What can Transient Photo-current measurements tell us about recombination, transport and the density of states in OPVs?

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Overview

What are TPC transients?

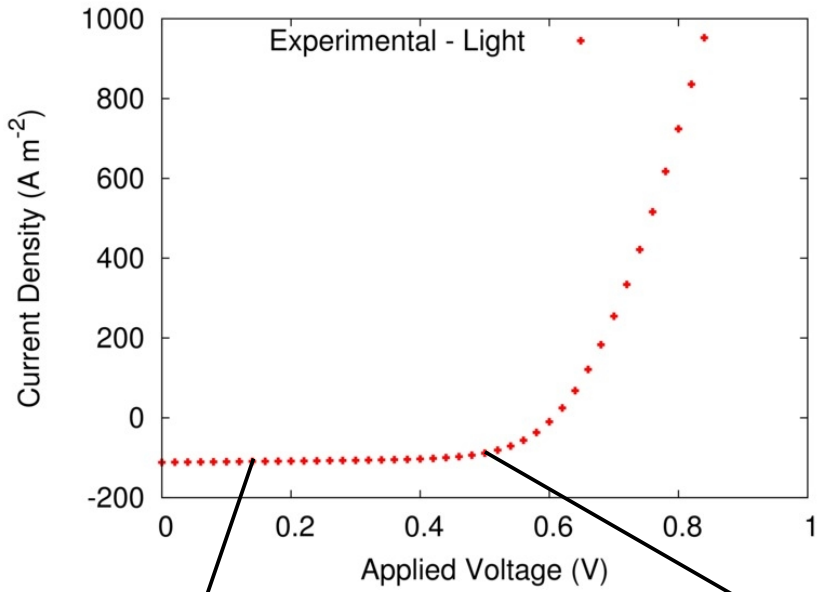
TPC transients away from Voc are very complex due to the interplay of recombination, trapping, de-trapping and transport.

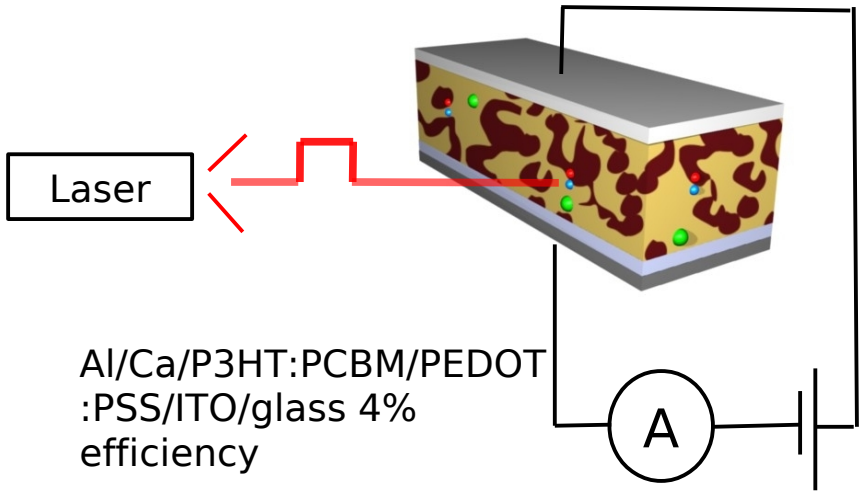
They therefore potentially contain a lot of information about device behavior

If we can model TPC transients then we will have correctly described carrier recombination, trapping and transport.

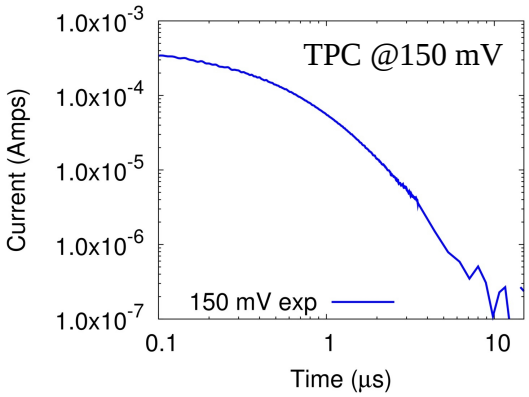
We will use TPC data to extract the HOMO and LUMO DoS from P3HT:PCBM data.

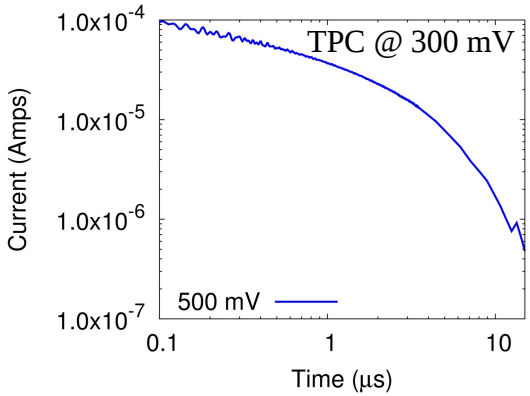
What is a transient Photo-current (TPC) measurement?





Al/Ca/P3HT:PCBM/PEDOT :PSS/ITO/glass 4% efficiency





- The transient contains information on carrier recombination, transport, and trapping across the entire JV curve.

