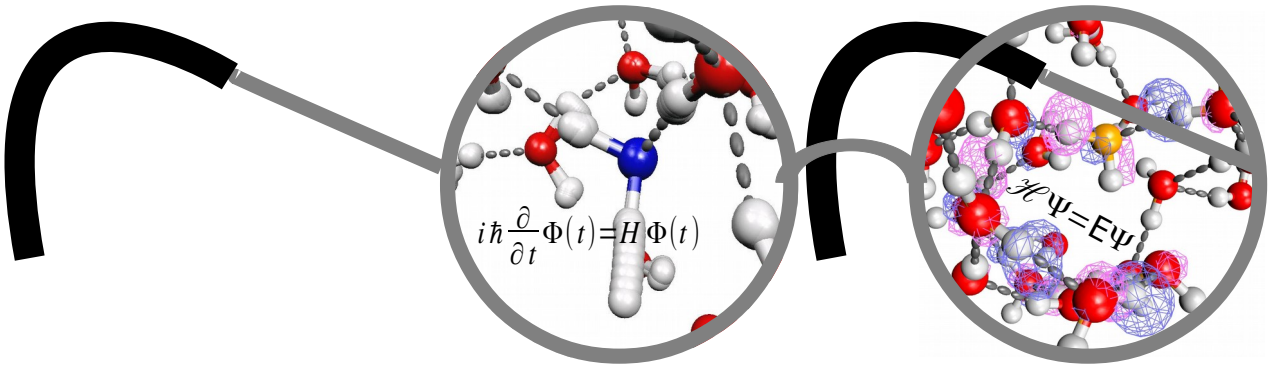


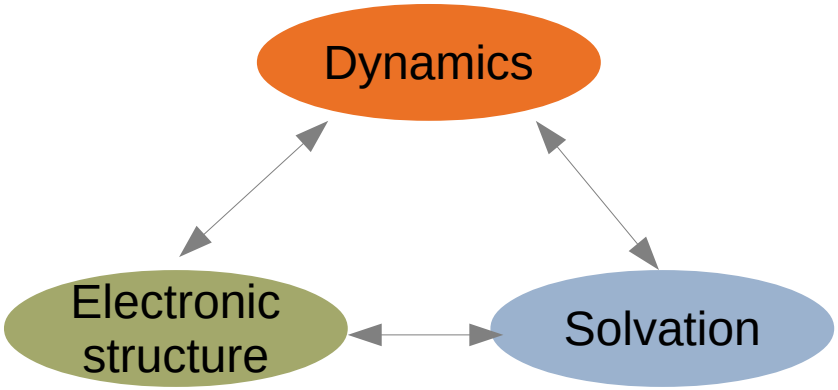
Modeling of X-ray spectroscopies

Michael Odelius
Department of Physics

4FUTURE Intensive course 2019:
Methods for Image and Spectral Data Analysis and Interpretation

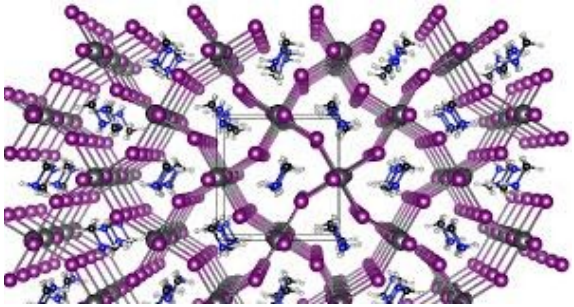
Stockholm University

Ultrafast dynamics in solution



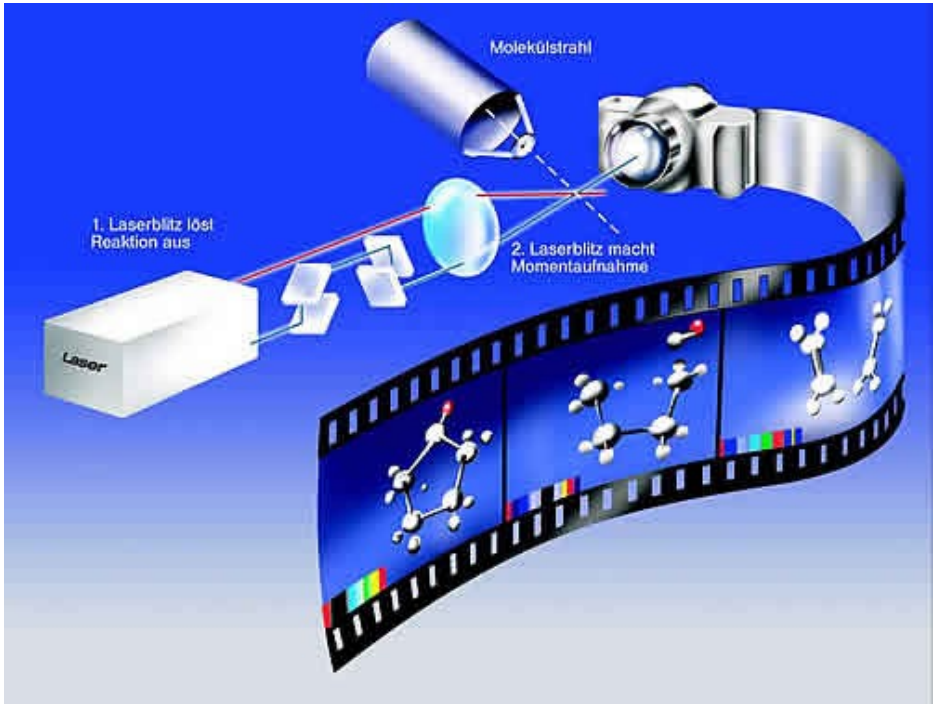
Solar cell materials

Hybridperovskites: Methylammonium leadtriiodide



Great photovoltaic properties, but environmental hazards and instability

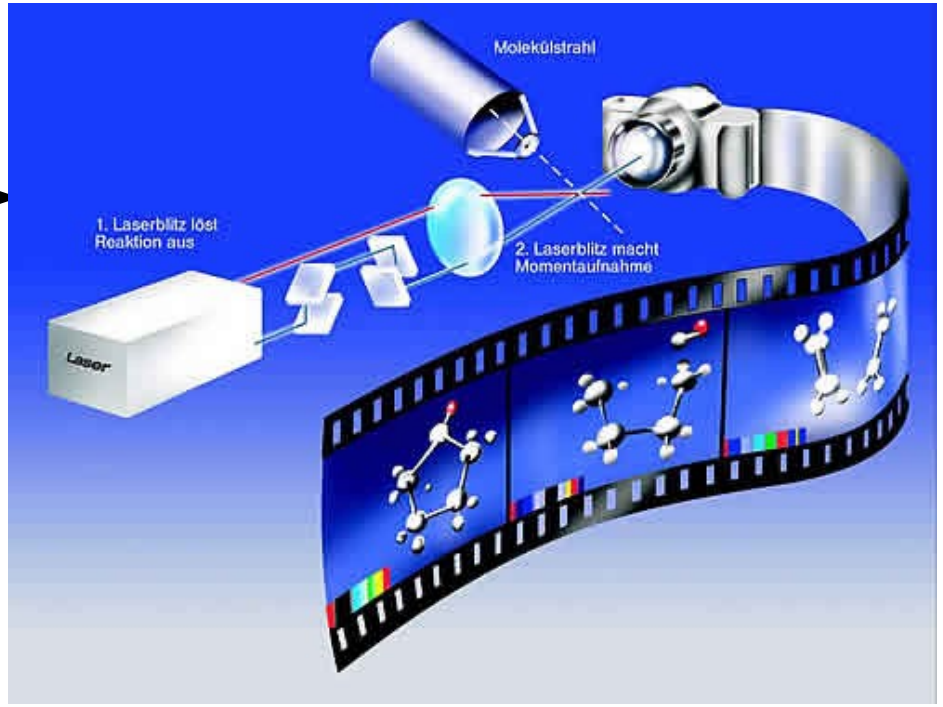
Theoretical spectrum simulations – Why bother?



Femtochemistry: "Filming" chemical reactions using ultra-fast lasers. (Source: DESY Hamburg)

Theoretical spectrum simulations – Why bother?

Theory is required to develop the film



Femtochemistry: "Filming" chemical reactions using ultra-fast lasers. (Source: DESY Hamburg)

Qualitative assignment

Evaluate theo. models

Quantitative analysis

Evaluate approximations

Outline

Spectrum simulations – Part I

Molecular orbital approach

Spectrum simulations – Part II

Electronic states approach

Dynamical effects

Excited state X-ray spectra

Core-level spectroscopy

X-ray photo-electron spectroscopy	Core-ionization (Valence-ionization)
X-ray absorption spectroscopy	Core-excitation
X-ray emission spectroscopy	Fluorescence decay
Resonant inelastic X-ray Scattering	Fluorescence decay

XPS XAS XES RIXS

Resonant photo-electron spectrosc.	Auger decay (dominate for small Z)

Quantum Chemistry $\mathcal{H}\Psi=E\Psi$

Hartree-Fock

1) Born-Oppenheimer
2) Mean-field approx.

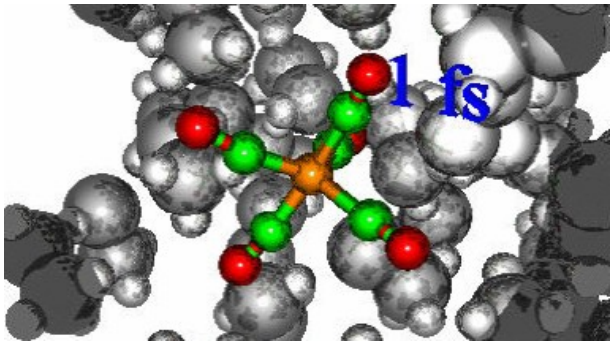
$$\Psi_{HF} = \det | \phi_1, \phi_2, \ldots \phi_N |$$

Momentary
$e^- - e^-$ correlation
missing!

DFT

Singlet determinant

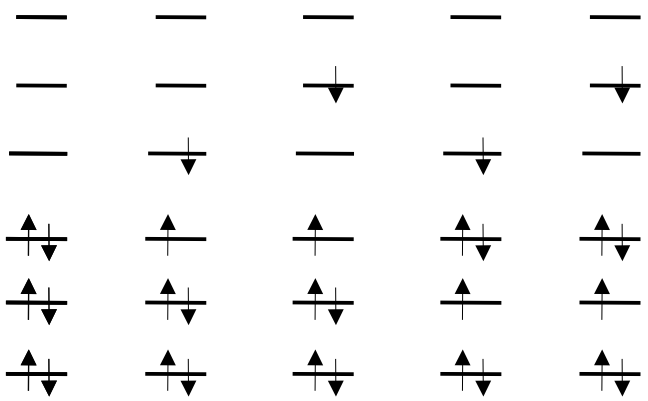
Correlation in $\mathcal{H}$



Post-HF

Multi-determinant

Wave function correlated



Ab initio Molecular dynamics

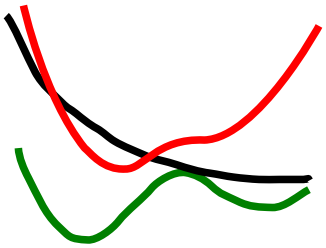
F=ma

$$\boldsymbol{F}_I = -\nabla_I \langle H_e \rangle \approx -\langle \Psi_0 | \nabla_I H_e | \Psi_0 \rangle$$

AIMD: CPMD Cp2k

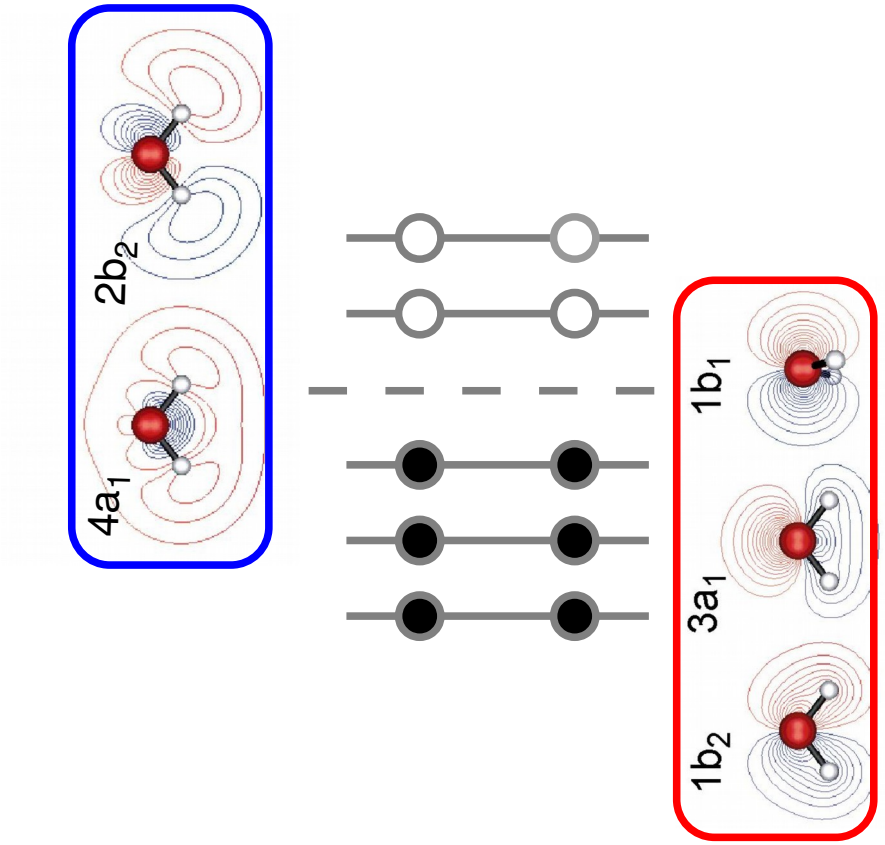
Quantum dynamics

$$i\hbar \frac{\partial}{\partial t} \Phi(\{\boldsymbol{r}_i\}, \{\boldsymbol{R}_I\}; t) = H \Phi(\{\boldsymbol{r}_i\}, \{\boldsymbol{R}_I\}; t)$$



QMD: Wave packet simulations

Molecular orbitals of $H_2O(g)$ – C_{2v} Point group



O2s (2a1)

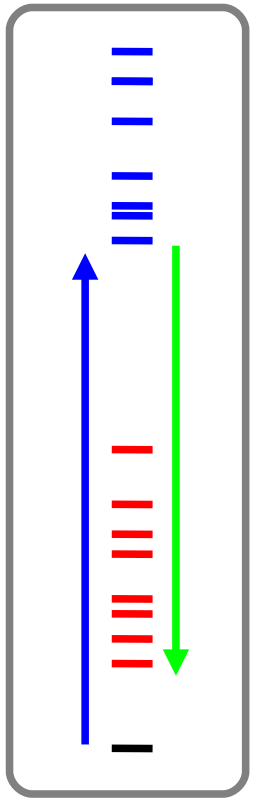
O1s (1a1)

Spectrum simulations $\mathcal{H}\Psi=E\Psi$

Accurate methods
Electronic states

$\Delta E = E_{tot}(\Psi_i) - E_{tot}(\Psi_j)$

$|\langle\Psi_i|O|\Psi_i\rangle|^2$

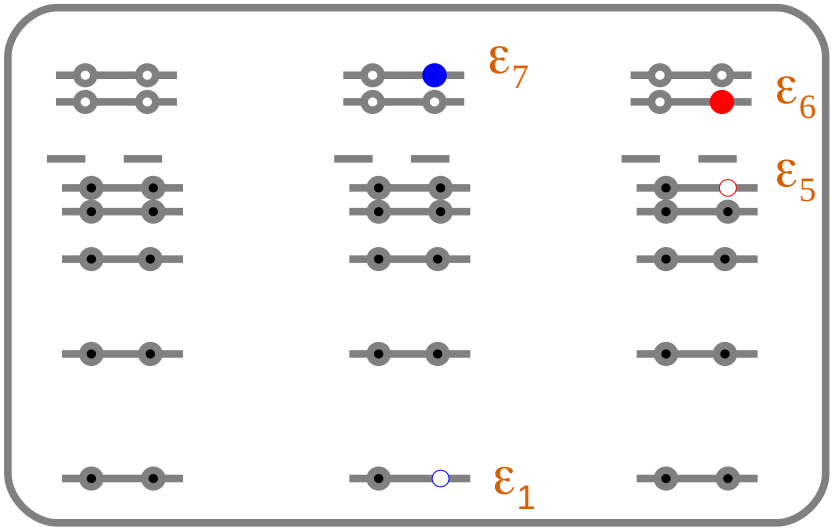


Core-excited

Valence excited

Ground state

Approximate methods
Molecular orbitals



GS $\quad \varepsilon_7 - \varepsilon_1 \quad \varepsilon_6 - \varepsilon_5$

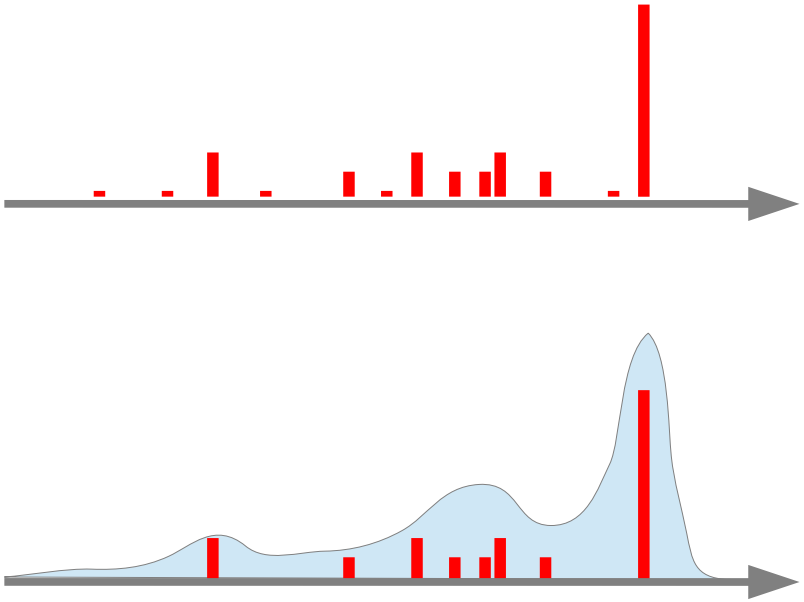
Transition potential DFT

$|\langle\Psi_i|O|\Psi_i\rangle|^2 = |\langle\phi_m|O|\phi_n\rangle|^2$

Spectrum simulations $\mathcal{H}\Psi=E\Psi$

$$E_{tot}(\Psi_i) - E_{tot}(\Psi_j)$$

$$|\langle\Psi_i|O|\Psi_i\rangle|^2$$



Broadening:

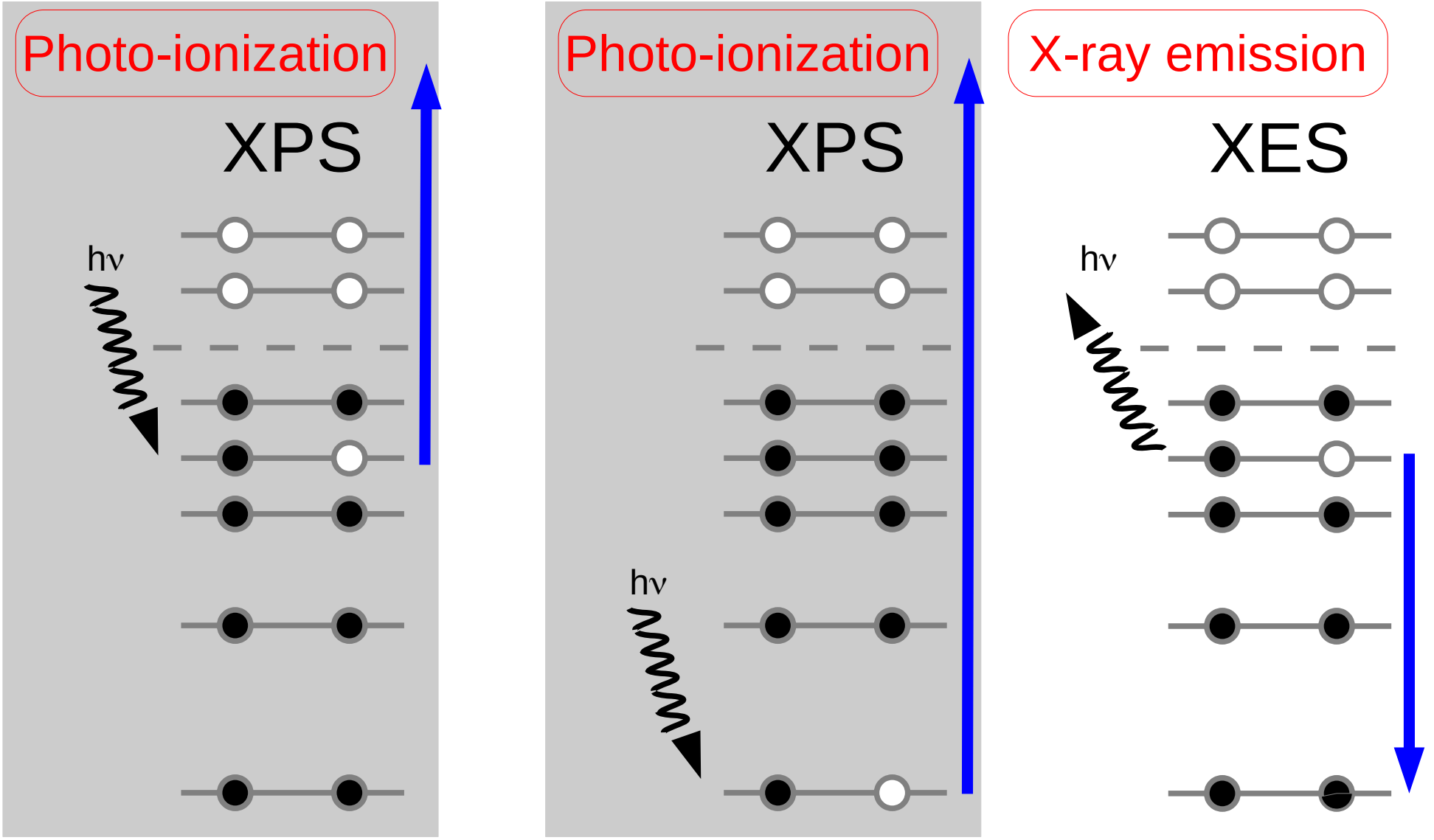
Core-hole life-time

Vibrational

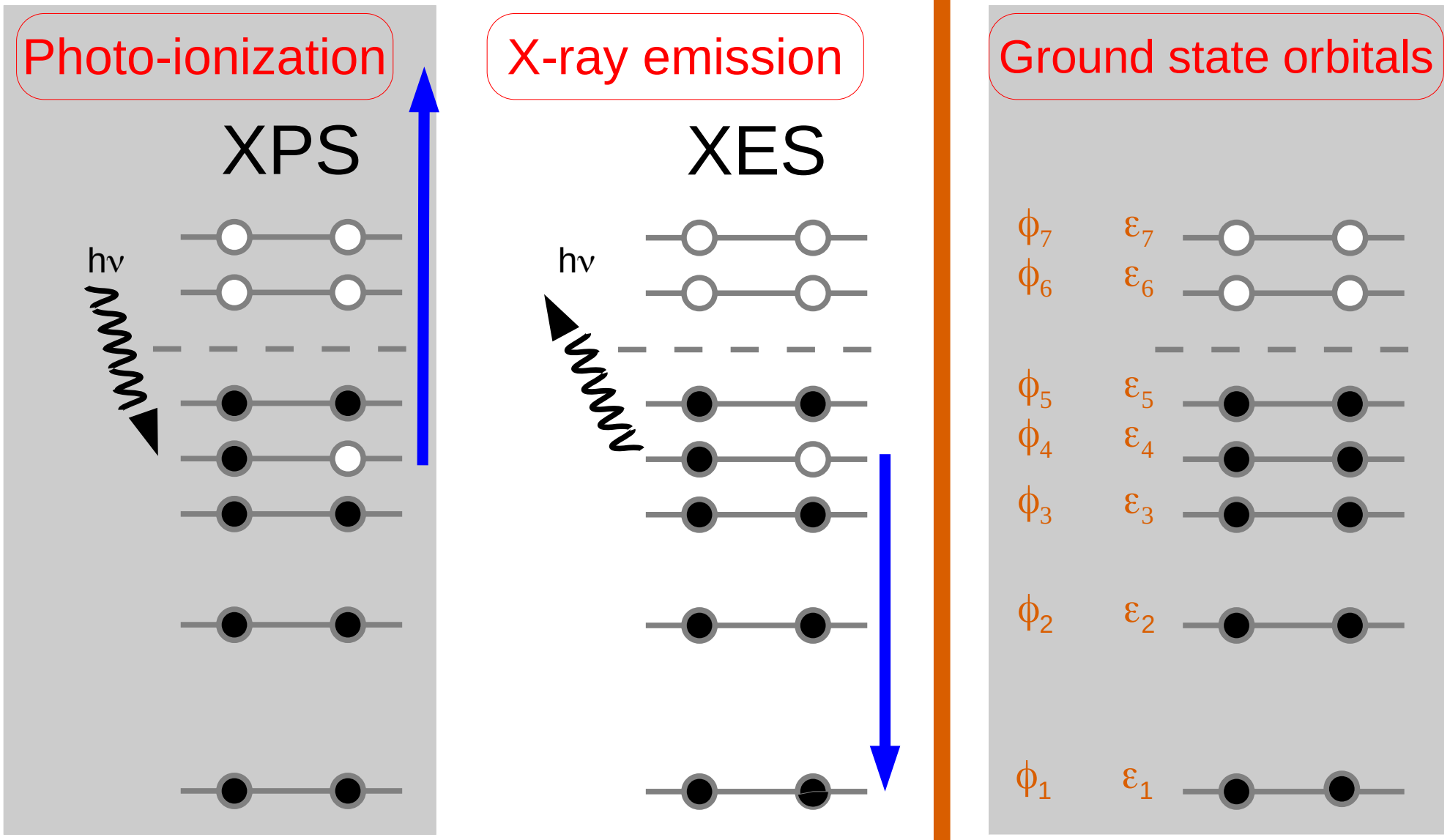
Configurational

Experimental

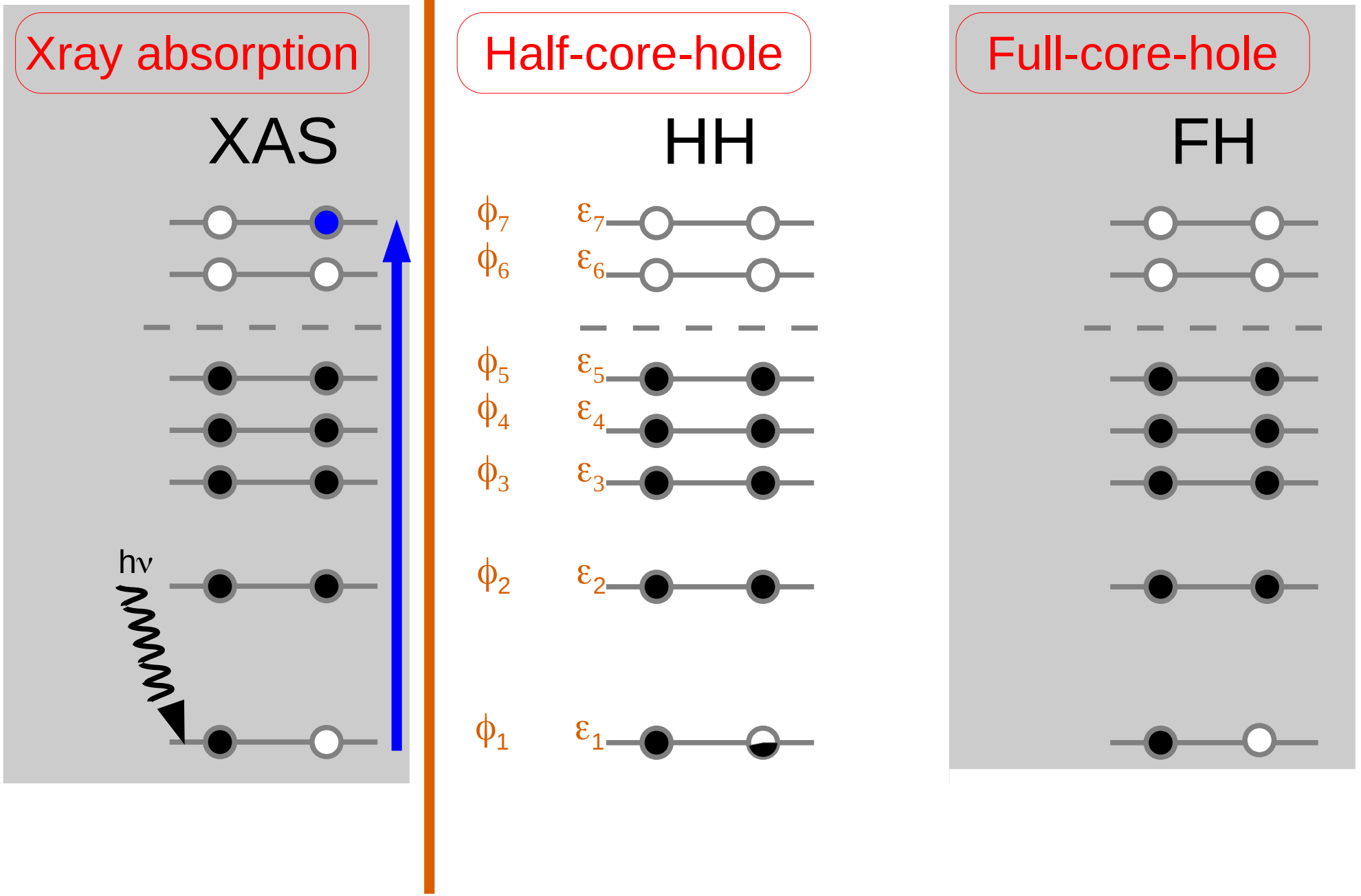
Orbital represention of the XPS and XES processes



Orbital represention of the XPS and XES processes



Orbital represention of the XA process



X-ray spectroscopy Case study: $H_2O(g)$

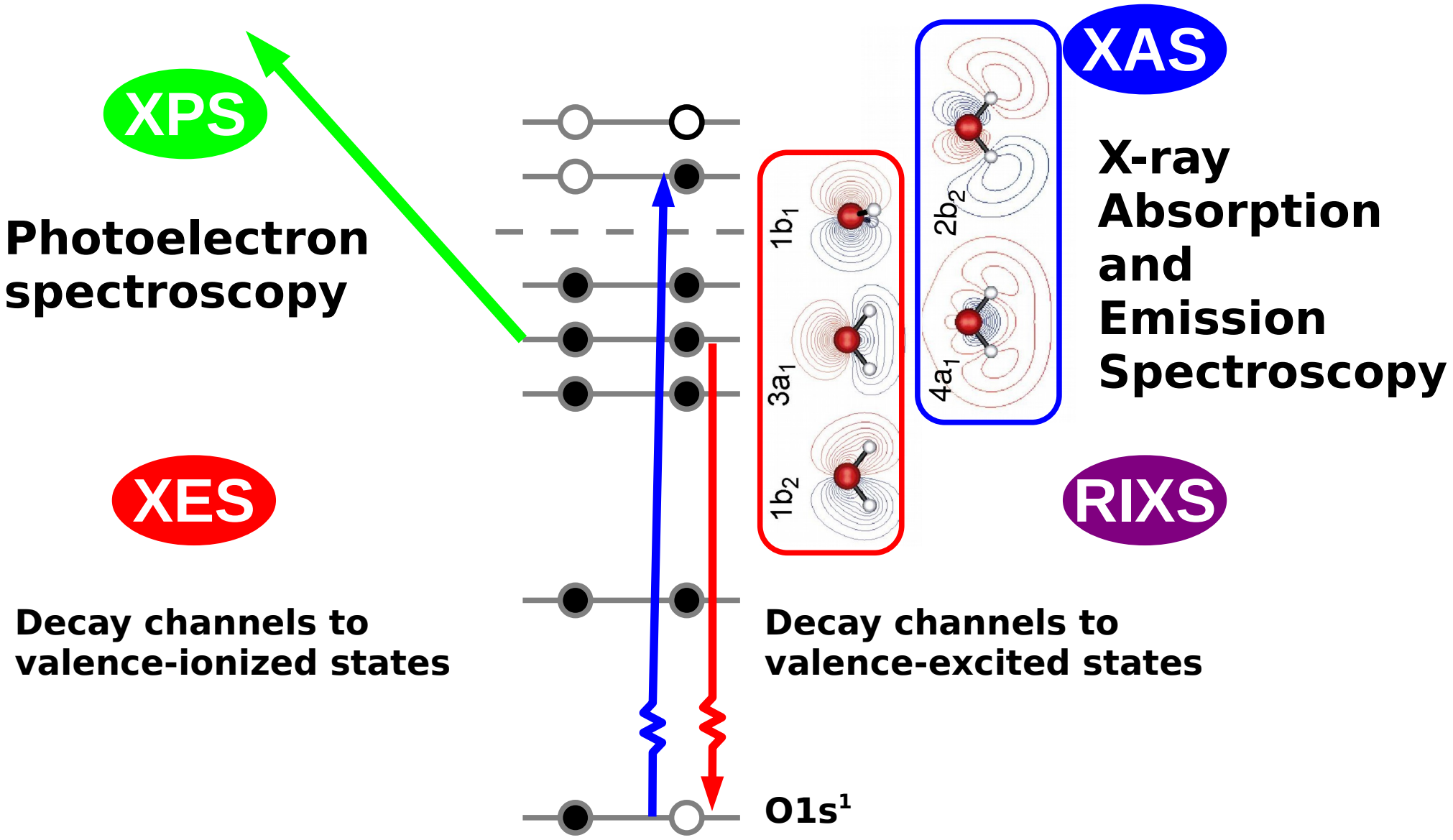
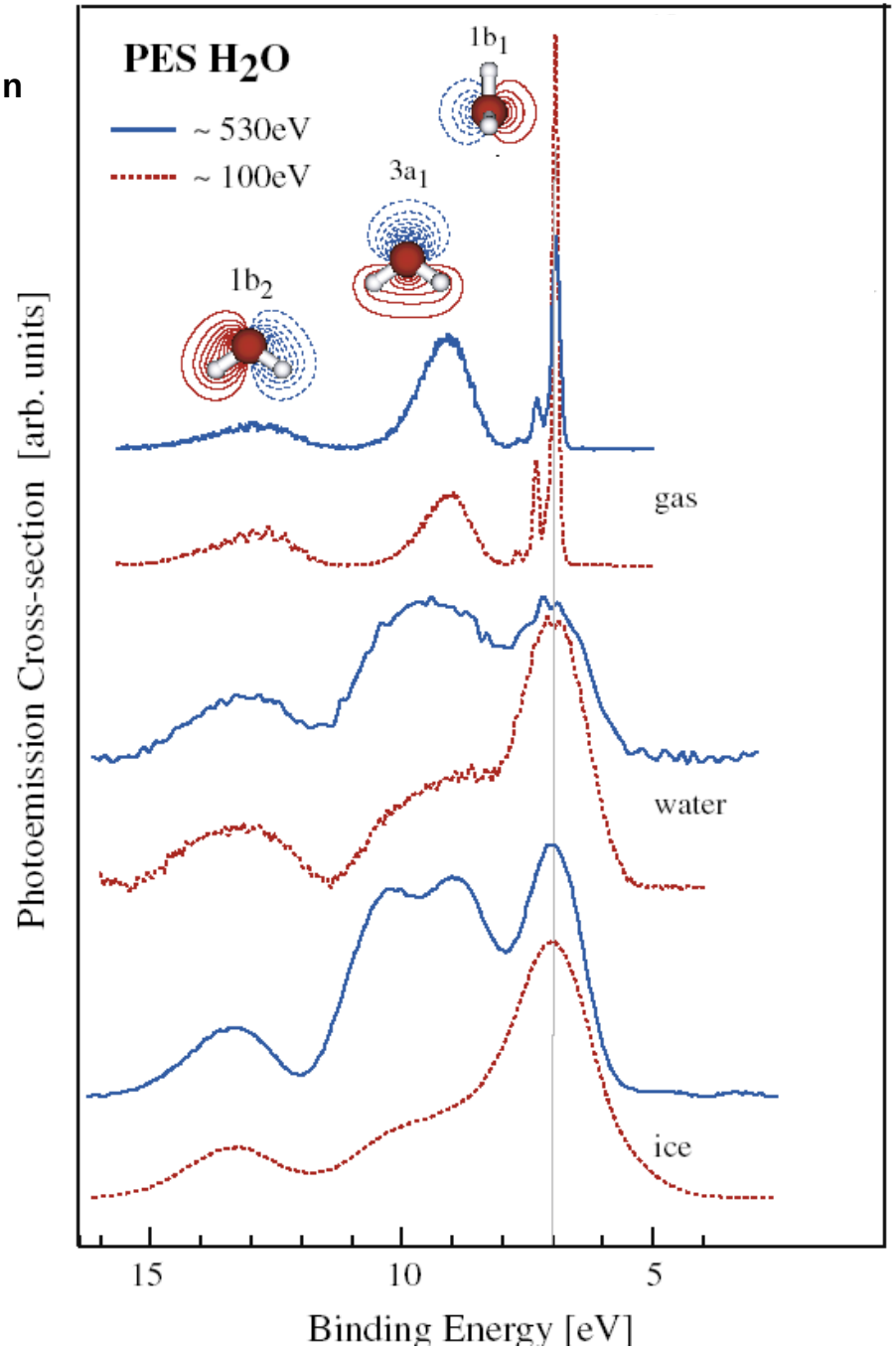


