Observation of ionic Coulomb blockade in nanopores

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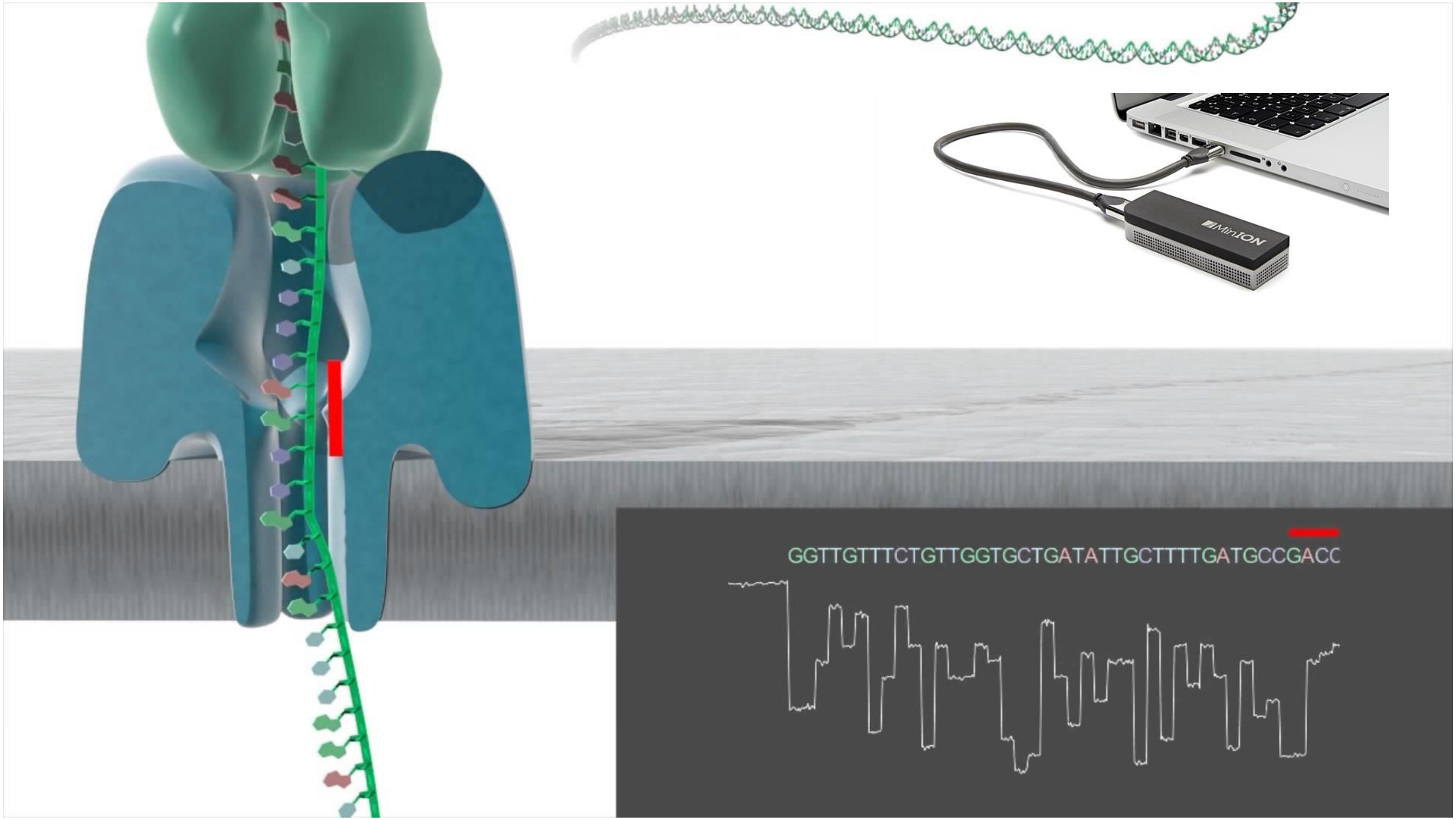
Nanopores: molecular transporters

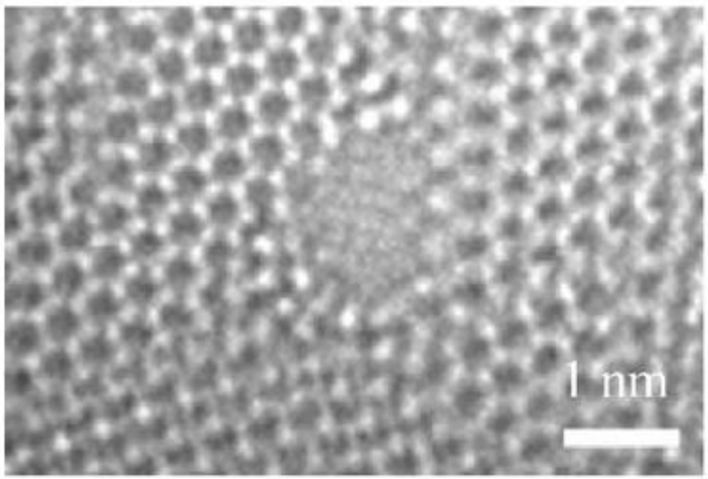
Nanopore sequencing, proposed by David Deamer and George Church, is now reality



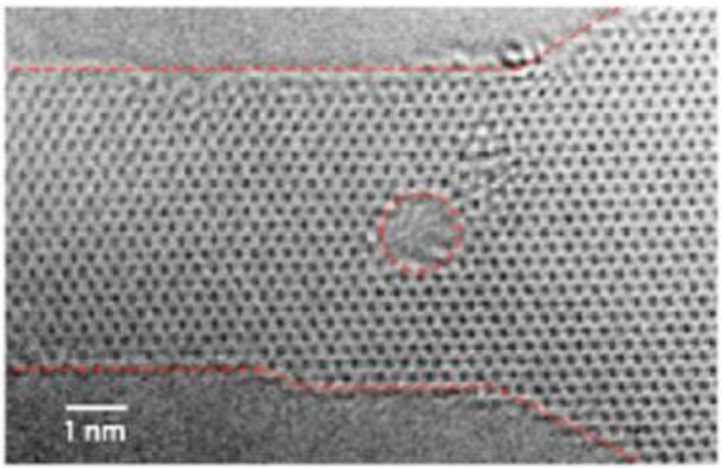
@ Oxford Nanopore

Nanopores: artificial ion channels

Second generation of solid-state nanopore: subnanometer in all dimensions made in 2-D material -they are artificial ion channels!

