KUNGL TEKNISKA HÖGSKOLAN

First Principle Study of Soft X-ray Spectroscopy

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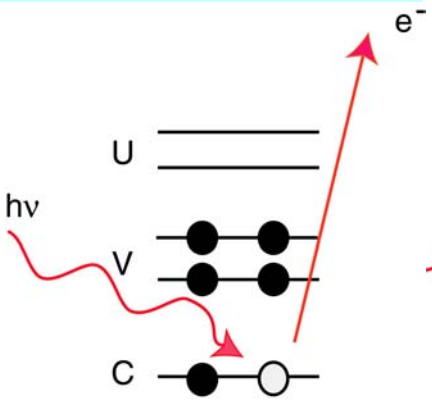
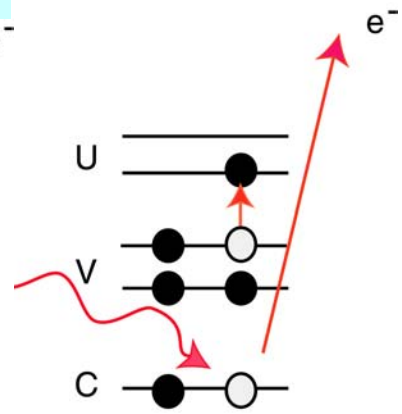
ALS, 2004-10-19

- Ionization/excitation of core electron (XPS-NEXAFS)
- Radiative decay of core excited/ionized state (XES-RIXS)

- core e^- B.Energy
- chemical environment
- satellite structures

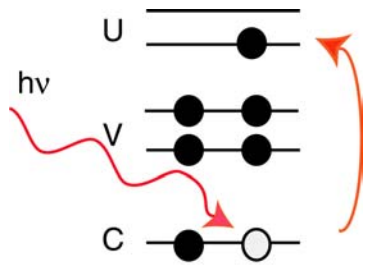


XPS

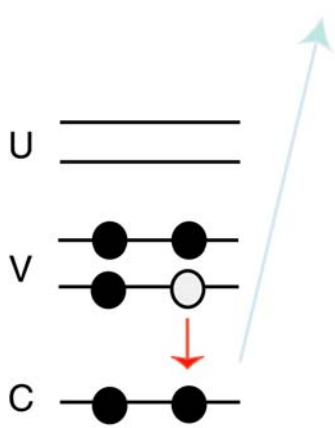


XPS - shake-up satellite

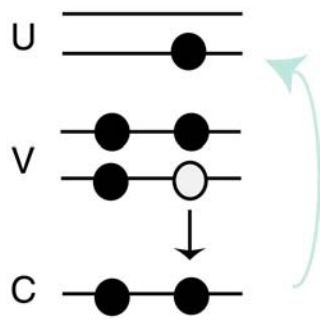
- picture of unoccupied pDOS



NEXAFS



XES



RIXS

- XES non resonantly excited
- RIXS resonantly excited selection rules
- information about occupied pDOS

For large molecular systems, two theoretical methods are normally used.

Hartree-Fock method (HF): without electron correlation

Wave-function based method, Ψ

Density Functional Theory (DFT): with electron correlation

Density based method: $\rho = \Sigma_{1}^{N} | \Psi_i |^2$

Program packages: DALTON, DeMon, GAMESS, GAUSSIAN

Density Functional Theory for X-ray Spectroscopy of Molecular Systems

Funtionals: LDA, gradient corrected, and hybrid

XPS:

Binding energy, shake-up and vibrational structures.

UPS:

Spectrum

NEXAFS:

Vibrationally resolved spectrum

XES:

Non-resonant emission and

resonant inelastic X-ray scattering (RIXS)

RIXS formulation

$$\langle \sigma(\omega', \omega_0) \rangle = \sum_{\nu n} \frac{\omega'}{\omega} \lambda_{\nu n} \Phi(\omega' + \omega_{\nu n} - \omega_0)$$

$$= \sum_{\nu n} \frac{\omega'}{\omega} (F\lambda^F_{\nu n} + G\lambda^G_{\nu n} + H\lambda^H_{\nu n}) \Phi(\omega' + \omega_{\nu n} - \omega_0).$$

$$\lambda^F_{\nu n} = \sum_\beta F^{\beta\beta}_{\nu n} \sum_\gamma F^{\gamma\gamma *}_{\nu n}$$

$$\lambda^G_{\nu n} = \sum_{\beta\gamma} F^{\beta\gamma}_{\nu n} F^{\beta\gamma *}_{\nu n}$$

$$\lambda^H_{\nu n} = \sum_{\beta\gamma} F^{\beta\gamma}_{\nu n} F^{\gamma\beta *}_{\nu n}.$$

$$F = -|e_1 e_2^*|^2 + 4|e_1 e_2|^2 - 1$$

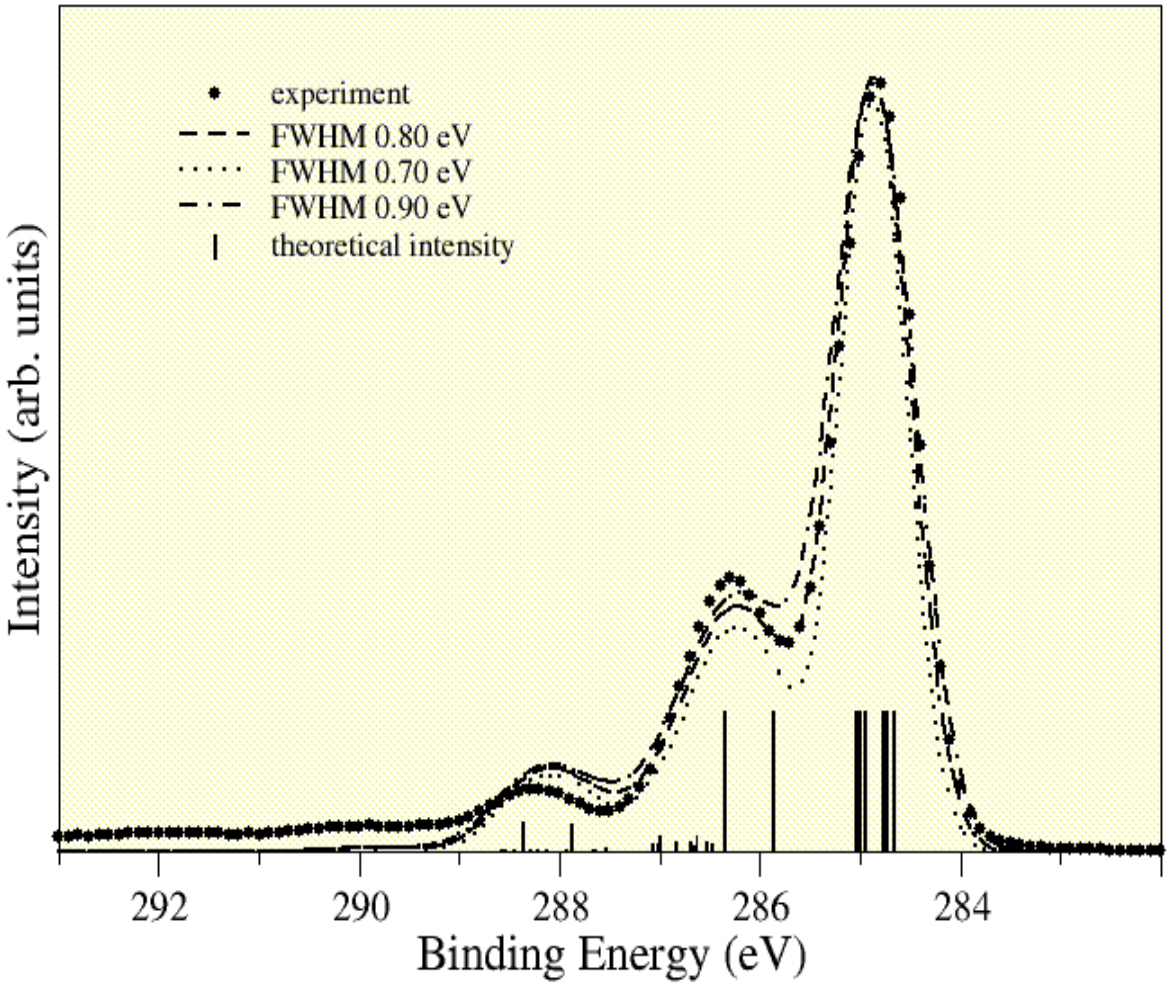
$$G = -|e_1 e_2^*|^2 - |e_1 e_2|^2 + 4$$

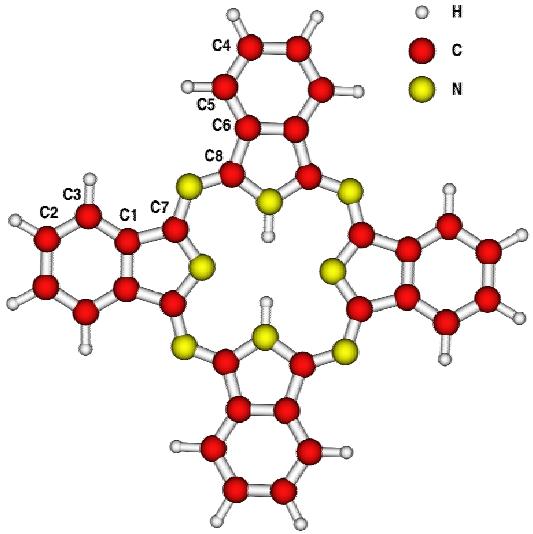
$$H = 4|e_1 e_2^*|^2 - |e_1 e_2|^2 - 1.$$

$$F^{\beta\gamma}_{\nu n} = \alpha \sum_k \omega_{\nu k} \omega_{nk}(\nu) \frac{d^\beta_{\nu k} d^\gamma_{kn}(\nu)}{\omega - \omega_{\nu k} + i\Gamma_{\nu k}}$$

Y. Luo, H. Ågren, and F. Gelmukhanov, J. Phys. B, 27 (1994) 4169

Theoretical results and simulation of the experimental spectrum of metal-free Phthalocyanine H2Pc



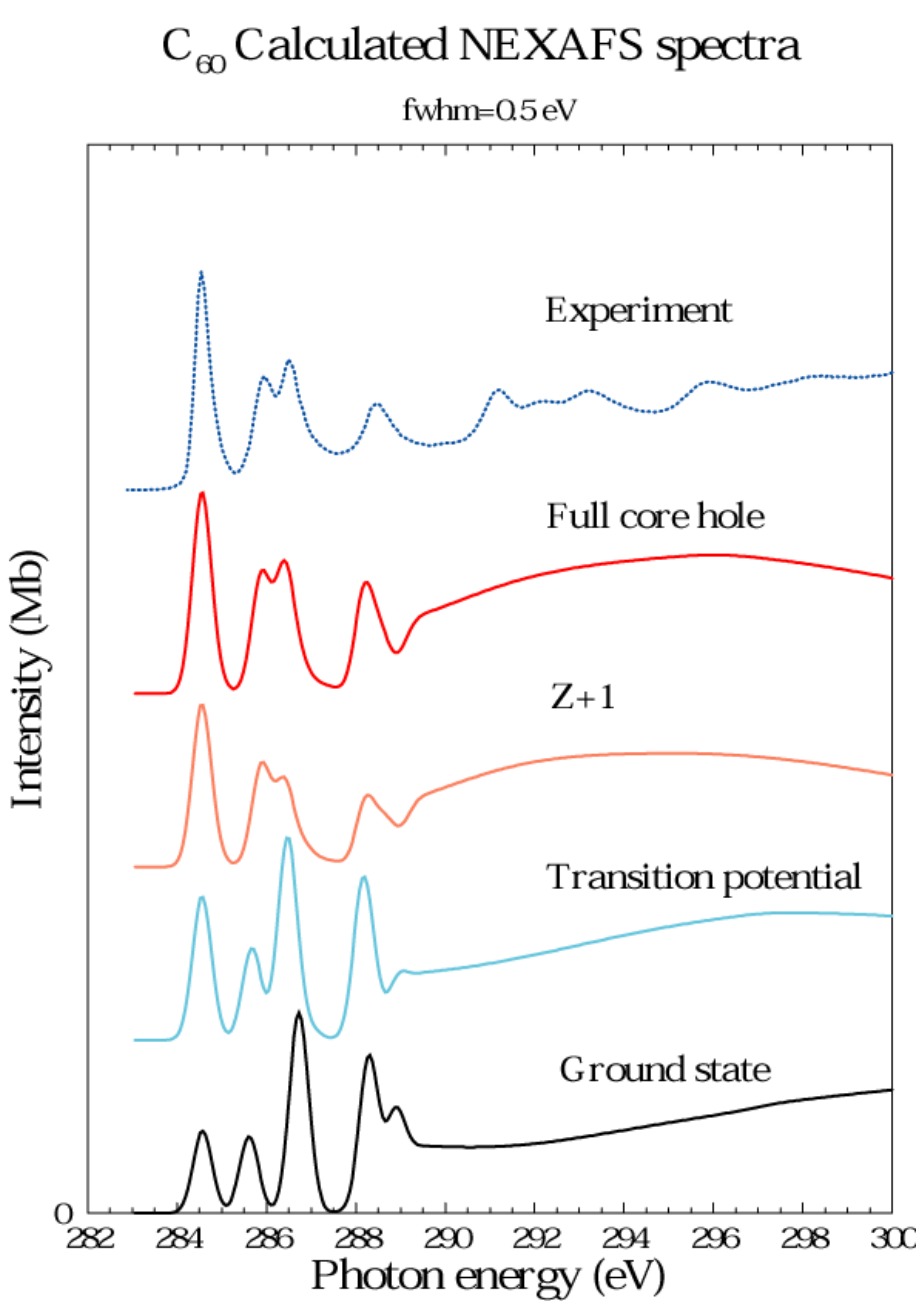


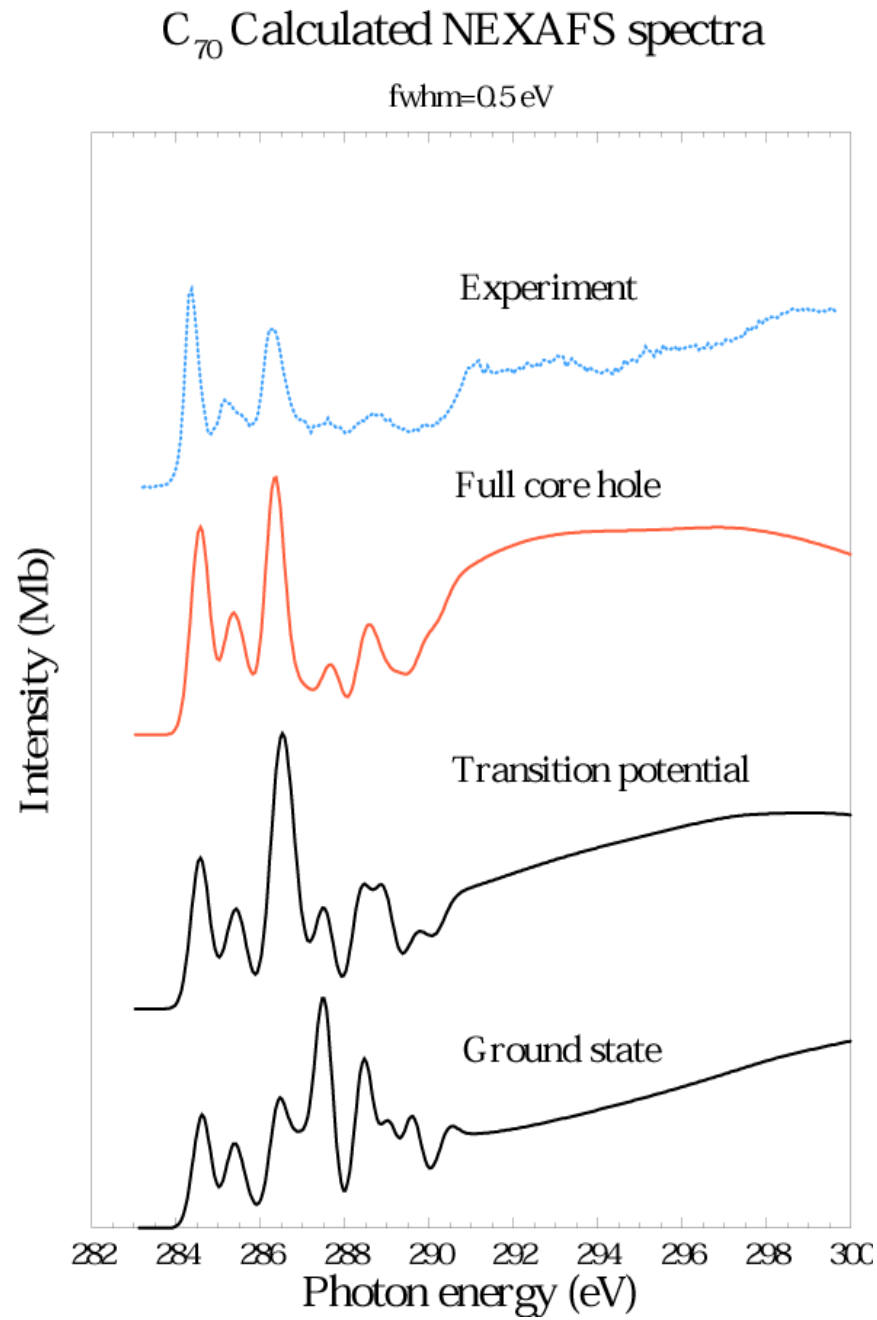
Benzene C1s shake-up peaks
Pyrrole C1s shake-up peaks
at about 2 eV from main line

Convoluted by gaussian curves
0.7, 0.8, 0.9 eV FWHM

First theoretical evidence of
benzene shake-up

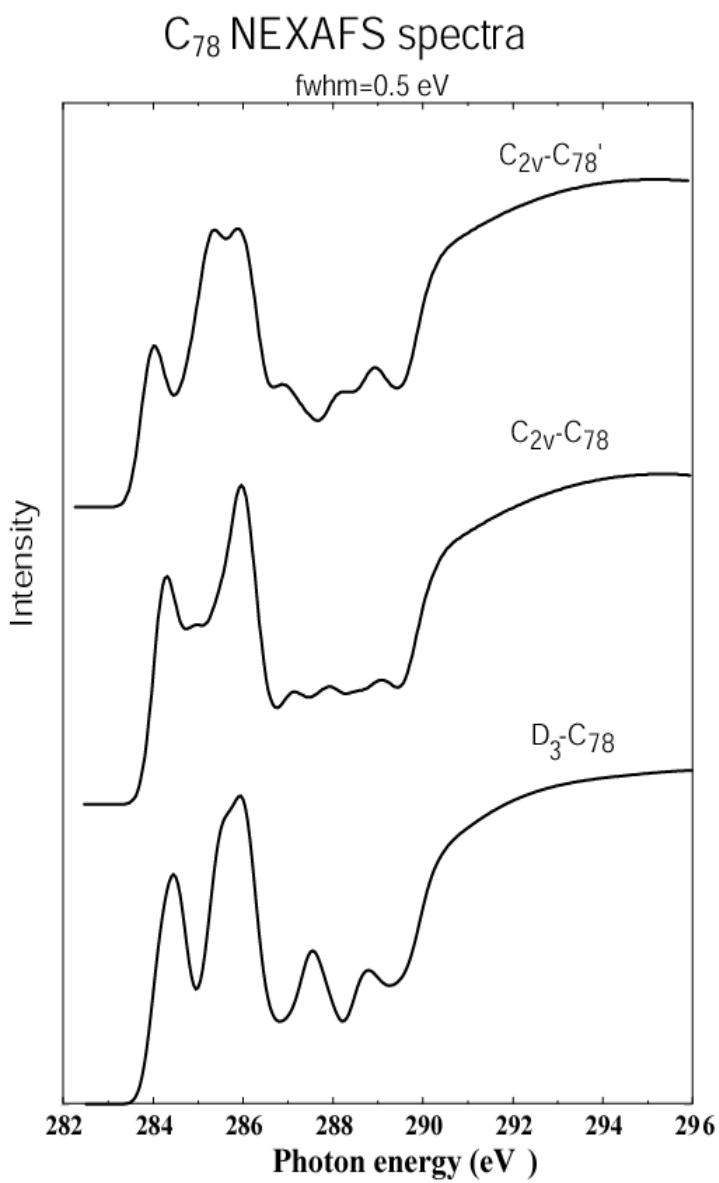
B. Brena, Y. Luo, M. Nyberg, S. Carniato, K. Nilsson, Y. Alfredsson, J. Ahlund, N. Mårtensson, H. Siegbahn, and C. Puglia, Phys. Rev. B, 00, 000, (2004)

