Structure, dynamics, and vibrational spectroscopy of acidic solutions

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Date- 21/10/2021

Why It is Important?

Chemistry	• Acid-base chemistry • Enzyme catalysis
Materials Science	• Fuel cells and batteries • Proton exchange membranes

Challenges of Proton Solvation and Transport

Model

Describes the continuously changing network of covalent and hydrogen-bonded water molecules surrounding the hydrated protons.

Excess proton

Traditional force fields

Not reactive

Lack the ability to describe formation and cleavage of chemical bonds

• Different solvation structures

• Dynamics and electrical charge defects

• Electron hole (missing electron)

3

Proton Transfer Mechanism in Hydrogen Bonded Network

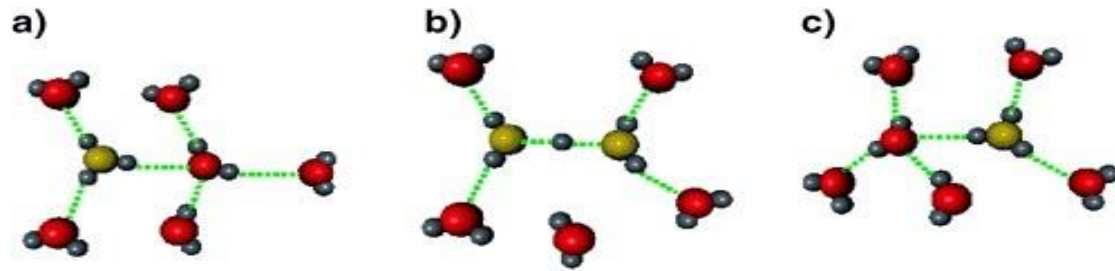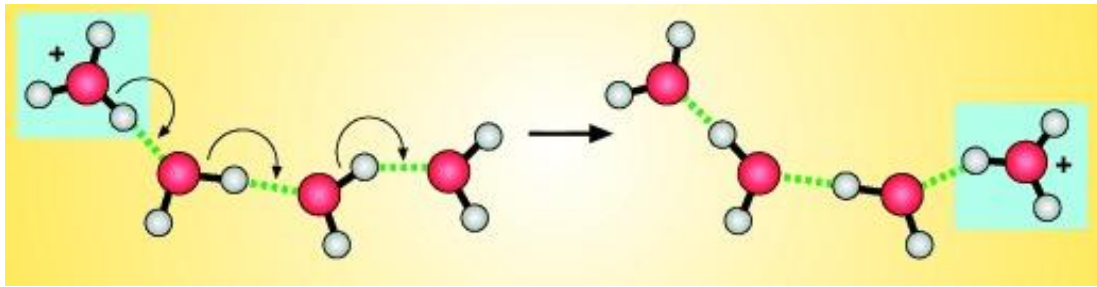**Grotthuss Mechanism (200 years old)**

Fig: Structural diffusion of H$^+$

- Structural diffusion

- Proton hoping

- Proton Transfer : Through Hydrogen bonded network

- Successive covalent O-H bonds breaking and forming

1. Grotthuss, C. J. T. d. *Ann. Chim. (Paris)* **1806,** 58, 54–74.
2. Marx, D. *Chem. Phys. Chem.* **2006**, 7(9), 1848-1870.

Pre-Solvation Concept

- Mechanism of structural diffusion during the proton transfer step.

- In the proton transfer step for aqueous solution :
- The solvation structure of protonic defect (H_3O^+) and water molecule accepting the excess proton must have similar solvation patterns during the proton transfer step.
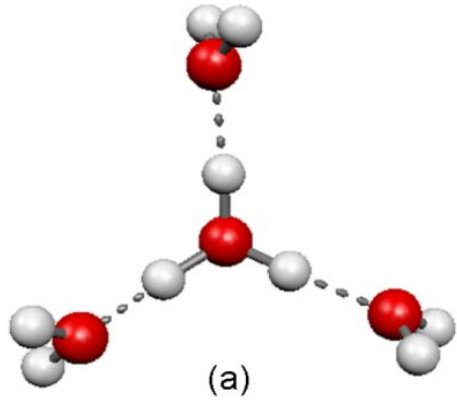
Species receiving the proton is to be solvated like the species it will become.
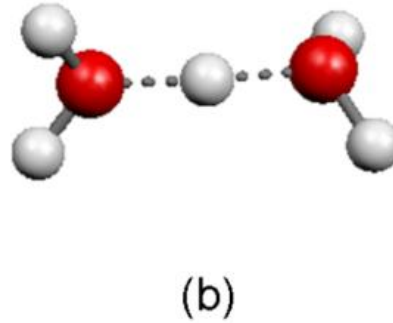
Solvent molecules

Hydronium ion

Marx, D. *Chem. Phys. Chem.* **2006**, *7*(9), 1848-1870.

Proton Transfer in Liquid Water

Excess proton is hydrated as :

Mismatch of coordination number of water and the hydronium ion!

(a)

(b)

3 coordinated (Eigen complex)

2 coordinated (Zundel complex)

- Hydronium ion coordination number cannot be 4 since it does not accept any hydrogen bond.

- Bulk water molecules prefer tetrahedral coordination shell.

Agmon, N.; Bakker, H.J.; Campen, R.K.; Henchman, R.H.; Pohl, P.; Roke, S.; Thämer, M.; Hassanali, A. *Chemical reviews.* **2016**, *116*(13), 7642-7672.

