Understanding Ion-Related Performance Losses in Perovskite-Based Solar Cells by Capacitance Measurements and Simulation

C. Messmer[1,2], J. Parion[3], C. V. Meza[3], S. Ramesh[3], M. Bivour[2], M. Heydarian[2], J. Schön[1,2], H. S. Radhakrishnan[3], M. C. Schubert[2], S. W. Glunz[1,2]

[1] INATECH, University of Freiburg, Germany
[2] Fraunhofer ISE, Germany
[3] IMEC, Belgium

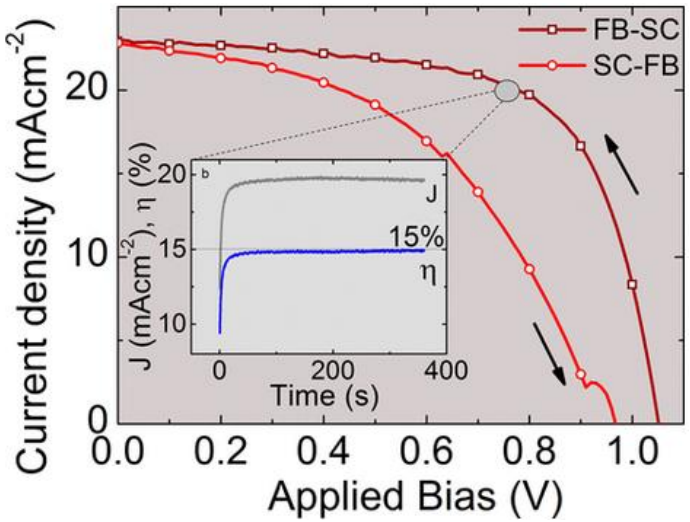
EU PVSEC, Vienna, Austria, 25th September 2024

Motivation

Understand Ion-related losses in Perovskite-Based Solar Cells (PSCs)

- **Hysteresis effects** impact the performance of PSCs [1-3]
- Origin: **Ion migration** within the perovskite absorber
- Goal: Understand and mitigate ion-related performance losses
- Approach: Small AC signal analysis [3,4]
  - Investigate frequency-dependent capacitances of PSCs
- **Learn about** device properties, e.g., ion diffusivities, built-in potential, …

[1] Snaith *et al.*

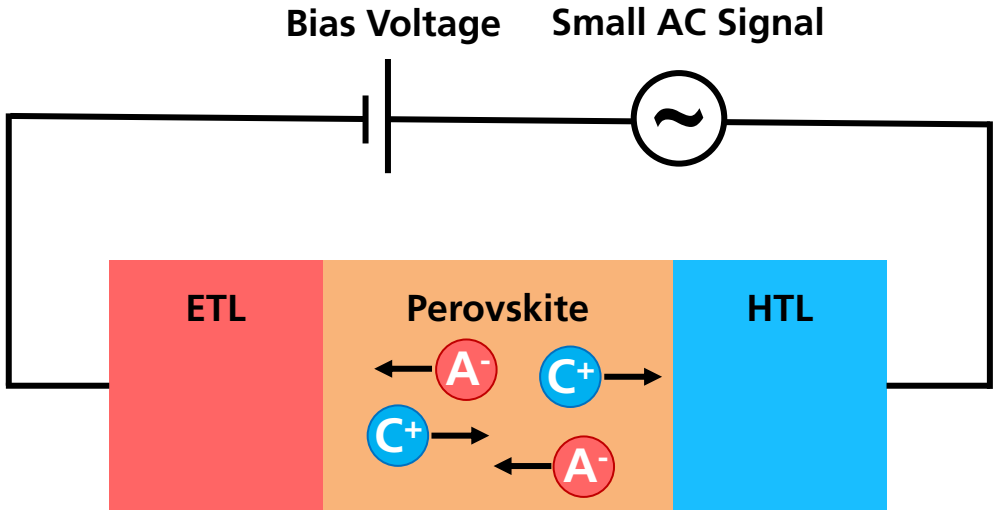


Experiments

Fraunhofer ISE

IMO-IMOMEC

UHASSELT imec



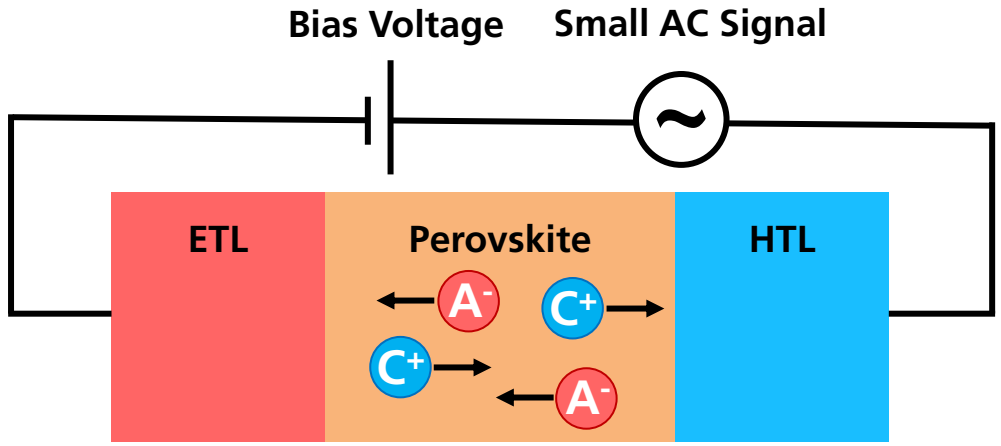
Simulation

universität freiburg

[1] Snaith *et al.*, „Anomalous Hysteresis in Perovskite Solar Cells", J. Phys. Chem. Lett. 2014
[2] Le Corre *et al.*, „Quantification of Efficiency Losses Due to Mobile Ions …," Sol. RRL, vol. 6(4), 2022
[3] Ravishankar *et al.*, "Multilayer Capacitances: How Selective Contacts Affect …," PRX Energy, vol. 1(1), 2022
[4] Recart, Cuevas, "Application of junction capacitance measurements…," IEEE Trans. Electron Dev., vol. 53(3), 2006

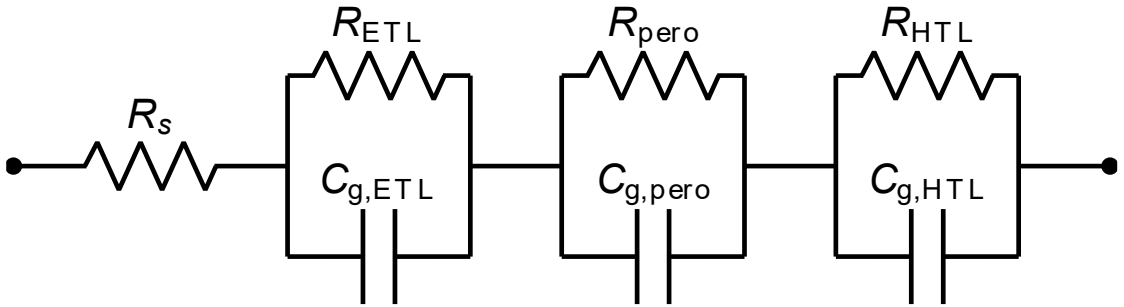
Modelling Approaches

Small AC signal analysis



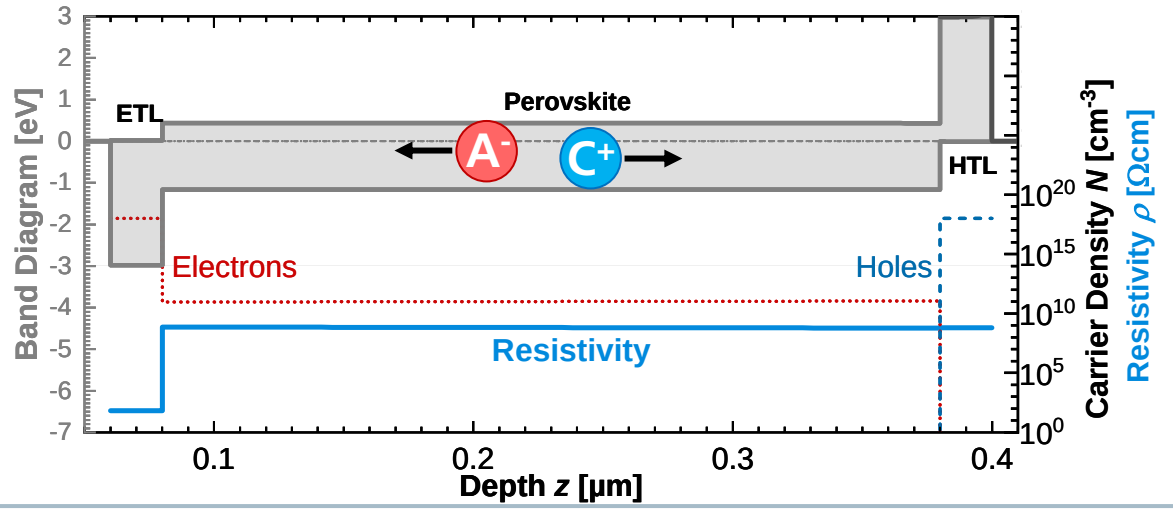
- **Equivalent-Circuit Modelling Approach:**
  - Each layer: RC circuit [1]
  - Geometrical capacitance (plate capacitor):

$$C_{g,L}/A = \epsilon_0 \epsilon_r / d_L$$



Equivalent Circuit

- **TCAD Modelling (this work):**
  - Detailed device modelling with Sentaurus TCAD [2]
    - Poisson equation and electron/hole drift diffusion (DD)
  - TCAD model was extended to AC signal analysis [3]
    - Compared to Eq.-Circuit Model
  - **Advantages**:
    - DD-Modelling of (several types of) ions incl. preconditioning
    - Study interfaces, full (tandem) stacks, tunneling transport, …
    - Same model for simulation of *JV* curves, …



TCAD Model

[1] Ravishankar *et al.*, „Multilayer Capacitances: …", PRX Energy, vol. 1, no. 1, 2022
[2] Messmer *et al.*, „Toward more reliable measurement procedures…", Prog Photovolt Res Appl. 2024
[3] Messmer *et al.*, „Understanding Ion-Related Performance Losses…", submitted to Solar RRL

universität freiburg

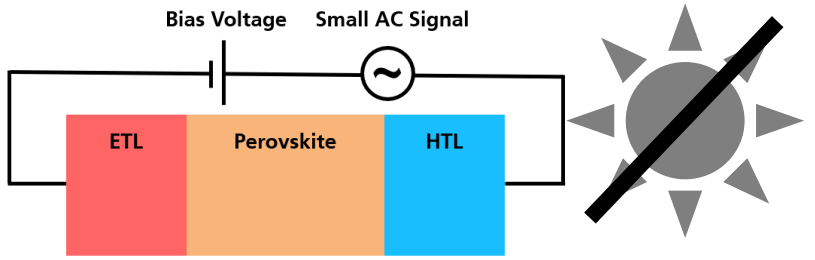
Fraunhofer ISE

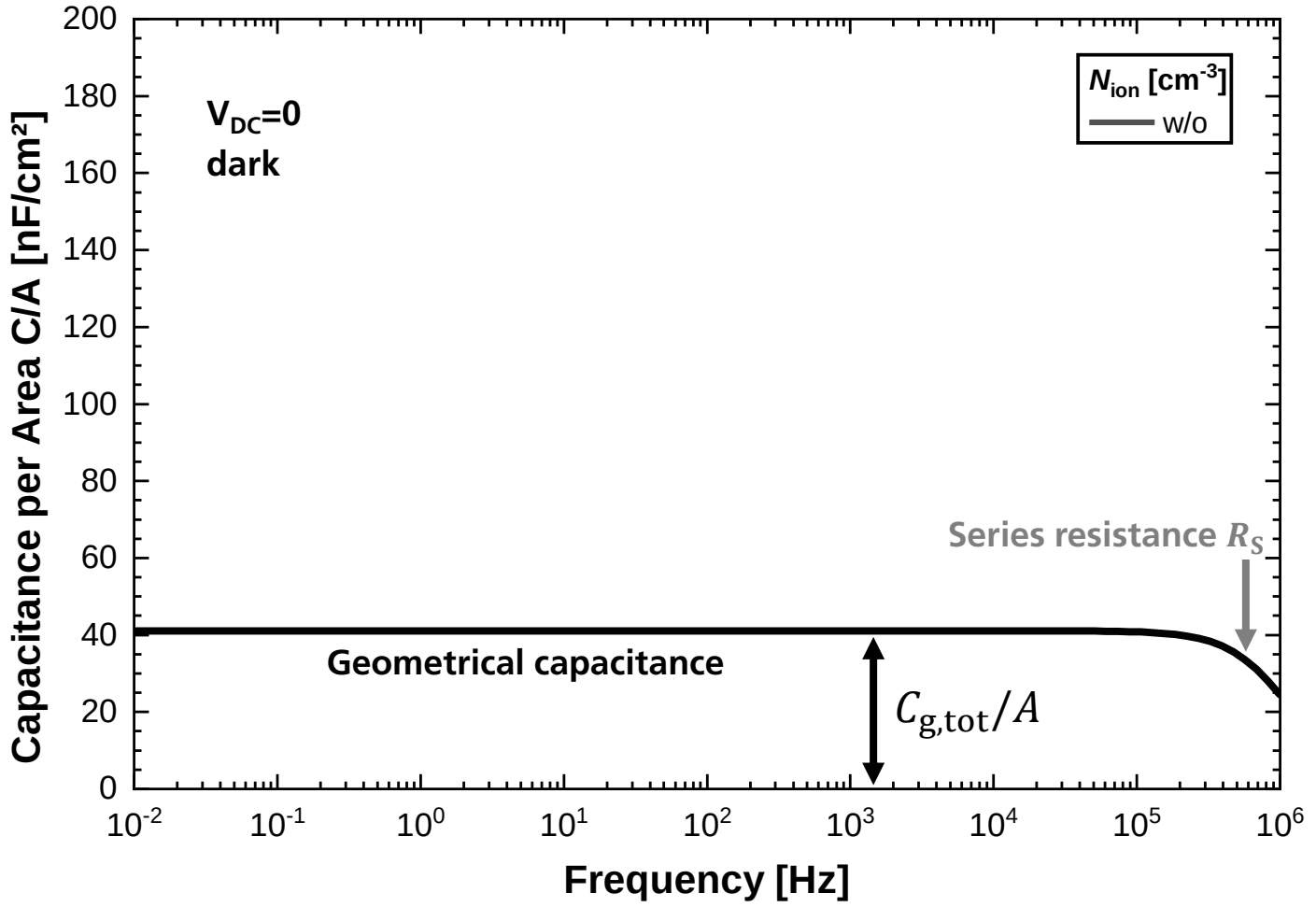
Ion-induced Capacitances in Perovskite Solar Cells

TCAD Simulation: Dark State

Presented at 41st EU PVSEC, 2024, Vienna, Austria

- Dark state, w/o DC bias, w/o ions, varied AC frequency
  - Geometrical capacitances in series connection
  - High-frequency capacitance reduced by series resistance



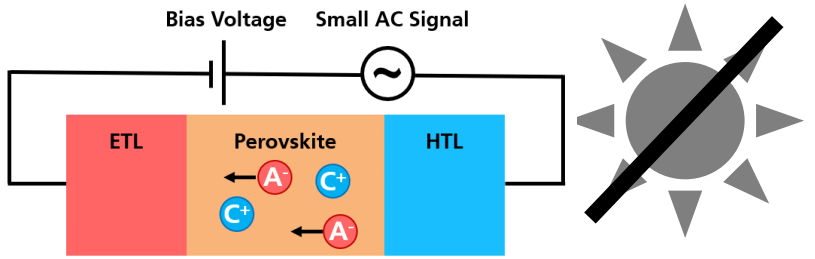


universität freiburg

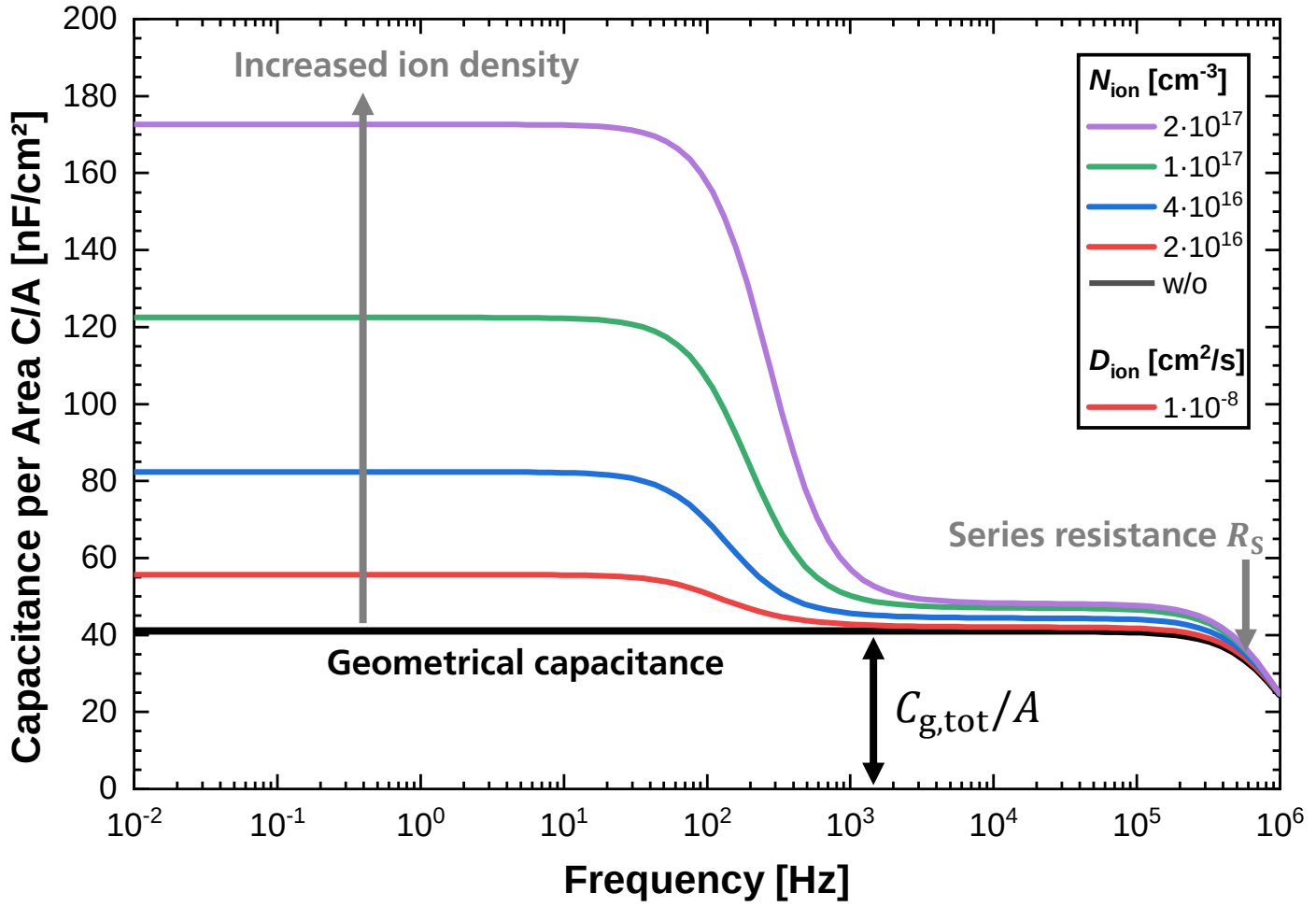
Fraunhofer ISE

Ion-induced Capacitances in Perovskite Solar Cells

TCAD Simulation: Dark State



- Dark state, w/o DC bias, w/o ions, varied AC frequency
  - Geometrical capacitances in series connection:
  - High-frequency capacitance reduced by series resistance
- Mobile anions with varied concentration (immobile cations)
  - Increased low-frequency response of capacitance



