf{E} \times \mathbf{B}_n(\mathbf{k})$]. Charge carriers with $s \cdot \tau \pm 1/2$, excitable by left- and right-circularly polarized light, respectively, will exhibit opposite transverse conductivity (σ_{xy}), which can be detected via the valley Hall effect similar to TMDC [4,5].

F. Ultrafast optical control of multivalley states

The rectangular unit cell, as marked by black squares in Figs. 5(a)–5(c), positions the X-X' (Y-Y') valleys near the BZ boundaries. As a result, the X-X' (Y-Y') distance on the k plane across the BZ boundaries (0.16 a.u.) is much smaller than it appears within the BZ (0.66 a.u.). This may

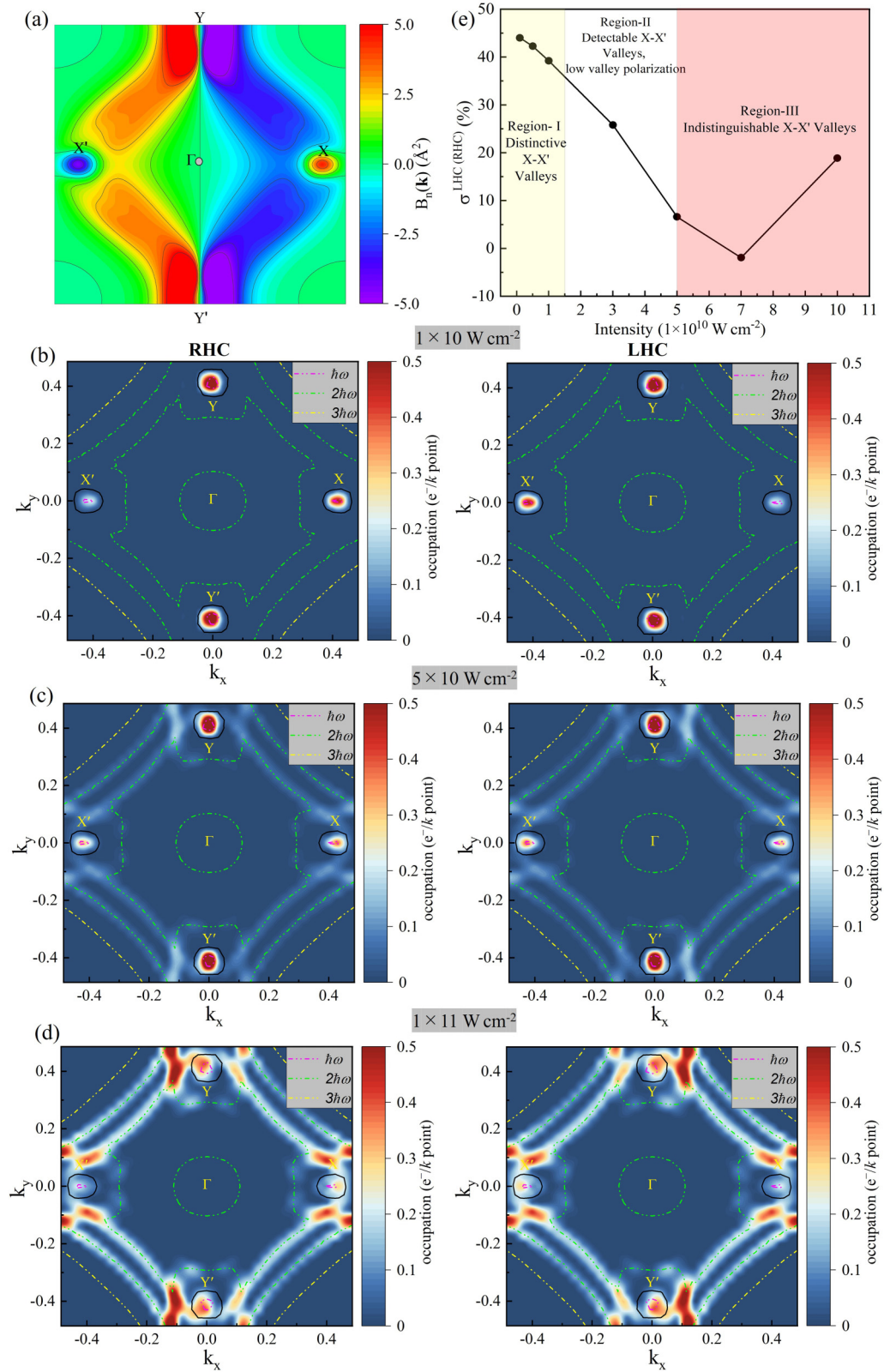


FIG. 4. (a) Momentum resolved out of plane (z component) of Berry curvature (calculated by OpenMX [49]), illustrating positive and negative peaks at X and X' points. Distribution of k -resolved electron populations by circularly polarized light at intensity (b) $1 \times 10^{10} \text{ W cm}^{-2}$, (c) $5 \times 10^{10} \text{ W cm}^{-2}$ and (d) $1 \times 10^{11} \text{ W cm}^{-2}$. The left and right panels show excited carrier population under right and left-handed circular polarization. (e) Circular valley polarization control relative to field strength. The dashed contour lines indicate resonance conditions where the energy difference between the valence and conduction band equals $n\hbar\omega$ ($\hbar\omega = 1.1 \text{ eV}$, $n = 1, 2, 3$).

