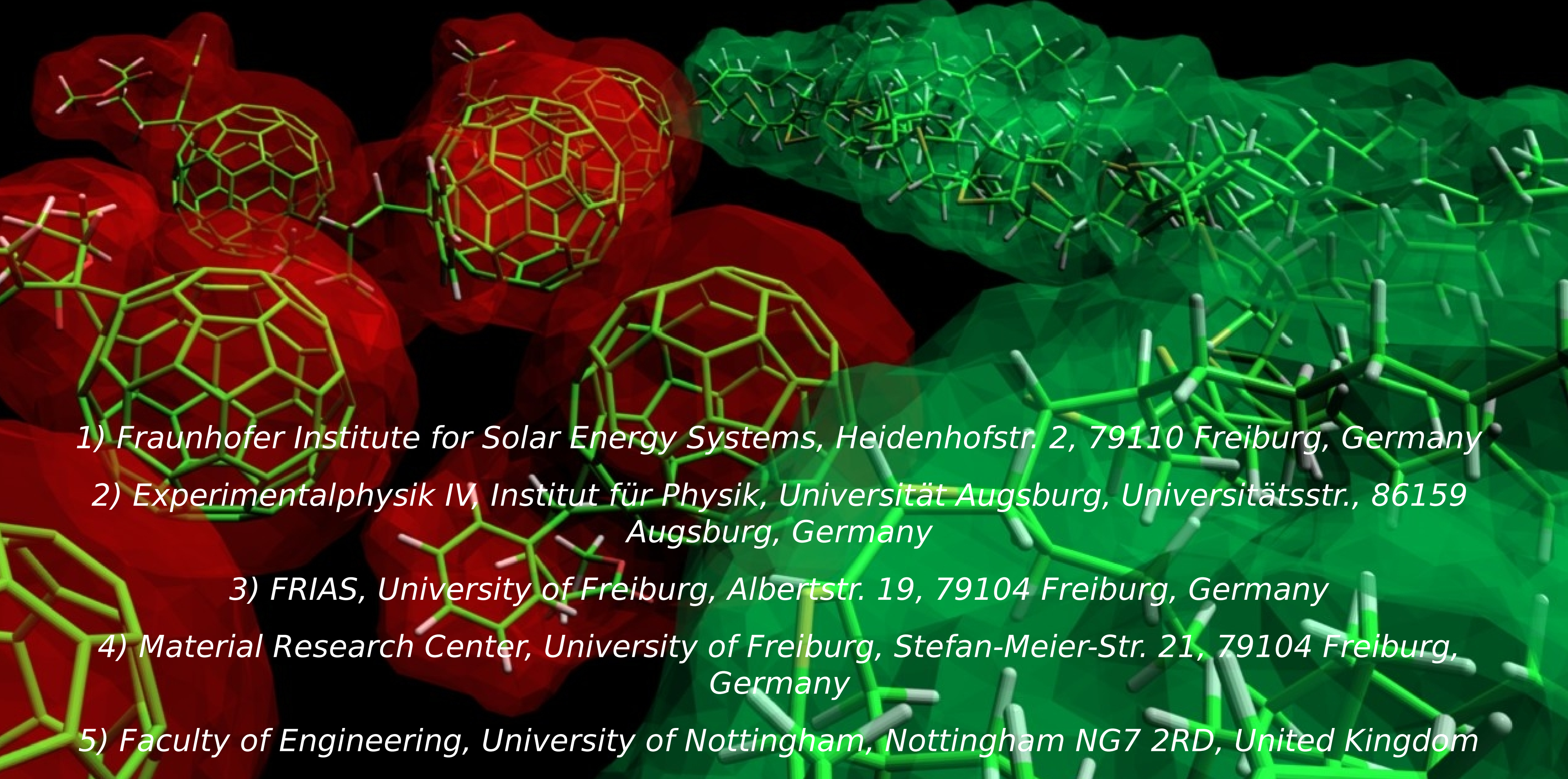
Understanding CELIV transients

Robert Hanfland,[1,2,3] Martin A. Fischer,[1] Wolfgang Brüting[2], Uli Würfel,[1,4] and Roderick C. I. MacKenzie[3,5]



1) Fraunhofer Institute for Solar Energy Systems, Heidenhofstr. 2, 79110 Freiburg, Germany

2) Experimentalphysik IV, Institut für Physik, Universität Augsburg, Universitätsstr., 86159 Augsburg, Germany

3) FRIAS, University of Freiburg, Albertstr. 19, 79104 Freiburg, Germany

4) Material Research Center, University of Freiburg, Stefan-Meier-Str. 21, 79104 Freiburg, Germany

5) Faculty of Engineering, University of Nottingham, Nottingham NG7 2RD, United Kingdom

Overview of talk

- Why are we interested in measuring mobility in organic solar cells?
- Methods for measuring mobility.
- Discuss CELIV in broad terms.
- Analyze CELIV in detail using a numerical model
- Conclusions

"The physical meaning of charge extraction by linearly increasing voltage transients from organic solar cells", Appl. Phys. Lett. 103, 063904 (2013); doi: 10.1063/1.4818267

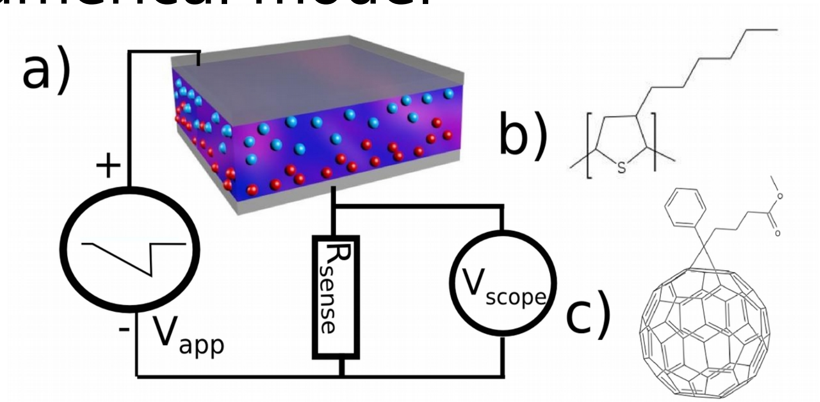
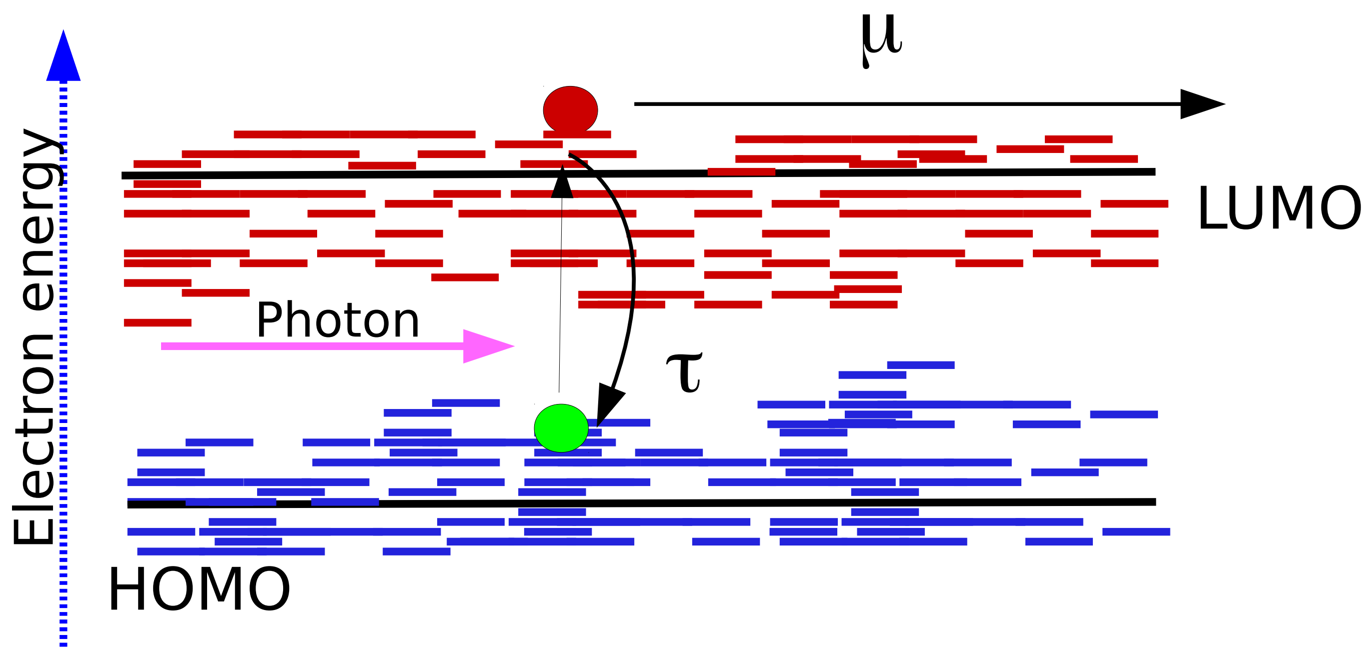


Figure 1: CELIV experimental system

Why are we interested in measuring mobility in organic solar cells?

$$Efficiency(\eta) \propto Mobility(\mu) \cdot Recombination\,time\,constant(\tau)$$



For an efficient solar cell we want a **high mobility** so the carriers can leave the cell quickly and do not have enough time to recombine.

