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Molecular dynamics in ice and water:

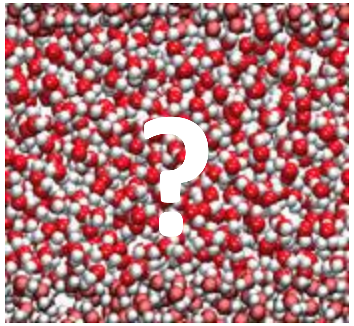
insights from broadband dielectric spectroscopy

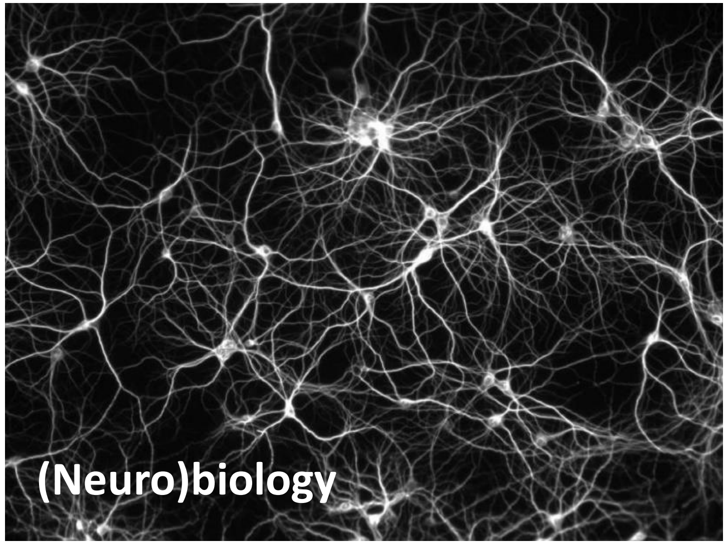
Vasily G. Artemov

5 August, 2021

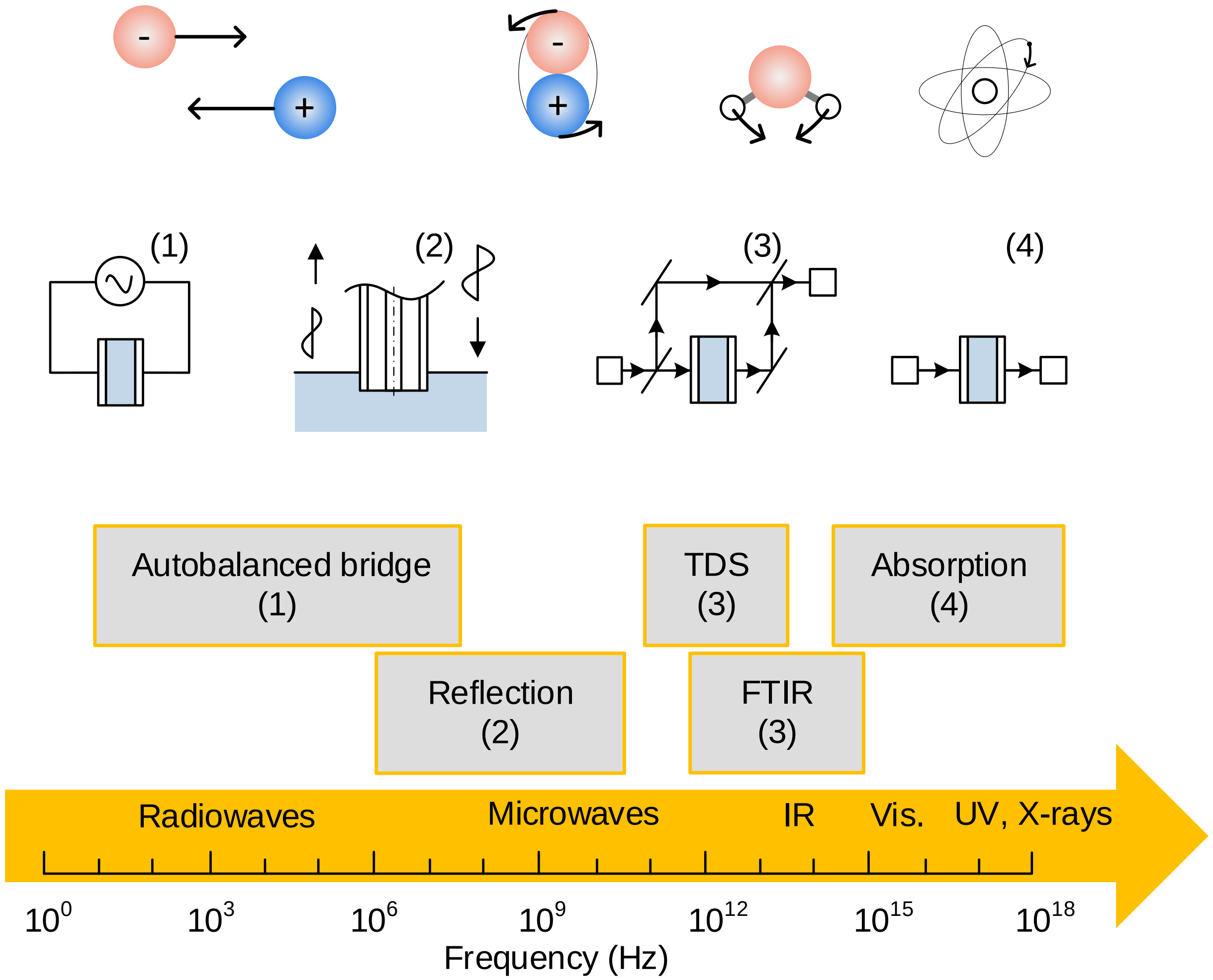
Motivation

Structure & Dynamics

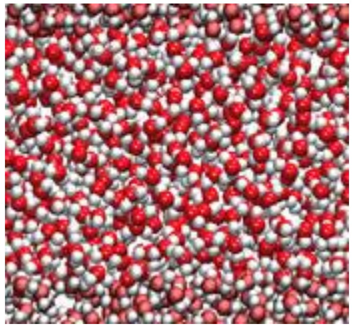




Broadband dielectric spectroscopy



Molecular dielectric



Maxwell's Equations

$$\nabla \times \boldsymbol{E} = -\frac{\partial \boldsymbol{B}}{\partial t}$$

$$\nabla \times \boldsymbol{H} = \boldsymbol{J} + \frac{\partial \boldsymbol{D}}{\partial t}$$

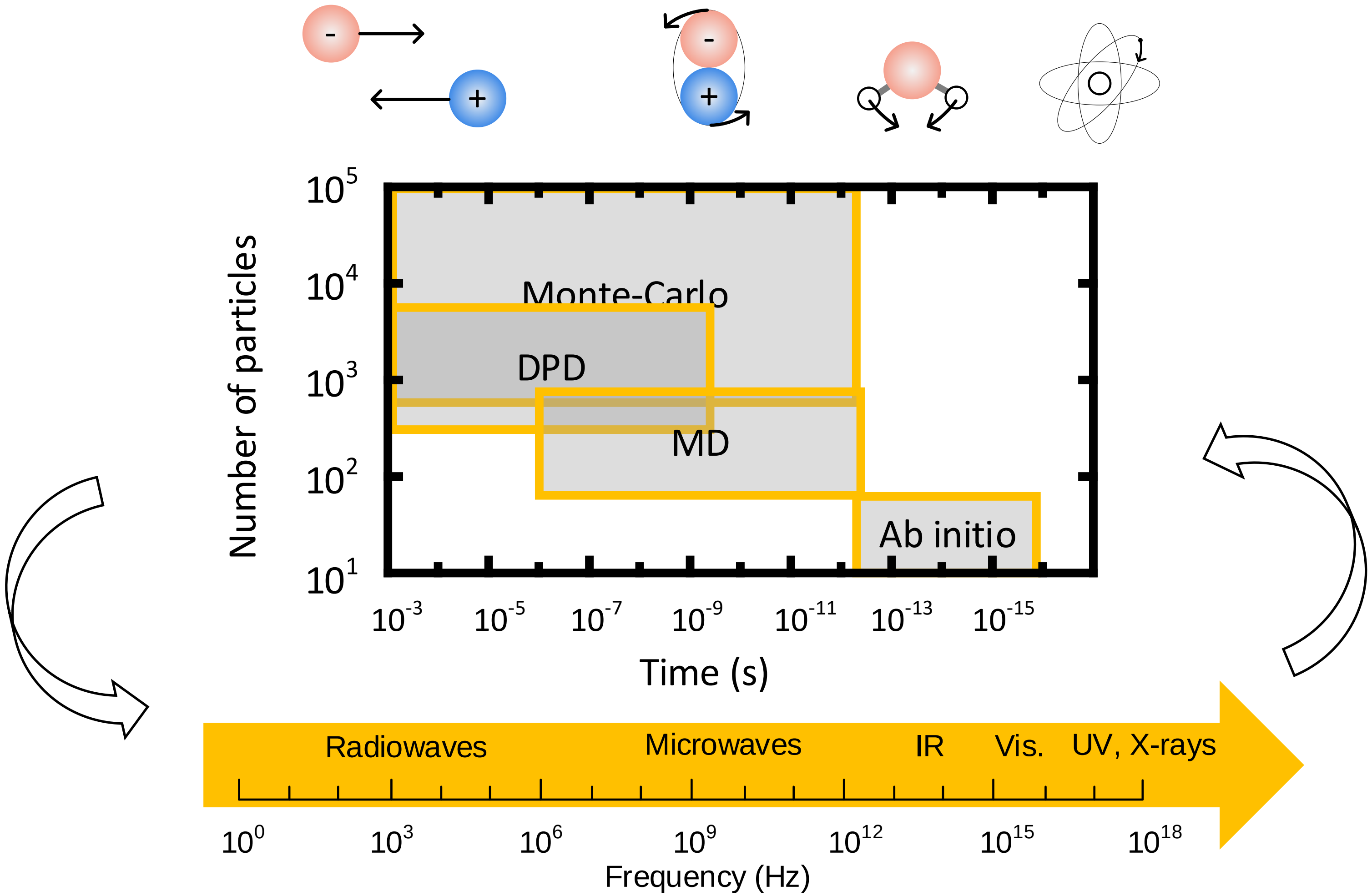
$$\nabla \cdot \boldsymbol{D} = \rho$$

$$\nabla \cdot \boldsymbol{B} = 0$$

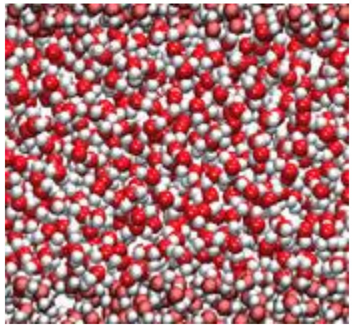
Constitutive relation

$$\boldsymbol{D}(\boldsymbol{r},\omega) = \epsilon(\omega)\boldsymbol{E}(\boldsymbol{r},\omega)$$

