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Nanostructured Interfaces and Surfaces
Centre of Excellence

Surface sites of nanomaterials: investigation of local structures by combining experimental and theoretical studies

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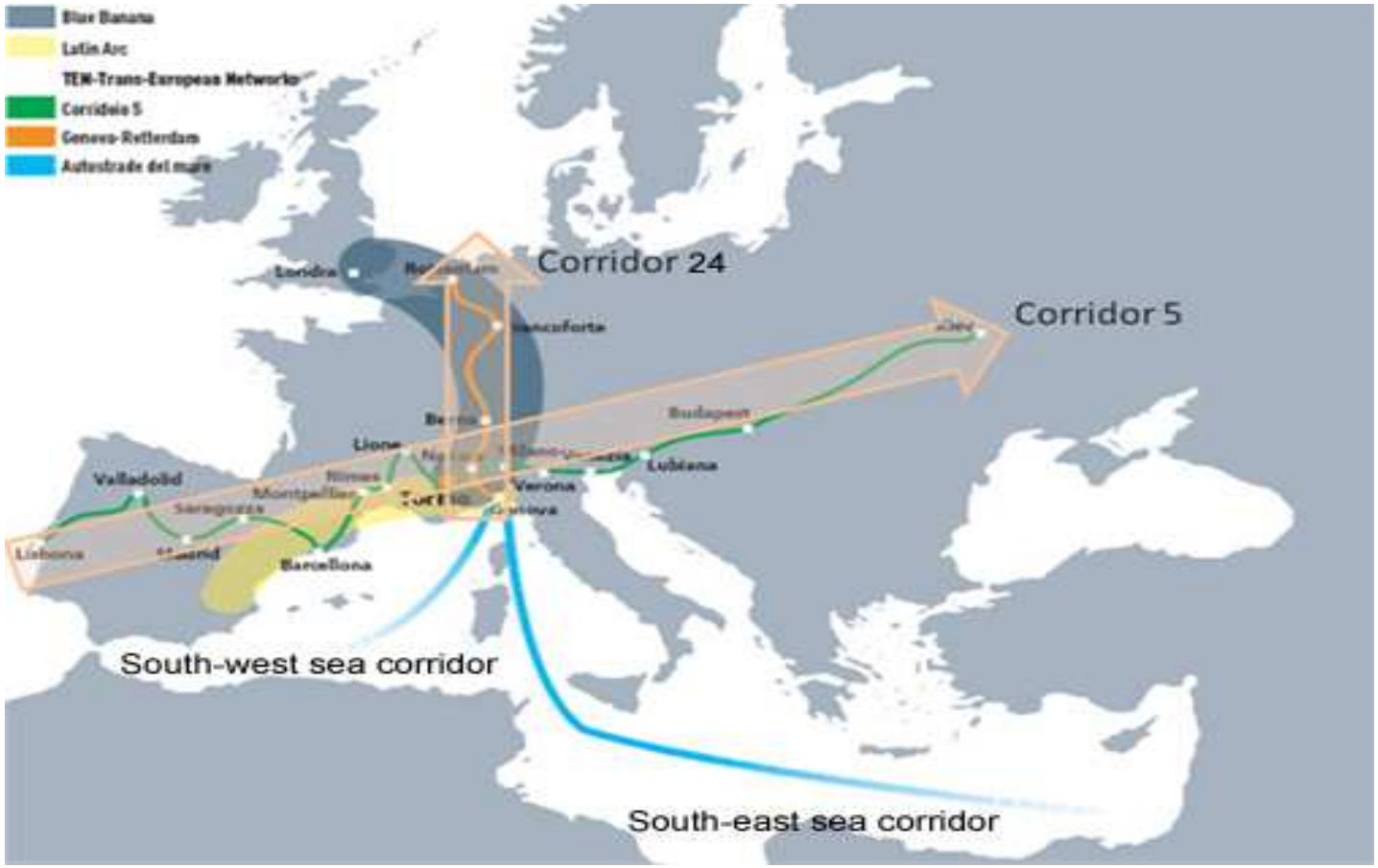
Department of Chemistry
&
Center of Excellence "Nanostructured Surfaces and Interfaces – NIS"
University of Torino - Italy

FP7 Nanotwinning Project

ISS on NANOTECHNOLOGY: from fundamental research to innovations

Torino & Piemonte: at the core of industrial Italy

- Three main markets within short reach: Western EU, Eastern EU, Africa and Middle Ea



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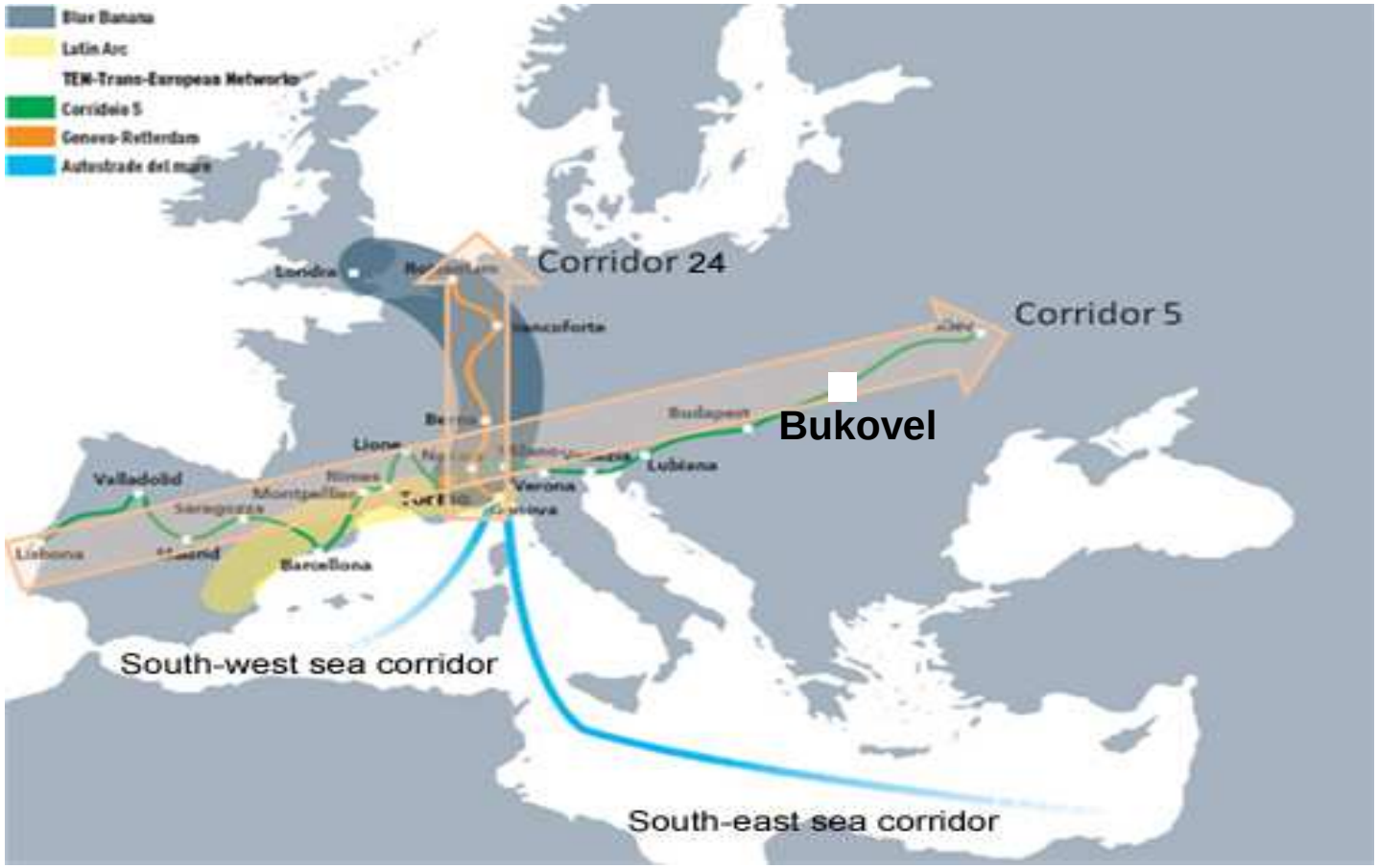

Summer School

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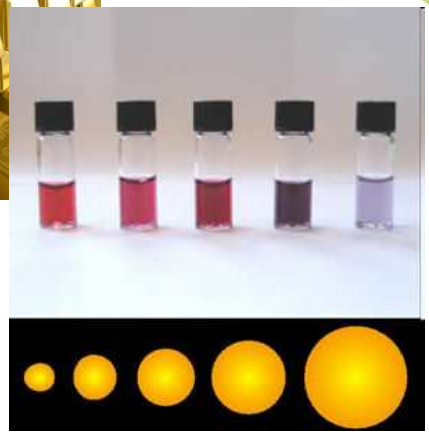
Nanoparticles

why “nano” is so passioning and important?

1. matter of size

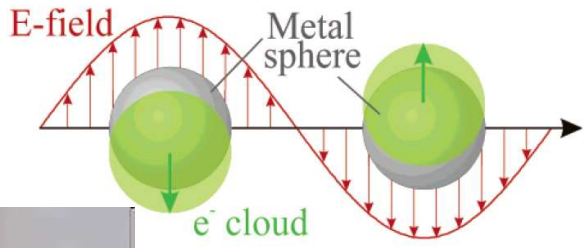


50 nm

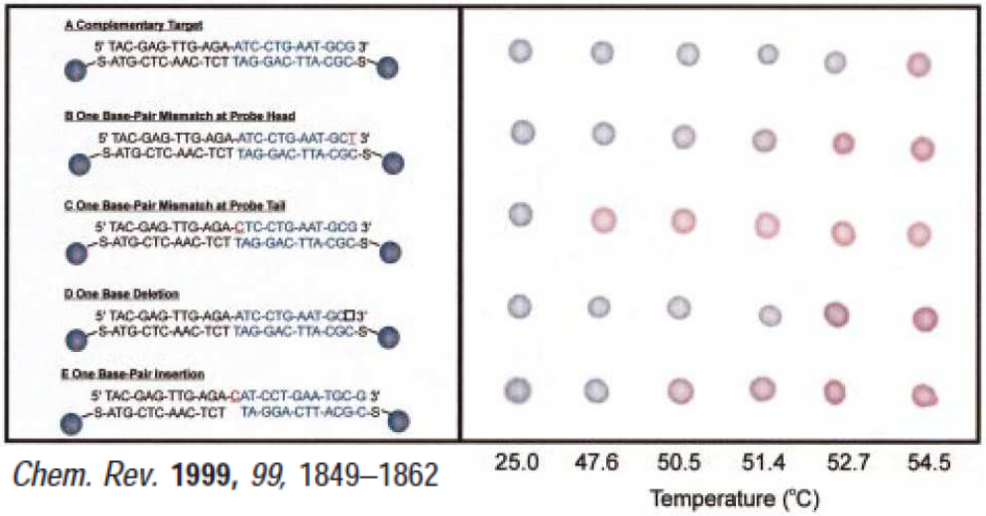
just a couple of examples

K. Lance Kelly, Eduardo Coronado, Lin Lin Zhao, and George C. Schatz*

J. Phys. Chem. B **2003,** *107,* 668−677

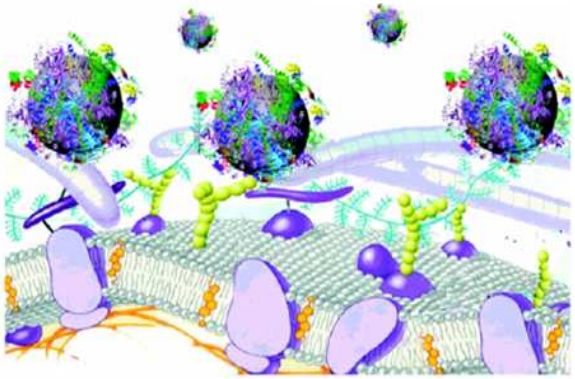


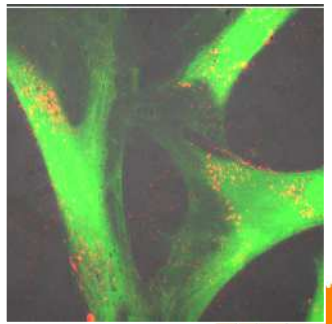
nanosize: peculiar optical features



Chem. Rev. **1999,** *99,* 1849–1862

nanosize: higly effective for uptake by cells



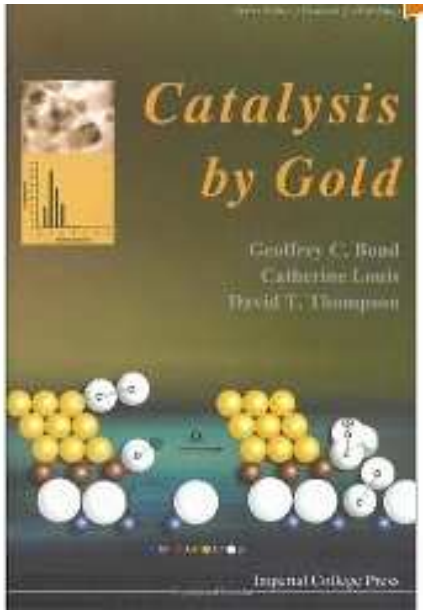


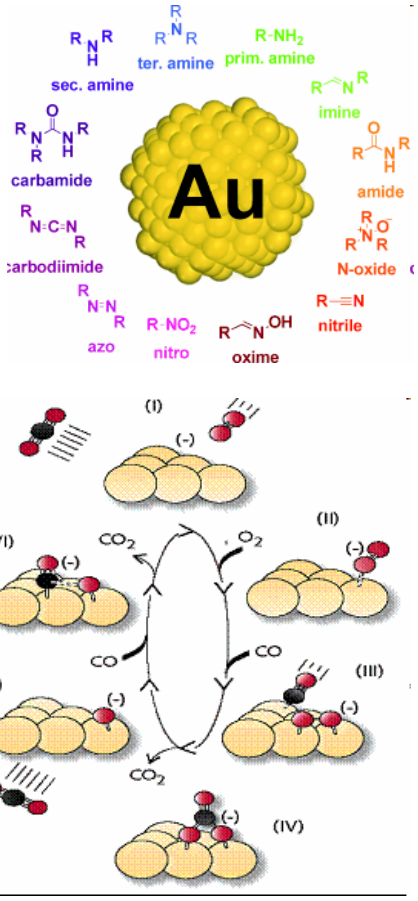
Nanoparticles

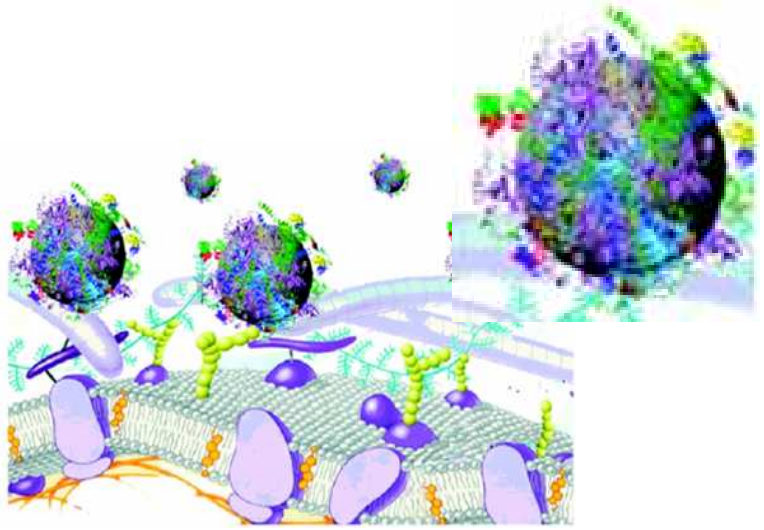
why “nano” is so passioning and important?

