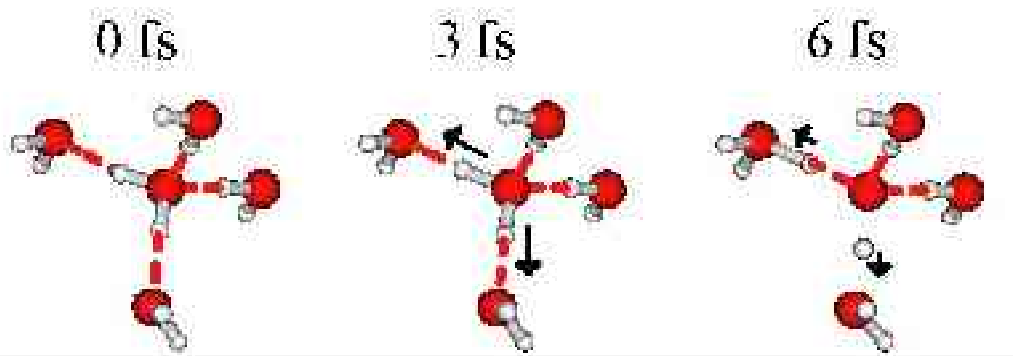
Ultrafast core hole induced dynamics in ice and water probed by xray emission spectroscopy

Michael Odelius

(Stockholm University)



Quantum Chemistry:

Lars G. M. Pettersson (Stockholm)

Barbara Brena

Experiment:

Anders Nilsson (Stockholm and Stanford)

Dennis Nordlund

Hirohito Ogasawara

More Experiments:

Clemens Heske (Würzburg -> Las Vegas)

Eberhard Umbach (Würzburg)

Oliver Fuchs

Lothar Weinhardt

Florian Maier

Michael Grunze (Heidelberg)

Yan Zubavichus

Jonathan D. Denlinger (ALS, Berkeley)

Michael.Odelius@physto.se

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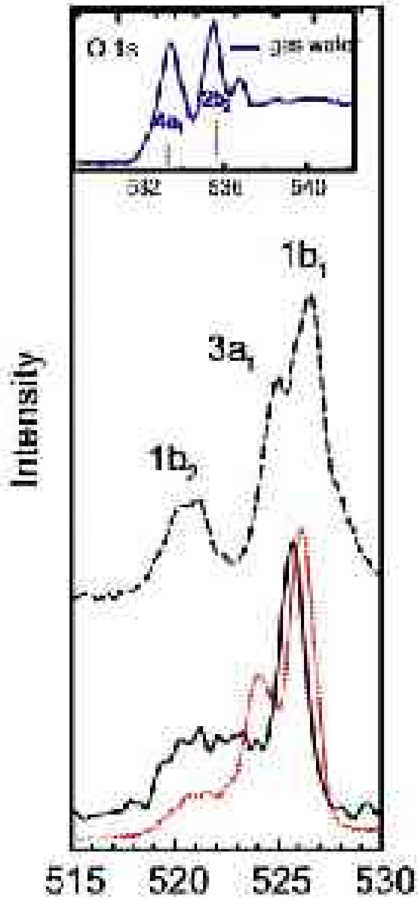
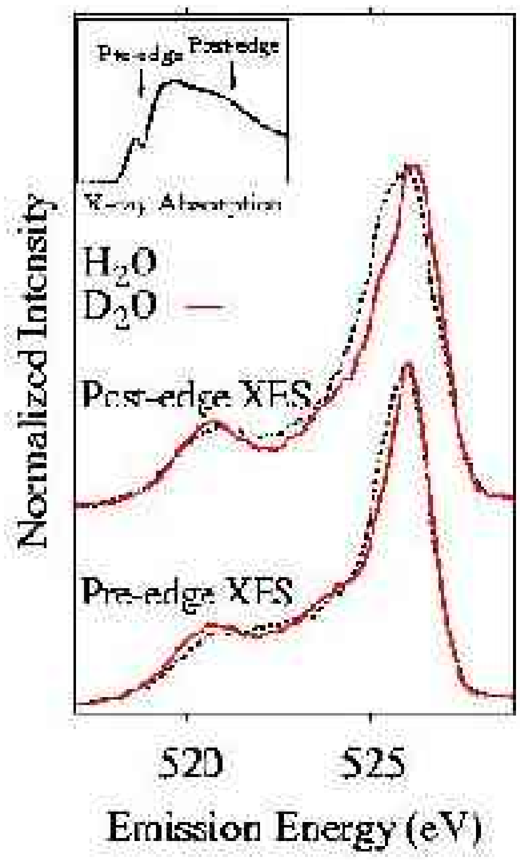
Simulations of Experimental XES of water

Gas Phase



Kastanov et al
PRB 69,024201 (2004)

Liquid Phase



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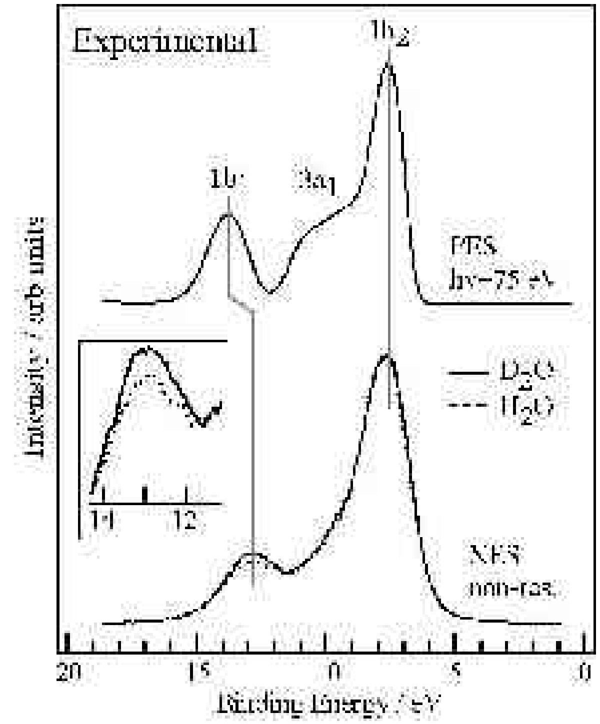
Submitted to PRL

Solid Phase



B.Brena et al. PRL
93,148302 (2004)

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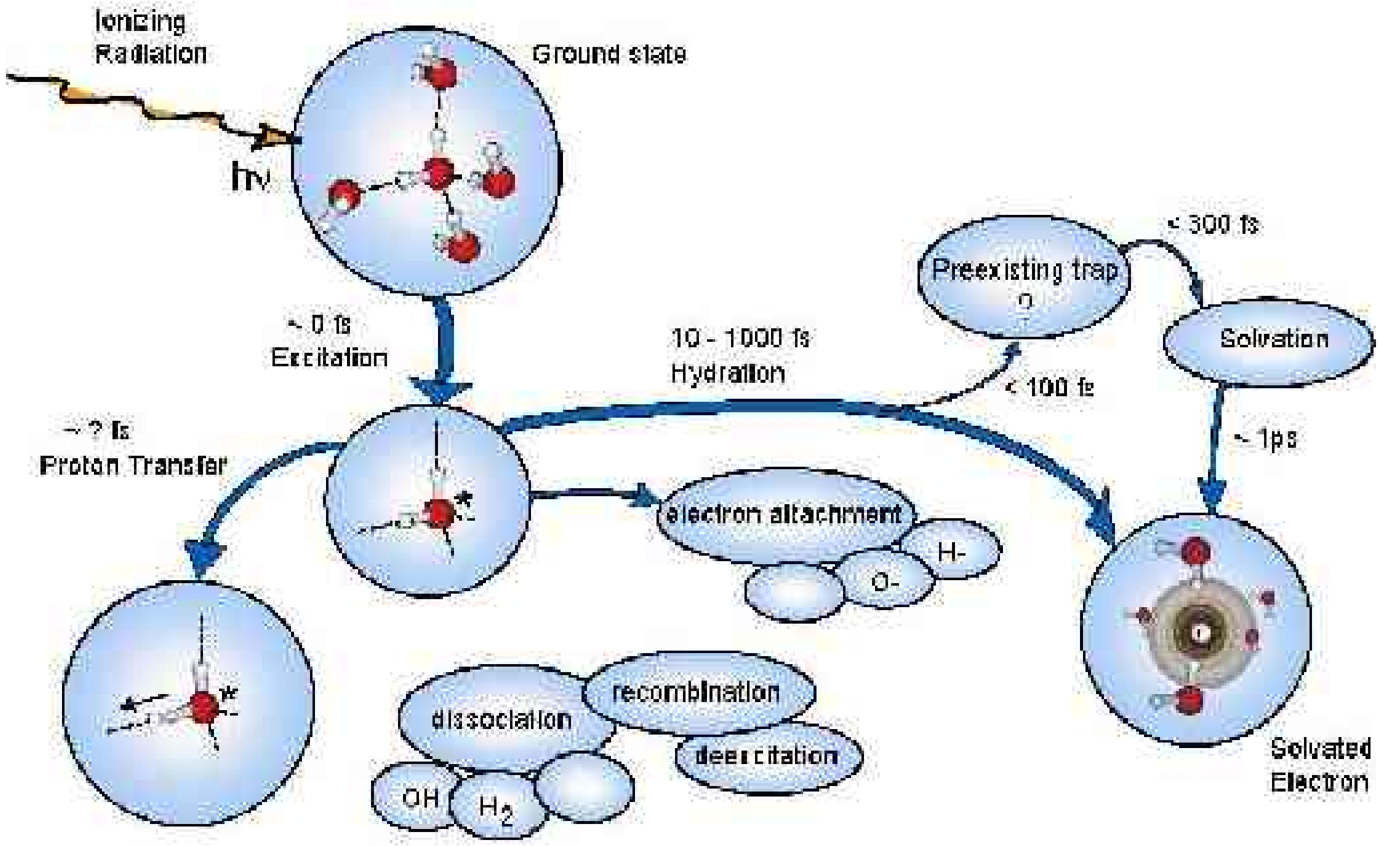
Objectives

- The electronic structure of water.
- Electron dynamics after core-excitations.
- How to correctly interpret x-ray emission spectra.