Methods to measure mobility in organic solar cells.

- There have been various methods proposed to measure mobility over the last 10 years, they include: **Transient photocurrent**, **space-charge limited current**, **Time-of-Flight** etc...

  - They all have advantages and disadvantages.

- However, one of the main methods used to measure mobility in working organic solar cells is **C**harge **E**xtraction **by L**inearly **I**ncreasing **V**oltage **(CELIV)***. (775 publications scholar.google.com)

- Because so much of our understanding is based upon this method,in this talk I will take a deeper look at the CELIV method using a combination of **modeling and experimentation**.

G. Juska, K. Arlauskas, M. Viliunas, and J. Kocka, Physical Review Letters 84, 4946 (2000).

The CELIV method (overview)

Juska said that if you apply a negative voltage ramp to a solar cell:

You will get a current transient which looks like this.

Then, Juska said that if you make some assumptions, mobility can be extracted using:

$$\mu = \frac{2}{3}\frac{d^2}{A t_{max}^2 \left(1 + 0.36 \frac{\Delta j}{j(0)}\right)}$$

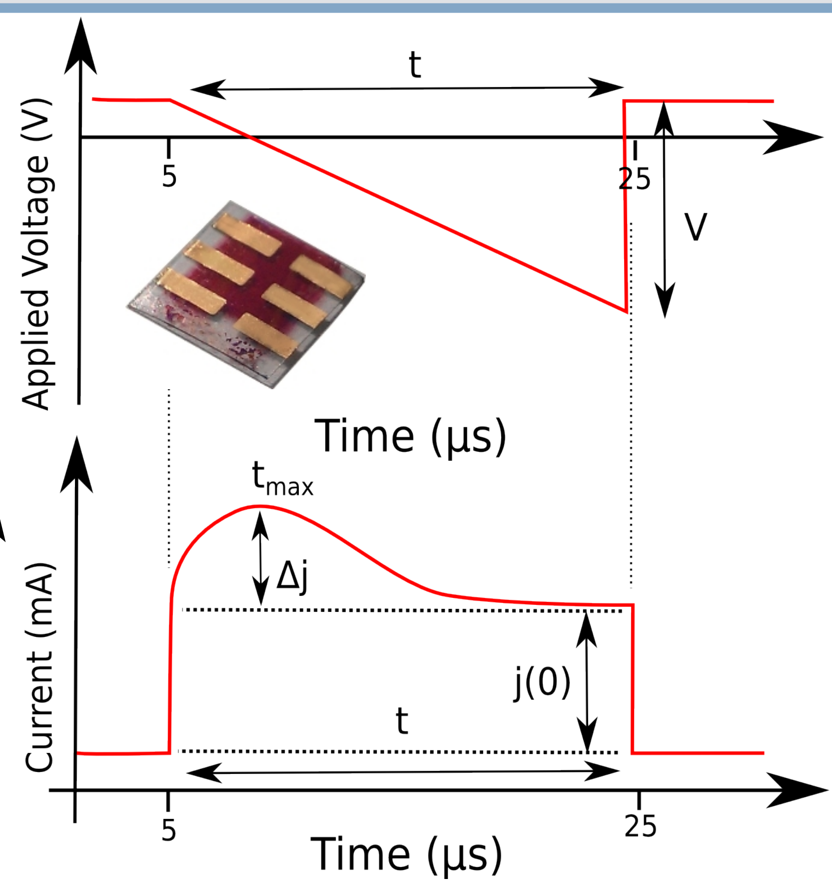
D: thickness of device

t_{max}: time of peak

j(0) : current due to capacitance

Δj: height of peak

A: max applied voltage/pulse length



G. Juska, K. Arlauskas, M. Viliunas, and J. Kocka, Physical Review Letters 84, 4946 (2000).

Juska's picture of a CELIV transient

To derive this $\mu=\frac{2}{3}\frac{d^2}{At_{max}^2\left(1+0.36\frac{\Delta j}{j(0)}\right)}$ equation Juska

Juska imagined that:

1) Charge is swept out of the device from one side to the other as a sheet of charge leaving a depletion region l(x)

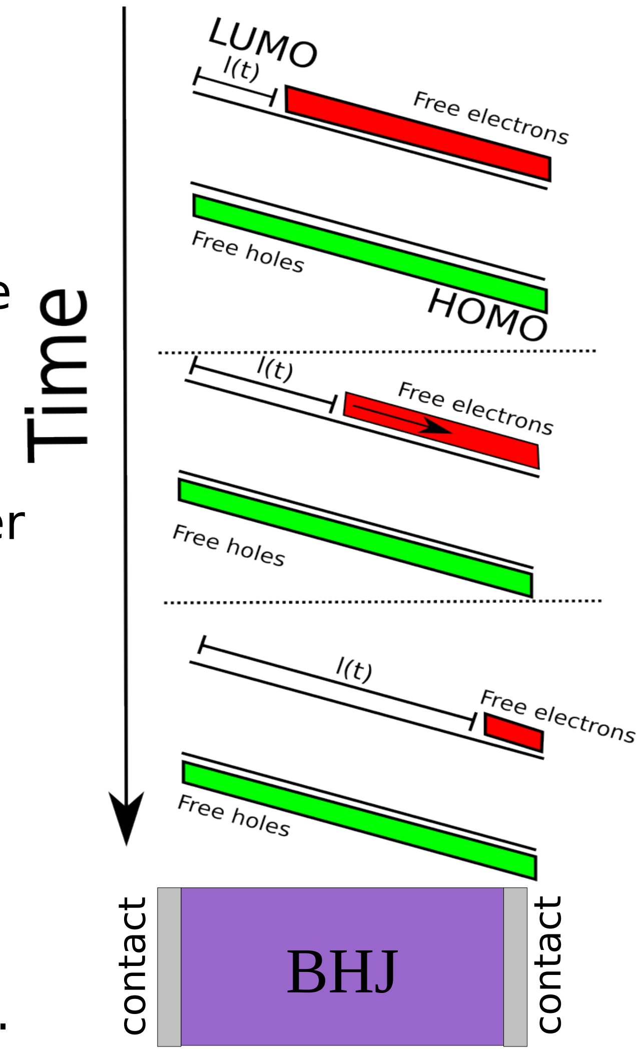
2) Only **one carrier species is mobile**. The other does not move.

To do this he assumed that:

1) There are **no carrier traps.**

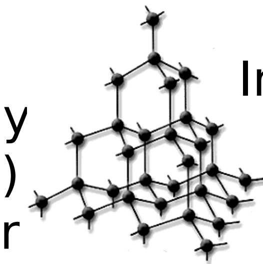
2) There is a **single constant value of mobility** for the fastest charge carrier

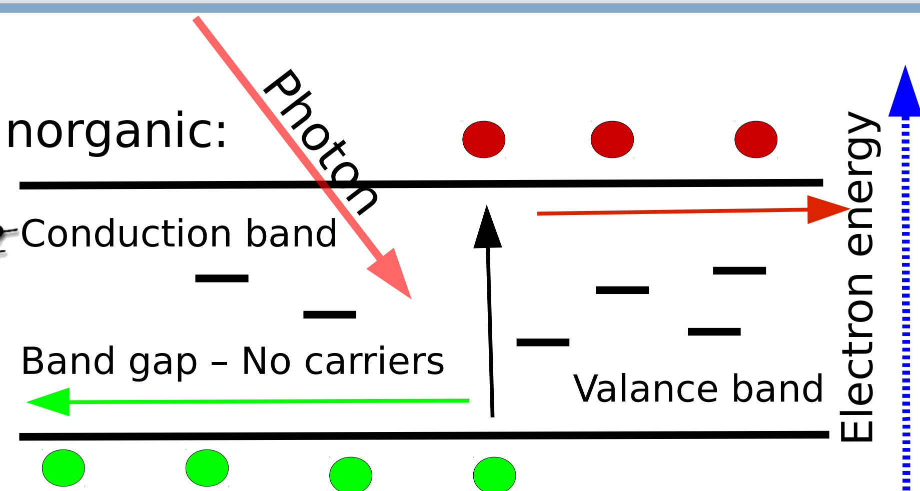
Let's look at these assumptions in more detail.......

