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Classify dynamic processes in water  
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DNN training dynamics  
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Conclusions  
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# Structure, Dynamics and Vibrational Spectroscopy of Interfacial Aqueous Solutions

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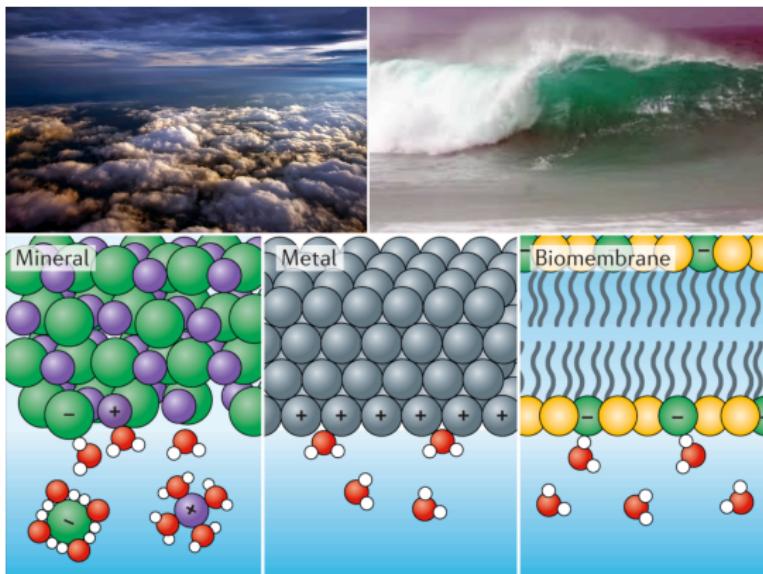
June 3, 2022

## Main arguments:

- (1) **Ab initio molecular dynamics simulations** → **The experimental spectra;**
- (2) **Hydrogen Bond (HB) dynamics + Instantaneous interface** → **Thickness of interfaces;**
- (3) **HB population + RNN** → **Classification of dynamical processes.**

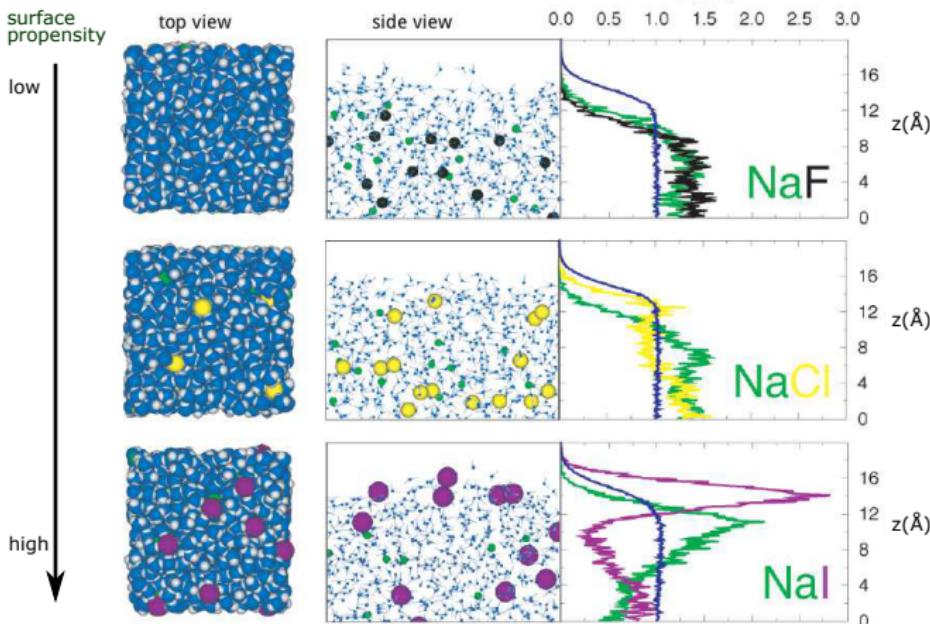
- ▶ **Introduction**
- ▶ **Methods:** Vibrational Sum-Frequency Generation (VSFG or SFG); Density Functional Theory-based Molecular Dynamics (DFTMD), Vibrational Density of States, HB dynamics
- ▶ **Results:** VSFG of alkali nitrate and alkali iodide solutions, Instantaneous interfaces and thickness of interfaces, Structural and features of solution/vapor interface; Classification of dynamical processes.
- ▶ **Conclusions and perspectives**

Aqueous interfaces are ubiquitous.



**Aqueous-vapor interfaces:** terminated HB network, statistical distribution of the position and orientation of molecules (Gonella, et al, *Nature Rev. Chem.* **5**, 466 (2021)).

Ions have different surface propensity.

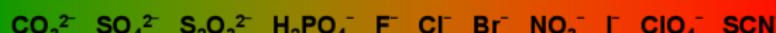


Ions' distribution with depth at the water-vapor interface are different. (Jungwirth, et al *Phys. Chem.* **105**, 10468 (2001)). Ions affect properties of interfaces significantly.

# Hofmeister anion effects

Anions' surface propensity and several different properties follow the **Hofmeister series** (Rogers, Thompson and Zhang, *J. Phys. Chem. B*, **120**, 49, 12596 (2016)).

Hofmeister Series



↑↑↑ surface tension

harder to make cavity

↓ solubility of proteins

salting out (aggregate)

↓ protein denaturation

↑ protein stability



↑ surface tension

easier to make cavity

↑ solubility of proteins

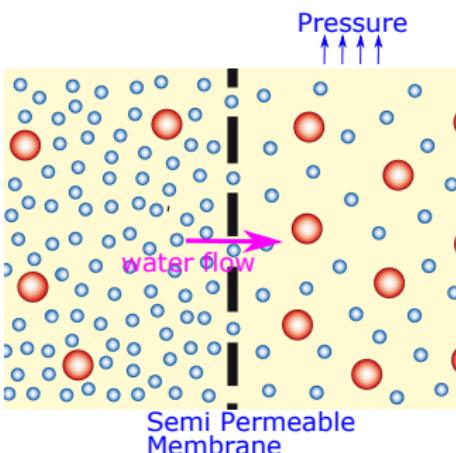
salting in (solubilize)

↑ protein denaturation

↓ protein stability

## Applications and problems

- ▶ Microscopic understanding of interfaces of aqueous solutions is essential to further energy and human development.