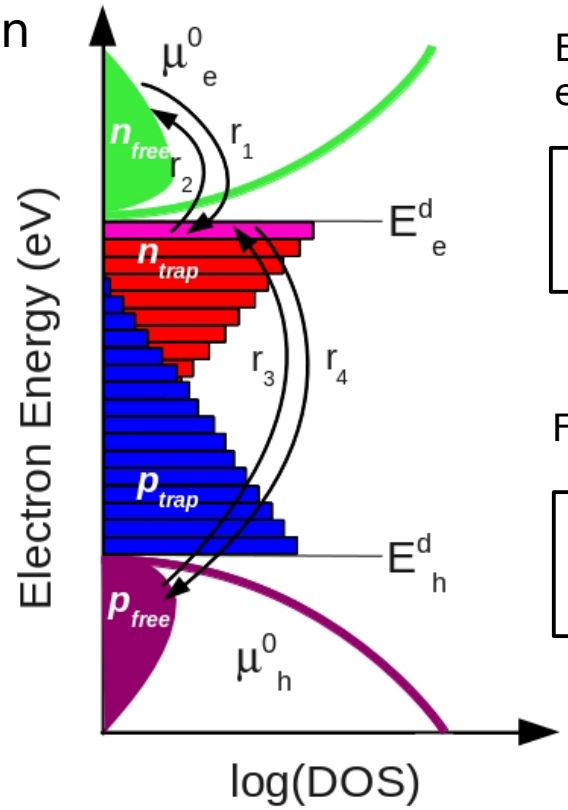
- They are quite complex therefore need a model to help us understand them.

Modeling carriers in 0D energy space

- To model a device in time domain we need to describe:
  - Free carriers
  - Capture/escape from traps

Process	
electron capture	r_1
electron emission	r_2
hole capture	r_3
hole emission	r_4

  - The DoS



Electron density of each trap:

$$\frac{\partial n}{\partial t} = r_1 - r_2 - r_3 + r_4$$

Free carrier recombination

$$R_n = \sum_0^{n_{band}} \left(r_1^e - r_2^e \right)$$

Detailed balance is maintained.

- **Shockley-Read-Hall**

but a solar cell is a 1D structures not 0D structures so we need a 1D charge transport model.....

Modeling carrier transport across the device.

Inputs

•Applied Voltage

•Light intensity

Inputs

Poisson's equation

$$\nabla \epsilon_o \epsilon_r \cdot \nabla \phi = q \cdot (n - p)$$

Current driving terms

$$J_n = q \mu_e n \nabla E_c + q D_n \nabla n$$

$$J_p = q \mu_h p \nabla E_v - q D_p \nabla p$$

Current continuity equations

Electron continuity

$$\nabla \cdot \boldsymbol{J}_n = q \cdot \left(\sum_0^{n_{band}} (r_1^e - r_2^e) + \sum_0^{p_{band}} (r_3^h - r_4^h) + \frac{\partial n_{free}}{\partial t} \right)$$

Hole continuity

$$\nabla \cdot \boldsymbol{J}_p = -q \cdot \left(\sum_0^{n_{band}} (r_3^e - r_4^e) + \sum_0^{p_{band}} (r_1^h - r_2^h) + \frac{\partial p_{free}}{\partial t} \right)$$