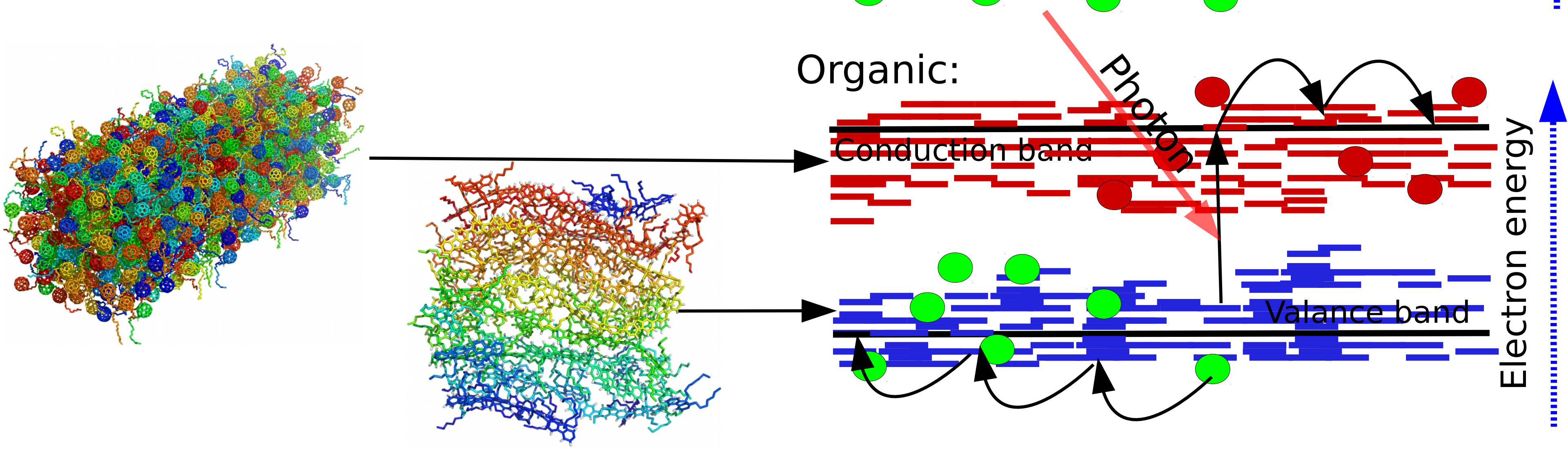


Assumption 1:
There are no carrier traps

We know that organic semiconductors consist mainly of traps, compare Silicon (top) and an organic semiconductor (bottom).







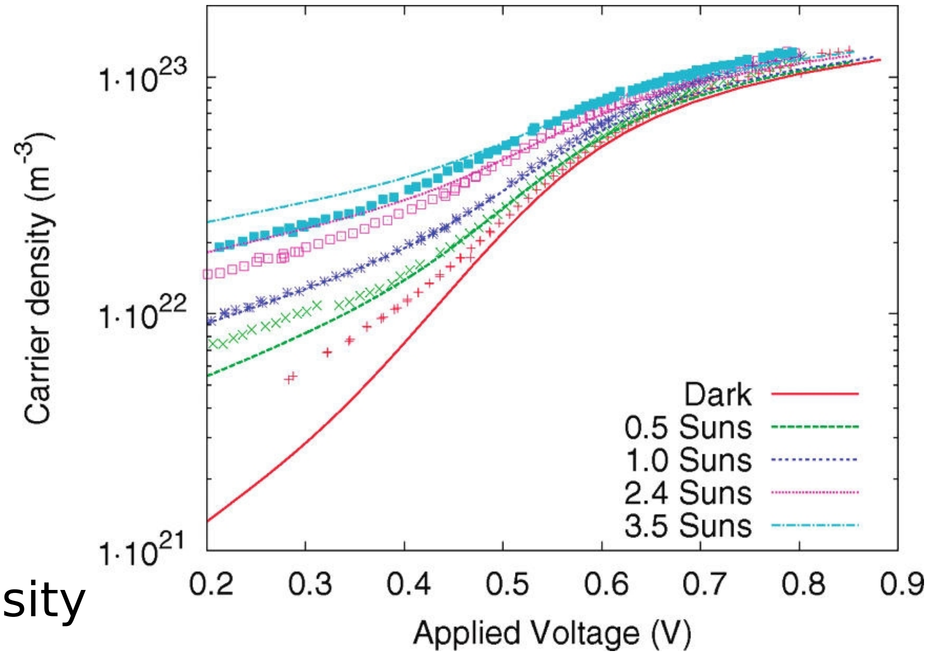
We can say that this is probably a risky assumption...

Assumption 2: The most mobile carrier has a single constant value of mobility.

and CELIV will give you the value of the faster of the mobilities if you apply:

$$\mu = \frac{2}{3} \frac{d^2}{A t_{max}^2 \left(1 + 0.36 \frac{\Delta j}{j(0)} \right)}$$

However, we know that charge density is a strong function of applied bias.



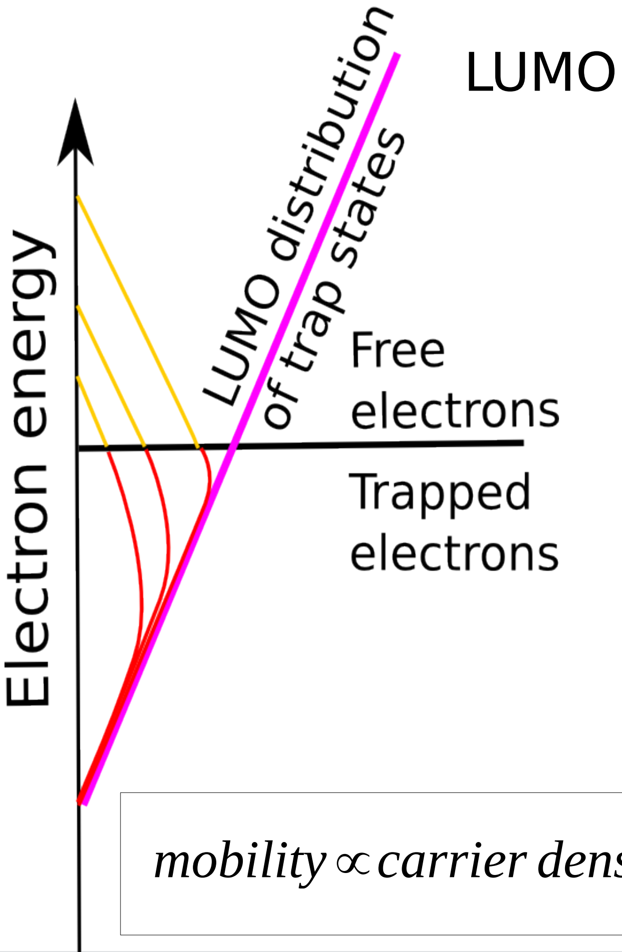
Carrier density as a function of applied voltage and light intensity.

MacKenzie et al. . Phys. Chem. C 2011, 115, 9806–9813

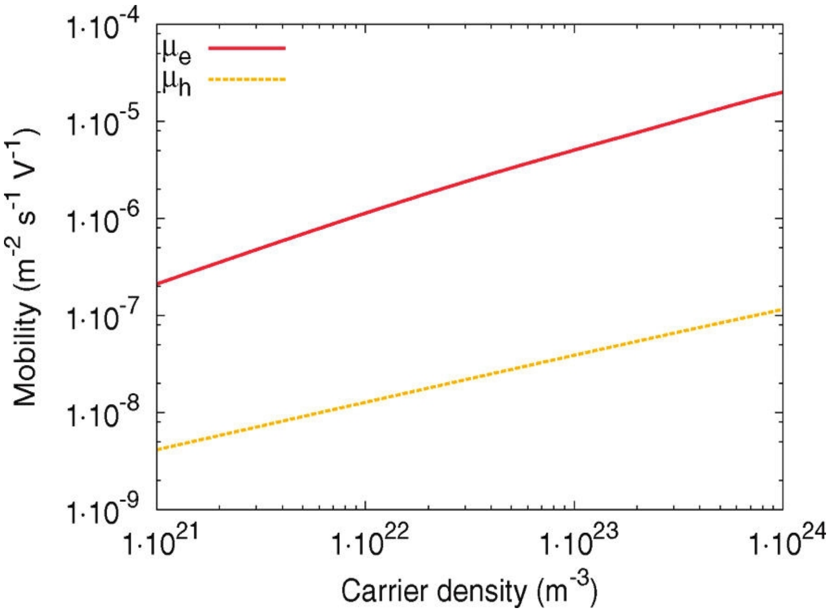
$$carrier\ density \propto applied\ bias$$

Assumption 2: The most mobile carrier has a single constant value of mobility.