Broadband dielectric spectroscopy and molecular dynamics simulations



Molecular dielectric



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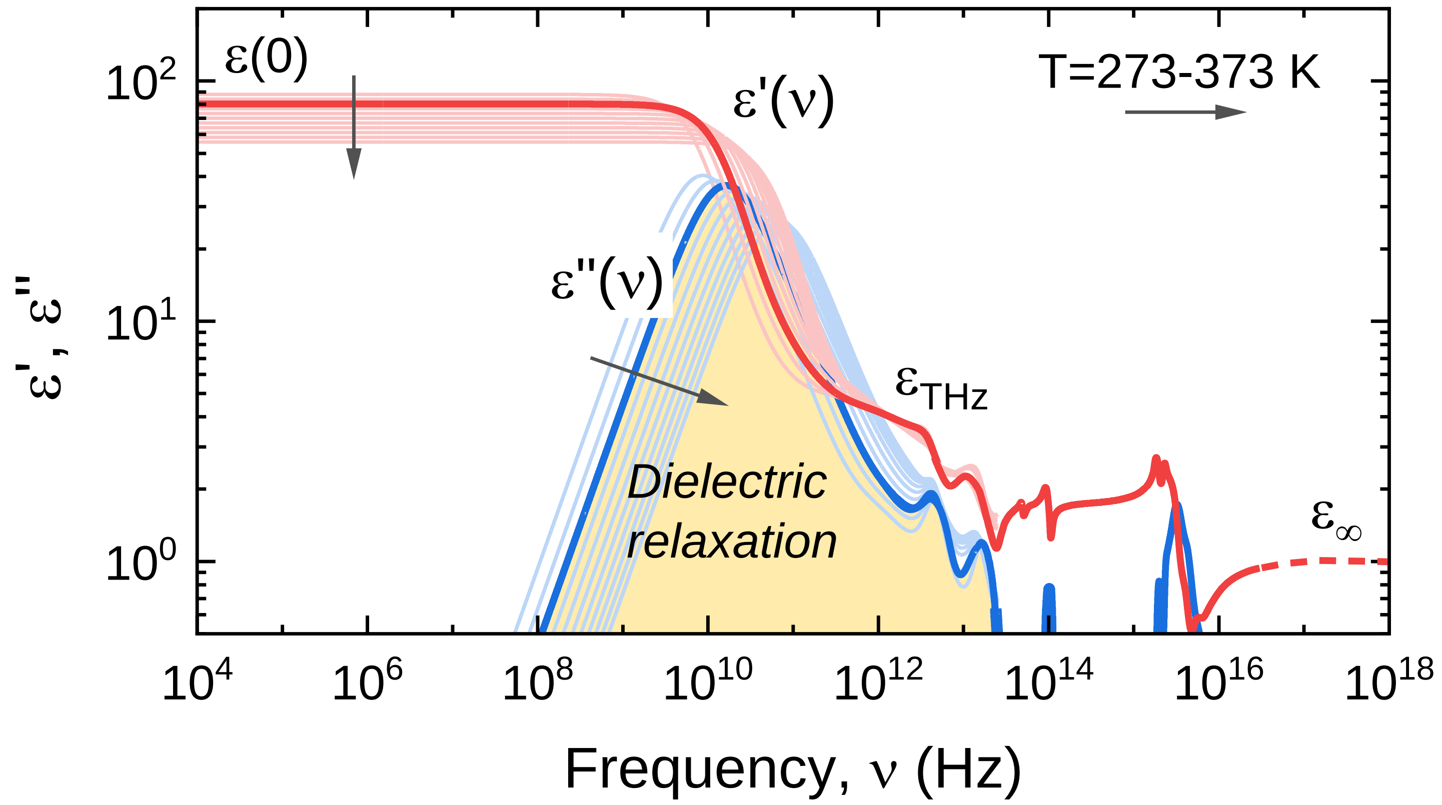
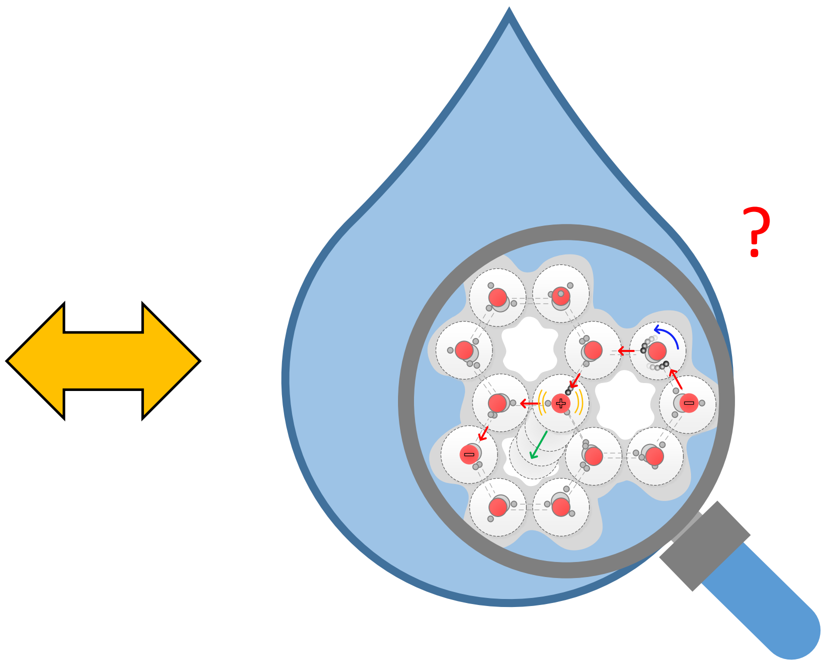
Broadband dielectric spectrum of water

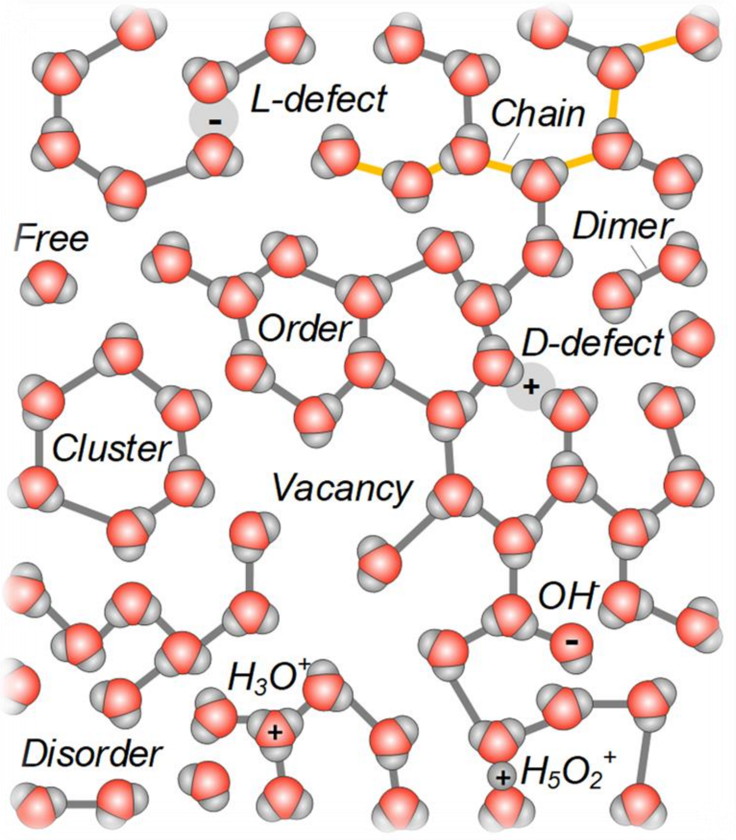




$$D(r,\omega) = \epsilon(\omega) E(r,\omega)$$

Bernal-Fowler water (1933)

Where did we get this structure of water?



THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 1 AUGUST, 1933 NUMBER 8

A Theory of Water and Ionic Solution, with Particular Reference to Hydrogen and Hydroxyl Ions

J. D. BERNAL AND R. H. FOWLER, *University of Cambridge, England*

(Received April 29, 1933)

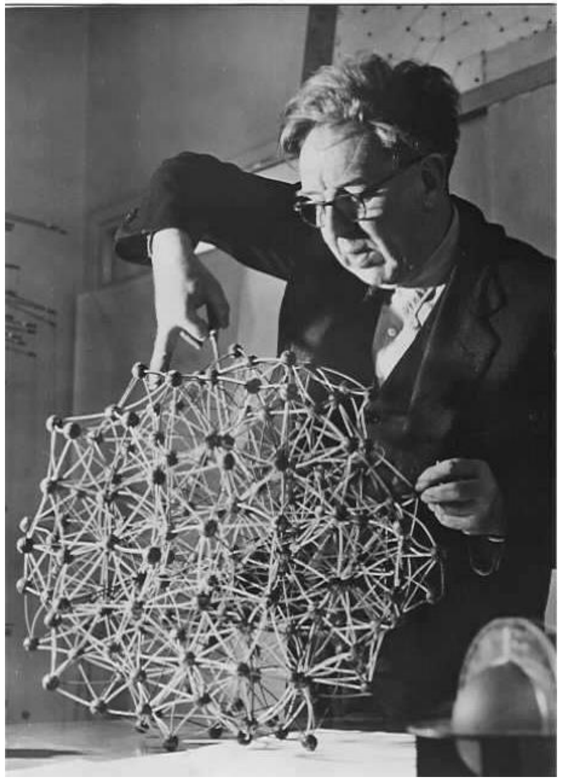
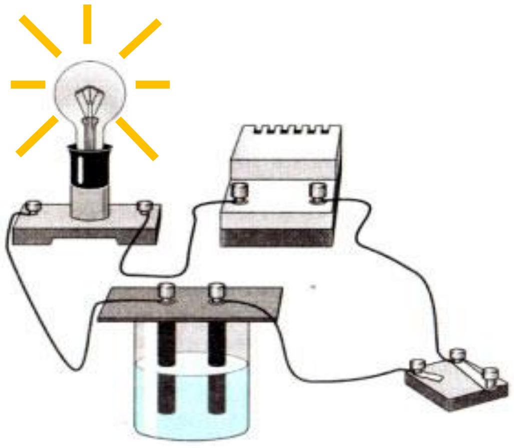
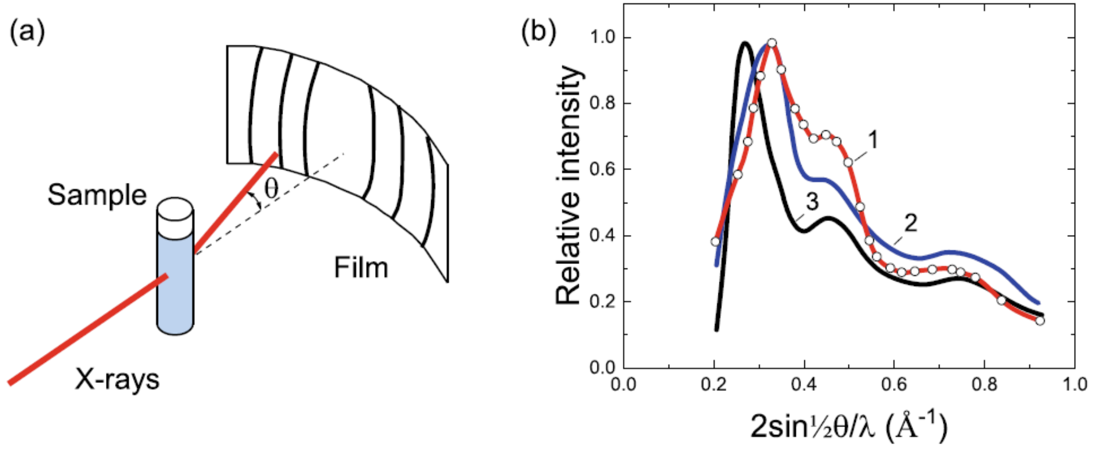


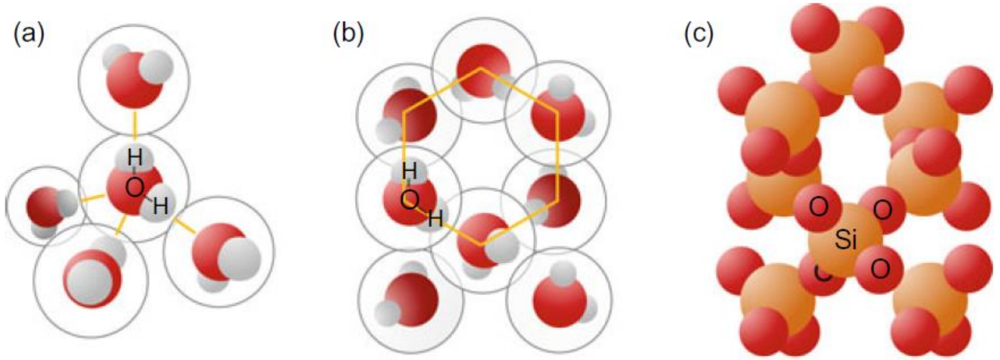
Photo from: J.L. Finney, J. Phys.: Conf. Ser. 57, 4 (2007)

Bernal-Fowler water (1933): experimental background



Assumption #1:
Pure water is a poor conductor, thus it has low concentration of H^+ and OH^-.



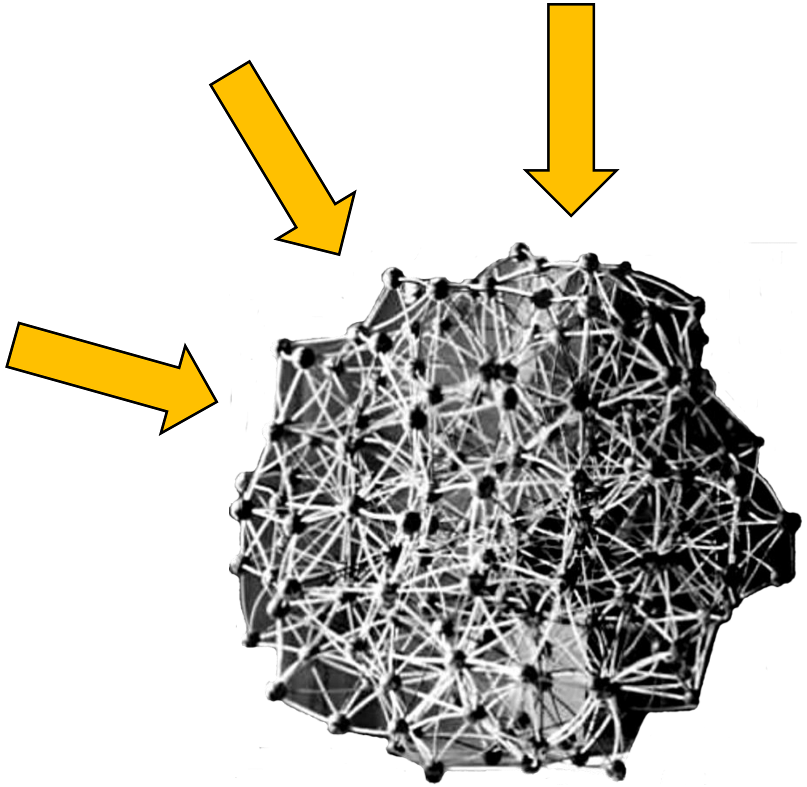


Assumption #2:
Water scatters X-rays just like quartz, thus, it has similar structure.