Special Pair Formation and Proton Transfer

H$_2$O molecule

- In the first solvation shell:

  4 coordinated water $\rightarrow$ 3 coordinated water

- Special pair formation
- Proton Transfer
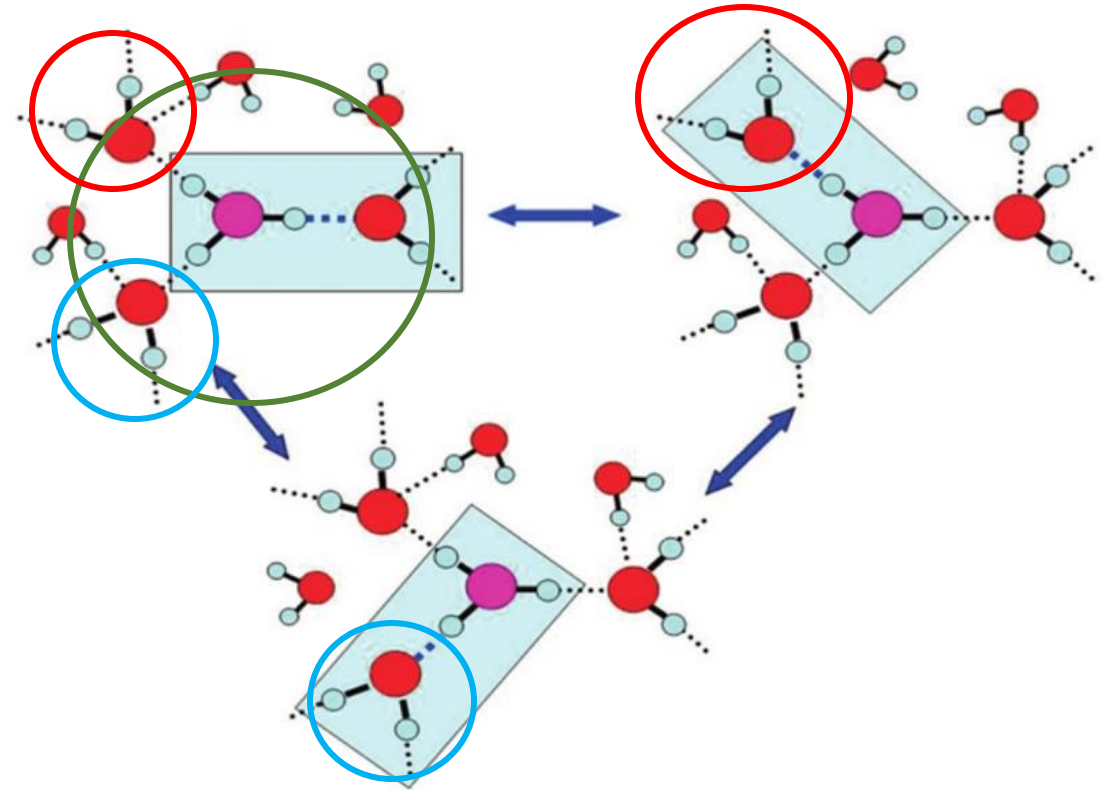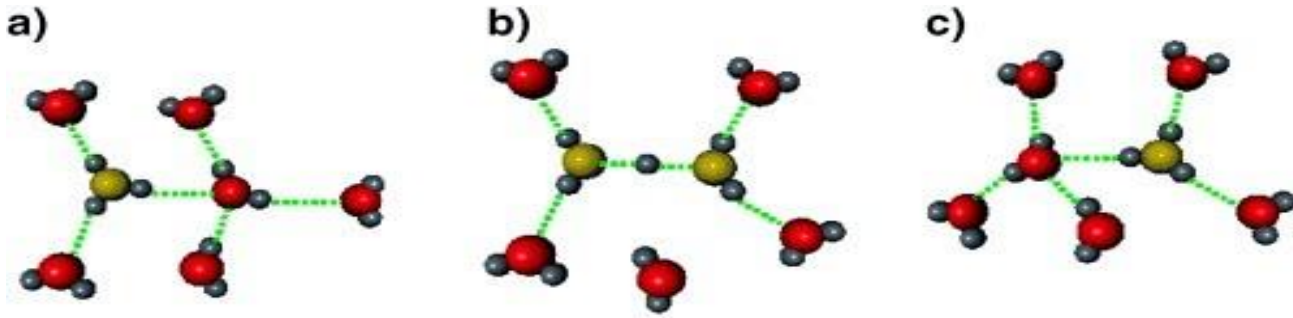
Breaking of H-bond between the 1st and the 2nd solvation shell leads to a picture where water in a coordination pattern similar to that of H$_3$O$^+$(H$_2$O)$_3$ cation.

1. Marx, D. *Chem. Phys. Chem.* **2006**, *7*(9), 1848-1870.
2. Agmon, N.; Bakker, H.J.; Campen, R.K.; Henchman, R.H.; Pohl, P.; Roke, S.; Thämer, M.; Hassanali, A. *Chemical reviews.* **2016,** *116*(13), 7642-7672.

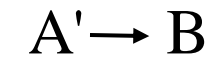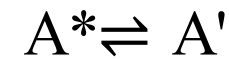# Population Correlation Function : Theory of Proton Transfer Kinetics

>>Theory connects particular defect's solvation structure and microscopic PT mechanism to macroscopic charge transport kinetics.

- Proton Transfer Correlation Function:

$$C_i(t) = \frac{\langle h(0)h(t)\rangle}{\langle h \rangle} \qquad C_c(t) = \frac{\langle h(0)H(t)\rangle}{\langle h \rangle}$$

$$A\text{–}H\cdots A$$

$$A^* \rightleftharpoons A'$$

$$A' \rightarrow B$$

- A = O atom of H_2O
- A^* = Cationic defects

- Where ,

h(t) = 1 ,	A is A^* at time t
= 0 ,	Otherwise
H(t) = 1 ,	A^* retain its identity

C_i and C_c computed directly from MD trajectories

1. Tuckerman, M. E.; Chandra, A.; Marx, D. *J. Chem. Phys.* **2010**, 133, 124108.
2. Chandra, A.; Tuckerman, M. E.; Marx, D. *Phys. Rev. Lett.* **2007**, 99, 145901.