Let's look at the energetic distribution of carriers as a function of carrier density.



$$mobility \propto carrier\ density \propto applied\ bias$$



Mobility as a function of carrier density

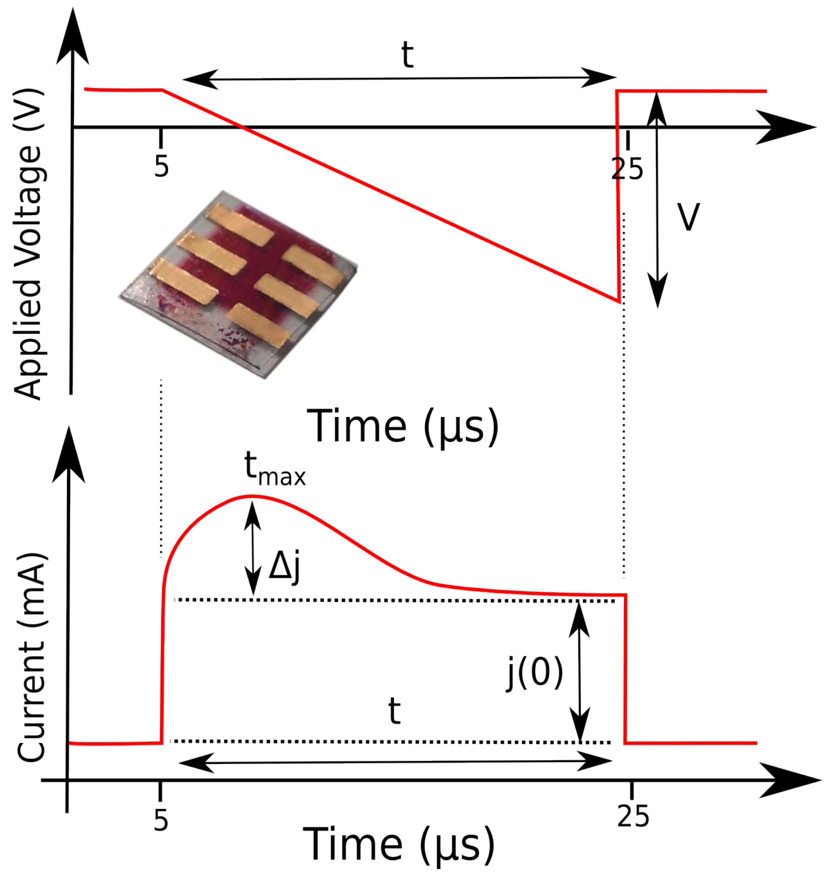
CELIV applies a changing voltage to the device, the very process of making the measurement will probably change the mobility within the device.

The most mobile carrier has a single constant value of mobility.(?)

$$mobility \propto carrier\ density \propto applied\ bias$$

?

$$\mu = \frac{2}{3} \frac{d^2}{A t_{max}^2 \left(1 + 0.36 \frac{\Delta j}{j(0)}\right)}$$



Let's use a model to look at this in more detail...

Transport

Gauss's Law

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

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

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

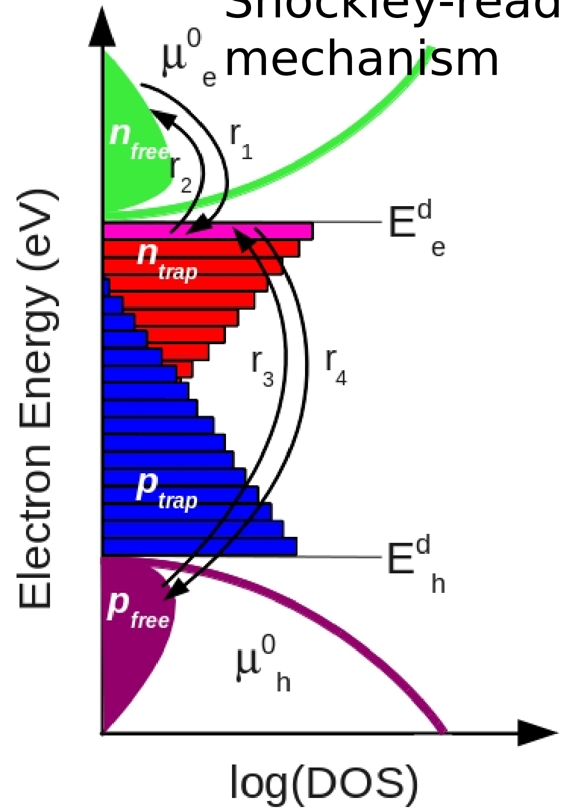
Hole continuity

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

MacKenzie et al. Adv. Energy Mater. 2012, DOI: 10.1002/aenm.201100709

+

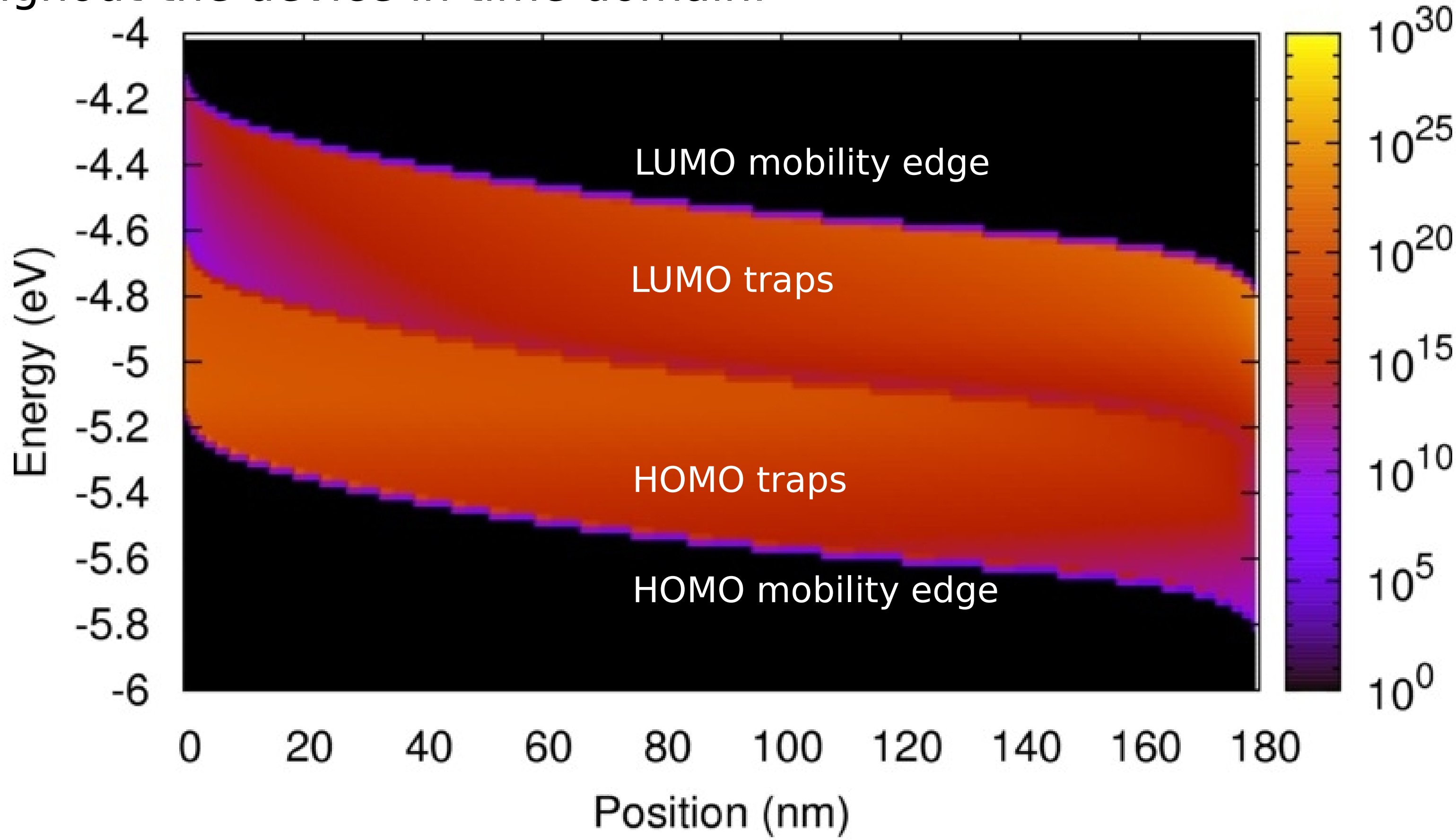
Trapping



download the source code from:
www.organicphotovoltaicdevicemodel.com

Carrier transport model + carrier trapping/recombination model

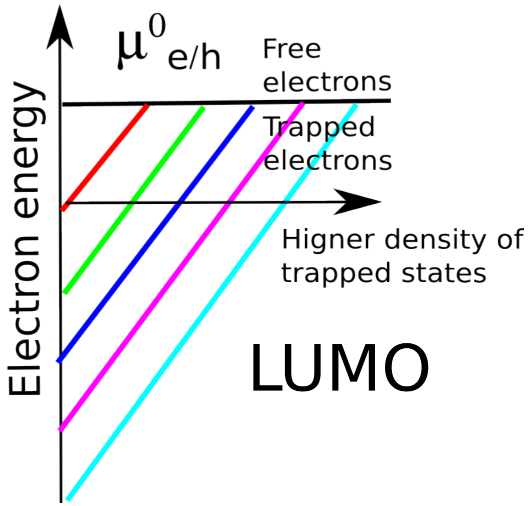
Using this formulation, we can describe carriers in position and energy space throughout the device in time domain.

