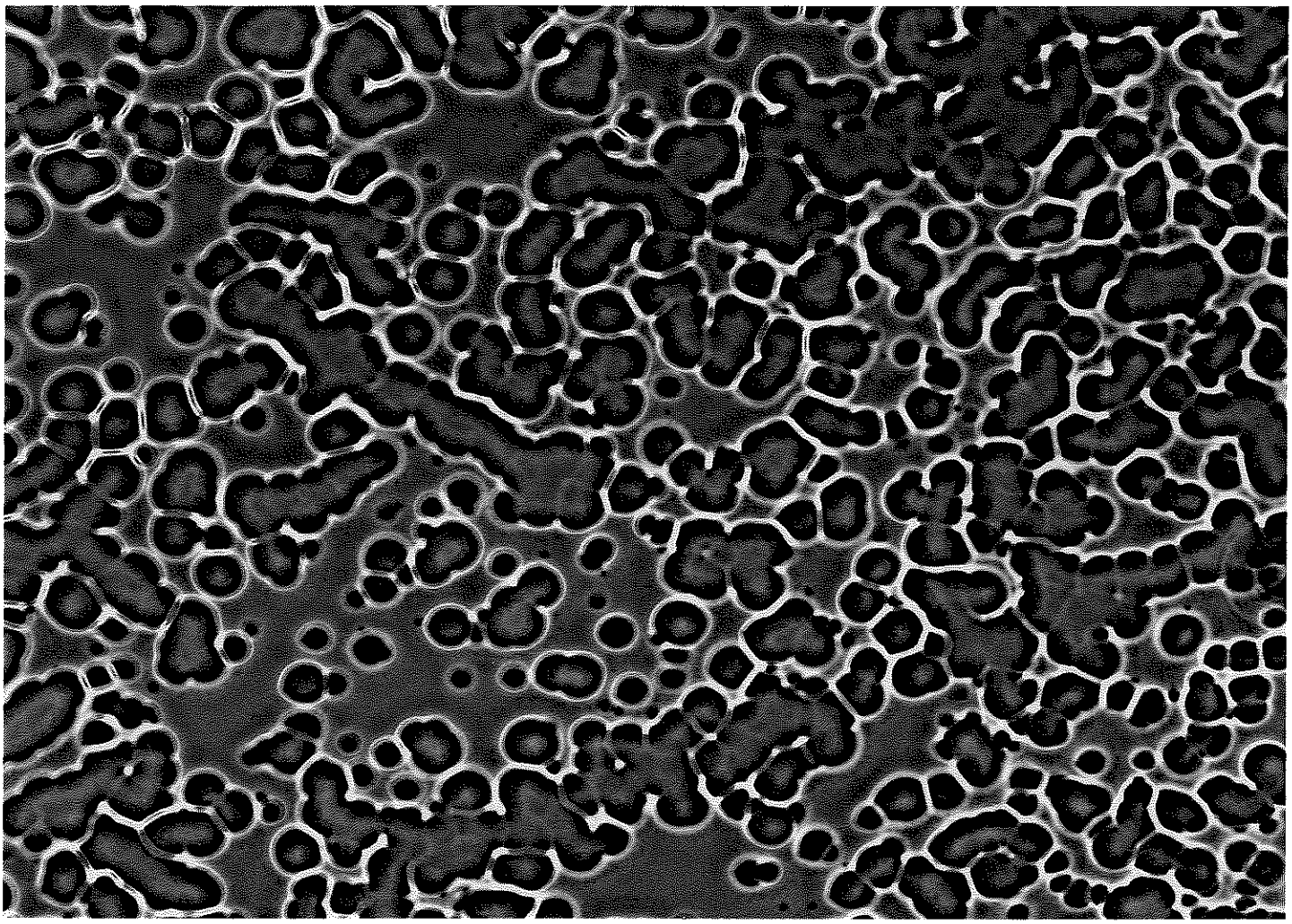
BOOK OF ABSTRACTS

Faraday Discussion 167

Mesostructure and Dynamics in Liquids and Solutions

18 - 20 September 2013
University of Bristol, UK



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Faraday Discussion 167: Mesostructure and Dynamics in Liquids and Solutions
is organised by the Faraday Division of the RSC.