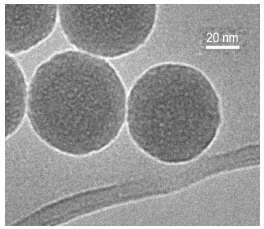
2. matter of enhanced surface/volume ratio

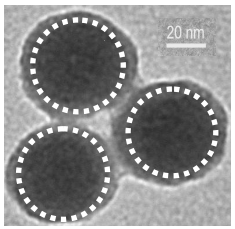
increased importance of surface/interfacial phenomena











0%FBS 10%FBS

L. Accomasso, F. Catalano,
G. Alberto et al, Small, 2012, in press

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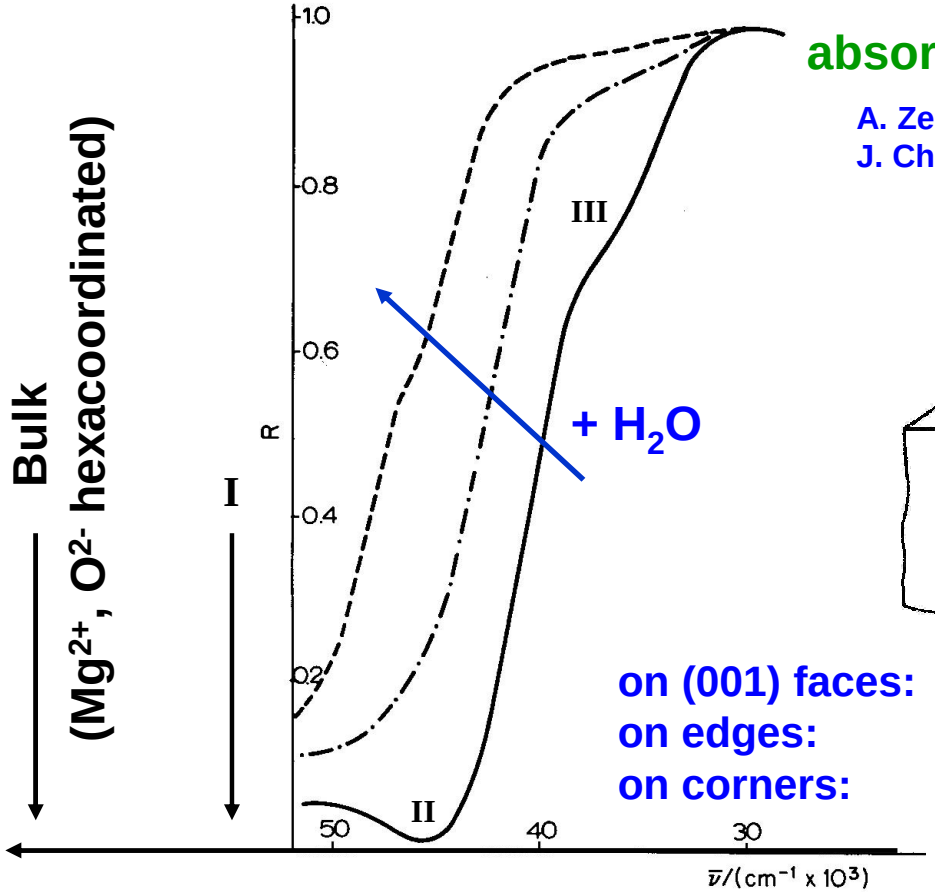
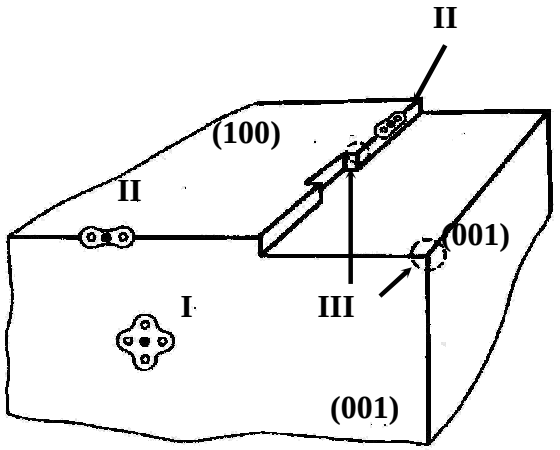
What special in surfaces?

Electronic spectra (diffuse reflectance mode) of MgO nanoparticles



absorptions due to CT transitions

A. Zecchina, M.G. Lofthouse and F.S. Stone,
J. Chem. Soc. Faraday Trans I, 71 (1975) 1476



on (001) faces: five coordinated ions, Mg_{5c}^{2+} and O_{5c}^{2-}
on edges: four coordinated ions, Mg_{4c}^{2+} and O_{4c}^{2-}
on corners: three coordinated ions, Mg_{3c}^{2+} and O_{3c}^{2-}

surface sites = surface electronic states,
dependent on the nature and local structure

effect on electron density, acidity, basicity, redox potential…

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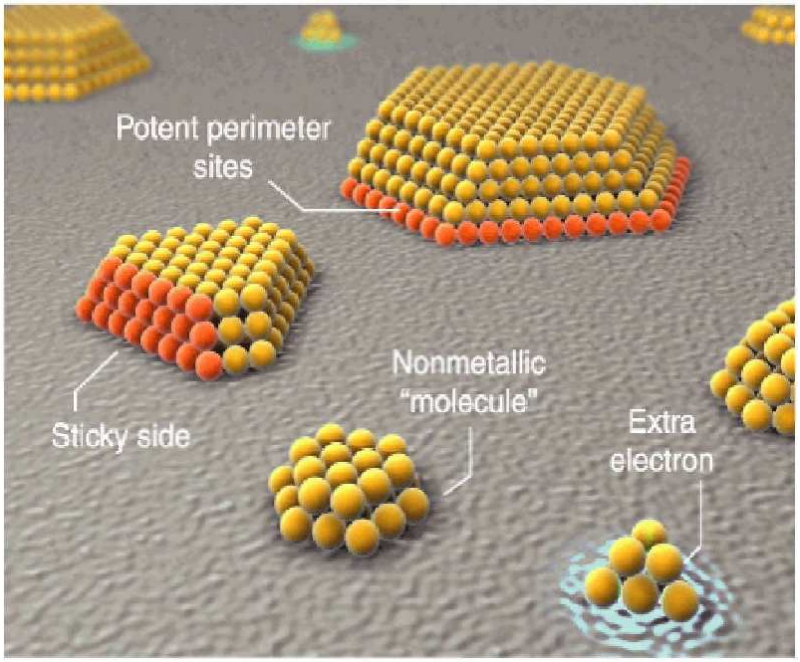
What's challenging in surfaces/interfaces?

two classes of systems

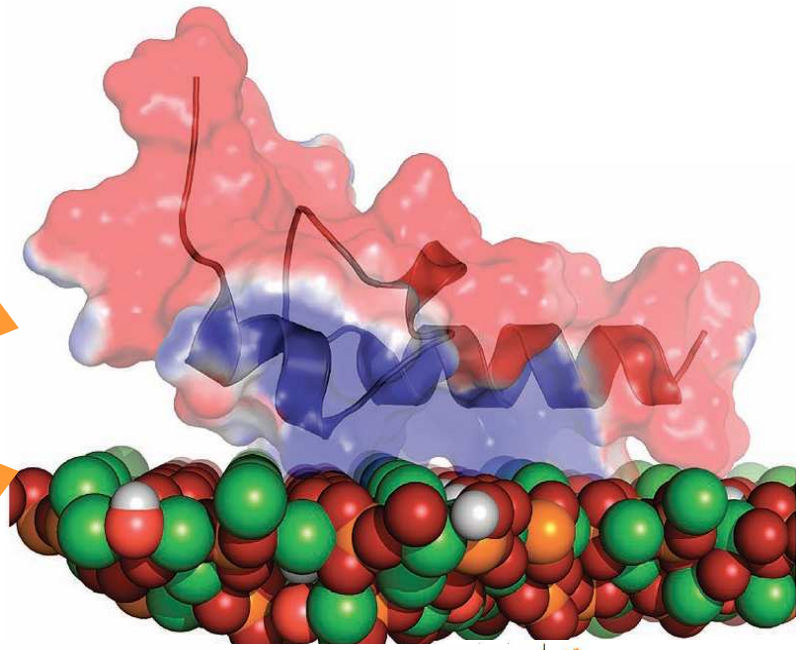


heterogeneous catalysts:
tailored surface sites
for specific chemical events

structure
of adsorbed biopolymers

nanobiomaterials:
complex surfaces &
complex molecules

biomaterial/biopolymer
interface



Kosta Makrodimitris,† David L. Masica,‡ Eric T. Kim,§ and Jeffrey J. Gray*,†

J. AM. CHEM. SOC. 2007, *129*, 13713–13722

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What we need to properly study surface sites?

Investigation tool(s) sensitive to:

- nature of surface sites
- oxidation state
- local structure
- isolated vs clusterized sites

chemical and physical “ultra high resolution”

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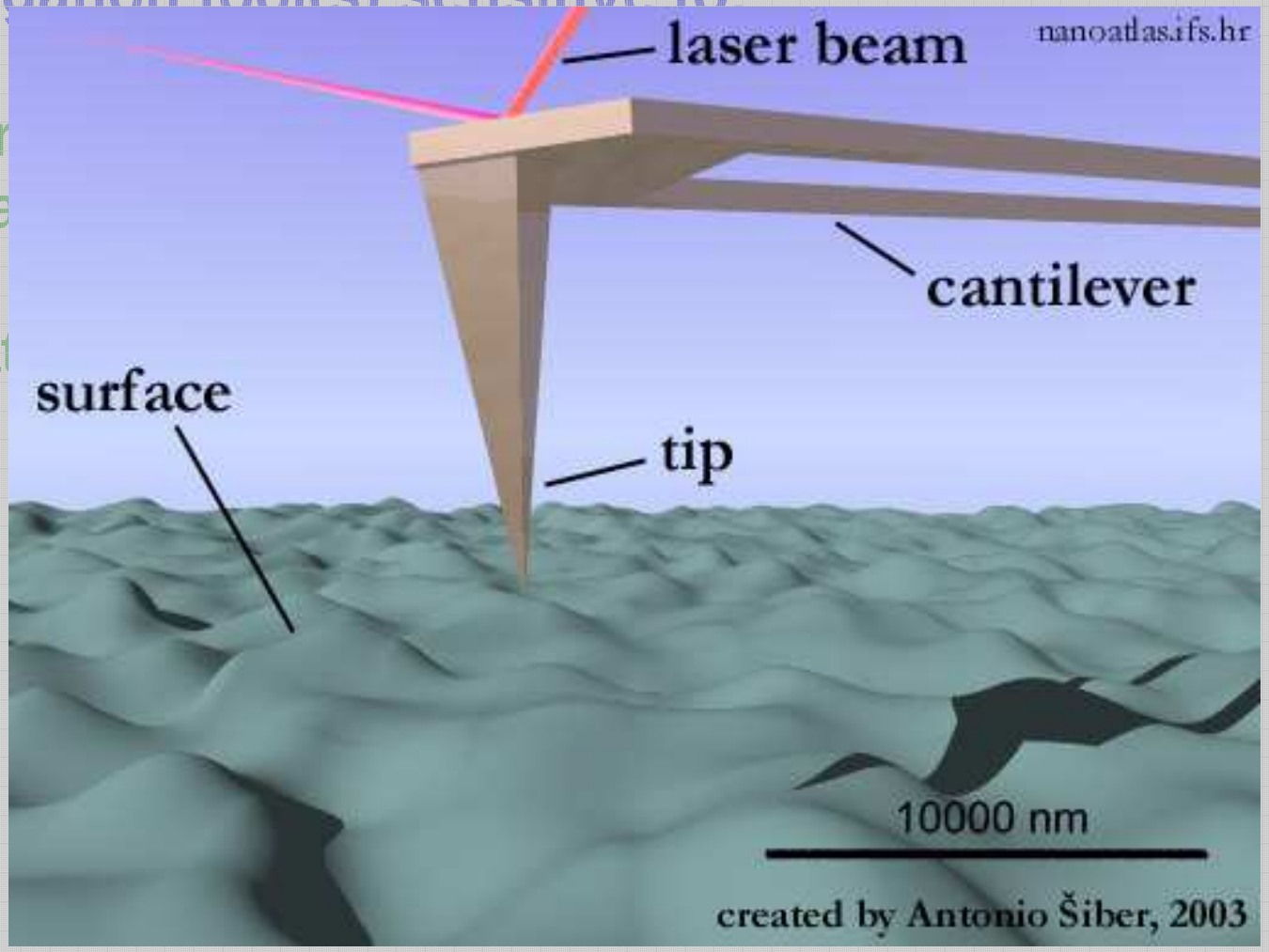

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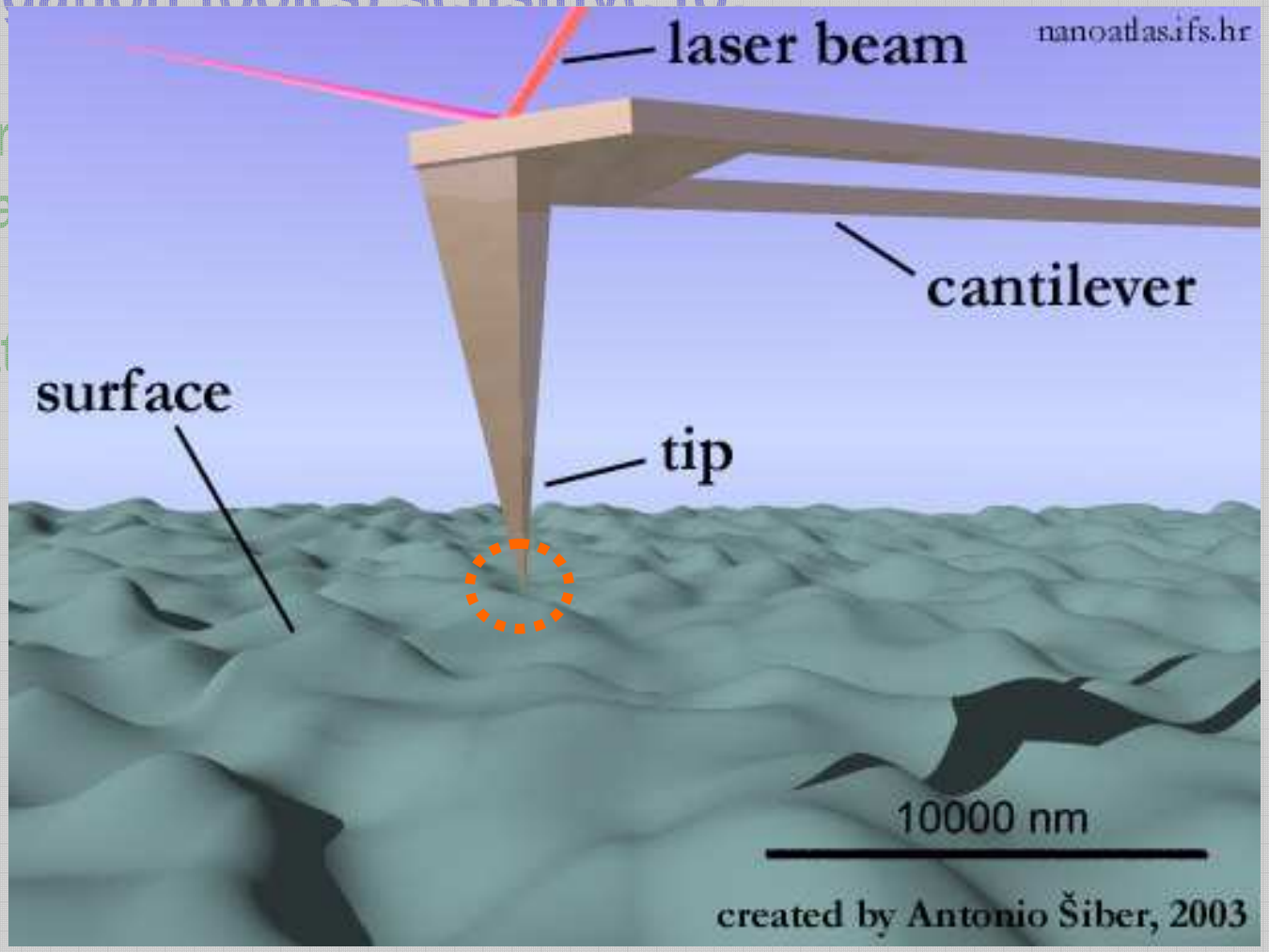

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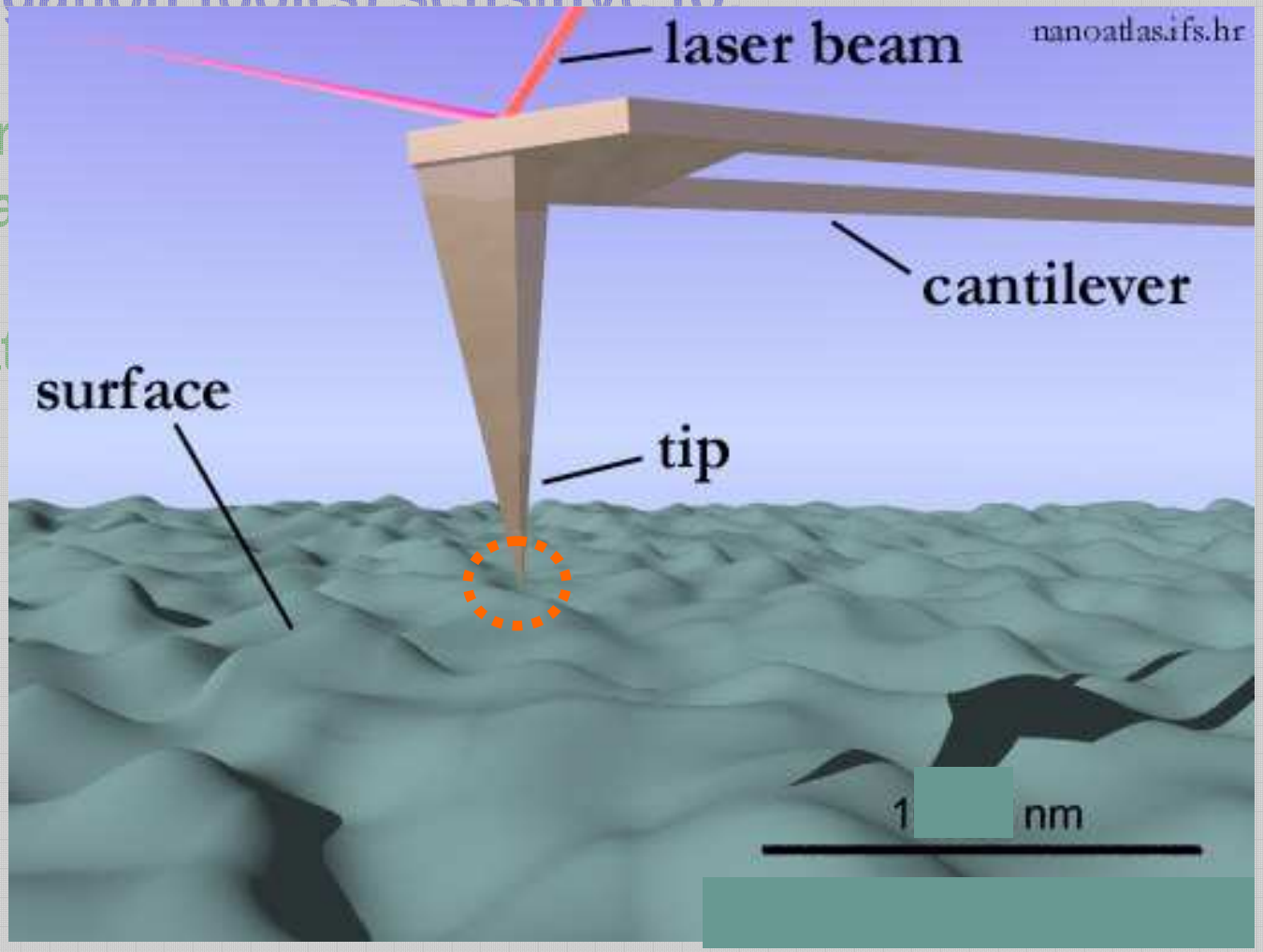