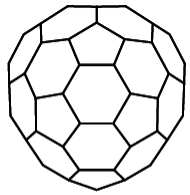




M. Nyberg, Y. Luo, L. Triguero, L. G.M. Pettersson, and H. Ågren, **Phys. Rev. B** 60, 7956 (1999)

Isomer Dependence



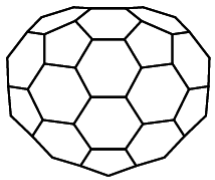


E=0

C_{2v}-C_{78}'

R_{cc}

Shortest: 1.373 Å
Longest: 1.477 Å
Average: 1.437 Å

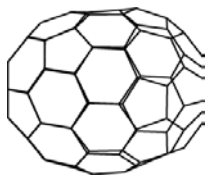


E=6.34

C_{2v}-C_{78}

R_{cc}

Shortest: 1.366 Å
Longest: 1.476 Å
Average: 1.437 Å

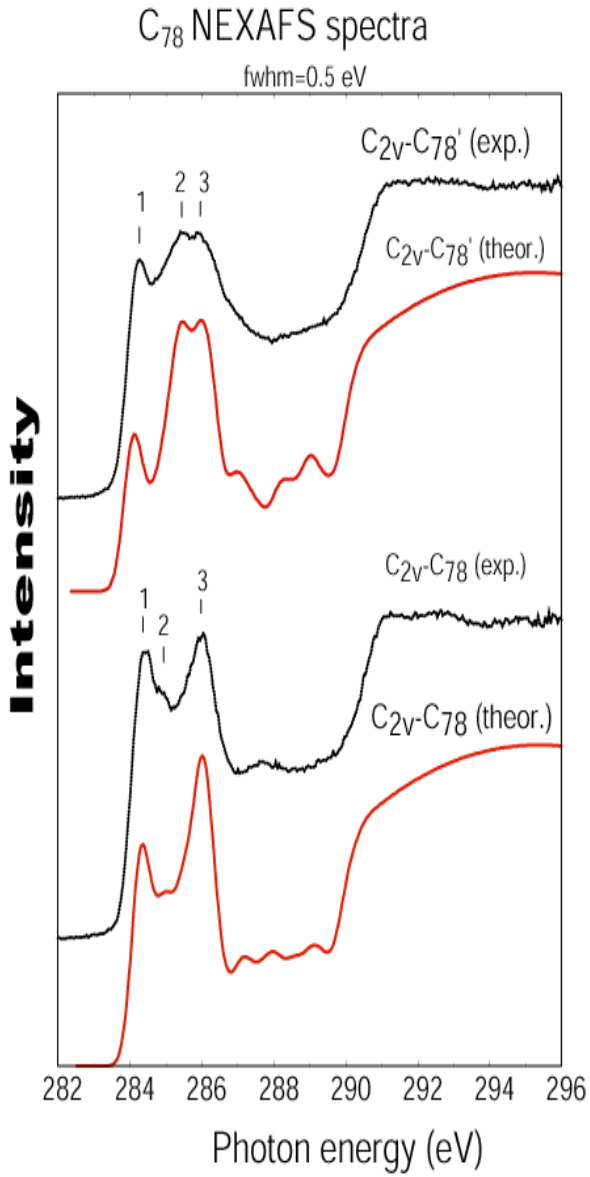


E=9.48
Kcal/mol

D_3 - C_{78}

R_{cc}

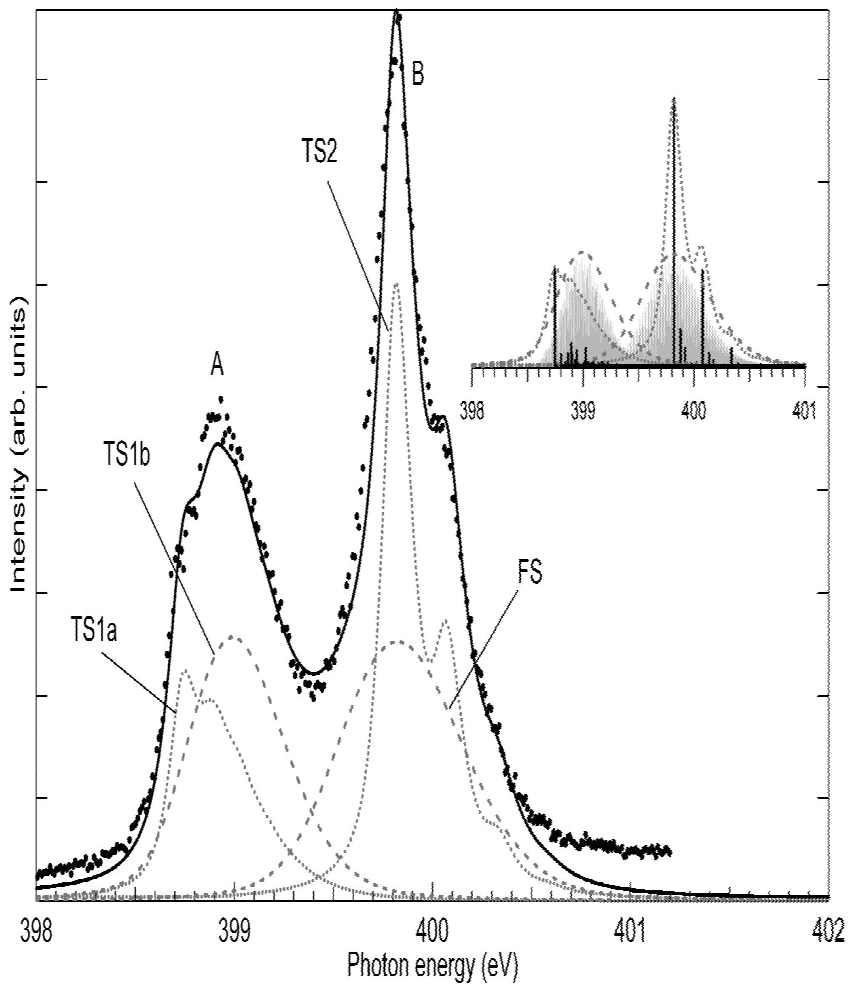
Shortest: 1.383 Å
Longest: 1.475 Å
Average: 1.437 Å

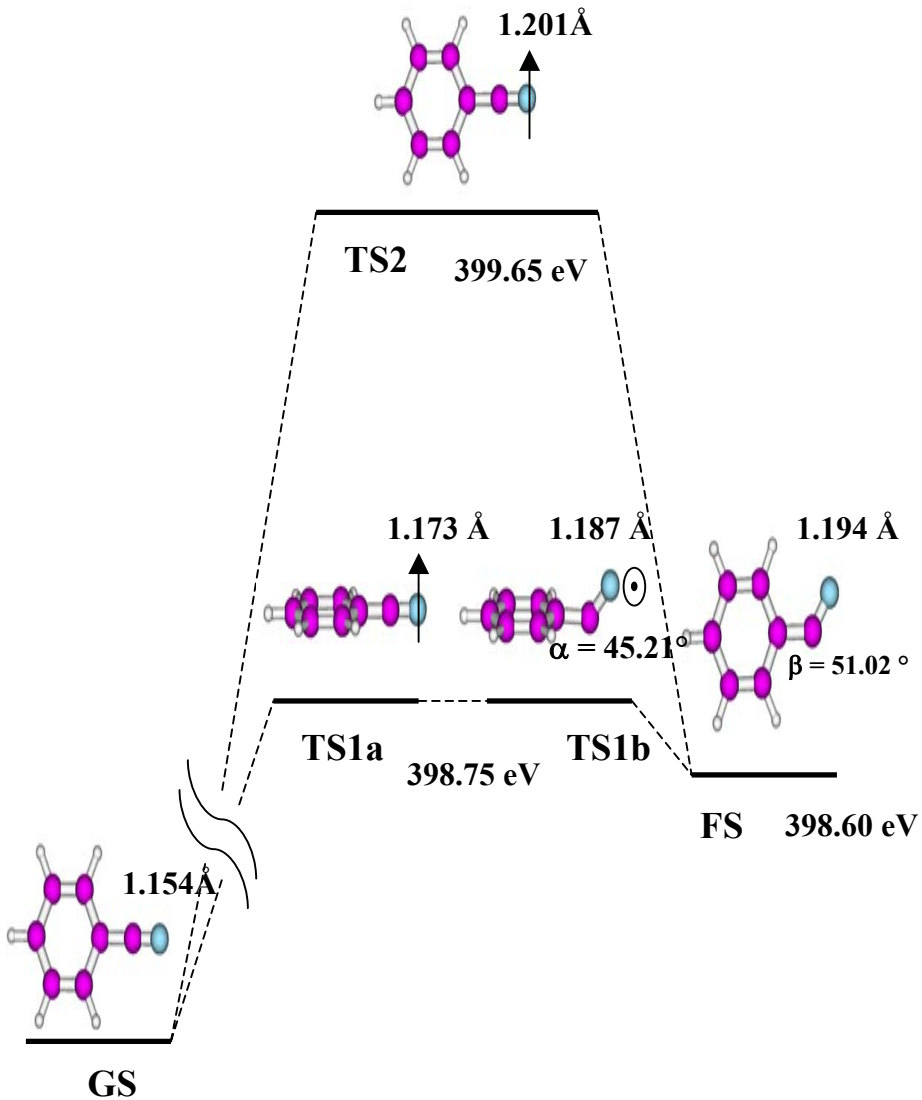


A. Bassan, M. Nyberg, and Y. Luo, Phys. Rev. B, 65, (2002) 165402.

Multidimensional transition-state theory calculations for nuclear dynamics of core excited benzonitrile molecule

S. Carniato, V. Ilakovac, J.-J. Gallet, E. Kukk, and Y. Luo, *Phys. Rev. A*, in press





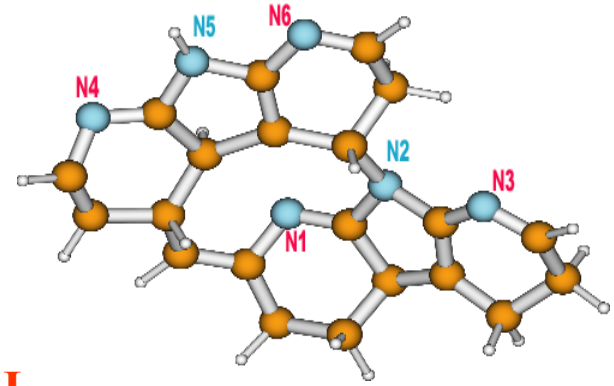
Carbon Nitride

Carbon nitride is today commercially used as a protective coating on hard discs and recorder heads by, e.g., IBM

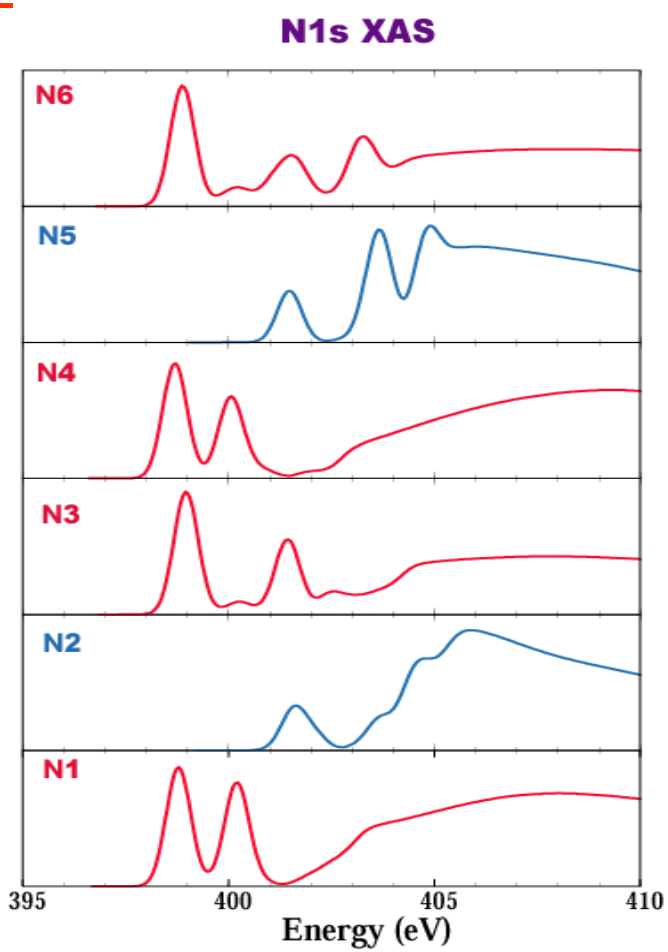
New fullerene-like phase of CNx (x = 0.1-0.3) films were discovered in 1995 in Linköping, Sweden. The phase is extremely hard and compliant (up to 95% elastic recovery!).

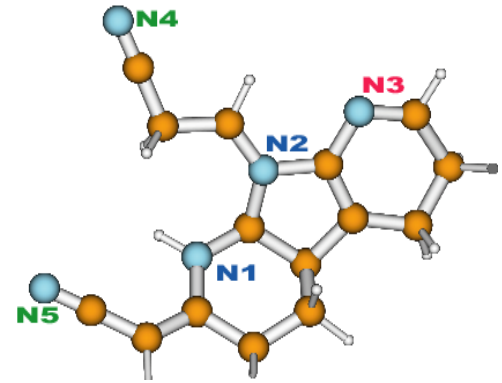
Many XPS and XAS studies have been reported.

