Giant valley-selective Stark and Bloch-Siegert shifts of exciton resonances in WSe$_2$ and MoS$_2$ monolayers

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In this letter we demonstrate that the valley degeneracy of exciton states in monolayers of WSe$_2$ and MoS$_2$ can be lifted by the interaction with strong circularly-polarized infrared pulses with durations of only few periods of the electric field whose photon energy is much lower than the energy of the excitonic transition. The observed valley-sensitive blue shifts of excitonic absorption lines are consequences of optical Stark and Bloch-Siegert shifts acting exclusively on the opposite valleys of the monolayer. We measured the transient valley-selective changes of sample reflectivity for 1sA as well as for 1sB exciton transitions corresponding to the two most intensive resonances in the studied materials. For the studied phenomena we developed a theoretical description based on semiconductor Bloch equations, which goes beyond the simple two-level model used in previous investigations. The theoretical approach takes into account Coulomb many-body effects in the monolayer and provides a unified description of both types of shifts. The detected room-temperature excitonic energy shifts of up to 30 meV pave the way for practical applications of these effects.

Valleytronics aims at information processing and storage by utilizing the valley degree of freedom of electrons instead of their charge. This new quantum number is associated with the inequivalent groups of energy degenerate valleys of the conduction or valence bands, which are occupied by an electron or a hole. Principles allowing to generate, control and read imbalanced valley populations have been demonstrated and studied in several dielectric and semiconductor materials such as diamond [1], silicon [2] or AlAs [3], in semimetallic bismuth [4] and in two-dimensional materials including graphene [5] and transition metal dichalcogenides monolayers (TMDs) [7, 8].

Among the other materials, two-dimensional TMDs have exceptional properties, which make them attractive for valleytronic applications. The two typical examples of TMDs are WSe$_2$ and MoS$_2$. These materials belong to direct band gap 2D semiconductors with band gap minima in K$^\pm$ points (valleys) of the Brillouin zone [9–11]. Due to the spatial and time-reversal symmetries of the electronic wave functions in the K$^+$ and K$^-$ points determined by the symmetry point group of the crystal D$_{3h}$, these materials demonstrate valley-dependent optical selection rules. Resonant light with right- ($\sigma^+$) or left-handed ($\sigma^-$) circular polarization induces optical transitions only in K$^+$ or K$^-$ valley, respectively. The optically allowed transitions lead to the generation of so-called intravalley bright excitons, the electron-hole pairs tightly bound by the Coulomb interaction that strongly interact with photons.

The exciton states in opposite valleys have the same energies, i.e. they are doubly degenerate by valley. They form a basis for a two-level system and superposition of these states belongs to the valley pseudospin space [12–14]. The controllable probing and manipulation of such states are necessary prerequisites for valleytronic devices [7, 8, 15, 16]. One of the crucial elements of the pseudospin operations is the control of the energies of the two-level system, i.e. the energies of the exciton states in each valley.

Lifting the energy degeneracy of the excitons in K$^+$ and K$^-$ valleys may be reached by Zeeman-type splitting in static magnetic field [17–20] or by DC Stark effect due to electric field [21] applied perpendicularly to the sample plane. However, these two effects are not practical for several reasons: (i) the fields required to observe significant shifts are extremely high, e.g. magnetic field of 10 T generates Zeeman splitting of the exciton states of only 1 meV, (ii) the application of static fields allows neither ultrafast operation nor high spatial resolution, (iii) the experiments are typically limited to low-temperatures due to small splitting.

An alternative approach, which simultaneously solves the aforementioned problems, is to use the strong coupling of the excitons to light fields and to lift the energy degeneracy of the exciton states by coherent optical phenomena. Off-resonant circularly-polarized light waves applied to TMDs generate valley-specific blue shifts of the excitonic resonances via the optical Stark (OS) or Bloch-Siegert (BS) effects [22–23]. The OS and BS effects can be described in the framework of a two-level system driven by light with photon energy $\hbar \omega_{\text{pump}}$ detuned from the energy of the transition $E_0$. In the case of small detuning $E_0 - \hbar \omega_{\text{pump}} \ll E_0$, rotating wave ap-
proximation can be applied and the OS shift dominates. The magnitude of the shift of the resonance energy can be expressed as 
\[ \Delta E_{OS} \propto E_{pump}^2 \left( E_0 - \hbar \omega_{pump} \right) \]
where \( E_{pump} \) is the amplitude of the electric field of the pump pulse. When the pump photon energy is small, \( E_0 - \hbar \omega_{pump} \approx E_0 \), then the contribution to the energy shift due to the Bloch-Siegert effect \[ \Delta E_{BS} \propto E_{pump}^2 \left( E_0 + \hbar \omega_{pump} \right) \]
becomes similar to OS. The simple two-level model, which was applied for the description of coherent optical phenomena in TMDs in the past, neglects the effects of the Coulomb interaction, which brings significant corrections to the OS and BS effects. Moreover, these coherent phenomena were observed only for the lowest resonance in system (1sA-exciton line) and in a limited number of materials. In this Letter we report on an ultrafast valley-selective control of blue spectral shifts of 1sA as well as 1sB exciton resonances in WSe\(_2\) and MoS\(_2\) monolayers via the interaction with off-resonant circularly polarized laser pulses with sub-50 femtosecond durations. We present a novel theoretical approach for the description of the observed effects, which is based on semiconductor Bloch equations (SBE) and goes beyond the simple two-level approximation, used in the previous works. This description takes into account i) the excitonic (many-body) nature of the observed shifts, and ii) the Rytova-Keldysh potential, i.e. the Coulomb potential in TMD monolayer, modified due to inhomogeneity of the system.

