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A phenomenological theory of dark exciton reservoirs in monolayer transition metal dichalcogenides

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Abstract: Dark excitons play a decisive role in governing the low-temperature optical and dynamical properties of monolayer transition metal dichalcogenides (TMDs). Owing to their spin- and momentum-forbidden nature, dark excitons possess long lifetimes and remain weakly coupled to light, rendering their direct experimental detection challenging. Nevertheless, a surge of recent experiments demonstrates that dark excitons act as long-lived population reservoirs that strongly influence bright exciton photoluminescence, relaxation pathways, and nonequilibrium dynamics. In this work, we develop a comprehensive phenomenological framework describing coupled bright and dark exciton populations using rate equations that incorporate phonon-mediated scattering. Analytical expressions for steady-state densities, temperature-dependent photoluminescence, and characteristic relaxation times are derived. The model captures a wide range of experimental observations, including emission quenching at low temperatures, thermal brightening, and bi-exponential decay dynamics. Beyond reproducing known trends, the framework provides physical insight into how dark excitons control excitonic response in two-dimensional semiconductors and offers a flexible platform for exploring collective and nonlinear dark-exciton-driven phenomena.

Keywords: Dark excitons, Exciton dynamics, Dark reservoir, Transition metal dichalcogenides, Phenomenological theory.

1. INTRODUCTION

Two-dimensional transition metal dichalcogenides (TMDs) have emerged as a remarkable platform for studying excitonic physics in the strong-coupling regime. The observation of intense photoluminescence from monolayer MoS_2, WS_2, $MoSe_2$, and WSe_2 established these materials as direct-gap semiconductors despite their atomic thickness [1-3]. Reduced dielectric screening combined with spatial confinement leads to exceptionally large exciton binding energies, often exceeding several hundred meV, allowing excitons to remain stable even at room temperature [4].

Beyond the existence of optically bright excitons, the excitonic fine structure of monolayer TMDs is enriched by strong spin–orbit coupling and spin–valley

locking. These effects give rise to a manifold of exciton states, including spin-forbidden and momentum-forbidden dark excitons [5, 6]. In tungsten-based TMDs (WSe_2, WS_2), dark excitons typically lie energetically below bright excitons, causing exciton populations to relax rapidly into optically inactive states at low temperatures [7, 8].

Experimental access to dark excitons has been achieved indirectly through magnetic-field-induced brightening [9-11], phonon-assisted recombination [12], and time-resolved photoluminescence (TRPL) experiments that reveal long-lived emission tails [13-14]. These observations consistently indicate that dark excitons dominate exciton relaxation dynamics. While microscopic theories involving GW-BSE calculations provide detailed band structures, a transparent phenomenological model is required to interpret macroscopic observables such as temperature-dependent yields and decay curves. In this work, we present such a framework, treating dark excitons as long-lived reservoirs coupled to optically bright excitons via phonon scattering and many-body interactions.

2. PHENOMENOLOGICAL MODEL

The excitonic landscape of monolayer TMDs is intrinsically complex, consisting of multiple spin- and valley-resolved exciton states. However, for the purpose of capturing experimentally observable optical dynamics, this complexity can be systematically reduced to an effective two-manifold description. In this phenomenological approach, we classify excitons into (i) optically bright states that couple efficiently to light and (ii) optically inactive dark states that possess long lifetimes and weak radiative coupling.

We therefore consider a simplified model in which the total exciton population is partitioned between a bright exciton mode with density N_b and an effective dark reservoir with density N_d, as schematically illustrated in figure 1. The dark reservoir aggregates both spin-forbidden intra-valley excitons and momentum forbidden intervalley excitons, which are experimentally difficult to distinguish but play a similar dynamical role. The time evolution of these populations is governed by the interplay of optical pumping, radiative decay, inter-species scattering.