Photo electron spectroscopy of H_2O(g,l,s)

$E_{binding} = E_{photon} - E_{kin}$



Koopman's theorem

HF orbital energies

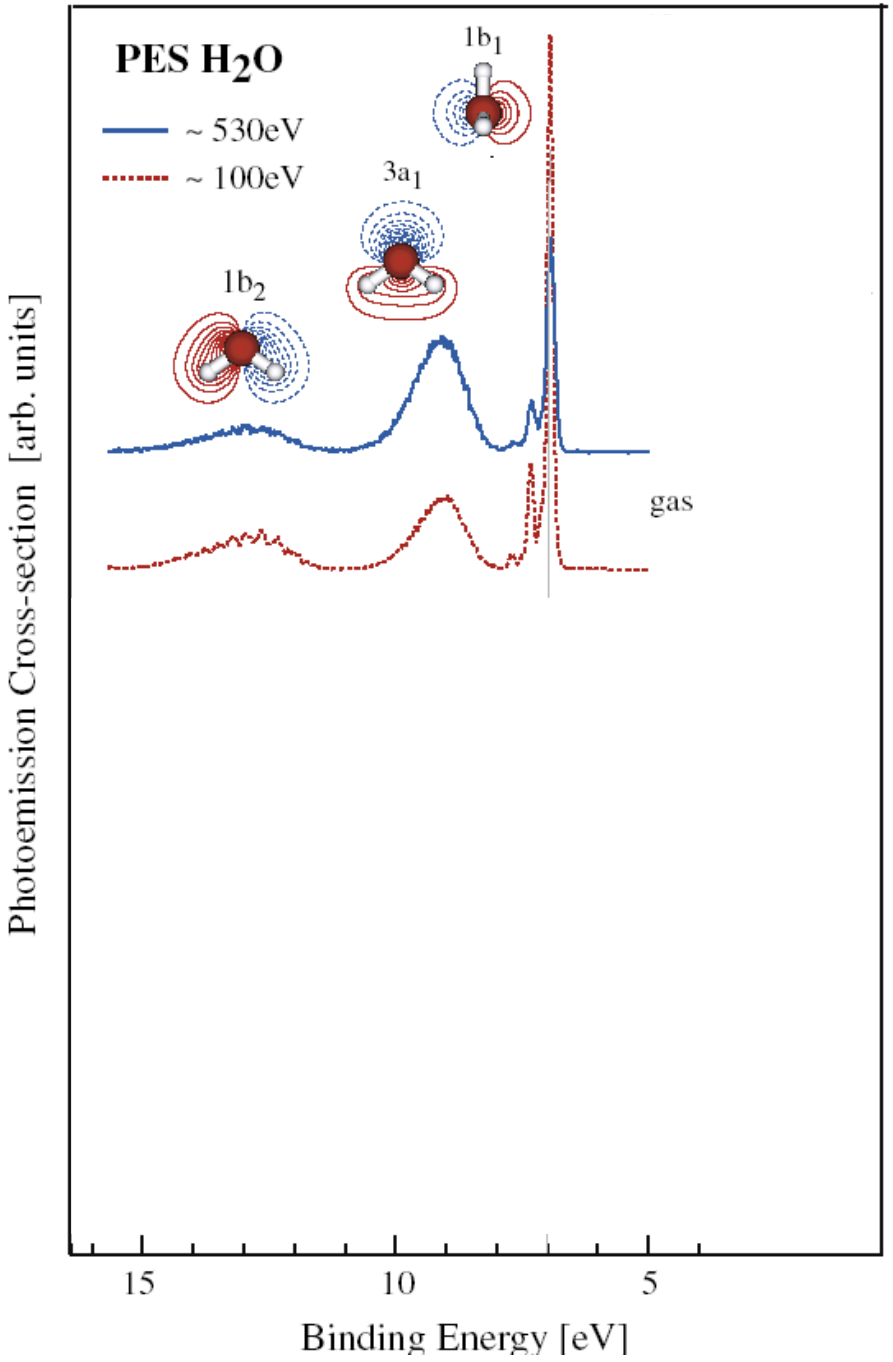
approximate

Ionization binding energies

(However, we will cheat and also use DFT Kohn-Sham energies which require ad hoc shifts)

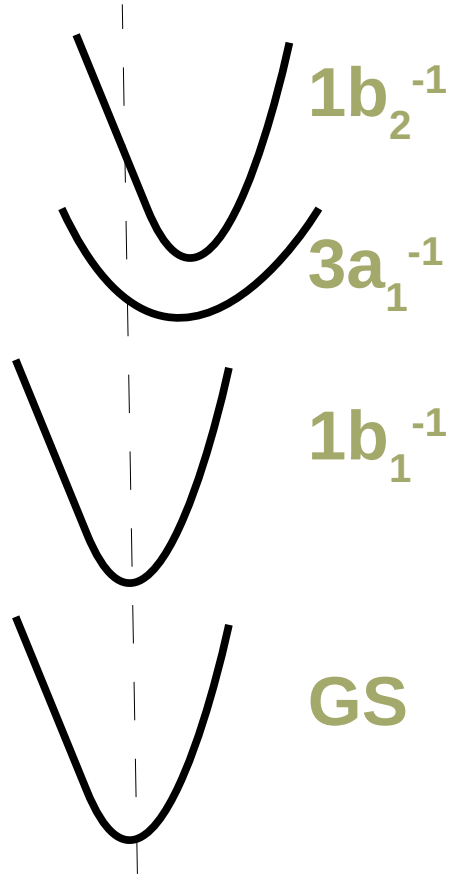
D. Nordlund et al
CPL **460** 86 (2008)

Photo electron spectroscopy of H_2O(g,l,s)



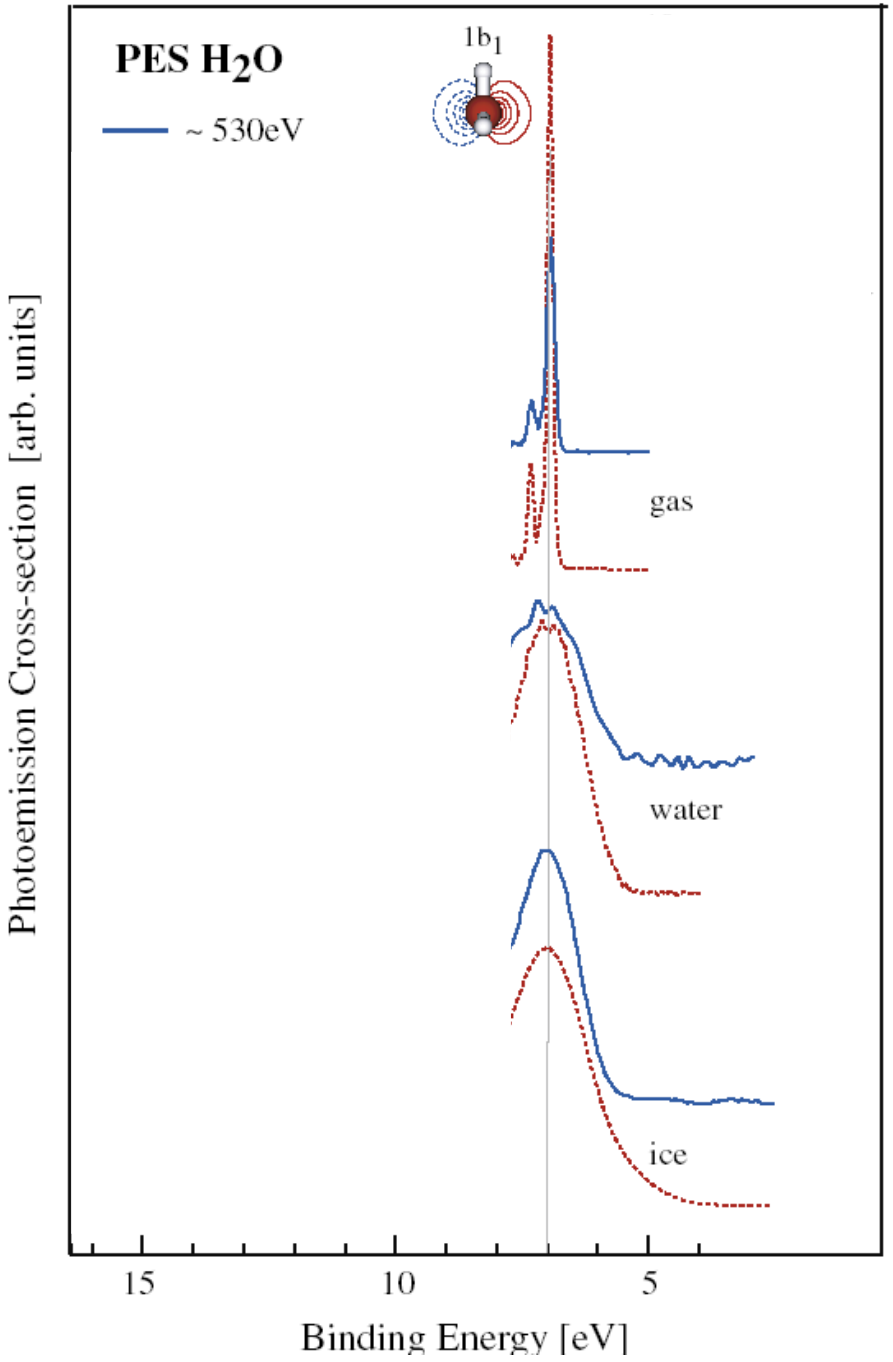
Franck-Condon

Vibrational excitations

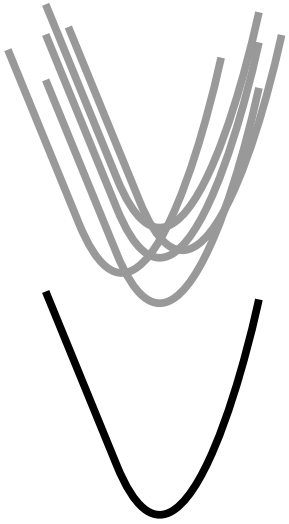


D. Nordlund et al
CPL **460** 86 (2008)

Photo electron spectroscopy of H_2O(g,l,s)



Inhomogeneous Broadening

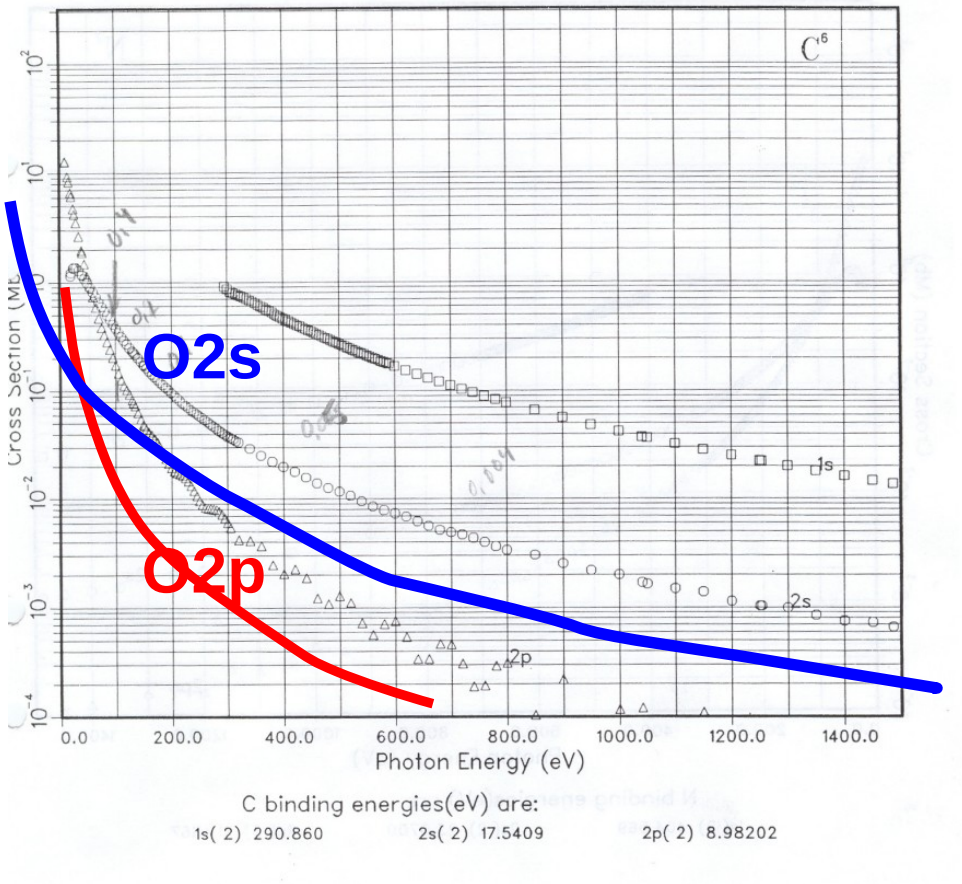


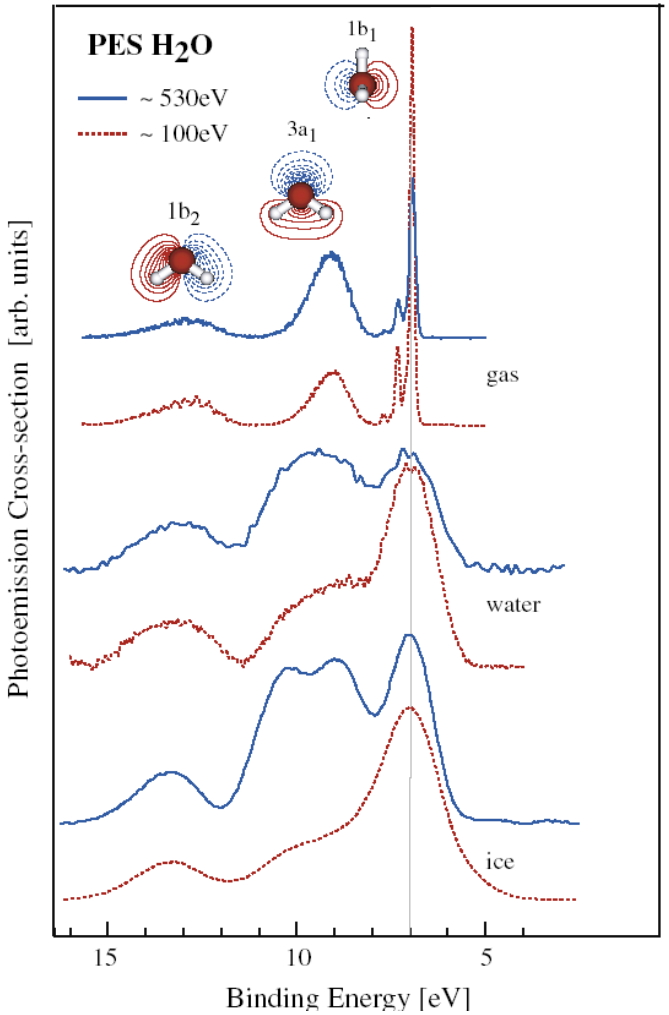
(Homogeneous broadening is due to finite life-times)

D. Nordlund et al
CPL **460** 86 (2008)

Photo electron spectroscopy of H_2O(g,l,s)