Average time needed for PT from A* to the 1st solvation shell:
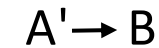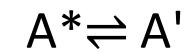
$$\tau_{exch} = \int_0^\infty C_c(t)\,dt$$

Decay of C_i depends on PT rate and reverse process

To disentangle the coupled forward and backward kinetics:

Nearest Neighbour PT correlation function

$$C_{nn}(t) = \frac{\langle h(0)g(t)\rangle}{\langle h \rangle}$$

Tuckerman, M. E.; Chandra, A.; Marx, D. *J. Chem. Phys.* **2010**, 133, 124108.

$$A* \rightleftharpoons A'$$
$$A' \rightarrow B$$

- A' = 1st solvation shell sites

$$\frac{d}{dt}[A^*](t) = -k_1^{PT}[A^*](t) + k_{-1}^{PT}[A'](t)$$

$$\frac{d}{dt}C_i(t) = -k_1^{PT}C_i(t) + k_{-1}^{PT}C_{nn}(t)$$

$$\frac{d}{dt}[A'](t) = -(k_2 + k_{-1}^{PT})[A'](t) + k_1^{PT}[A^*](t)$$

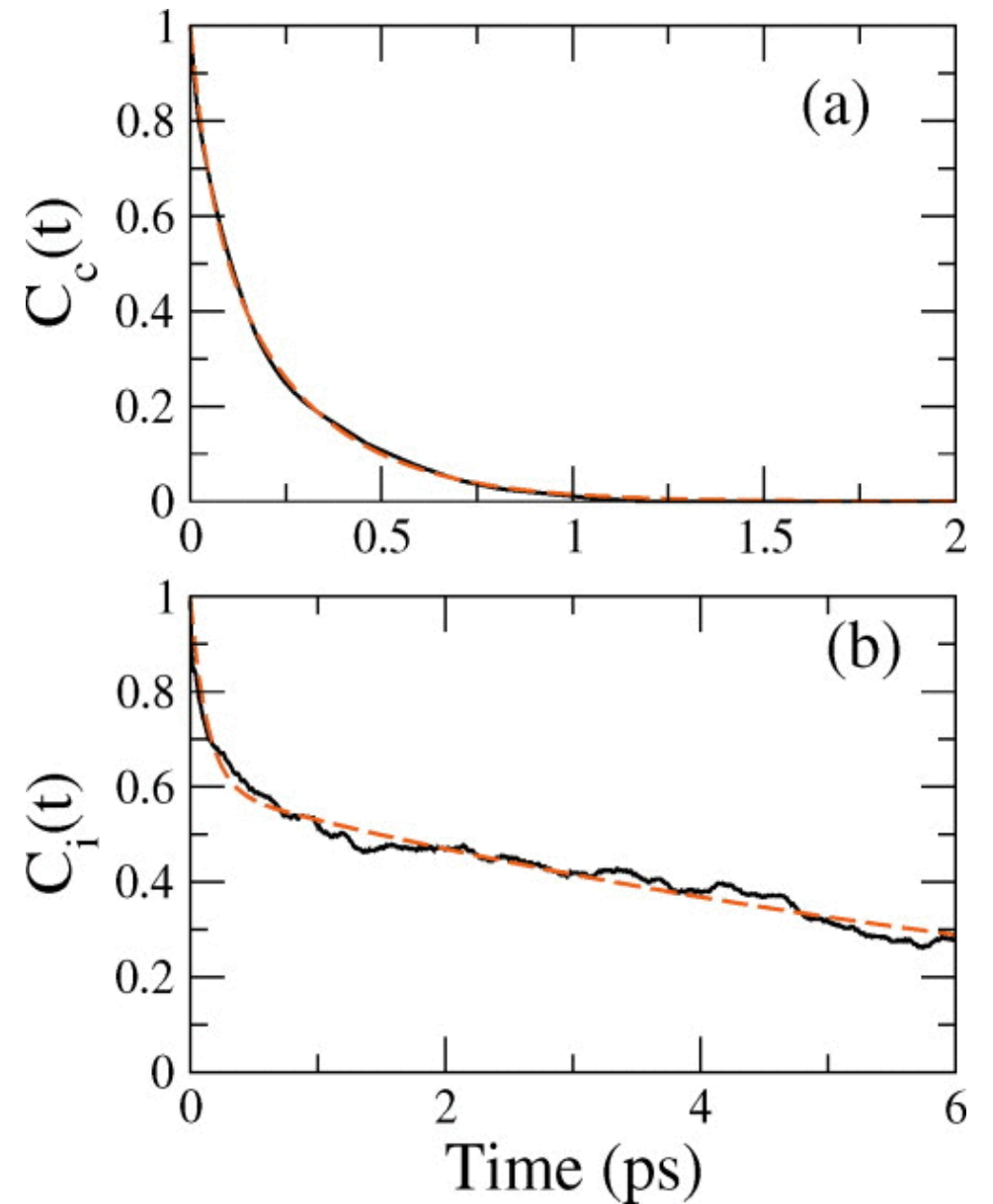$$\frac{d}{dt}C_{nn}(t) = -(k_2 + k_{-1}^{PT})C_{nn}(t) + k_1^{PT}C_i(t)$$

$$C_i(t) = a_0 e^{-a_1 t} + (1 - a_0) e^{-a_2 t}$$

$$k_1^{PT} = a_1 a_2 + a_2 (1 - a_0)$$

$$k_{-1}^{PT} = \frac{(a_1 - a_2)^2 \, a_0 (1 - a_0)}{a_0 a_1 + a_2 (1 - a_1)}$$

$$k_2^{PT} = \frac{a_1 a_2}{a_1 a_0 + a_2 (1 - a_0)}$$

Proton rattling: Defect (Hydronium ion) returns to original site A* after two successive PTs

Tuckerman, M. E.; Chandra, A.; Marx, D. *J. Chem. Phys.* **2010**, 133, 124108.

Proton Solvation and Transport

Methods and Techniques

- *Ab-initio* Molecular Dynamics
- Population correlation functions
- Two-Dimensional Infrared (2DIR) Spectroscopy.
- Vibrational Sum Frequency Generation (VSFG) Spectroscopy.