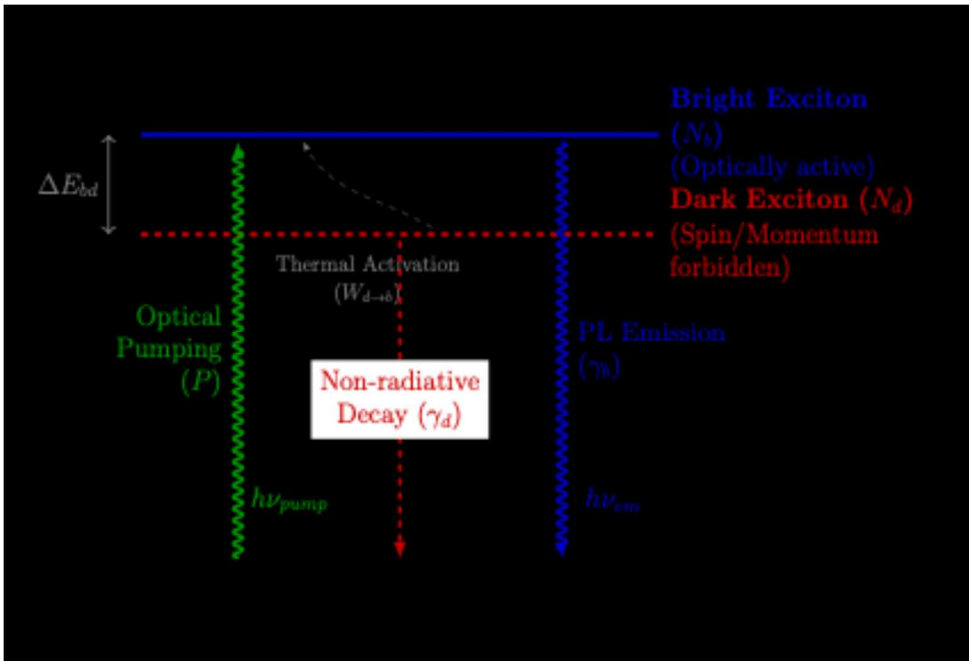

Figure 1: Schematic energy-level diagram illustrating the phenomenological model. Optically active bright excitons (N_b) are generated by pumping (P) and decay radiatively (γ_b). Dark excitons (N_d), which lie at lower energy ΔE_{bd}, are generated via rapid intersystem scattering ($W_{b\to d}$) from the bright state. They act as a population reservoir, decaying non-radiatively (γ_d) or scattering back to the bright state via thermal activation ($W_{d\to b}$).

The coupled rate equations are given by:

$$\frac{dN_b}{dt} = P - \Gamma_b N_b - \Gamma_{bd} N_b + \Gamma_{db} N_d \tag{1}$$

$$\frac{dN_d}{dt} = \Gamma_{bd} N_b - \Gamma_d N_d - \Gamma_{db} N_d \tag{2}$$

where

P is the generation rate proportional to the optical pump intensity.

$\Gamma_b = \frac{1}{\tau_b}$ is the recombination rate of bright excitons (typically ~ ps scale).

$\Gamma_d = \frac{1}{\tau_d}$ is the non-radiative decay rate of dark excitons (typically ~ ns scale)

Γ_{bd} is the scattering rate from bright to dark states (down-conversion)

Γ_{db} is the scattering rate from dark to bright states (up-conversion)

A defining feature of TMDs, particularly W-based monolayers, is the energetic splitting $\Delta E_{bd} = E_b - E_d > 0$. Consequently, the scattering rates must satisfy the principle of detailed balance:

$$\frac{\Gamma_{db}}{\Gamma_{bd}} = \exp\left(-\frac{\Delta E_{bd}}{k_B T}\right) \tag{3}$$

This constraint ensures that in the absence of pumping and decay, the populations would thermalize according to Boltzmann statistics. As a result, dark excitons act as a thermo-dynamically favored population reservoir at low temperatures, fundamentally reshaping the optical response of the system. In the continuous-wave (CW) excitation regime $\frac{dN}{dt} = 0$ and assuming the low-excitation limit, the steady-state solution for the bright exciton density is:

$$N_b^{SS} = \frac{P}{\Gamma_b + \Gamma_{bd}\left(1 - \frac{\Gamma_{db}}{\Gamma_d + \Gamma_{db}}\right)} \tag{4}$$

The photoluminescence intensity $I_{PL} \propto N_b^{SS}\Gamma_b$. We define the internal quantum efficiency (IQE), η, as the ratio of radiative recombination to the generation rate:

$$\eta = \frac{\Gamma_b N_b^{SS}}{P} = \frac{\Gamma_b}{\Gamma_b + \Gamma_{bd}\left(\frac{\Gamma_d}{\Gamma_d + \Gamma_{db}}\right)} \tag{5}$$

This expression highlights the reservoir effect. If the dark decay rate Γ_d is negligible ($\Gamma_d \to 0$), the efficiency approaches unity regardless of Γ_{bd}, as all dark excitons eventually scatter back to the bright state and radiate. However, in reality, Γ_d is finite, acting as a loss channel. The term $\Gamma_{bd}\left(\frac{\Gamma_d}{\Gamma_d + \Gamma_{db}}\right)$ represents the effective non-radiative loss rate mediated by the dark reservoir. This interpretation tells us that photoluminescence quenching at low temperatures does not necessarily imply enhanced defect-mediated losses. Instead, it can arise purely from population trapping in long-lived dark states. This distinction is crucial for correctly interpreting optical experiments and assessing material quality in monolayer TMDs.