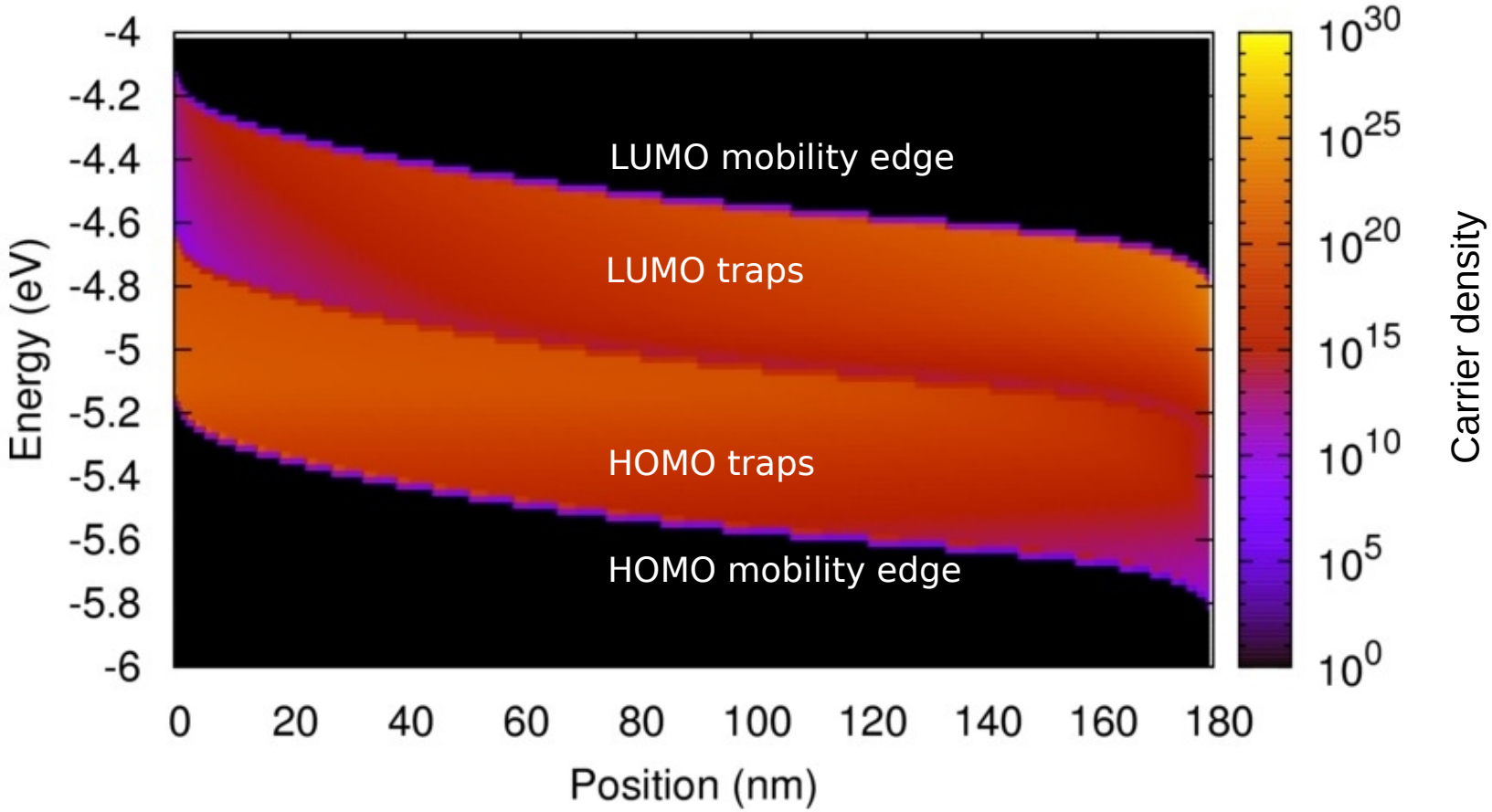
Outputs

•Current density

•Recombination rates

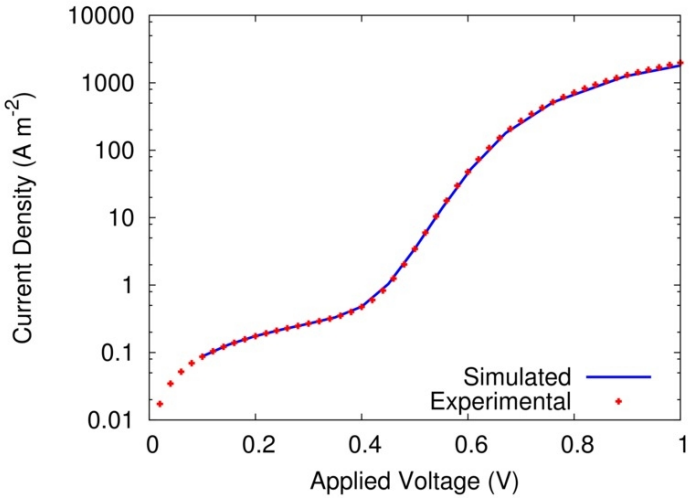
•Average charge density

0D energy model + 1D device model

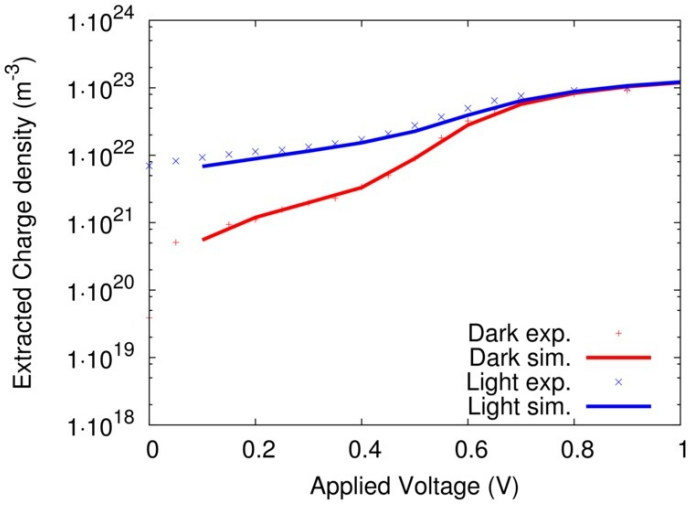


We have a device model, but can it reproduce experimental results?

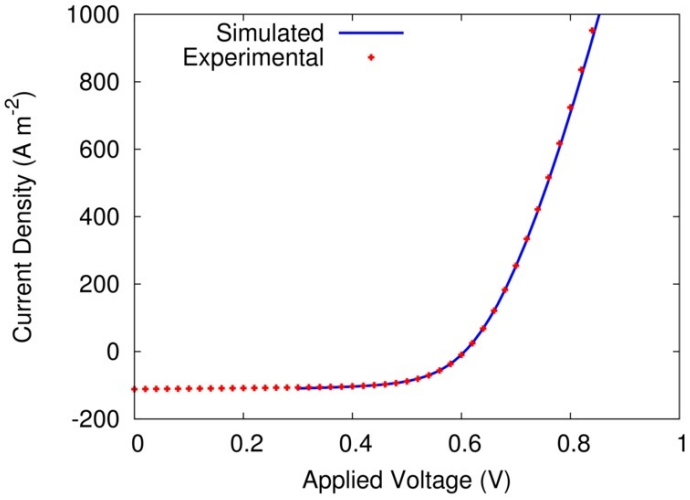
Reproducing steady state JV/CE curves



Dark simulated and experimental JV curves



Light and dark charge extraction curves.



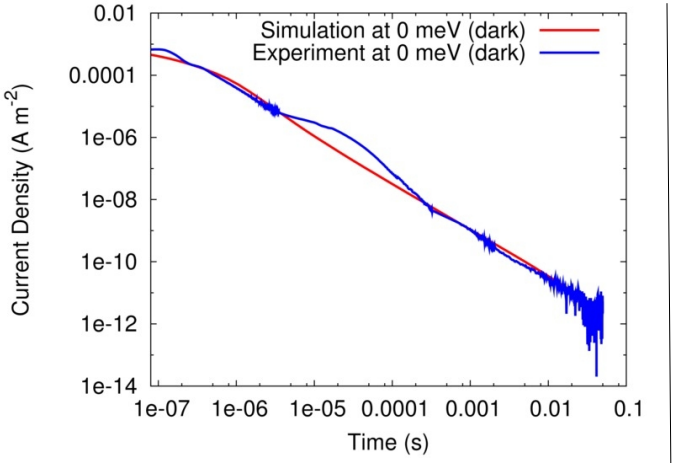
One sun simulated and experimental JV curves

