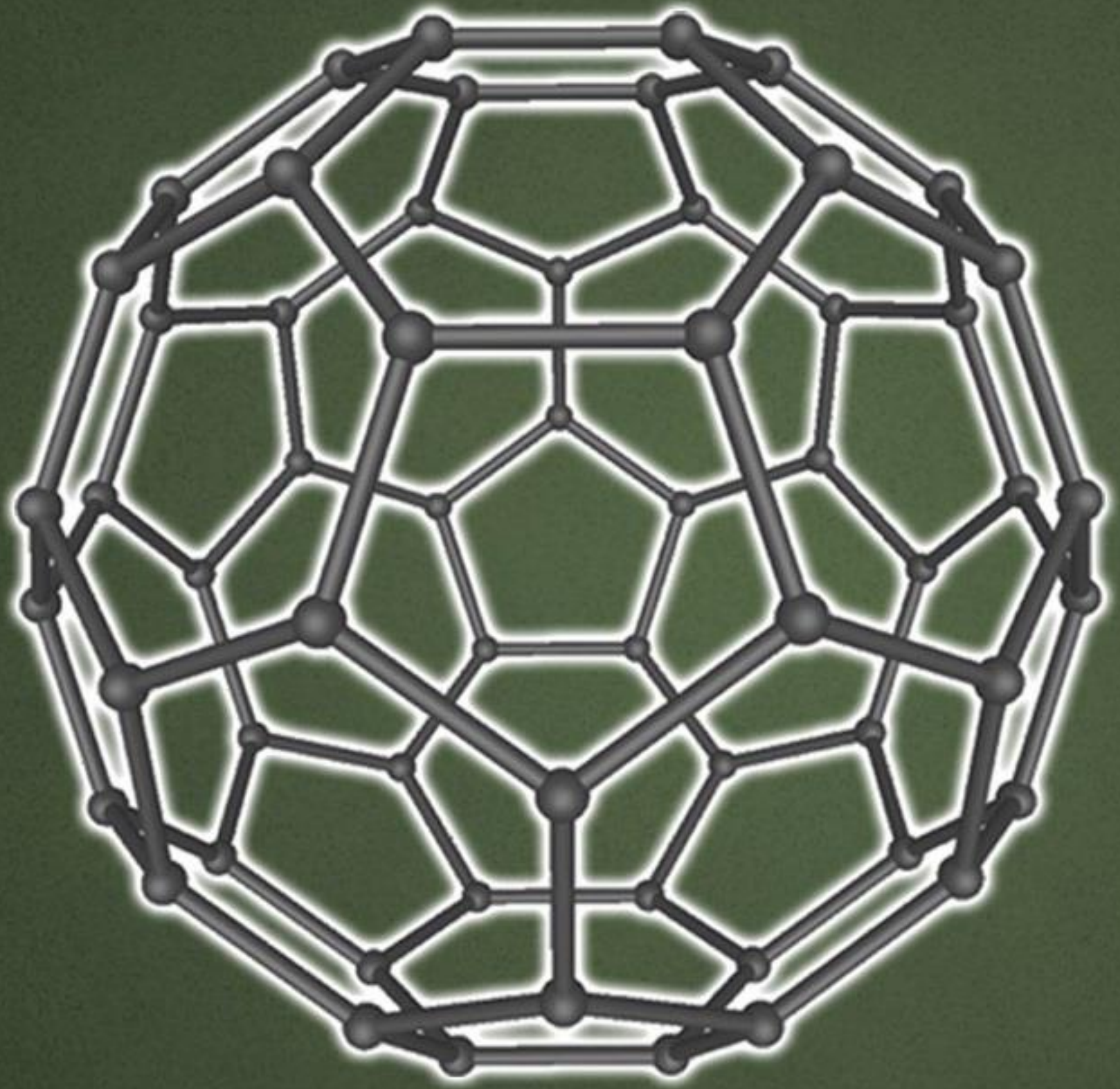


Optically Induced Capacitance Changes in Organic Semiconductor Based Structures

J.W.E. Kneller and T. Kreouzis

School of Physics and Astronomy,
Queen Mary University of London, UK

A.S. Andy, C.G. Parini, M. Pigeon and O. Sushko and R.S Donnan

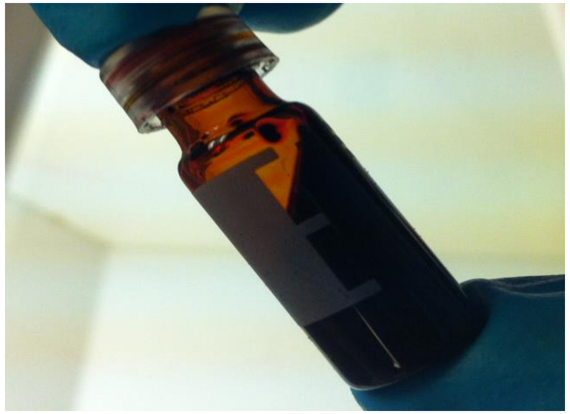
School of Electronic Engineering and Computer Science,
Queen Mary University of London, UK

Contents

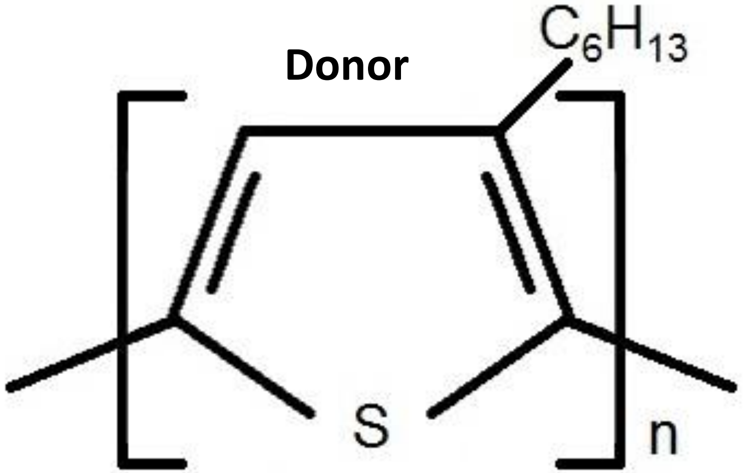
- Brief introduction to organic electronics
- Dielectric constant change $\Delta\varepsilon_{Theory} \Rightarrow \Delta\varepsilon_{Plasma} = \Delta\varepsilon_{(\mu,\Delta n)}$
  $\Rightarrow \Delta\varepsilon_{Space\text{charge}} = \Delta\varepsilon_{(\mu,G)}$
  $\Rightarrow \Delta\varepsilon_{e-h} = \Delta\varepsilon_{(r_c,\Delta n)}$
  - Time of Flight
  - Steady State Photocurrent
- $\Delta\varepsilon_{Experimental} = \Delta\varepsilon_{(\upsilon)}$
  - Impedance Spectroscopy
  - *GHz - Quasi-Optical Free Space propagation*
- $\Delta\varepsilon_{Theory}\ vs\ \Delta\varepsilon_{Experimental}$
- Conclusions

Organic Materials

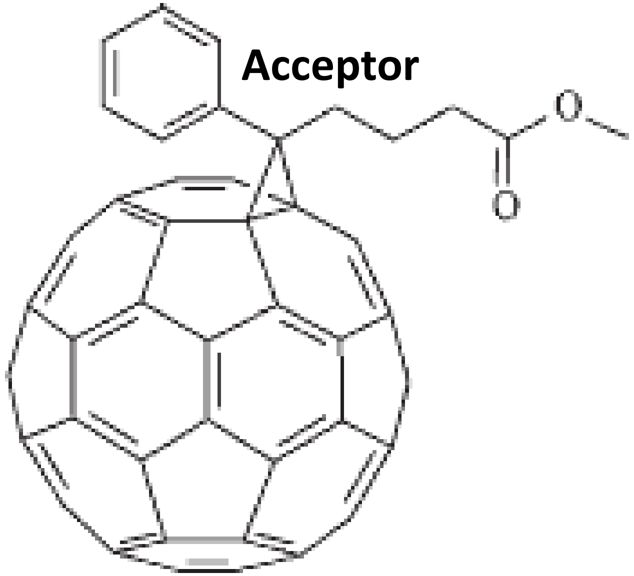
- Two semi-conducting organic materials used,
- P3HT and PCBM mixed in a 95:5 ratio respectively.
- When excited, one material donates an electron while the other accepts an electron.