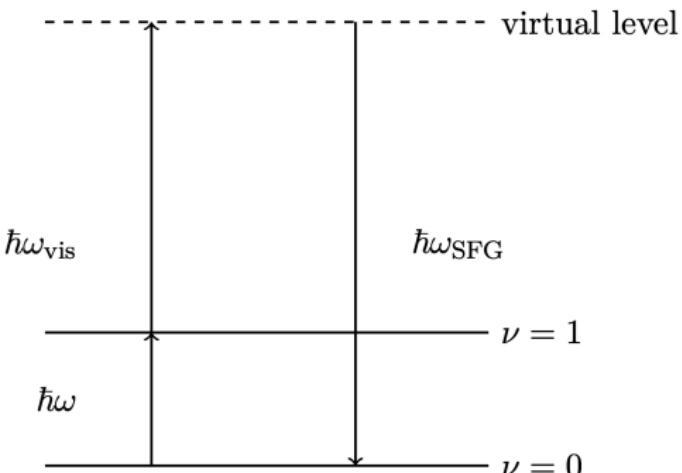
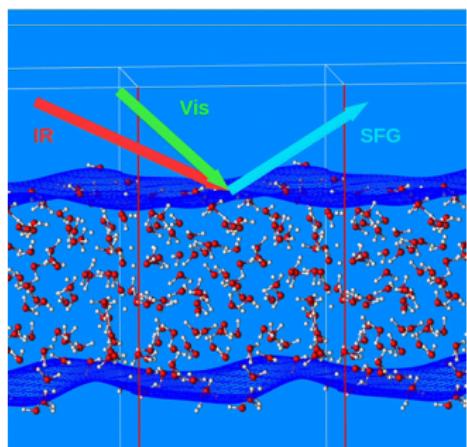


The water flow in Osmotic power plant.

- ▶ When the solution contains **larger molecular anions** such as **nitrate, sulfate and carbonate ions**, the processes occurring at the interface need to be further studied. (Gopalakrishnan et al, *J. Phys. B* **109** (2005); Jungwirth and Tobias, *Chem. Rev.*, **106**, 1259 (2006))

## Selectively probing the interface: VSFG spectroscopy

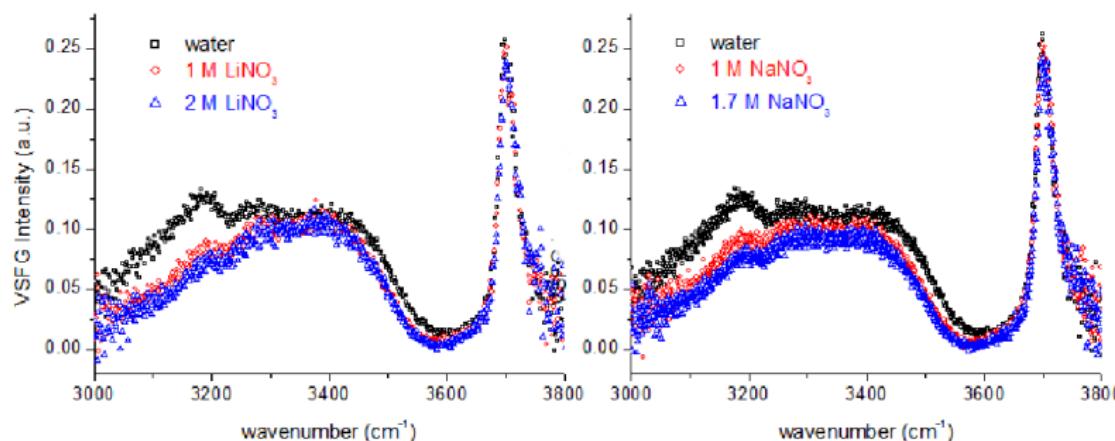
- ▶ VSFG (SFG) is used to get **vibrational information** of water molecules at the water/vapor interface (Shen, et al, *Chem. Phys. Lett.*, **133**, 189 (1987)).
- ▶ Sensitive only to regions of a material where **inversion symmetry is broken**.



VSFG process which involves IR and Raman transitions (Sulpizi, Salanne, Sprik and Gaigeot, *J. Phys. Chem. Lett.*, **83** (2013)).

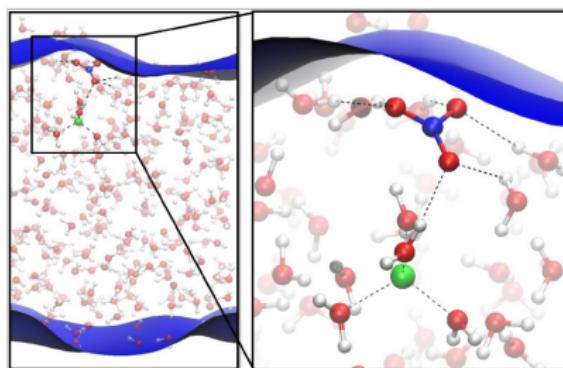
# VSFG spectra: Ions modify hydrogen bond structure at the interfaces.

The intensity spectra of nitrate solution show a **depletion of the  $3200\text{ cm}^{-1}$  region** in the experiments (Hua, Verreault and Allen, *J. Phys. Chem. C*, **118**, 24941 (2014) ).



# *ab initio* Molecular Dynamics (AIMD)

- ▶ Molecular Dynamics: **Born-Oppenheimer dynamics**;
- ▶ Exchange-Correlation functional: **BLYP**;
- ▶ Basis sets: **DZVP-MOLOPT-GTH**;
- ▶ Plane wave cut off: **280 Ry**;
- ▶ NVT ensemble ( $T = 300 \text{ K}$ );
- ▶ **Grimme correction**;
- ▶ PBC Box:  $19.7 \times 19.7 \times 40.0 \text{ (\AA}^3\text{)}$ ; Time step: 0.5 fs; Simulation time: **60 ps**.



The lithium and nitrate ions are **separated by water** and remain in this configuration stably at the interface of  $\text{LiNO}_3$  solution.

# VSFG spectra from molecular dynamics simulations

- ▶ **Intensity** of the SFG spectra is proportional to 2nd-order susceptibility's absolute value squared,  $|\chi^{(2)}(\omega)|^2$ :

$$\chi_{ssp}^{(2)}(\omega) = \frac{i\omega}{k_B T} \sum_{j=1}^{N_m} \int dt \langle A_{xx}^j(t) M_z^j(0) \rangle e^{i\omega t}. \quad (1)$$

(Morita, et al, *Phys. Chem. Chem. Phys.*, **10**, 5801 (2008))

- ▶ Assume

- (1) Bond elongation is **small**;
- (2) **Derivatives** of dipole moments/polarizability w.r.t. bond length **vary slowly**:

$$\begin{aligned} \chi_{ssp}^{(2)}(\omega) = & \frac{i\omega}{k_B T} \frac{1}{\pm\omega^2} \sum_{j=1}^{N_m} \sum_{a=1}^{N_{mode}} \left\langle \frac{\partial A_{xx}^j(0)}{\partial q_a} \right\rangle \left\langle \frac{\partial M_z^j(0)}{\partial q_a} \right\rangle \\ & \times \int e^{i\omega t} \left\langle \frac{dq_a(t)}{dt} \frac{dq_a(0)}{dt} \right\rangle. \end{aligned} \quad (2)$$

(Khatib and Sulpizi, *J. Phys. Chem. Lett.*, **8** (6), 1310 (2017))

# Vibrational density of states (VDOS)

The calculations and analysis of the Vibrational Density Of States (VDOS) permits to obtain **information on the HB strength**.

