ESPCI PARIS
EDUCATION SCIENCE INNOVATION

SIMM

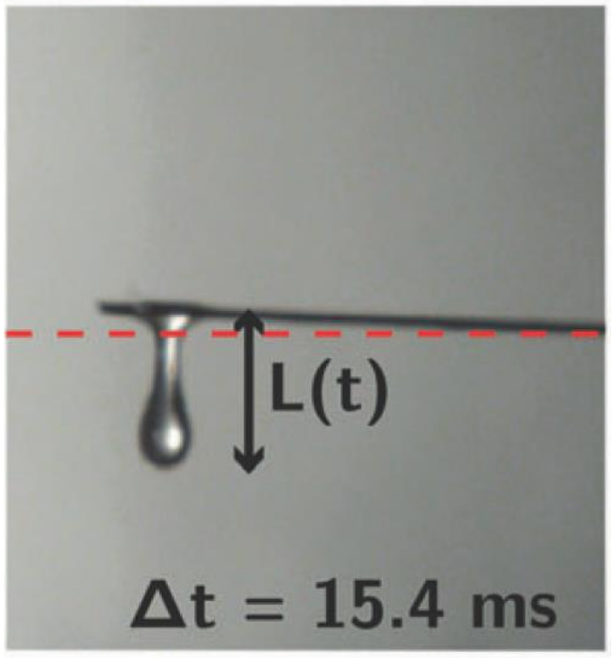
cnrs

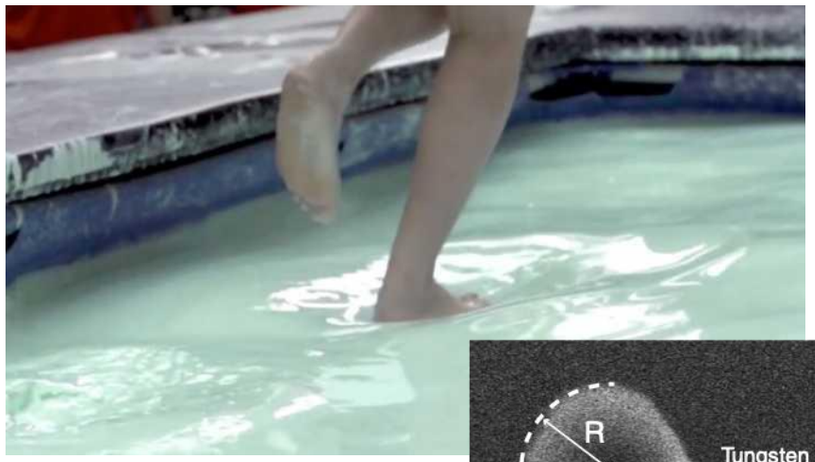
Voir la dynamique des interfaces en matière molle aux échelles nanométriques

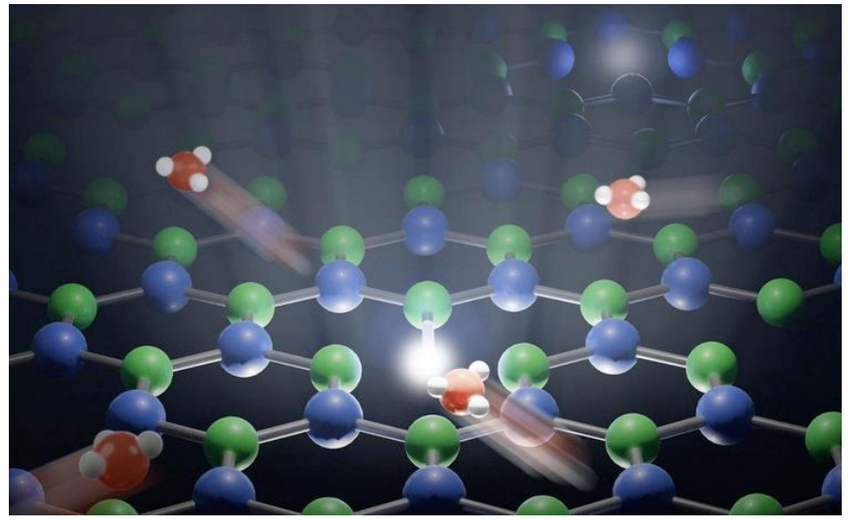
Jean Comtet

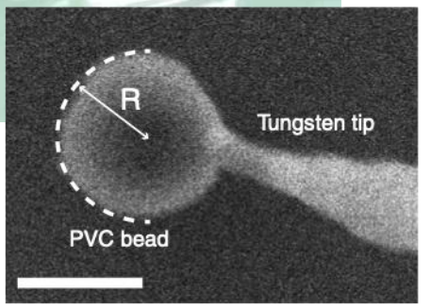
Prix Branly 2021

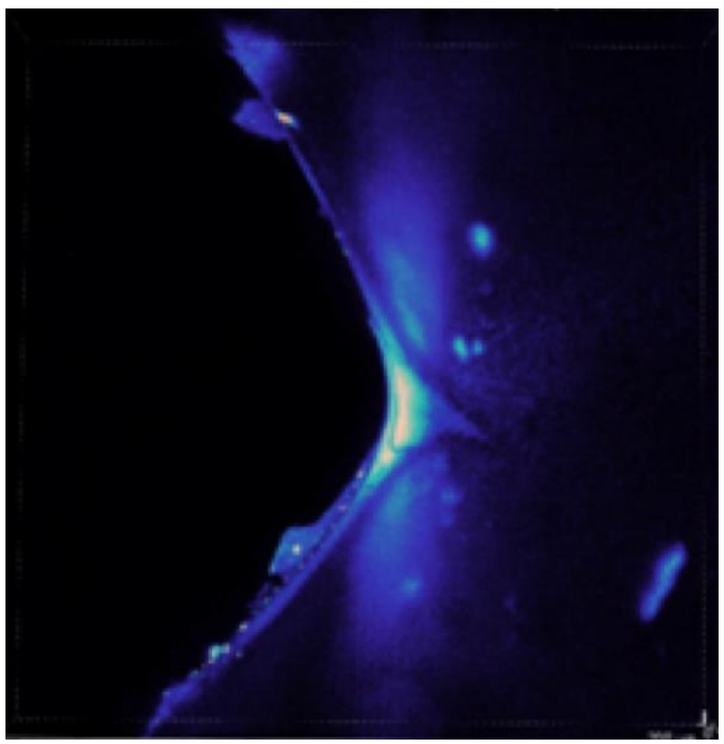
A (short) journey through soft matter (2013-2022)

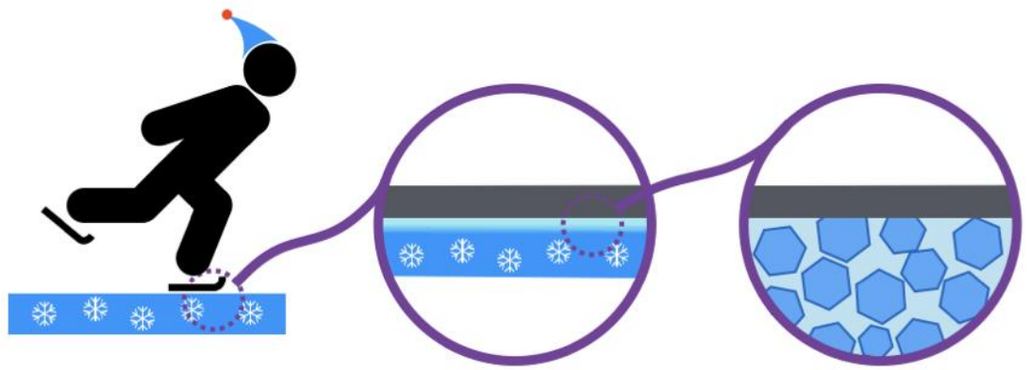


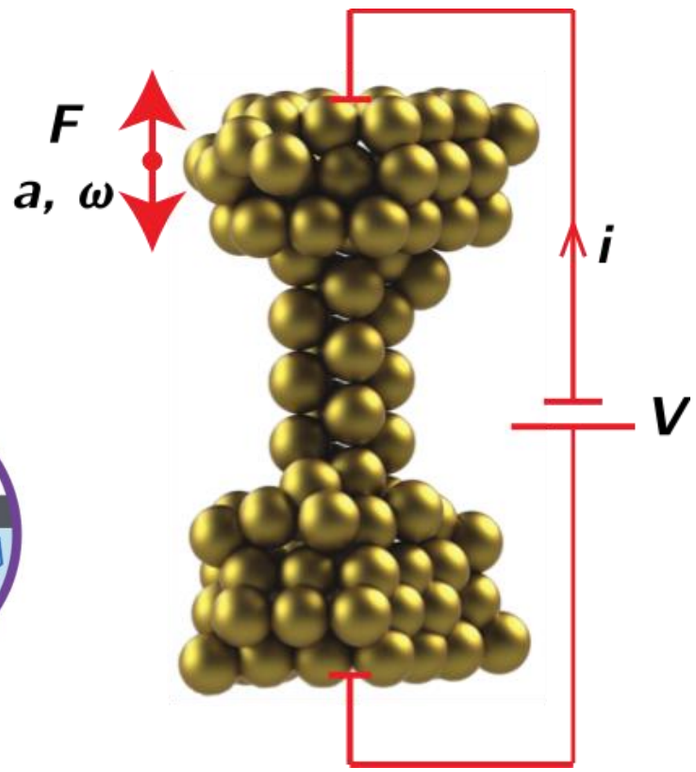








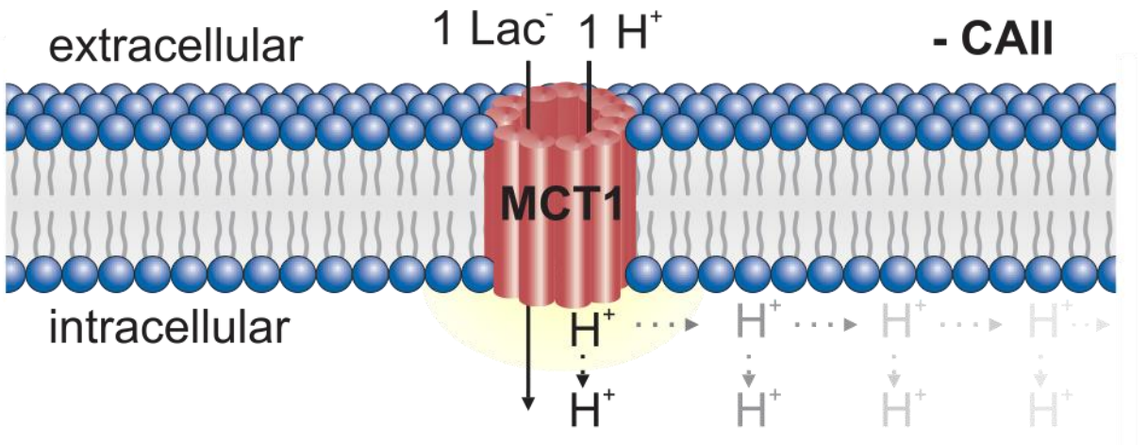




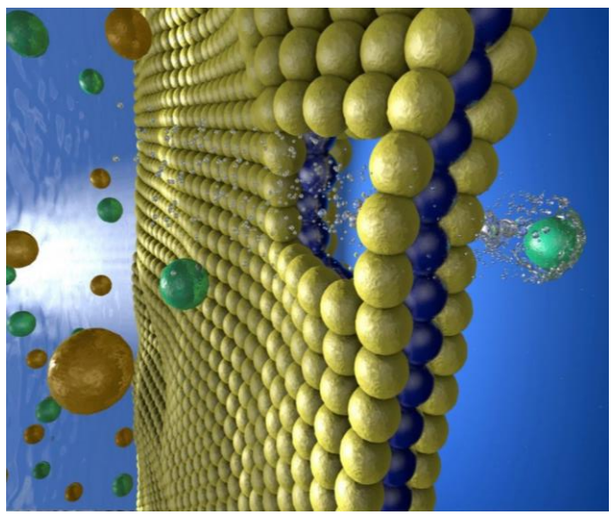
with C. Creton, A. Radenovic, L. Bocquet, A. Siria, A.E. Hosoi, J. Bush

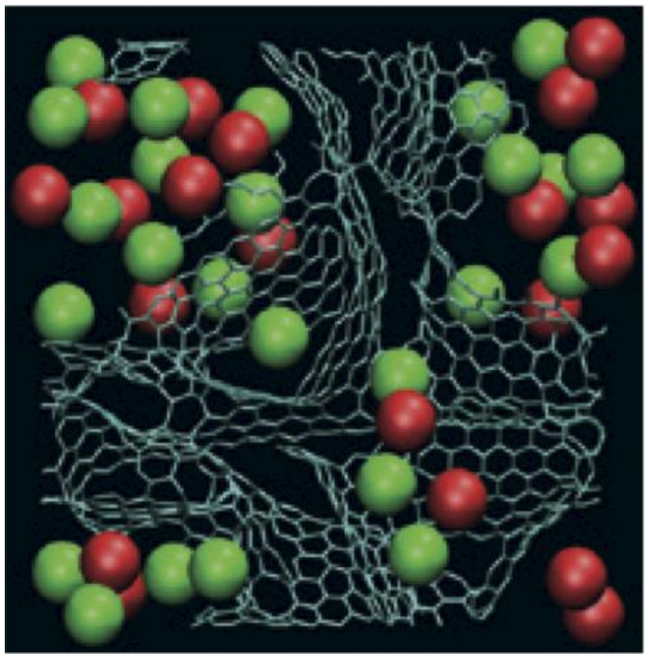
Ion dynamics at solid/liquid interfaces

Biological signaling



Deitmer et al. Journal of Biological Chemistry (2008)





Energy storage

Salanne et al. Nature Energy (2016)

Membrane science and nanofluidics

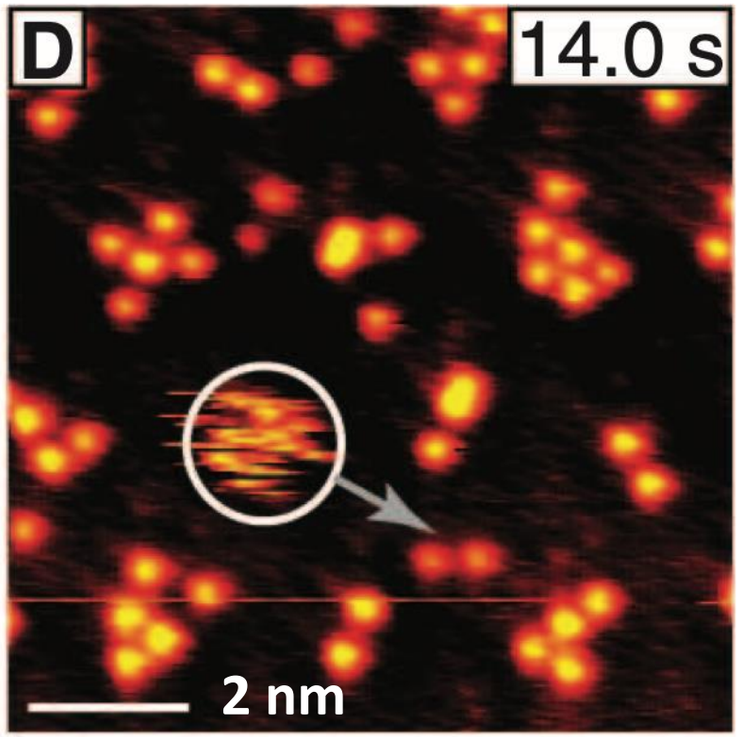
Radenovic et al.
Bocquet et al.