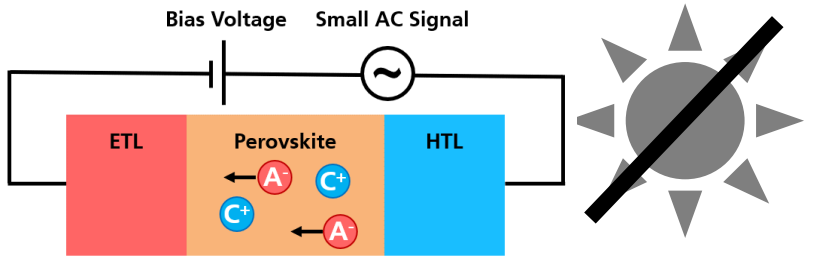
Presented at 41st EU PVSEC, 2024, Vienna, Austria

universität freiburg

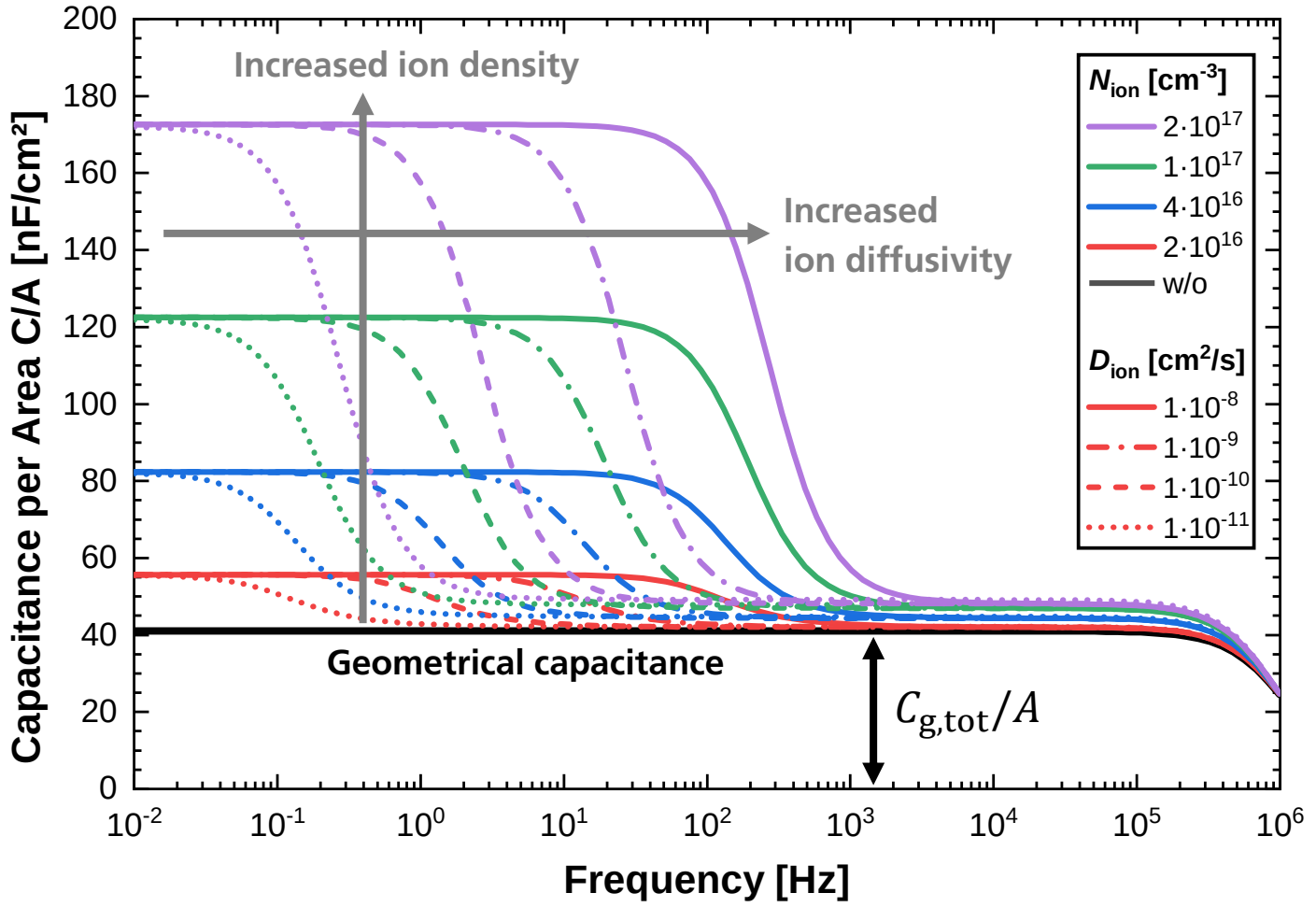
Fraunhofer ISE

Ion-induced Capacitances in Perovskite Solar Cells

TCAD Simulation: Dark State



- Dark state, w/o DC bias, w/o ions, varied AC frequency
  - Geometrical capacitances in series connection:
  - High-frequency capacitance reduced by series resistance
- Mobile anions with varied concentration (immobile cations)
  - Increased low-frequency response of capacitance
- Mobile anions with varied diffusivity
  - Characteristic frequency shifts

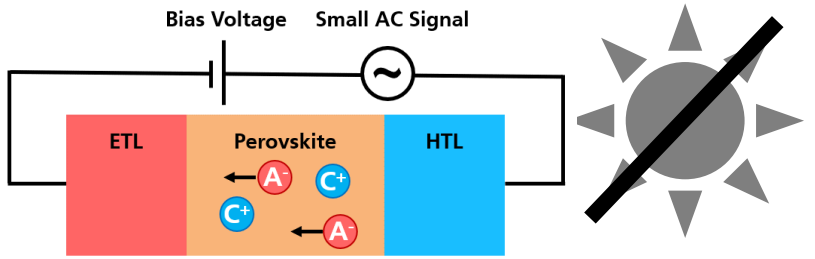


Presented at 41st EU PVSEC, 2024, Vienna, Austria

universität freiburg Fraunhofer ISE

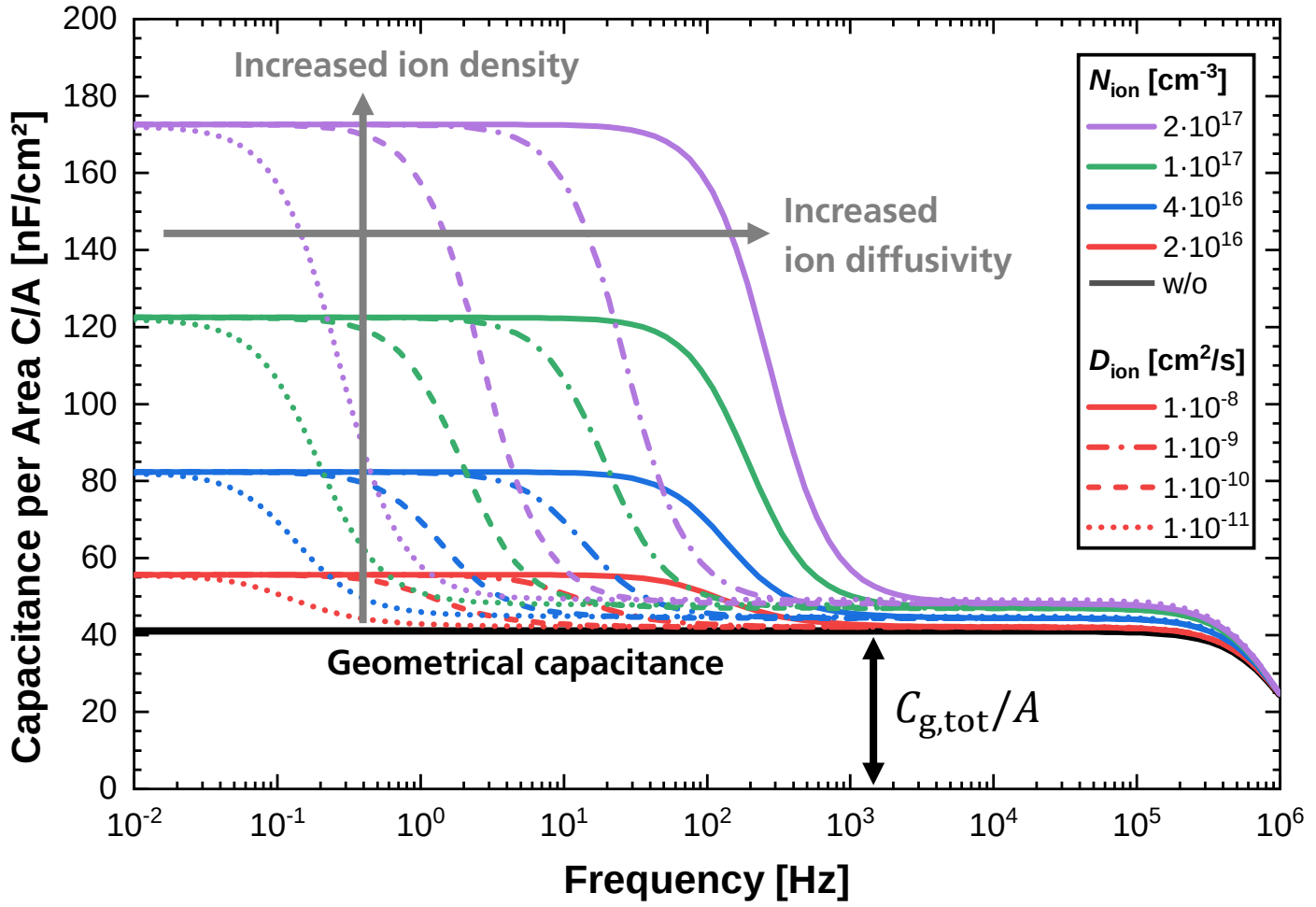
Ion-induced Capacitances in Perovskite Solar Cells

Experimental Evidence



- Perovskite single junction fabricated and measured at IMEC

IMO-IMOMEC
UHASSELT imec

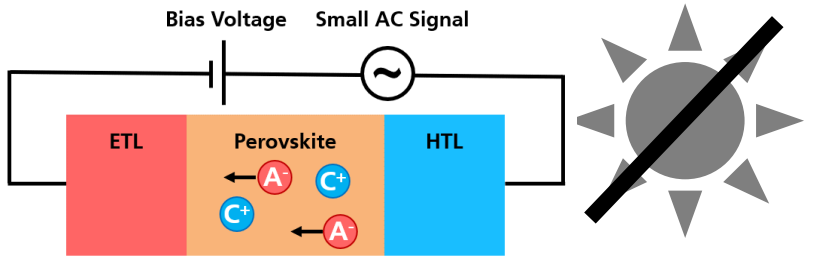


Presented at 41st EU PVSEC, 2024, Vienna, Austria

universität freiburg
Fraunhofer ISE

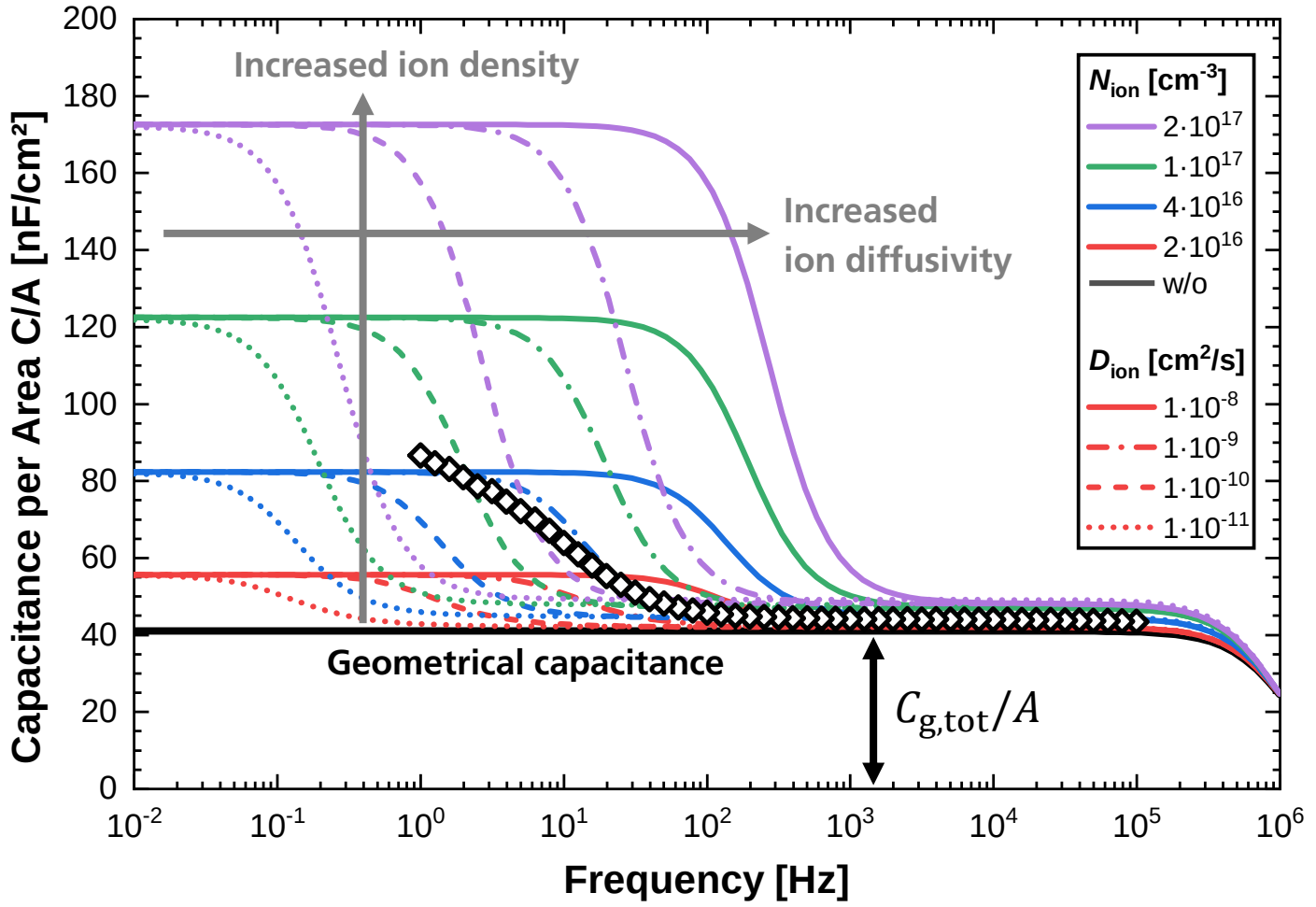
Ion-induced Capacitances in Perovskite Solar Cells

Experimental Evidence



- Perovskite single junction fabricated and measured at IMEC
- What can we deduce from *C-f* characteristics?

IMO-IMOMEC
UHASSELT imec

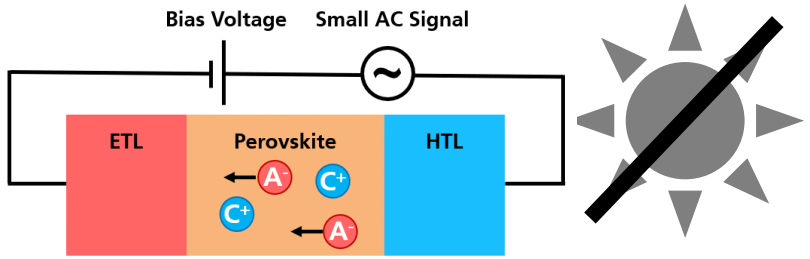


Presented at 41st EU PVSEC, 2024, Vienna, Austria

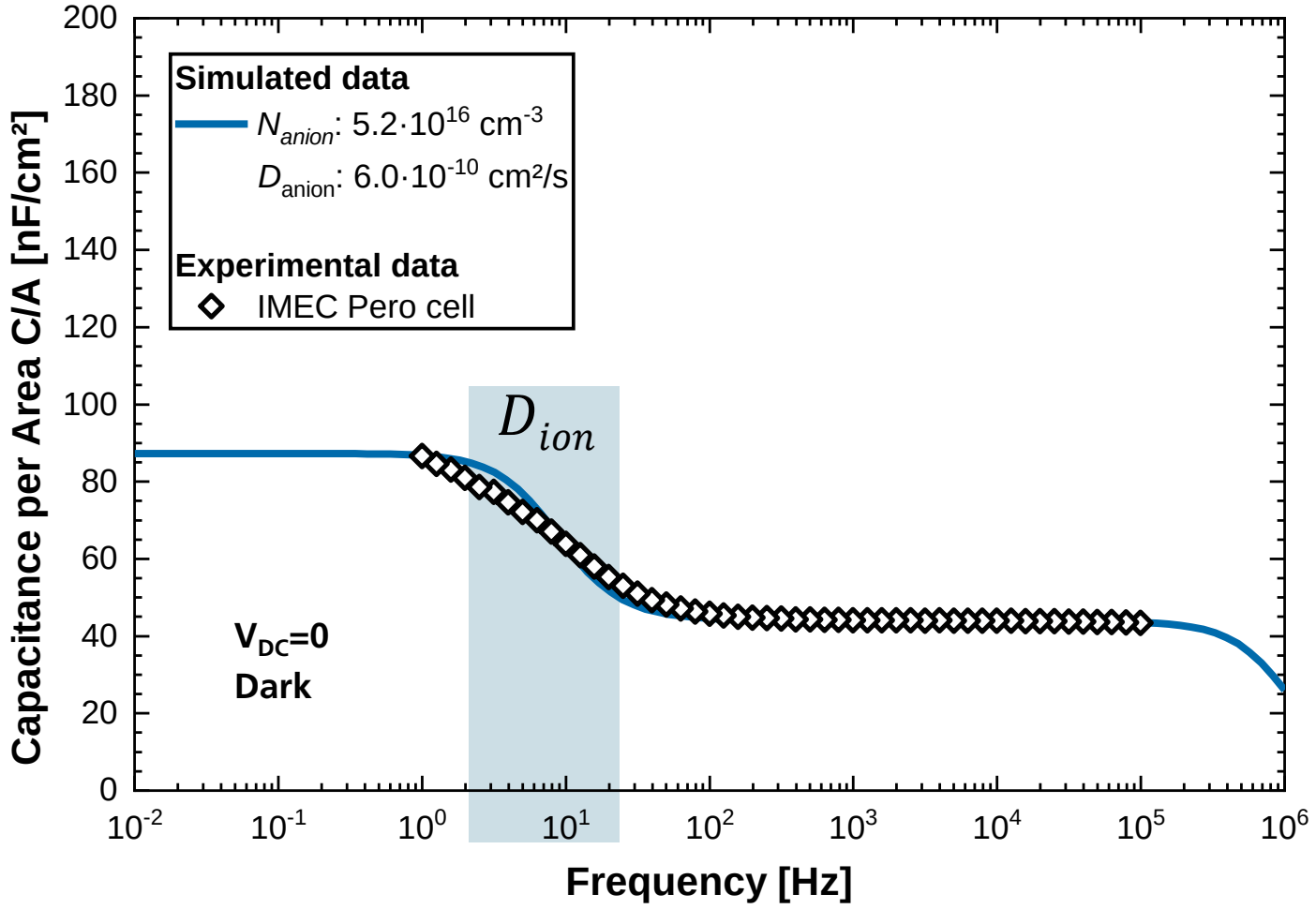
universität freiburg
Fraunhofer ISE

Ion-induced Capacitances in Perovskite Solar Cells

Experimental Evidence



- Perovskite single junction fabricated and measured at IMEC
- What can we deduce from *C-f* characteristics?
  - Characteristic frequency f, here around 10 Hz
    → **Ion diffusivity** of $6 \cdot 10^{-10}$ cm²/s



