Reveling Phonon-Bottleneck Effect in 2D Perovskites

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Two dimensional (2D) metal-halide perovskites have emerged as revolutionary semiconductor materials for light emission and energy harvesting applications. They also constitute fascinating playground for the fundamental physics studies. In this natural quantum wells, excitonic effects are strongly enhanced governing the optical response. Excitons in 2D perovskites exhibits a characteristic fine structure comprising bright triplet and dark singlet states. Recent studies have shown that the dark state is situated several to tens of meV below the bright states in 2D perovskites [1]. Despite this significant splitting, these materials exhibit surprisingly intense PL emission even at cryogenic temperatures, pointing on non-Boltzmann distribution of excitons. However, the origin of this high bright-state occupation has remained elusive.

Here, we address this problem for, $(PEA)_2PbI_4$ 2D perovskites which demonstrates 20 meV splitting between the bright and dark states. Using magnetooptical spectroscopy (which offer access to the dark exciton population) we show that exciton population is characterized with higher temperature than the crystal lattice. To explain this observation we used detailed microscopic and material-specific many-particle theory, exploring the formation, relaxation and decay dynamics of excitons. Our modeling show that the energy mismatch between the fine structure of exciton and phonons leads to a pronounced phonon-bottleneck effect. The consequence is an inefficient exciton relaxation to the energetically lowest dark state resulting in an enhanced non-thermal population of bright excitons. We find an excellent agreement between theory and experiment. Our work [2] provides a comprehensive microscopic picture of the phonon-bottleneck effect between bright and dark exciton states in the family of 2D perovskites, explaining their strong PL emission at low temperatures.

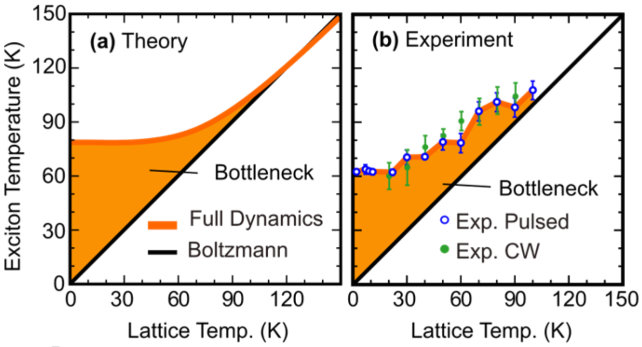

Figure 1. *Effective steady-state temperature T_{exc} of the bright exciton as a function of the lattice temperature extracted from Theory and Experiment. The shaded region indicates the phonon-bottleneck effect.*

[1] Dyksik et al., Sci. Adv. 7, eabk0904 (2021)
[2] Thompson et al., Adv. Energy Mater. (accepted for publication)