The possible bonding structures have been under debate

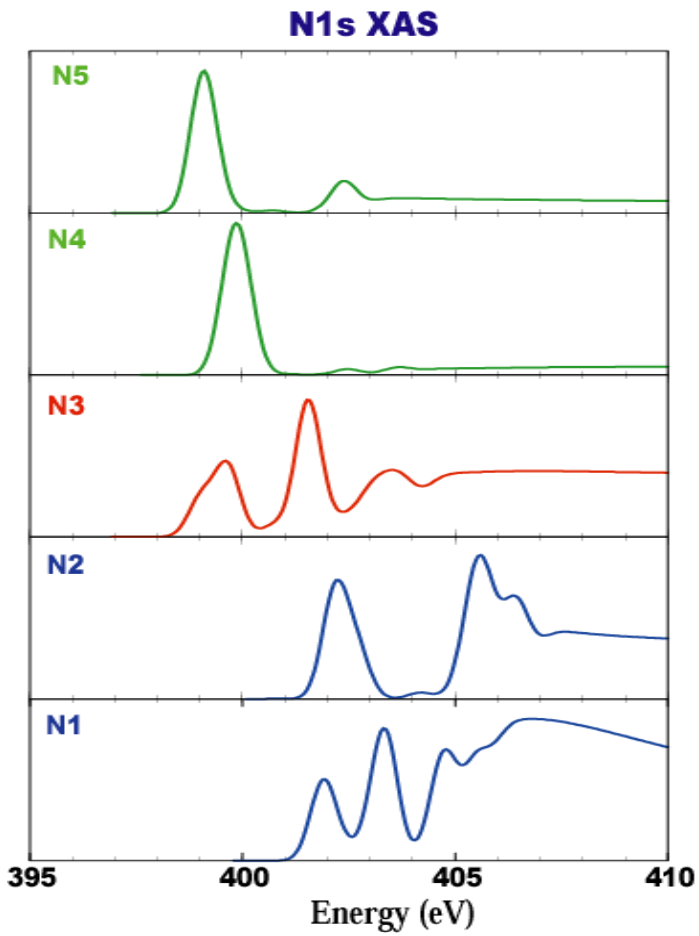


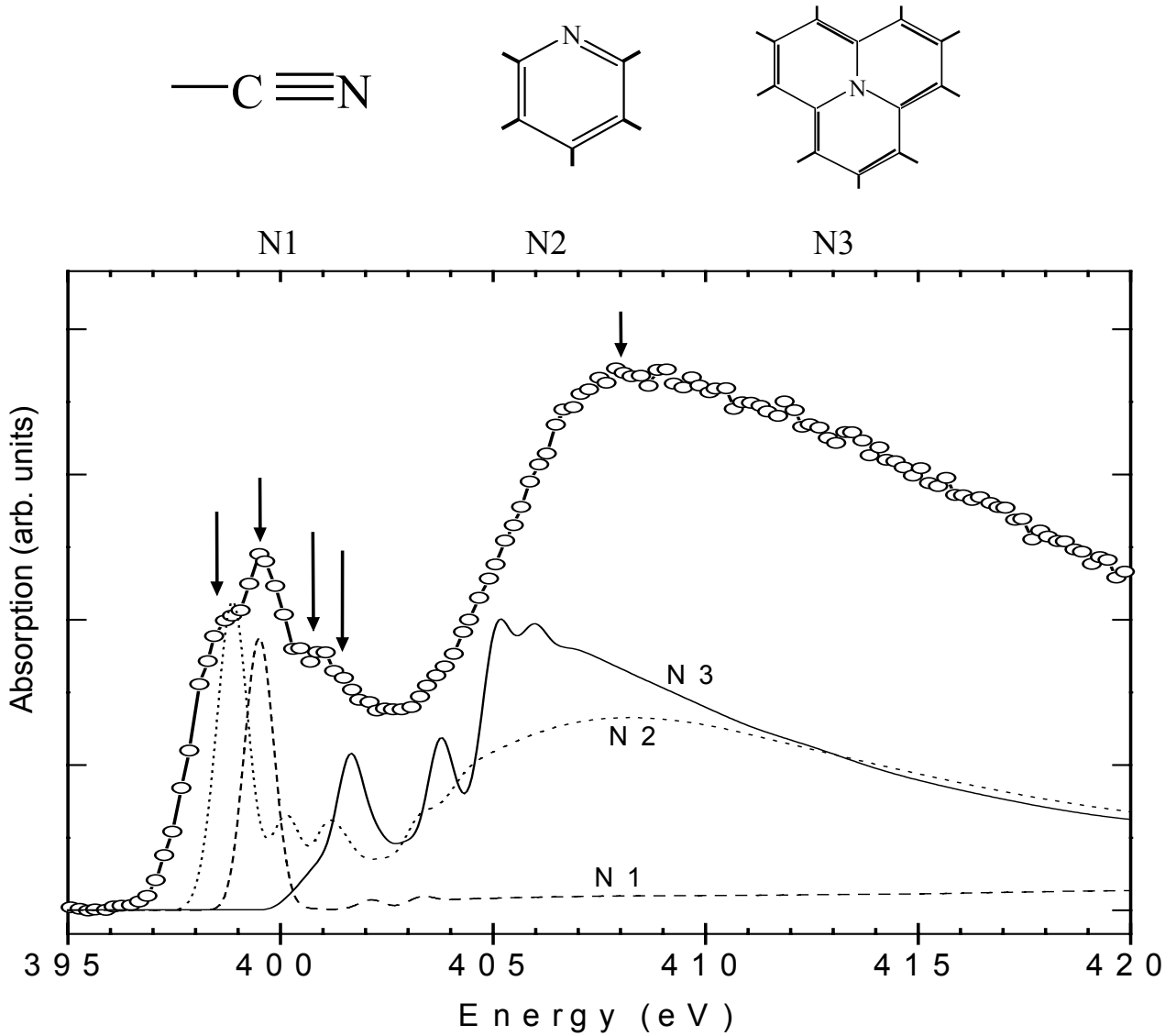
Model I





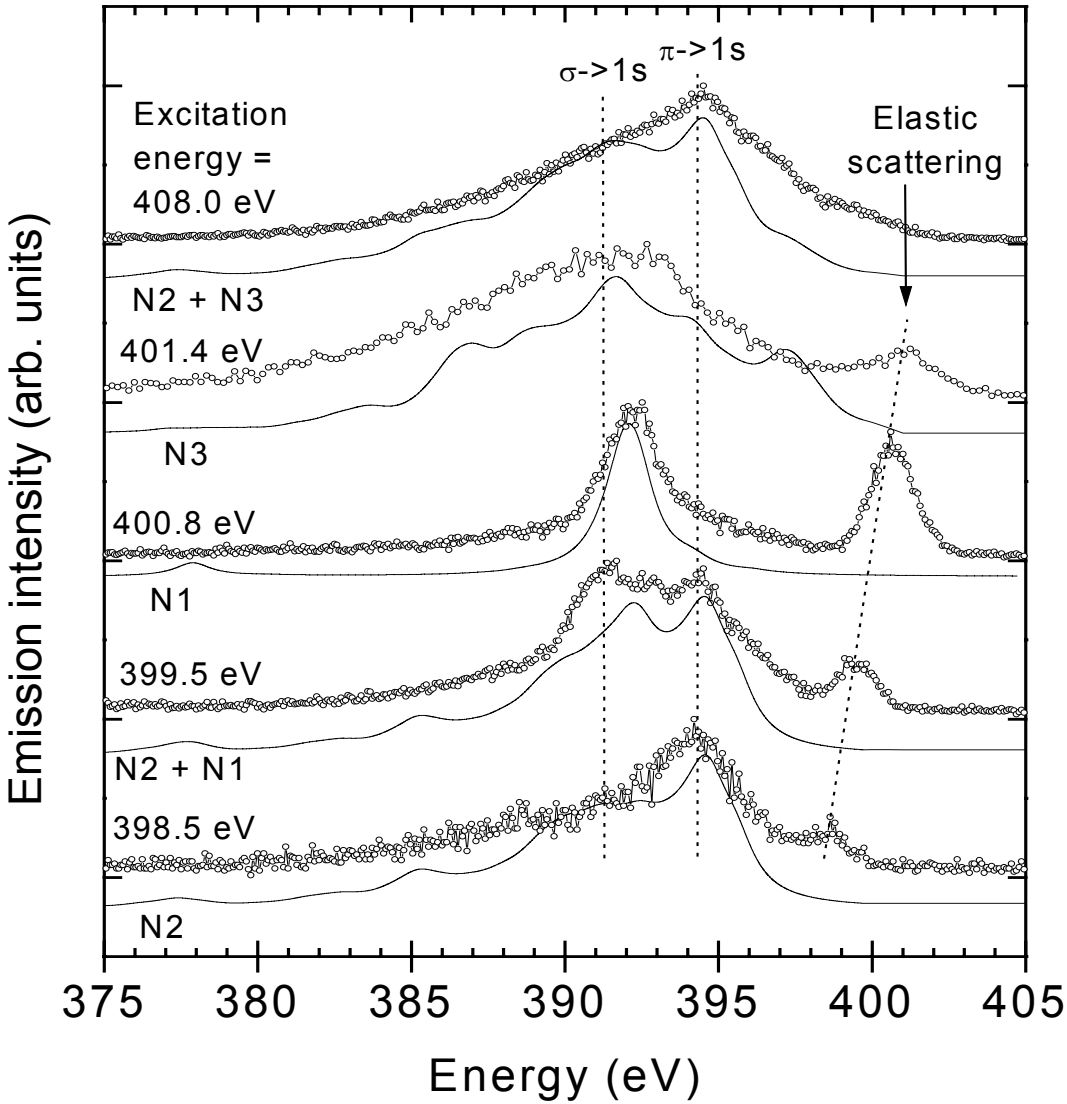
Model II





SXAS N K-edge spectrum from a magnetron sputtered $CN_{0.25}$ films, grown at 350 °C (open circles), and calculated spectra from nitrile structures (N1), pyridine-like N (N2) and graphite-like N (N3). The relative intensity for the N1 spectra has been scaled to 50%, relative to N2 and N3.

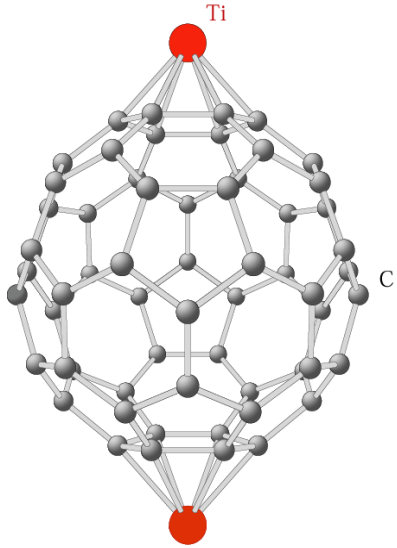
N. Hellgren, J.-H. Guo, C. Såthe, A. Agui, J. Nordgren, Y. Luo, H. Ågren, and J.-E. Sundgren, **Appl. Phys. Lett.,** *26 (2001) 4348.*



Experimental (open circles) SXES N K emission spectra achieved using different excitation energies (marked by arrows in XAS), and calculated spectra (solid lines) from nitrile structures (N1), pyridine-like N (N2) and graphite-like N (N3).

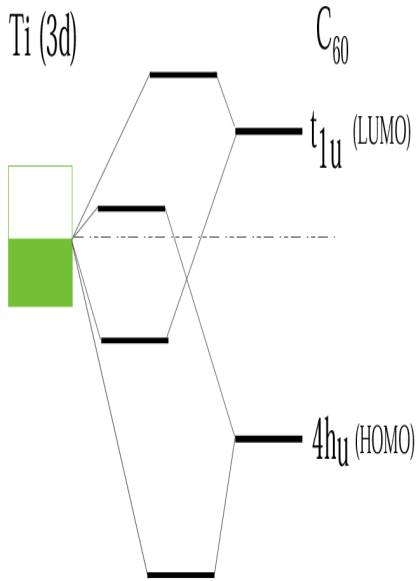
Bonding Sites and Energies:

System	B.E. (eV/atom)	distance Ti-C (Å)
$C_{60}Ti$		
Bridge	3.57	2.03
5-ring	3.35	1.92(1), 2.09(2), 2.37(2)
6-ring	4.01	2.16(2), 2.17(4)
$C_{60}Ti_2$		
Bridge	3.43	2.03
5-ring	3.42	1.94(1), 2.09(2), 2.39(2)
6-ring	3.78	2.17(2), 2.21(4)



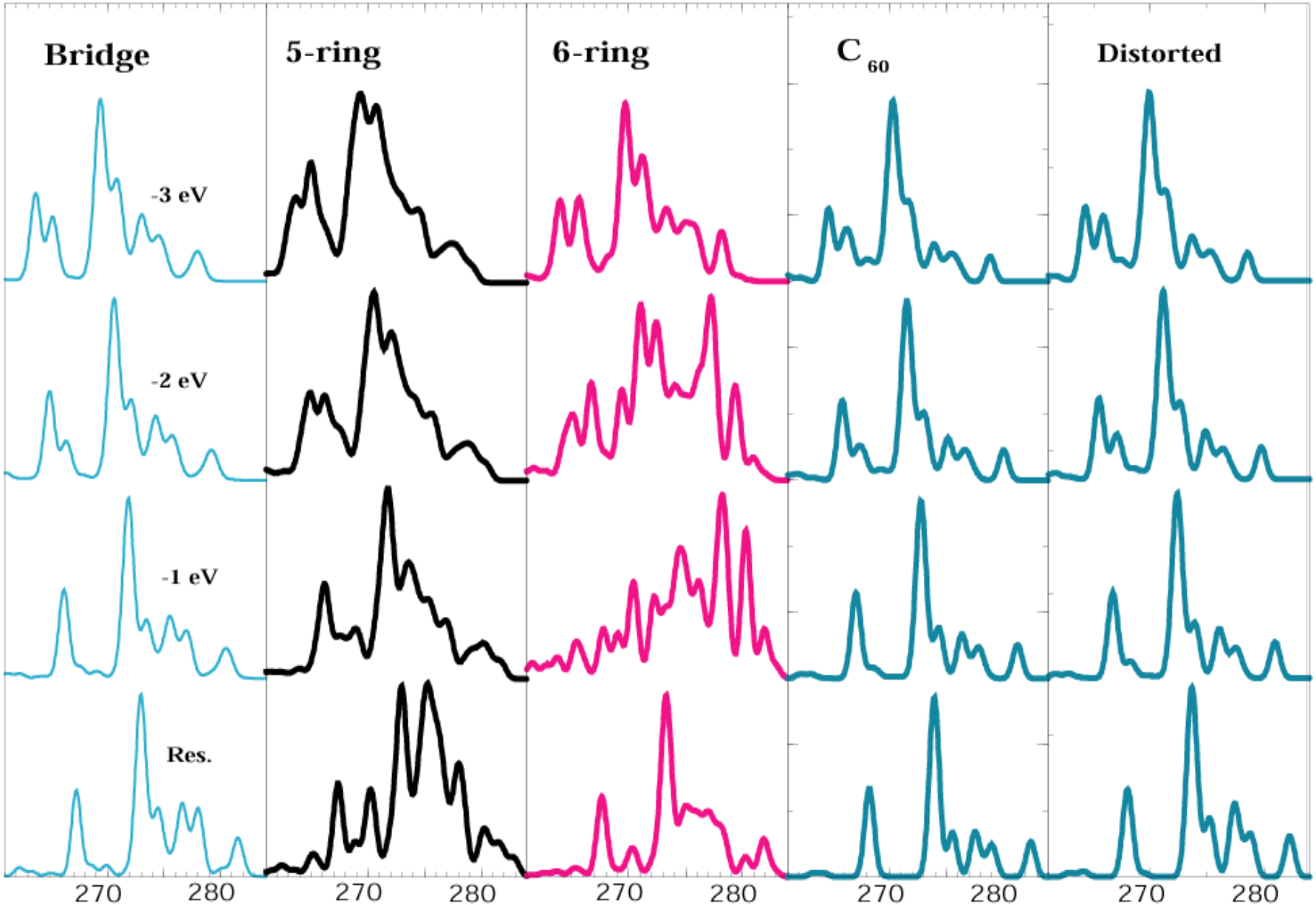
Bonding Formation

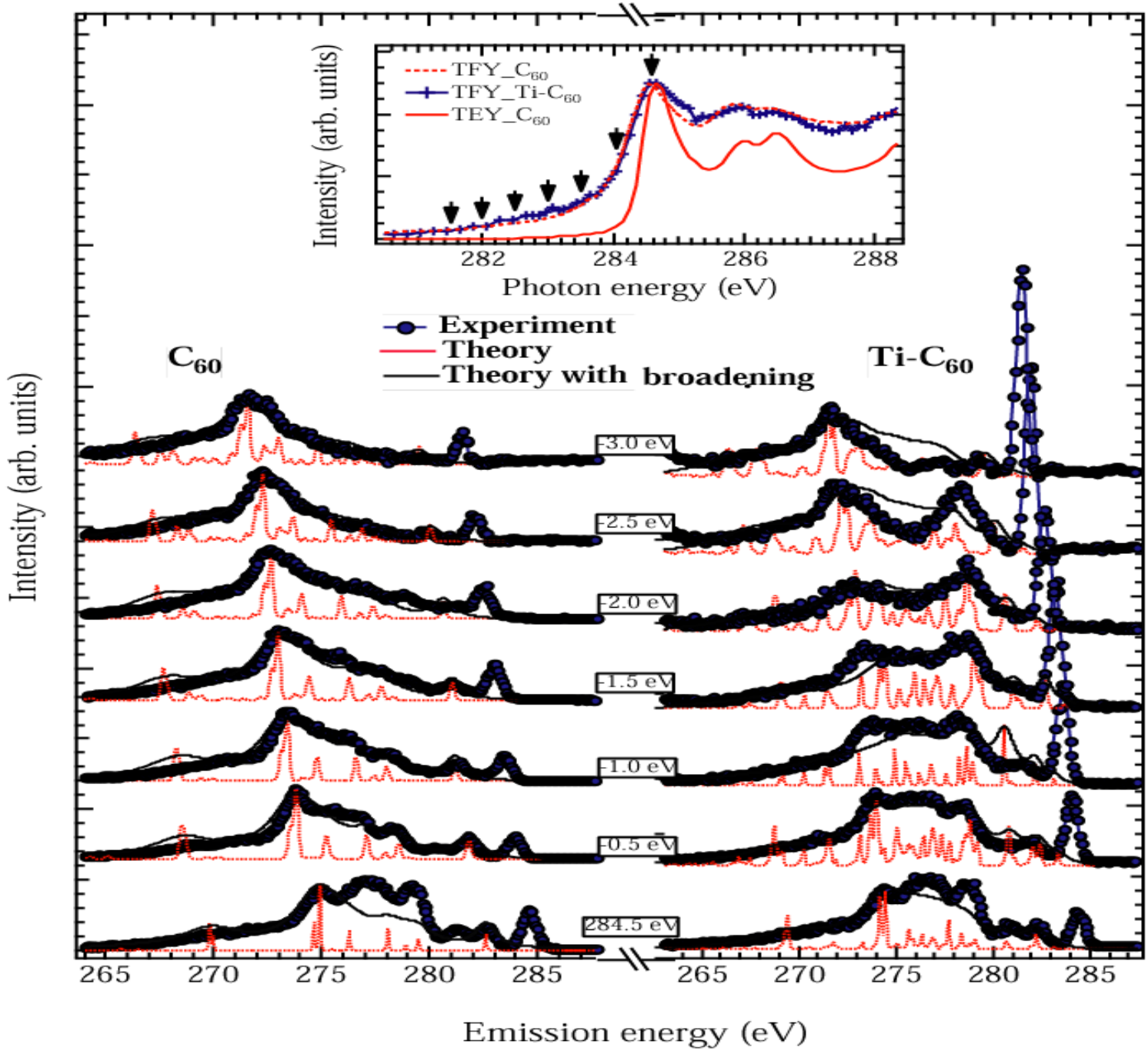
Dewar, Chatt and Duncanson (DCD) model



M. Nyberg, Y. Luo, L. Qian, J. E. Rubensson, C. Såthe, D. Ding, J. -H Guo, T. Käämbre, and J. Nordgren, Phys. Rev. B, 63, 115117 (2001)

C_{60} Ti calculated RIXS detuning spectra



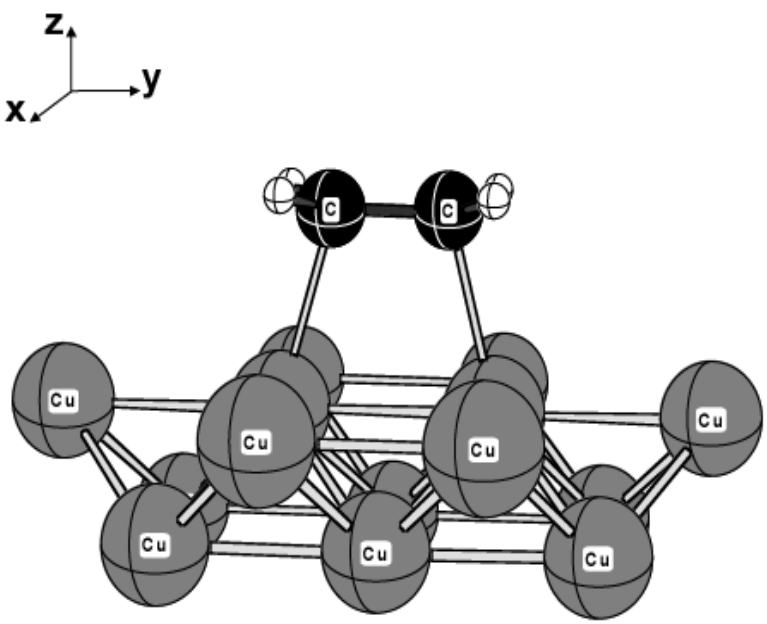

TFY_C60
TFY_Ti-C60
TEY_C60
Intensity (arb. units)
282
284
286
288
Photon energy (eV)
Experiment
Theory
Theory with broadening
C60
Ti-C60
-3.0 eV
-2.5 eV
-2.0 eV
-1.5 eV
-1.0 eV
-0.5 eV
284.5 eV
Intensity (arb. units)
265
270
275
280
285
Emission energy (eV)

RIXS of ethylene on Cu(110)

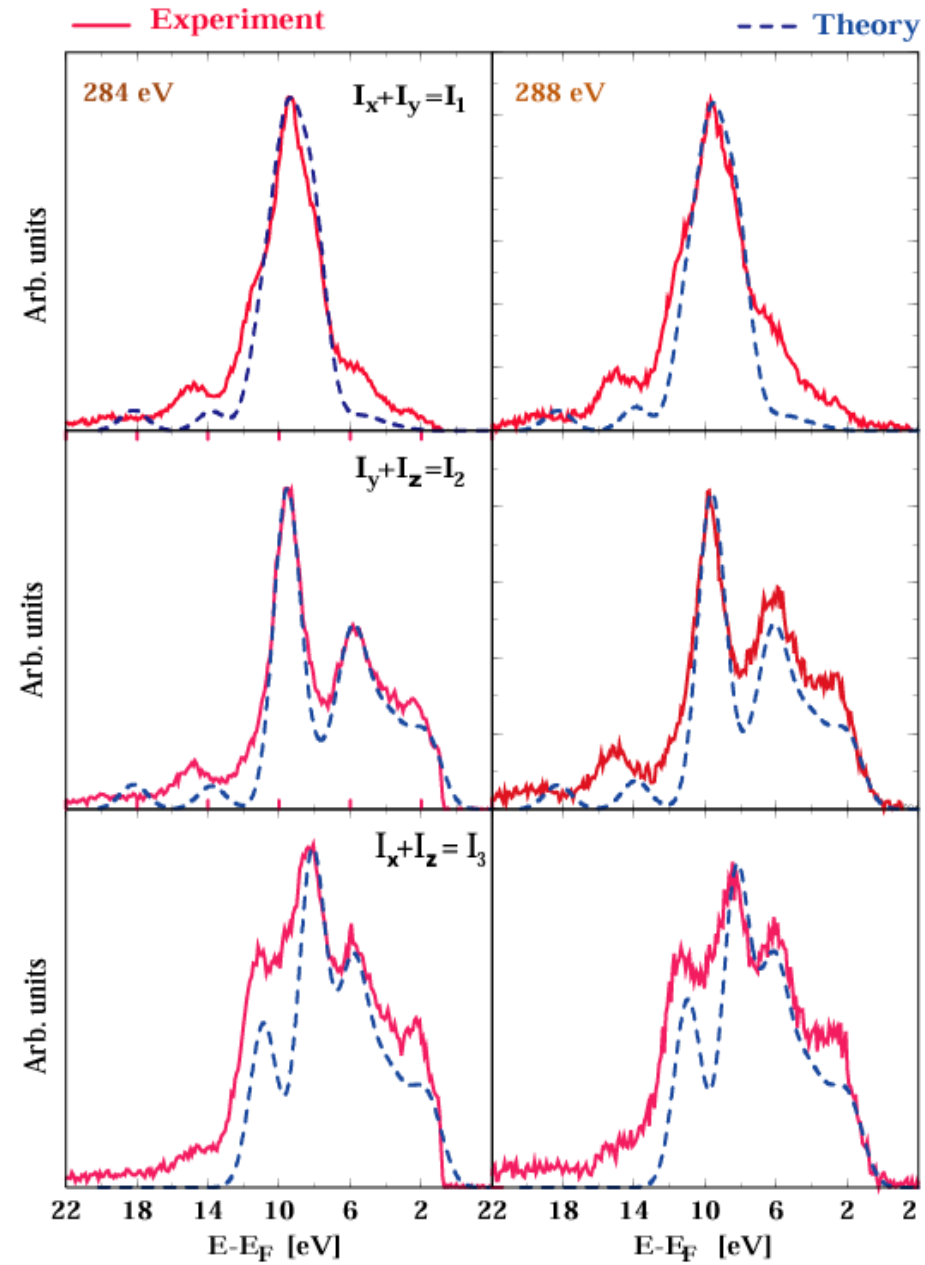
L.Triguero, Y.Luo, L.G.M.Pettersson, H.Ågren, P.Väterlein, M.Weinelt, A.Föhlisch, J.Hasselström, O.Karis, and A.Nilsson, ***Phys.Rev.B*** *59,5189 (1999)*