Proton dynamics at interfaces

T = 180 K
P = 10^{-7} mbar

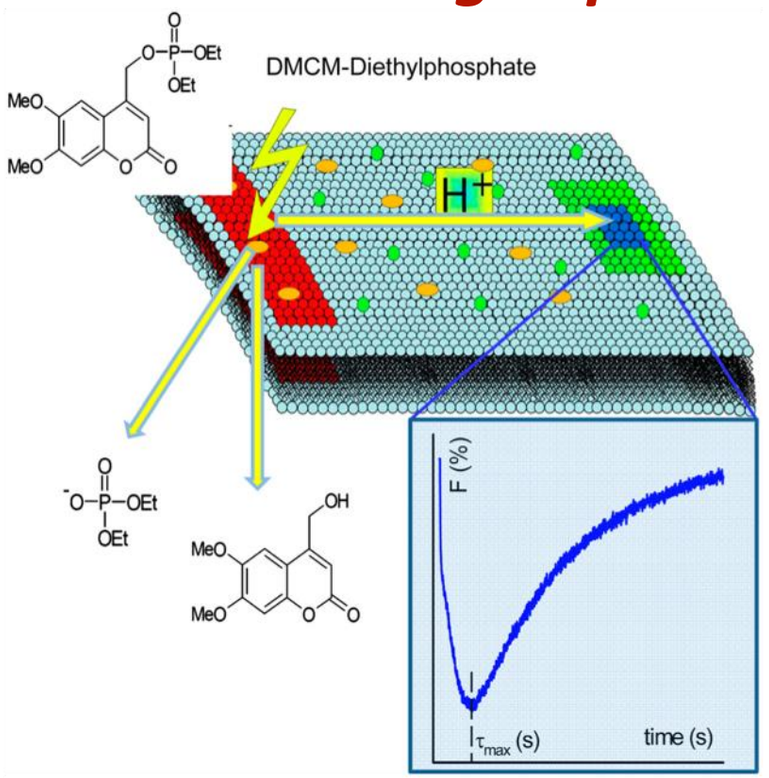
Room Temperature
Liquid Environment

Single Proton transport



Scanning Tuneling Microscopy
Besenbacher et al. Science (2012)

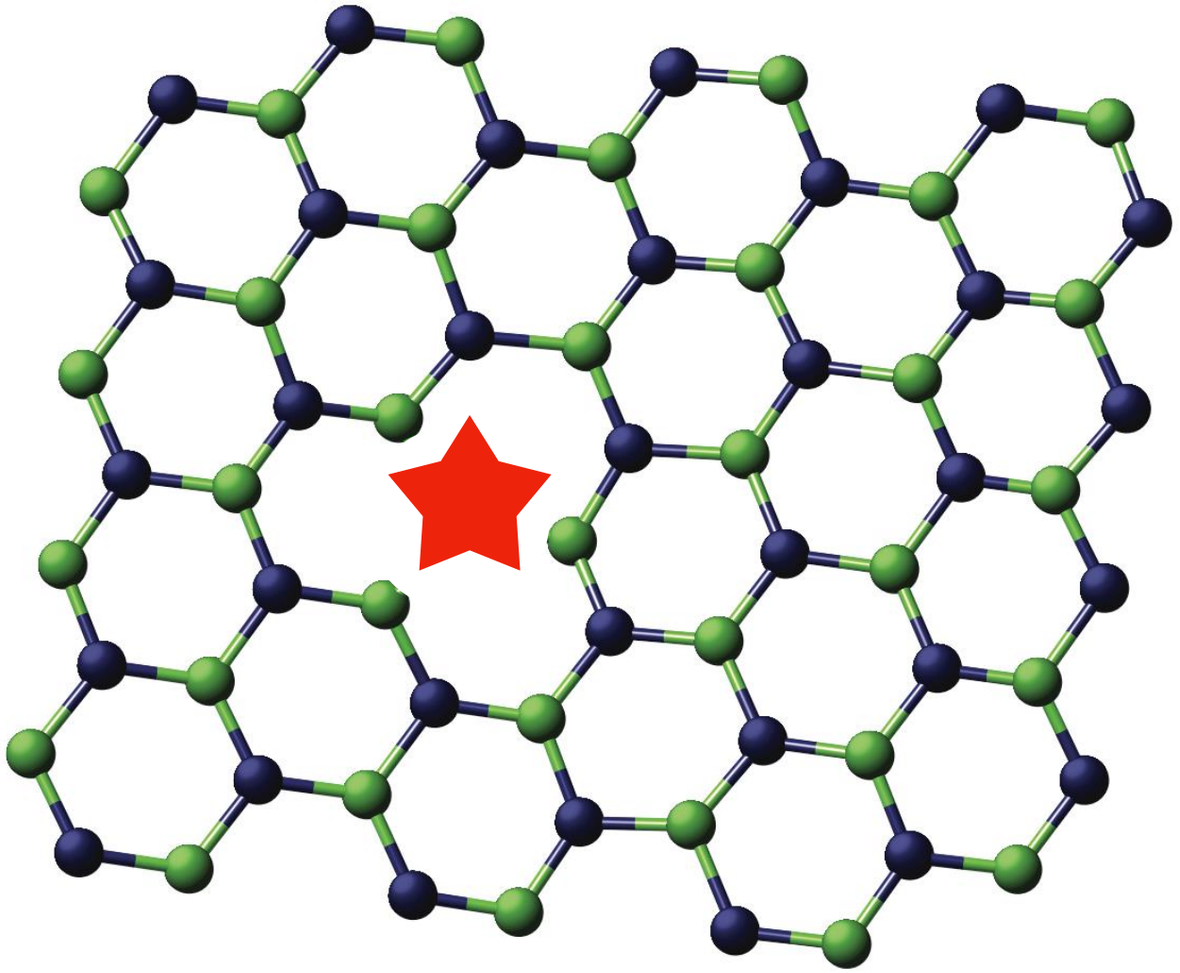
Ensemble Averaged proton transport



Proton-sensitive dyes
Second Harmonic Generation
Pohl et al. PNAS (2011)

Can we directly see single proton charge transport
at solid/liquid interfaces?

Defects in hexagonal Boron Nitride (hBN)