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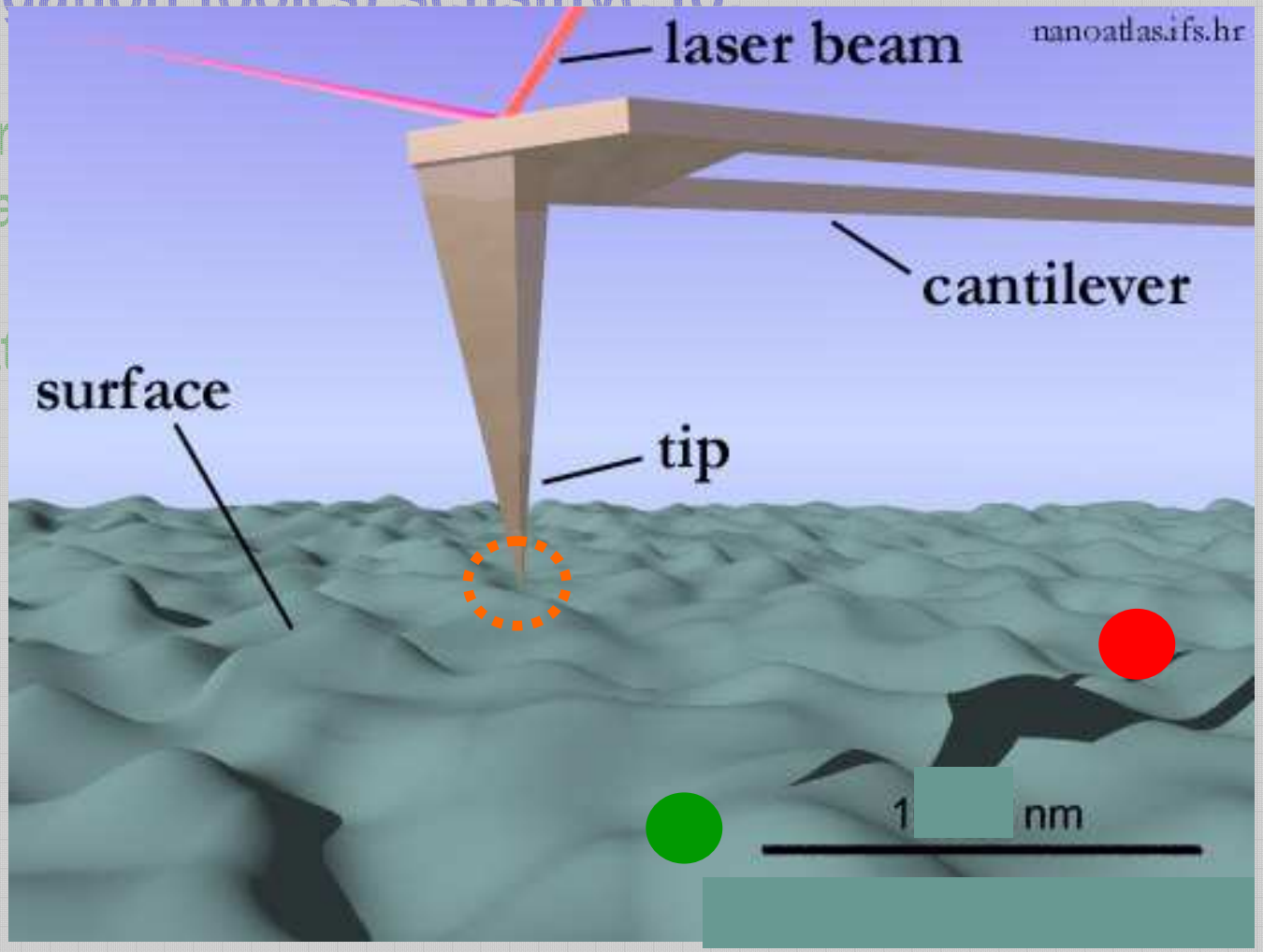

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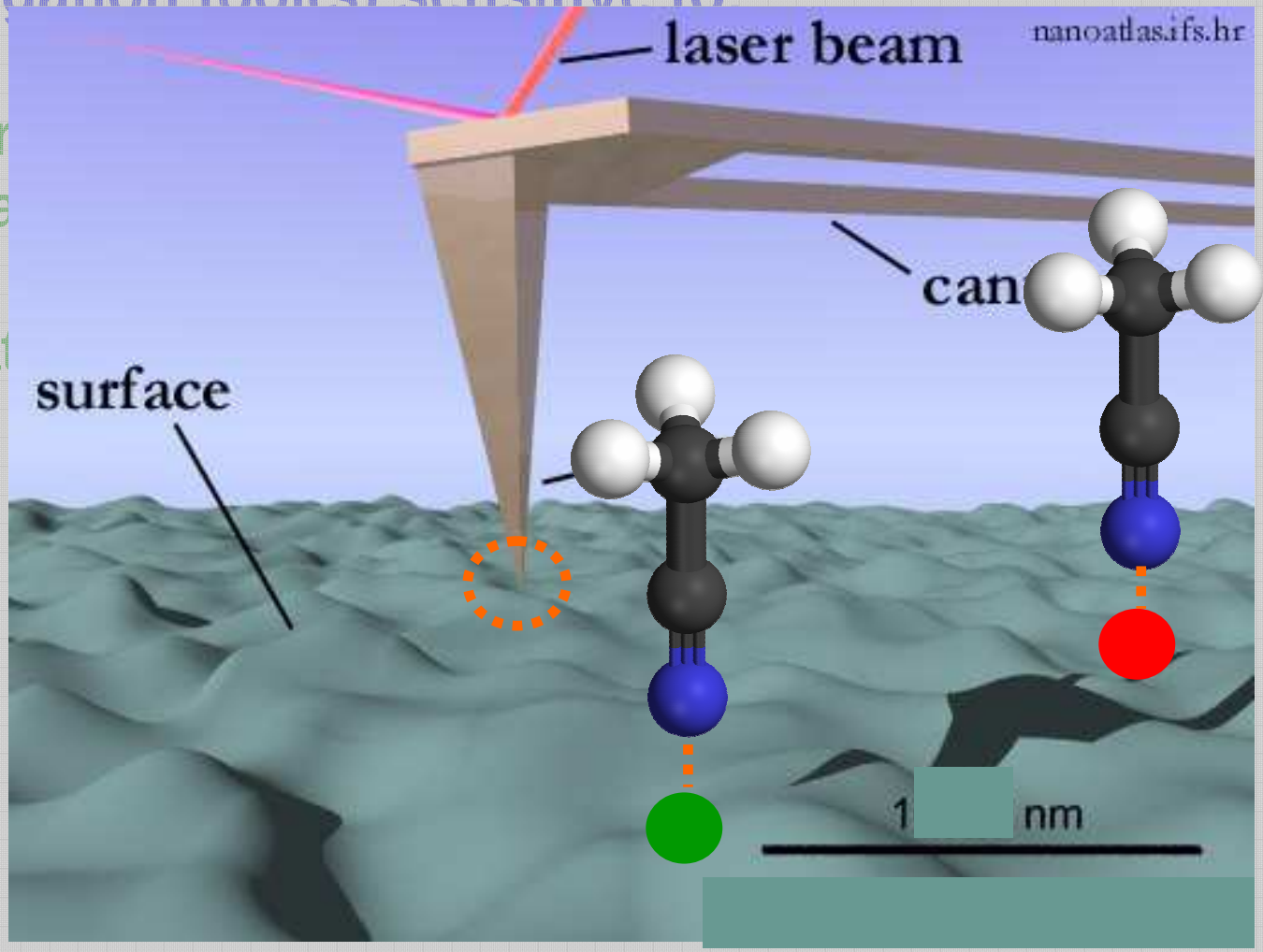

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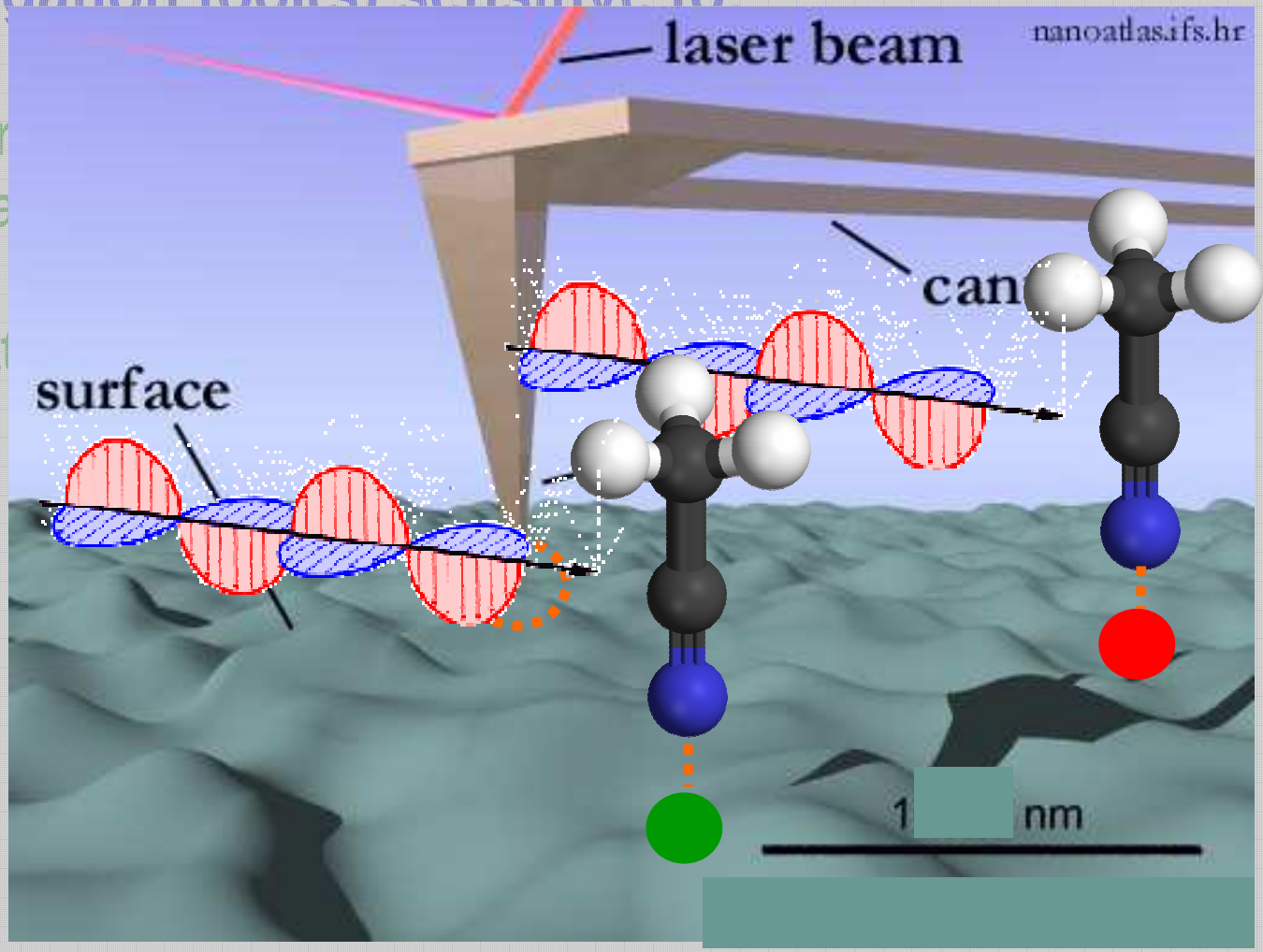

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chemical and physical “ultra high resolution”

adsorbed molecules acting as probes of the surface sites

“seen” by molecular spectroscopies

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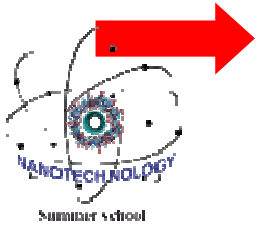
chemical and physical "ultra high resolution"

adsorbed molecules acting as probes of the surface sites

"seen" by molecular spectroscopies

IR: structural sensitivity, quantitative sensitivity, wide applicability (trasmission, reflectance, different T, P)



In-situ IR spectroscopy of adsorbed molecules

1. proper sample form

Powders compressed in self supporting pellet (no KBr)