Test of Bernal-Fowler water

1933 - 2021

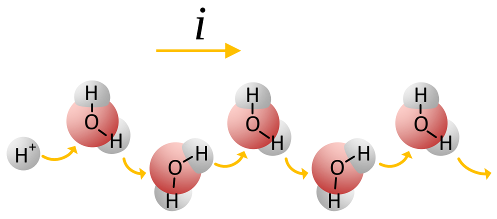
- Ab-initio, Monte Carlo and Molecular dynamics simulations
- Diffusion measurements with isotopic tracers
- NMR spectroscopy
- Neutron Scattering
- X-ray scattering

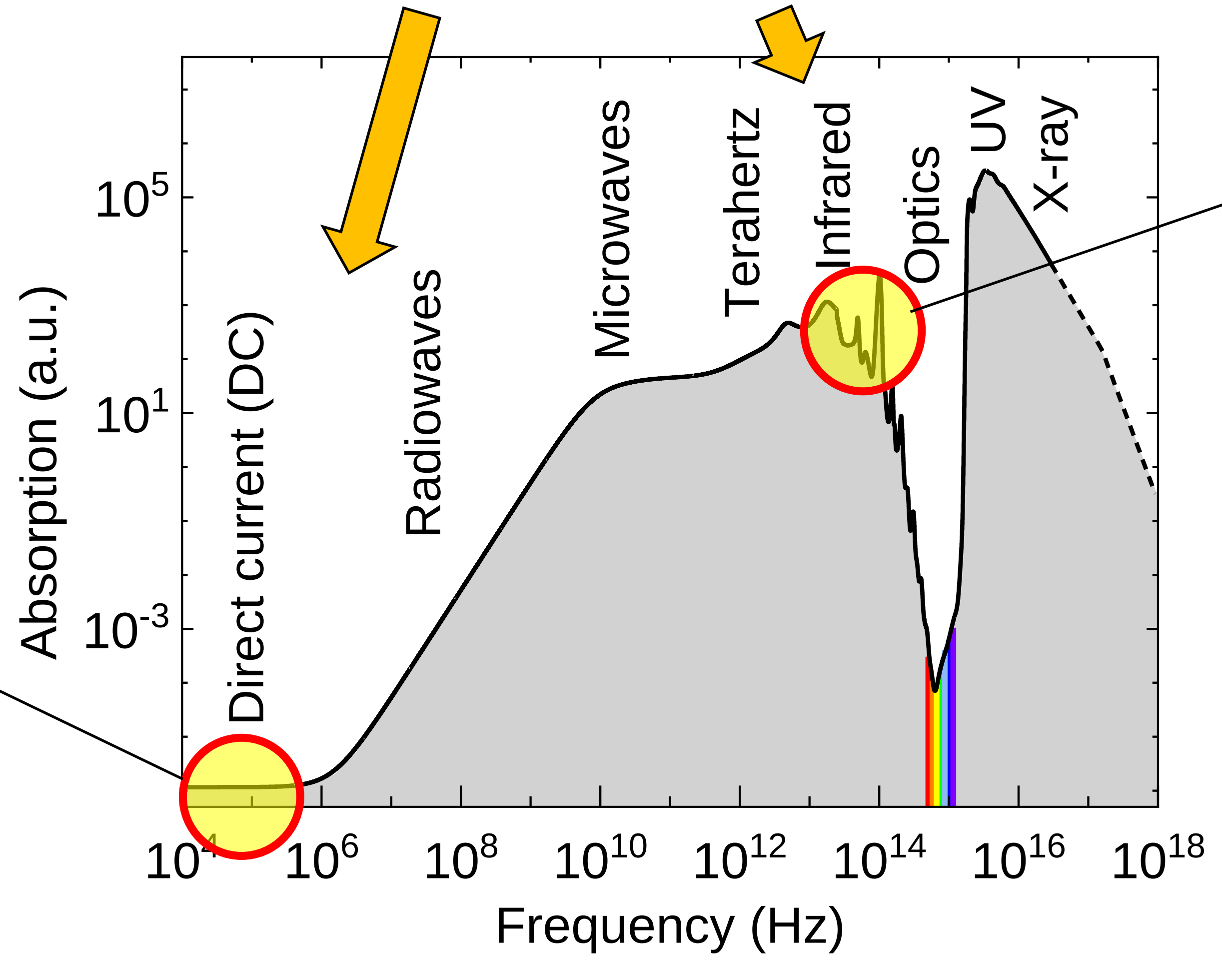


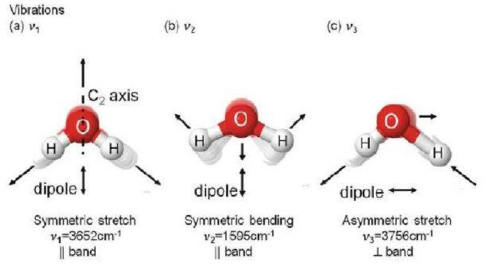
What about electrodynamics?

Absorption of electromagnetic waves by water

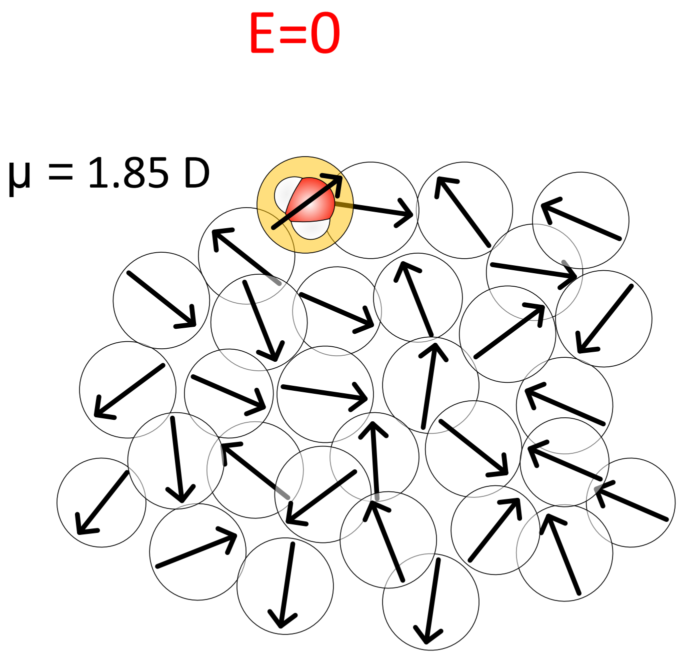
Range of validity of the Bernal-Fowler model

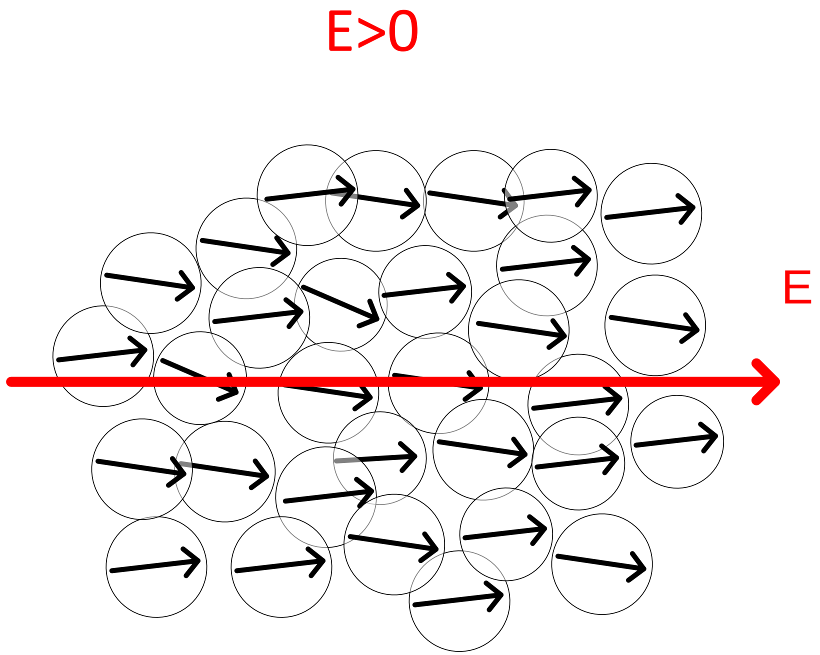






Bernal-Fowler water in electric field

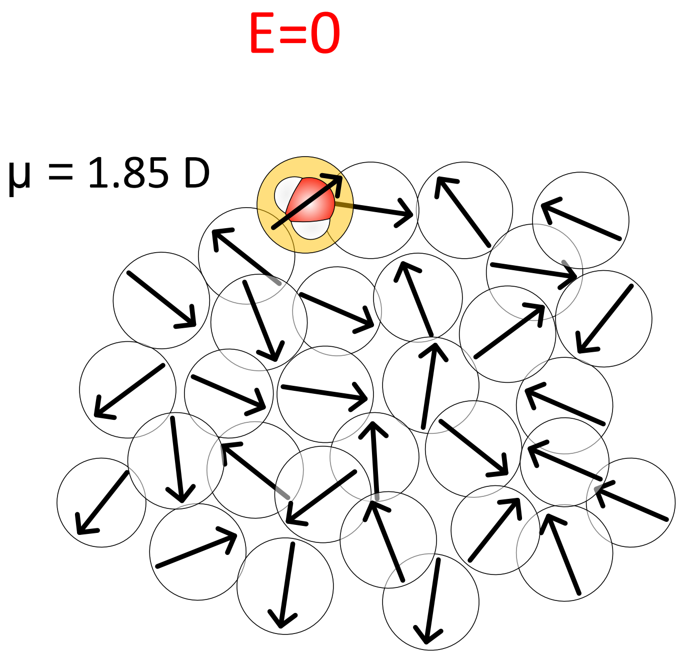


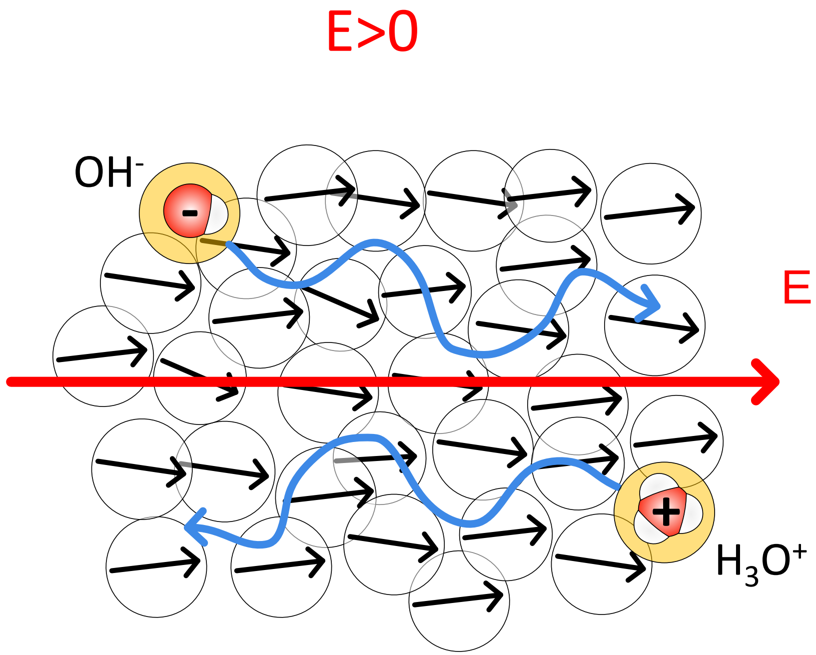


Dielectric constant: $\varepsilon(0) = 1 + \frac{4\pi}{3}\frac{N\mu^2}{Vk_BT}$ ⇨ $\varepsilon(0)_{calc} \approx 14$ ⟷ ? $\varepsilon(0)_{exp} \approx 80$

A. von Hippel, 1988

Bernal-Fowler water in electric field





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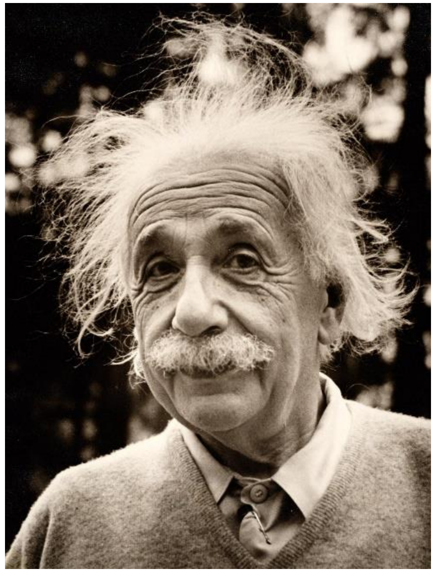
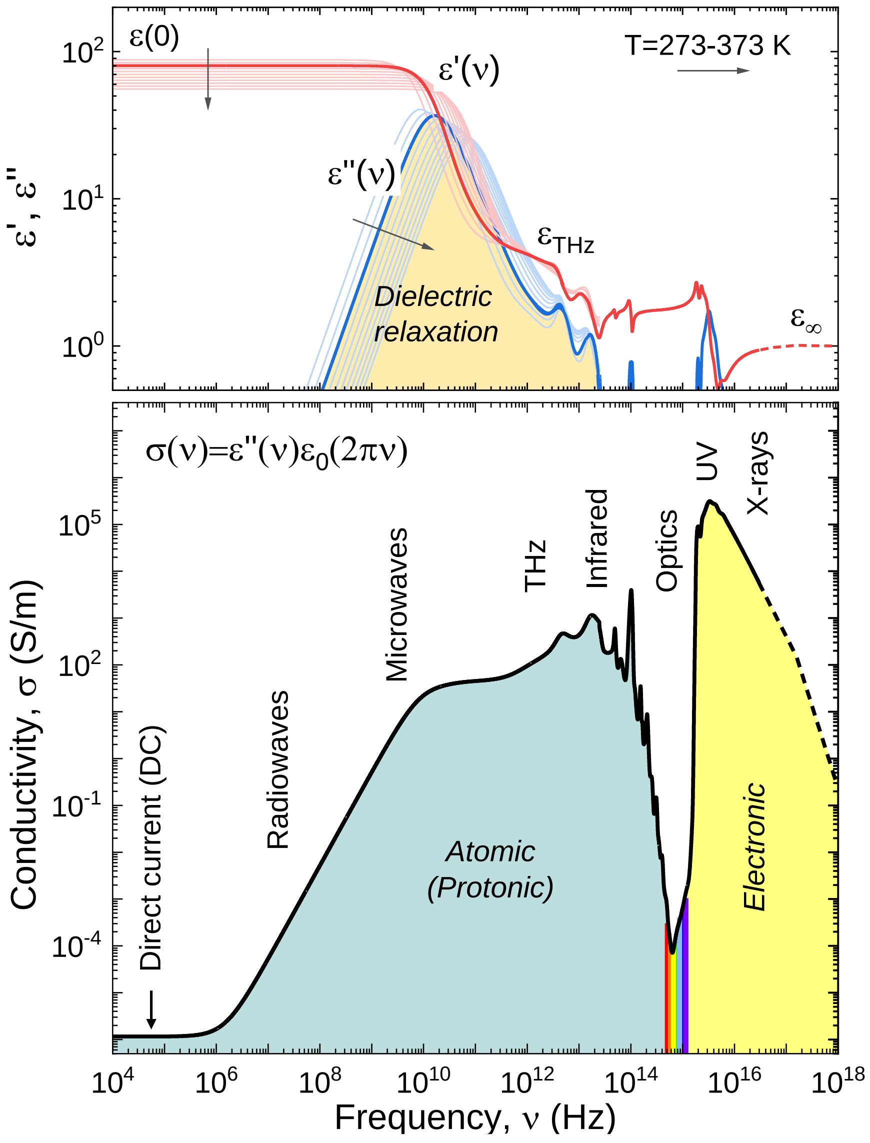


“We can't solve problems by using the same kind of thinking we used when we created them.”