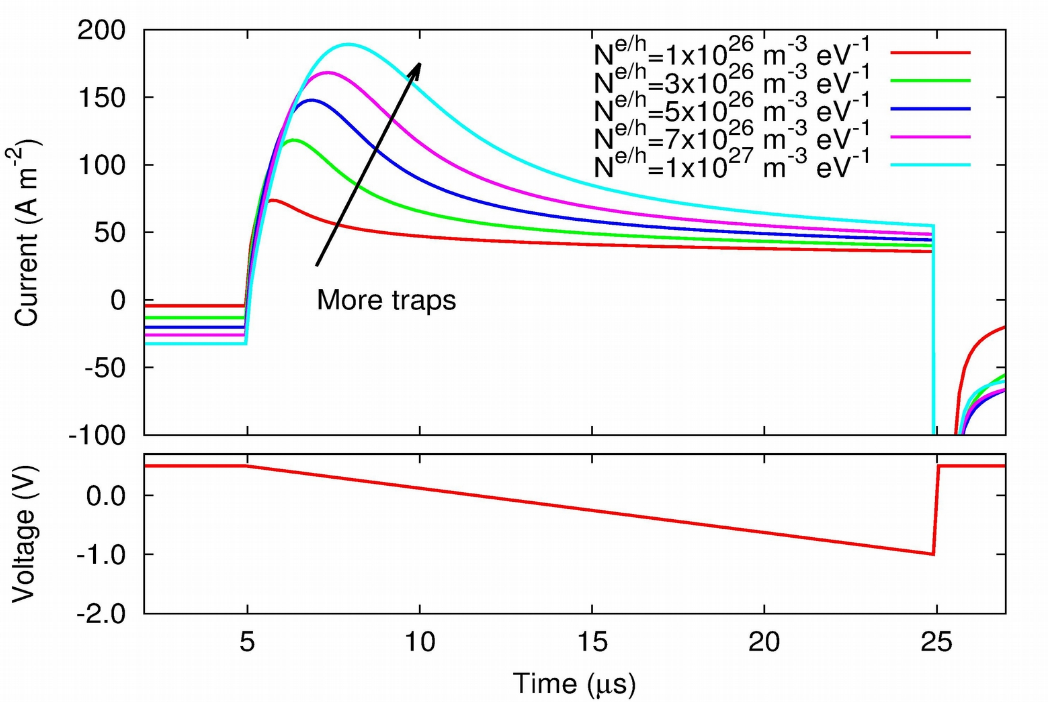


Question 1: Do carrier trap states affect the CELIV transient?

Yes, they do.

This means CELIV will probably not measure the 'free' carrier mobility as Juska described but an averaged carrier mobility of trapped and free carriers.

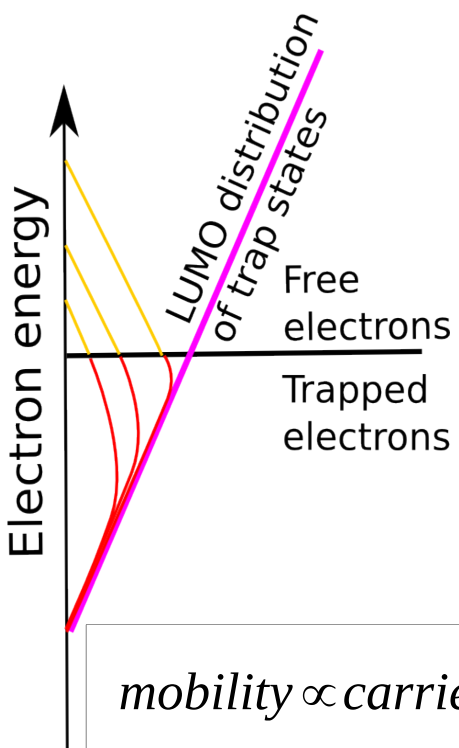


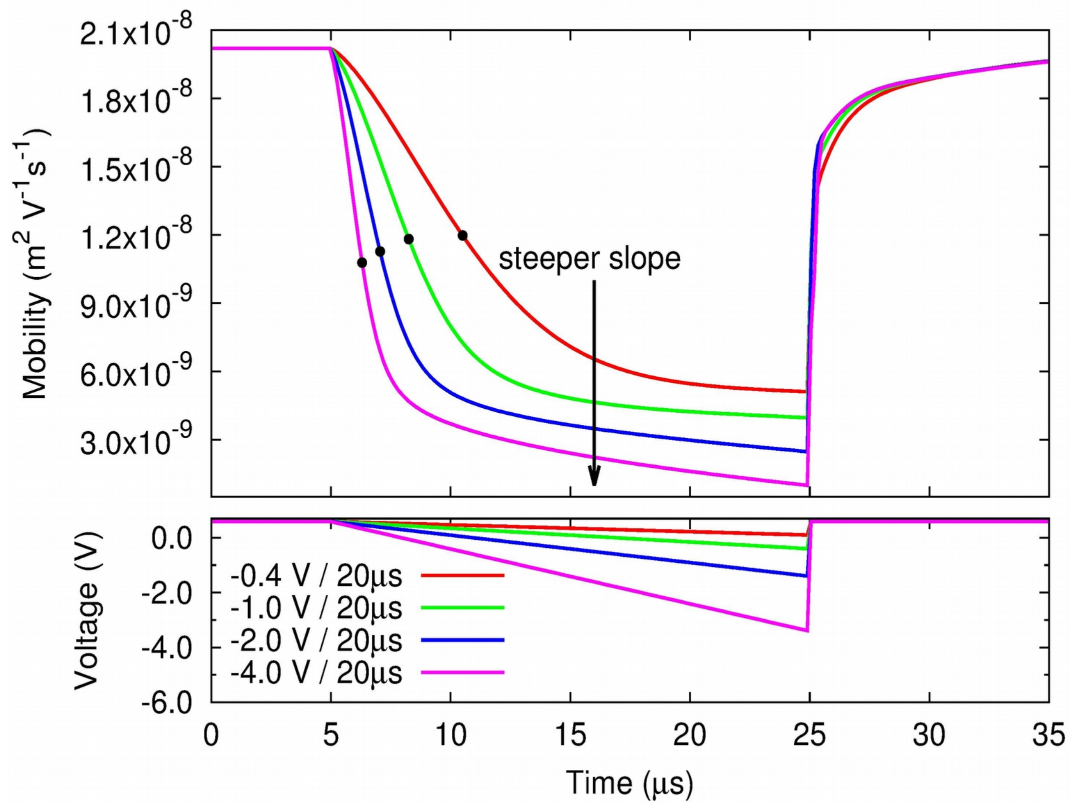


This could mean the we need to take trap states into account in the derivation of the CELIV method.

Question 2: How does the CELIV voltage ramp affect device mobility?

By merely applying the CELIV transient the mobility within the device changes by up to 50%.