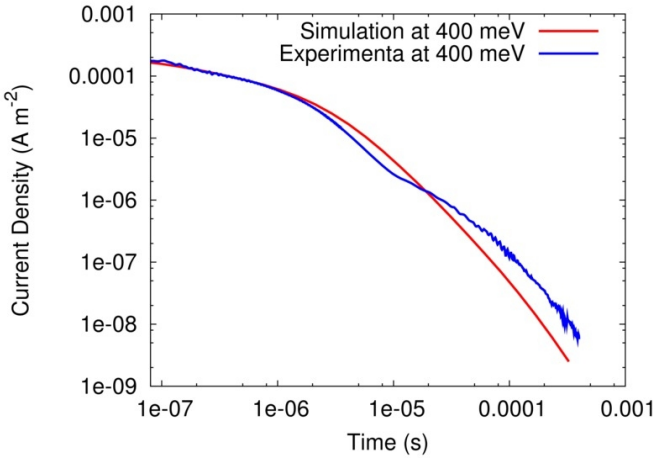
- The deep trap tail slope
- Absolute value of the DoS
- The carrier trapping times
- The recombination times
- Carrier mobilities
- Contact carrier densities

MacKenzie et al. J. Phys. Chem. C, 10.1021/jp200234m

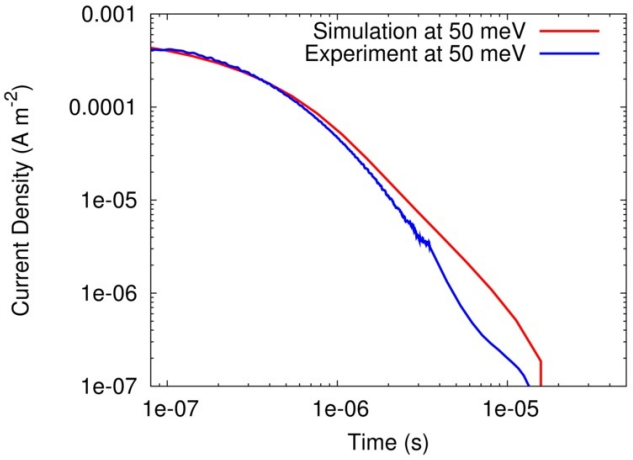
Reproducing TPC transients

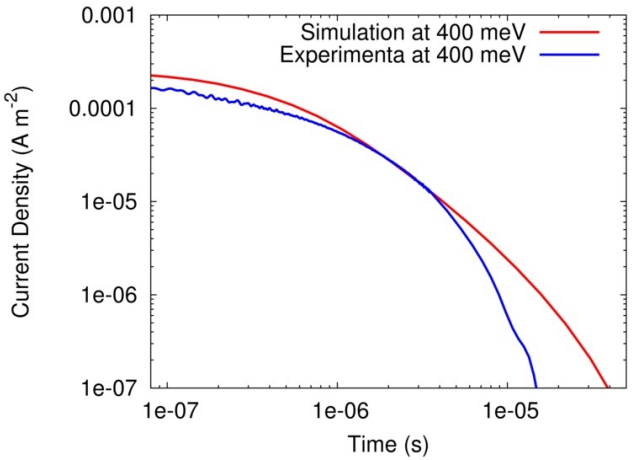
Dark





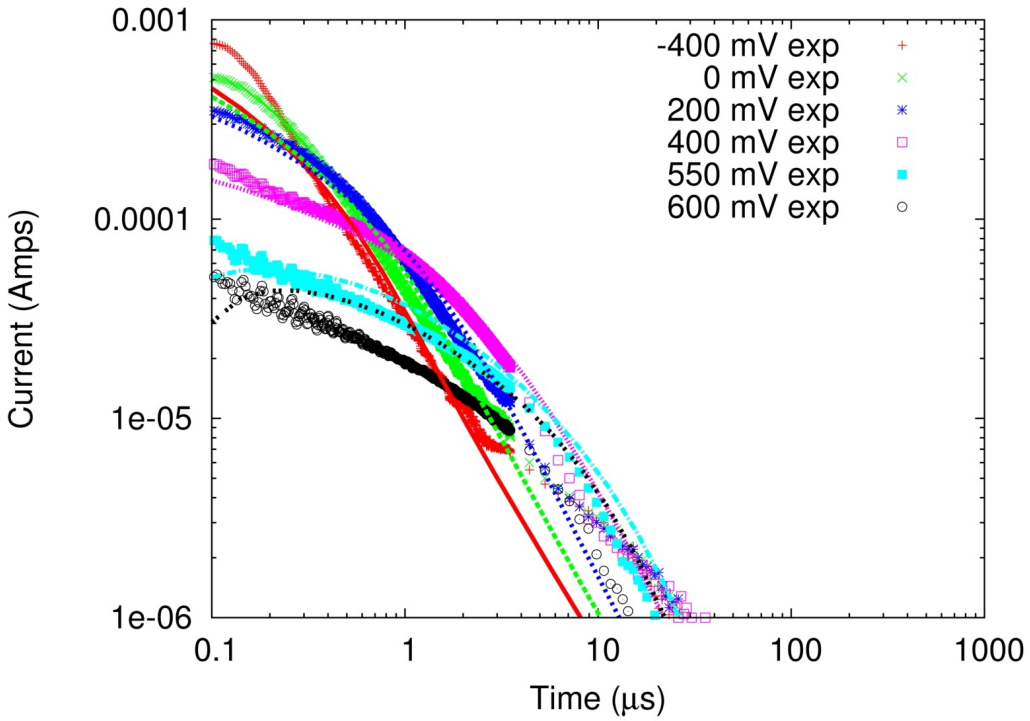
Light





- We can also reproduce the TPC curves at two points on the JV in both the light and in the dark.
- One model and one set of parameters which can self-consistently reproduce 8 different experimental curves from three different types of measurement.