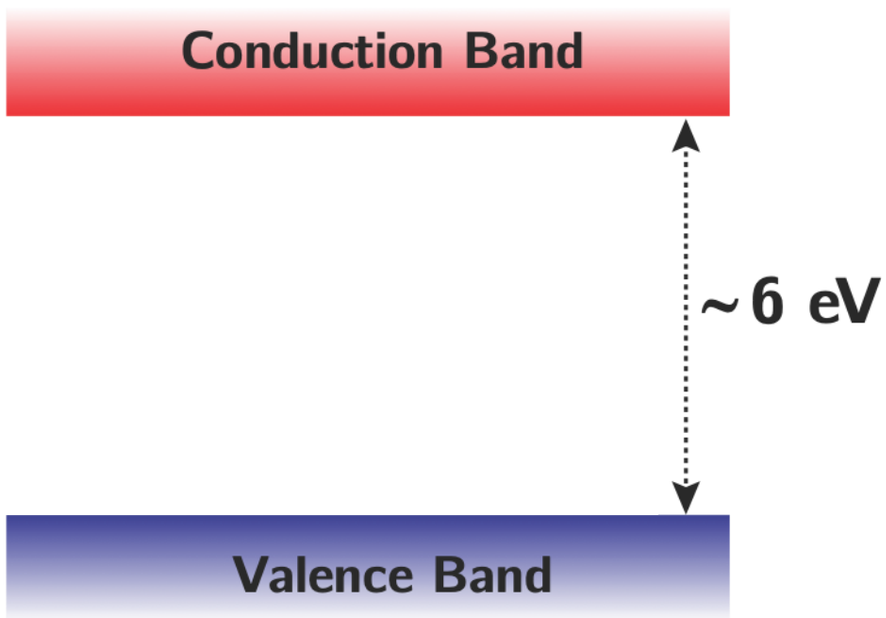


0.5 nm

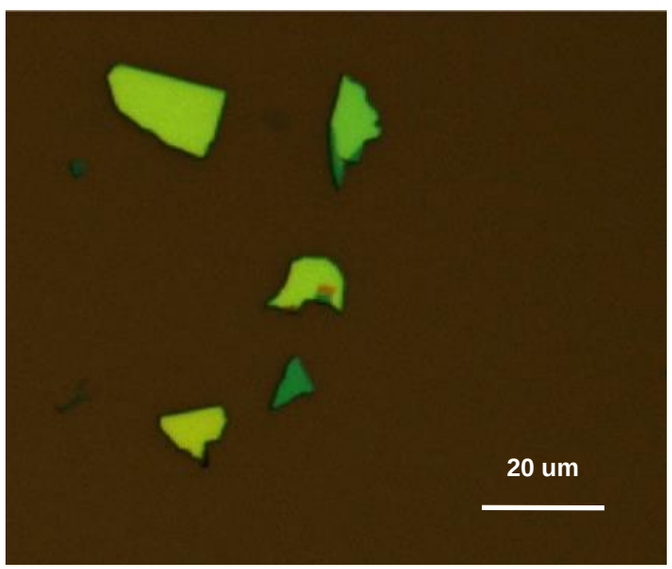
hBN can host fluorescent defects

Ionic layered crystal

Wide band-gap insulator

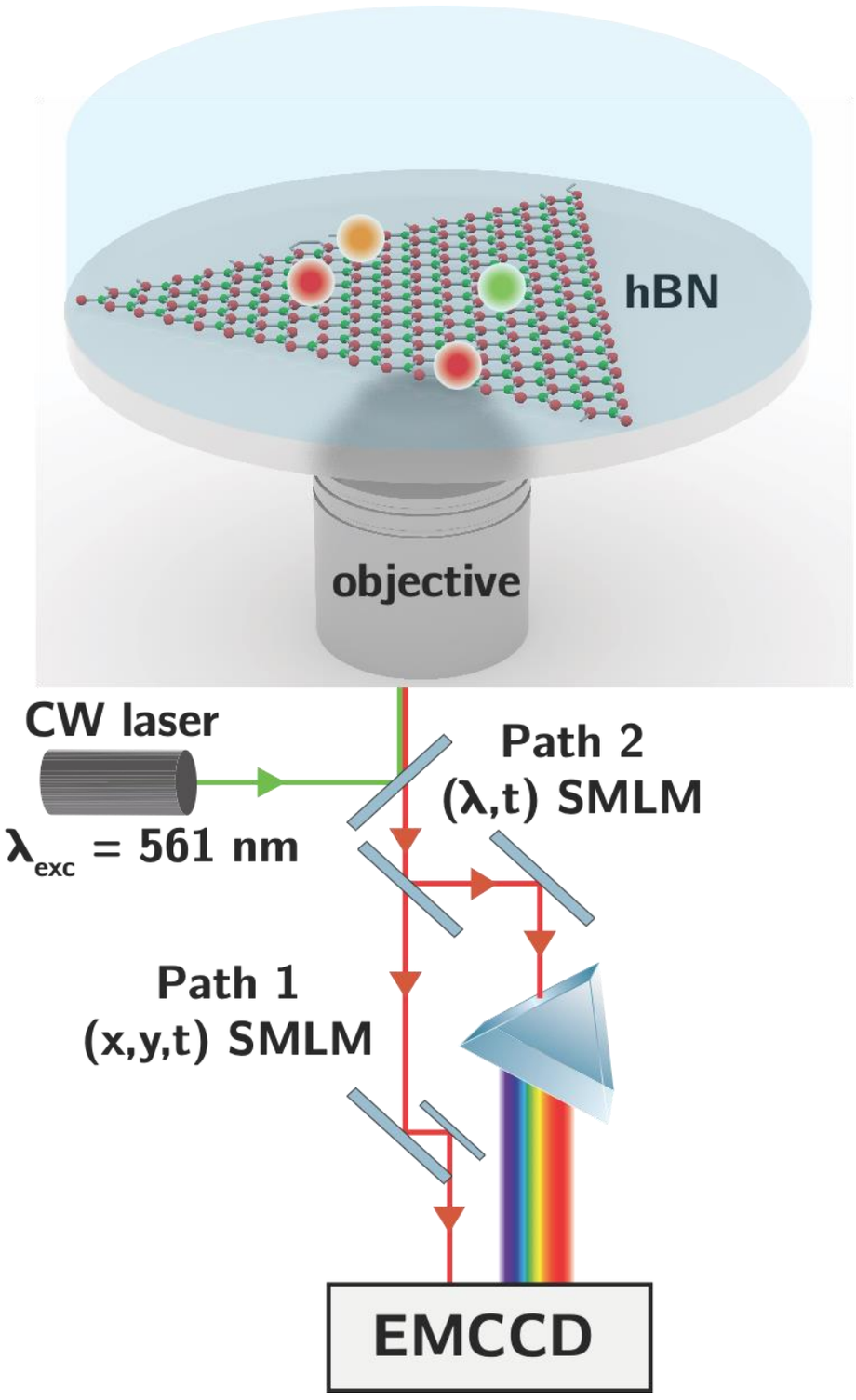


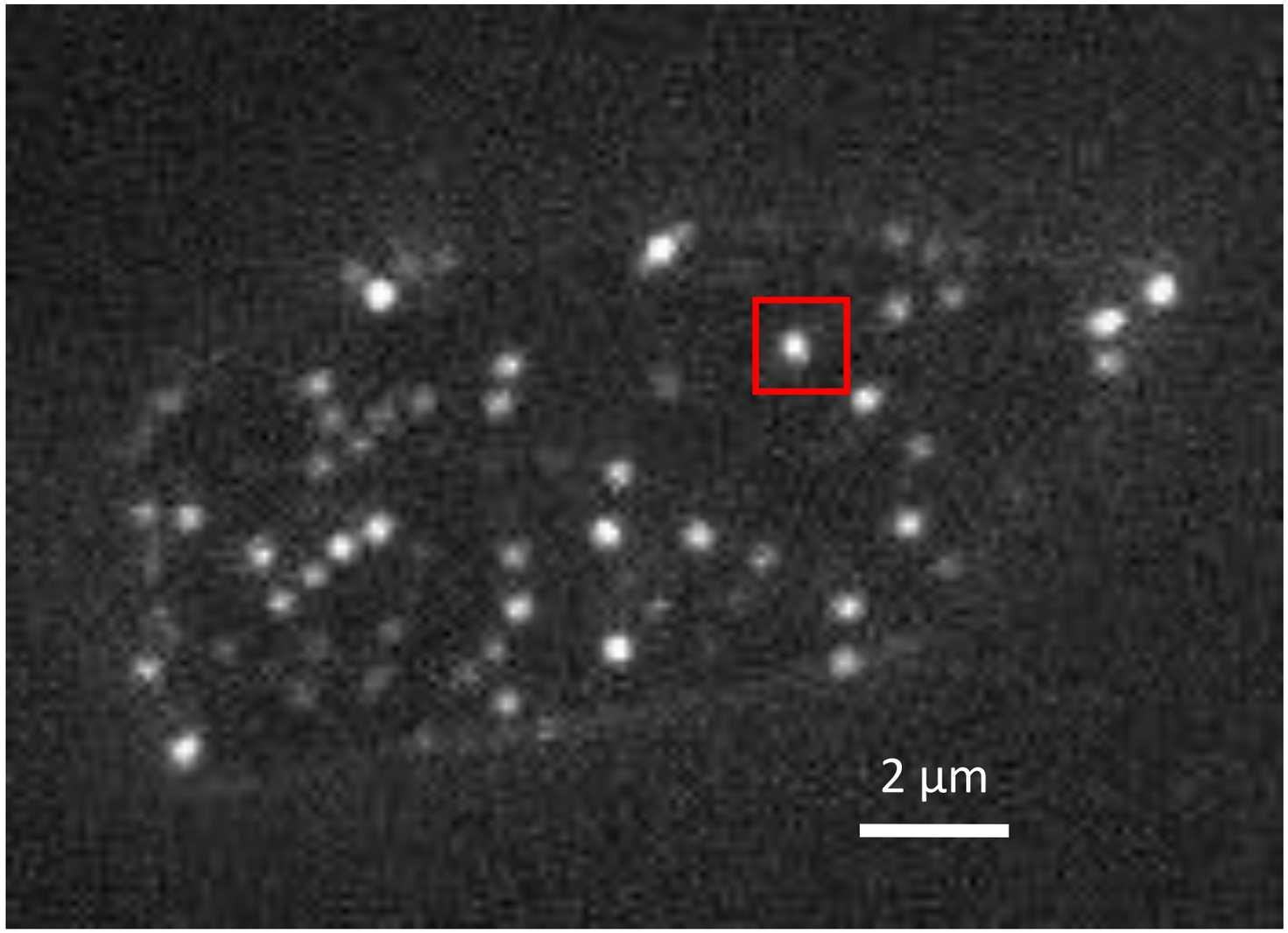
Exfoliation + O_2 plasma treatment



Aharonovich, Nature Nanotechnology, 2015

Super-resolution of optically active defects in hBN





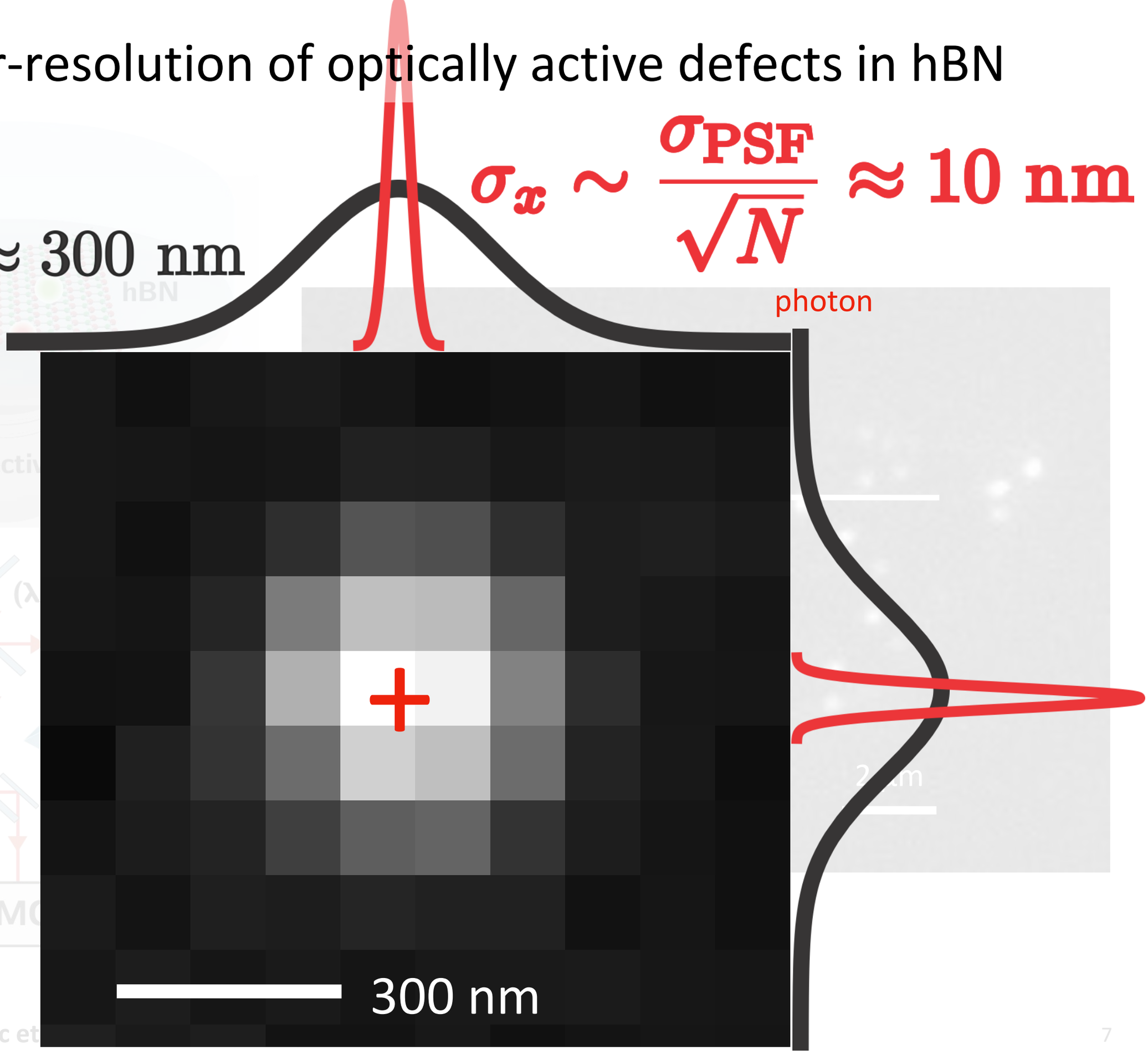
Comtet, Radenovic et al. *Nano letters* (2019)

K Xu et al. Nature Methods (2015)

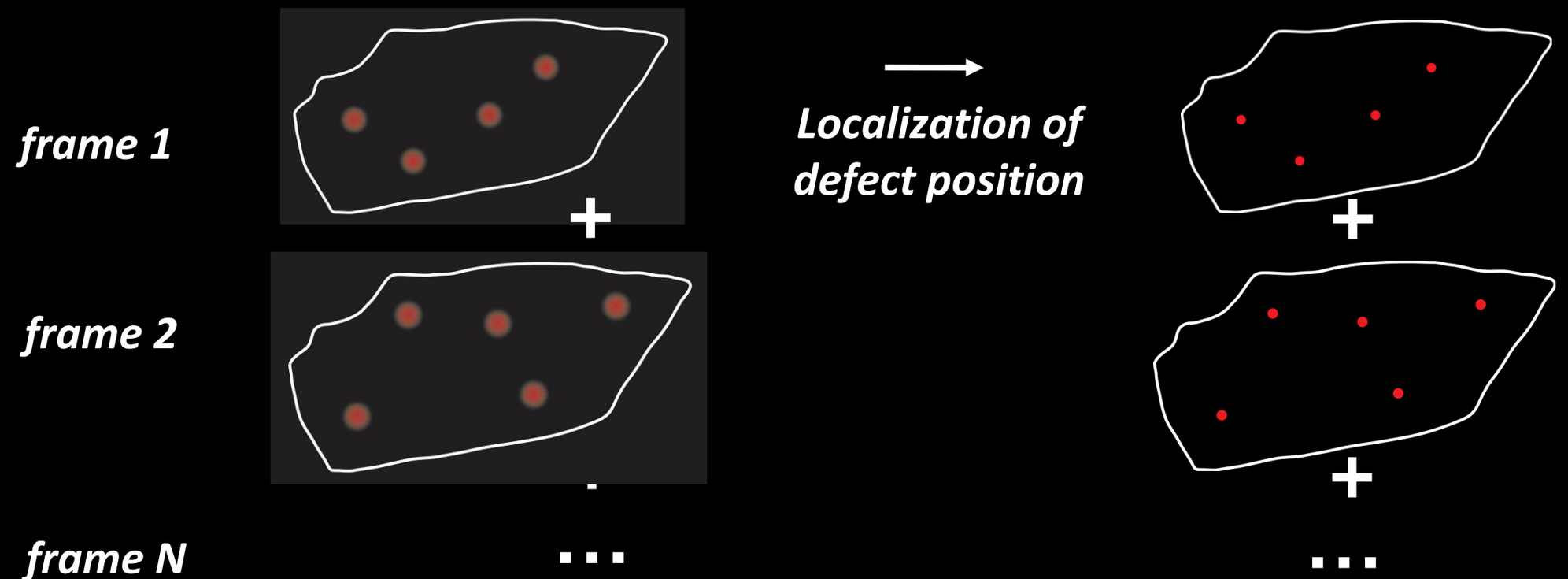
Super-resolution of optically active defects in hBN