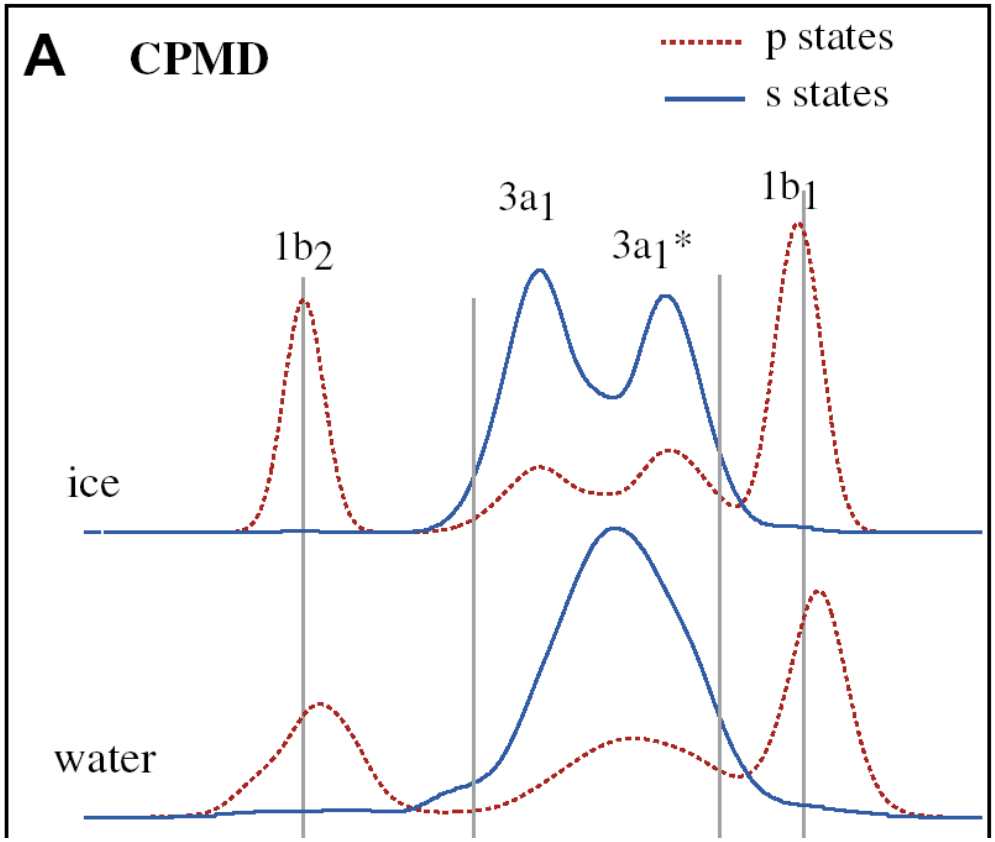
Cross-sections vary with photonenergy

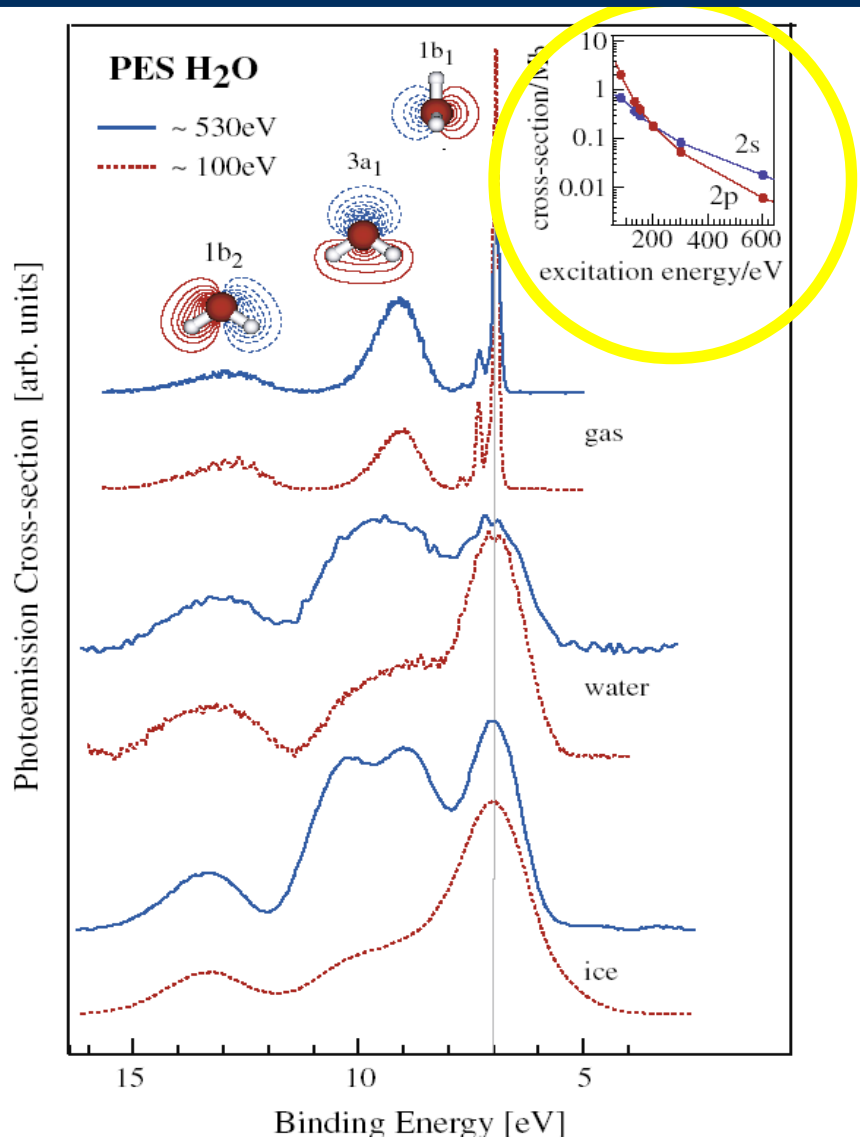




D. Nordlund et al
CPL **460** 86 (2008)

Photo electron spectroscopy of H_2O(l,s)





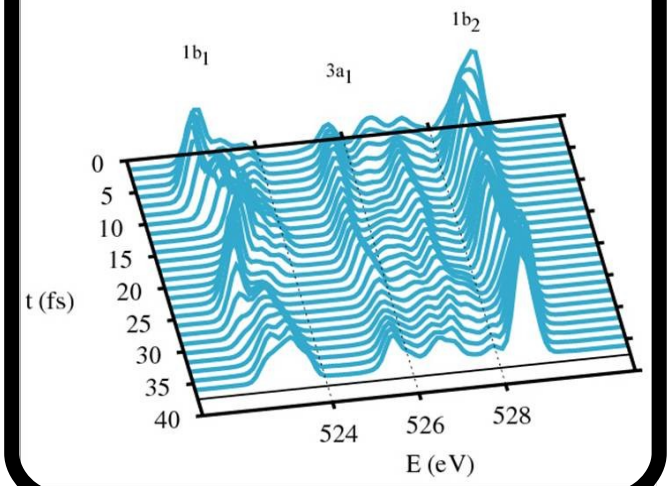
Notice: In C_{2v} symmetry only a_1 can have oxygen s-sym.

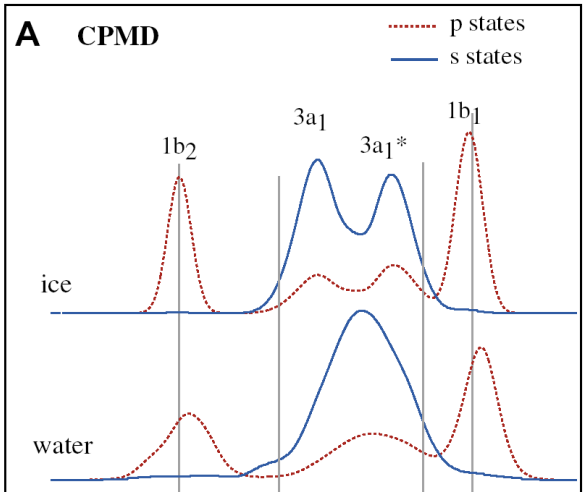
D. Nordlund et al
CPL **460** 86 (2008)

Time evolution of the electronic structure due to hydrogen bond dynamics

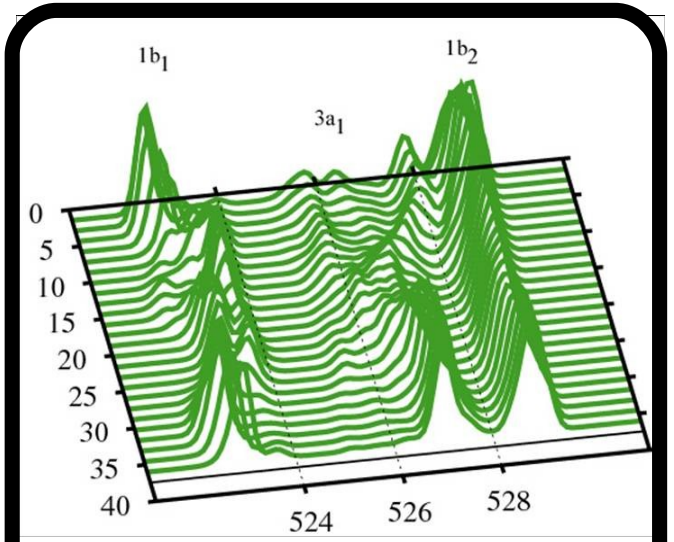
Hydrogen bond dynamics

Intact H-bonds





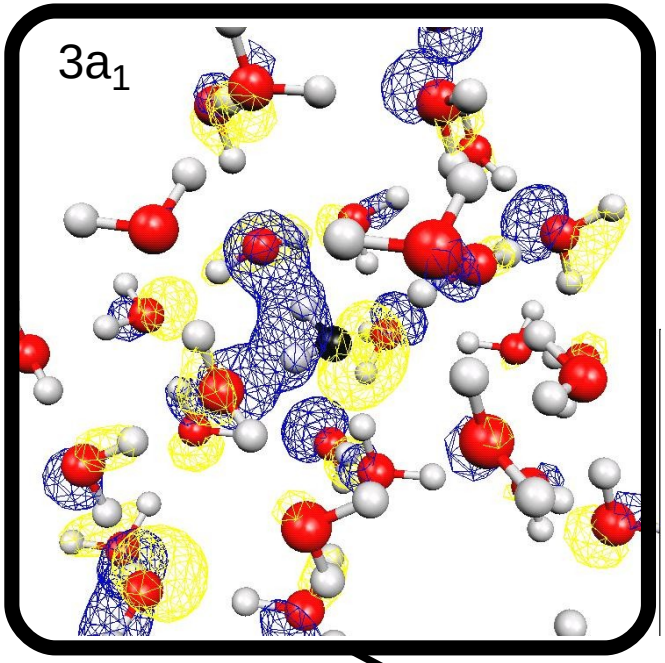
D. Nordlund et al
CPL **460** 86 (2008)

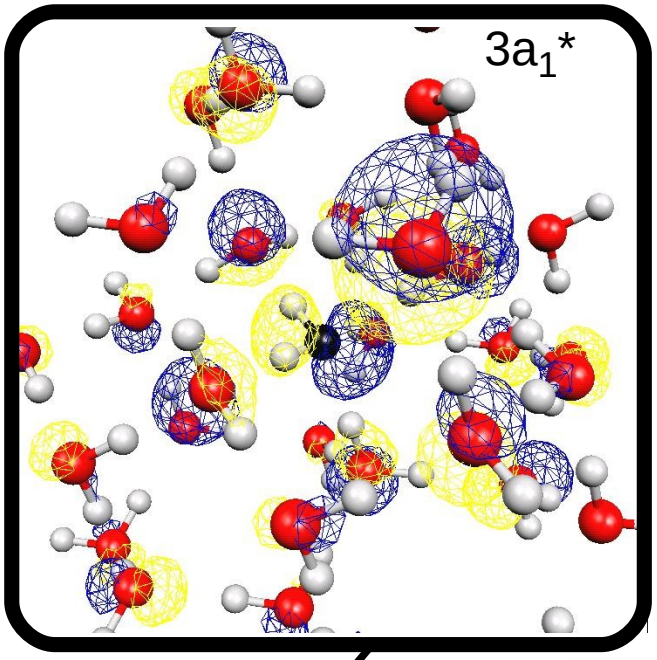


H-bond breakage

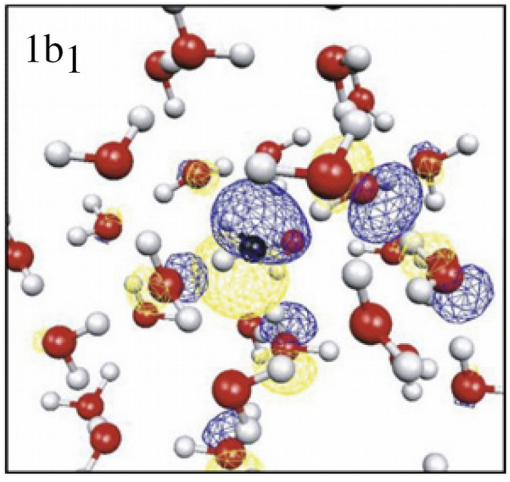
Car-Parrinello MD simulations

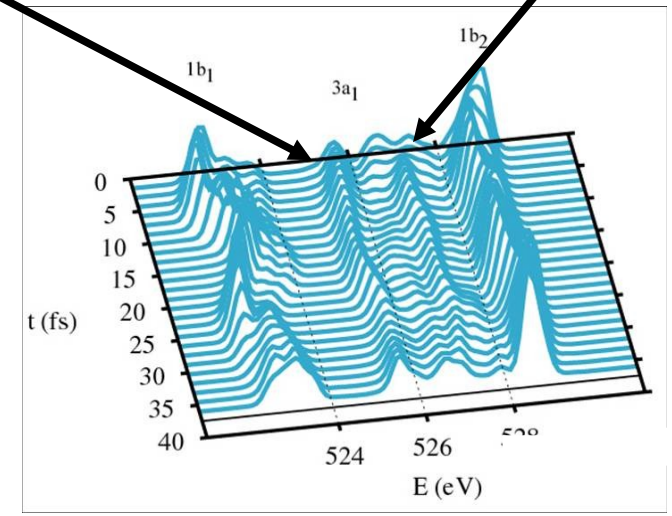
Hydrogen bonding in water

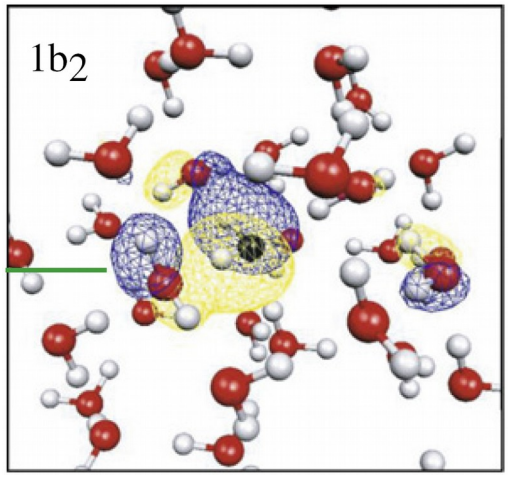




Strong overlap in $3a_1$

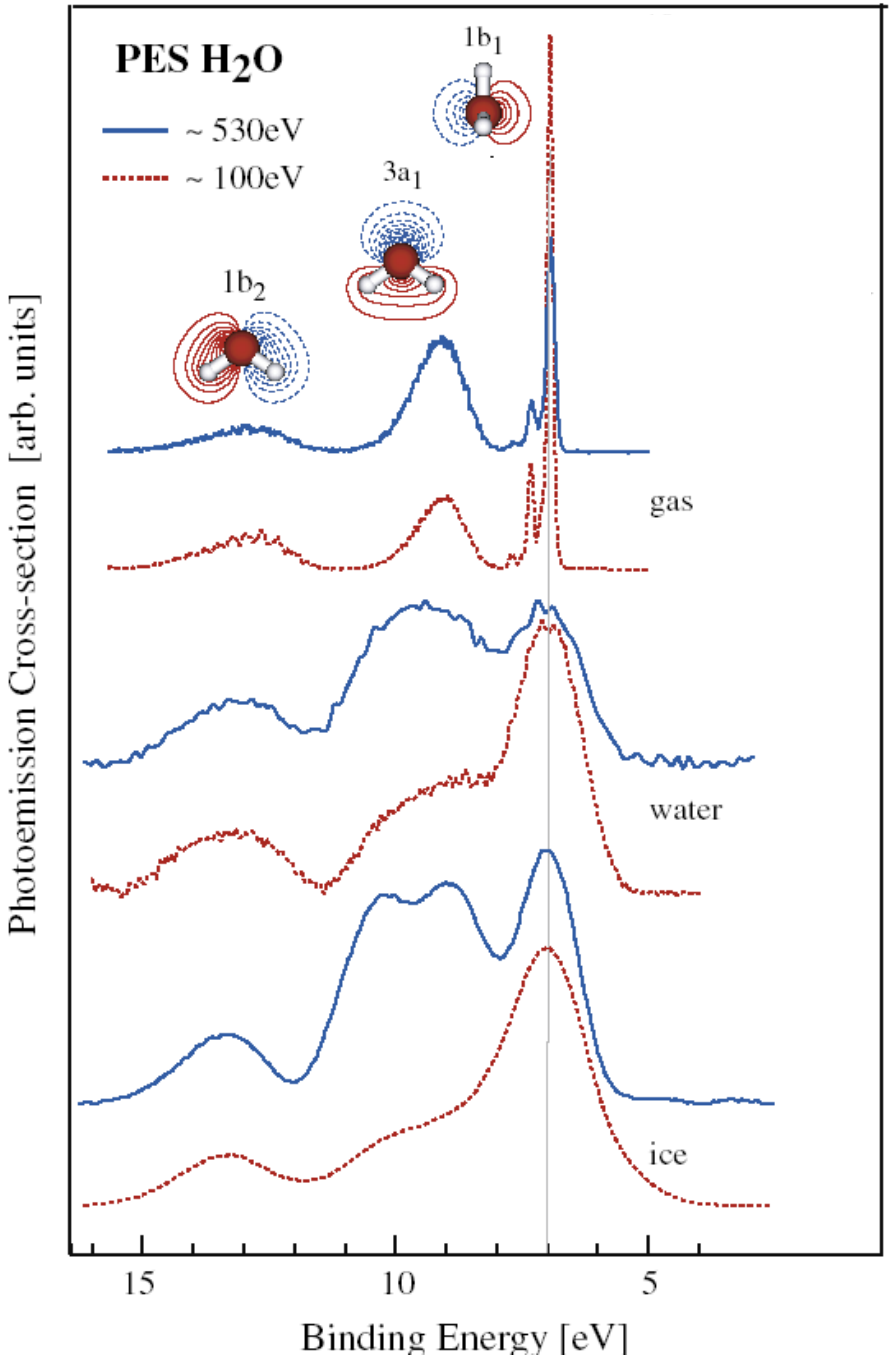






D. Nordlund et al
CPL **460** 86 (2008)

Photo electron spectroscopy of H_2O(g,l,s)



Franck-Condon

Inhomogeneous broadening

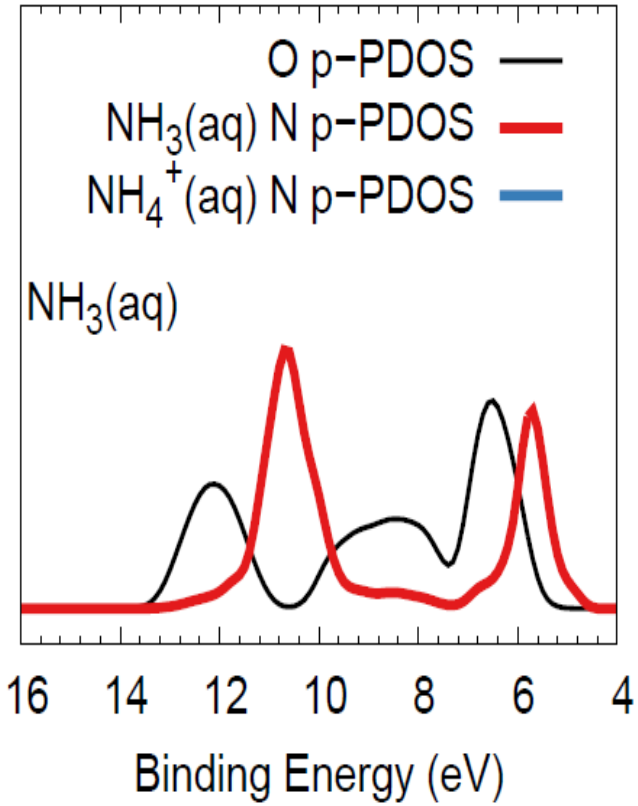
Chemical bonding

Hydrogen bonding and dynamics

D. Nordlund et al
CPL **460** 86 (2008)

XES allows us to access N p-DPOS in NH_3(aq)

