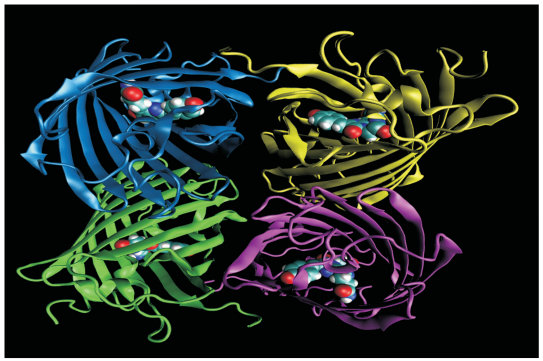
Clusters-in-liquid IR identifies the proton transfer mode in acidic aqueous solution

Waldemar Kulig

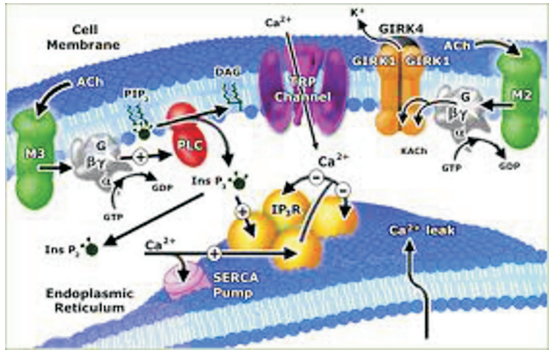
The Fritz Haber Center for Molecular Dynamics
The Hebrew University of Jerusalem

September 19, 2012

Protein folding

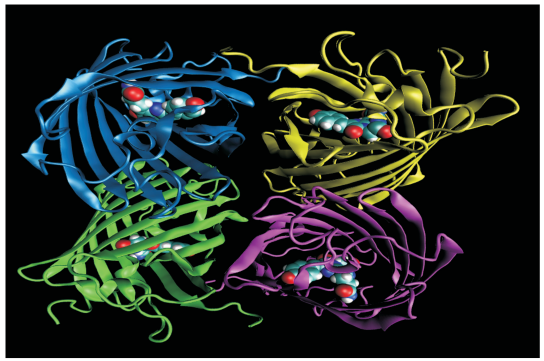


Prepared by Ai Shinobu



Source: Clapham Lab

Protein folding



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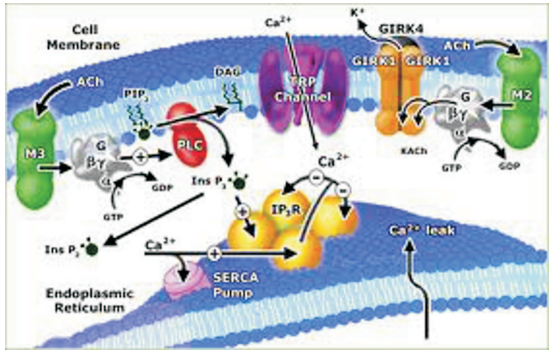

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Acid-base reactions

Source: Jones Collage Prep

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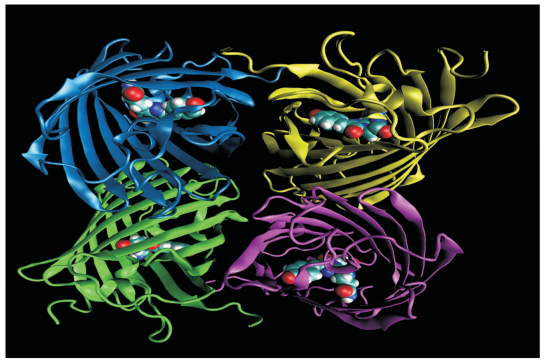

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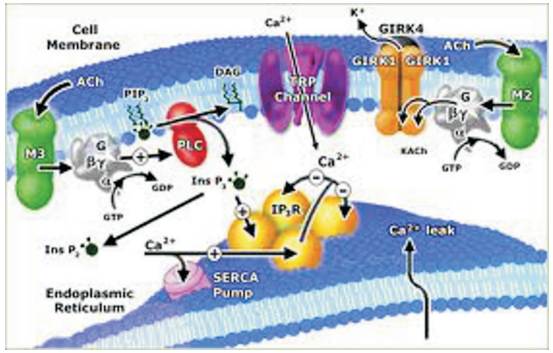

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Acid-base reactions

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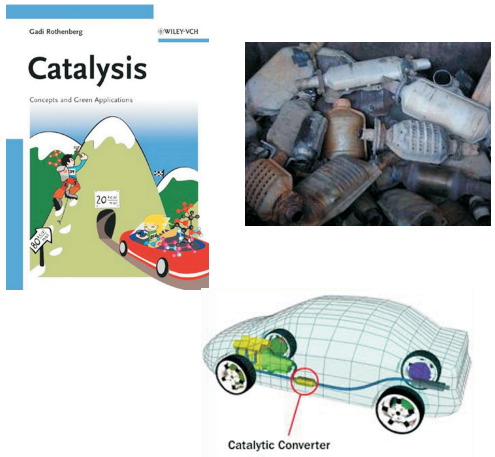
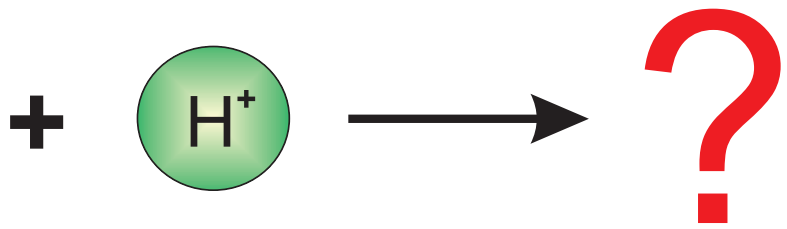
Catalysis



Source: www.wikipedia.com

Proton transfer

Banias Waterfall, Israel



The kinetics of proton in water cannot be measured experimentally

but the IR spectrum can!

Proton transfer

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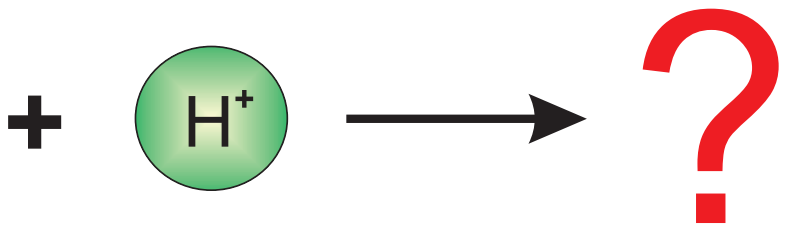

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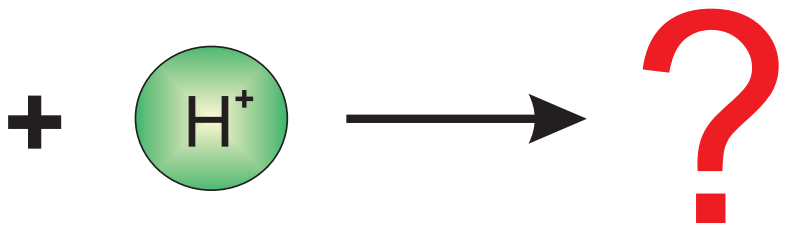

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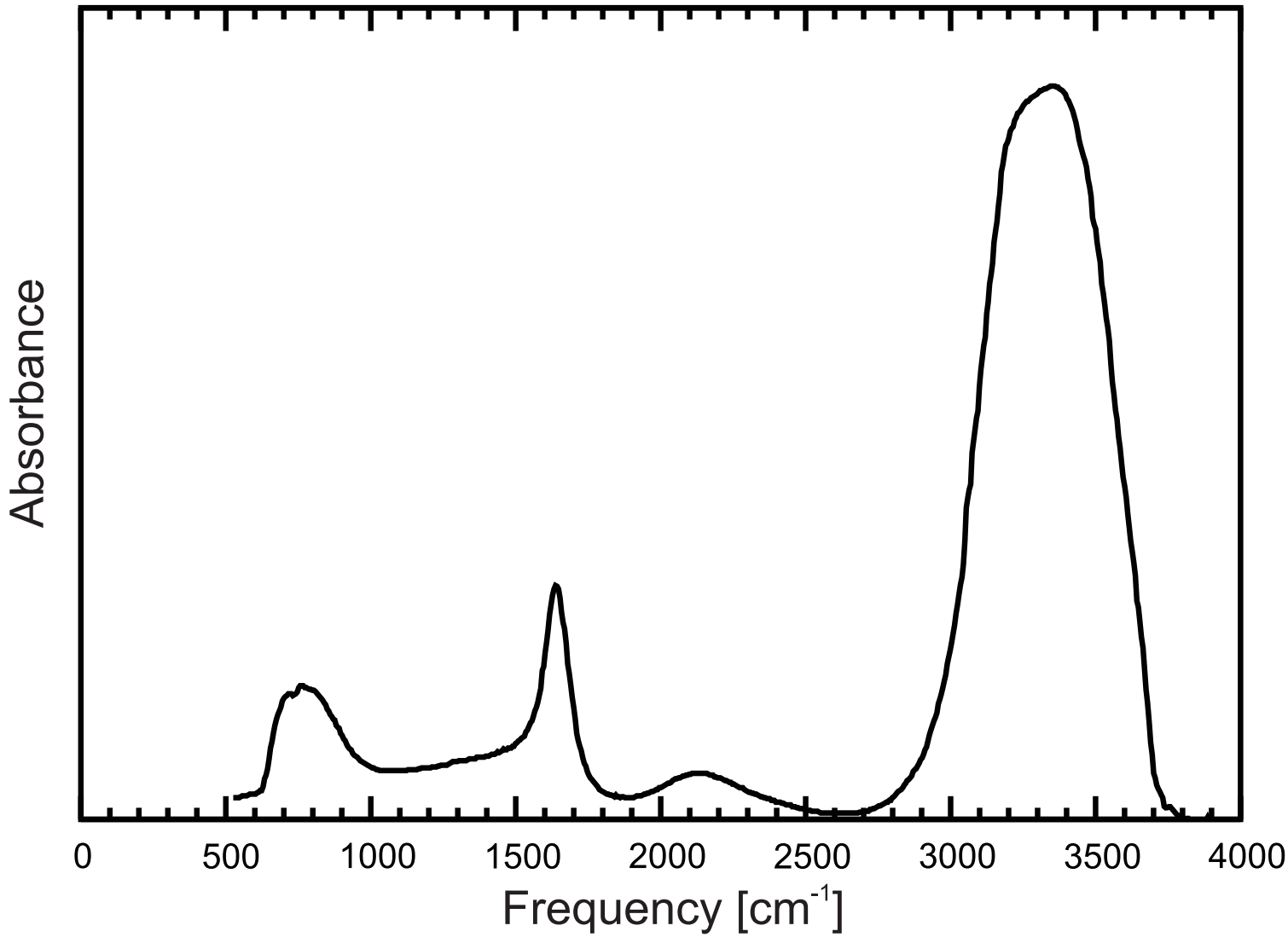
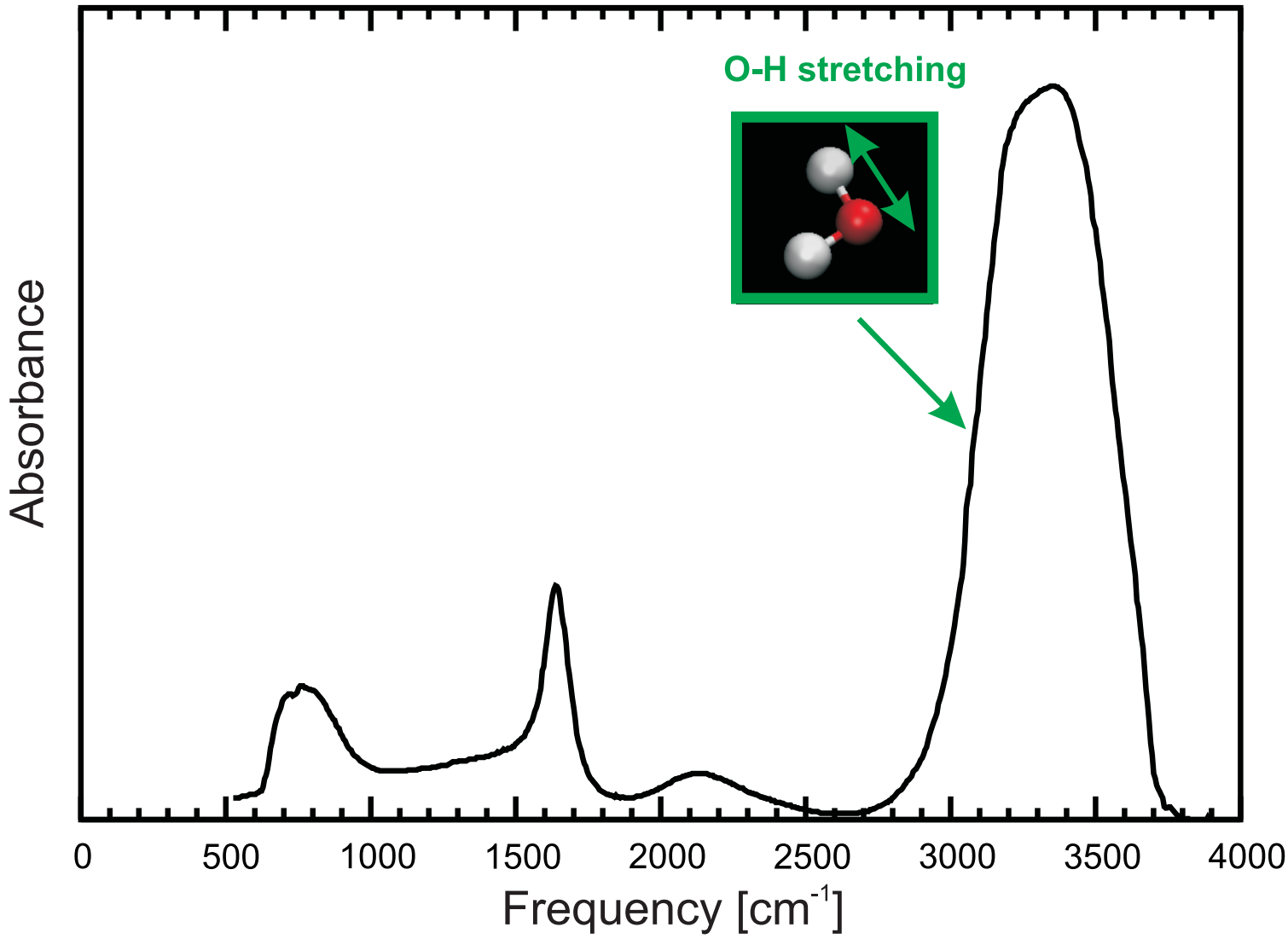
IR spectrum of pure water



J. Kim *et al.* **J. Chem. Phys.** 116 (2002) 737

IR spectrum of pure water



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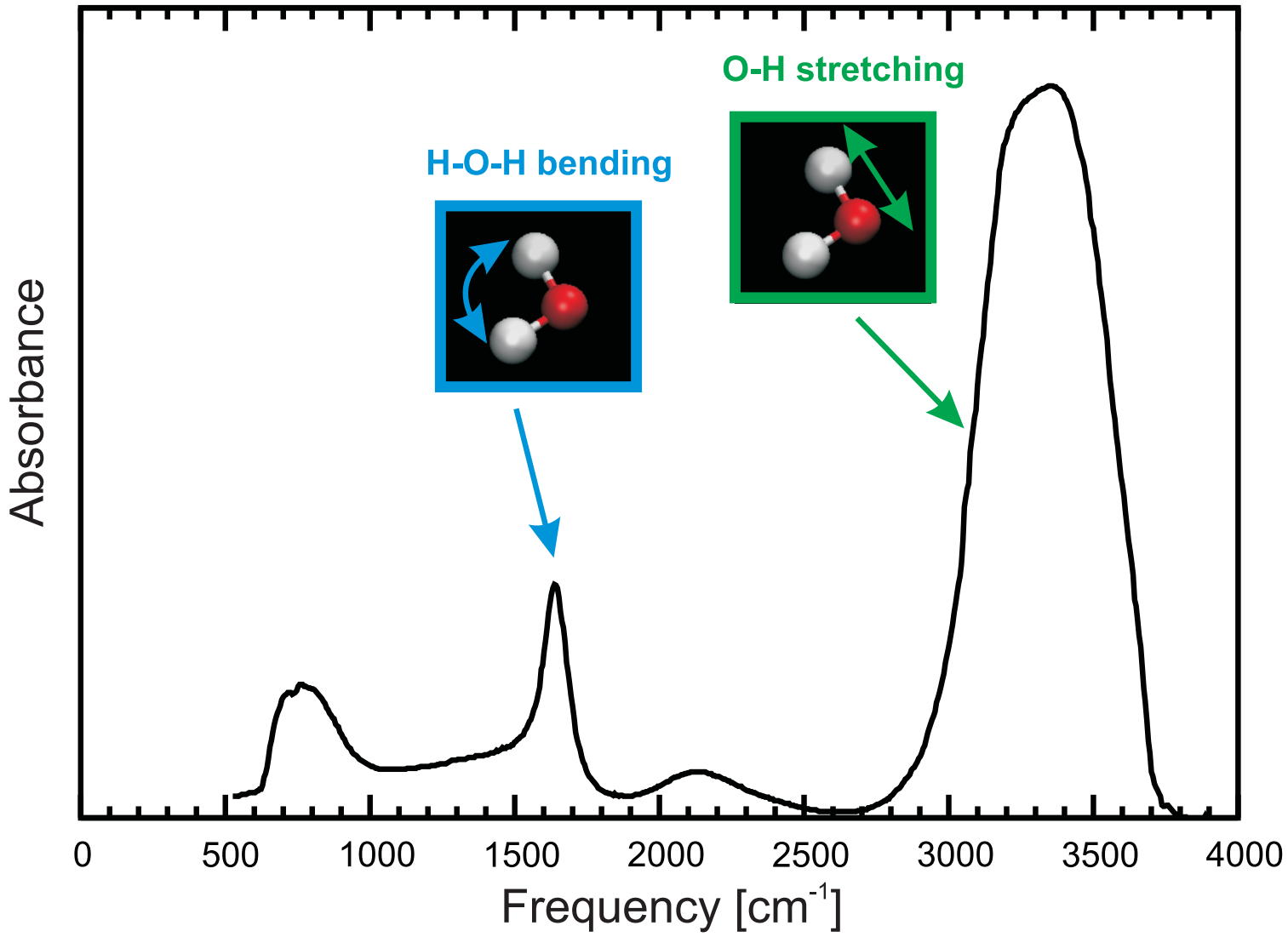