$$2 \cdot \sigma_{\mathrm{PSF}} \approx 300 \text{ nm}$$

$$\sigma_x \sim \frac{\sigma_{\mathrm{PSF}}}{\sqrt{N}} \approx 10 \text{ nm}$$



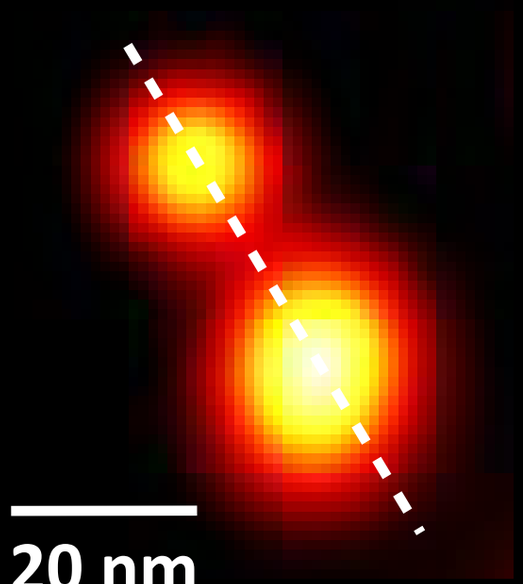
Super-Resolved Image in water

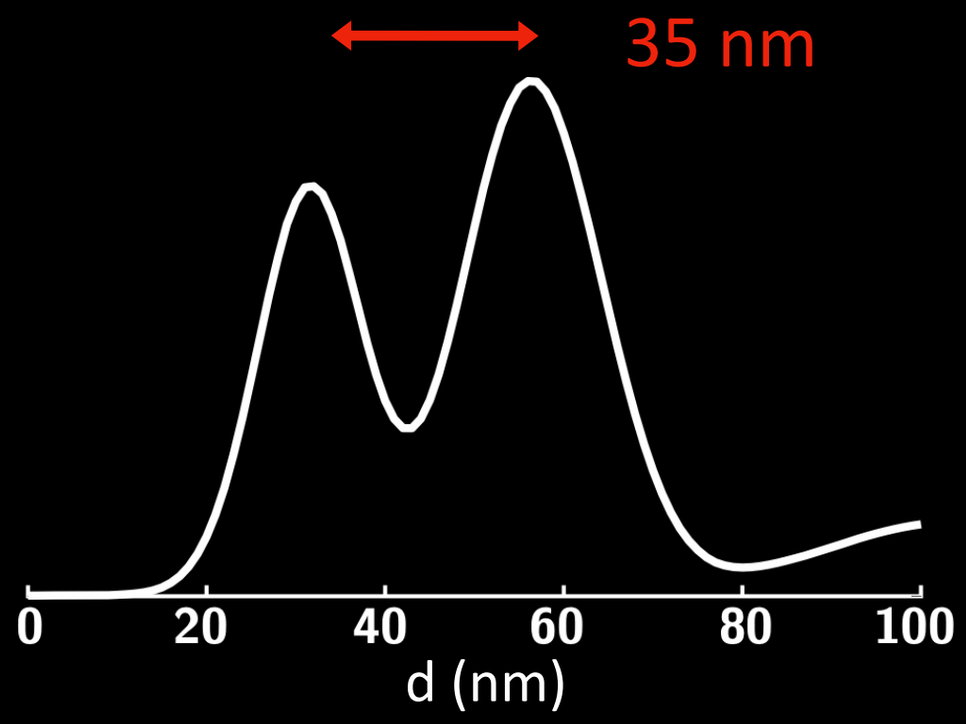


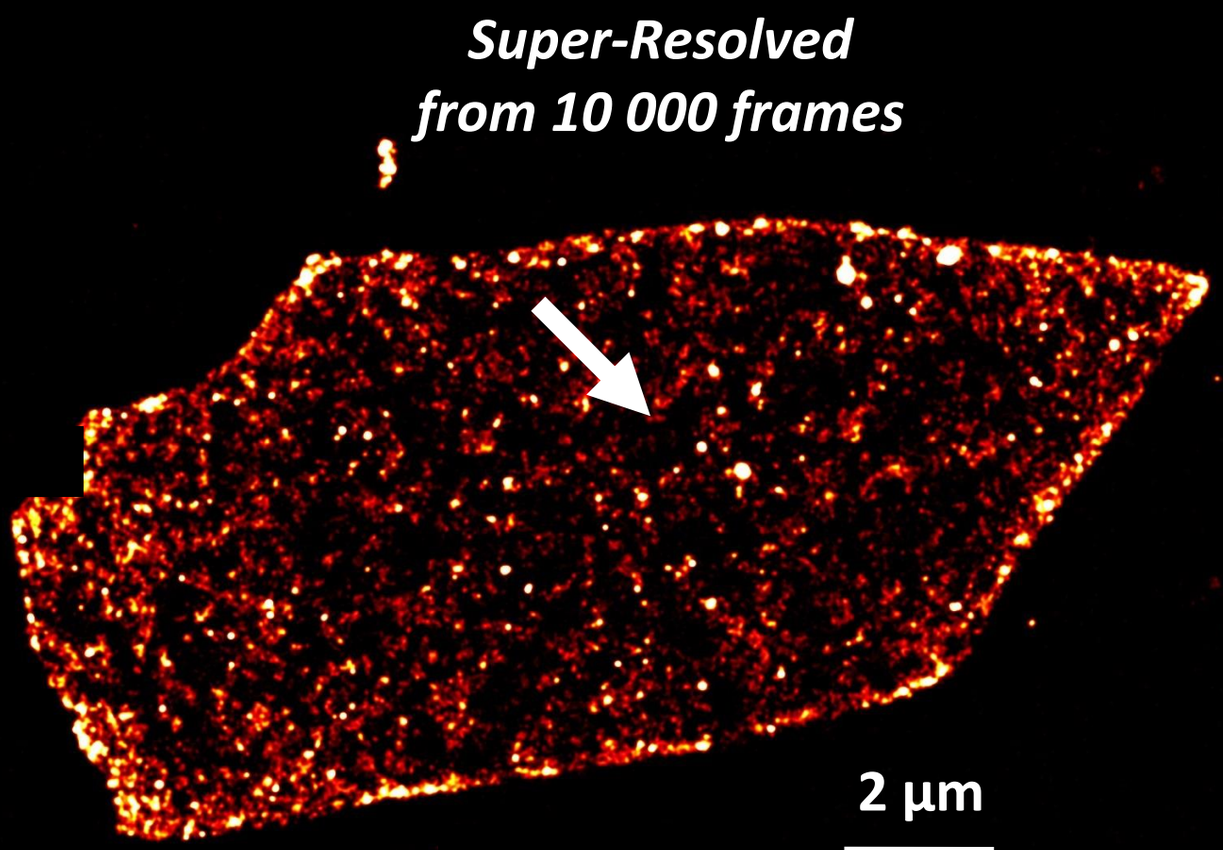
Diffraction-limited

Super-Resolved from 10 000 frames

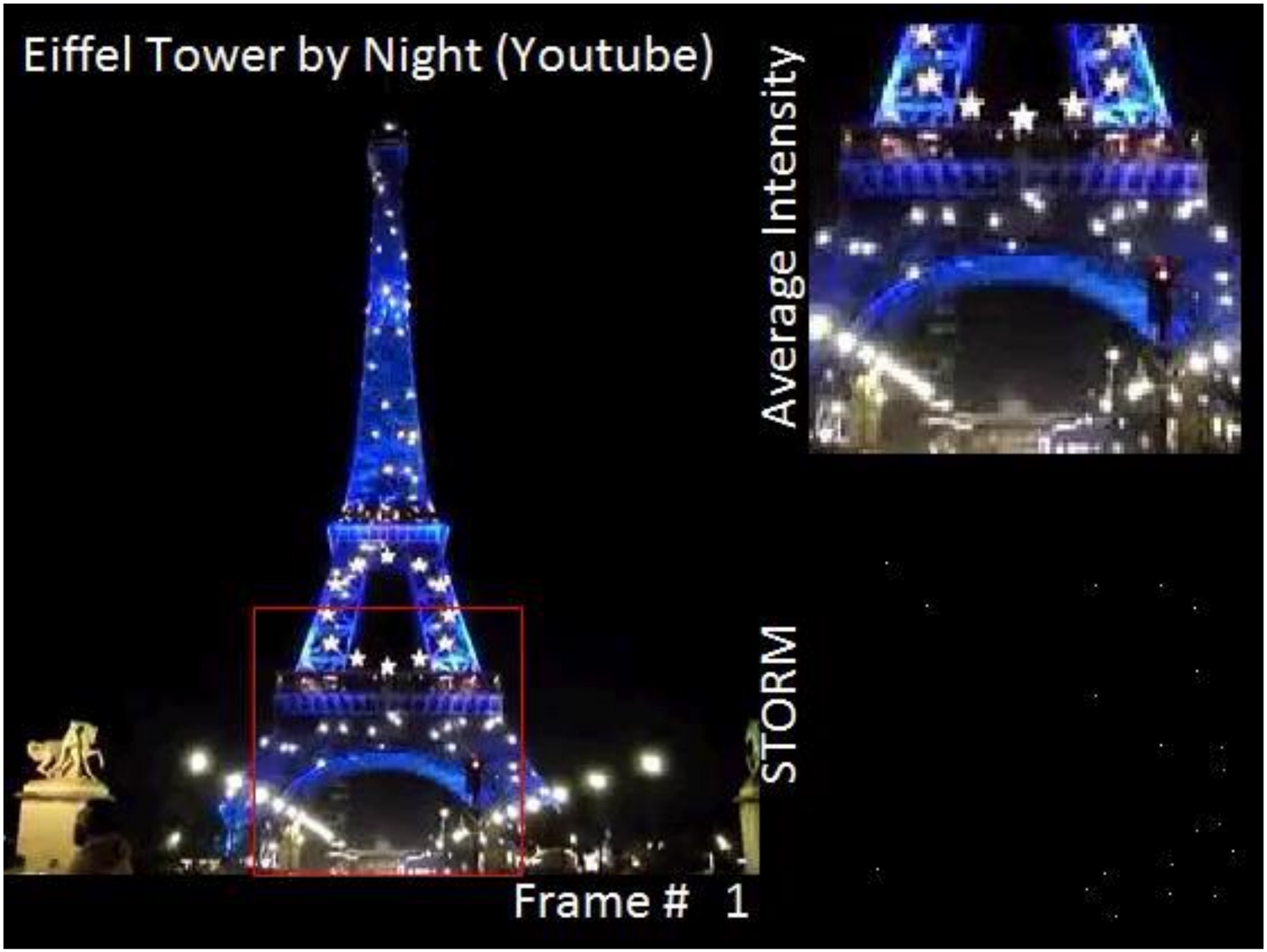
Super-Resolved Image in water







Another illustration of Super Resolution principle

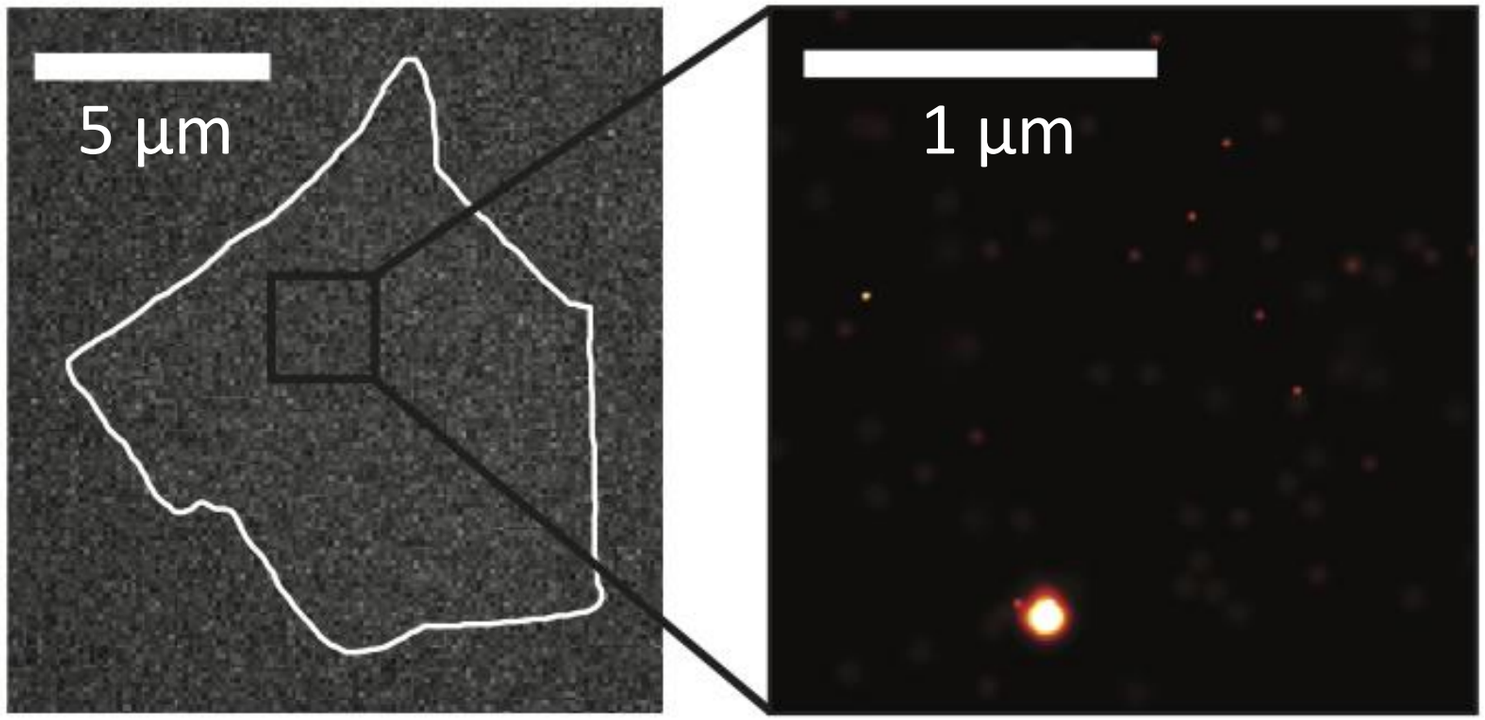


credit: Ricardo Henriques

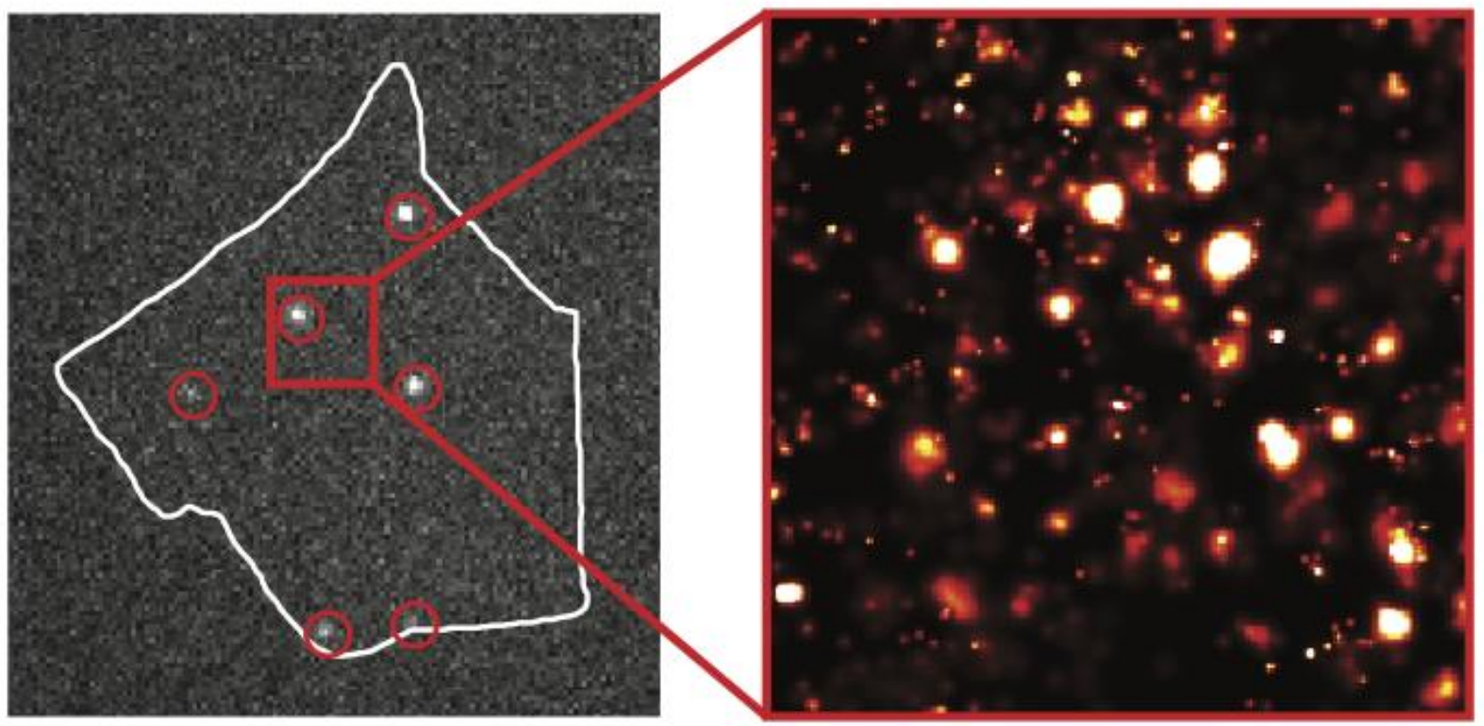
Defect reactivity in water

Wide-field image ***Super-resolved image***

Sample in air



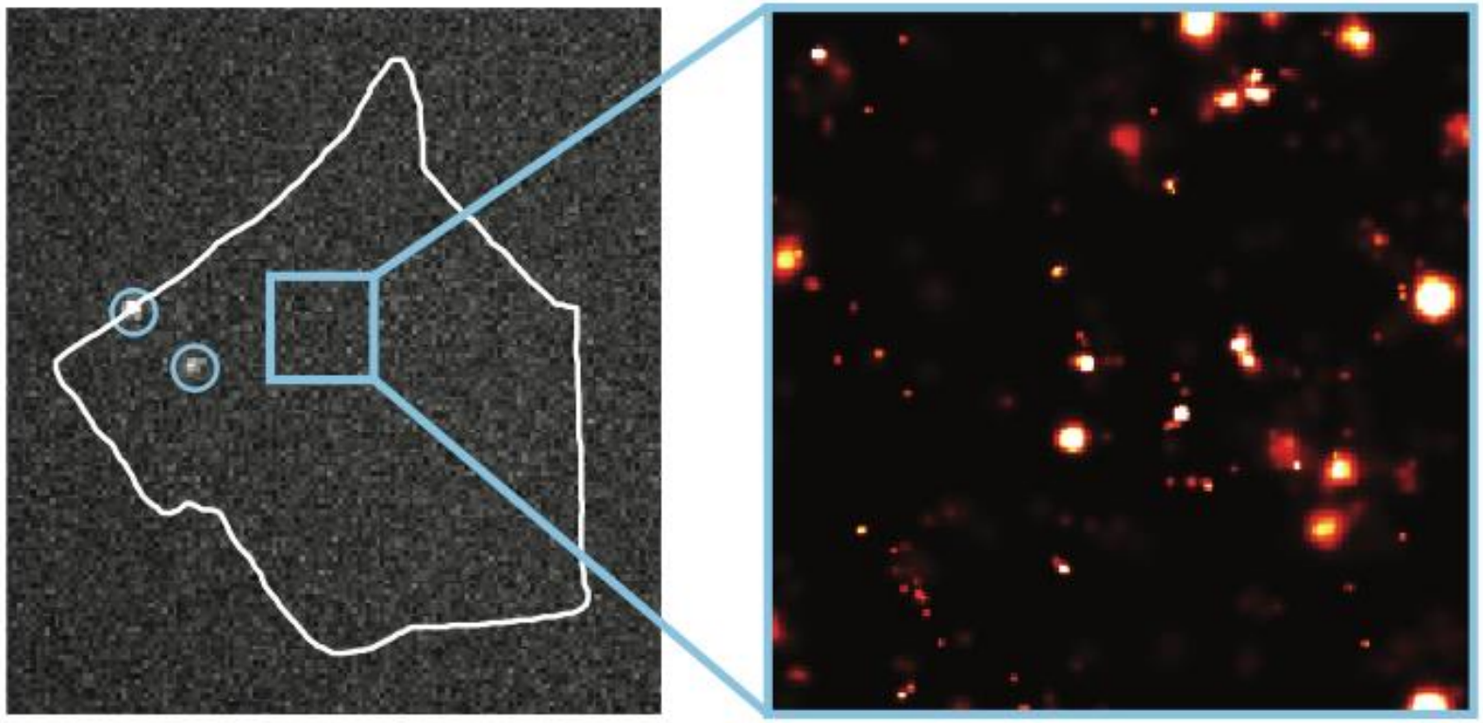
Sample in water
(pH 3)