Dynamic conductivity of water: a different type of thinking

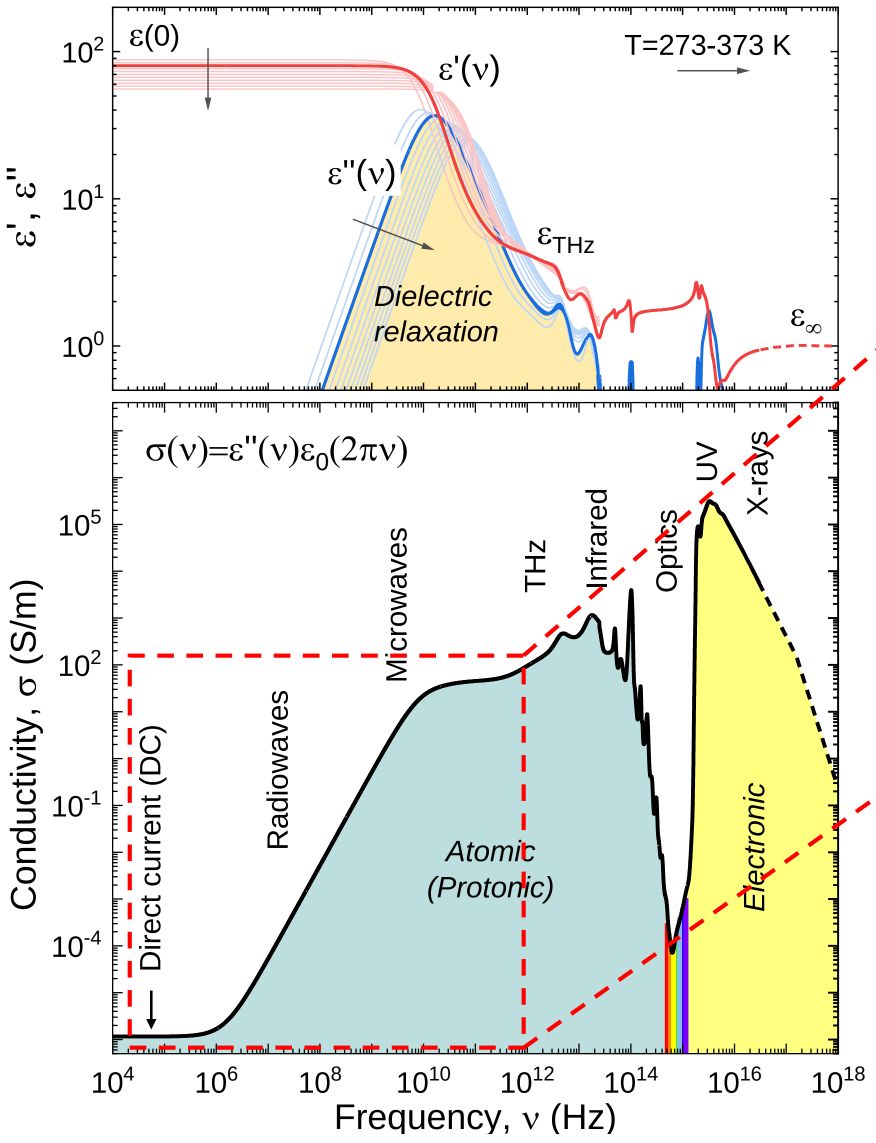


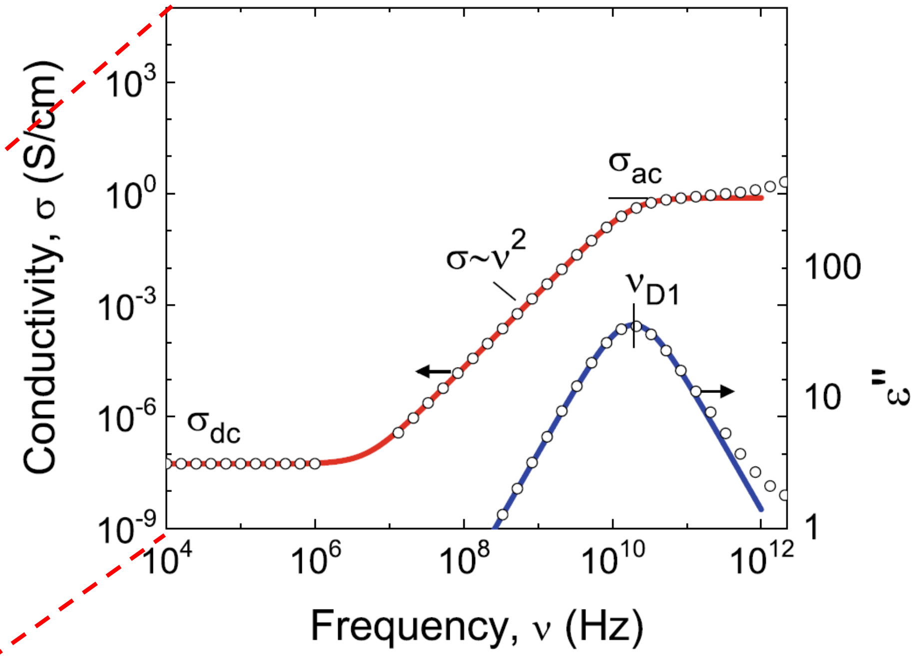
Dielectric permittivity
(dielectric loses per period of the field)

Dynamic conductivity
(dielectric loses per period of time)