The studied TMDs are fabricated by exfoliation from bulk crystals. The monolayers are transferred to a Si/SiO\(_2\) substrate and are covered by multilayer of hBN to preserve their optical properties in ambient air. In our experiments we measure the spectrum of transient change of reflectivity of monolayers WSe\(_2\) and MoS\(_2\) as a function of the time delay between a femtosecond infrared pump pulse (central photon energy 0.62 eV, FWHM pulse duration of \( \tau_{pump} = 38 \) fs) and a broadband supercontinuum probe pulse (photon energy 1.3-2.25 eV). The layout of the experimental setup is shown in Fig. 1a. During the experiments, the samples are imaged in situ using an optical microscope setup to ensure the spatial overlap of the pump and probe pulses and their position at the monolayer (each sample is about 20-30 \( \mu \)m in size, see Figs. 1b and c). The polarization state of both pump and probe beams is controlled using broadband quarter-wave plates, which generate circular polarizations. The experiments are carried out at room temperature with laser repetition rate of 25 kHz.

Because the samples are prepared on an absorptive substrate, an increase of absorption in the monolayer corresponds to a decrease of reflectivity of the sample. This was verified both by measuring the differential reflectivity \[ R_0(h\omega) - R_{sab}(h\omega) \] of the monolayers, where \( R_0(h\omega) \) is the reflectivity of the sample (substrate), and by using FDTD simulations (for details see Ref. [26]). The energies of 1sA and 1sB exciton transitions obtained from our differential reflectivity measurements in the WSe\(_2\) monolayer (Fig. 1) are \( E_{1sA}^{\text{WSe}_2} = 1.639 \) eV and \( E_{1sB}^{\text{WSe}_2} = 2.083 \) eV.

When the sample is illuminated by the non-resonant pump pulse, the excitonic transitions move to higher energies leading to a blue shift \( \Delta E \) of the resonances in the reflectivity spectra. The information about this shift is encoded in reflectivity of the sample \( R(h\omega, \delta t) \) after time \( \delta t \) of the pulse application (see Fig. 1). We consider the difference \( \Delta R(h\omega, \delta t) = R(h\omega, \delta t) - R_0(h\omega) \) to eliminate the contribution of the optical response of the Si/SiO\(_2\) substrate. Hence, \( \Delta R(h\omega, \delta t) \) contains only the contribution from the excitons in the monolayer. In the following we consider the experimentally measurable ratio \( \Delta R(h\omega, \delta t = 0)/R_0(h\omega) \), sketched in Fig. 1e.

In Figs. 2a and 3a we show the delay time dependence of the transient reflectivity (TR) spectra \( \Delta R(h\omega, \delta t)/R_0(h\omega) \) in monolayers WSe\(_2\) and MoS\(_2\). In Figs. 2b and 3b the temporal profile of the signal is presented for WSe\(_2\) and MoS\(_2\), respectively. In both materials we identify two features corresponding to the shifts of 1sA and 1sB excitons. The spectra at the zero time delay are plotted in Figs. 2 and 3 for different combinations of circular polarization handedness of pump and probe pulses, namely for \( \sigma^+_{pump}/\sigma^+_{probe} \) and \( \sigma^+_{pump}/\sigma^-_{probe} \). The measurements with opposite combinations of the polarizations, i.e. \( \sigma^-_{pump}/\sigma^+_{probe} \) and \( \sigma^-_{pump}/\sigma^-_{probe} \), provide the same shifts in full accordance with the time-reversal symmetry of TMDs.