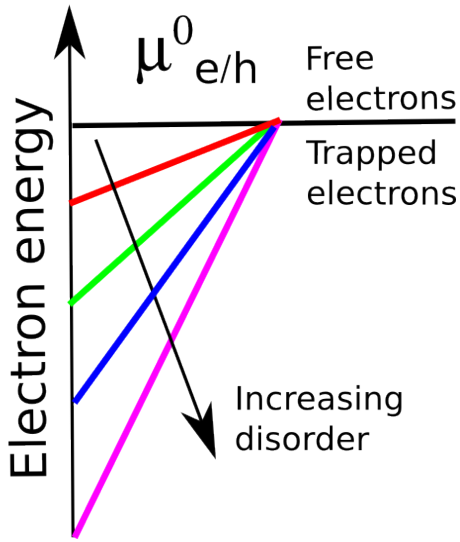


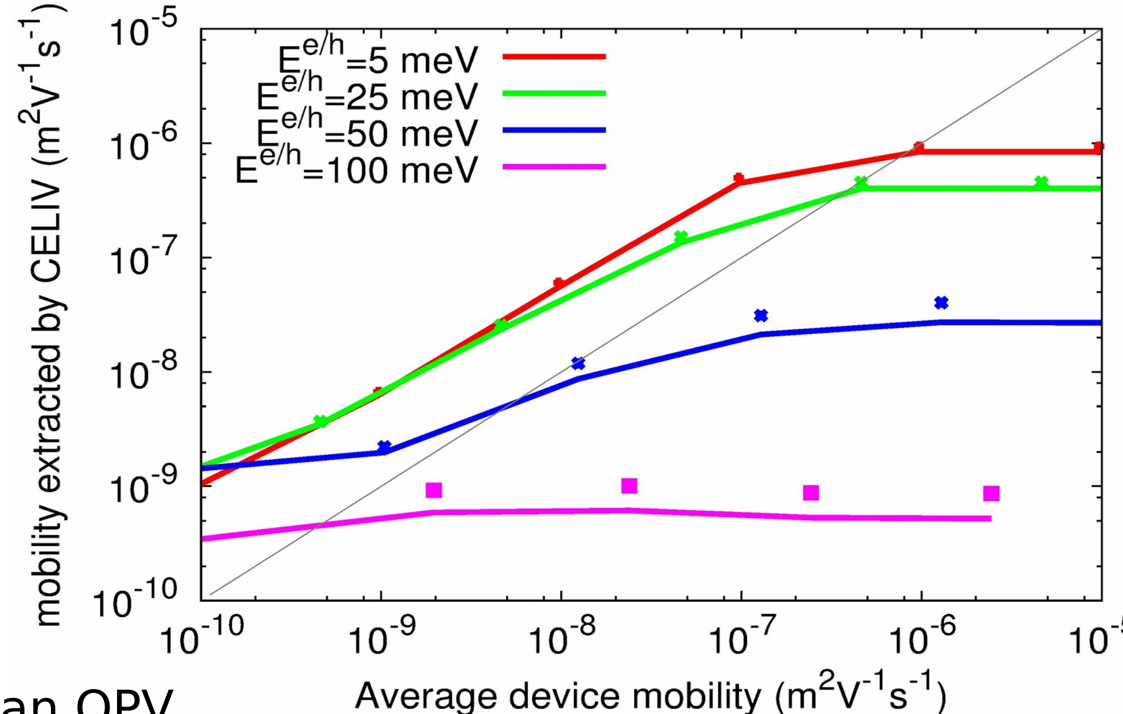


$$mobility \propto carrier\ density \propto applied\ bias$$

$$\mu_{e/h} = \frac{1}{d} \int_0^d \mu^0_{e/h} \frac{n^{free}_{e/h}(V)}{n^{free}_{e/h}(V) + n^{trapped}_{e/h}(V)} dx$$

Knowing this, how reliable is CELIV for organic solar cells?





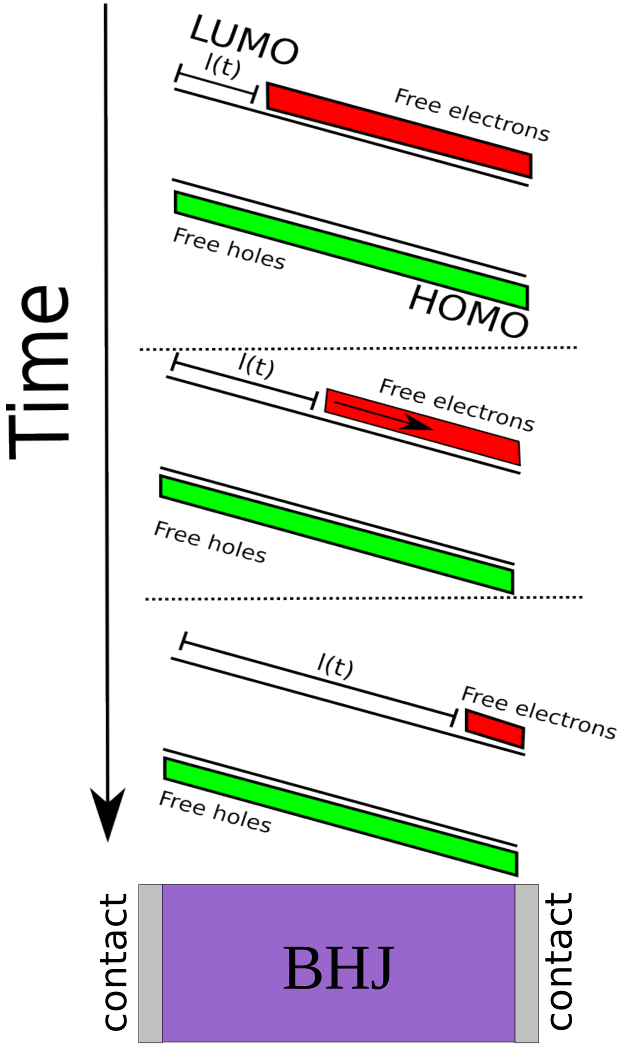
Hanfland, et al., Appl. Phys. Lett. 103, 063904 (2013)

When disorder is high (as in an OPV device) CELIV can only give you an estimate of mobility within about two orders of magnitude.

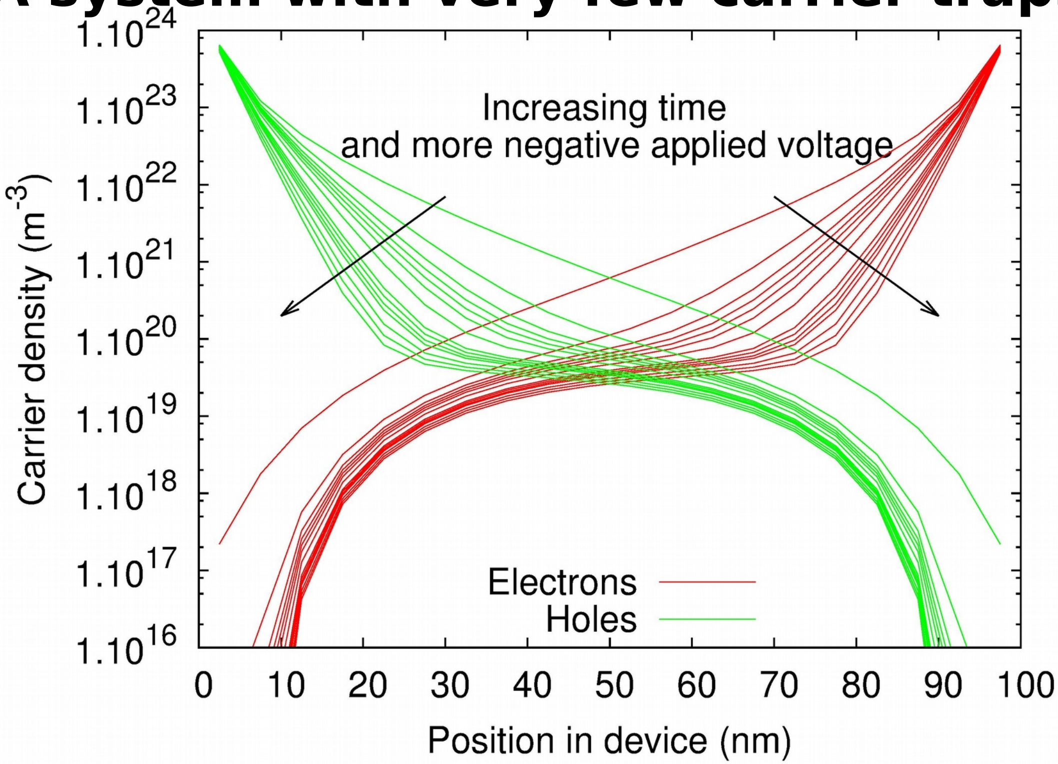
$$\mu_{e/h}=\frac{1}{d}\int_0^d \mu^0_{e/h}\frac{n^{free}_{e/h}(V)}{n^{free}_{e/h}(V)+n^{trapped}_{e/h}(V)}dx$$

Note – this cell is symmetric

What happens in a CELIV transient? (low disorder)