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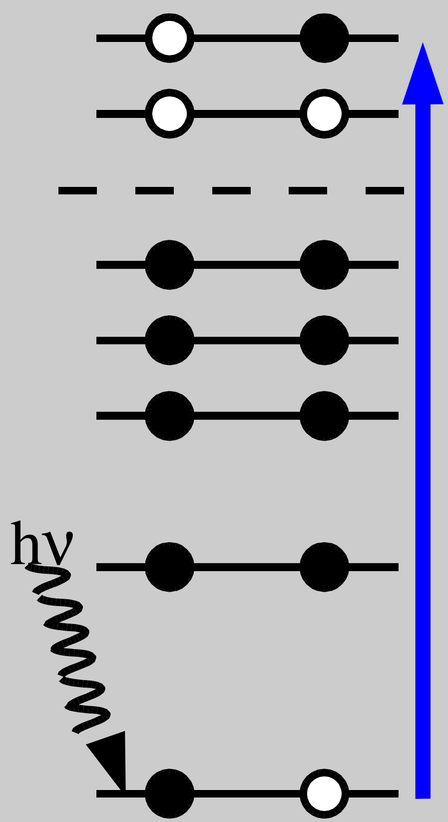
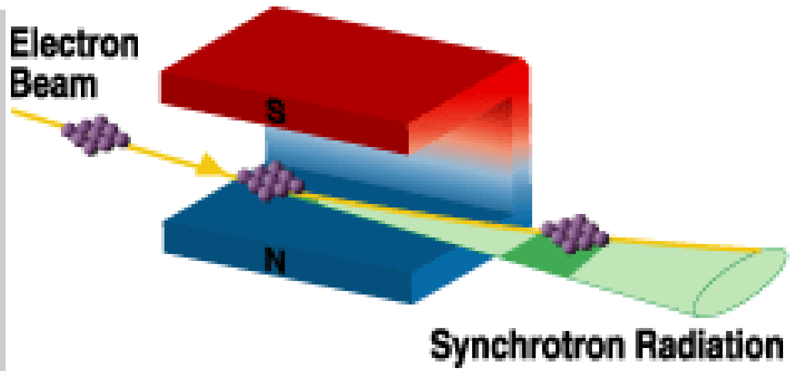
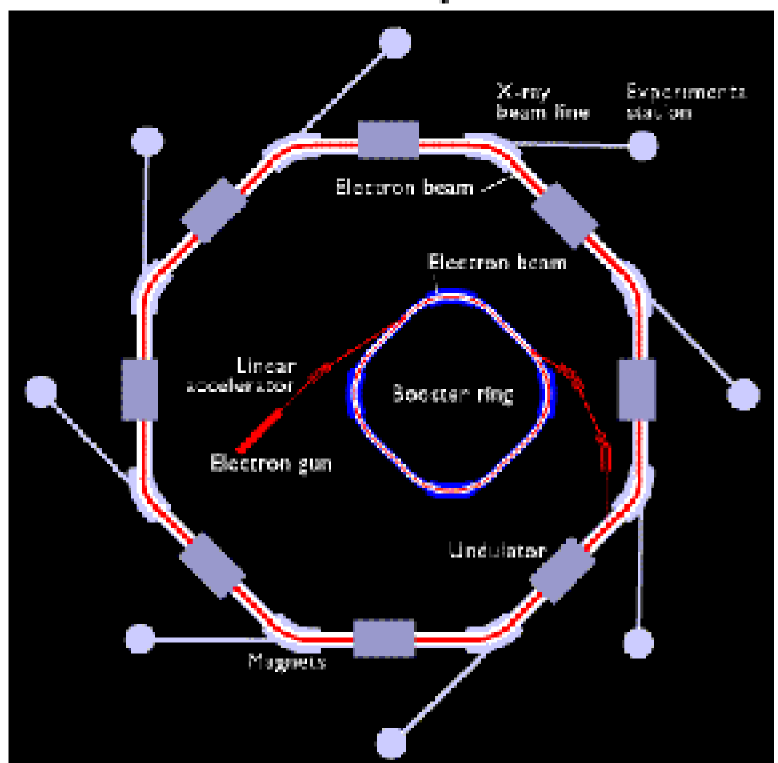
X-ray Absorption & Emission Spectroscopies

Core-excitation

XAS

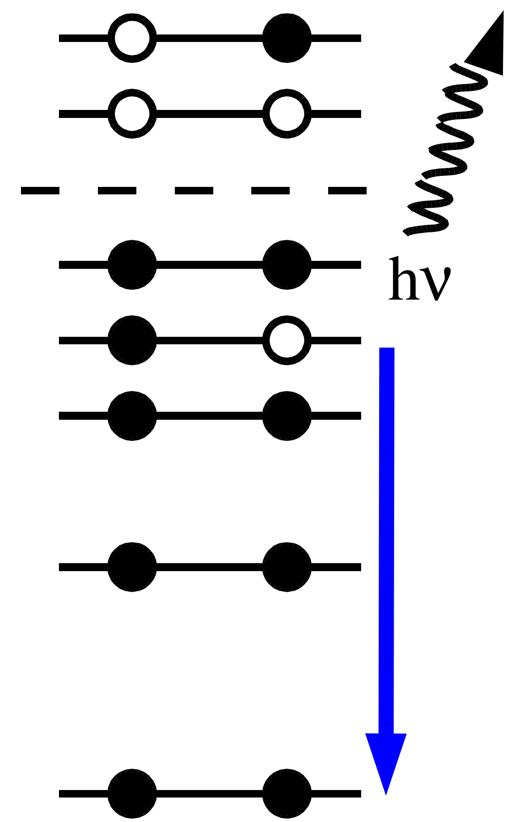






1% Radiant

XES



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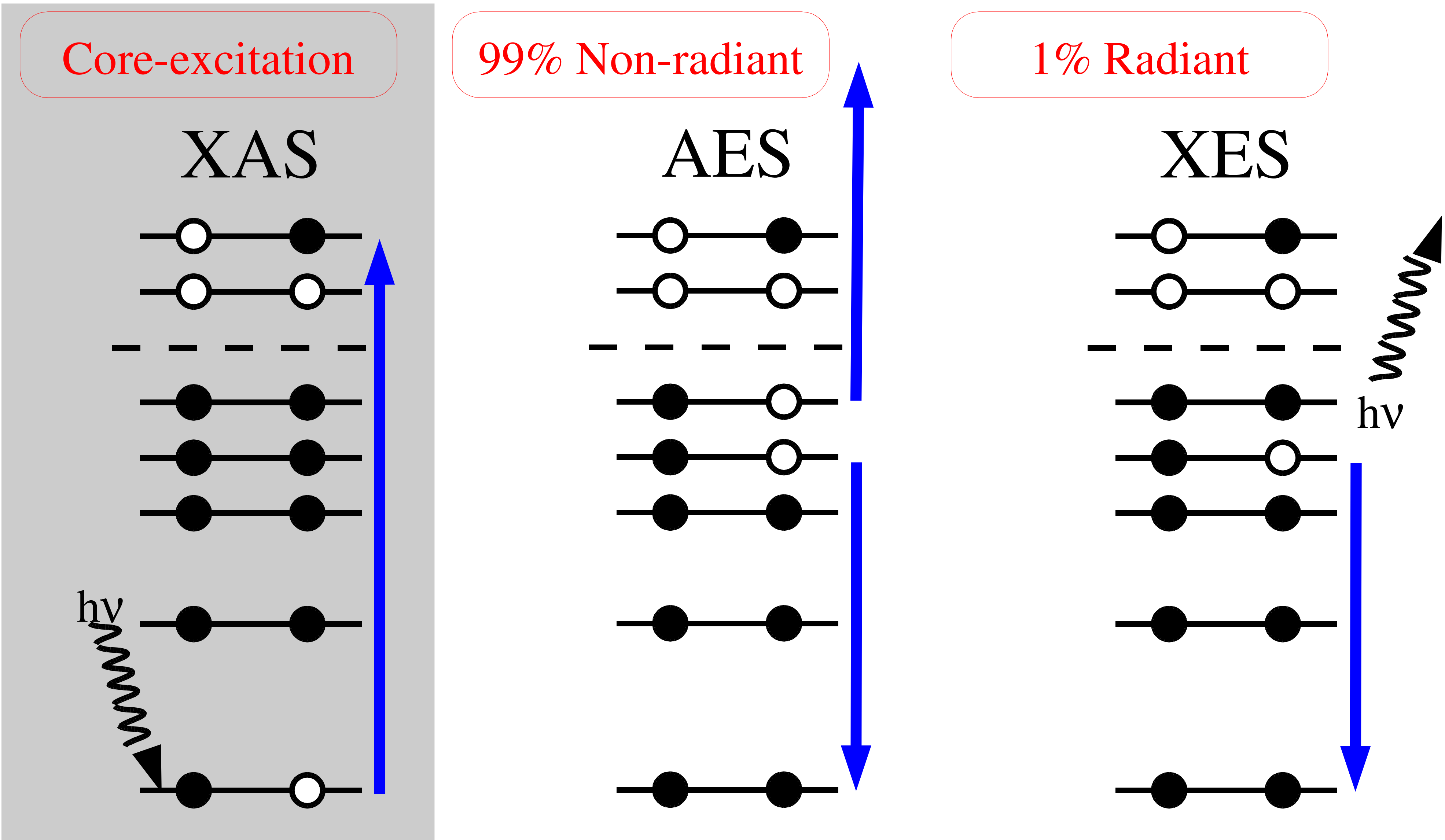
Core-level Decay Spectroscopies



