Electronic Supplementary Material (ESI) for Nanoscale.

Suplementary Information: Phonon-assisted Exciton Dissociation in Transition Metal Dichalcogenide Monolayers

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CONTENTS

A. CURRENT DENSITY

The current operator reads in second quantization formalism $\boldsymbol{j} = \sum_{\lambda'\lambda\boldsymbol{k}\boldsymbol{k}'} \boldsymbol{J}^{\lambda\lambda'}_{\boldsymbol{k}\boldsymbol{k}'} a^\dagger_{\lambda\boldsymbol{k}} a_{\lambda'\boldsymbol{k}'}$, with the current matrix $\boldsymbol{J}^{\lambda\lambda'}_{\boldsymbol{k}\boldsymbol{k}'} = \frac{e_0}{m_0}\langle\lambda\boldsymbol{k}|\boldsymbol{p}|\lambda'\boldsymbol{k}'\rangle = \frac{e_0\hbar}{m_\lambda}\boldsymbol{k}\delta_{\boldsymbol{k}\boldsymbol{k}'}\delta_{\lambda\lambda'}$ and the ladder operators $a^{(\dagger)}_{\lambda\boldsymbol{k}}$ describing the annihilation (creation) of an electron at the band $\lambda = v, c$ with momentum $\boldsymbol{k}$. The current density can be then written as $\langle\boldsymbol{j}\rangle = A^{-1}e_0\hbar\sum_{\lambda\boldsymbol{k}} m_\lambda^{-1}\boldsymbol{k} f^\lambda_{\boldsymbol{k}}$, where we have defined the carrier occupation $f^\lambda_{\boldsymbol{k}} = \langle a^\dagger_{\lambda\boldsymbol{k}} a_{\lambda\boldsymbol{k}}\rangle$. One can introduce a unit operator [1, 2] to express the carrier occupations $f^e_{\boldsymbol{k}} = \sum_{\boldsymbol{k}'}\langle P^\dagger_{\boldsymbol{k}\boldsymbol{k}'} P_{\boldsymbol{k}\boldsymbol{k}'}\rangle$ and $f^h_{\boldsymbol{k}} = \sum_{\boldsymbol{k}'}\langle P^\dagger_{\boldsymbol{k}'\boldsymbol{k}} P_{\boldsymbol{k}'\boldsymbol{k}}\rangle$ in terms of pair operators $P^\dagger_{\boldsymbol{k}\boldsymbol{k}'} = a^\dagger_{c\boldsymbol{k}} a_{v\boldsymbol{k}'}$, which in turn can be expanded in a basis of excitonic states, $P^\dagger_{\boldsymbol{k}\boldsymbol{k}'} = \sum_\nu \phi^\nu_{\alpha_h\boldsymbol{k}+\alpha_e\boldsymbol{k}'} X^{\nu\dagger}_{\boldsymbol{k}-\boldsymbol{k}'}$. Here $X^{\nu\dagger}_{\boldsymbol{Q}}$ is the creation operator for an exciton at the ν-level with center-of-mass momentum $\boldsymbol{Q}$, $\phi^\nu_{\boldsymbol{k}}$ is the excitonic wavefunction with relative momentum $\boldsymbol{k}$ fulfilling the Wannier equation [3], and $\alpha_\lambda = m_\lambda/(m_h + m_e)$. Considering only diagonal terms describing incoherent occupation of excitons, i.e. $\langle X^{\nu\dagger}_{\boldsymbol{Q}} X^\mu_{\boldsymbol{Q}}\rangle = \langle X^{\nu\dagger}_{\boldsymbol{Q}} X^\nu_{\boldsymbol{Q}}\rangle\,\delta_{\nu\mu}$, the current density reads $\langle\boldsymbol{j}\rangle = e_0\hbar m_r^{-1}\sum_{\nu\boldsymbol{k}}\boldsymbol{k}|\phi^\nu_{\boldsymbol{k}}|^2 n_\nu$, with the reduced mass $m_r^{-1} = m_h^{-1} + m_e^{-1}$ and the exciton density $n_\nu = A^{-1}\sum_{\boldsymbol{Q}}\langle X^{\nu\dagger}_{\boldsymbol{Q}} X^\nu_{\boldsymbol{Q}}\rangle$. It is important here to distinguish between free and bound excitonic states. The probability functions $|\phi^\nu_{\boldsymbol{k}}|^2$ for bound states are even, and hence the integration over momentum with the even function $\boldsymbol{k}$ yields zero current. This is not the case for continuum (free) states, which can be approximately described by plane waves. Therefore the current only has contributions from excitonic states in the continuum

(free electron-hole pairs): $\langle \boldsymbol{j} \rangle = e_0 \hbar m_r^{-1} \sum_{\boldsymbol{k}\boldsymbol{k}'} \boldsymbol{k} |\psi_{\boldsymbol{k}}^{\boldsymbol{k}'}|^2 n_\nu$, where the quantum number ν has become a continuous momentum $\boldsymbol{k}'$ and we have redefined the exciton wavefunction for continuum states to $\psi_{\boldsymbol{k}}^{\boldsymbol{k}'}$. The current is thus governed by free electron-hole pairs.