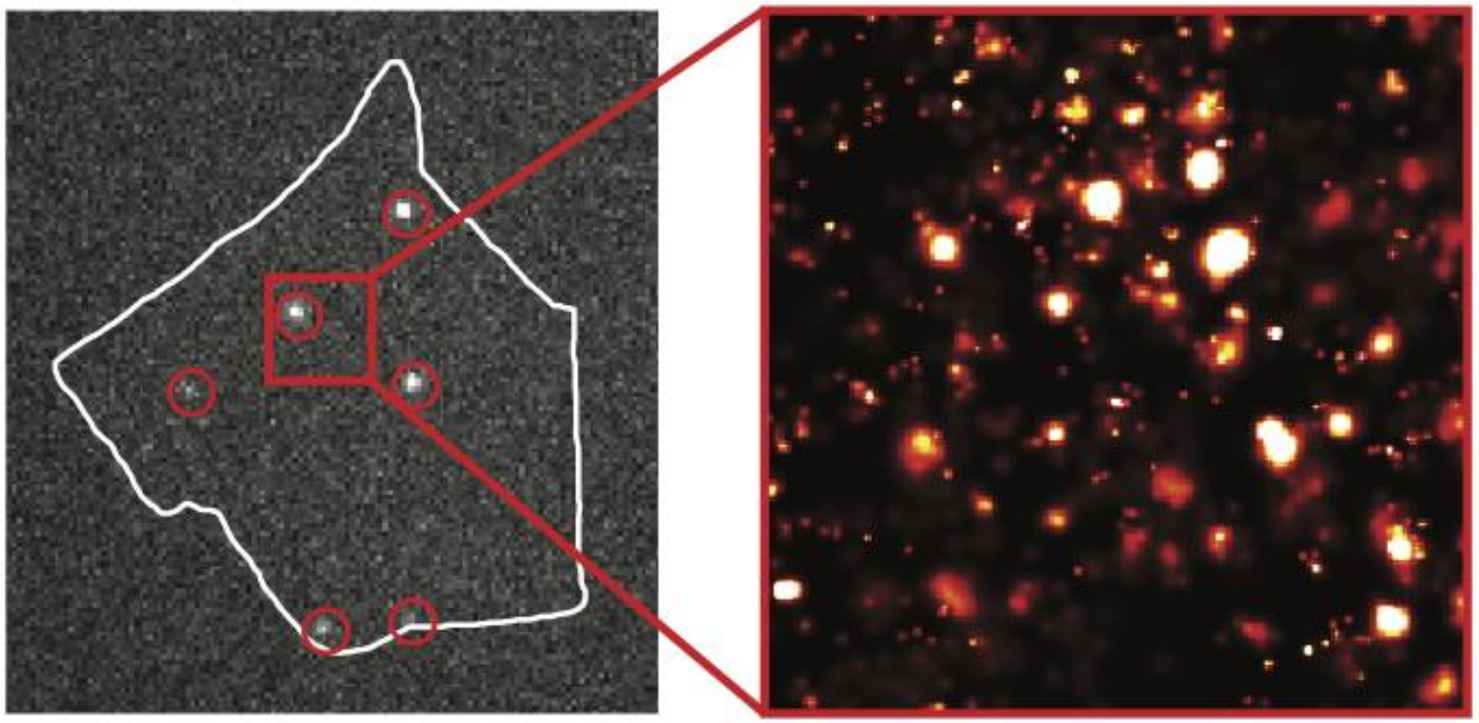
Defect reactivity in water

Wide-field image ***Super-resolved image***

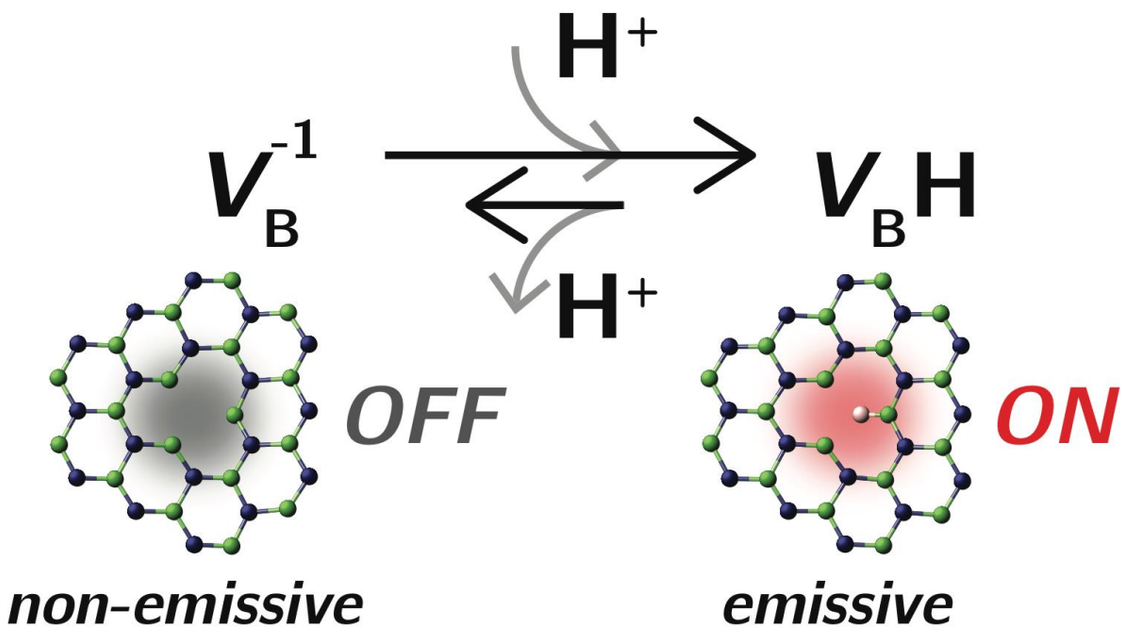
pH 10



pH 3



Emission due to protonated boron vacancy



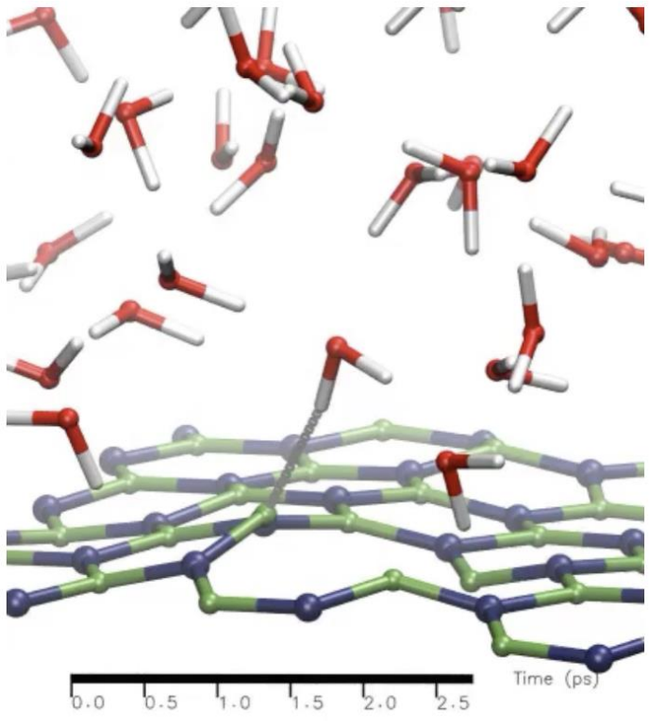
—> Emission is due to a defect in its protonated form (here boron vacancy)

Collaboration with theoretical chemists at ENS B Grosjean, ML Bocquet, R Vuilleumier