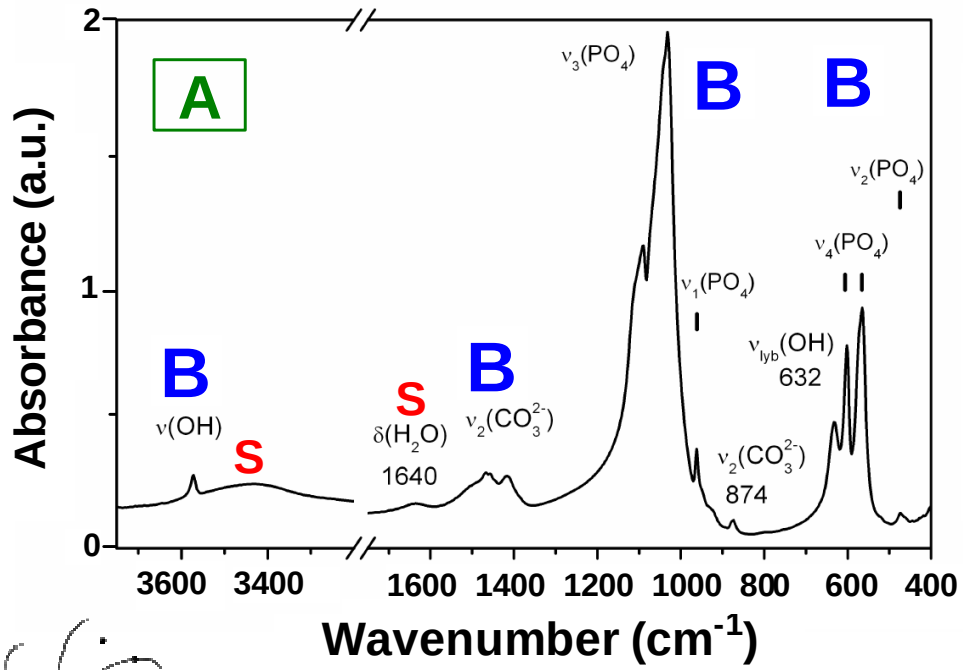
Pellets of sample dispersed in KBr

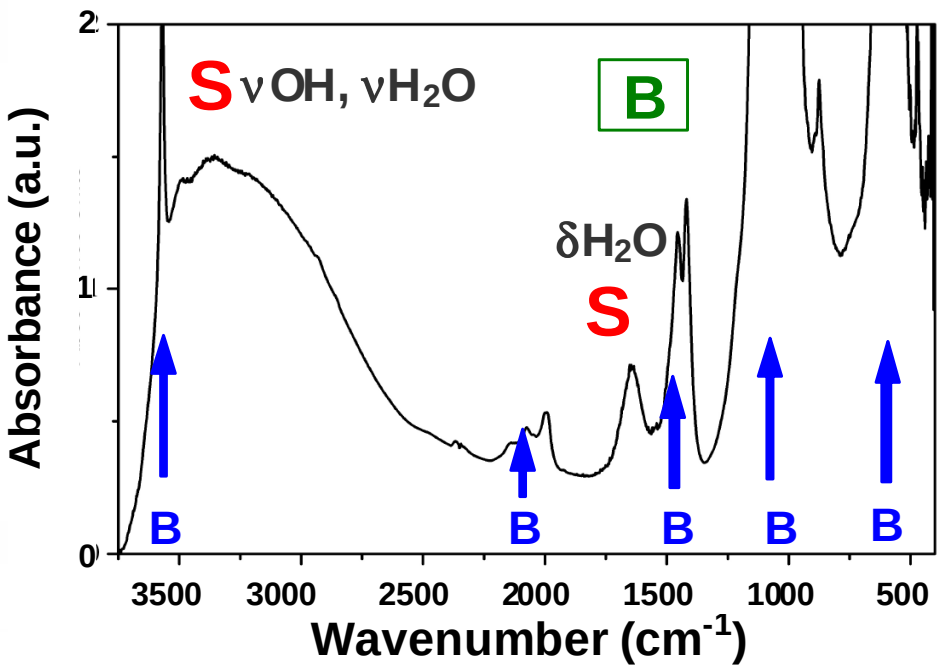
$$A = \varepsilon b c$$

Pellet of pure sample

B=Bulk absorptions

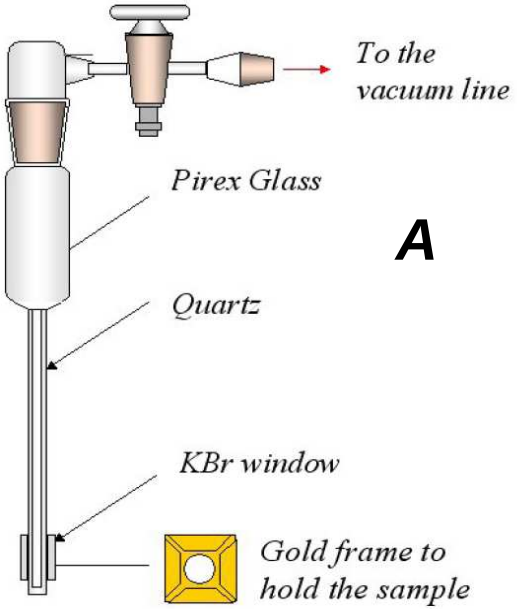
S= Absorption due to surface species

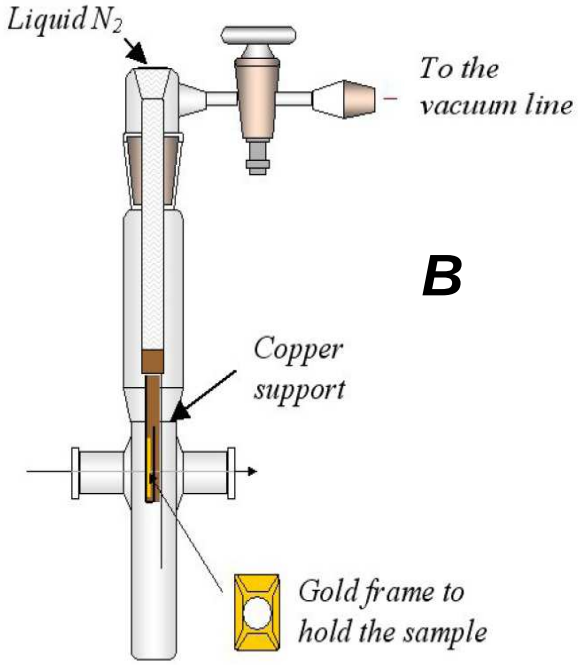




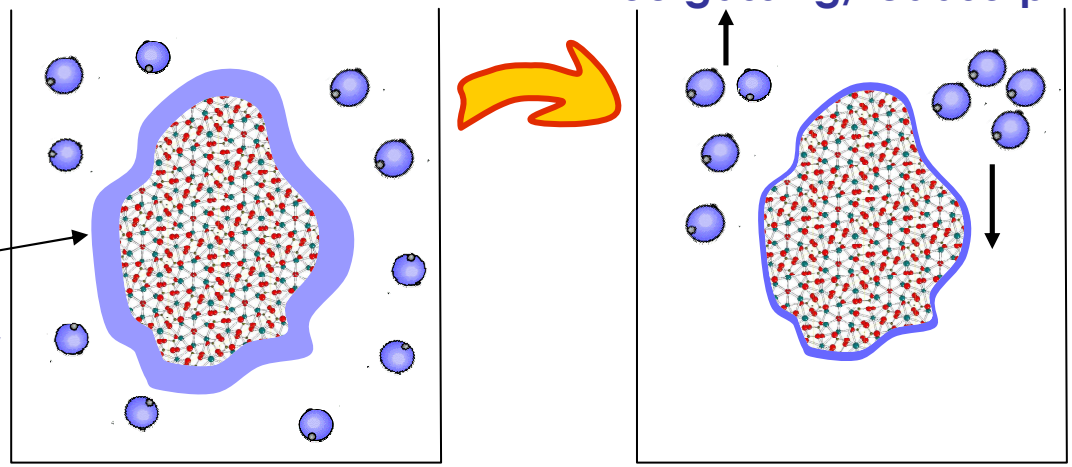
In-situ IR spectroscopy of adsorbed molecules

2. Proper cells





outgassing/readsorption



control of the amount of adsorbed H_2O

Outline

experimental and theoretical studies of adsorbed molecules aimed to the elucidation of surface structure and/or interfacial behavior of:

- **MgO nanocubelets: a model system for oxide catalysts**

- **Nanohydroxyapatite: an example of biomimetic, bioresorbable material**

Heterogeneous catalysts & Nanomaterials

G.A. Somorjai and Y.G. Borodko,
"Research in nanoscience – Great opportunity for catalysis science"
Catal. Lett., 76 (2001) 1

….”Many heterogenoeus catalysts utilize nanoparticles. Nanoparticles of metals, oxides and sulfides have been developed and used as catalyst for hydrocarbon conversion, partial oxidation and combustion since the 1920’s; as such they represent the oldest commercial application of nanotechnology.”…

20th century: activity (productivity per site per second)
new generation Z-N heterogeneous polymerization catalysts:
$\sim 10^6$ C-C bonds site^{-1}s^{-1}

21th century: 100% Selectivity

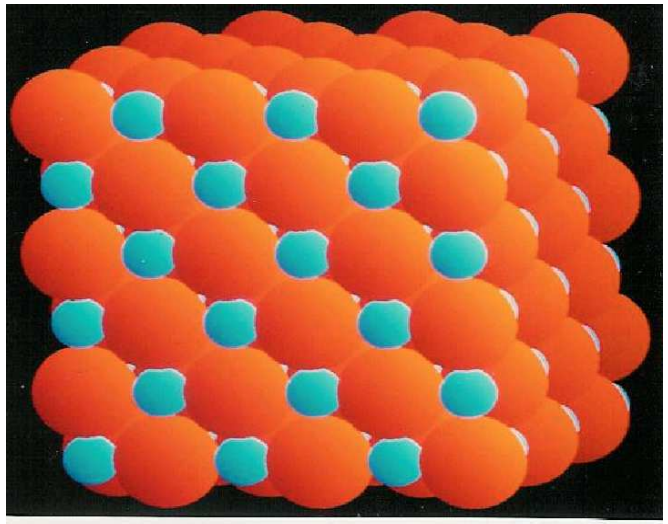
for both

central role: structure of the catalytic surface site(s)

MgO: a case hystory

- Definite ionic character
- Simple (rock-salt) crystalline structure
- Absence of surface relaxation

➡ Excellent **model system** for both → experimental studies / theoretical



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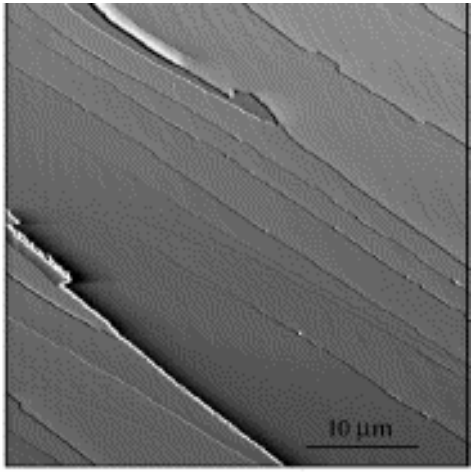
MgO: a wide knowledge background

➡ **“defect free” MgO (001) films**

➡ **cleaved MgO single crystals**



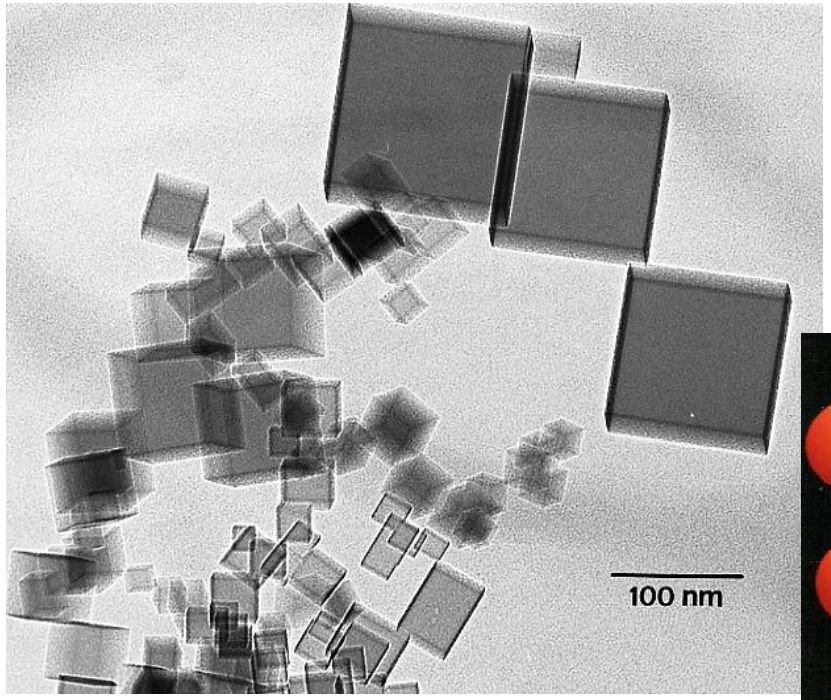
M. Foster et al, Surf. Sci., 502-503 (2002) 102

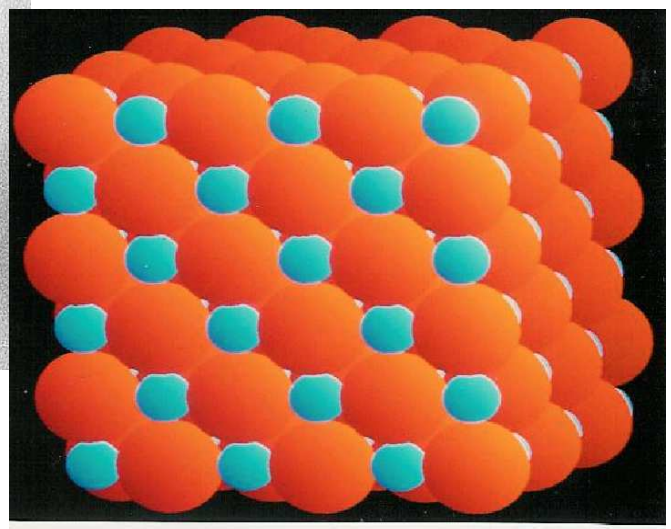
➡ **highly defective surfaces: nanosized MgO (powders)**

The MgO model system at nanoscale

A: simple morphology

MgO "smoke": MgO-s
SSA: 10 m^2g^{-1}



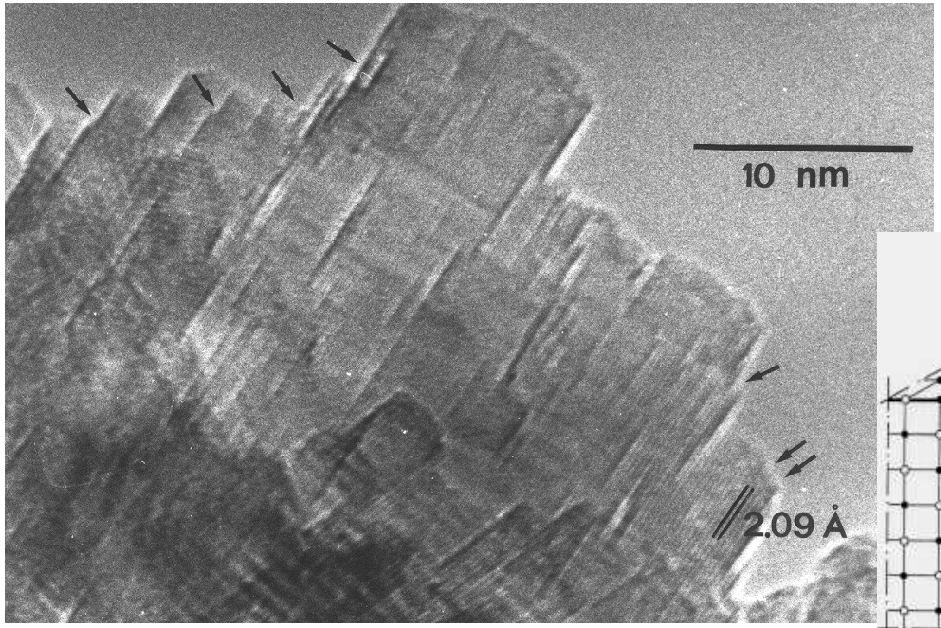


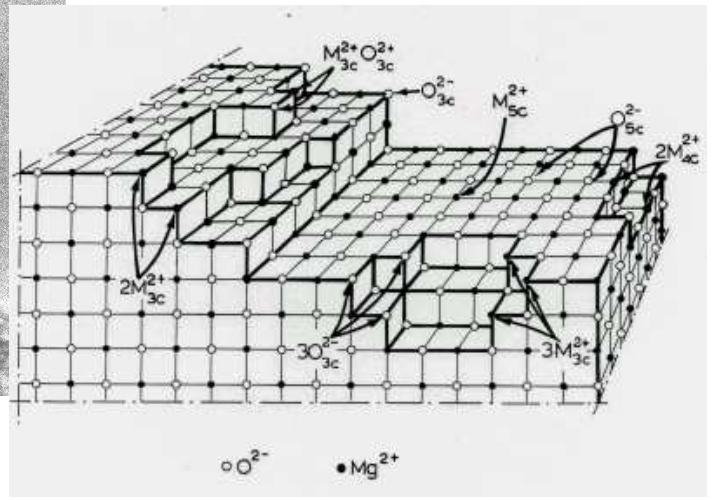
Flat surfaces, regular edges: absolute predominance of 5c sites
extended rows of 4c
"isolated" 3c

The MgO model system at nanoscale

B: complex morphology

MgO "ex-hydroxide": MgO-h
SSA, 200 $m^2 \cdot g^{-1}$





Rough surfaces: increased amount of 3c and 4c sites
variety of "clusters" of sites in low coordination (LC)

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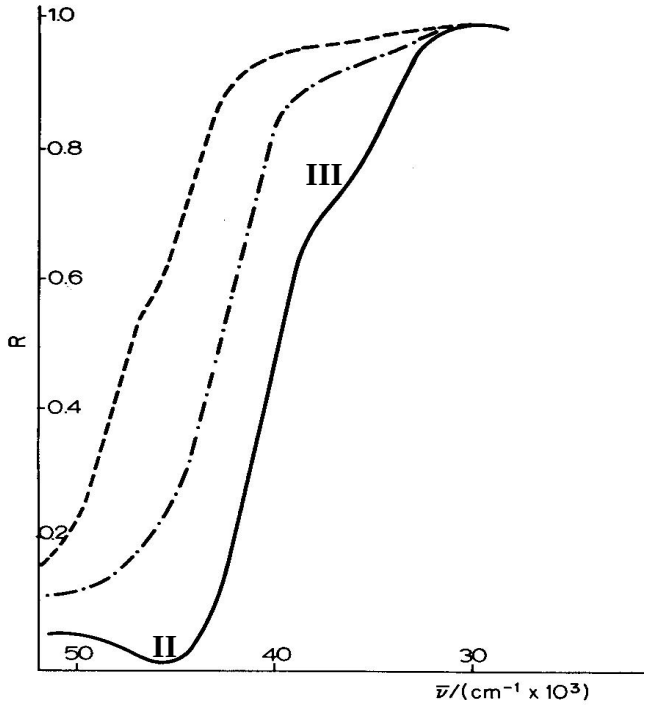
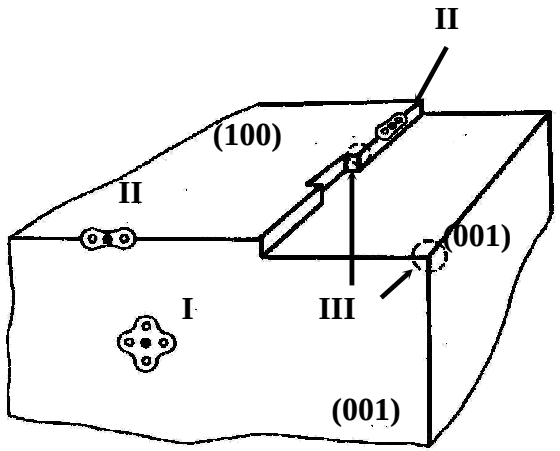
Surface states and surface reactivity of nano-MgO





Nanosized MgO (and other AEO also) able to activate:

X-H bonds

(H_2/D_2, NH_3, idrocarbons, heterocycles)

CO

to be stressed:

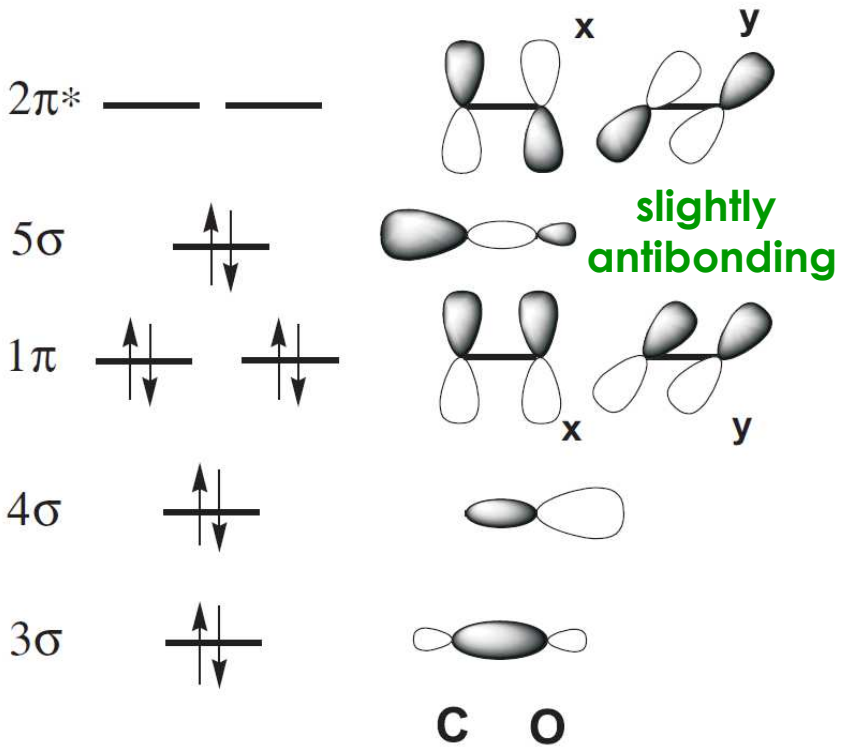
for C-containing molecules → *carbanion chemistry*