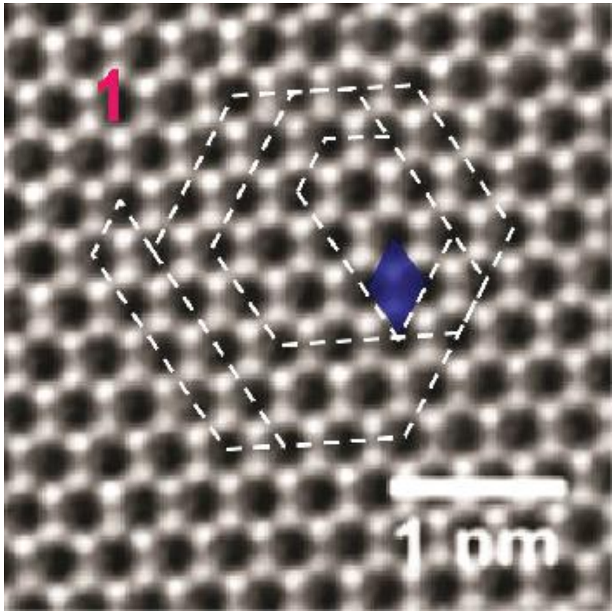


1-nm MoS2 pore@ EPFL

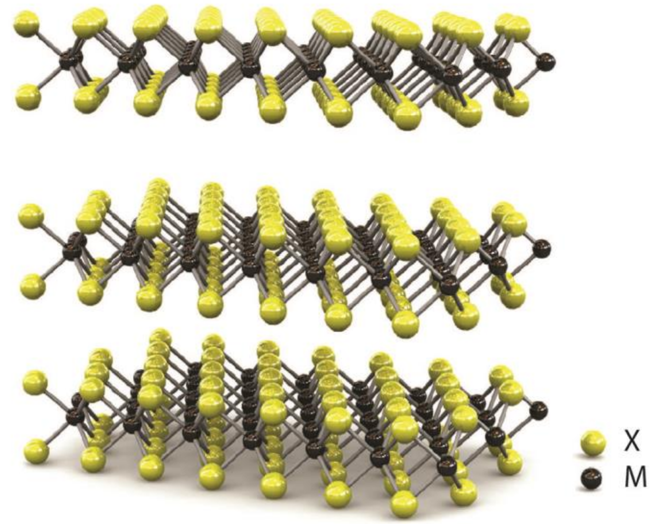


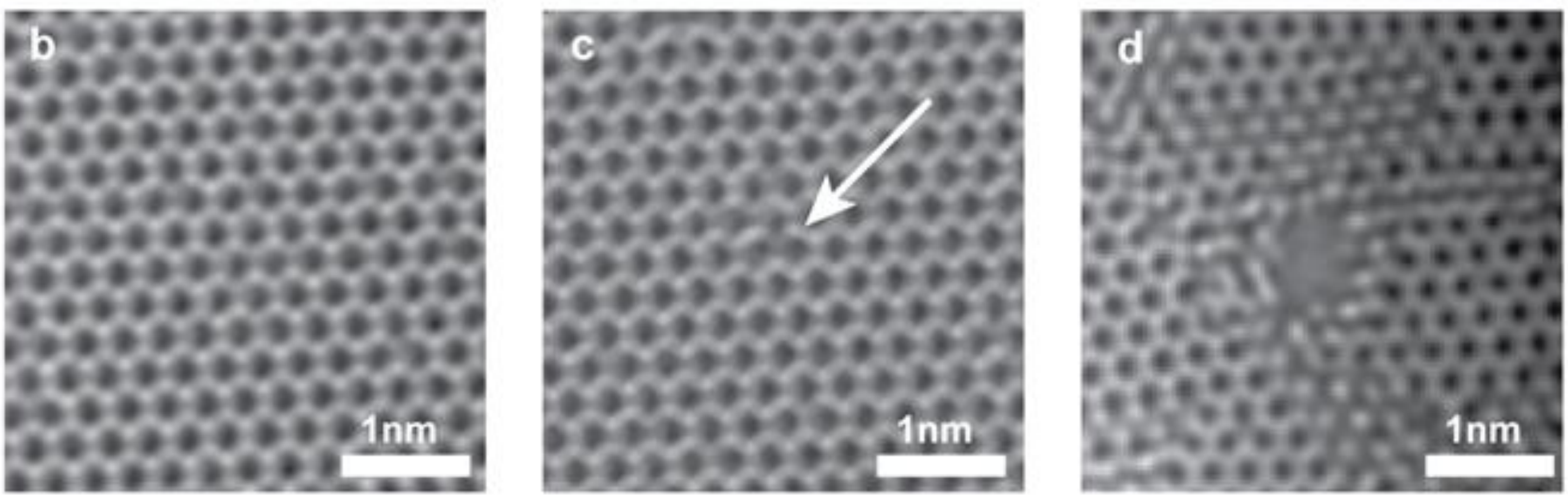
Gate-integrated 1 nm graphene pore @ Dekker, Delft

Engineering sub-nanometer pores

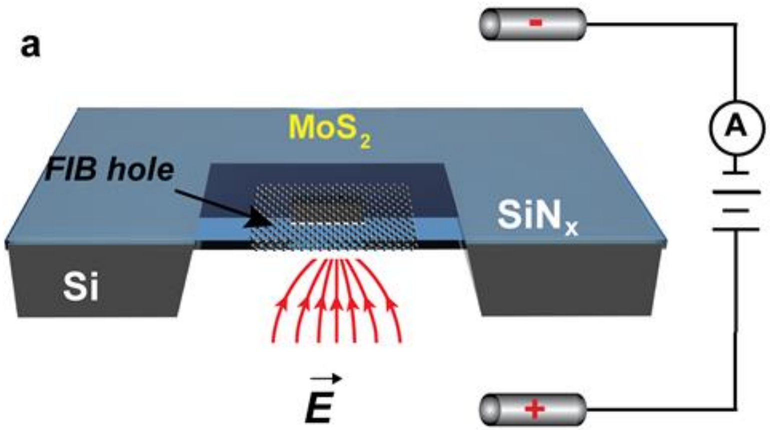


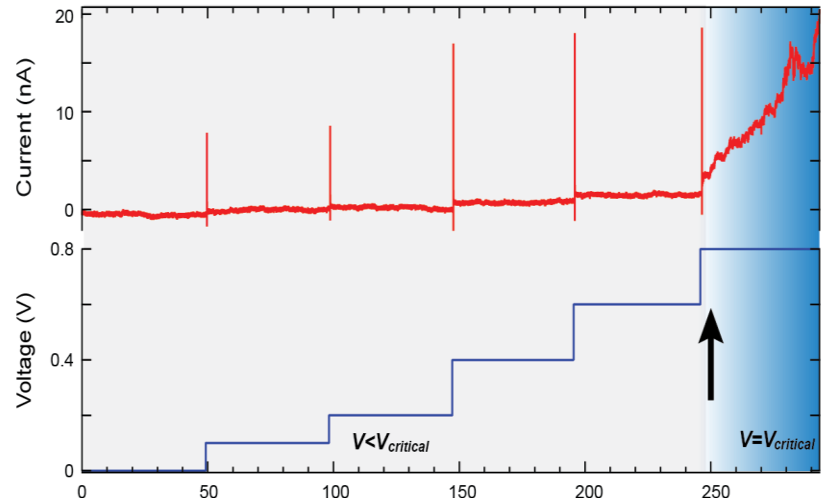
Aberration corrected TEM (Titan Themis @ EPFL)

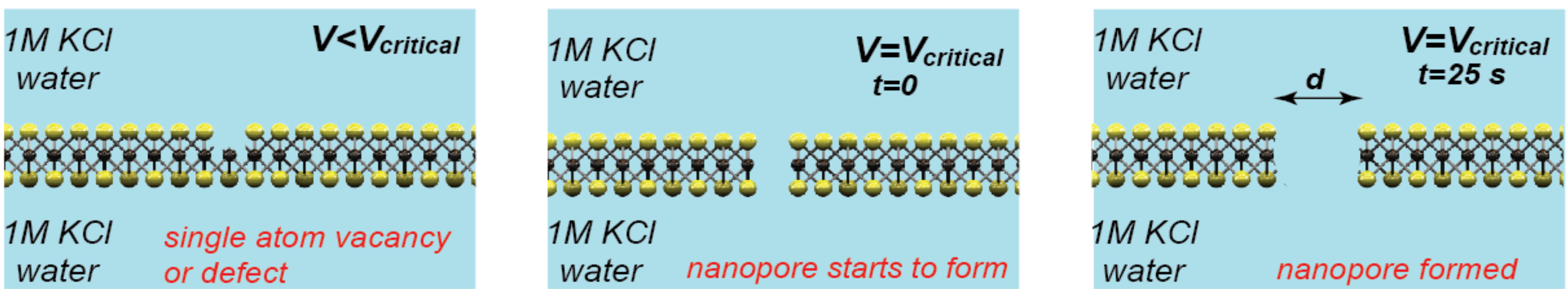


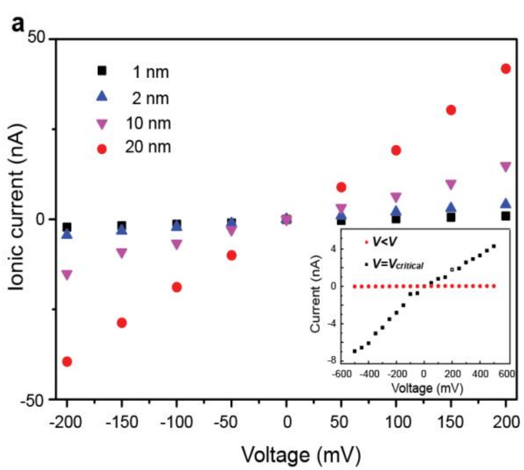


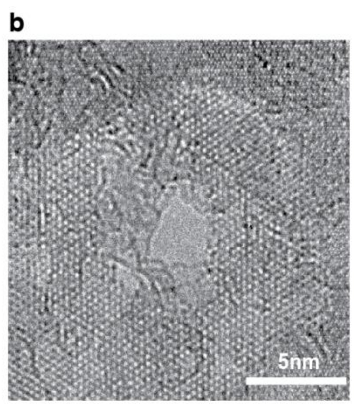
Engineering nanopores at atomic precision









