

Computing Inner-Shell Spectra

- Energies typically in the range a few hundred eV (soft x-ray) or keV (hard x-ray)
- Core-ionized or excited states embedded in the continuum (not the lowest ionized states...)
- Core-levels spatially and energetically well separated
- Resolution typically not superhigh (tenths of eV to meV)
- Relaxation effects large ($O 1s^{-1}$ in water ~ 20 eV)
- Challenge for ground state approach
- Dynamical correlation "simple" – mainly in ground state
- Relativistic effects affect energy scale ($O 1s^{-1} \sim 0.3$ eV)
- Many states needed
- Continuum treatment

Origin-independent calculation of quadrupole intensities in X-ray spectroscopy

Stephan Bernadotte, Andrew J. Atkins, and Christoph R. Jacob^{a)}
Karlsruhe Institute of Technology (KIT), Center for Functional Nanostructures and Institute of Physical Chemistry, Wolfgang-Gaede-Str. 1a, 76131 Karlsruhe, Germany

(Received 10 September 2012; accepted 23 October 2012; published online 26 November 2012)

II. THEORY

For the theoretical description of spectroscopic processes, quantum chemistry commonly employs a semi-classical theory. In this framework, the molecules are described with (nonrelativistic) quantum-mechanics, whereas the electromagnetic radiation is treated classically (for a discussion, see also Ref. 60). This theoretical framework is also appropriate for absorption and emission processes in X-ray spectroscopy. Here, we will focus on the case of absorption, but the results can be transferred to other types of experiments.

A. Electromagnetic radiation

Within the Coulomb gauge (i.e., if one chooses the vector potential such that $\nabla \cdot \mathbf{A} = 0$), a monochromatic, linearly polarized electromagnetic wave is defined by the scalar and vector potentials,^{61–63}

$$\phi(\mathbf{r}, t) = 0, \quad (1)$$

$$\mathbf{A}(\mathbf{r}, t) = -A_0 \mathcal{E} \cos(\mathbf{k} \cdot \mathbf{r} - \omega t), \quad (2)$$

where the wave vector \mathbf{k} points in the direction of propagation and its magnitude is related to the wavelength by $\lambda = 2\pi/k$, where $k = |\mathbf{k}|$. The angular frequency ω is $\omega = 2\pi\nu$ with the frequency ν , and frequency and wavelength are related by $c = \lambda\nu = \omega/k$, where c is the speed of light. Finally, the polarization vector \mathcal{E} is a real unit vector that is perpendicular to the direction of propagation (i.e., $\mathcal{E} \cdot \mathbf{k} = 0$).

From these scalar and vector potentials, one obtains for the electric and magnetic fields,

$$\mathbf{E}(\mathbf{r}, t) = -\nabla\phi(\mathbf{r}, t) - \frac{1}{c} \frac{\partial \mathbf{A}(\mathbf{r}, t)}{\partial t} = A_0 k \mathcal{E} \sin(\mathbf{k} \cdot \mathbf{r} - \omega t), \quad (3)$$

$$\mathbf{B}(\mathbf{r}, t) = \nabla \times \mathbf{A}(\mathbf{r}, t) = A_0 (\mathbf{k} \times \mathcal{E}) \sin(\mathbf{k} \cdot \mathbf{r} - \omega t). \quad (4)$$

Here and in the following, we are using the Gaussian system of units. The electric and magnetic fields are perpendicular to each other and to the direction of propagation and are oscillating with angular frequency ω and the wavelength λ . The amplitudes of the electric and magnetic fields are $E_0 = B_0 = A_0 k$.

The intensity $I(\omega)$ of the electromagnetic radiation is defined as the energy flux per area through a surface perpendicular to the propagation direction. It can be calculated from the Poynting vector,⁶¹

$$\mathbf{S} = \frac{c}{4\pi} (\mathbf{E} \times \mathbf{B}), \quad (5)$$

by taking the absolute value and averaging over one period of the oscillations,

$$I(\omega) = \int_0^{1/\nu} |\mathbf{S}| dt = \frac{1}{8\pi} \frac{\omega^2}{c} A_0^2 = \frac{c}{8\pi} k^2 A_0^2. \quad (6)$$

B. Molecules in an electromagnetic field

In the absence of an external electromagnetic field, a molecular system within the Born–Oppenheimer approximation is described by the nonrelativistic Hamiltonian

$$\hat{H}_0 = \sum_{i=1}^N \frac{\hat{\mathbf{p}}_i^2}{2m_e} + V(\mathbf{r}_1, \dots, \mathbf{r}_N), \quad (7)$$

where the momentum operator is given by $\hat{\mathbf{p}} = -i\hbar\nabla$, m_e and e are the mass and the charge of the electron, respectively, and the potential energy $V(\mathbf{r}_1, \dots, \mathbf{r}_N)$ contains the electron–nuclei attraction as well as the electron–electron repulsion. Here and in the following, the index i is used to label the electrons.

An external vector potential can be included in this Hamiltonian via^{62–64}

$$\begin{aligned} \hat{H} &= \sum_i \frac{1}{2m_e} \left[\hat{\mathbf{p}}_i - \frac{e}{c} \mathbf{A}(\mathbf{r}_i, t) \right]^2 \\ &\quad - \frac{ge}{2m_e c} \sum_i \mathbf{B}(\mathbf{r}_i, t) \cdot \hat{\mathbf{s}}_i + V(\mathbf{r}_1, \dots, \mathbf{r}_N) \\ &= \sum_i \left[\frac{\hat{\mathbf{p}}_i^2}{2m_e} - \frac{e}{m_e c} \mathbf{A}(\mathbf{r}_i, t) \cdot \hat{\mathbf{p}}_i + \frac{e^2}{2m_e c^2} A^2(\mathbf{r}_i, t) \right] \\ &\quad - \frac{ge}{2m_e c} \sum_i \mathbf{B}(\mathbf{r}_i, t) \cdot \hat{\mathbf{s}}_i + V(\mathbf{r}_1, \dots, \mathbf{r}_N), \quad (8) \end{aligned}$$

where g is the electron g -factor. In the second line we used that in the Coulomb gauge, $\mathbf{p}_i \cdot \mathbf{A} = \mathbf{A} \cdot \mathbf{p}_i$. After neglecting the term that is quadratic in \mathbf{A} , which is justified for weak electromagnetic fields, this can be expressed as

$$\hat{H} = \hat{H}_0 + \hat{U}(t), \quad (9)$$

where the time-dependent perturbation is given by

$$\begin{aligned} \hat{U}(t) &= -\frac{e}{m_e c} \sum_i \mathbf{A}(\mathbf{r}_i, t) \cdot \hat{\mathbf{p}}_i - \frac{ge}{2m_e c} \sum_i \mathbf{B}(\mathbf{r}_i, t) \cdot \hat{\mathbf{s}}_i \\ &= \frac{eA_0}{m_e c} \sum_i \left[\cos(\mathbf{k} \cdot \mathbf{r}_i - \omega t) (\mathcal{E} \cdot \hat{\mathbf{p}}_i) \right. \\ &\quad \left. - \frac{g}{2} \sin(\mathbf{k} \cdot \mathbf{r}_i - \omega t) (\mathbf{k} \times \mathcal{E}) \cdot \hat{\mathbf{s}}_i \right], \quad (10) \end{aligned}$$

Here, we inserted the vector potential and the magnetic field of an electromagnetic wave given in Eqs. (2) and (4). Using $\sin(x) = \frac{1}{2i}[\exp(ix) - \exp(-ix)]$, this can be expressed in the form

$$\hat{U}(t) = \hat{U} \exp(-i\omega t) + \hat{U}^* \exp(i\omega t), \quad (11)$$

with the time-independent perturbation operator,

$$\begin{aligned} \hat{U} &= \frac{eA_0}{2m_e c} \sum_i \left[\exp(i\mathbf{k} \cdot \mathbf{r}_i) (\mathcal{E} \cdot \hat{\mathbf{p}}_i) \right. \\ &\quad \left. + i \frac{g}{2} \exp(i\mathbf{k} \cdot \mathbf{r}_i) (\mathbf{k} \times \mathcal{E}) \cdot \hat{\mathbf{s}}_i \right]. \quad (12) \end{aligned}$$

With this form of the perturbation, we can apply Fermi's golden rule to obtain the transition rate (i.e., the rate of change in the probability of finding the molecule in the n th excited state)^{62,63,65}

$$\begin{aligned} \Gamma_{0n}(\omega) &= \frac{2\pi}{\hbar} |\langle 0 | \hat{U} | n \rangle|^2 \delta(\omega - \omega_{0n}) \\ &= \frac{\pi A_0^2}{2\hbar c^2} |T_{0n}|^2 \delta(\omega - \omega_{0n}), \quad (13) \end{aligned}$$

where we introduced the transition moments

$$\begin{aligned} T_{0n} &= \frac{e}{m_e} \sum_i \langle 0 | \exp(i\mathbf{k} \cdot \mathbf{r}_i) (\hat{\mathbf{p}}_i \cdot \mathcal{E}) \\ &\quad + i \frac{g}{2} \exp(i\mathbf{k} \cdot \mathbf{r}_i) (\mathbf{k} \times \mathcal{E}) \cdot \hat{\mathbf{s}}_i | n \rangle. \quad (14) \end{aligned}$$

Here, $|0\rangle$ and $|n\rangle$ are the eigenfunctions of the time-independent Hamiltonian \hat{H}_0 with $\hat{H}_0|n\rangle = E_n|n\rangle$, and transitions only occur if the frequency of the perturbation matches the energy differences between eigenstates of the unperturbed molecule, i.e., for $\omega = \omega_{0n} = (E_n - E_0)/\hbar$.

Now, Eq. (6) can be used to eliminate A_0^2 from the equation for the transition rate to arrive at

$$\Gamma_{0n}(\omega) = \frac{4\pi^2}{c\hbar\omega^2} |T_{0n}|^2 I(\omega) \delta(\omega - \omega_{0n}). \quad (15)$$

The absorption cross section, describing the rate of energy transfer from the electromagnetic radiation to the molecule, is defined as

$$\sigma_{0n} = \int \frac{\Gamma(\omega)\hbar\omega}{I(\omega)} d\omega = \frac{4\pi^2\hbar}{cE_{0n}} |T_{0n}|^2, \quad (16)$$

where $E_{0n} = E_n - E_0$. Finally, one usually introduces the dimensionless oscillator strengths,

$$f_{0n} = \frac{m_e c}{2\pi^2 e^2 \hbar} \sigma_{0n} = \frac{2m_e}{e^2 E_{0n}} |T_{0n}|^2. \quad (17)$$

These are defined as transition rates relative to a harmonic oscillator model,^{63,65} which fixes the prefactor connecting the absorption cross section and the oscillator strengths.

C. Multipole expansion

Calculating the oscillator strengths via the matrix elements of Eq. (14) would in principle be possible, but is cumbersome and in general not feasible. The required integrals are difficult to compute analytically (for a possible approach, see Ref. 66), and because of its dependence on the wave vector \mathbf{k} , the operator in T_{0n} is different for each excitation. Therefore, one usually performs a multipole expansion. The starting point for this expansion is a development of the exponential in a Taylor series,

$$\exp(i\mathbf{k} \cdot \mathbf{r}_i) = 1 + i(\mathbf{k} \cdot \mathbf{r}_i) - \frac{1}{2}(\mathbf{k} \cdot \mathbf{r}_i)^2 + \dots \quad (18)$$

This is substituted into Eq. (14) and, subsequently, one collects the terms of different orders in the wave vector \mathbf{k} , i.e.,

$$T_{0n} = T_{0n}^{(0)} + T_{0n}^{(1)} + T_{0n}^{(2)} + \dots \quad (19)$$

In the following, we will consider terms up to second order in \mathbf{k} . Here, $|\mathbf{k}| = 2\pi/\lambda$ acts as the expansion parameter, and we note that for larger wavelengths λ , the convergence of the Taylor expansion will be faster. For typical molecules and wavelengths in the ultraviolet or visible range, the wavelength is large compared to the molecular size, and it is sufficient to include only the first (zeroth-order) term in this expansion. This corresponds to assuming that the oscillating electric field is constant over the whole molecule. However, for the short wavelengths used in hard X-ray spectroscopy this approximation is not adequate and higher-order terms need to be included.

Note: XAS through hard x-ray Raman in dipole limit for low q-transfer

1. Zeroth order: Electric-dipole moment

In zeroth order in the wave vector \mathbf{k} , we have

$$T_{0n}^{(0)} = \frac{e}{m_e} \sum_i \langle 0 | \hat{\mathbf{p}}_i \cdot \boldsymbol{\mathcal{E}} | n \rangle = \boldsymbol{\mathcal{E}} \cdot \langle 0 | \hat{\boldsymbol{\mu}}^p | n \rangle, \quad (20)$$

where we have introduced the electric-dipole moment operator in the velocity representation

$$\hat{\boldsymbol{\mu}}^p = \frac{e}{m_e} \sum_i \hat{\mathbf{p}}_i. \quad (21)$$

By using the relation

$$[r_{i,\alpha}, \hat{H}_0] = \frac{\hbar^2}{m} \hat{p}_{i,\alpha}, \quad (A1)$$

Next, we employ that the matrix elements of the commutator of an operator \hat{A} and \hat{H}_0 are given by

$$\begin{aligned} \langle 0 | [\hat{A}, \hat{H}_0] | n \rangle &= \langle 0 | \hat{A} \hat{H}_0 - \hat{H}_0 \hat{A} | n \rangle = E_n \langle 0 | \hat{A} | n \rangle - E_0 \langle 0 | \hat{A} | n \rangle \\ &= E_{0n} \langle 0 | \hat{A} | n \rangle. \end{aligned} \quad (A4)$$

Here, it is important to point out that this relation is only valid for the exact eigenfunctions of \hat{H}_0 and that it only holds approximately for approximate wavefunctions.