IMO-IMOMEC
UHASSELT imec

Presented at 41st EU PVSEC, 2024, Vienna, Austria

universität freiburg Fraunhofer ISE

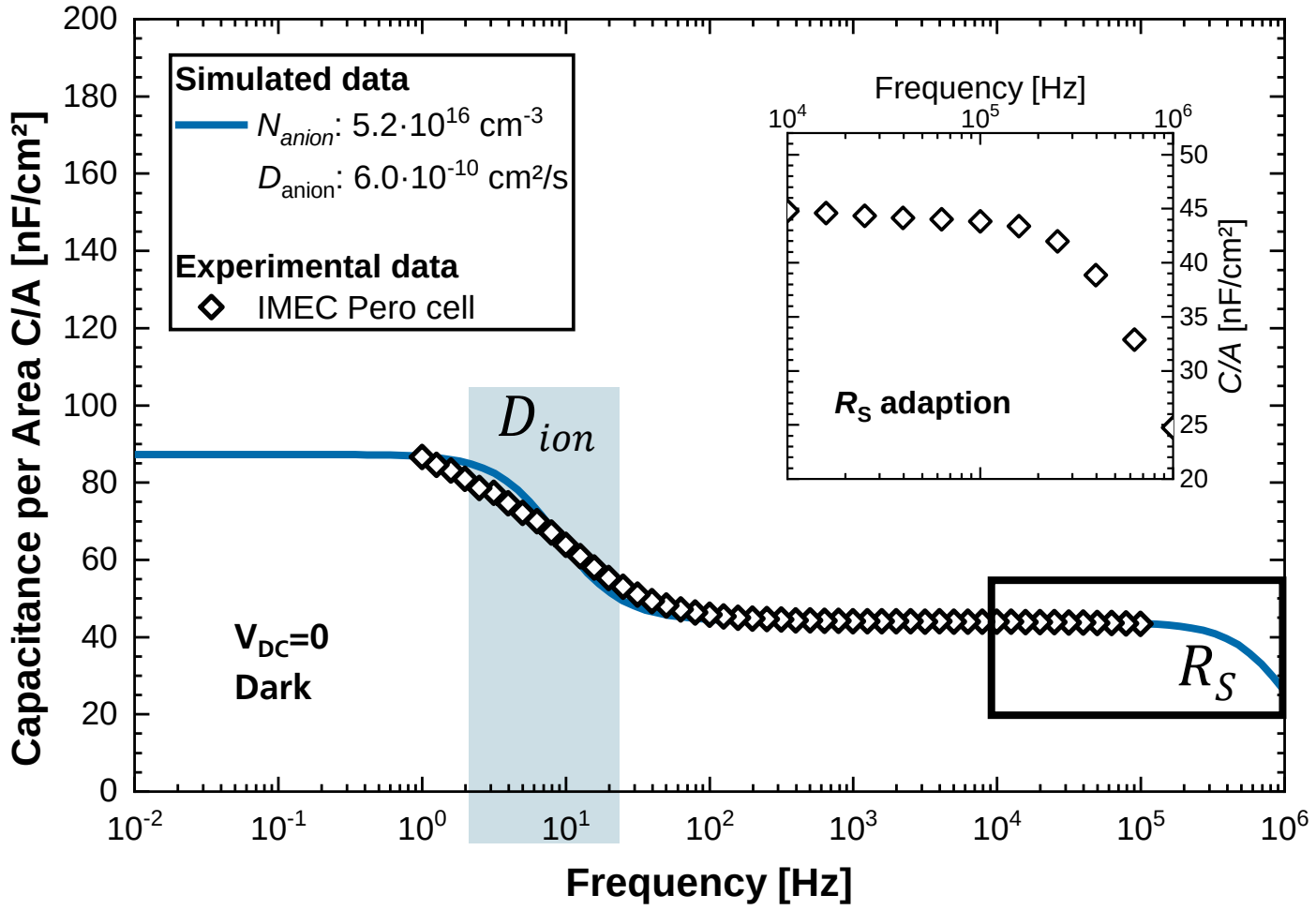
Ion-induced Capacitances in Perovskite Solar Cells

Experimental Evidence

Presented at 41st EU PVSEC, 2024, Vienna, Austria

- Perovskite single junction fabricated and measured at IMEC
- What can we deduce from *C-f* characteristics?
  - Characteristic frequency f, here around 10 Hz
    → **Ion diffusivity** of $6 \cdot 10^{-10}$ cm²/s
  - High-frequency regime (measured on similar sample)

IMO-IMOMEC
UHASSELT imec



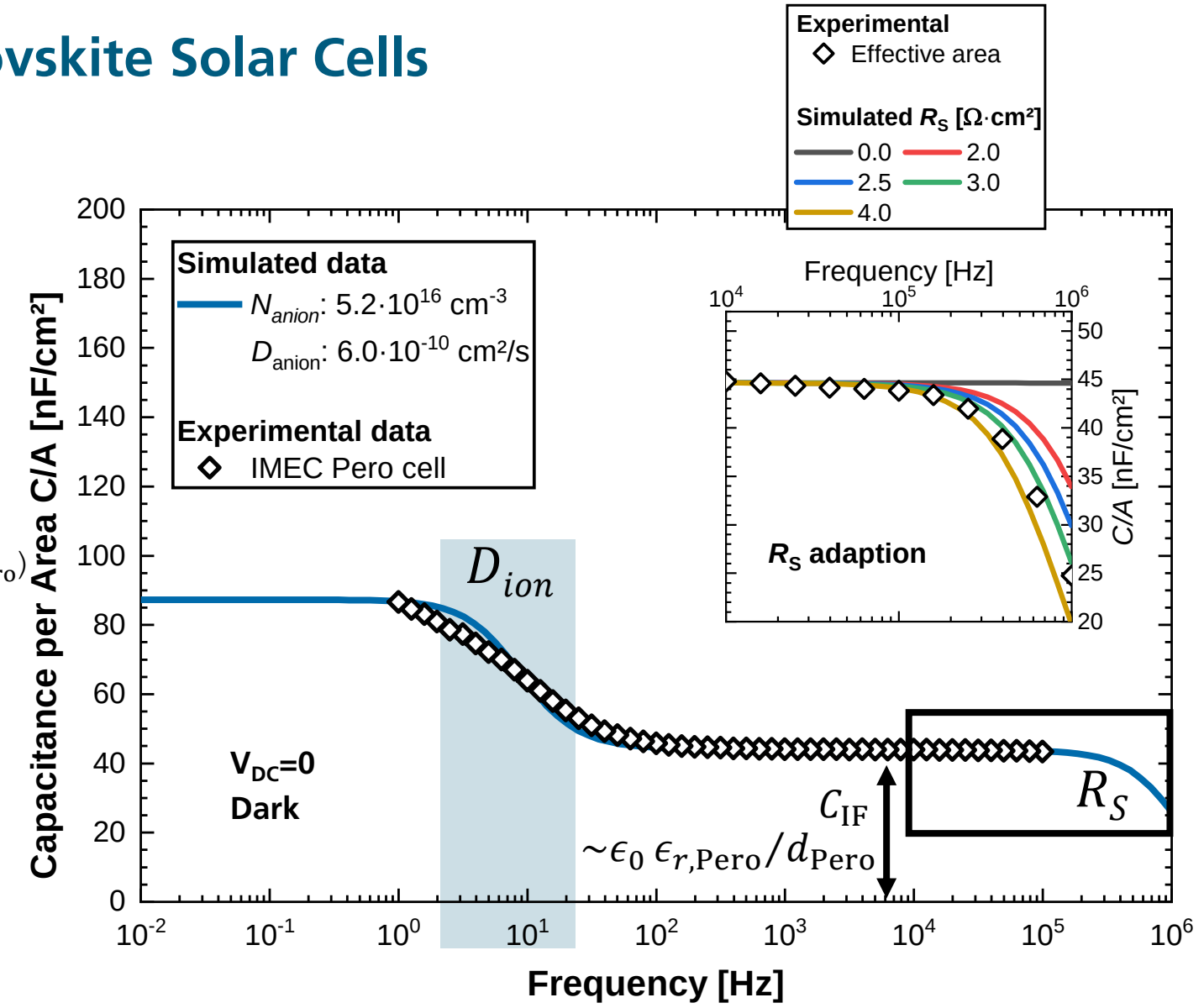
universität freiburg Fraunhofer ISE

Ion-induced Capacitances in Perovskite Solar Cells

Experimental Evidence

Presented at 41st EU PVSEC, 2024, Vienna, Austria

- Perovskite single junction fabricated and measured at IMEC
- What can we deduce from *C-f* characteristics?
  - Characteristic frequency f, here around 10 Hz
    → **Ion diffusivity** of $6 \cdot 10^{-10}$ cm²/s
  - High-frequency regime (measured on similar sample)
    → **Series resistance** of device is about 3 Ω·cm²
  - C_{IF} (for negligible capacitances of CTLs):
    → **Dielectric permittivity** of perovskite (for known d_{Pero})



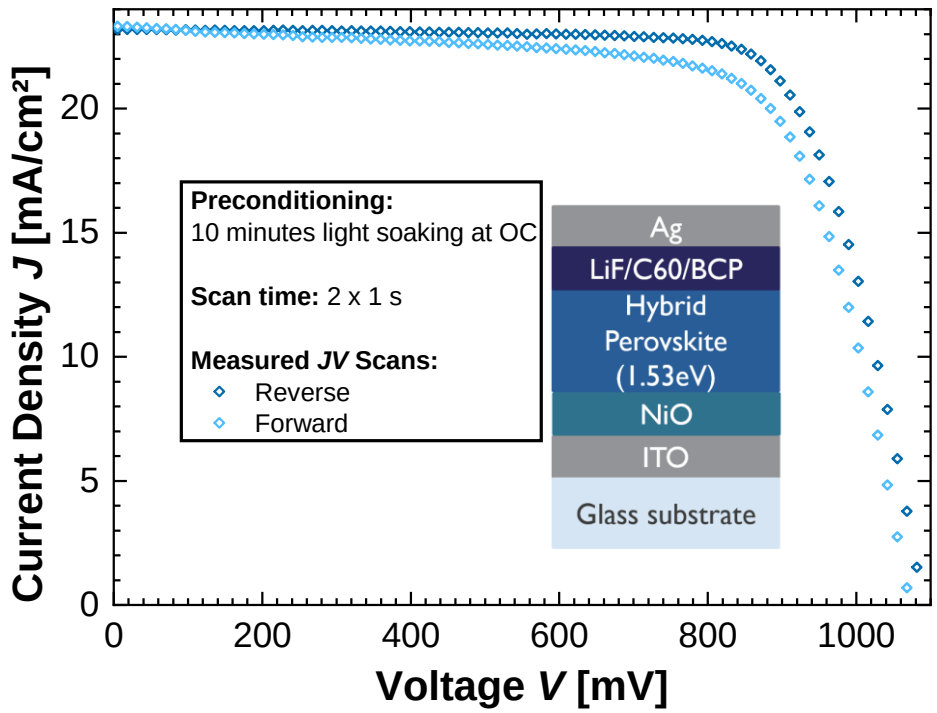
IMO-IMOMEC
UHASSELT imec

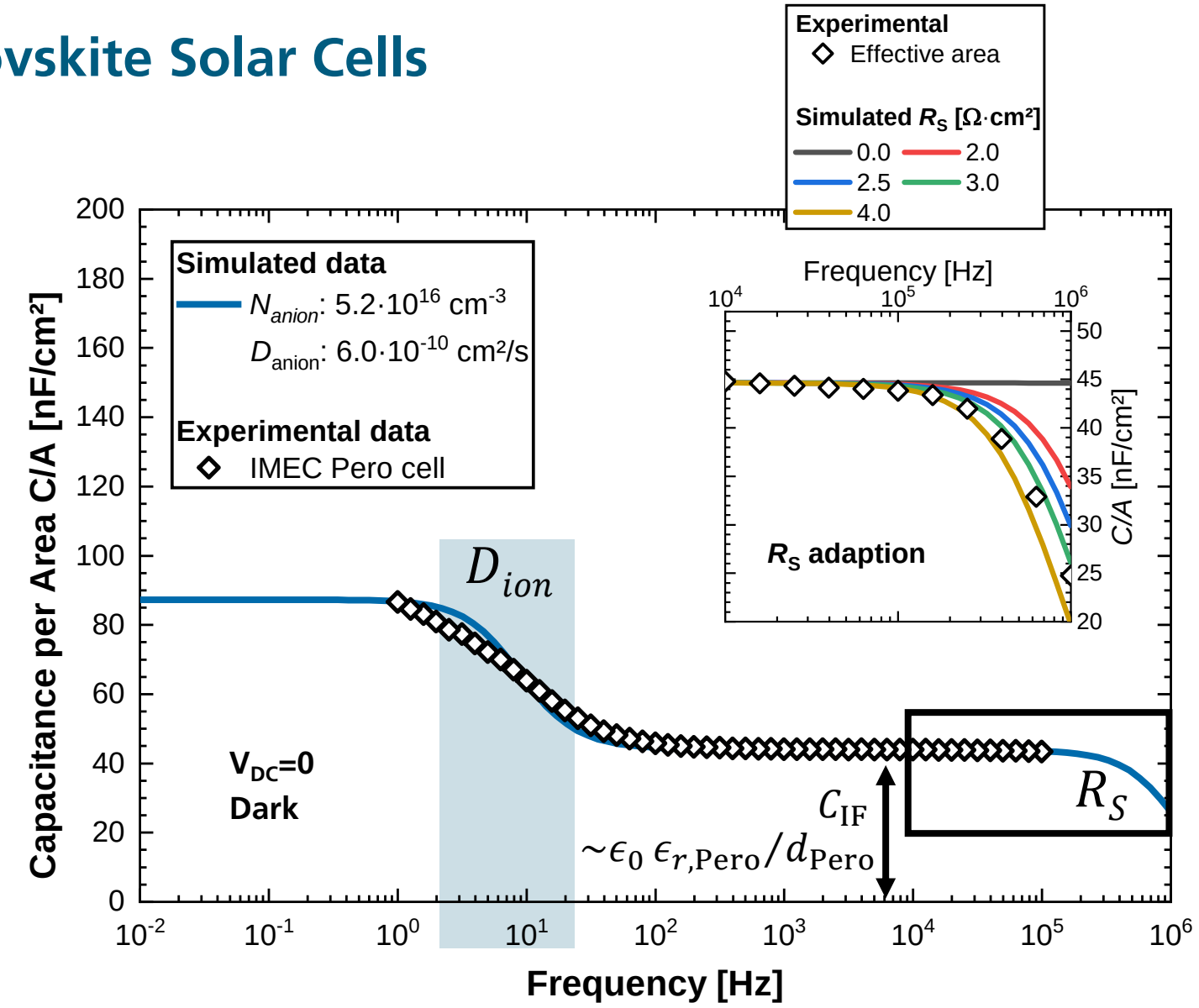
universität freiburg Fraunhofer ISE

Ion-induced Capacitances in Perovskite Solar Cells

Relation to *JV* Hysteresis

- Measured *JV* reverse and forward scan for same sample



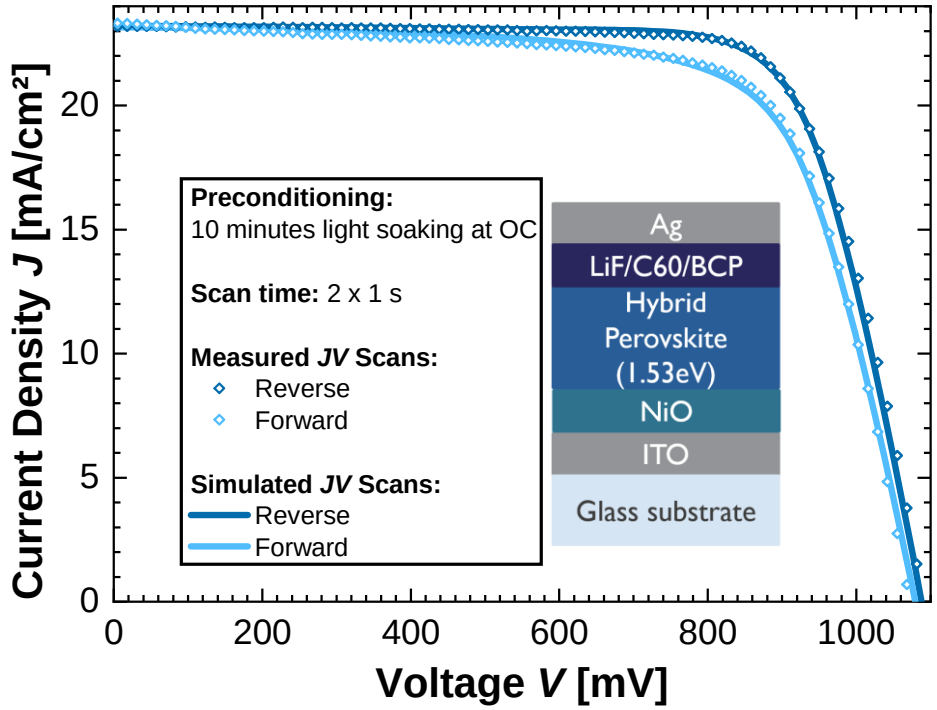


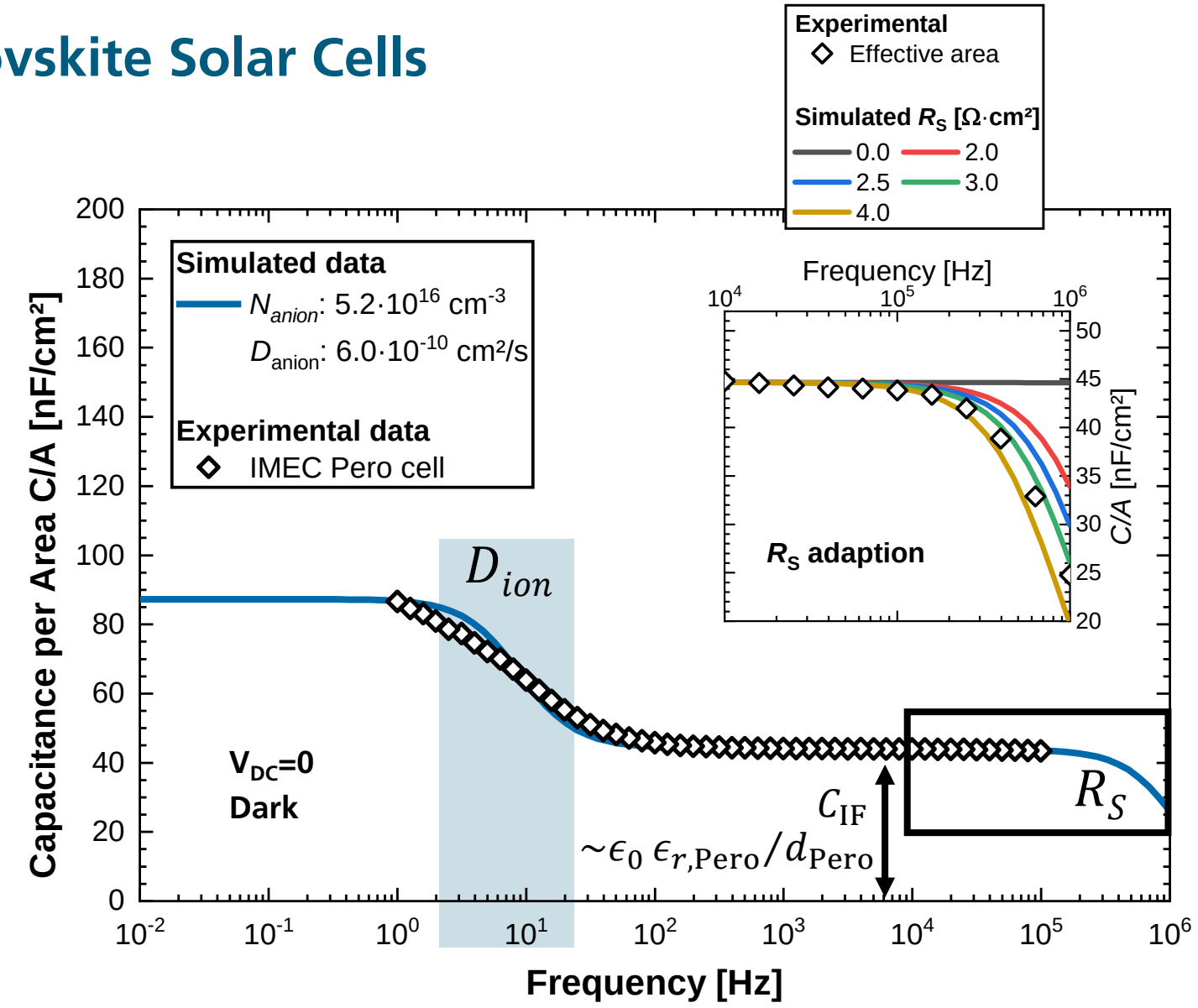
Presented at 41st EU PVSEC, 2024, Vienna, Austria

