Electronic Supplementary Material (ESI) for Nanoscale Horizons.

Supplementary Information: Valley-Exchange Coupling Probed by Angle-Resolved Photoluminescence

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I. THEORETICAL MODEL

In this section, we outline the theoretical model.

A. Exciton-Exchange coupling

We define the intervalley exchnage as

$$\hat{\boldsymbol{H}}_{\text{ex, inter}} = \sum_{\boldsymbol{k}'\boldsymbol{k}\boldsymbol{q}} J_{\boldsymbol{k}'\boldsymbol{k}\boldsymbol{q}} \hat{\boldsymbol{c}}^{K\dagger}_{\boldsymbol{k}+\boldsymbol{q}} \hat{\boldsymbol{v}}^{K'\dagger}_{\boldsymbol{k}'-\boldsymbol{q}} \hat{\boldsymbol{c}}^{K'}_{\boldsymbol{k}'} \hat{\boldsymbol{v}}^{K}_{\boldsymbol{k}} + h.c. \tag{1}$$

where we have

$$J_{\boldsymbol{k}'\boldsymbol{k}\boldsymbol{q}} = \int drdr' \psi^{\dagger cK}_{\boldsymbol{k}+\boldsymbol{q}}(r) \psi^{\dagger vK'}_{\boldsymbol{k}'-\boldsymbol{q}}(r') V(r-r') \psi^{vK}_{\boldsymbol{k}}(r) \psi^{cK'}_{\boldsymbol{k}'}(r') \tag{2}$$

$$\hat{\boldsymbol{H}}_{\text{ex, intra}} = \sum_{\xi} \sum_{\boldsymbol{k}'\boldsymbol{k}\boldsymbol{q}} K^{\xi}_{\boldsymbol{k}'\boldsymbol{k}\boldsymbol{q}} \hat{\boldsymbol{c}}^{\xi\dagger}_{\boldsymbol{k}+\boldsymbol{q}} \hat{\boldsymbol{v}}^{\xi\dagger}_{\boldsymbol{k}'-\boldsymbol{q}} \hat{\boldsymbol{c}}^{\xi}_{\boldsymbol{k}'} \hat{\boldsymbol{v}}^{\xi}_{\boldsymbol{k}} \tag{3}$$

$$K^{\xi}_{\boldsymbol{k}'\boldsymbol{k}\boldsymbol{q}} = \int drdr' \psi^{\dagger cK}_{\boldsymbol{k}+\boldsymbol{q}}(r) \psi^{\dagger vK}_{\boldsymbol{k}'-\boldsymbol{q}}(r') V(r-r') \psi^{vK}_{\boldsymbol{k}}(r) \psi^{cK}_{\boldsymbol{k}'}(r') \tag{4}$$

where we used the fact that the wavefunctions are spin degenerate. We can transform these into the exciton basis

$$\hat{\boldsymbol{H}}_{\text{X, inter}} = \sum_{\boldsymbol{Q}} \mathcal{J}_{\boldsymbol{Q}} \hat{\boldsymbol{X}}^{K\dagger}_{\boldsymbol{Q}} \hat{\boldsymbol{X}}^{K'}_{\boldsymbol{Q}} \tag{5}$$

$$\hat{\boldsymbol{H}}_{\text{X, intra}} = \sum_{\boldsymbol{Q},\xi} \mathcal{K}^{\xi}_{\boldsymbol{Q}} \hat{\boldsymbol{X}}^{\xi\dagger}_{\boldsymbol{Q}} \hat{\boldsymbol{X}}^{\xi}_{\boldsymbol{Q}} \tag{6}$$