95:5 P3HT:PCBM Mixture



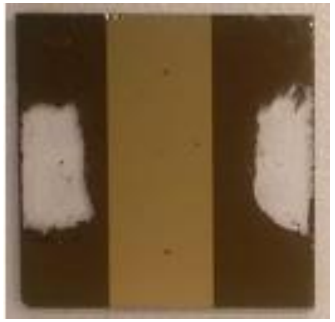
P3HT, poly(3-hexylthiophene)



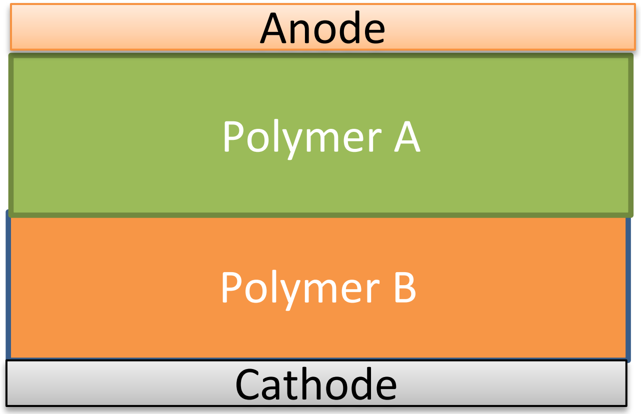
PCBM, phenyl-C61-butyric-acid methyl ester

Organic Electronics

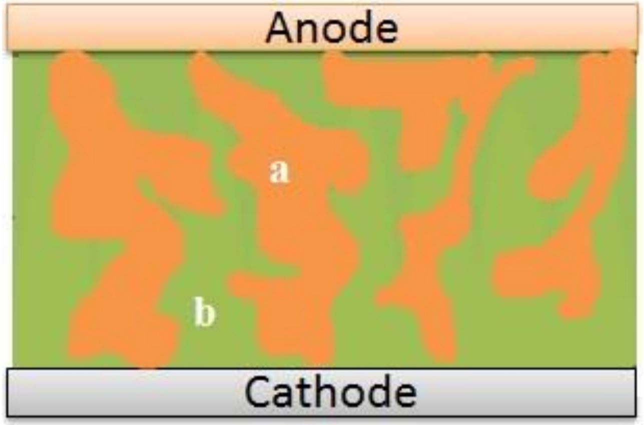
- The polymers are in contact with each other in a junction and in contact to electrodes
- Best way to achieve this is with a Bulk-Heterojunction which maximises dissociation at interface
- Devise: ITO:P3HT:PCBM:Al



95:5 P3HT:PCBM device layout showing the layers of deposited material, the design and the finished device.



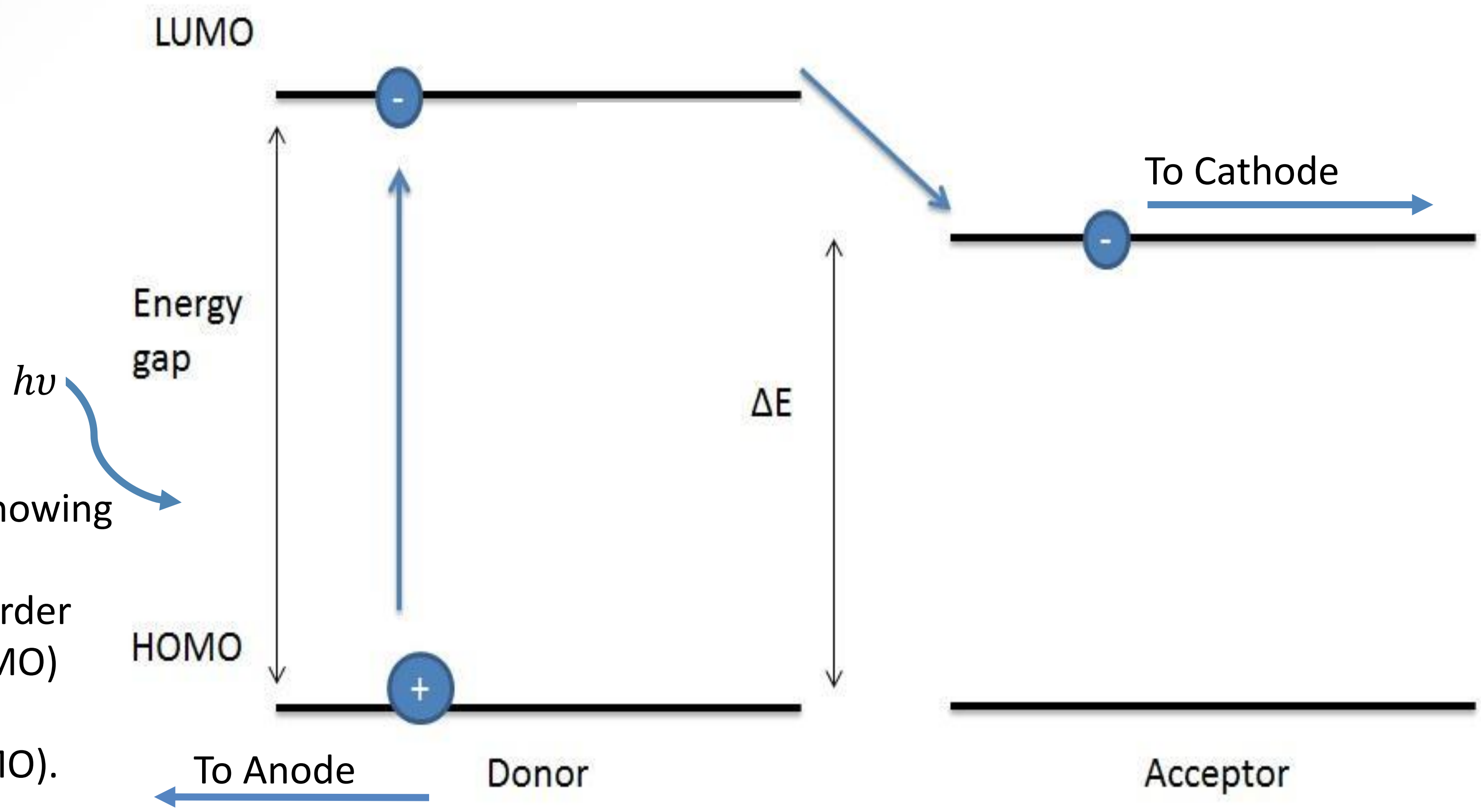
A simple bi-layer design



A Bulk-Heterojunction

Organic Charge Transfer

- LUMO P3HT = 3.7eV
- LUMO PCBM = 3.0eV



Energy level diagram showing electron/hole transfer between the Highest Order Molecular Orbital (HOMO) and the Lowest Order Molecular Orbital (LUMO).

