Pump-probe spectroscopy of layered halide perovskites with different organic spacers

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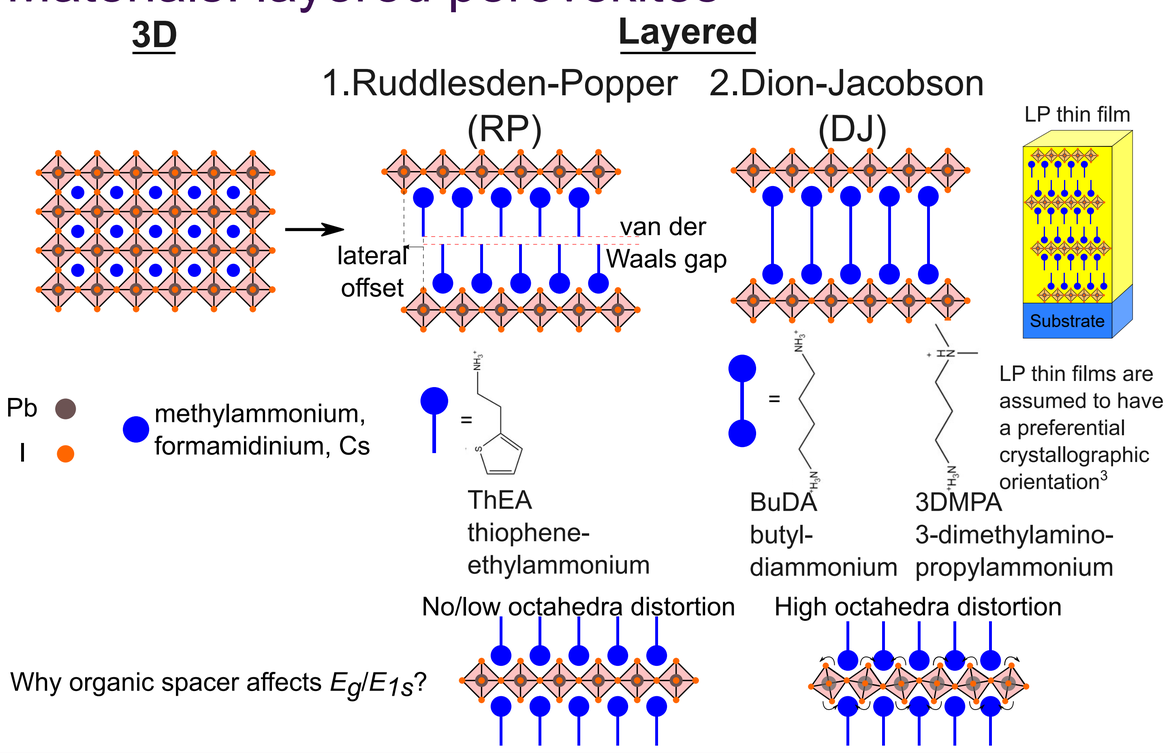
Introduction