We find that the exchange elements can be expressed in terms of the interband optical matrix element[1,2] $d^{cv,\xi}_{\boldsymbol{p}}$ at momentum $\boldsymbol{p}$

$$\mathcal{J}_{\boldsymbol{Q}} = \frac{V(-\boldsymbol{Q})}{A} \left(\sum_{\boldsymbol{k}} \psi(\boldsymbol{k}) \boldsymbol{Q} \cdot d^{cv,K}_{\boldsymbol{k}+\boldsymbol{Q}} \right) \left(\sum_{\boldsymbol{k}} \psi(\boldsymbol{k}) \boldsymbol{Q} \cdot d^{cv,K'}_{\boldsymbol{k}'-\boldsymbol{Q}} \right) \tag{7}$$

$$K^{\xi}_{\boldsymbol{Q}} = \frac{V(-\boldsymbol{Q})}{A} \left(\sum_{\boldsymbol{k}} \psi(\boldsymbol{k}) \boldsymbol{Q} \cdot d^{cv,\xi}_{\boldsymbol{k}+\boldsymbol{Q}} \right) \left(\sum_{\boldsymbol{k}} \psi(\boldsymbol{k}) \boldsymbol{Q} \cdot d^{cv,\xi}_{\boldsymbol{k}'-\boldsymbol{Q}} \right) \tag{8}$$

After closer inspection of these expression, one finds that the intervalley and intravalley exchange elements differ only by a phase, $\mathcal{J}_{\boldsymbol{Q}} = \mathcal{K}^{K/K'}_{\boldsymbol{Q}} e^{-2i\theta_{\boldsymbol{Q}}}$, while $\mathcal{K}_{\boldsymbol{Q}}$ is valley degenerate. As outlined in the main text, the final Hamiltonian can be solved by taking a valley-spinor approach

$$\hat{\boldsymbol{H}}_{\text{valley-spinor}} = \begin{pmatrix} E_{\boldsymbol{Q}} + \mathcal{K}_{\boldsymbol{Q}} + g_L \mu_B B & \mathcal{K}_{\boldsymbol{Q}} e^{-2i\theta_{\boldsymbol{Q}}} \\ \mathcal{K}_{\boldsymbol{Q}} e^{2i\theta_{\boldsymbol{Q}}} & E_{\boldsymbol{Q}} + \mathcal{K}_{\boldsymbol{Q}} - g_L \mu_B B \end{pmatrix} \tag{9}$$

where we include the valley-Zeeman term[3], $g_L \mu_B B$ arising from an externally applied magnetic field B. Diagonal terms correspond to intravalley processes while the off-diagonal elements lead to valley-mixing in the eigenstate.

$$\mathcal{E}^{\eta}_{\boldsymbol{Q}} = E_{\boldsymbol{Q}} + \mathcal{K}_{\boldsymbol{Q}} + \eta \sqrt{(g_L \mu_B B)^2 + |\mathcal{K}_{\boldsymbol{Q}}|^2}, \tag{10}$$

$$\psi^{\eta}_{\text{VS}} = \frac{1}{\sqrt{1 + |\alpha^{\eta}_{\boldsymbol{Q}}|^2}} \begin{pmatrix} 1 \\ \alpha^{\eta}_{\boldsymbol{Q}} e^{-2i\theta_{\boldsymbol{Q}}} \end{pmatrix}, \tag{11}$$

$$\alpha^{\eta}_{\boldsymbol{Q}} = \frac{g_L \mu_B B + \eta \sqrt{(g_L \mu_B B)^2 + |\mathcal{K}_{\boldsymbol{Q}}|^2}}{|\mathcal{K}_{\boldsymbol{Q}}|}. \tag{12}$$

where ψ^{η}_{VS} is the valley-spinor wavefunction and $\alpha^{\eta}_{\boldsymbol{Q}}$ determines the relative valley distribution on the upper and lower bands. At $B = 0$, $\alpha^{\eta}_{\boldsymbol{Q}} = \eta$ implying even valley distribution.