Theoretical model: C_2H_4/Cu_{86} + DFT

Experiment: ALS beamline 8.0

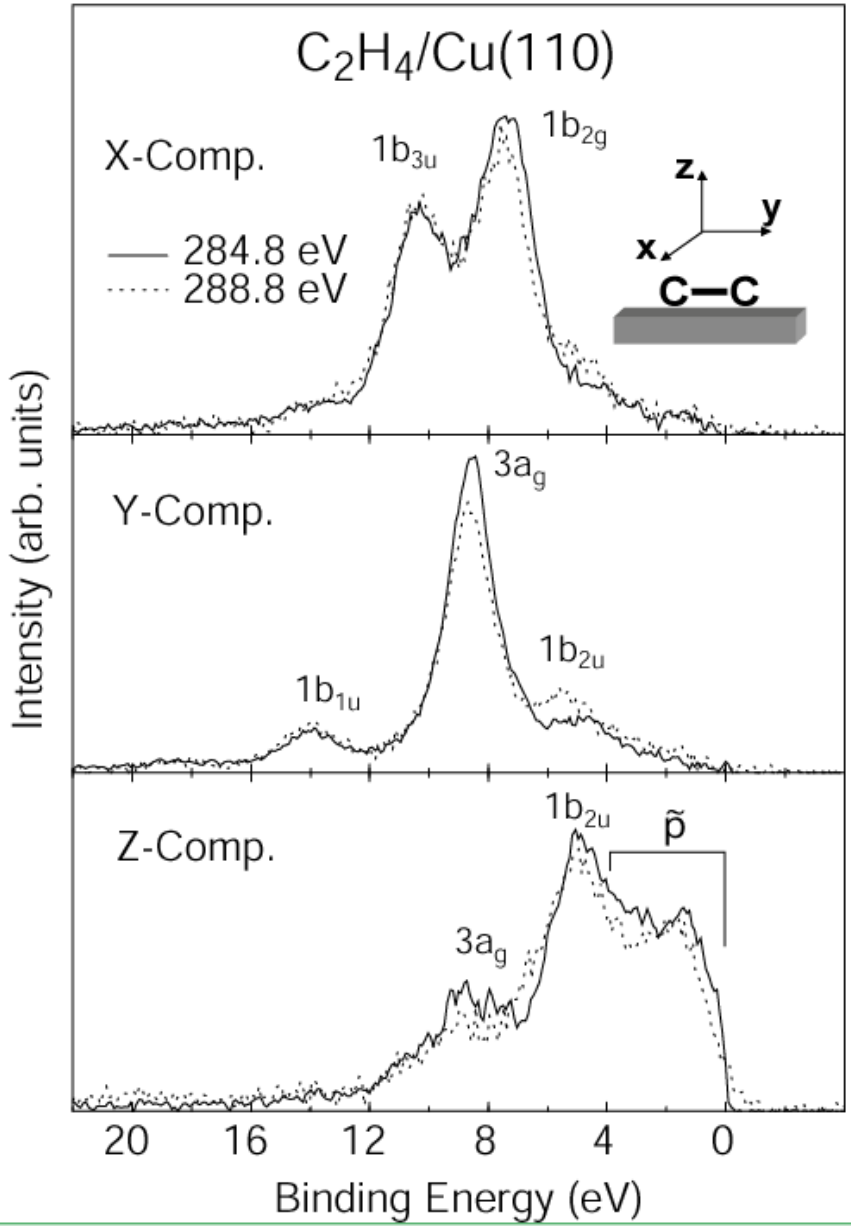


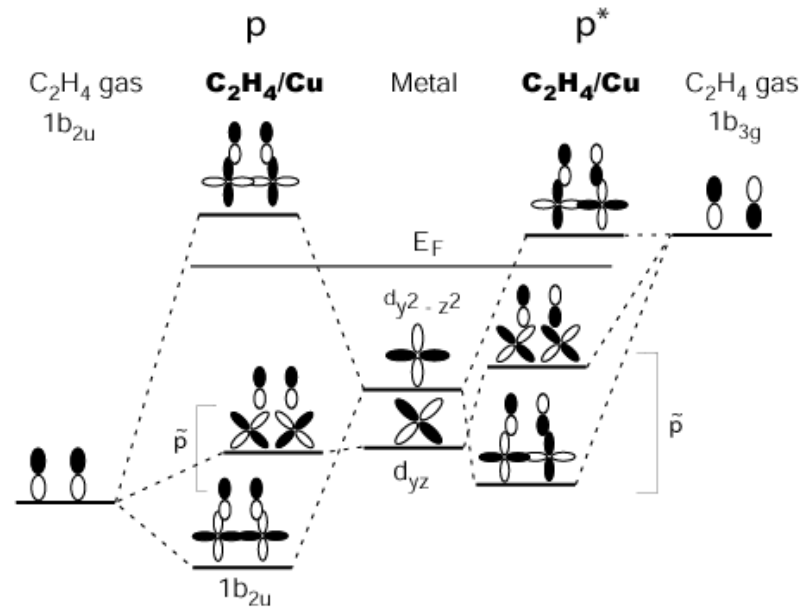
Chemisorbed ethylene on Cu(110); di-s site

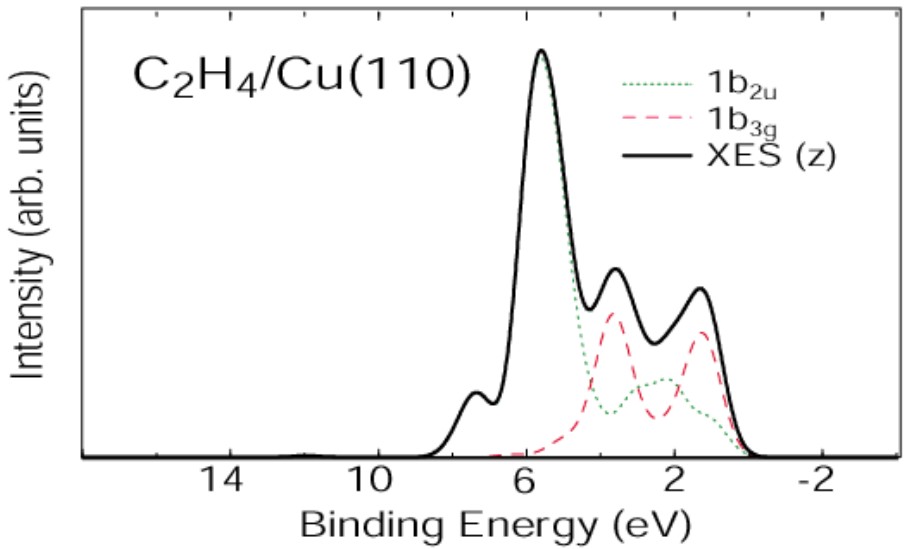


Bonding formation of Ethylen on Cu(110)

experiment

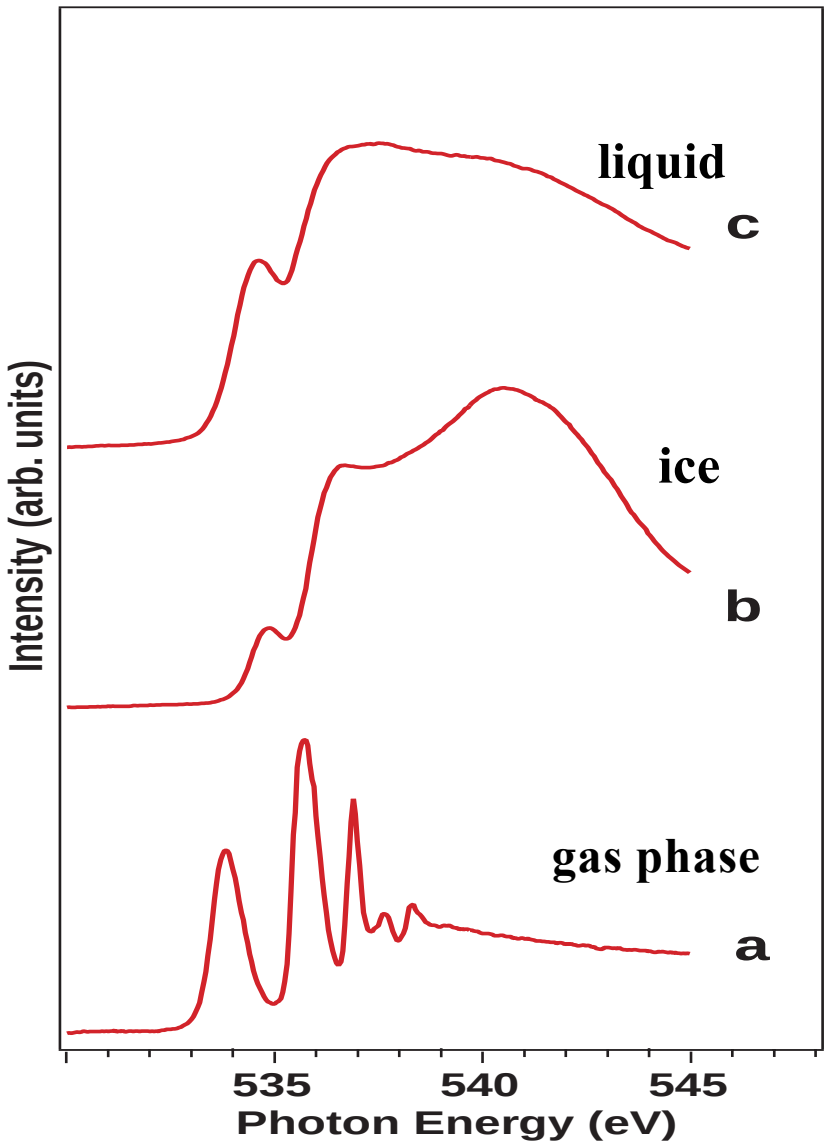


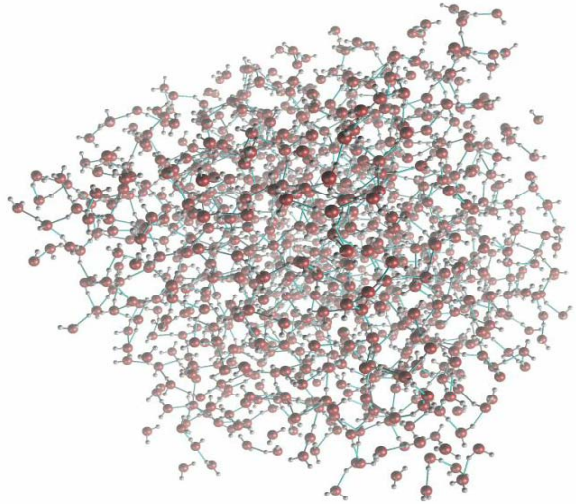


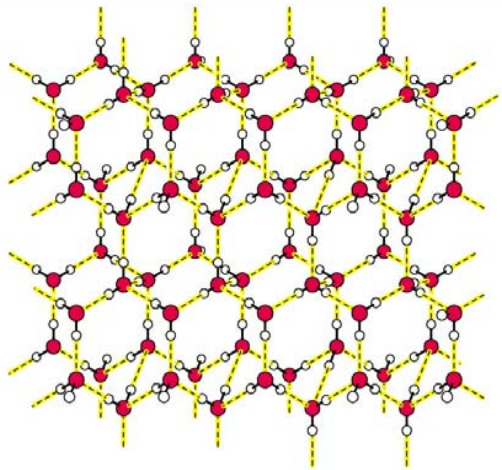


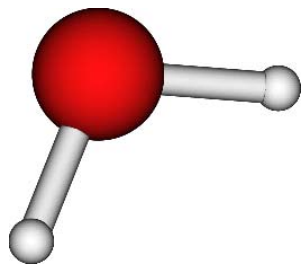
L. Triguero, A. Föhlisch, P. Väterlein, J. Hasselström, M. Weinelt, L.G.M. Pettersson, Y. Luo, H. Ågren and A. Nilsson, J. Am. Chem. Soc, 122. 12310 (2000)

X-ray absorption of water



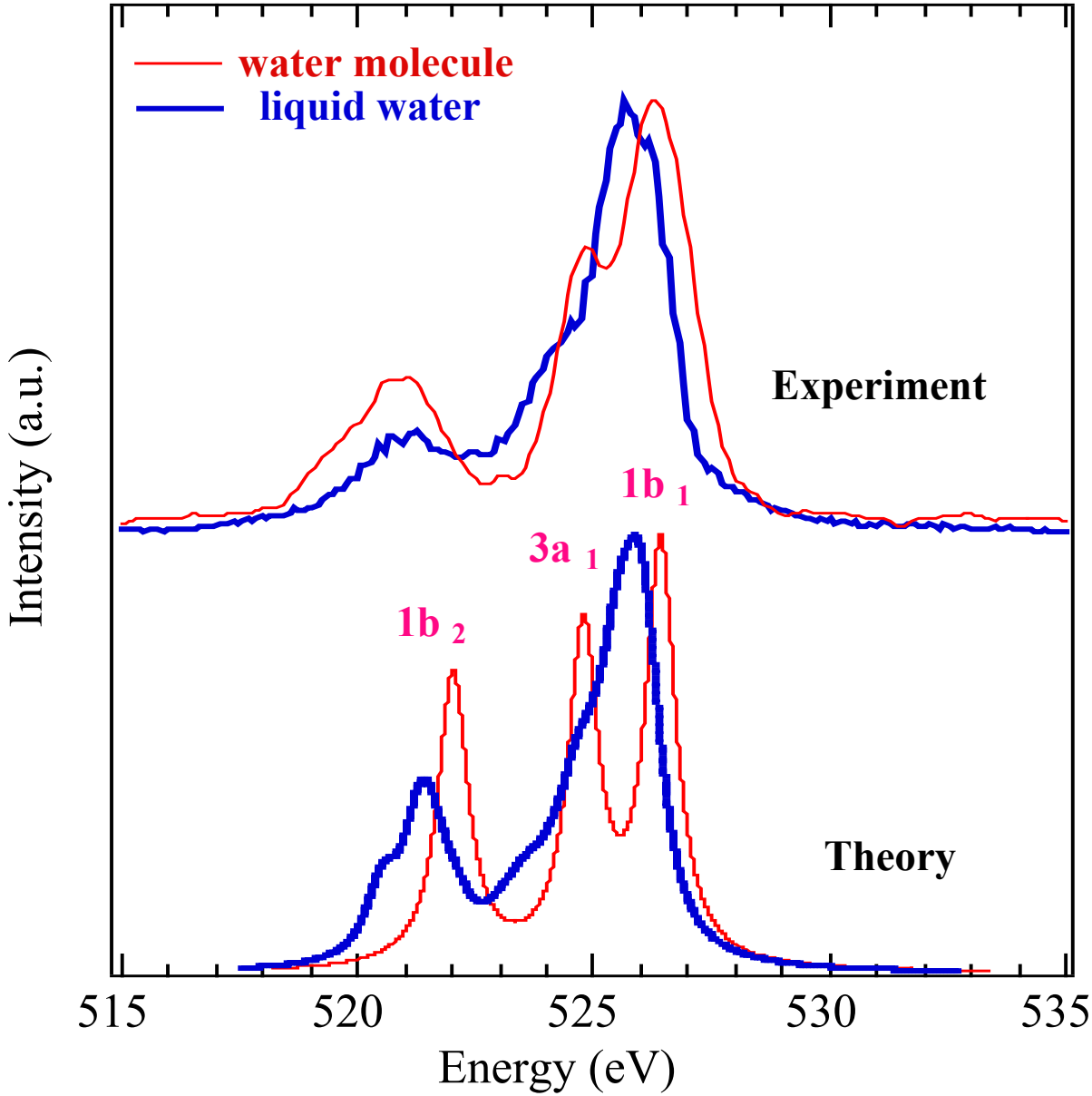


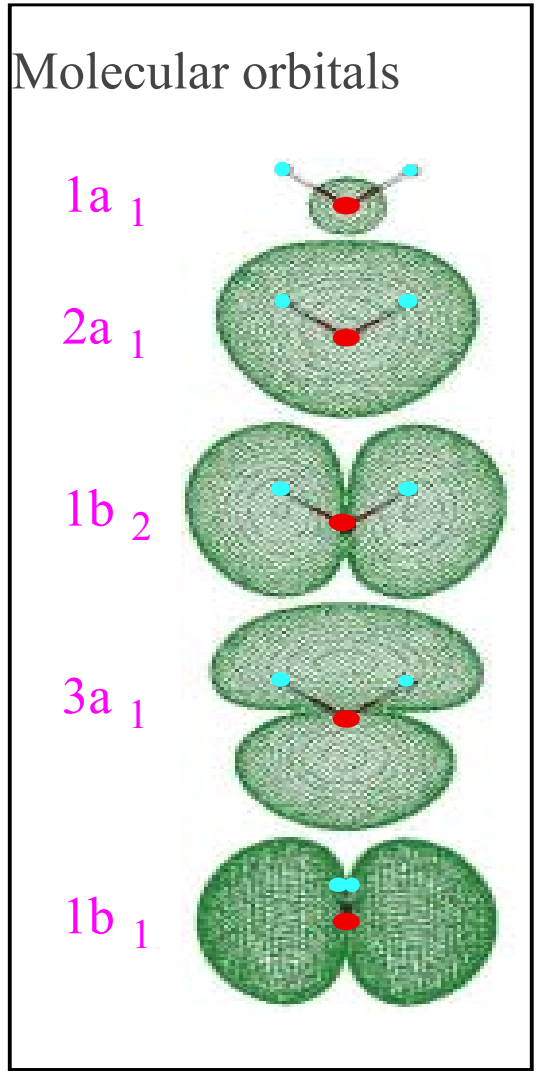




S. Myneni, Y. Luo, L.Å. Näslund, M. Cavalleri, L. Ojamäe, H. Ogasawara, A. Pelmenschikov, Ph. Wernet, P. Väterlein, C. Heske, Z. Hussain, L.G.M. Pettersson, and A. Nilsson J. Phys. Cond. Matter, 14 (2002) L213.

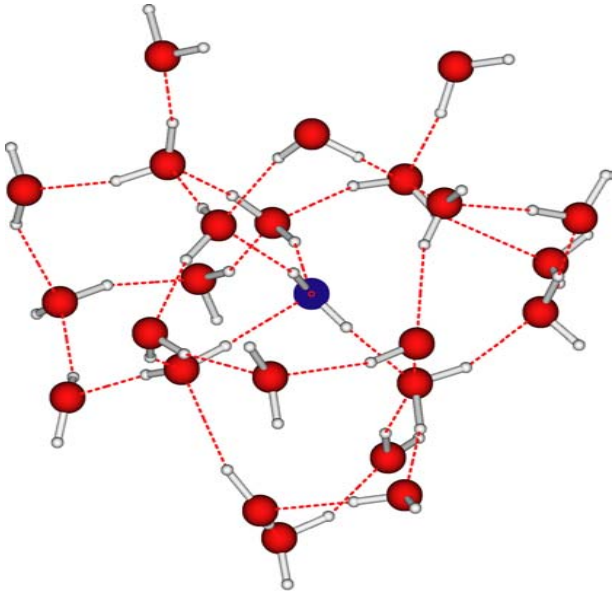
XES of Liquid Water



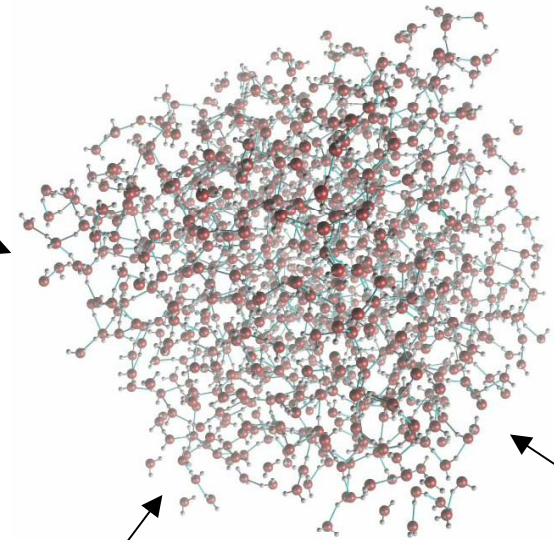


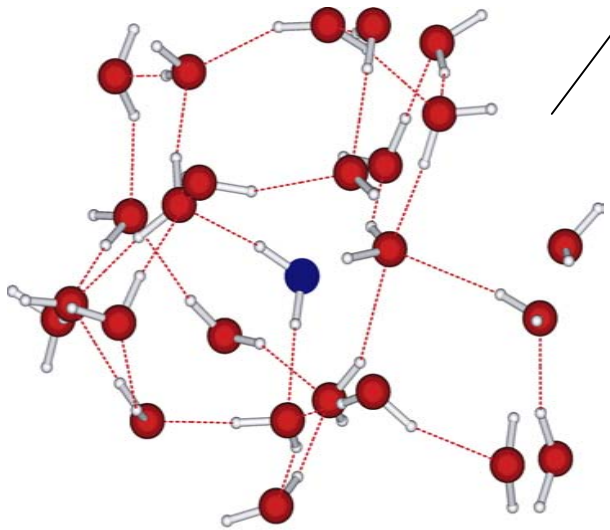
J.-H. Guo, Y. Luo, A. Augustsson, J.-E. Rubensson, C. Såthe, H. Ågren, H. Siegbahn, and J. Nordgren, *Phys. Rev. Lett.*, 89, (2002) 137402.