Aqueous ammonia:
Energy mismatch in orbital mixing

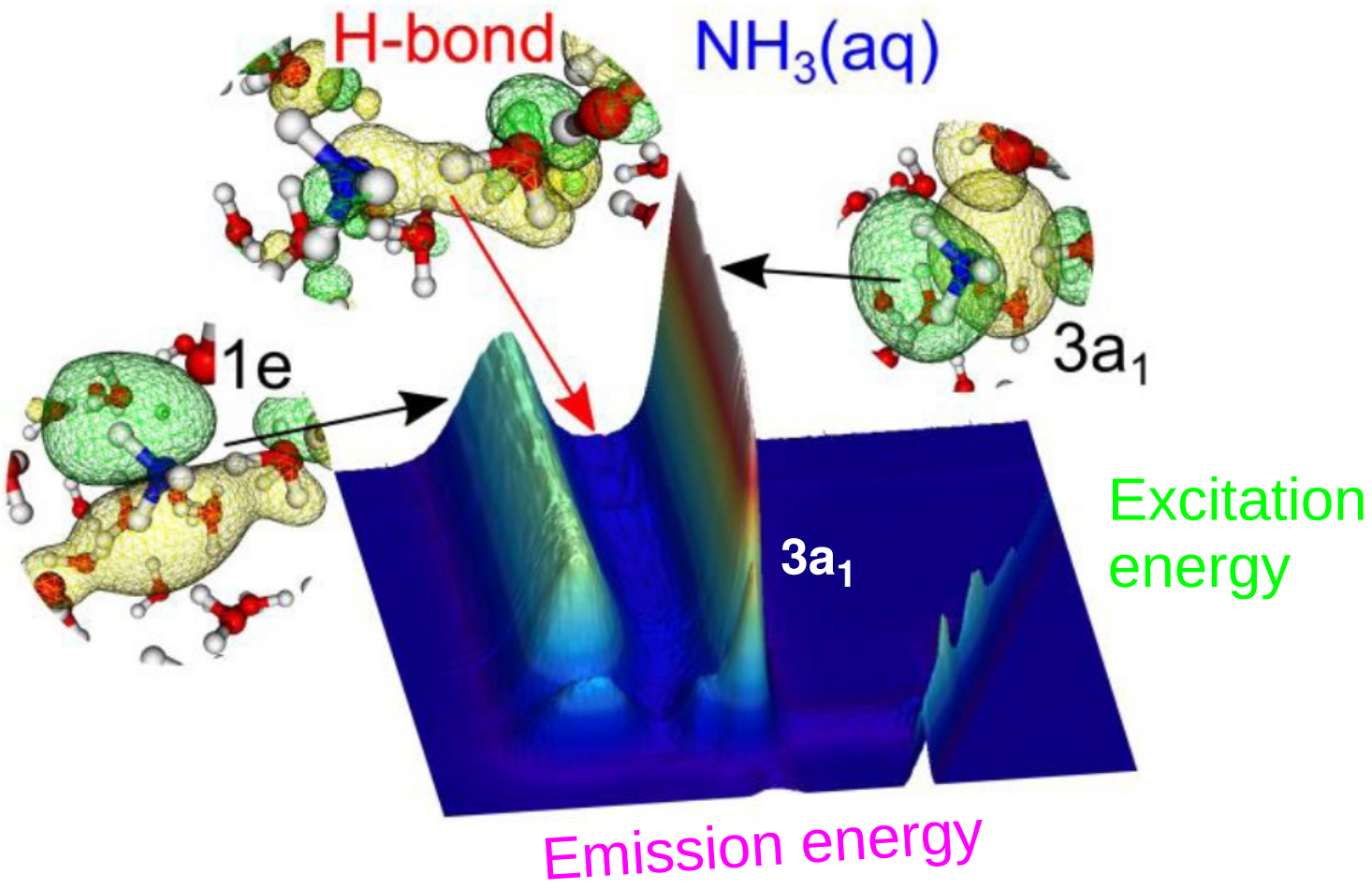


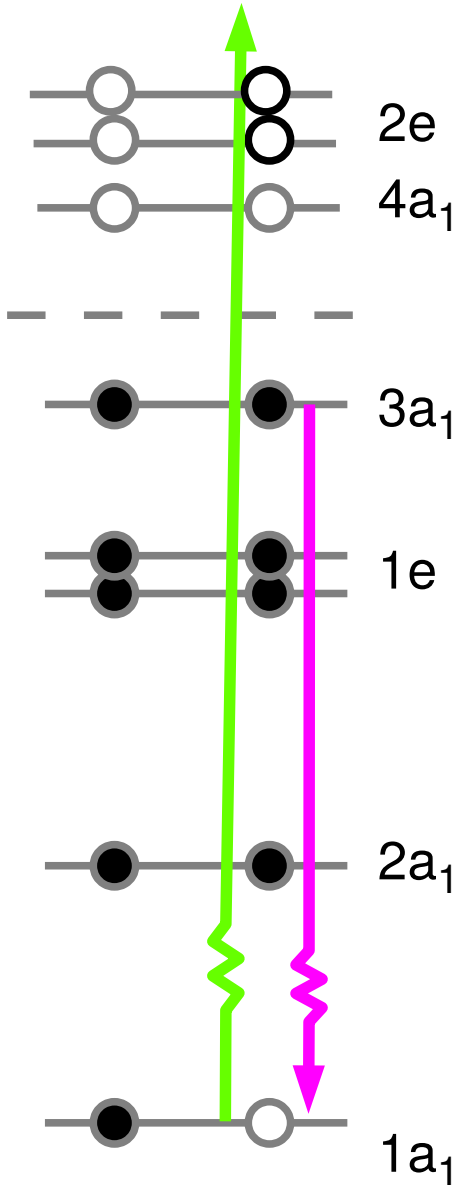
O PDOS would dominate in valence XPS

N K-edge XES can cut-out N p-PDOS

M. Ekimova et al. DOI: 10.1021/jacs.7b07207
J. Am. Chem. Soc. 2017, 139, 12773−12783

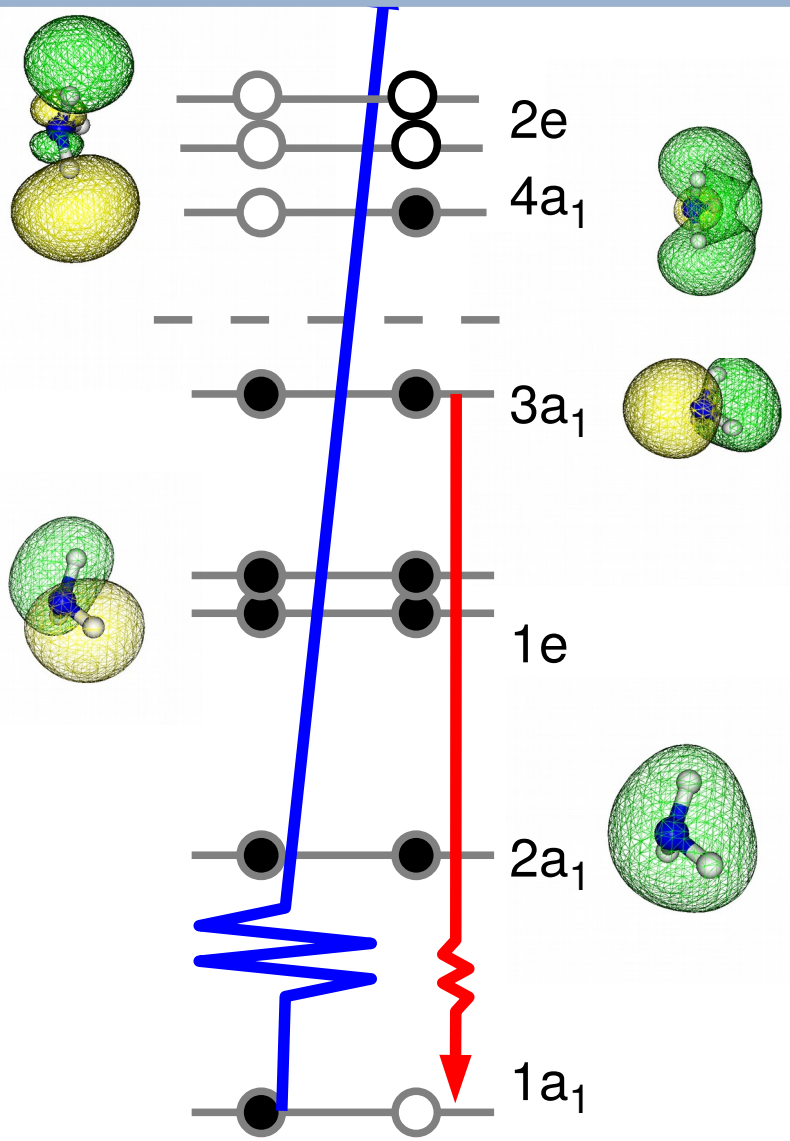
X-ray emission spectroscopy of NH_3(g) and NH_3(aq)

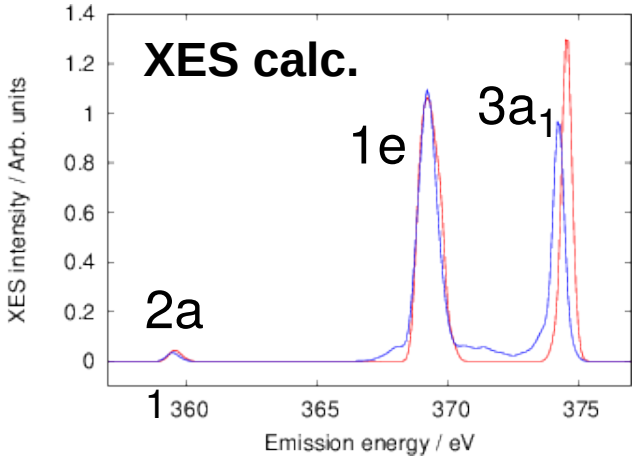




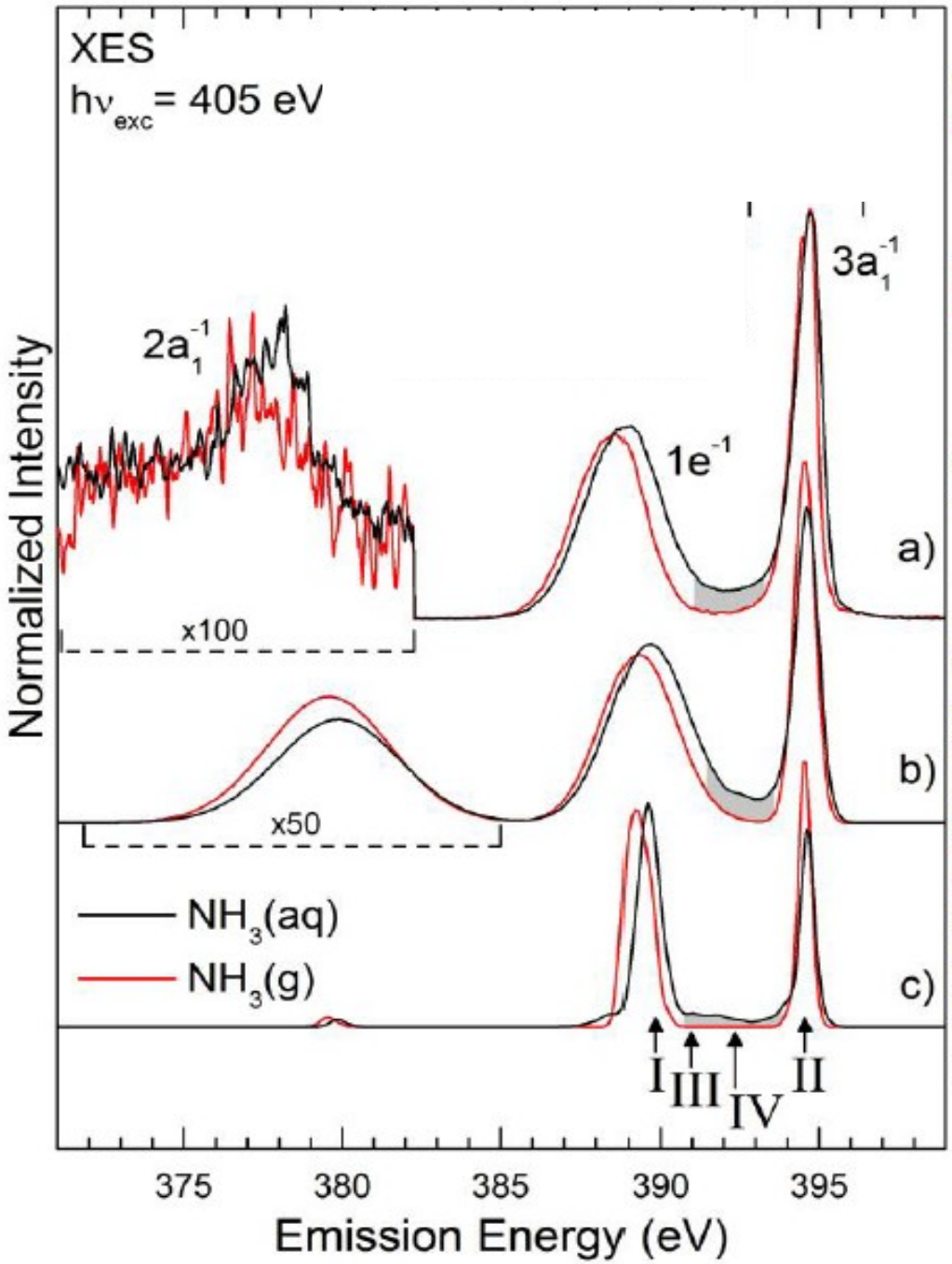
L. Weinhardt, E. Ertan, M. Iannuzzi, M. Weigand, O. Fuchs, M. Bär, M. Blum, J. D. Denlinger, W. Yang, M. Odelius E. Umbach, and C. Heske. Phys. Chem. Chem.Phys., **17**, 27145 (2015)

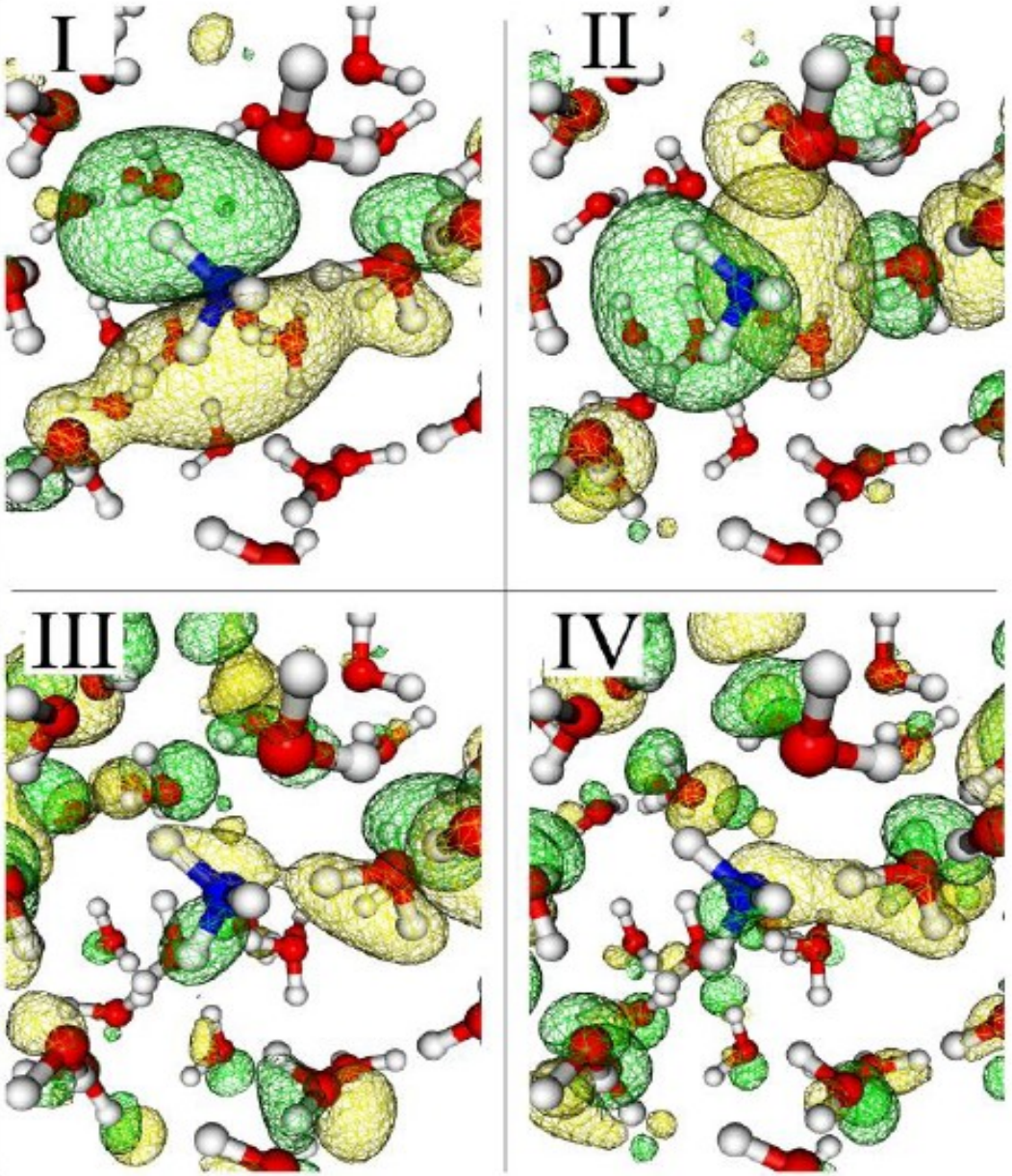
Electronic structure of NH_3(g) and NH_3(aq)