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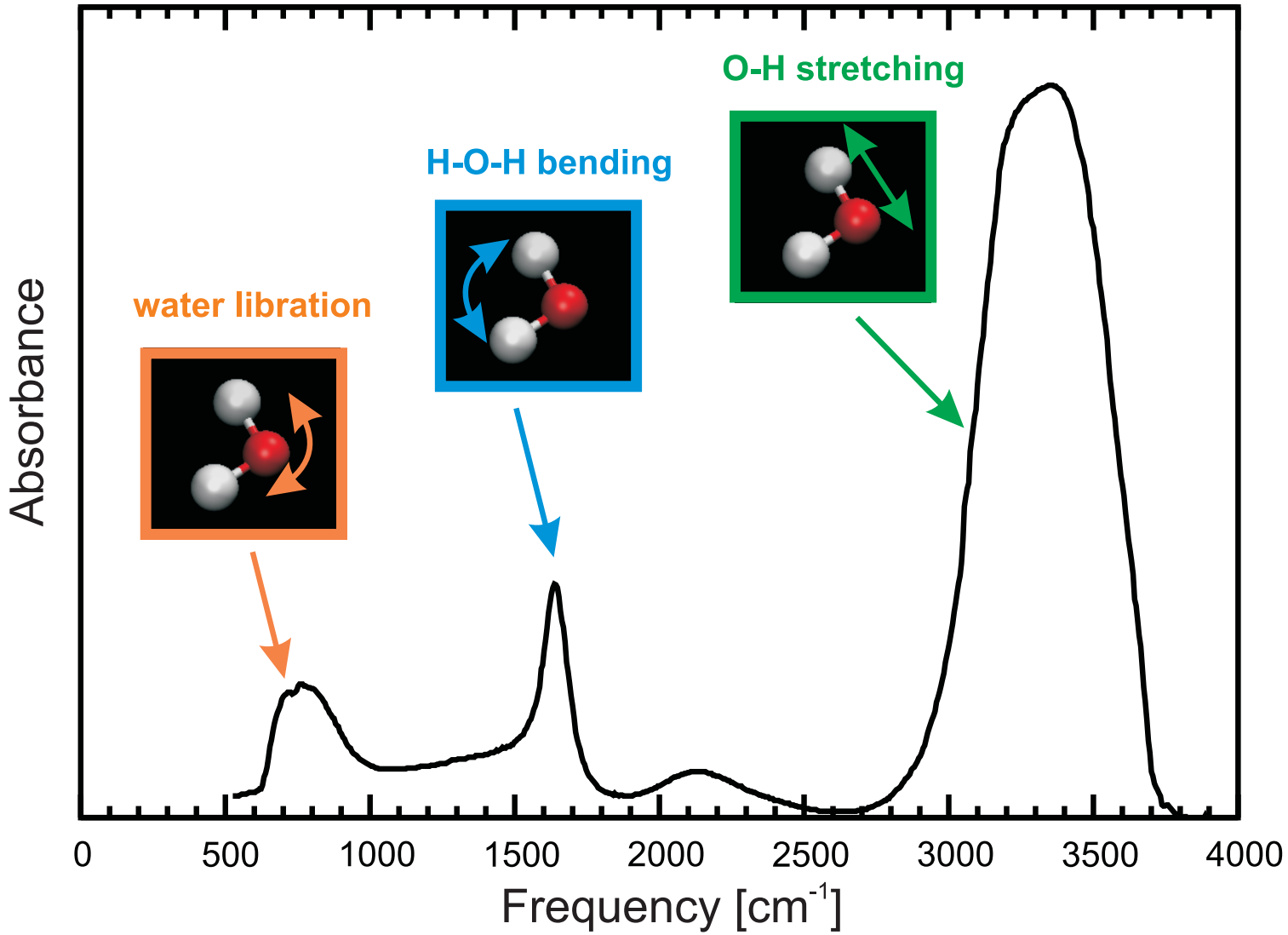

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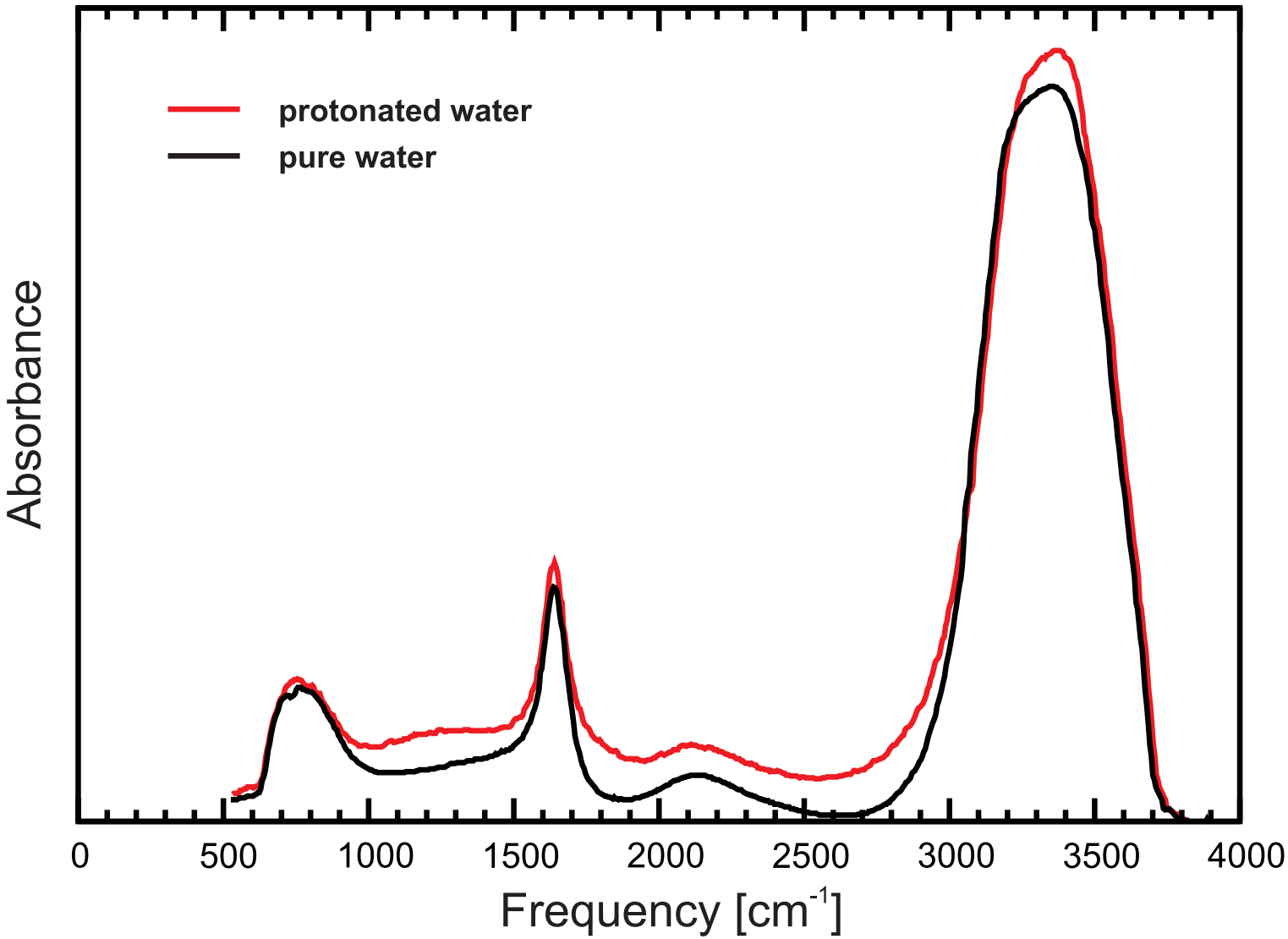
IR spectrum of protonated water



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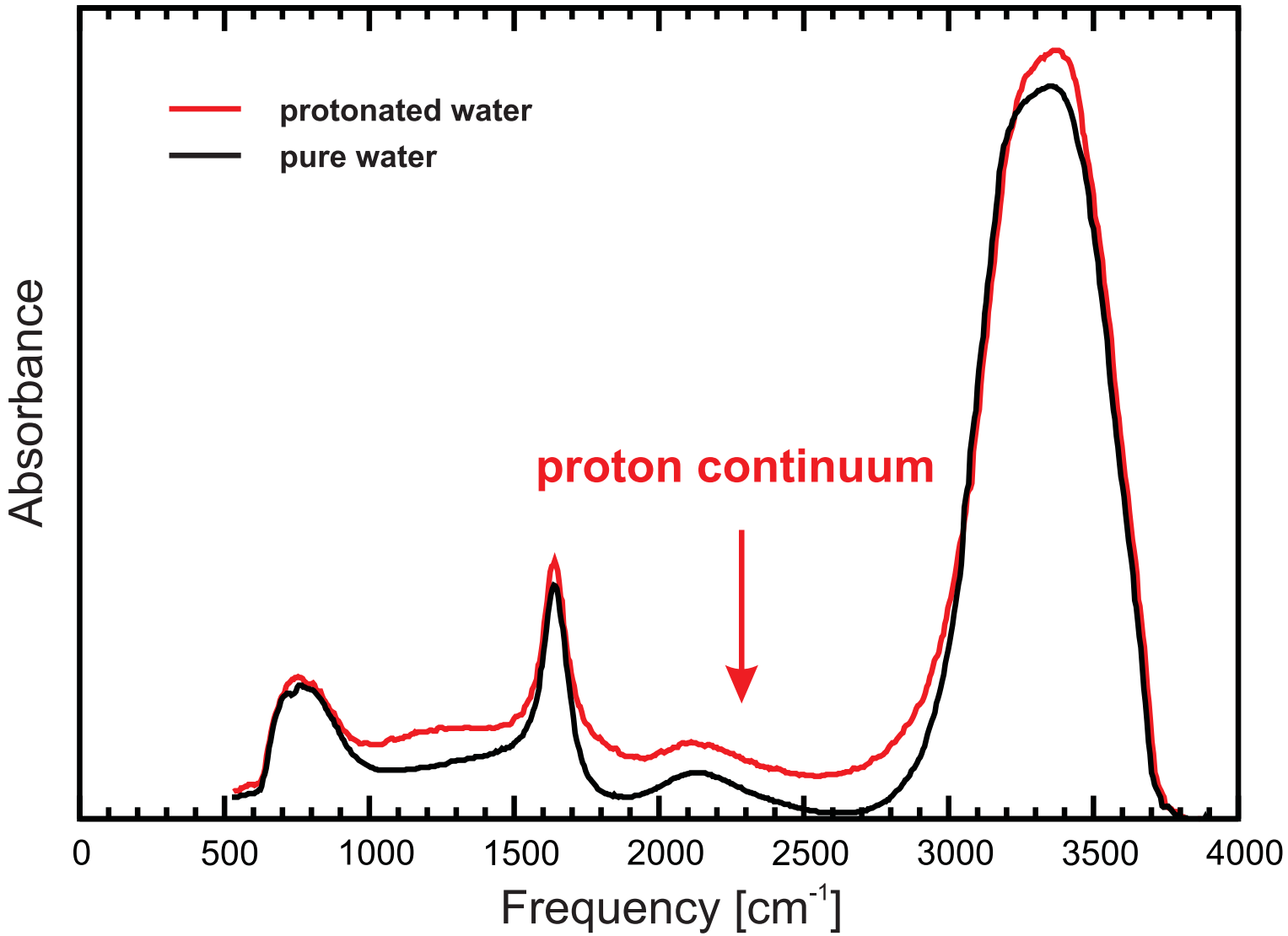
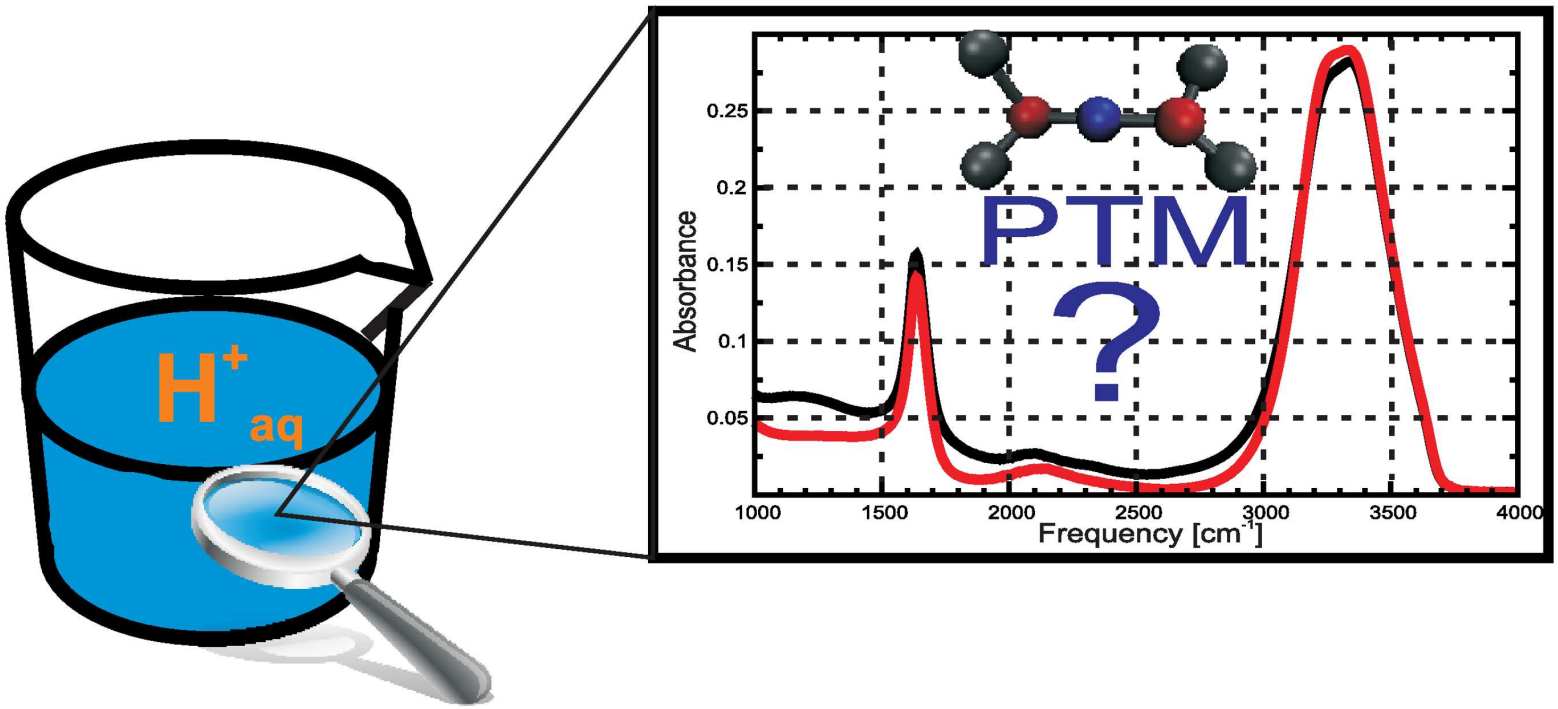
IR spectrum of protonated water



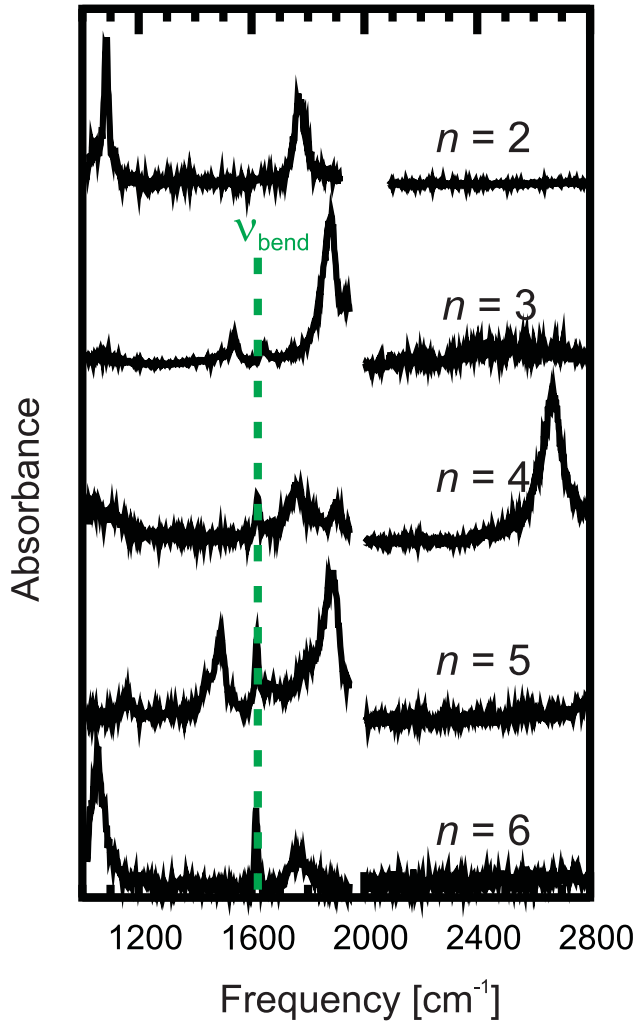
J. Kim *et al.* **J. Chem. Phys.** 116 (2002) 737

Where is a signal from a proton transfer mode (PTM)?



