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Femtosecond mid-infrared spectroscopy of polaron dynamics in a 3D hybrid perovskite

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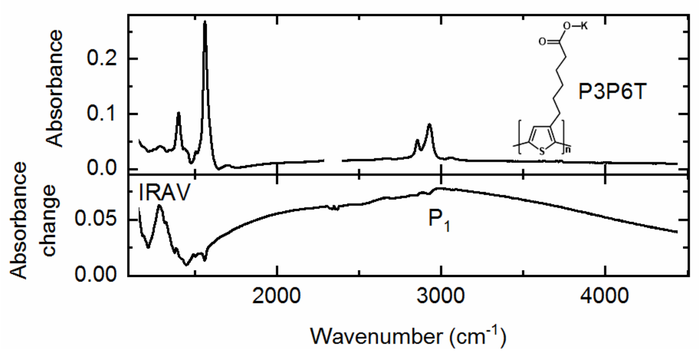
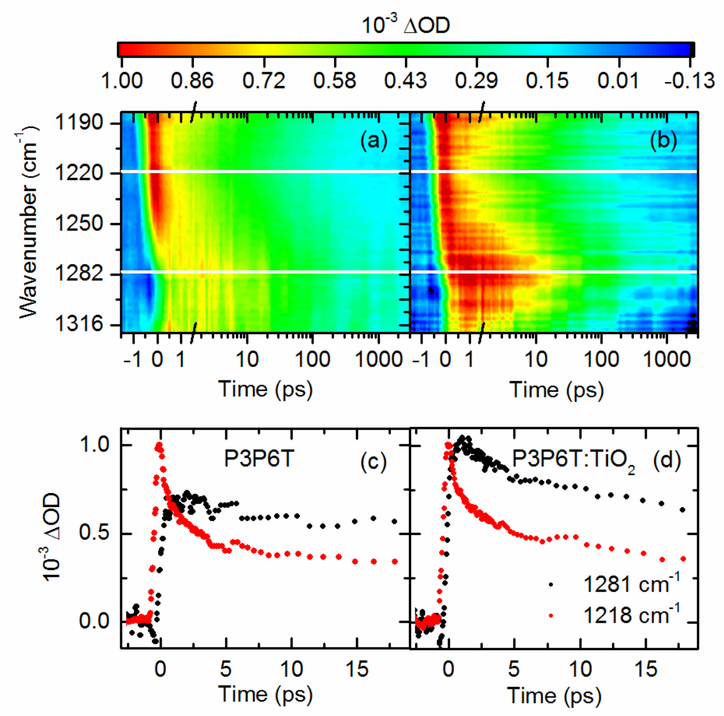
Introduction

In perovskites, different polaronic species have been stipulated: ‚small' polarons, as well as ‚large' ones, involving the organic cations. Generation, recombination and dissociation of charged species on time scales from femtoseconds to picoseconds can be accessed by time resolved visible-pump/infrared-probe spectroscopy. Here we focus on vibrational signatures in the polaron bands of the 3D methylammonium lead iodide (MAPI) perovskite and infer polaron characteristics similar to prototypical conjugated polymers, in which the vibrational modes in the 'fingerprint' spectral region allow distinguishing between different polaronic species and observing their distinct dynamics. In MAPI, we find the coexistence of polaron bands with distinct dynamics, pointing to a possible role of traps in polaron localization.

Distinguishing polaronic species in conjugated polymers by their spectral ‚fingerprint'



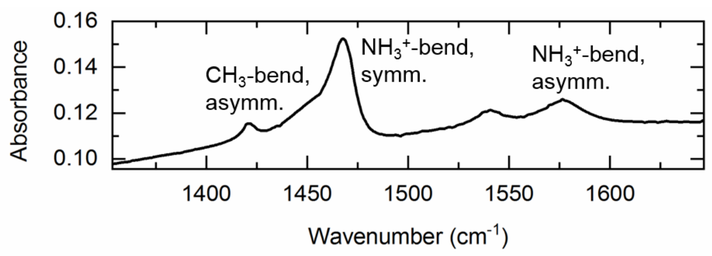
Infrared activated vibrations (IRAV) are sensitive to charges on the polymer backbone.



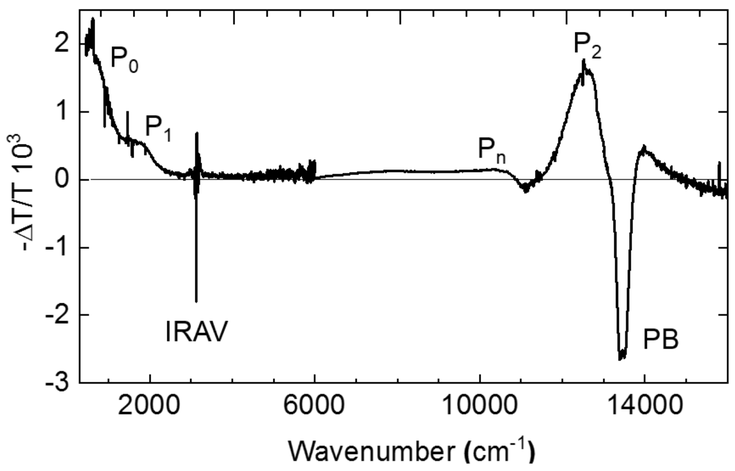
Short-lived polaron pairs (τ = 5 ps in P3P6T) are followed by polarons. The ratio of their amplitudes changes, when an acceptor is present.