B. Optical Matrix Element

In the absence of exchange interaction, the exciton-photon Hamiltonian is[4,5]

$$H_{\text{X-pt}} = \sum_{\xi,\boldsymbol{Q}} \sum_{\sigma,\boldsymbol{q}} \hat{\boldsymbol{c}}^{\dagger}_{\sigma\boldsymbol{q}} \hat{\boldsymbol{X}}^{\xi}_{\boldsymbol{Q}} \delta_{\boldsymbol{q}_{||},\boldsymbol{Q}} \left(M^{\xi,\sigma}_{\boldsymbol{q}} \sum_{\boldsymbol{k}} \phi_{\boldsymbol{k}} \right) + h.c \tag{13}$$

such that $M^{\xi,\sigma}_{\boldsymbol{q}}$ is the optical matrix element for an exciton in valley ξ, interacting with a photon with polarisation σ and momentum $\boldsymbol{q}$. The delta function ensures conservation of in-plane momenta between the 2D exciton, with momentum $\boldsymbol{Q}$ and the photon with in-plane momentum $\boldsymbol{q}_{||}$. The excitonic wavefunction, $\phi_{\boldsymbol{k}}$, is deduced from the Wannier equation[6], with summation over the relative exciton mometa $\boldsymbol{k}$. $\hat{\boldsymbol{c}}$ are photon operators.

The valley-spinor wavefunction in Eq. (11) allows a unitary matrix to be deduced transforming the valley excitons, $\hat{\boldsymbol{X}}^{\xi}_{\boldsymbol{Q}}$, to the new valley mixed basis, $\hat{\boldsymbol{Y}}^{\eta}_{\boldsymbol{Q}}$. We find

$$\begin{pmatrix} \hat{\boldsymbol{X}}^{K}_{\boldsymbol{Q}} \\ \hat{\boldsymbol{X}}^{K'}_{\boldsymbol{Q}} \end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{1+|\alpha^{\eta=+1}_{\boldsymbol{Q}}|^2}} & \frac{1}{\sqrt{1+|\alpha^{\eta=-1}_{\boldsymbol{Q}}|^2}} \\ \frac{\alpha^{\eta=+1}_{\boldsymbol{Q}} e^{2i\theta_{\boldsymbol{Q}}}}{\sqrt{1+|\alpha^{\eta=+1}_{\boldsymbol{Q}}|^2}} & \frac{\alpha^{\eta=-1}_{\boldsymbol{Q}} e^{2i\theta_{\boldsymbol{Q}}}}{\sqrt{1+|\alpha^{\eta=-1}_{\boldsymbol{Q}}|^2}} \end{pmatrix} \begin{pmatrix} \hat{\boldsymbol{Y}}^{\eta=+1}_{\boldsymbol{Q}} \\ \hat{\boldsymbol{Y}}^{\eta=-1}_{\boldsymbol{Q}} \end{pmatrix} \tag{14}$$

which we can relabel as

$$U^{K}_{\eta,\boldsymbol{Q}} = \frac{1}{\sqrt{1+|\alpha^{\eta}_{\boldsymbol{Q}}|^2}}, \quad U^{K'}_{\eta,\boldsymbol{Q}} = \frac{\alpha^{\eta}_{\boldsymbol{Q}} e^{2i\theta_{\boldsymbol{Q}}}}{\sqrt{1+|\alpha^{\eta}_{\boldsymbol{Q}}|^2}},. \tag{15}$$

We can rewrite the exciton-photon Hamiltonian as

$$H_{\text{X-pt}} = \sum_{\eta} \sum_{\sigma,\boldsymbol{q}} \hat{\boldsymbol{c}}^{\dagger}_{\sigma\boldsymbol{q}} \hat{\boldsymbol{Y}}^{\eta}_{\boldsymbol{q}_{||}} \sum_{\xi} U^{\xi}_{\eta,\boldsymbol{q}_{||}} M^{\xi,\sigma}_{\boldsymbol{q}} \left(\sum_{\boldsymbol{k}} \phi_{\boldsymbol{k}} \right) + h.c \tag{16}$$