Ion-induced Capacitances in Perovskite Solar Cells

Relation to *JV* Hysteresis

- Measured *JV* reverse and forward scan for same sample
- Simulated *JV* scans with parameters from *C-f* analysis
  - Very good agreement indicating the relation between C-f characteristics and *JV* hysteresis

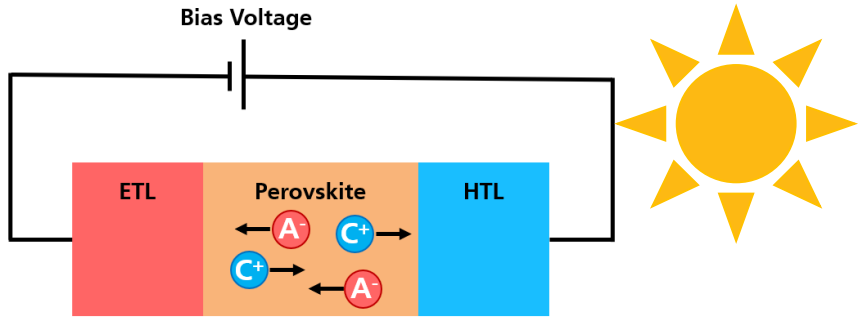




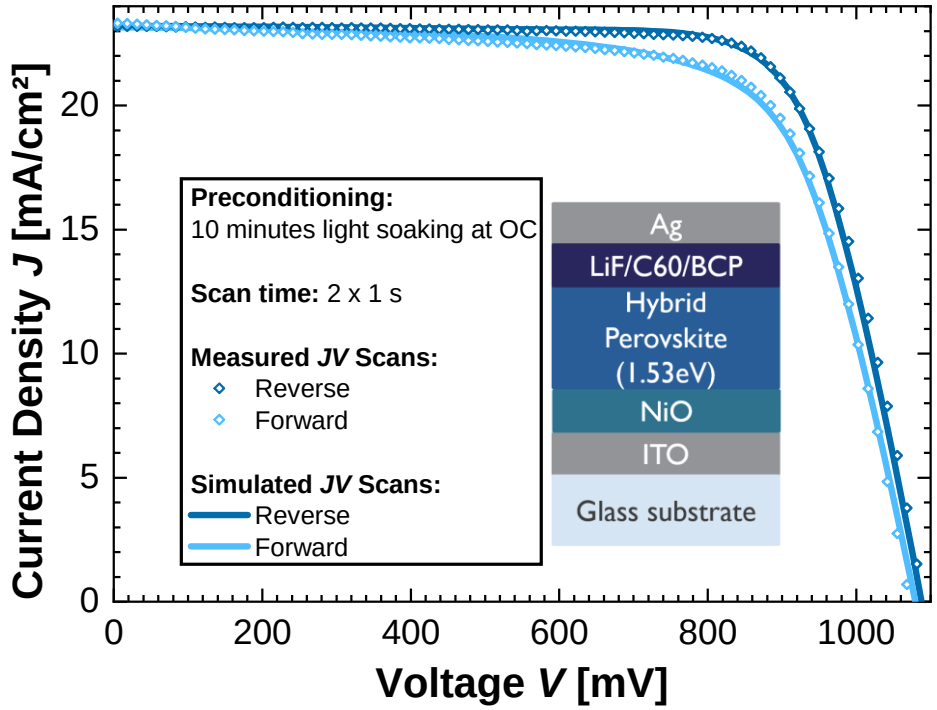
Presented at 41st EU PVSEC, 2024, Vienna, Austria

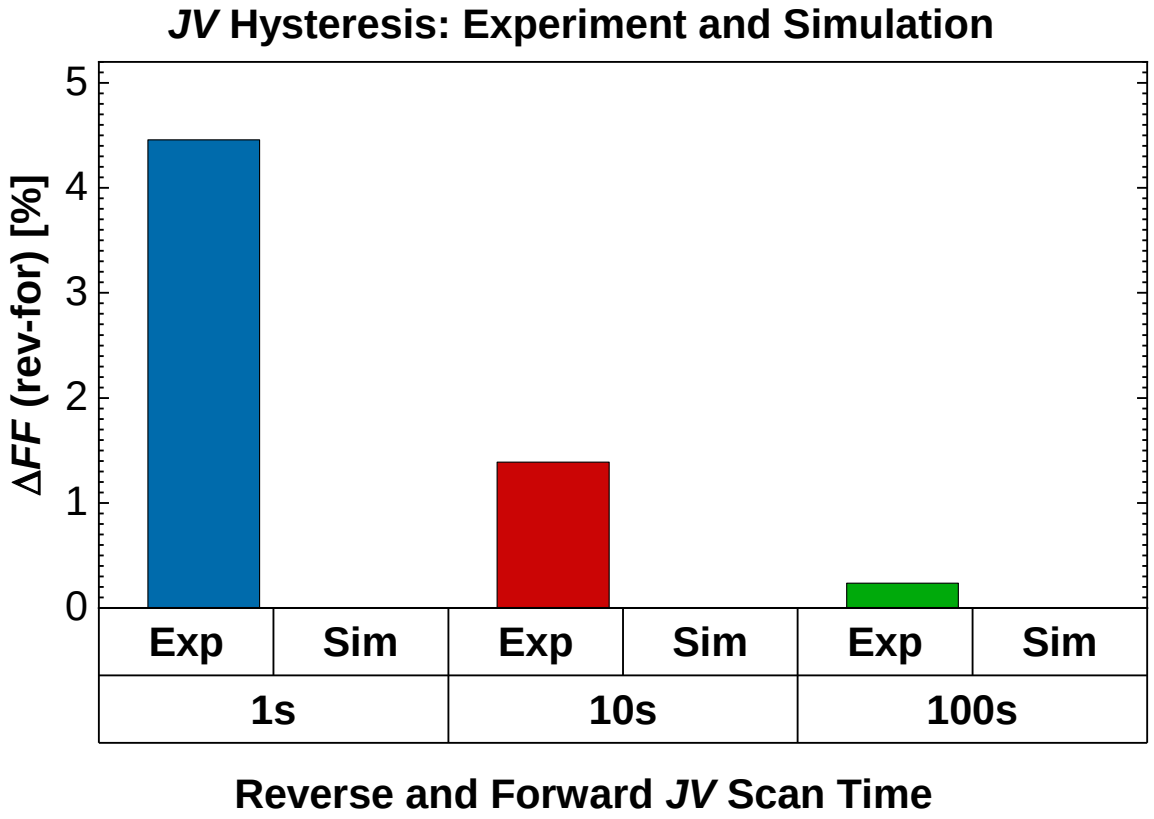
Ion-induced Capacitances in Perovskite Solar Cells

Relation to *JV* Hysteresis



- Measured *JV* reverse and forward scan for same sample
- Simulated *JV* scans with parameters from *C-f* analysis
  - Very good agreement indicating the relation between C-f characteristics and *JV* hysteresis



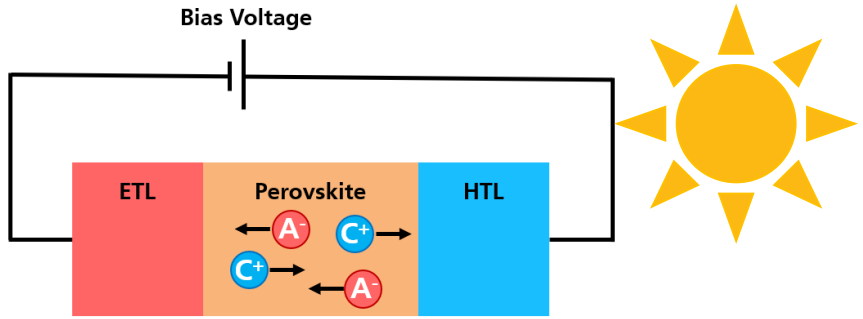


Presented at 41st EU PVSEC, 2024, Vienna, Austria

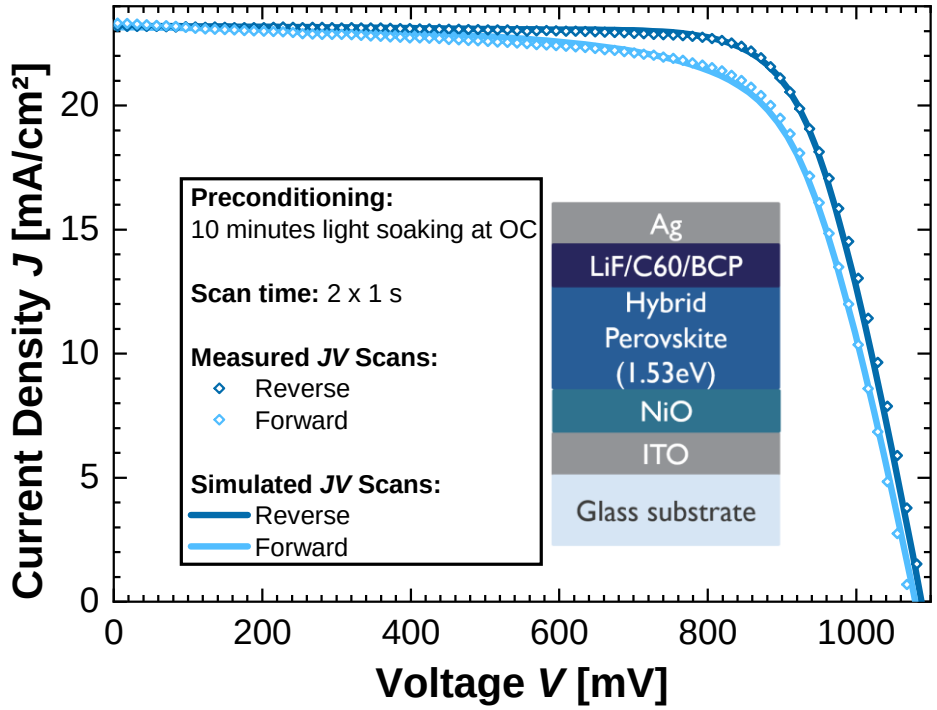
universität freiburg Fraunhofer ISE

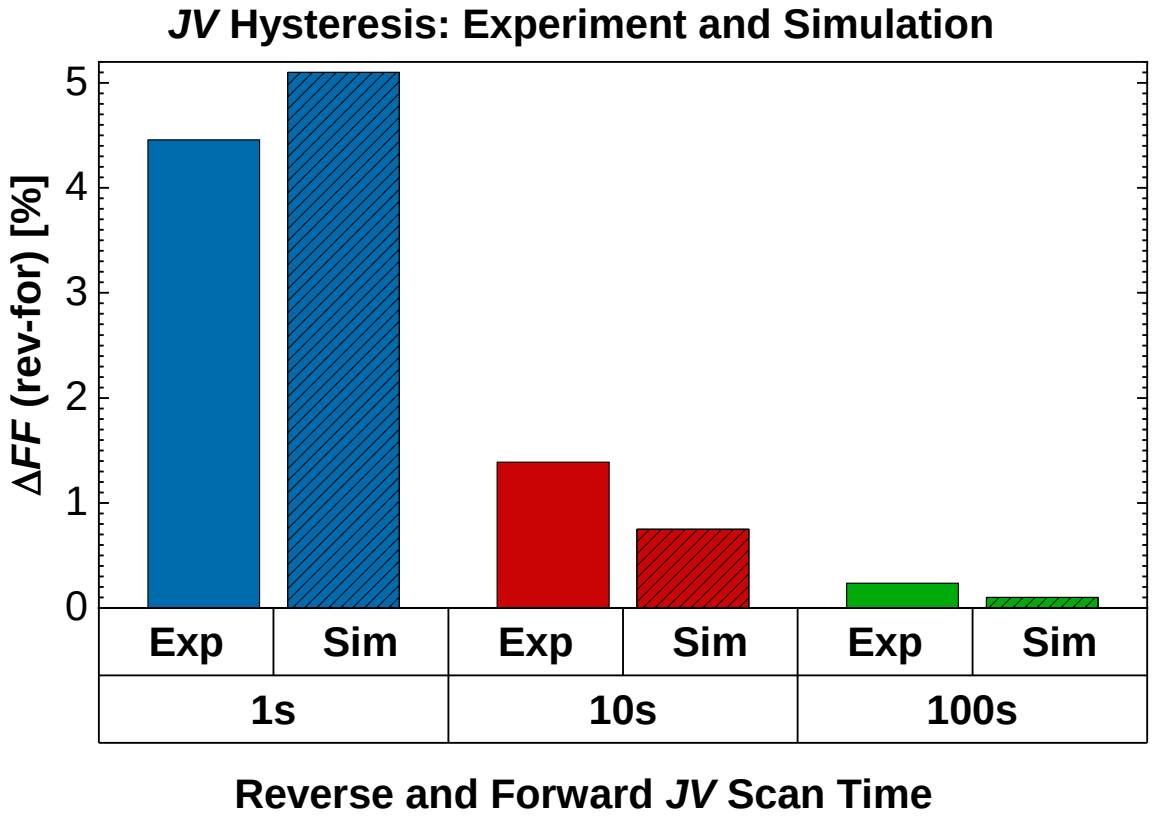
Ion-induced Capacitances in Perovskite Solar Cells

Relation to *JV* Hysteresis



- Measured *JV* reverse and forward scan for same sample
- Simulated *JV* scans with parameters from *C-f* analysis
  - Very good agreement indicating the relation between C-f characteristics and *JV* hysteresis for varied scan-times





Presented at 41st EU PVSEC, 2024, Vienna, Austria

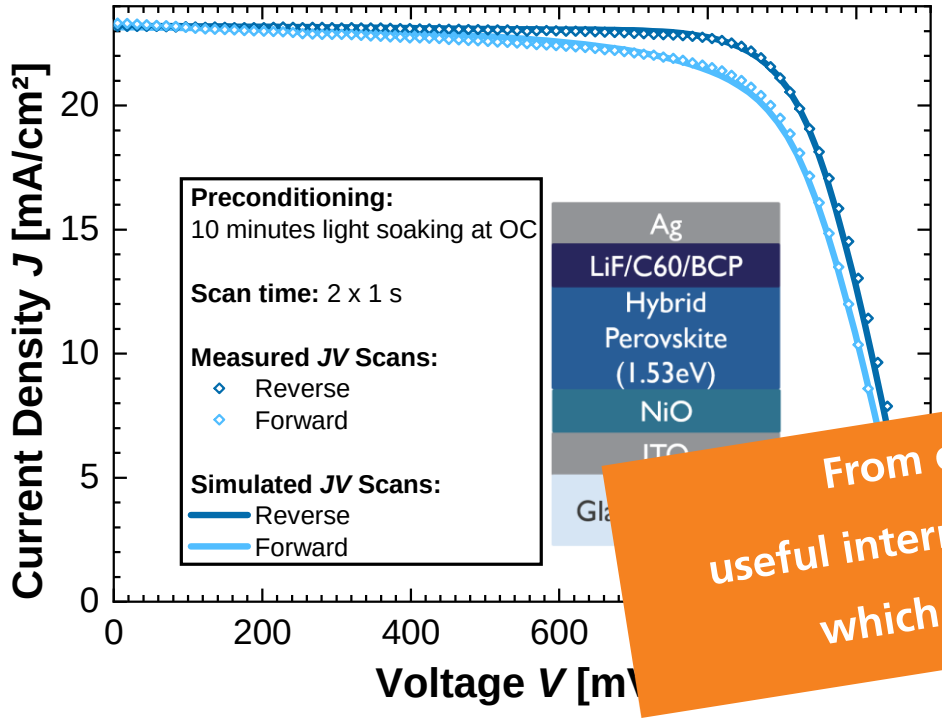
universität freiburg

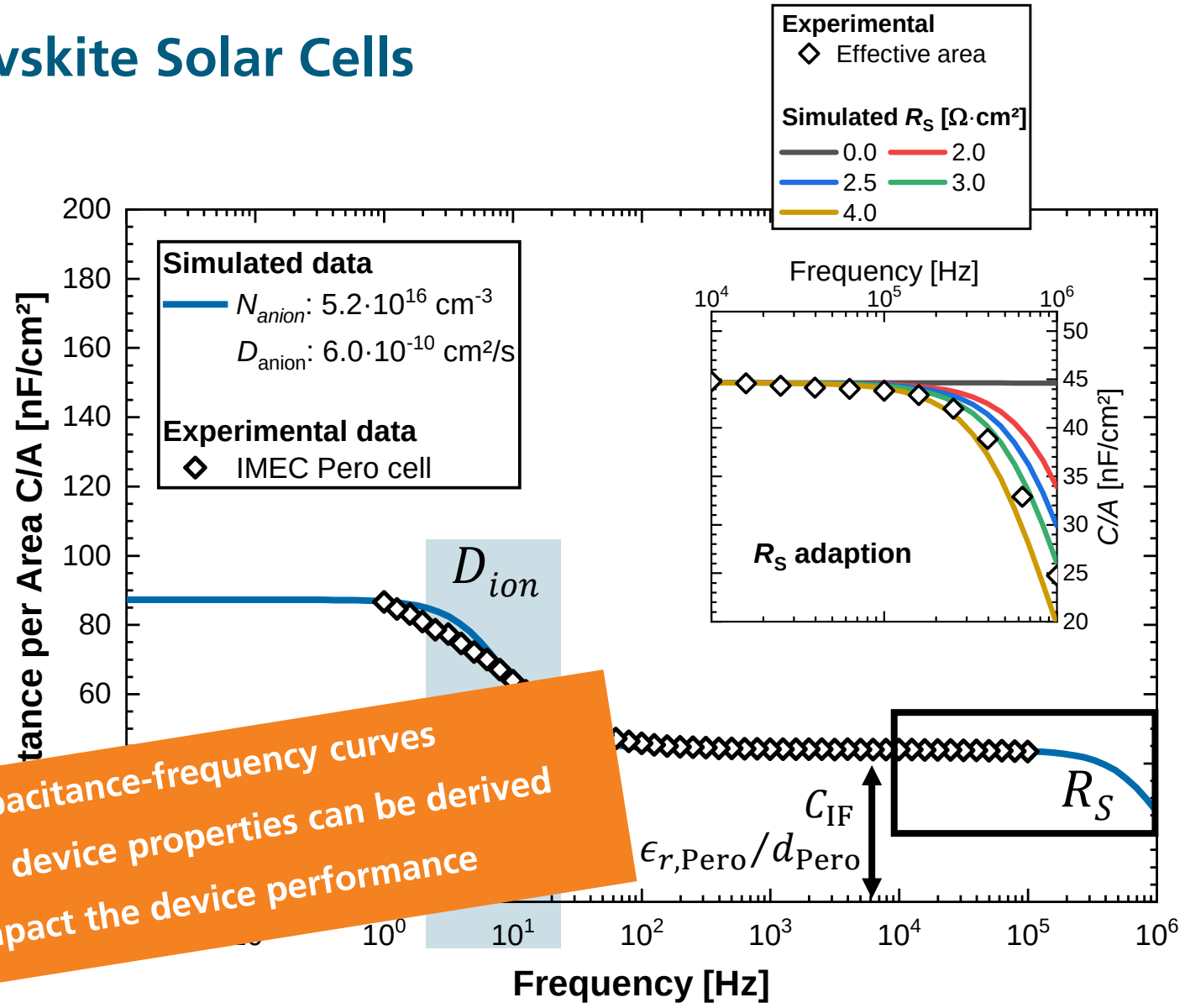
Fraunhofer ISE

Ion-induced Capacitances in Perovskite Solar Cells

Relation to *JV* Hysteresis

- Measured *JV* reverse and forward scan for same sample
- Simulated *JV* scans with parameters from *C-f* analysis
  - Very good agreement indicating the relation between C-f characteristics and *JV* hysteresis for varied scan-times