Osamu Takahashi (Hiroshima)

Michael.Odelius@physto.se

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Case study: Water

2b1 2b2 Anti-bonding (O-H)

4a1 4a1 Anti-bonding (O-H)

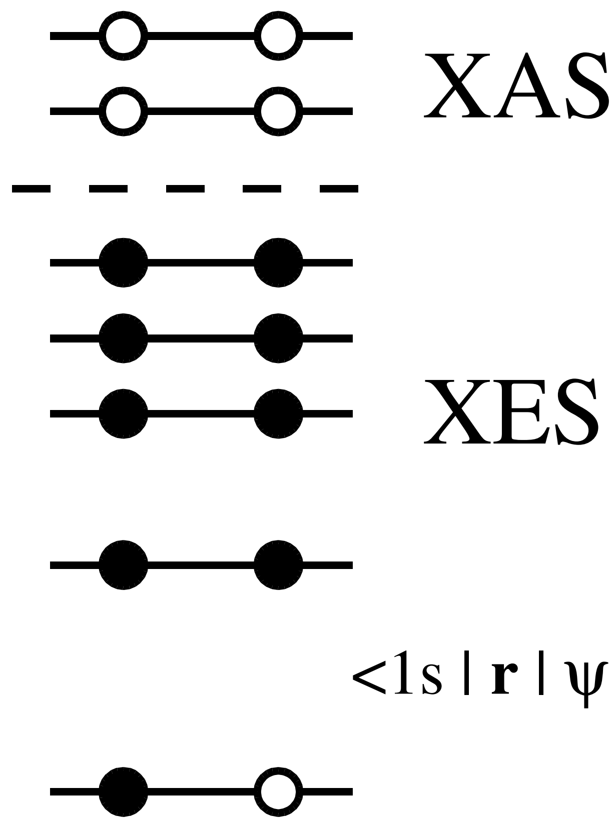
1b2 1b1 Non-bonding (O2p)

3a1 3a1 Bonding(O-H)

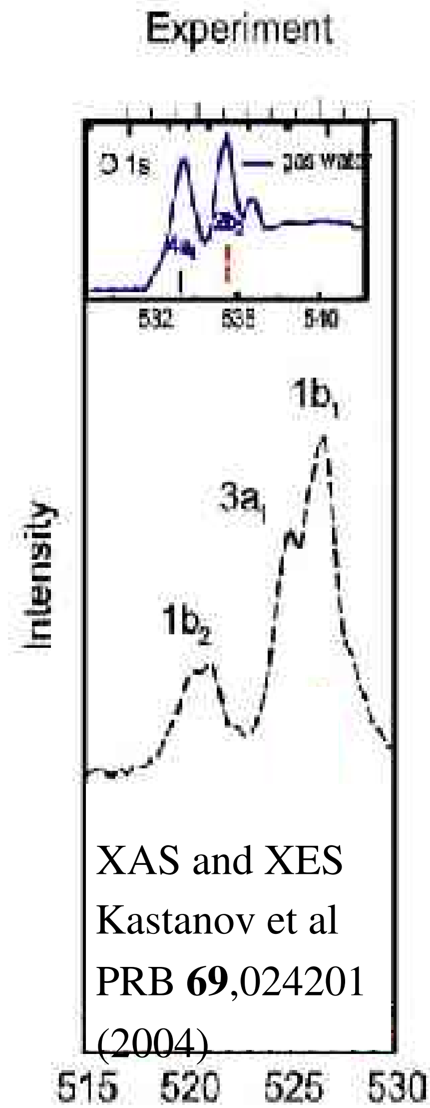
1b1 1b2 Bonding(O-H)

2a1 Dominantly O2s
("Invisible" in XES)

1a1 O1s core-orbit



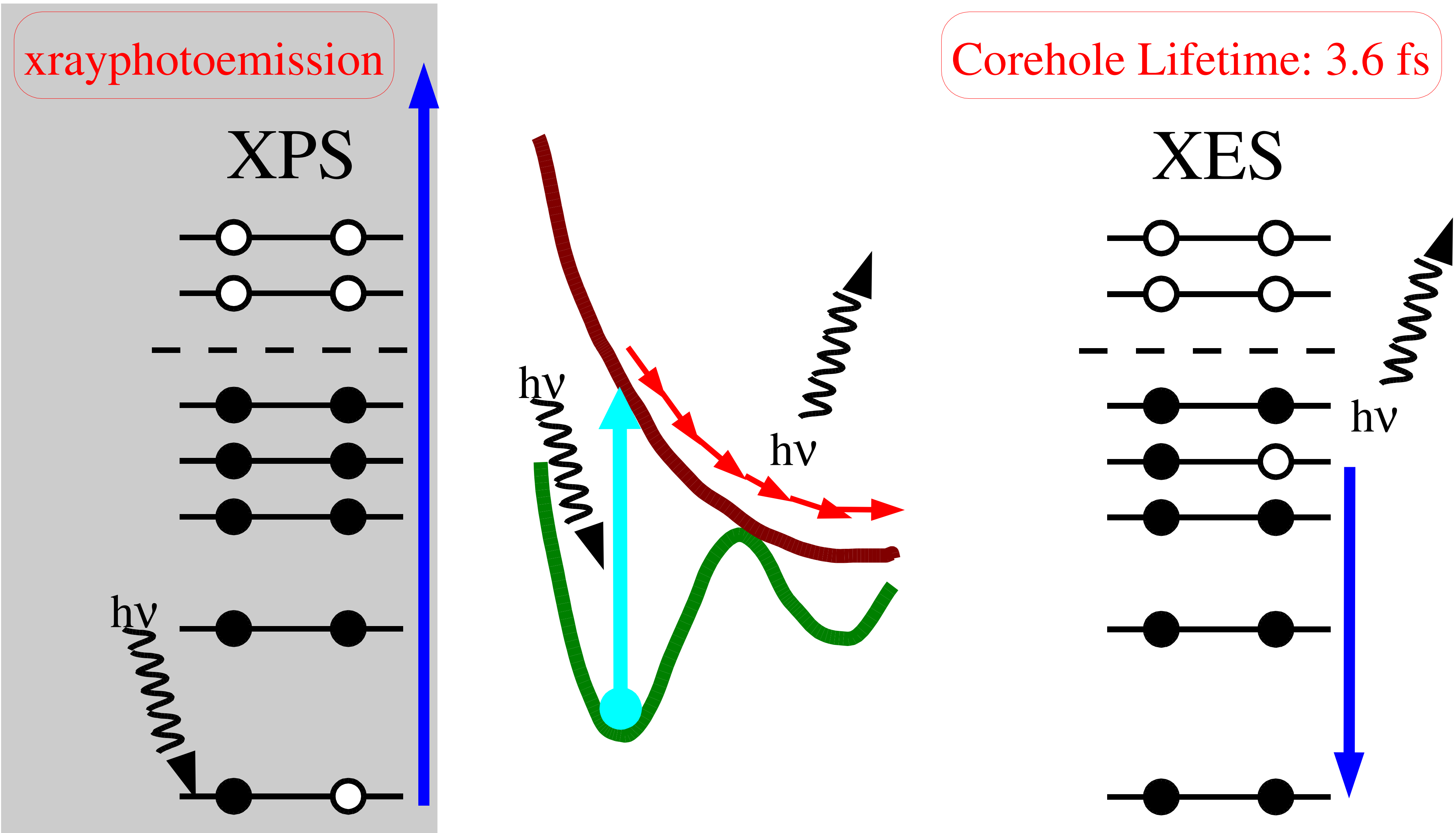
$<1s \mid \mathbf{r} \mid \psi>$



XAS and XES
Kastanov et al
PRB **69**,024201
(2004)

