Brightening of dark excitons in 2D perovskites by in-plane magnetic field

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In 2D perovskites, as in all semiconductors, the degeneracy of the dark and bright exciton states is lifted by the exchange interaction between the electron and hole. This exciton *fine structure* is essential to understand the interaction of matter with light, and reflects the underlying symmetry of the system [1]. The bright-dark splitting is of paramount importance for light emitters which rely on the radiative recombination of excitons, since the excitons usually relax to the lowest lying dark state, which is detrimental for the device efficiency. It is expected that the enhanced Coulomb interaction in the 2D limit strongly increases the splitting of dark and bright excitonic states [2], however, such a splitting has never been measured directly in 2D perovskites.

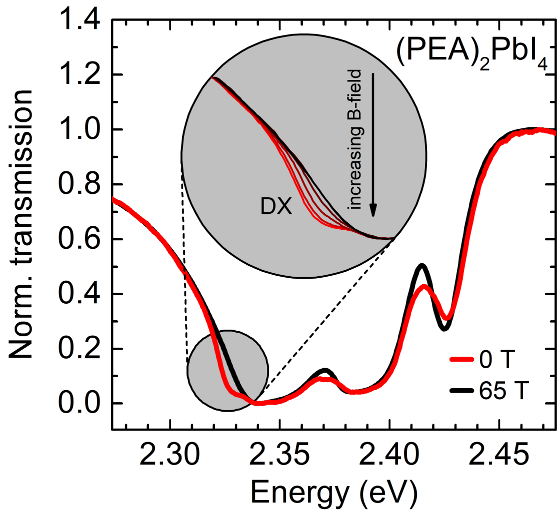

Figure. Transmission spectra of $(PEA)_2PbI_4$ measured in Voigt geometry. The circle at the low energy side indicates an appearance of the brightened dark state. Inset shows evolution of this state with increasing magnetic field.

Here we report on optical spectroscopy measurements with an applied in-plane magnetic field to mix the bright and dark excitonic states in PEA-based family of 2D perovskites ($(PEA)_2(Pb,Sn)(I,Br)_4$), providing the first direct measurement of the bright-dark splitting. The induced brightening of the dark state allows us to directly observe an enhancement of the absorption at the low-energy side of the spectrum related to the dark state (cf. Fig.). With the signature of dark state in the optical spectra we are able precisely determine the bright-dark exciton state splitting of $21.6 \pm 3.3\,\mathrm{meV}$ for $(PEA)_2PbI_4$ at $B = 0\,\mathrm{T}$. The brightening of the dark state was also visible in photoluminescence, dominating the emission already at a moderate magnetic field of $\simeq 6\,\mathrm{T}$. The evolution of the PL signal in the magnetic field suggests that, at low temperatures, the exciton population is not fully thermalized because of the existence of a phonon bottleneck, which occurs due to the specific nature of the exciton-phonon coupling in soft perovskite materials. Our observations explain why 2D perovskites are ideal light emitters although its lowest-lying excitation is optically inactive.

[1] Baranowski *et al.*, Nano Lett. **19**, 10 (2019)
[2] Bayer *et al.*, Phys. Rev. Lett. **82**, 1748 (1999)