Correlation functions of atomic velocity in a system of  $N$  atoms:

$$C_{(z)}(t) = \frac{\langle \sum_{i=1}^N \vec{v}_{i(z)}(t) \cdot \vec{v}_{i(z)}(0) \rangle}{\langle \sum_{i=1}^N \vec{v}_i(0) \cdot \vec{v}_i(0) \rangle},$$

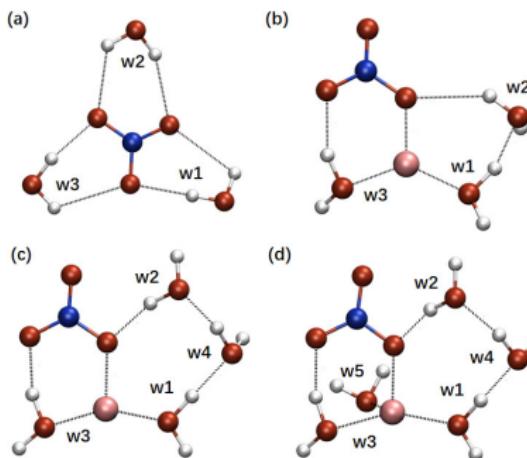
VDOS  $g(\nu)$  ( $g_z(\nu)$ ):

$$g_{(z)}(\nu) = \sqrt{\frac{2}{\pi}} \int_0^\infty dt \cos(2\pi\nu t) C_{(z)}(t).$$

1. VDOS and SEG spectra

Cluster models sufficient to explain the spectral features?

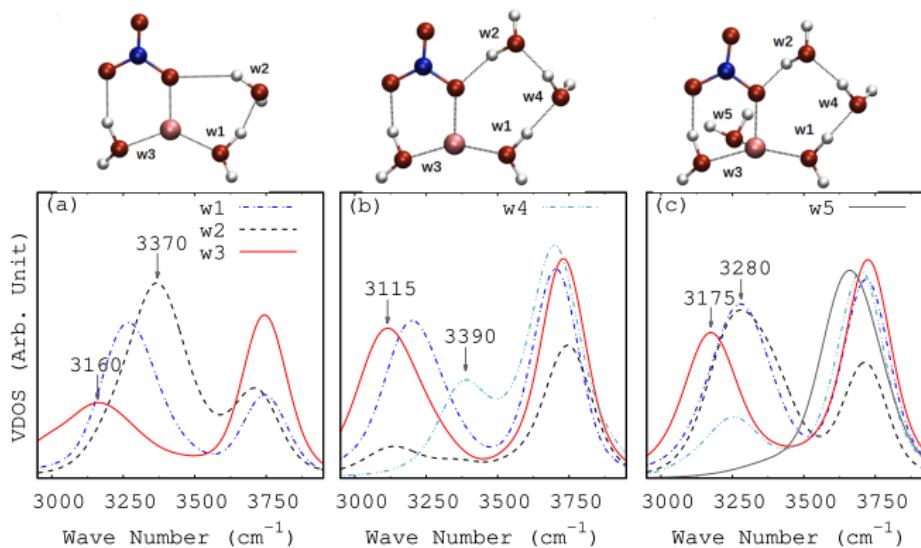
Geometry optimized clusters of water molecules with nitrate and alkali metal ions and increasing number of waters.



## 1. VDOS and SFG spectra

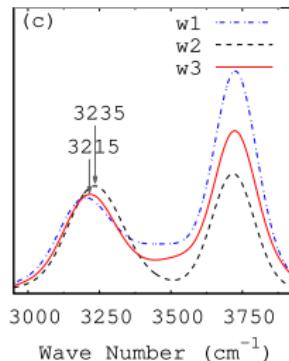
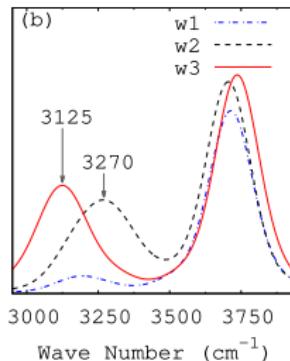
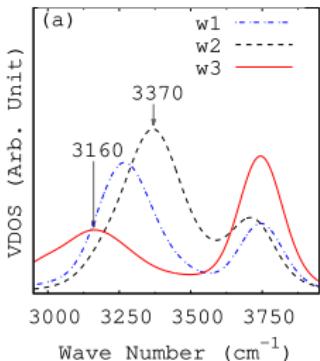
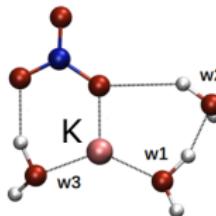
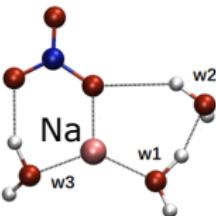
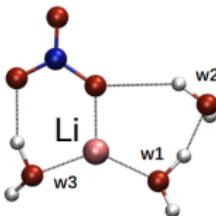
Increasing the number of waters:  $\text{LiNO}_3(\text{H}_2\text{O})_n$  ( $n = 3 - 5$ ), strong red-shift

The OH stretching peaks in the HB region is quite strong **red-shifted** around  $3200 \text{ cm}^{-1}$ . This is **not observed in the experiment!**



Specific cation effect:  $\text{RNO}_3(\text{H}_2\text{O})_3$  ( $\text{R}=\text{Li, Na, K}$ ), also quite red-shifted

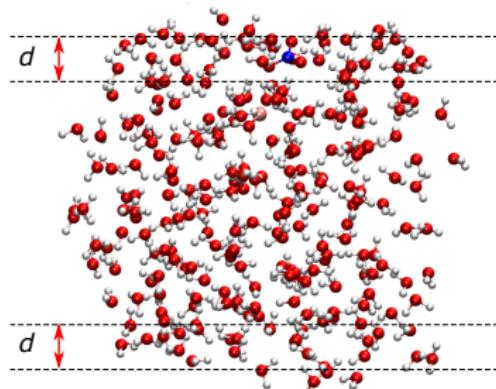
The OH stretching peaks in the HB region are also quite red-shifted. Not observed in the experiment!



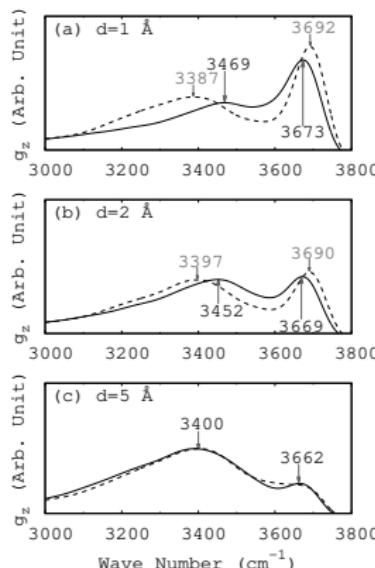
## 1. VDOS and SFG spectra

## A more complete model: the aqueous/vapor interface

**The salty interface has a blue shifted HB band.** → Aqueous/vapor interface is a better model to calculate the SFG spectra.



Definition of horizontal interface and the thickness for  $\text{LiNO}_3/\text{vapor}$  interface system by Gibbs dividing surface.