Surface heterogeneity: tools for a detailed investigation

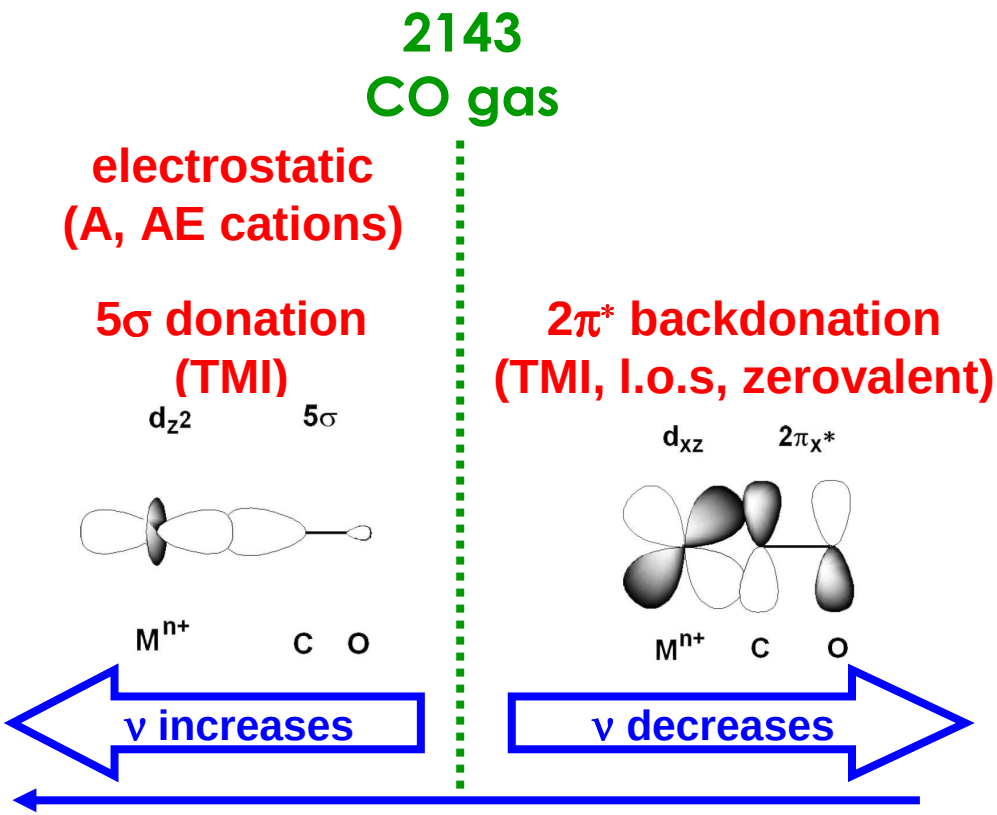
- microscopies (HRTEM, AFM)
- Spectroscopies: UV-Vis, PL, EPR, vibrational IR
- Molecular probes: H_2, O_2, CO, NO_x, H_2O, CO_2, NH_3, CH_4, CD_3CN, Py
- Quantum chemical calculations

CO as vibrational probe molecule (only 1 internal mode!)

electronic structure



effect of the interaction with surface sites on the ν of the internal mode

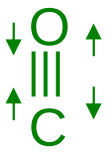


K.I. Hadjiivanov, G.N. Vayssilov, Adv. Catal., 47 (2002) 307-511)

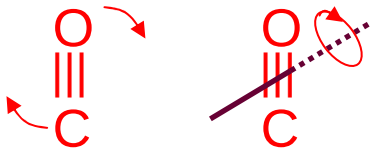
Other vibrational features of adsorbed CO

CO gas phase

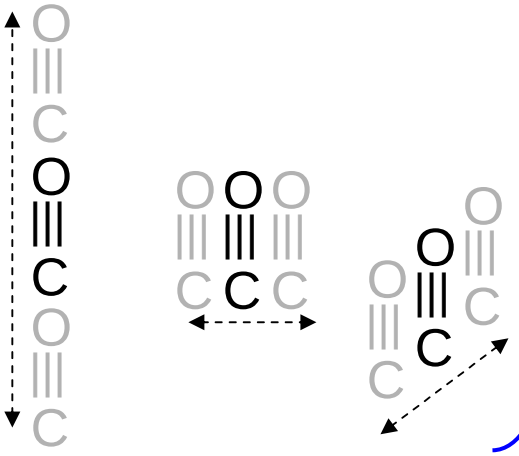
only one internal mode ν(C-O)



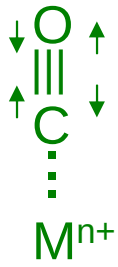
2 rotations



3 translations



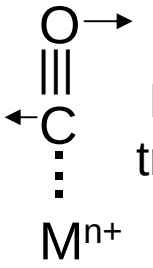
Adsorbed CO



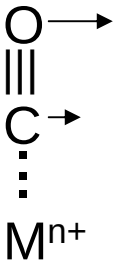
ν(C-O)

Mn+-CO bends

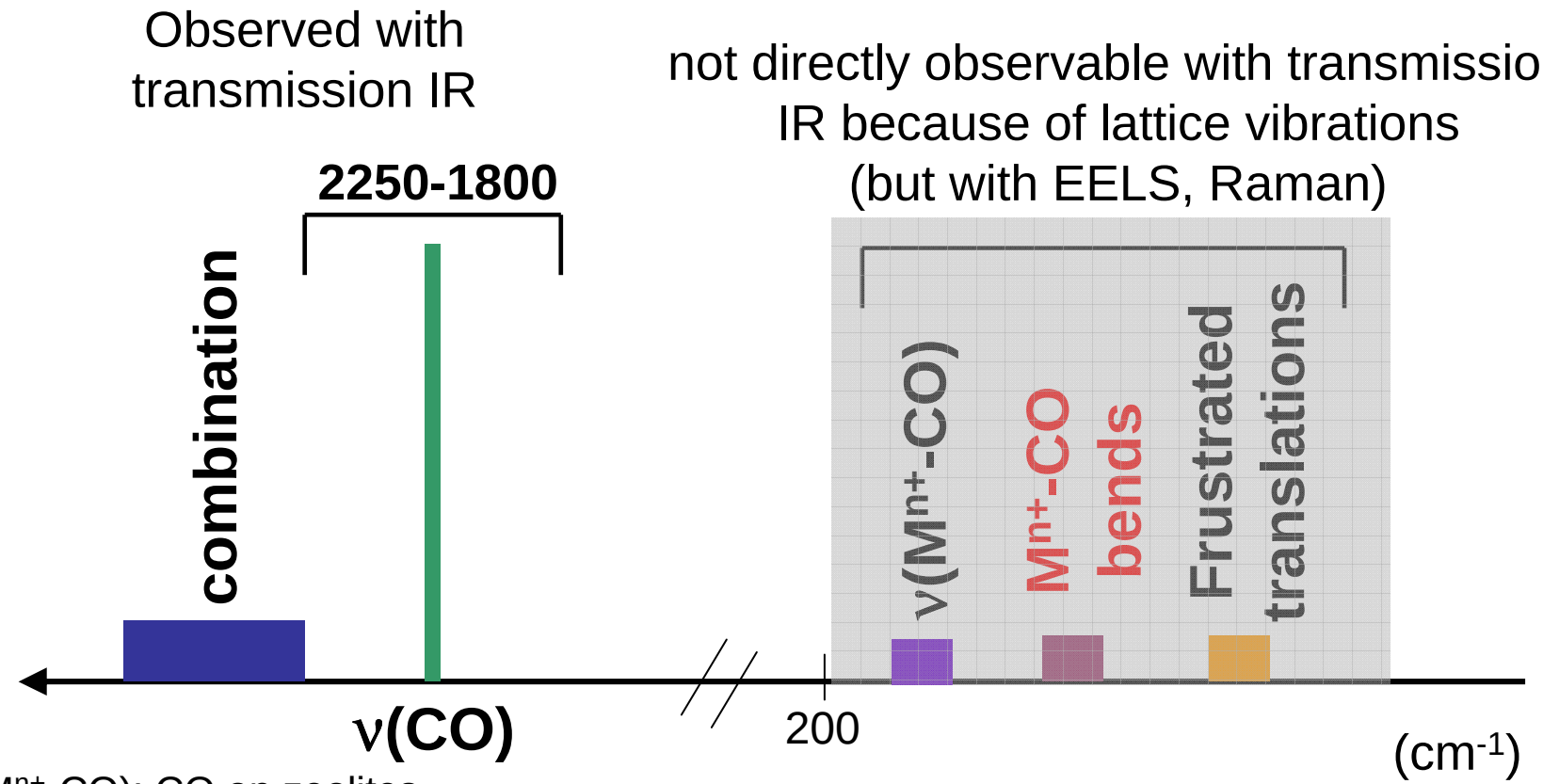
ν(Mn+-CO)



Frustrated translations



Other vibrational features of adsorbed CO



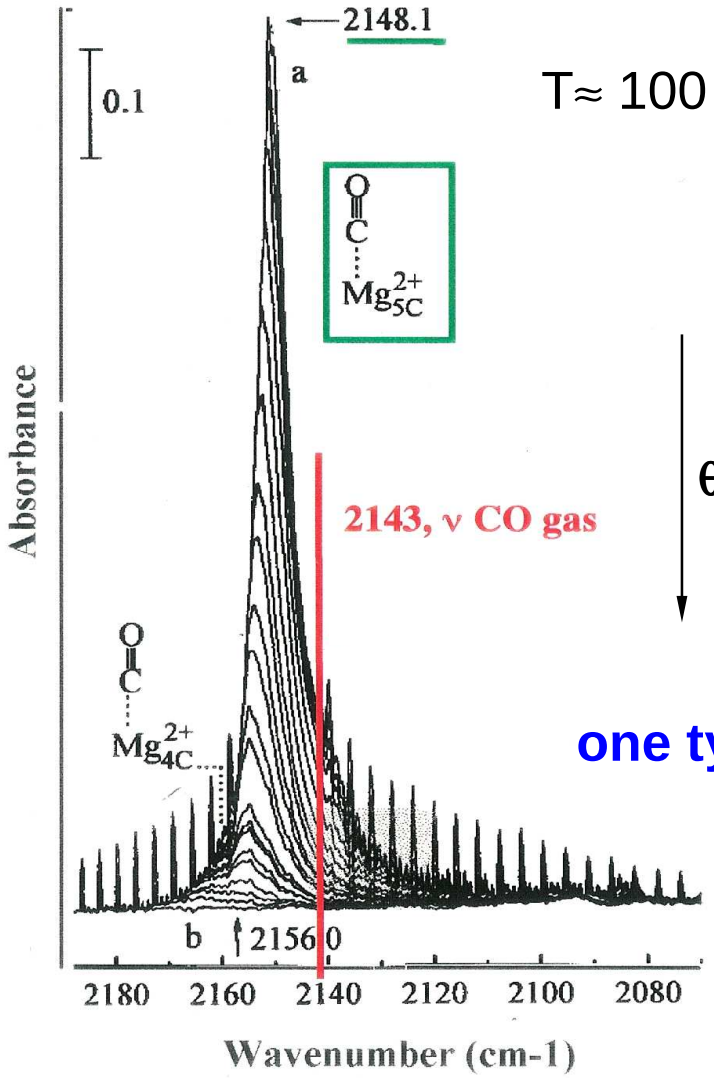
ν(M^{n+}-CO): CO on zeolites
frustrated rotation: CO on NaCl
frustrated translation: CO on NaCl; CO on TiO_2

Arean, C. O. et al., *Phys. Chem. Chem. Phys.* **1999** (1), 4139
Richardson, H. H. et al., *Surf. Sci.* **1987** (185), 15
Martra, G. et al, *Langmuir,* **2010** (26), 2521

Probing Mg^{2+}_{LC} single sites:

CO physisorption

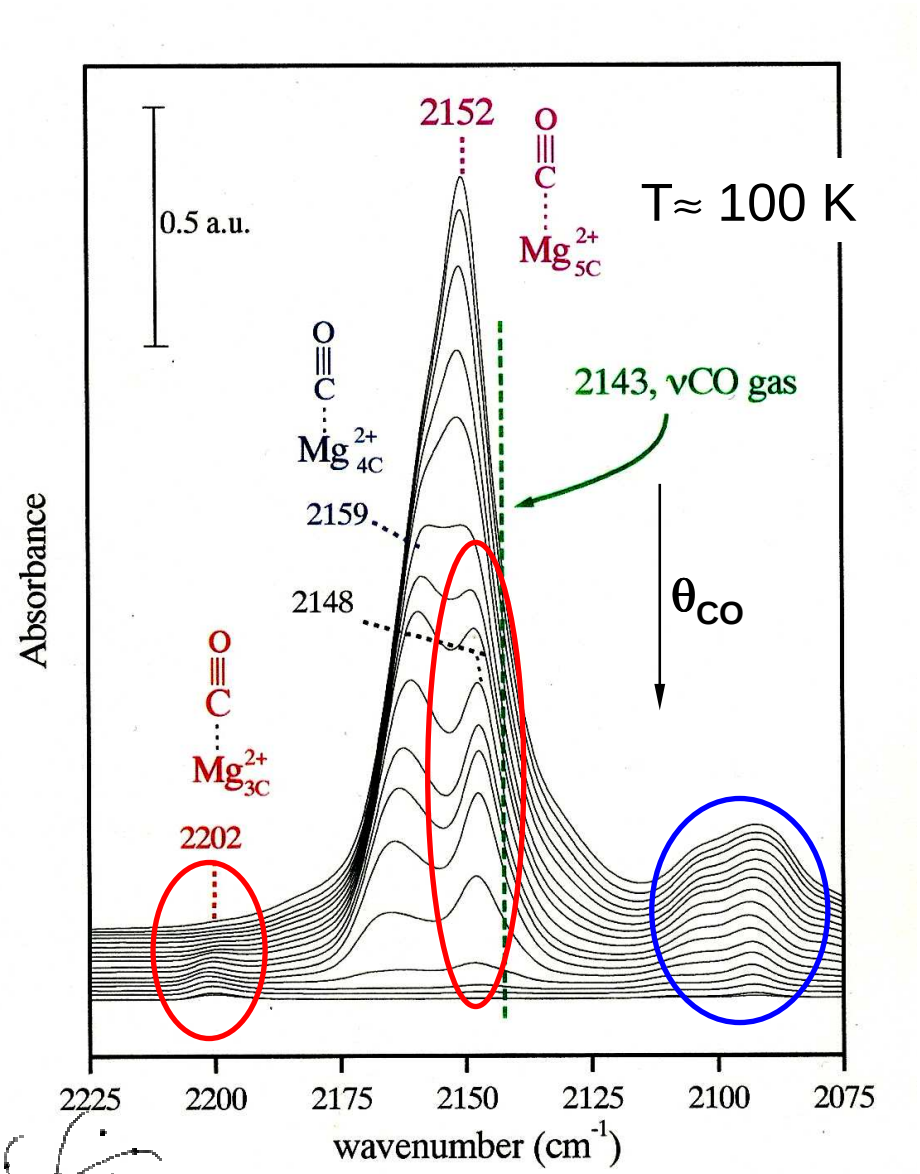
CO on MgO-s



Essentially one type of cations (Mg^{2+}_{5c}) are exposed

L. Marchese et al., Surf. Sci, 269-270 (1992) 135

CO on MgO-s



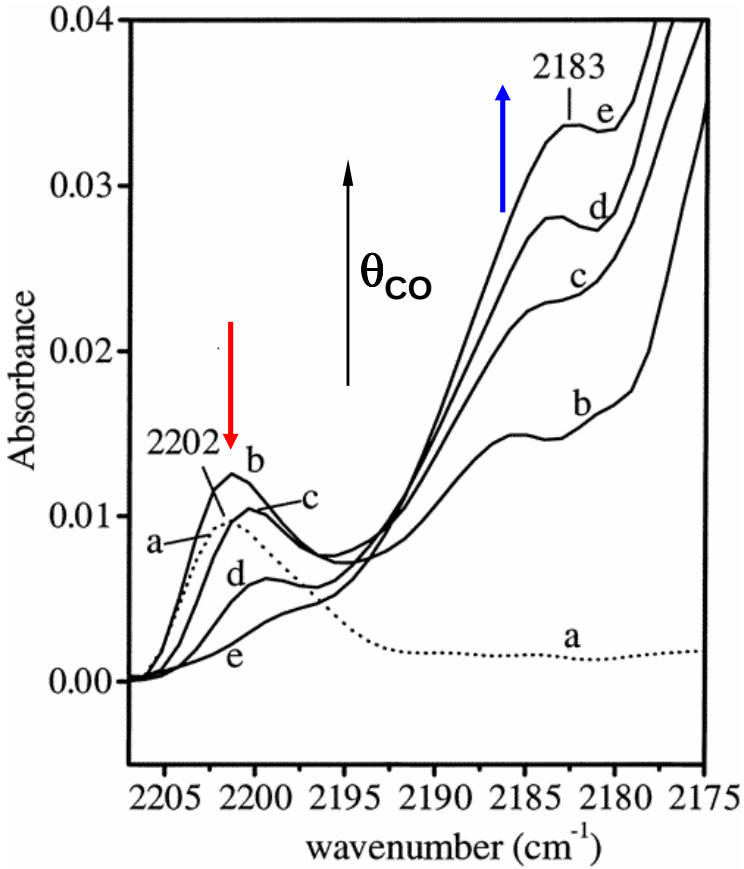
in agreement with quantum chemical calculations

- 2202 cm^{-1}: CO on Mg_{3C}^{2+}
- 2159 cm^{-1}: CO on Mg_{4C}^{2+}
- 2152 cm^{-1}: CO on Mg_{5C}^{2+}