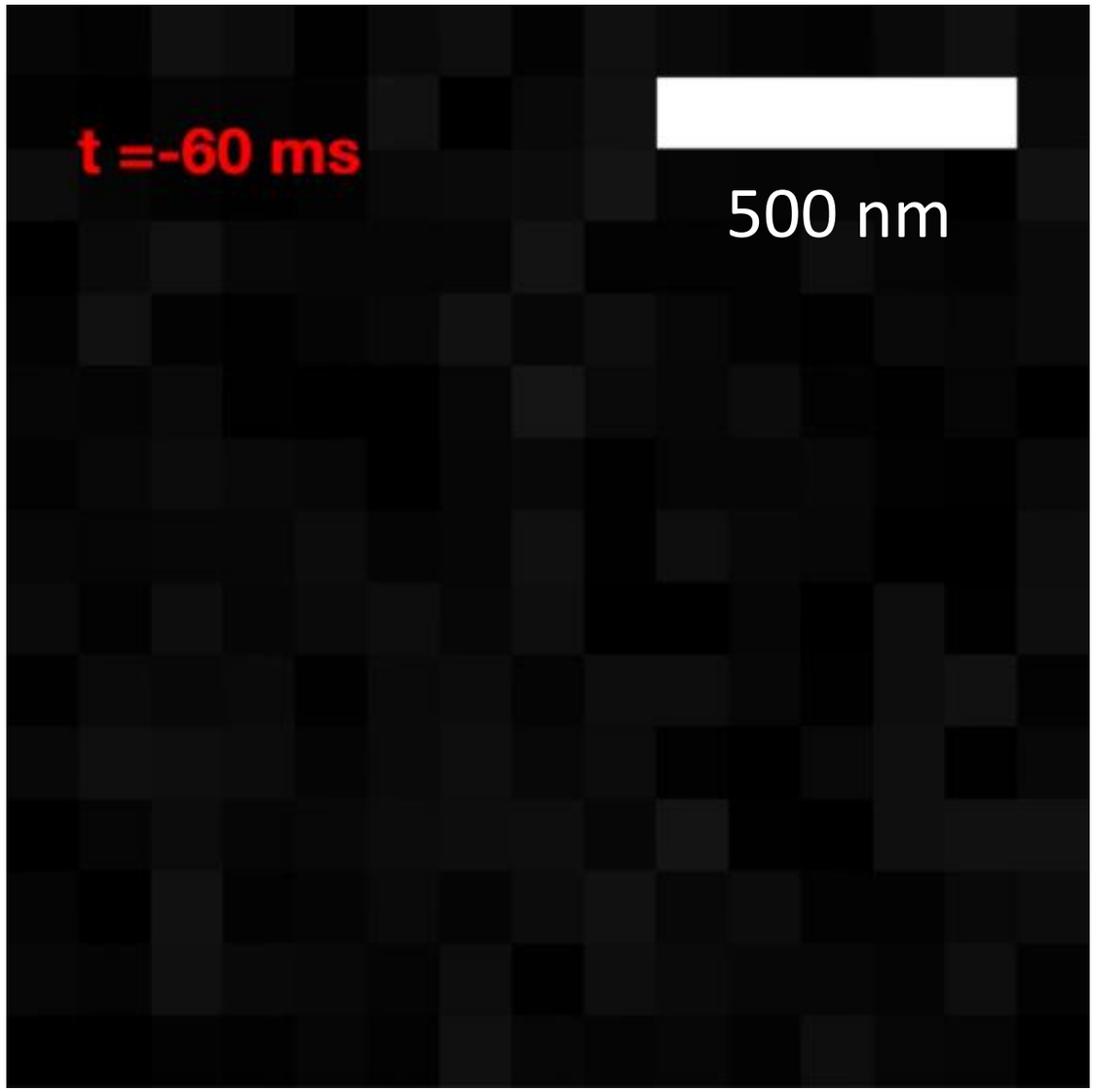
+DFT calculations

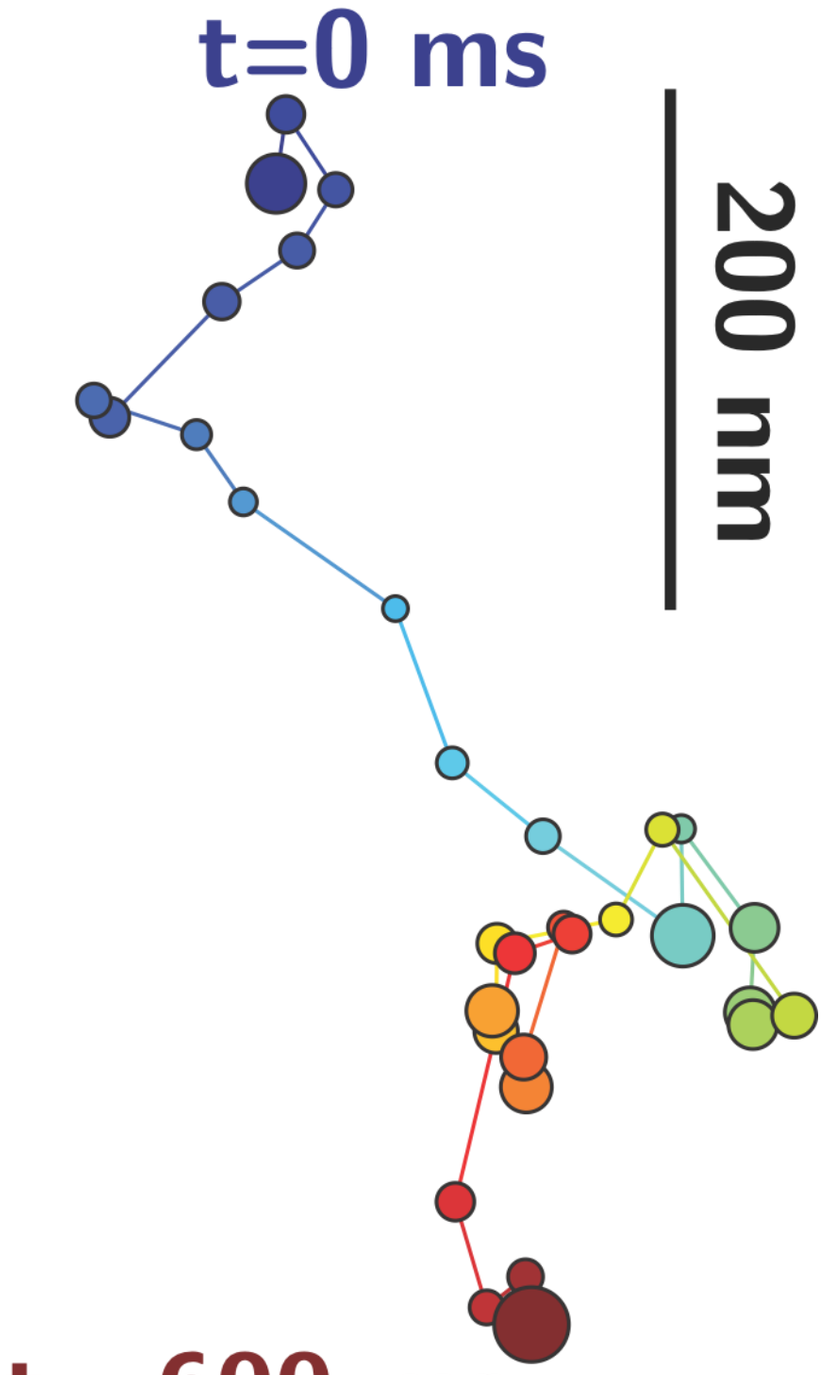
Van de Walle, PRB, 2018

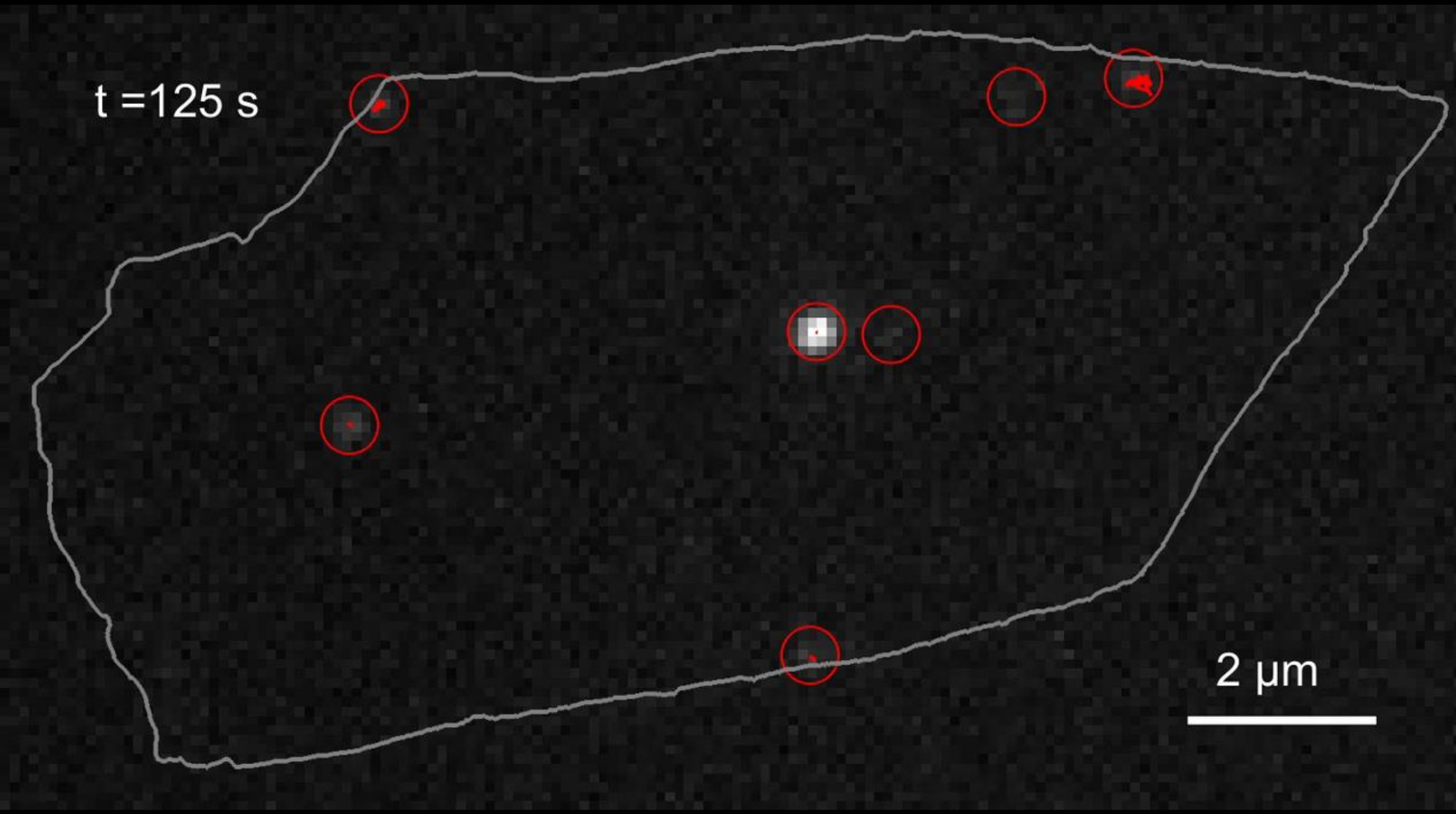
Ab-initio simulations

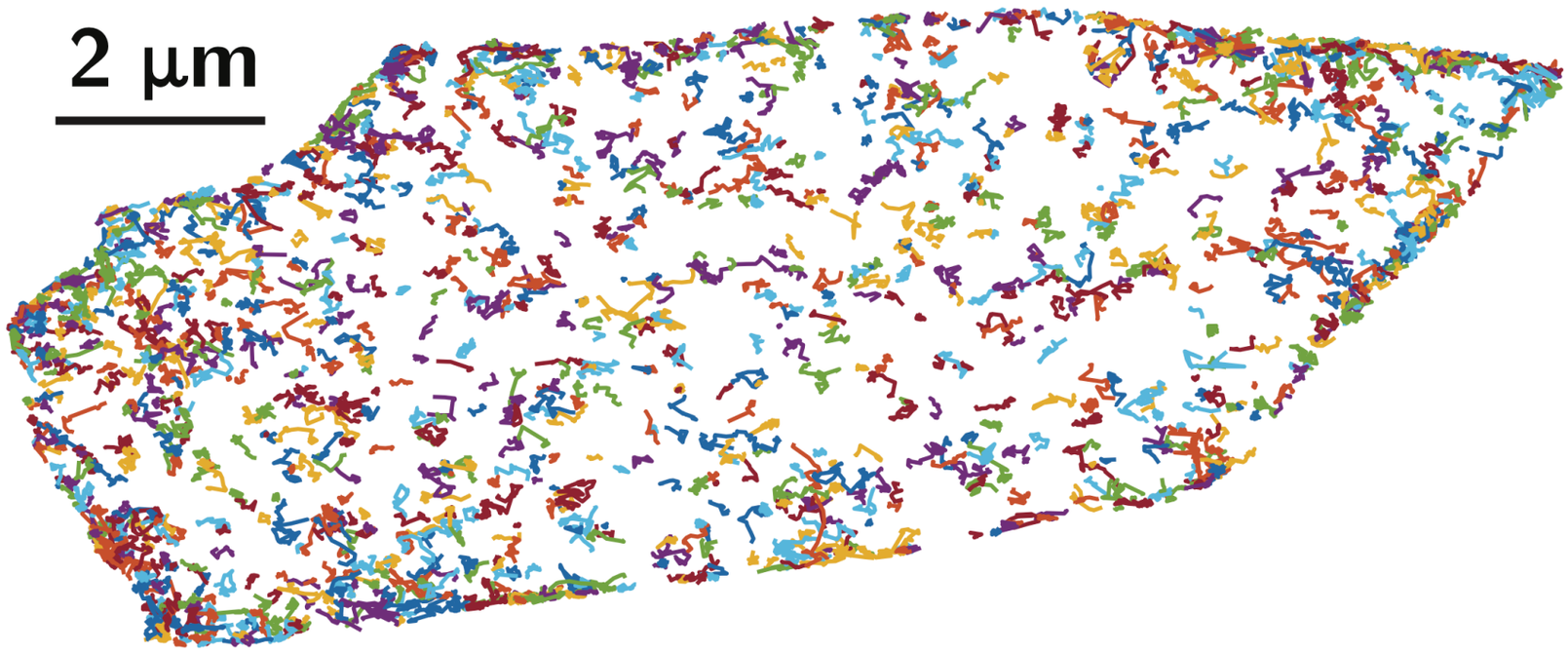


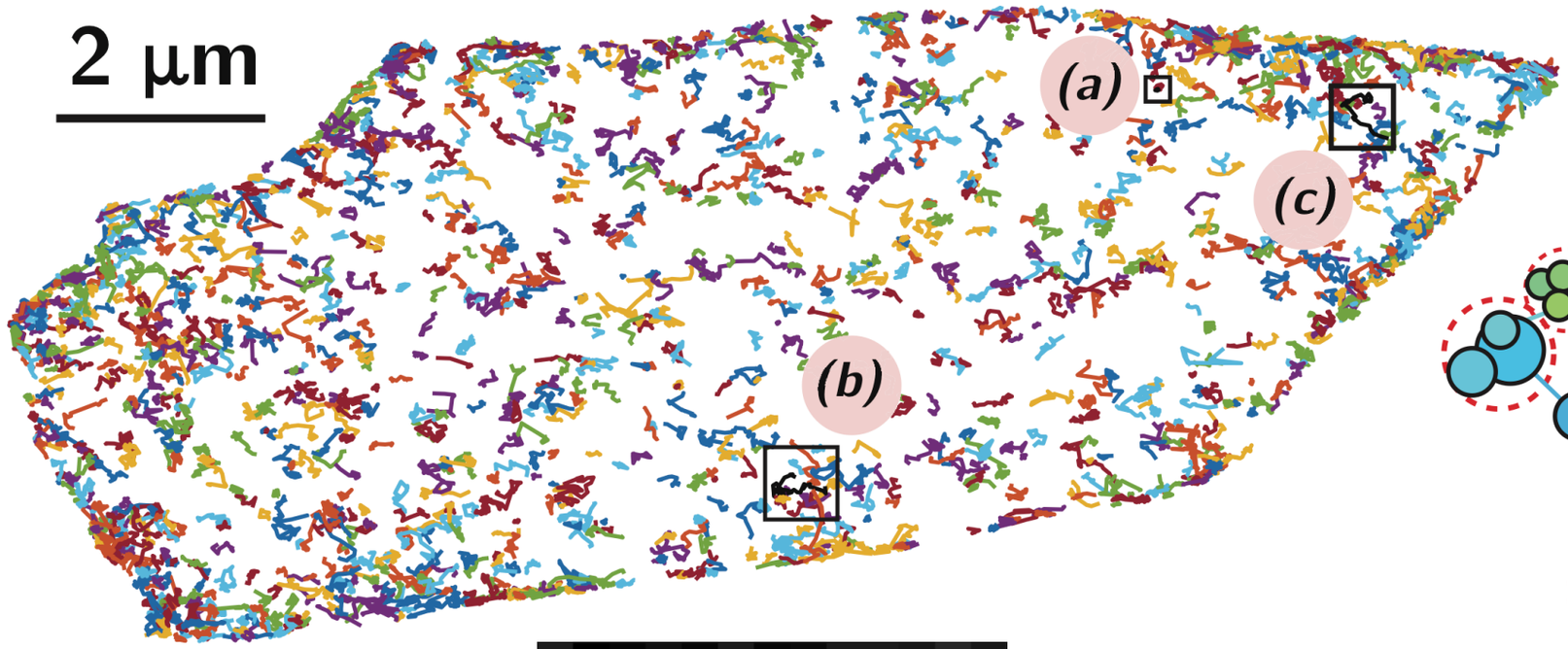
Tracking proton trajectories using defects

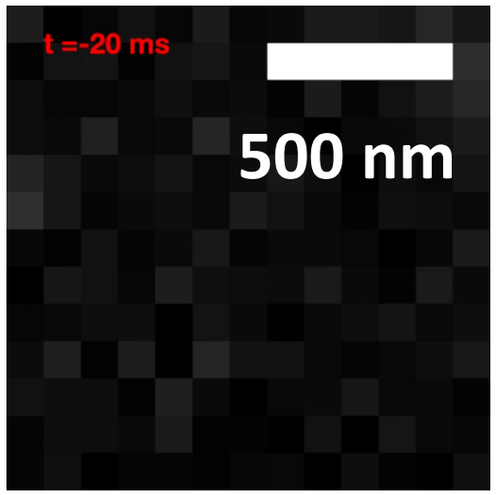


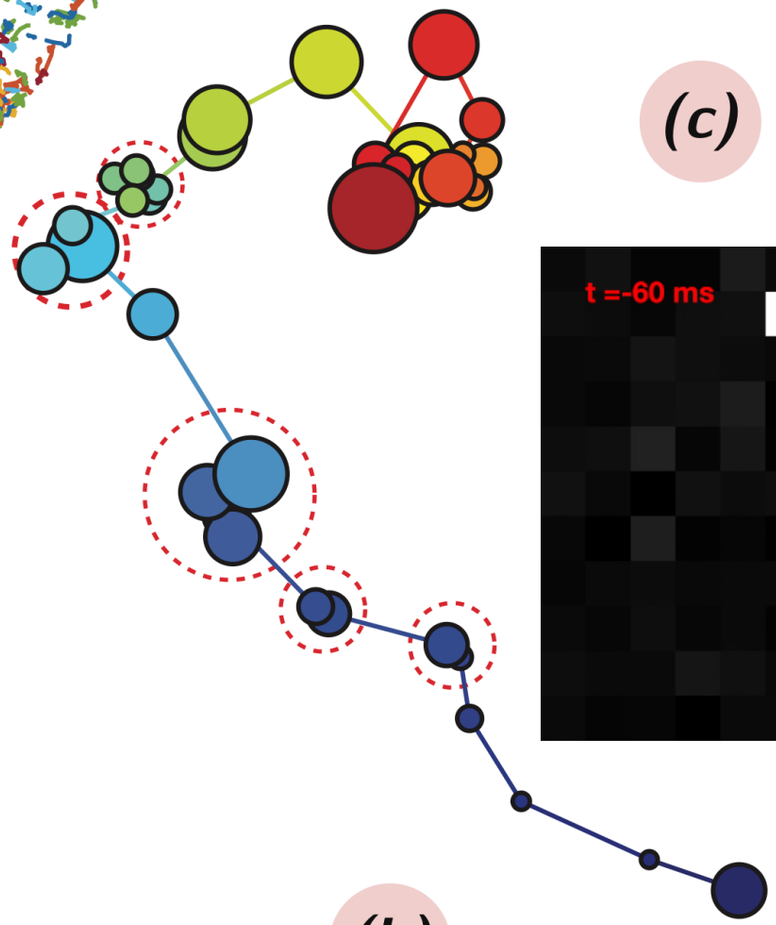



t =125 s
2 µm


2 µm

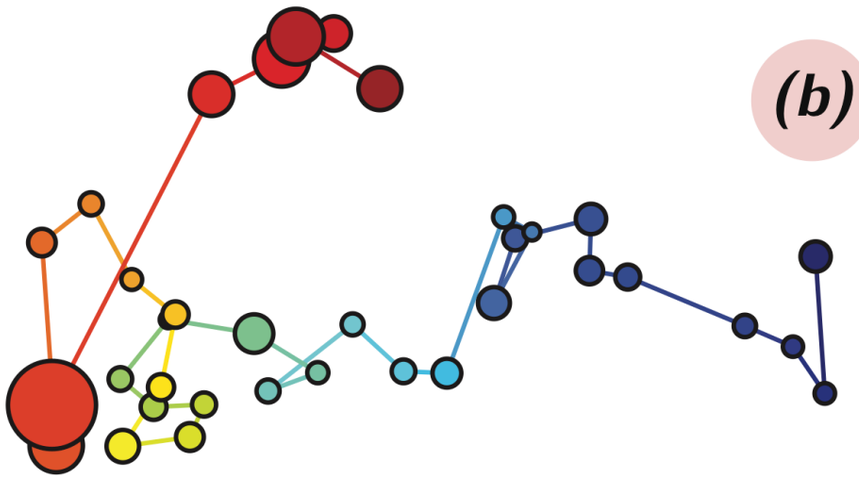

2 µm
(a)
(b)
(c)