Modeling the TPC curves across the JV using the calibrated model - dark.

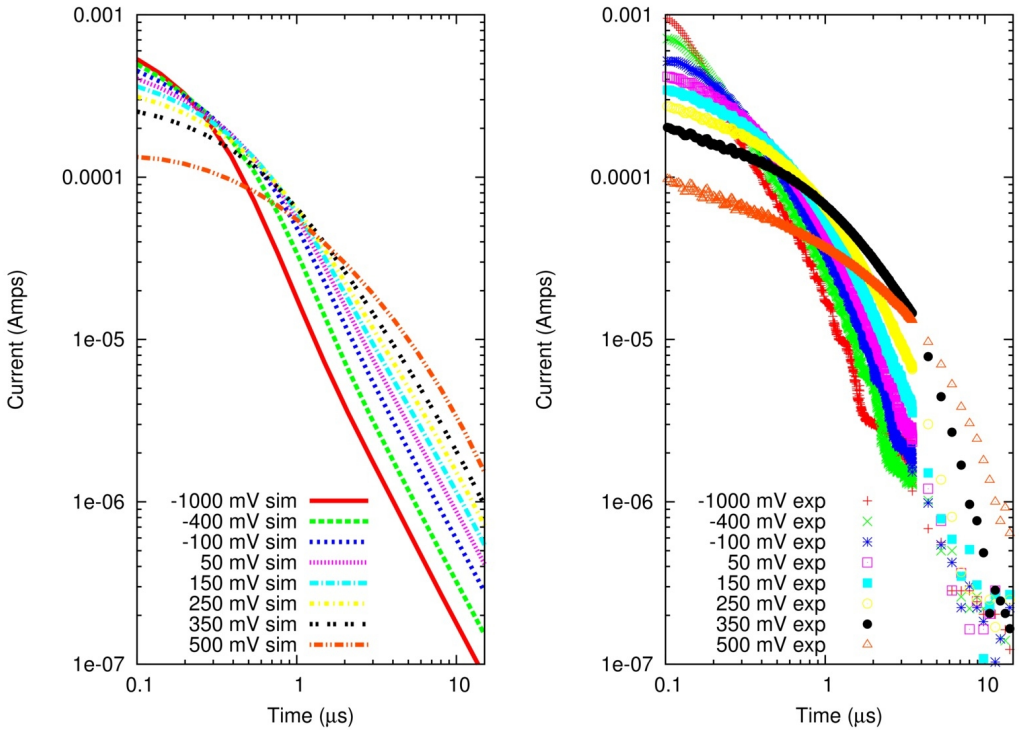


- After having calibrated the model it is now able to reproduce the TPC curves across the entire JV curve

- Even at negative voltages – no negative voltage TPC transients were used in the calibration.

- Simulated = lines
- Experimental = points

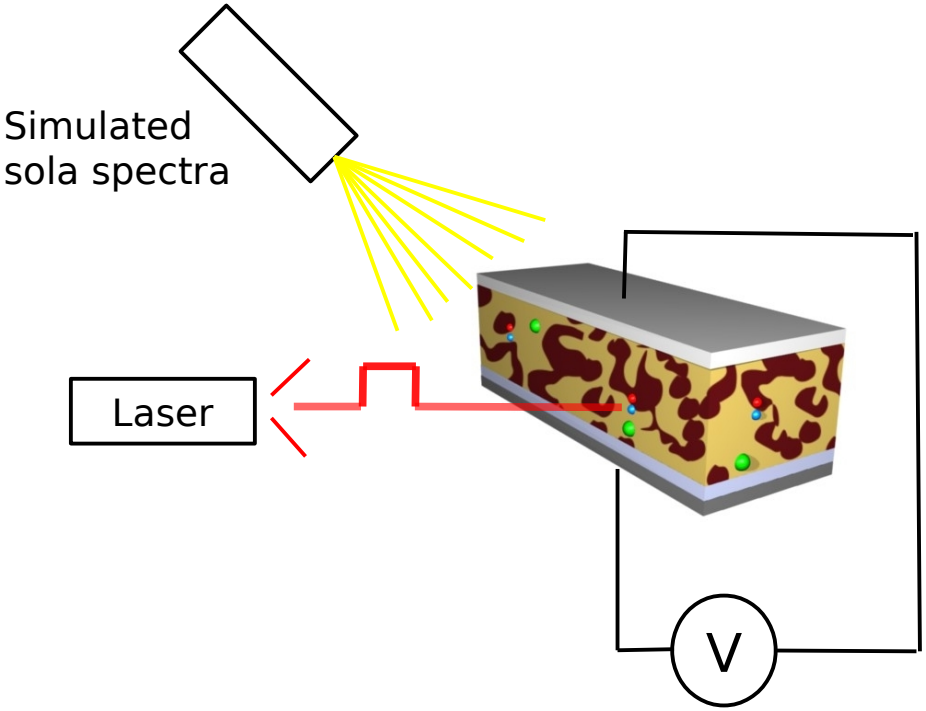
Modeling the TPC curves across the JV using the calibrated mode - light.