Proton (H$^+$)
- Solvation pattern
- Proton transfer Kinetics
- Hydrogen-bond dynamics

2D IR Spectroscopy as a Probe

Linear IR Spectroscopy

- More the degrees of freedom more complex the spectra
- Measures the intrinsic vibrations of the molecule
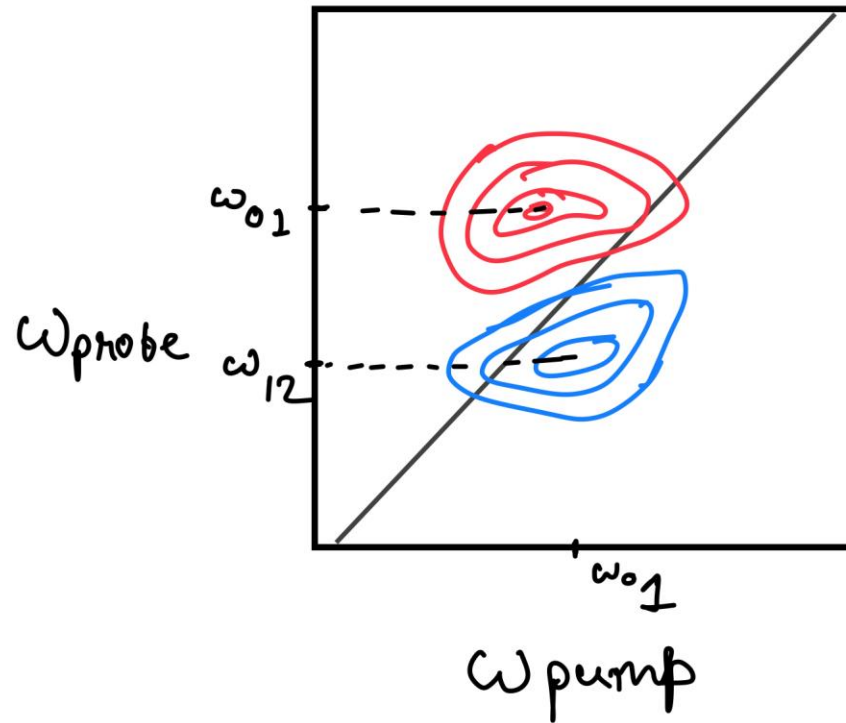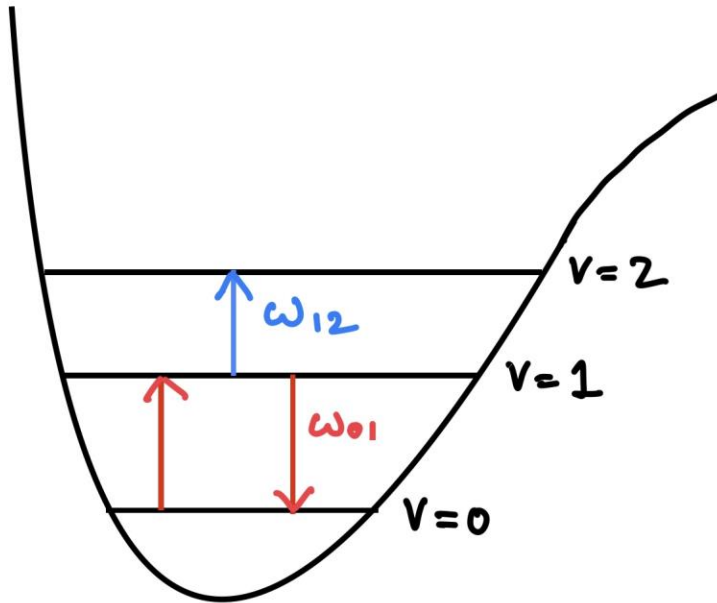- Unable to capture dynamics in aqueous solutions