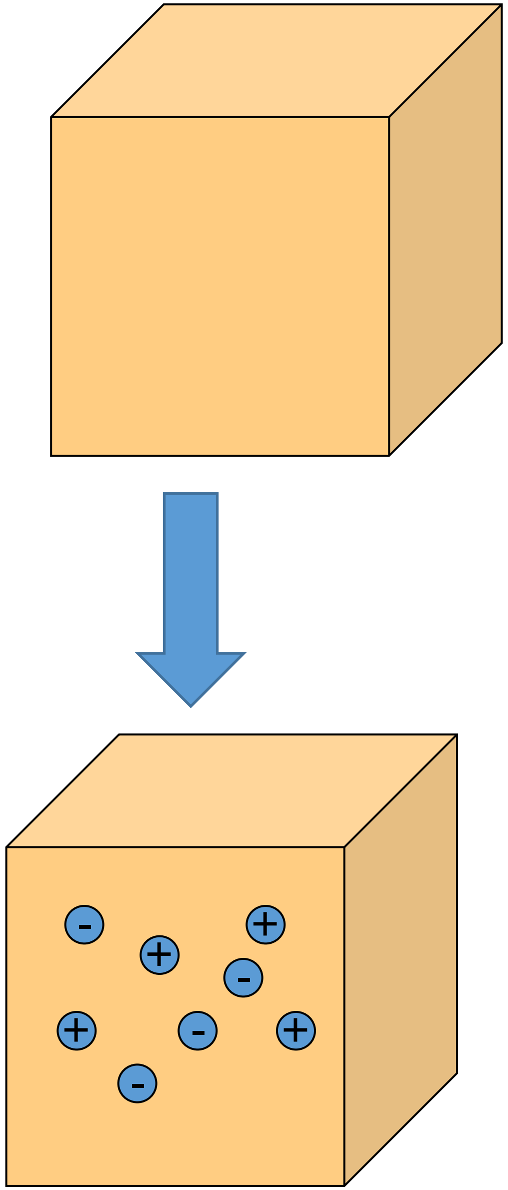
Dielectric Constant

- A slab of conjugated polymer
  will have some dielectric properties:

$$\varepsilon = \varepsilon_{dark}$$

- A slab of conjugated polymer under illumination
  will have different dielectric properties:

$$\varepsilon_{illuminated} = \varepsilon_{dark} + \Delta\varepsilon$$



$\Delta\varepsilon$

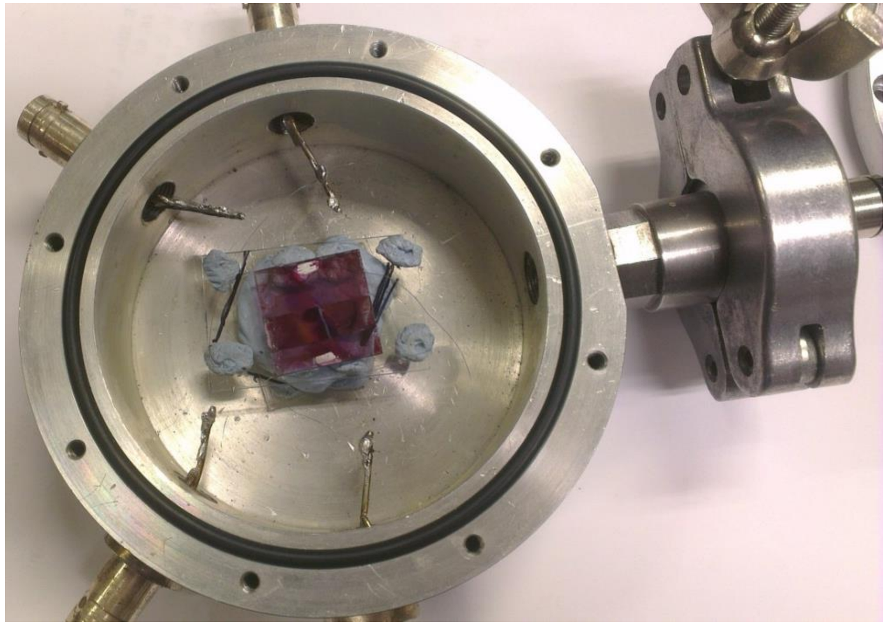
- Three different theoretical approaches:
- $\Delta\varepsilon_{Theory} \Rightarrow \Delta\varepsilon_{Plasma} = \Delta\varepsilon_{(\mu,\Delta n)}$

  $\Rightarrow \Delta\varepsilon_{Spacecharge} = \Delta\varepsilon_{(\mu,G)}$

  $\Rightarrow \Delta\varepsilon_{e-h} = \Delta\varepsilon_{(r_c,\Delta n_{e-h})}$

- $\Delta\varepsilon_{Experimental} \Rightarrow \Delta\varepsilon_{(v)}$ (DC and GHZ)

P3HT:PCBM device in an open vacuum chamber



$$\boldsymbol{\Delta\varepsilon_{Theory} \Rightarrow \Delta\varepsilon_{Plasma} = \Delta\varepsilon_{(\mu,\Delta n)}}$$

- Change in dielectric constant can be calculated according to established plasma theory: (for high mobility silicon)
- $\Delta\varepsilon_{Plasma} = -\left(m_e\mu_e^2 + m_h\mu_h^2\right)\frac{\Delta n}{\varepsilon_0} \in \mathbb{R}$

Dielectric Constant Change

Electron/Hole Mobility

Charge Carrier Density

- $\Delta\varepsilon_{Plasma}$ is dependant on the density and mobility of the charge carriers
- These can be easily measured, thus $\Delta\varepsilon_{Plasma}$ can be calculated.

$$\boldsymbol{\Delta\varepsilon_{Plasma}} \Rightarrow \mu = 10^{-4}\text{cm}^2\text{v}^{-1}\text{s}^{-1}$$
$$\Rightarrow \Delta n$$

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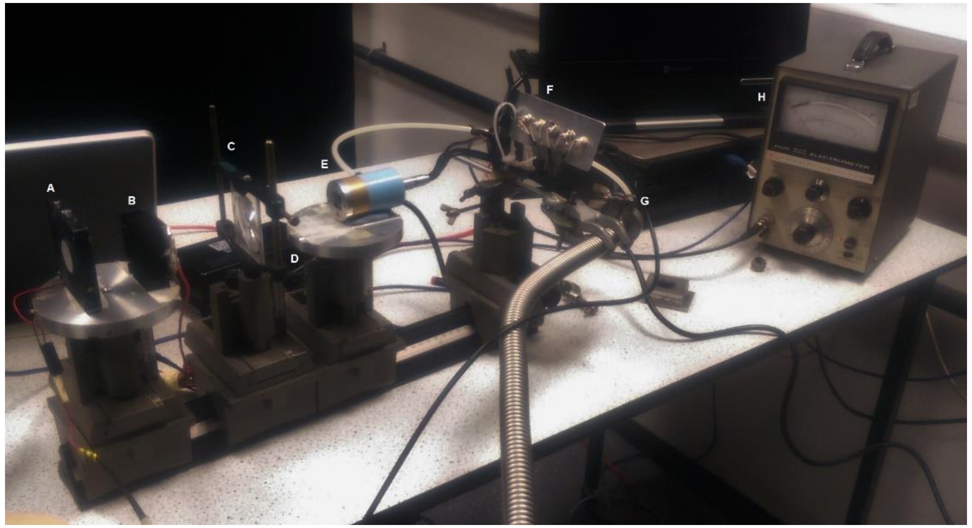
M. El Khaldi, F. Podevin, and A. Vilcot, Microwave and Optical Technology Letters 47 (6), 570 (2005).