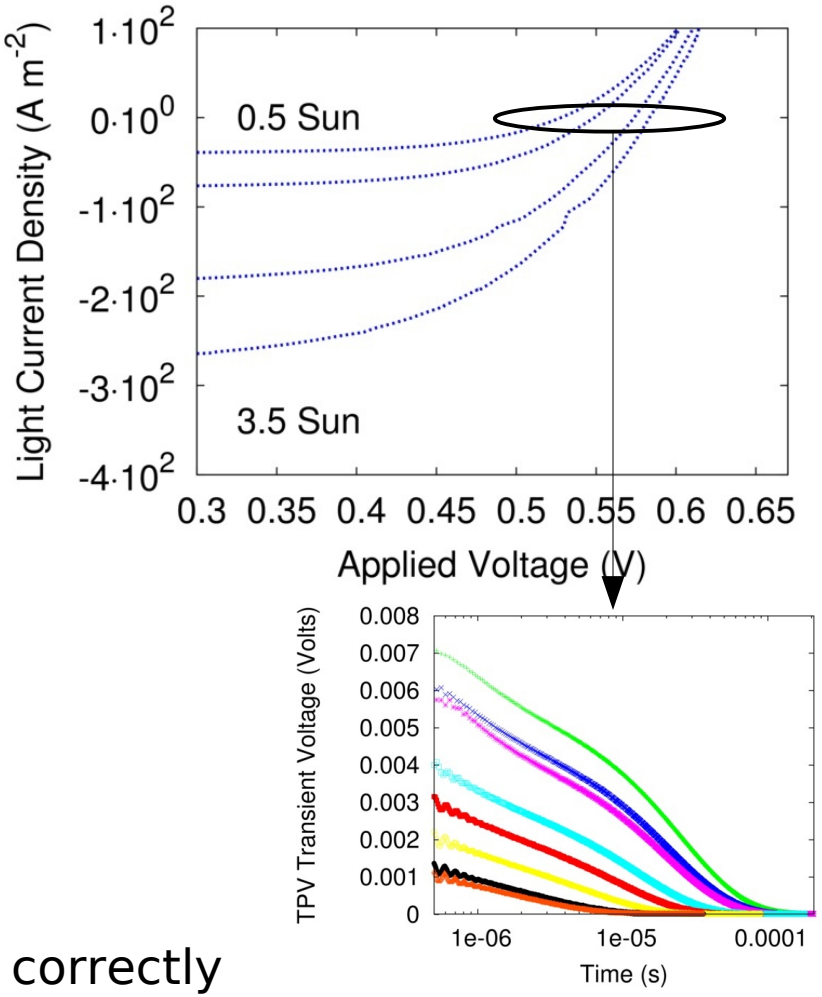


- The model can also reproduce the TPC transients across the JV in the light.
- In summary we now have a model capable of reproducing steady state and transients TPC measurements from a P3HT:PCBM solar cell.
- This suggests that we are modeling recombination, detrapping and transport correctly.

- It would be better if we could test the model against another experimental technique.

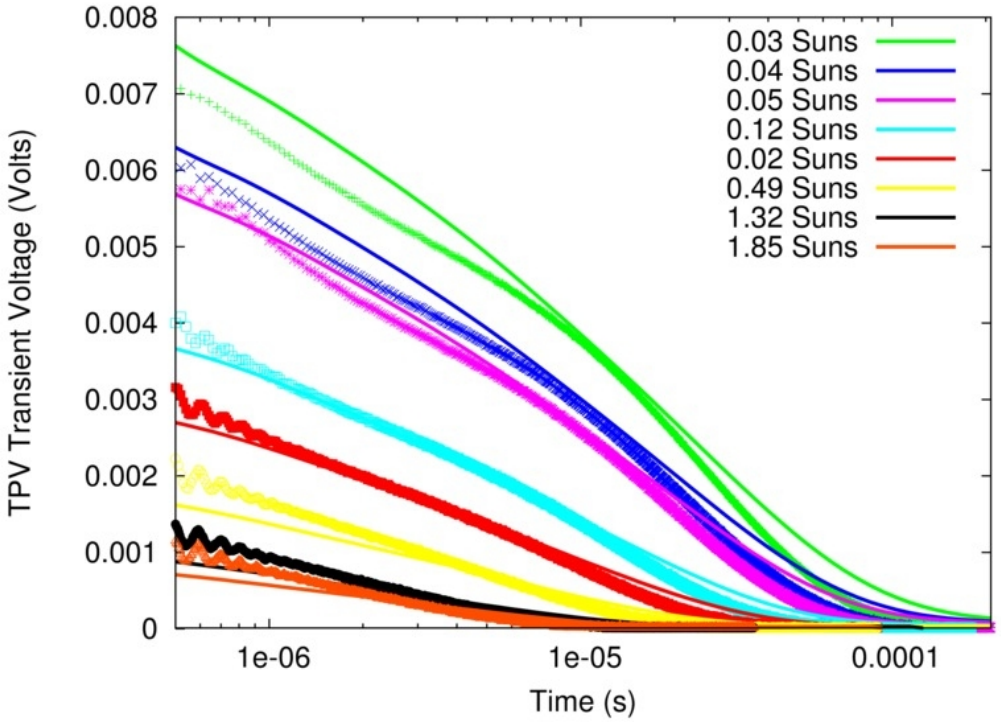
Another measurement technique
Transient photo-voltage





- Device is held at Voc with high impedance volt meter.
- Unlike TPC no current flows.
- So if our model is modeling recombination correctly we should be able to predict experimental TPV data.

Predicting TPV from TPC



- If the model is correctly modeling recombination, traps and transport we should be able to predict another type of measurement technique without any further model calibration.

- We compare the model against TPV.

- With out any further fitting we can **predict** TPV transients.

- This validates the model and suggests that we are modeling carrier recombination, trapping and transport correctly.