Representative water clusters

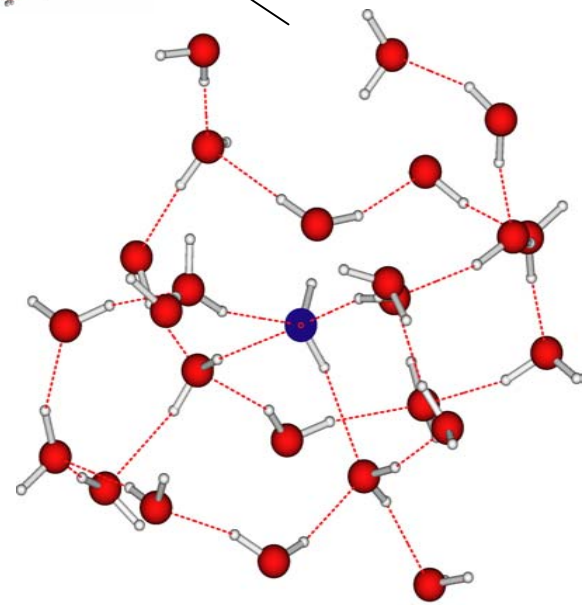


SYM

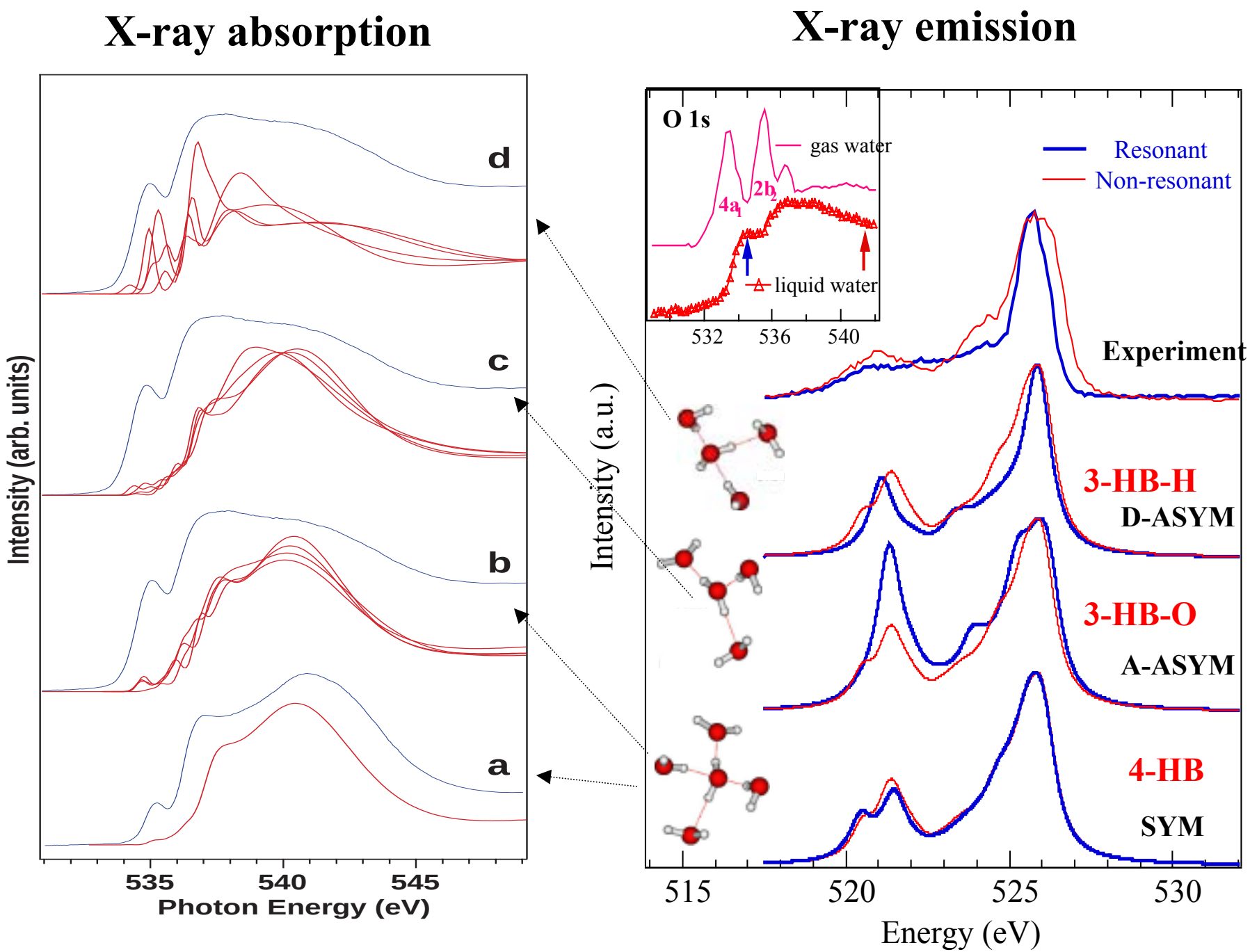




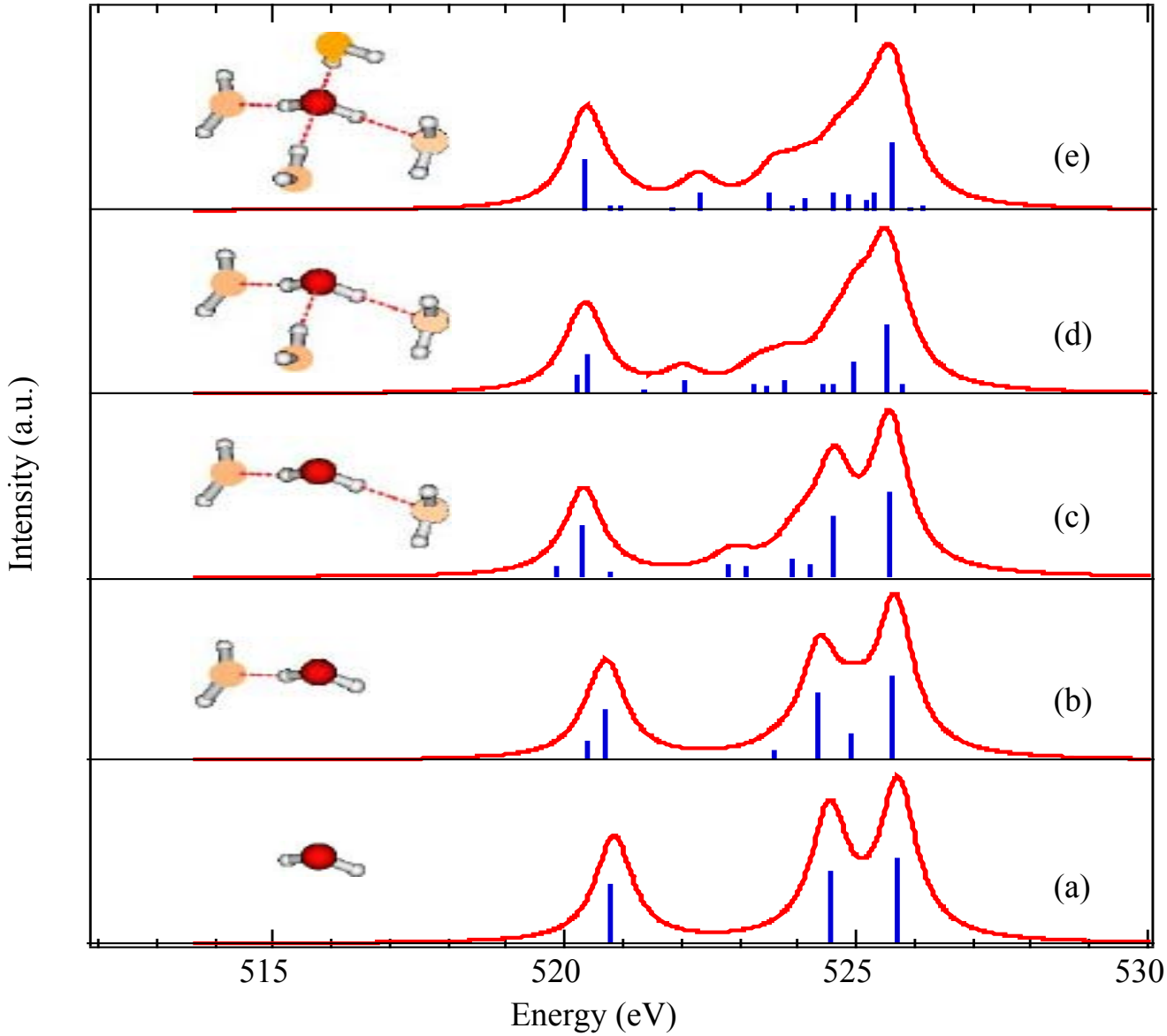
A-ASYM



D-ASYM

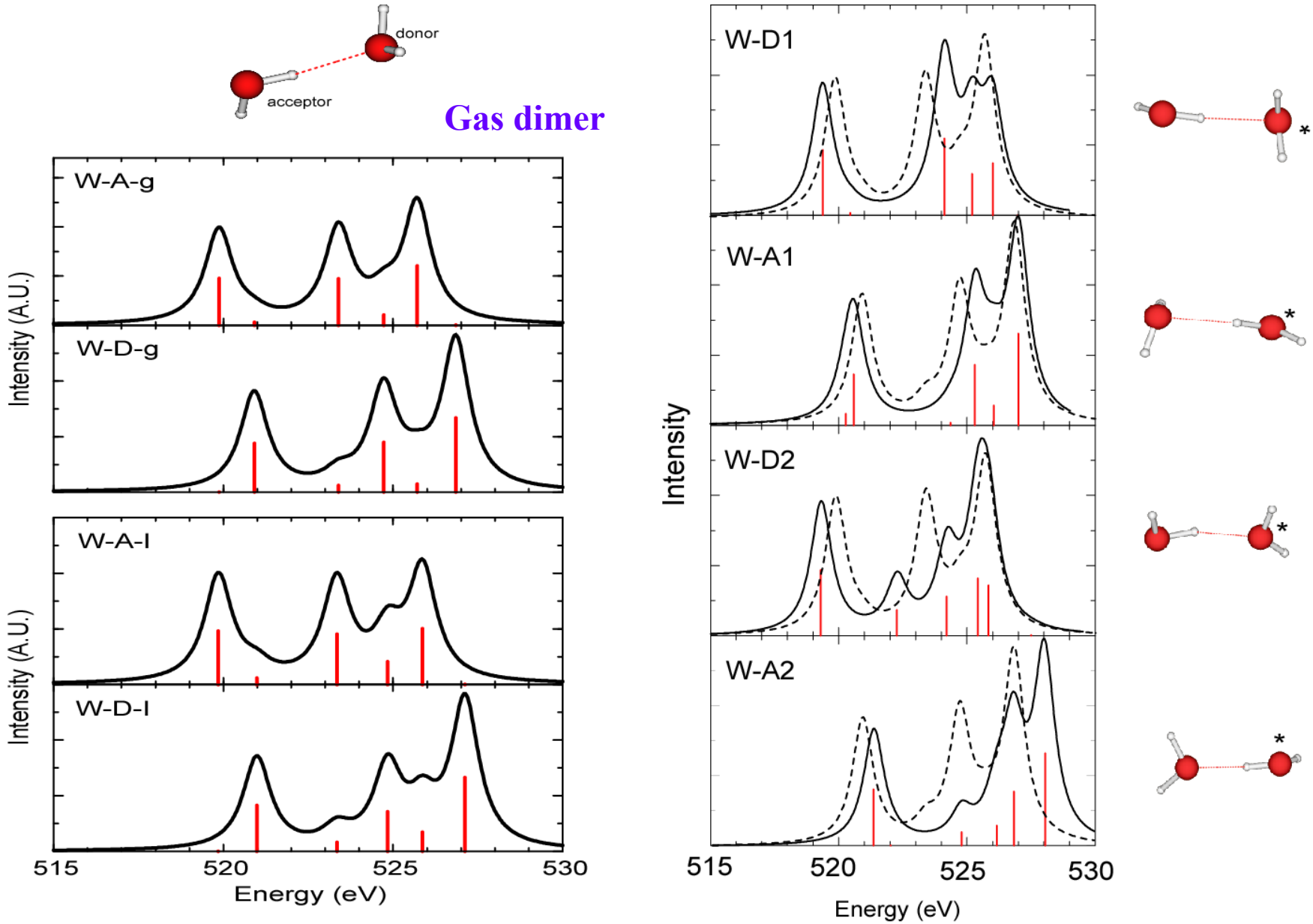

X-ray absorption
X-ray emission
d
c
b
a
Intensity (arb. units)
535
540
545
Photon Energy (eV)
O 1s
gas water
liquid water
4a1
2b2
532
536
540
Resonant
Non-resonant
Experiment
3-HB-H
D-ASYM
3-HB-O
A-ASYM
4-HB
SYM
Intensity (a.u.)
515
520
525
530
Energy (eV)

Effects of hydrogen bond on the electronic structure of liquid water

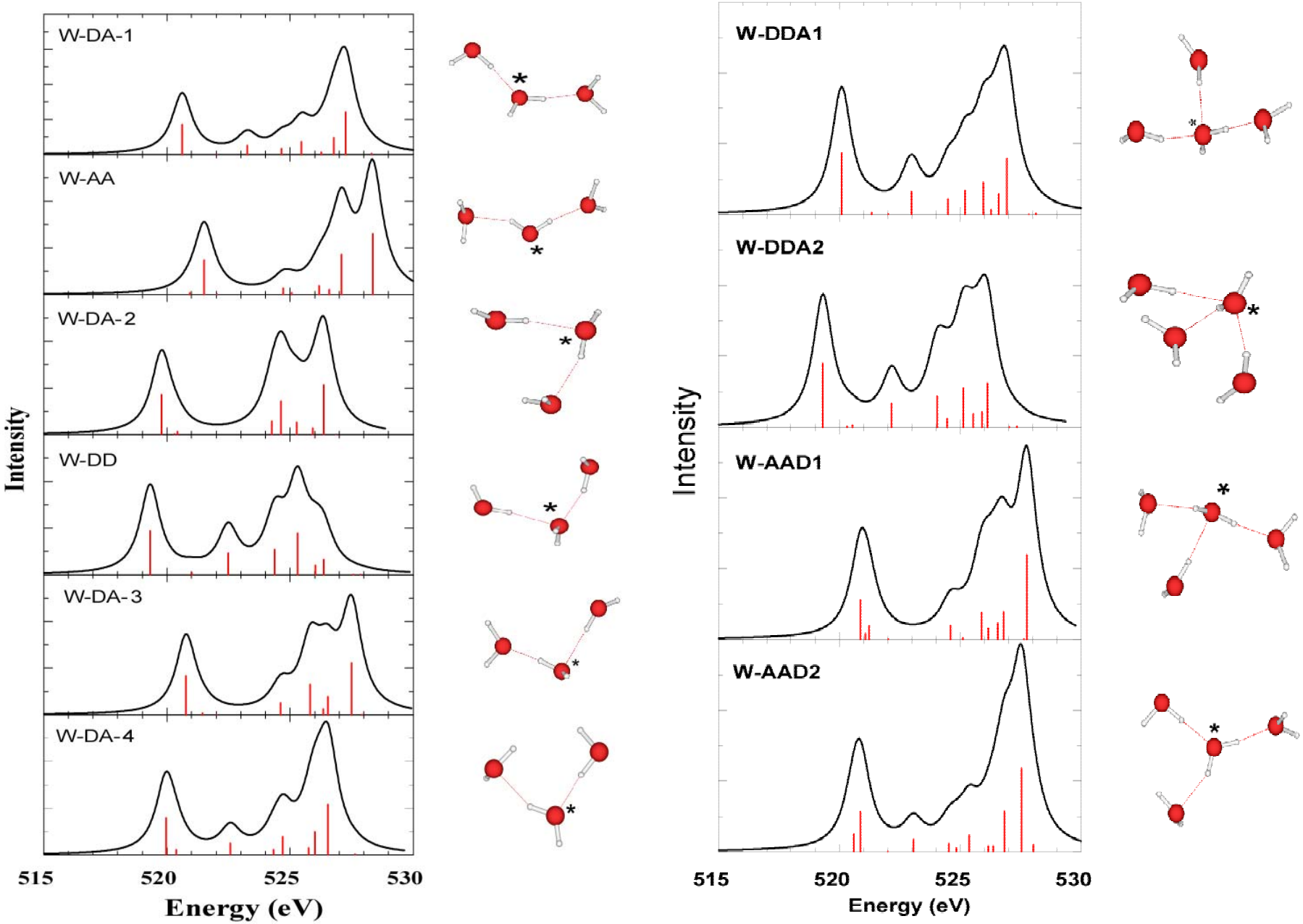


J.-H. Guo, Y. Luo, A. Augustsson, J.-E. Rubensson, C. Såthe, H. Ågren, H. Siegbahn, and J. Nordgren, *Phys. Rev. Lett.*, 89, (2002) 137402.