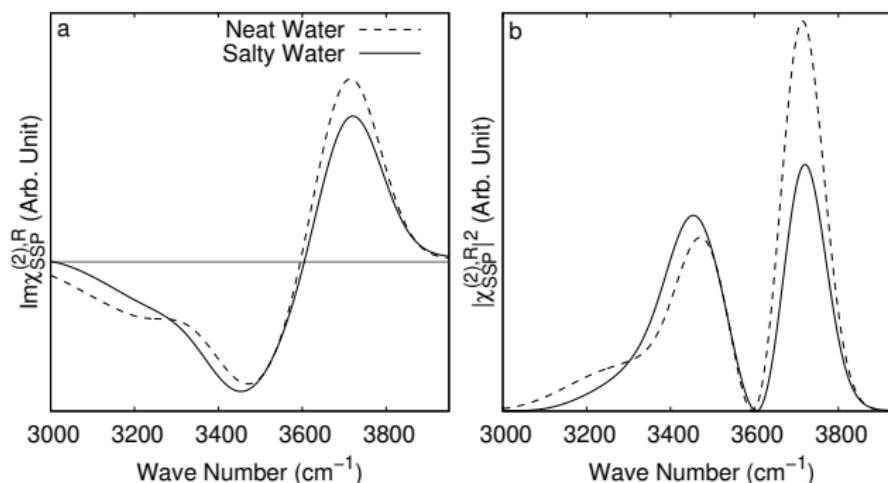


VDOS for water at  $\text{LiNO}_3$  interface (solid line) and water/vapor interface (dashed line):

## 1. VDOS and SEG spectra

Calculated SFG spectra: Consistent with experiment!

The intensity spectra show a **depletion** of the  $3200\text{ cm}^{-1}$  region as in the experiments.



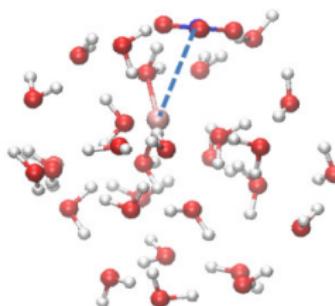
Calculated SFG intensity for LiNO<sub>3</sub> solution shows: 1. **Lower intensity** around 3200 cm<sup>-1</sup> comes from nitrate at the interface; 2. **Nitrate prefer to stay at surface.** (G. Huang, *PhD Dissertation, Johannes Gutenberg-Universität Mainz*, <http://doi.org/10.25358/openscience-6865>)

## 1. VDOS and SEG spectra

## Connecting the cluster and interface view (1)

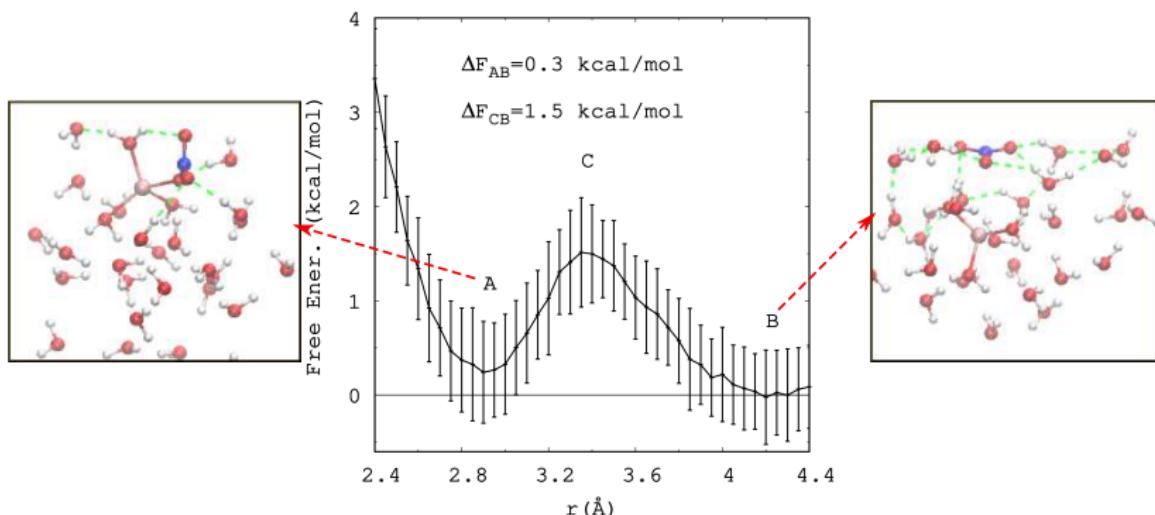
**Question: Is it possible to find a contact ion pair at the interface?**

- ▶ Use cluster  $\text{LiNO}_3(\text{H}_2\text{O})_{30}$  to model the interface with constraint MD.
  - ▶ Reaction coordinate ( $r$ ): distance  $d_{\text{Li}-\text{N}}$ .
  - ▶ Calculate free energy difference between the contact ion pair and separated ion pair at the interface.



## 1. VDOS and SFG spectra

## Connecting the cluster and interface view (2)



Free energy as a function of the reaction coordinate  $d_{\text{Li-N}}$ .

- ▶ Two minima exist for config.s A and B.
- ▶ Separated ion pair (config. B) is more stable than contact ion pair (config. A).

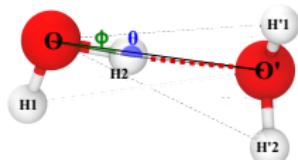
(G. Huang, *PhD Dissertation, Johannes Gutenberg-Universität Mainz*, <http://doi.org/10.25358/openscience-6865>)

### 3. HB dynamics of the interface of electrolyte solutions

Definitions of hydrogen bond (HB) and HB population

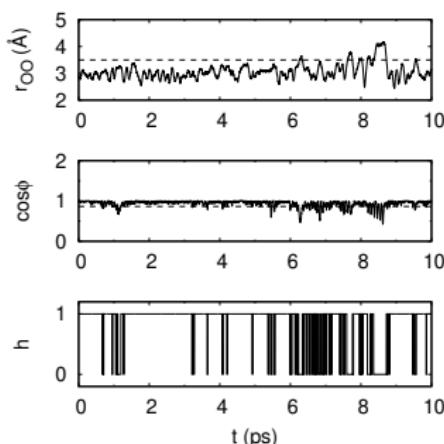
For a particular tagged pair of molecules  $i, j$ , define

$$h[r(t)] = \begin{cases} 1 & i, j \text{ are H-bonded} \\ 0 & \text{otherwise} \end{cases}$$



Hydrogen bonds. **ADH** criterion:  
 $|OO'| < 3.5 \text{ \AA}$  and the  $\text{H}_2\text{O} \cdots \text{O}'$   
angle  $\phi < 30^\circ$ ; **AHD** criterion:  
 $|OO'| < 3.5 \text{ \AA}$  and the  $\text{O}-\text{H}_2 \cdots \text{O}'$   
angle  $\theta > 120^\circ$ .

(Luzar, Chandler, *Nature*, **379**, 55 (1996))



The HB population  $h(t)$ .