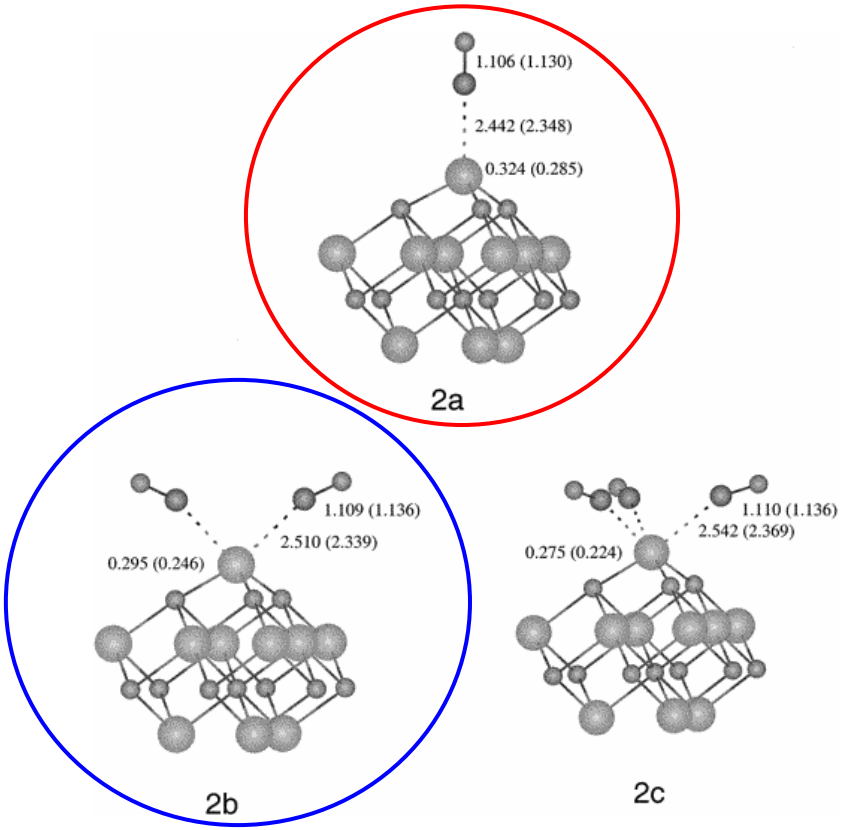
CO molecules adsorbed on ***single*** Mg_{LC}^{2+} cations, surrounded by a different number of O^{2-} ions

S. Coluccia et al., Spectrochim. Acta A, 49 (1993) 1289

CO on Mg2+3c

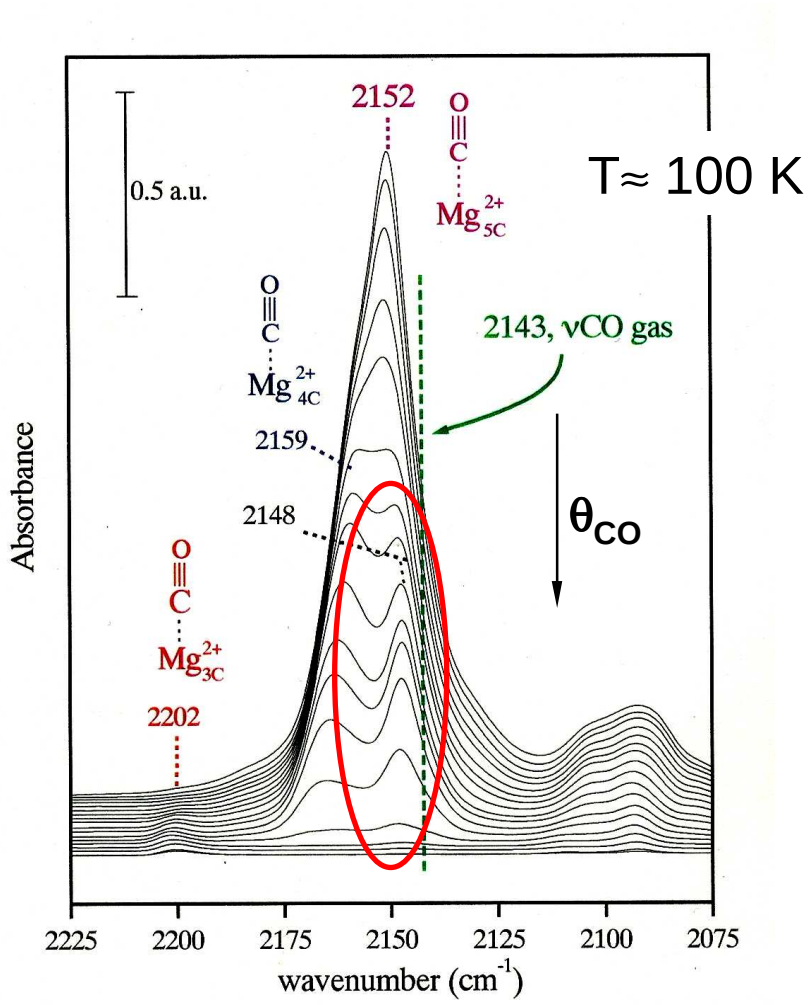


A. G. Pelmenshikov et al.,
J. Phys. Chem B, 104 (2000) 11947



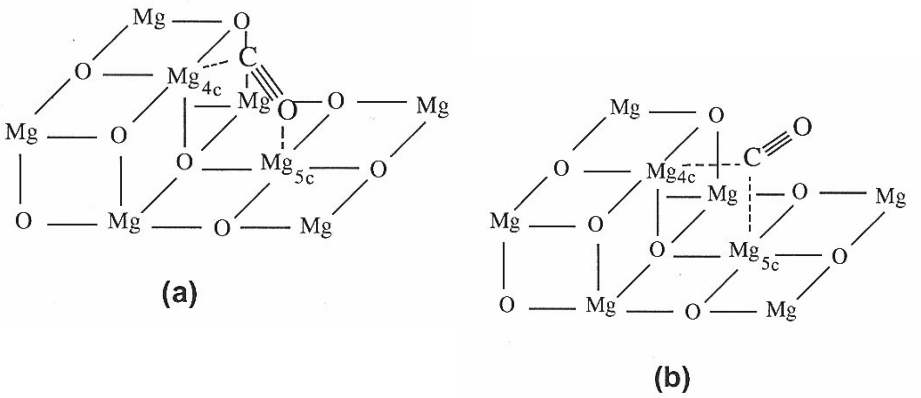
Mg^{2+} on corners are able to adsorb up two CO molecules

Band at 2148 cm^{-1}



position + stability

~~linear Mg^{2+}_{LC}•••CO~~



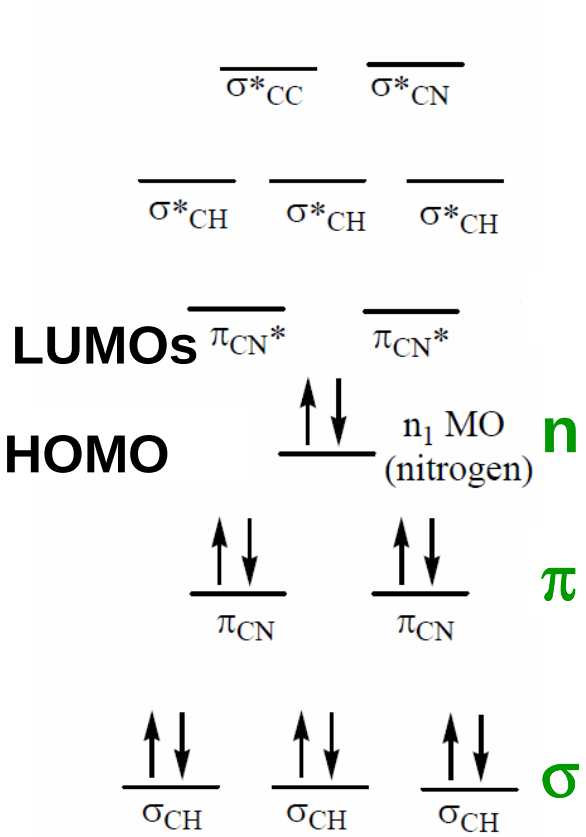
b: favoured by ab-initio calculations

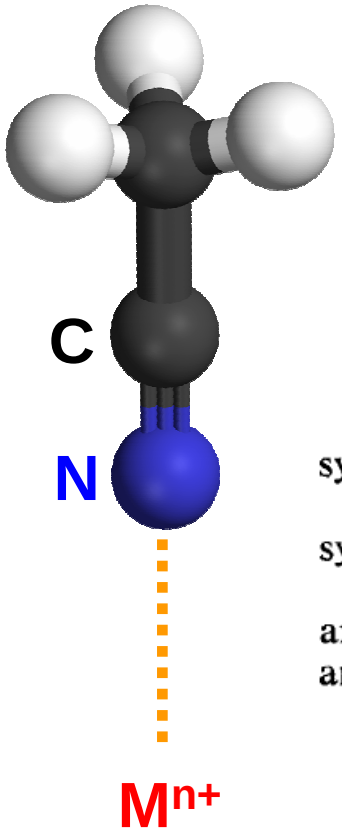
R. Soave and G. Pacchioni,
Chem. Phys. Lett 320 (2000) 345

band at 2148 cm^{-1}: fingerprint of monoatomic steps "edge-terrace"

A step forward from single to mutiple cationic sites

probing the surface with CD_3CN





for the use as IR probe, deuteration is required to avoid Fermi resonance between ν_2 and $\nu_3+\nu_4$ vibrations

description	designation	symmetry species
symmetric C—H stretching	$\bar{\nu}_1$	A_1
C≡N stretching	$\bar{\nu}_2$	A_1
symmetric CH_3 deformation	$\bar{\nu}_3$	A_1
C—C stretching	$\bar{\nu}_4$	A_1
antisymmetric CH_3 deforma	$\bar{\nu}_5$	E
antisymmetric C—H stretch	$\bar{\nu}_6$	E
CH_3 rocking	$\bar{\nu}_7$	E
C—C≡N bending	$\bar{\nu}_8$	E
	$\bar{\nu}_3+\bar{\nu}_4$	A_1

donation from n:

stabilization of σ ⇒ νC≡N ↑

destabilization of π ⇒ νC≡N ↑

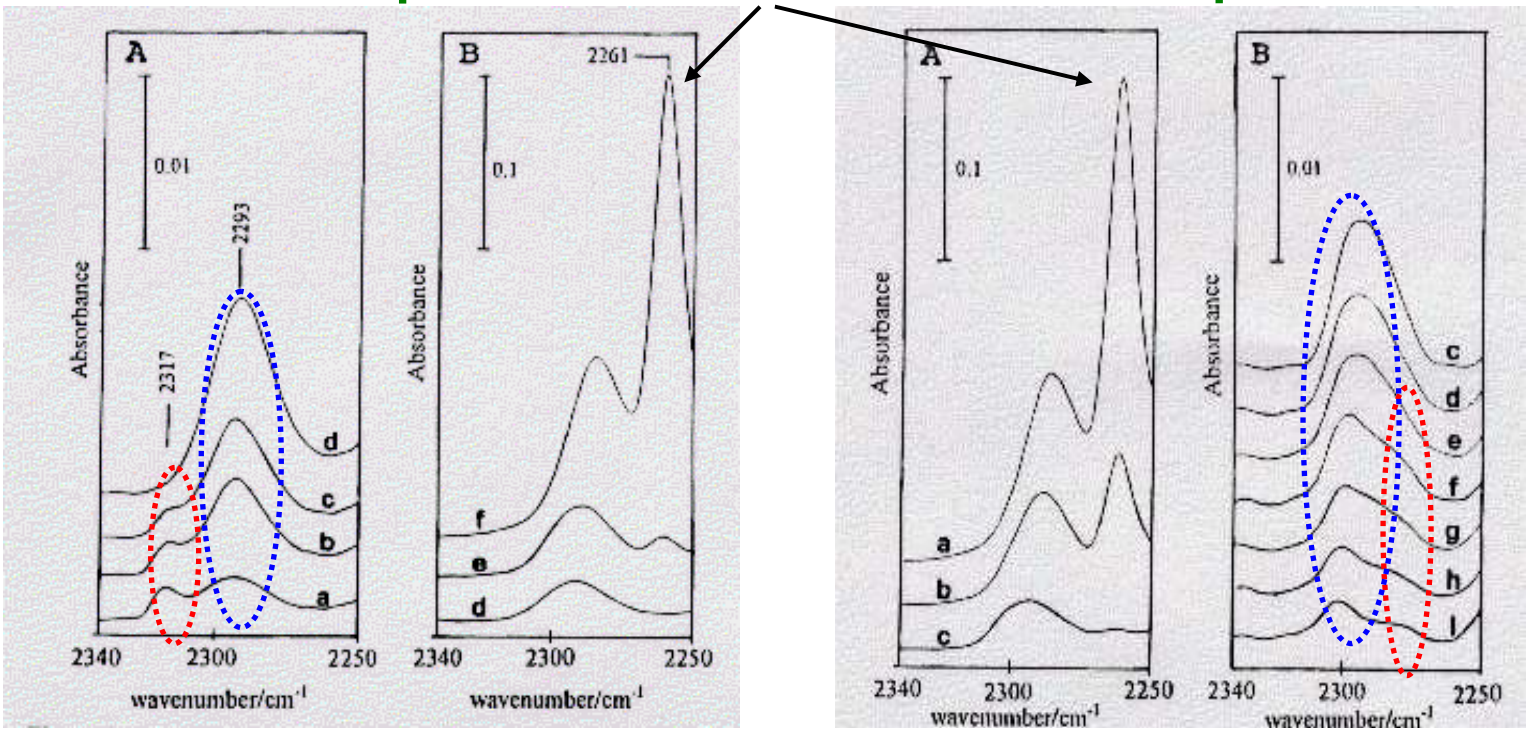
V.N. Filimonov, D.S. Bistrov, Opt. Spectrosc., 73, 1962, 31

K.F. Purcell, JACS, 89, 1967, 247

Evidence for additional types of multiple Mg^{2+}_{LC} sites

IR spectra of CD_3CN adsorbed on MgO-h

adsorption **liquid-like CD_3CN** **desorption**



Assignment: support of quantum chemical calculation *molecular models*

A. Pelmenshikov, G. Morosi, A. Gamba, S. Coluccia, G. Martra, E.A. Paukshtis, J.Phys.Chem. B, 100 (1996) 5011-5016

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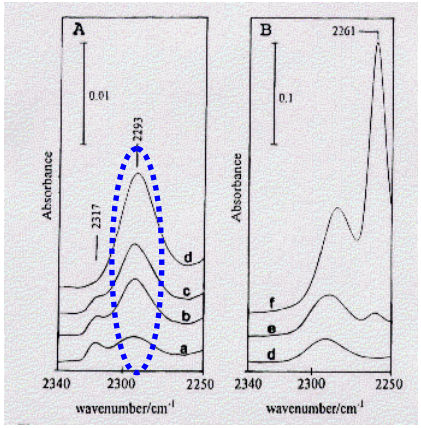
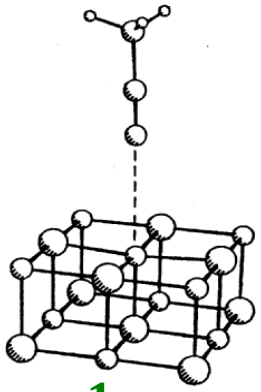
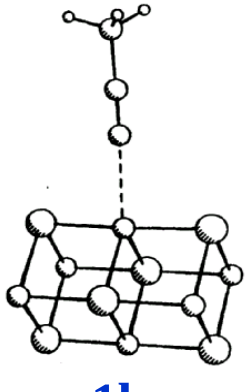
CD_3CN coordination on SINGLE Mg^{2+}_{LC} sites

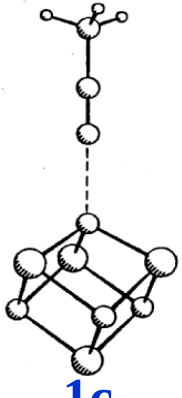




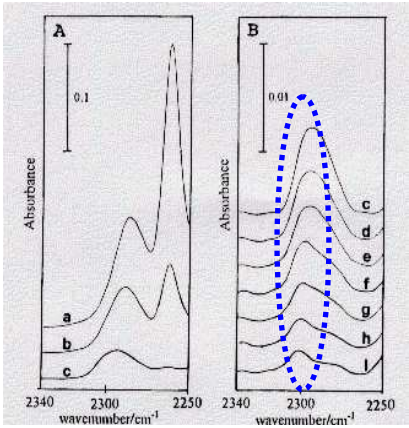
1a



1b



1c



$\Delta\nu_{CN}$ shift of CD_3CN (cm^{-1})

adsorbing site	model	calc	exp
Mg_{5c}^{2+}	1a	1	(not determined)
Mg_{4c}^{2+}	1b	24	21
Mg_{3c}^{2+}	1c	26	30

ab initio SCF, 6-31G*, CBS1, CBS2

similar $\Delta\nu_{CN}$ shift for CD_3CN adsorbed on Mg_{3c}^{2+} and Mg_{4c}^{2+}:

the stabilisation of the σ orbital (Mg_{3c}^{2+}> Mg_{4c}^{2+})
is compensated by
the destabilisation of the π orbitals (Mg_{3c}^{2+}>Mg_{4c}^{2+})