2D IR spectroscopy

- Resolves the broad spectrum
- Captures dynamical information
- Defeats inhomogenous broadening
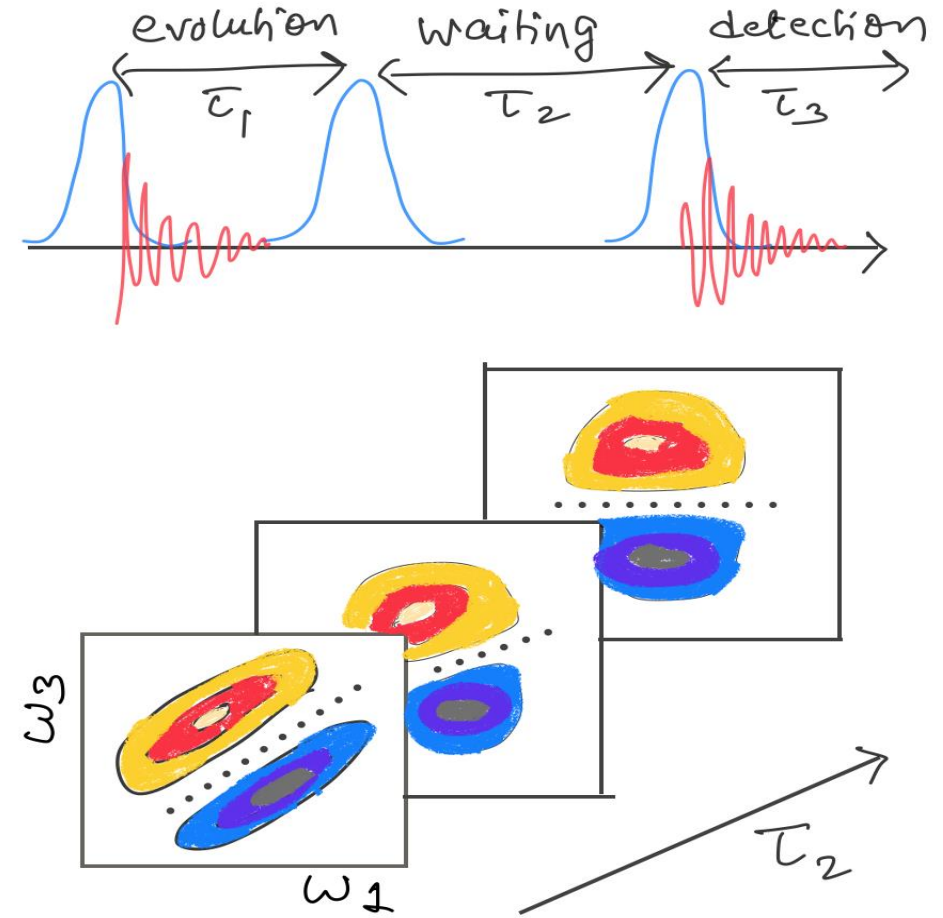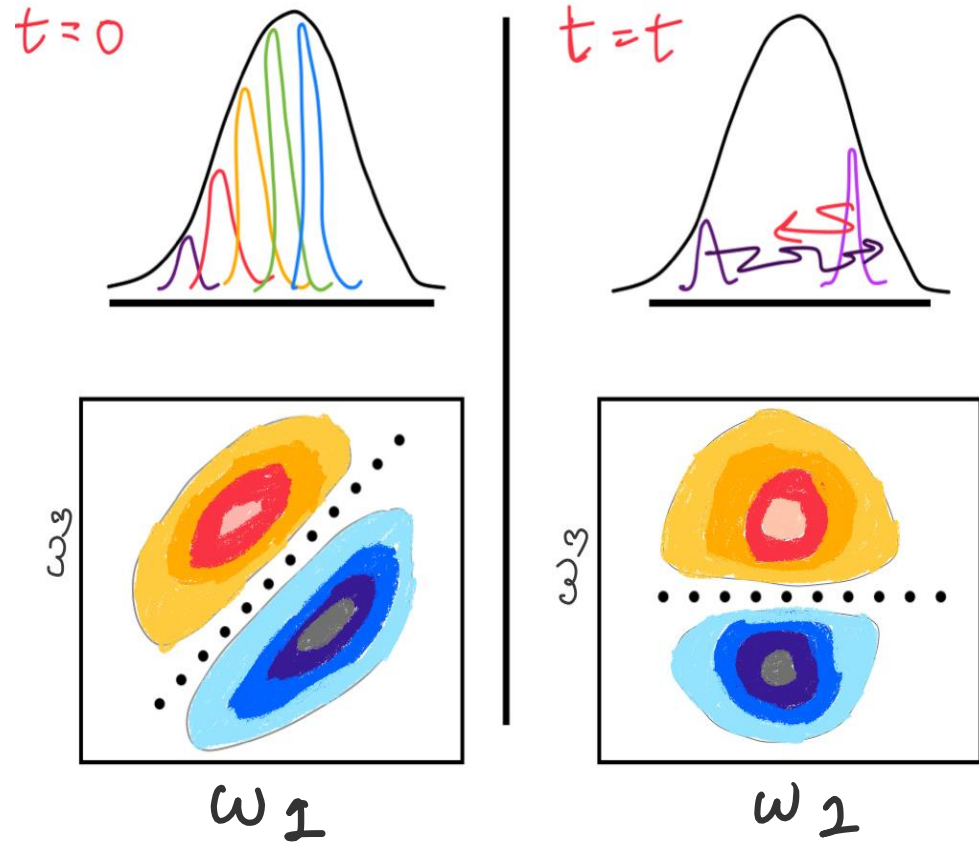- Spectral