Charge Carrier Concentration, Δn

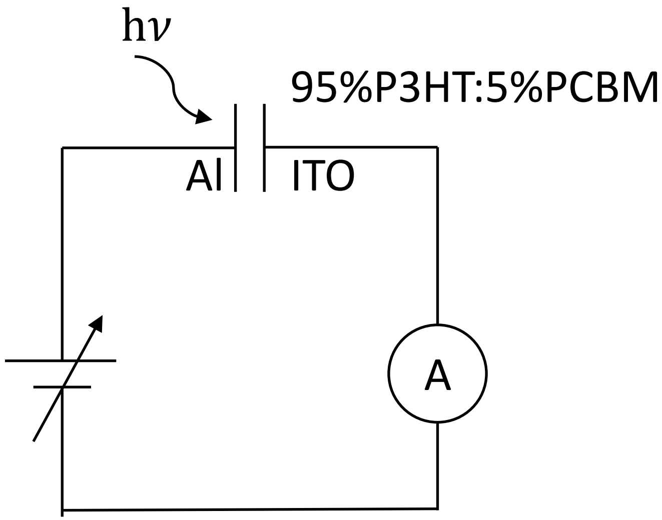
- From Ohms Law: $J = \Delta n e \mu E$
- And Charge definition between two plates:

$$E = \frac{\Delta\phi}{d} = \frac{V_{eff}}{d} = \frac{V_{Bias} - V_{Built-IN}}{d}$$



- We get Δn as a function of photocurrent, mobility and voltage:

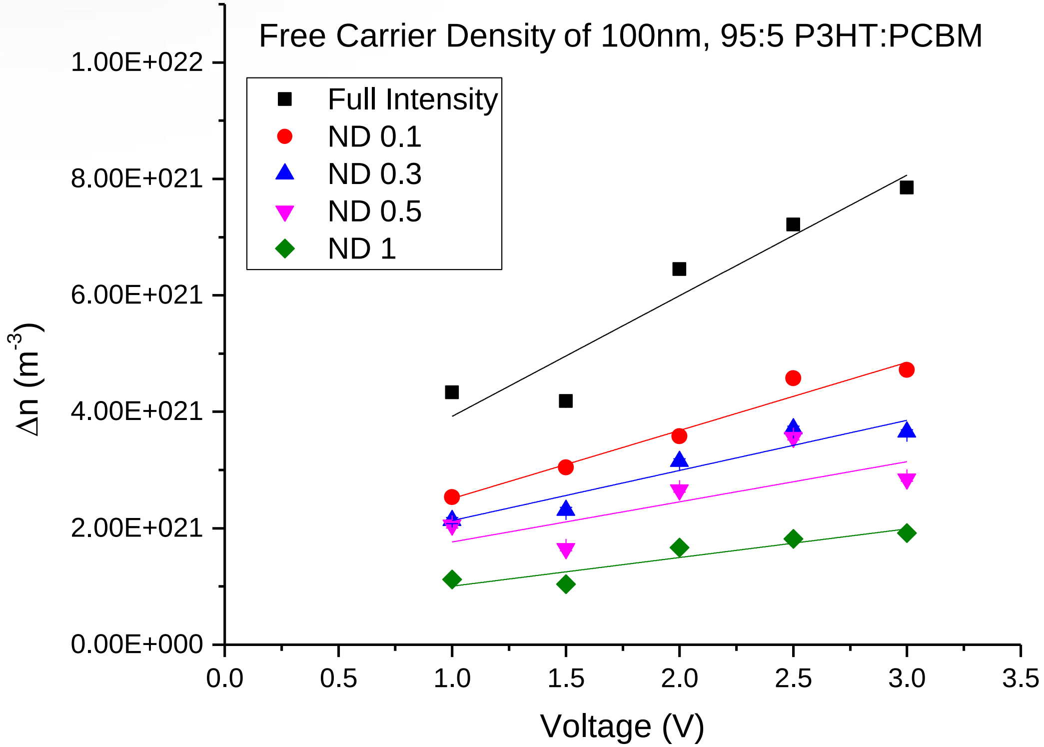
$$\Delta n = \frac{Id}{Ae\mu V_{eff}}$$

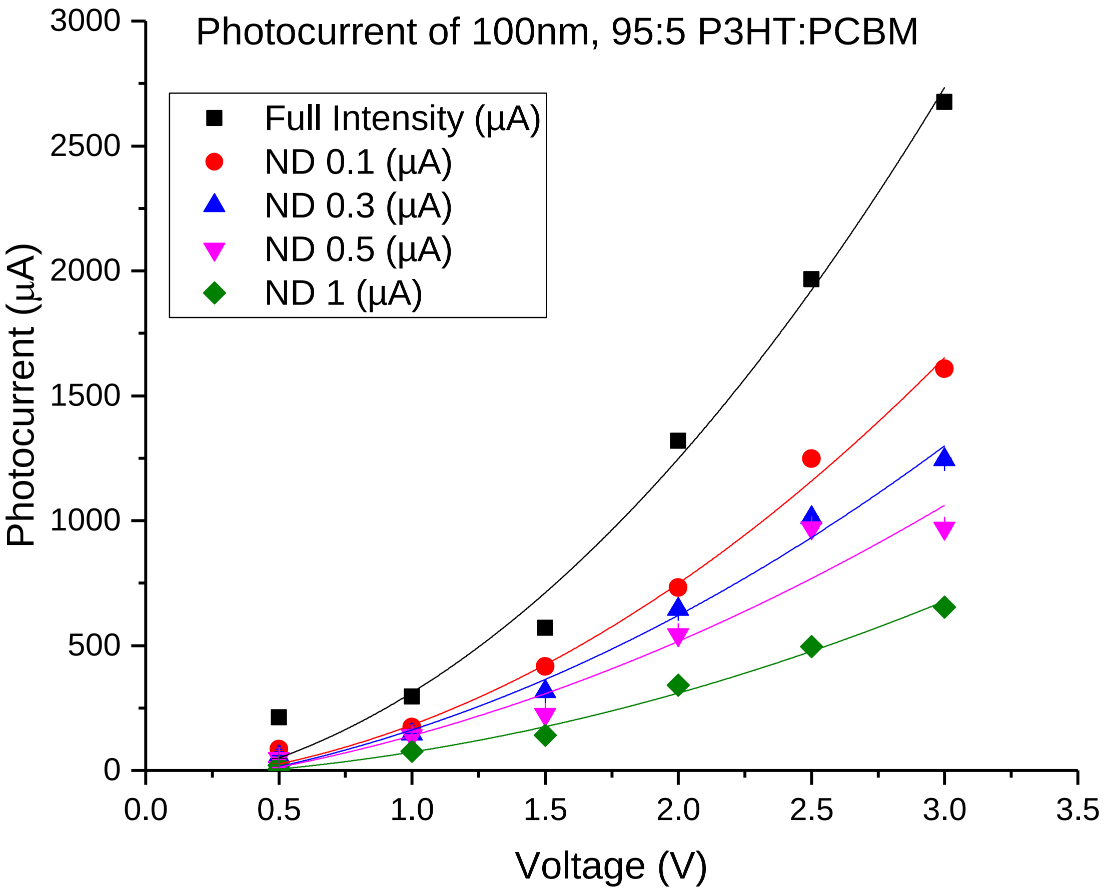


- So simply excite and measure photocurrent under a bias voltage.