Experiment

Sharp peak at 1620 cm^{-1} assigned to HOH bend of flanking water molecules



Headrick, J. M. *et al.*, Science 308, 1765-1769 (2005)

Experiment

THE JOURNAL OF CHEMICAL PHYSICS 127, 184303 (2007)

Full dimensional (15-dimensional) quantum-dynamical simulation of the protonated water dimer. II. Infrared spectrum and vibrational dynamics

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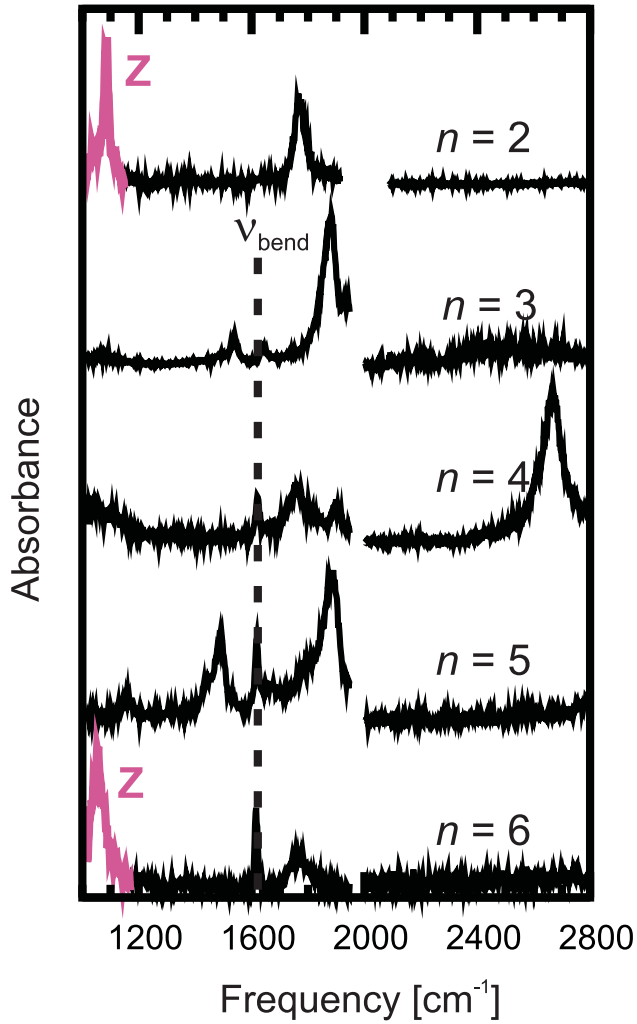
Hans-Dieter Meyer[c)]
Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg, INF 229, D-69120 Heidelberg, Germany

(Received 6 July 2007; accepted 29 August 2007; published online 9 November 2007)

The infrared absorption spectrum of the protonated water dimer ($H_5O_2^+$) is simulated in full dimensionality (15 dimensional) in the spectral range of 0–4000 cm^{-1}. The calculations are performed using the multiconfiguration time-dependent Hartree (MCTDH) method for propagation of wavepackets. All the fundamentals and several overtones of the vibrational motion are computed. The spectrum of $H_5O_2^+$ is shaped to a large extent by couplings of the proton-transfer motion to large amplitude fluxional motions of the water molecules, water bending and water-water stretch motions. These couplings are identified and discussed, and the corresponding spectral lines are assigned. The large couplings featured by $H_5O_2^+$ do not hinder, however, to describe the coupled vibrational motion by well defined simple types of vibration (stretching, bending; etc.) based on well defined modes of vibration, in terms of which the spectral lines are assigned. Comparison of our results to recent experiments and calculations on the system is given. The reported MCTDH IR spectrum is in very good agreement to the recently measured spectrum by Hammer *et al.* [J. Chem. Phys. **122**, 244301 (2005)]. © 2007 American Institute of Physics. [DOI: 10.1063/1.2787596]

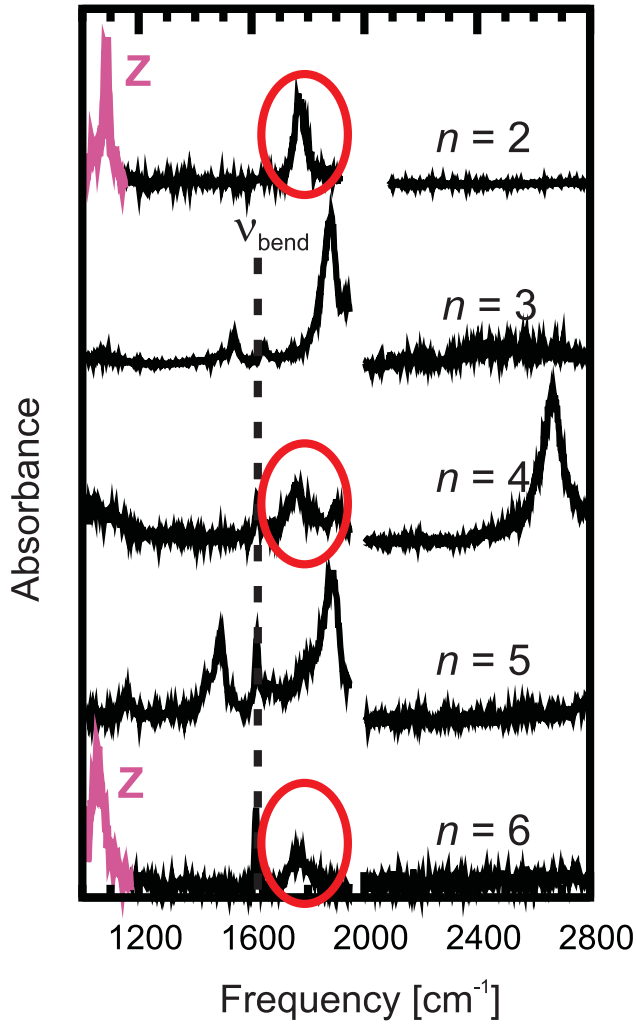
Strong peak near 1080cm^{-1} assigned previously to the PTM in symetric Zundel conformers



Headrick, J. M. *et al.*, Science 308, 1765-1769 (2005)

Experiment

?



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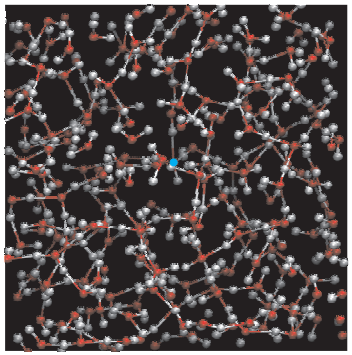
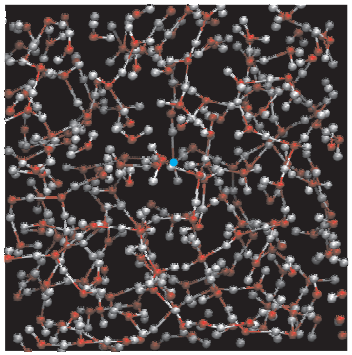
Default calculations



proton in water box

Default calculations



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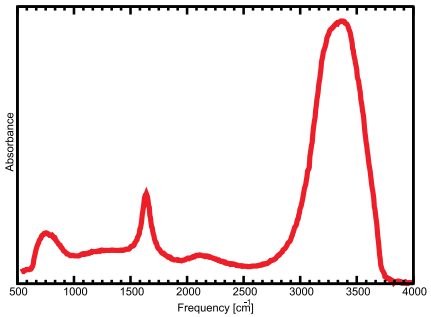

IR proton in water box

$$I(\omega) \approx \int dt\, e^{-i\omega t} \langle \dot{\boldsymbol{\mu}}(0) \dot{\boldsymbol{\mu}}(t) \rangle$$

$$\dot{\boldsymbol{\mu}}(t) = \sum_{i}^{N} \left(\dot{q}_i(t) \boldsymbol{R}_i(t) + q_i(t) \dot{\boldsymbol{R}}_i(t) \right)$$

The summation runs over all atoms in the system

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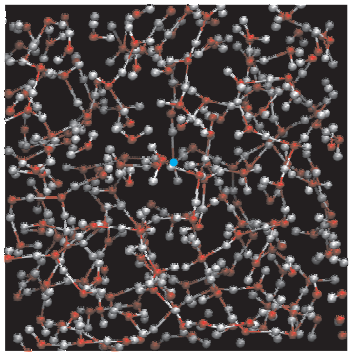

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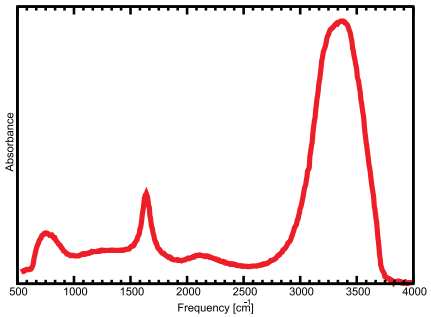

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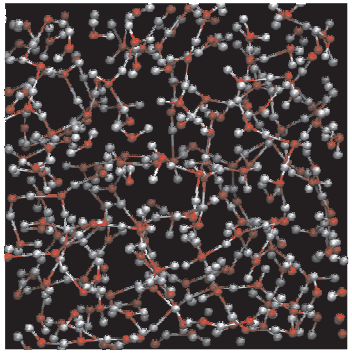
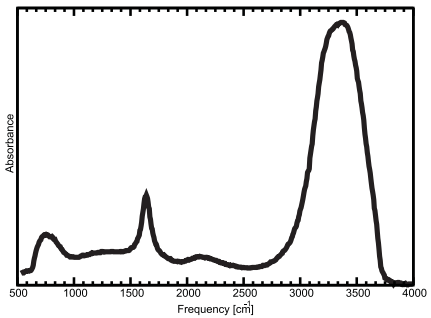


water box



IR water box

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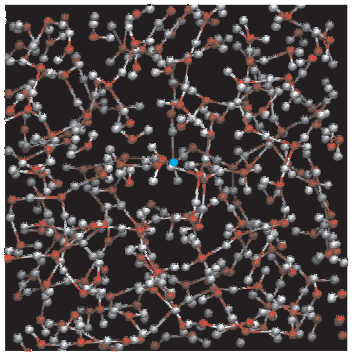

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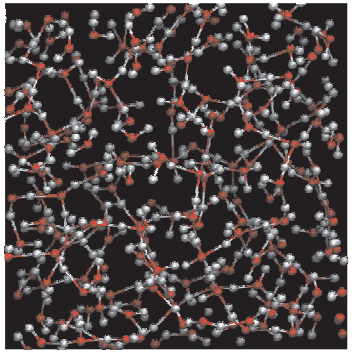

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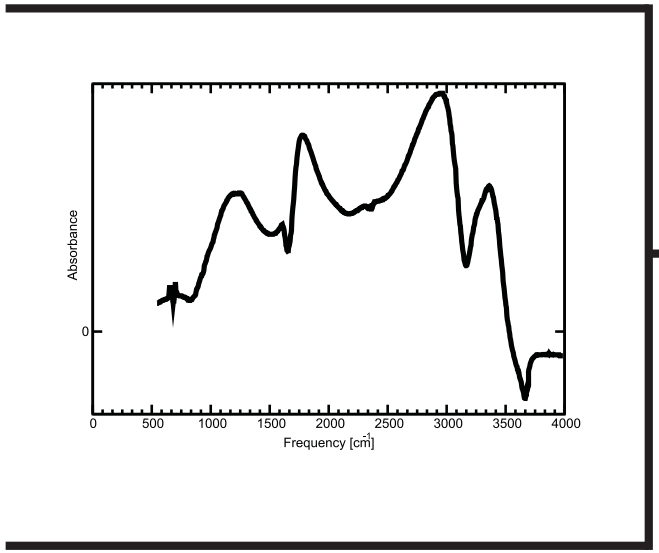
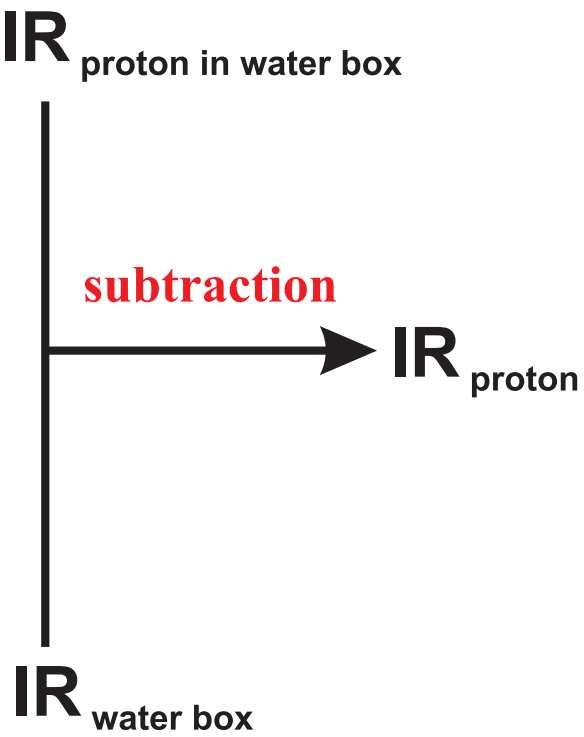
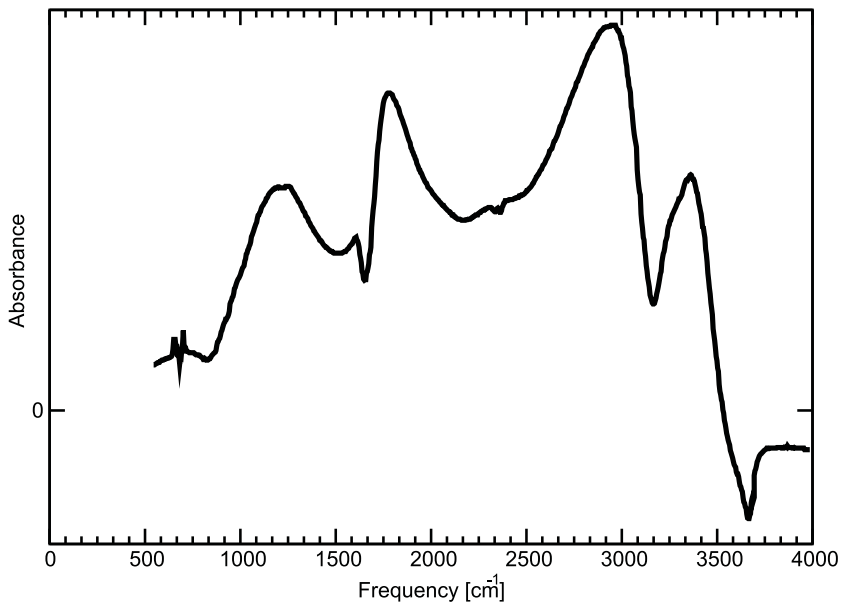


subtraction

IR_{proton}

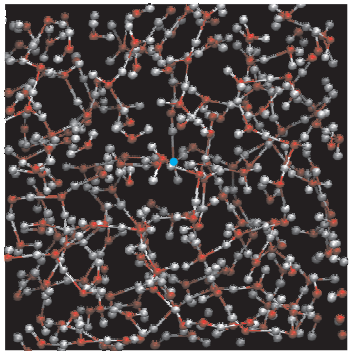
Default calculations





molecular motions assignment

Clusters-in-liquid approach



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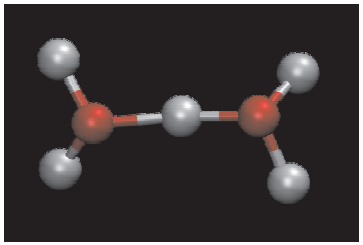

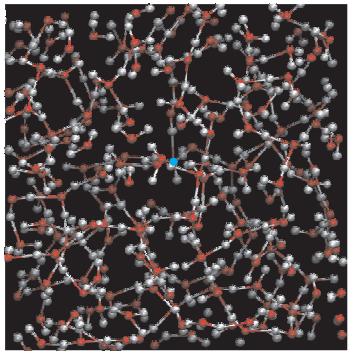

proton in water box

$$\mathbf{IR}_{\text{Zundel ion}}$$

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The summation runs only over a part of a system

where t - time, ω - frequency, μ - dipole moment, N - number of atoms, q - atomic charge, $\boldsymbol{R}$ - position of atom

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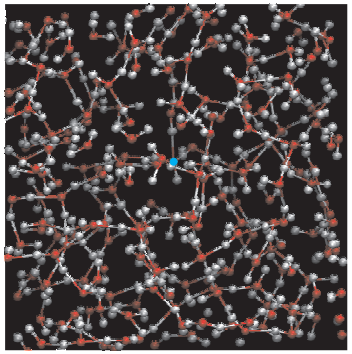

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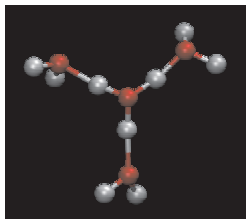

IR Eigen ion

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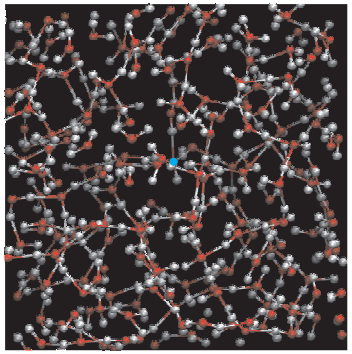
Clusters-in-liquid approach



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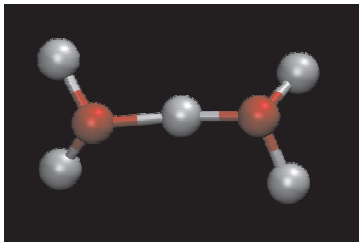
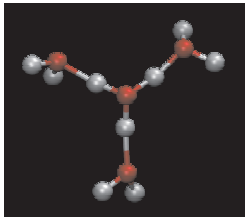




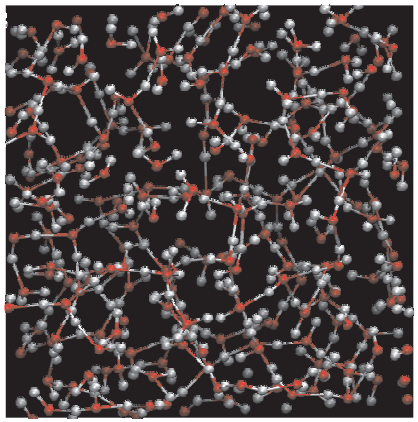
IR Zundel ion

IR Eigen ion

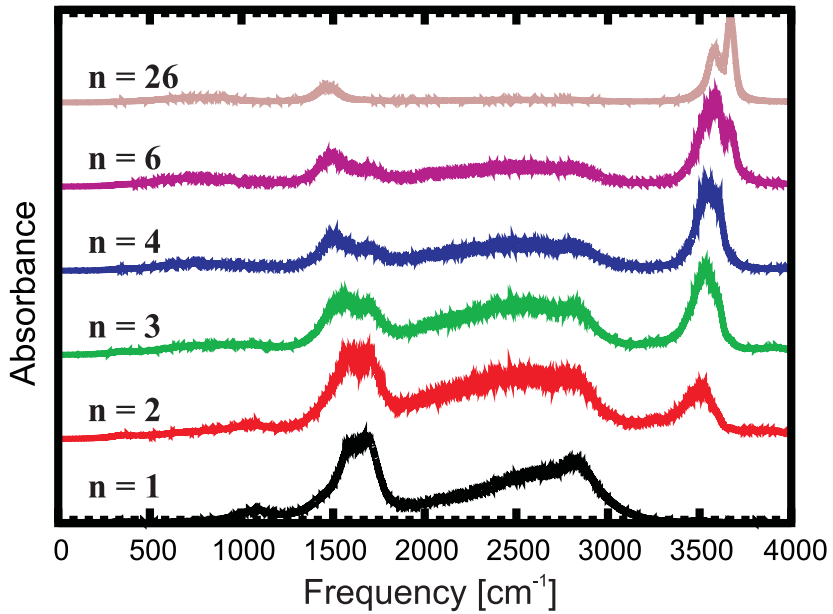
one simulation, no subtraction
IR signal from specific part of the system

Simulation protocol

- proton and 216 water molecules
- 8 starting configurations / at least 500 ps of equilibration (NVT)
- 300K (Nose-Hoover) and 1 atm
- 8 ns 'production run' (NVE), timestep 0.5 fs
- MS-EVB3 methodology, SPC/Fω water model
- hydronium ion - oxygen atom with three shortest O-H bonds
- $H^+(H_2O)_n$, where $n = 1, 2, 3, 4, 6, 26$, clusters cut out from simulation box