Now, we can use these results to obtain

$$\langle 0 | \hat{p}_{i,\alpha} | n \rangle = \frac{m}{i\hbar} \langle 0 | [r_{i,\alpha}, \hat{H}_0] | n \rangle = -i E_{0n} \frac{m}{\hbar} \langle 0 | r_{i,\alpha} | n \rangle \quad (A5)$$

and get for the electric-dipole transition moments

$$\begin{aligned} \langle 0 | \hat{\boldsymbol{\mu}}_\alpha^p | n \rangle &= \sum_i \frac{e}{m} \langle 0 | \hat{p}_{i,\alpha} | n \rangle = -i \frac{E_{0n}}{\hbar} e \sum_i \langle 0 | r_{i,\alpha} | n \rangle \\ &= -i \frac{E_{0n}}{\hbar} \langle 0 | \hat{\boldsymbol{\mu}}_\alpha | n \rangle. \end{aligned} \quad (A6)$$

Thus, for the zeroth-order contribution, we arrive at

$$T_{0n}^{(0)} = T_{0n}^{(\mu)} = -i \frac{E_{0n}}{\hbar} (\boldsymbol{\mathcal{E}} \cdot \langle 0 | \hat{\boldsymbol{\mu}} | n \rangle). \quad (24)$$

Basic Methods for X-ray Spectra

STATIC EXCHANGE APPROXIMATION (STEX) - single channel,
single up excitations

TAMM-DANCOFF APPROXIMATION (TDA) - multichannel,
single up excitations

RANDOM PHASE APPROXIMATION - multi channel, single up and
down excitations

STEX $h\{p\}$: **TDA** $\{hp\}$: **RPA** $\{hp\} + \{ph\}$: **SOPPA** $\{hhpp\} +$
 $\{pphh\}$

TRANSITION POTENTIAL and **EQUIVALENT CORE** models are important
approximations of **STEX**

STATE SPECIFIC - CI, MCSCF, CCSD...
RESPONSE THEORY

TDDFT
BETHE-SALPETER

X-ray Polarization Propagator

- The cross section for linear absorption of radiation by a randomly oriented molecule sample is

$$\sigma(\omega) = \frac{4\pi\omega}{c} \text{Im } \bar{\alpha}(\omega)$$

- $\bar{\alpha}$ denotes the trace of the complex electric dipole polarizability tensor.

$$\alpha_{kl}(\omega) = \hbar^{-1} \sum_{n>0} \left\{ \frac{\langle 0 | \hat{\mu}_k | n \rangle \langle n | \hat{\mu}_l | 0 \rangle}{\omega_{0n} - \omega - i\gamma_n} + \frac{\langle 0 | \hat{\mu}_l | n \rangle \langle n | \hat{\mu}_k | 0 \rangle}{\omega_{0n} + \omega + i\gamma_n} \right\}$$

Carbon X-ray absorption spectra of fluoroethenes and acetone: A study at the coupled cluster, density functional, and static-exchange levels of theory

Thomas Fransson,¹ Sonia Coriani,² Ove Christiansen,³ and Patrick Norman¹

¹Department of Physics, Chemistry and Biology, Linköping University, SE-581 83 Linköping, Sweden

²Dipartimento di Scienze Chimiche e Farmaceutiche, Università degli Studi di Trieste, Via Licio Giorgieri 1, I-34127 Trieste, Italy

³Department of Chemistry, University of Aarhus, DK-8000 Århus C, Denmark

(Received 4 October 2012; accepted 5 March 2013; published online 29 March 2013)

Formalism independent of QC wave function – calibrate for CC2, CCSD, DFT

124311-10 Fransson *et al.*

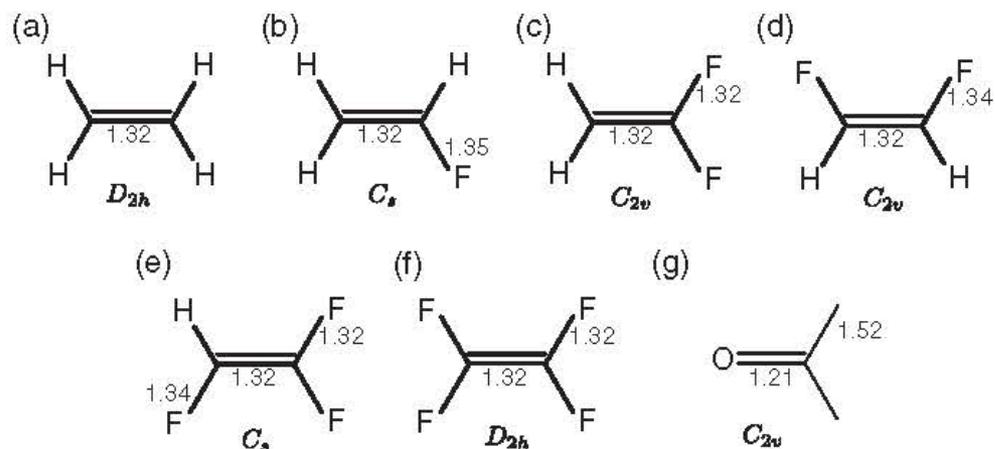
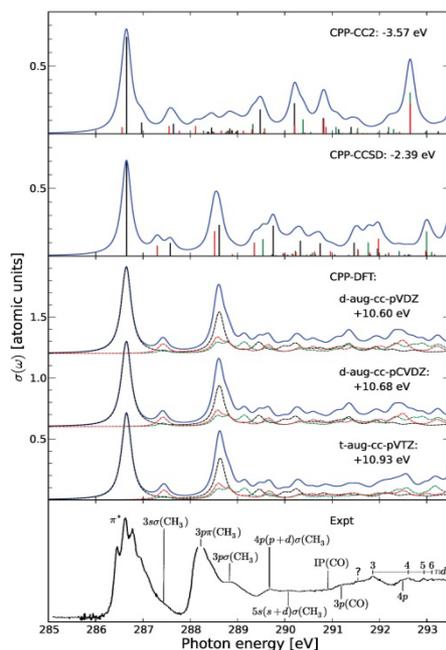
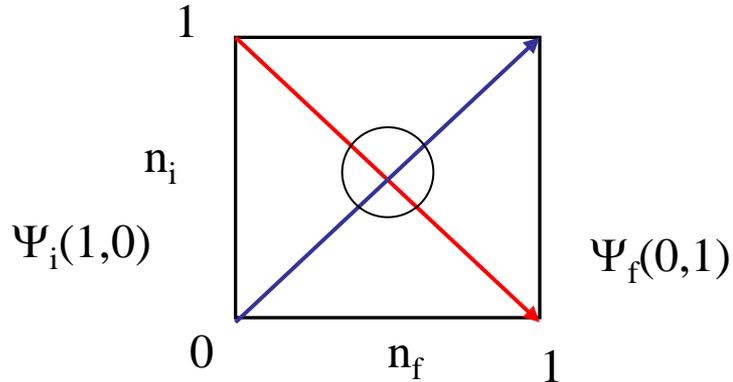


FIG. 1. Molecular structure of (a) ethene, (b) vinylfluoride, (c) 1,1-difluoroethene, (d) *cis*-1,2-difluoroethene, (e) trifluoroethene, (f) tetrafluoroethene, and (g) acetone. Bond lengths are given in Å.

Acetone

Slater Transition State



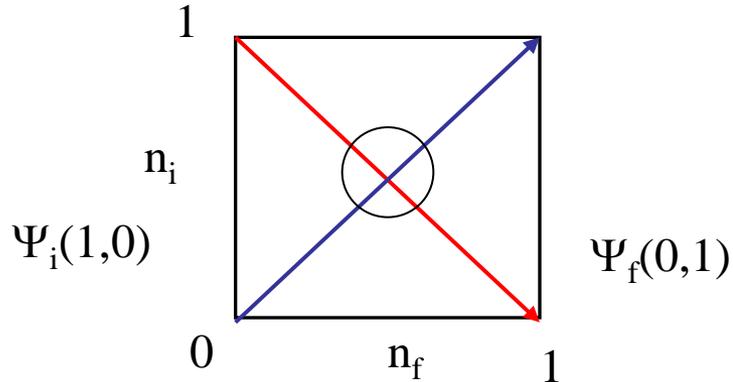
View the excitation as going continuously from GS occupation to one electron excited

Focus on orbitals that change occupation

Energy $E \equiv E(\rho(\mathbf{r}))$

$$\rho(\mathbf{r}) = \sum_i n_i |\varphi_i(\mathbf{r})|^2$$

Slater Transition State



Optimize orbitals at midpoint ($n_i=n_f=1/2$)

Reach GS and excited state by Taylor expansion

Ground state:

$$E(n_i + 1/2, n_f - 1/2) = E(n_i, n_f) + \frac{1}{2} \frac{\partial E}{\partial n_i} - \frac{1}{2} \frac{\partial E}{\partial n_f} + \frac{1}{2!} \left(\frac{1}{2}\right)^2 \left(\frac{\partial^2 E}{\partial^2 n_i} - 2 \frac{\partial^2 E}{\partial n_i \partial n_f} + \frac{\partial^2 E}{\partial^2 n_f} \right) + O(\partial^3)$$

Excited state:

$$E(n_i - 1/2, n_f + 1/2) = E(n_i, n_f) - \frac{1}{2} \frac{\partial E}{\partial n_i} + \frac{1}{2} \frac{\partial E}{\partial n_f} + \frac{1}{2!} \left(\frac{1}{2}\right)^2 \left(\frac{\partial^2 E}{\partial^2 n_i} - 2 \frac{\partial^2 E}{\partial n_i \partial n_f} + \frac{\partial^2 E}{\partial^2 n_f} \right) + O(\partial^3)$$

Excitation energy:

$$\Delta E_{fi} = E_f - E_i = E(n_i - 1/2, n_f + 1/2) - E(n_i + 1/2, n_f - 1/2) = \frac{\partial E}{\partial n_f} - \frac{\partial E}{\partial n_i} + O(\partial^3)$$

Janak's Theorem: $\frac{\partial E}{\partial n_i} = \varepsilon_i$



$$\Delta E_{fi} = \varepsilon_{+1/2}^f - \varepsilon_{-1/2}^i + O(\partial^3)$$

Transition Potential

- Excitation energies can be obtained as orbital energy difference

$$\Delta E_{exc}^{i \rightarrow j} = \epsilon_j^{1/2} - \epsilon_i^{-1/2}$$

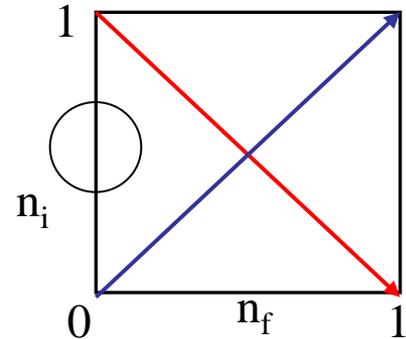
- Remove half an electron, put it back in excited level
- Slater's **transition state**
- Relaxations correct to second-order
- **Drawback**: requires state-by-state calculation

Approximation: **Half-occupied core hole only (biggest effect)**

- Gives density/potential for excited level
- **Double basis set**: Add large diffuse basis set to excitation center \Rightarrow more states **Now “bring back electron”**
- Compute transition moments

XAS: StoBe-deMon DFT code

StoBe version: **Lars G.M.Pettersson**, Stockholm
Klaus Hermann, Berlin

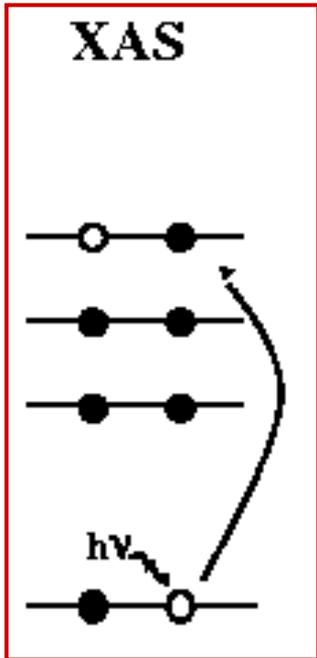


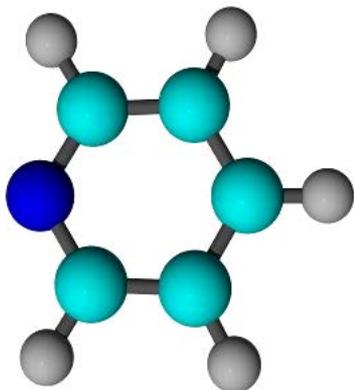
- Determine transition potential *i.e.* half-occupied core hole
- Build K-S matrix again in much larger (augmented) basis
- Use same orbitals for initial and final states
- Orthogonal transition moments

$$\sigma \propto \left| \langle \varphi_{1s} | \mathbf{r} | \varphi_{\varepsilon} \rangle \right|^2$$

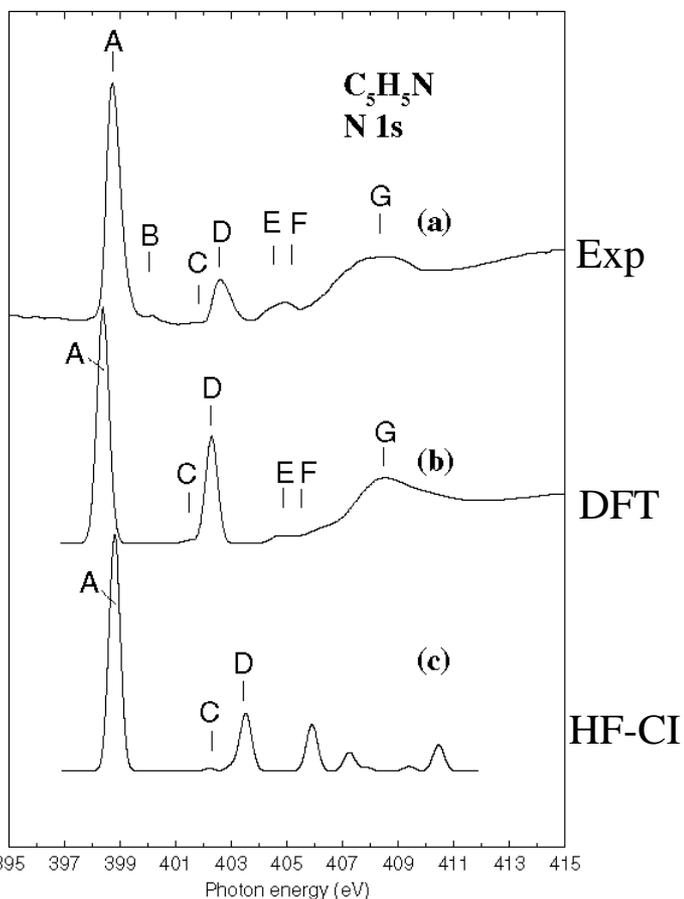
- Continuum through convolution (energy dependent)