Michael.Odelius@physto.se

Core-excited State Dynamics



Michael.Odelius@physto.se

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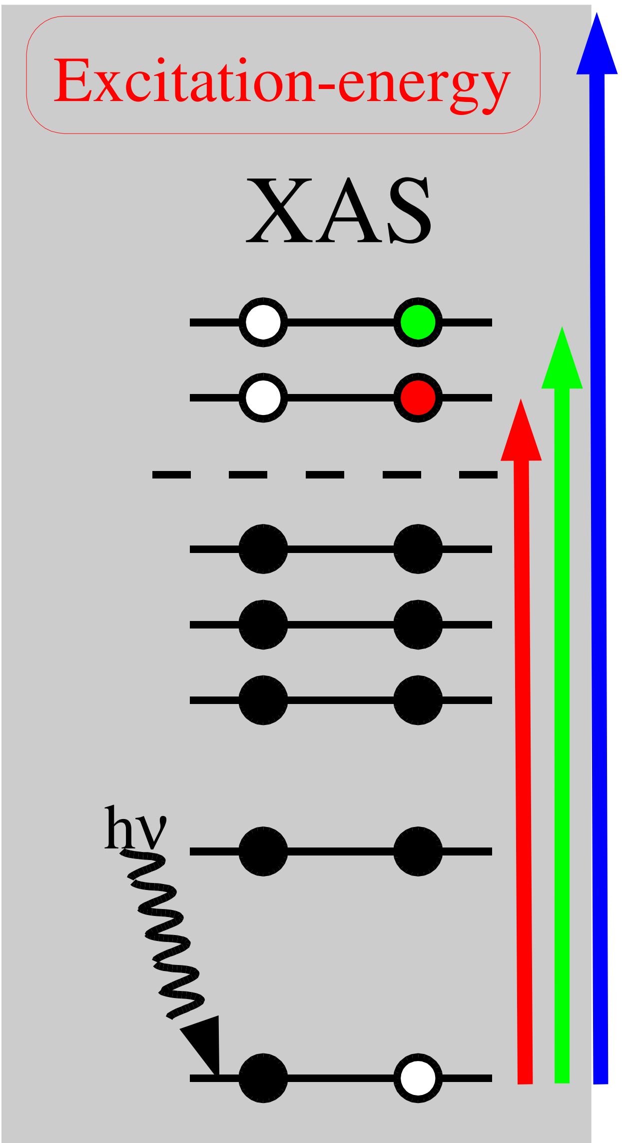
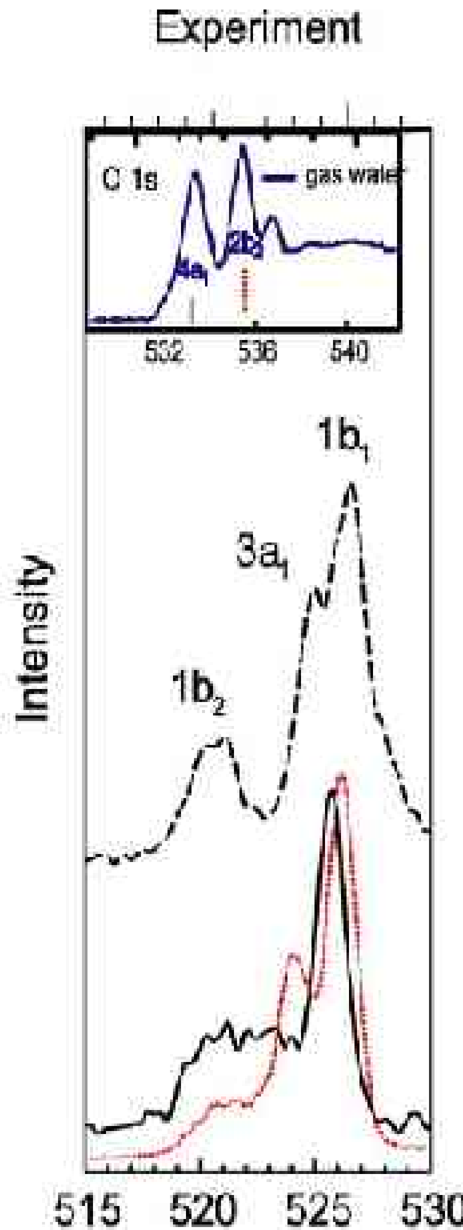
$H2O(g)$

Michael.Odelius@physto.se

The X-ray Emission Spectrum of H_2O(g)





Experimental data
Kastanov et al
PRB 69,024201 (2004)

Non-resonant XES (decay after Core-ionization)

Resonant XES (decay after Core-excitations)

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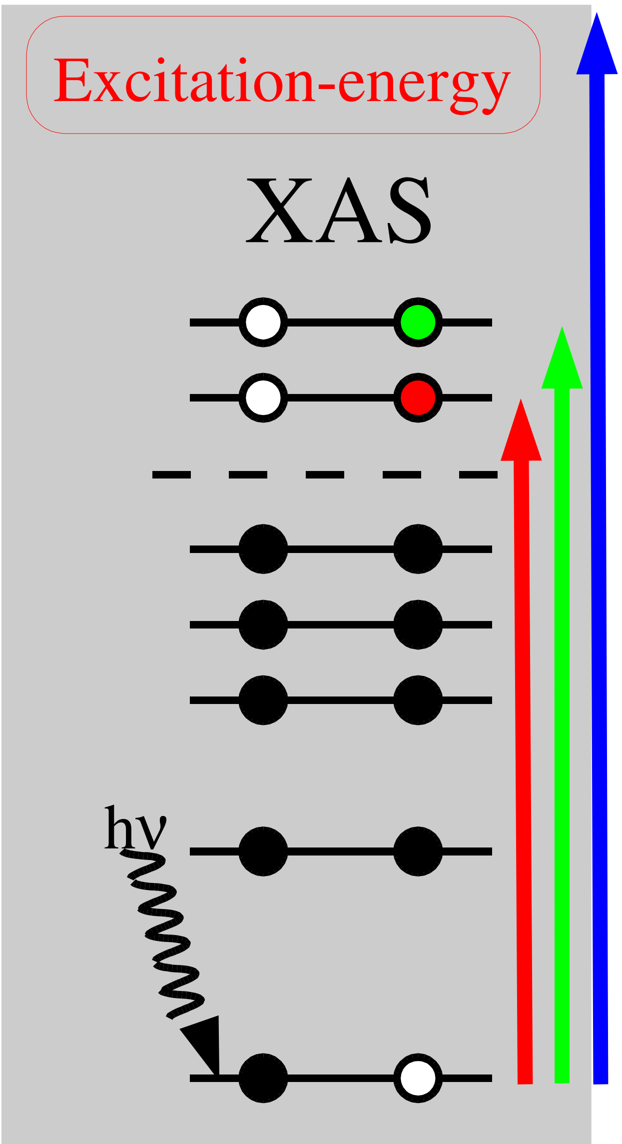
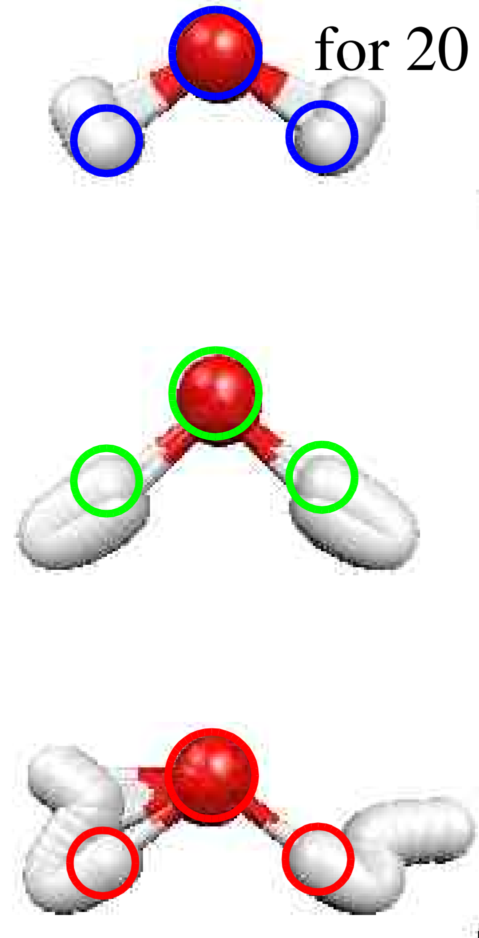
The X-ray Emission Spectrum of H2O(g)



Superimposed snapshots for 20 fs



Simulations performed with Stobe

- The core-ionized state only involves a change in bond angle
- The next-lowest core-hole excited state is bound but involves large O-H distortions
- Lowest (4a1) core-hole excited state is dissociative