The inter-band optical matrix element $M^{\xi,\sigma}_{\boldsymbol{q}}$ depends on the photon emission angle. The polarisation of the electric field is orthogonal to the propagation direction of the emitted photon, hence as the angle of emission tilts from out-of-plane to in-plane, the interaction between this electric field and the in-plane excitonic dipole should principally decrease. We assume emission is confined to the x-z plane (it can be easily shown that the matrix element is independent of in-plane angle apart from a phase), such that we can calculate the optical matrix element as

$$M^{\xi,\sigma}_{\boldsymbol{q}} \propto \frac{1}{\sqrt{|\sigma_x|^2+|\sigma_y|^2}} \begin{pmatrix} \sigma_x \cos(\theta) \\ \sigma_y \\ \sigma_x \sin(\theta) \end{pmatrix} \cdot \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \xi i \\ 0 \end{pmatrix} \tag{17}$$

where the vector on the left is the three-dimensional polarisation Jones vector after rotation about the y-axis. The vector on the right is the optical dipole matrix element about valley ξ. We asssume that for normal emission ($\theta = 0$), $\sigma_z = 0$ and σ_x and σ_y are defined by the choice of polarisation. Circular polarisation is defined independently of the emission plane, therefore $\sigma_x = 1$ and $\sigma_y = i(-i)$ for σ_+ (σ_-) polarised light. For s-polarised (p-polarised) linearly polarised light we have $\sigma_x = 0, \sigma_y = 1$ ($\sigma_x = 1, \sigma_y = 0$). The angle response is therefore primarily driven by the sum over valleys appearing in Eq. 17. We summarise here the results for different polarisations, in the absence of a magnetic field

$$\sum_{\xi} U^{\xi}_{\eta,\boldsymbol{q}_{||}} M^{\xi,\sigma_{\pm}}_{\boldsymbol{q}} \propto (1+\eta)\cos\theta \mp (1-\eta), \tag{18}$$

$$\sum_{\xi} U^{\xi}_{\eta,\boldsymbol{q}_{||}} M^{\xi,\text{s-pol}}_{\boldsymbol{q}} \propto i(1-\eta), \tag{19}$$

$$\sum_{\xi} U^{\xi}_{\eta,\boldsymbol{q}_{||}} M^{\xi,\text{p-pol}}_{\boldsymbol{q}} \propto \cos\theta(1+\eta), \tag{20}$$

In the presence of a magnetic field these optical matrix elements change.

C. Elliot formula

Heisenberg's equations of motion can be used to derive the PL intensity, arriving at a modified version of the Elliot Formula[4–6]

$$I_\sigma(\theta,\omega,T) = \frac{2}{\hbar}\sum_\eta \mathrm{Im}\left[\frac{f_\eta(\theta,T)|\sum_\xi U^\xi_{\eta,\theta} M^{\xi,\sigma}_\theta|^2}{\mathcal{E}^\eta_\theta - \hbar\omega - i(\gamma^\eta_\theta + \Gamma^\eta_\theta(T))}\right] \tag{21}$$

where we used the fact that $\theta = \sin^{-1}\left(\frac{|\boldsymbol{q}_{||}|}{|\boldsymbol{q}|}\right)$. The term $f_\eta(\theta,T)$, determines the exciton occupation while γ^η_θ and $\Gamma^\eta_\theta(T)$ are the radiative and non-radiative (phonon-induced) broadening. In the presence of an external magnetic field we have the magneto-PL intensity

$$I_\sigma(\theta,\omega,T,B) = \frac{2}{\hbar}\sum_\eta \mathrm{Im}\left[\frac{f_\eta(\theta,T,B)|\sum_\xi U^\xi_{\eta,\theta}(B) M^{\xi,\sigma}_\theta|^2}{\mathcal{E}^\eta_\theta(B) - \hbar\omega - i(\gamma^\eta_\theta(B) + \Gamma^\eta_\theta(T,B))}\right] \tag{22}$$