Interactions correct but static ("Static Exchange")
i.e. not self-consistent when adding electron to
 $\hat{a}_{1s} \Psi^{\text{TP}}$
 Relaxation effects: Continuum < Rydberg < Valence





Example: Gas phase Pyridine N 1s Spectrum



1. Do Transition Potential ($1s^{-1/2}$) calculation to define potential and relative energies
 → overall spectrum
2. Compute full core hole for fully relaxed IP
 Add relativity (+0.3 eV)
 → overall shift
3. Compute excited states separately for the lowest excitations (trick) to get relaxation



Energy positions 0.4 ± 0.1 eV too low
 Also good intensities

- *Peak D goes from valence to valence + Rydberg with relaxation*
 - *Peak B from vibronic coupling*
- Assignment and analysis can be made

Variational H-K Method

Procedure: Determine E_{GS} and ρ by means of a constrained energy minimization of the energy functional $E[\rho]$

N = total number of particles;
 $\phi[\rho]$ is the functional of the density

$$E[\rho] = \langle \phi[\rho] | T + V_{ext} + V_{coul} + V_{xc} | \phi[\rho] \rangle \geq E_{GS}$$
$$E[\rho] = E_{GS}$$

Note that lowest triplet state is also variational in Kohn-Sham

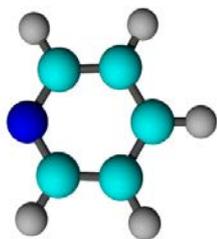
Lowest core-hole state is variational under restriction that core is singly occupied (Δ KS)

Adding an electron to core-hole state gives lowest core-excited state variationally (1s \rightarrow LUMO)

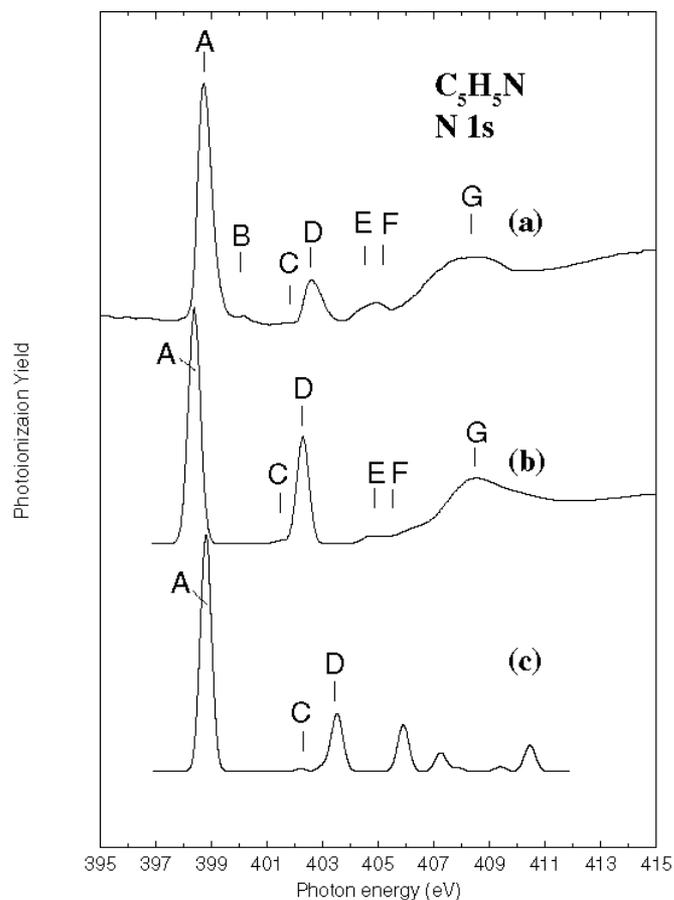
Removing LUMO from orbital space gives 1s \rightarrow LUMO+1 variationally

Removing LUMO+1....

Eventually convergence becomes difficult, but ~ 5 states/symmetry can be obtained



Differential Relaxation Effects: Variationally Determined Excited States



Peak	Resonance	DFT		Experiment gas phase	
		TP	Δ Kohn-Sham		
	IP	406.1	404.5	404.8 ^a	-0.3 eV
A	$N 1s^{-1}$ $1\pi^*(b_1)$	400.5	398.4	398.8	-0.4 eV
B	$N 1s^{-1}$ $2\pi^*(a_2)$	401.2	399.7	400.2	-0.5 eV
C	$N 1s^{-1}$ $\sigma^*(a_1)$	403.7	401.5	402.0	-0.5 eV
D	$N 1s^{-1}$ $3\pi^*(b_1)$	404.7	402.3	402.6	-0.3 eV

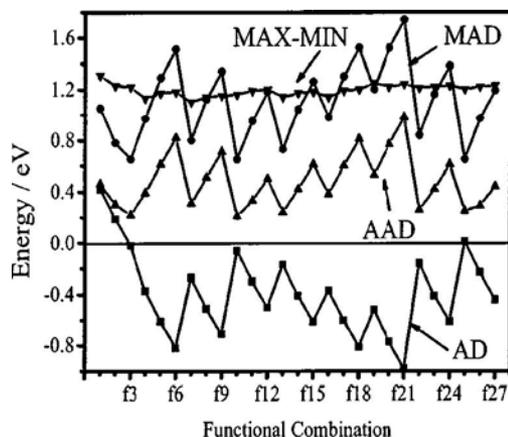
- Hohenberg-Kohn theorem uses variational principle (and unique potential with density)
- Δ KS IP – restrict to singly occupied 1s
- First excited – add electron to LUMO
- Second excited – remove LUMO, LUMO+1 now lowest etc

Kolczewski *et al*, JCP **115**, 6426 (2001)

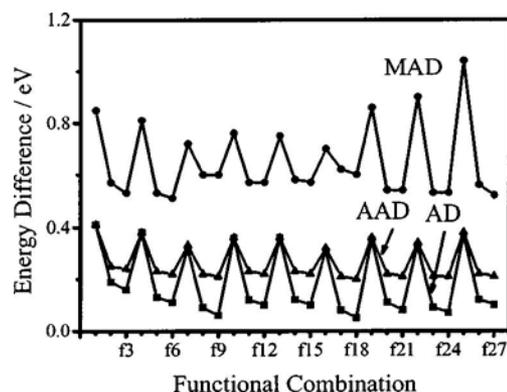
Takahashi&Pettersson, JCP **121**, 10339(2004)

Functional Dependence of XPS and XAS

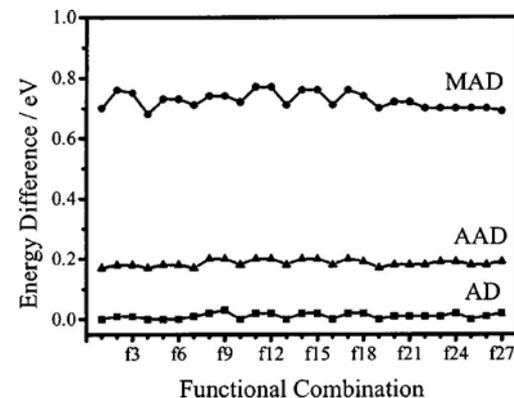
18 molecules with well-established CEBE and term-values (XAS)
9 exchange functionals x 3 correlation functionals



CEBE deviation from experiment



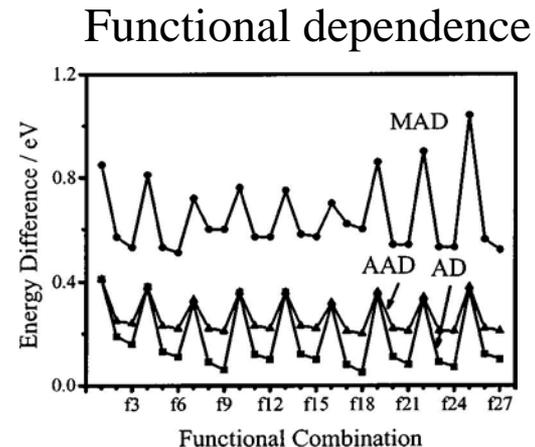
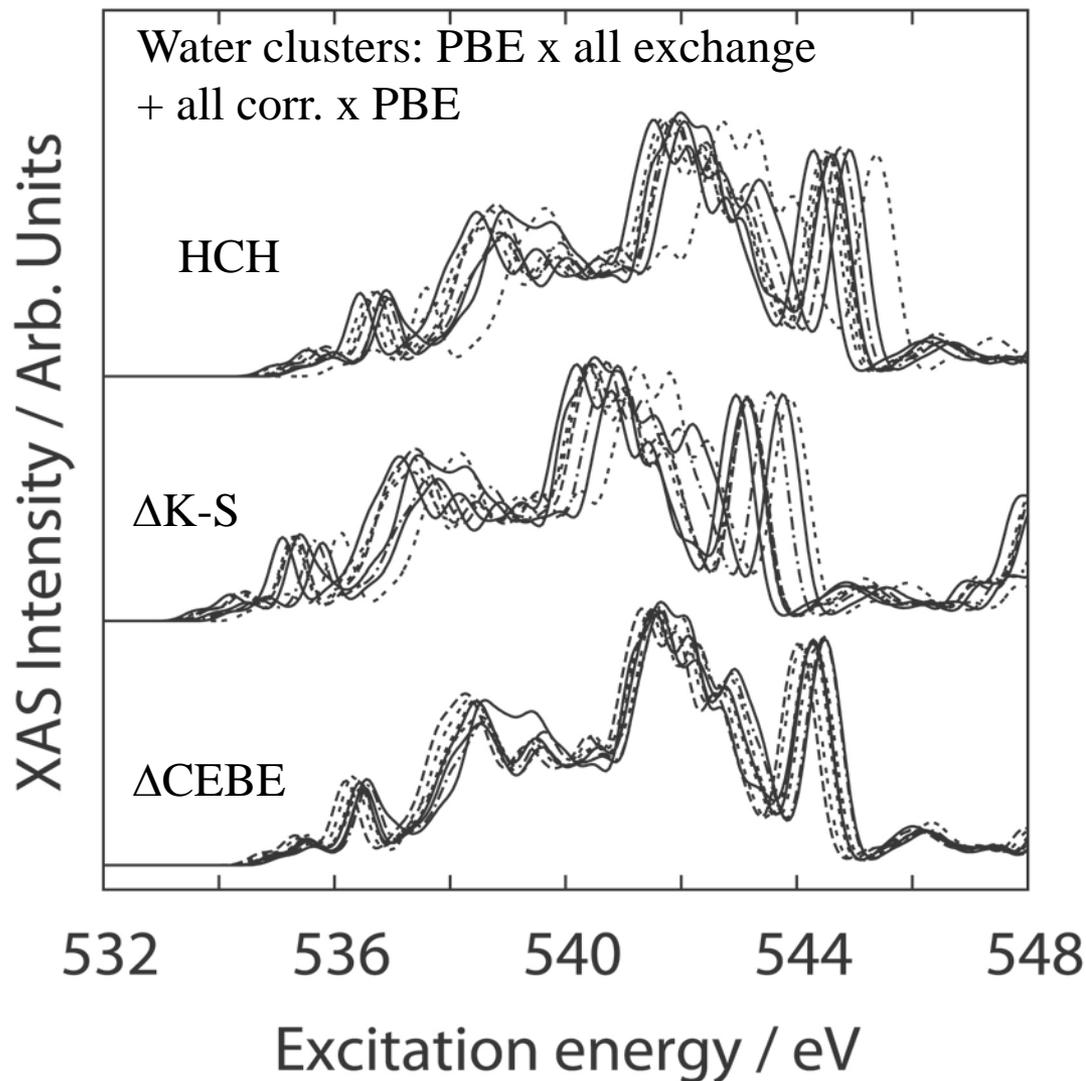
T_1 deviation from experiment



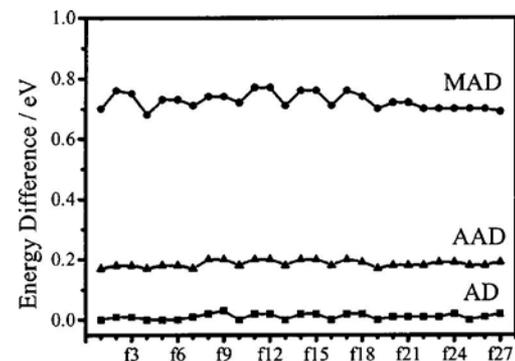
Differences between term-values (3 states)
84 excitations

Most of the error due the functionals are associated with the electron dense inner shell. **Cancels for excitation energy differences and XPS shifts.** Calibrate against exp. CEBE

Spectrum Calculations – Energy Scale



T_1 deviation from experiment



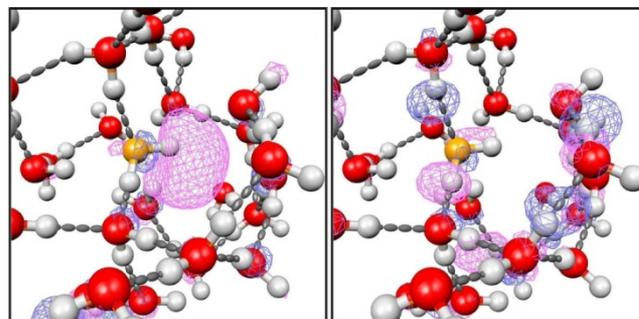
Differences between term-values (3 states)
84 excitations

Leetmaa *et al.*, J. Electron Spec. Rel. Phen. **177**, 135 (2010).