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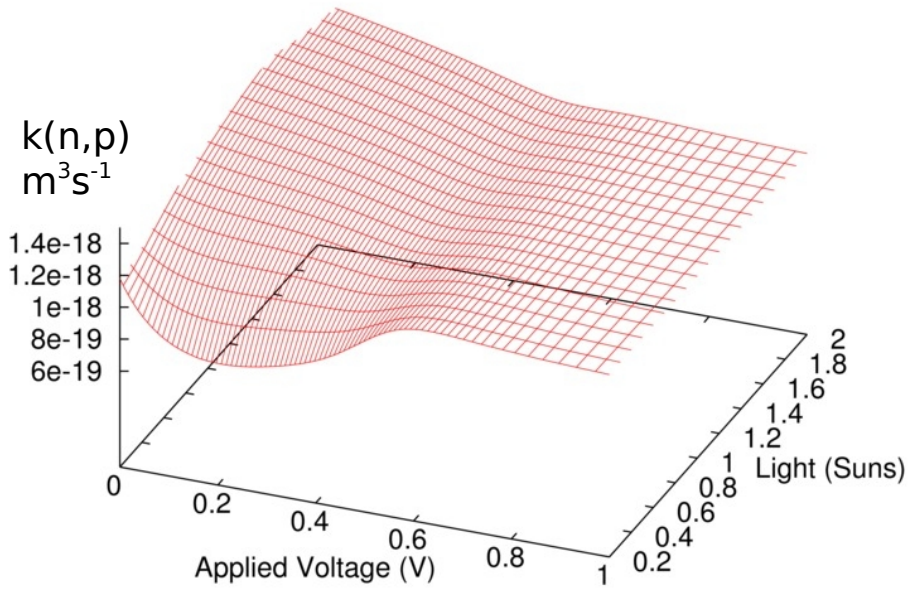
Extracting recombination data across the JV



Macroscopic Langevin recombination pre-factor

$$k(n,p) = \frac{\int_0^d \frac{R(n,p)}{np}\,dx}{d}$$

- As the model can predict TPV transients at Voc and TPC transients across the JV it would appear that model is modeling carrier recombination, transport and trapping correctly.

- We can therefore directly relate microscopic and macroscopic device parameters anywhere on the JV curve at any light intensity.

- Here we have extracted the macroscopic Langevin recombination rate from the model.

- This would not be possible with TPV alone as we could not have got recombination data far away for Voc.

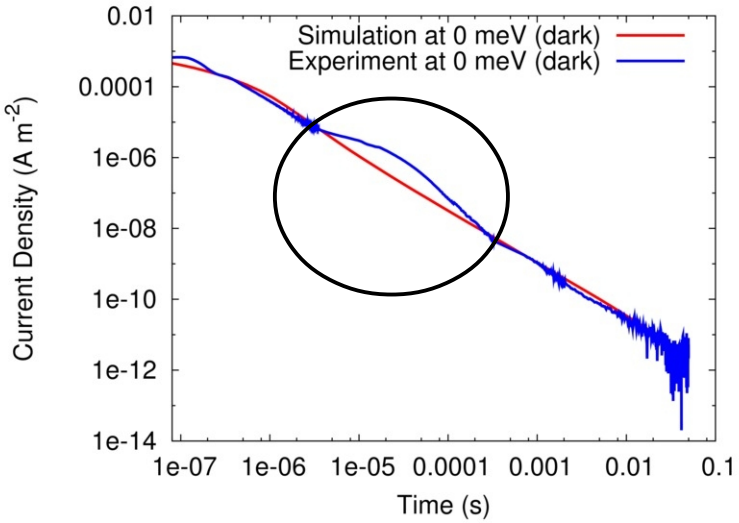
Summary so far....

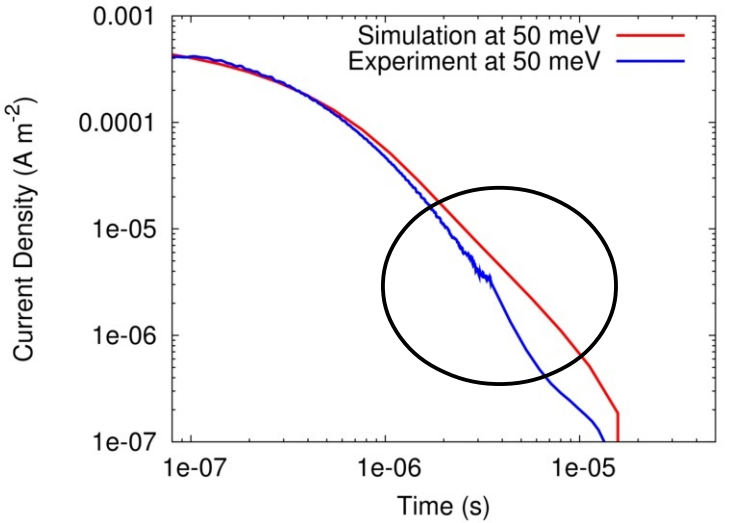
- We have a model which can describe the both the steady state and transient behavior of OPVs across the JV curve and over a range of light intensities.

- TPC transients are complex and we need a model to understand the transients.

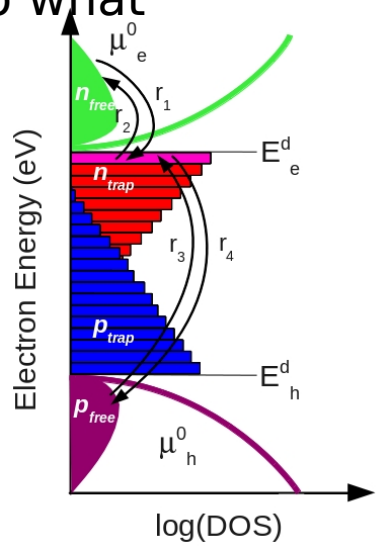
- But can TPC give us any more information about what is going on in the device?

Can we extract more data from the TPC transients?