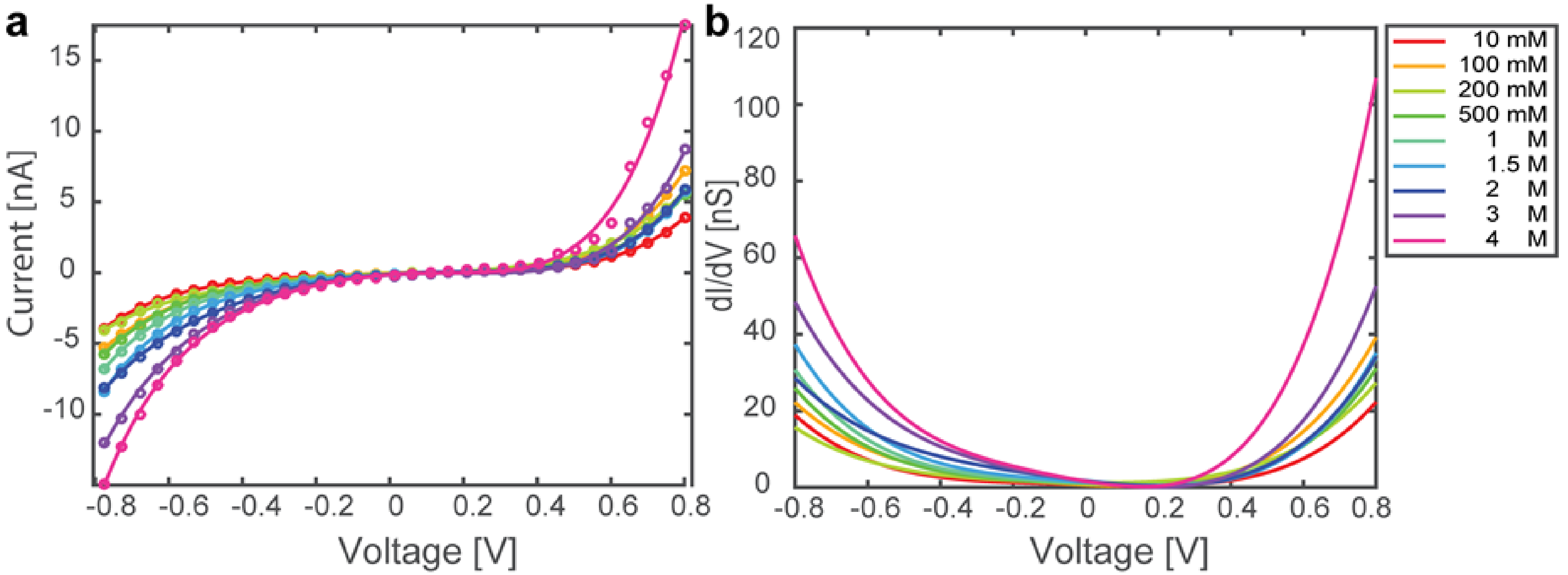


Feedback-controlled electrochemistry

$$MoS_2 + 11H_2O = MoO_3 + 2SO_4^{2-} + 22H^+ + 18e^-$$

Feng, Radenovic et al, Nano Letters, 2015

Ionic transport through sub-nm nanopore junction

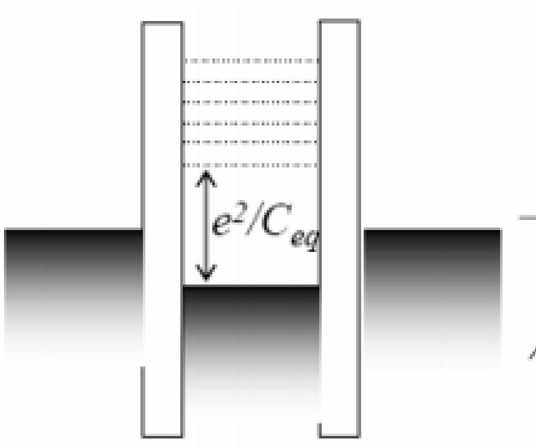


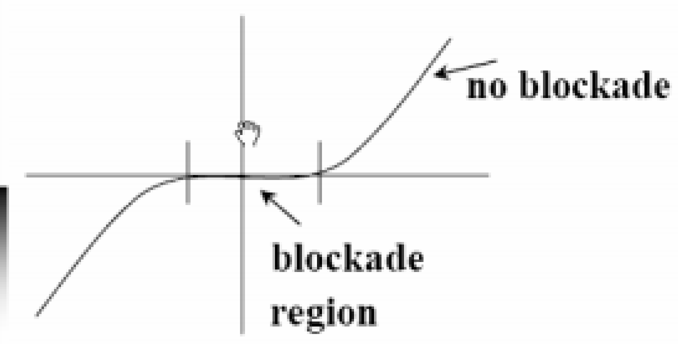
Energy gaps are observed in the I-V through a sub-nm pore!

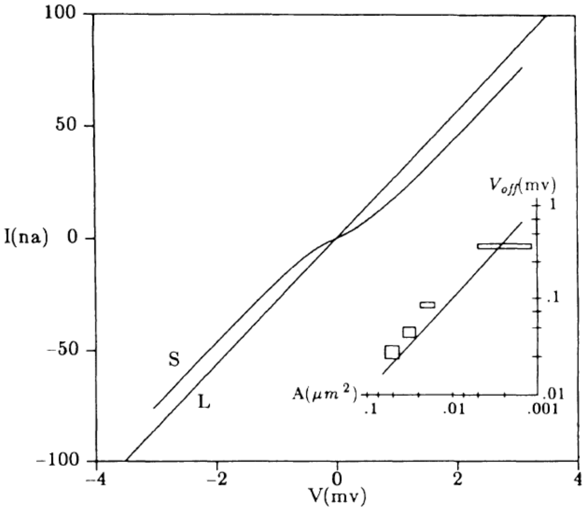
Feng, Radenovic et al, Nature Materials, 2016

Electronic transport

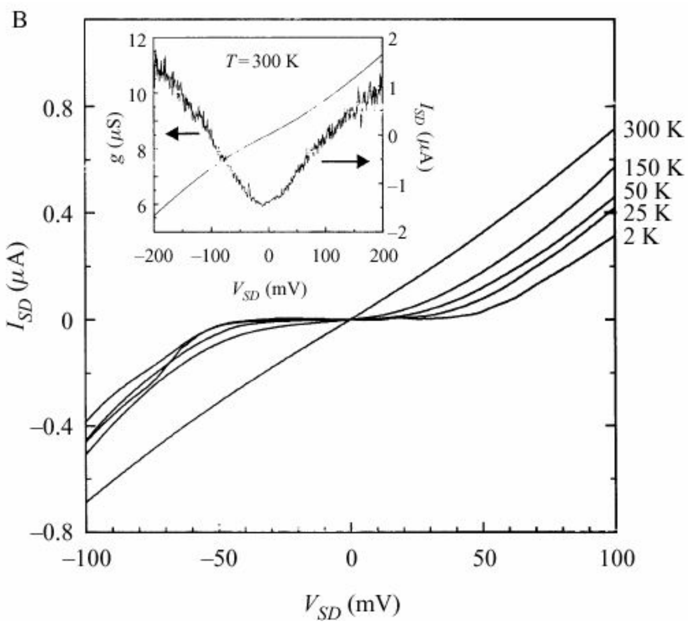
Coulomb blockade: charging energy $e^2/2C > kT$ $|V| \geq \frac{|e|}{2C}$