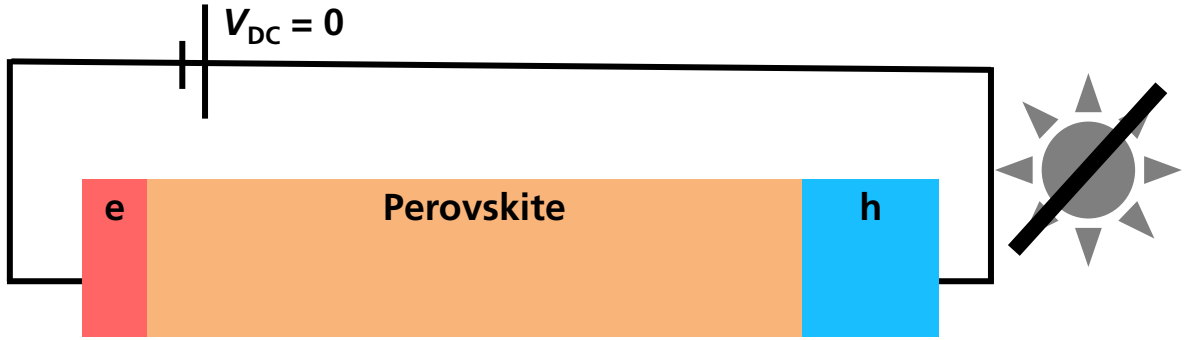
From capacitance-frequency curves useful internal device properties can be derived which impact the device performance

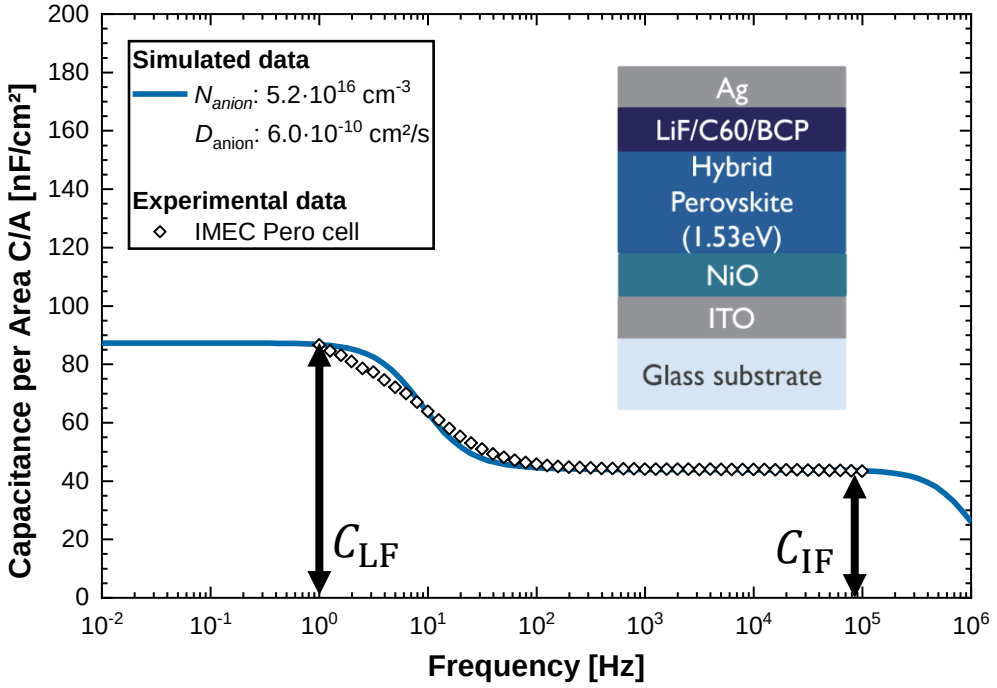
Presented at 41st EU PVSEC, 2024, Vienna, Austria