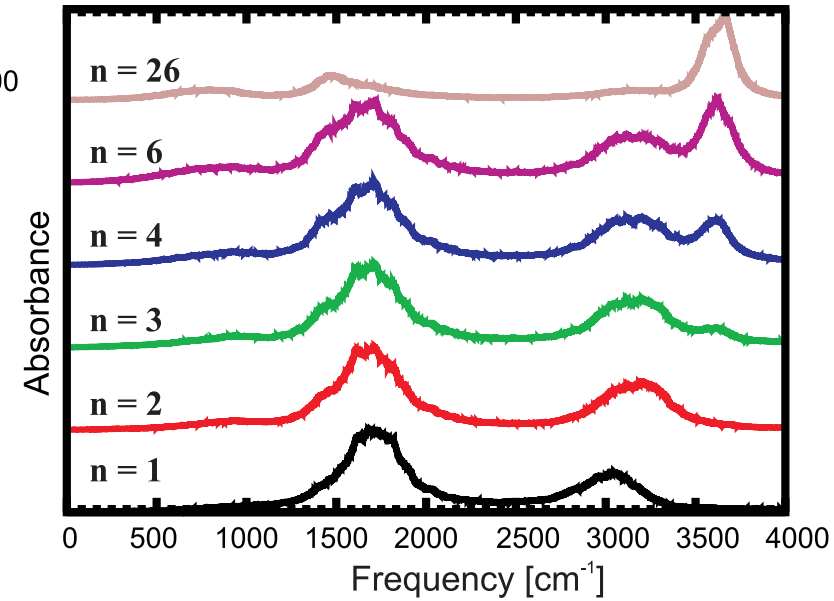


$H^+(H_2O)_n$ clusters



Eigen-like part

Zundel-like part



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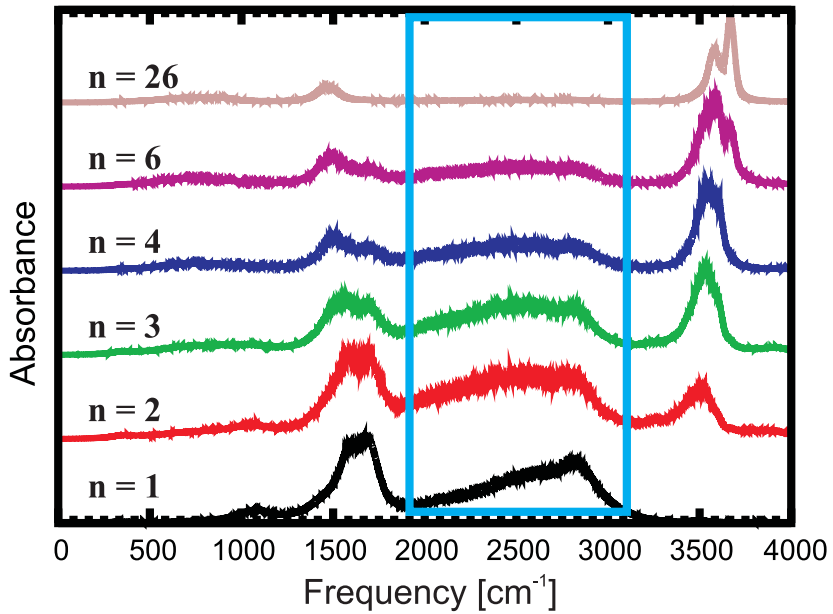
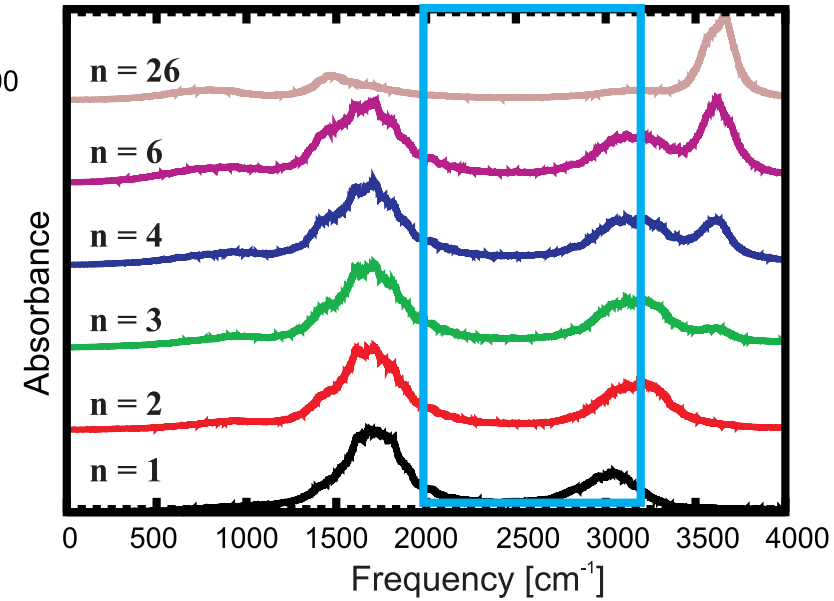
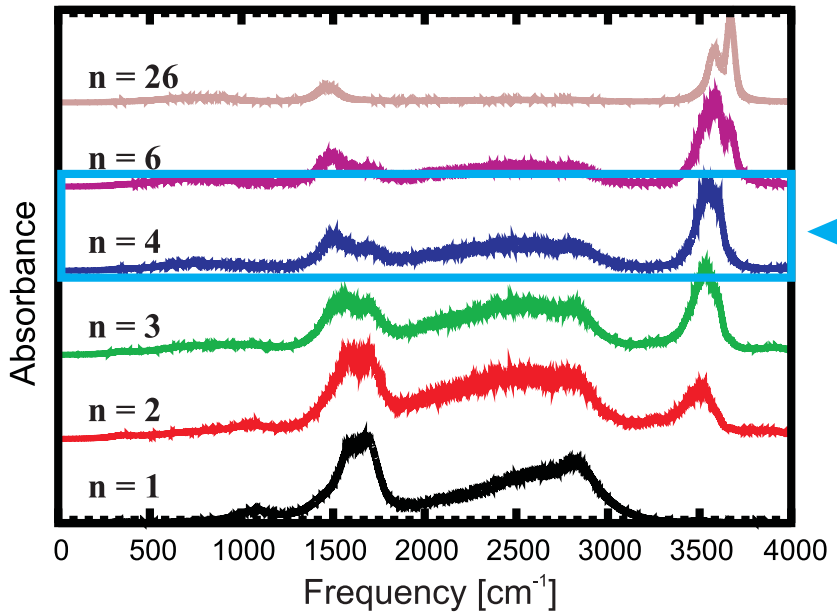


The proton continuum is dominated by Eigen-like structures

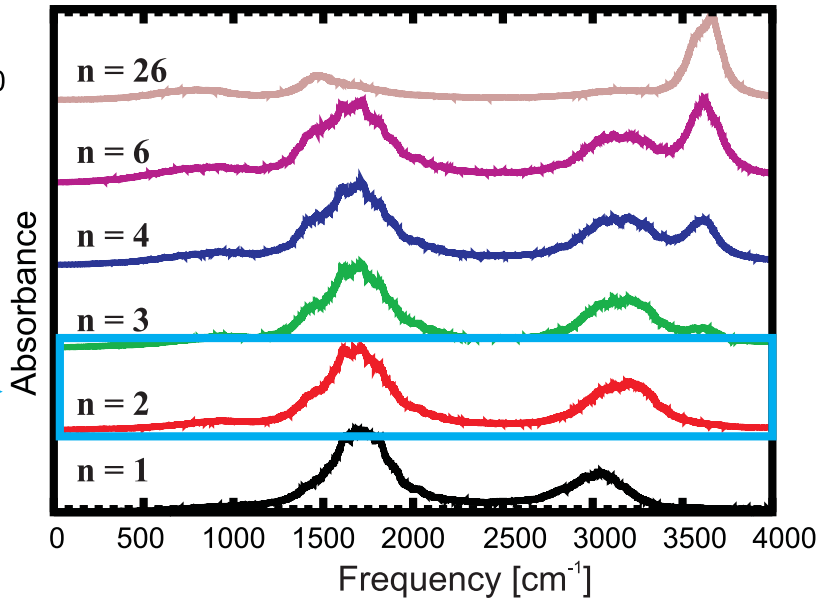


$H^+(H_2O)_n$ clusters

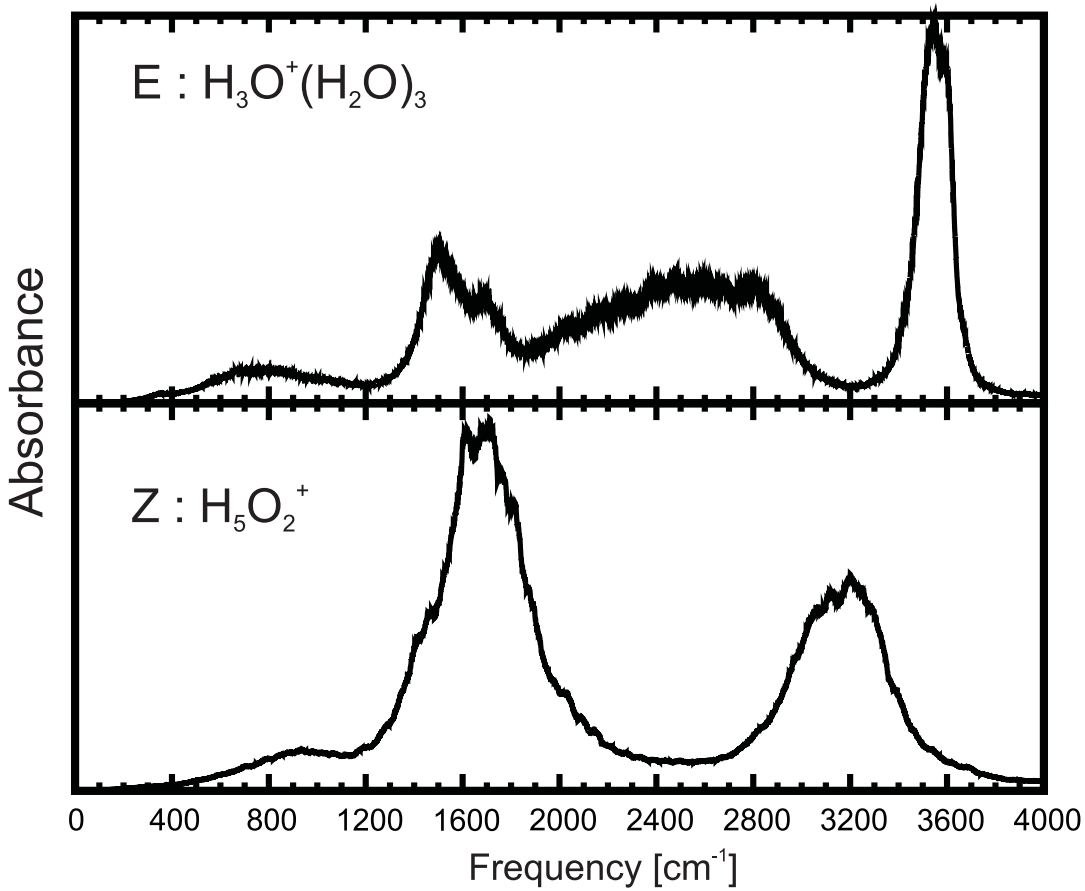


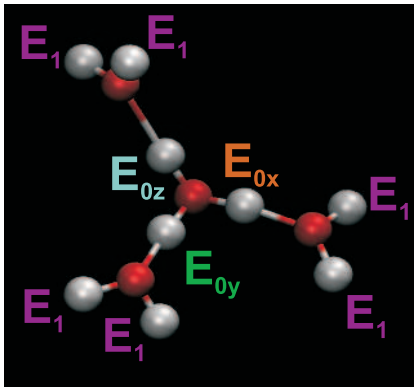
E: $H_3O^+(H_2O)_3$

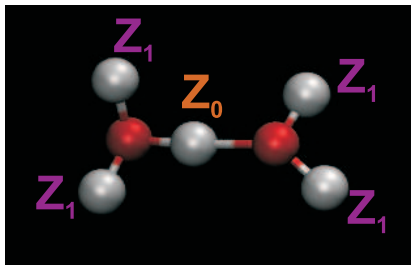
Z: $H_2O_5^+$



Looking for an excess proton . . .







W. Kulig and N. Agmon, *A 'clusters-in-liquid' method for calculating infrared spectra identifies the proton transfer mode in acidic aqueous solution*, **Nature Chemistry**, accepted

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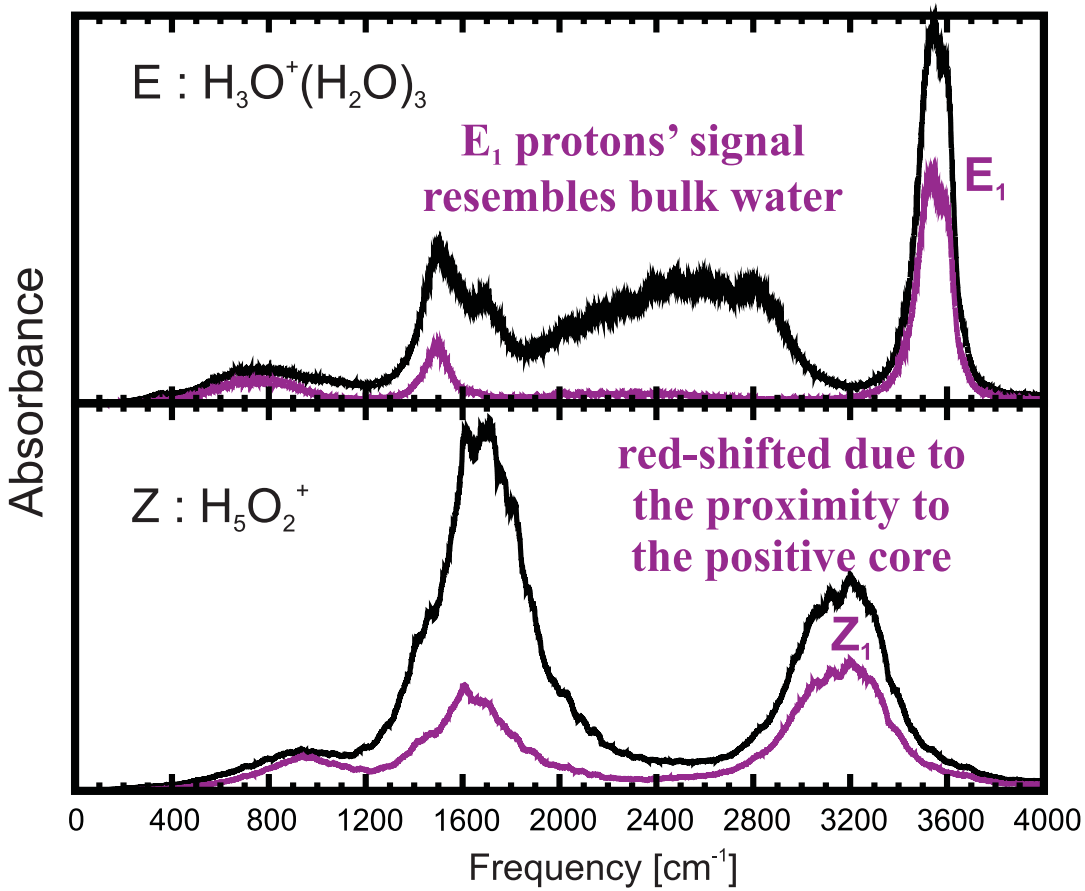

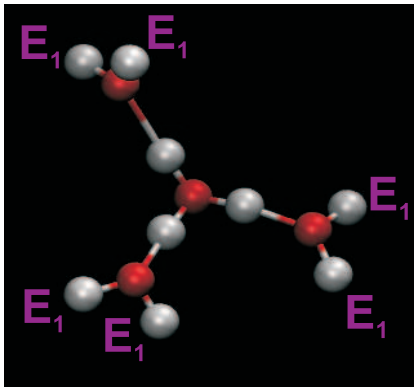

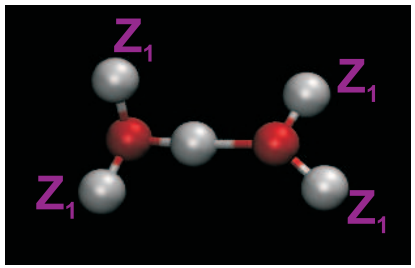

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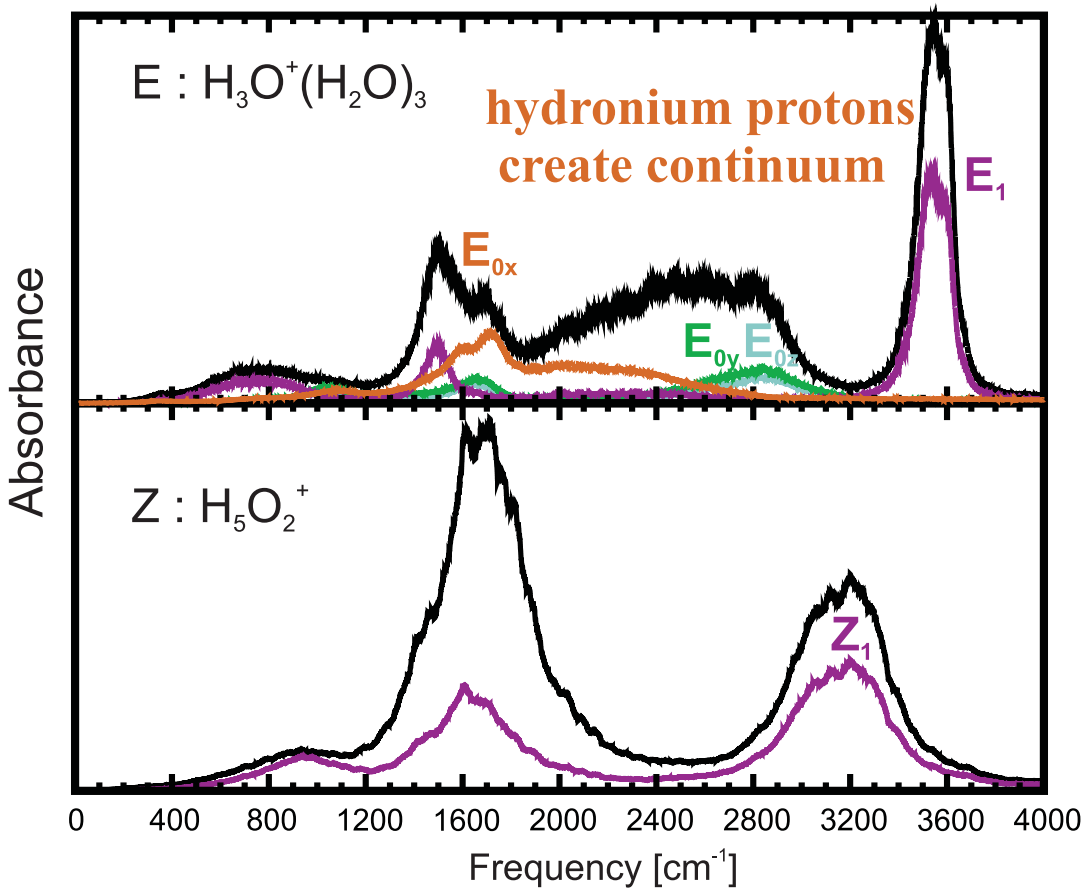