correlations
  >> Coupling, exchange.
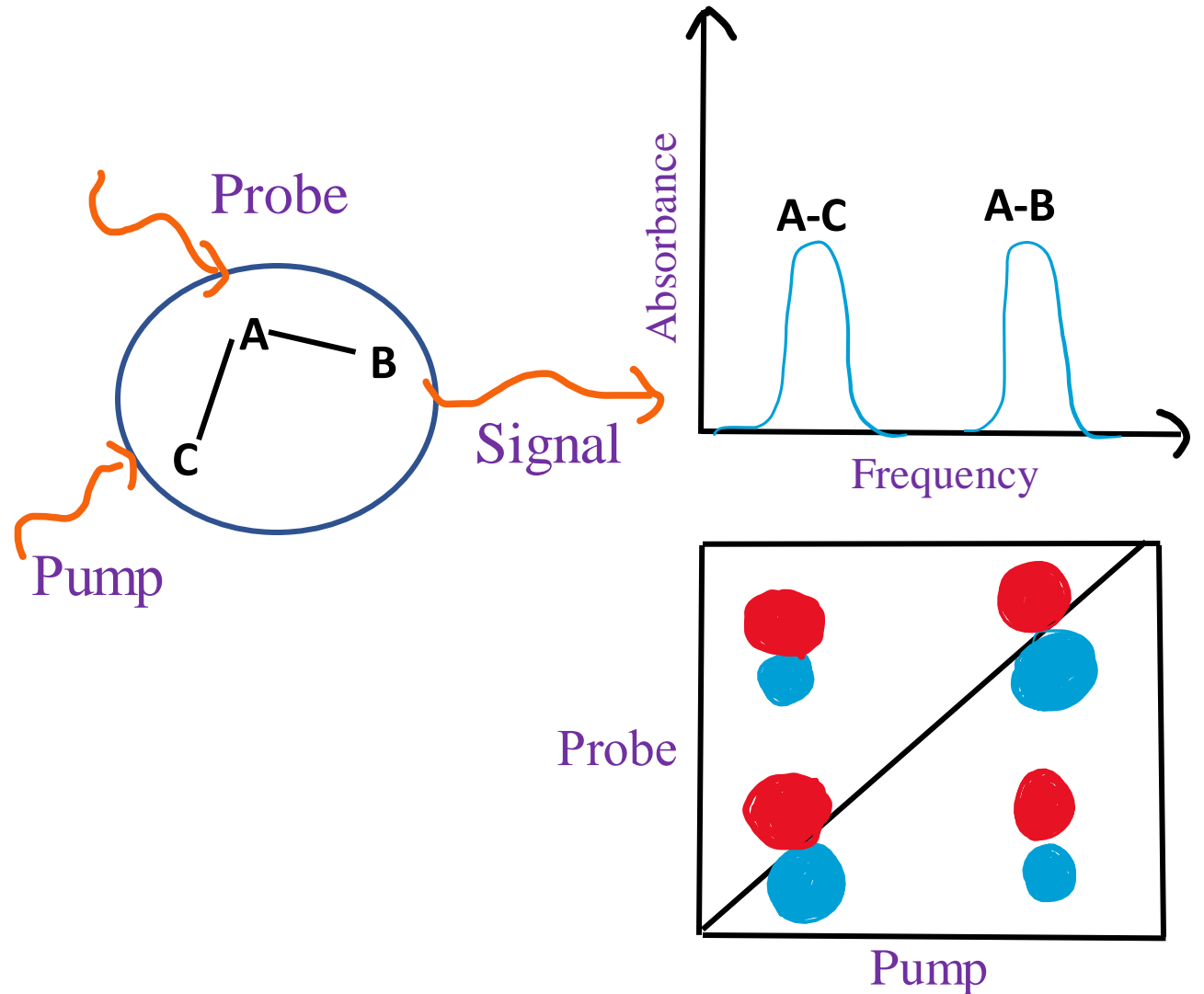
2D IR Spectroscopy as a Probe
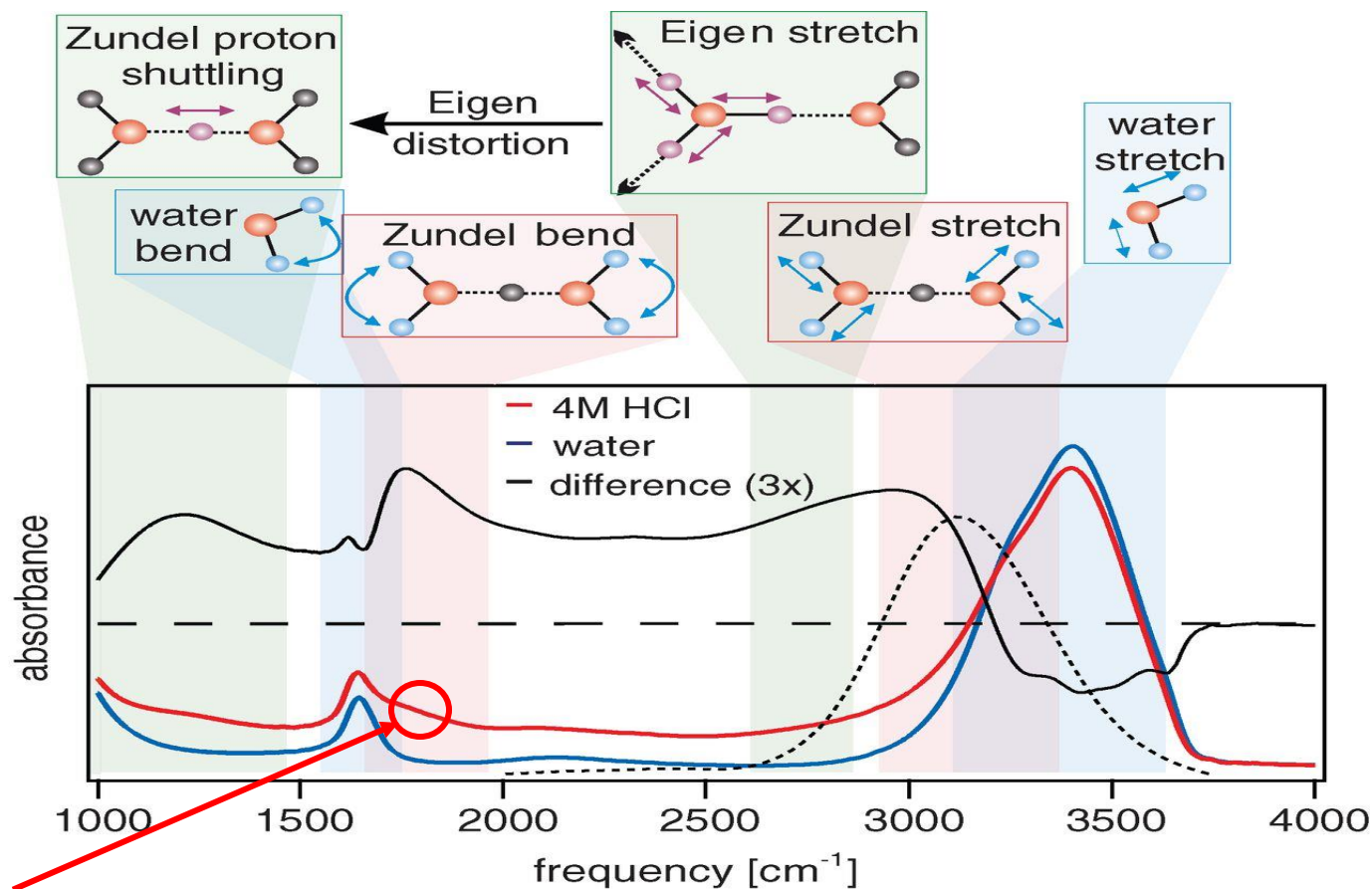
Pictorial representation

