Supporting Information for

Spin-Valley Dynamics in Monolayer WSe_2 Excited by Circularly Polarised Light

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The Hamiltonian that includes the electromagnetic field can be written as：

$$H^{tot} = \frac{(p - e\mathcal{A})}{2m} + V_0(r)$$

Expand the above Hamiltonian：

$$H^{tot} = \left(\frac{p^2}{2m} + V_0(r)\right) + \left(\frac{e\mathcal{A} \cdot p}{m} + \frac{e^2\mathcal{A}^2}{2m}\right)$$

$$H^{tot}(r,R,t) = H^0(r,R,t) + H^{LMI}(r,R,t)$$

Where $H^0(r,R,t) = \left(\frac{p^2}{2m} + V_0(r)\right)$, $H^{LMI}(r,R,t) = \left(\frac{e\mathcal{A} \cdot p}{m} + \frac{e^2\mathcal{A}^2}{2m}\right)$

$\mathcal{A}$ represents the vector potential, and $E = -\frac{\partial \mathcal{A}}{\partial t}$, under electric dipole approximation:

$$\mathcal{A}(r,t) \approx \mathcal{A}(t)$$

In non-adiabatic molecular dynamics, the wave function can be expanded using any complete set of basis:

$$|\psi\rangle = \sum_j |\phi_j\rangle\langle\phi_j|\psi\rangle = \sum_j c_j|\phi_j\rangle$$

Substituting the total Hamiltonian and wave function into the time-dependent Schrödinger equation gives:

$$i\hbar\frac{\partial|\psi(r,R,t)\rangle}{\partial t} = H^{tot}(r,R,t)|\psi(r,R,t)\rangle$$

$$\frac{\partial c_{j(t)}}{\partial t} = \sum_k \left[i\hbar^{-1} < \phi_j|H^{tot}|\phi_k > + \left\langle \phi_j|\frac{\partial}{\partial t}|\phi_k \right\rangle \right]$$

$$= \sum_k \left[i\hbar^{-1} H^0_{jk}\delta_{jk} + i\hbar^{-1} H^{LMI}_{jk} + T_{jk} \right]$$

Where $H^{LMI}_{jk} = -\frac{e}{m} < \phi_j|p|\phi_k > \cdot A$, $T_{jk} = < \phi_j|\frac{\partial}{\partial t}|\phi_k >$

In the momentum space approach, electron-phonon coupling takes the place of nonadiabatic coupling in the real space method：

Starting from the time-dependent Schrödinger equation:

$$i\hbar\frac{\partial|\Psi(r;R(t))\rangle}{\partial t} = \hat{\mathrm{H}}^{\mathrm{el}}(r;R(t))|\Psi(r;R(t))\rangle$$

Consider the motion of atoms as vibrations around their equilibrium positions. At this time, the total Hamiltonian can be written as:

$$\hat{H}^{tot}(r;R(t)) = \hat{H}^{el}(r;R_0) + \Delta V(r;R(t))$$

$$\hat{H}^{el} = \left(\frac{p^2}{2m} + V_0(r)\right) + \left(\frac{e A \cdot p}{m} + \frac{e^2 A^2}{2m}\right)$$

Consider the basis set as the eigenstates $\hat{H}^{el}(r;R_0)$ of the equilibrium Hamiltonian $\{|\psi_{nk}(r;R_0)\rangle\}$

Expand the electronic wave function as：

$$|\Psi(r;R(t))\rangle = \sum_{nk} c_{nk}(t)|\psi_{nk}(r;R_0)\rangle$$

$$i\hbar\frac{d}{dt}c_{mk'}(t) = \sum_{nk}(H^0_{mk',nk} + H^{LMI}_{mk',nk} + H^{ep}_{mk',nk})c_{nk}(t)$$

Here, $H^{0}_{mk,nk}$ represents the eigenenergy term, $H^{LMI}_{mk,nk}$ is the light-matter interaction term, $H^{ep}_{mk,nk}$ is the electron-phonon coupling term.

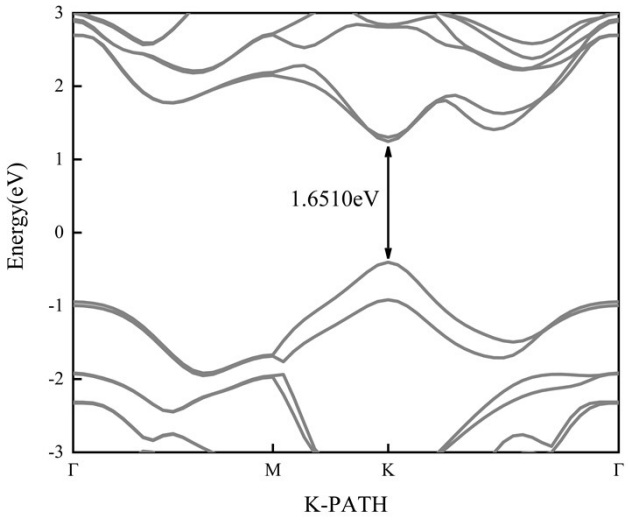

Figure S1. Energy band structure calculated using HSE06 with SOC.