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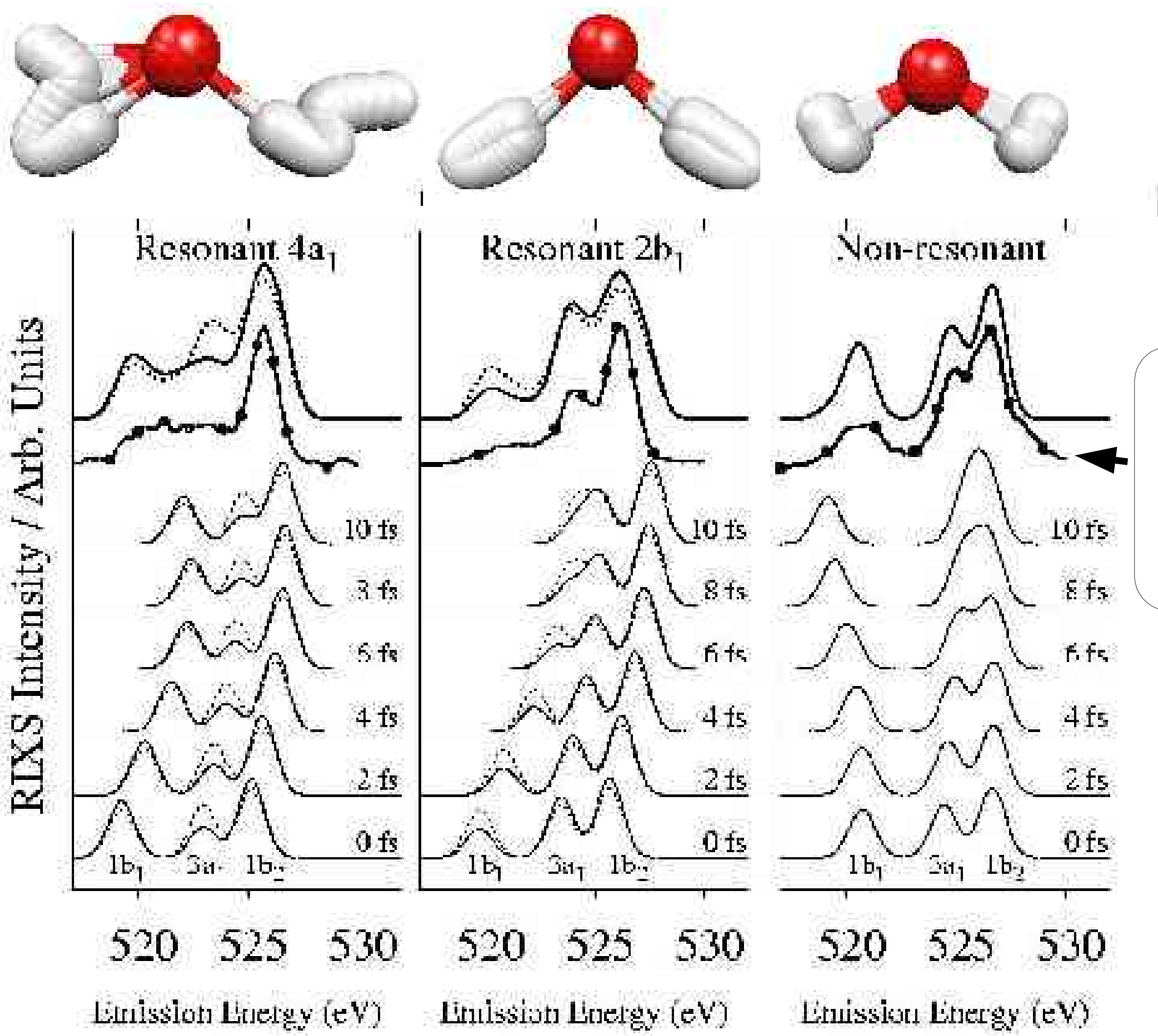
Michael.Odelius@physto.se

The X-ray Emission Spectrum of H2O(g)



Experimental data
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PRB 69,024201 (2004)

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H2O(s)

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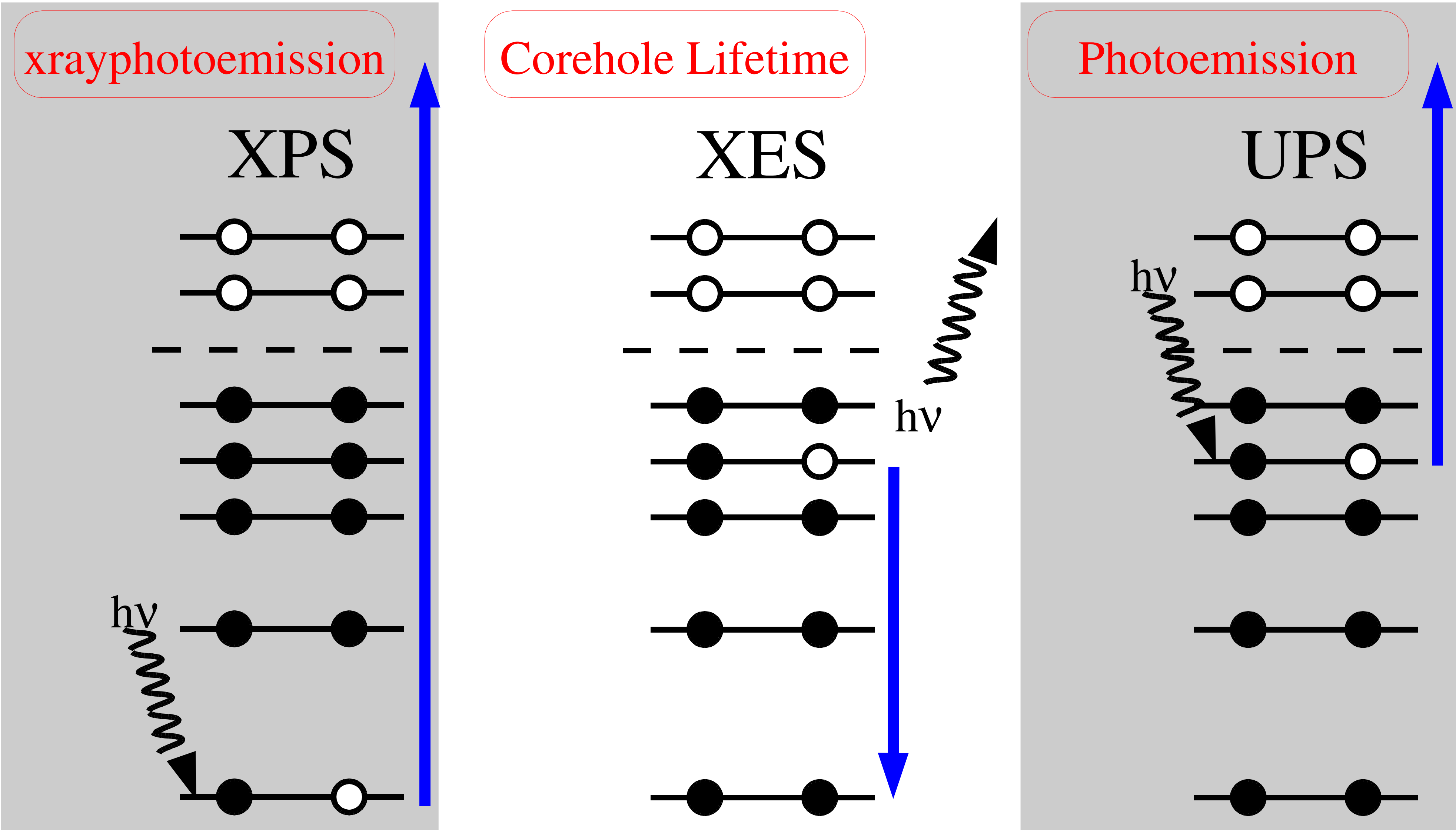
UPS versus XPS+XES: Same final state