B. ORTHOGONAL PLANE WAVES

Plane waves in momentum space are described by a delta function. We describe free states as plane waves but note that the complete basis is also formed by bound states. Hence we add a correction to the plane waves and obtain the so-called orthogonal plane waves (OPWs)

$$\psi_{\boldsymbol{k}}^{\boldsymbol{p}} = N_{\boldsymbol{p}} \left(\delta_{\boldsymbol{p}\boldsymbol{k}} - \sum_{\nu}^{N_\mathrm{b}} c_{\boldsymbol{p}}^{\nu} \phi_{\boldsymbol{k}}^{\nu} \right), \tag{B.1}$$

where $N_{\boldsymbol{p}}$ is a normalization factor and $c_{\boldsymbol{p}}^{\nu}$ is an orthogonalization coefficient. In order for free and bound states to be orthogonal, the following condition must be fulfilled:

$$\sum_{\boldsymbol{k}} \psi_{\boldsymbol{k}}^{\boldsymbol{p}*} \phi_{\boldsymbol{k}}^{\nu} = 0 \implies c_{\boldsymbol{p}}^{\nu} = \phi_{\boldsymbol{p}}^{\nu *}. \tag{B.2}$$

In a similar manner, we find the normalization factor,

$$\sum_{\boldsymbol{k}} |\psi_{\boldsymbol{k}}^{\boldsymbol{p}}|^2 = 1 \implies N_{\boldsymbol{p}} = \left(1 - \sum_{\nu}^{N_\mathrm{b}} \left| \phi_{\boldsymbol{p}}^{\nu} \right|^2 \right)^{-\frac{1}{2}}. \tag{B.3}$$

The contribution from the few bound states $\sum_{\nu}^{N_\mathrm{b}} \left| \phi_{\boldsymbol{p}}^{\nu} \right|^2$,is insignificant and hence can be neglected. Another way to argue why this factor can be neglected is that $\left| \phi_{\boldsymbol{p}}^{\nu} \right|^2 \propto \frac{1}{A} \to 0$ for $A \to \infty$. The final expression for the OPWs describing free states is

$$\psi_{\boldsymbol{k}}^{\boldsymbol{p}} = \delta_{\boldsymbol{p}\boldsymbol{k}} - \sum_{\nu}^{N_\mathrm{b}} \phi_{\boldsymbol{p}}^{\nu *} \phi_{\boldsymbol{k}}^{\nu}. \tag{B.4}$$

C. OPTICAL EXCITATION AND RADIATIVE RECOMBINATION

An optical excitation first generates coherent excitons (also referred to as microscopic polarization, $p^\nu = \langle X_{\boldsymbol{0}}^{\nu \dagger} \rangle$), which then either decay radiatively or are transferred into the incoherent population $N_{\boldsymbol{Q}}^{\nu}$ via phonon scattering. Since we will focus on continuous wave excitation, we will assume the temporal evolution of p^ν to be slow. In a rotating wave approximation, we obtain

$$p^\nu = \frac{\hbar \Omega^\nu}{E_{\boldsymbol{0}}^{\nu} - \hbar\omega + i\hbar\gamma^\nu}, \tag{C.1}$$

where ω is the frequency of the incident light, $\Omega_\sigma^\nu = i\frac{e_0}{\hbar m_0}\boldsymbol{M}^\nu \cdot \boldsymbol{A}(t)$ is the Rabi frequency [4], with the excitonic optical matrix element $\boldsymbol{M}^\nu$ and the vector potential $\boldsymbol{A}(t)$ [5], and $\gamma^\nu = \gamma^\nu_{\mathrm{rad}} + \frac{1}{2}\sum_{\mu \boldsymbol{Q}} \Gamma^{\nu\mu}_{\boldsymbol{0Q}}$ is the total dephasing [6]. We assume here circulary-polarized light for optimal absorption and set $\boldsymbol{M}^\nu$ to match oscillator strengths extracted from experimental absorption spectra [7]. Note that the difference between the calculated absorption values that determine the EQE in the main manuscript and the ones reported in Ref. 7 is due to different linewidths—in the experiment the linewidths might be larger due to disorder, while our linewidths are in agreement with clean samples [6]. It is noteworthy to mention that when one sums the optical absorption term in Eq. (2) over momentum and all excitonic states one obtains $\dot{n}_x = \frac{I}{\hbar\omega}\alpha(\omega)$, which can be intuitively understood as the exciton generation corresponding to the photon flux weighted by the absorption profile.