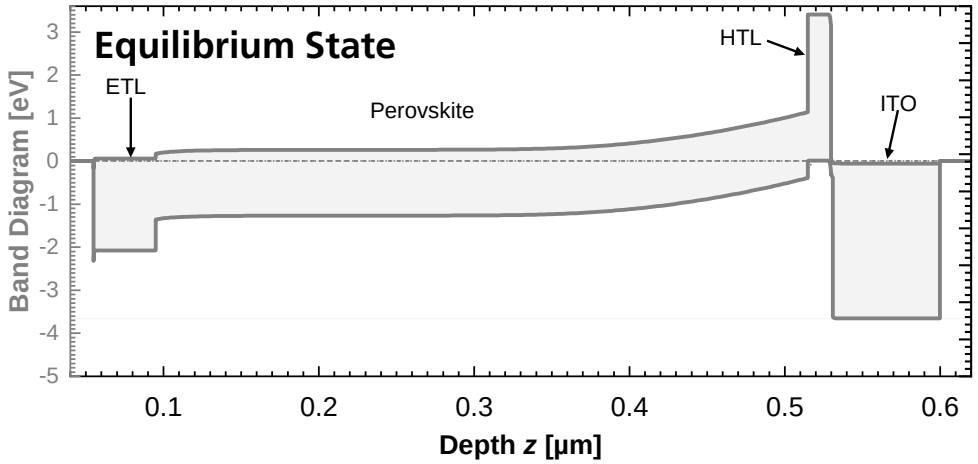
Ion-Induced Capacitances

In-Depth Analysis of the Capacitance Plateau

Presented at 41st EU PVSEC, 2024, Vienna, Austria





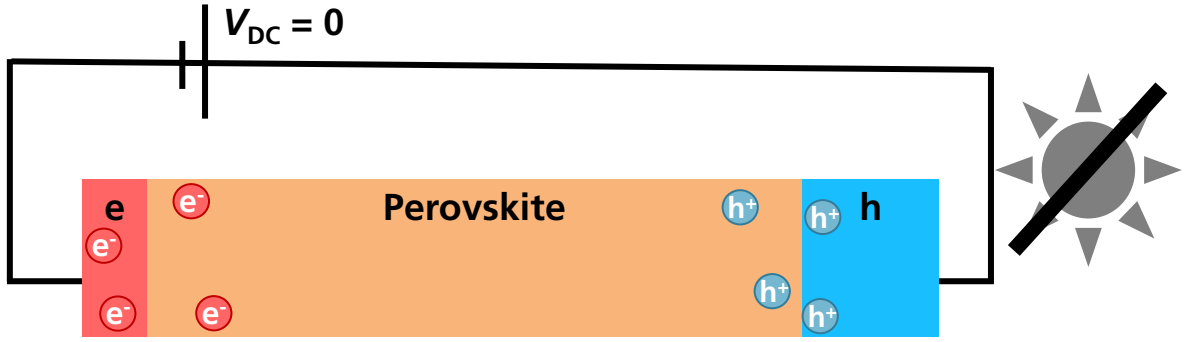


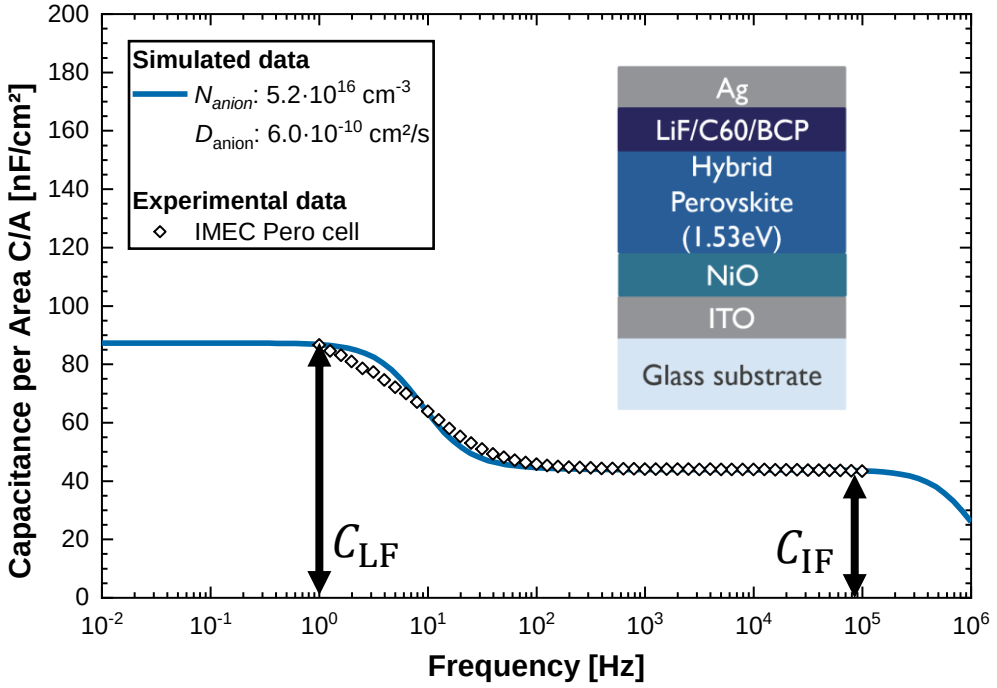
universität freiburg

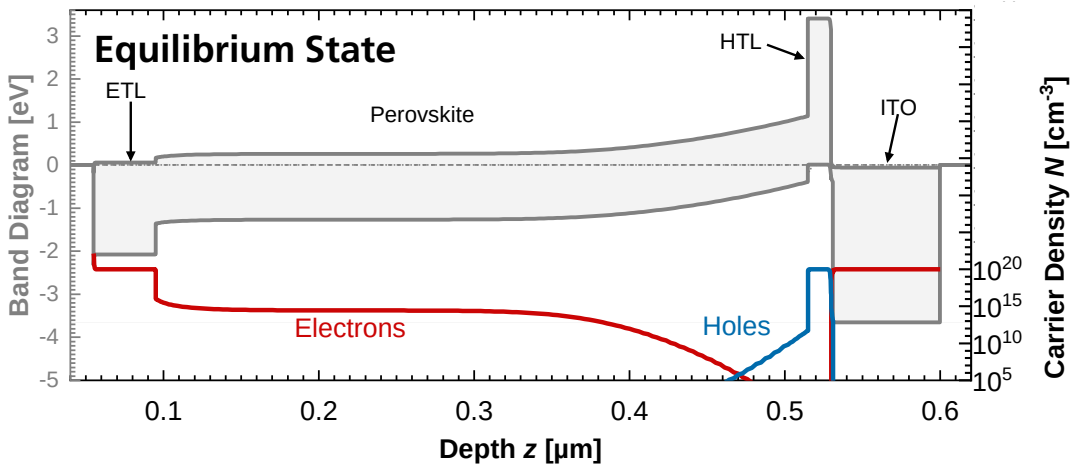
Fraunhofer ISE

Ion-Induced Capacitances

In-Depth Analysis of the Capacitance Plateau





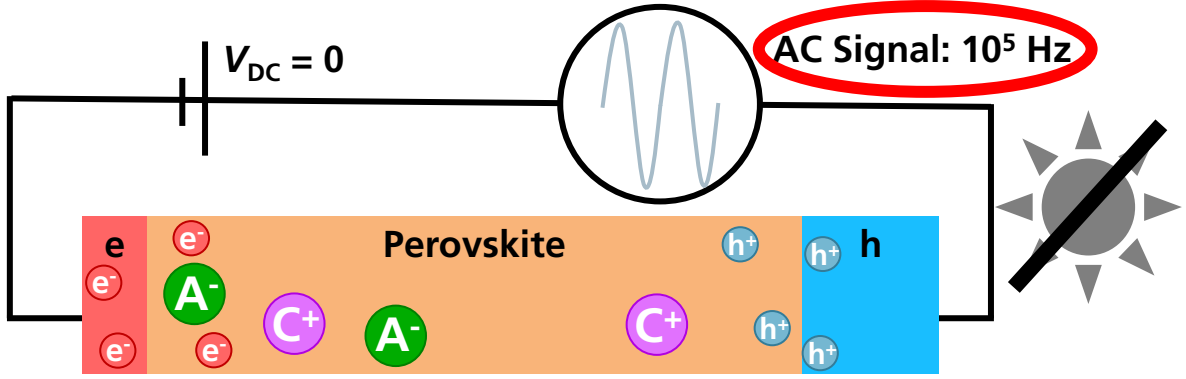


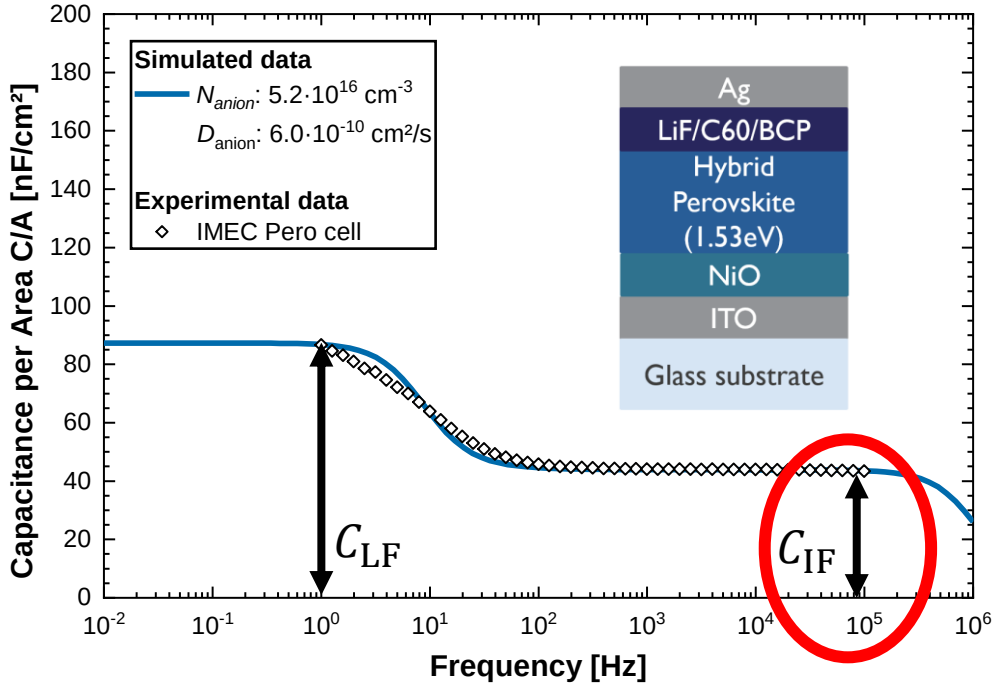
universität freiburg

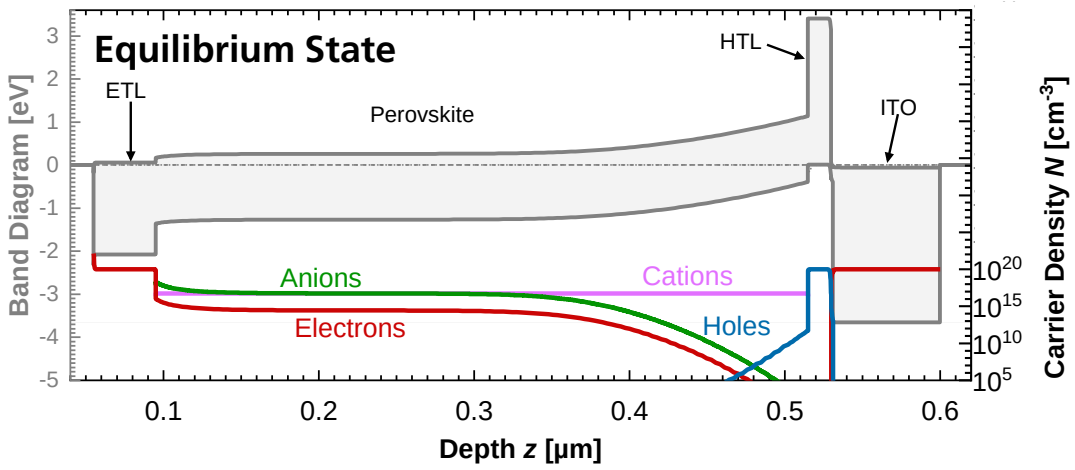
Fraunhofer ISE

Ion-Induced Capacitances

In-Depth Analysis of the Capacitance Plateau







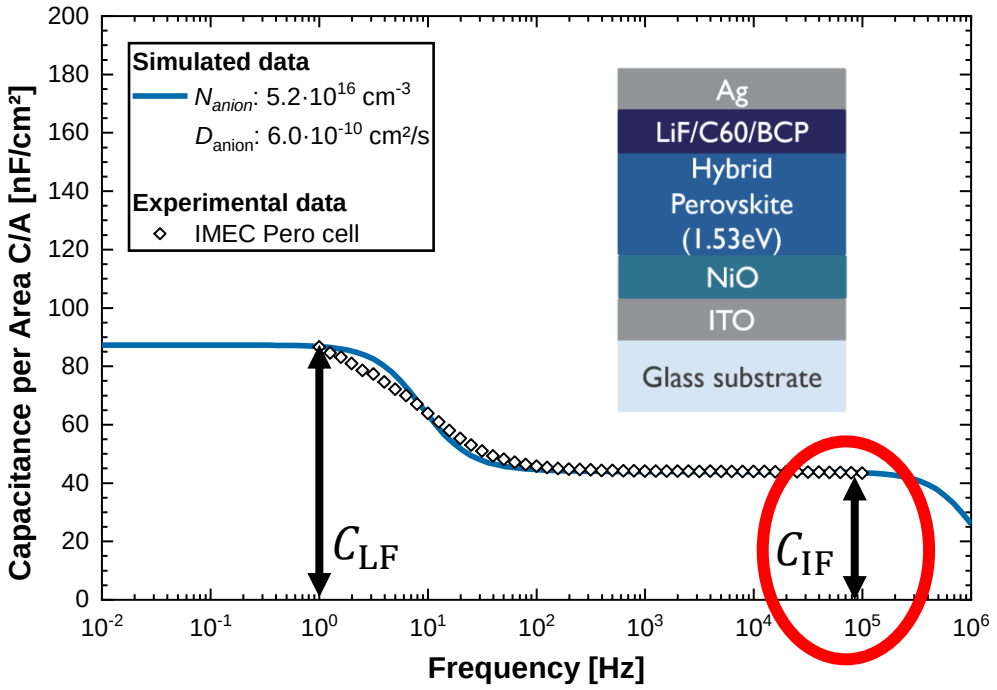
universität freiburg

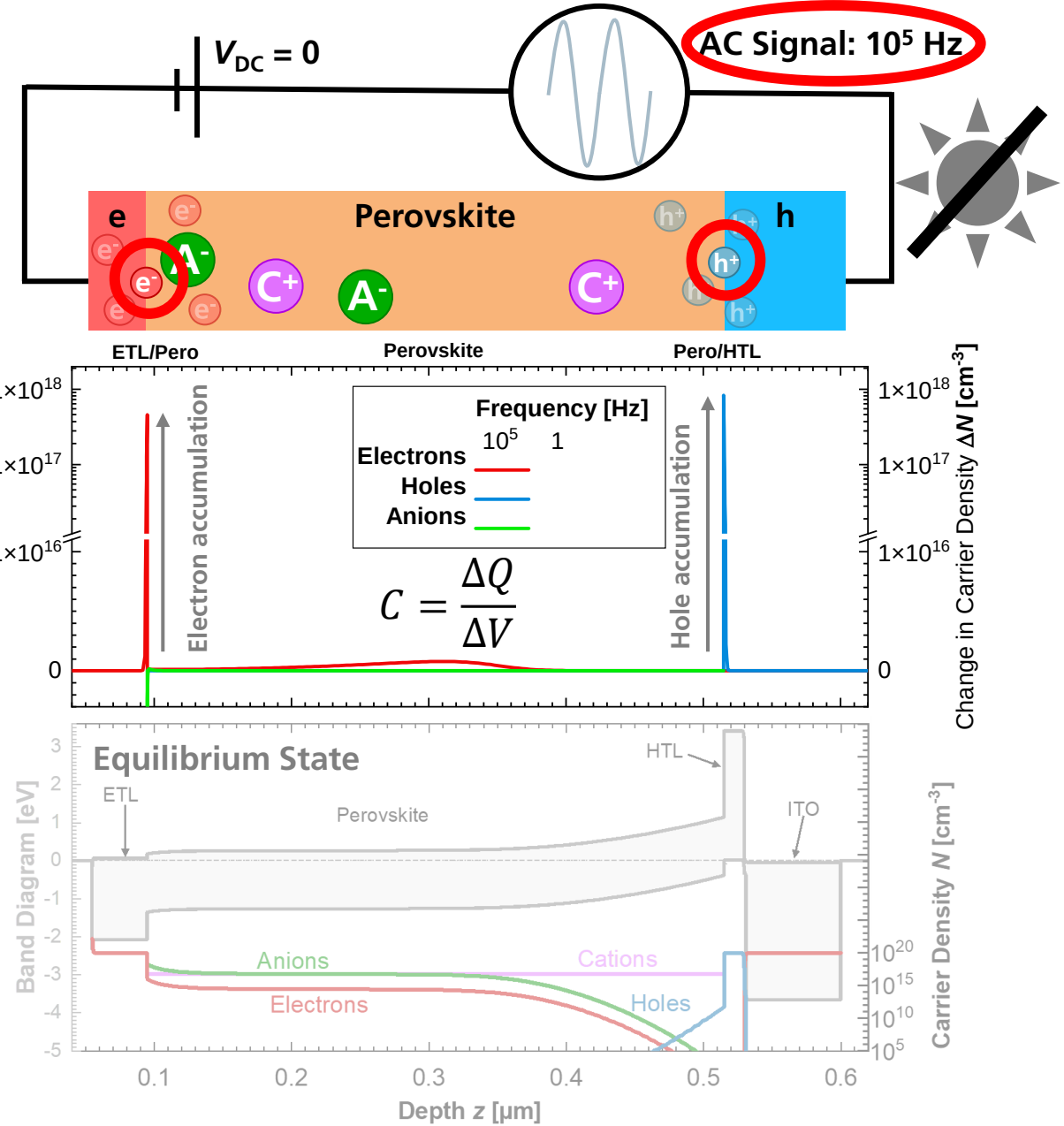
Fraunhofer ISE

Ion-Induced Capacitances

In-Depth Analysis of the Capacitance Plateau

- C_{IF} corresponds to charge accumulation at Pero/ETL, Pero/HTL interface





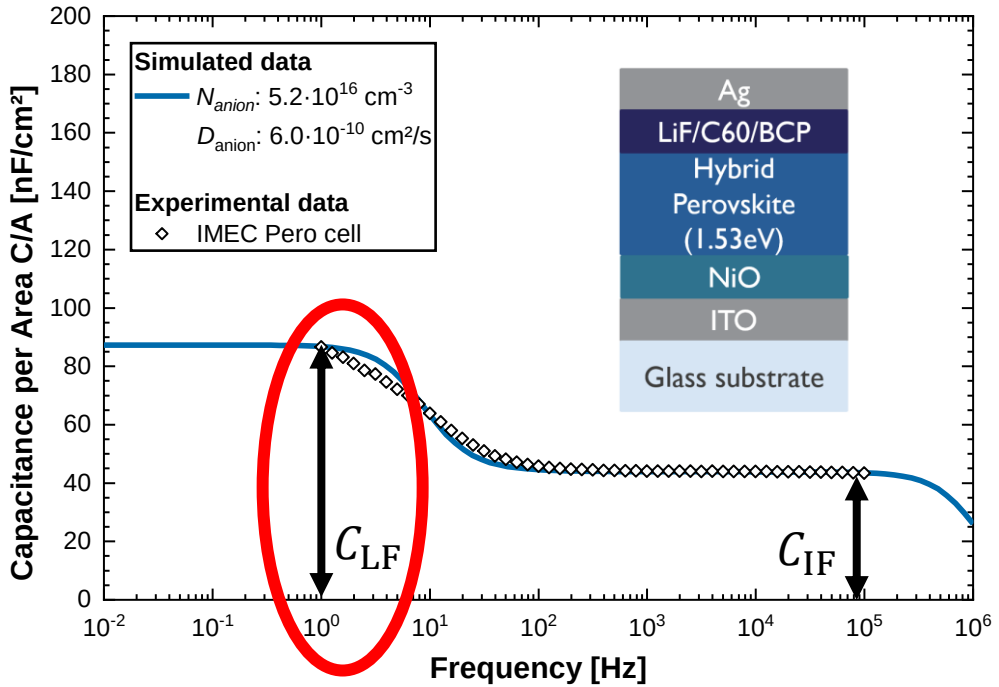
universität freiburg

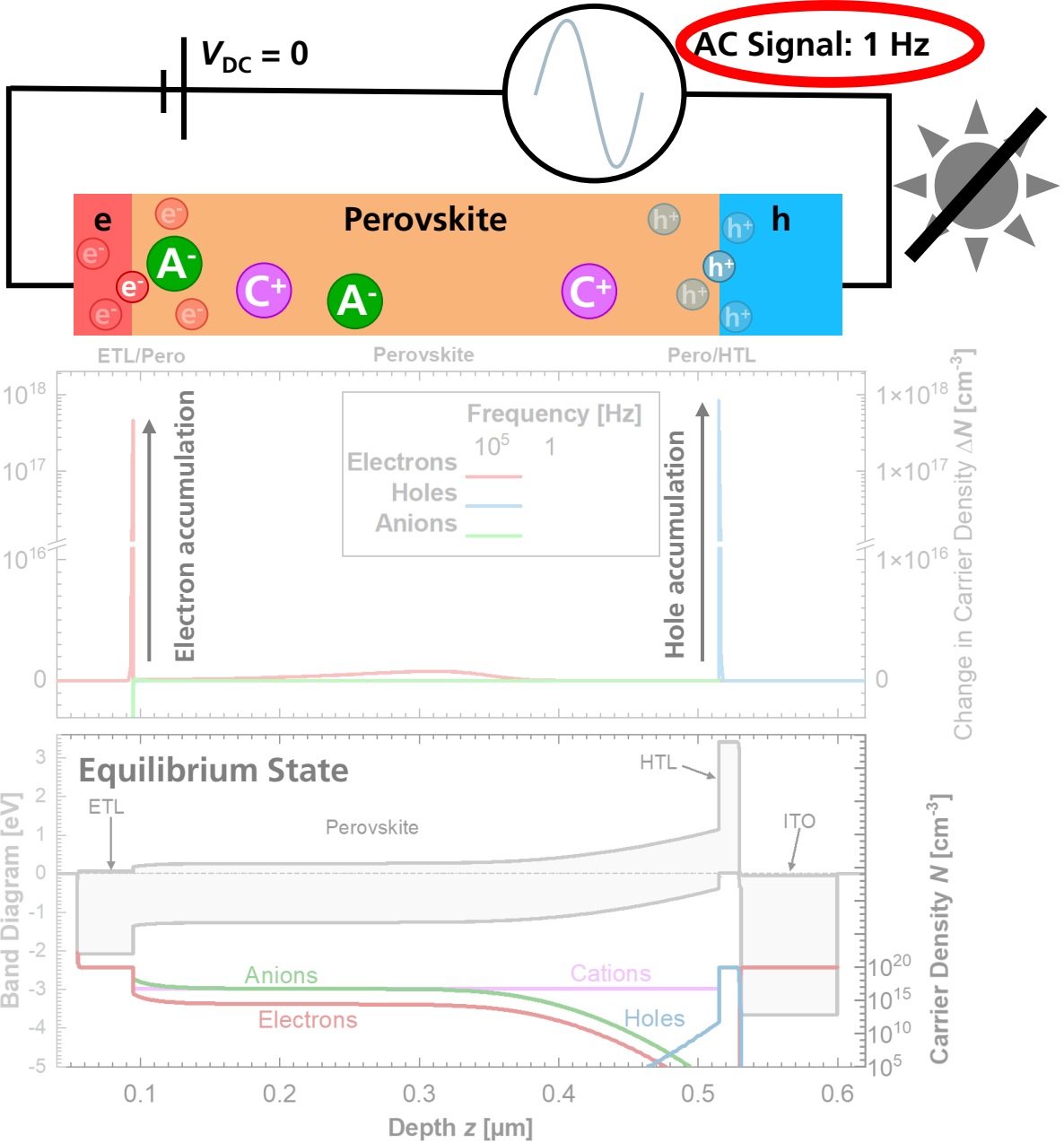
Fraunhofer ISE

Ion-Induced Capacitances

In-Depth Analysis of the Capacitance Plateau

- C_{IF} corresponds to charge accumulation at Pero/ETL, Pero/HTL interface



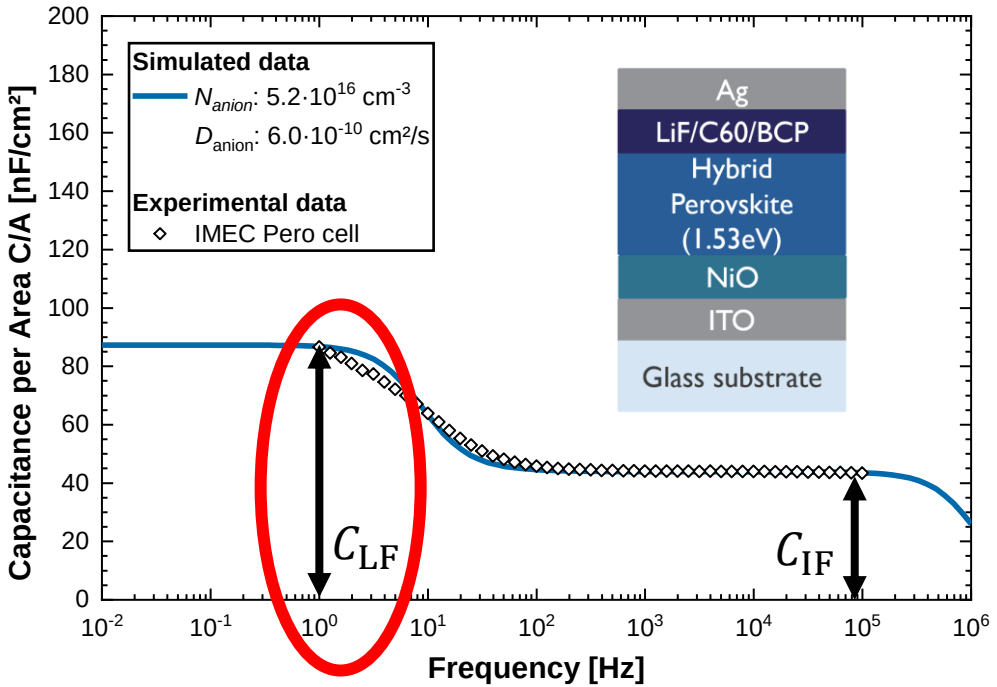


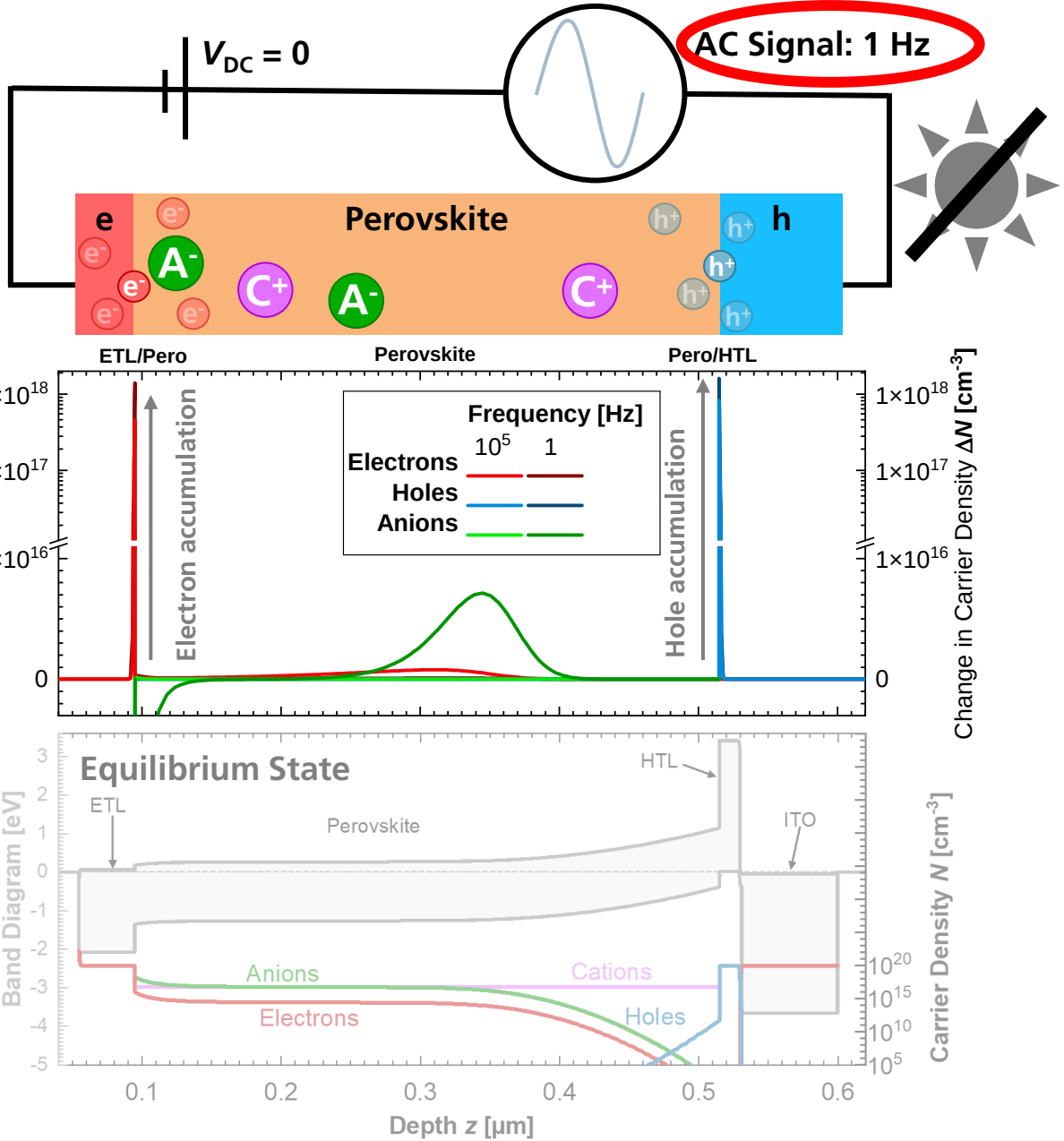
Presented at 41st EU PVSEC, 2024, Vienna, Austria

Ion-Induced Capacitances

In-Depth Analysis of the Capacitance Plateau

- C_{IF} corresponds to charge accumulation at Pero/ETL, Pero/HTL interface





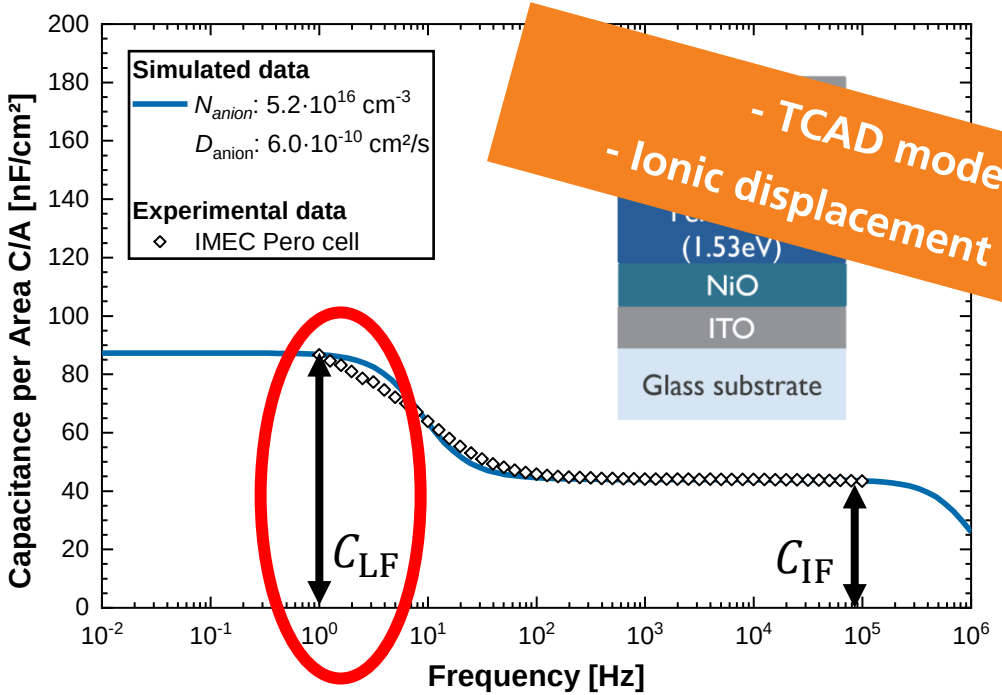
universität freiburg

Fraunhofer ISE

Ion-Induced Capacitances

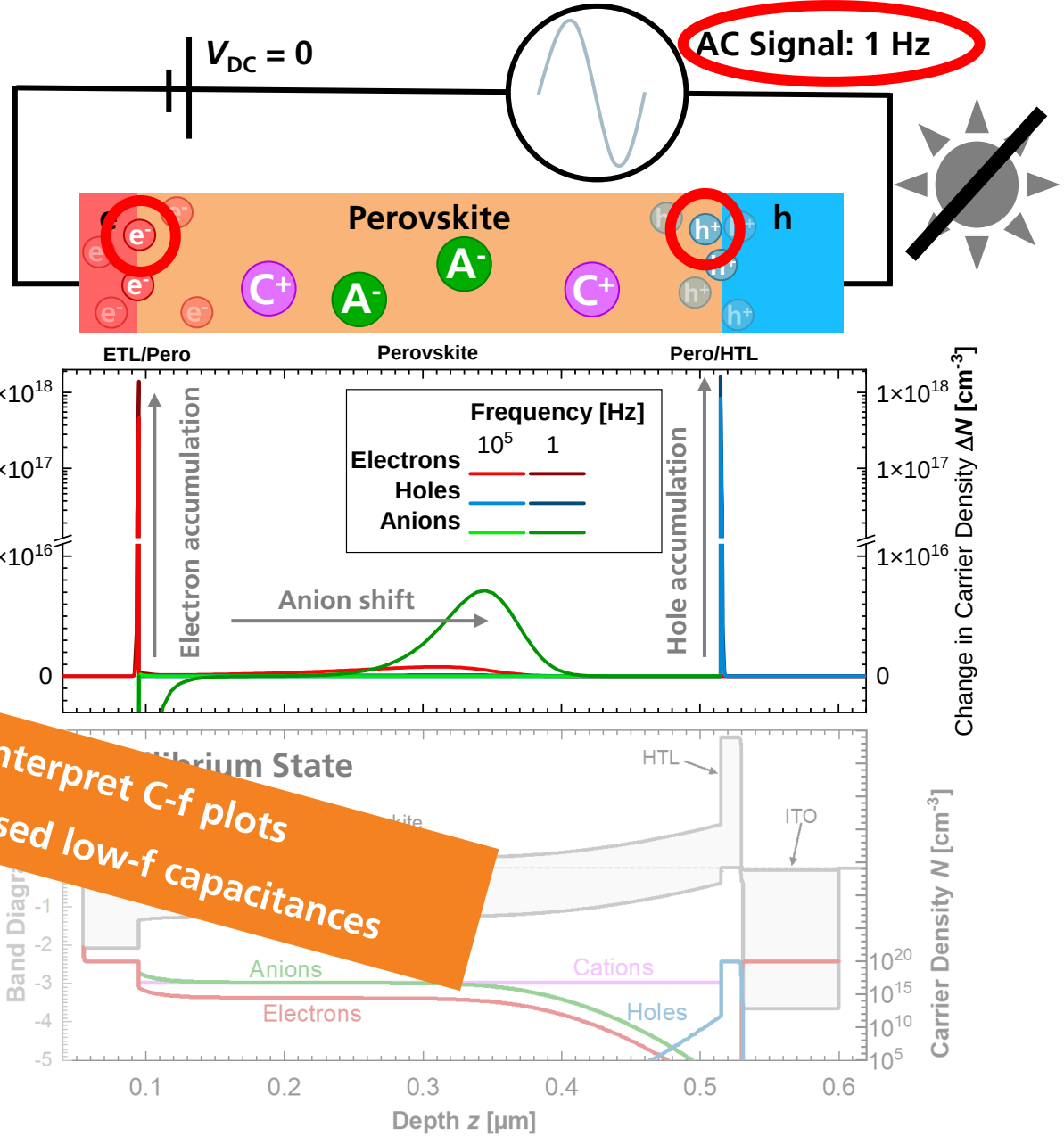
In-Depth Analysis of the Capacitance Plateau