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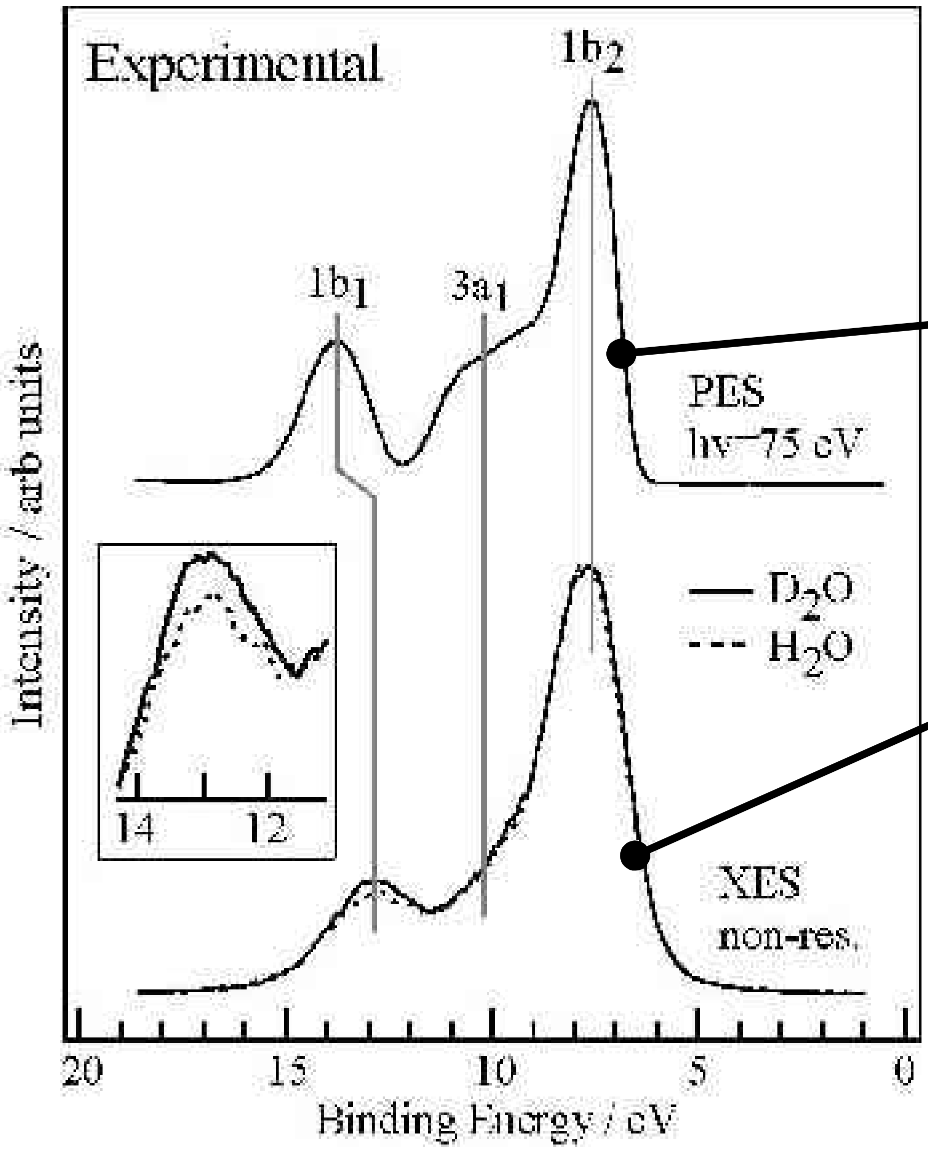
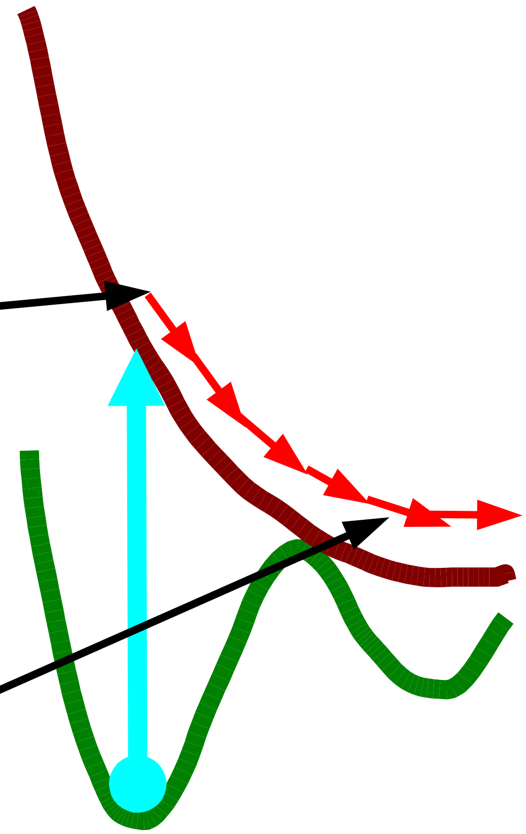
The X-ray Emission Spectrum of Ice





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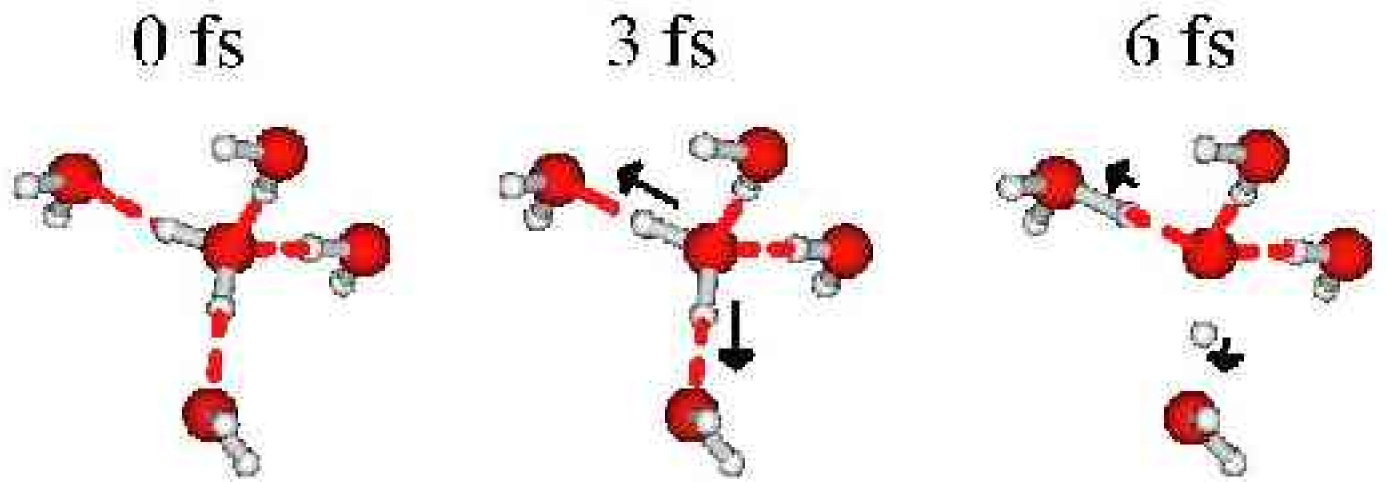
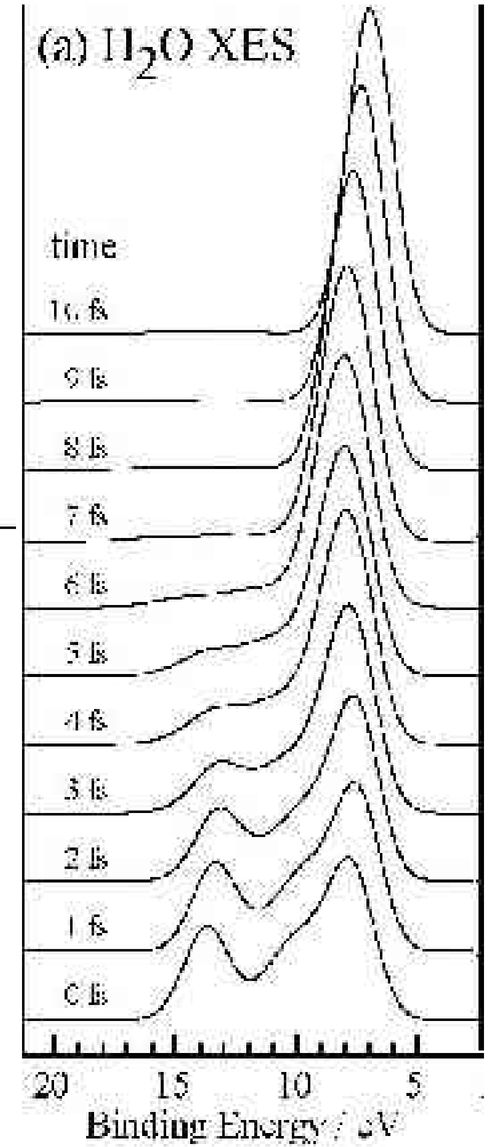
The X-ray Emission Spectrum of Ice





- Core-ionized state is also dissociative due to hydrogen bonding
- Sampling over many ground state configurations
- H2O and D2O MD simulations

