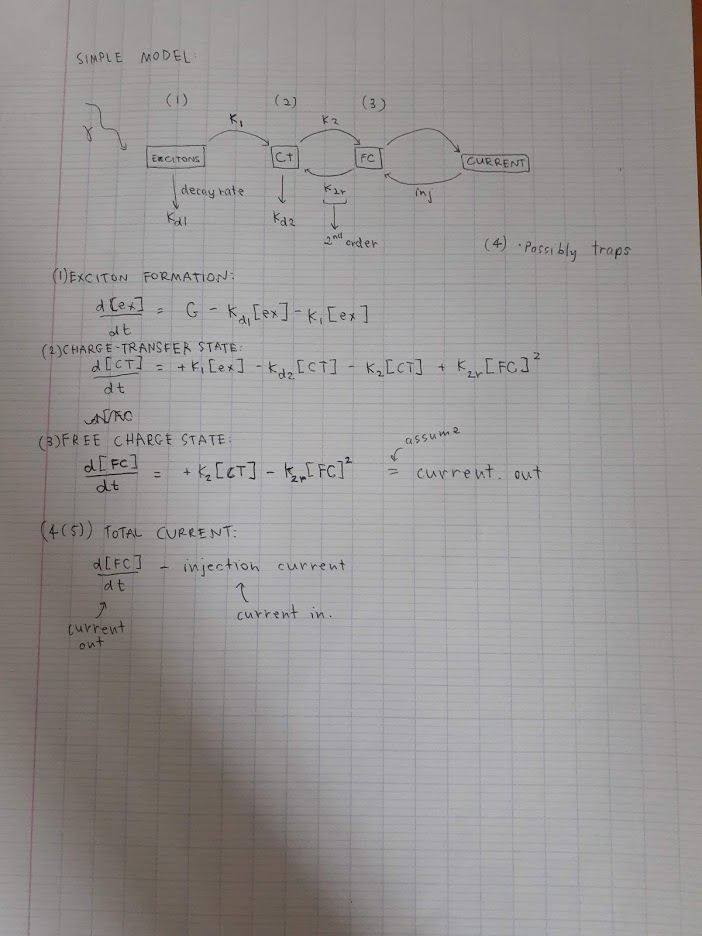
The equations of interest:



Charges are generated (excitons form), separated (charge transfer state) and escape the cell (free charge).

Rate constants reqd:

|  |  |  |
| --- | --- | --- |
| Symbol | Description | Value |
| G | Rate at which excitons are generated, given a certain incident light intensity | Calculated (with Students guide as reference) as: 3.7756e+27 (photons per m^3 per second) |
| k1 | Rate at which excitons dissociate into the charge transfer state | Assuming together: ~1012s-1, Arrehnius activated? |
| k2 | Rate at which the charger transfer state becomes free charges |
| kd1 | Rate at which excitons decay (non-radiatively) | 1 – 250 cm3s-1 |
| kd2 | Rate at which charge transfer state decays (non-radiatively) |  |
| K2r | Rate at which free charges meet and recombine in CT state | 10-3 to 10-5 m3s-1 |
| Inj | Quantity of injection current |  |

RATE CONSTANTS VERSION 2:

|  |  |  |
| --- | --- | --- |
| Symbol | Description | Value |
| G0 | Rate at which excitons are generated, given a certain incident light intensity | Calculated (with Students guide as reference) as: 3.7756e+27 (photons per m^3 per second) |
| k1 | Rate at which excitons dissociate into the free charge | Assuming together: ~1012s-1, Arrehnius activated? |
| kd1 | Rate at which excitons decay (non-radiatively, excluding traps) | 1.4e7 s-1 (STRANKS 2014) |
| K2r | Rate at which free charges meet and recombine in CT state | 10-3 to 10-5 m3s-1 |
| Kt & kdt | Trapping and detrapping rates |  |
| Inj | Quantity of injection current |  |

**Important specs:**

The perovskite: always methyl ammonium, lead, and then either indeterminate halide or specifically iodide.

**Equations:**

*Generation rate (G):*

Lambert-Beer Law: photon intensity falls off exponentially with thickness of absorber and the absorption coefficient.

Spectral generation rate: how many photons do you get at each wavelength.

Optical generation rate:

In units .

Assumptions: Ignore the profile term by assuming the film is “very thin”: we are at at all times. The quantum efficiency of generation is unity ( such that every absorbed photon generates one and only one electron-hole pair, we illuminate with a narrow enough light range that there is no change in , and we illuminate with a step function in wavelength across a range .