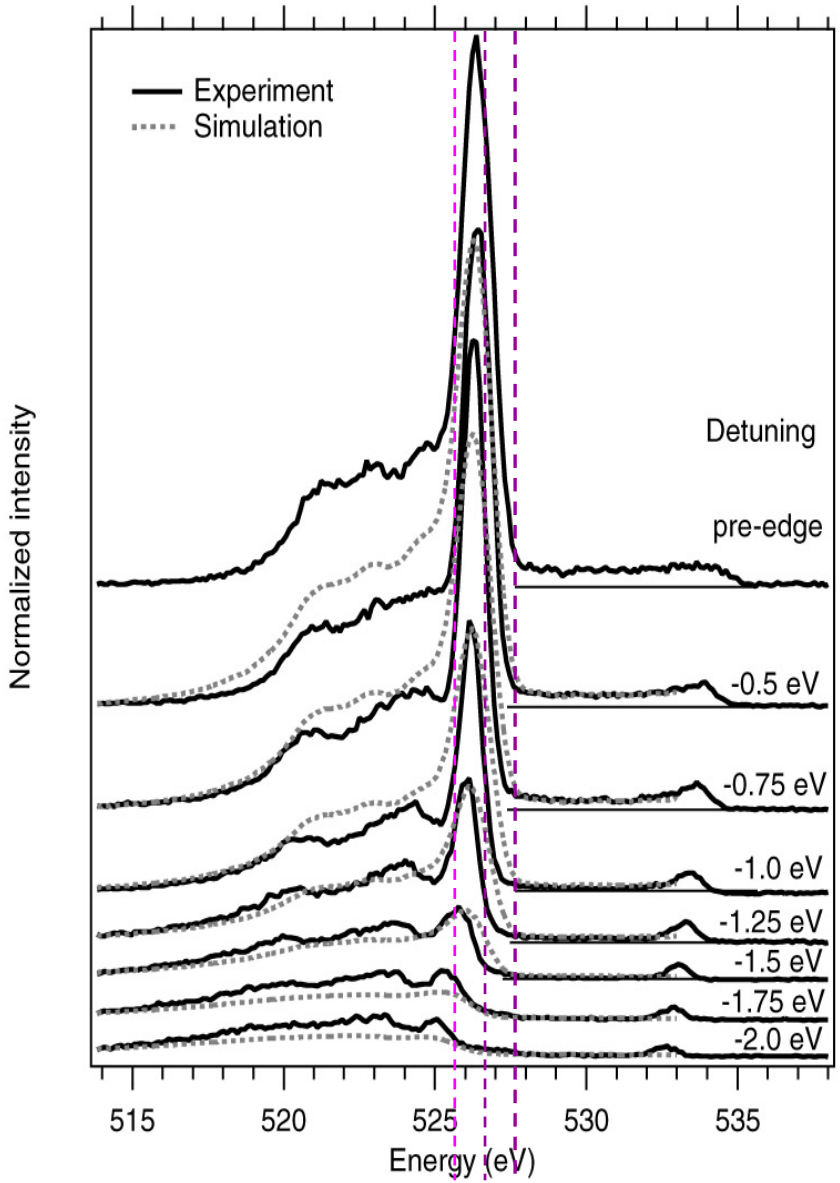
Effects of local arrangements on the covalency of hydrogen bonding

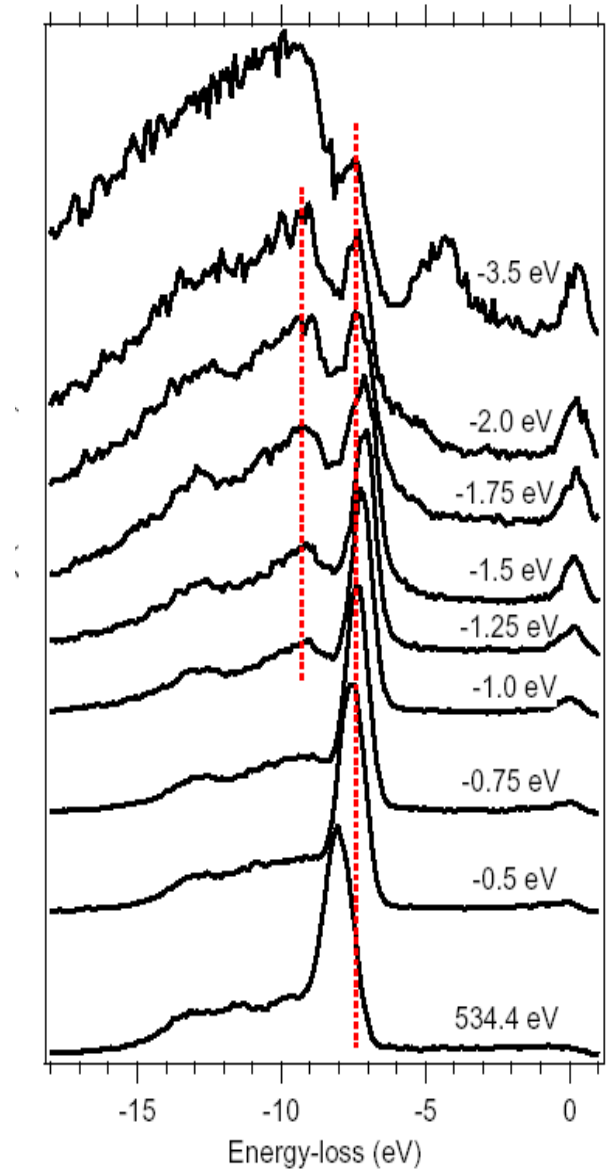


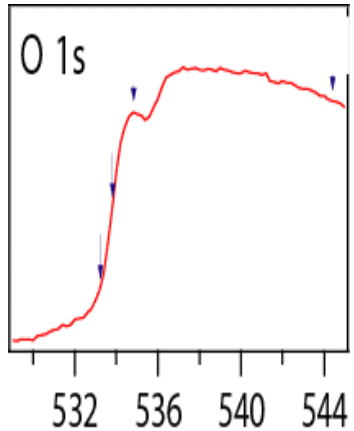
S. Kashtanov, A. Augustsson, Y. Luo, J.-H. Guo, C. Såthe, J.-E. Rubensson, H. Siegbahn, J. Nordgren, and H. Ågren ., **Phys. Rev. B**, 69, 024201, (2004)


W-DA-1
W-AA
W-DA-2
W-DD
W-DA-3
W-DA-4
Intensity
515
520
525
530
Energy (eV)
W-DDA1
W-DDA2
W-AAD1
W-AAD2
Intensity
515
520
525
530
Energy (eV)

Dynamics of core-excitation in liquid water







A. Augustsson, S. Kashtanov, Y. Luo, J.-H. Guo, C.-L. Dong, C. L. Chang, J.-E. Rubensson, and J. Nordgren, to be published.

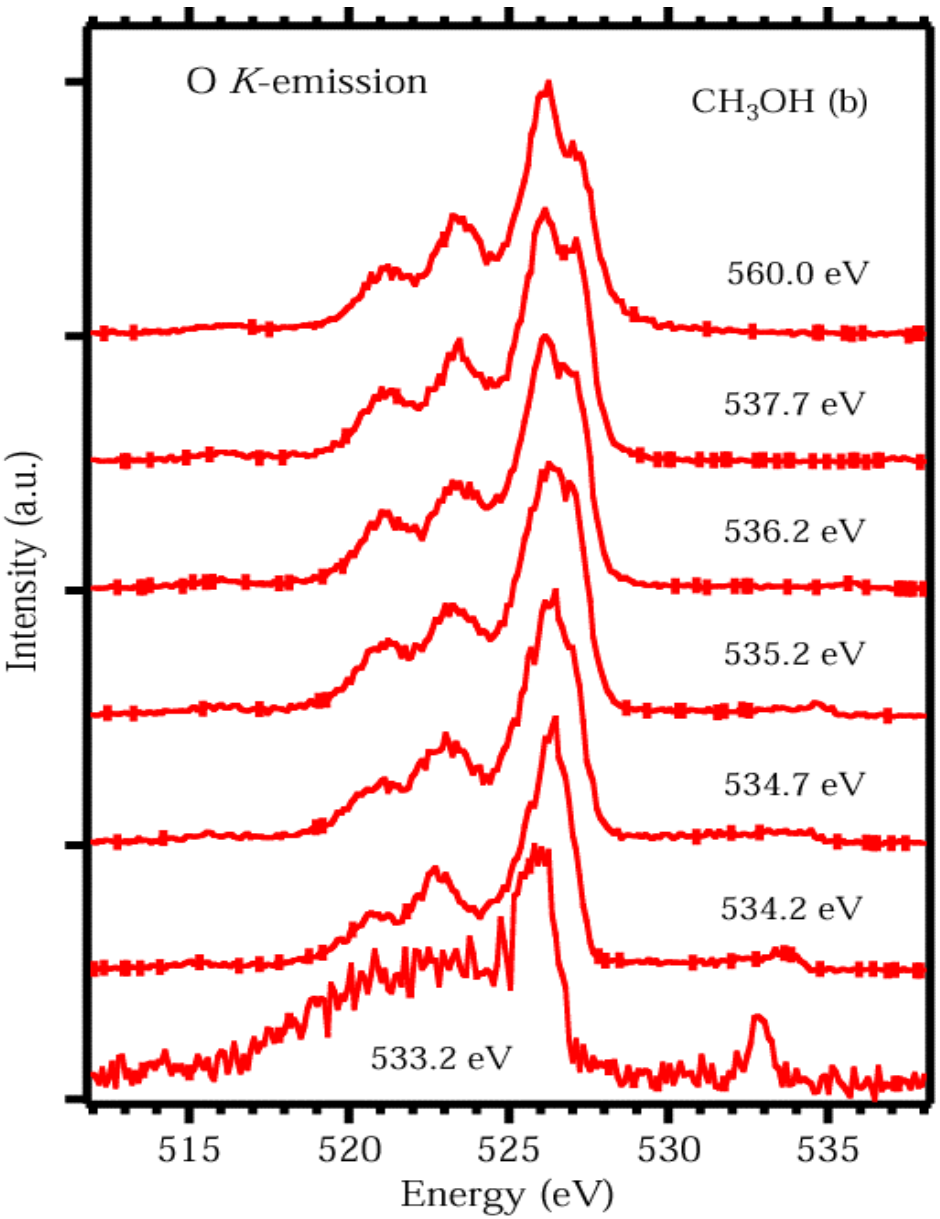
Liquid Methanol

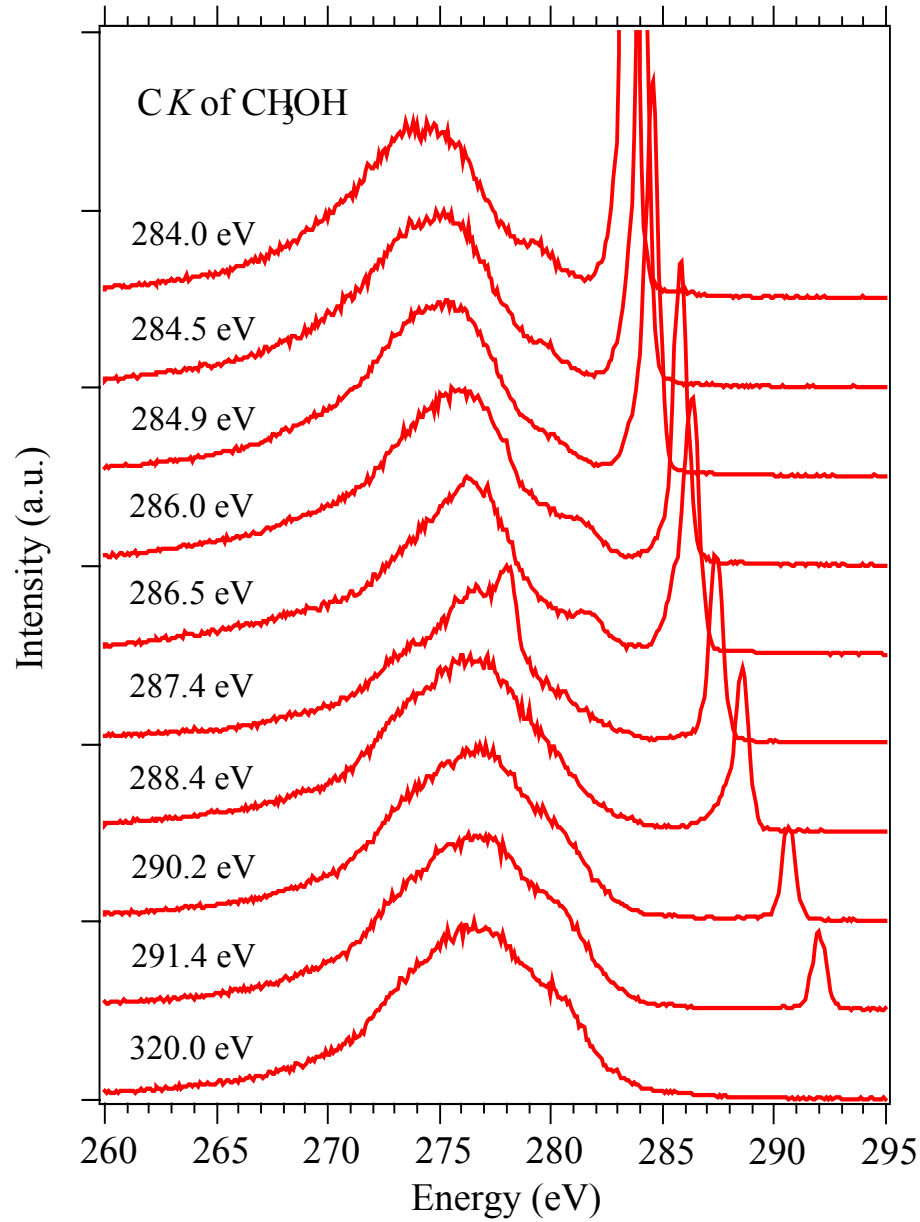
(1) Methanol crystal: infinite hydrogen-bonded chains; liquid methanol: non consensus after decades of studies

(2) Based on neutron diffraction data: It was found experimentally that **chains up to ten molecules** with average of **six molecules** in liquid methanol [Yamaguchi, K. Hidaka, and A.K. Soper, *Molecular Physics* ***96****, 1159 (1999)];* Haughney et al., *J. Phys. Chem.* ***91****, 4934 (1987)*; S. & Joarder, R. N., *J. Chem. Phys.* ***99****, 2032 (1993)* revealed a different picture of **cyclic hexamers** (six-rings); Using the same diffraction data, Tanaka found **linear trimer and tetramer chains** [*Bull. Chem. Soc. Jpn.* ***58****, 270 (1985)*]

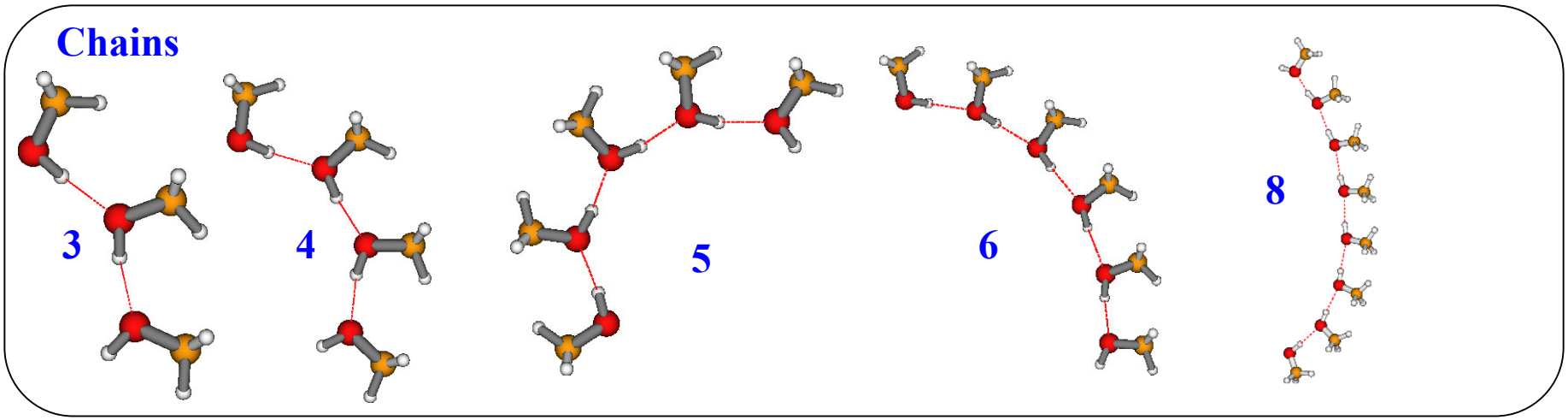
(3) All molecular dynamics /Monte Carlo simulations give chain structures of different sizes.

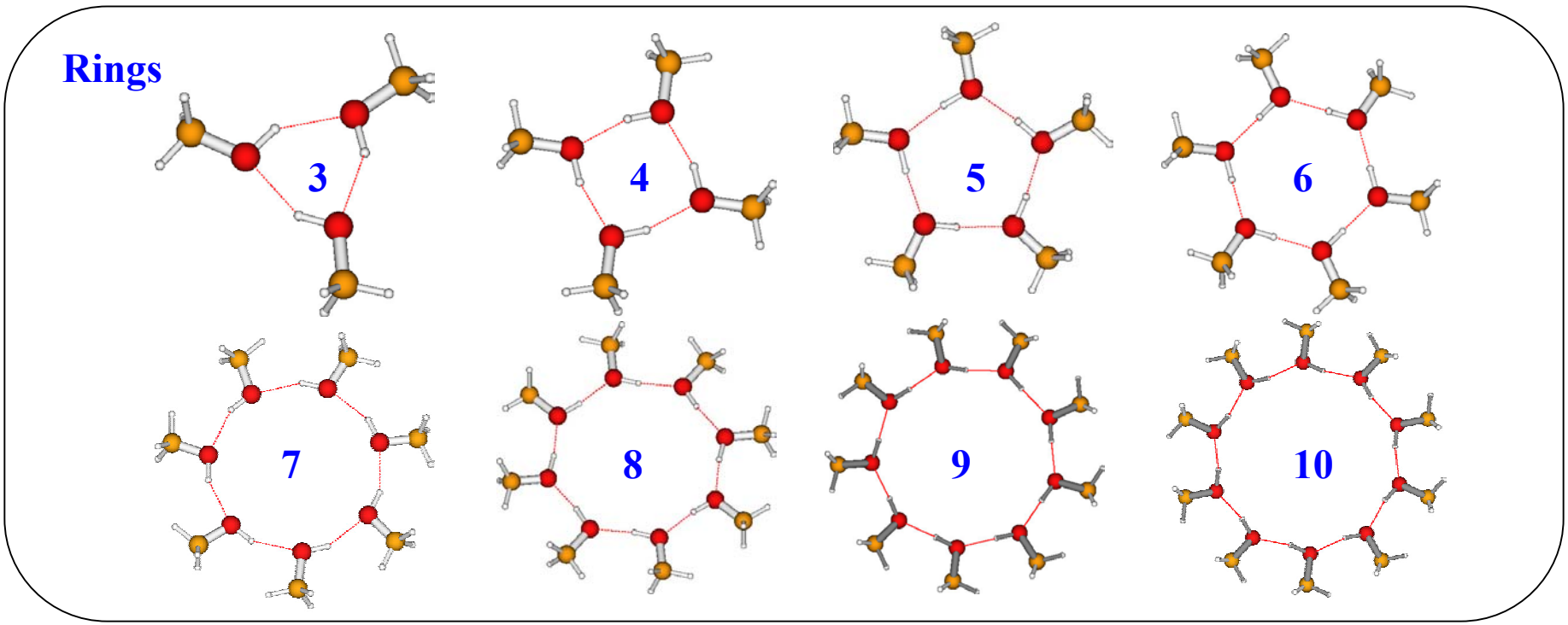
Experimental RIXS spectra of methanol liquid



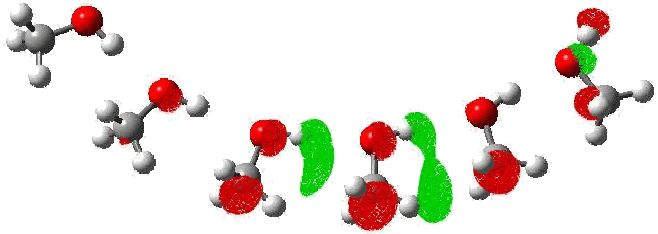


Possible structure of liquid methanol?