Charge Carrier Concentration, Δn

- Measure photocurrent
- Calculate Δn
- Extrapolate to Zero Field, $\Delta n_{E=0}$
- Calculate $\Delta \varepsilon_{Plasma}$

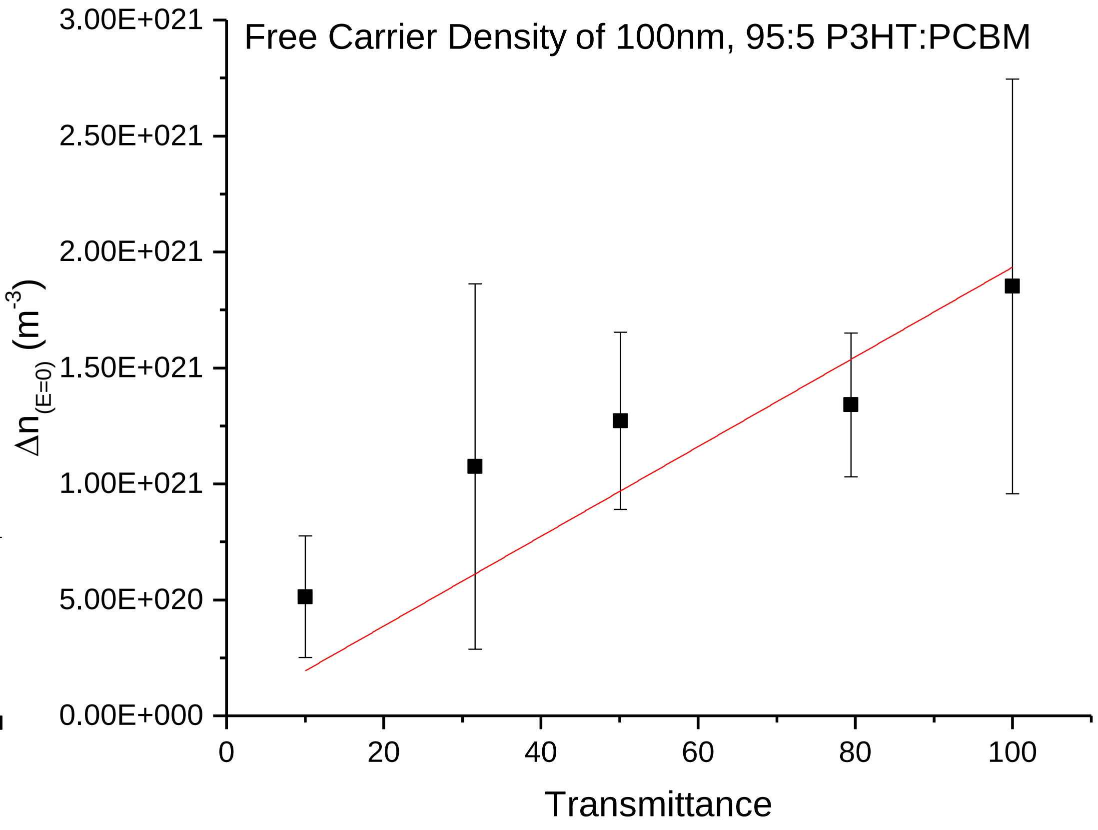


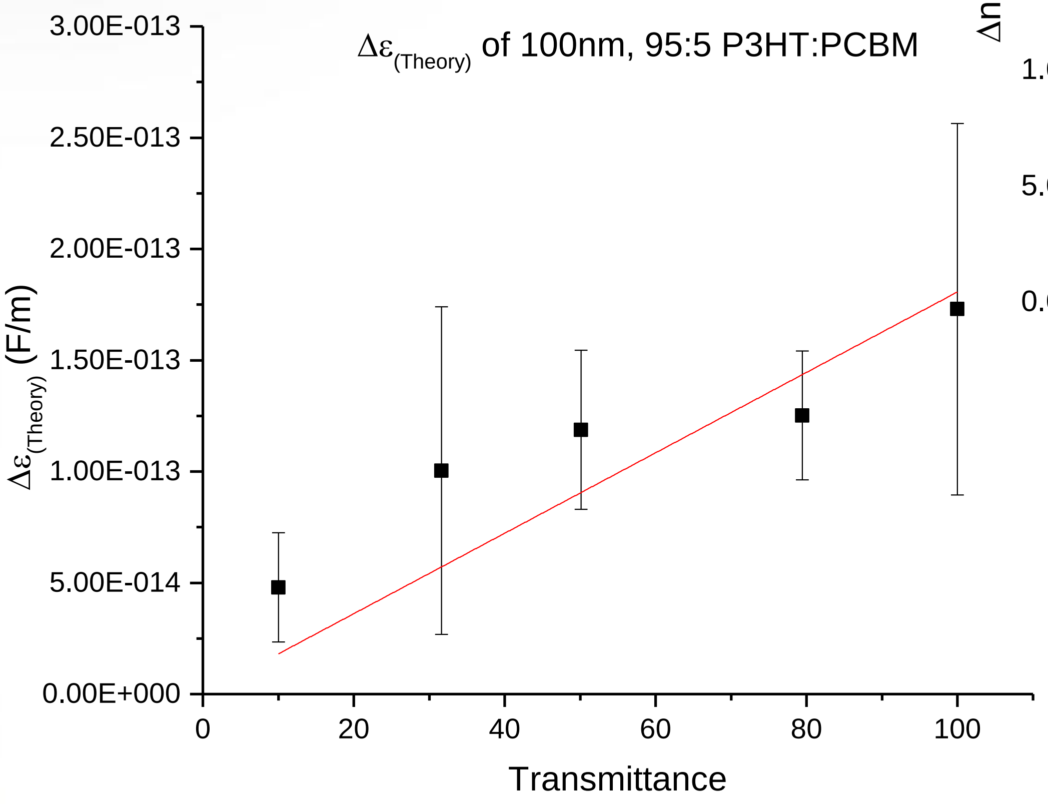


Graphs showing Photocurrent I (above) (quadratic as both V and μ dependant) and charge carrier concentration Δn (left) against effective voltage V_{eff}.

Charge Carrier Concentration, Δn

- Measure photocurrent
- Calculate Δn
- Extrapolate to Zero Field, $\Delta n_{E=0}$
- Calculate $\Delta\varepsilon_{Plasma}$





Graphs showing zero field concentration $\Delta n_{E=0}$ (above) and change in dielectric constant $\Delta\varepsilon_{Theory}$ (left) against % light transmittance. (100%=1234Wm-2)

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$\boldsymbol{\Delta\varepsilon_{Theory} \Rightarrow \Delta\varepsilon_{Spacecharge} = \Delta\varepsilon_{(\mu,G)}}$

- Can model photocapacitance as a spacecharge:

$$C_p = \left(\frac{eGd}{2E_0^2}\right)\left(\frac{1}{(\mu_n + \mu_p)}\right)$$

- Dependant on conductance G and mobility μ
- As $c = \frac{\varepsilon\varepsilon_0 A}{d}$ and $E_0 = \frac{V}{d}$
- $c \propto d^3$ $c \approx 10^{-38}F$

- $\Delta\varepsilon_{Space\ Charges} = \Delta\varepsilon_{(\mu,G)} = 10^{-26}$

Richard S. Crandall, Journal of Applied Physics 54 (12), 7176 (1983).

$$\Delta\boldsymbol{\varepsilon}_{\boldsymbol{Theory}} \Rightarrow \Delta\boldsymbol{\varepsilon}_{\boldsymbol{e-h}} = \Delta\boldsymbol{\varepsilon}_{(\boldsymbol{r_c}, \Delta n_{e-h})}$$

- $\Delta\varepsilon = \Delta\varepsilon_{static\ charges} + \Delta\varepsilon_{free\ charges}$

Coulombically bound e-h pairs

- rotating with the electronic field
- Traditionally assumed to be negligible
- Derived via:
  - Richard Friend
  - New QMUL Model

Free electrons and holes

- $\Delta\varepsilon_{Plasma}$
- $\Delta\varepsilon_{Spacecharge}$

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$$\boldsymbol{\Delta\varepsilon_{Theory}} \Rightarrow \boldsymbol{\Delta\varepsilon_{e-h}} = \boldsymbol{\Delta\varepsilon_{(r_c,\Delta n_{e-h})}}$$

$$\Delta\varepsilon_{static\ charges} = ?$$

- Can define polarizability per unit dipole as:
  - $\Delta P = \varepsilon_0(\Delta\varepsilon - 1)E$
  - $\Delta P = \overline{p_{\parallel}}\Delta n$
- Dipole moment parallel to Field:
  - $\overline{p_{\parallel}} \leq p_{e-h} \leq er_c$
- e-h pair density:
  - $\Delta n_{e-h} \geq \frac{\varepsilon_0(\Delta\varepsilon - 1)E}{er_c}$
  - Using $\Delta\varepsilon$ of order unity
  - $\Delta n_{e-h} \geq 10^{22}\ \mathrm{m}^{-3}$
  - which is smaller than the maximum pair density of 10^{24} m^{-3}