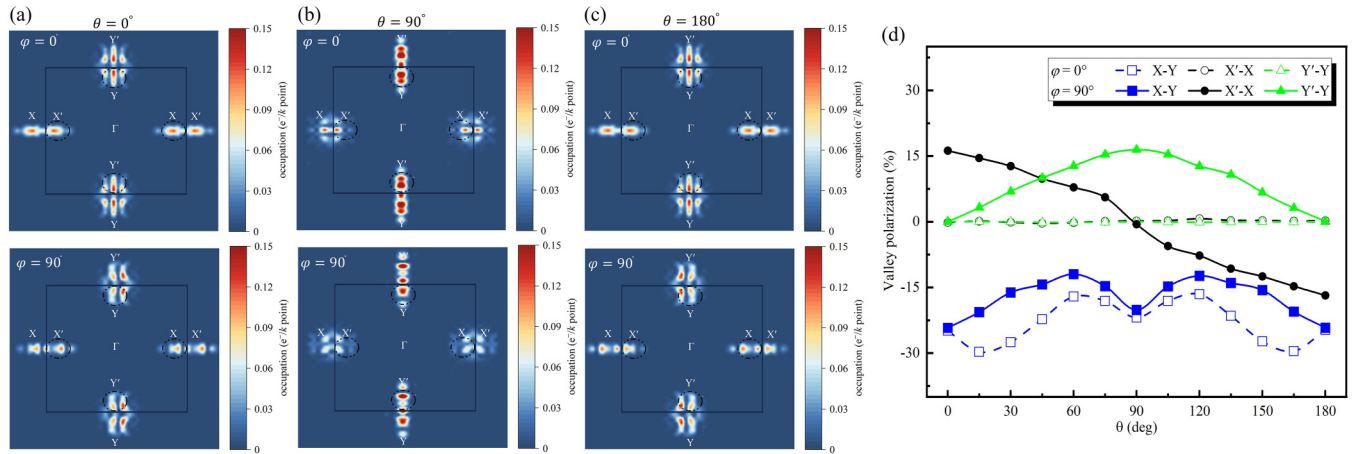


FIG. 5. Valley selection by ultrashort linearly polarized three-cycle pulses with a photon energy of 0.4 eV and field strength of $5 \times 10^{10} \text{ W cm}^{-2}$. Distribution of k -resolved electron populations at the end of the pulse for polarization direction (a) $\theta = 0^\circ$ (x -polarized), (b) $\theta = 90^\circ$ (y -polarized) and (c) $\theta = 180^\circ$ ($-x$ -polarized). The upper panels are for $\varphi = 0^\circ$ while the lower panels are for $\varphi = 90^\circ$. (d) Valley polarization as a function of θ for X-Y, X-X', and Y-Y' valleys for $\varphi = 0^\circ$ and 90° . To calculate the valley polarization, the electron densities are obtained by integrating the conduction band electron population around the X(Y) points within black dashed circles.

result in faster intervalley scattering than in TMD. Inspired by this conjecture, let us now explore the possibility of controlling carrier excitation at multiple valley points through the polarization and CEP φ [see Eq. (9)] of linearly polarized ultrashort laser pulses. Figure 5 presents the dependence of valley polarization on the laser polarization angle θ for $\varphi = 0^\circ$ and $\varphi = 90^\circ$. Figures 5(a)–5(c) displays the k -resolved electron population at the end of the pulse with 0.4 eV photon energy (much smaller than the bandgap) and $5 \times 10^{10} \text{ W cm}^{-2}$ peak intensity. Practically no valley asymmetry is observed at $10^{10} \text{ W cm}^{-2}$ (not shown). At $5 \times 10^{10} \text{ W cm}^{-2}$, for which the vector potential $A(t)$ (0.16 a.u.) is comparable to the distance between X-X' (or Y-Y') separation across the BZ boundaries, a clear valley asymmetry is observed. When the laser polarization is parallel to Γ -X ($\theta = 0^\circ$) and $\varphi = 0^\circ$, both X and X' valleys are equally excited [Fig. 5(a), upper panel]. In contrast, for $\theta = 0^\circ$ and $\varphi = 90^\circ$, a strong valley asymmetry is observed [Fig. 5(a), lower panel]. Consequently, we see a substantial valley polarization [Fig. 5(d)]. When the laser is polarized parallel to Γ -Y direction ($\theta = 90^\circ$) and $\varphi = 90^\circ$ [Fig. 5(b)], either Y or Y' is more excited than the other. Thus, V_Y valley results in two inequivalent valleys, and, therefore, in spite of the absence of opposite spin splitting and Berry curvature, 15% valley polarization is achieved at Y-Y' points. The electron distribution for $\theta = 180^\circ$ [Fig. 5(c)] is reversed with respect to the Y-Y' line, compared to the case of $\theta = 0^\circ$, as is expected from the symmetry of the band structure, and the opposite valley [see Fig. 5(c)] is selected. For this nonresonant $\hbar\omega \ll E_g$ (bandgap) process, the absorbed energy per electron is ~ 1.7 eV, corresponding to ~ 4 photons. Thus, while the valley selection rule for the case of circularly polarized light with a photon energy close to the bandgap depends on Berry curvature as we have seen in the previous subsection, valley polarization under a linearly polarized ultrashort laser pulse with a photon energy much smaller than the bandgap is driven by multiphoton excitation, Bragg scattering, and the interference of the wave packets [60–63].