Takahashi and Pettersson JCP 121 (2004) 10339

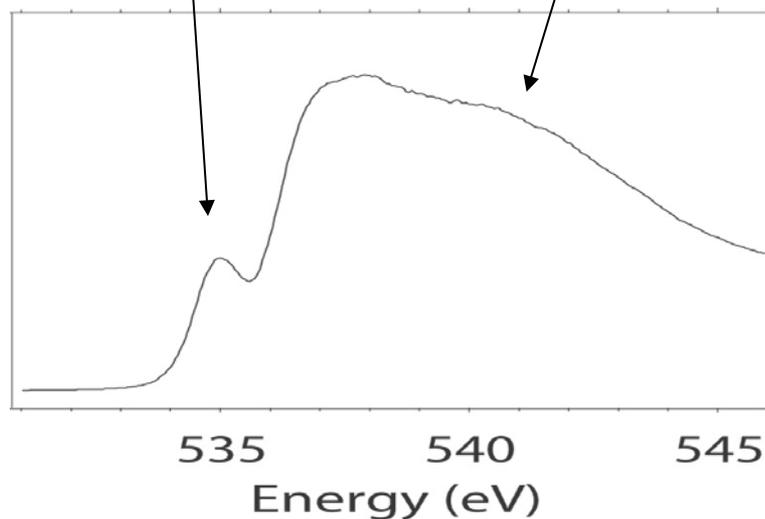
Absolute Energy Scale

- Hole-quasiparticle interaction included (half-core-hole)
- Full hole-quasiparticle for the first state. Shifts energy for all states (\sim GW)
- Full response for the first state in the energy (\sim BSE)
- Higher states delocalized
- No arbitrary shifts

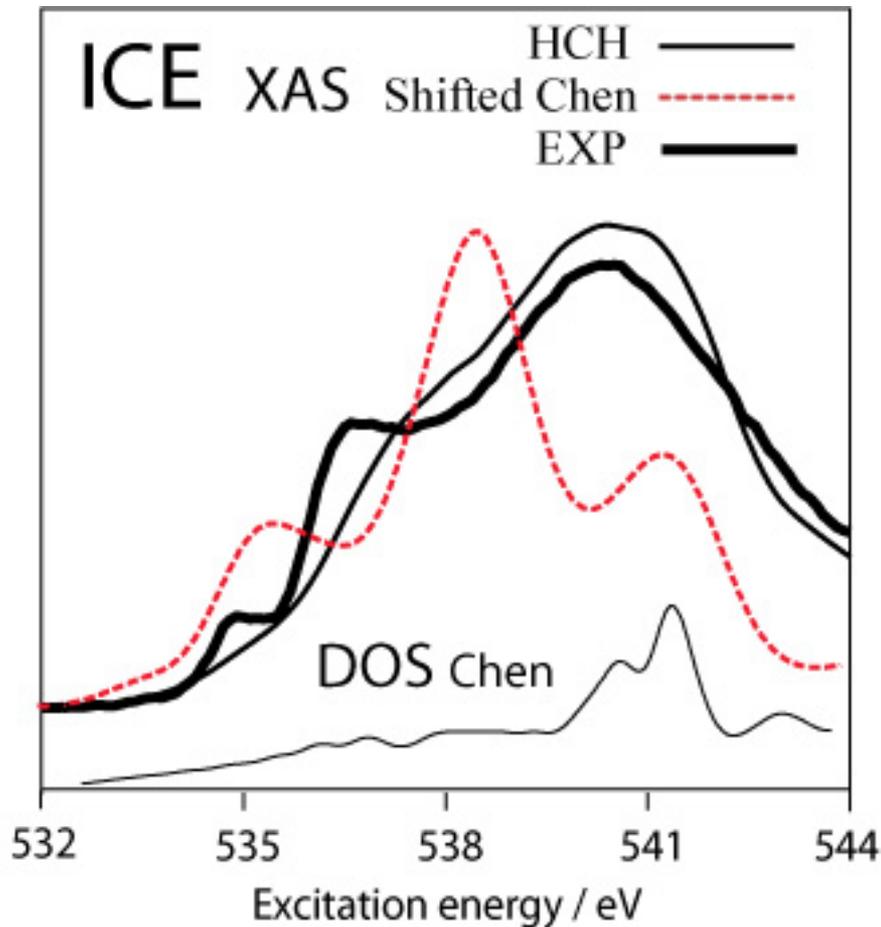


Localized
on free OH

Delocalized



Chen et al., PRL 105, 017802 (2010)



Chen et al. spectrum shifted to have onset as in experiment (and HCH)
GS DOS on same energy scale
Pettersson & Nilsson, PRL submitted

COHSEX calculations on CPMD structures

O-O rdf overstructured compared to Soper ND data (2000)

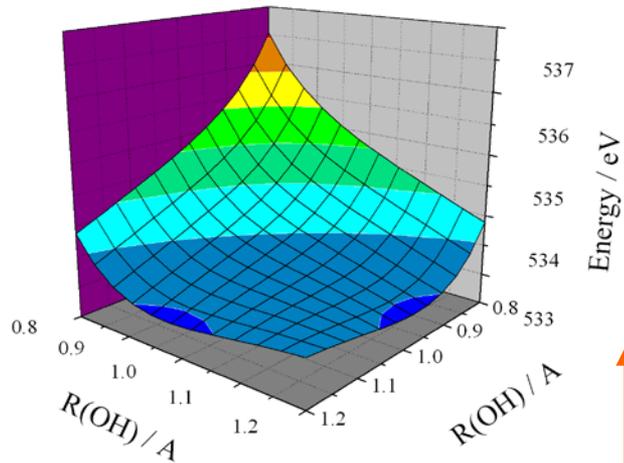
Pseudopotential – **no energy scale**
Static full core-hole

Post-edge in ice at **lower** energy than in liquid model.

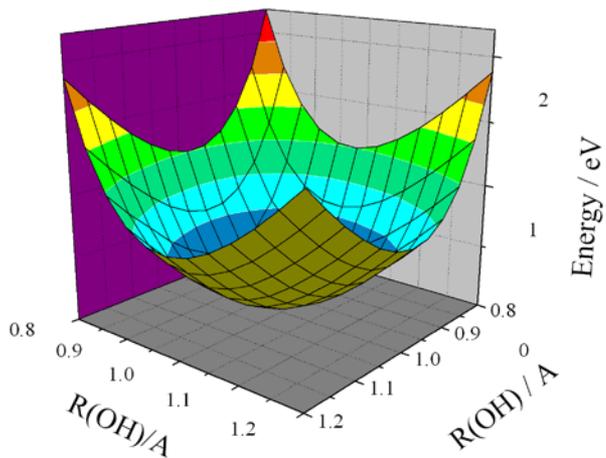
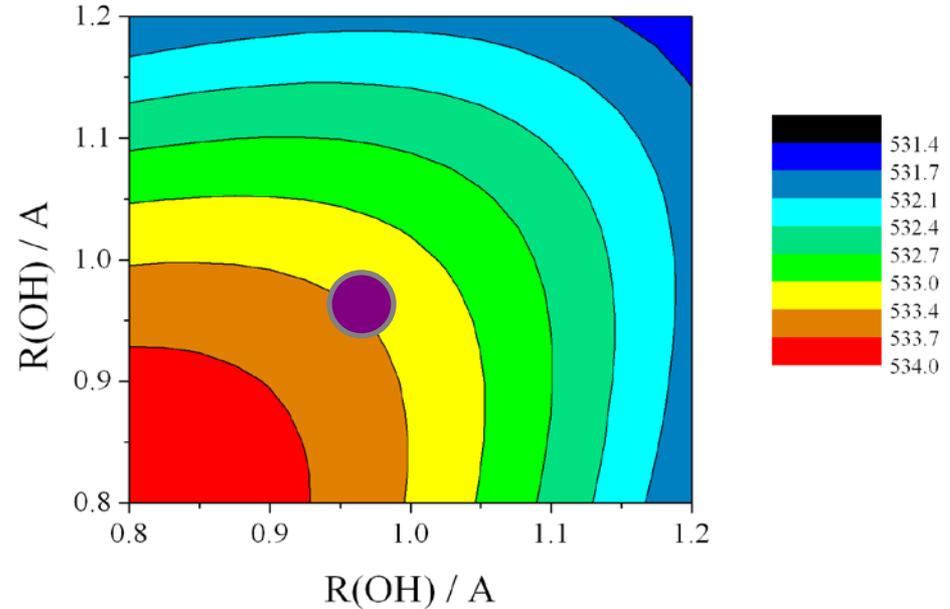
Difference between ice and liquid **not reproduced**

Large shift in intensity from GS DOS:
Experimentally no excitonic effects in post-edge region – only in pre-edge

Potential Energy Surface of Water Molecule



$1s \rightarrow 4a_1$



Ground state

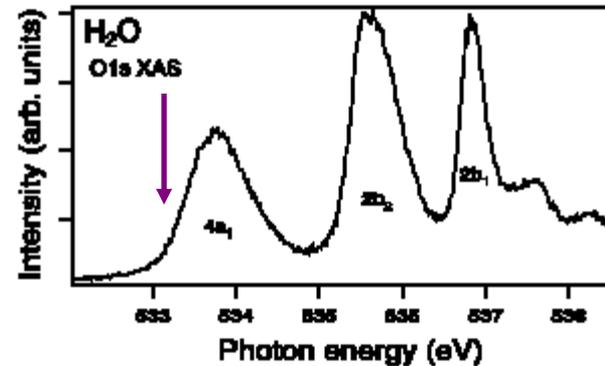
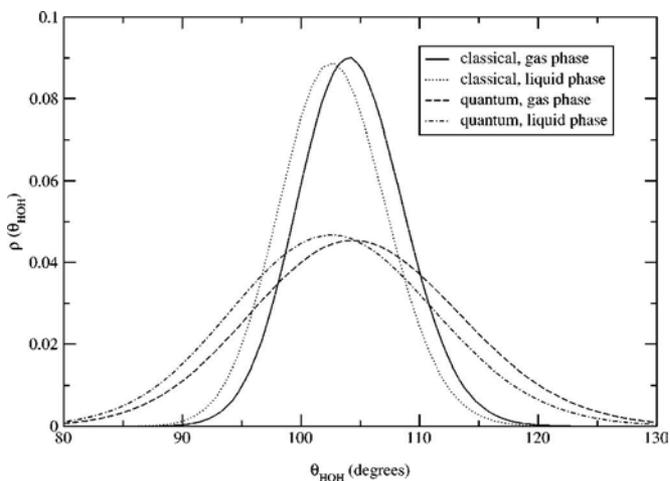
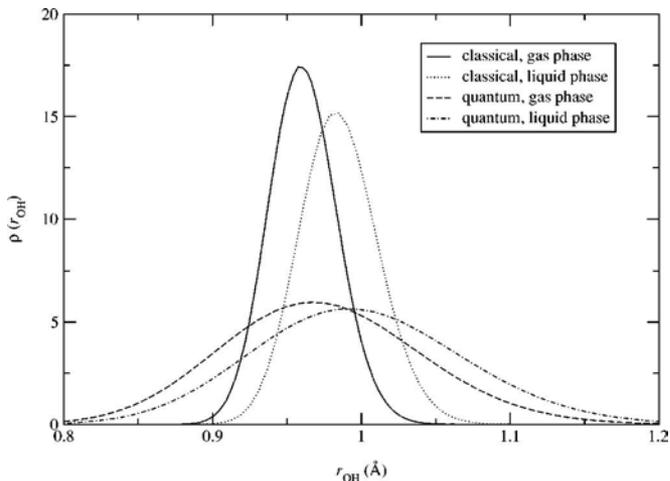
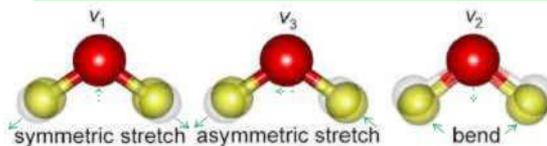


Fig. 2. The O1s X-ray absorption spectrum of molecular water as measured by the partial Auger electron yield. The assignments of the orbitals into which the core electron is excited are given for each absorption peak.

Build up Franck-Condon Profile: XAS as Position Measurement



With classical dynamics only a fraction of real surface probed

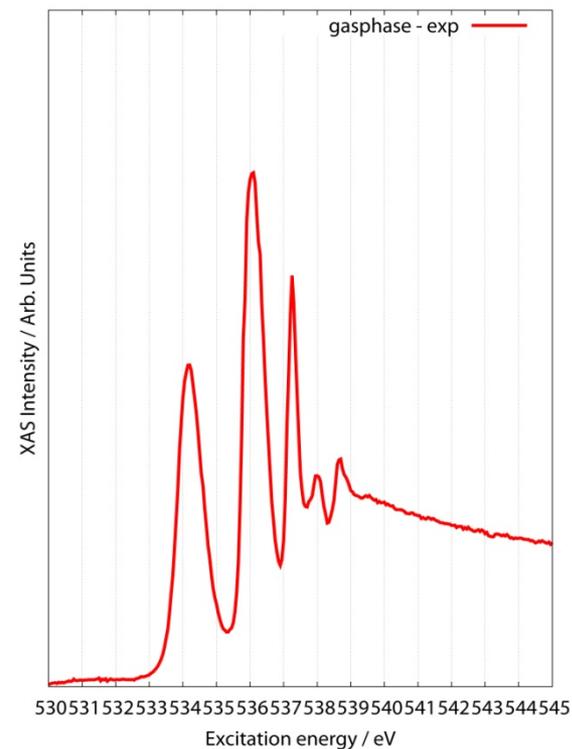


Mikael Leetmaa: "I will probe FC profile computing 8000 spectra...."