- Assuming a cube of coulomb radius completely filled with *e-h* dipoles:
- $\Delta\varepsilon_{e-h} \leq \frac{er_c\Delta n_{e-h}V}{d}$
- $\Delta\varepsilon_{e-h} \leq 10^5$

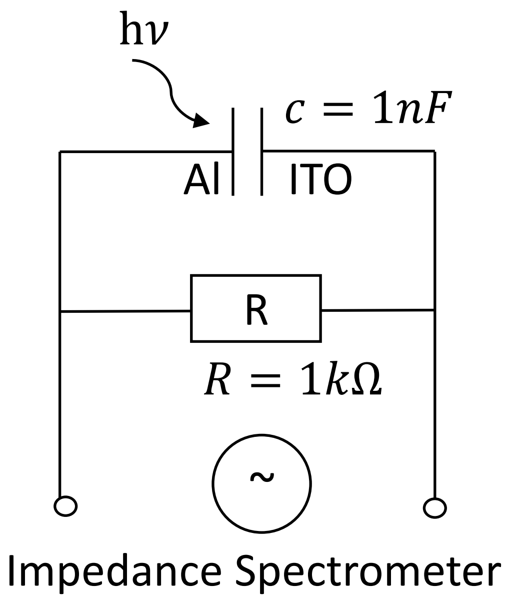
A. D. Chepelianskii, J. Wang, and R. H. Friend, Phys Rev Lett 112 (12), 126802 (2014).

$\Delta\boldsymbol{\varepsilon}_{\boldsymbol{Experimental}} = \Delta\boldsymbol{\varepsilon}_{(\boldsymbol{v})}$

- From capacitance definition: $c = \frac{\varepsilon\varepsilon_0 A}{d}$
- And RC circuits: $\omega_{Resonant} = \frac{1}{RC}$
- We get: $\frac{\Delta\varepsilon}{\varepsilon} = \frac{\Delta\upsilon}{\upsilon}$
- Any change in υ

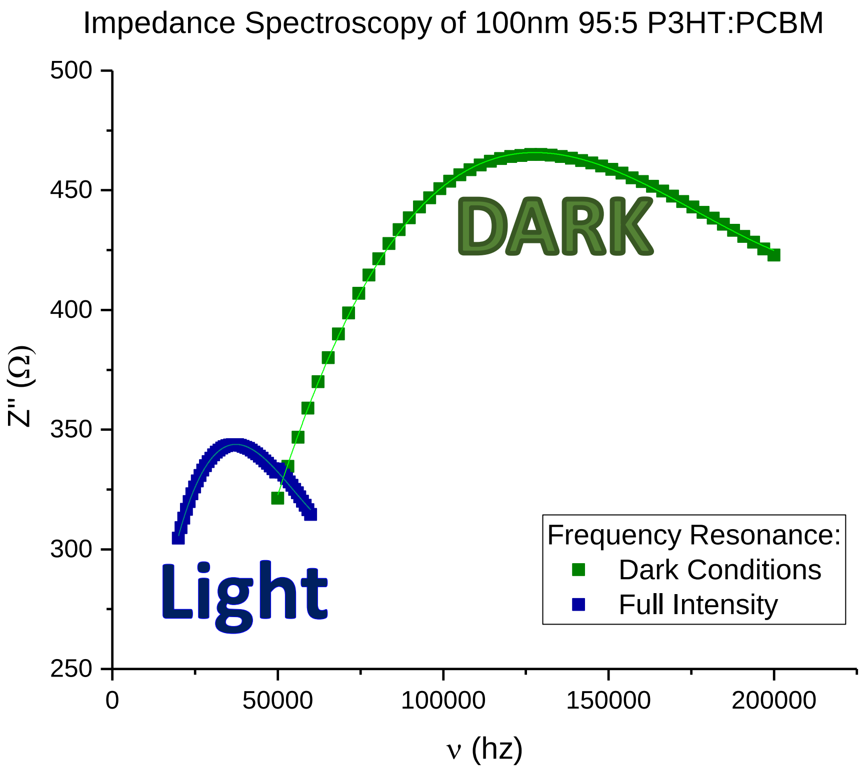
  comes from change in C

  from change in ε
- Measurable via Impedance Spectroscopy.
- $\Delta\upsilon = \Delta\upsilon_{Light} - \Delta\upsilon_{Dark}$

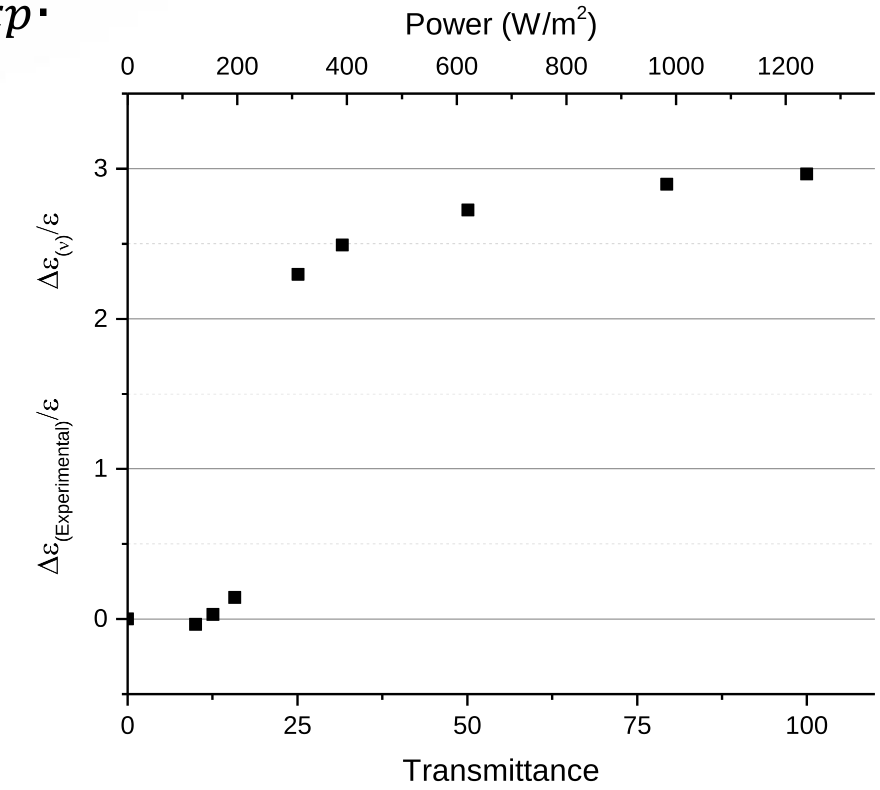


Impedance Spectroscopy

- Sweeps over a range of frequencies
- Finds Imaginary Impedance $Z'' = \frac{1}{c\omega i}$ as a function of frequency.
- Can find resonance frequency and hence $\Delta\varepsilon_{Exp}$.



Impedance Spectroscopy data showing highly reproducible frequency shifts between active and dark states.



$\Delta\varepsilon_{Exp}$ vs % of light (100% = 1234Wm^{-2})

$$\boldsymbol{\Delta\varepsilon = 0.1}\ \text{(unsaturated)}$$

Impedance Spectroscopy –REPRODUCIBLE!