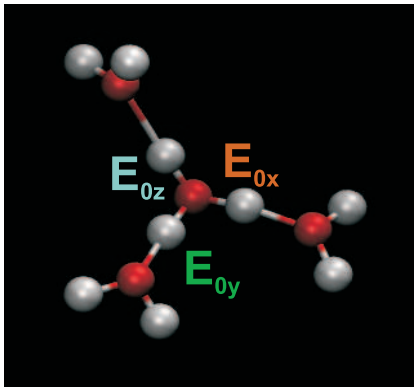

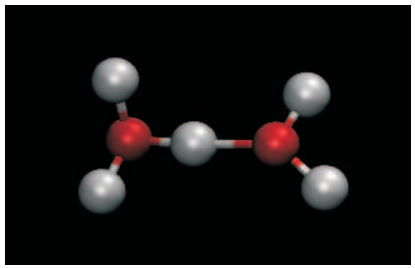

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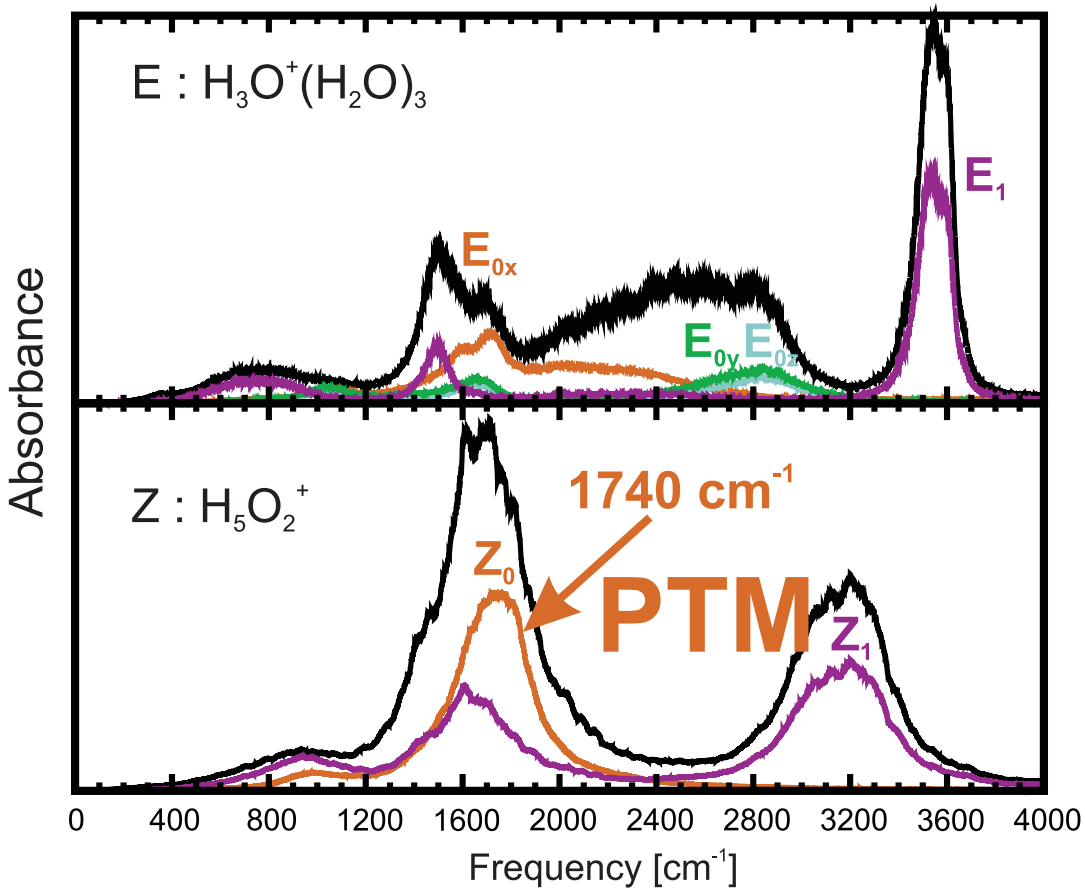

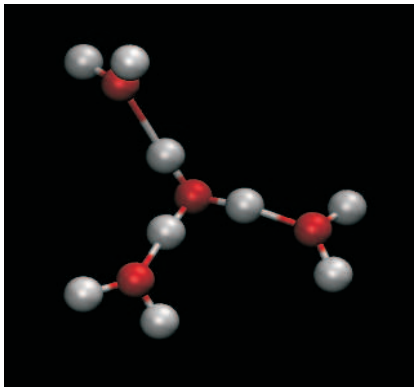

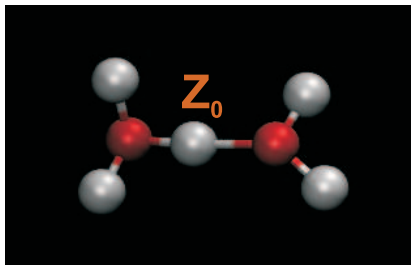

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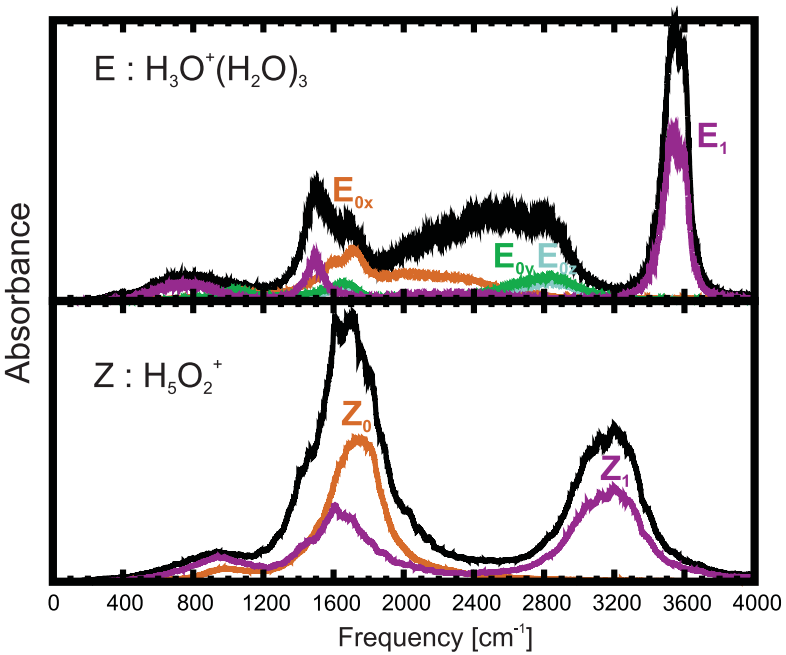
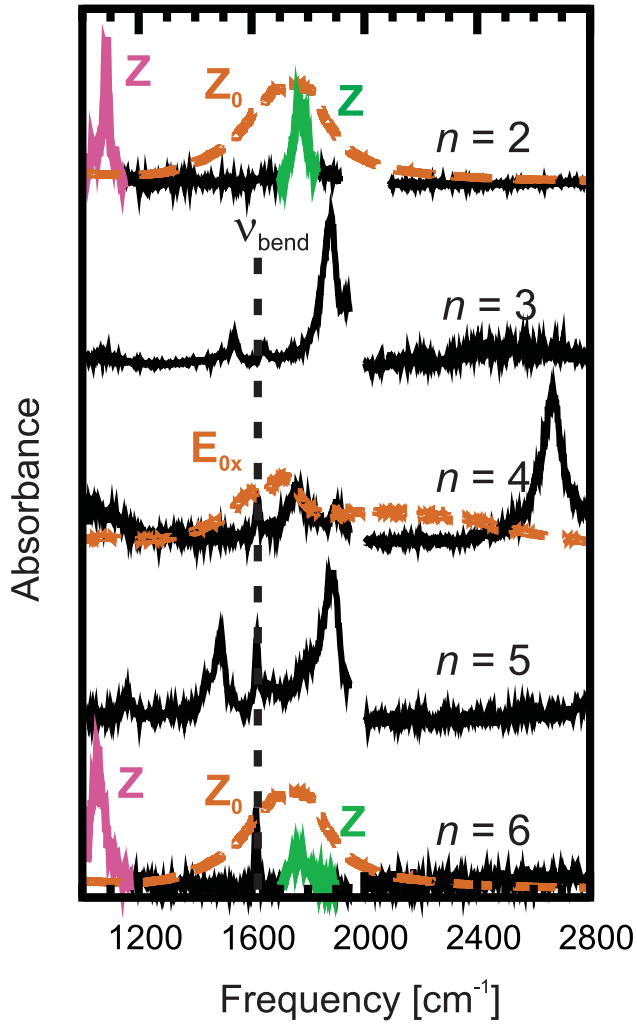
Comparison with experiment

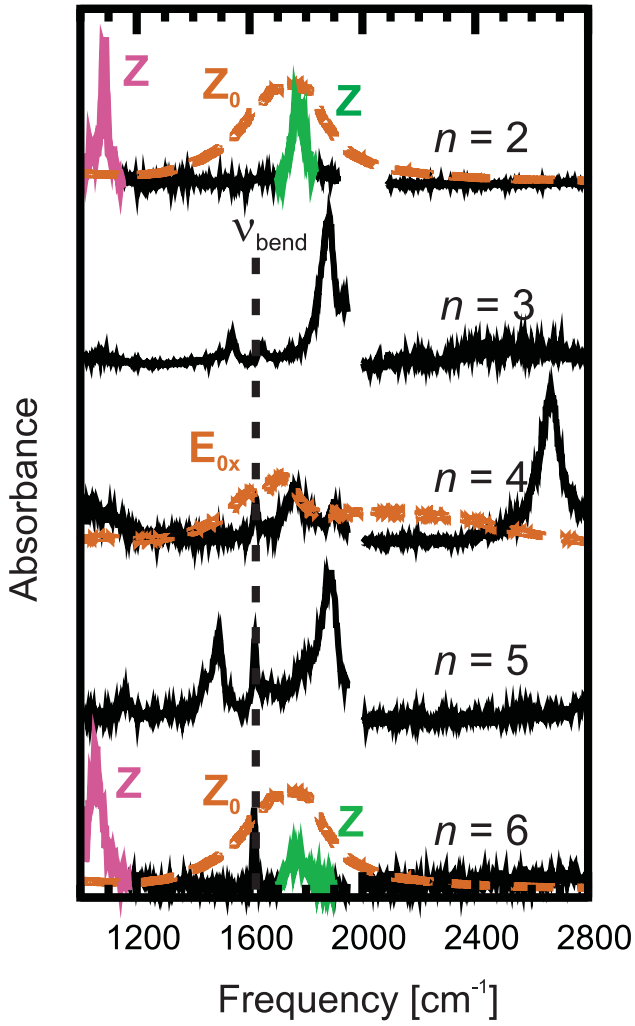




Headrick, J. M. *et al.*, Science 308, 1765-1769 (2005)

Comparison with experiment

The IR signal of the excess proton corresponds to an unidentified peak at 1740 cm^{-1} of protonated gas-phase water clusters with n=2, 4, and 6



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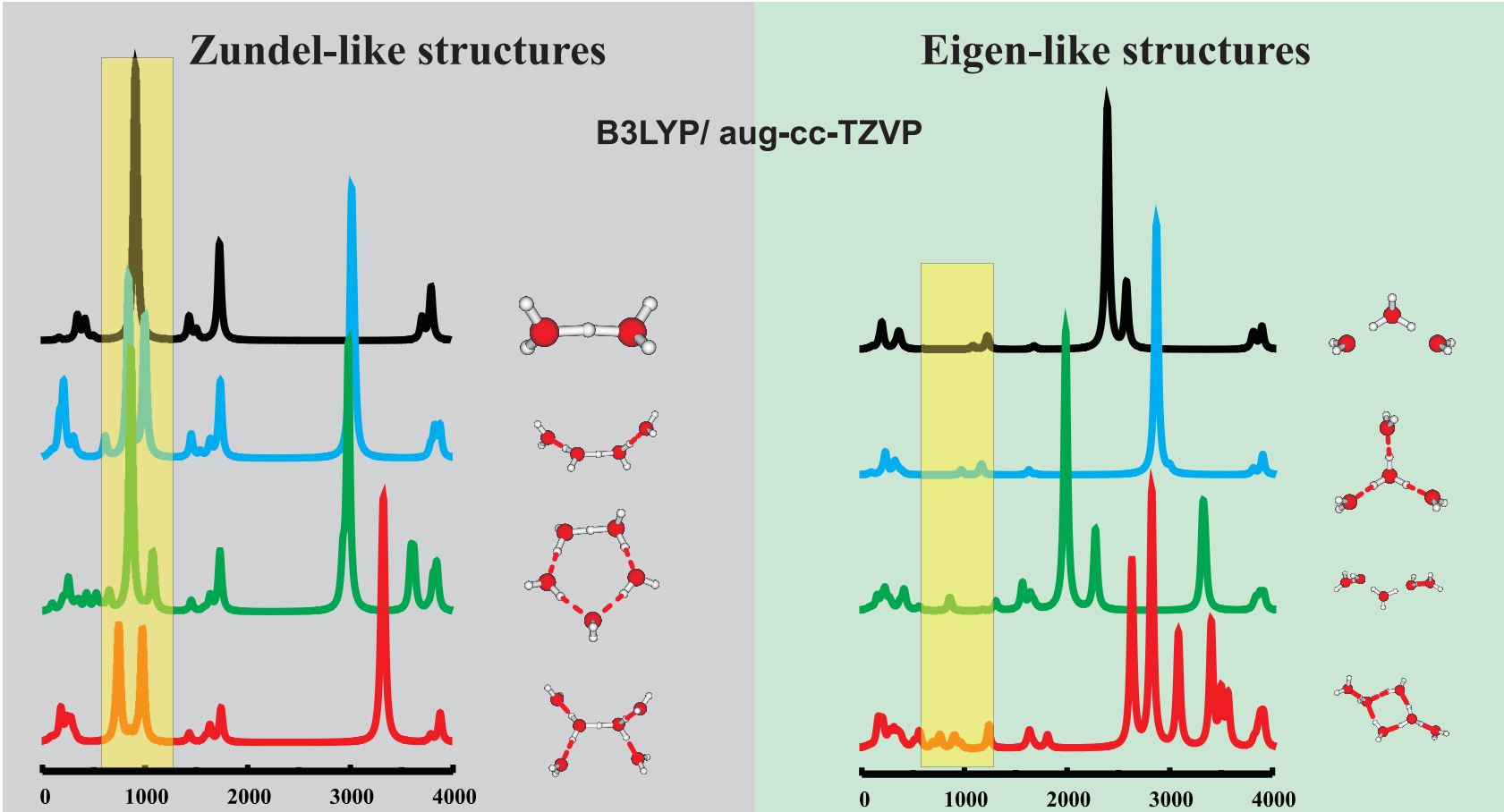
Gaussian clusters - Zundel-like structures



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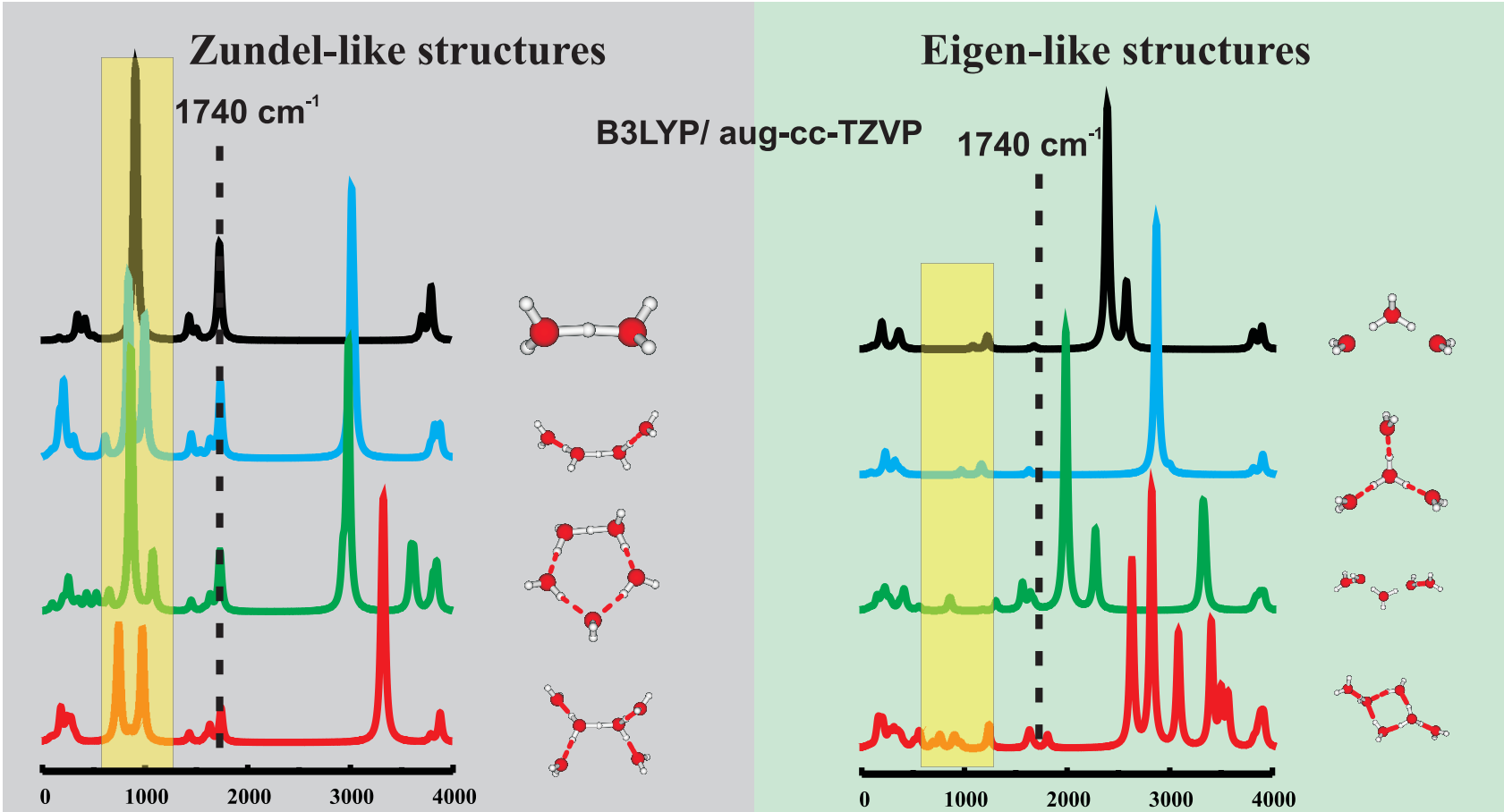
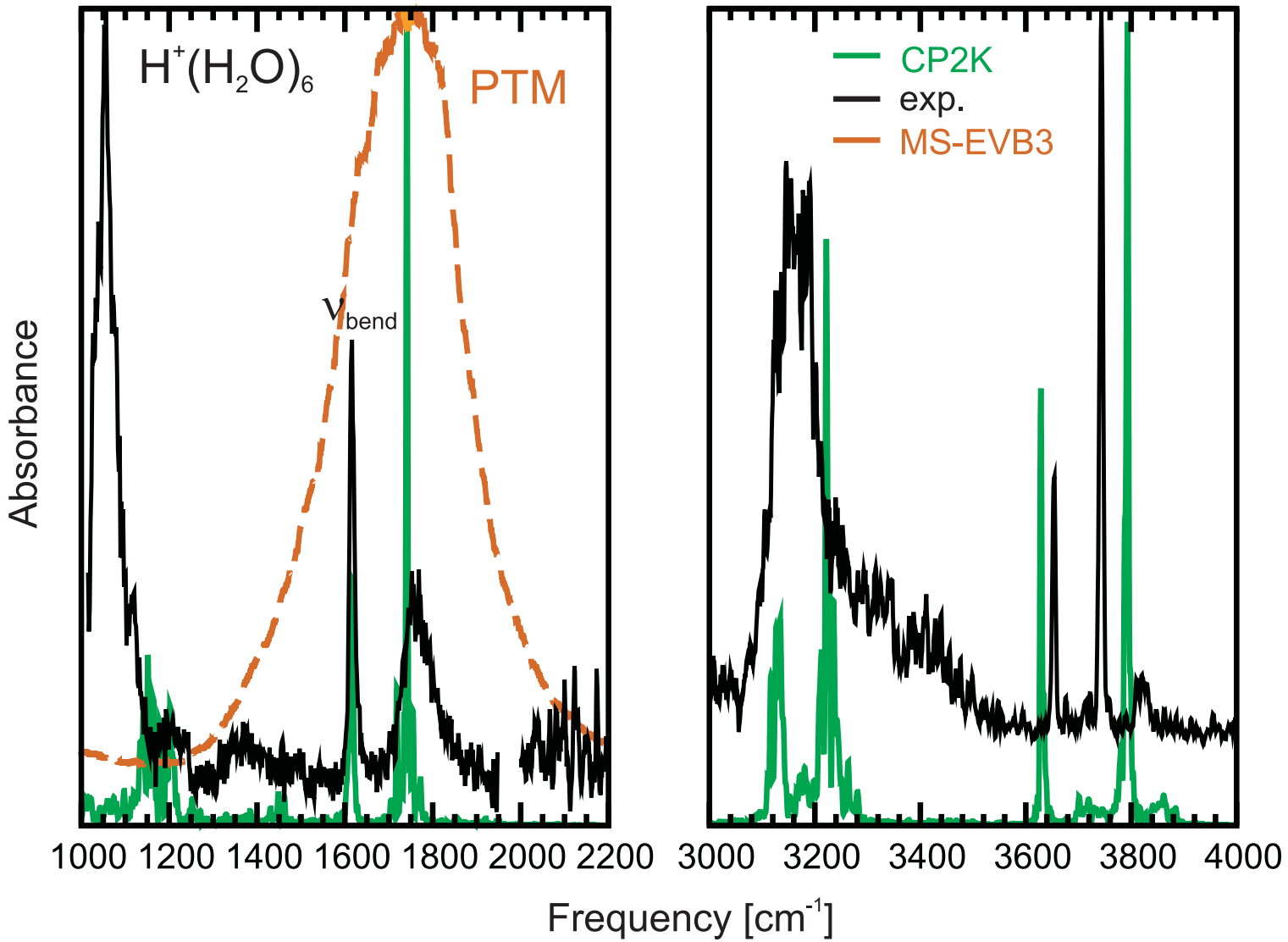