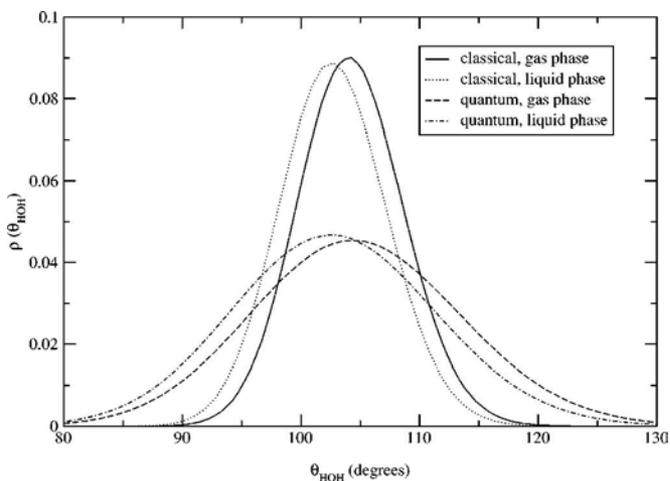
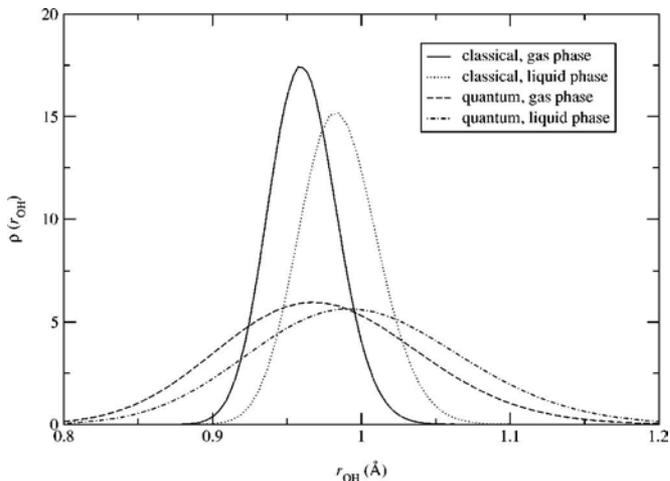
Experiment

water - gasphase exp. XAS

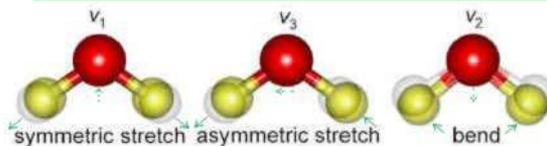


H.A. Sterne and B.J. Bern, J. Chem. Phys. **115** (2001) 7622

Build up Franck-Condon Profile: XAS as Position Measurement



With classical dynamics only a fraction of real surface probed

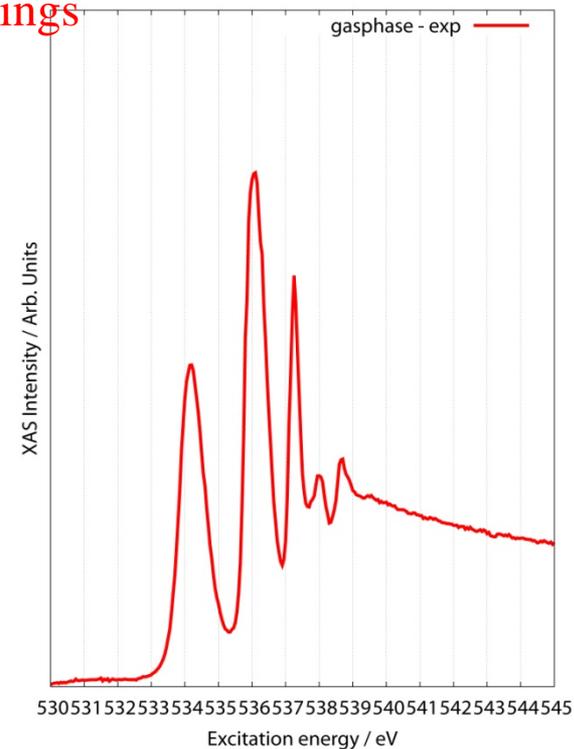


No way! More Important Things to do!



Experiment

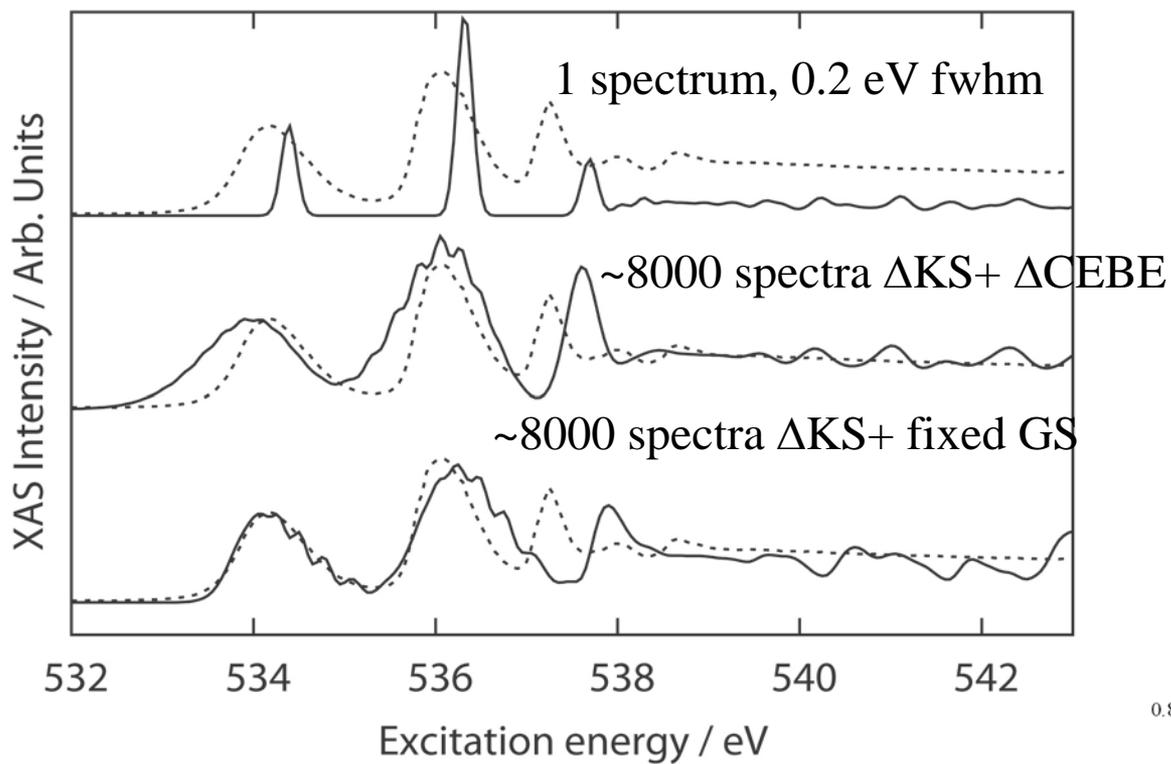
water - gasphase exp. XAS



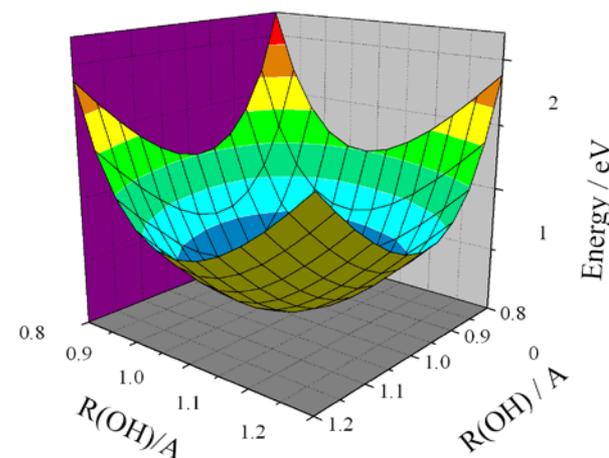
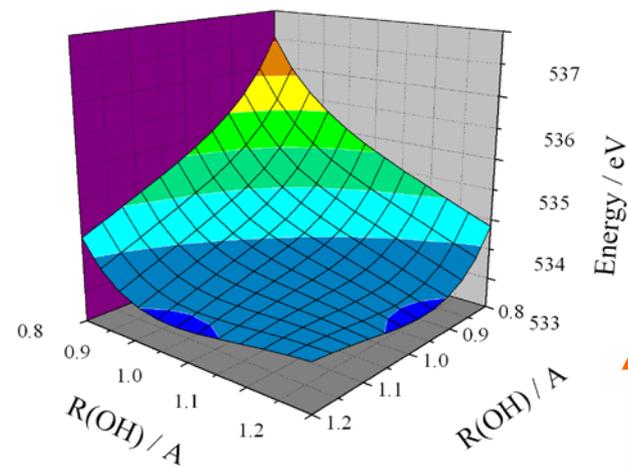
H.A. Sterne and B.J. Bern, J. Chem. Phys. **115** (2001) 7622

Gas Phase H₂O: Build up Franck-Condon Profile

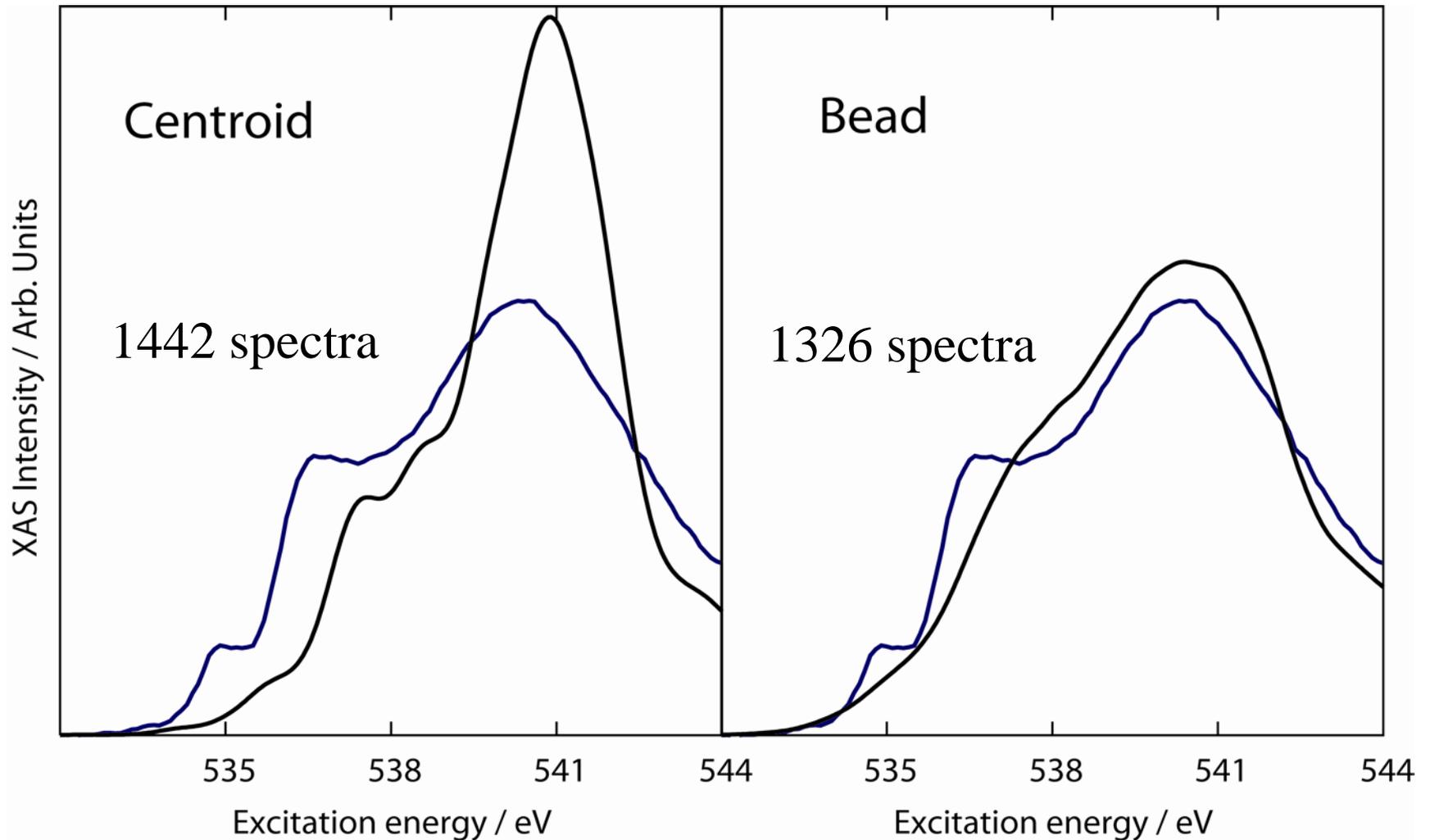
- Sampling ZPE distribution (3D)
 - FC profile
- ∴ XAS position measurement



Franck-Condon profile perfect; uncertainty in ZPE

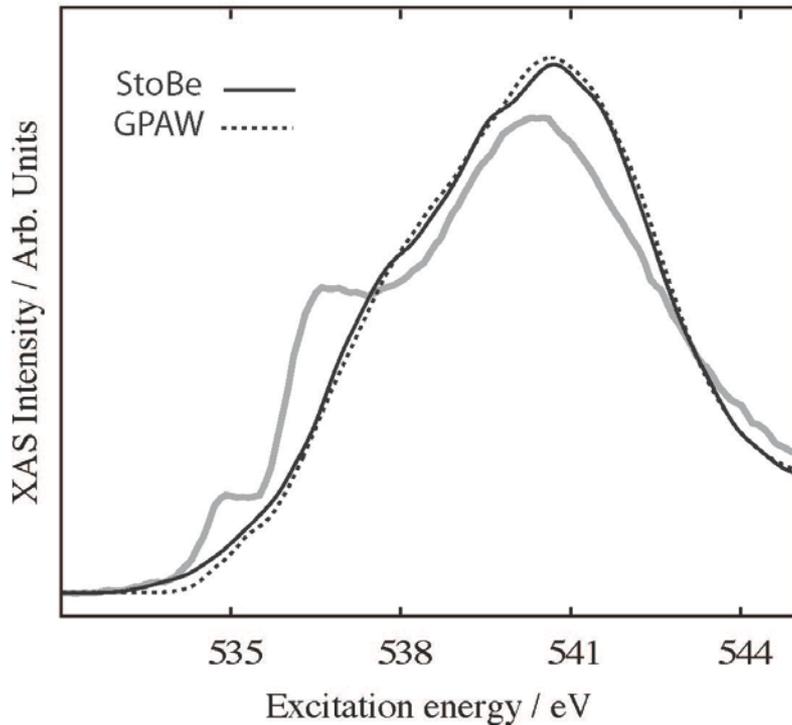


Sampling Internal OH in Ice

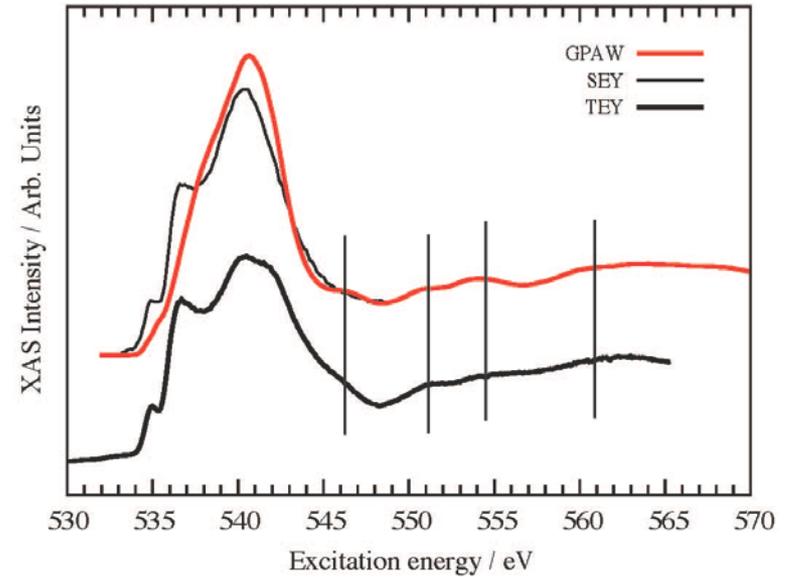


Ice Ih – sampling structures from PIMD; 39 molecules

Calibrate Cluster XAS Calculations



Compare grid-based periodic (GPAW)
2x2x2 k -points with cluster model
(StoBe) 39 waters
Sum of 174 spectra from PIMD
Excellent agreement!