This book contains abstracts of the 34 posters presented at Faraday Discussion 167. All abstracts are produced directly from typescripts supplied by authors.

Posters

Posters have been numbered consecutively: **P01 –P34.**
The formal poster viewing session has been scheduled to take place on Wednesday 18th September.

Poster Prizes

The RSC Skinner poster prize will be awarded to the best RSC student member poster as judged by the committee.

Faraday Discussion Volume

Copies of the Discussion Volume will be distributed approximately 6 months after the meeting. To expedite this, it is essential that summaries of contributions to the discussion are received no later than Monday 7th October 2013 for questions and comments and Monday 21st October 2013 for responses. In order to keep the students fees low the Discussion Volume is NOT included in the student conference fees. A copy of the publication may be purchased at a reduced price, only for orders placed at the meeting; an application form is available from the information desk at the meeting.

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Poster Presentations

P01 **Terahertz spectroscopy of hydrogen-bonded glass-forming liquids**
Juraj Sibik* and J. Axel Zeitler
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P02 **The cluster fluid phase of fluids with competing short and long-ranged interactions**
Martin Sweetman*, Rui Fartaria and Leo Lue
University of Edinburgh, UK

P03 **An anomalous behaviour of water-glycerol solutions in a confined geometry**
Jan Swenson*, Khalid Elamin, Helén Jansson and Shigeharu Kittaka
Chalmers University of Technology, Sweden

P04 **Dynamics and vibrational spectroscopy of water at the solid-liquid interface**
Prashant Kumar Gupta and Markus Meuwly*
University of Basel, Switzerland

P05 **Ionic diffusion and solvation : from applications to theory**
Riccardo Spezia*, Fausto Martelli, Dominika Lesnicki and Rodolphe Vuilleumier
CNRS, France

P06 **Fluids Confined Between a Solvophilic and a Solvophobic Substrate: Interfaces, Local Structure and Layering Transitions**
Robert Evans* and Maria C. Stewart
University of Bristol, UK

P07 **Investigating the liquid-liquid phase transition in supercooled water on the coupled cluster quality potential energy surface**
Yaping Li, Jicun Li and Feng Wang*
University of Arkansas, USA

P08 **Experiments at negative pressure to probe nanoscale structures in water**
Frédéric Caupin*, Mouna El Mekki Azouzi and Gaël Pallares
Université Claude Bernard Lyon, France

P09 **Investigations into the structure of confined liquids in mesoporous materials with terahertz time-domain spectroscopy**
Nicholas Y. Tan*, Lynn F. Gladden and J. Axel Zeitler
University of Cambridge, UK

P10 **Inter Molecular Dynamics of Monohydroxy Alcohol 2-Propanol in the Liquid and Supercooled State**
Antonio Faraone*, Michihiro Nagao, Kenji Nakajima and Tatsuya Kikuchi
University of Maryland & NIST Center for Neutron Research, USA

P11 **Single pairs of densely charged anions and cations cooperatively slowdown water rotation**
Ana C. A. Vila Verde* and Reinhard Lipowsky
Max Planck Institute of Colloids and Interfaces, Germany

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P12 **Dynamic properties of water-xylitol solutions**
Khalid Elamin*, Stefano Cazzato, Johan Sjöström, Stephen M. King and Jan Swenson
Chalmers University of Technology, Sweden

P13 **Chlorine-chlorine interactions and dipole alignments in liquid chloroform**
Jacob J. Shephard*, John S. O. Evans and Christoph G. Salzmann
Durham University and University College London, UK

P14 **A Self-Consistent-Field Theory for the Reorganization Energy in Solvent Mixtures**
Bilin Zhuang* and Zhen-Gang Wang
California Institute of Technology, USA

P15 **Dynamics and Structure of a Typical Room Temperature Ionic Liquid Across Glass Transition: A Multinuclear NMR Study**
Takatsugu Endo*, Derrick C. Kaseman and Sabyasachi Sen
University of California, Davis, USA

P16 **Cavitation of water at negative pressures**
Georg Menzl *, Philipp Geiger and Christoph Dellago
Faculty of Physics, University of Vienna, Austria