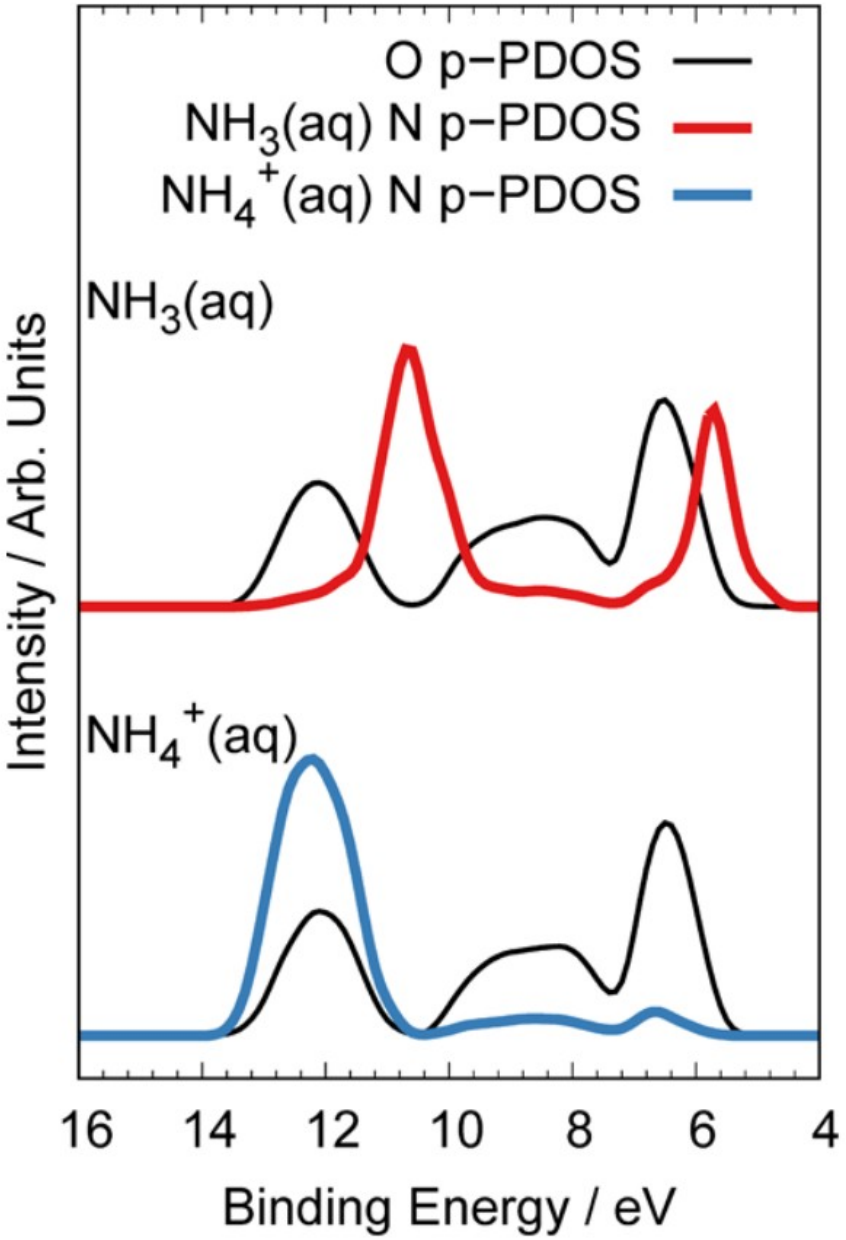
RIXS spectroscopy of NH_3(aq)





The effect of pH

Aqueous ammonia: Energy mismatch

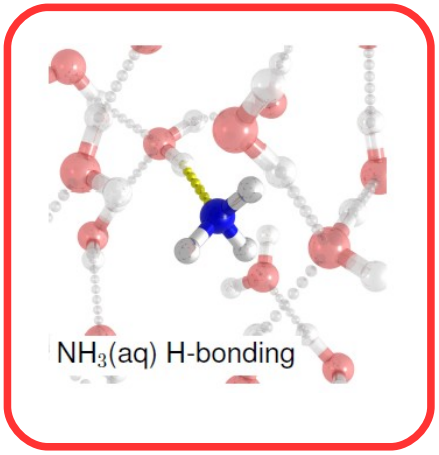


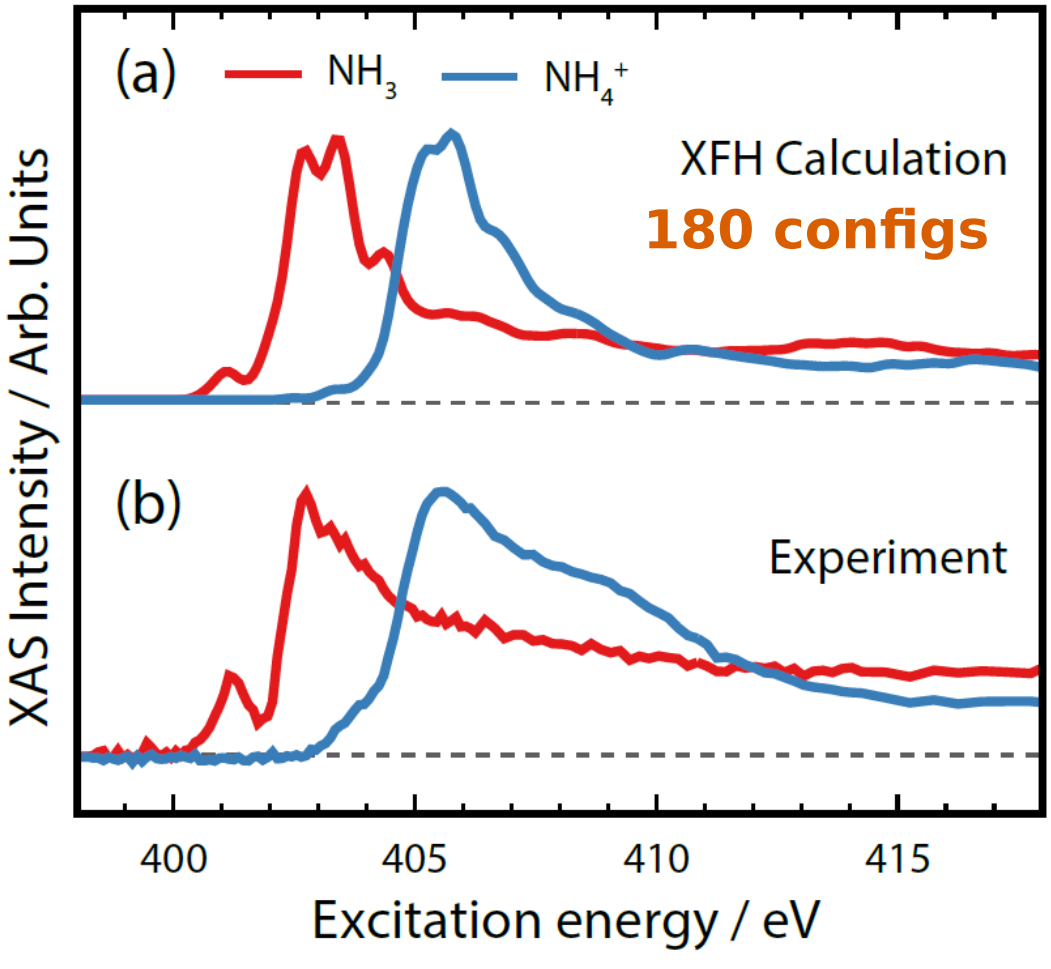
M. Ekimova et al. DOI: 10.1021/jacs.7b07207
J. Am. Chem. Soc. 2017, 139, 12773−12783

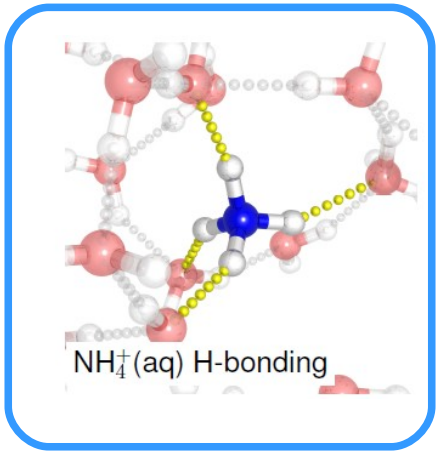
Hydration structure of NH_3(aq) and NH_4^+(aq)

pH dependence in N K-edge X-ray absorption

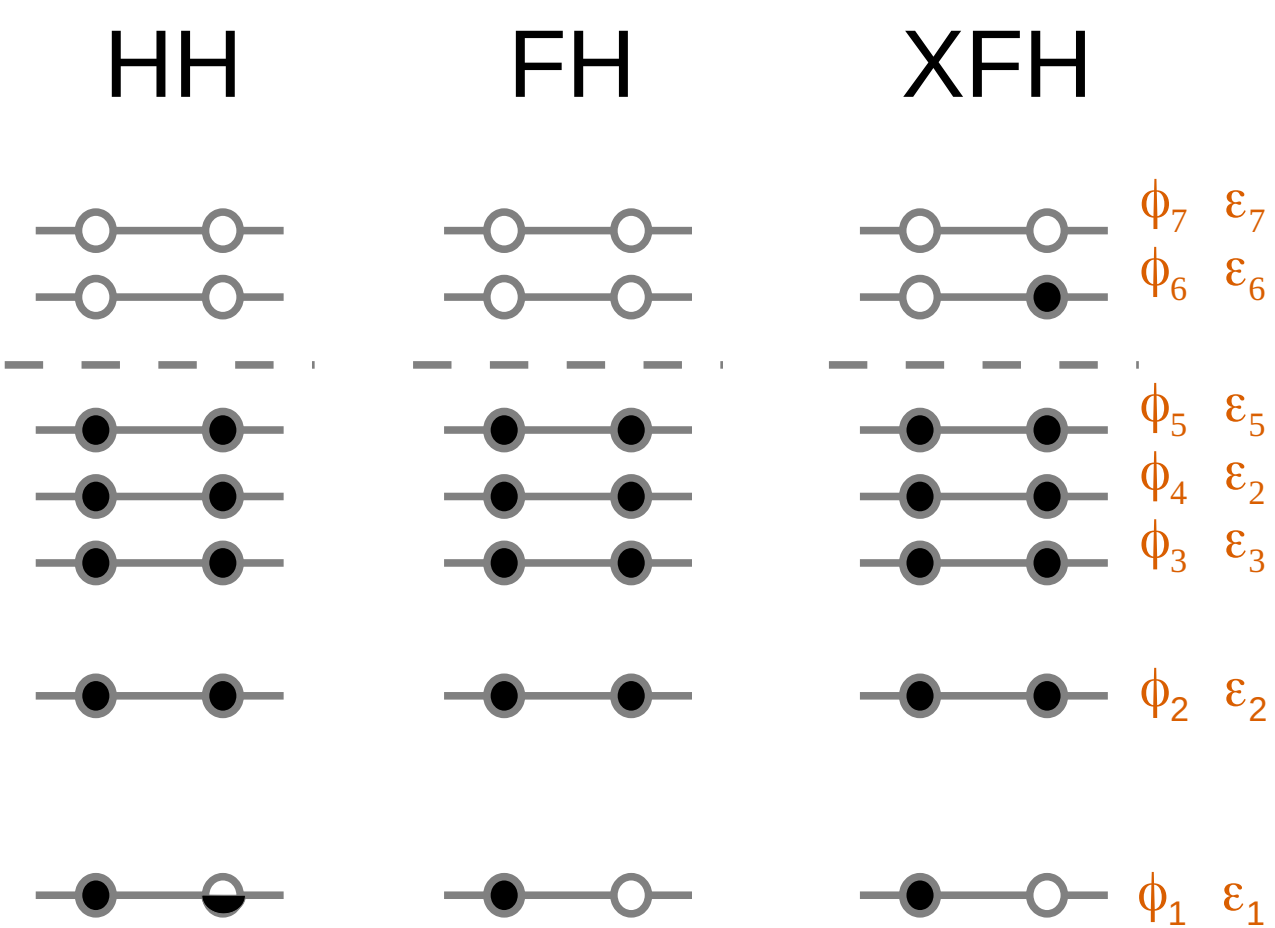
M. Ekimova et al. DOI: 10.1021/jacs.7b07207
J. Am. Chem. Soc. 2017, 139, 12773−12783

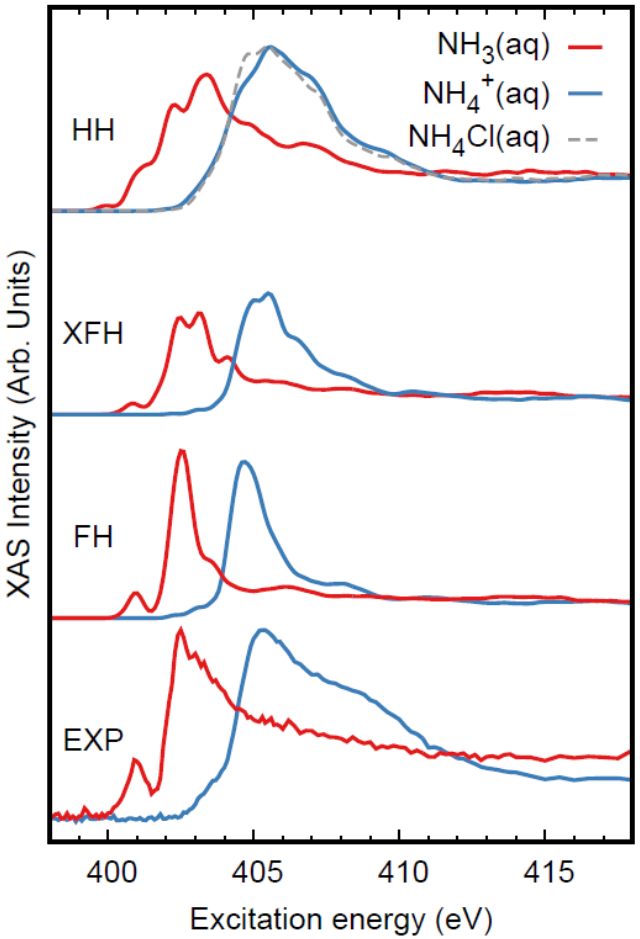






Transition potential approximations of N K-edge XAS

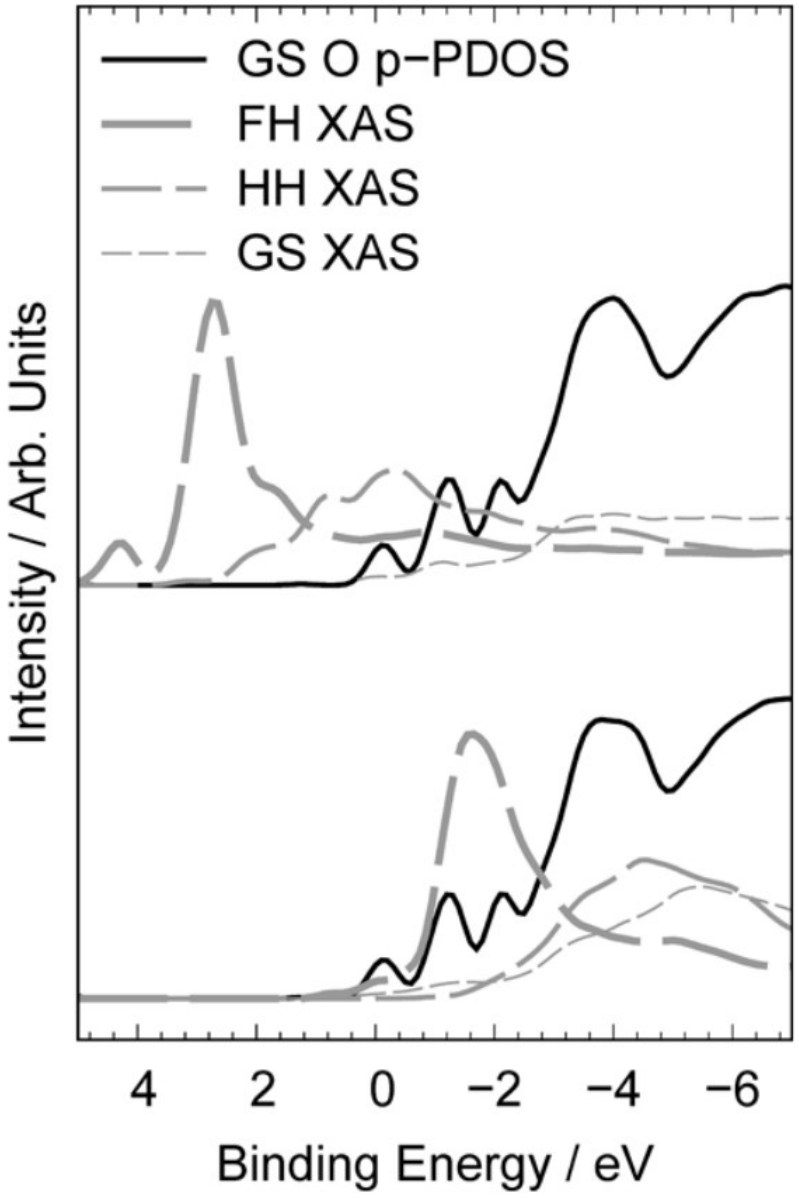




In our case,
XFH and FH are superior to HH

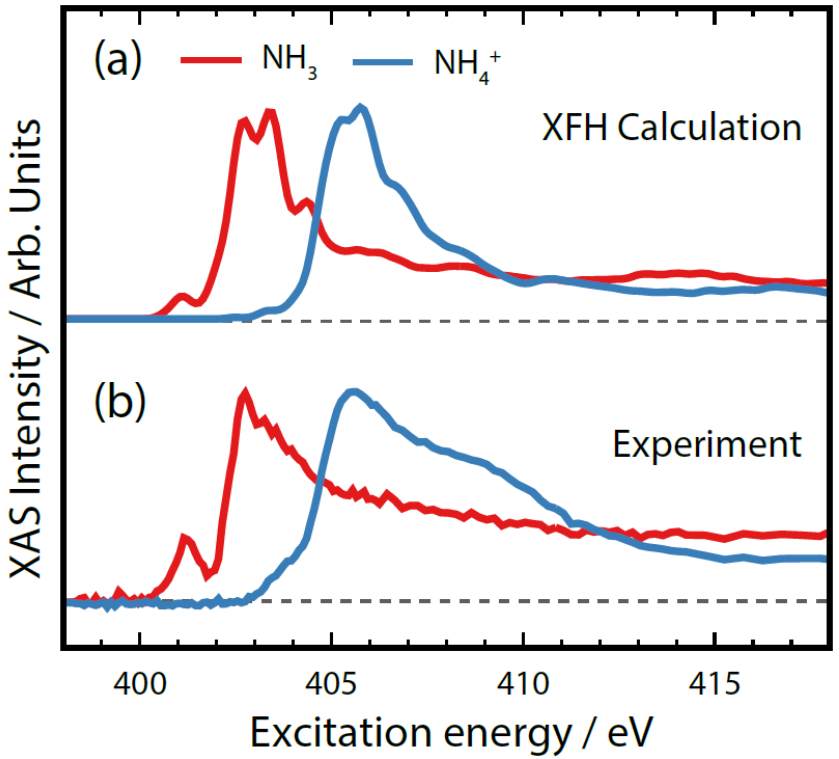
M. Ekimova et al. DOI: 10.1021/jacs.7b07207
J. Am. Chem. Soc. 2017, 139, 12773−12783