- C_{IF} corresponds to charge accumulation at Pero/ETL, Pero/HTL interface
- C_{LF}: **Anion displacement** from ETL interface towards bulk leads to further charge carrier accumulation
  - → C_{LF} depends on N_{ion}, **but also on** built-in potential, cations, …



- TCAD modelling helps to interpret C-f plots

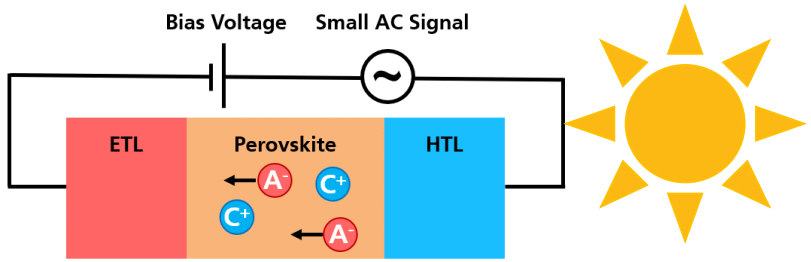
- Ionic displacement leads to increased low-f capacitances

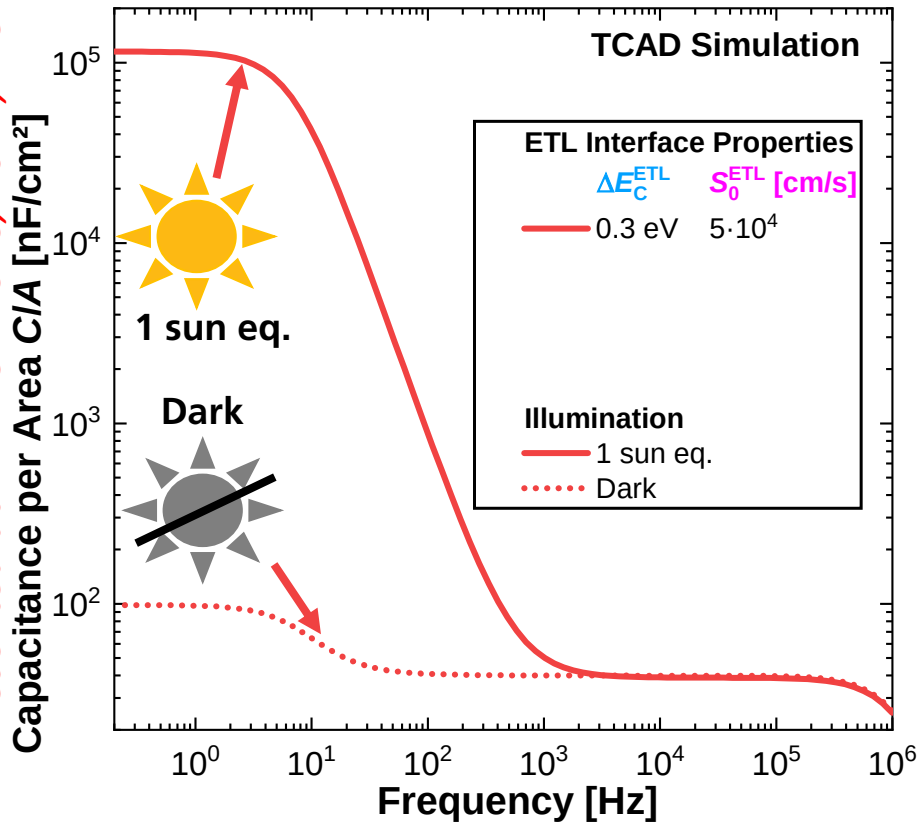


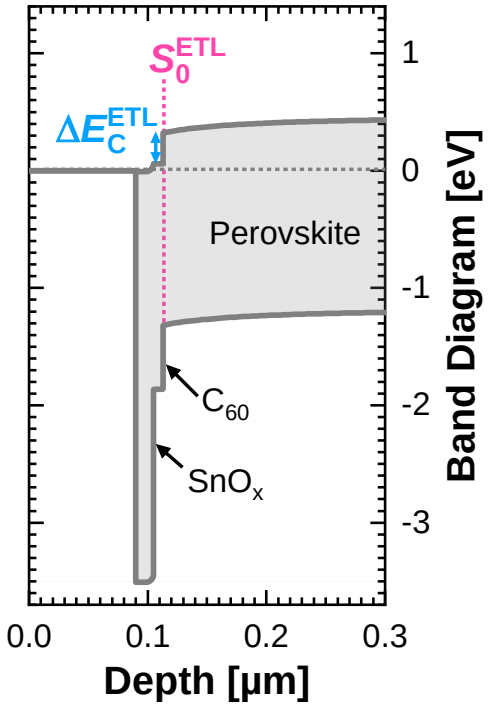
Ion-Induced Capacitances under Illumination

TCAD Simulation

Presented at 41st EU PVSEC, 2024, Vienna, Austria







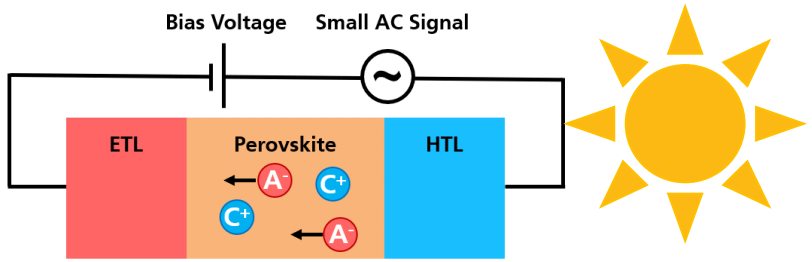
- **Simulated dark and light *C-f* curves** for different ETL interface properties
  - Capacitance under illumination increases by several orders of magnitude

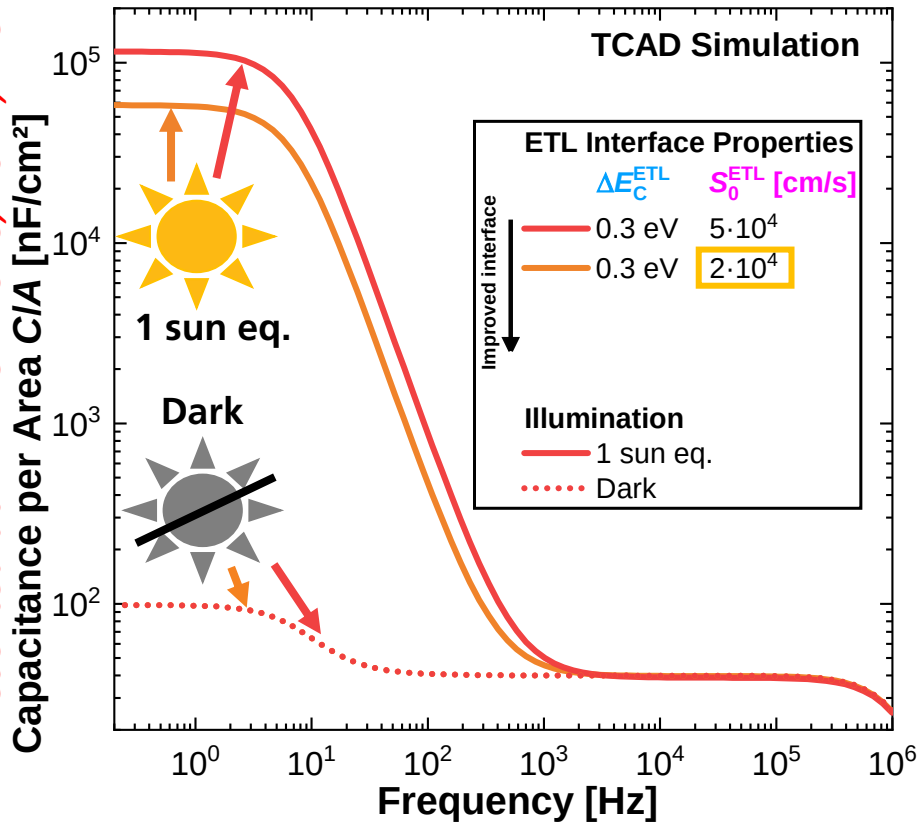
universität freiburg Fraunhofer ISE

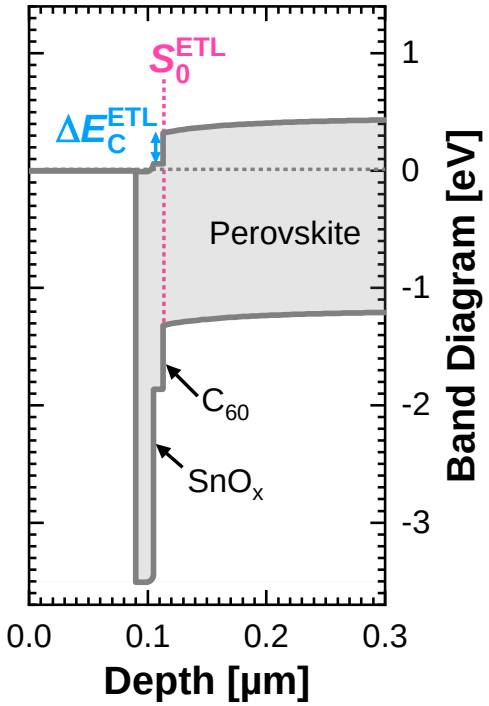
Ion-Induced Capacitances under Illumination

TCAD Simulation

Presented at 41st EU PVSEC, 2024, Vienna, Austria







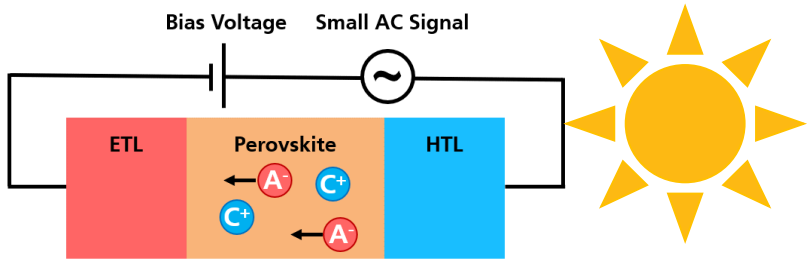
- **Simulated dark and light *C-f* curves** for different ETL interface properties
  - Capacitance under illumination increases by several orders of magnitude
- **For lower surface recombination velocity (SRV) at ETL/Pero interface:**
  - Illuminated *C-f* curve shifts down
  - Dark *C-f* curve is unchanged

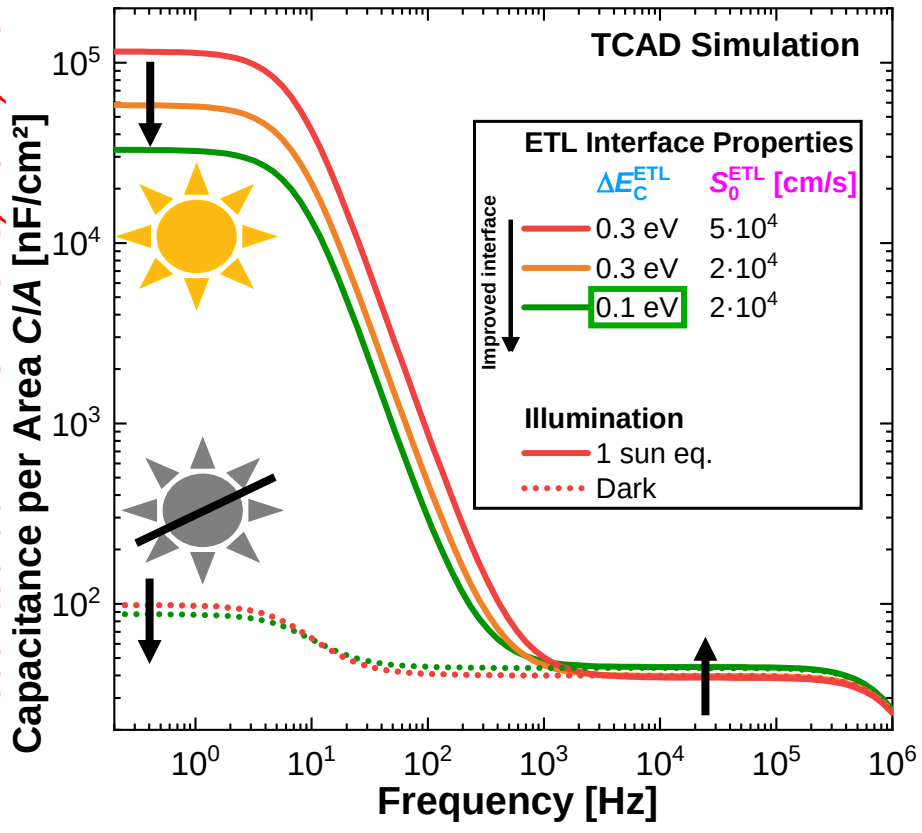
universität freiburg Fraunhofer ISE

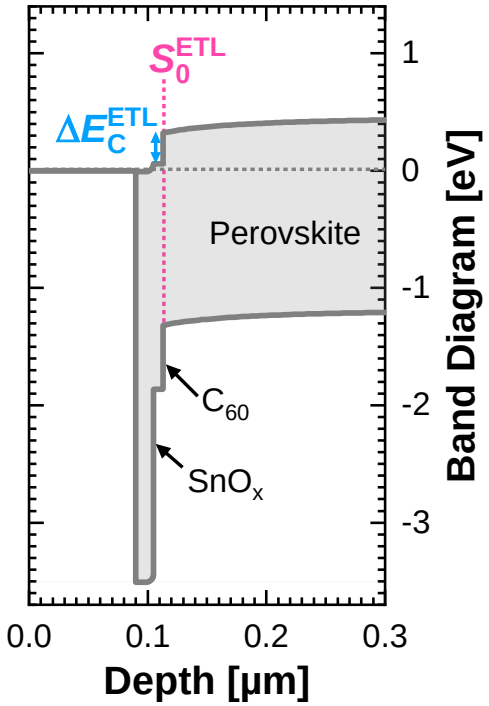
Ion-Induced Capacitances under Illumination

TCAD Simulation

Presented at 41st EU PVSEC, 2024, Vienna, Austria





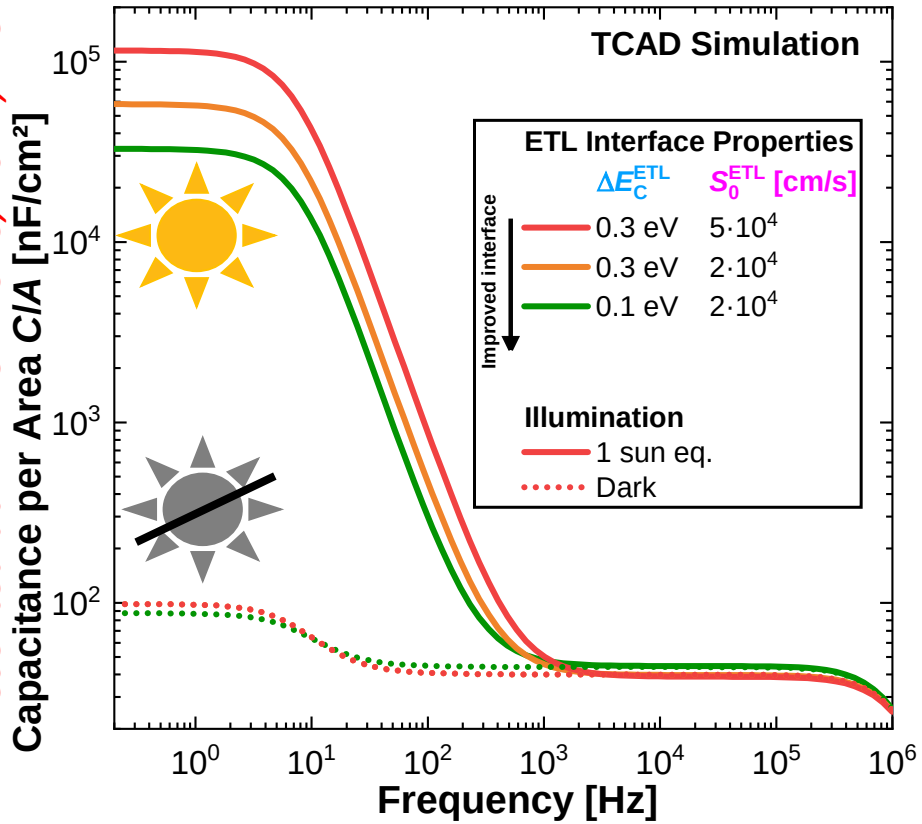


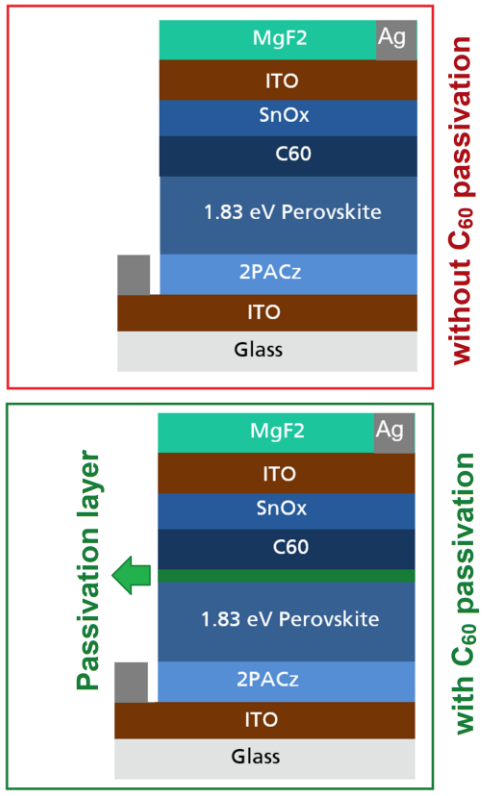
- **Simulated dark and light *C-f* curves** for different ETL interface properties
  - Capacitance under illumination increases by several orders of magnitude
- **For lower surface recombination velocity (SRV) at ETL/Pero interface:**
  - Illuminated *C-f* curve shifts down
  - Dark *C-f* curve is unchanged
- **For change in band alignment (reduced ETL/Pero conduction band offset):**
  - Both illuminated and dark *C-f* curve change
  - **Low frequency plateau**: Capacitance decreases
  - **High frequency plateau**: Capacitance increases