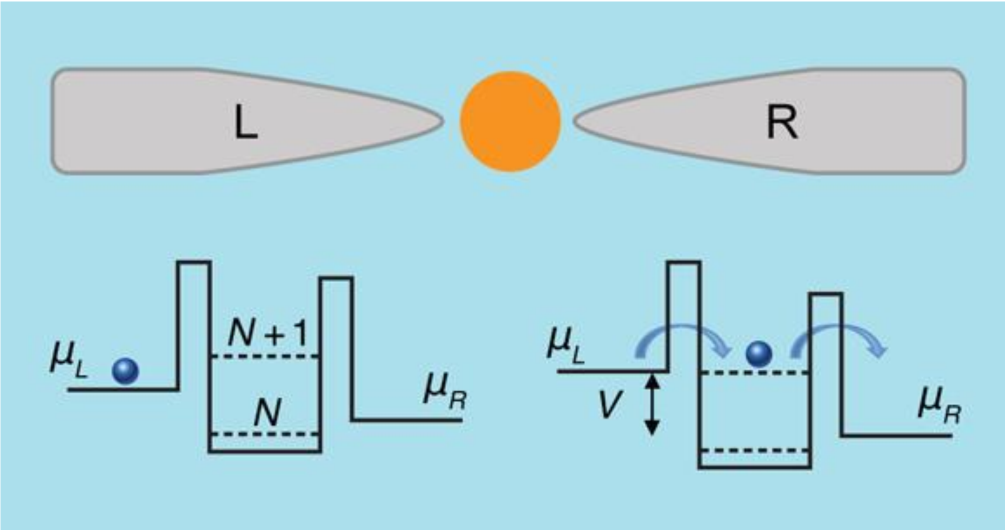




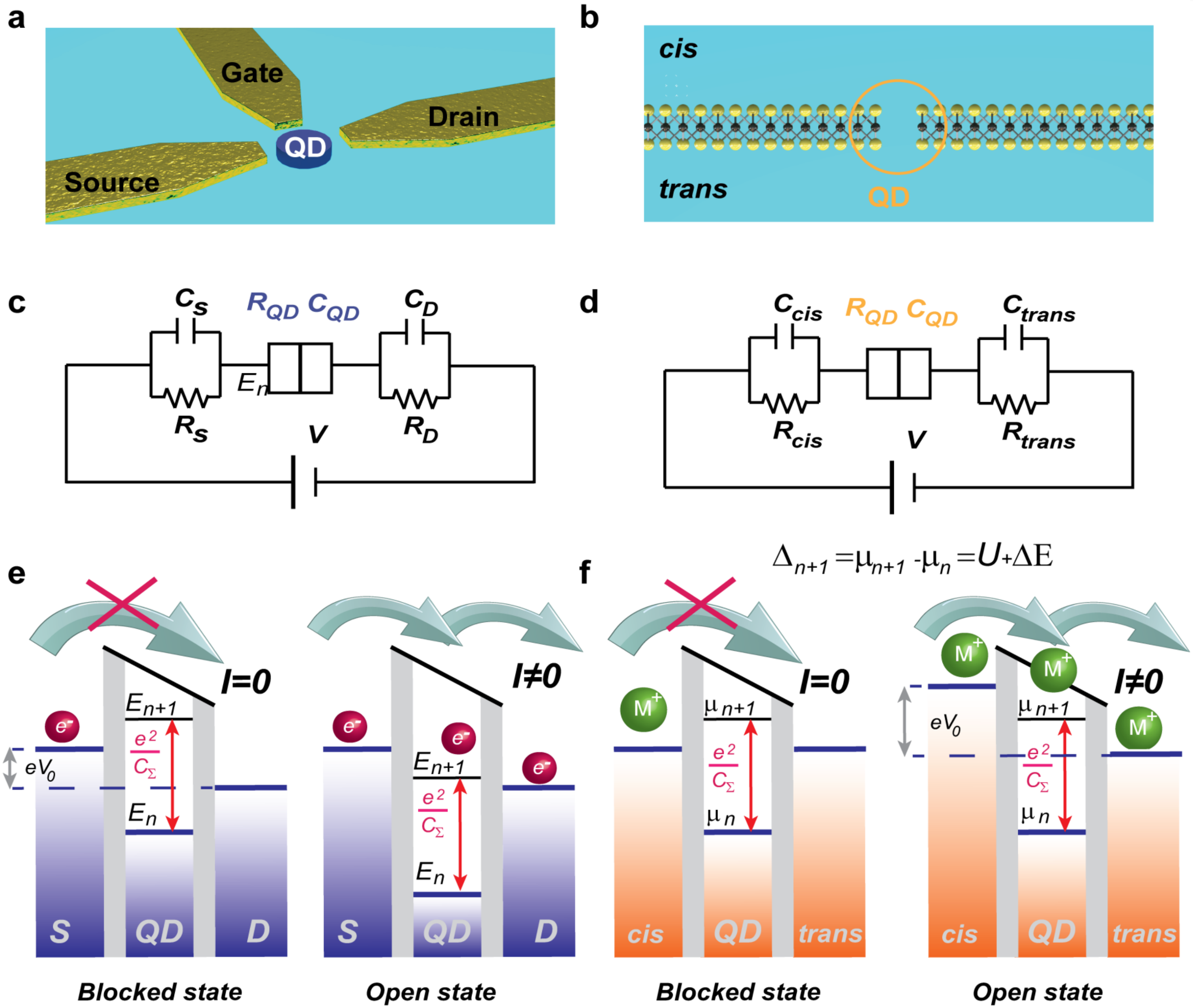
Fulton, PRL, 1987



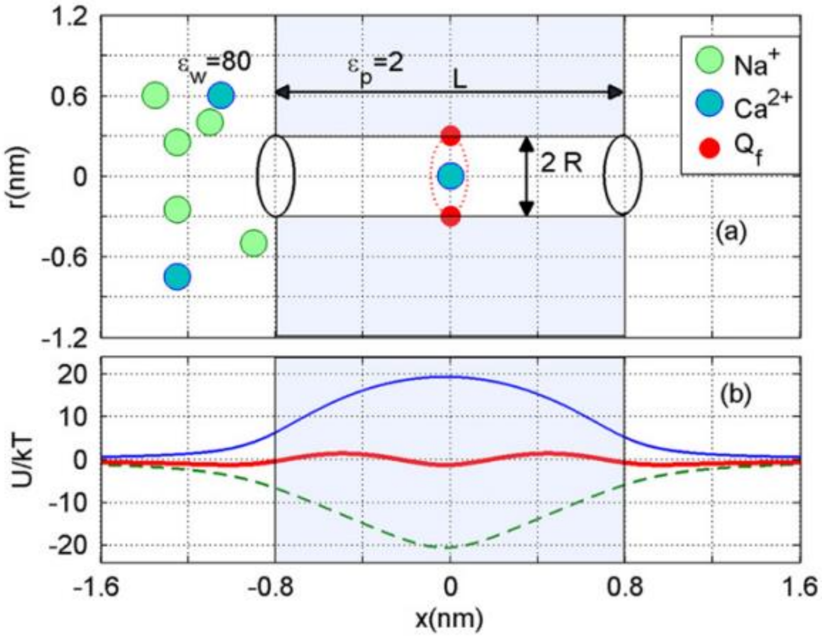
Jörg P. Kotthaus @ Munich



Quantum analogies in ion transport



Ionic Coulomb blockade model

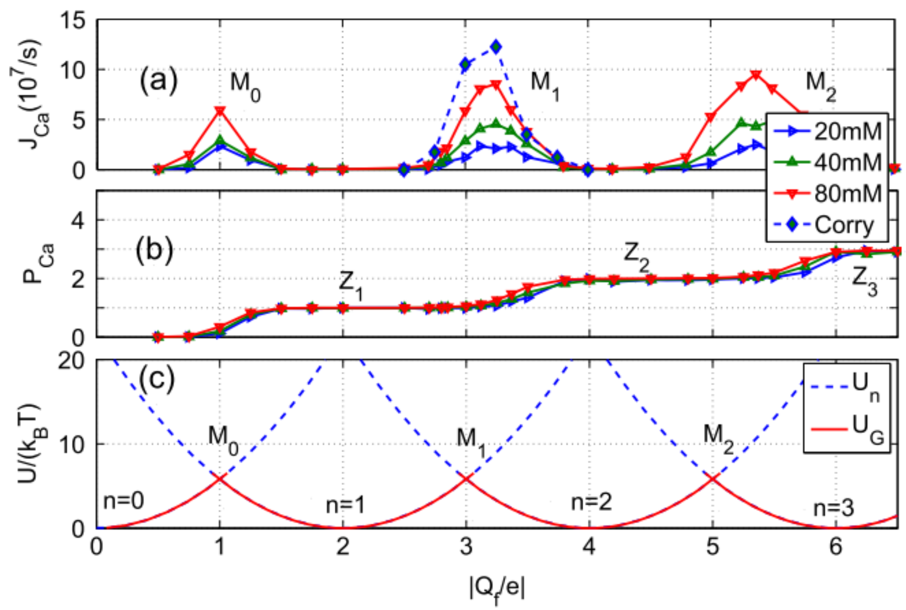


$$U_s = \frac{e^2}{2C_s} = \frac{\lambda_B L}{2R^2}, \quad U_{s,z} = z^2 U_s \gg 1 \quad \text{(Coulomb gap)}$$

$$Z_n = -zen \pm \delta Z_n, \quad \text{(Coulomb blockade)},$$

$$M_n = -ze\,(n + 1/2) \pm \delta M_n \quad \text{(Resonant conduction)}$$

$$\frac{J_c}{J_{max}} = U_c \sinh^{-1}\left(U_c\right) \approx \cosh^{-2}\left(\frac{U_c}{2.5}\right)$$