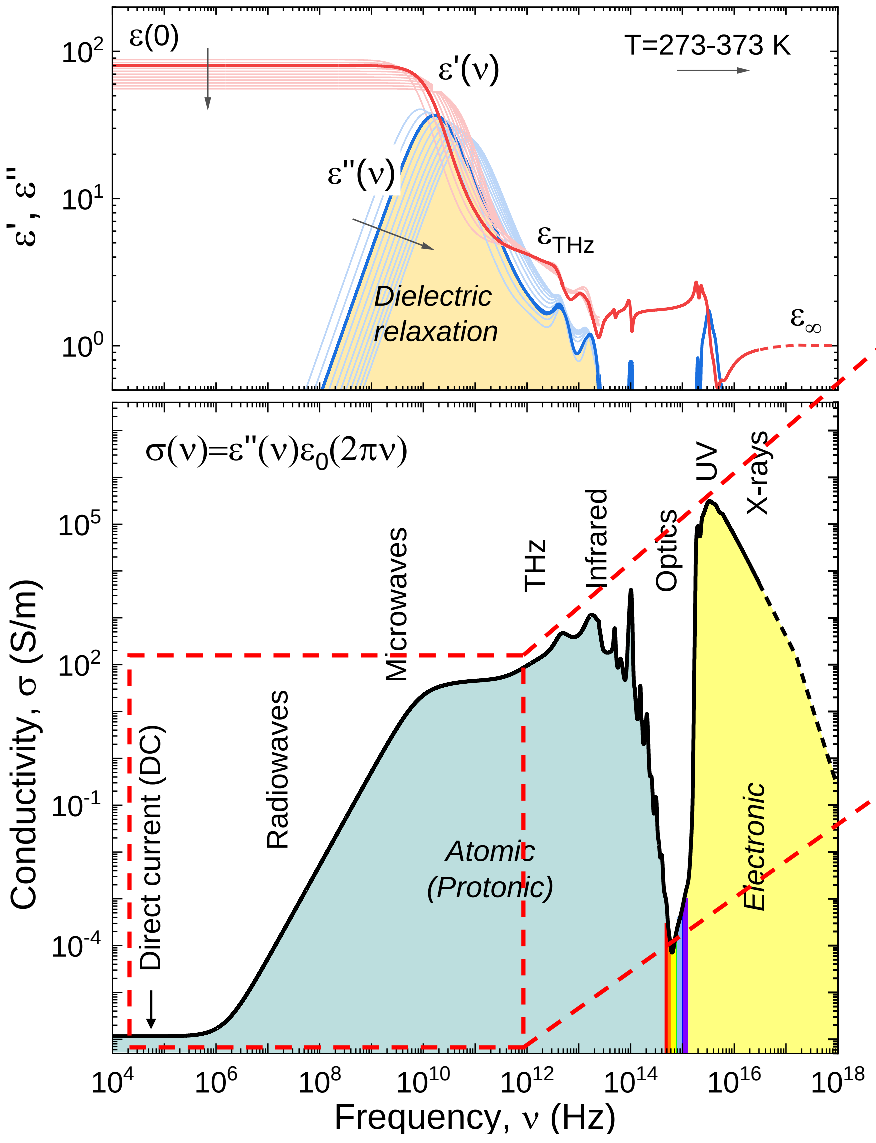
Vasily Artemov, 2021

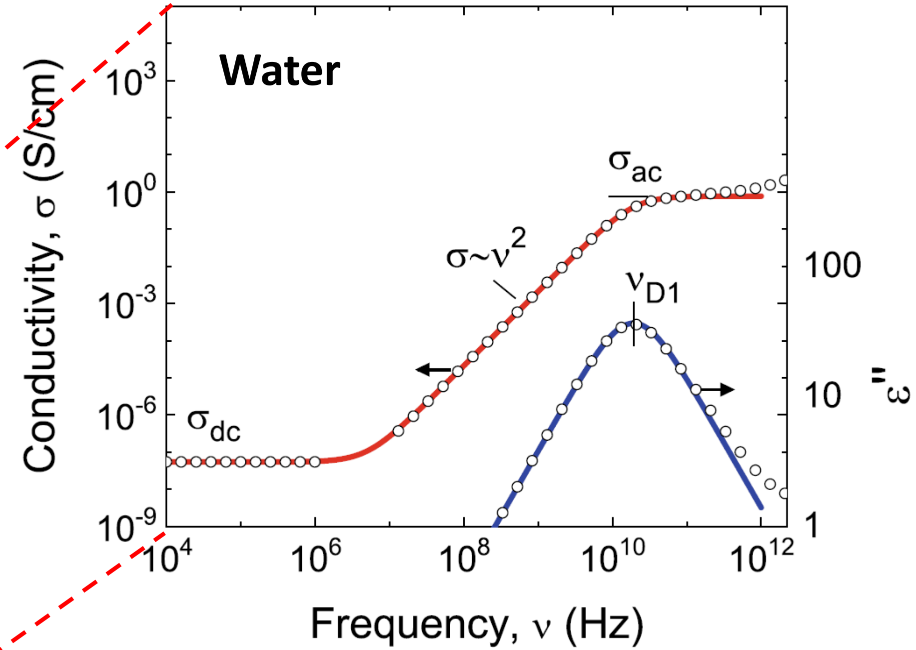
Dynamic conductivity of water

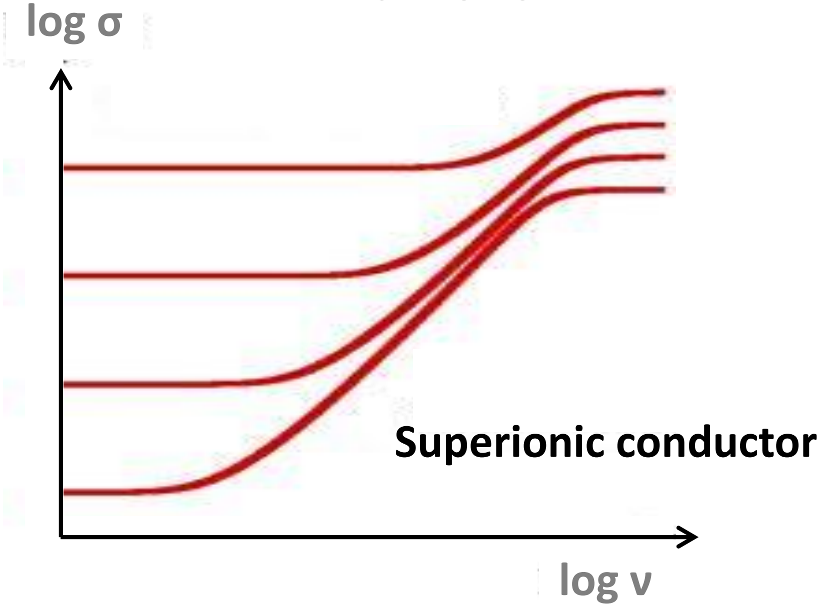




Dynamic conductivity of water

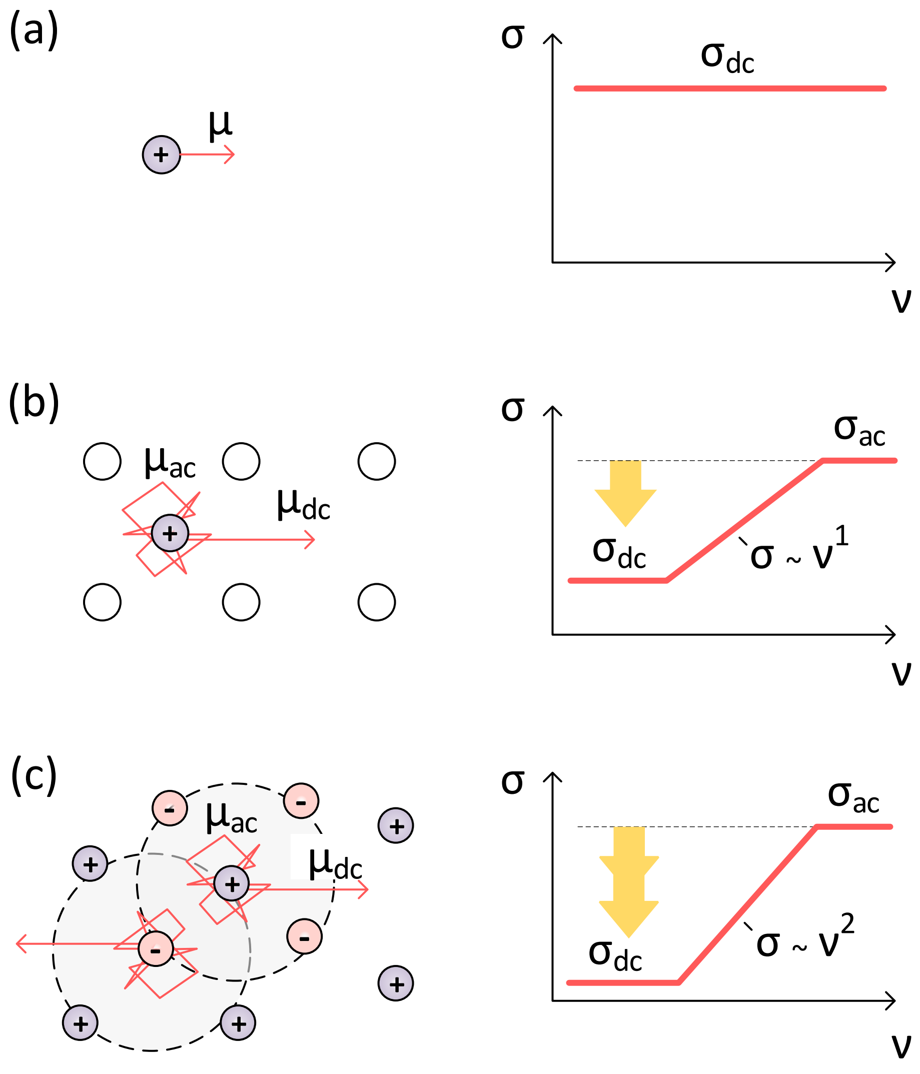


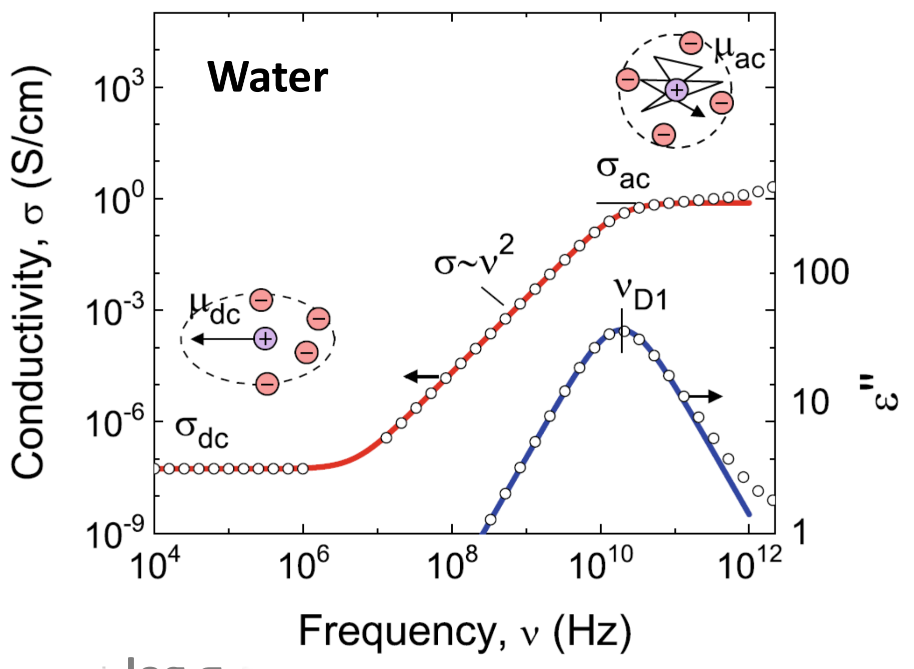


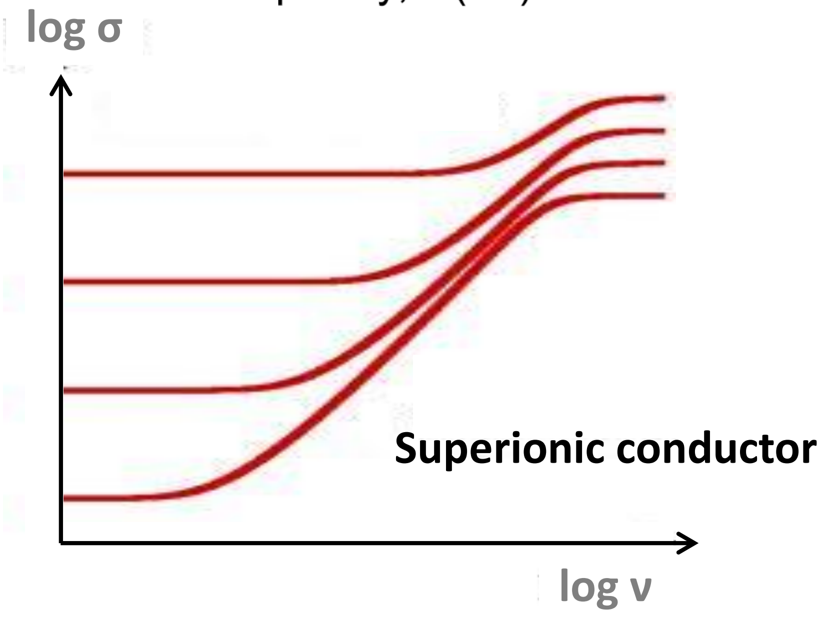


Vasily Artemov, 2021

Dynamic conductivity and mobility

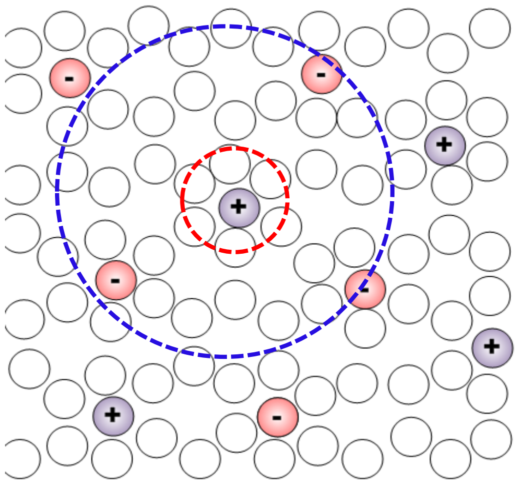


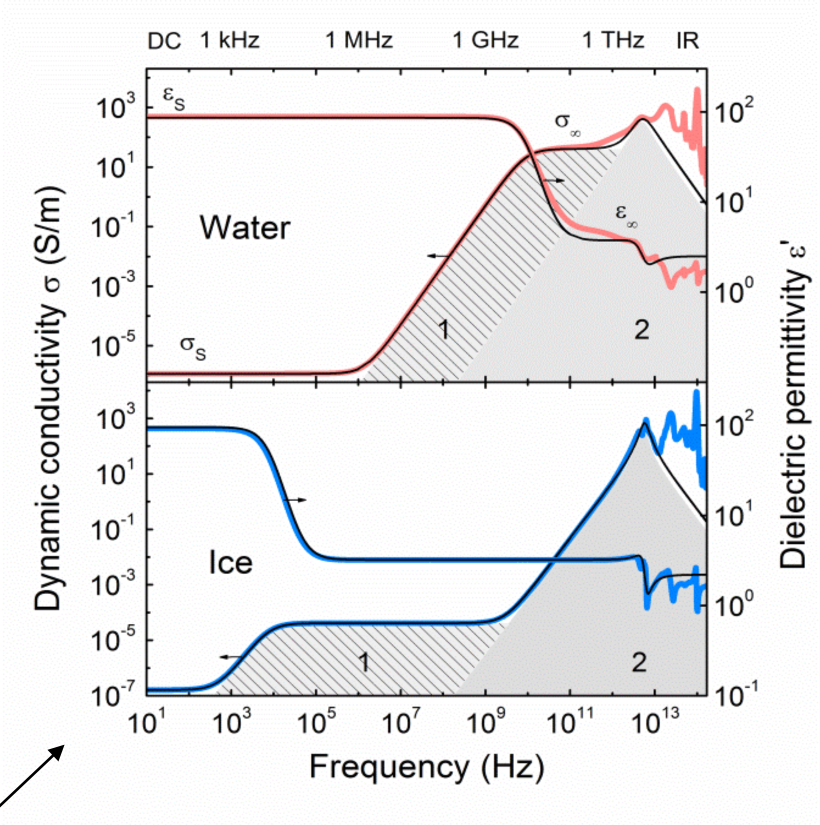




Vasily Artemov, 2021

Turning on ion-ion interaction





$$\begin{cases} m\ddot{x} + m\gamma\dot{x} + \kappa_2\int_0^t M(t-t')\dot{x}(t')dt' + K = f(t) \\ m^*\ddot{X} + m^*\Gamma\dot{X} - K = F(t), \end{cases}$$

$$\sigma(\omega) = \frac{i n_i q^2 B}{(\kappa_1 / \omega)^2 - AB}$$

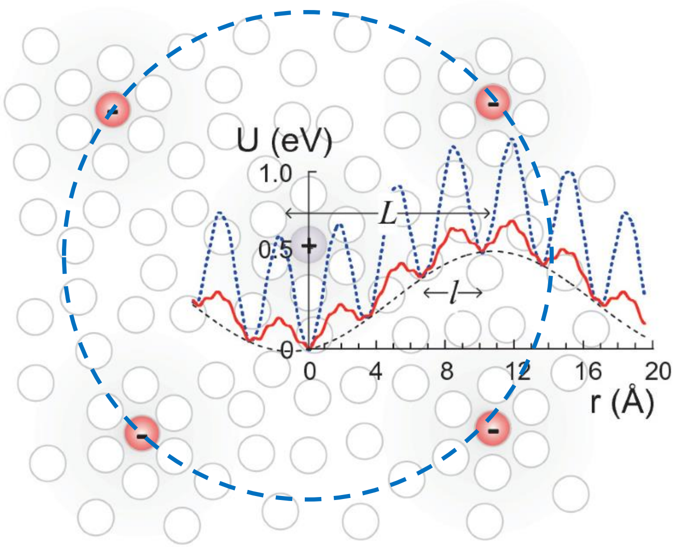
$A = \kappa_1/\omega - m[\omega + i(\gamma + \omega_0^2 M(\omega))]$ and
$B = \kappa_1/\omega - m^*\omega + i m^*\Gamma$, $M(\omega) = 1/(\tau_c^{-1} - i\omega)$

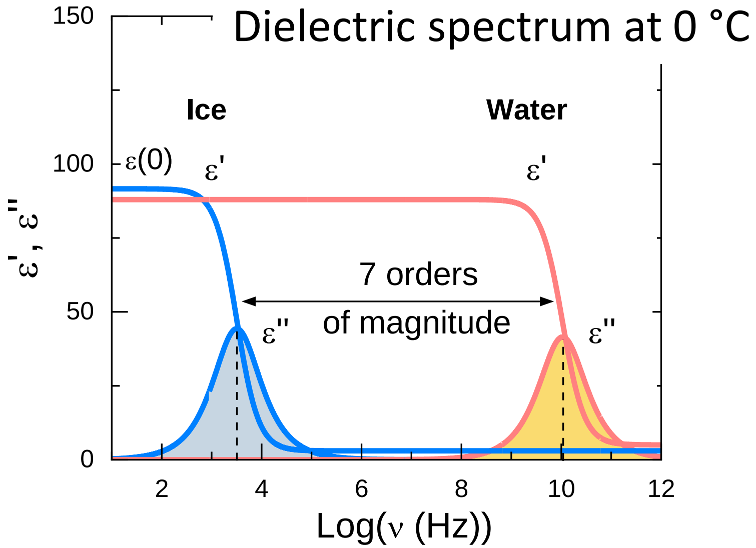
Fit parameters for water: n_i=1 M (**2%**), γ =4 THz, Γ=2.2 THz, τ_C =0.7 ms, ω_0=0.7 THz, Ω_0=5 THz