Figure 5(d) shows the valley polarization as a function of in-plane laser polarization angle θ . The valley polarization is calculated by Eq. (11), in which the electron densities are obtained by integrating the conduction band electron population around valley points (X-Y, X-X', and Y-Y') as indicated by black dashed circles in Figs. 5(a)–5(c). As mentioned above, the valley polarization for X-X' (Y-Y') vanishes in the weak intensity limit ($10^{10} \text{ W cm}^{-2}$). On the other hand, we see from Fig. 5(d) that as the intensity increases to $5 \times 10^{10} \text{ W cm}^{-2}$ the nonlinear processes lead to a substantial valley polarization. This behavior contrasts with the previously described linear and circular dichroism, which diminishes with increasing intensity. For $\varphi = 90^\circ$, the valley polarization along the X-X' direction is maximized at $\theta = 0^\circ$ ($\parallel x$) and monotonically decreases as θ increases, eventually reaching zero at $\theta = 90^\circ$ ($\parallel y$); the valley polarization along the Y-Y' direction is maximized at $\theta = 90^\circ$ ($\parallel y$) and monotonically decreases as θ moves away from 90° , eventually vanishing at $\theta = 0^\circ$ and 180° ($\parallel x$). Thus, the valley polarization is maximized (vanishes) when the laser polarization is parallel (perpendicular) to the valley direction. The maximum valley polarization between X-X' (Y-Y') is 16%, which is expected to be observed experimentally [29,64]. Though less prominent than in the case of the resonant 1.1 eV photon energy (Fig. 2), we still obtain a sizable inter-valley (X-Y) polarization of up to $\sim 30\%$ [Fig. 5(d)]. Its dependence on φ and θ is more complicated than for the X-X' (Y-Y') polarization. Hence, these findings indicate that tailoring the wave form of ultrashort laser pulses enables the control of electron dynamics across multiple valleys on a timescale even faster than electron-electron and electron-phonon scattering.

Let us briefly comment on the experimental feasibility of our proposed scheme for ultrafast valley control in SnS monolayers. The pulse durations and field strengths used in our simulations are within reach of existing setups [16,28,29]. The valley-selective dynamics discussed in our work stem from intrinsic crystal symmetry and electronic structure. In realistic

samples, defects, impurities, or structural disorder can locally break symmetry, affecting valley-selective optical transitions. Previous experimental and theoretical studies in related 2D materials suggest that moderate levels of disorder do not completely suppress valley polarization, although they may reduce its magnitude or introduce additional scattering channels [65,66]. Thus, ensuring high crystalline integrity is essential. Recent advances in chemical vapor deposition, solution-phase techniques, and mechanical exfoliation have enabled the synthesis of SnS monolayers with superior structural purity [19,23,67]. To observe the valley polarization, techniques which have been successfully applied to TMDC monolayers [10], such as time-resolved Kerr rotation, transient absorption spectroscopy [68], and time- and angle-resolved photoemission spectroscopy (TR-ARPES) [69,70], may be used.

IV. CONCLUSION

Using TDDFT calculations, we have investigated valley control in 2D SnS monolayers. In contrast to conventional materials that typically rely on a single valley pair, SnS offers the possibility of exploiting multiple valley states, including $X-X'$, $Y-Y'$, and $X-Y$, thereby enhancing the degrees of freedom for valley manipulation. Moreover, SnS monolayers exhibit both linear and circular dichroism due to the corrugated phosphorene-like crystal structure, allowing valley-selective excitation to be tuned by adjusting the light polarization. Furthermore, the interplay between inversion symmetry breaking and strong spin-orbit coupling in SnS produces Berry curvatures of opposite signs at the X and X' points. As a result, circularly polarized light can induce spin-valley coupling, allowing for the simultaneous manipulation of both spin and valley. We have also proposed a method of rapidly switching

among multiple valley states on a subcycle timescale using femtosecond laser pulses. CEP manipulation enables the selective excitation of multiple valley states, which may be useful for developing ultrafast valley-based technologies.

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The authors declare no competing financial interest.

DATA AVAILABILITY

All calculations were performed using SALMON, an open-source TDDFT code, as cited in Ref. [31]. The figures data were generated using SALMON input files, which are available in the SALMON GitHub repository at Ref. [71]. Additional data are available from the corresponding author upon reasonable request.

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