Finally, the radiative decay can be determined by self-consistently solving the semiconductor Bloch equation for the excitonic polarization and the Maxwell equations for the vector potential $\boldsymbol{A}$ in a 2D geometry [6, 8, 9], obtaining the rate

$$\gamma^\nu_{\mathrm{rad}} = \frac{e_0^2 |\boldsymbol{M}^\nu \cdot \boldsymbol{e}_\sigma|^2}{2m_0^2 \epsilon_0 n c_0 E^\nu_{\boldsymbol{0}}}. \tag{C.2}$$

Here we have defined the Jones vector $\boldsymbol{e}_\sigma$ describing the polarization of the light and the refractive index of the medium n.

D. RESPONSE TIME AND STATIONARY STATE

From our microscopic theory, we can set up a simple model for the macroscopic dynamics in order to identify key parameters. Eq. (2) can be summed over $\boldsymbol{Q}$ and ν to obtain the equation of motion for the exciton density $\dot{n} = G - \tau^{-1} n$, where $G = \frac{I}{\hbar\omega}\alpha(\omega)$ is the optical generation current, I the power density of the incident light, and τ the lifetime corresponding to the sum of different decay times $\tau^{-1} = \sum_i \tau_i^{-1}$. The different decay mechanisms are dissociation $\tau_{\mathrm{d}}^{-1} = \frac{1}{nA}\sum_{\nu \boldsymbol{Q}} \Gamma^{\mathrm{diss}}_{\nu \boldsymbol{Q}} N^\nu_{\boldsymbol{Q}}$, radiative recombination $\tau_{\mathrm{r}}^{-1} = \frac{1}{nA}\sum_\nu 2\delta_{\boldsymbol{Q0}} \gamma^\nu_{\mathrm{rad}} N^\nu_{\boldsymbol{Q}}$, and non-radiative recombination τ_{nr}. The solution to this equation of motion reads $n(t) = n(0)\mathrm{e}^{-t/\tau} + G\tau(1 - \mathrm{e}^{-t/\tau})$. Here, we can identify the stationary solution $n(\infty) = G\tau$ and the response time τ. Hence, the mechanism governing the stationary exciton density and the response time τ will be the one with the shortest characteristic time τ_i.

E. MODEL PARAMETERS

We assume a parabolic dispersion for each electronic valley and use ab-initio parameters for the effective mass, lattice constant, valley energy offsets, and dielectric constants [10, 11]. We treat scattering with phonons in an effective deformation potential approach and use ab-initio parameters for the phonon energies and deformation potentials, considering transversal and longitudinal acoustic (TA, LA) and optical (TO, LO) modes, as well as the out-of-plane A_1 mode, in the Γ, $K^{(')}$, $\Lambda^{(')}$ and $M^{(')}$ valleys [12]. In order to study the effect of strain, we take parameters for the energetic shift of the electronic valleys from Ref. 13.

F. TRANSITION RATES

In Table I we list the values for the transition rates that are depicted in Fig. 2(c) in the main manuscript.

	KK_{1s}	KK_{2s}	KK'_{1s}	KK'_{2s}	$K\Lambda_{1s}$	$K\Lambda_{2s}$	$KK'_{cont.}$
KK_{1s}	0	$5.3 \cdot 10^{-2}$	1.4	$4.2 \cdot 10^{-2}$	6.3	$9.4 \cdot 10^{-2}$	$3.6 \cdot 10^{-2}$
KK_{2s}	$-5.3 \cdot 10^{-2}$	0	$-9.5 \cdot 10^{-3}$	$-3.8 \cdot 10^{-3}$	$-4.2 \cdot 10^{-2}$	$-4.8 \cdot 10^{-3}$	$9.0 \cdot 10^{-2}$
KK'_{1s}	-1.4	$9.5 \cdot 10^{-3}$	0	$4.9 \cdot 10^{-1}$	$-4.2 \cdot 10^{-2}$	1.7	$2.6 \cdot 10^{-2}$
KK'_{2s}	$-4.2 \cdot 10^{-2}$	$3.8 \cdot 10^{-3}$	$-4.9 \cdot 10^{-1}$	0	-3.5	3.3	$2.8 \cdot 10^{-1}$
$K\Lambda_{1s}$	-6.3	$4.2 \cdot 10^{-2}$	$4.2 \cdot 10^{-2}$	3.5	0	$8.6 \cdot 10^{-1}$	2.8
$K\Lambda_{2s}$	$-9.4 \cdot 10^{-2}$	$4.8 \cdot 10^{-2}$	-1.7	-3.3	$-8.6 \cdot 10^{-1}$	0	5.8

TABLE I. Transition rates $\Gamma_{\nu\mu}$ from excitonic states ν (rows) into other bound states μ (columns) or the KK' continuum (last column). The values are in units of $cm^{-2}ps^{-1}$. Only the main states involved in the dynamics are included.

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