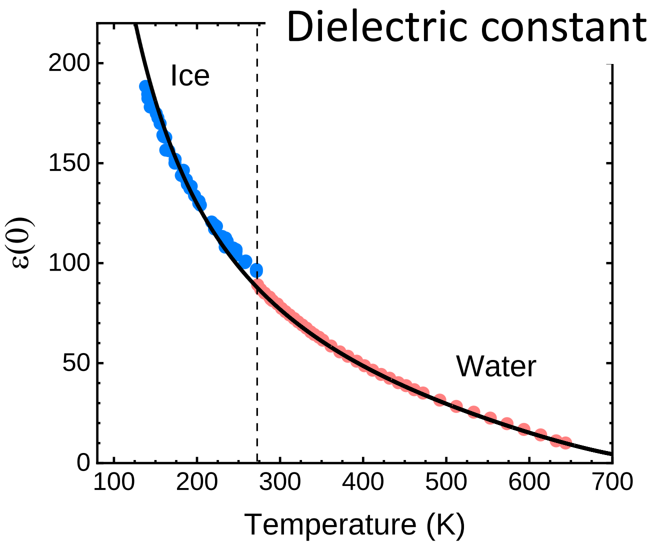
Fit parameters for ice: n_i=1 M (**2%**), γ =3 THz, Γ=2.4 kHz, τ_C =0.6 ms, ω_0=0.6 THz, Ω_0=5 THz

V. G. Artemov, *Phys. Chem. Chem. Phys.*, 21, 8067 (**2019**)

Ice and water: similar structures, different dynamics







$$\varepsilon_s = \frac{n_i q^2 (m^* \Gamma + \kappa_1 \tau_c)}{\varepsilon_0 \kappa_1 (m\gamma + \kappa_2 \tau_c + m^* \Gamma)} \approx \frac{n_i q^2}{\varepsilon_0 \kappa_2}.$$

Fit parameters for water: n_i=1 M (**2%**), γ =4 THz, Γ=2.2 THz, τ_C =0.7 ms, ω_0=0.7 THz, Ω_0=5 THz

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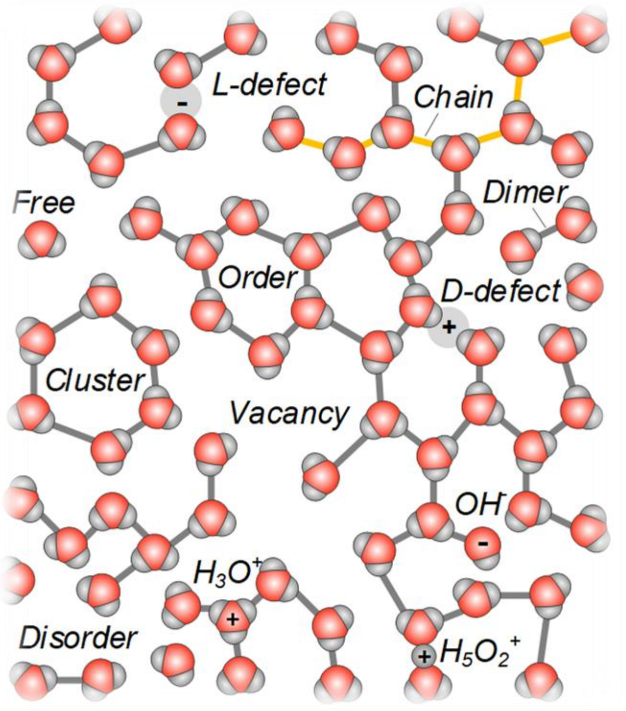
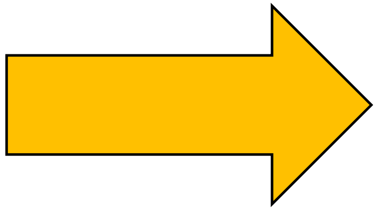
V. G. Artemov et al., *Ferroelectrics*, 466, 158 (**2014**)

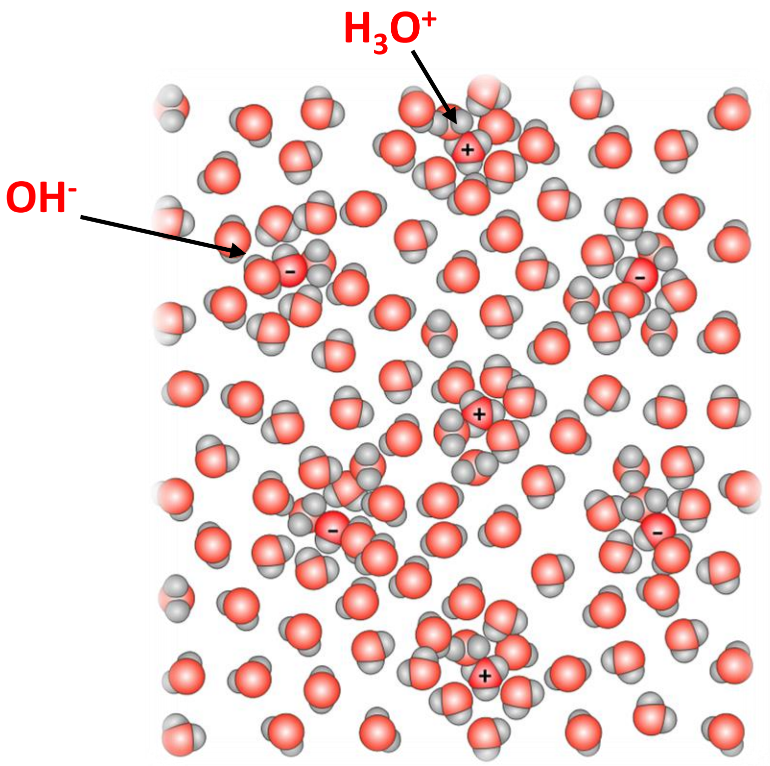
A comparison of water structures

Bernal-Fowler model of water





The ionic model of water



2% of H_3O^+ and OH^-

pH and ion concentration

Concentration of ions according to the standard pH concept:

pH=7 $[H_3O^+] + [OH^-] \approx \mathbf{10^{-9}}$ %

Compare with:

$HDO \approx 10^{-2}$ %

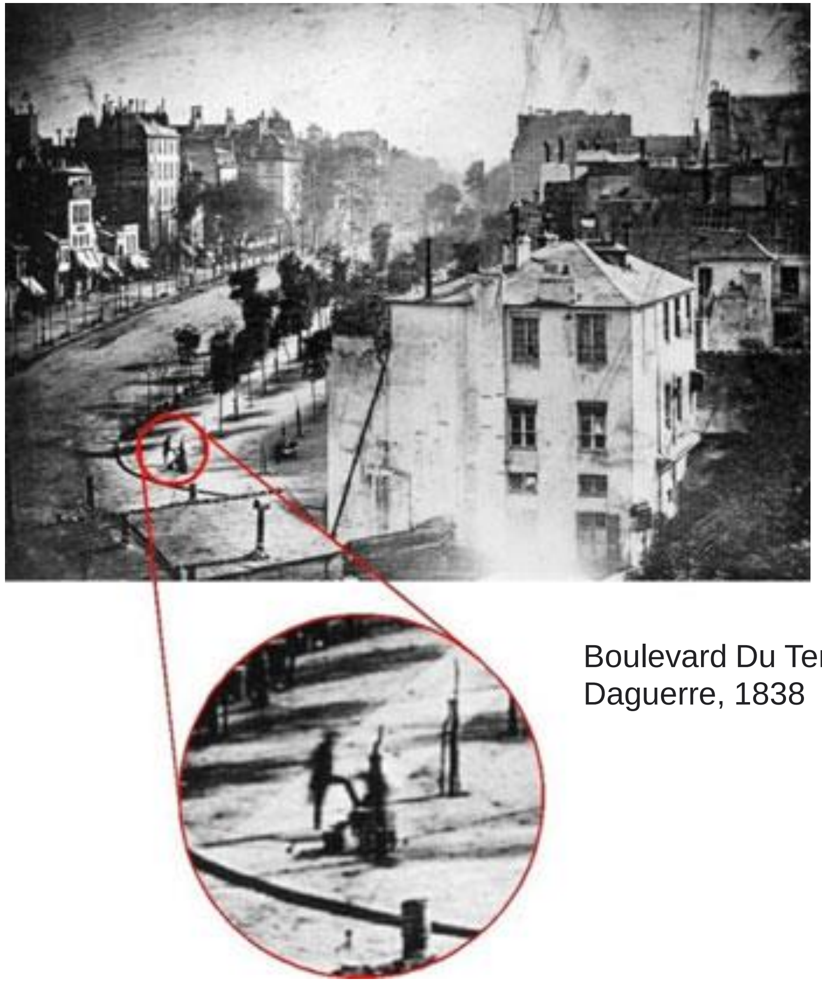
$H_2O_2 \approx 10^{-7}$ %

$CO_2 \approx 10^{-4}$ %

$O_2 \approx 10^{-4}$ %

$N_2 \approx 10^{-3}$ %

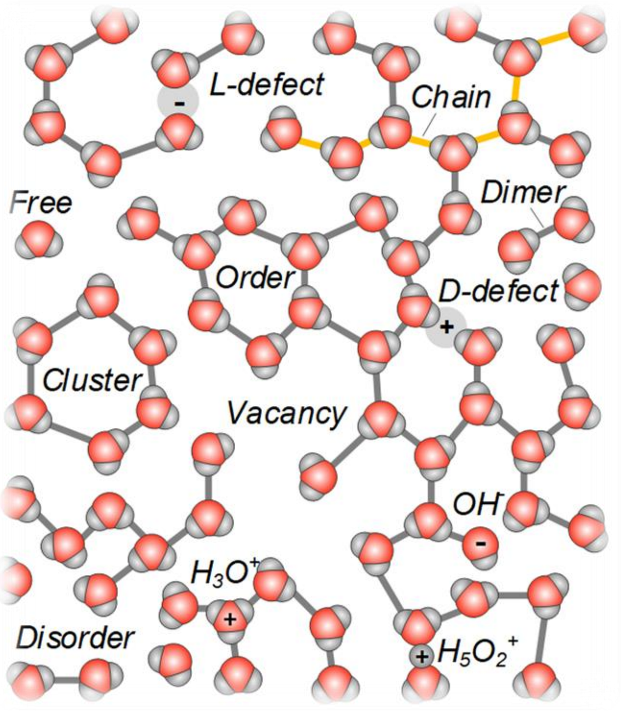
V. G. Artemov et al., *Doklady Physics,* 61, 1 (**2016**)



Boulevard Du Temple, Louis Daguerre, 1838

A comparison of water structures

Bernal-Fowler model of water
(Diffusion averaged picture)

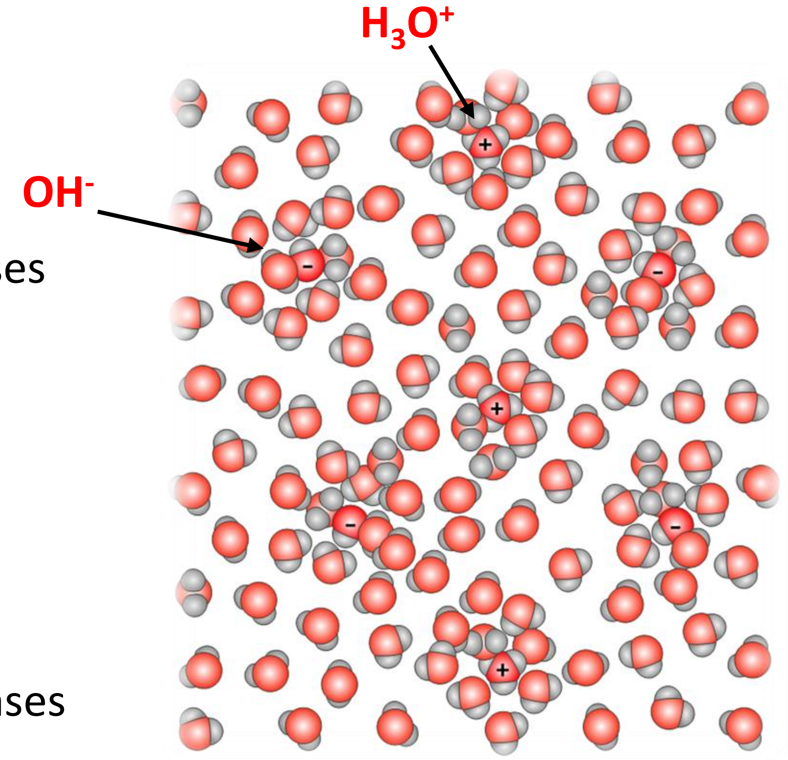


$[H_3O^+] + [OH^-] \approx$ **10^{-9}** %

Observation time increases

Observation time decreases

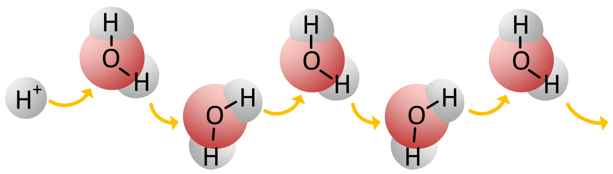
The ionic model of water
(Instantaneous structure)