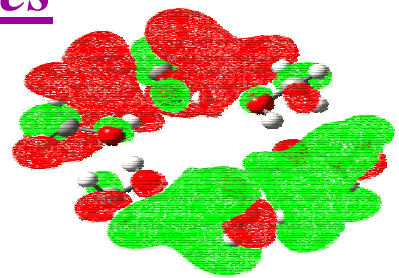


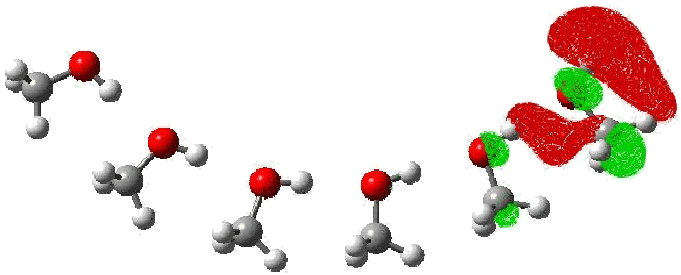


Six Methanol Molecules

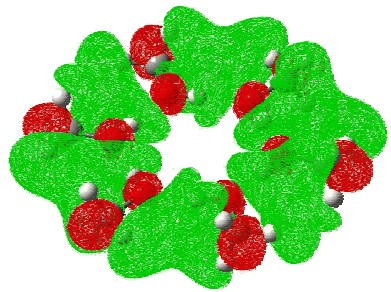


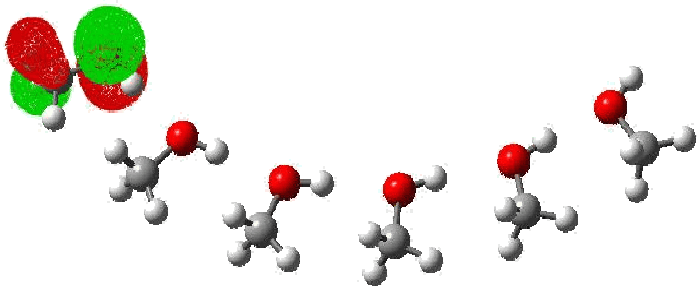
LUMO+1



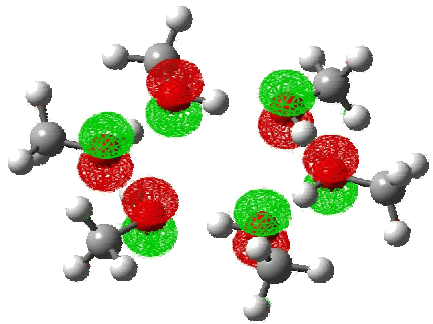


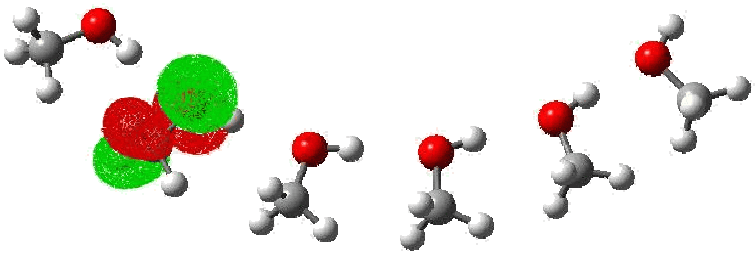
LUMO



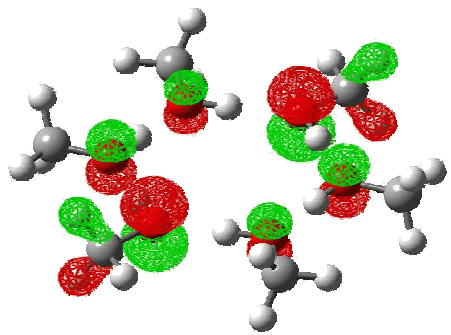


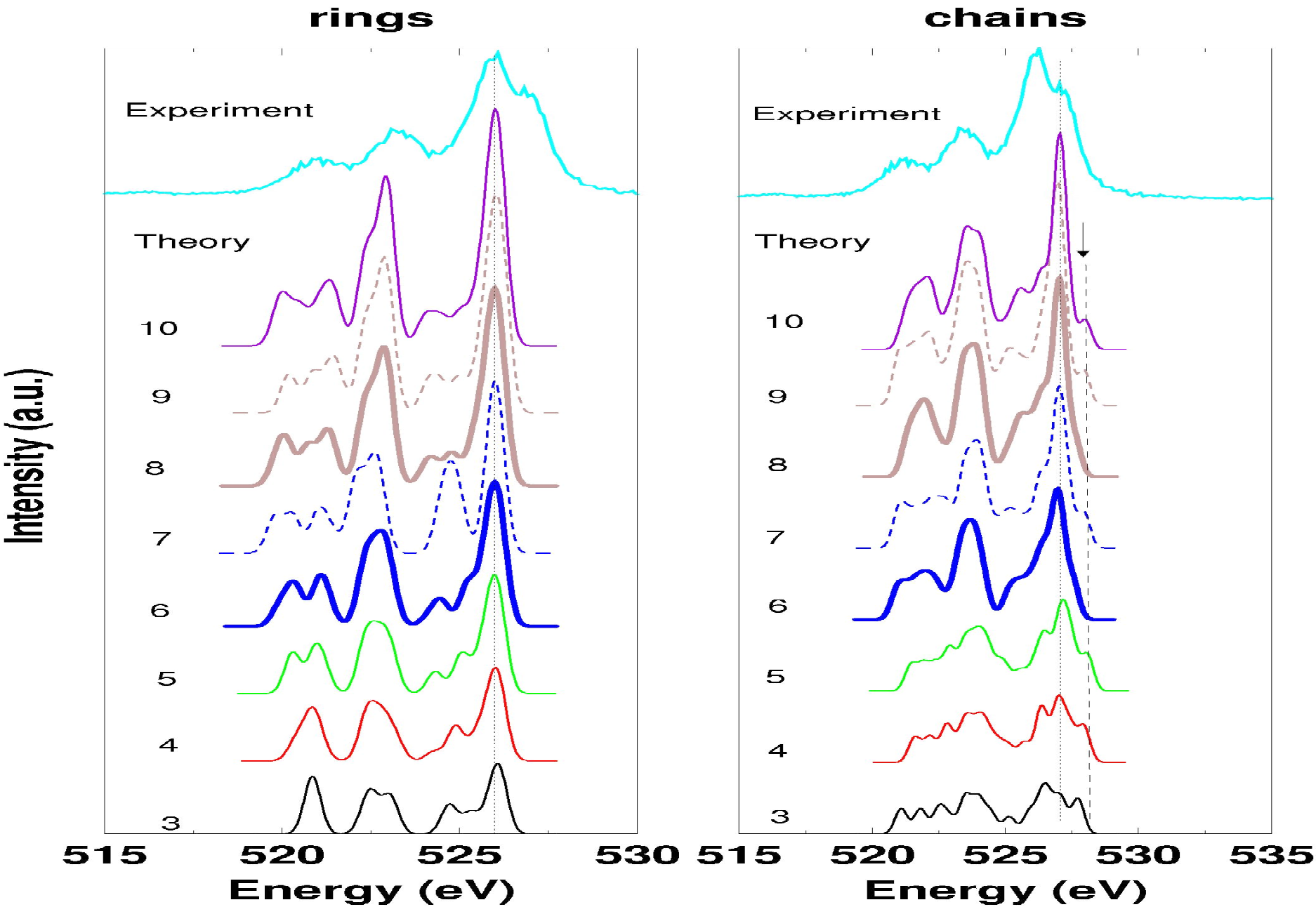
HOMO

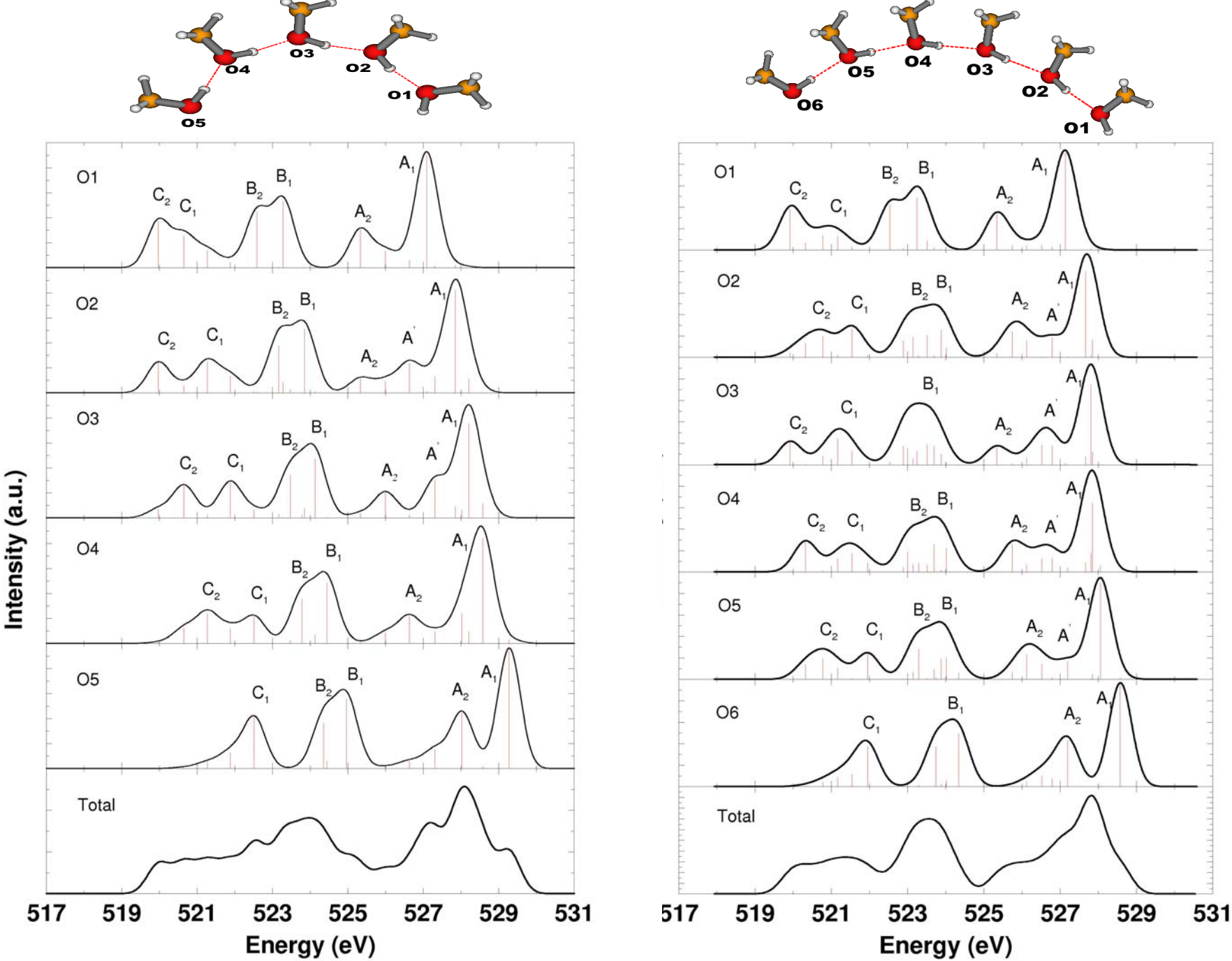




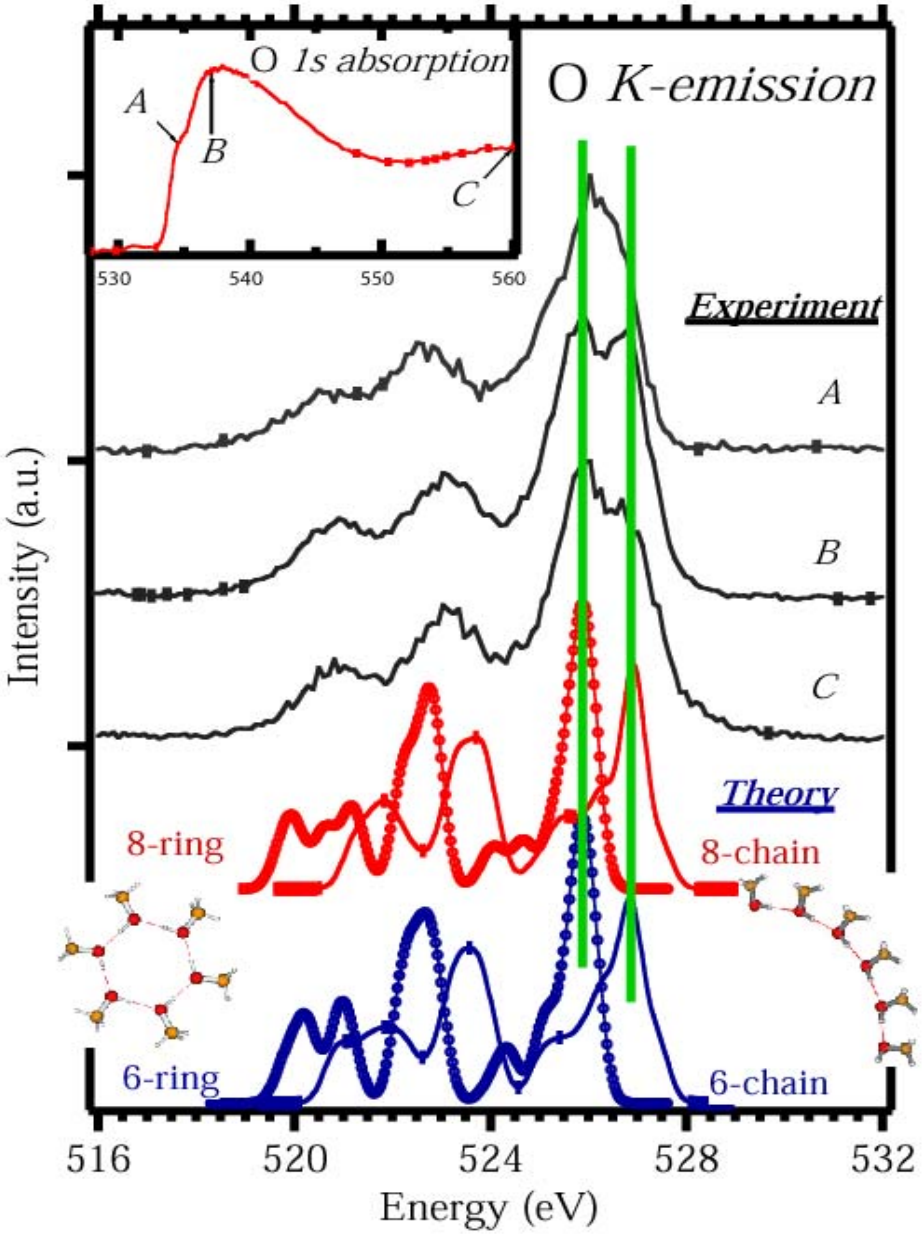
HOMO-1

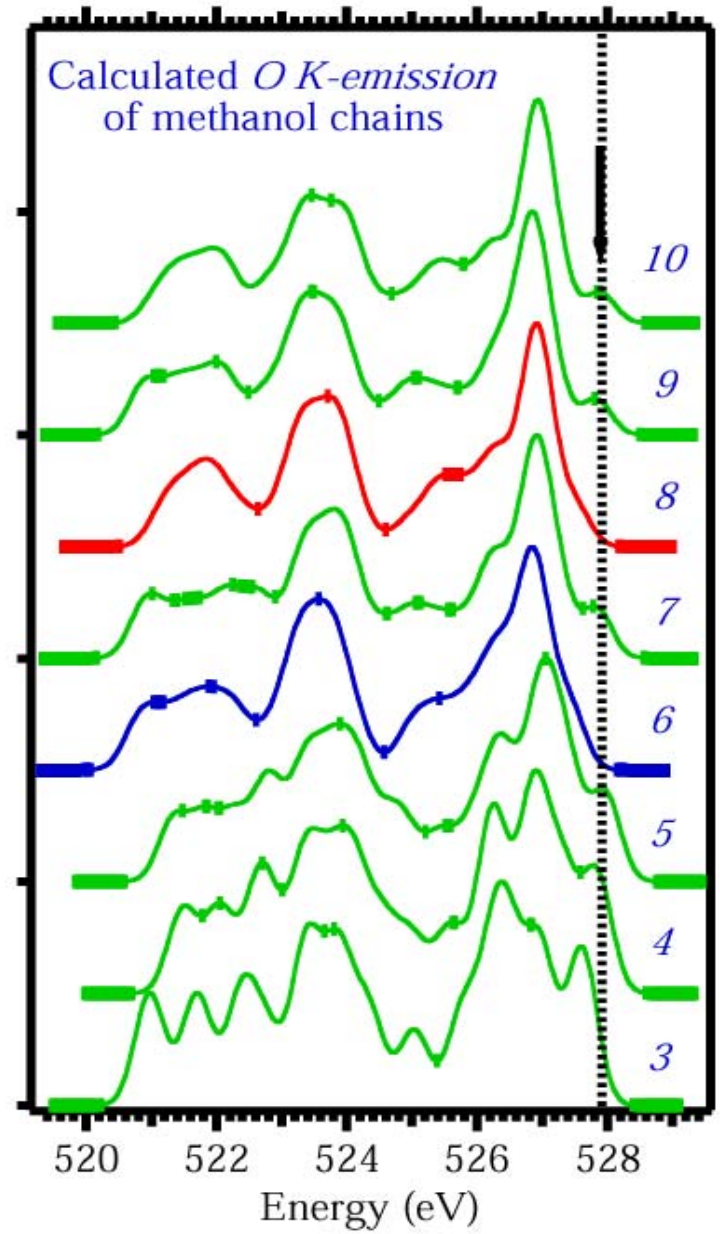



rings
chains
Experiment
Theory
Experiment
Theory
10
9
8
7
6
5
4
3
10
9
8
7
6
5
4
3
Intensity (a.u.)
515
520
525
530
515
520
525
530
535
Energy (eV)
Energy (eV)

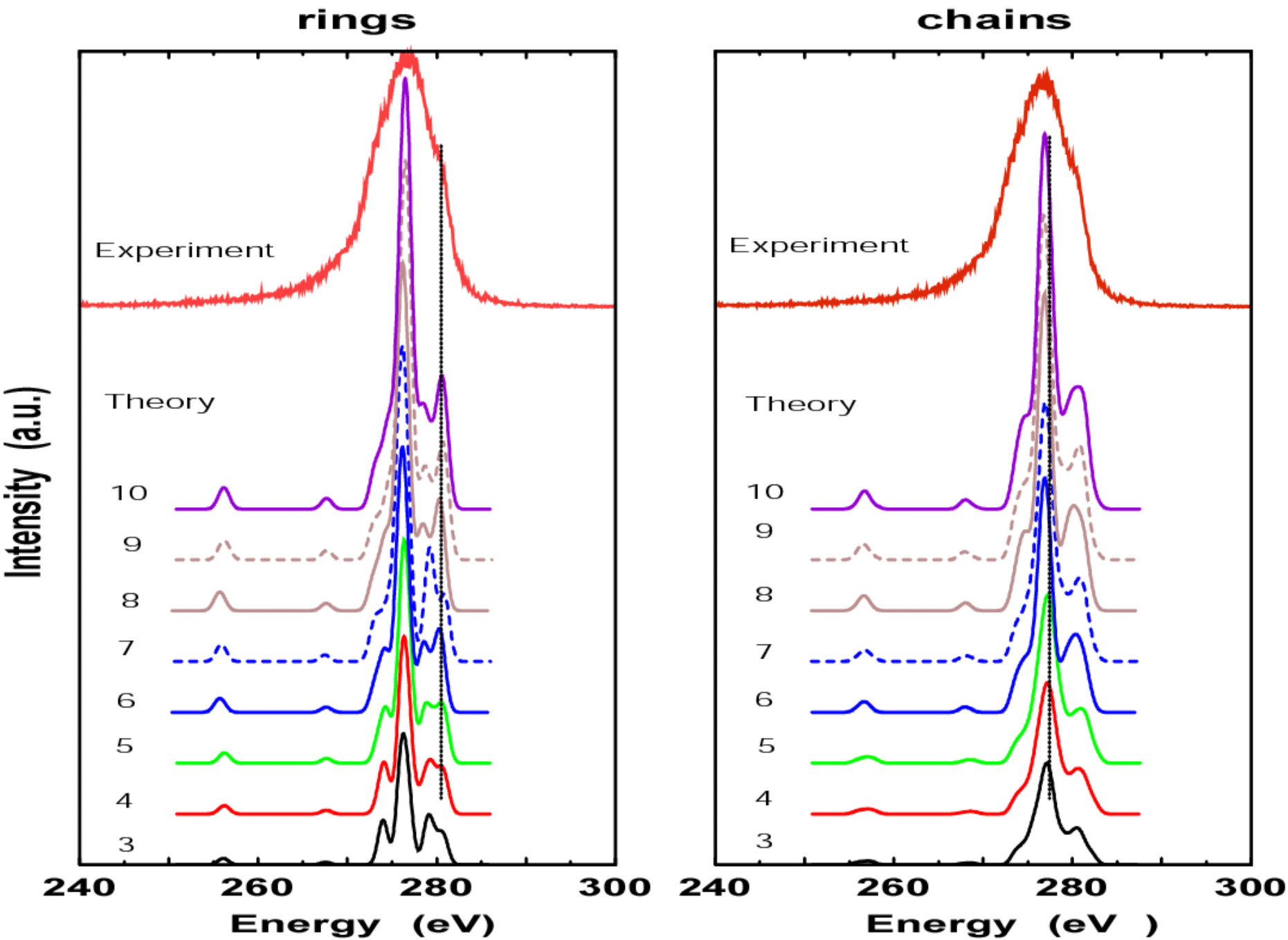

O1
O2
O3
O4
O5
O6
Total
Intensity (a.u.)
Energy (eV)
517
519
521
523
525
527
529
531

Molecules in the pure liquid methanol predominantly persist as hydrogen-bonded chains and rings with six and/or eight molecules of equal abundance.