t =-20 ms
500 nm

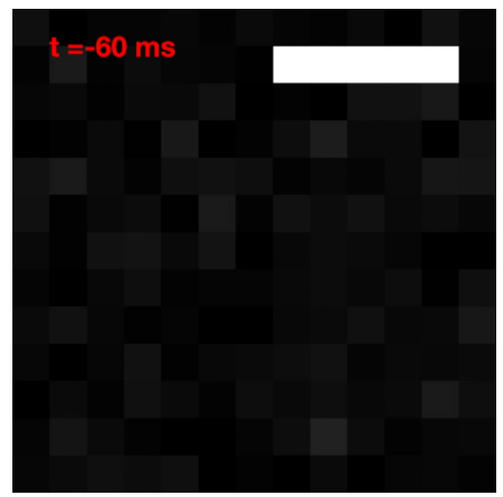

(c)


t =-60 ms

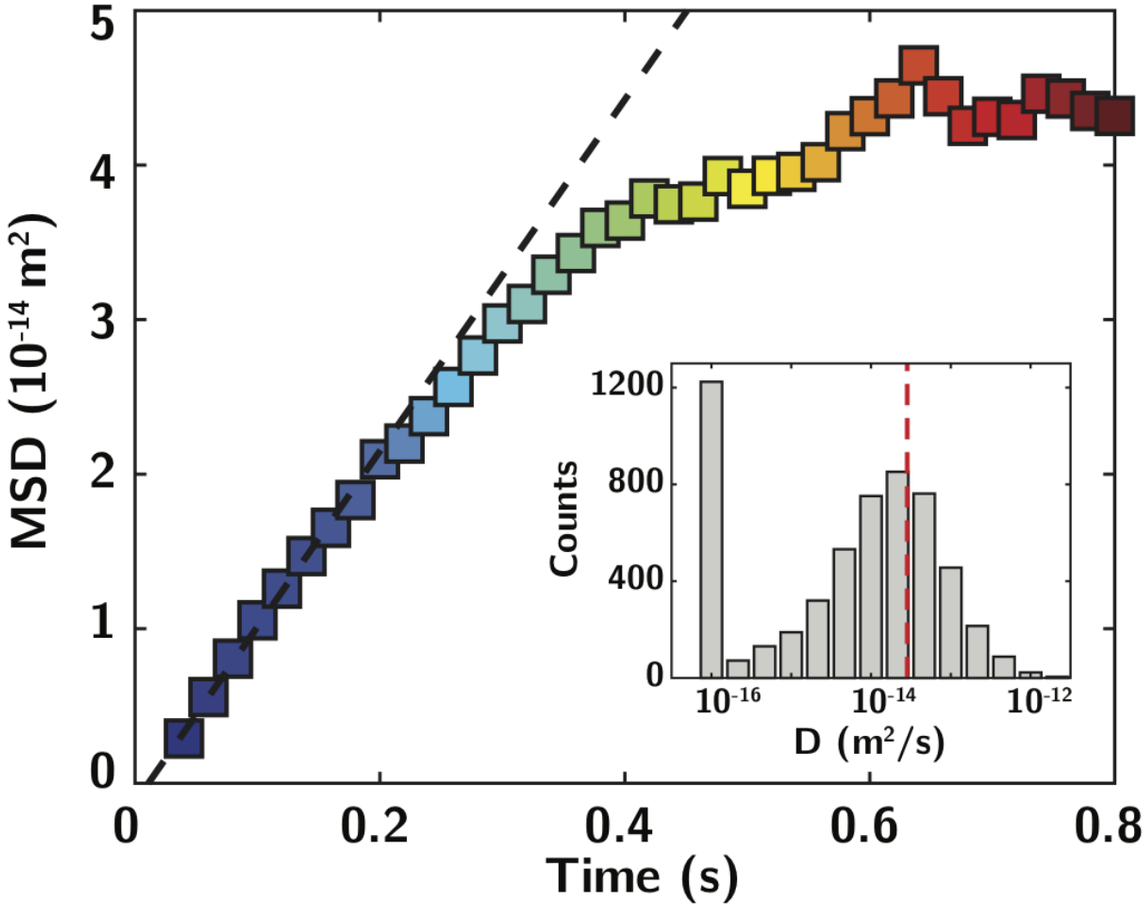

(a)


250 nm

(b)

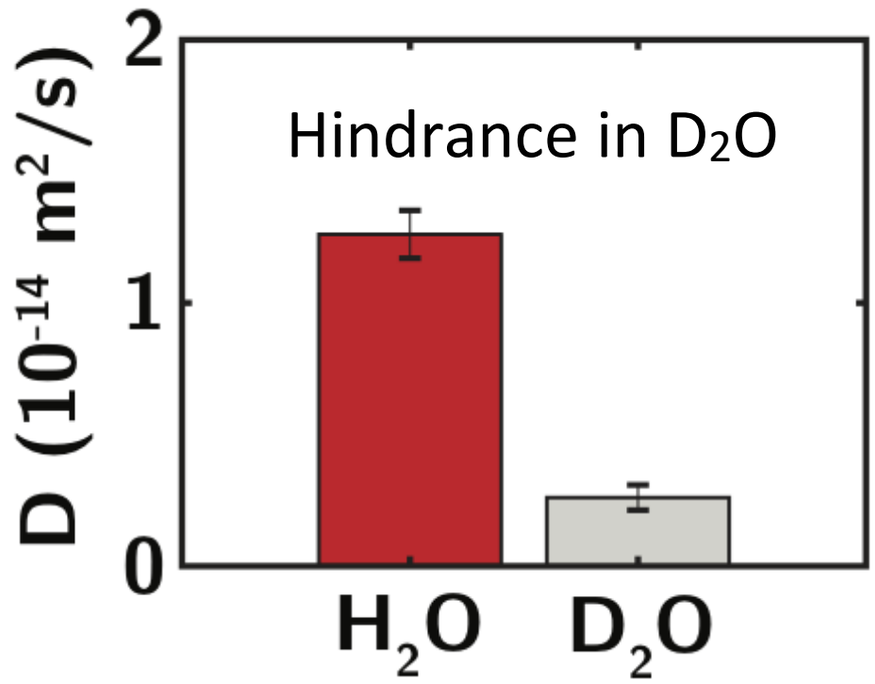

t =-60 ms

Diffusive behavior



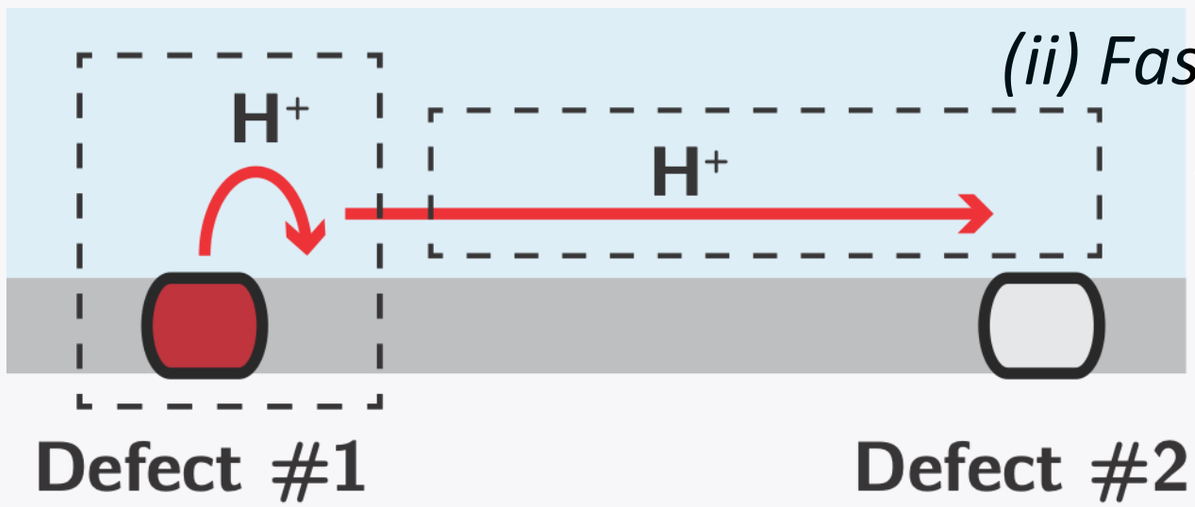
$D \approx 10^{-14}$ m^2/s $\ll D_{bulk} \approx 10^{-8}$ m^2/s

Strongly hindered transport



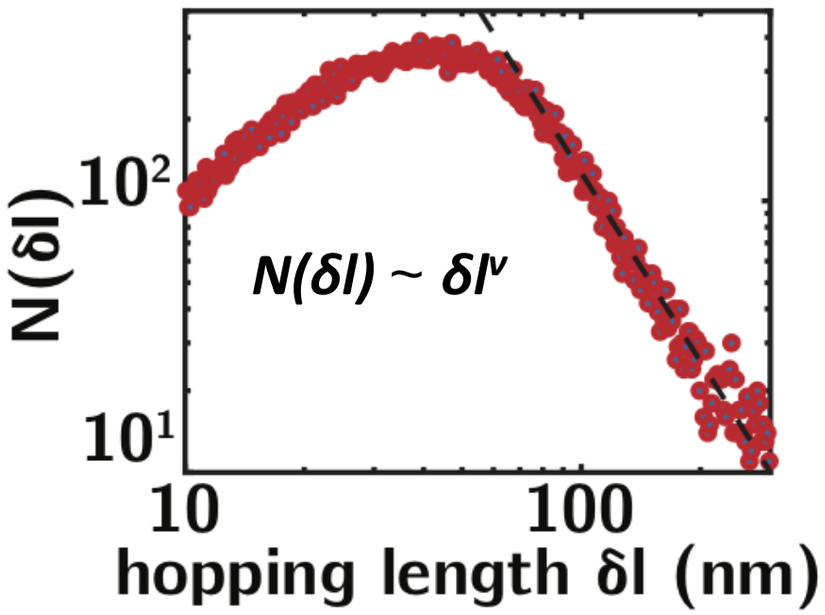
$MSD(t) = \langle (x(t)-x(0))^2 \rangle \sim 4Dt$

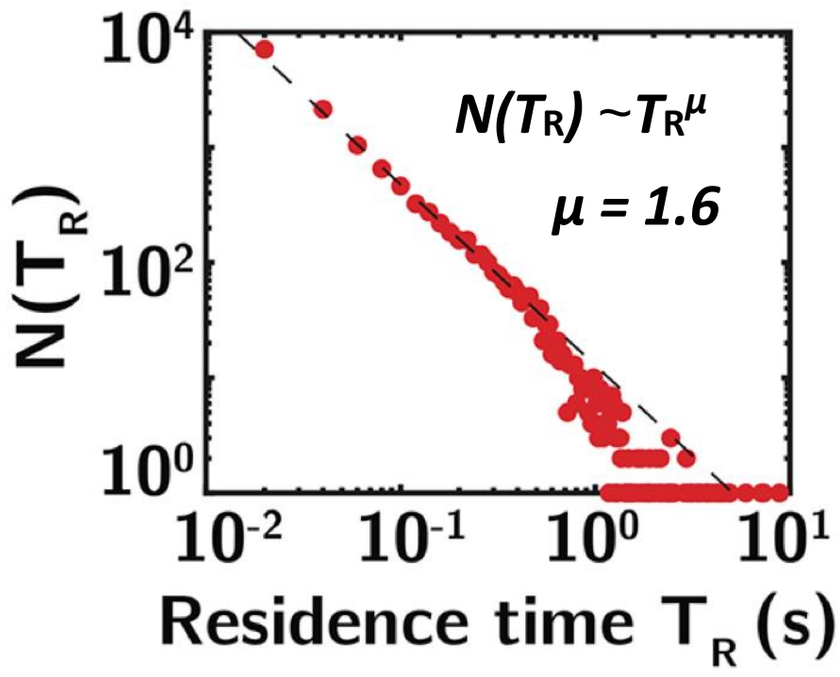
(i) Rate-limiting desorption



(ii) Fast transport to the next defect

Beyond Mean-Field behavior





—> *Anomalous random walk*

Desorption-limited transport

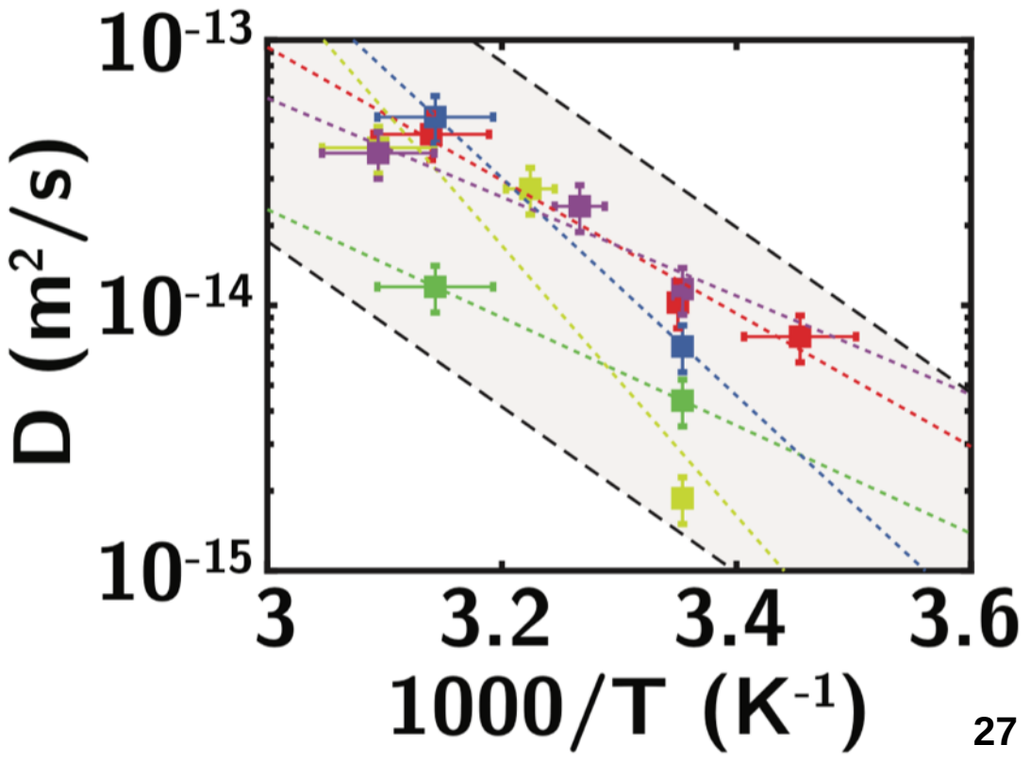
~ GHz

interdefect distance (10-100 nm)

