

Cooling dynamics of electrons in MAPbBr₃ probed in the deep-UV

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Abstract. Transient absorption in the Visible and in the deep-UV is performed on MAPbBr₃ thin films with 3.1 eV pump excitation. The UV probe can access higher order transitions in the material exploring different high-symmetry points of the Brillouin zone. Uncorrelated electron-hole pairs are generated within the instrument response function of 150 fs. The photobleaching at 3.3 eV shows that electron cooling happens in ~ 1 ps.

Introduction

Hybrid organic-inorganic methylammonium lead halide perovskites (HOIP) with formula MAPbX₃ (X=Cl, Br, I) are very promising materials for applications in photovoltaic [1], light-emitting [2] and sensor devices [3]. HOIP can be easily synthesized with cheap production costs. MAPbBr₃ is a popular HOIP, generating high open circuit voltages in solar cells. Charge-carrier dynamics in MAPbBr₃ with above band gap excitation has been intensively investigated by femtosecond transient absorption spectroscopy (TAS) in the Visible [4], [5]-[7]. A slow charge-carrier cooling time in the subpicosecond range is often reported [4]-[5], [6], partially explaining the efficiency of electron injection at interfaces. However, TAS in the Visible does not distinguish between the type of charge carrier (electron or hole). Here, using deep-UV TAS with 150 fs time resolution from 270 to 370 nm [8], higher order interband transitions can be reached in MAPbBr₃, from which we specifically observe the electron dynamics.

Results

Figure 1a) shows spectral traces from MAPbBr₃ thin film excited at 3.1 eV above the band gap and probe from the Visible to the UV. The transient spectra exhibit four photobleaches (PBs) centred at 2.35, 3.35, 3.75 and 4.45 eV labelled PB1 to PB4 in the following. The PBs positions correspond to specific features of the optical spectrum (Figure 1a) and agree with the resonances retrieved in previous ellipsometry studies [9], [10].

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In the Visible, the PB1 lineshape with positive wings after 100 fs is consistent with the large number of works available nowadays. The PB1 minimum is reached after ~ 2 ps (Figure 1b) due to charge-carrier cooling and accumulation at the R-point (Figure 2). However, the competing cooling rates of electrons and holes cannot be disentangled which can be overcome by TAS of higher energy transitions at different points in the Brillouin zone (BZ) in the UV.

Time traces close to the PB minima in the UV are depicted in Figure 1b) together with the instrument response function (IRF). Contrary to PB3 and PB4, PB2 follows a bimodal rise with a prompt bleach within the IRF followed by a further bleach in ~ 1 ps. Such bimodal bleach is also observed for PB1 and can be related to charge carrier-cooling as previously reported [4], [6].

The initial negative signal over a wide spectral range in the UV within the IRF points towards an IRF limited suppression of the Coulomb enhancement, corroborating the ultrafast dissociation of electron-hole pairs into free charge carriers [4].

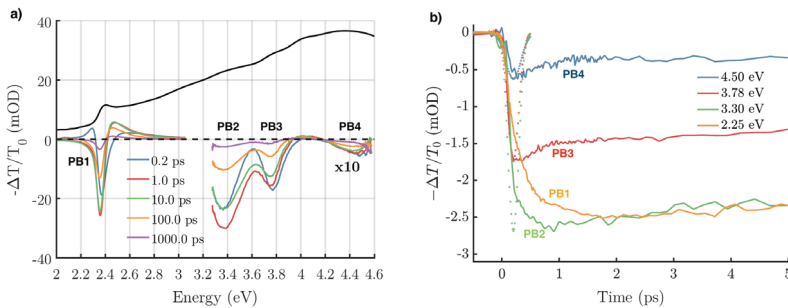


Fig. 1. a) Transient absorption signal of MAPbBr₃ following 3.1 eV excitation (density $1.3 \times 10^{17} \text{ cm}^{-3}$) and UV-Vis spectrum. b) Time traces at the positions of the photobleaches.

Discussion

The link between the observed MAPbBr₃ transient response and the band diagram is of utmost importance for the understanding of the optoelectronic properties of HOIPs. The reported band structures of MAPbX₃ are similar despite the halogen substitution [10], the main changes being the energy spacing between the bands. Hence, a plausible universal behaviour of the transient optical responses may be expected.

A few TAS studies on MAPbI₃ focused on the dynamics above the optical band gap where the corresponding PBs appear at 1.65 (PB1), 2.58 (PB2) and 3.13 eV (PB3) [11]-[14]. Especially, PB2 in MAPbI₃ shows a prompt rise independent of the pump energy [12] while the bands therein involved are directly populated with 3.1 eV pump. This contrasts with the ~ 500 fs time required for PB2 in MAPbBr₃ to reach its minimum inferring a non-universal photodynamics under halogen substitution.