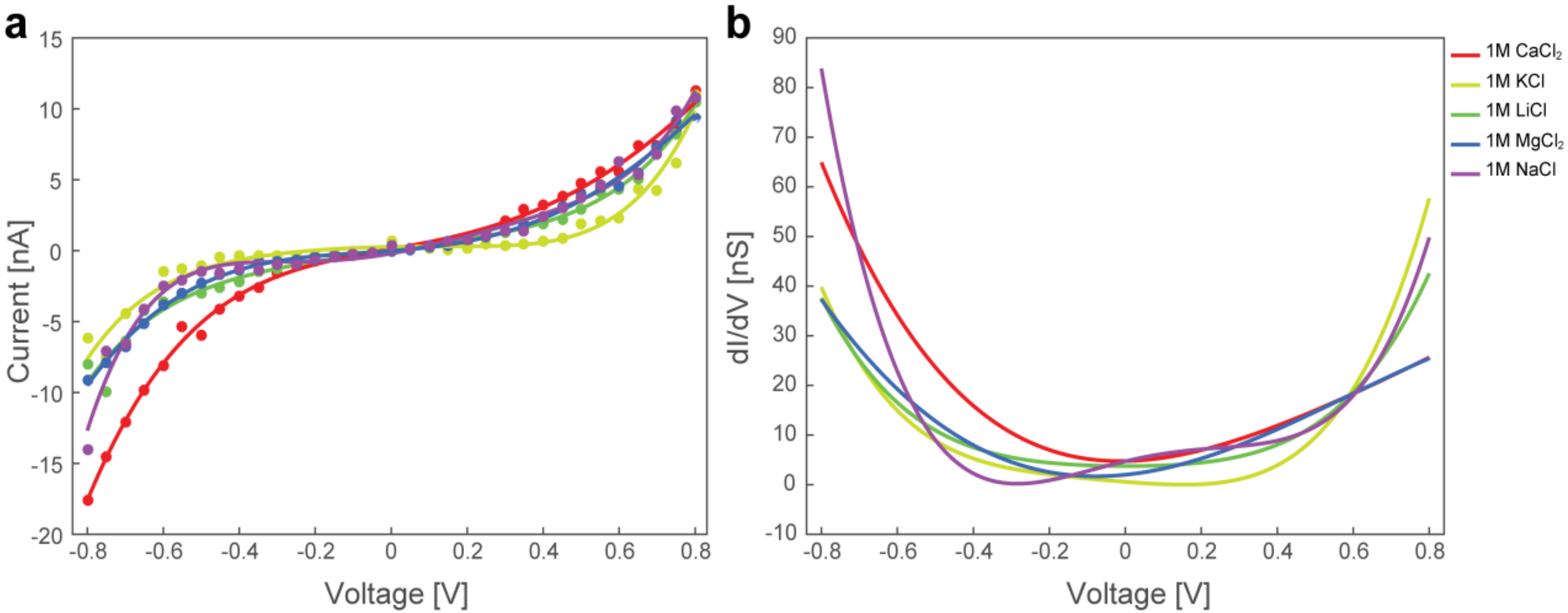


Calcium conduction

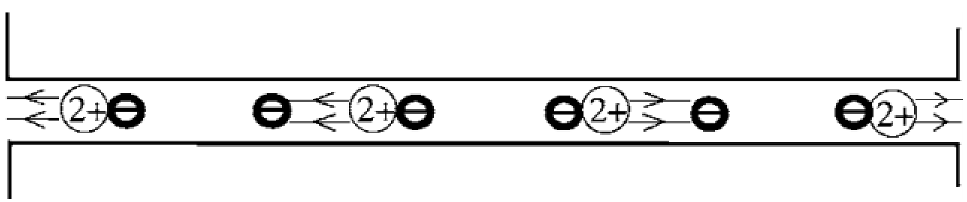
Parsegian, Nature, 1969
Shklovskii, PRL, 2005, PRE, 2006
Di Ventra, JPCM, 2013
Kaufman et al, NJP, 2015

Ionic valence dependence

However, ions have non-zero diameter and valence

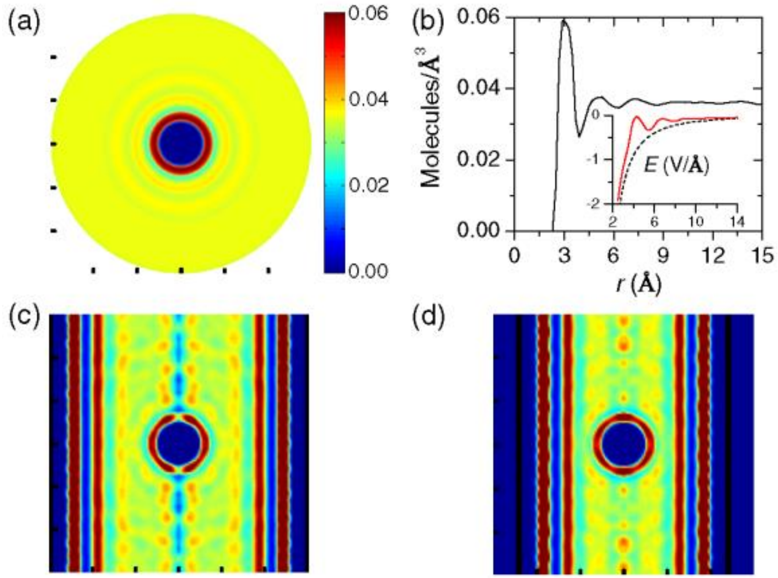


Observed smaller gap for divalent Ca ions can be interpreted by their fractionalization into two separate excitations

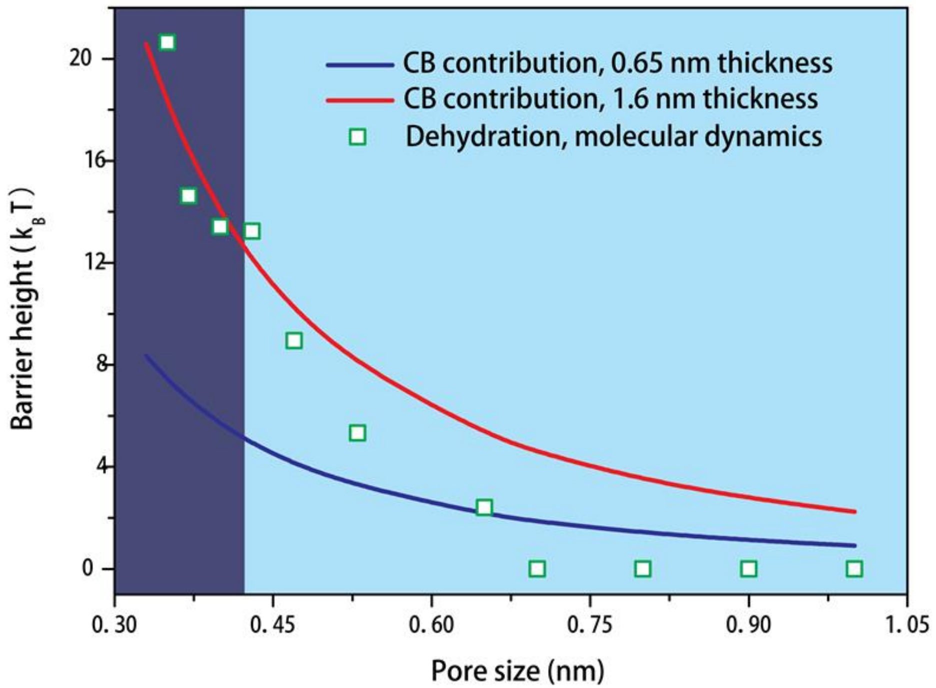


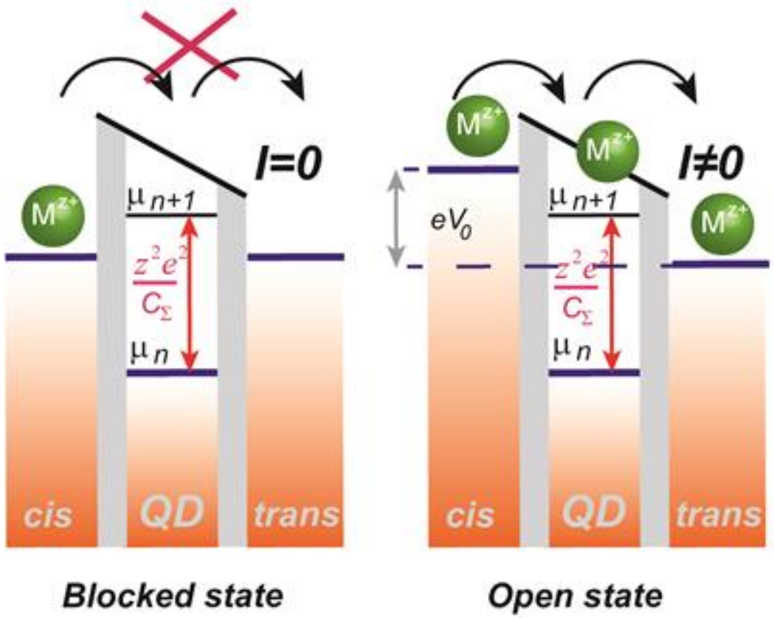
Shklovskii, PRL, 2005, PRE, 2006 and Kaufman, NJP, 2015