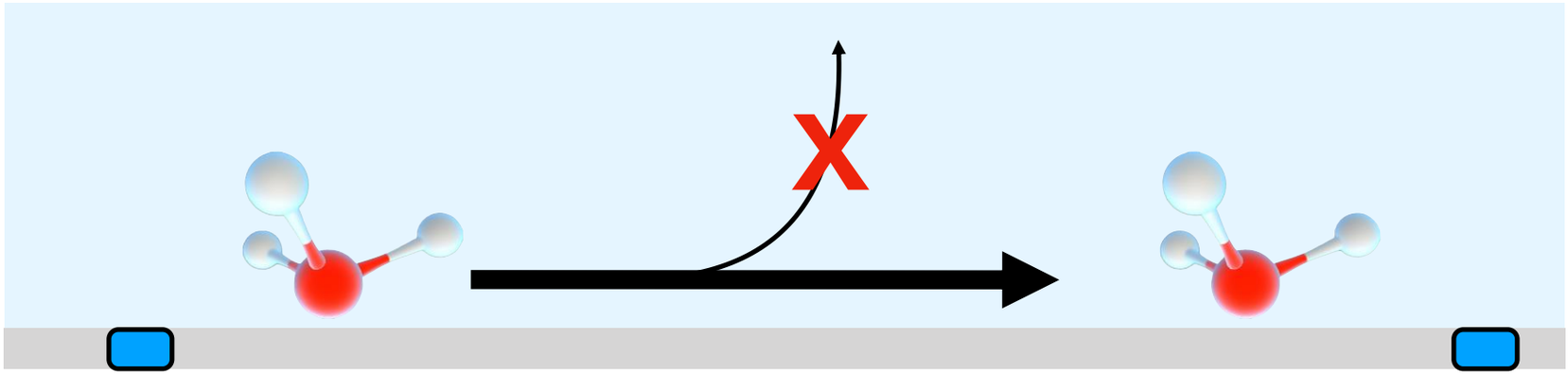
$$D \sim \nu \cdot a^2 \cdot \exp\left(-\frac{\Delta F}{kT}\right)$$

—> Enthalpic barrier

$\Delta E = 0.62 \pm 0.12$ eV ~ 24 $k_B T$



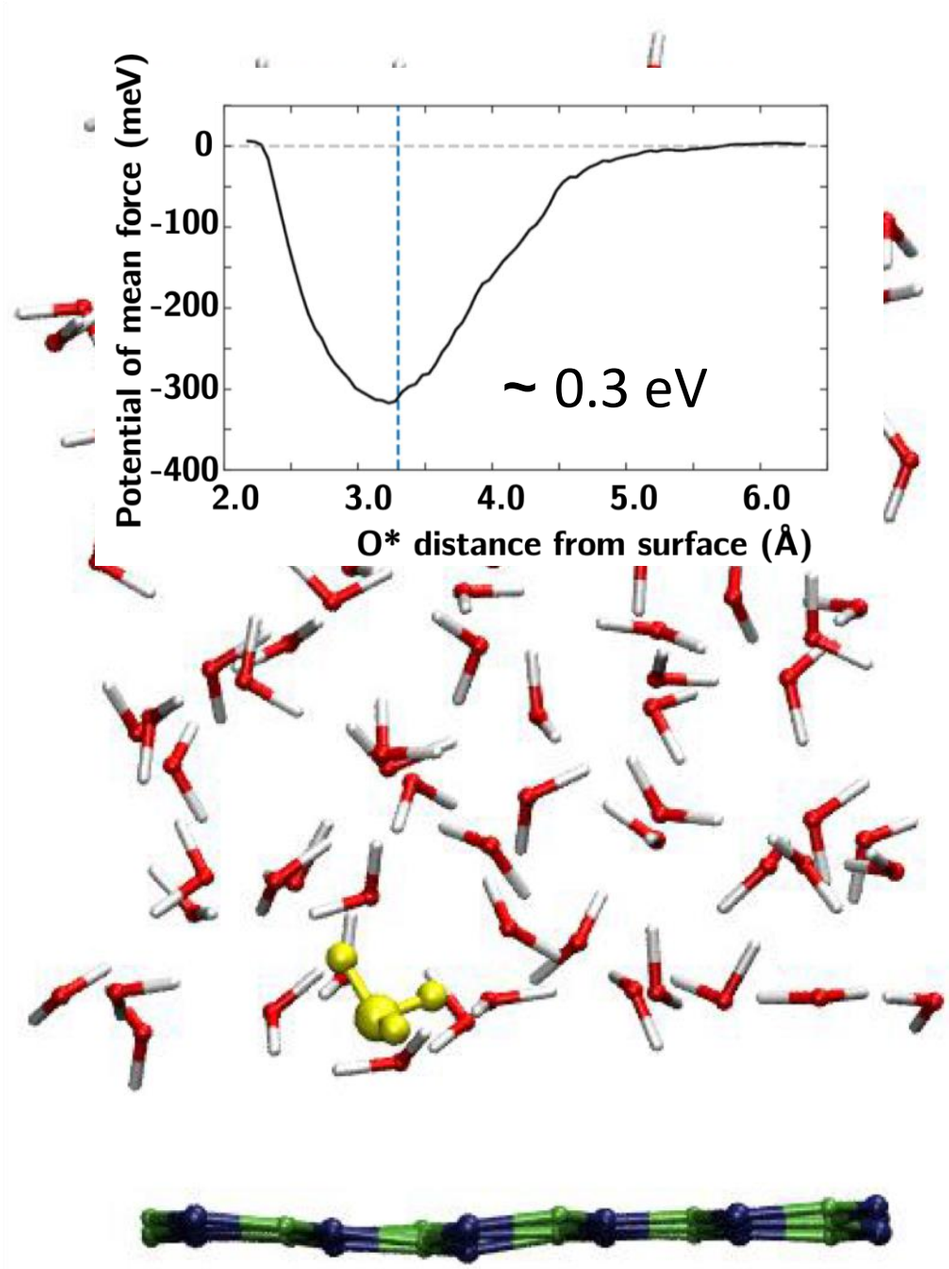
Surface affinity of protons



Defect #1

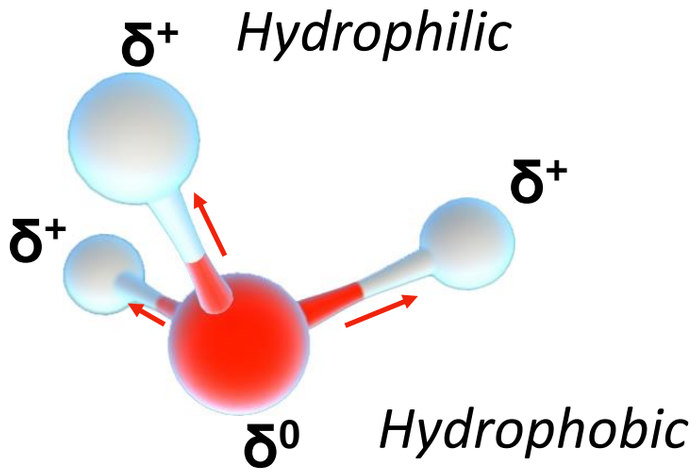
Defect #2

Free energy barrier preventing proton desorption from the interface

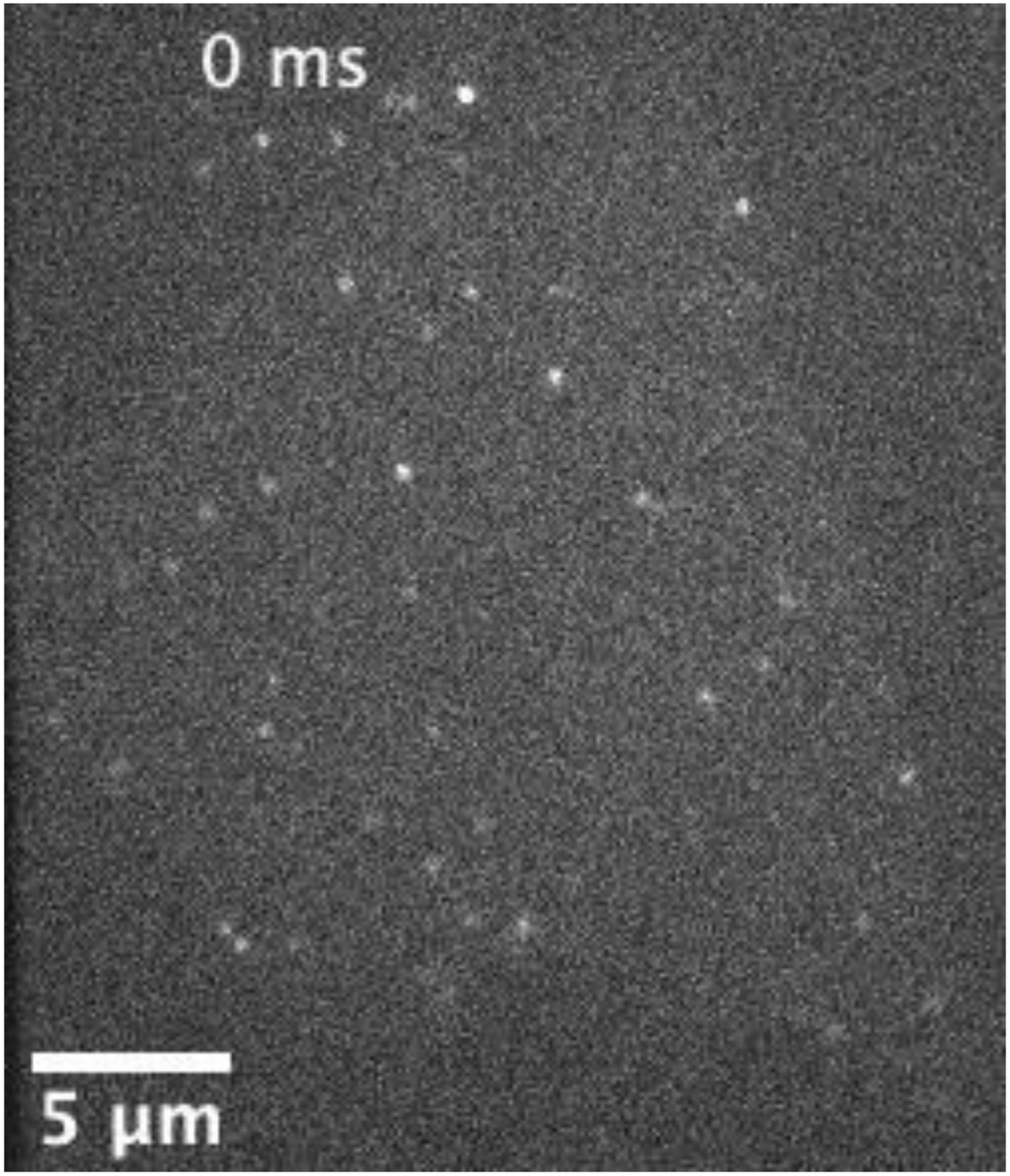


Amphiphilic behavior at interfaces

Kudin, K. N., & Car, R. (2008).JACS 130(12), 3915-3919.



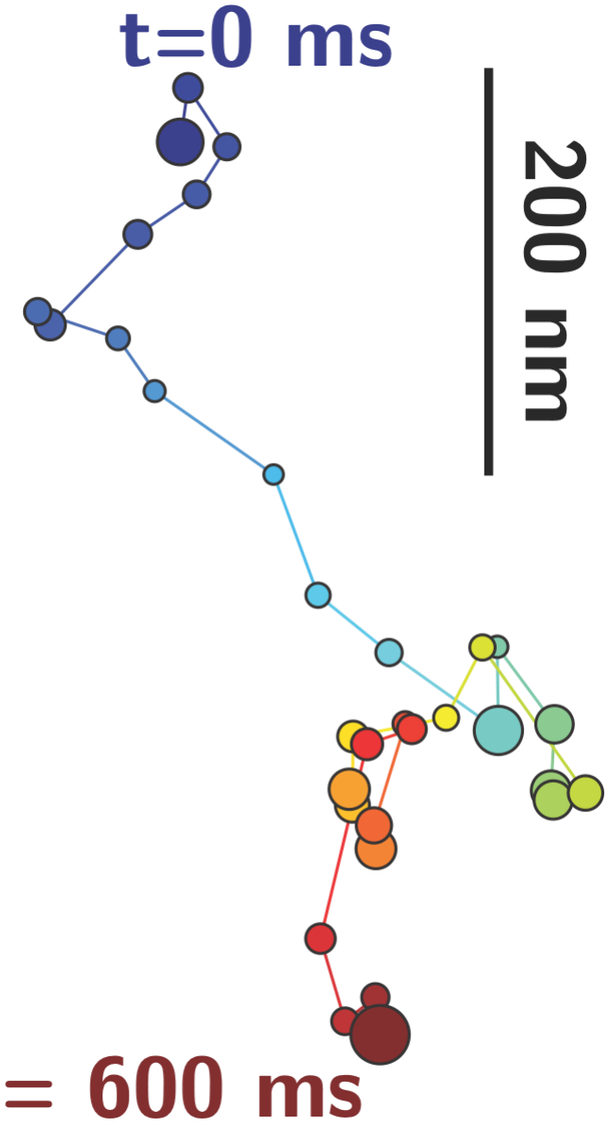
Towards more complex solvents



Dynamics in water/ethanol mixture

Perspective

Platform to study interfacial dynamics at solid/liquid interfaces **at the** single charge **and** single-molecule scale



Acknowledgment

A. Radenovic (EPFL), C. Creton (ESPCI), L. Bocquet and A. Siria (ENS Paris)

Nano letters **(2019)** ***Nature Nanotechnology*** **(2020)** ***Science Advances*** **(2021)**