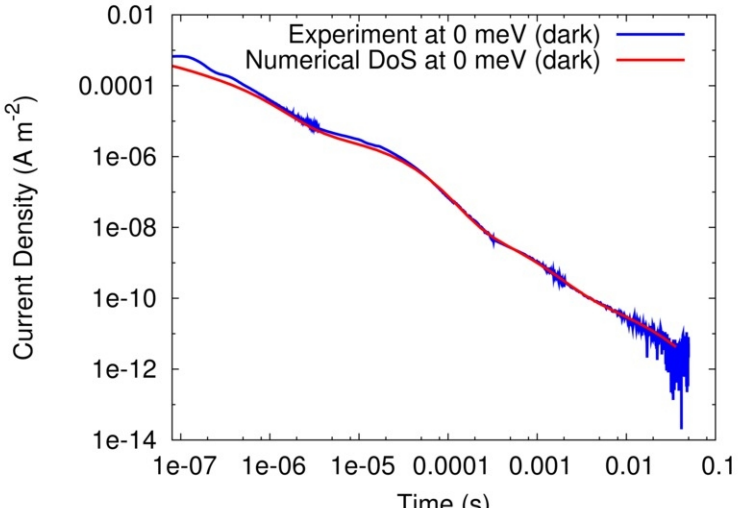


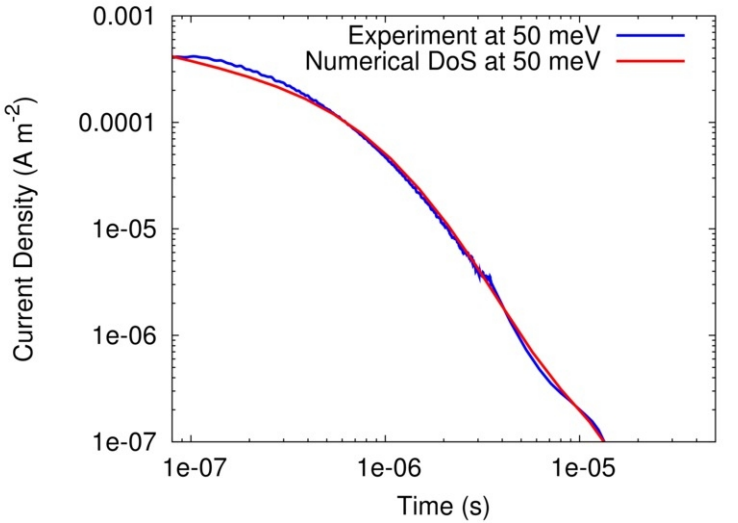


- We could not fit the TPC transients perfectly.
- The largest assumption made in the model is an exponential DoS.
- Can we change the DoS to reproduce the experimental TPC data and thus gain an insight into what the DoS looks like?



Can we change the DoS to make the TPC data fit better?





- Yes we can
- So what does the new DoS look like?

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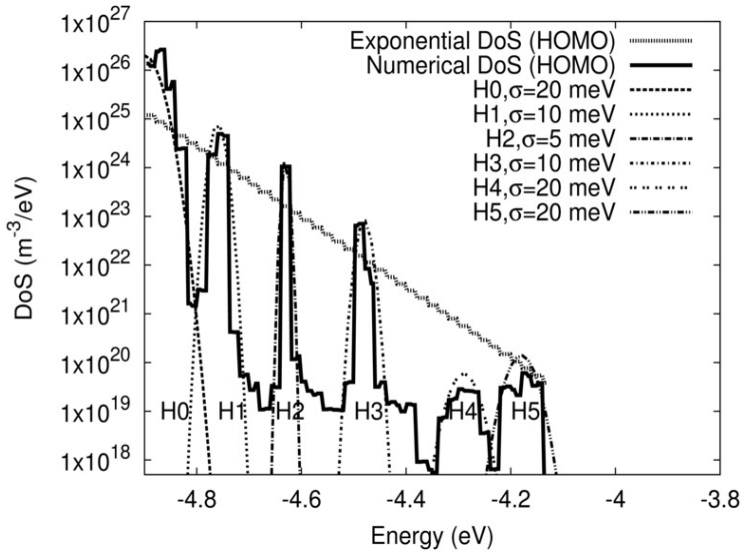
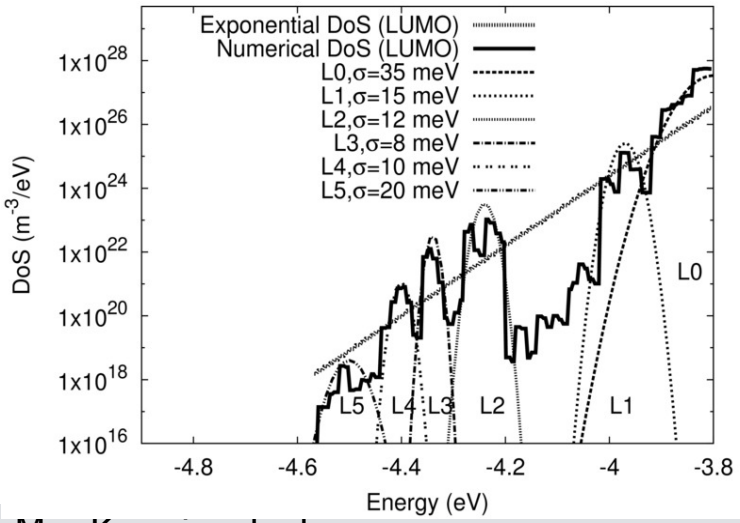
What shape is the DoS deep within the band of an OPV?





- 4-5 trap levels offset in energy are clearly visible in the DoS.
- They superimpose to form an approximation to an exponential.
- These could be due to molecular packing affecting the DoS.
- A better understanding of how the molecular packing affects the DoS could help reduce recombination losses and thus boost OPV efficiency

Conclusions

•We can reproduce the steady state and transient behavior of an OPV.

•We can use the model to predict TPV data and TPC data across the JV curve in the dark and light.

•This suggests that we are modeling recombination, transport and trapping correctly.

•By adjusting the DoS from we can extract an estimate of the DoS of HOMO and LUMO in and P3HT:PCBM.

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