Large, valley-exclusive Bloch-Siegert shift in monolayer WS$_2$

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Coherent interaction with off-resonance light can be used to shift the energy levels of atoms, molecules, and solids. The dominant effect is the optical Stark shift, but there is an additional contribution from the so-called Bloch-Siegert shift that has eluded direct and exclusive observation in solids. We observed an exceptionally large Bloch-Siegert shift in monolayer tungsten disulfide (WS$_2$) under infrared optical driving. By controlling the light helicity, we could confine the Bloch-Siegert shift to occur only at one valley, and the optical Stark shift at the other valley, because the two effects obey opposite selection rules at different valleys. Such a large and valley-exclusive Bloch-Siegert shift allows for enhanced control over the valleytronic properties of two-dimensional materials.

Fig. 1. Comparison of the optical Stark shift and the Bloch-Siegert shift in a two-level system. (A) Energy diagram for optical Stark shift. $|a\rangle$ and $|b\rangle$ denote the two original states with resonance energy $E_0$ before they are optically driven; $|a + h\omega\rangle$ and $|b - h\omega\rangle$ are photon-dressed (Floquet) states driven by the corotating optical field. Hybridization of these Floquet states causes the resonance energy to blueshift by $\Delta E_{\text{OS}}$, which is proportional to the light intensity ($E_0^2$) and inversely proportional to $(E_0 - h\omega)$. (B) Energy diagram for Bloch-Siegert shift. $|a - h\omega\rangle$ and $|b + h\omega\rangle$ are two different Floquet states driven by the counterrotating optical field. Hybridization with these Floquet states causes the Bloch-Siegert shift, with magnitude $\Delta E_{\text{BS}}$ inversely proportional to $(E_0 + h\omega)$.
the $K$ valley (23, 24). The $K'$ valley exhibits only a very weak (but observable) signal. However, as we lower the pumping photon energy to 0.59 eV, the signal at the $K'$ valley becomes comparable to the signal at the $K$ valley (Fig. 2E). This observation indicates a pronounced energy blueshift at the $K'$ valley, a phenomenon that apparently violates the well-established valley selection rules in monolayer TMDs. Some modulations also appear in the $\Delta \alpha$ spectrum. These minor features are possibly induced by electron-phonon coupling and warrant further investigation; here, we average out these modulations by smoothing the curves (black lines). We further examined the signals at different pump-probe time delays. The $\Delta \alpha$ signals at both valleys emerge only at zero time delay, with temporal profiles very similar to the 160-fs duration of the pump pulses (Fig. 2F). These results indicate the coherent nature of the energy shift; they also exclude the influence of intervalley scattering of possible excited carriers, which typically occurs on the picosecond time scale (25–27).

To investigate the underlying mechanism of the anomalous energy shift at the $K'$ valley, we measured the zero-delay $\Delta \alpha$ spectra for both valleys at various pump photon energies ($h\omega = 0.59, 0.69, 0.89$, or 0.98 eV) and different pump fluences ($F = 30$ to 800 $\mu$J/cm$^2$). In Fig. 2G, we show the fluence-dependent spectra for $h\omega = 0.59$ eV (see fig. S1 for the remaining spectra). The $\Delta \alpha$ spectra at both valleys are found to grow with increasing pump fluence. For a more quantitative analysis, we extracted the energy shift from each spectrum, plotted as a function of $F/(E_0 + h\omega)$ in Fig. 3A. The shift at the $K$ valley exhibits an excellent linear dependence regardless of the different pump photon energies (solid symbols), indicating that it arises from the optical Stark effect. The shift at the $K'$ valley, however, spreads out with no rigorous linear dependence (open symbols). Such a contrast indicates that the $K'$-valley shift does not arise from the optical Stark effect. In Fig. 3B, we replot the $K'$-valley shift as a function of $F/(E_0 + h\omega)$ with the same axis scales; the data now exhibit an excellent linear dependence. Moreover, the slope of the $K'$-valley shift in this new plot is identical to the slope of the $K$-valley shift in Fig. 3A. This observation strongly suggests that the $K'$-valley shift arises from the Bloch-Siegert effect.

Our finding can be verified quantitatively by using either a semiclassical theory or a fully quantum-mechanical theory (28) (see supplementary text). Because we probe only the lowest-energy exciton state ($1s$), which shows properties similar to those of hydrogen atoms, it is appropriate and sufficient to use a simple two-level framework, as shown in earlier studies (22, 25, 23, 24).