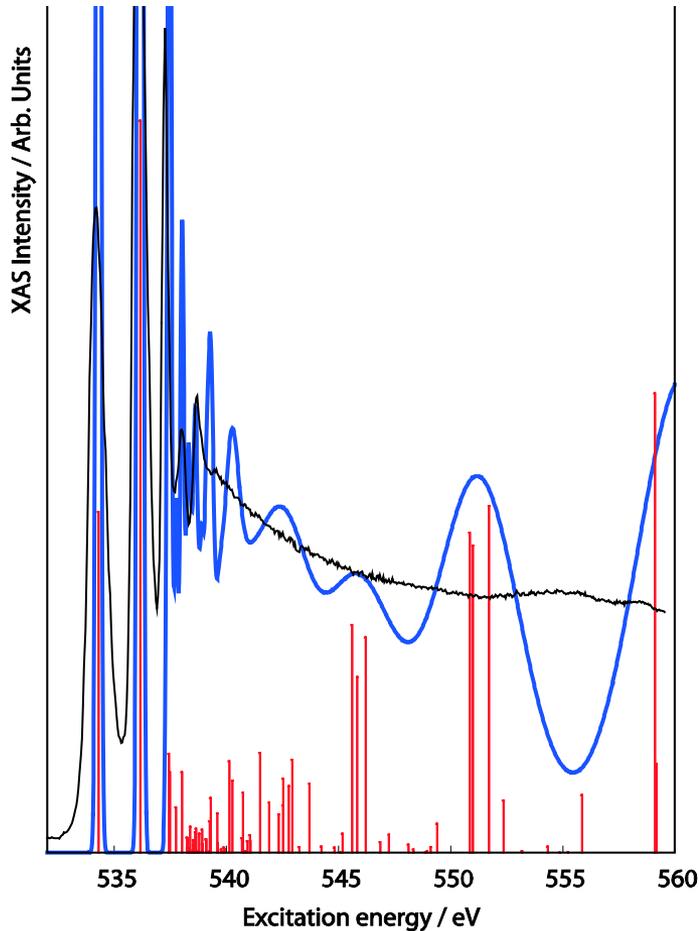
GPAW vs two different measured
ice spectra. Higher resonances excellent
Redistribution of intensity in main region

Structure in experiment different?
Semi-local correlations important?

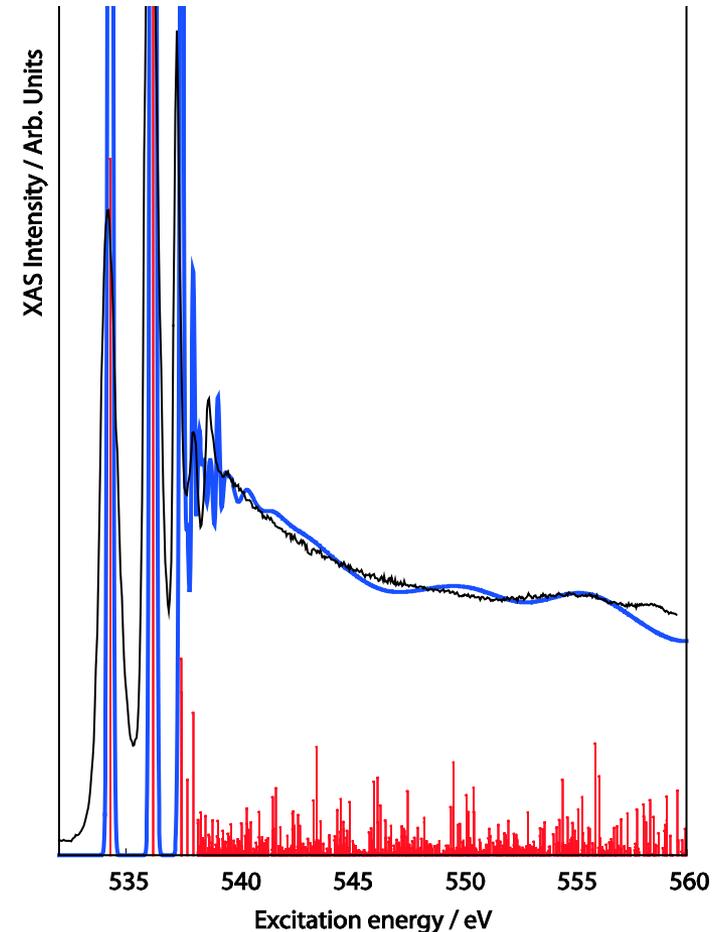
Double-Basis Set Technique

- Occupied density well-described by molecular (Gaussian) basis set
- For excited states a much more diffuse and extended basis is needed to describe Rydberg and unbound states
- Determine molecular ion density using molecular basis
- Add large, diffuse augmentation basis and rebuild KS
- Diagonalize once to get excited states in half-core-hole potential
- Increase augmentation to improve sampling of continuum
- Continuum functions incorrectly described by Gaussians
- Description valid to 10-20 eV beyond the edge (slow oscillations)

Convergence with augmentation basis

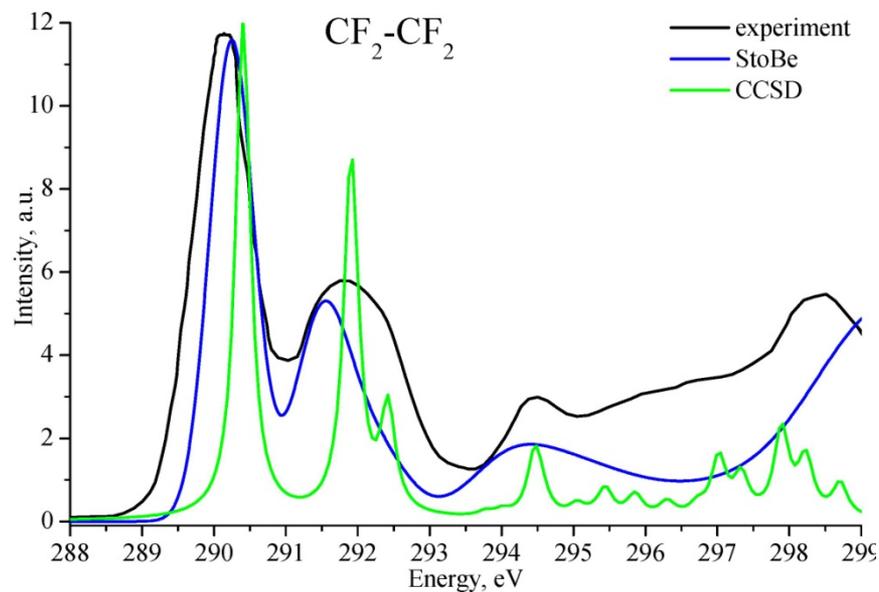
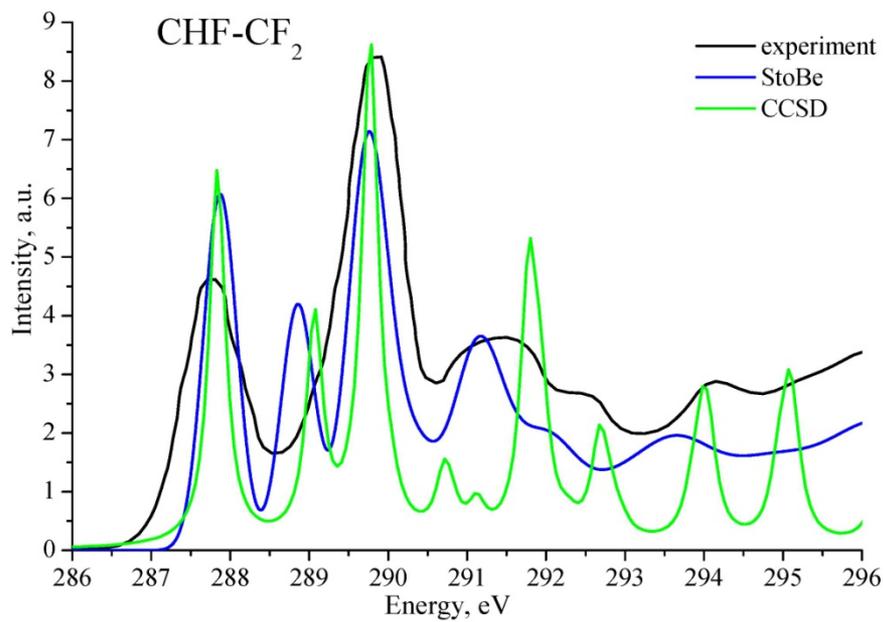
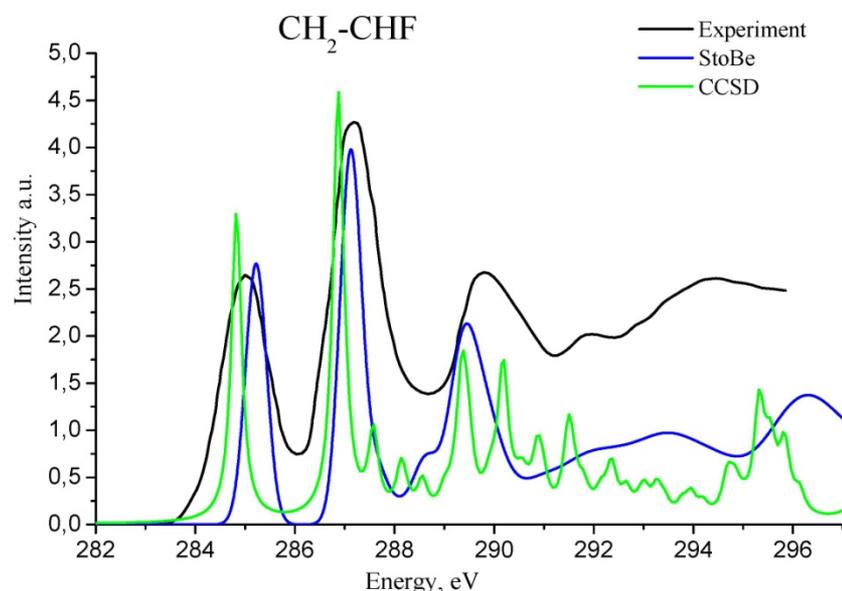
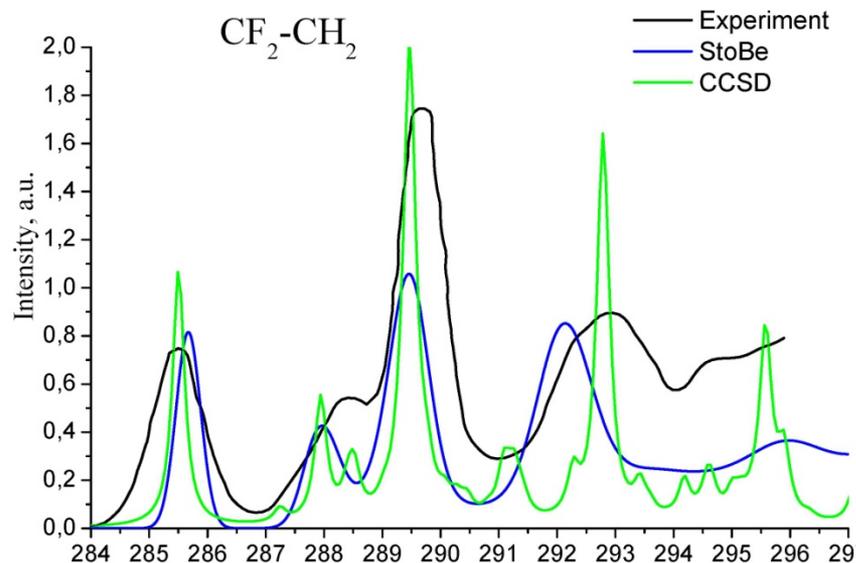


Augmentation basis on oxygen
Broaden up to 4.5 eV
~150 functions

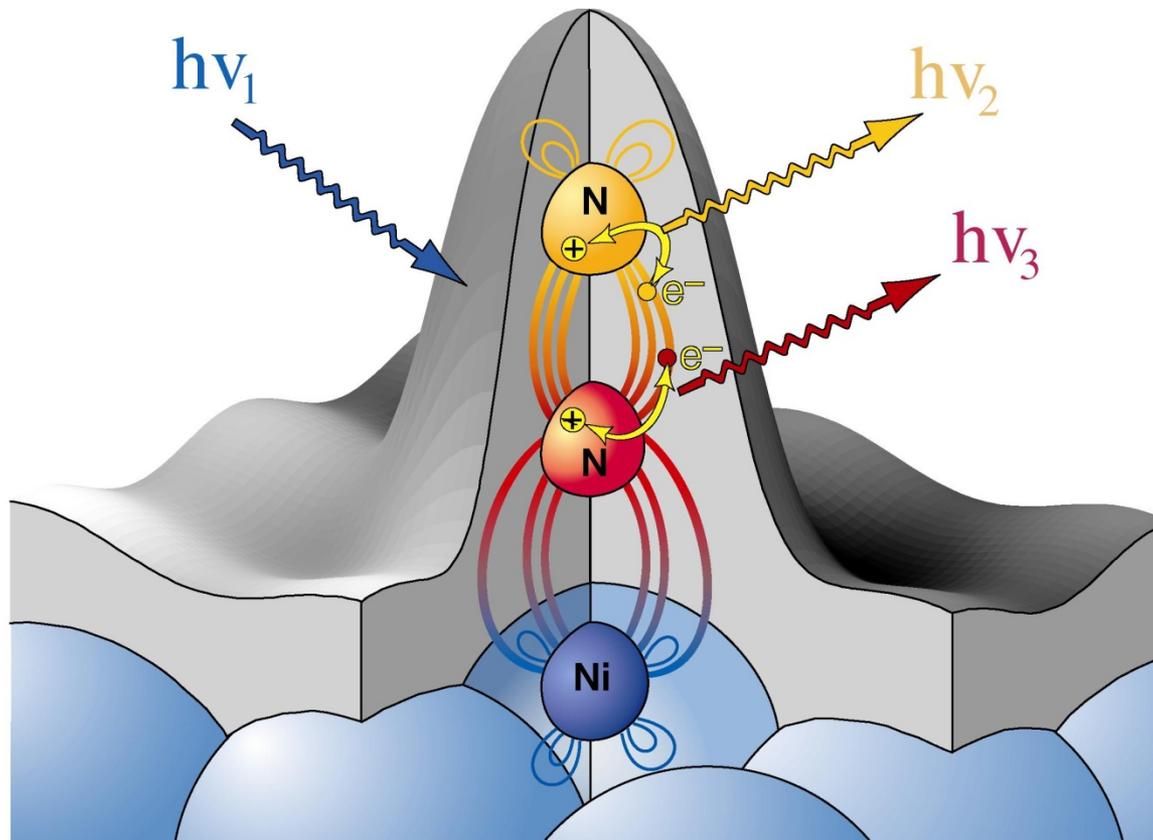


Augmentation basis on oxygen
plus 11 more + 35 with limited basis
Broaden up to 4.5 eV; ~2000 fctns