P17 **Long-range hydrogen-bond structure in aqueous solutions**
Sheeba Jem Irudayam and Richard H. Henchman*
The University of Manchester, UK

P18 **Correlation of ionic liquid nanostructure, cohesive energy density and their ability to promote amphiphile self-assembly**
Tamar L. Greaves* and Calum J. Drummond
CSIRO Materials Science and Engineering, Australia

P19 **NMR Relaxation Study of Ionic Liquids in Bulk and Under Confinement in Porous Media**
Amin Ordikhani Seyedlar*, Siegfried Stapf and Carlos Mattea
Ilmenau University of Technology, Germany

P20 **Measuring the Critical Micelle Concentration (CMC) of Molecular Solvents as Amphiphile Self-Assembly Media**
Emmy C. Wijaya*, Tamar L. Greaves and Calum J. Drummond
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P21 **Glass transition and structural relaxation of low-density amorphous ice**
Christoph G. Salzmann*, Jacob J. Shephard and John S. O. Evans
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P22 **Supression of Nucleation by Increase in Five-Fold Symmetric Local Structures**
Jade Taffs* and C. Patrick Royall
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P23 **Development of an electrical method for inducing mesoscale state transitions in polar liquids**
Adam D. Wexler*, Sandra Drusová, Elmar C. Fuchs and Jakob Woisetschläger
Wetsus - Center for Sustainable Water Technology, The Netherlands

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P24 **Amphiphile meets amphiphile: from affinity to demixing.**
Olga Russina, Silvia Imberti, Ruggero Caminiti and Alessandro Triolo*
ISM-CNR, Italy

P25 **Structural examination of the interactions of glutamine: a model system for understanding hydrophilic association**
Natasha H. Rhys*, Alan K. Soper and Lorna Dougan
University of Leeds, UK

P26 **Fluorescence lifetime imaging of liquid–liquid phase transition of triphenyl phosphite**
Joanna E. Mosses*, Christopher D. Syme, Christopher Gordon and Klaas Wynne
University of Glasgow, UK

P27 **Second-harmonic scattering in aqueous urea solutions: evidence for solute clusters?**
Martin R. Ward*, Stanley W. Botchway, Andrew D. Ward and Andrew J. Alexander
University of Edinburgh, UK

P28 **Lipidic Mesophases as Tools for Biological Investigation**
Thomas G. Meikle*, Charlotte E. Conn, Calum J. Drummond and Frances Separovic
CSIRO/University of Melbourne, Australia

P29 **Phase transitions and self-assembly in liquids confined to thin films**
Alexander M. Smith, Kevin R. J. Lovelock, Nitya Nand Gosvami and Susan Perkin
University of Oxford, UK

P30 **Understanding the Ionic Liquid/Gas Surface Structure: a Combined Approach**
Kevin R. J. Lovelock*, Sarah Fearn and Alexander M. Smith
Imperial College London, UK

P31 **Do H-Bonds Explain Strong Ion Aggregation in Ethylammonium Nitrate + Acetonitrile Mixtures?**
Thomas Sonnleitner, Viktoriya A. Nikitina and Richard Buchner*
Universität Regensburg, Germany

P32 **Evidence for a dynamical crossover in liquid metal dynamics**
Franz Demmel
ISIS Facility, UK

P33 **Self-association process in urea, acetone, acetamide and isopropanol aqueous solutions: Molecular dynamics simulation**
A. Idrissi, M. Barj, A. P. Seitsonen, M. Kiselev, V. Spiwok and M. V. Fedorov
LASIR, France

P34 **Ionic diffusion and solvation**
Riccardo Spezia, Fausto Martelli, Dominika Lesnicki* and Rodolphe Vuilleumier
École normale supérieure, France

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Single pairs of densely charged anions and cations cooperatively slowdown water rotation