## 3. HB dynamics of the interface of electrolyte solutions

Correlation functions:  $c(t)$  and  $s(t)$ 

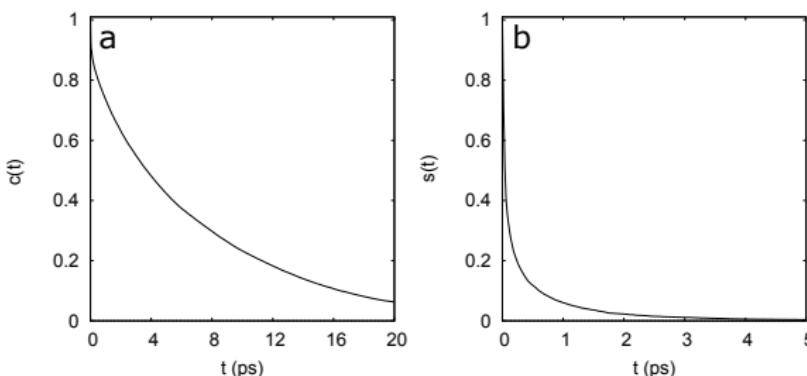
$$c(t) = \langle h(0)h(t) \rangle / \langle h \rangle,$$

$$s(t) = \langle h(0)H(t) \rangle / \langle h \rangle.$$

$\langle \dots \rangle$ : an average over all molecular pairs,

$$H(t) = \begin{cases} 1 & i, j \text{ are continuously H-bonded in time interval } [0, t], \\ 0 & \text{otherwise.} \end{cases}$$

(Luzar, *J. Chem. Phys.* **113**, 10663 (2000))



Calculated  $c(t)$  and  $s(t)$  for bulk water.

### 3. HB dynamics of the interface of electrolyte solutions

## Correlation functions: $k(t)$

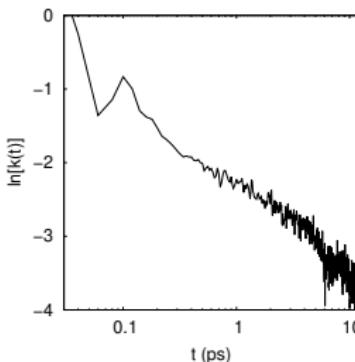
- Reactive flux  $k(t)$ .

$$k(t) = -\frac{dc(t)}{dt}; n(t) = \langle h(0)[1 - h(t)]h^{(d)}(t) \rangle / \langle h \rangle;$$

$$k(t) = kc(t) - k'n(t) \xrightarrow[\text{fit}]{\text{least squares}} k \text{ and } k'$$

$$h^{(d)}(t) = \begin{cases} 1 & \text{O-O distace of molecules } i,j \text{ is less than } R = 3.5 \text{ \AA} \\ 0 & \text{otherwise} \end{cases}$$

$k$  and  $k'$  are the forward and backward rate constants. (Luzar, *J. Chem. Phys.* **113**, 10663 (2000); Khaliullin and Kühne, *Phys. Chem. Chem. Phys.*, **15**, 15746 (2013))



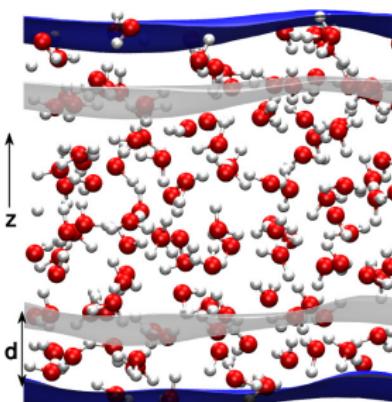
## 3. HB dynamics of the interface of electrolyte solutions

## Definition of instantaneous interfaces

The density at  $(\mathbf{r}, t)$ :

$$\bar{\rho}(\mathbf{r}, t) = \sum_i \phi(|\mathbf{r} - \mathbf{r}_i(t)|; \xi), \quad \phi(\mathbf{r}; \xi) = (2\pi\xi^2)^{-3/2} \exp(-r^2/2\xi^2),$$

$\phi(\mathbf{r}; \xi)$  is a normalized **Gaussian function**.  $\bar{\rho}(\mathbf{r}, t) = \rho_c$  defines the **instantaneous interface**,  $\rho_c$  is a reference density.

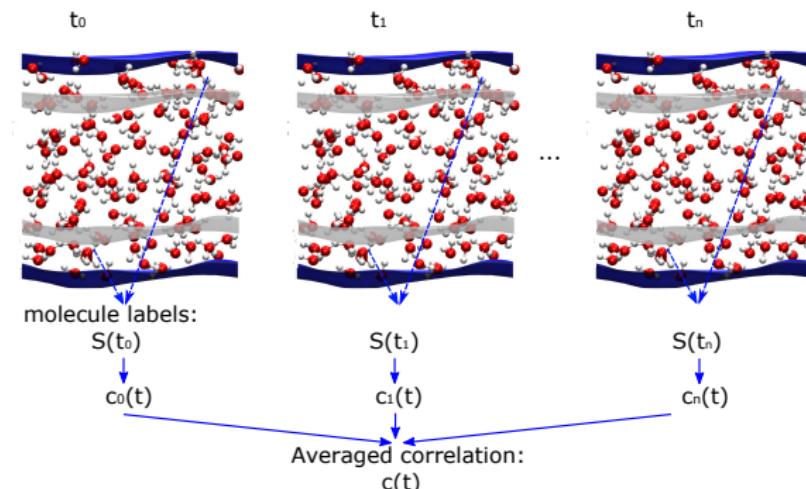


A slab of water with the instantaneous interface represented as a blue mesh on the upper and lower boundary.

## 3. HB dynamics of the interface of electrolyte solutions

## Extracting interfacial bonds (1): Interfacial Molecule Sampling (IMS)

The **first method** to extract interfacial HB dynamics: Directly sampling. (**Slower** than the real interfacial HB dynamics.)



- (1) Define interfacial layers with thickness  $d$ ;
- (2) Identify molecules in these layers, for sampling time  $t_0, \dots, t_n$ ;
- (3) Calculate functions  $c_i(t)$  of those molecules;
- (4) Average:  $c(t) = \sum_{i=1}^n c_i(t)/n$ .



## 3. HB dynamics of the interface of electrolyte solutions

## Extracting interfacial bonds (2): Interfacial HB population

The **second method** to extract the interfacial HB dynamics.

- ▶ Define **IHB population**

$$h^{(s)}[r(t)] = \begin{cases} 1 & i, j \text{ are H-bonded, and} \\ & i, j \text{ are inside the interfacial layer} \\ 0 & \text{otherwise} \end{cases}$$