Comparison to Complex Polarization Operator (CCSD)

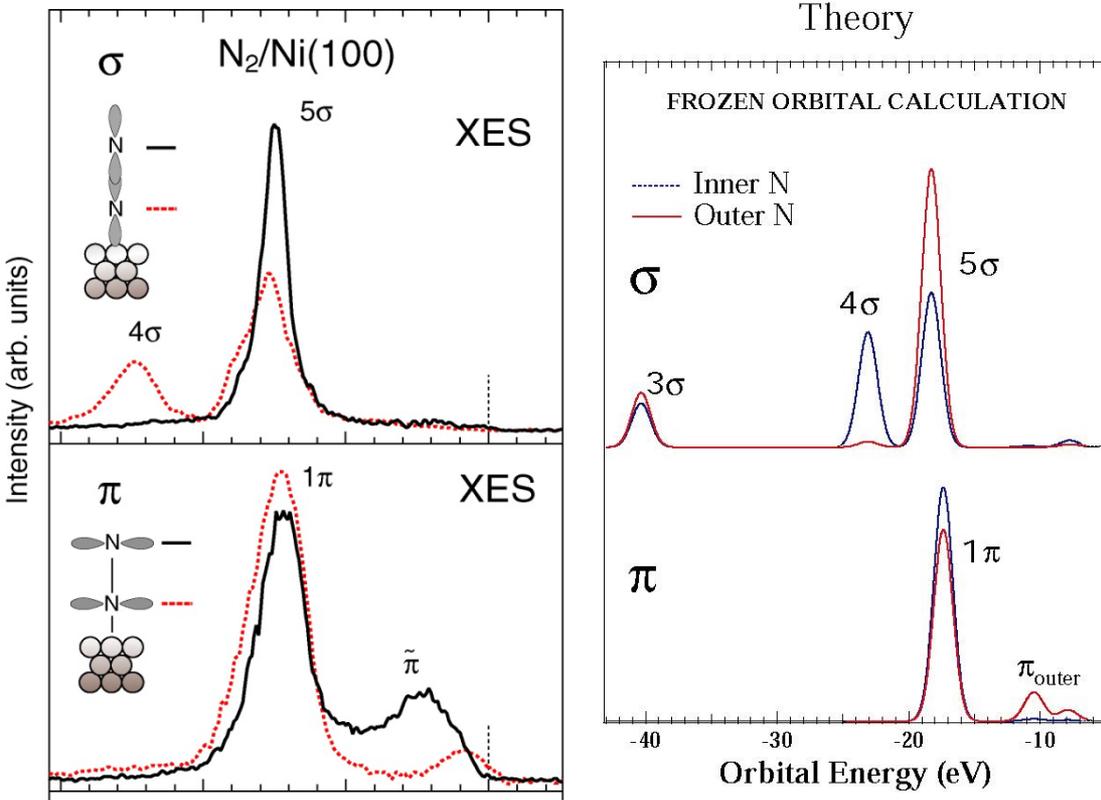


X-ray Emission Spectroscopy (XES)



Resonantly Excited Chemisorbed N₂

$$I_{\text{RIXS}}(\omega', \omega) \propto \sum_F \left| \sum_M \frac{\langle F | \vec{D} \cdot \vec{E}' | M \rangle \langle M | \vec{D} \cdot \vec{E} | G \rangle}{\hbar\omega - (E_M - E_F) + i\Gamma_{M/2}} \right|^2 \delta(\hbar\omega - \hbar\omega' + E_G - E_F)$$



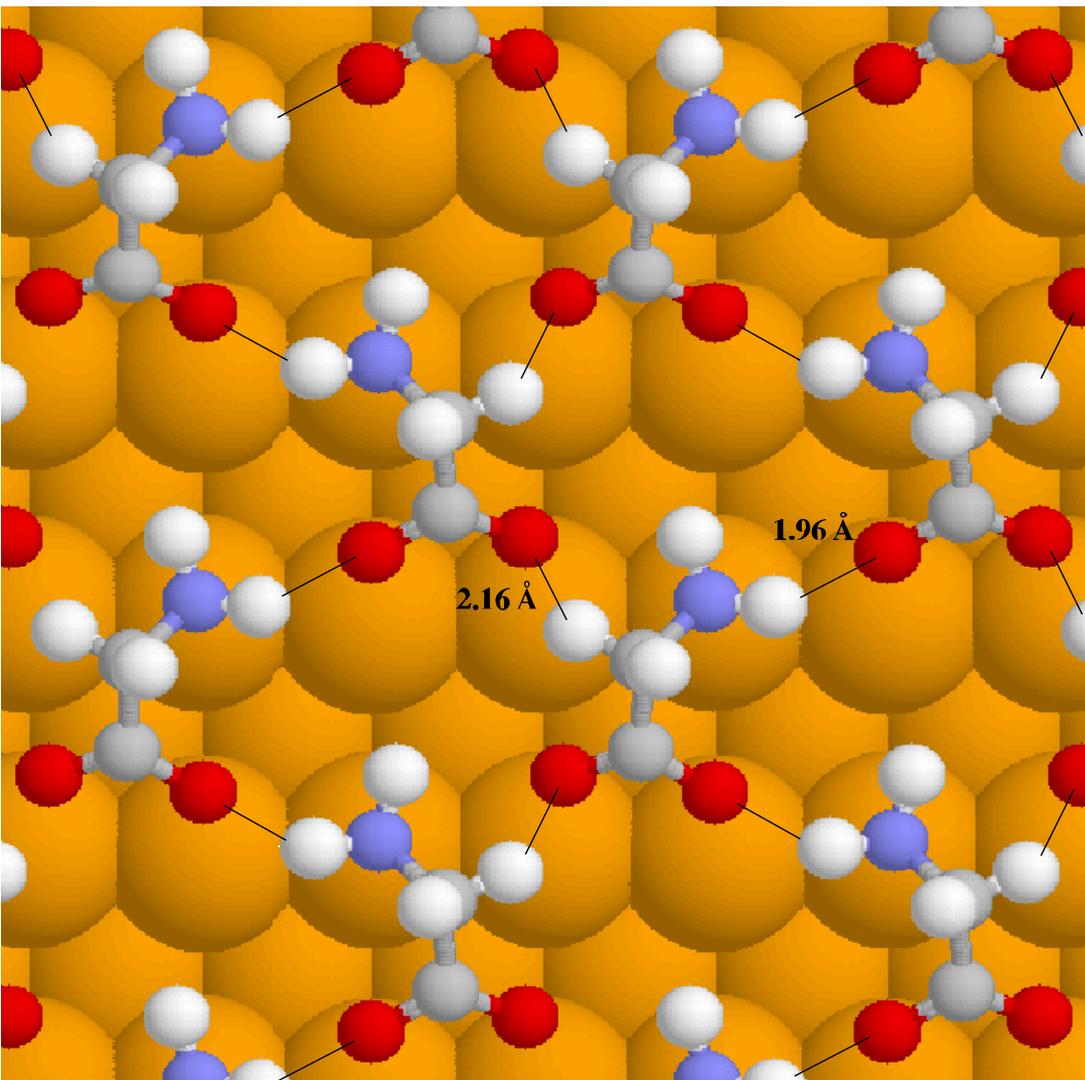
Typically the intermediate state enters and when more than one you get interference effects

For chemisorbed molecules the excited electron delocalizes and only one intermediate electronic state important

Vibrations can still be important for light atoms

Compute transition for ground state orbitals

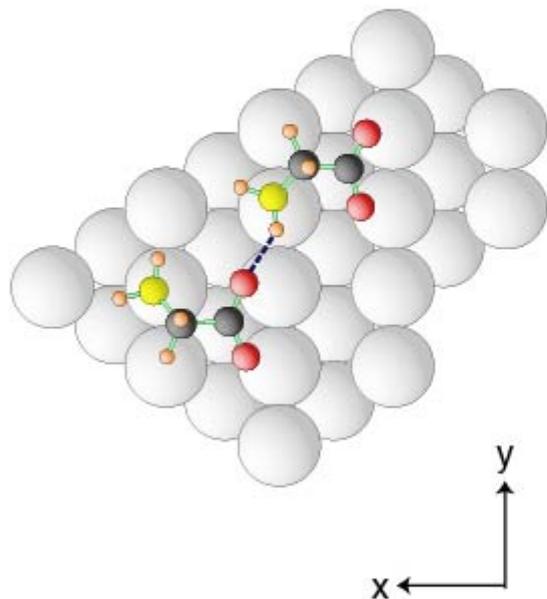
Glycinate/Cu(110)



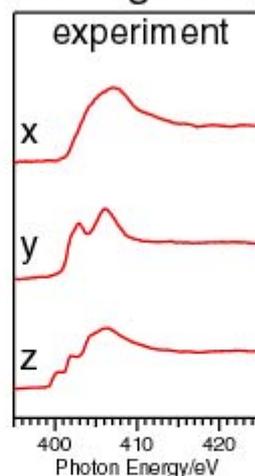
- 3-layer slab
- 2 glycines/cell
- Optimize first layer plus adsorbate

- Two short distances:
N-H \cdots O-C 1.96 Å
C-H \cdots O-C 2.16 Å

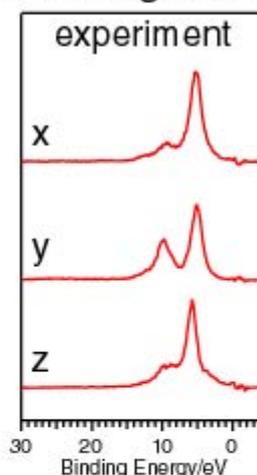
Hydrogen bonding in glycine



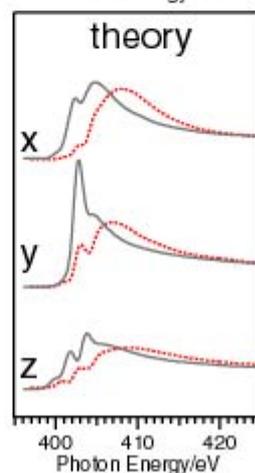
N K edge XAS



O K edge XES

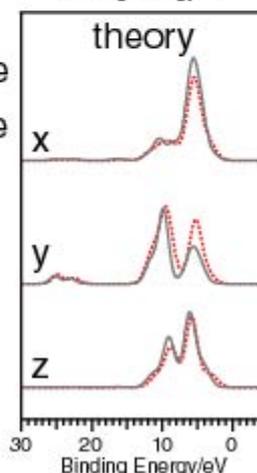


theory



— 1 glycine
- - - 2 glycine

theory



Introduce H-bond

XAS: Unoccupied \Rightarrow Effects on donor

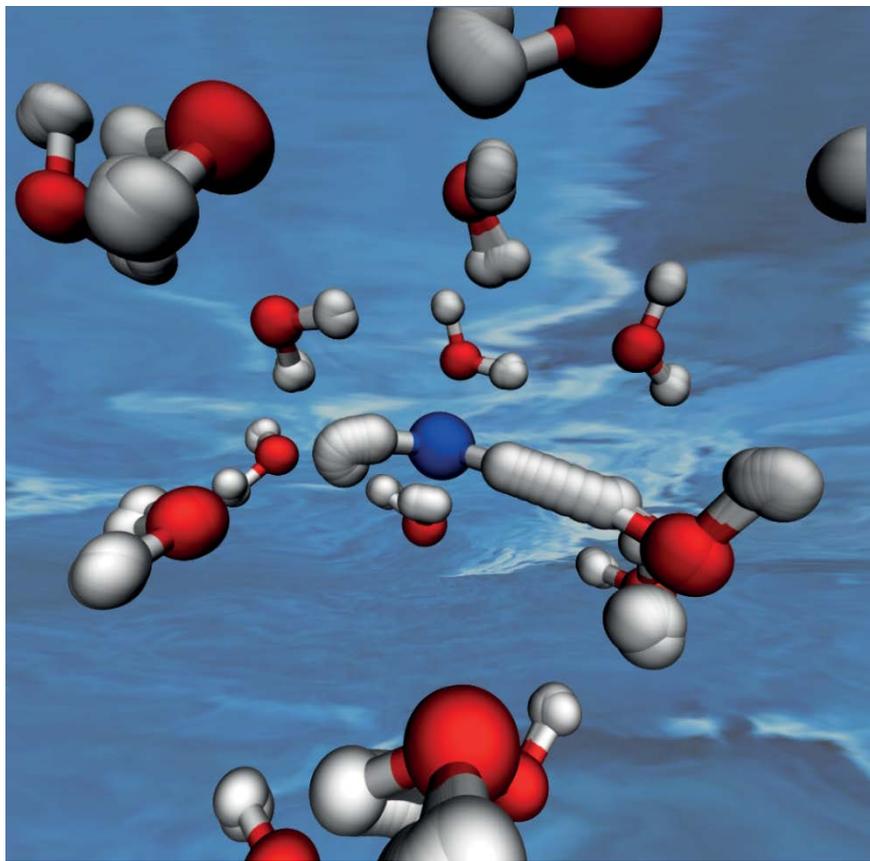
XES: Occupied \Rightarrow Effects on acceptor

Nyberg *et al*, JCP **119**, 12577 (2003).