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We use classical atomistic molecular dynamics simulations and polarizable models to investigate the dynamics of rotation of water in the vicinity of single pairs of magnesium sulfate or cesium chloride ions at varying anion-cation separation. At an anion-cation separation of 23 Å, a distance sufficiently large that each ion can be considered isolated, we find that the four ions impact the rotational dynamics of water in very distinct ways. Water rotation is markedly slowed down in the first and second hydration layers of the isolated magnesium ion and in the first hydration layer of isolated sulfate and chloride ions; in contrast, isolated cesium ions have almost no effect on water rotational dynamics. At 12 Å anion-cation separation, a small population of water molecules halfway between the magnesium and sulfate ions rotates more slowly than the equivalent population near the isolated ions or near the cesium chloride pair. This result indicates that pairs of densely charged anions and cations weakly slow down water rotation in a cooperative manner already at this large anion-cation separation. Surprisingly, this subpopulation consists exclusively of water molecules in the second or third hydration layers of either ion. For a 5 Å anion-cation separation, intense cooperative slowdown of water rotation is observed in the first hydration layer of all four ions, and weak cooperative slowdown is present in the outer hydration layers. Our results broadly support the existence of both short- and long-range cooperative slowdown of water rotation by ions, initially proposed based on experimental measurements, but suggest that intense cooperative slowdown is limited to the first hydration layers of the ions and that long-range cooperative slowdown is weak. Our results also indicate that ion cooperativity affects both the magnitude and the spatial range of the slowdown. The dependence of cooperative slowdown on the identity of the ions, anion-cation distance and the position of water molecules relative to the ions obtained from simulations can be used to refine the interpretation of experimental measurements to gain further insight into these systems.

Single pairs of densely charged anions and cations cooperatively slowdown water rotation

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1. Motivation and Method

ION SOLVATION STRUCTURE/ DYNAMICS

•Solvent structure and dynamics are important for biological function.

•Experimental studies of water near small, inorganic, ions suggest that particular ion combinations cooperatively slowdown water rotation[1,2,4].

- Some studies indicate that cooperative effects can be intense and long range for densely charged ions, whereas others indicate that they are always limited to the first hydration shell of the ions.

•Experimental data is often analyzed using a two-population model:

- Only two populations of water exist: bulk-like (τ_{reor}=2.5 ps) and slow (τ_{reor}=10 ps); different salt solutions differ only in the fraction of slow waters;
- The fraction of slow waters differs between solutions because:
  - Anions and cations anisotropically slowdown water rotation: anions slowdown OH rotation, cations slowdown dipole rotation;
  - Combining densely charged anions and cations locks the hydrogen bond network between them.

QUESTIONS

- Does cooperative slowdown occur for isolated pairs of ions?
- What is the spatial range of the slowdown?
- Is a two-population model reasonable?
- Do anions and cations anisotropically slowdown water dynamics?

MOLECULES AND METHODS

CLASSICAL ATOMISTIC MD WITH POLARIZABLE MODELS

MODELS
SWM4-NDP water and ions[3,7]

Bonded Interactions

$$U_{bond} = K_b (b - b_0)^2$$

$$U_{angle} = K_\theta (\theta - \theta_0)^2$$

Polarizability - Drude oscillators

$$U_{Drude} = k_D (b_D - 0)^2$$

$$q = q_1 - q_D \quad \alpha = \frac{q_D^2}{k_D}$$

$$k_D = 1000\,\text{kcal/mol/A}^2$$

Non-bonded Interactions

$$U_{LJ} = \varepsilon\left[\left(\frac{\sigma_{i,j}}{r_{i,j}}\right)^{12} - 2\left(\frac{\sigma_{i,j}}{r_{i,j}}\right)^{6}\right]$$

$$U_c = K\frac{q_1 q_2}{r}$$

PARAMETERIZATION OF SO_4^{2-}

Target properties:

- experimental[6] $\Delta\Delta G^{hydr}$
  $\Delta\Delta G^{hydr} = \Delta G^{hydr}_{sulfate} - \Delta G^{hydr}_{chloride}$
- monohydrate properties from ab initio simulations[5]: (E_{min}, $R_{S\text{-}Ow}$)