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Michael.Odelius@physto.se

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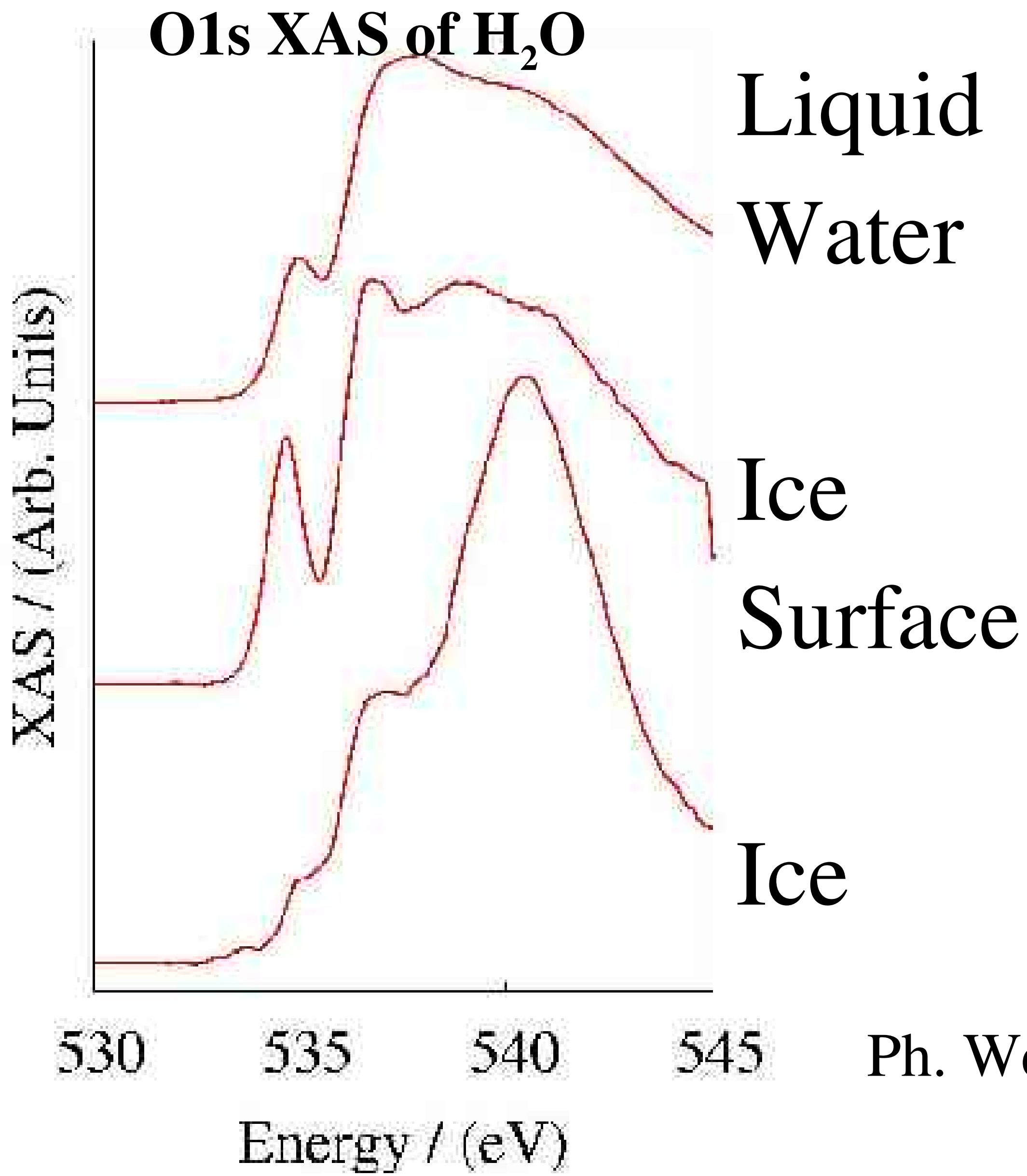
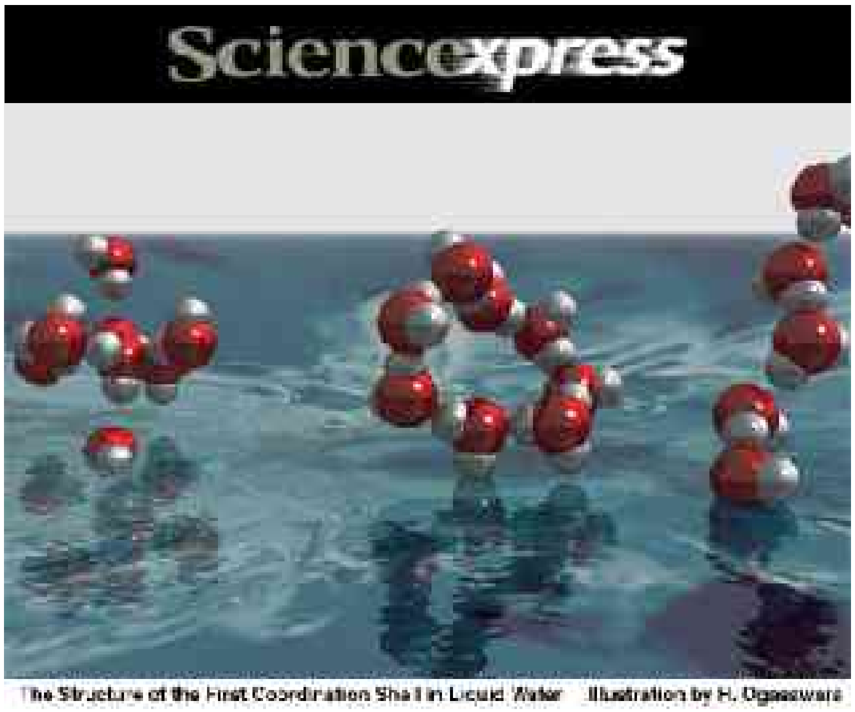
H2O(l)

Michael.Odelius@physto.se

The X-ray Absorption Spectrum of Water



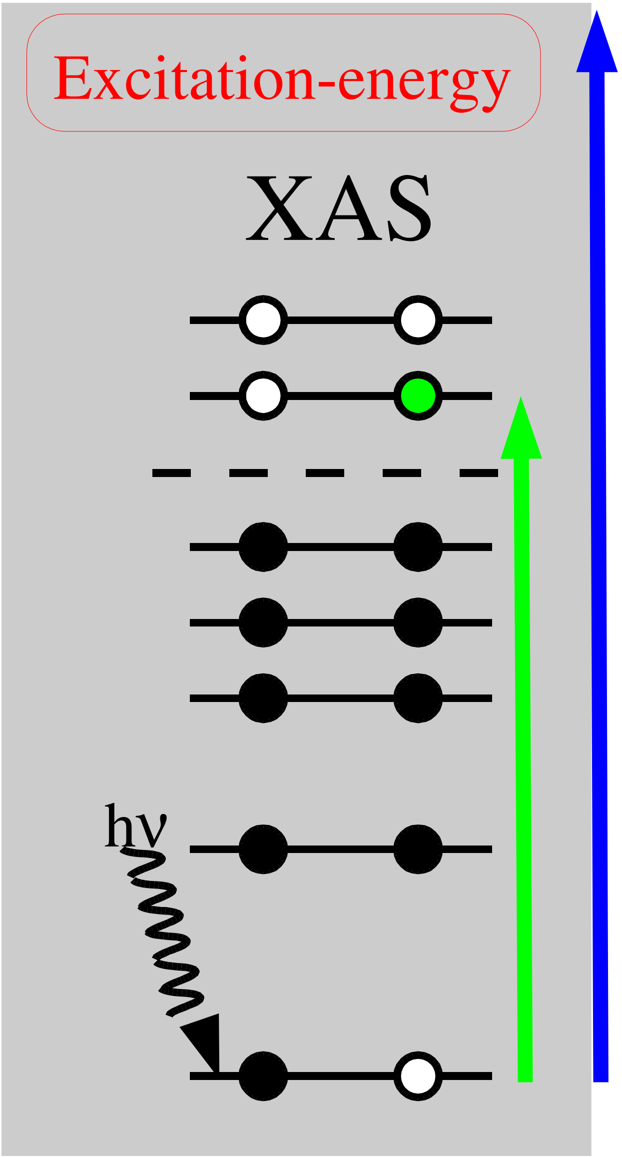
Water contains a large fraction of uncoordinated H-bonds



Ph. Wernet et al. Science **304**, 995 (2004)