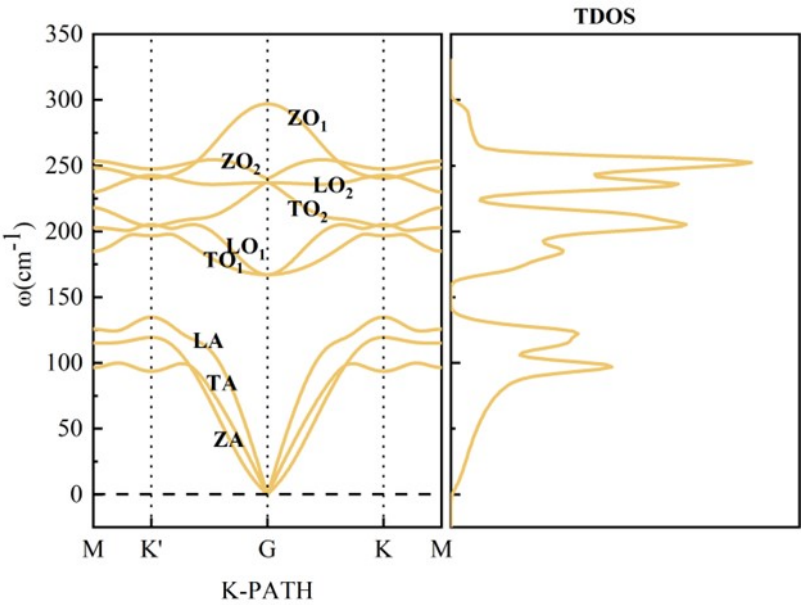

Figure S2. Phonon spectra and phonon density of states calculated using time-dependent density functional theory.

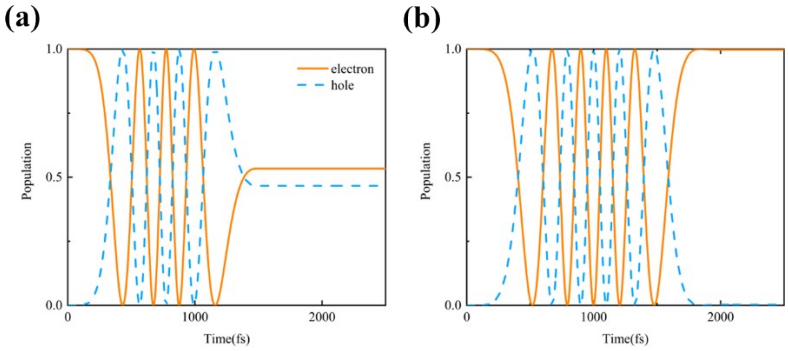

Figure S3. (a) The evolution of the electronic configuration of correlated energy states at 0K with a pulse duration of 1000 fs and a pulse intensity of 0.01 eV/Å. (b) The evolution of the electronic configuration of correlated energy states at 0K with a pulse duration of 2000 fs and a pulse intensity of 0.005 eV/Å.

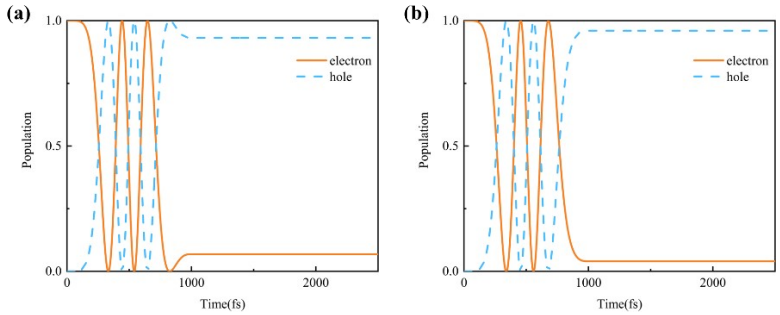

Figure S4. (a) Time-dependent evolution of the left-handed circularly polarised light-excited K-valley electron distribution with a pulse duration of 1000 fs and a pulse intensity of 0.005 eV/Å. And the band gap is shifted to 1.6010 eV using the "scissors operator". (b) Time-dependent evolution of the left-handed circularly polarised light-excited K-valley electron distribution with a pulse duration of 1000 fs and a pulse intensity of 0.005 eV/Å. And the band gap is shifted to 1.7010 eV using the "scissors operator".

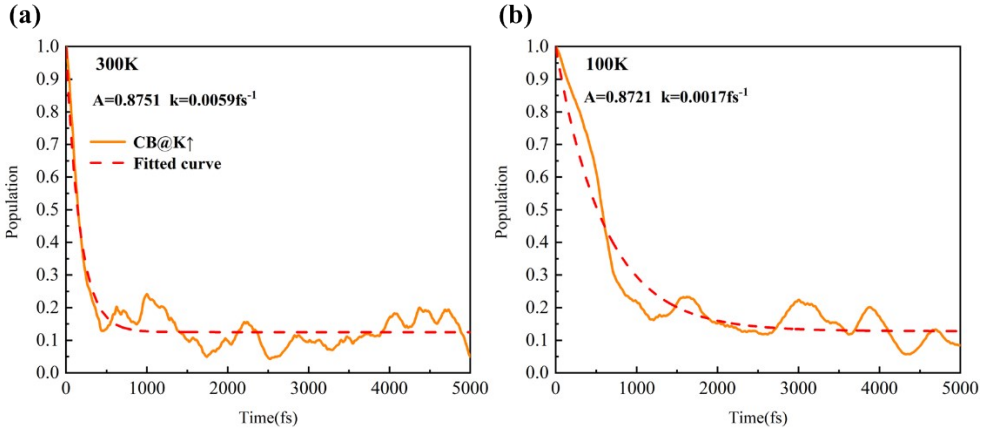

Figure S5. The electron population on CB@K↑ using the exponential function $y = 1 - A(1 - exp(-kt))$, for(a)300K(b)100K.