MAPI

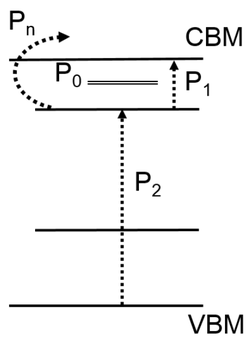
Vibrational modes



Polaron bands



Photoinduced absorption spectrum reveals two polaron bands P_0 and P_1 in ‚fingerprinting' spectral range at 78 K.



P_1 vanishes together with P_2 at room temperature, pointing towards different origin of P_0, possibly traps.

Pump-probe measurements focusing on 'fingerprinting' spectral region

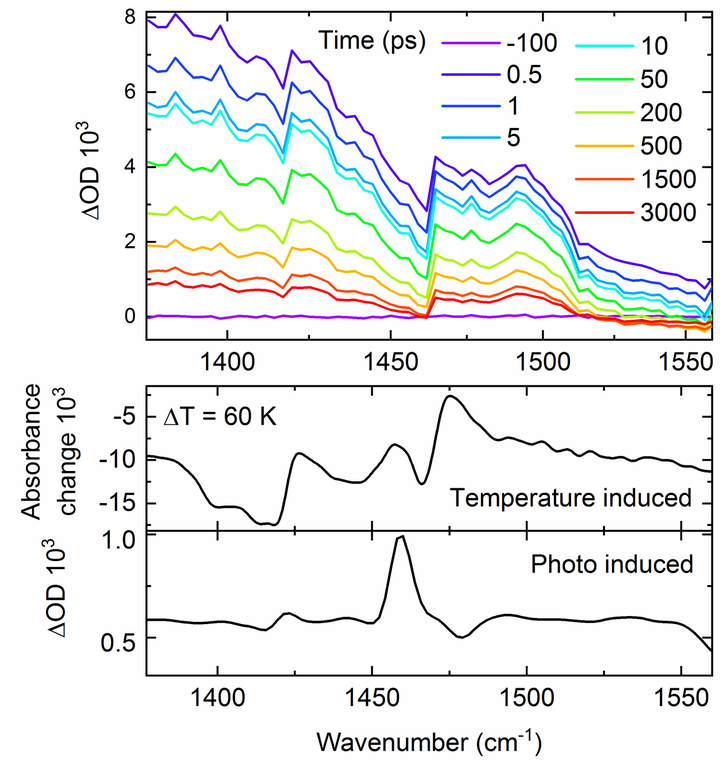
→ Distinct dynamics of P_0 and P_1 band on ultrashort timescales?

→ Inferences on interplay between electronic and vibrational exciatation by observing polaron bands and signatures of vibrational modes at the same time.

Transient Spectra

Temperature induced absorption changes and long-lived photoinduced effects represent possible contributions to the transient absorption.

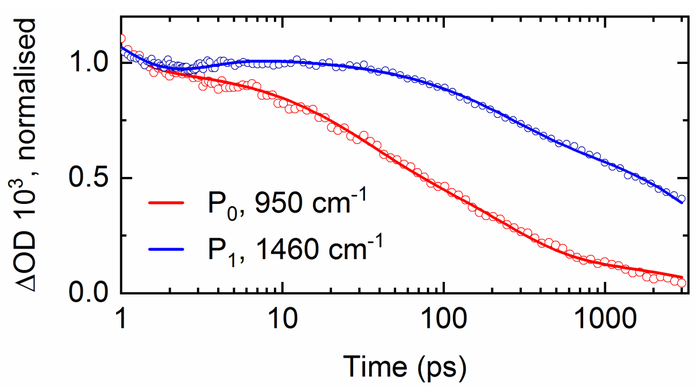
Sharp spectral signatures are present at the position of the CH_3 asymmetric and the NH_3^+ symmetric bend.



Distinct dynamics of P_1 and P_0 band

Excitation: ~55 µJ/cm² at 500 nm,
multi-exponential fit:
P_1: τ_1 = 0.4 , τ_2 = 28 , τ_3 = 225, τ_4 = 3582
P_0: τ_1 = 0.8 , τ_2 = 1.4, τ_3 = 259, τ_4 = 5497

→ Distinct dynamics for P_0 and P_1 band: additional lifetime of ~ 30 ps for P_1.



Additional decay constant with few picoseconds lifetime for higher excitation densities ascribed to bimolecular recombination.

Conclusions

→ Different dynamics of polaron bands P_0 and P_1 on picosecond timescale and distinct temperature dependence observed in quasi-steady state photoinduced absorption measurements point towards their different origin.

→ Vibrational signatures observed in P_0 band promise insight on role of organic cation vibrational relaxation for polaron dynamics.