In Figs. 2c and 3a, we show the measured energy shifts of the exciton lines for the two combinations of circular polarization handedness of the pump and probe pulses as functions of the peak intensity of the pump pulse. In all cases, the observed blue shift changes linearly with the pump intensity. From linear fits of the data we obtained the ratios between the shifts caused by OS and BS effects, which are summarized in Table 1 and compared to the theoretical values. The observer deviation of the experimental and theoretical results can be explained by an inaccuracy of the parameters of the monolayer, used for the theoretical estimation as well as 2D crystal’s imperfections which reduce the its valley-dependent optical response.

The maximum observed energy shift of 1sA exciton in both materials is about 30 meV, which is a much larger value compared to the previously published results. Such a large transient shift is reached due to high peak intensity of the pump pulse of 30-50 GW/cm\(^2\). Thanks to the short pump pulse duration (\( \tau_{pump} = 38 \) fs), the transient signal is not accompanied by a long signal component corresponding to the real carrier population generated.
TABLE I. The ratio $\chi = \Delta E_{OS}/\Delta E_{BS}$ of OS to BS shifts for 1sA and 1sB excitons, derived experimentally (ex.) and calculated theoretically (th.).

|     | 1sA, ex. | 1sA, th. | 1sB, ex. | 1sB, th. |
|-----|----------|----------|----------|----------|
| WSe$_2$ | 1.62 ± 0.08 | 2.48 | 1.58 ± 0.17 | 1.95 |
| MoS$_2$ | 1.67 ± 0.09 | 2.19 | 1.75 ± 0.14 | 2 |

by nonlinear absorption of the pump pulse. The maximum relative transient change of the sample reflectivity of about 20% is promising for applications of this effect in valleytronic devices working on femtosecond time scales. Note that this reflectivity change is reached at room temperature and without an enhancement by an optical cavity, which could further increase the transient signal [39].

The theoretical description of the observed blue shifts of the exciton resonances is based on a perturbative solution of the SBE. Since the 1sA and 1sB exciton transitions couple the valence and conduction bands with the same spin, i.e. the fixed pair of the bands, we restrict our consideration to an effective two band model [41]. The interaction between $\sigma^\pm$ polarized light, characterized by electric field $\mathbf{E}_\pm = \mathcal{E}(\cos(\omega t), \pm \sin(\omega t))$, with charged carries in $K^\pm(\tau = \pm)$ valleys of TMDs is defined by the Hamiltonian $H^\tau = H^\tau_0 + H^\tau_{\text{int}}$. Here

$$H^\tau_0 = \sum_k (E_{e,k} \alpha_k^\tau + E_{h,k} \beta_k^\tau)$$

$$+ \sum_{k,k',q \neq 0} V_q \left( \alpha_k^\tau \alpha_{k+q}^\tau \alpha_{k-q}^\tau \beta_{k-q}^\tau \right) - \sum_{k,k',q \neq 0} V_q \left( \beta_k^\tau \beta_{k+q}^\tau \beta_{k-q}^\tau \alpha_{k-q}^\tau \right)$$

(1) is the two-band Hamiltonian with included Coulomb interaction. The first term defines a spectrum of electrons $E_{e,k} = \hbar^2 k^2/2m_e + E_g$ and holes $E_{h,k} = \hbar^2 k^2/2m_h$ in TMDs, where $k = |k|$, $m_e, m_h > 0$ are the electron and hole effective masses, $E_g$ is the bandgap in the system, $\alpha_k^\tau$ and $\beta_k^\tau$ are the annihilation operators for electrons and holes, with momentum $k$ in $\tau$ valley. The remaining terms describe the Coulomb interaction between quasi-particles in the system. Here $V_q$ is the Fourier transform of the Rytova-Keldysh potential The light-matter interaction term reads

$$H^\tau_{\text{int}} = -\mathbf{P}^\tau \cdot \mathbf{E}_\pm = -\sum_k d_{cv}^\tau \mathcal{E}_\pm^*(t) \alpha_k^\tau \beta_{-k}^\tau + \text{h.c.}$$

(2) where $\mathbf{P}^\tau$ is the polarization operator of the system in $\tau$ valley, $d_{cv}^\tau = r \tau d_{cv}$ is the transition dipole moment between the valence and conduction bands and $\mathcal{E}_\pm^*(t) = \mathcal{E} \exp(\mp i \omega t)$. Note that $H^\tau_{\text{int}}$ has a similar form as the light-matter interaction for a two-level system in the rotating-wave approximation. However, $H^\tau_{\text{int}}$ is exact and its form originates from the specific structure of the interband transition dipole moments in $K^\pm$ points of TMDs. To describe the energy shift of the exciton transitions we introduce the quantum average of polarization $r_k^\tau(t) \equiv \langle \beta_{-k}^\tau \alpha_k^\tau \rangle$ and electron and hole population