Then, define functions

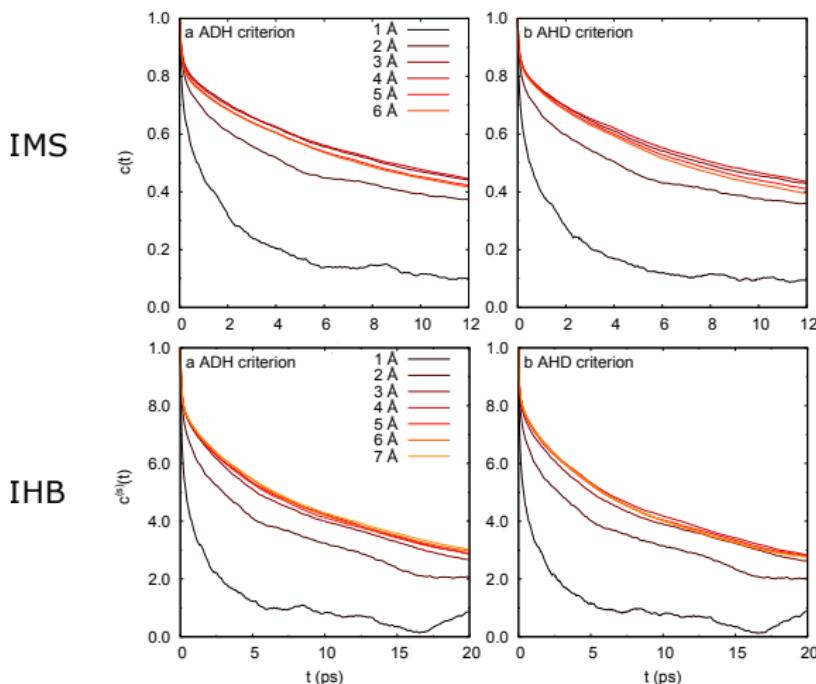
$$\begin{aligned} c^{(s)}(t) &= \langle h^{(s)}(0)h^{(s)}(t) \rangle / \langle h^{(s)} \rangle \\ n^{(s)}(t) &= \langle h^{(s)}(0)[1 - h^{(s)}(t)]h^{(d,s)} \rangle / \langle h^{(s)} \rangle \\ k^{(s)}(t) &= -\frac{dc^{(s)}(t)}{dt} \end{aligned}$$

**Difference from the IMS method:** IHB dynamics are **faster than the real interfacial HB dynamics.** (G. Huang, J. Huang, arXiv:2204.13941, <https://arxiv.org/abs/2204.13941>)



## 3. HB dynamics of the interface of electrolyte solutions

Both correlation functions ( $c(t)$ ,  $c^{(s)}(t)$ ) converge as  $d$  is larger than 4 Å.

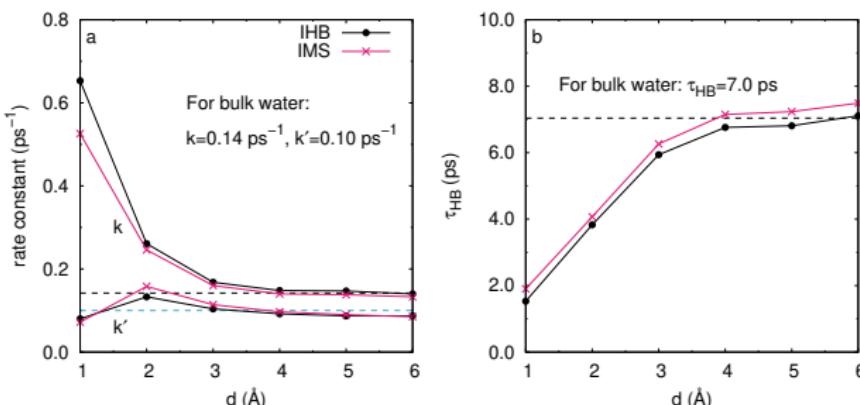


$c(t)$  ( $c^{(s)}(t)$ ) for instantaneous interfacial H-bonds with different thicknesses.

### 3. HB dynamics of the interface of electrolyte solutions

Thickness of the water/vapor interface is 4 Å.

As  $d$  increases, values of  $k$  and  $k'$  converge to bulk values. → Thickness of the water/vapor interface is 4 Å.



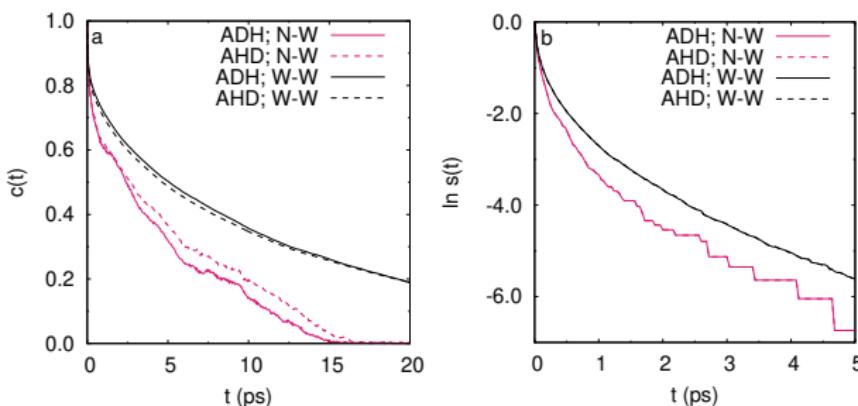
(a) Reaction rate constants  $k$  and  $k'$  and (b) the HB lifetime  $\tau_{\text{HB}} = 1/k$ , obtained by the IHB and the IMS method, respectively.

(G. Huang, J. Huang, arXiv:2204.13941, <https://arxiv.org/abs/2204.13941>)

## 3. HB dynamics of the interface of electrolyte solutions

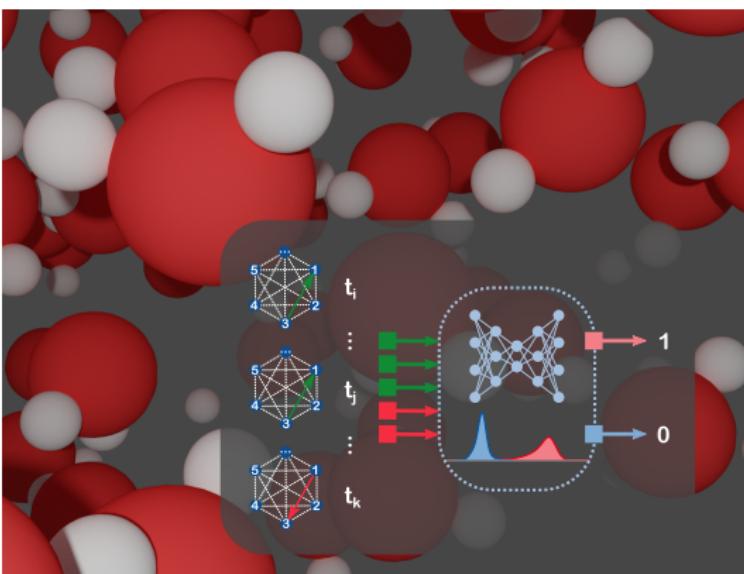
$c(t)$  and  $s(t)$ :  $\text{NO}_3^-$ -water bonds are weaker than water-water bonds!

$c(t)$  and  $s(t)$  of **nitrate–water** (N-W) bonds decay **faster** than that of **water–water** (W-W) bonds (nitrate–water bonds are **weaker** than water–water bonds).



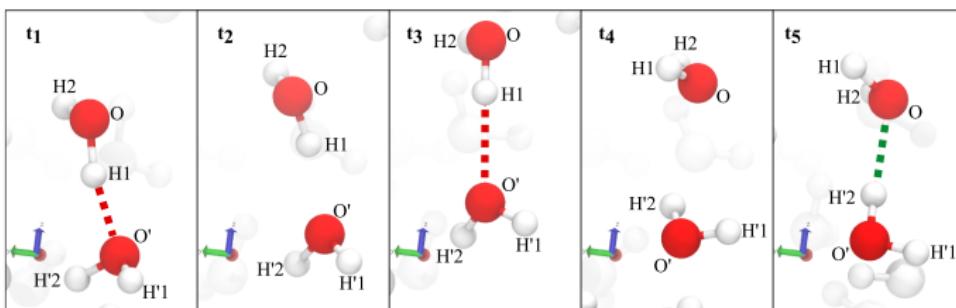
(a)  $c(t)$  and (b)  $\ln s(t)$  of all W-W and N-W bonds for the slab of LiNO<sub>3</sub> solution.