- ω_{01} (emission and ground-state bleach)
- ω_{12} (Excited-state absorption)
- Bleach and emission in red
- Excited-state absorption in blue

Spectral Diffusion

IR Spectroscopy Of Excess Proton

- Characteristic frequency beneath the overlapping spectra of solvated proton.

Fig: Linear IR spectra for water and 4 M HCl

- Shoulder at 1760 cm^{-1}

Thämer, M.; De Marco, L.; Ramasesha, K.; Mandal, A.; Tokmakoff, A. Science 2015, 350, 78−82.

2D IR Spectroscopy Of Excess Proton

- The appearance of stretch bend cross peak at 1760 cm^{-1}

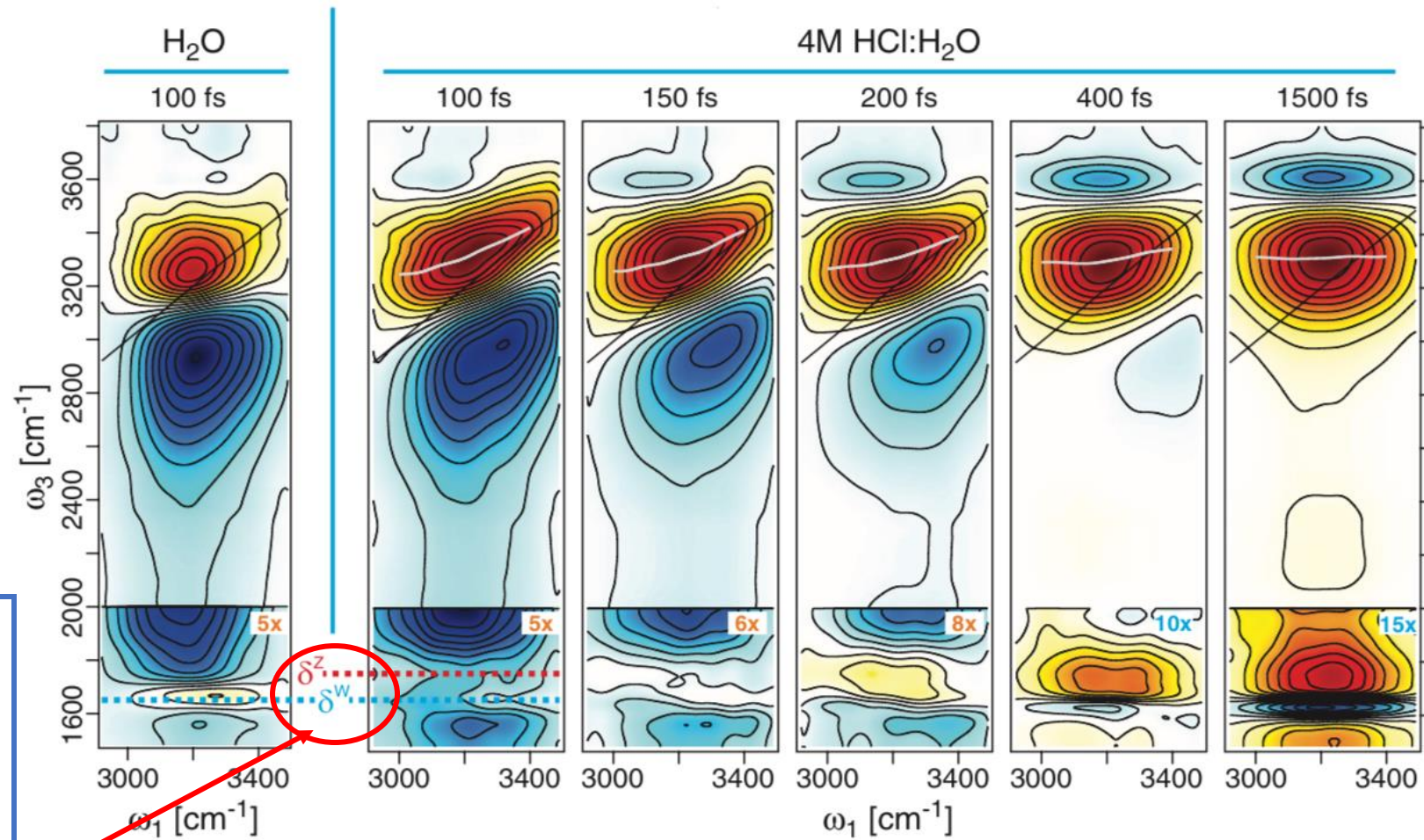Frequencies corresponding to Zundel complex bend and H$_2$O bend