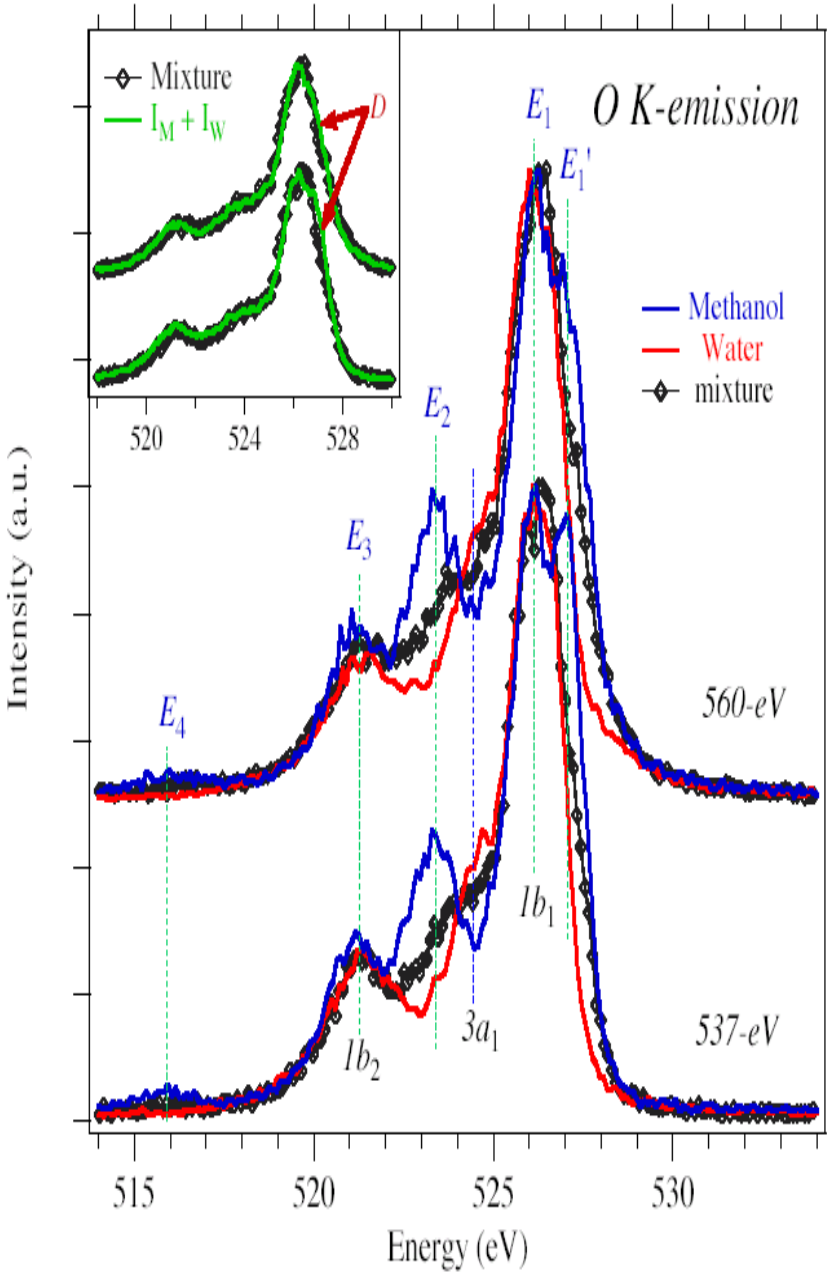


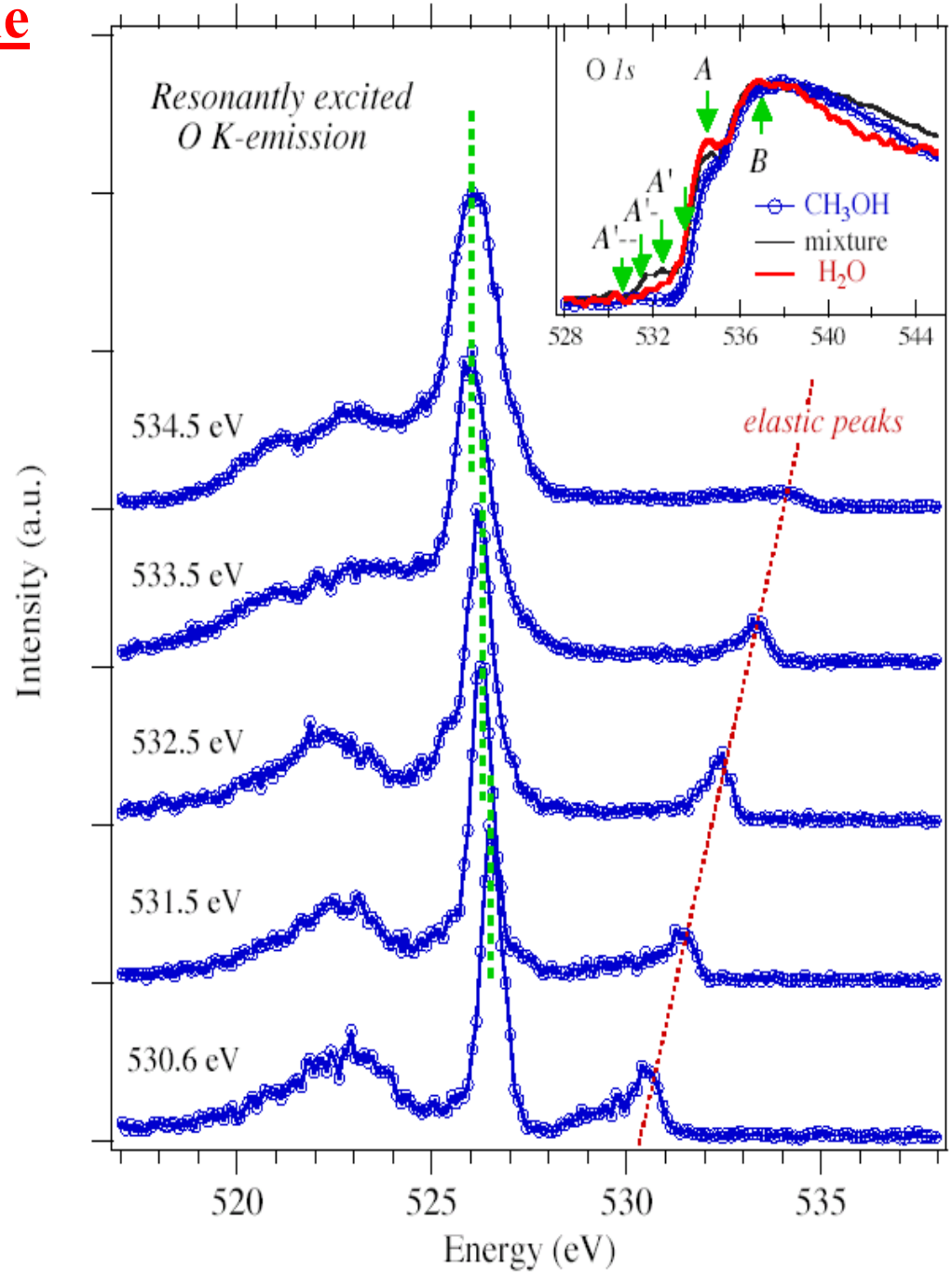


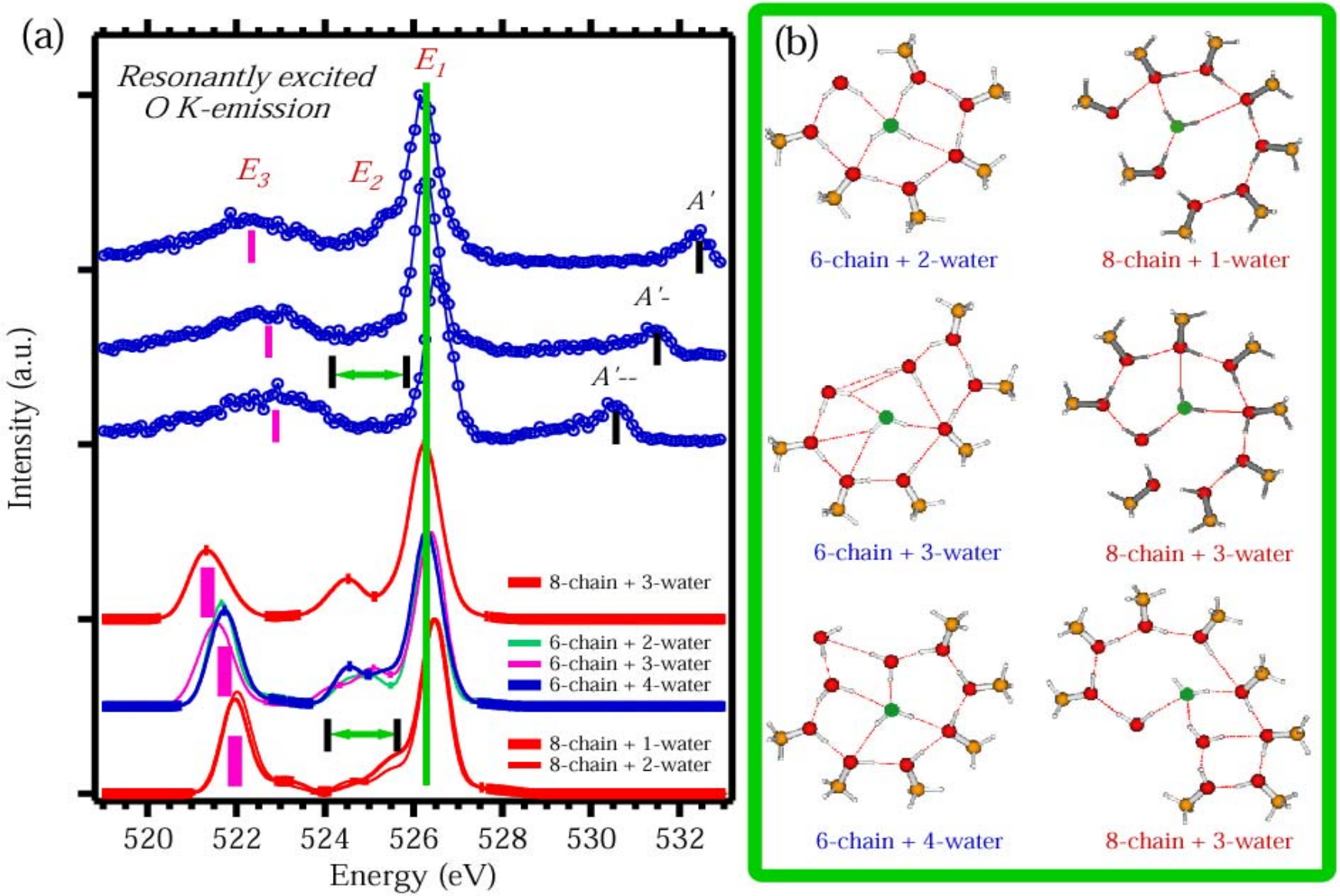
J.-H. Guo, Y. Luo, A. Augustsson, S. Kashtanov, J.-E. Rubensson, D. Shuh , H. Ågren, and J. Nordgren, **Phys. Rev. Lett.**, 91 (2003) 157410


rings
chains
Experiment
Theory
Intensity (a.u.)
10
9
8
7
6
5
4
3
240
260
280
300
Energy (eV)
Energy (eV)

XES of methanol/water mixtue

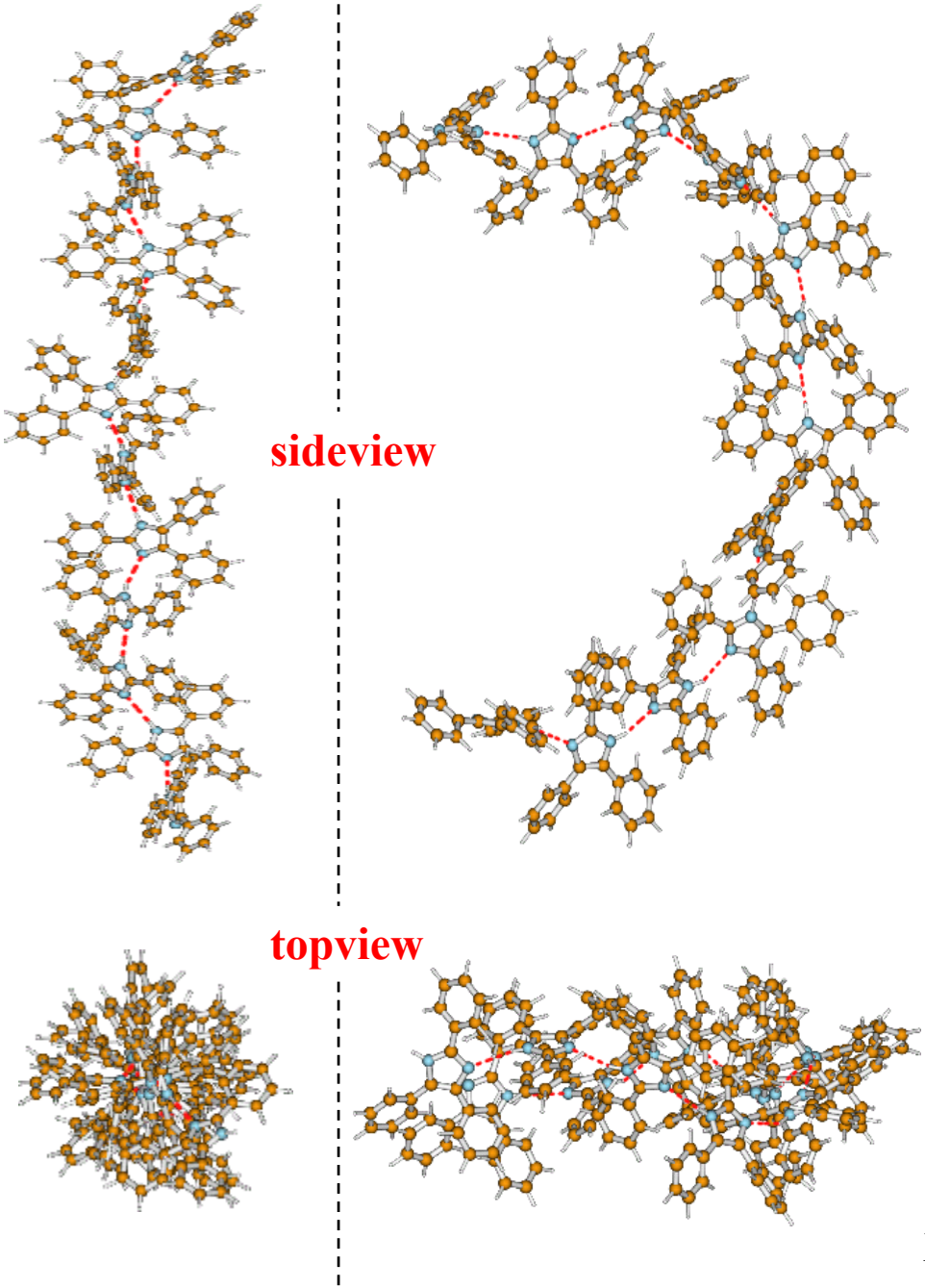


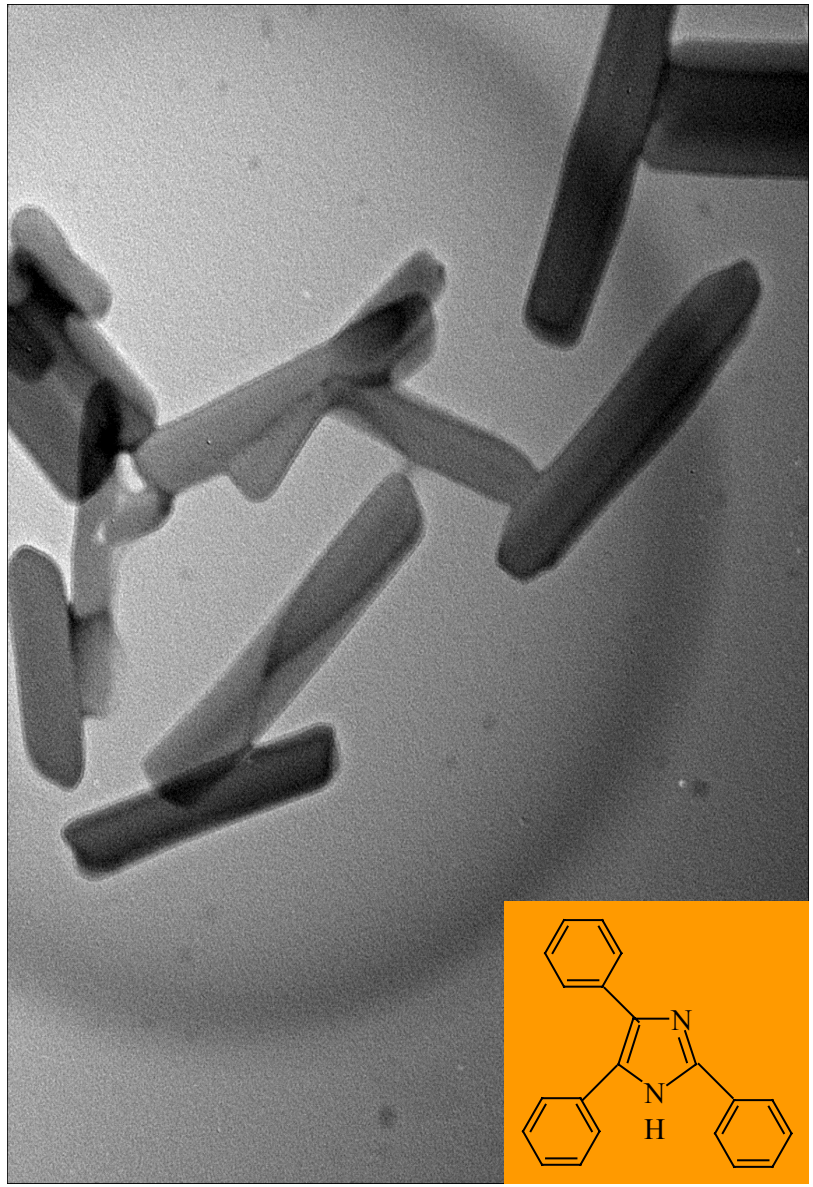




We find evidence of incomplete mixing at the microscopic level, and of water molecules bridging methanol chains to form rings.

Sheet **Folding**





Y. S. Zhao, J. N. Yao, and Y. Luo, to be published

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Andreas Augustsson	Uppsala University
Jan-Erik Rubensson	Uppsala University
Joseph Nordgren	Uppsala University

Main theoretical collaborator

Stepan Kashtanov	Royal Institute of Technology / ALS
Barbara Brena	Royal Institute of Technology
Hans Ågren	Royal Institute of Technology
Stephane Carniato	P&M Curie University, Paris

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Uppsala University (Joseph Nordgren)
Carl-Trygger Foundation (CTS)