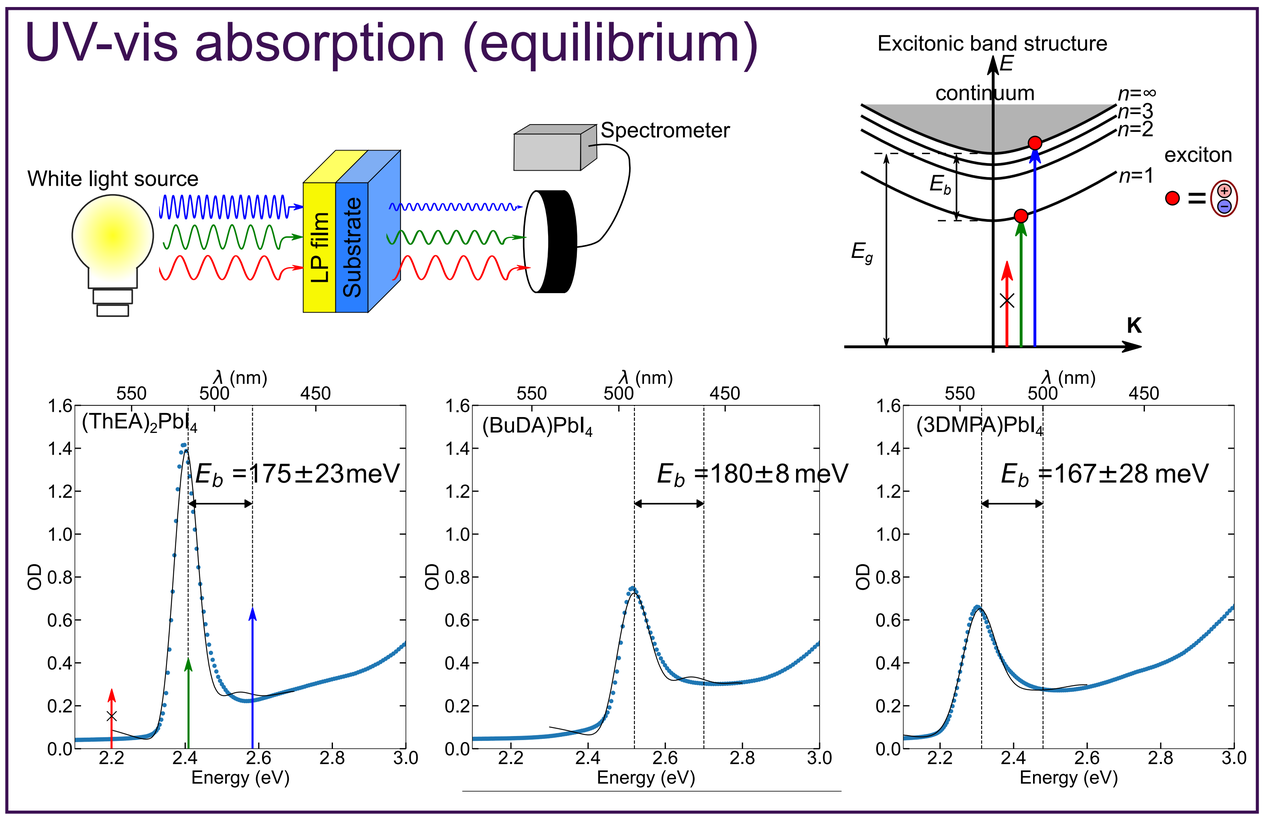
Metal halide perovskites are solution processed semiconductors that possess high power conversion efficiencies (>25%) with the drawback of being unstable[1]. To address the stability problems, long organic cations were incorporated in the lattice creating layered perovskite (LP) structure. Although more stable, LPs have high exciton binding energies caused by the quantum confinement of the inorganic layers, which significantly decreases photoconversion efficiency[2]. To enable the progress of the LPs, understanding of organic spacer's effect on the fundamental optoelectronic processes is critical.

In this study, we employ pump-probe spectroscopy on technologically applicable LPs to analyse the exciton formation and recombination dynamics. The structure characterisation method revealed the lack of preferential crystallographic orientation in certain phases.

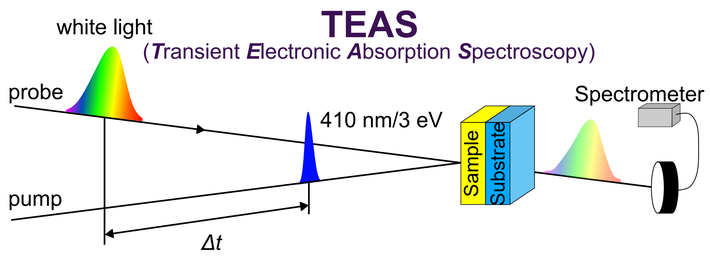
Materials: layered perovskites



UV-vis absorption (equilibrium)



Pump-probe spectroscopy

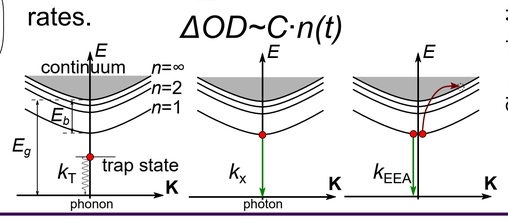


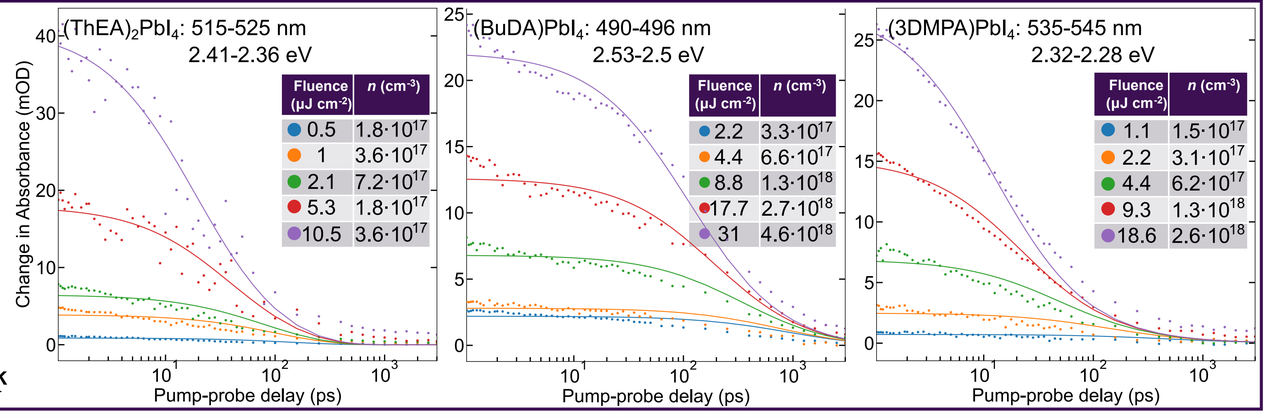
Excitonic recombination rate equation[4]:

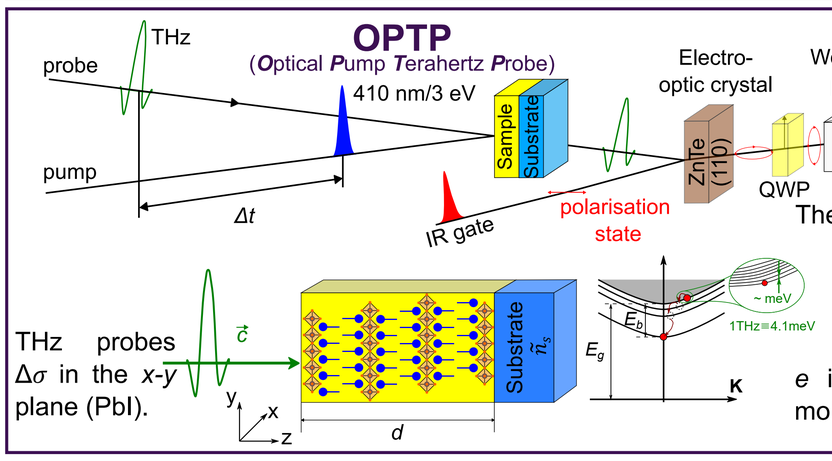
$$\frac{dn}{dt} = -(k_T + k_X)n - k_{EEA}n^2$$

n is the exciton density (cm^{-3}); k_T, k_X and k_{EEA} are recombination rates.

$\Delta OD \sim C \cdot n(t)$





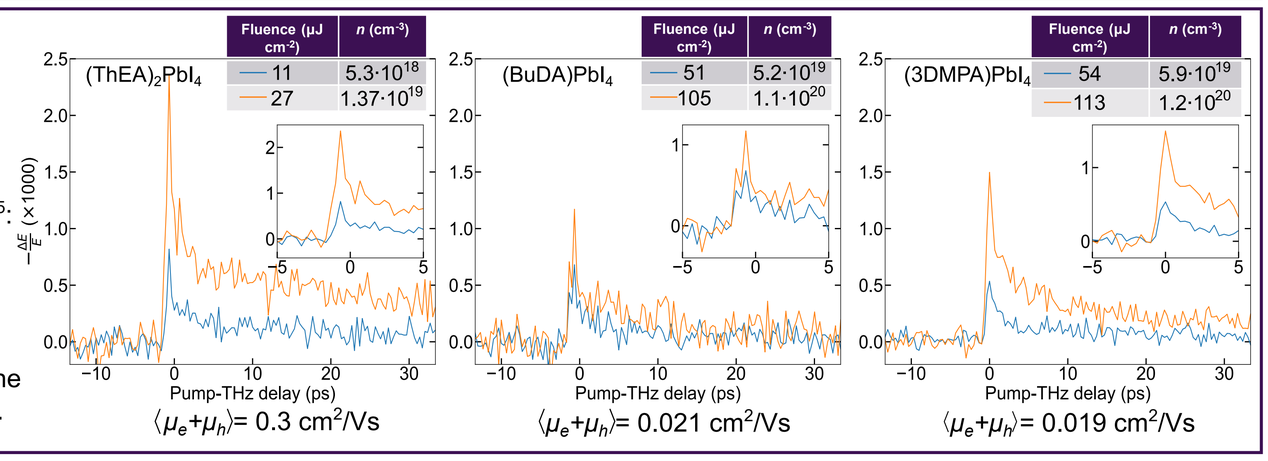


The change of photoconductivity $\Delta\sigma$[5]:

$$\Delta\sigma = ne\mu$$

$$\Delta\sigma = -\frac{\epsilon_0 c(1+\tilde{n}_s)}{d}\frac{\Delta E}{E}$$

e is the electron charge; μ is the mobility; ϵ_0 is the vacuum permittivity.



Exciton-exciton annihilation rate constant of LPs with different organic spacers:

X-ray diffraction

Bragg's law: $m\lambda = 2d\sin\theta$

where m is the order of diffraction; λ is the wavelength of X-ray; θ is the angle of incidence.

Conclusions

1. Exciton dynamics from visible pump-probe spectroscopy suggested that exciton-exciton annihilation rate depends on the bandgap energy.
2. Optical pump-Terahertz probe spectroscopy showed the fast exciton formation times (~1ps) and the Ruddlesden-Popper phase yielding significantly higher THz photoconductivity than Dion-Jacobson.
3. X-ray diffraction revealed the lack of preferential crystallographic direction in Dion-Jacobson phase, unlike Ruddlesden-Popper.

References

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Acknowledgements

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