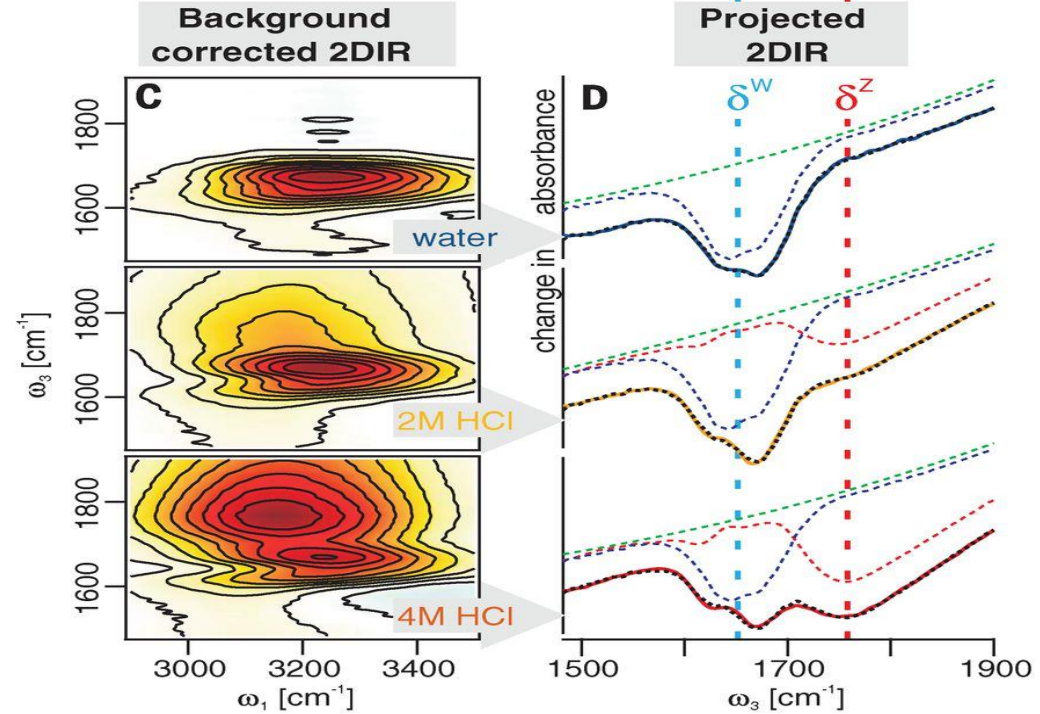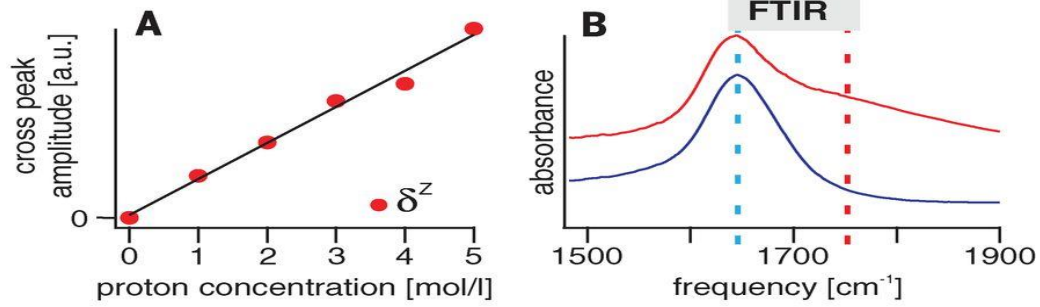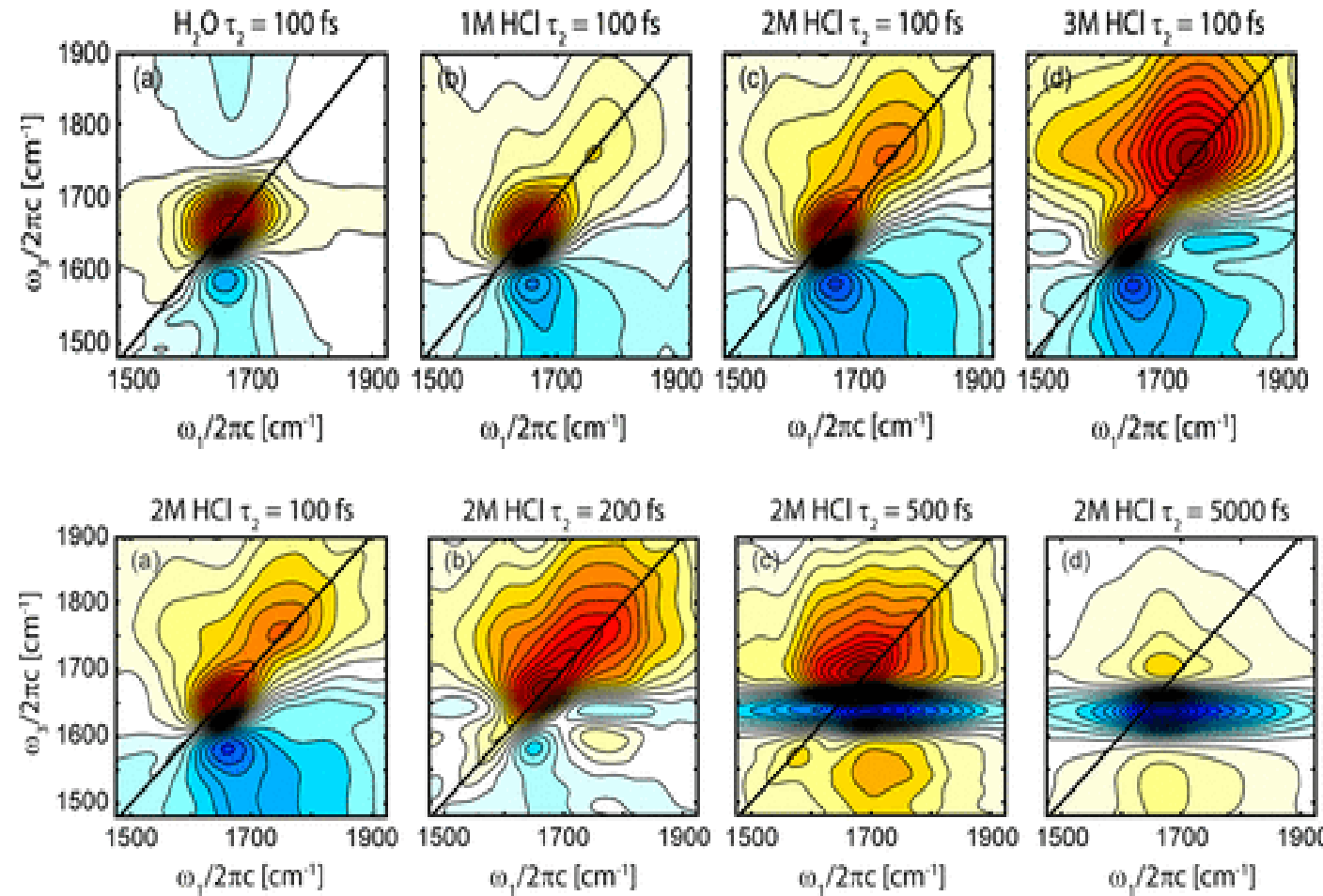Fig: 2D IR spectra of 4M HCl:H$_2$O as a function of waiting time.

Thämer, M.; De Marco, L.; Ramasesha, K.; Mandal, A.; Tokmakoff, A. Science 2015, 350, 78−82.

(1)

(2)

Thämer, M.; De Marco, L.; Ramasesha, K.; Mandal, A.; Tokmakoff, A. *Science* 2015, 350, 78−82.

Carpenter, W.B.; Fournier, J.A.; Lewis, N.H.; Tokmakoff, A. *The Journal of Physical Chemistry B*, **2018,** *122*(10), 2792-2802.

Conclusion

- The proton solvation pattern keeps changing and the predominant solvation species are Eigen and Zundel complexes.

- The hydrogen bond dynamics plays important role in proton transfer mechanism.

- Population correlation gives kinetics of proton transfer in a hydrogen-bonded network.

- 2D IR spectroscopic technique successfully captures the evolving structure and dynamics.

Thank You!