Ionic dehydration effect



Zwolak, PRL, 2009





The total charging energy,

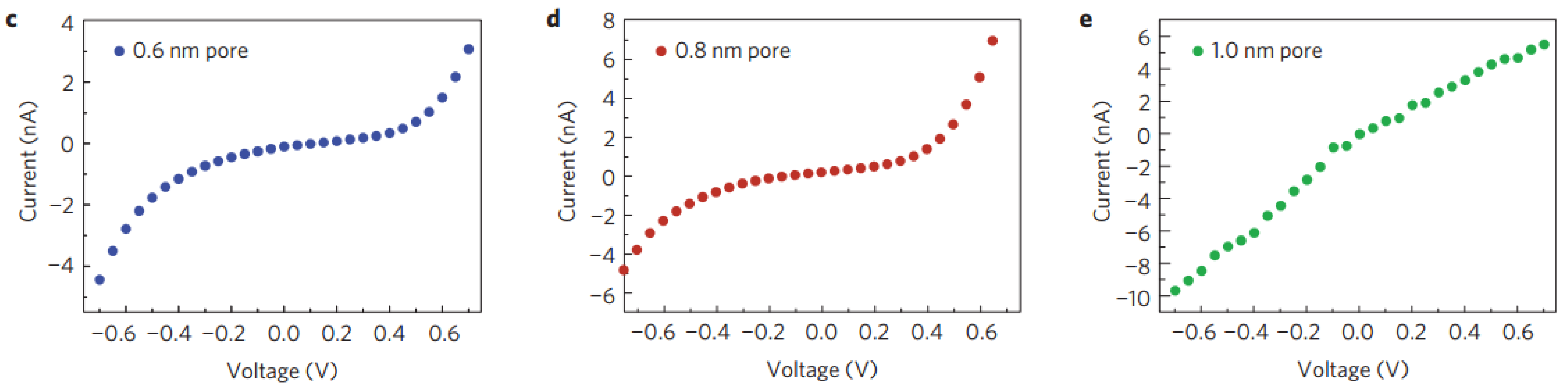
$$\Delta_{N+1} = \mu_{N+1} - \mu_N = U + \Delta E$$

Coulomb gap

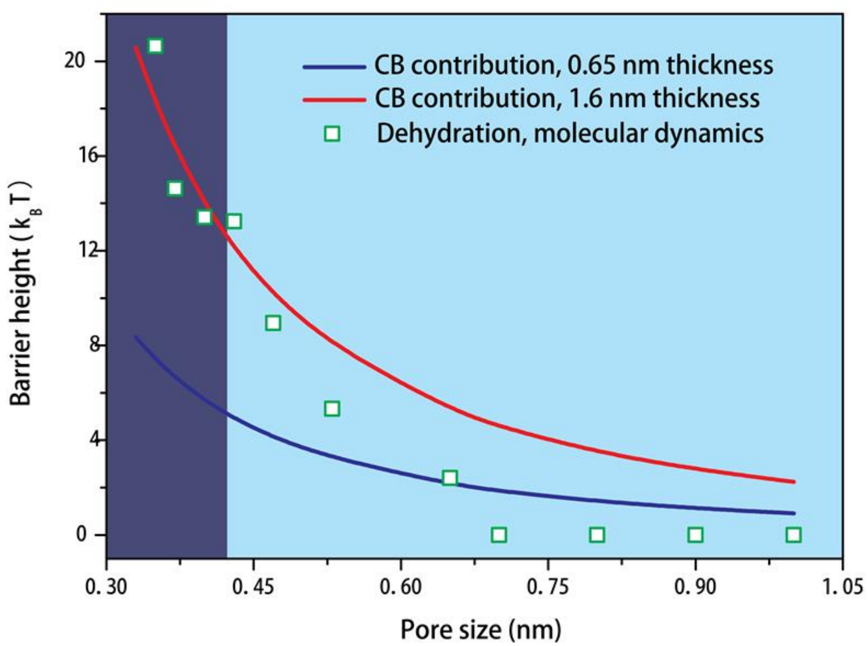
$$U = \frac{z^2e^2}{2C} = \frac{1}{4\pi\varepsilon_0}\frac{z^2e^2L}{2\varepsilon_W r^2}$$

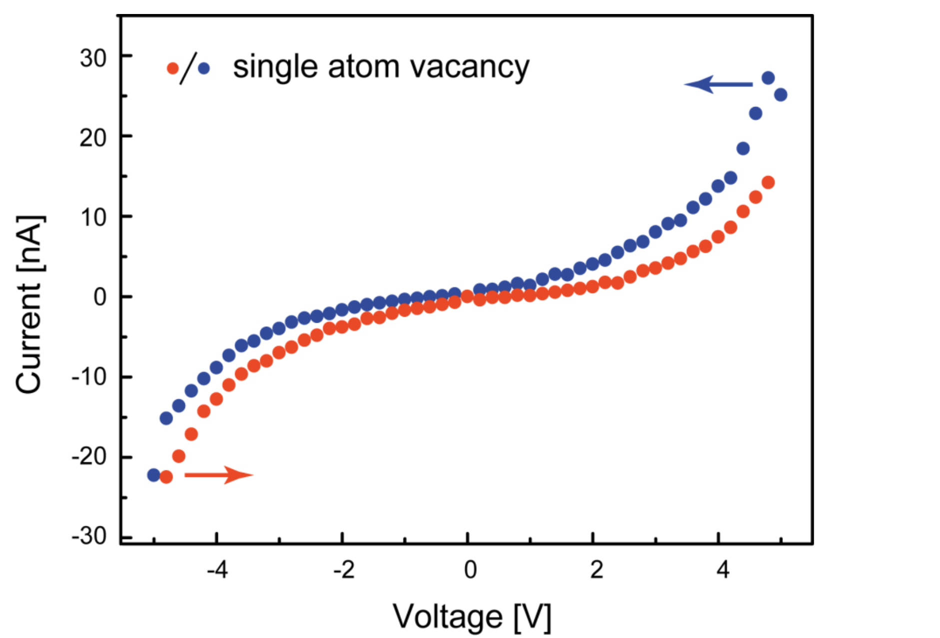
Dehydration energy (excitation) ΔE

Pore size



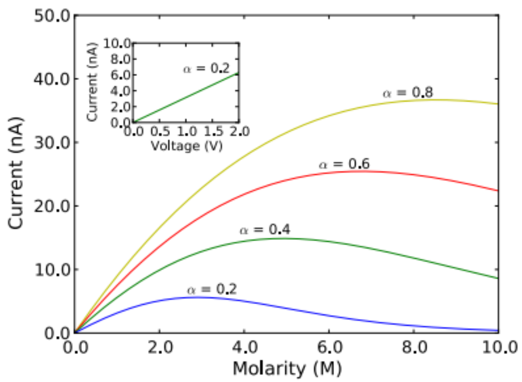
Energy gaps only observed when pore size is smaller than 1 nm