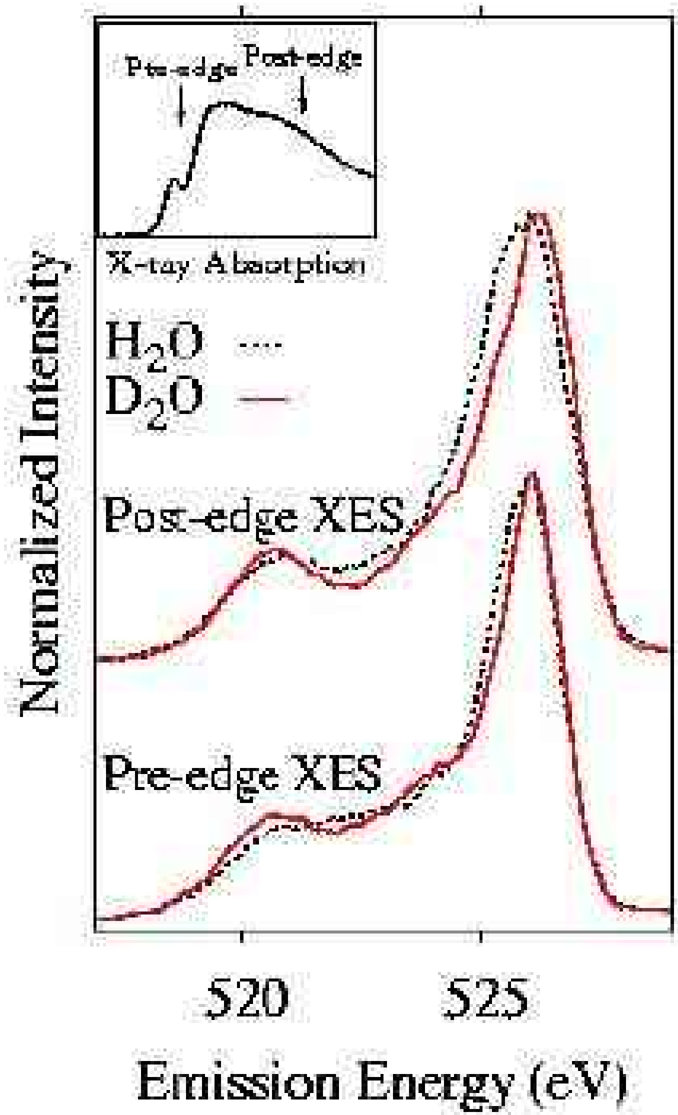
Michael.Odelius@physto.se

The X-ray Emission Spectrum of Liquid Water



Non-resonant

Resonant



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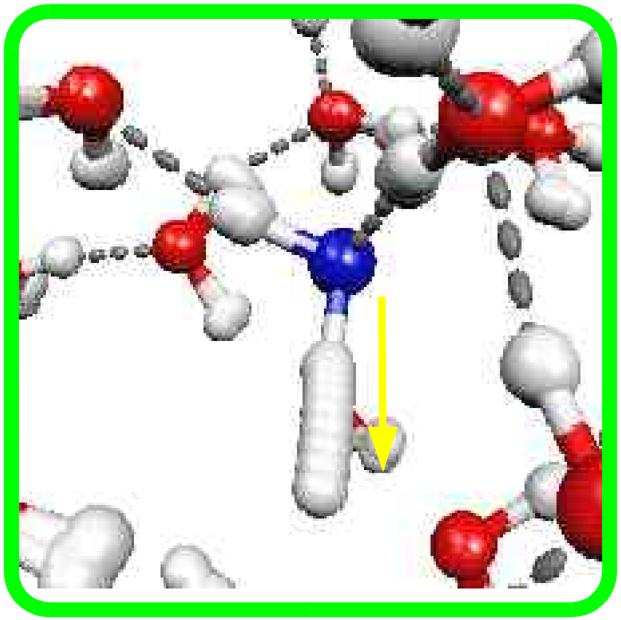
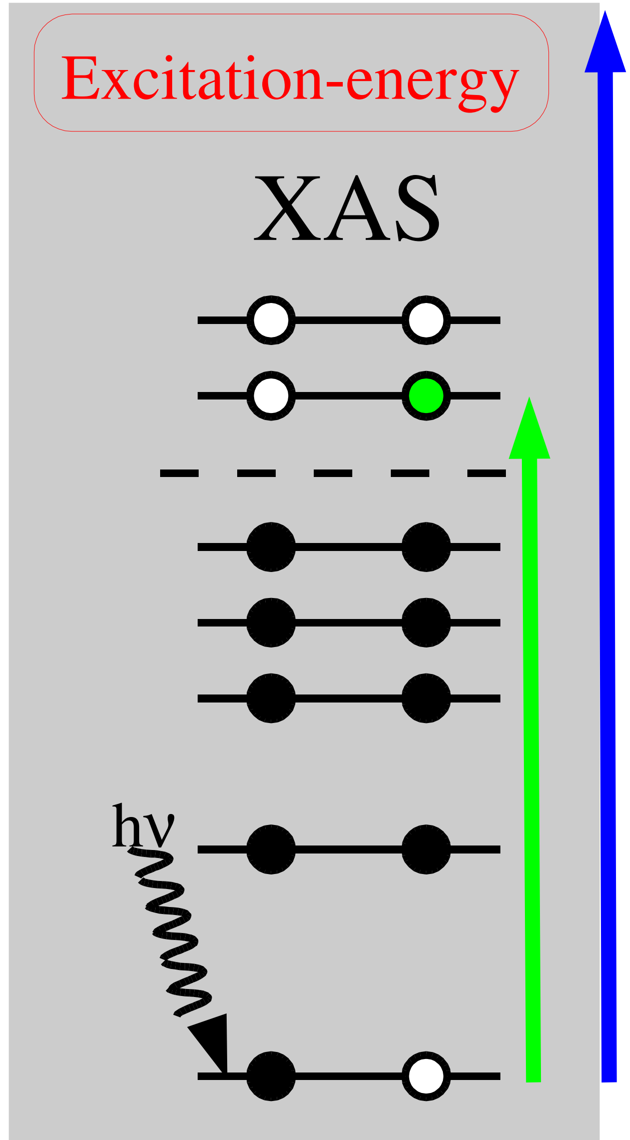
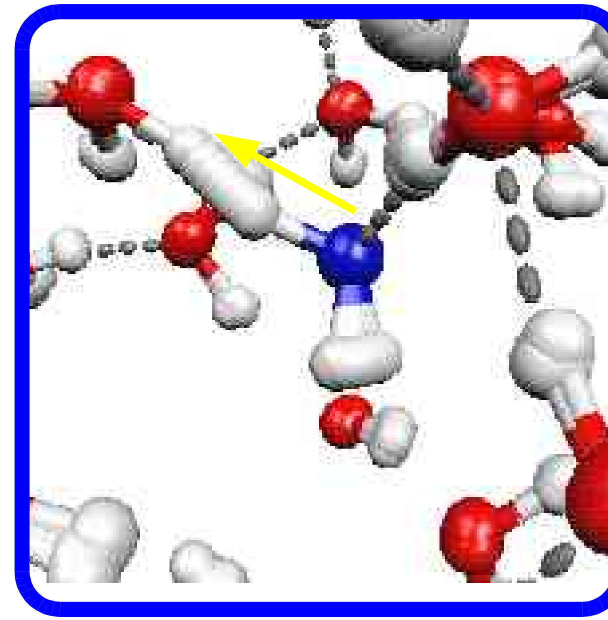
The X-ray Emission Spectrum of Liquid Water







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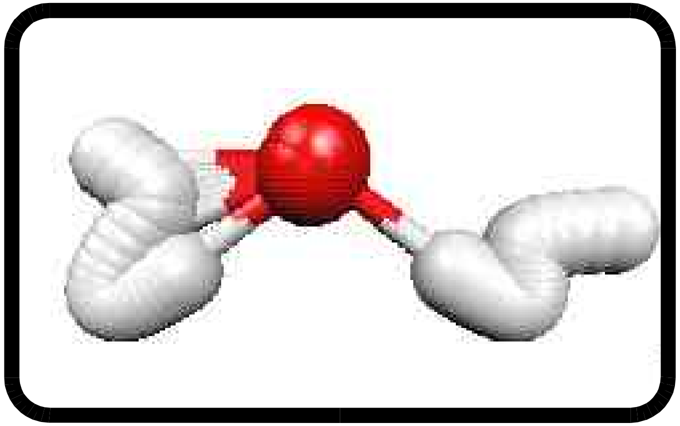
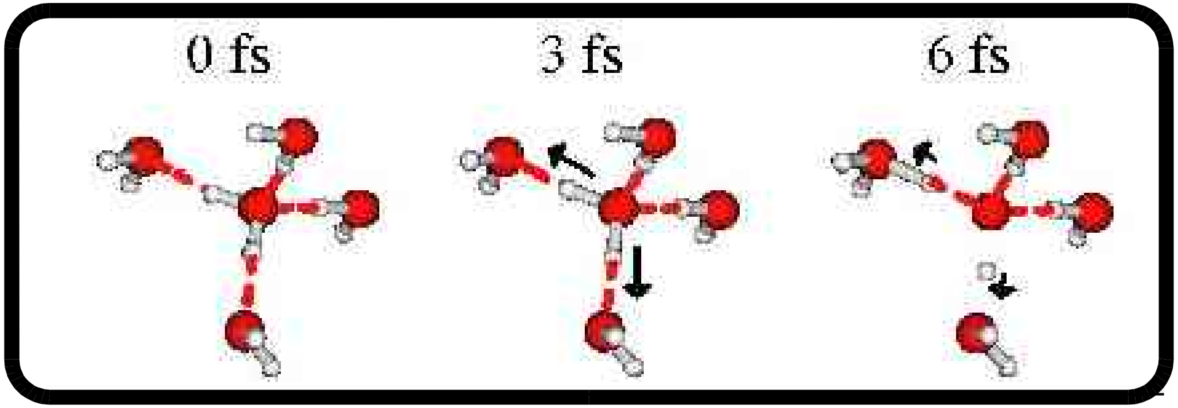
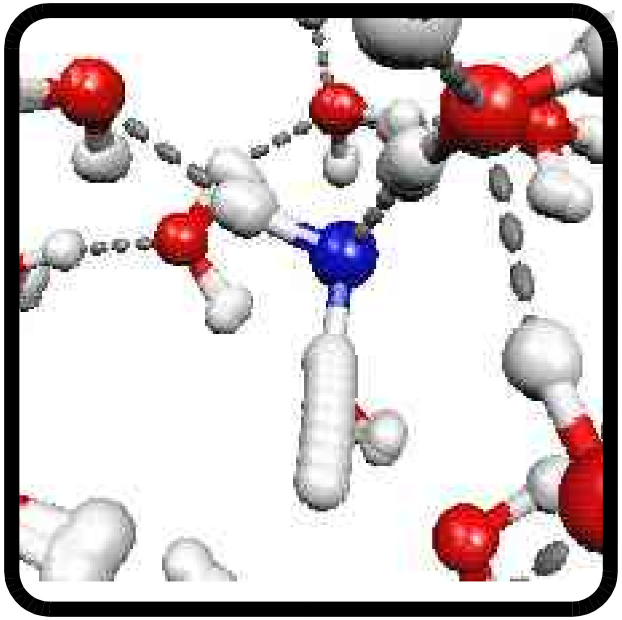
Conclusions

XES contains a valuable information on H-bonding and ultra-fast core-hole excited-state dynamics.







Michael.Odelius@physto.se

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