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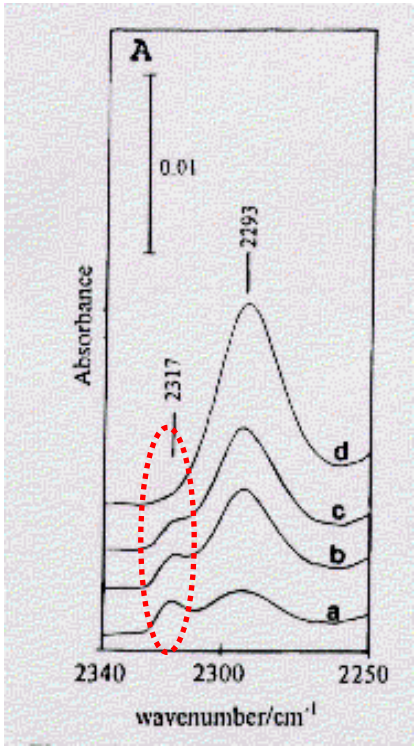
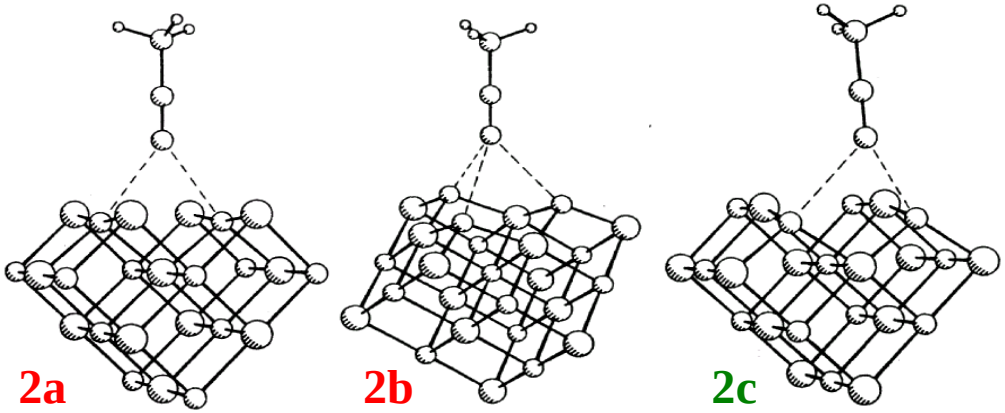
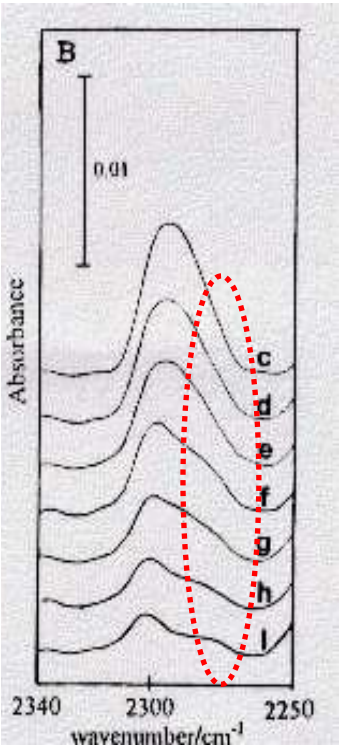
CD_3CN coordination on MULTIPLE Mg^{2+}_{LC} sites







$\Delta\nu_{CN}$ shift of CD_3CN (cm^{-1})

adsorbing site	model	calc	exp
double-Mg_{4c}^{2+}	2a	42	45
triple-Mg_{3c}^{2+}	2c	-26	(not found)
double-Mg_{3c}^{2+}	2b	4	8

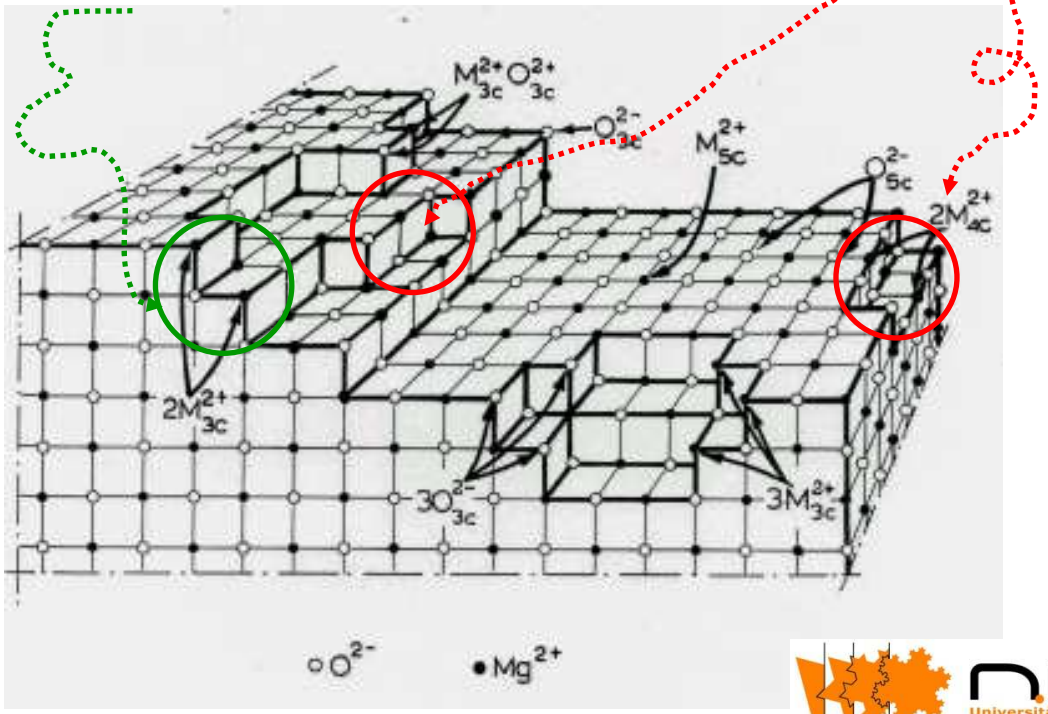
$\Delta\nu_{CN}$ (>0):

$CD_3CN{\cdot}$double-Mg_{4c}^{2+} >> $CD_3CN{\cdot}$double-Mg_{3c}^{2+}

consequence of the the deviation of the C≡N•••Mg fragment from the linearity

CD_3CN reveals:

- single Mg_{4C}^{2+} , Mg_{3C}^{2+} sites
- double Mg_{4C}^{2+}- Mg_{4C}^{2+} cationic sites
  (one unit cell steps edge-edge)
- double Mg_{3C}^{2+}- Mg_{3C}^{2+} cationic sites
  (one unit cell steps corner-corner)



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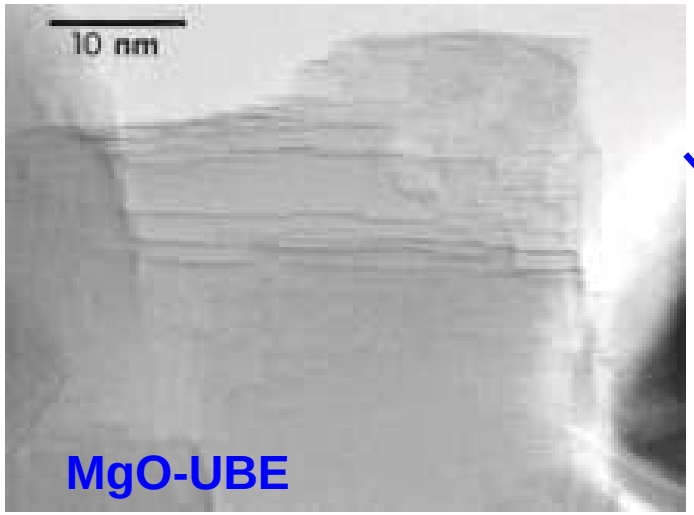
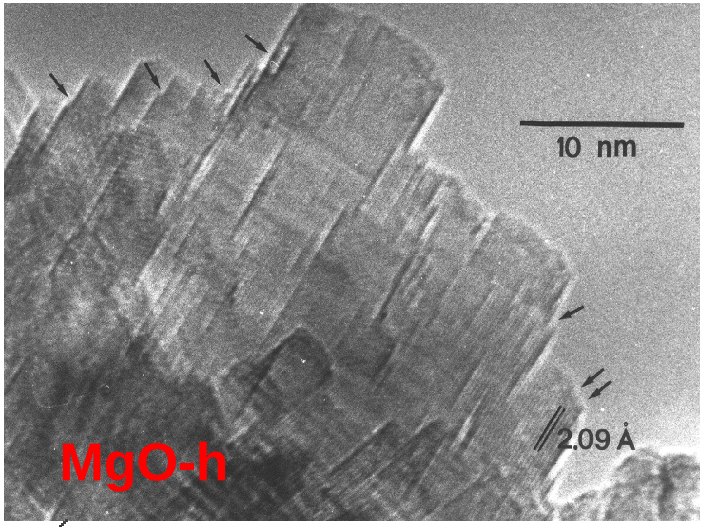
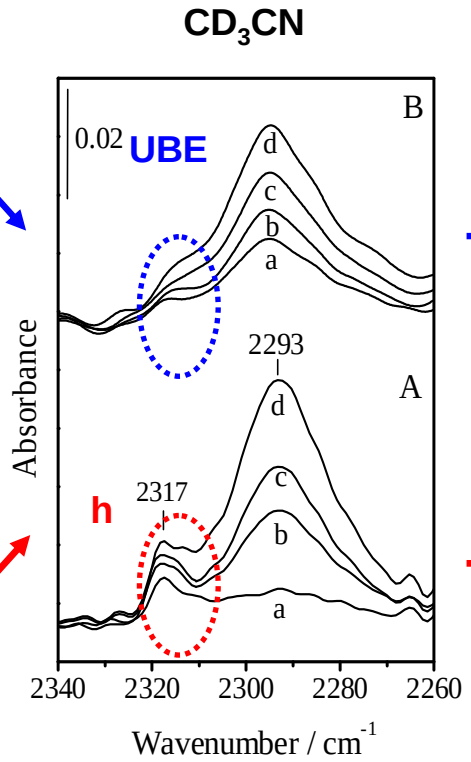
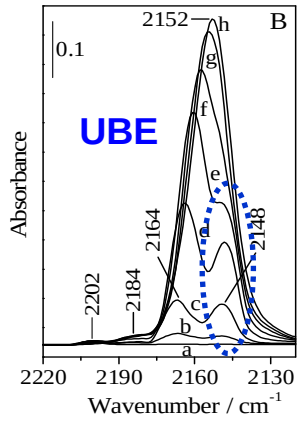
Playing with surface stepping

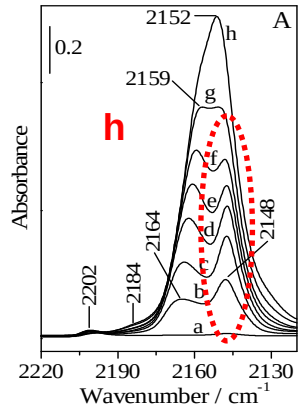








CO



on *MgO-h* *one unit-cell steps* prevail

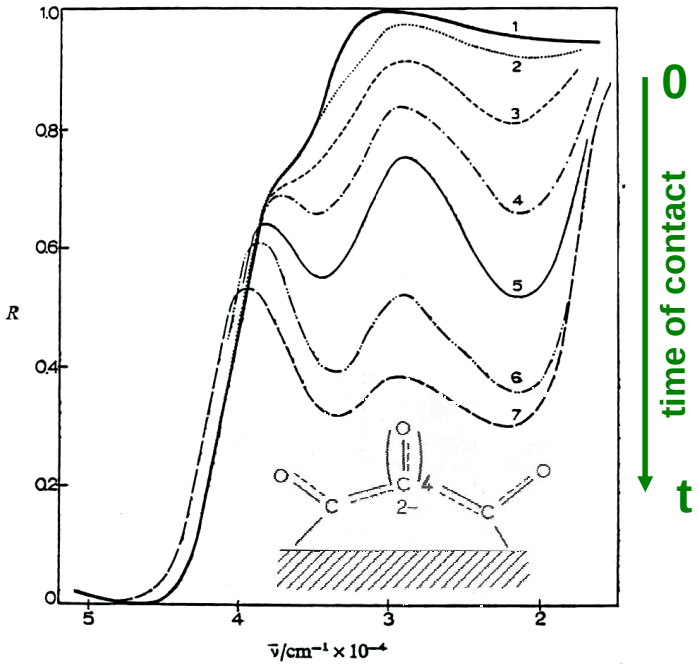
G. Martra et al., Catal. Today, 70 (2001) 121

Any effect of the arrangement of steps on surface chemistry?

CO on MgO at r.t.: a complex reactivity

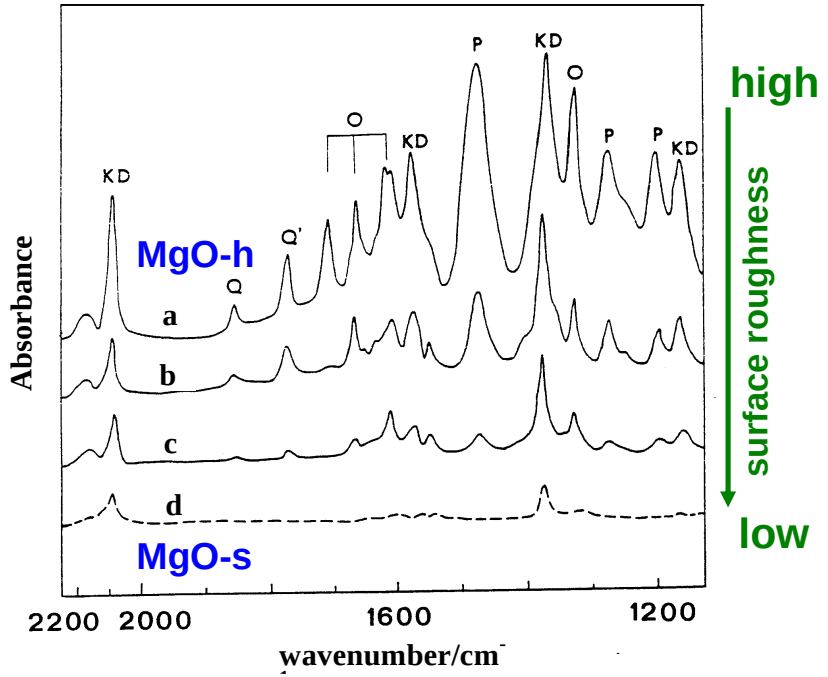
$P_{CO} \sim 40$ Torr, $T \sim 300$ K

DR UV-Vis; CO on MgO-h



A. Zecchina, F.S. Stone,
J. Chem. Soc. Comm. (1974) 1476

IR; CO on various MgO



S. Coluccia et al.,
Spectrochim. Acta A, 49 (1993) 1289

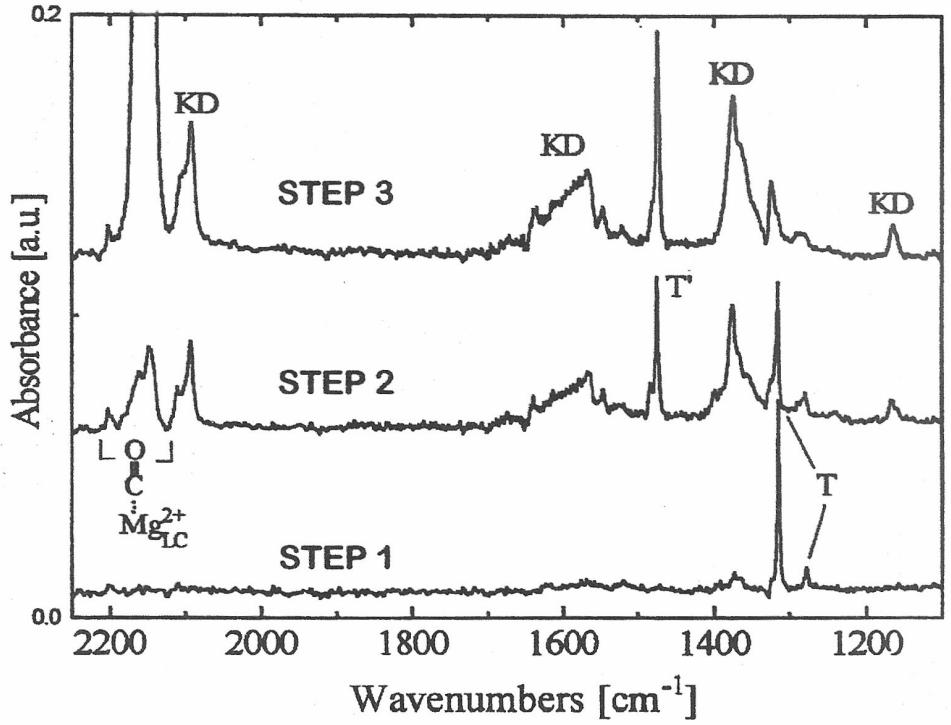
➡ surface O^{2-} in the lowest coordination are the active sites

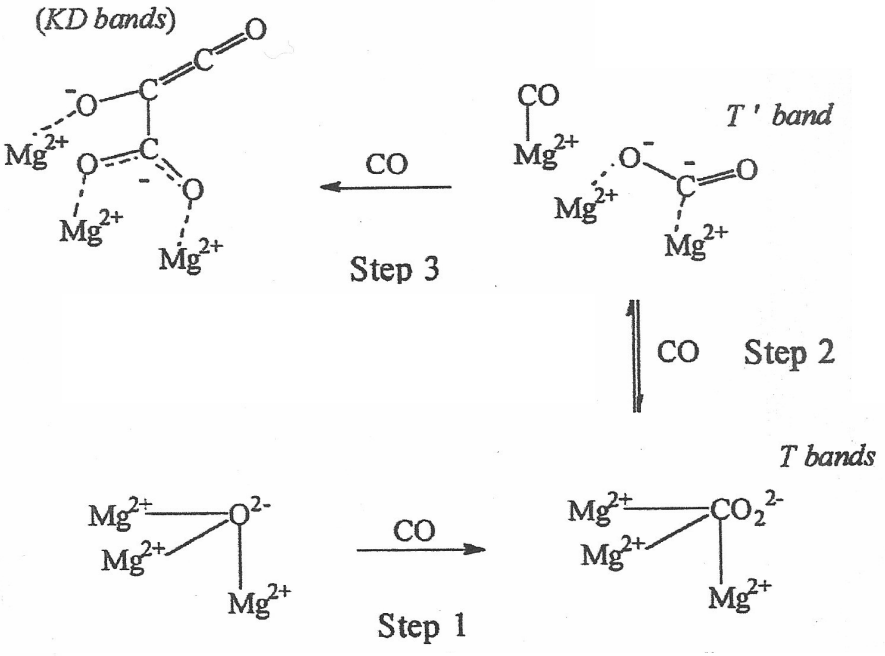
➡ variety of products: heterogeneity of active sites