$H^+(H_2O)_6$ cluster

CP2K: BLYP/DZVP-GTH-BLYP/300Ry/50K/SIC



Summary

- IR signal of an excess proton in protonated liquid water is located near 1740 cm^{-1}
- a signal around 1000 cm^{-1} fades away in clusters with $n > 2$, which is supported both by MS-EVB3 and CP2K calculations
- proton continuum arises mostly from Eigen-like structures
- clusters-in-liquid approach is generic and could be applied to any simulation protocol that generates a charge distribution, therefore it may be useful for probing mixed solvents, interfaces, proteins and membranes.

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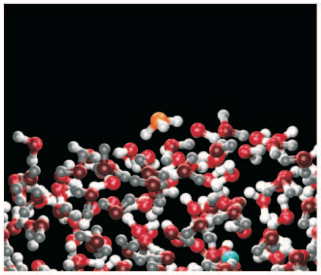
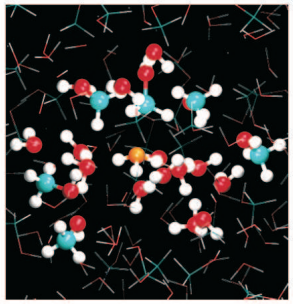
Applications of MS-EVB methodology

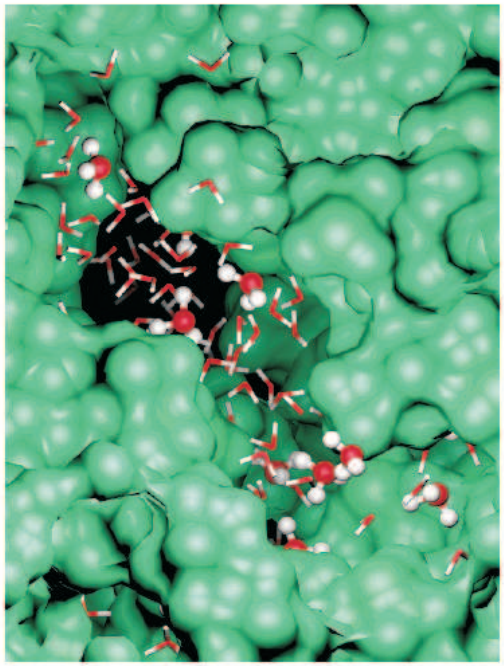


water - vaccum

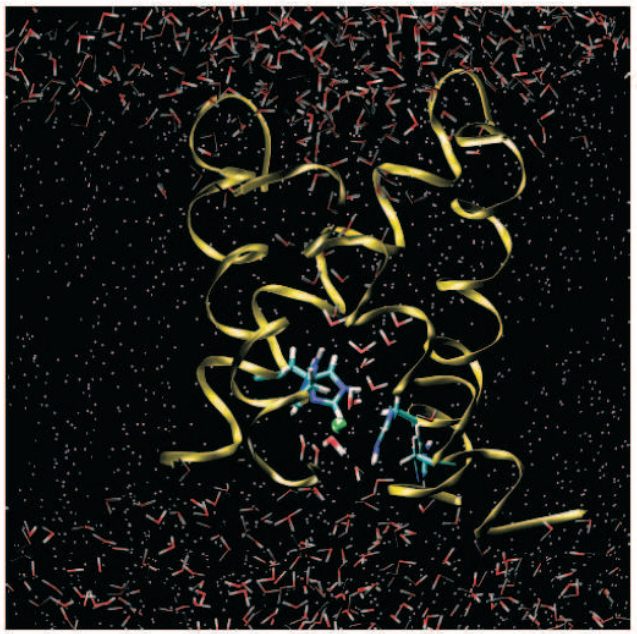


water - methanol

G. Voth, Acc. Chem. Res., 39 (2006) 143



40 excess protons in Nafion polymer electrolyte membrane



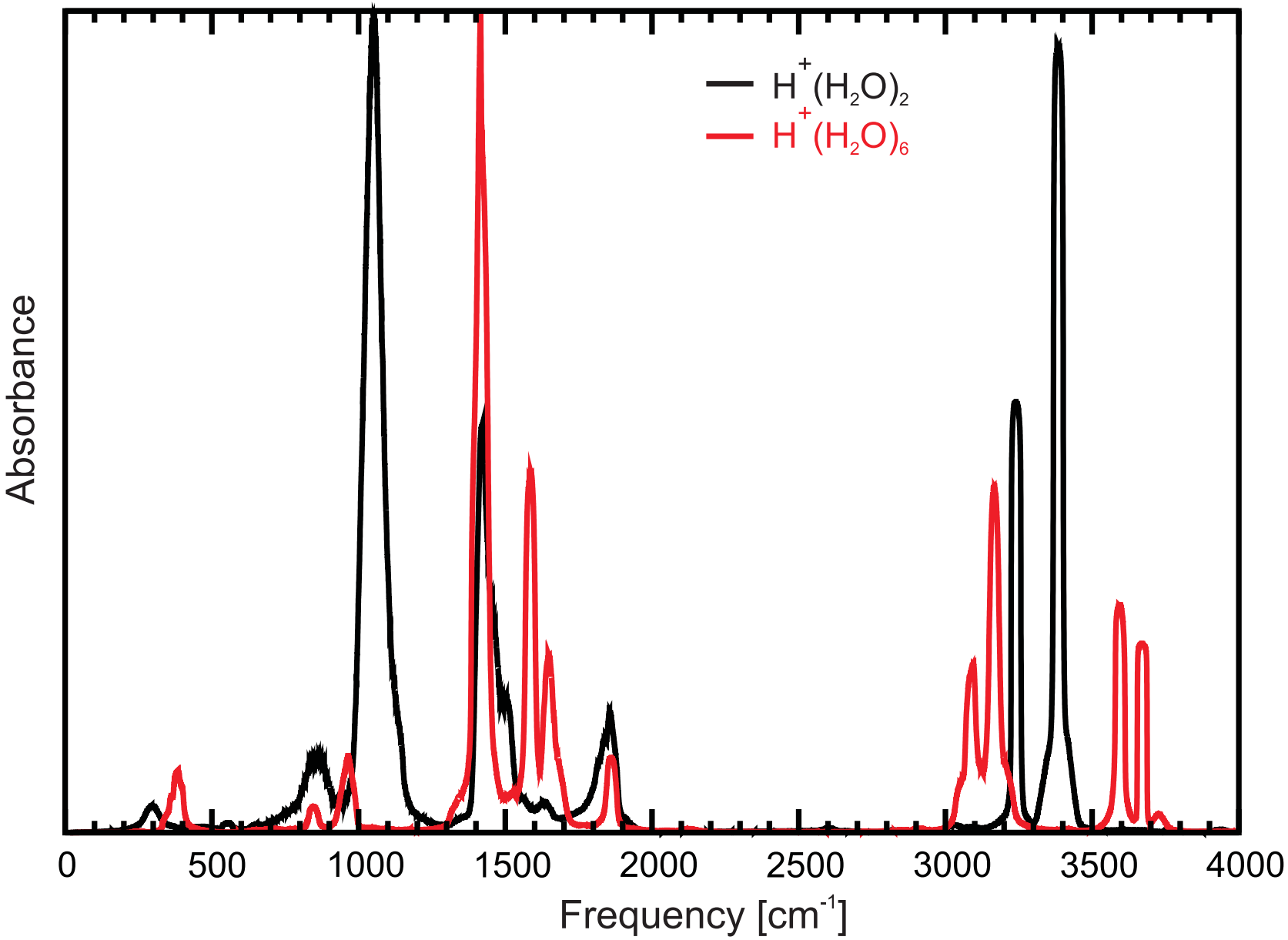
M2 proton channel in DMPC lipid bilayer

Acknowledgement

- Experimental results:
  - Mark A. Johnson
  - Maciej Śmiechowski
- Financial support:
  - The Minerwa Gesellschaft Für die Forschung
  - Binational Science Foundation