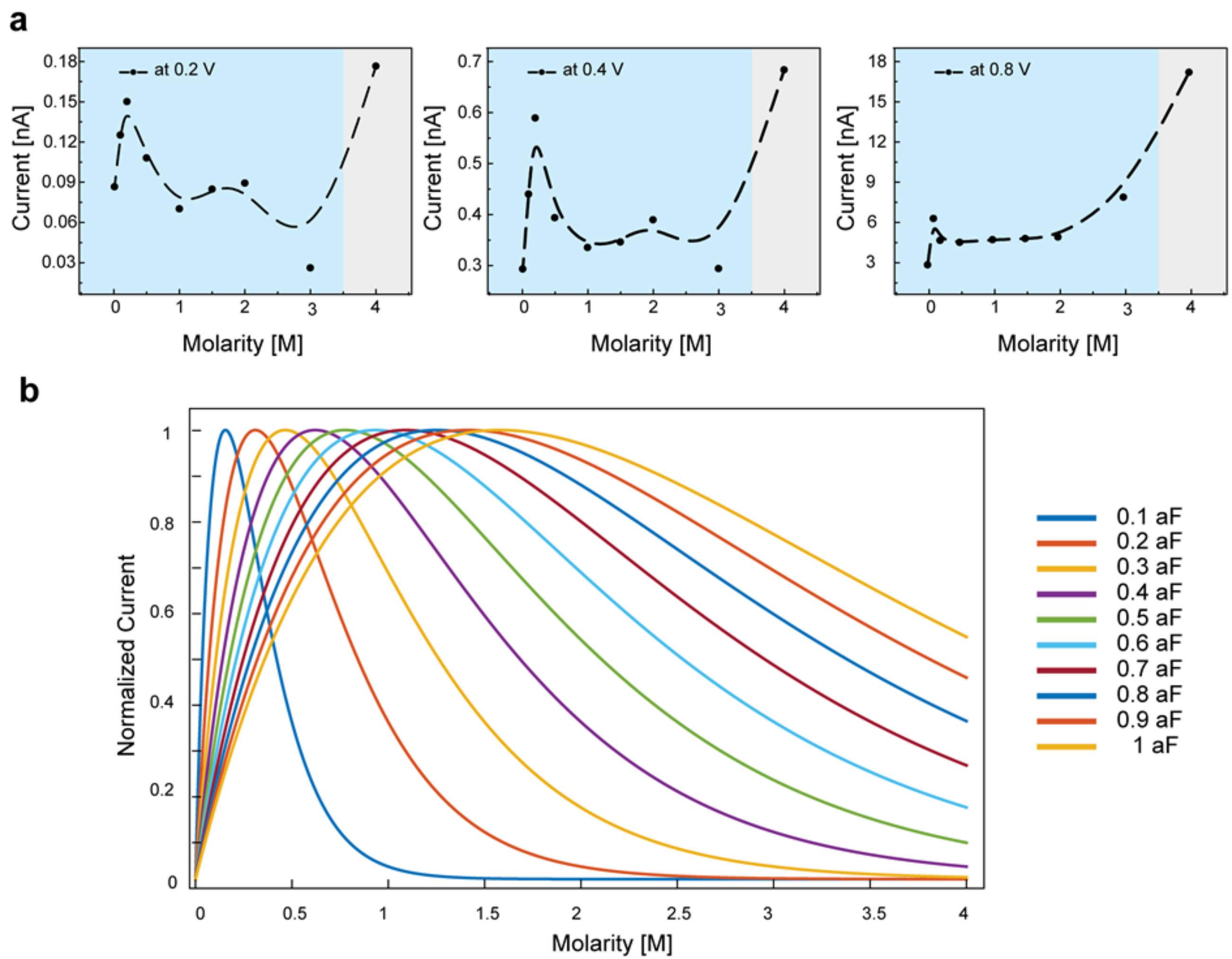


Current-molarity relation

$$I_b = e\alpha\gamma_t \left(\frac{\exp(-\epsilon_C/kT)}{\exp(-\epsilon_C/kT) + \alpha} \right)$$



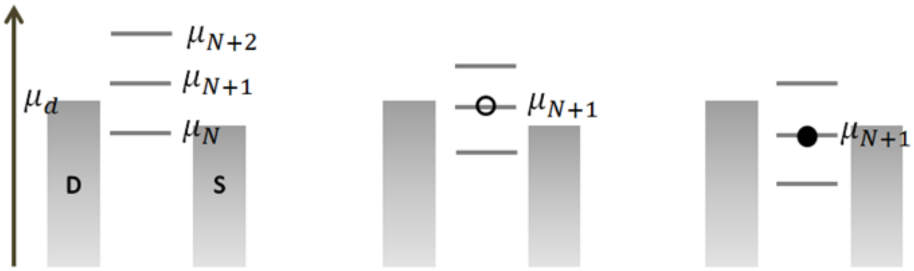
Massimiliano Di Ventra
@UCSD, JPCM, 2013



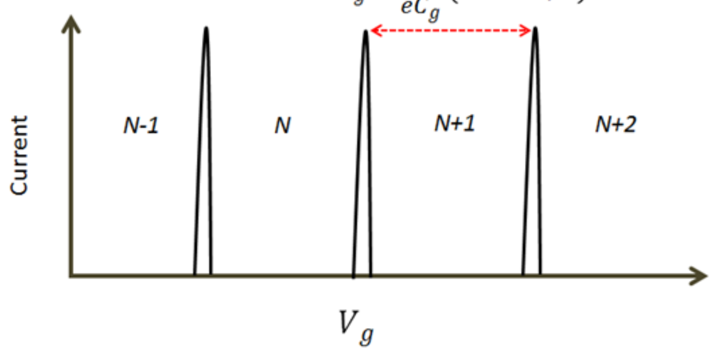
Capacitance obtained: 0.2 aF for experimental peak at 200 mM and 1 aF at 2 M

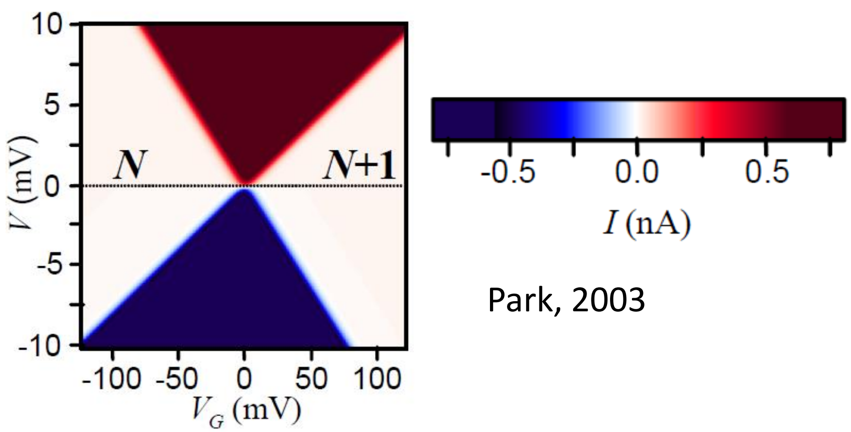
Coulomb oscillations

Electronic transport



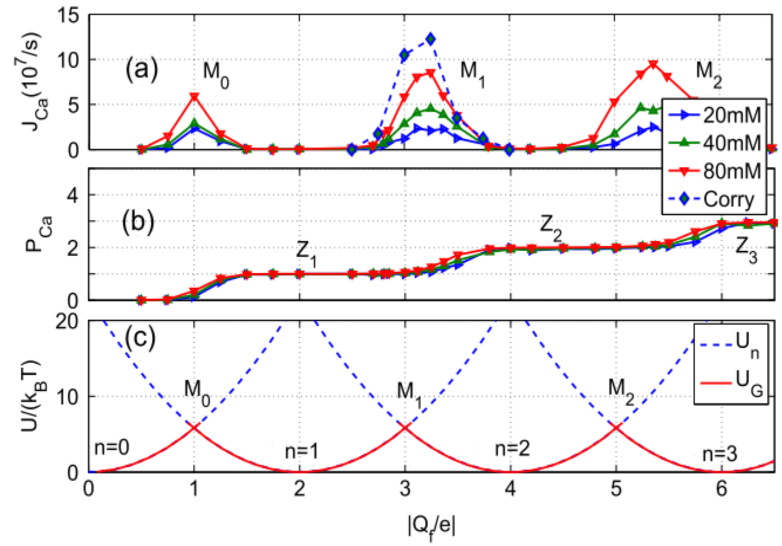
$$\Delta V_g = \frac{C}{eC_g}\left(\Delta E + e^2/C\right)$$