FIG. 1. (a) Layout of the experimental setup used for transient reflection spectroscopy of TMDs. The monolayer is pumped with an infrared circularly polarized pump pulse and probed by a broadband circularly polarized pulse, whose spectrum is measured. (b), (c) Optical microscope images of the studied samples of TMDs. White polygons mark the monolayers. (d), (e) Differential reflectivity spectra of WSe$_2$ (d) and MoS$_2$ (e) monolayers. (f) Sketch of the monolayer reflectivities without $R_0(h\omega)$ and with the pump pulse at zero delay time $\delta t = 0$ between pump and probe pulses $R(h\omega, \delta t = 0)$. The distance $\Delta E$ between two extrema of the reflectivities manifests the shift of exciton energy due to pump pulse. (g) Sketch of the transient reflectance contrast $[R(h\omega, \delta t = 0) - R_0(h\omega)]/R_0(h\omega)$. Its peak-and-deep shape explains the experimental data presented in Figs. 2c and 3c.
\[ \Delta E = \frac{2|d_{cv}|}{\rho_{s}^{2}} \left( \frac{E_{ex} + \hbar \omega_{pump}}{E_{ex} + \hbar \omega_{pump}} \right) \left( \rho_{1s} + \frac{\eta_{1s}}{E_{ex} + \hbar \omega_{pump}} \right). \]

Here \( \Delta E_{\pm} \) correspond to the OS and BS shifts in \( K^{\pm} \) points, respectively. The first term of Eq. (5) corresponds to the exciton-pump-field interaction, while the second term provides a correction due to exciton-exciton interaction in the system [37]. To evaluate \( \rho_{1s} \) and \( \eta_{1s} \) we use the hydrogen-like 1s wavefunction, which is a remarkably good approximation for the ground-state excitons [38]. In this case \( \rho_{1s} = 16/7 \), while the exciton-exciton correction is material dependent and reaches ~ 10% – 20% of \( \rho_{1s} \) for the studied monolayers. Hence, our predicted energy shift is approximately 2-3 times larger than the two-level approximation result [24]. It demonstrates the importance of Coulomb interaction and many-body effects in the evaluation of the OS and BS shifts.

Using the presented theory we numerically calculated the expected energy shifts for the parameters used in our experiments [28]. The results in form of coefficient \( k \equiv \Delta E/E_{\text{pump}}^{2} \) are presented in Tab. II. Almost all experimental results are close to the theoretical estimations. The observed deviations of both results, in particular for...
1sB excitons in WSe$_2$, can be explained either by an inaccuracy of the parameters of the monolayer, used for the theoretical study or by the peculiarities of 2D crystals used in the experiment.

$$\kappa \equiv \Delta E/E_{\text{pump}}$$

|                  | OS,1sA | BS,1sA | OS,1sB | BS,1sB |
|------------------|--------|--------|--------|--------|
| WSe$_2$, th.     | 33.6   | 13.5   | 12.7   | 6.5    |
| WSe$_2$, ex.     | 26.4 ± 0.7 | 16.3 ± 0.5 | 4.1 ± 0.4 | 2.6 ± 0.4 |
| MoS$_2$, th.     | 17.7   | 8.1    | 13.1   | 6.4    |
| MoS$_2$, ex.     | 16.0 ± 0.6 | 9.6 ± 0.4 | 14.7 ± 0.5 | 8.4 ± 0.4 |

Table II. The coefficient $\kappa \equiv \Delta E/E_{\text{pump}}$ calculated theoretically (th.) and experimentally (ex.) for OS ($\Delta E_{\text{OS}}$) and BS ($\Delta E_{\text{BS}}$) shifts of 1sA and 1sB excitons, in WSe$_2$ and MoS$_2$ samples.

The observed valley-specific energy shifts of excitonic resonances in 2D TMDs WSe$_2$ and MoS$_2$ allow to lift the valley degeneracy in these materials at extremely short time scales of several tens of femtoseconds. The observed maximum relative transient change of the reflectivity of the WSe$_2$ monolayer at the 1sA exciton resonance reaches 20%. Together with the large circular dichroism of $\xi_{\text{max}} = (\Delta R_{\sigma+/\sigma} - \Delta R_{\sigma-/\sigma})/\Delta R_{\sigma+/\sigma} = 38\%$ ($\Delta R_{\sigma+/\sigma+}$ and $\Delta R_{\sigma+/\sigma-}$ are reflectivity changes of the probe pulse for the co- and counter-rotating circularly polarized pump and probe fields) and the nonresonant ultrafast operation without a significant population of real excitons, this effect is promising for ultrafast valleytronics applications. Furthermore, by applying circularly polarized pump pulses with low photon energy and high intensity, strong-field nonlinear coherent phenomena may lead to generation of valley-polarized currents observable in transport [39, 40] or optical [11] measurements.

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