$R_{S\text{-}OW}$

side view | top view

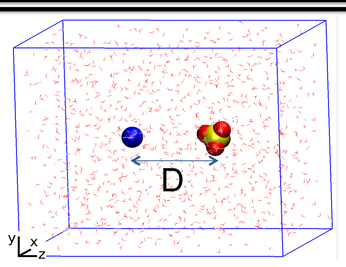
	Target	Model	%diff
E_{min} (kcal/mol)	-25.65	-23.84	-7
$R_{S\text{-}Ow}$ (A)	3.44	3.47	1
$\Delta\Delta G^{hydr}$ (kcal/mol)	-177.58	-177.42	0

SYSTEMS AND SIMULATION SETUP

$MgSO_4$ – strongly cooperative

CsCl – weakly cooperative

1040 H_2O
Ions in fixed positions
Ion pairs: D = 5, 6, 7, 8, 10, 12 A
Isolated ions: D = 24 A



300 K, NVT
Langevin thermostat γ = 0.05 ps
Drude thermostat γ = 0.1 ps
Periodic boundary conditions
dt = 0.5 fs, duration = 100 ns

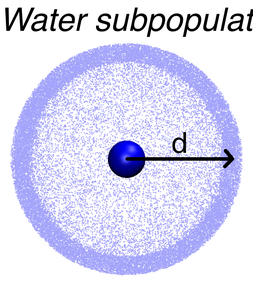
2. Mapping Rotational Anisotropy

Rotational anisotropy of OH or water dipole

$$P_2(\tau) = 0.5\left\langle 3\cos^2(\phi_\tau) - 1\right\rangle$$

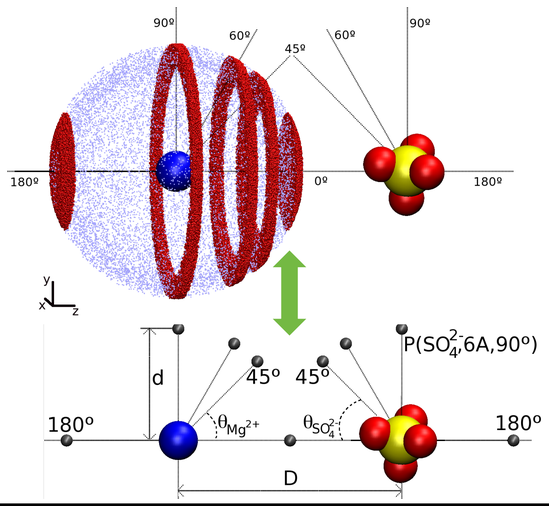
ϕ_τ – angle traveled by OH or water dipole in time τ.

Water subpopulations near single ions



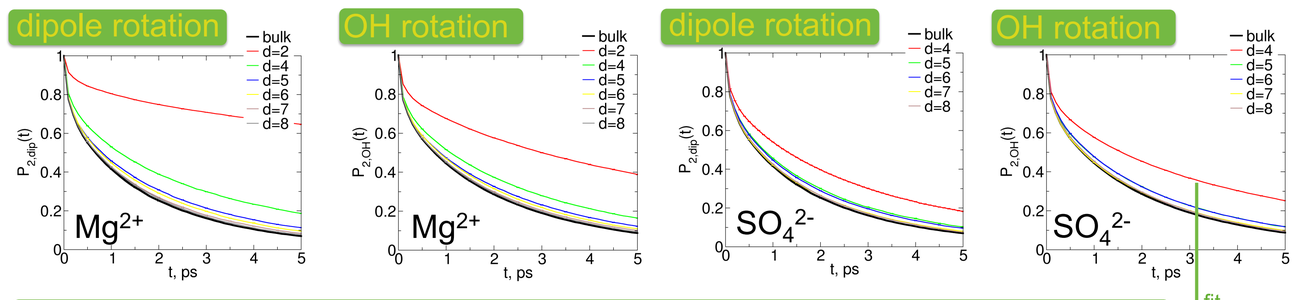
waters at distance *d* from the ion at t=0