H-bond seen in spectra and calculation

Interference Effects

$$\sigma(\omega') \propto \sum_f \left| \sum_n \frac{\langle f | D'_{FN} | n \rangle \langle n | D_{NI} | i \rangle}{\omega' - (E_n - E_f) + i\Gamma} \right|^2$$



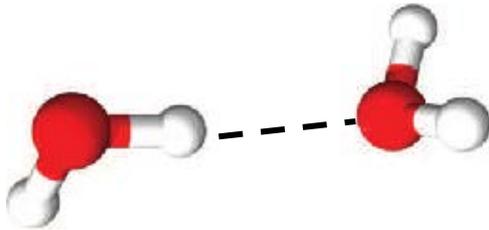
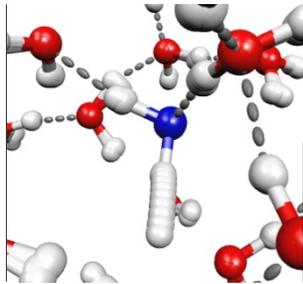
- Example: H-bonded water
- Z+1 approximation : $\text{H}_2\text{O} \rightarrow \text{H}_2\text{F}^+$ strong H-donor
- Potential curve changes
- Wave packet propagation

- Number of involved intermediate vibrational states contributing to ω' depends on life-time broadening Γ
- Interference effects
- Core-hole life-time (O 1s) 3-4 fs
- Important for light atoms

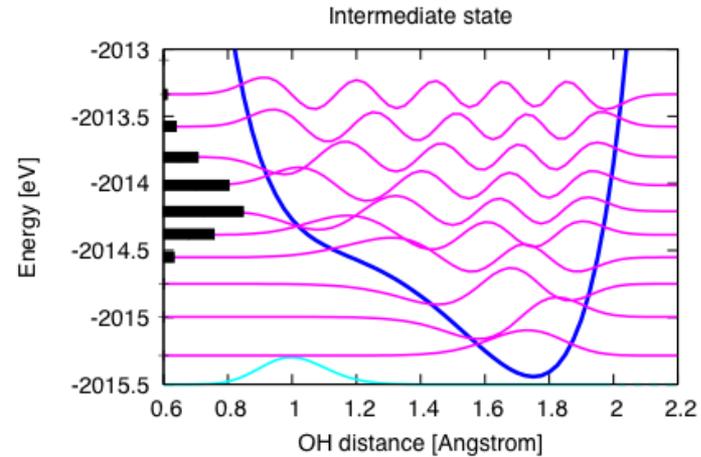
Kramers-Heisenberg

$$\sigma(\omega') \propto \sum_f \left| \sum_n \frac{\langle f | D'_{FN} | n \rangle \langle n | D_{NI} | i \rangle}{\omega' - (E_n - E_f) + i\Gamma} \right|^2$$

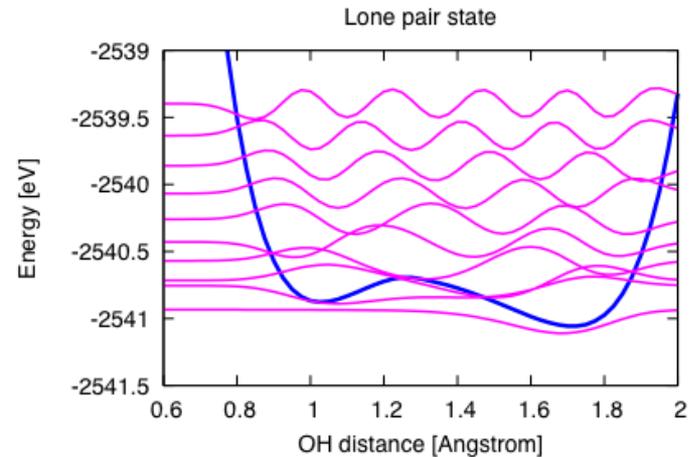
Core-hole induced
dynamics on the
3-4 fs time-scale



Water dimer 1-D as model
Wave packet propagation



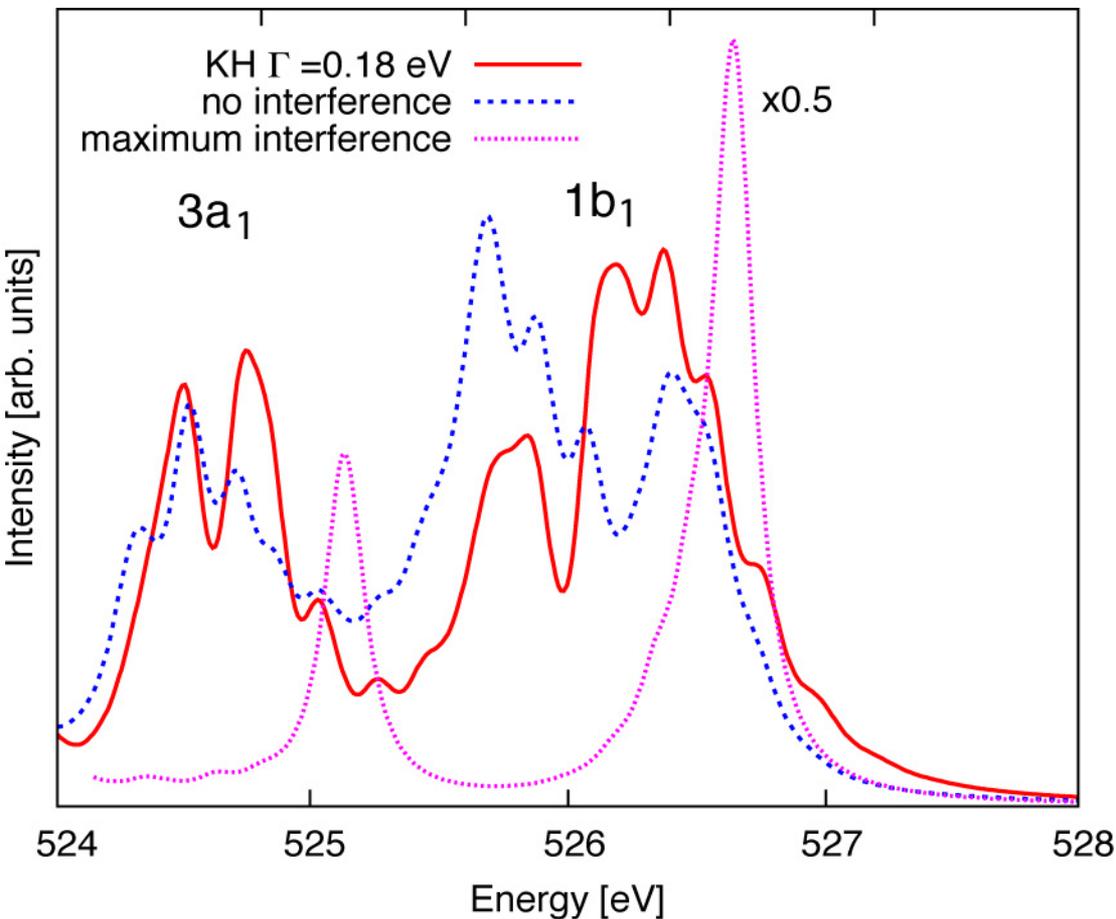
CH state



l.p. state

Vibrational Interference

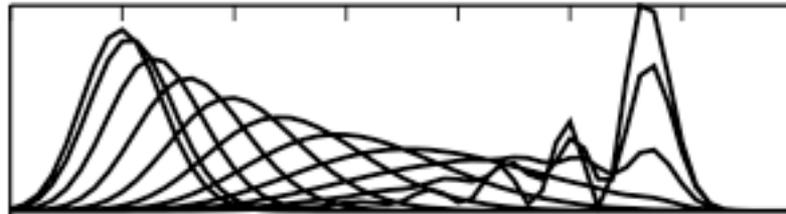
$$\sigma(\omega') \propto \sum_f \left| \sum_n \frac{\langle f | D'_{FN} | n \rangle \langle n | D_{NI} | i \rangle}{\omega' - (E_n - E_f) + i\Gamma} \right|^2$$



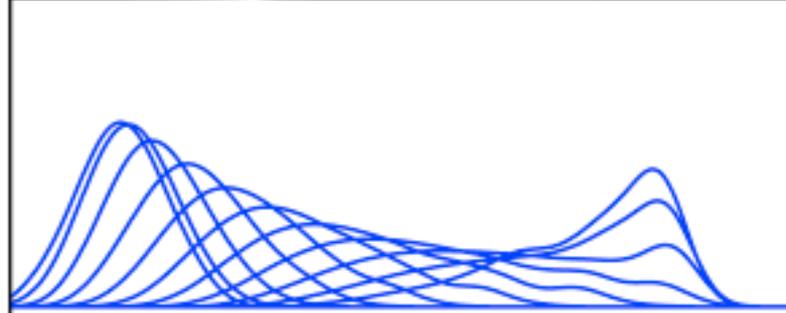
- Maximum interference: no influence of intermediate state
- No interference: resolved vibrational transitions + shift to lower emission energy of $1b_1$
- Intermediate case: asymmetric broadening
- Dissociation NOT giving spectrum

Core-Induced Dynamics – Zero-point Energy

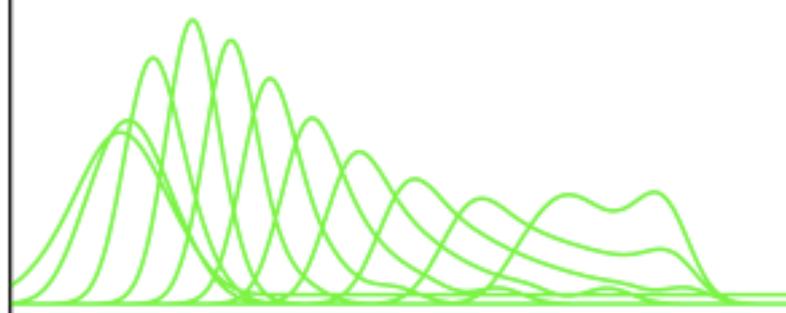
Quantum wave packet



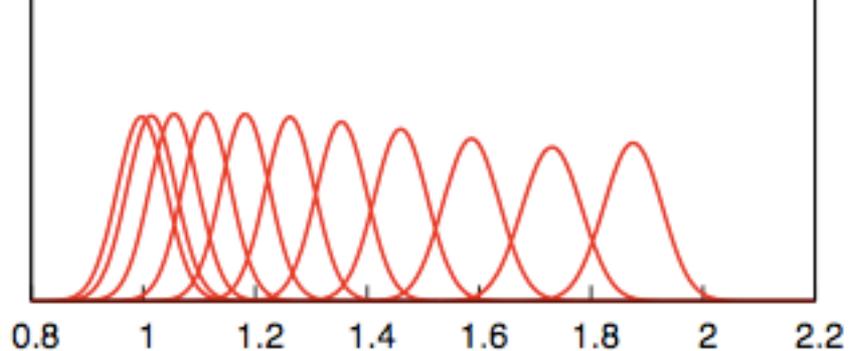
Classical dynamics
Quantum initial cond.



Classical dynamics
Sample QM OH position



Classical dynamics
Classical initial cond.



Semiclassical Approximation

Non-resonant K-H

Need reliable technique to compute XES including life-time vibrational interference for large clusters with many degrees of freedom

- treat the nuclear degrees of freedom in the time domain
- sum over classical trajectories with QM initial conditions

$$\sigma^{class}(\omega') = \sum_{traj} \sum_F |D_F^{+class}(\omega')|^2$$

- approximate nuclear Hamiltonians with corresponding energies

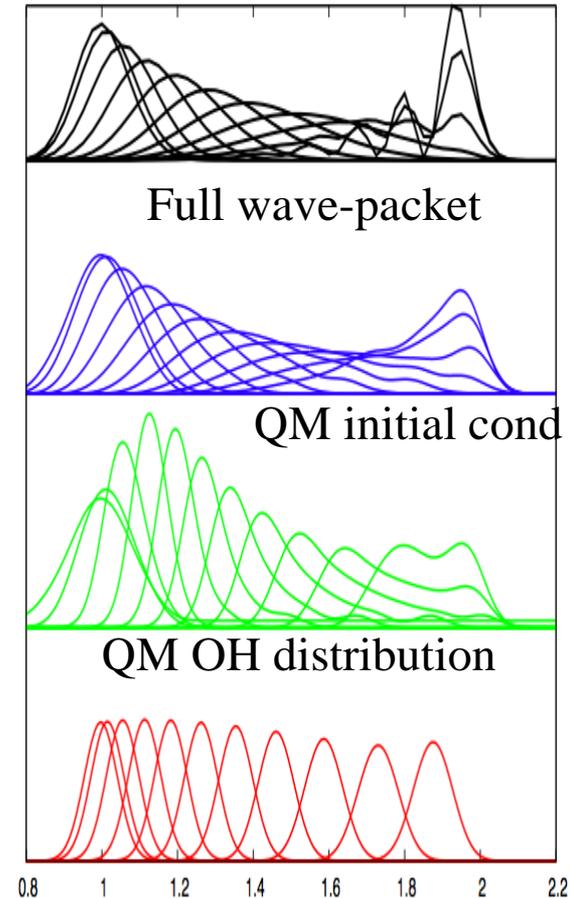
$$D_F^{+class}(\omega') = \int_0^\infty dt D_{NI}^+(0) D_{FN}^+(t) e^{-i \int_0^t (E_F(\tau) - E_N(\tau)) d\tau} e^{-\Gamma t} e^{-i\omega' t}$$

Sample structure model

Sample QM O-H and momentum distributions for the two hydrogens

Run trajectories and sum to get one spectrum

Sample many to get spectrum for the model...



Classical thermal distribution in r_{OH} and p

Semiclassical Approximation

Non-resonant K-H

Need reliable technique to compute XES including life-time vibrational interference for large clusters with many degrees of freedom

- treat the nuclear degrees of freedom in the time domain
- sum over classical trajectories with QM initial conditions

$$\sigma^{class}(\omega') = \sum_{traj} \sum_F |D_F^{+class}(\omega')|^2$$

- approximate nuclear Hamiltonians with corresponding electronic states

$$D_F^{+class}(\omega') = \int_0^\infty dt D_{NI}^+(0) D_{FN}'^+(t) e^{-i \int_0^t (E_F(\tau) - E_N(\tau)) d\tau} e^{-\Gamma t'} e^{-i\omega t'}$$

Sample structure model

Sample QM O-H and momentum distributions for the two hydrogens

Run trajectories and sum to get one spectrum

Sample many to get spectrum for the model...