In our semiclassical analysis, we treat the ground state and the $1s$ exciton state as a two-level system ($\langle \mu \rangle$ and $\langle b \rangle$) with a resonance energy $E_0$, driven by a classical electromagnetic wave with amplitude $E_0$ and frequency $\omega$. We use a left-circularly polarized pump beam,

$$E(t) = E_0 [\cos(kz - \omega t) \hat{x} + \sin(kz - \omega t) \hat{y}]$$ (1)
Here, $\mu_0$ and $\mu_K$ are the dipole matrix elements at the $K$ and $K'$ valleys, respectively, and they have equal magnitudes $|\mu_0| = |\mu_K|$. However, they are associated with opposite time-evolution factors, which leads to a more general theory of valley selection rules in monolayer TMDs. Under the resonant absorption condition ($\hbar \omega = E_0$), the left-circularly polarized light couples only to the $K$-valley. By contrast, under the off-resonance condition ($\hbar \omega < E_0$), the coupling to the $K'$-valley can become appreciable through the time-reversed process, giving rise to a noticeable energy shift. The induced energy shifts at the respective valleys can be evaluated by the time-dependent perturbation theory as

$$
\Delta E_K = \frac{\mu_0^2}{2 \hbar^2} \frac{1}{E_0 - \hbar \omega}
$$

$$
\Delta E_{K'} = \frac{\mu_K^2}{2 \hbar^2} \frac{1}{E_0 + \hbar \omega}
$$

The two energy shifts have different energy dependence, from which we can readily identify $\Delta E_K$ to be the optical Stark shift and $\Delta E_{K'}$ the Bloch-Siegert shift. When plotted as a function of their respective energy denominators ($E_0 - \hbar \omega$ or $E_0 + \hbar \omega$), both shifts exhibit an identical slope. The prediction of common slope and opposite valley indices agrees well with our experimental observation (Fig. 3A and B). From our data, we can deduce the dipole matrix elements to be $\mu = 55$ debye, in excellent agreement with previous measurements (23). In addition, the ratio between $\Delta E_{OS}$ and $\Delta E_{BS}$ is predicted to be $(E_0 - \hbar \omega)/(E_0 + \hbar \omega)$, the same as $\Delta E_{BS}/\Delta E_{OS}$ for a generic two-level system. By plotting the average shift ratio measured for each pump photon energy, we find good agreement between our experiment and theory (Fig. 3B, inset).

The physics of this valley-exclusive energy shift can be illustrated in the energy diagrams shown in Fig. 3, C and D. The corroborating field generates a Floquet state $\hbar \omega$ above the ground state in both valleys, with energy separation $E_0 - \hbar \omega$ from the excited state. Because of the matching condition of angular momentum, repulsion between the Floquet state and the excited state only occurs at the $K$ valley, giving rise to the ordinary optical Stark shift (Fig. 3C). On the other hand, the counterrotating field generates a Floquet state $\hbar \omega$ below the ground state, with energy separation $E_0 + \hbar \omega$ from the excited state (Fig. 3D). The matching condition of angular momentum forbids the level repulsion at the $K$ valley but allows it at the $K'$ valley. This gives rise to the Bloch-Siegert shift at the opposite ($K'$) valley. In other words, the left-circularly polarized light can be understood as stimulating the $\sigma^-$ absorption ($\Delta m = -1$) and $\sigma^+$ emission ($\Delta m = +1$) processes at the $K$ and $K'$ valleys, respectively. This makes it possible for the circularly polarized light with a given helicity to couple to both valleys in a distinct manner, thus enriching the valley selection rules.

The Bloch-Siegert shift we observed exhibits valley selection rules opposite from those of the...
ordinary optical Stark effect, which allows us to completely separate the two effects. This is possible because, as time-reversed partners, the two effects share a similar relationship with the two time-reversed valleys in monolayer WS$_2$, which can be disentangled under circularly polarized light that breaks the time-reversal symmetry. Our finding reveals more general polarized light that breaks the time-reversal which can be disentangled under circularly

REFERENCES AND NOTES

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SUPPLEMENTARY MATERIALS
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**Going way off resonance**
Single atomic layers of transition metal dichalcogenide (TMD) materials have two nonequivalent valleys in their electronic structure. When researchers shine visible light on these monolayers, left-circularly polarized light modifies the electronic levels in one valley but not the other. Sie *et al.* studied the material WS₂. They found that in the infrared regime, if the frequency of the light was far away from the resonance, energy levels in both valleys were affected. The so-called Bloch-Siegert effect could explain the energy shift in the "wrong" valley. The findings should be important for the manipulation of valleytronic properties of TMDs.

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