Ion-Induced Capacitances under Illumination

Experimental Comparison

Presented at 41st EU PVSEC, 2024, Vienna, Austria





- Perovskite single junctions (used as top cells) fabricated at Fraunhofer ISE and measured at IMEC
  1. **ETL/Pero interface unpassivated**
  2. **ETL/Pero interface passivated with PI***

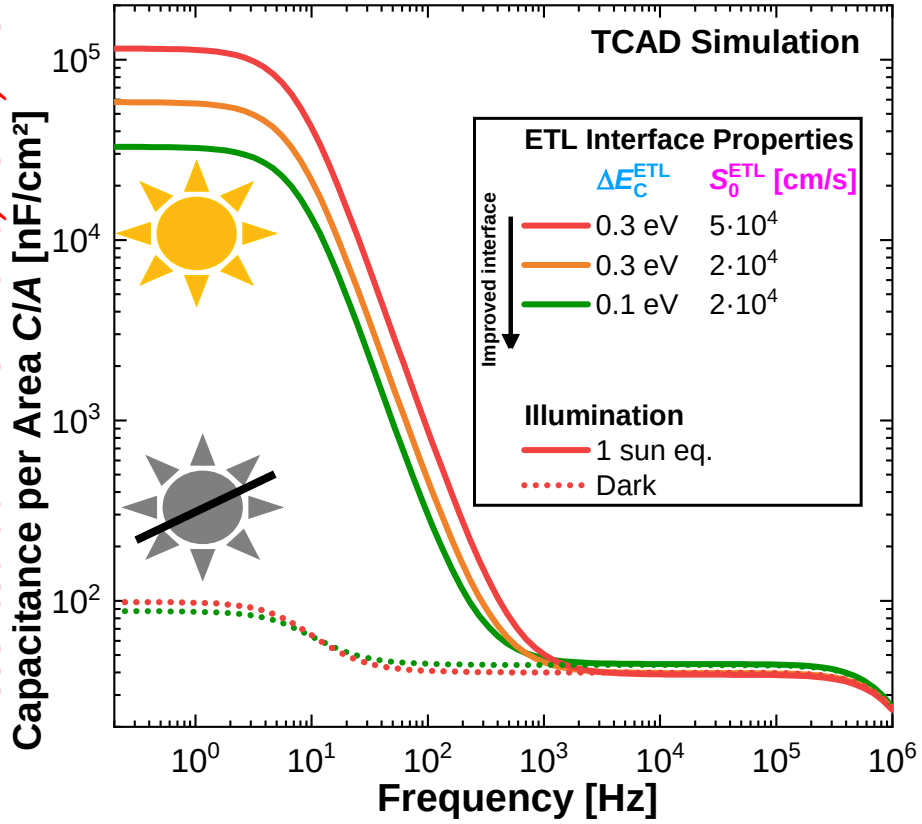
*PI = piperazinium iodide

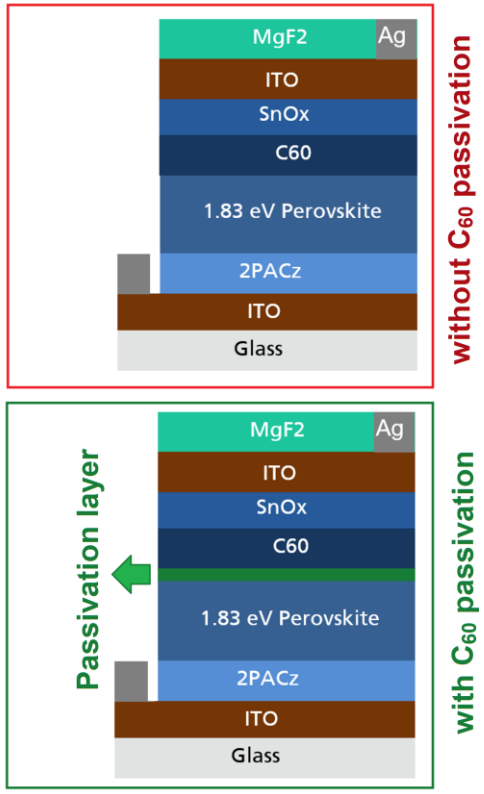
universität freiburg Fraunhofer ISE

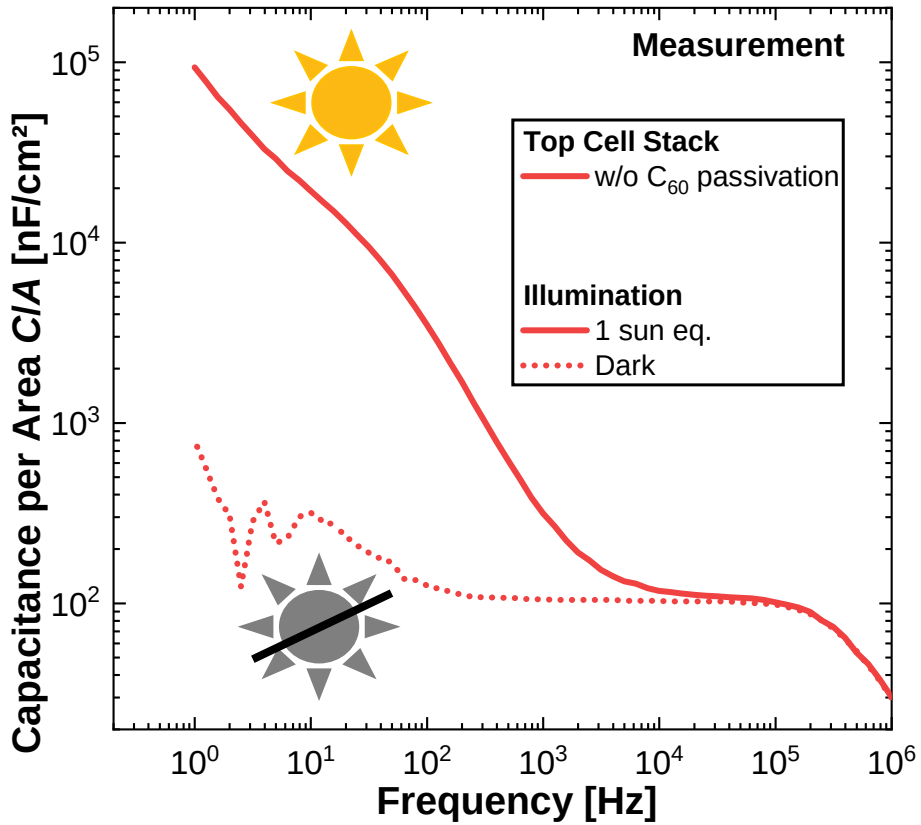
Ion-Induced Capacitances under Illumination

Experimental Comparison

Presented at 41st EU PVSEC, 2024, Vienna, Austria







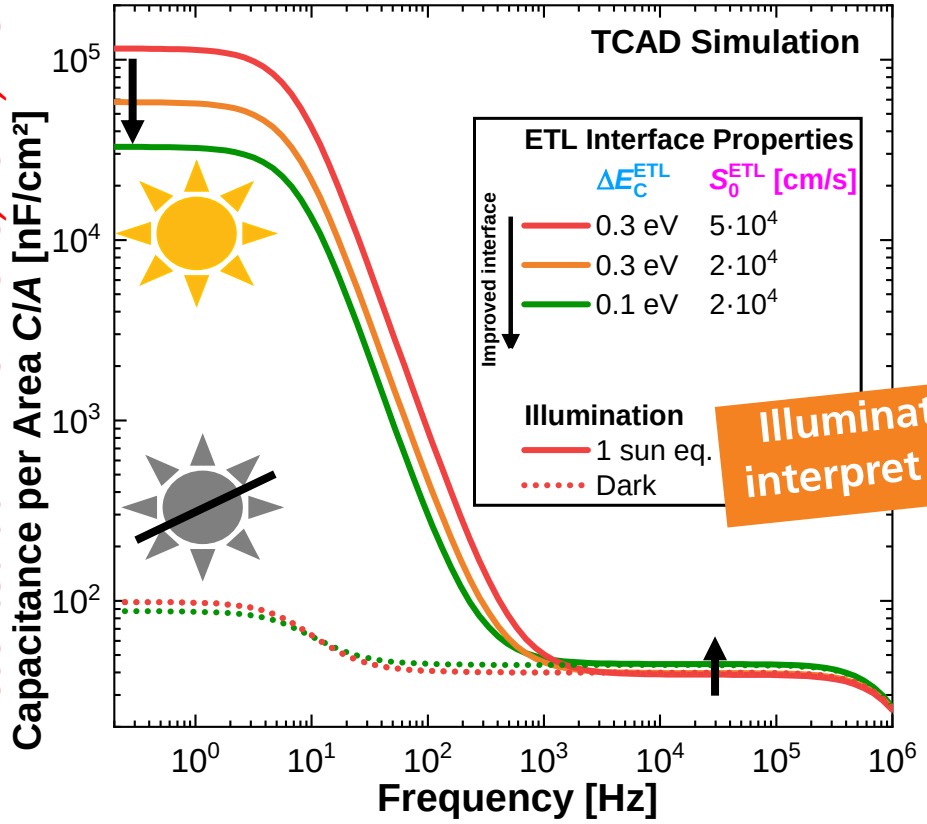
universität freiburg Fraunhofer ISE

Ion-Induced Capacitances under Illumination

Experimental Comparison

Presented at 41st EU PVSEC, 2024, Vienna, Austria

- Good qualitative agreement of TCAD model and measurements

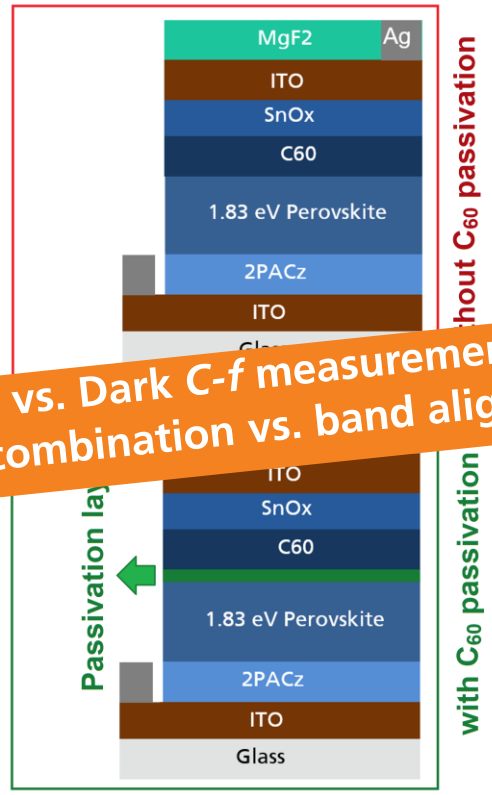


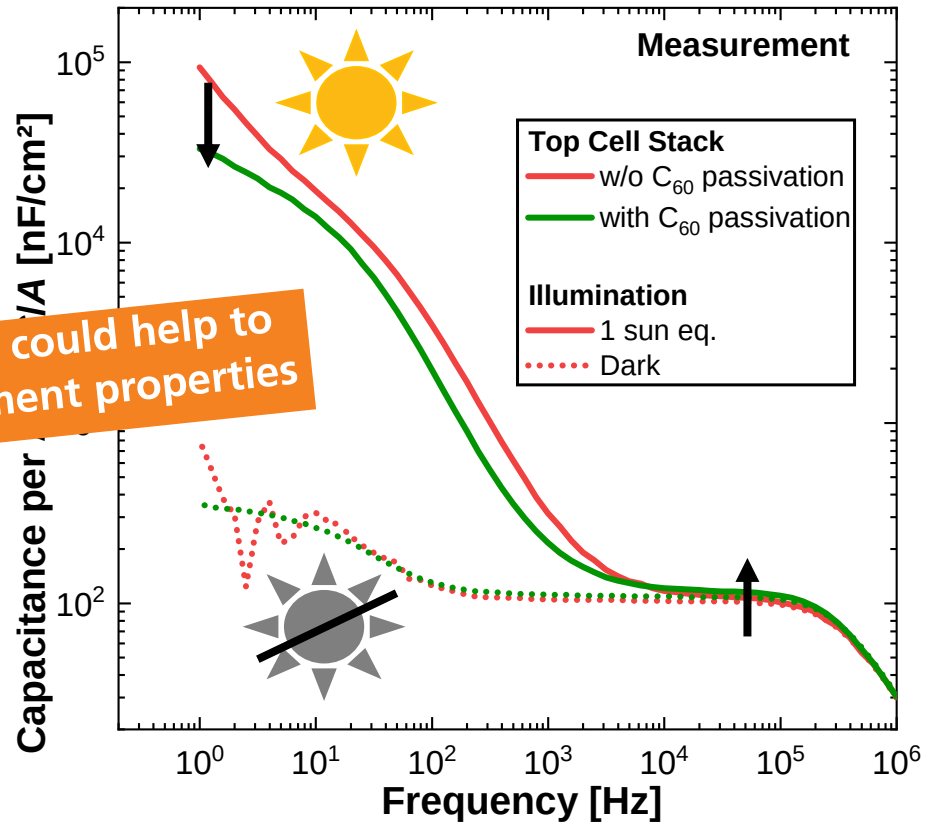
Passivation layer leads to:

- Reduced low-f capacitance
- Increased high-f capacitance

→ Indicates lower recombination

→ Possibly also better ETL/Pero band alignment



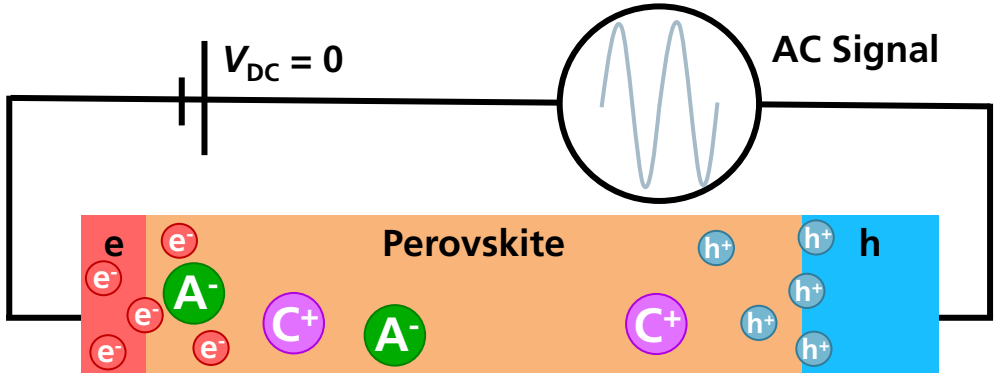


Illuminated vs. Dark *C-f* measurements could help to interpret recombination vs. band alignment properties

universität freiburg

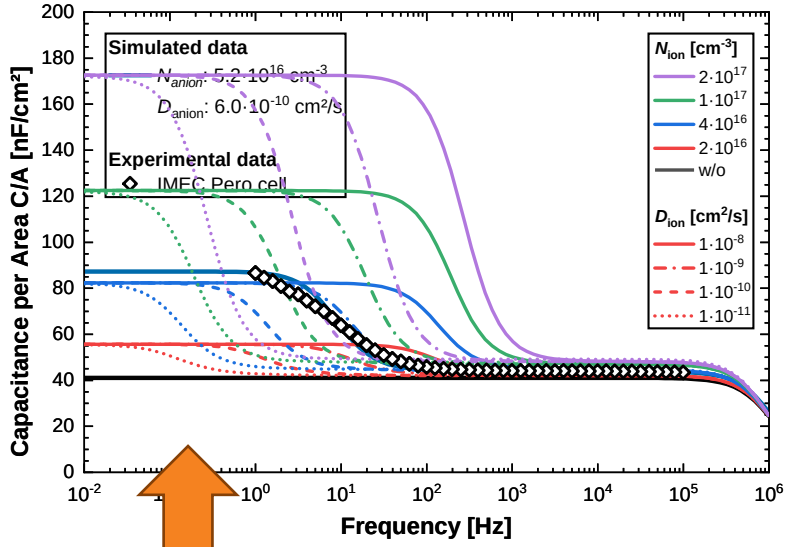
Fraunhofer ISE

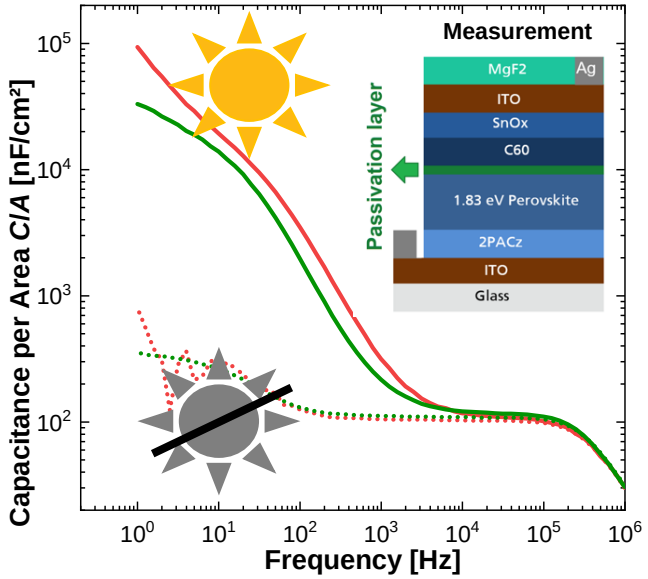
Conclusion

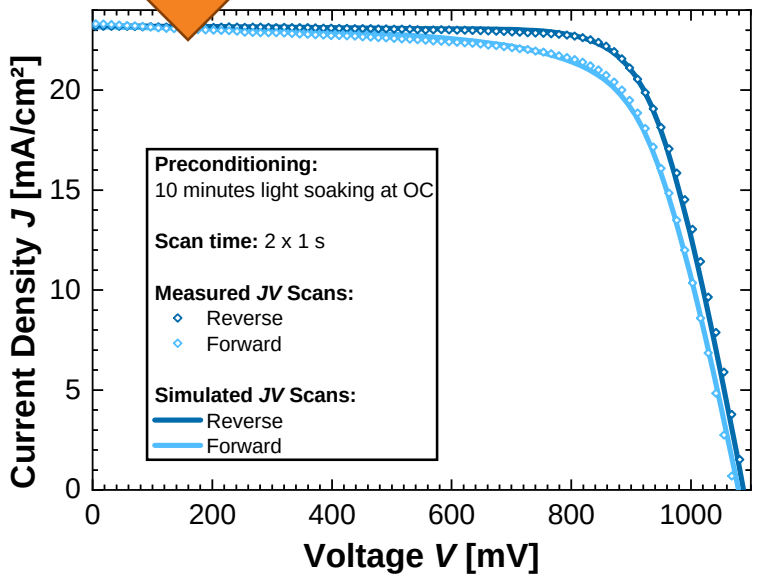


- TCAD Simulation of capacitance response of PSCs:
  - Impact of ionic properties
  - Good agreement with experimental data
  - Insights into physical origin of ionic capacitance
- Link ***C-f* response** to scan-time dependent ***JV* hysteresis**
- Investigation of ***C-f* curves under illumination**
  - Effect of band alignment and interface recombination
  - Experimental evidence

→Simulation-aided analysis of *C-f* curves contributes to **enhanced understanding**
→**Careful interpretation** of data is essential
→Measurements are **non-destructive** and on device level







Presented at 41st EU PVSEC, 2024, Vienna, Austria

Thanks for your attention!

Upcoming Journal Publication in Solar RRL [1]

Dr. Christoph Messmer
Tel. +49 761 203 54176
christoph.messmer@inatech.de

[1] Messmer *et al.*, „Understanding Ion-Related Performance Losses in Perovskite-Based Solar Cells by Capacitance Measurements and Simulation“, submitted to Solar RRL

universität freiburg

INATECH
INSTITUT FÜR NACHHALTIGE TECHNISCHE SYSTEME

Fraunhofer ISE

contributions of

Fraunhofer ISE 41th EU PVSEC

ise.link/eupvsec2024

TRIUMPH

Federal Ministry for Economic Affairs and Climate Action

on the basis of a decision by the German Bundestag