# A machine learning model to classify dynamic processes in liquid water.



(J. Huang, G. Huang, S. B. Li, *ChemPhysChem*, (2022), 23, e202100599 (Front cover))

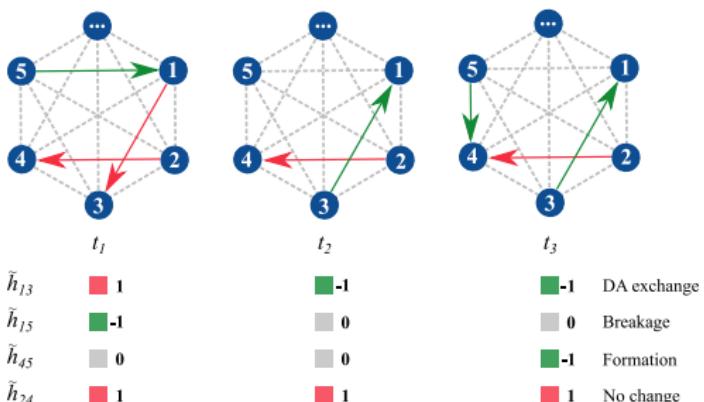
# Donor-Acceptor exchange processes in water



A typical interchange process, where two water molecules exchange their roles as H-bond donor and acceptor via water molecules' reorientation in an concerted manner.

(J. Huang, G. Huang, S. B. Li, *ChemPhysChem* 2022, **23**, e202100599)

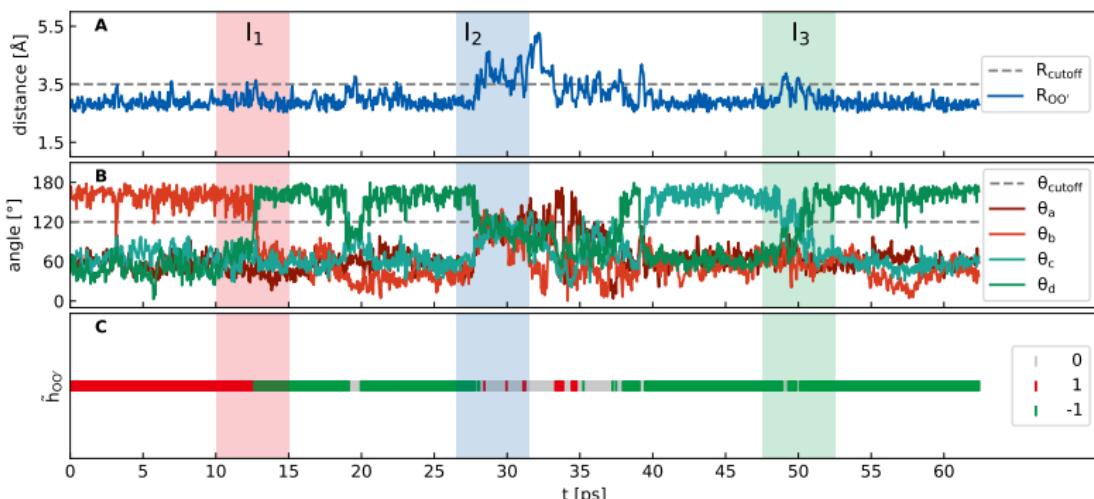
# Dynamic graph representation of H-bond networks



**Dynamic graph representation** of the H-bond network in simulated bulk water. Nodes represent **water molecules**; solid red or green arrows represent **H-bonds**. The colors **red**, **grey**, and **green** indicate  $\tilde{h}_{ij}=1$ ,  $\tilde{h}_{ij}=0$ , and  $\tilde{h}_{ij}=-1$ , respectively.

$$\tilde{h}_{ij}(t) = \begin{cases} 1 & \text{H-bonded, } i \text{ is the donor} \\ 0 & \text{Not H-bonded} \\ -1 & \text{H-bonded, } j \text{ is the donor} \end{cases}$$

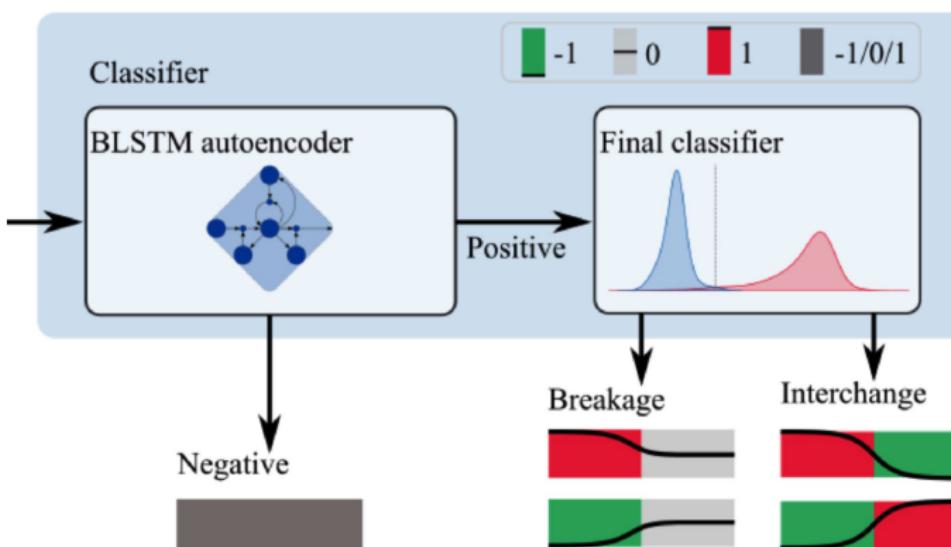
## H-bond configuration change processes