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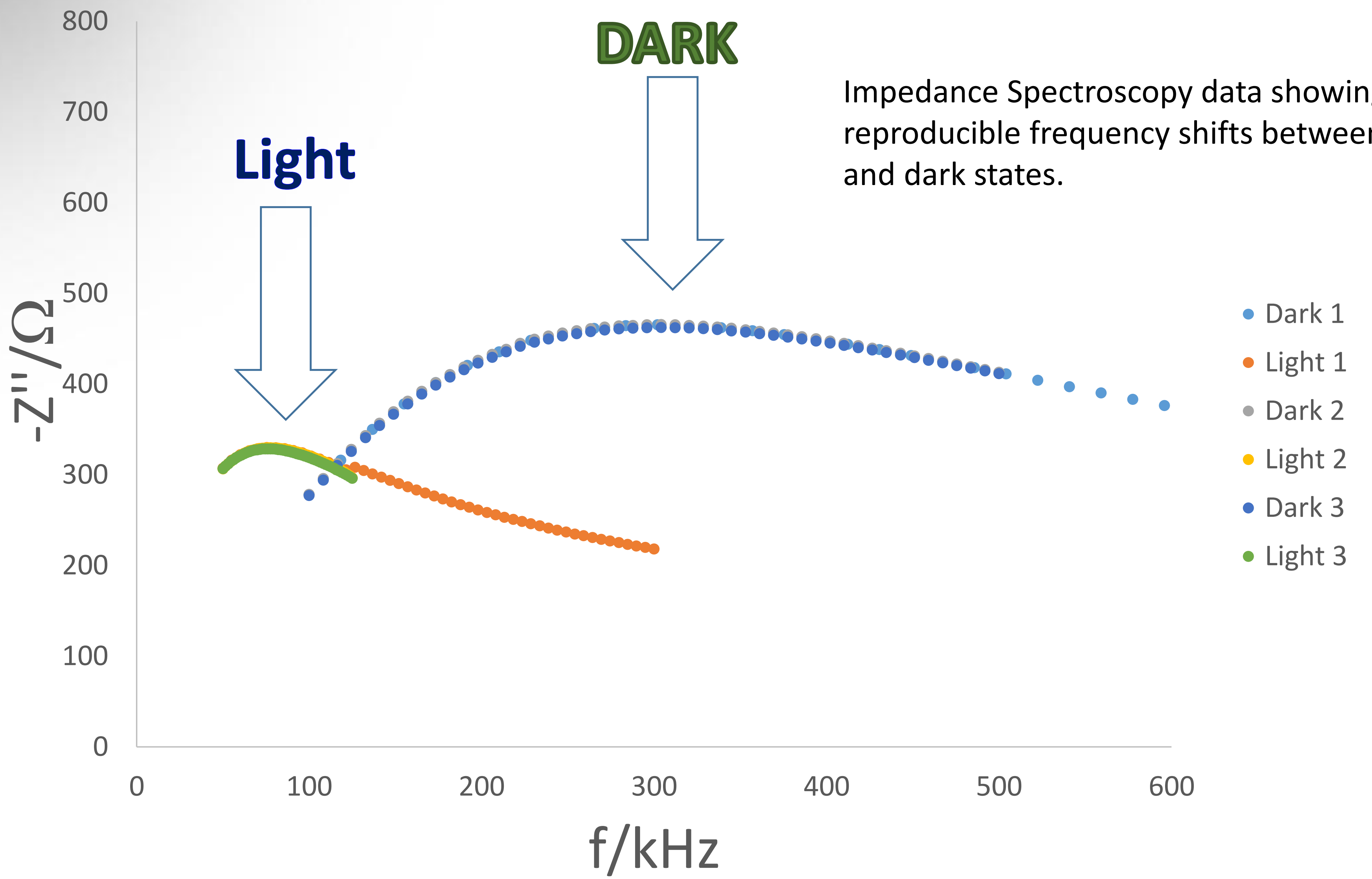
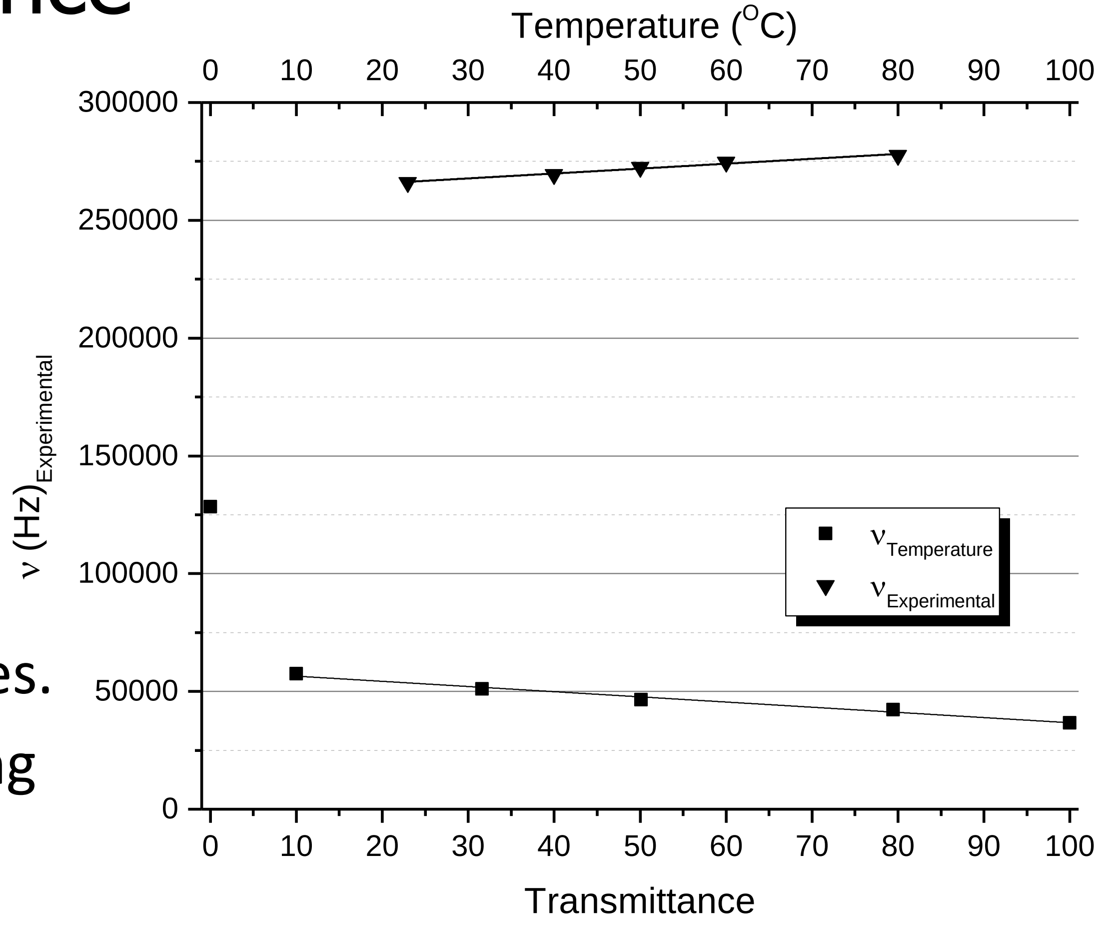


Impedance Spectroscopy data showing highly reproducible frequency shifts between active and dark states.

Temperature Dependence

- Mobility is highly dependant on temperature, T:
- $\mu_{(T,E)} = \mu_{(T,E=0)} e^{\gamma_{(T)}\sqrt{E}}$
- From Graph:
    - As T increases, υ increases.
    - As Light increases, υ decreases.
- So heating of device not affecting results.



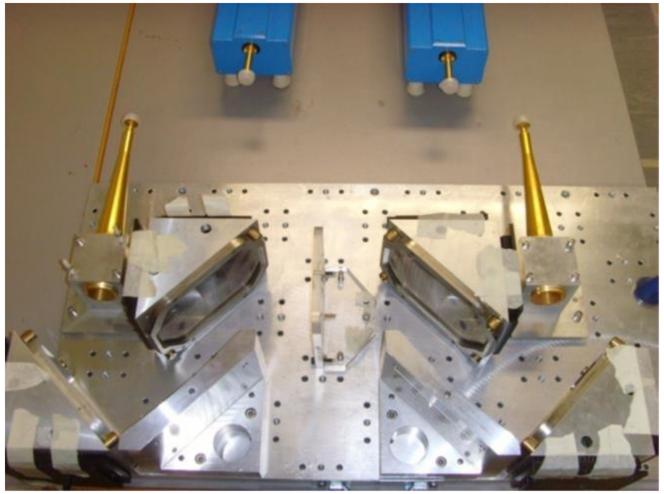
Left-bottom axis – Frequency resonance against % light (100% = 1234Wm^{-2})

Left-top axis – Frequency resonance against temperature.