2. 1 Temperature-dependent brightening

The temperature dependence of PL intensity is governed by the activation of up-scattering channel Γ_{db}. Substituting Eq. (3) into the efficiency equation, and assuming Γ_{bd} is dominated by spontaneous phonon emission (weakly temperature dependent) while Γ_{db} is thermally activated, we obtain:

$$I_{PL}(T) \propto \frac{1}{1 + A\left[1 + B\exp\left(-\frac{\Delta E_{bd}}{k_B T}\right)\right]^{-1}} \tag{6}$$

where $A = \Gamma_{bd}/\Gamma_b$ and B relates to the density of states ratio. At cryogenic temperatures $\Delta E_{bd} \ll k_B T$, the exponential term vanishes, and excitons are

trapped in the dark state, leading to PL quenching (dark state shelving). As T increases, thermal energy facilitates back-scattering from the reservoir to the bright state, increasing the observable PL. This phenomenological derivation reproduces the characteristic "thermal brightening" observed in WSe_2 and WS_2 monolayers [9, 12]. The resulting temperature dependence of the photoluminescence intensity, shown in figure 2, demonstrates strong emission quenching at low temperatures due to population trapping in the dark exciton reservoir, followed by thermal brightening driven by phonon-assisted activation into optically bright states.

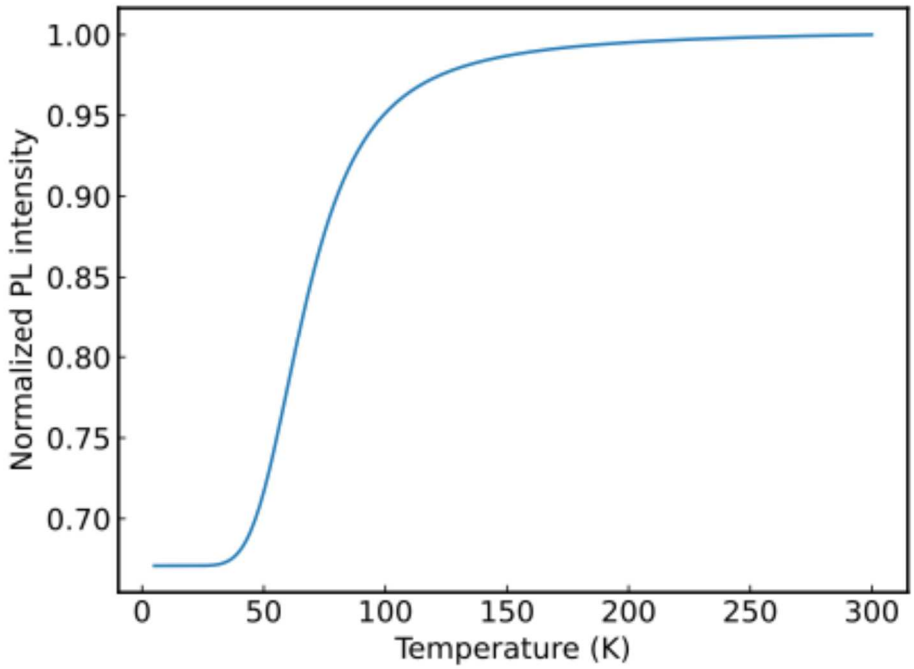

Figure 2: Temperature-dependent photoluminescence intensity calculated from the steady-state phenomenological model. At low temperatures (T < 50 K), exciton populations are trapped in the momentum-dark reservoir, quenching emission. As temperature increases, thermal activation (Γ_{db}) repopulates the bright state, leading to characteristic thermal brightening.