D. Radiative and Non-Radiative decay

Following[4,5] the radiative decay rate is

$$\gamma^\eta_\theta(B) = \frac{1}{2}\frac{e_0^2}{2\epsilon_0 c n E_{\mathrm{Gap}}}\frac{a_0^2 t^2}{\hbar}|\sum_\xi U^\xi_{\eta,\theta}(B) M^{\xi,\sigma}_\theta|^2 \tag{23}$$

which carries an angle dependence. n is the refractive index of the surrounding medium, $t = \hbar/a_0\sqrt{E_{\mathrm{Gap}}/M}$ is the nearest neighbour hopping integral in the TMD and M is the exciton mass.

The exciton-photon Hamiltonian can be written as

$$H_{X-pn} = \sum_{\eta,\eta'}\sum_{\boldsymbol{Q},\boldsymbol{k},m} G^{\eta,\eta',m}_{\boldsymbol{Q},\boldsymbol{k}} \hat{\boldsymbol{Y}}^{\eta',\dagger}_{\boldsymbol{Q}+\boldsymbol{k}} \hat{\boldsymbol{Y}}^{\eta}_{\boldsymbol{Q}} \left(\hat{\boldsymbol{b}}_{\boldsymbol{k}} + \hat{\boldsymbol{b}}^\dagger_{-\boldsymbol{k}}\right), \tag{24}$$

$$G^{\eta,\eta',m}_{\boldsymbol{Q},\boldsymbol{k}} = g^m_{\boldsymbol{k}} \sum_\xi (U^\xi_{\eta',\boldsymbol{Q}+\boldsymbol{k}})^* U^\xi_{\eta,\boldsymbol{Q}} \tag{25}$$

where $\hat{\boldsymbol{b}}$ are creation/annihilation operators of phonons with momentum $\boldsymbol{k}$ in mode m. $g^m_{\boldsymbol{k}}$ is the corresponding exciton phonon matrix element. The non-radiative contribution to the dephasing can be computed using Heisenberg's equations of motion and the Markov approximation[4,5], arriving at the result,

$$\Gamma^\eta_{\boldsymbol{Q}}(T) = \pi\sum_{\eta'}\sum_{\boldsymbol{k},m,\pm} |G^{\eta,\eta',m}_{\boldsymbol{Q},\boldsymbol{k}}|^2 \left(\frac{1}{2} \pm \frac{1}{2} + n^m_{\boldsymbol{k}}(T)\right) \delta\left(\mathcal{E}^{\eta'}_{\boldsymbol{Q}+\boldsymbol{k}} - \mathcal{E}^\eta_{\boldsymbol{Q}} + \hbar\omega^m_{\boldsymbol{k}}\right) \tag{26}$$

where $\pm$ corresponds to the absorption/emission of phonons with frequency $\omega^m_{\boldsymbol{k}}$. $n^m_{\boldsymbol{k}}(T)$ is the Maxwell-Boltzmann distribution of phonons. In a magnetic field we find,

$$\Gamma^\eta_{\boldsymbol{Q}}(T,B) = \pi\sum_{\eta'}\sum_{\boldsymbol{k},m,\pm} |G^{\eta,\eta',m}_{\boldsymbol{Q},\boldsymbol{k}}(B)|^2 \left(\frac{1}{2} \pm \frac{1}{2} + n^m_{\boldsymbol{k}}(T)\right) \delta\left(\mathcal{E}^{\eta'}_{\boldsymbol{Q}+\boldsymbol{k}}(B) - \mathcal{E}^\eta_{\boldsymbol{Q}}(B) + \hbar\omega^m_{\boldsymbol{k}}\right) \tag{27}$$

The sum of both the radiative and non-radiative decay gives a good estimate of the theoretical PL linewidth, although higher-order, less significant processes such as exciton-exciton interactions are neglected [].

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