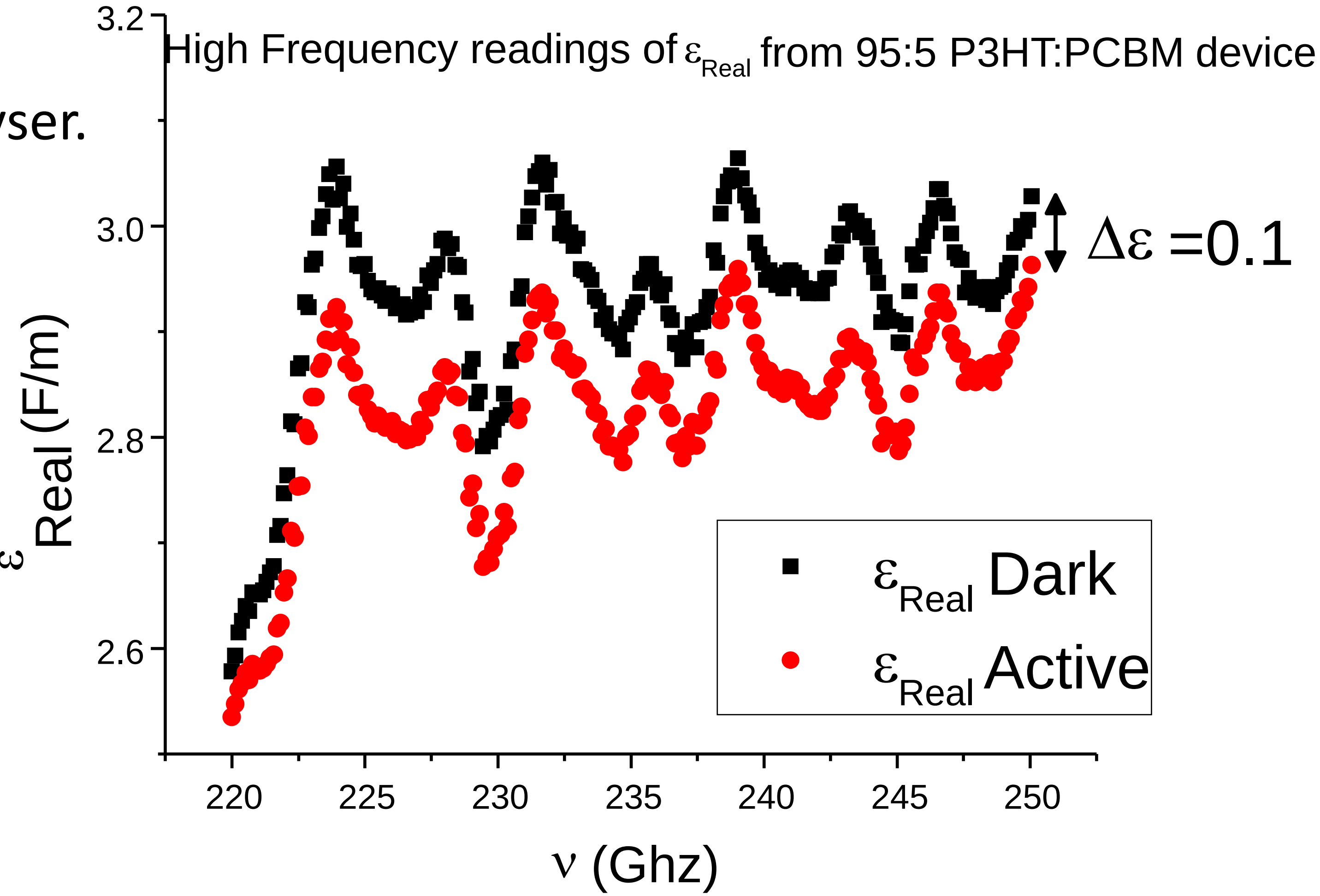
T. Kreouzis *et. al.* Physical Review B 73 235201 (2006)

$\Delta\varepsilon_{Experimental} \Rightarrow \Delta\varepsilon_{GHz}$

- Can measure at GHz frequencies.
- Uses free space propagation on quasi-optical setup
  - mm-wave transition
  - Vector Network Analyser.



$$\Delta\boldsymbol{\varepsilon} = \mathbf{0.1}$$



A.S. Andy
School of Electronic Engineering and Computer Science
Queen Mary, University of London

$\Delta\varepsilon_{Theory}\ vs\ \Delta\varepsilon_{Experimental}$

- $\Delta\varepsilon_{Theory}$

  $\Rightarrow \Delta\varepsilon_{Plasma} = \Delta\varepsilon_{(\mu,\Delta n)} \approx -10^{-9}$

  $\Rightarrow \Delta\varepsilon_{Space\ Charges} = \Delta\varepsilon_{(\mu,G)} \approx 10^{-26}$

  $\Rightarrow \Delta\varepsilon_{e-h} = \Delta\varepsilon_{(r_c,\Delta n_{e-h})} \leq +10^{+5}$

- $\Delta\varepsilon_{Experimental}$

  $\Rightarrow \Delta\varepsilon_{(\upsilon=100kHz)}$ *Low light Intensity* ≈ -0.1

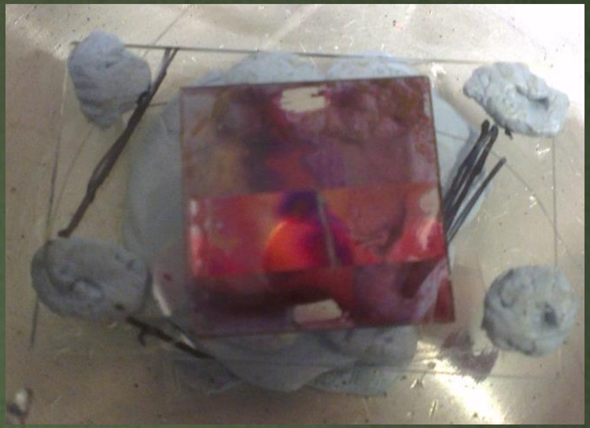
  $\Rightarrow \Delta\varepsilon_{(\upsilon=100kHz)}$ *High light Intensity* $\approx +1$

  $\Rightarrow \Delta\varepsilon_{(\upsilon=100GHz)}$ *High light Intensity* ≈ -0.1

  $\Rightarrow |\Delta\varepsilon|_{(\upsilon=100GHz)}$ *High light Intensity* ≈ 0.1

  (from phase shift)

Conclusions



An ITO:P3HT:PCBM:Al device

- Can optically induce dielectric changes in P3HT:PCBM
- Can measure said changes:
- $\Delta\varepsilon_{Exp} = \Delta\varepsilon_{(v)}$

- $$\begin{aligned} \Delta\varepsilon_{Theory} &\Rightarrow \Delta\varepsilon_{Plasma} &&= \Delta\varepsilon_{(\mu,\Delta n)} \quad ✗ \\ &\Rightarrow \Delta\varepsilon_{Space\ Charges} &&= \Delta\varepsilon_{(\mu,G)} \quad ✗ \\ &\Rightarrow \Delta\varepsilon_{e-h} &&= \Delta\varepsilon_{(r_c,\Delta n)} \quad \surd \end{aligned}$$

- Only theoretical model that can explain dielectric change is that of static charges ⇒ e-h pairs