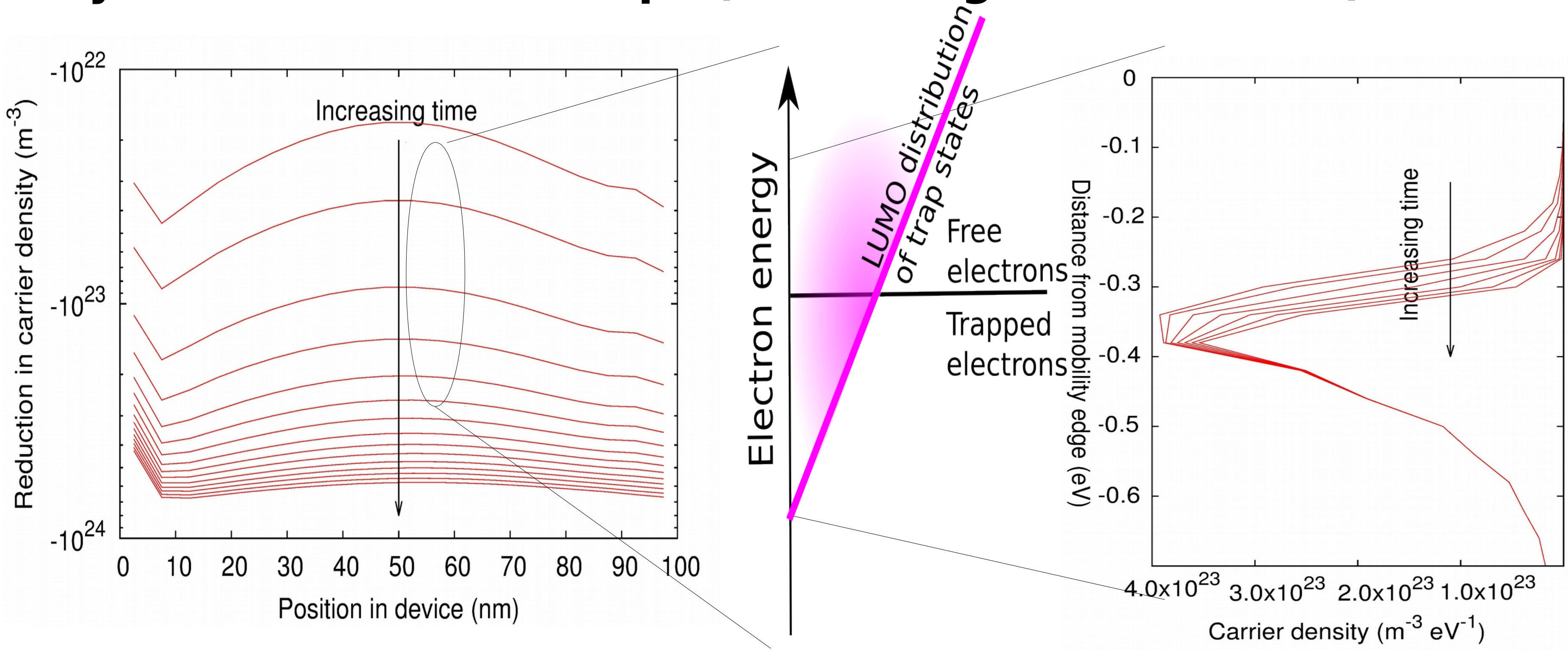
A system with very few carrier traps



For an ordered system – Juska's picture is not too far off – hence CELIV works for an ordered system.

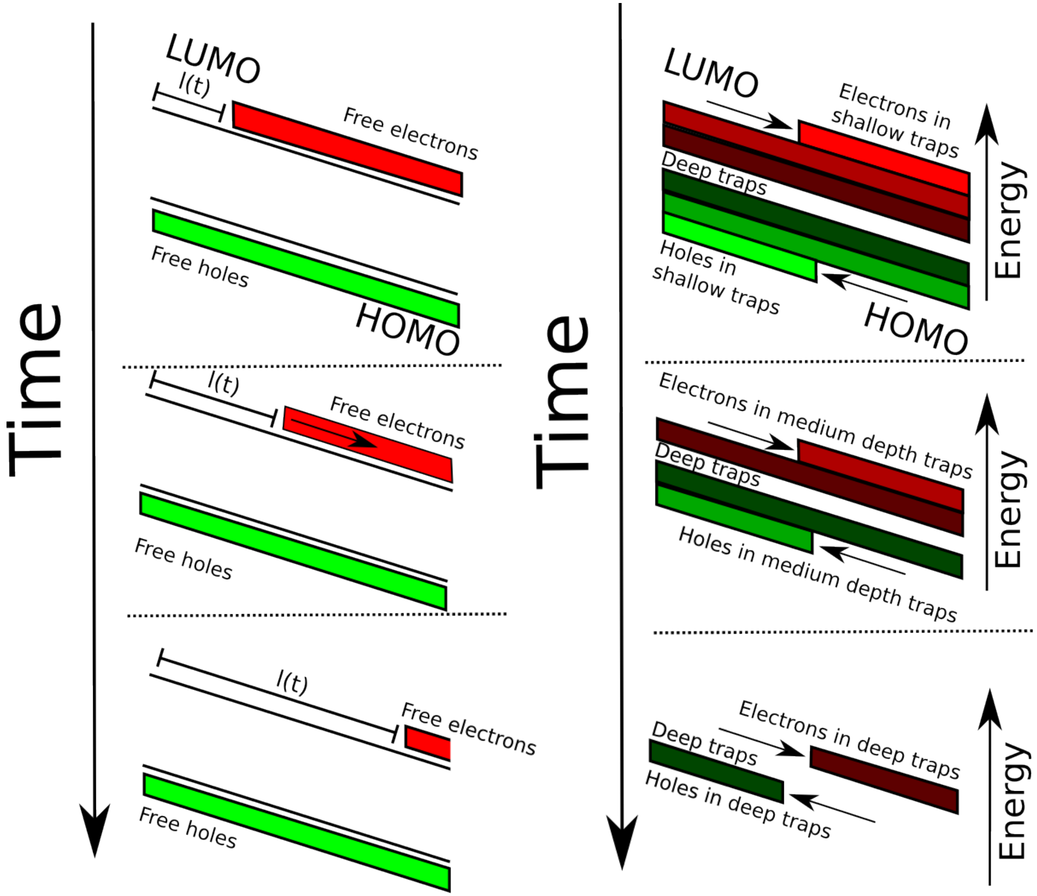
What happens in a CELIV transient? (high disorder)

A system with lots of traps (i.e. an organic solar cell)



Carriers progressively de-trap from deeper and deeper traps as time progresses.

Juska's picture of CELIV v.s. what is really happening in an organic solar cell.



Ideal CELIV extraction

CELIV extraction with traps

This means that Juska's I(t) is ill defined and thus the equation

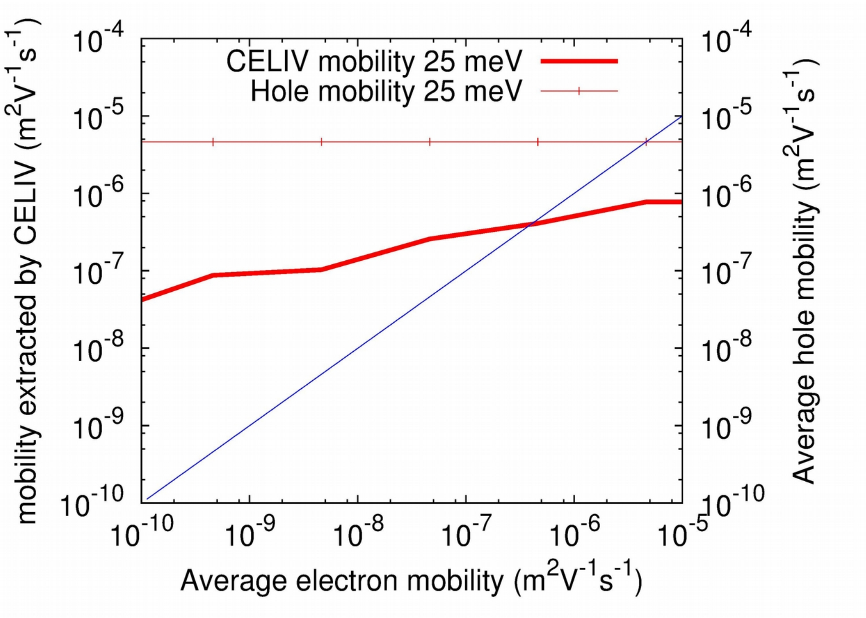
$$\mu = \frac{2}{3} \frac{d^2}{A t_{max}^2 \left(1 + 0.36 \frac{\Delta j}{j(0)}\right)}$$

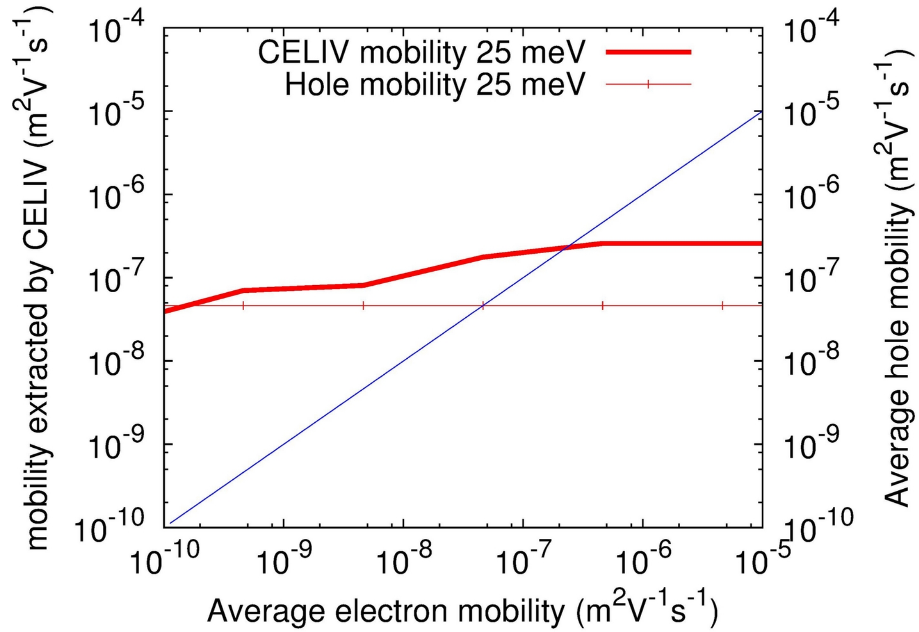
Is not as accurate as we would hope for a device with disorder.

Now we move on to answer some other common questions about CELIV.

Hanfland, et al., Appl. Phys. Lett. 103, 063904 (2013)

Does CELIV measure the mobility of the slowest or fastest carrier?