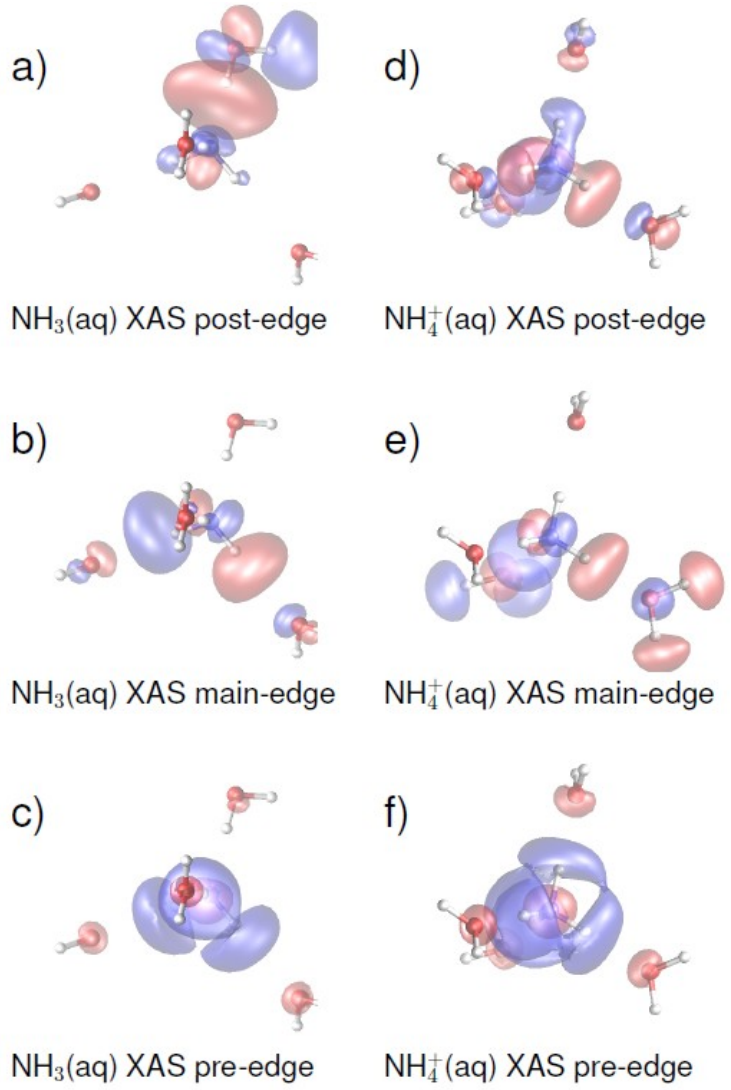
Electronic relaxation in the presence of the core-hole



M. Ekimova et al. DOI: 10.1021/jacs.7b07207
J. Am. Chem. Soc. 2017, 139, 12773−12783

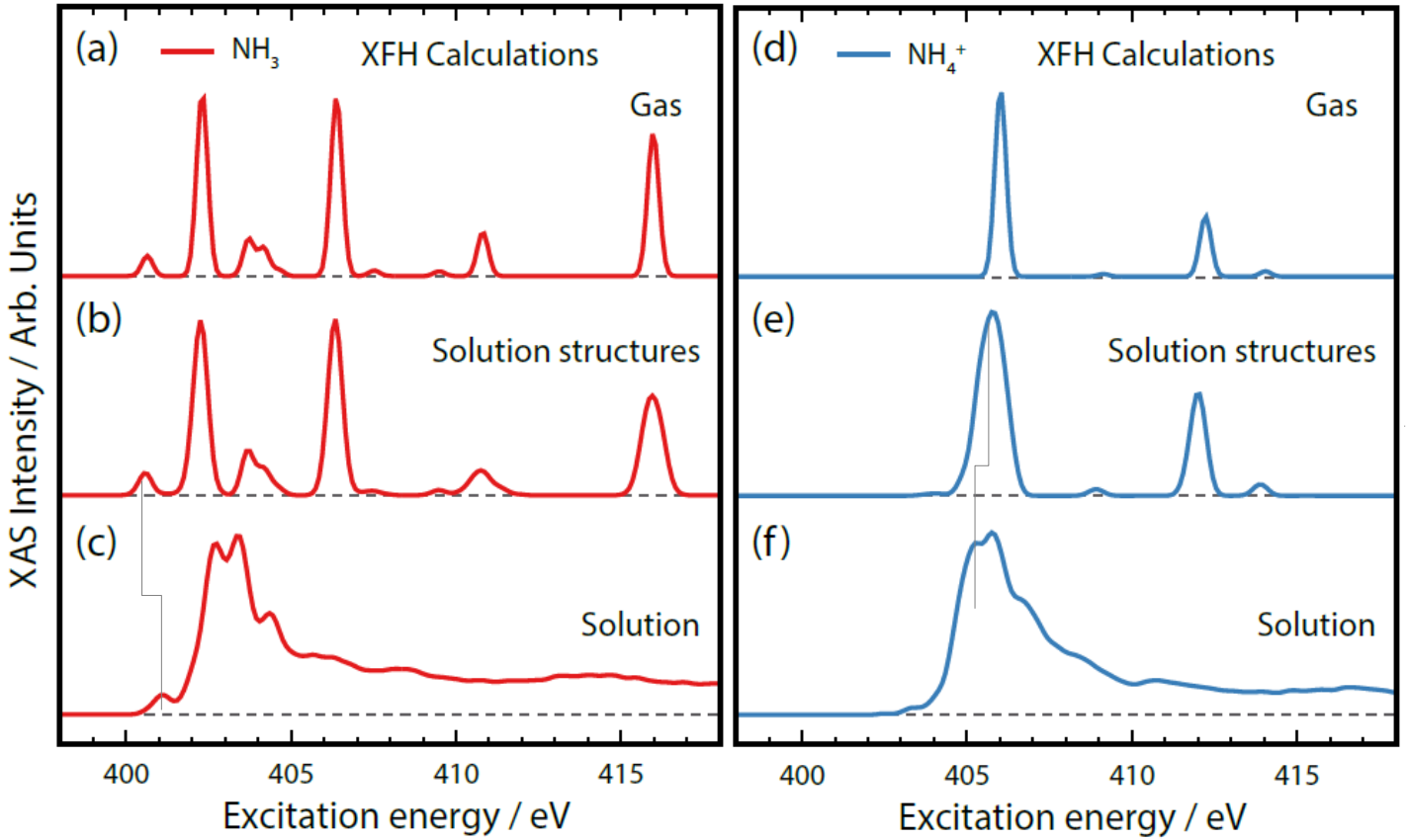
N K-edge XAS of NH_3(aq) and NH_4^+(aq)

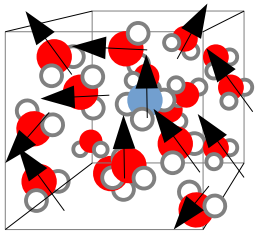




M. Ekimova et al. DOI: 10.1021/jacs.7b07207
J. Am. Chem. Soc. 2017, 139, 12773−12783

N K-edge XAS of NH_3(aq) and NH_4^+(aq)





NH_3(aq):

Whole XAS blue-shifted by accepting H-bonding

NH_4^+(aq):

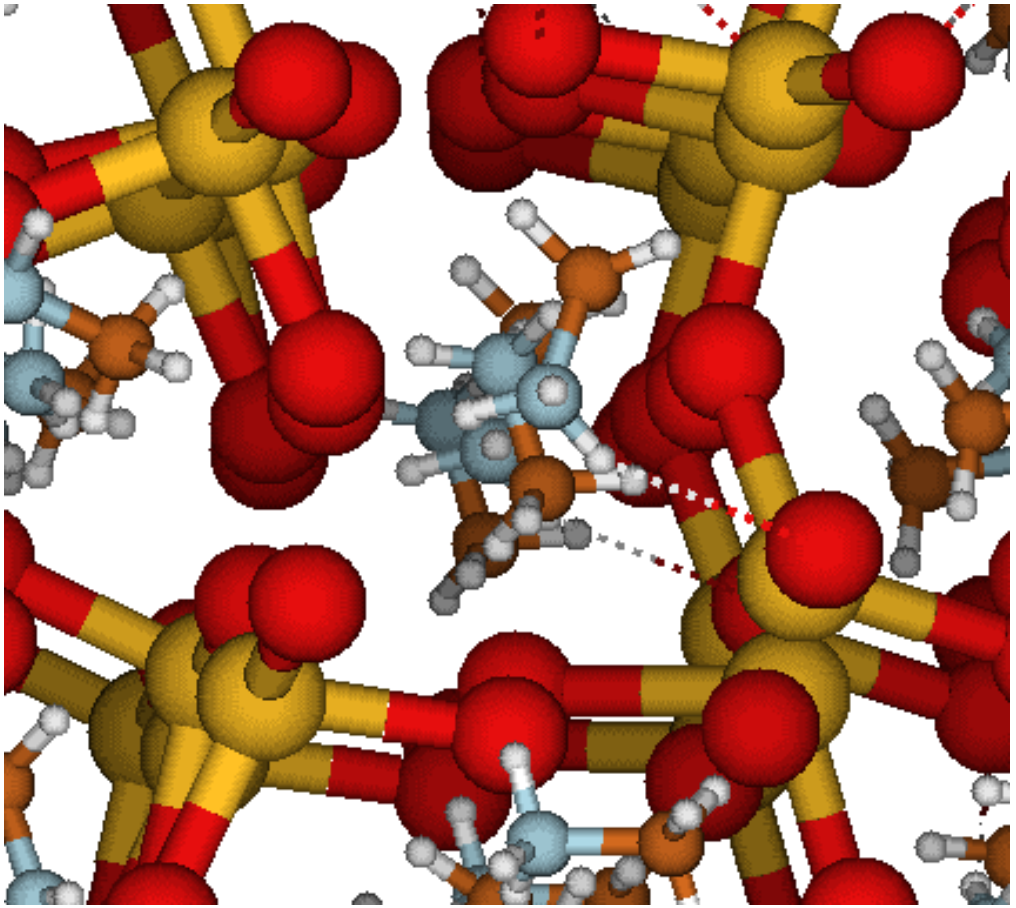
Pre-edge intensity due to distortions
Main-edge slightly red-shifted by donating H-bonding
Post-edge not well reproduced

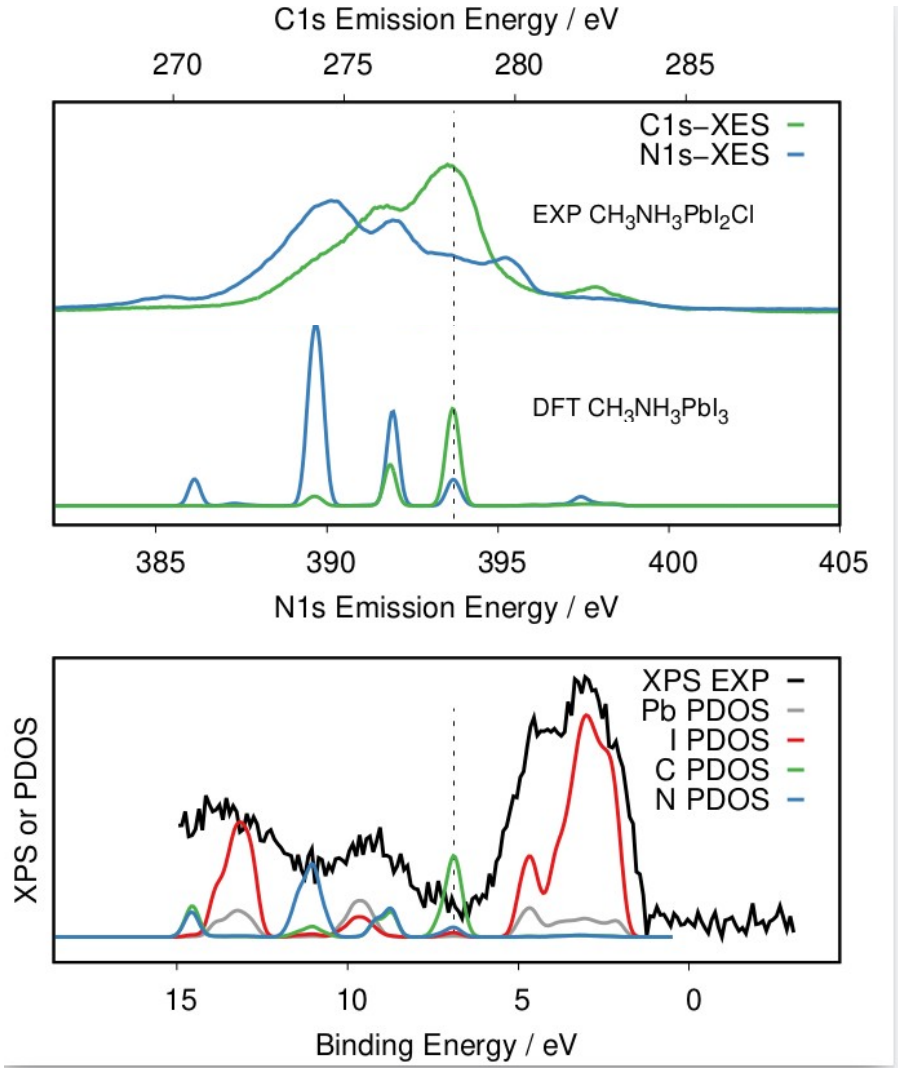
M. Ekimova et al. DOI: 10.1021/jacs.7b07207
J. Am. Chem. Soc. 2017, 139, 12773−12783

Perovskite solar cells: $PbI_3CH_3NH_3$

XPS and XES

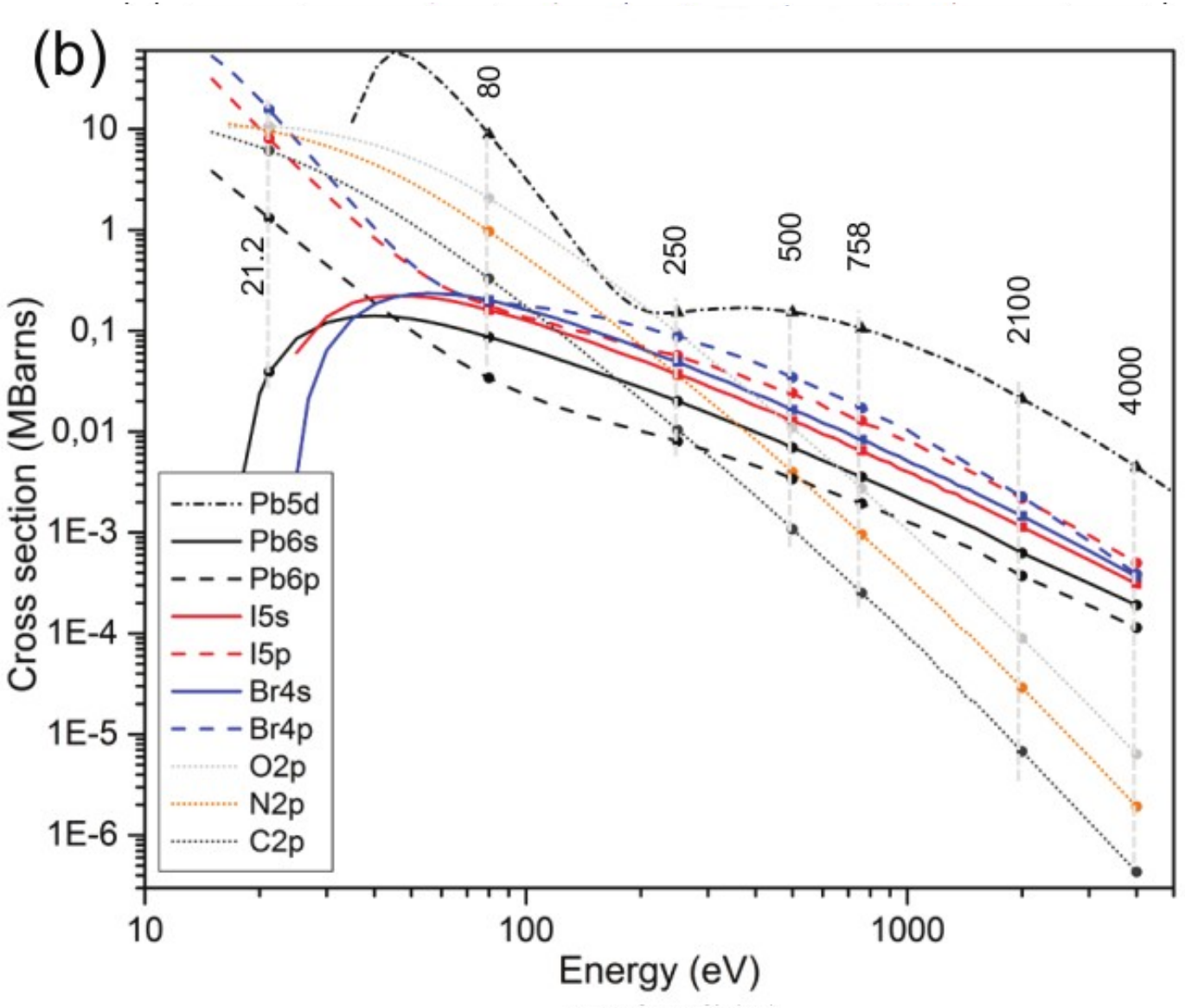
R. Wilks, M. Bär ….A. Erbing, M. Odelius