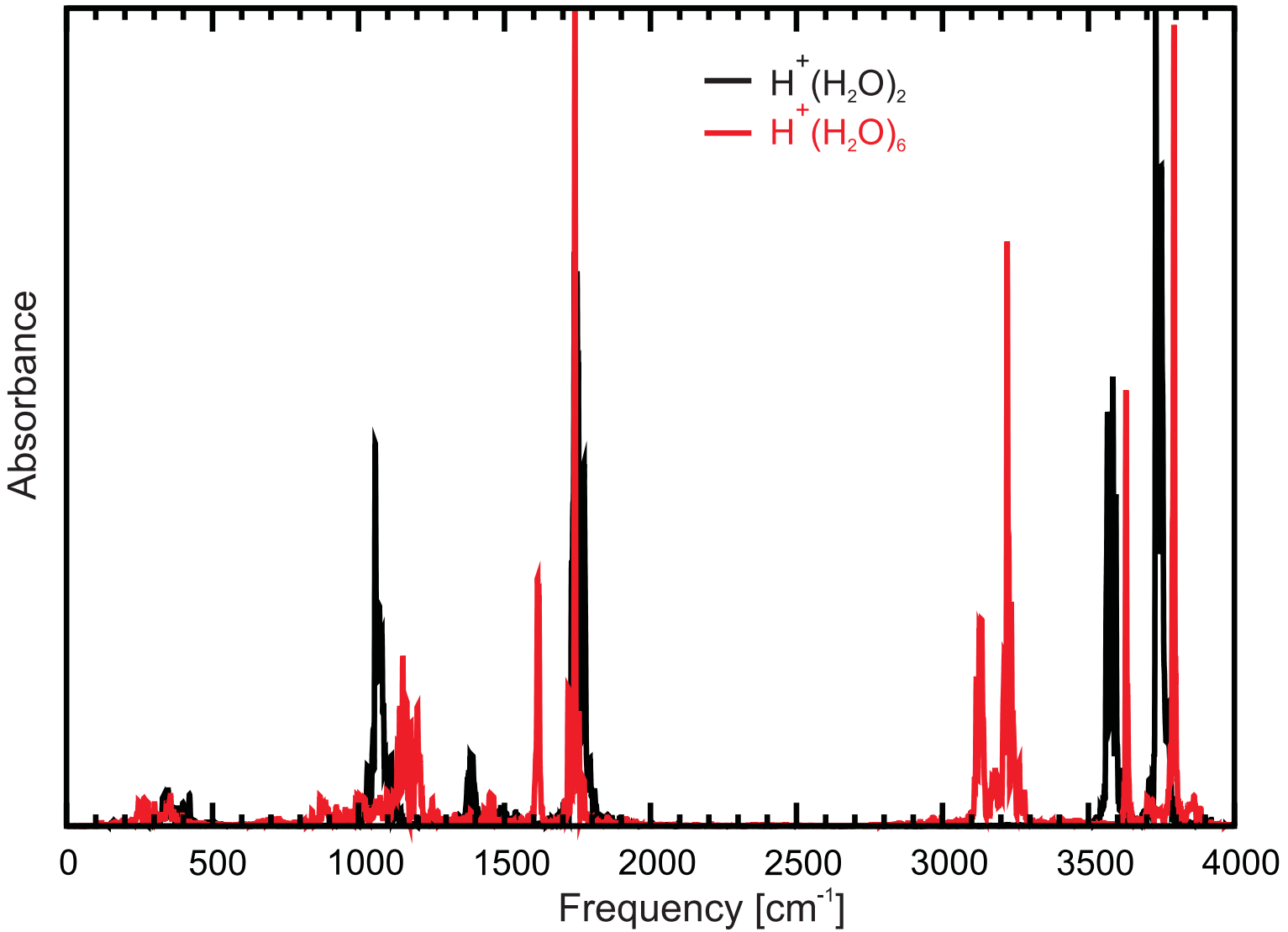
Thank you for attention

MS-EVB3 clusters

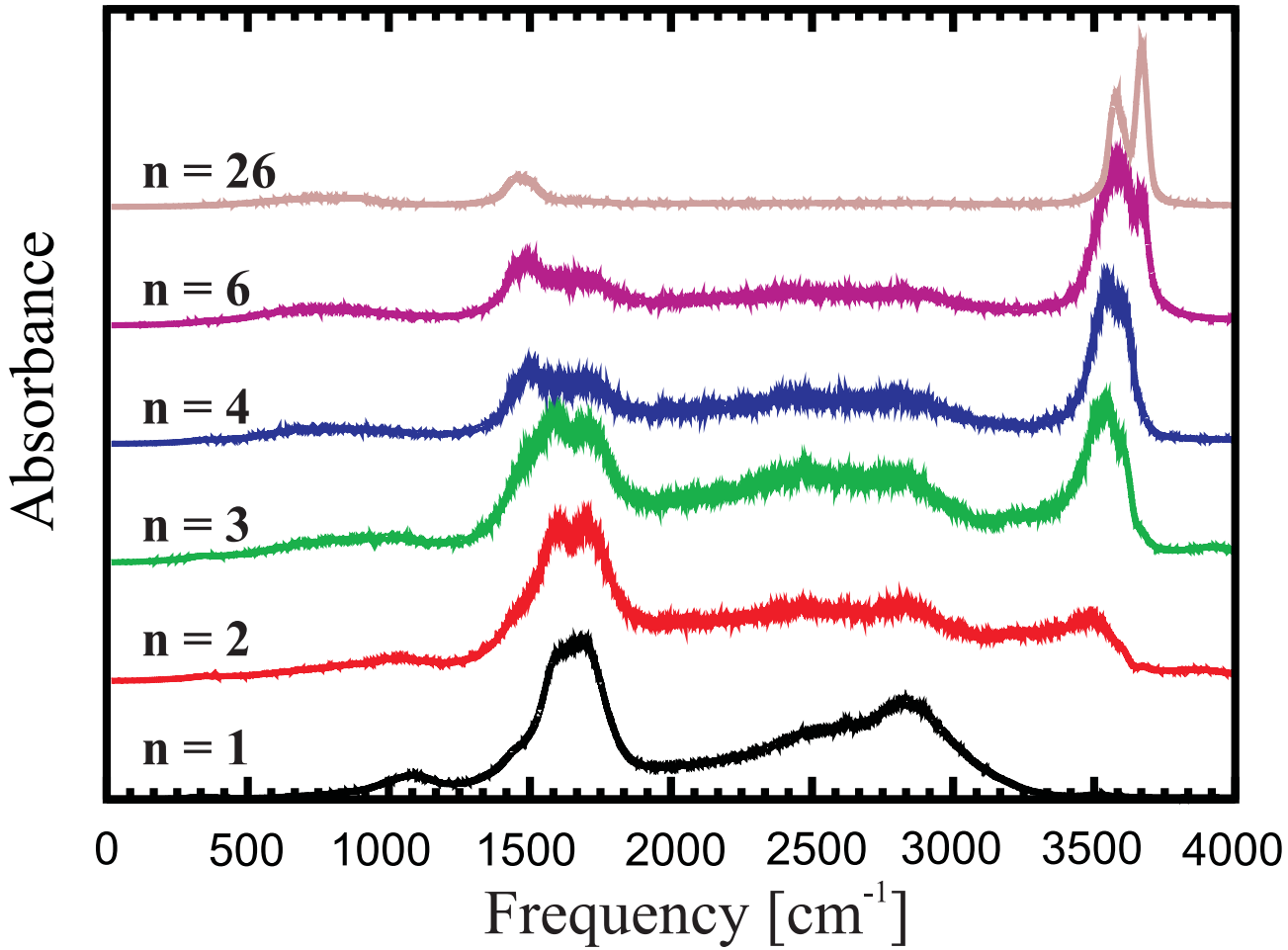


CP2K clusters

CP2K: BLYP/DZVP-GTH-BLYP/300Ry/50K/SIC



$H^+(H_2O)_n$ clusters



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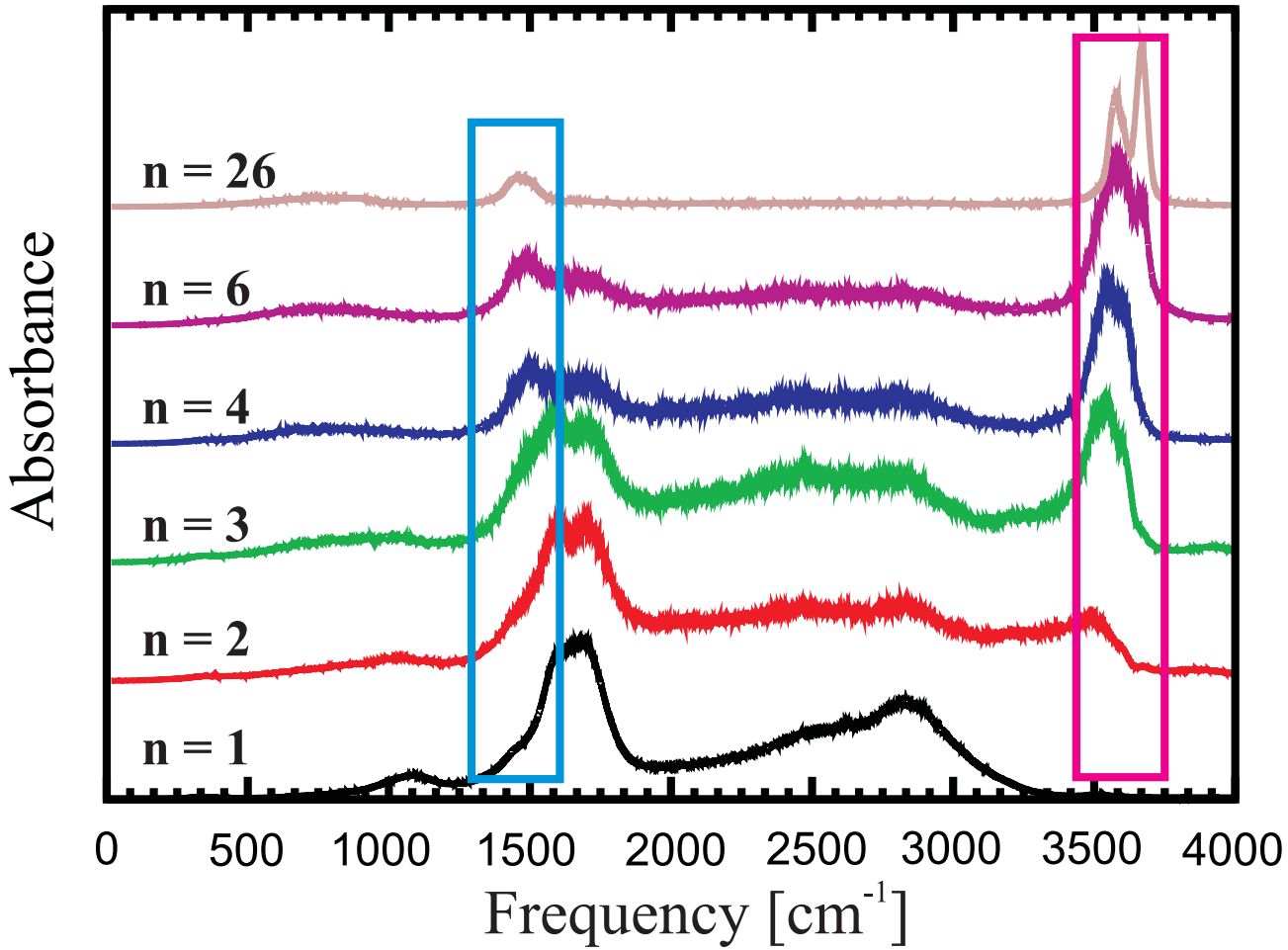
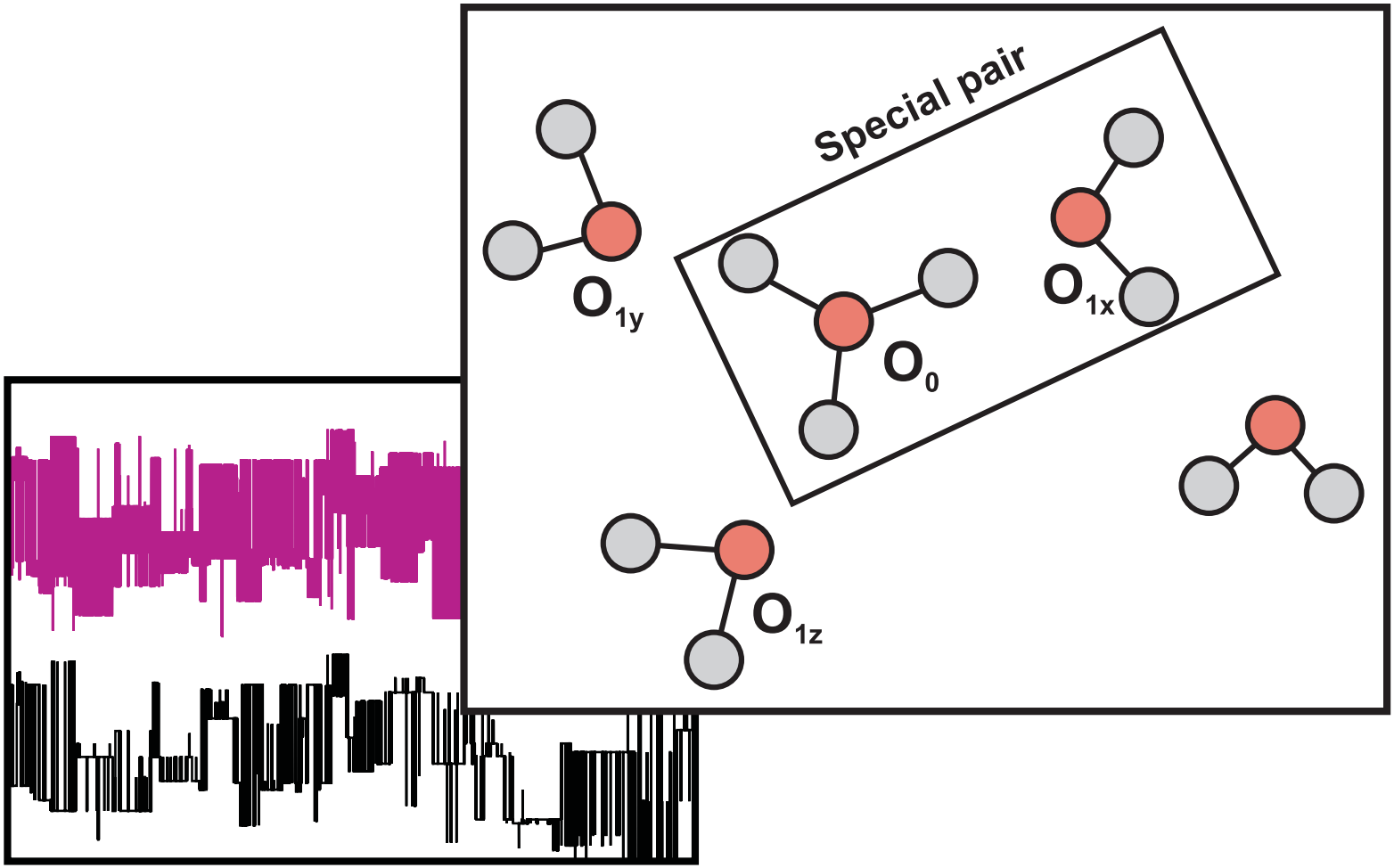


free H-O-H bending mode

free O-H stretching mode

Identity criterion



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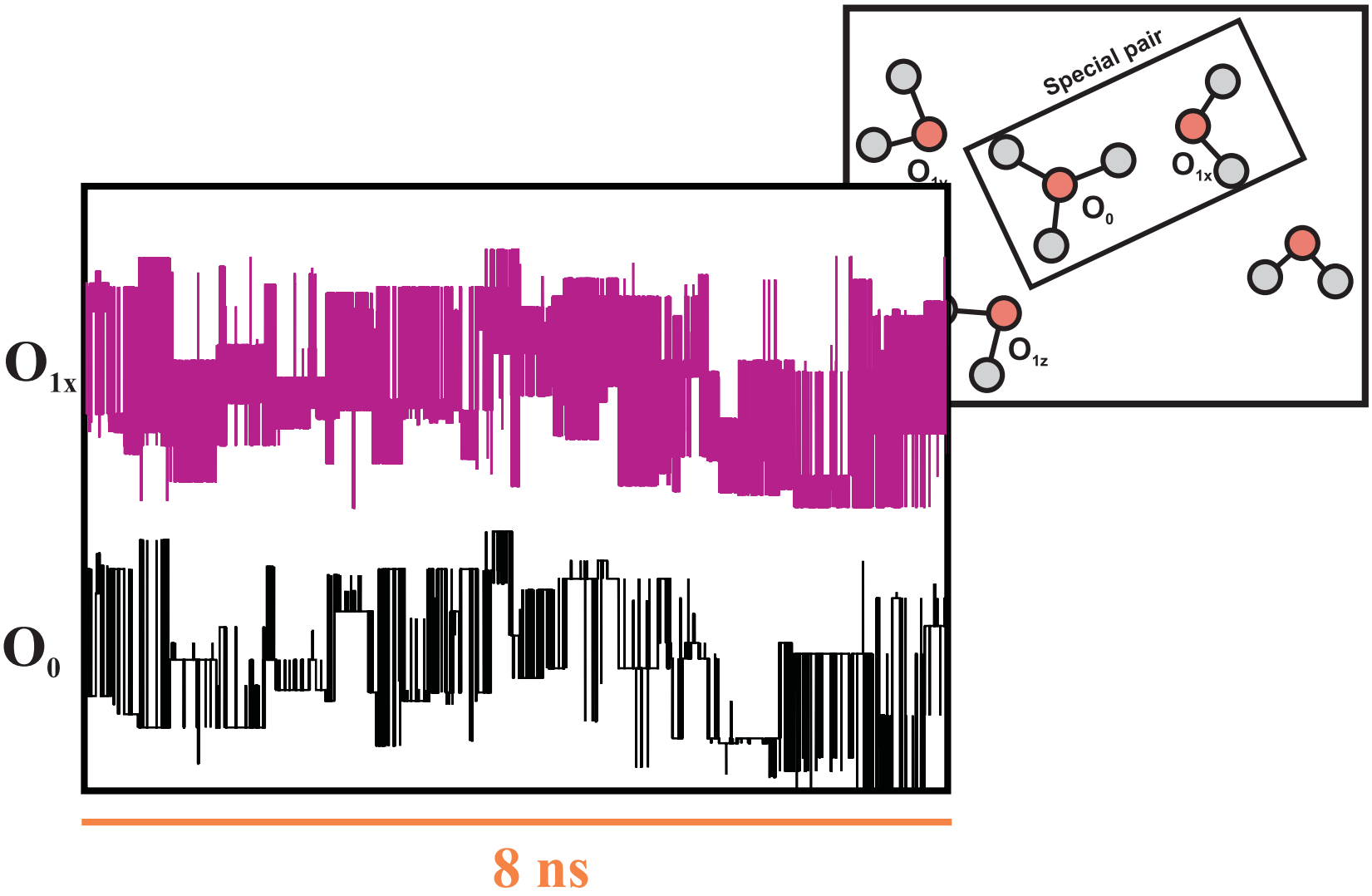

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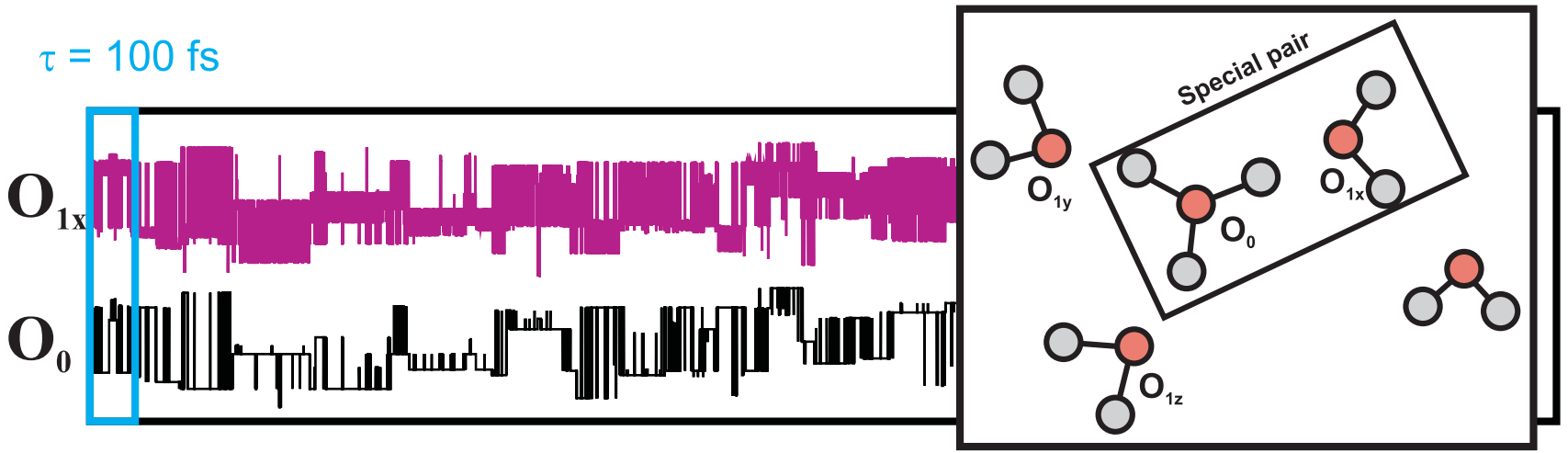
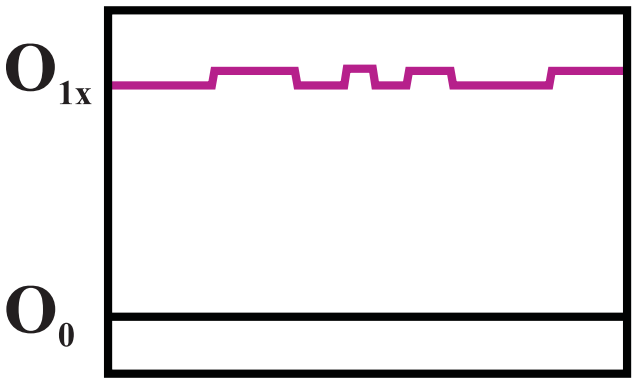


8 ns



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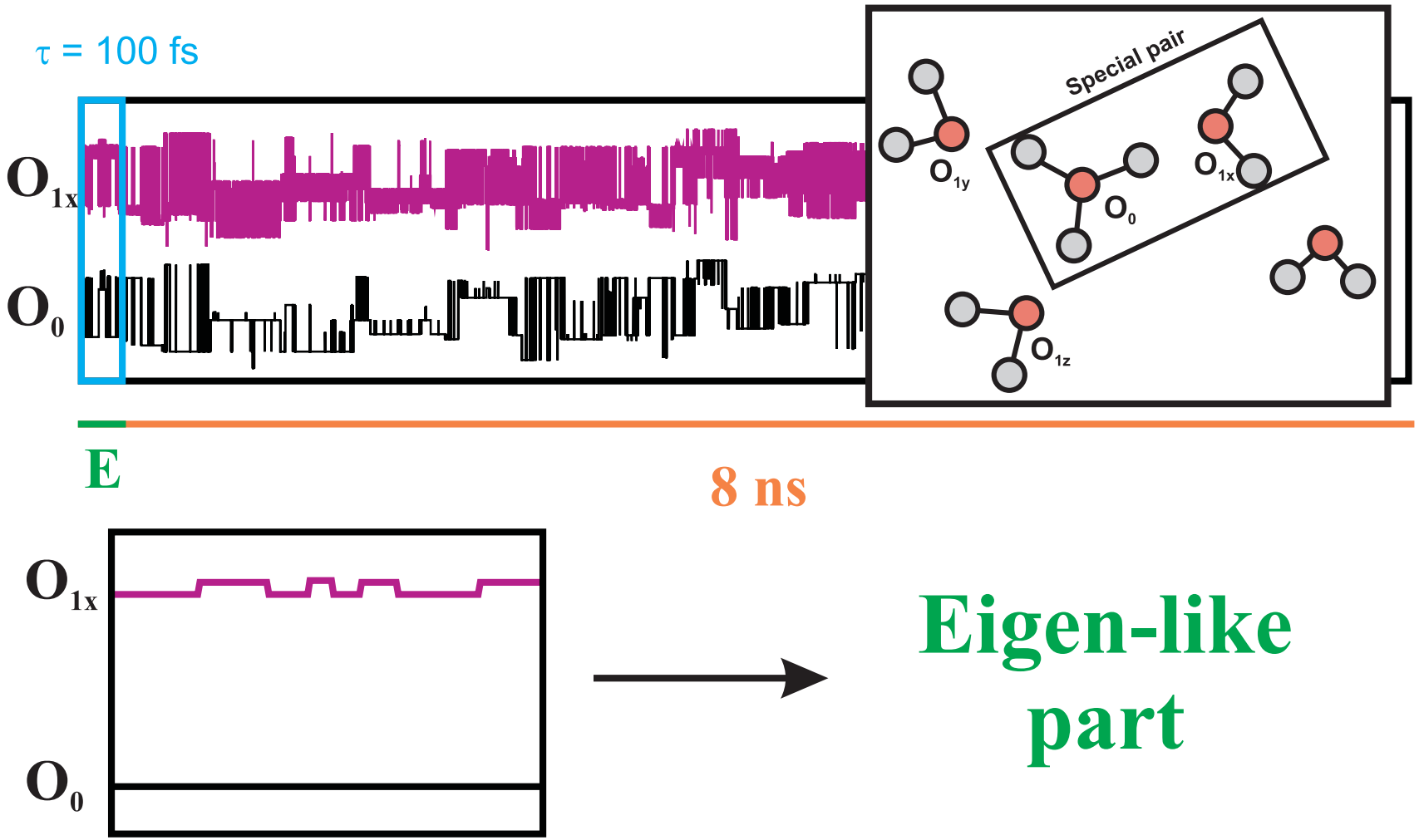