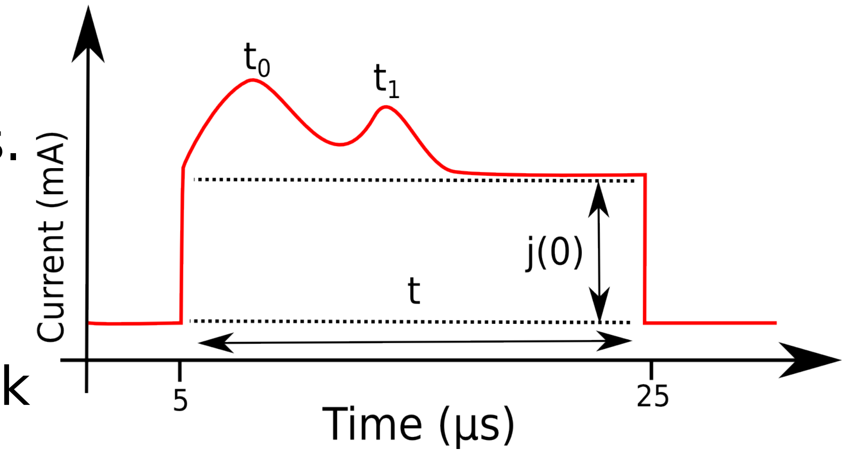
Hanfland, et al., Appl. Phys. Lett. 103, 063904 (2013)

- All previous simulations were perfomed with symmetric values of mobility.
- Above simulations were performed with asymmetric mobilities.
- CELIV attempts to measure the mobility of the fastest carrier.

The double CELIV peak of Anderson et al.

Anderson famously observed a double peak in his CELIV transients.

He attributed it to asymetric mobilities. **However,** we were unable to recreate this double peak with; asymmetric mobilities; asymmetric carrier trapping/recombination rates; and deep Gausian trap states.



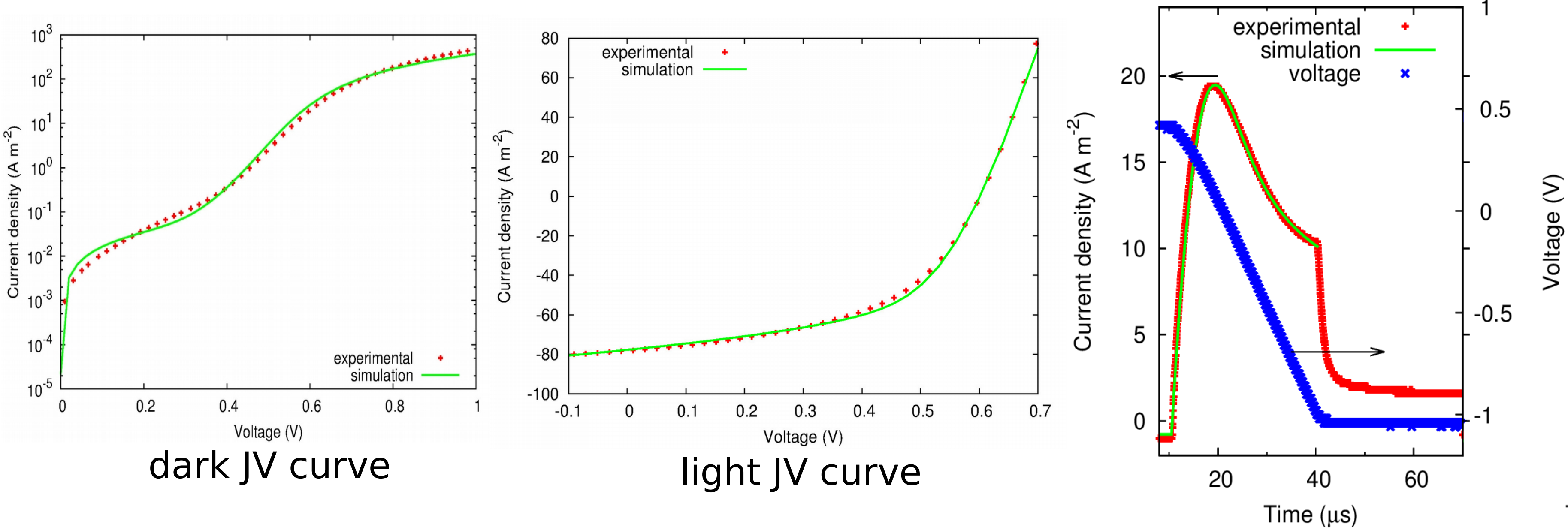
L. M. Andersson, Applied Physics Letters, 89(14):142111, 2006.

Anerson used a very high loading of PCBM (80%) so it is probable that he had a very odd morphology and not a normal BHJ.

Summary: **Asymmetric mobilities alone do not cause double peaks.**

Can CELIV be used for other things: Understanding aging using CELIV

Unaged JV curves + CELIV transient



dark JV curve

light JV curve

Dark CELIV transient

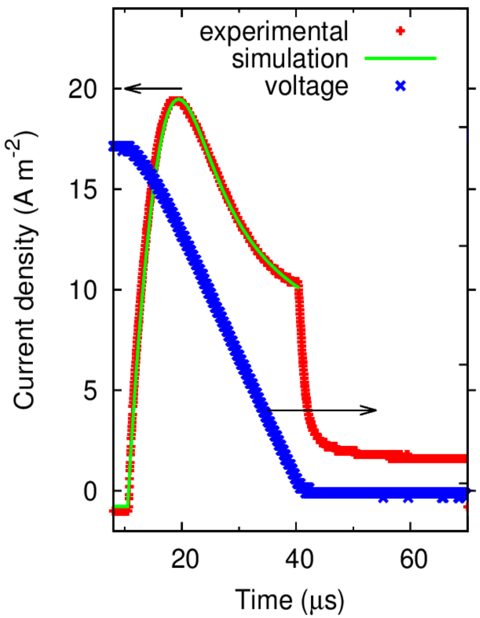
Hanfland, et al., Appl. Phys. Lett. 103, 063904 (2013)

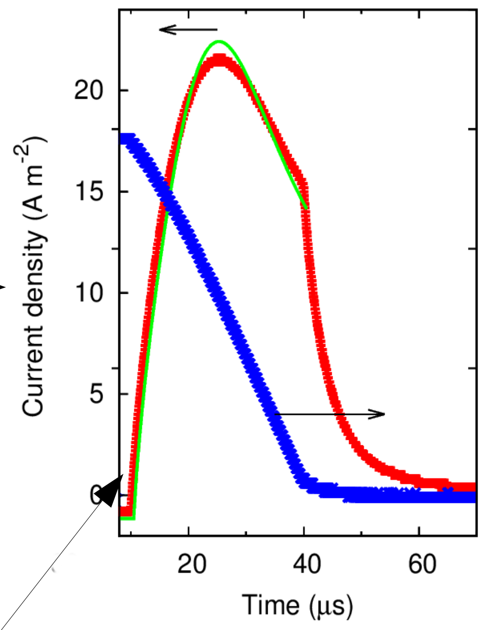
We fit the model to a non-aged P3HT:PCBM cell, by varying mobilities, recombination rates, trapping rates and trap densities.

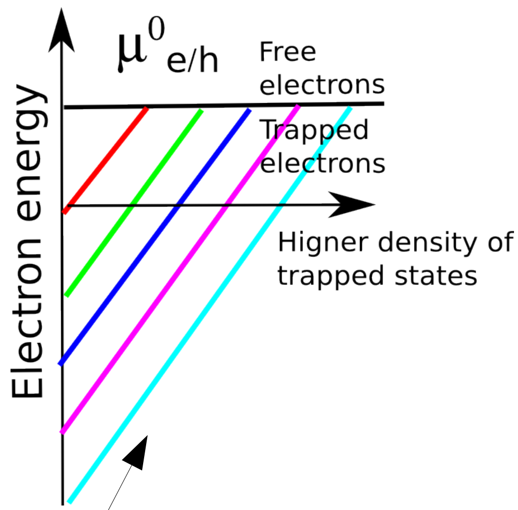
Then we aged the cell for 1176 h using a UV source equivalent to exposure at 1 Sun at 45 C with a relative humidity of 6%.

Understanding what happens to cells as they age.

Hanfland, et al., Appl. Phys. Lett. 103, 063904 (2013)







- After aging the CELIV transient changed significantly.
- To make the model fit the aged transient we only had to increase the trap density by a factor of two. ($5x10^{25}m^{-3}$->$1x10^{26}m^{-3}$)
- So we can conclude that although this could be attributed to a change in mobility it can also be attributed to an increase in trap density.

Conclusions

- Carrier trap states change the shape of the CELIV transient significantly

- The CELIV measurement itself changes the average carrier mobility by up to 50%

- The mobility as measured by CELIV can provide a good estimate to the mobility of the most mobile charge carrier for ordered materials.

- However, for materials with a **high density of trap states**, the estimate may be less reliable. For typical organic solar cells the accuracy of CELIV is within one or two orders of magnitude.

- You can download an open-source steady state version of the model at *www.organicphotovoltaicdevicemodel.com*

- I will make a copy of the talk available on-line later at *www.roderickmackenzie.eu*