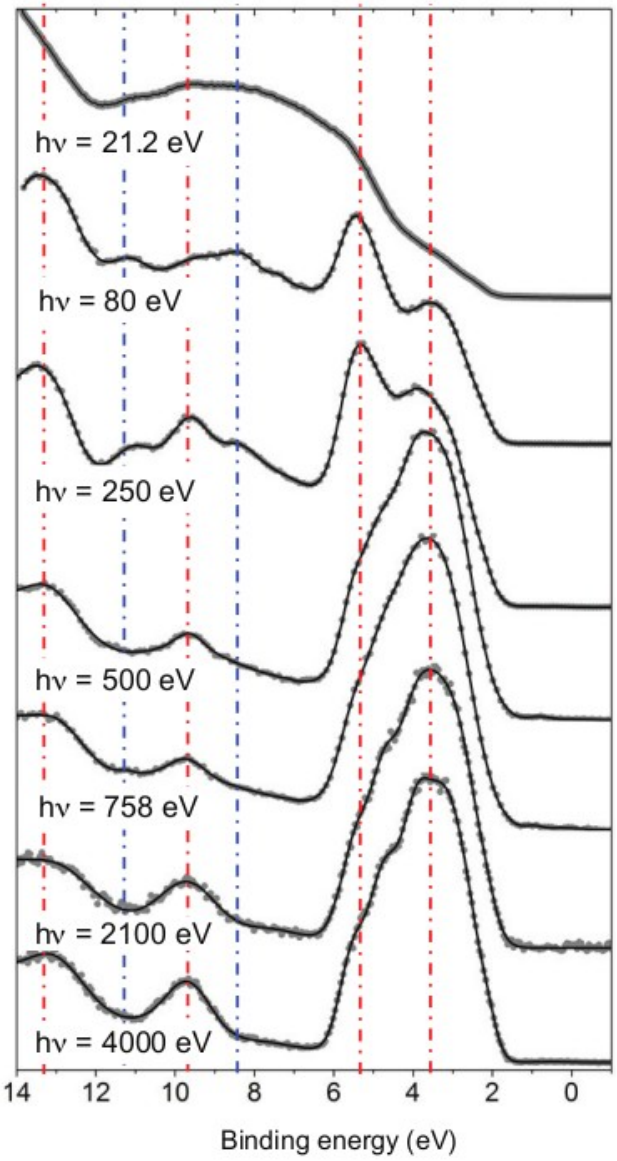




Perovskite solar cells: $PbI_3CH_3NH_3$

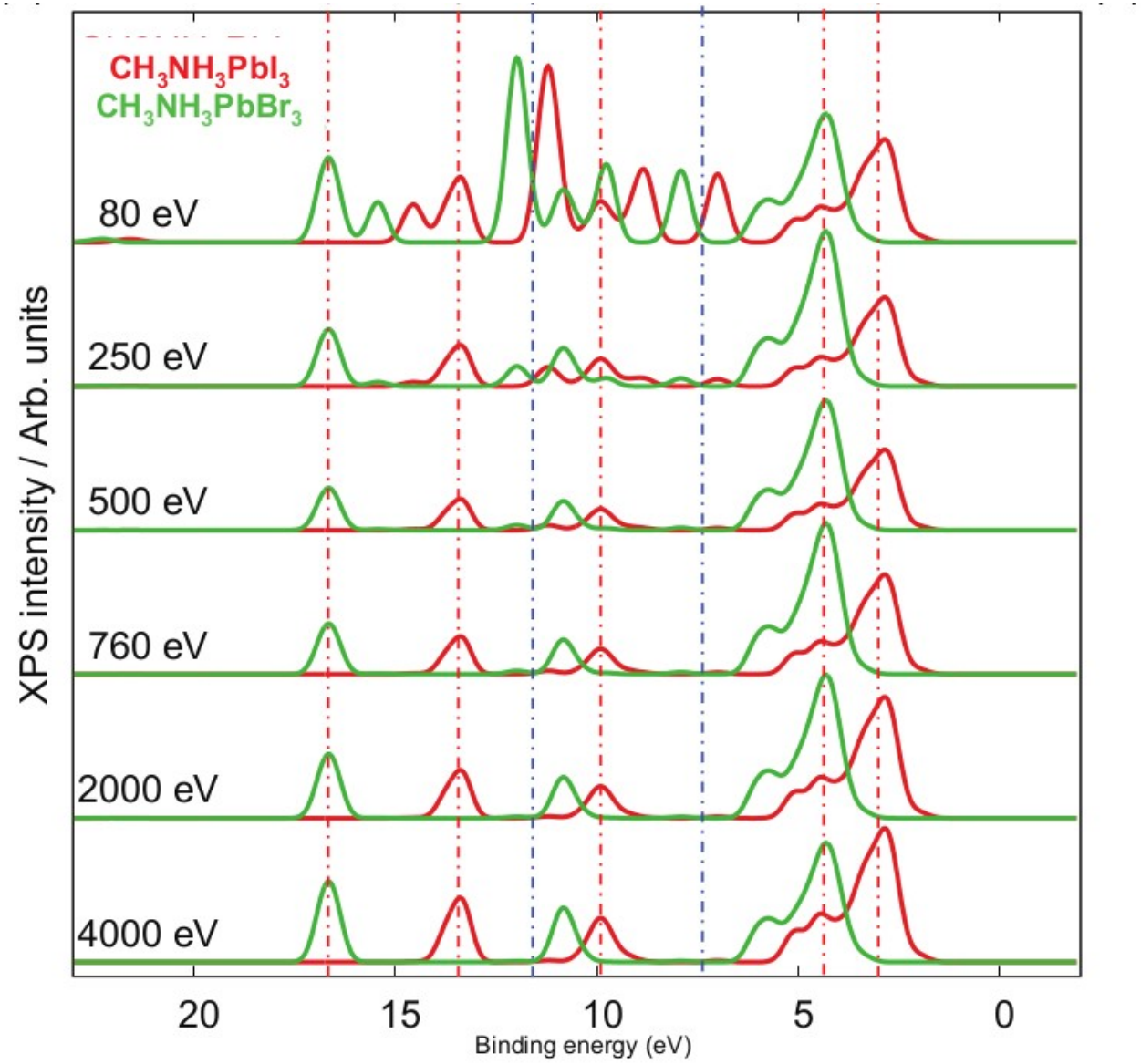
Photo-energy dependence in XPS

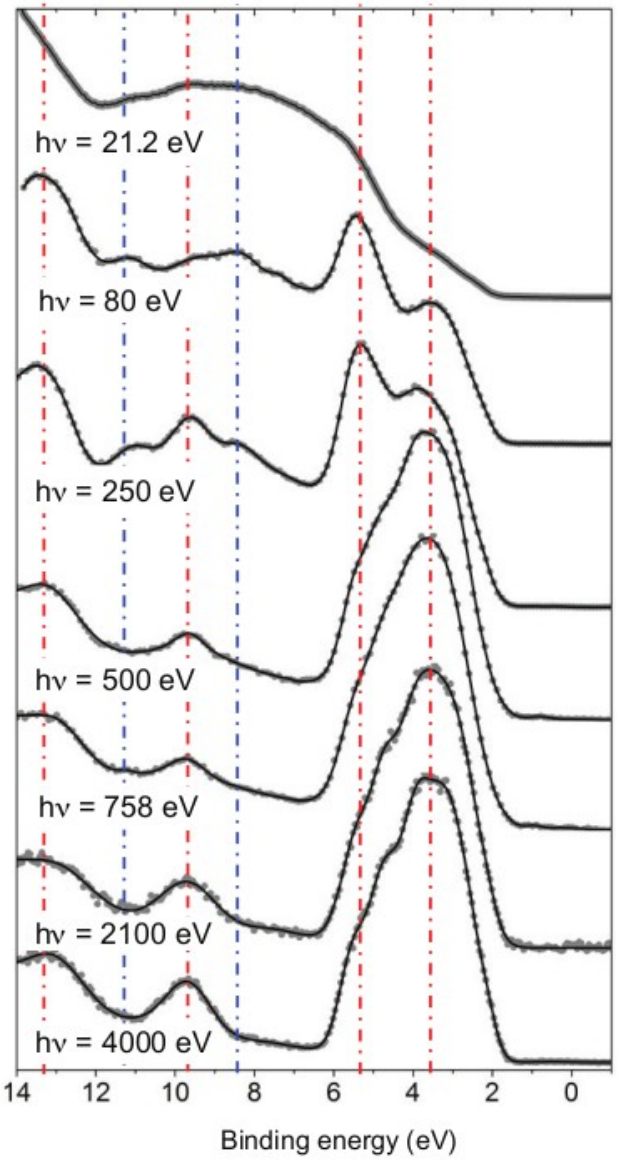




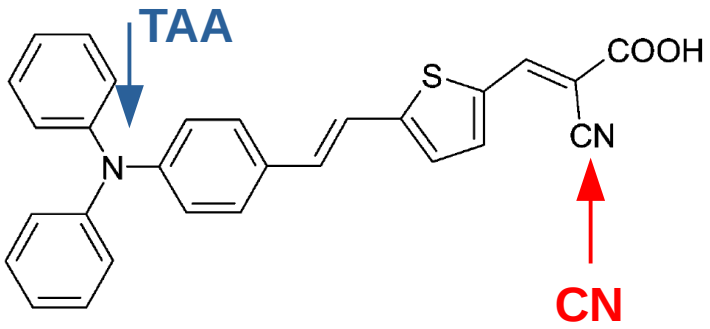
Perovskite solar cells: $PbI_3CH_3NH_3$

Photo-energy dependence in XPS



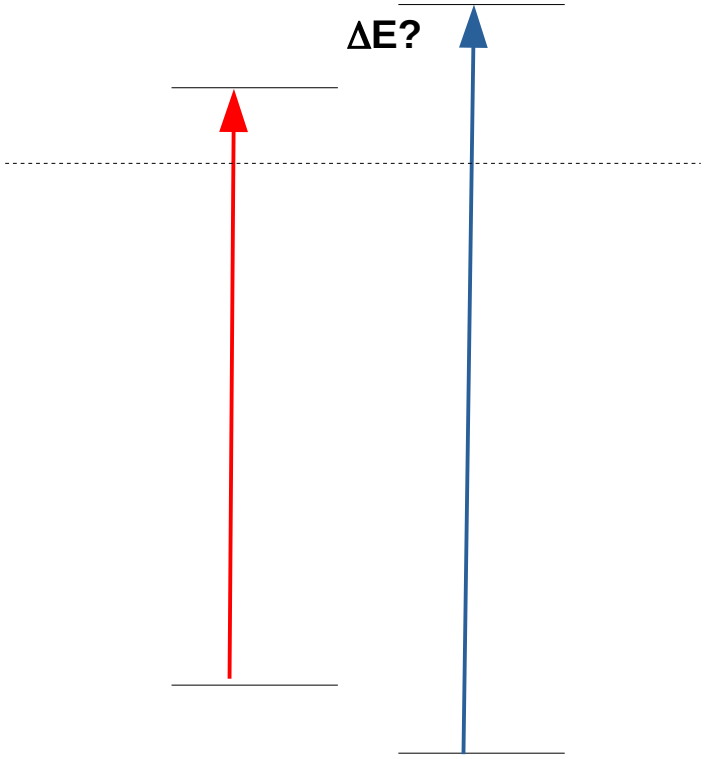


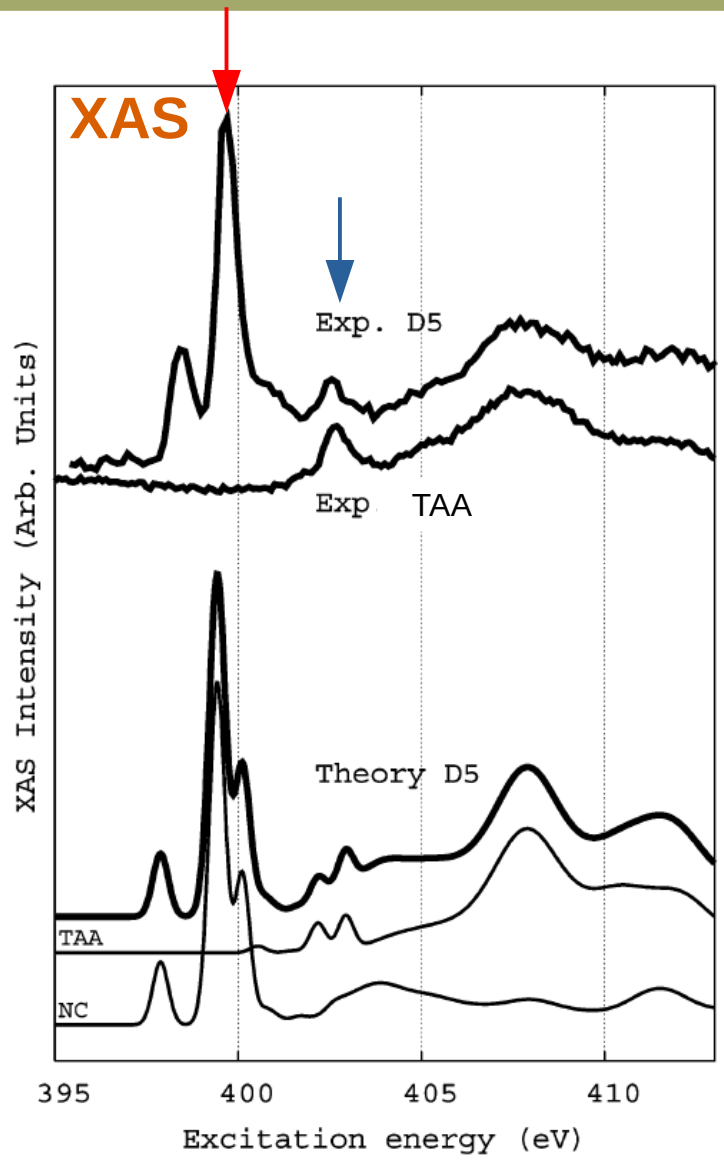
Orbital energies derived from XAS and XPS of an organic dye



Molecular structure of D5.

XAS

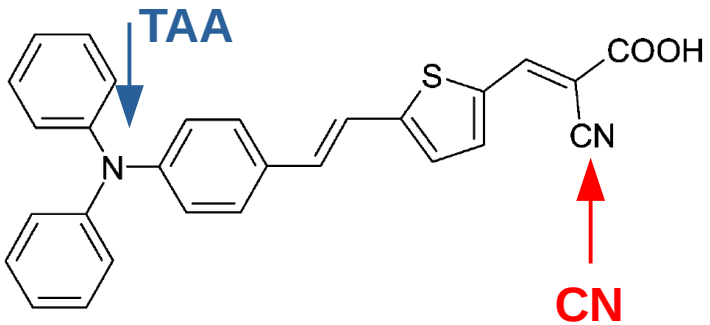




E. Johansson et al

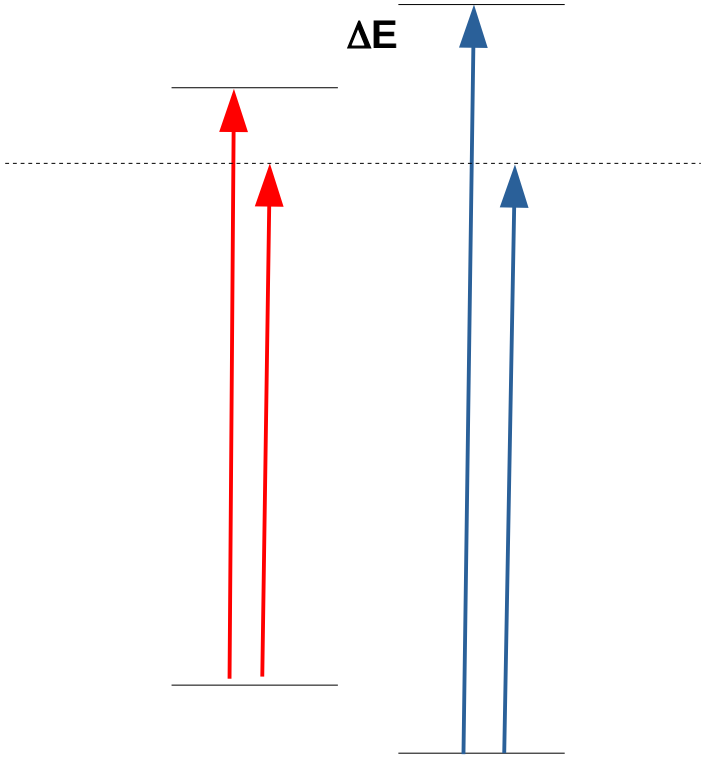
J. Phys. Chem. C **2007**, *111*, 8580−8586

Orbital energies derived from XAS and XPS of an organic dye

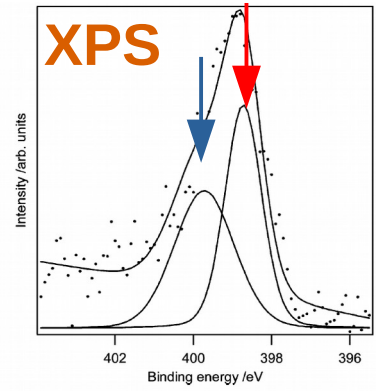


Molecular structure of D5.

XAS-XPS

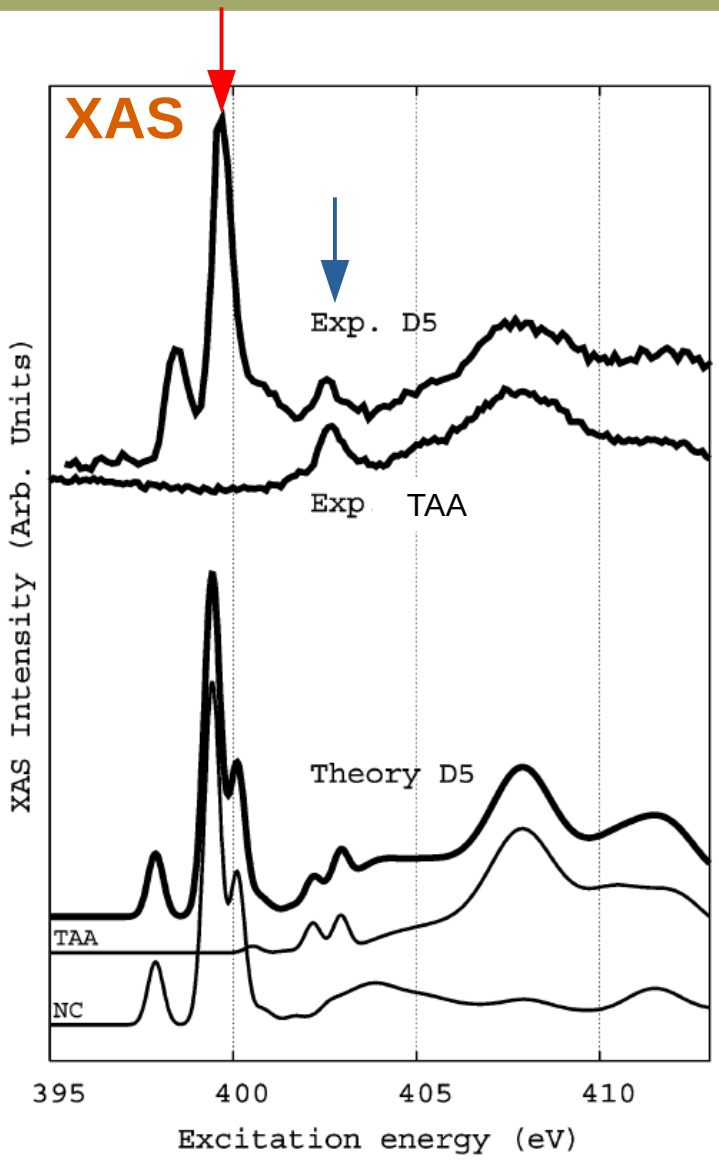


N1s core-levels



Valence XPS show that HOMO resides on TAA

Lowest UV excitation is a TAA → CN charge transfer



E. Johansson et al

J. Phys. Chem. C **2007**, *111*, 8580−8586

Outline

Spectrum simulations – Part I

Molecular orbital representation

XPS - Chemical environment
- Chemical bonding

XES - Local element-specific projection

XAS - Local element-specific projection
- Relaxation in presence of core-hole
- Alignment of energy scales