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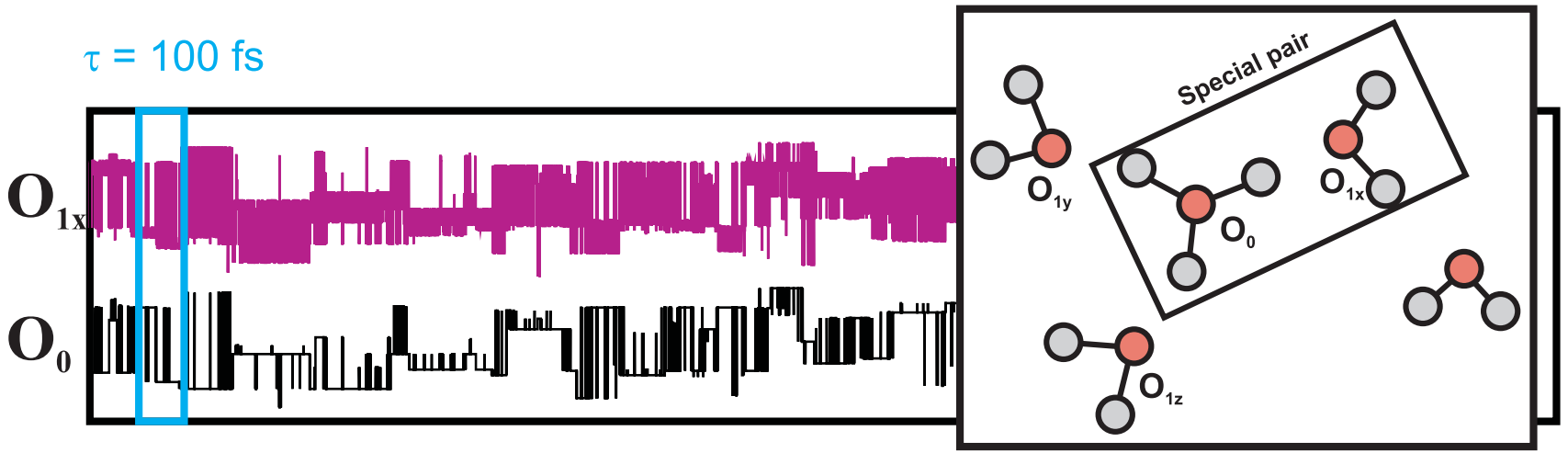
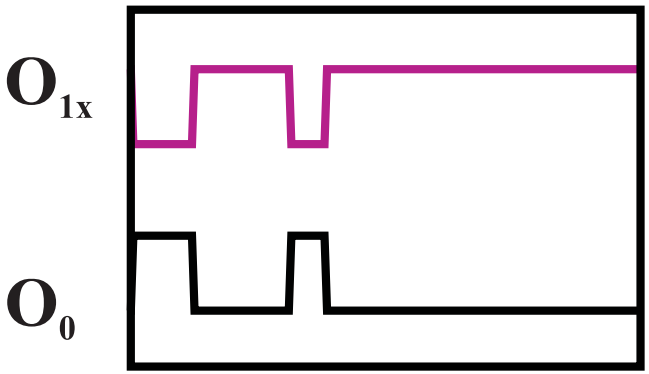


E

8 ns



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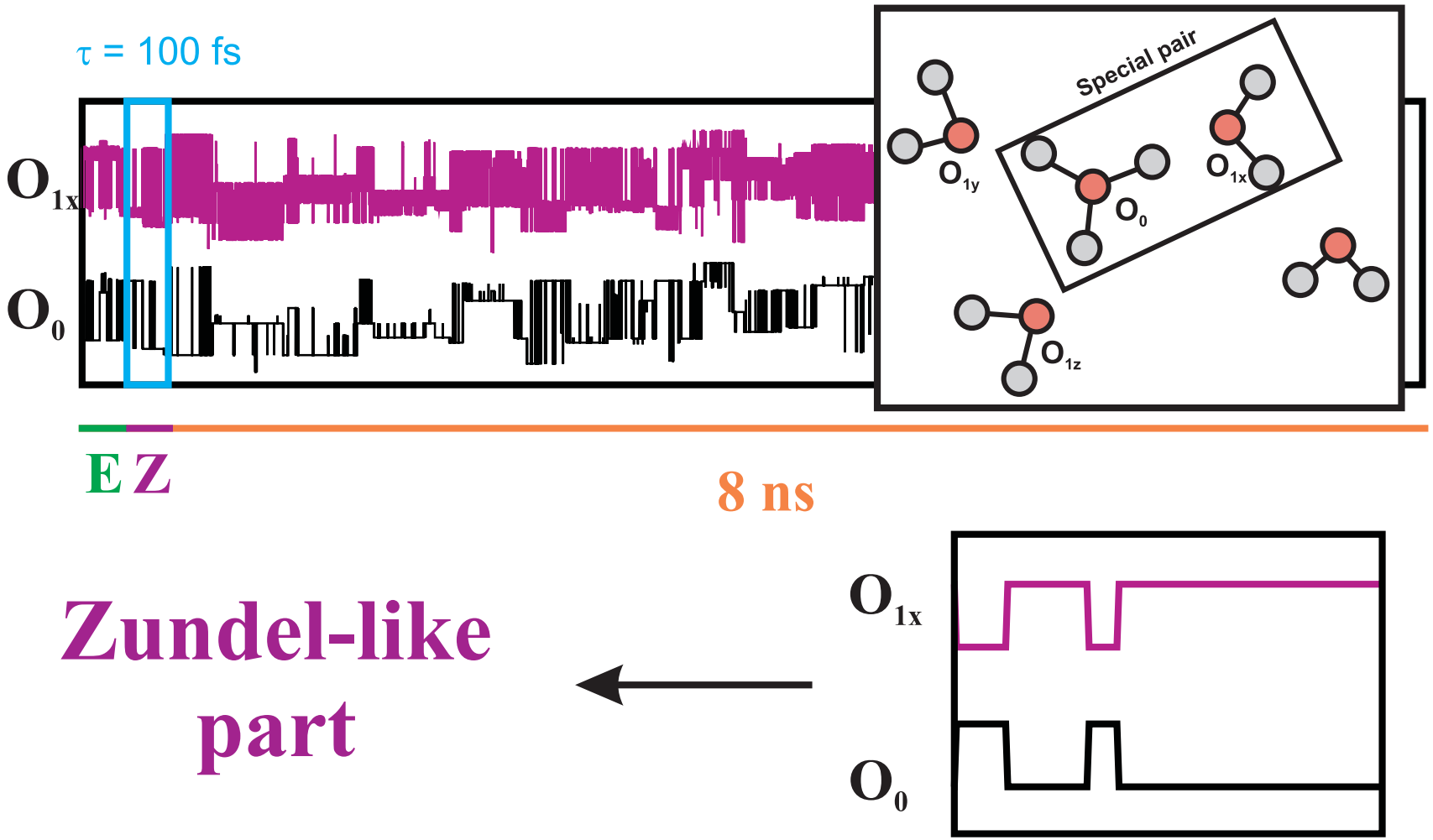

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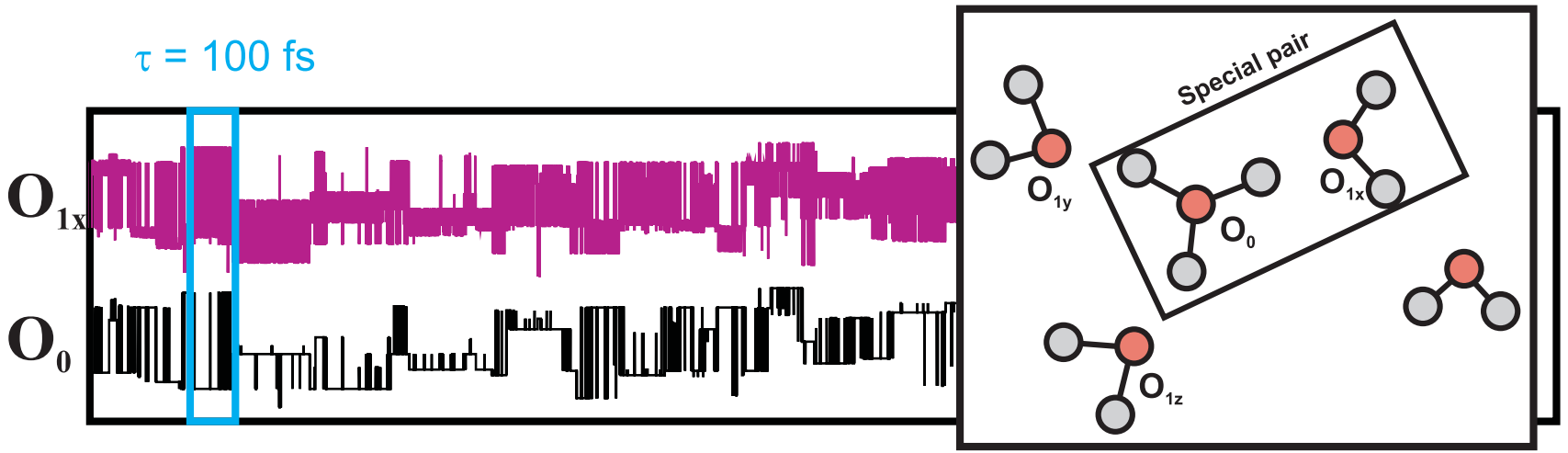
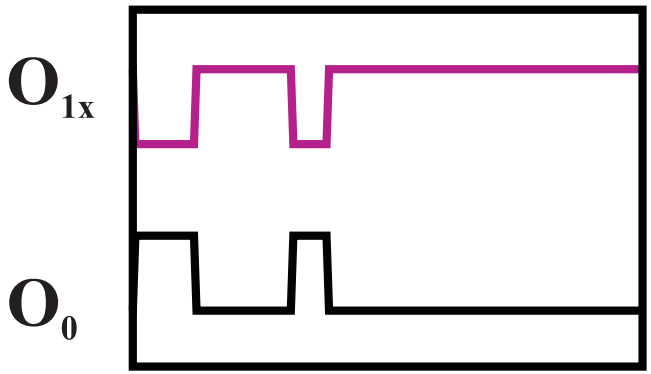


EZZ

8 ns

Zundel-like part



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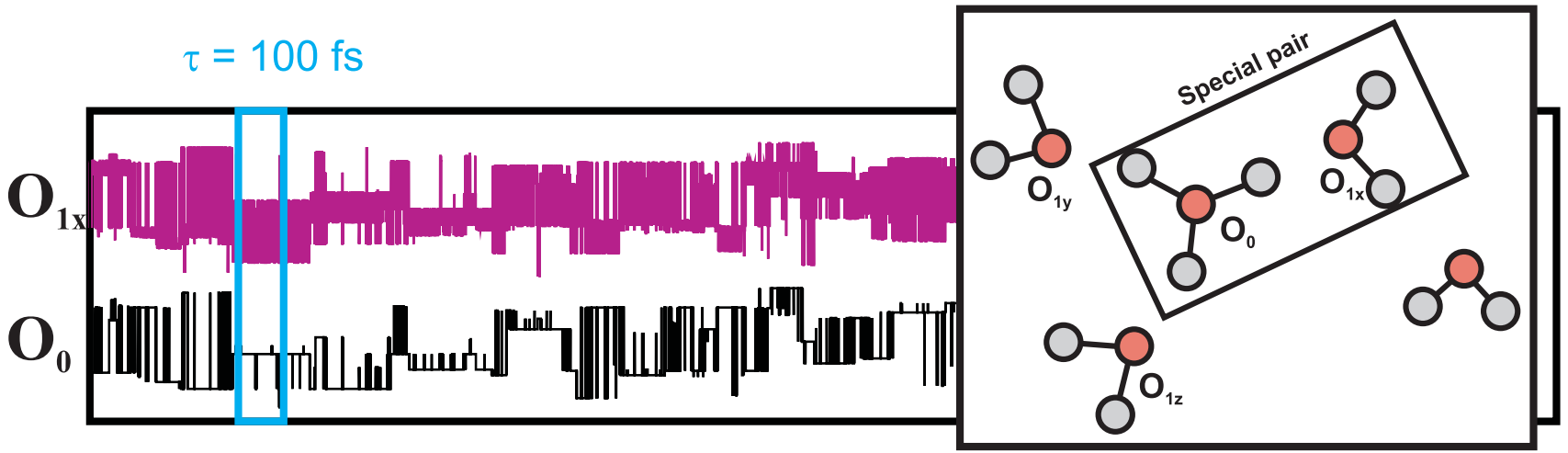
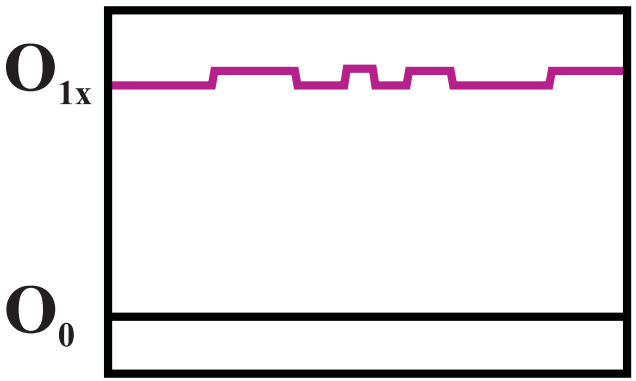
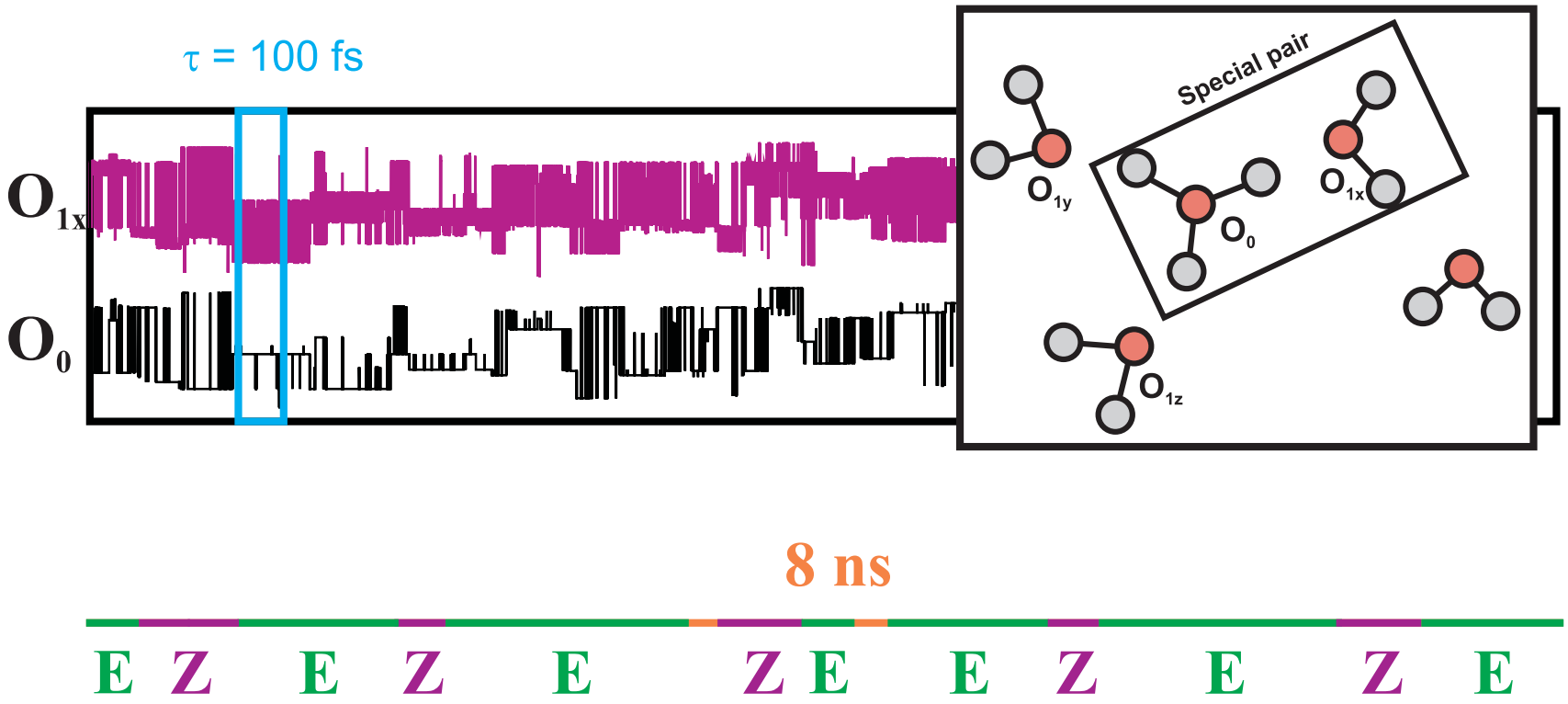


E Z Z E **8 ns**



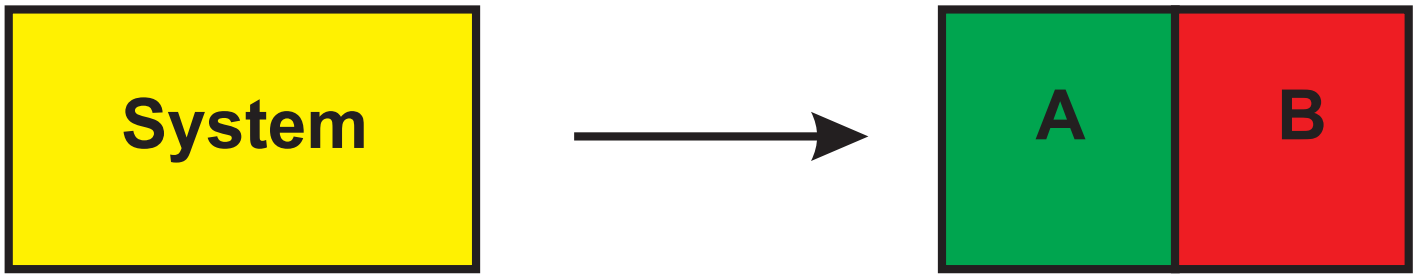
Eigen-like part

Identity criterion



ACF in *'clusters-in-liquid'* approach

$$I(\omega) \approx \int dt\, e^{-i\omega t} \langle \dot{\boldsymbol{\mu}}(0) \dot{\boldsymbol{\mu}}(t) \rangle$$



$$\mathrm{ACF}_{\mathrm{system}} \overset{?}{=} \mathrm{ACF}_{\mathrm{A}} + \mathrm{ACF}_{\mathrm{B}}$$

ACF in *'clusters-in-liquid'* approach

$$I(\omega) \approx \int dt\, e^{-i\omega t} \langle \dot{\boldsymbol{\mu}}(0) \dot{\boldsymbol{\mu}}(t) \rangle$$

$$ACF_A = \langle \dot{\boldsymbol{\mu}}_A(0) \dot{\boldsymbol{\mu}}_A(t) \rangle$$
$$ACF_B = \langle \dot{\boldsymbol{\mu}}_B(0) \dot{\boldsymbol{\mu}}_B(t) \rangle$$

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$$ACF_{AB} = \langle \dot{\boldsymbol{\mu}}_{AB}(0)\dot{\boldsymbol{\mu}}_{AB}(t)\rangle = \langle \dot{\boldsymbol{\mu}}_A(0)\dot{\boldsymbol{\mu}}_A(t) + \dot{\boldsymbol{\mu}}_B(0)\dot{\boldsymbol{\mu}}_B(t) + \dot{\boldsymbol{\mu}}_A(0)\dot{\boldsymbol{\mu}}_B(t) + \dot{\boldsymbol{\mu}}_B(0)\dot{\boldsymbol{\mu}}_A(t)\rangle$$

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$$ACF_{AB} = ACF_A + ACF_B + \langle \dot{\boldsymbol{\mu}}_A(0)\dot{\boldsymbol{\mu}}_B(t) + \dot{\boldsymbol{\mu}}_B(0)\dot{\boldsymbol{\mu}}_A(t)\rangle$$

ACF in *'clusters-in-liquid'* approach

$$I(\omega) \approx \int dt\, e^{-i\omega t} \langle \dot{\boldsymbol{\mu}}(0) \dot{\boldsymbol{\mu}}(t) \rangle$$

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$$I_{AB}(\omega) \neq I_A(\omega) + I_B(\omega)$$