**DA exchange ( $I_1$ ), diffusion ( $I_2$ ), and HH exchange ( $I_3$ ) process for one typical Q-bond in bulk water.**

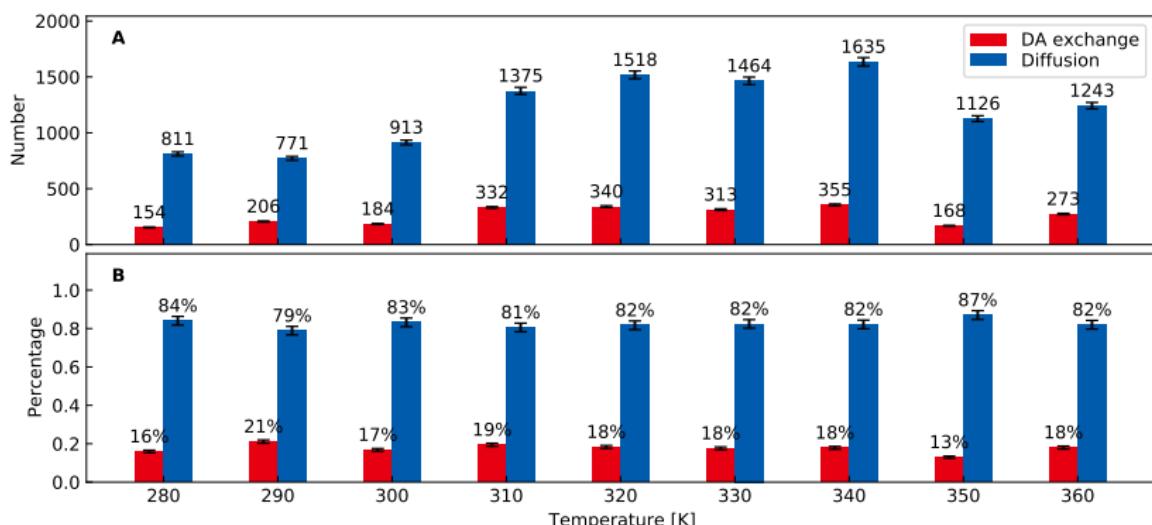
(J. Huang, G. Huang, S. B. Li, *ChemPhysChem* 2022, **23**, e202100599)

# To classify the dynamical processes!



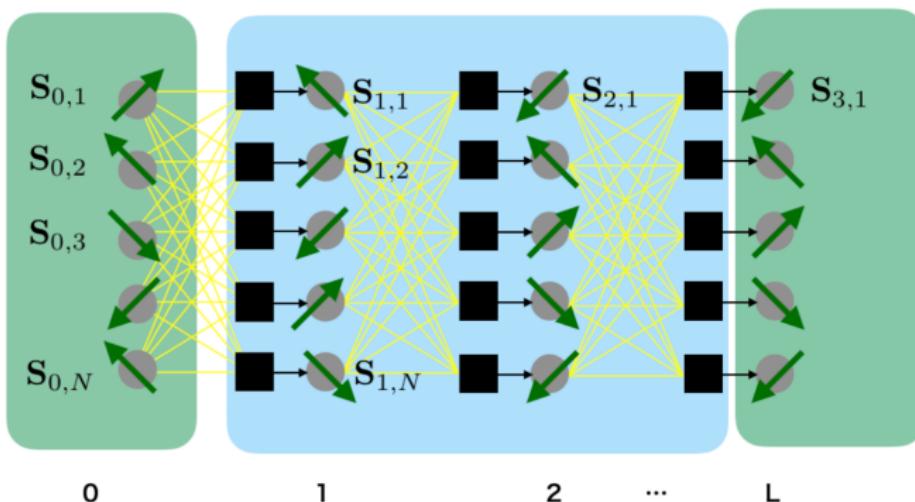
The classifier includes a **BLSTM auto encoder** to separate the positive and negative sequences and a **final classifier** to distinguish DA exchange and breakage processes.

## Proportions of DA exchange



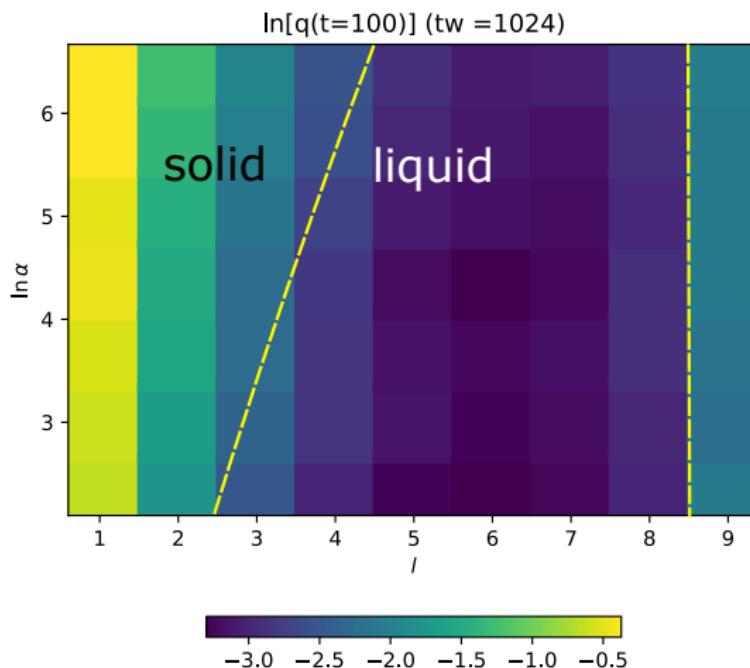
The **number** (A) and **proportion** (B) of DA exchange and diffusion processes determined by the RNN-based classifier at different temperatures. The **relative ratio** (0.25) of DA exchange to diffusion basically does not depend on temperature.

## A $L$ -layer Neural Network (NN).



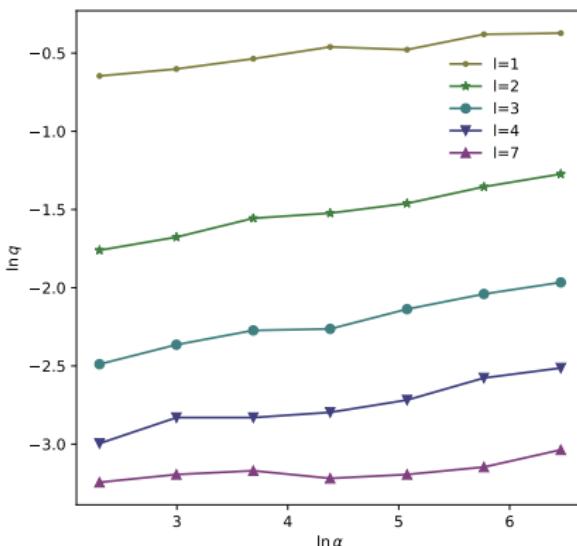
A  $L$ -layer NN. Totally  $L + 1$  layers. ( $L = 10$ )  $l = 0$  denotes input layer;  $l = L$  denotes the output layer.(H. Yoshino, SciPost Phys. Core 2, 005 (2020) )

# $\ln q(\ln \alpha, l)$



Similarity between **two DNN's nodes' states**, for the training process of DNN on the **MNIST dataset**. The two DNN have the same structure and the same initial condition.

# $\ln q(\ln \alpha)$



Similarity between **two DNN's nodes' states**, for the training process of DNN on the **MNIST dataset**. The two DNN have the same structure and the same initial condition.

## Conclusions

- ▶ The experimental spectra (**lower intensity for bonded OH stretch**) can be explained by the calculations. The **lower intensity** is due to the presence of a **water separated ion pair** where the nitrate resides on the surfaces and the alkali cation is in the subsequent layer.
- ▶ **Thickness** of the water/vapor interface: **4 Å**.
- ▶ Based on **instantaneous interface**, combination of IHB and IMS provide a basis for determining the **thickness** of interface layer.
- ▶ The **relative ratio** of DA exchange to diffusion basically is about **0.25** and it does **not depend on temperature**.

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Outline



Introduction



Methods



Results



Classify dynamic processes in water



DNN training dynamics



Conclusions



# THANK YOU!