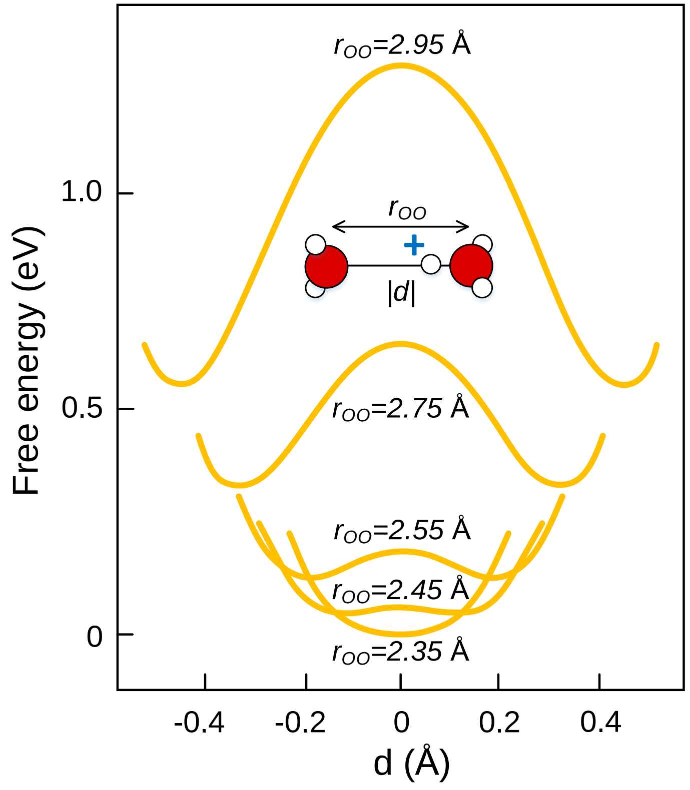
2% of H_3O^+ and OH^-

Quantum effects in water

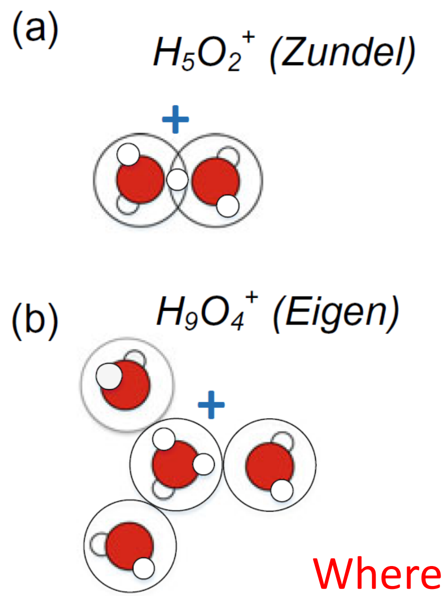
Grotthuss mechanism:



Proton tunneling:

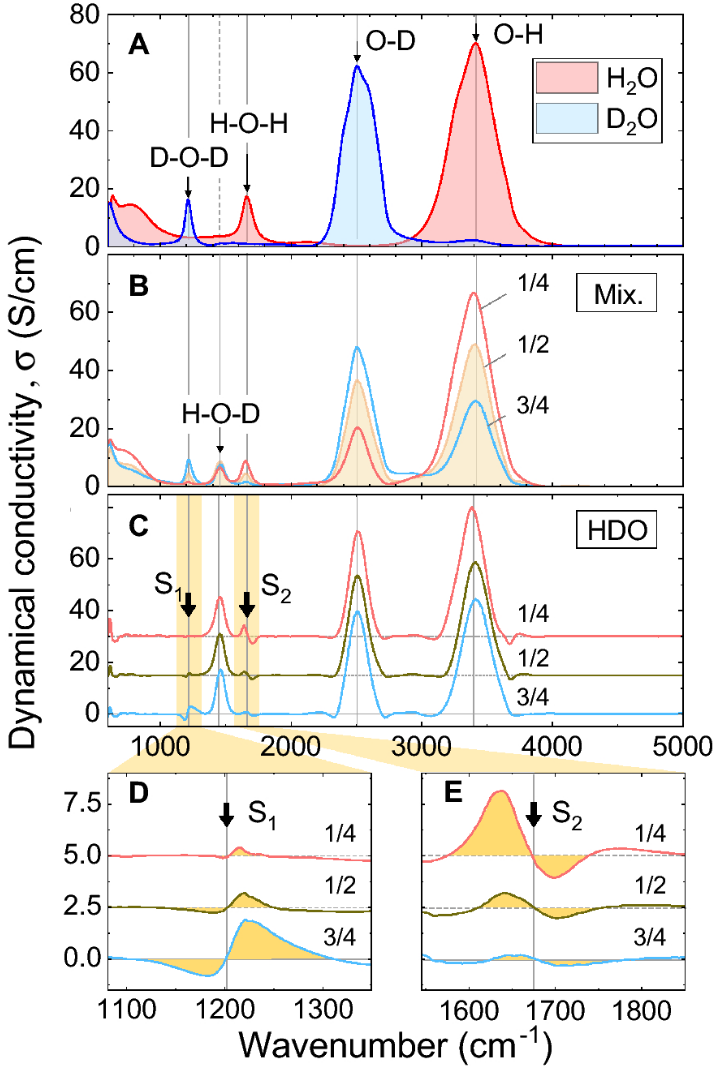


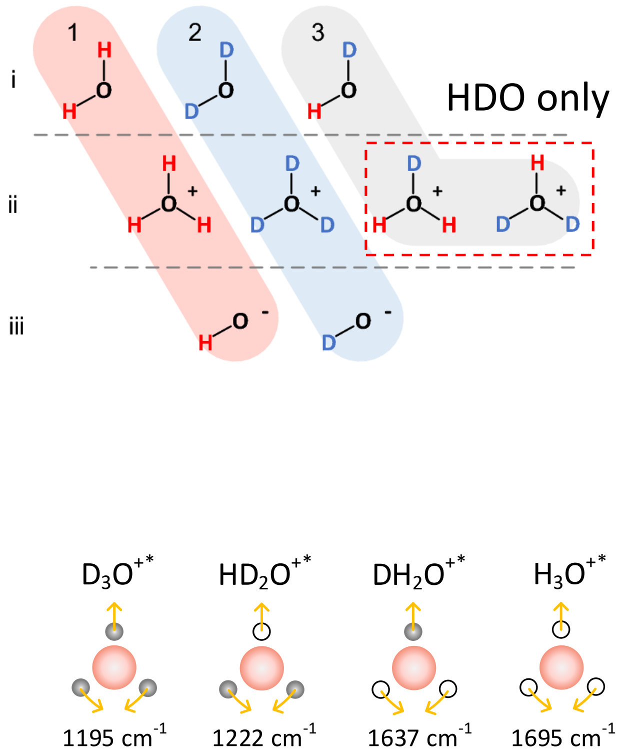
Two states of excess proton:



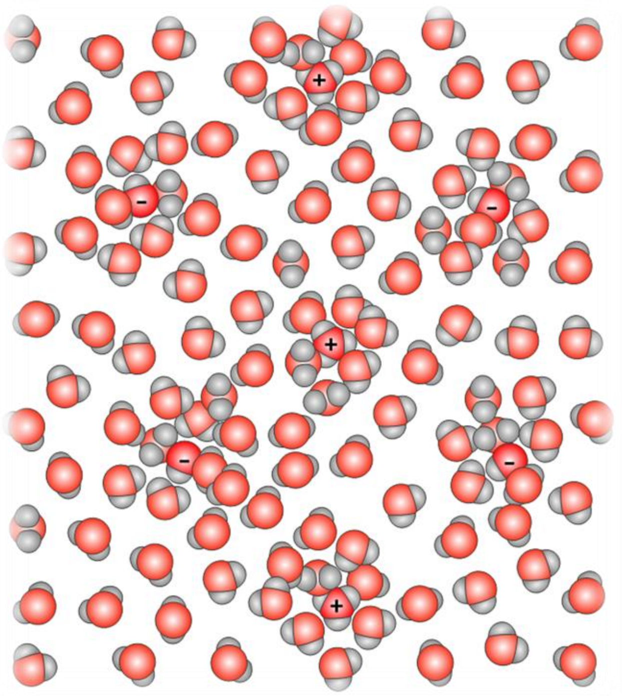
Where is the infrared signature of the excess protons?

Revealing excess protons in IR spectrum of water





The ionic model of water



2% of H_3O^+ and OH^- **confirmed**

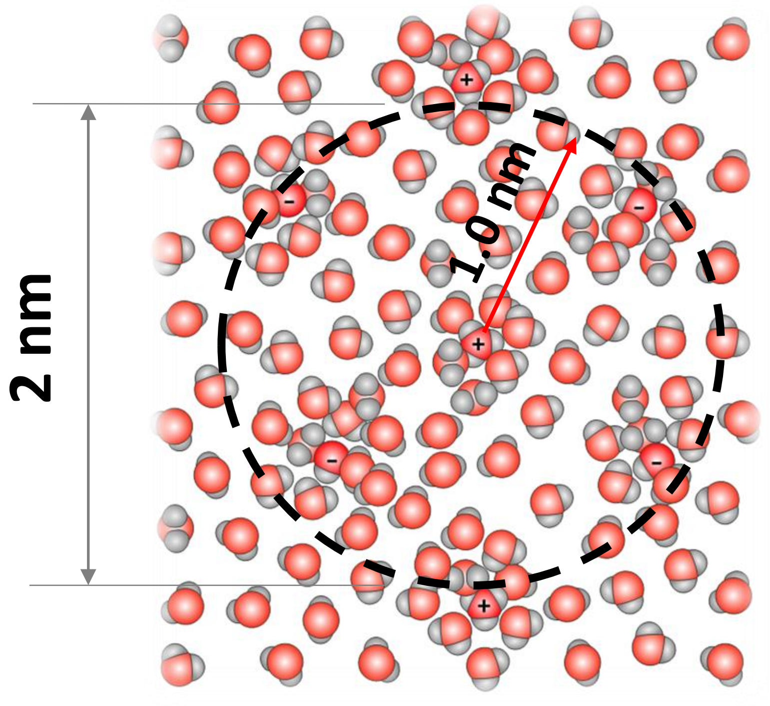
Lifetime of ion is 3 ps → **time heterogeneity**

V.G. Artemov et al., Scientific Reports, 10, 1132 (**2020**)

Space-time heterogeneity of water

The ionic model of water

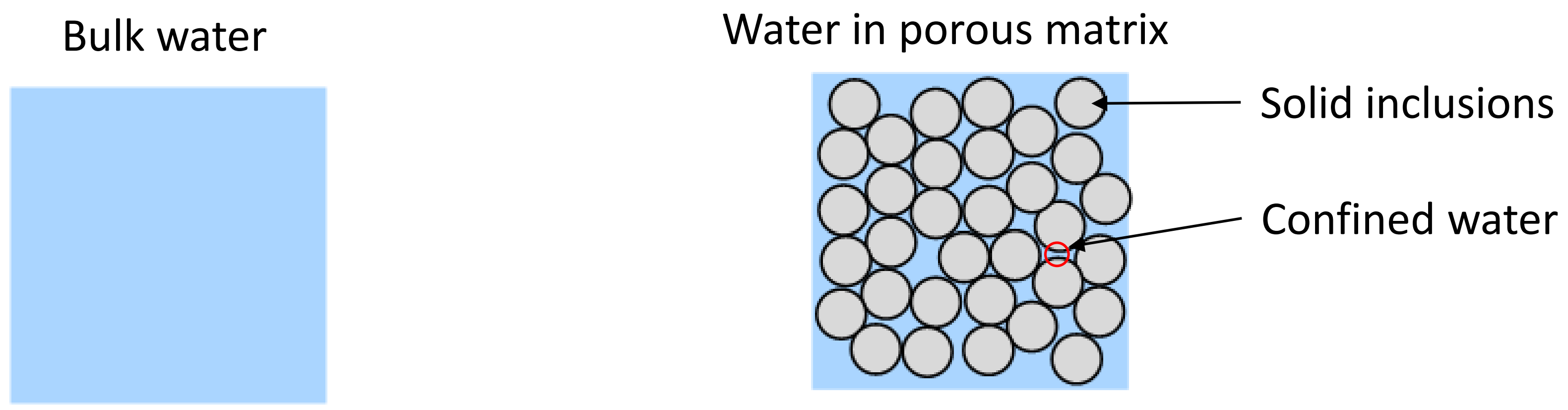
2% of H_3O^+ and OH^-



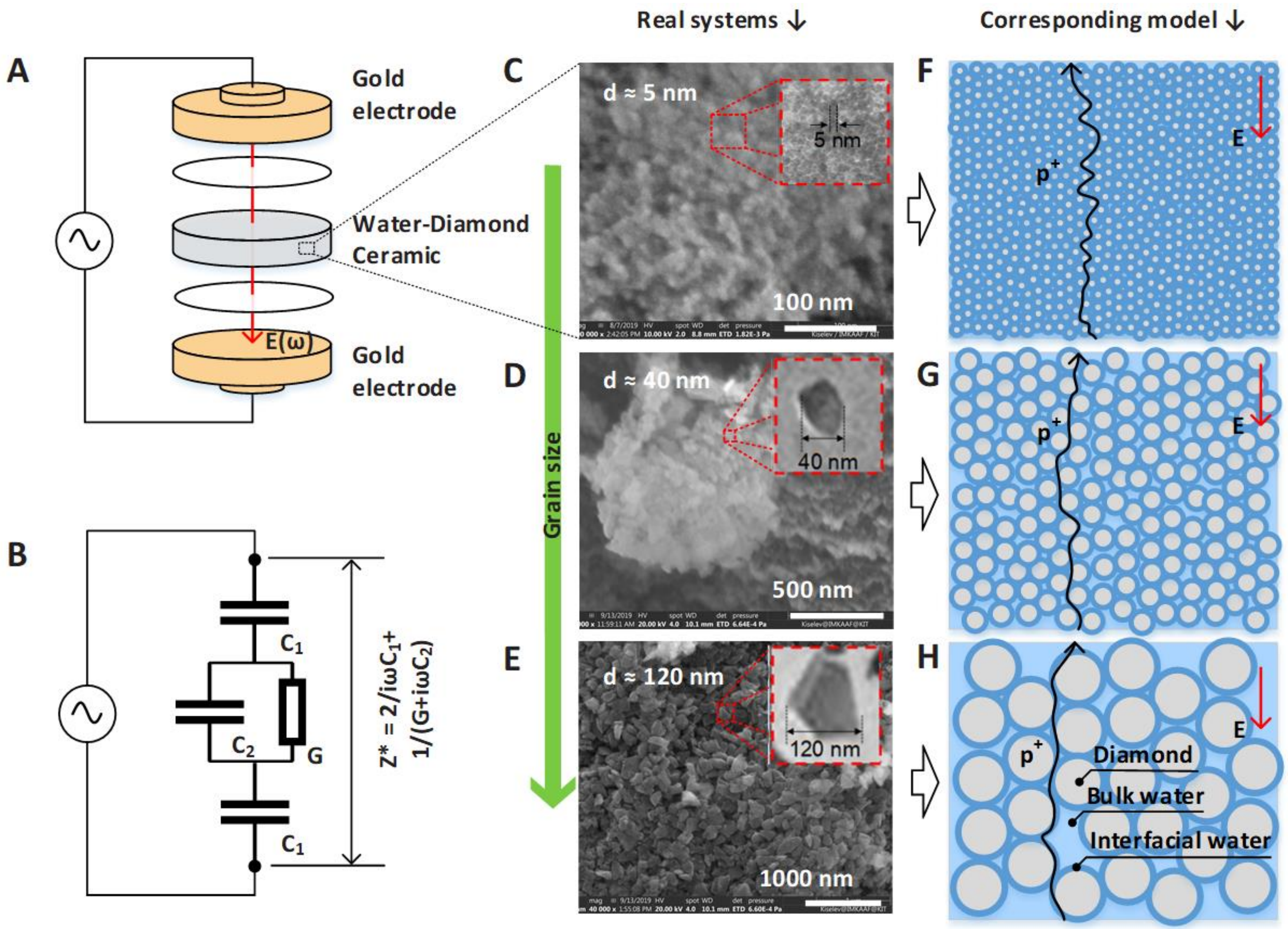
V. G. Artemov, *PCCP*, **2019**, 21, 8067