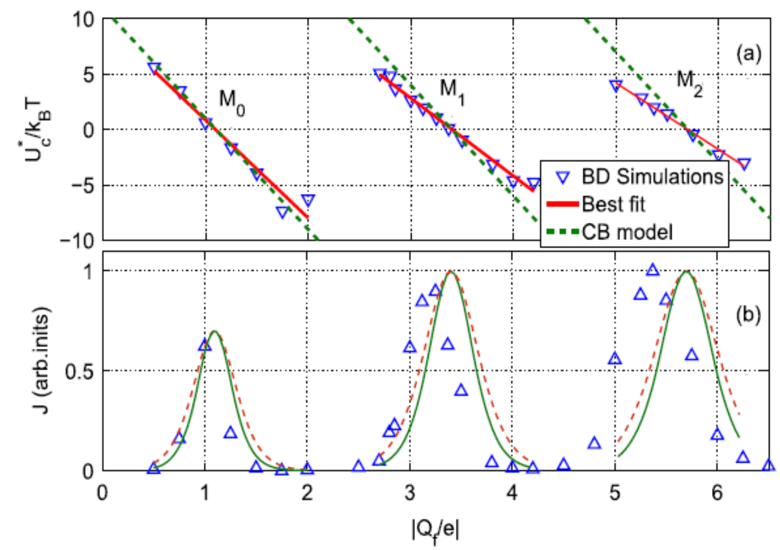




Park, 2003

Ionic transport

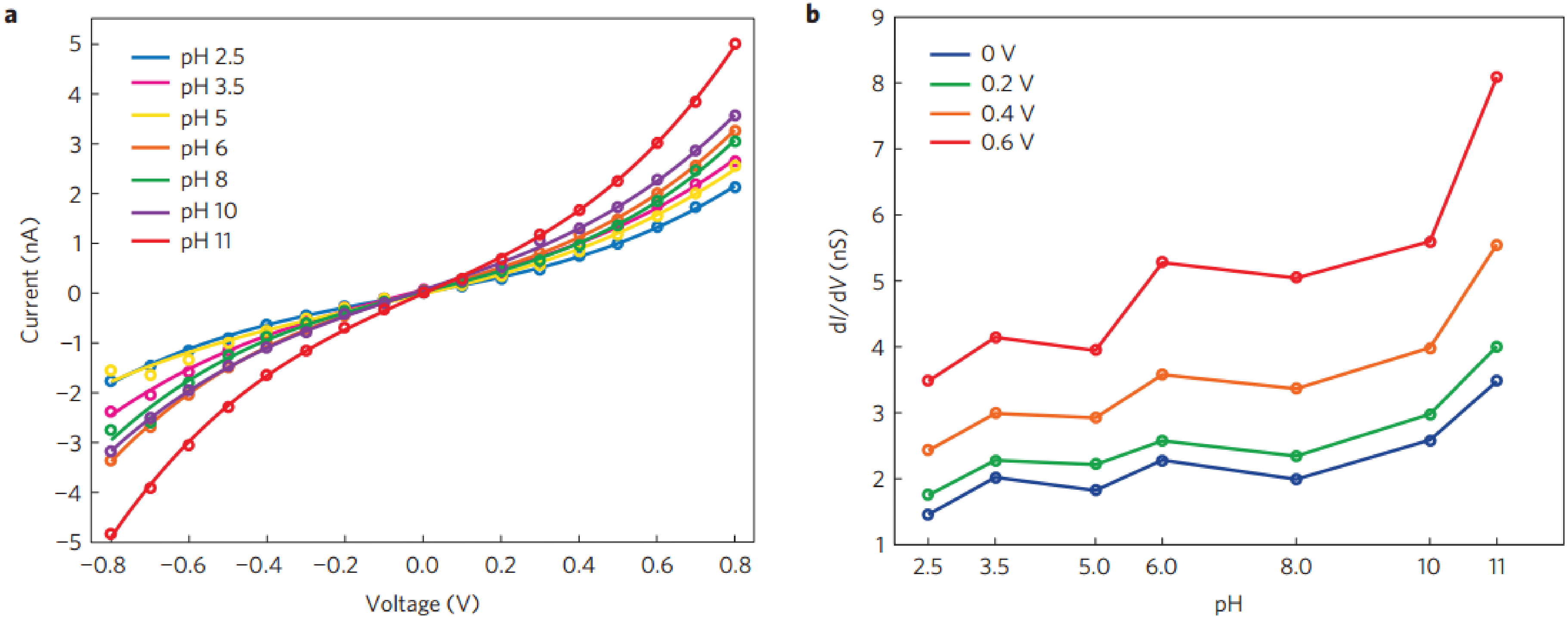




Kaufman et al, NJP, 2015

pH-induced conductance oscillations

Pore surface charge modulation $MoS_2 + H_2O \rightleftharpoons MoS_2 - OH^- + H^+$



Feng, Radenovic et al, Nature Materials, 2016

Conclusion

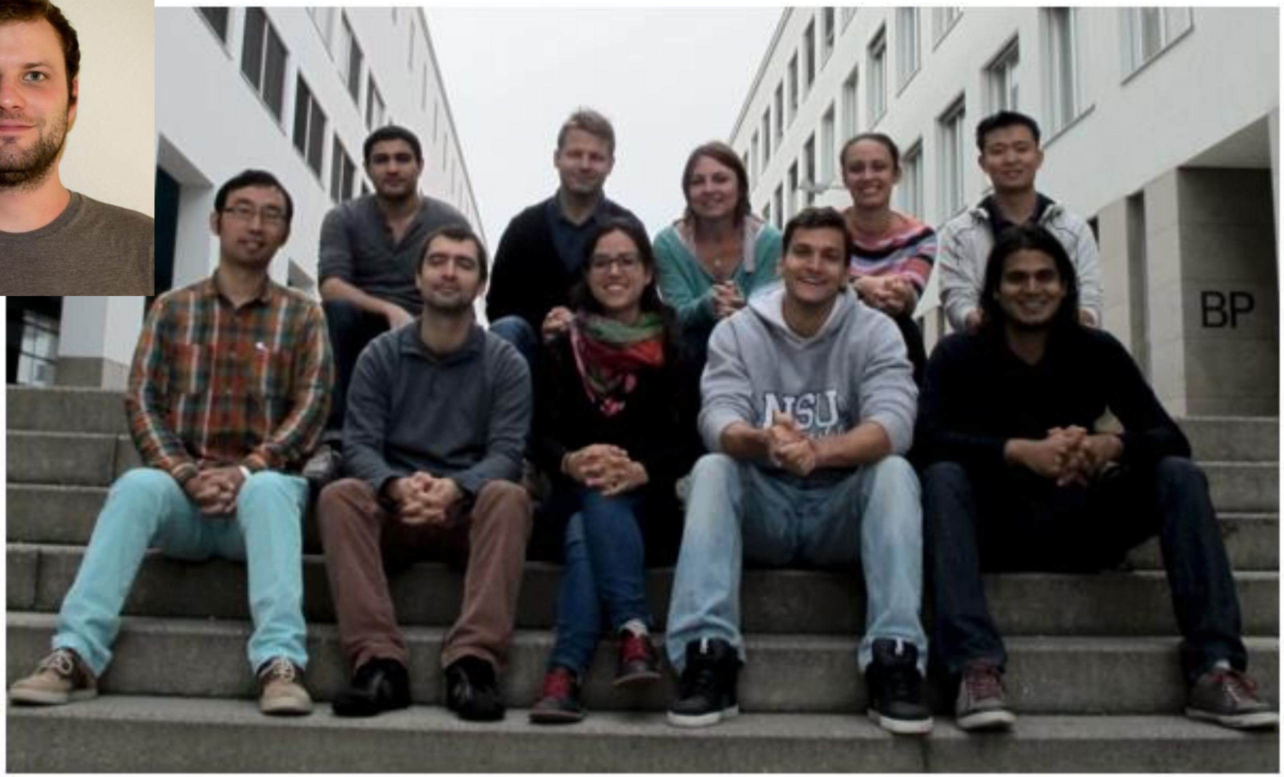
Although Coulomb blockade (a many-body effect) is concomitant with the single particle dehydration effect -**Observed Energy gaps**, the following four observations support the contribution from Coulomb blockade:

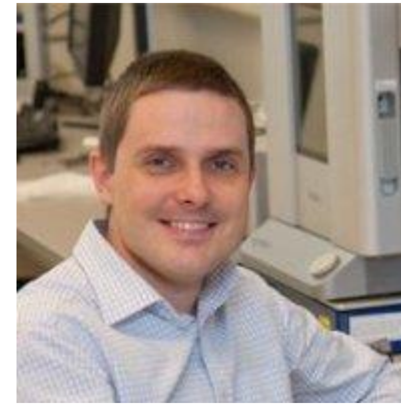
- **Low capacitance of the experimental configuration**
- **Valence dependence**
- **Current–molarity relation as charging results**
- **Conductance oscillations from pH-induced surface charge modulation**

Can we apply Coulomb blockade model to life's transistor: ion channels?

Acknowledgement

Prof. Aleksandra Radenovic and Laboratory of Nanoscale Biology





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