Following previous assignments for PB2 and especially the band structure calculations by Leguy and coworkers [10], PB2 is due to the transition from valence band 2 (VB2) to conduction band 1 (CB1) at the R-point sensitive to electron cooling in ~ 1 ps, while PB3 and PB4 are due to transitions between VB1 and CB1 at the M and X-points of the BZ respectively (Figure 2). While the CB1 involved in PB2 is directly populated upon 3.1 eV excitation, no direct population is involved at the high-symmetry points for PB3 and PB4. This is clearly visible from the sensitivity of PB2 to carrier cooling on the one hand

while both PB3 and PB4 undergo a prompt rise and decay. Instead, the observed transient optical non-linearities of PB3 and PB4 are due to Coulomb screening, explaining the red shift of PB3 over ~ 1 ps (Figure 1a). The transitions involved in PB3 and PB4 are mainly excitonic, in agreement with the retrieved excitonic phase factors [10] and recent temperature dependent ellipsometry measurements [15].

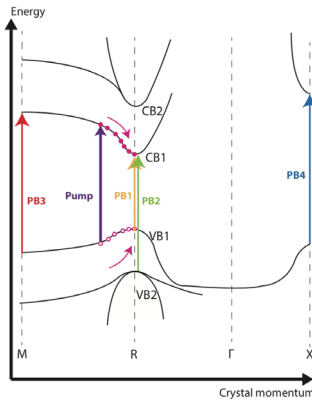


Fig. 2. Schematic band diagram with the expected assigned photobleached transitions in MAPbBr₃ following 3.1 eV excitation.

References

- [1] M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami, and H. J. Snaith, *Science*, **338**, 643 (2012).
- [2] S. D. Stranks and H. J. Snaith, *Nat. Nanotechnol.*, **10**, 391 (2015).
- [3] S. Yakunin, M. Sytnyk, D. Kriegner, S. Shrestha, M. Richter, G. J. Matt, H. Azimi, C. J. Brabec, J. Stangl, M. V. Kovalenko, and W. Heiss, *Nat. Photonics*, **9**, 444 (2015).
- [4] T. Ghosh, S. Aharon, L. Etgar, and S. Ruhman, *J. Am. Chem. Soc.*, **139**, 18262 (2017).
- [5] M. Li, S. Bhaumik, T. W. Goh, M. S. Kumar, N. Yantara, M. Grätzel, S. Mhaisalkar, N. Mathews, and T. C. Sum, *Nat. Comm.*, **8**, 14350 (2017).
- [6] V. Sharma, S. Aharon, I. Gdor, C. Yang, L. Etgar, and S. Ruhman, *J. Mater. Chem. A*, **4**, 3546 (2016).
- [7] J. Yang, H. Xia, R. Sheng, Q. Ma, J. Kim, P. Tapping, T. Harada, T. W. Kee, F. Huang, Y.-B. Cheng, M. Green, A. Ho-Baillie, S. Huang, S. Shrestha, R. Patterson, G. Conibeer, and X. Wen, *Nat. Comm.*, **8**, 1 (2017).
- [8] G. Auböck, C. Consani, R. Monni, A. Cannizzo, F. van Mourik, and M. Chergui, *Rev. Sci. Instrum.*, **83**, 093105 (2012).
- [9] M. S. Alias, I. Dursun, M. I. Saidaminov, E. M. Diallo, P. Mishra, T. K. Ng, O. M. Bakr, and B. S. Ooi, *Opt. Express*, **24**, 16586 (2016).
- [10] A. M. A. Leguy, P. Azarhoosh, M. I. Alonso, M. Campoy-Quiles, O. J. Weber, J. Yao, D. Bryant, M. T. Weller, J. Nelson, A. Walsh, M. van Schilfgaarde, and P. R. F. Barnes, *Nanoscale*, **8**, 6317 (2016).
- [11] T. Ghosh, S. Aharon, A. Shpatz, L. Etgar, and S. Ruhman, *ACS Nano*, **12**, 5719 (2018).
- [12] B. Anand, S. Sampat, E. O. Danilov, W. Peng, S. M. Rupich, Y. J. Chabal, Y. N. Gartstein, and A. V. Malko, *Phys. Rev. B*, **93**, 161205 (2016).
- [13] J. C. Brauer, Y. H. Lee, M. K. Nazeeruddin, and N. Banerji, *J. Mater. Chem. C*, **4**, 5922 (2016).
- [14] J. S. Manser and P. V. Kamat, *Nat. Photonics*, **8**, 737 (2014).
- [15] X. Chi, K. Leng, B. Wu, D. Shi, Y. Choy, Z. Chen, Z. Chen, X. Yu, P. Yang, Q.-H. Xu, T. C. Sum, A. Rusydi, and K. P. Loh, *Adv. Opt. Mater.*, **338**, 1800470 (2018).