Water subpopulations near ion pairs

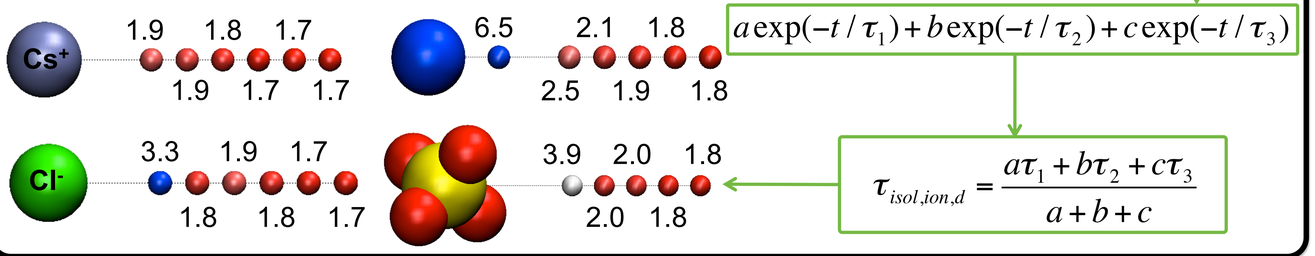


3. Water Dynamics Near Isolated Ions

Slowdown of OH and dipole rotation is weakly anisotropic

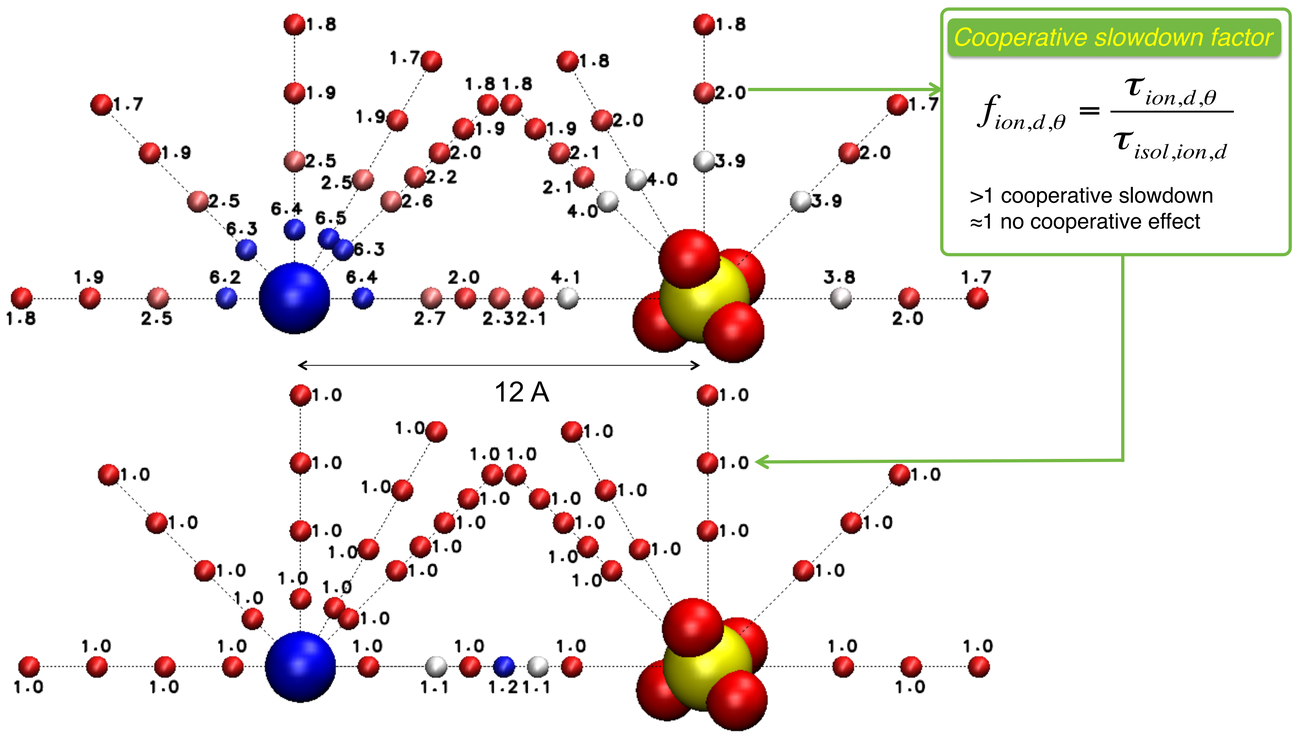


Average OH reorientation time for each water subpopulation

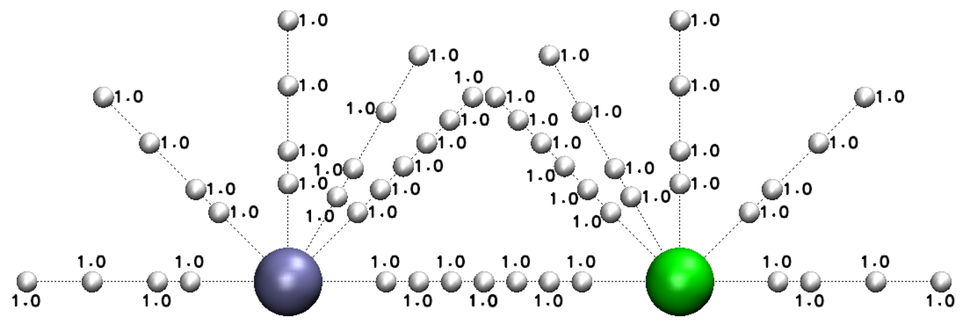


4. Water Dynamics Near Ion Pairs

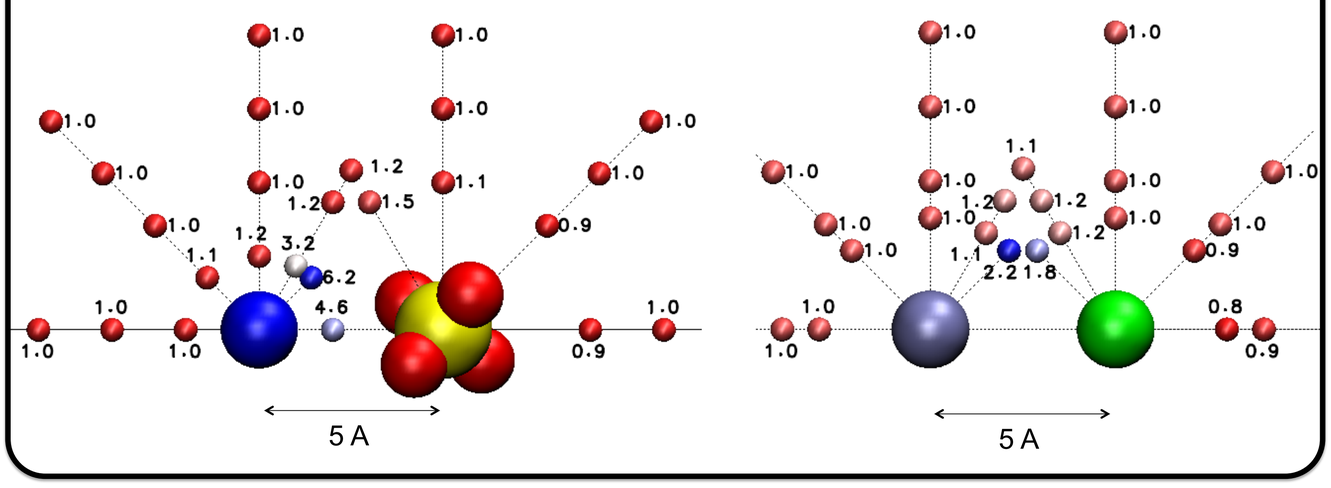
Mg^{2+} - SO_4^{2-} at large separation induce long range but weak cooperative slowdown



Cs^+ - Cl^- at large separation do not induce cooperative slowdown



Mg^{2+} - SO_4^{2-} and Cs^+ - Cl^- at short separation induce intense cooperative slowdown in the first hydration shell



5. Conclusions

•The effect of cations (anions) on the rotation of OH groups is comparable to their effect on the rotation of water dipoles: anions and cations have a weakly anisotropic effect on water dynamics.

•Strong cooperative slowdown is limited to water in the first hydration shell of the ions.

•Long range (6 A) cooperative slowdown exists, but is weak and exists only for densely charged ions.

•Ions cooperatively affect both the magnitude of slowdown and the spatial distribution of slow water populations, i.e., the simulations do not support the two-population model of cooperative slowdown commonly used to interpret experiments.

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