Lifetime of ions: 3 ps
Lifetime of H_2O: 50 ps

Confined water: the test of spatial heterogeneity

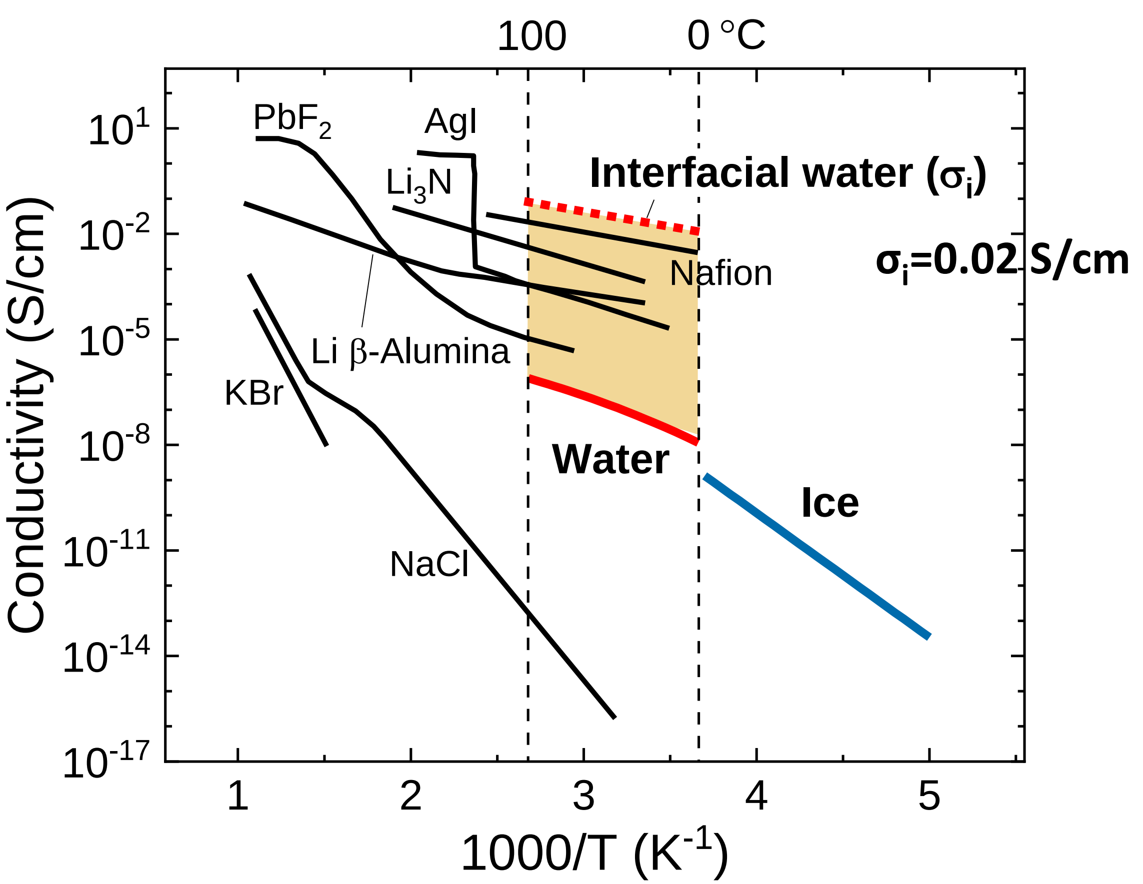


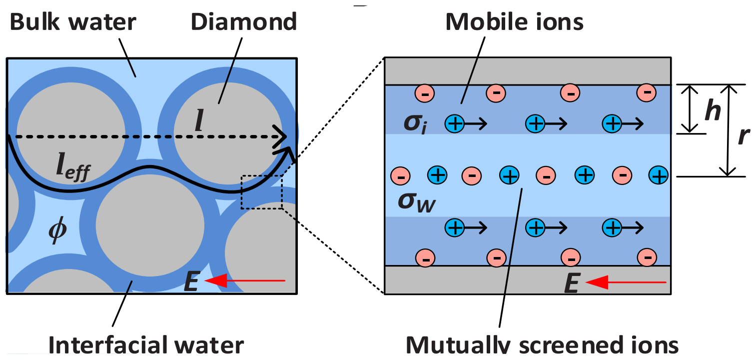
Electric properties of water confined in nanopores



V. G. Artemov et al., *J. Phys. Chem. Lett.* **2020**, 11, 3623-3628

Water as superionic conductor





V. G. Artemov et al., *J. Phys. Chem. Lett.* **2020**, 11, 3623

Conclusions (insights from broadband dielectric spectroscopy)

1. The century-old Bernal-Fowler model misses a part of the information because it is based on either static or optic data and excludes quantum effects.

2. We suggest the ionic model of water, which accounts for the quantum effects. According to the model, the concentration of H_3O^+ and OH^- ions of 2% and a lifetime of 3 ps. The model works for various electrodynamic properties in bulk and confinement.

3. The ionic model of water has a spatial heterogeneity period of 2 nm and a time heterogeneity period of 3 ps. We anticipate the changes in the properties of water near these points, such as change of viscosity, change of the dielectric constant, thermodynamic anomalies, etc.

4. We observed anomalously high proton conduction of the interfacial water. The effect paves the way for cheap and ecologically friendly devices for electrochemical energy storage.

Acknowledgments

Pavel Kapralov
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Alexander Ryzhov
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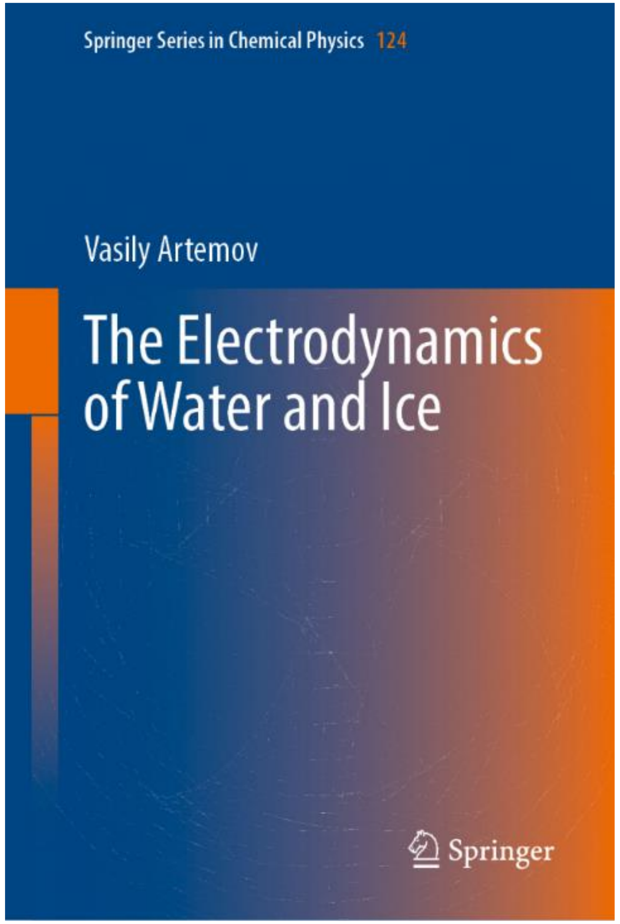
Ece Uykur
Artem Pronin
Seulki Roh
Martin Dressel
Svetlana Ponomarenko

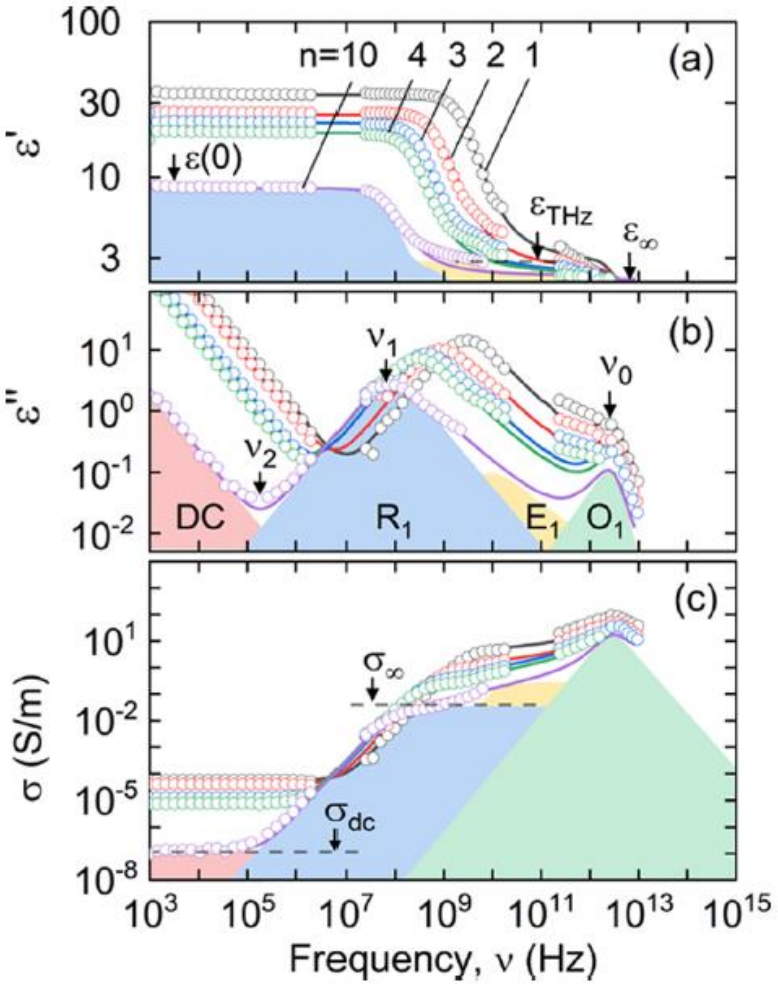
KIT Karlsruher Institut für Technologie
RQC Russian Quantum Center
Universität Stuttgart
Max-Planck-Institut für Festkörperforschung
Skoltech Skolkovo Institute of Science and Technology

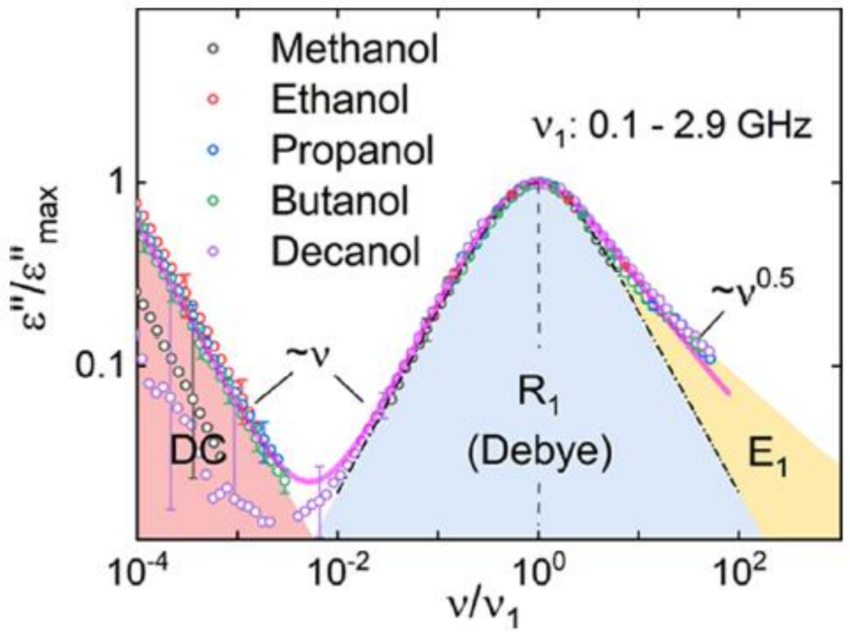
Thank you.

v.artemov@skoltech.ru



Dielectric relaxation of monohydric alcohols





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