Spectator exciton effects in nanocrystals

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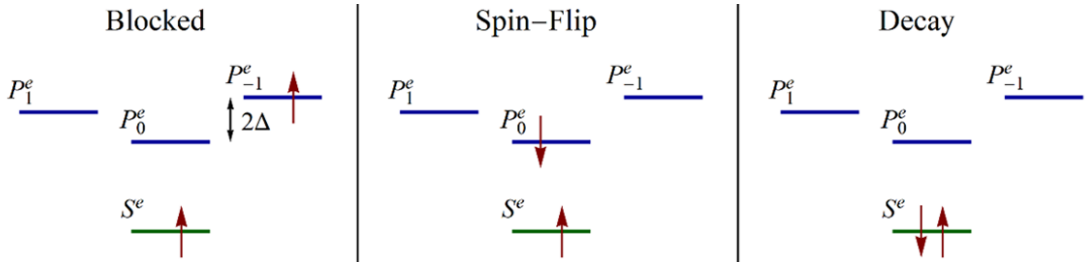
Femtosecond pump-probe experiments on nanocrystals (NC) are interpreted in terms of filling of the states involved in the intense band edge absorption features, and bi-exciton shifting which changes the resonance energy of the probe pulse due to presence of pump induced excitations. Results have habitually been interpreted to show 1) that "hot" excitons will relax to the lowest available levels in the conduction band in ~1 ps, and 2) that band edge exciton transitions will be bleached linearly with loading of additional excitons until the underlying states are completely filled. Testing this is complicated by difficulties in selectively generating a particular multi exciton state, due to the stochastic nature of consecutive multiple exciton absorption. Here we describe a new approach involving "spectator excitons" to test this view.[1] It consists of comparing pump-probe experiments on pristine samples, with equivalent scans conducted on the same sample after it has been saturated in cold mono-excitons. It uniquely allows clean spectral comparison of the pristine NC with that of the mono- and bi-exciton states thereof. We show how this method uncovered previously unrecognized spin blockades in the relaxation of hot multi-exciton states in CdSe and CdTe NCs.[2] An electron at the conduction band edge will selectively block a hot electron from joining it unless its spin orientation is correct. This can prolong the lifetime of hot bi-exciton states, limited by the rate of spin flipping which is also quantified in this experiment (see scheme below). More recently we have used the same approach to measure the cross section for stimulated emission from the relaxed mono-exciton state of quantum confined perovskite nanocrystals. results show that in 5-6 nm $CsPbBr_3$ NCs, a single exciton bleaches more than half of the intense band edge absorption band, while the cross section for stimulated emission from the same state is nearly 6 times weaker.[3] Discussion of these findings in light of several recent electronic structure models for this material proves them unable of simultaneously explaining both measures proving the importance of this new input to resolving this debate.



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