Then , .

If we illuminate with a light source with intensity given in a power, we need to convert to a photon flux density based on energy, using . Suppose incident intensity is at a wavelength of . One 500 nm photon has energy E=hf, divide incident power intensity by photon energy to get number of photons per second, .

Absorbance: , assume a thickness of 100 nm. <https://click.endnote.com/viewer?doi=10.1016%2Fj.mattod.2014.07.007&token=WzMxNjgwNTYsIjEwLjEwMTYvai5tYXR0b2QuMjAxNC4wNy4wMDciXQ.cr_4GWvaRcnI4hJ4grHAVgfhk1U>

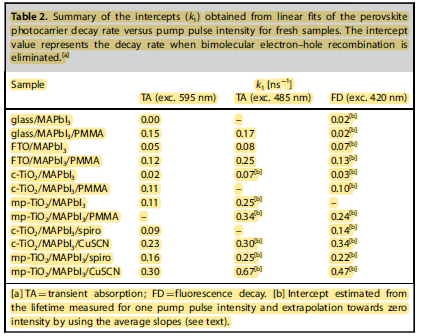
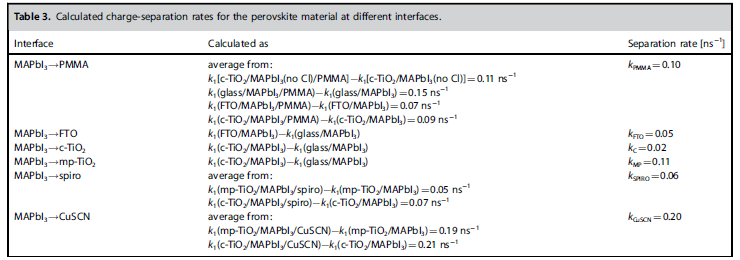
*Non-radiative decay: Decay rates 1 and 2 (kd1 & kd2).*

*Kd1:* Herz 2016 - Charge-carrier dynamics in org-inorg perovskite cells 1-250 cm3s-1

*Bimolecular recombination (k2r):*

<https://click.endnote.com/viewer?doi=10.1007%2Fs40820-018-0205-5&token=WzMxNjgwNTYsIjEwLjEwMDcvczQwODIwLTAxOC0wMjA1LTUiXQ.V9KqUJzPp14_S6WjXCgmXgz7DnQ>

*k1 & k2: transfer from excitons all the way to free charges*From Stranks 2014 – Recombination kinetics…  
Assumed to be an Arrhenius activated process, pre-exponential factor assumed related to the binding energy, exciton binding energy of approx. 50 meV. **This paper also gives some trapping and de-trapping rates and other details**.

*: rate at which electrons and holes escape the perovskite into the electron-selective and hole-selective contacts. Below images:  
*From paper: *Determination of Interfacial Charge-Transfer Rate Constants in Perovskite Solar Cells: Pydzińska.*

**General paper reading notes:**

*Determination of Interfacial Charge-Transfer Rate Constants in Perovskite Solar Cells: Pydzińska.***Note: this is charge transfer rates OUT of the perovskite (ie like extraction and injection current)**

* Transient absorption studies: later time absorption (blue line) corresponds to the excited population of the perovskite (out of ground) and is the mirror image of the fluorescence spectrum at 750 nm. AKA “bleaching band”. The time that this takes to decay reflects the decay in electron-hole population in the material (caused by first, second, and third order recombination OR charge transfer across interfaces with electron and hole-selective materials).



*Recombination kinetics in organic-inorganic perovskites: Stranks.*

* Langevin theory was found not to fit perovskites well
* Approaching the Shockley-Queisser efficiency limit requires that all recombination is radiative, but the efficiency limit is also maximsed at high excitation intensities wherein non-radiative decay pathways tend to dominate. Aka it’s a balance.
* This paper: PL measurements from pulsed and continuous excitation of CH3NH3PbIx-3Clx thin films with a theoretical model.
  + Low excitation fluences (including similar to solar cell operation): evolution of charge populations is dominated by traps.
  + High excitation fluences: all traps are filled and the evolution is dominated by radiative bimolecular recombination.

*Wen 2016 – Defect trapping states and charge carrier recombination in organic-inorganic halide perovskites*

QUESTIONS:

* Is 10 microseconds reasonable?
  + Is the low excitation fluences not coming up at all reasonable? (they seem to be completely going into traps and never saturating the traps)
* Current
* Check Anita trap-detrap paper
* How would we incorporate ion movement
* Get a radiative exciton decay rate