2. 2 Time-resolved dynamics

To analyze Time-Resolved Photoluminescence (TRPL), we solve Eqs. (1) and (2) for $P = 0$ after an initial pulse excitation. Assuming linear dynamics, the system yields a general solution of the form:

$$N_b(t) = C_1 e^{-\lambda_{fast} t} + C_2 e^{-\lambda_{slow} t} \quad (7)$$

λ_{fast} and λ_{slow}correspond to the rapid radiative decay and the slow reservoir feeding, respectively. Given the hierarchy of rates $\Gamma_b \gg \Gamma_{bd} \gg \Gamma_d$, we can approximate the decay rates as:

$$\lambda_{fast} \approx \Gamma_b + \Gamma_{bd} \quad (8)$$

$$\lambda_{slow} \approx \Gamma_d + \frac{\Gamma_{bd}\Gamma_{db}}{\Gamma_b + \Gamma_{bd}} \quad (9)$$

The initial fast decay corresponds to the immediate recombination of bright excitons and their scattering into the dark state. The slow component, often observed as a long-lived tail in experimental TRPL, signifies the delayed luminescence arising from dark excitons scattering back into the bright manifold. The amplitude ratio C_2/C_1 serves as a direct measure of the dark-bright coupling strength.

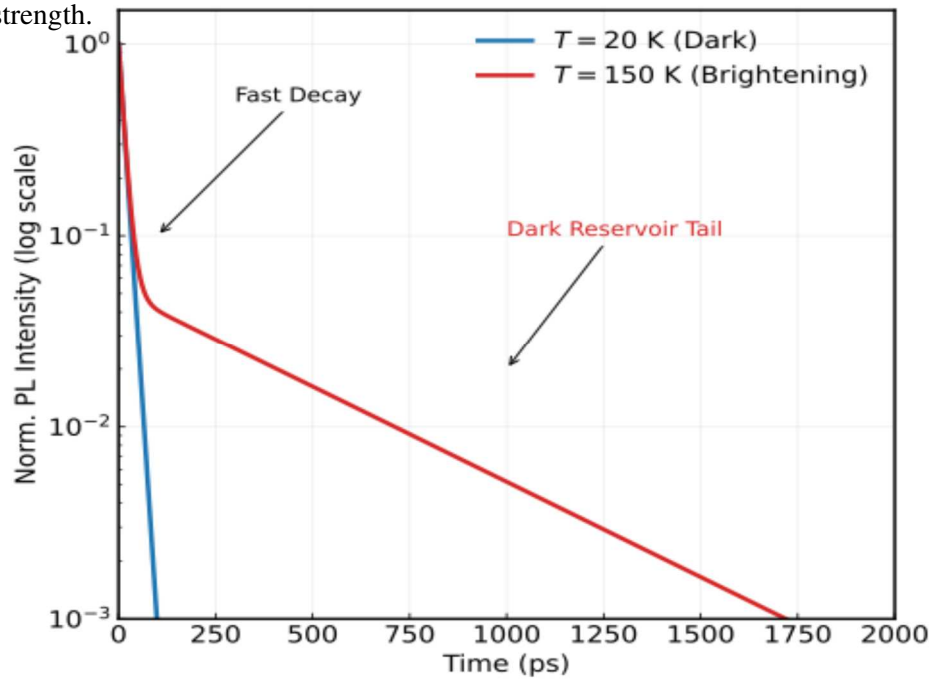

Figure 3: Simulated Time-Resolved Photoluminescence (TRPL) transients. The decay exhibits bi-exponential behavior characterized by an initial fast radiative decay (~ps) followed by a slow, long-lived tail (~ ns). The amplitude of the slow component increases with temperature due to enhanced back-scattering from the dark reservoir.

2. 3 Coherence and collective effects

The reservoir picture developed here offers insight into collective excitonic phenomena. The accumulation of a high-density population in the dark state ($N_d \gg N_b$) creates conditions favorable for Bose-Einstein Condensation (BEC). Since dark excitons have long lifetimes (τ_d) and integer spin, they can thermalize to the lattice temperature before recombining. In TMD heterostructures or external strain, the dark excitons can be confined, further enhancing critical phase space density. The rate equations suggest that pumping bright excitons essentially pumps the dark reservoir. If the inter-exciton interaction strength is repulsive, a stable dark condensate may form, detectable only through the coherence of the weak up-converted luminescence or distinctive signatures in the transport properties.

3. CONCLUSION

We have presented a phenomenological theory describing dark excitons as dynamic reservoirs in monolayer TMDs. By enforcing detailed balance, the model successfully reproduces key experimental features: low-temperature quenching, thermal brightening, and bi-exponential decay. The analytical results high-light that the "dark" nature of these excitons does not preclude them from dictating the optical response; rather, they act as a massive energy storage buffer. This framework provides a basis for future studies on dark exciton hydrodynamics and condensate formation in van der Waals heterostructures.

Acknowledgements

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