Slowing the reaction rate

CO on MgO-h

P_{CO} ~ 0.01 Torr, T ~ 100 K

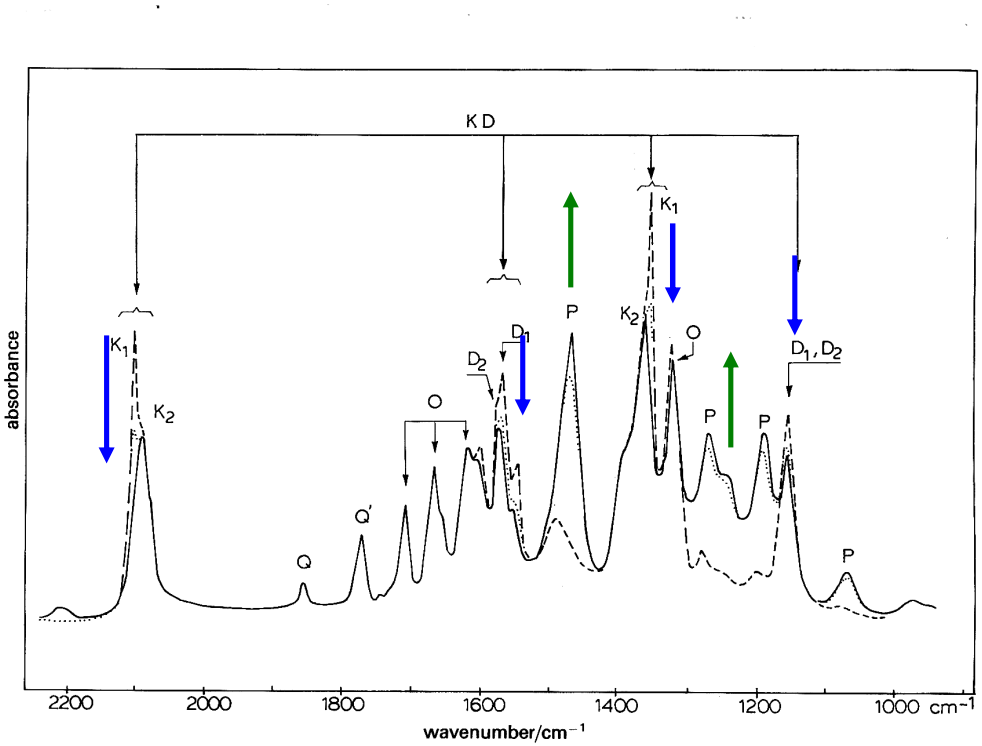




Carbonite, (T, T'): essentially one type

Ketenic species (KD): at least two families

Back to CO reactive adsorption at r.t.



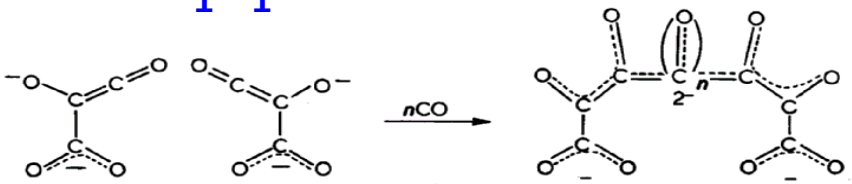
P_{CO} ~ *up to 40 Torr, T ~ 300 K*

K_2D_2: no evolution

K_1D_1: evolution to polymers (P)

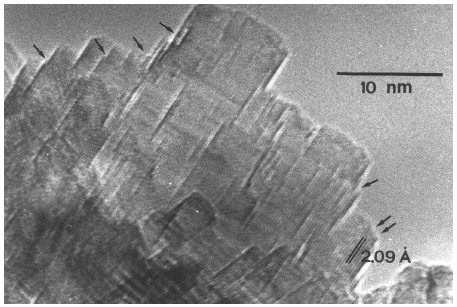
A. Zecchina et al., J. Chem. Soc. Faraday Trans., 86 (1990) 703

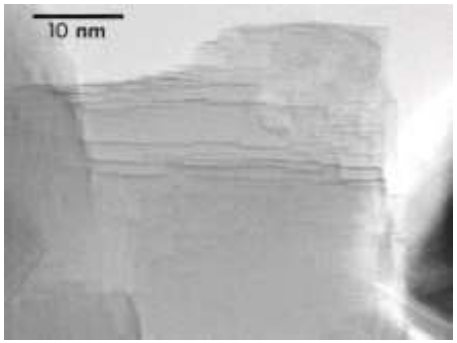
K_1D_1 → **P**



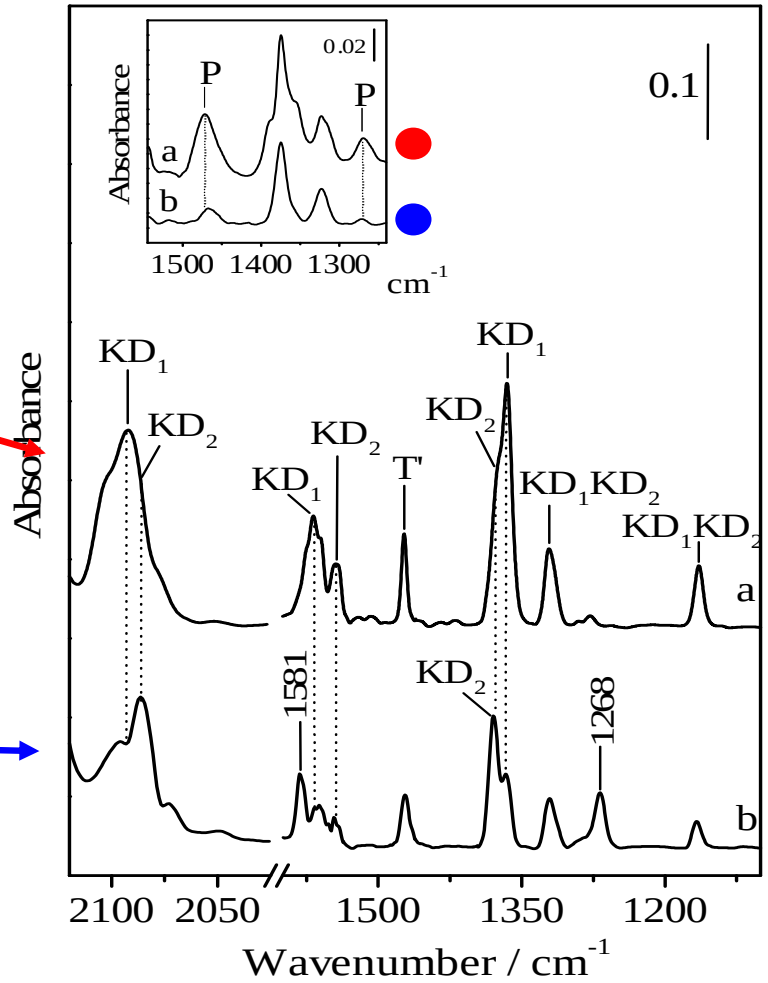
Role in polymerization of ketenic species

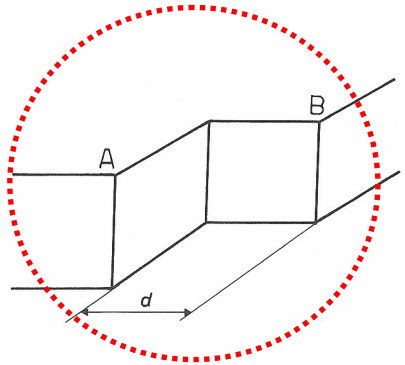
MgO-h





MgO-UBE





K_1D_1 species prevail on *MgO-h*

K_2D_2: on "isolated" steps **K_1D_1: on "staircases" of steps**

⇒ polymerization

Summary on MgO

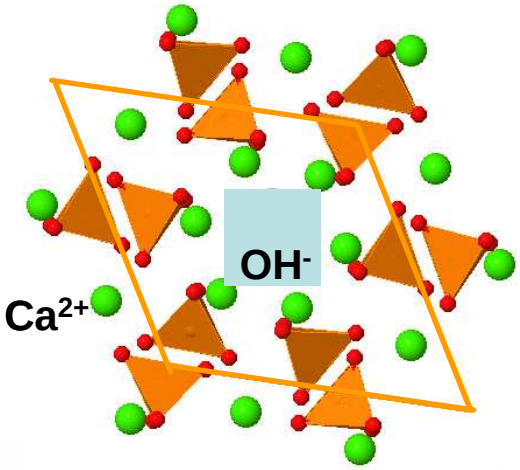
IR spectroscopy of adsorbed CO and CD_3CN revealed the presence of three levels of surface heterogeneity

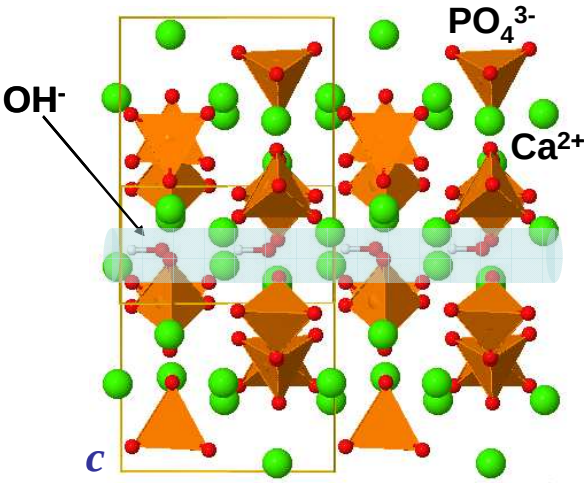
- **Coordinative state of ions as single sites**
- **Coordinative state of partners in cation-anion pairs**
- **Relative location of ensamble of proximal acid-base pairs in low coordination**

Nanohydroxyapatite: a biomimetic ceramic biomaterials

biomaterial for bone filling

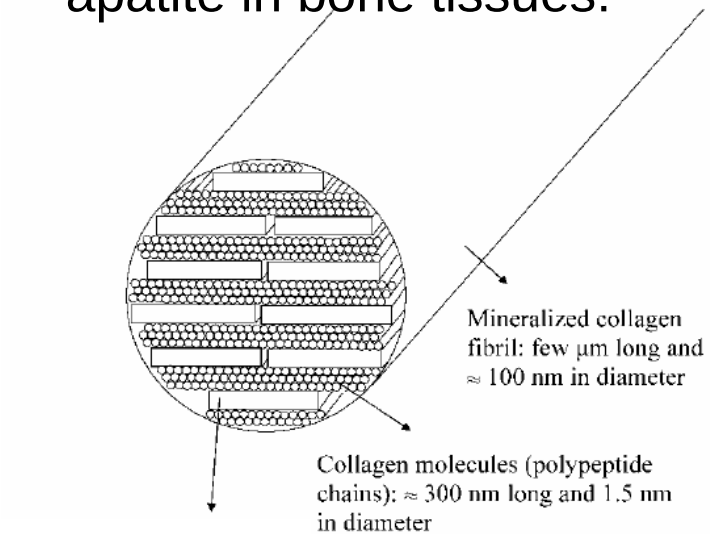
- resorbable
- bioactive
- osteoconductive
- osteoinductive





hexagonal, enamel formation

apatite in bone tissues:



Crystal size of HA: ≈ 50 x 25 x 4 nm

natural apatite composition

$(Ca^{2+},M^{n+})_{10}(PO_4^{3-},CO_3^{2-},Y)_6(OH^-,F^-,Cl^-)_2$

M: Mg^{2+},Na^+,K^+… Y: HPO_4^{3-},SO_4^{2-}…

Nanometric

biomimetism

Nanocomposite

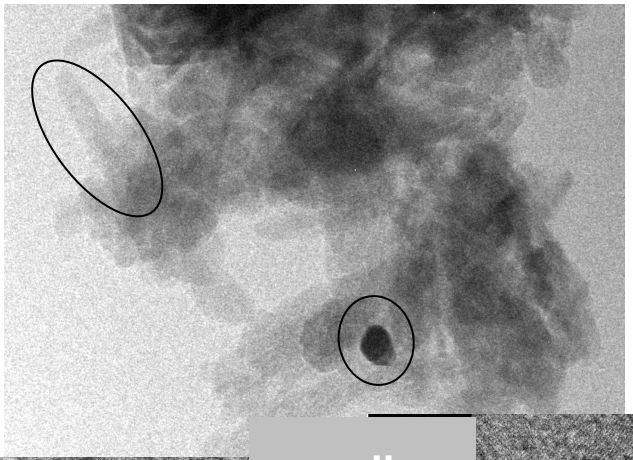
Nano-hydroxyapatite: tailoring of shape and structure

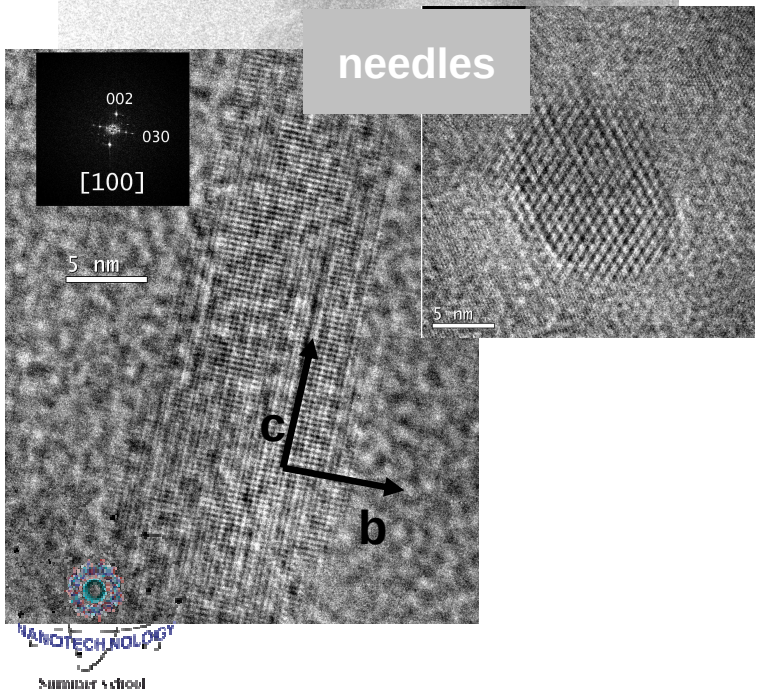
$$5Ca(OH)_2 + 3H_3PO_4 \rightarrow Ca_5(PO_4)_3OH + 9H_2O$$

L.Bertinetti et al.

J. Phys. Chem. C **2007**, *111*, 4027−4035

T = 25 ℃





needles

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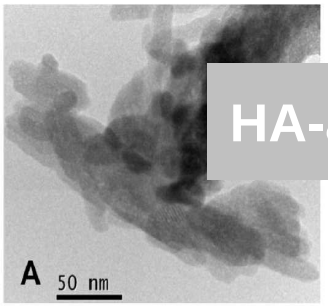
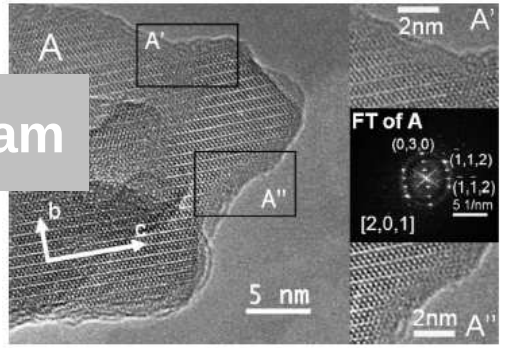
istec
cnr



HA-am



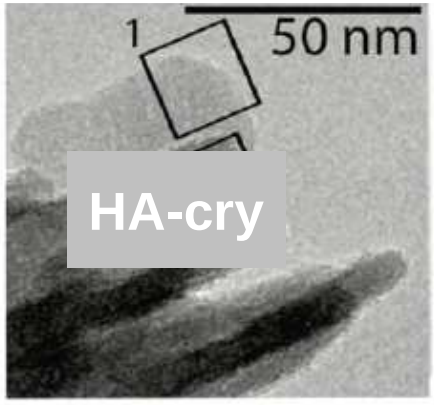
T = 40℃

platelets

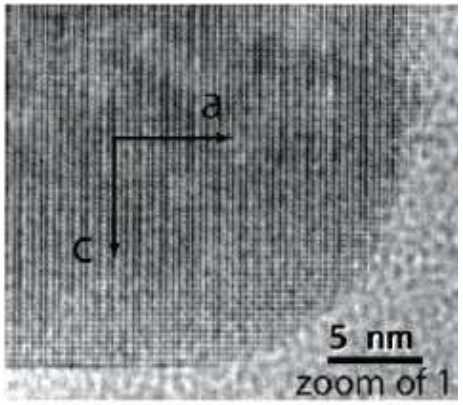
Y. Sakhno et al.

J. Phys. Chem. C **2010**, *114*, 16640–16648

T = 95℃



HA-cry



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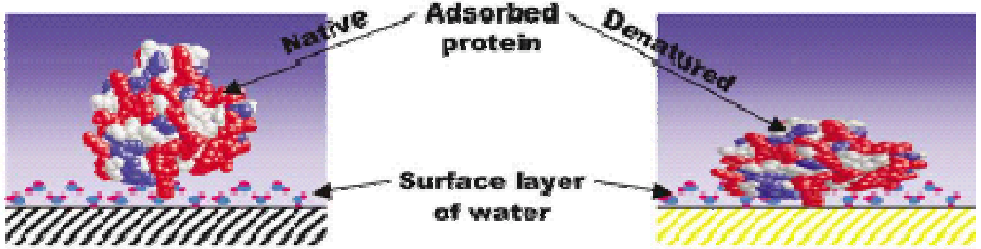
Biomaterials & Surface Science

1 Surface + water

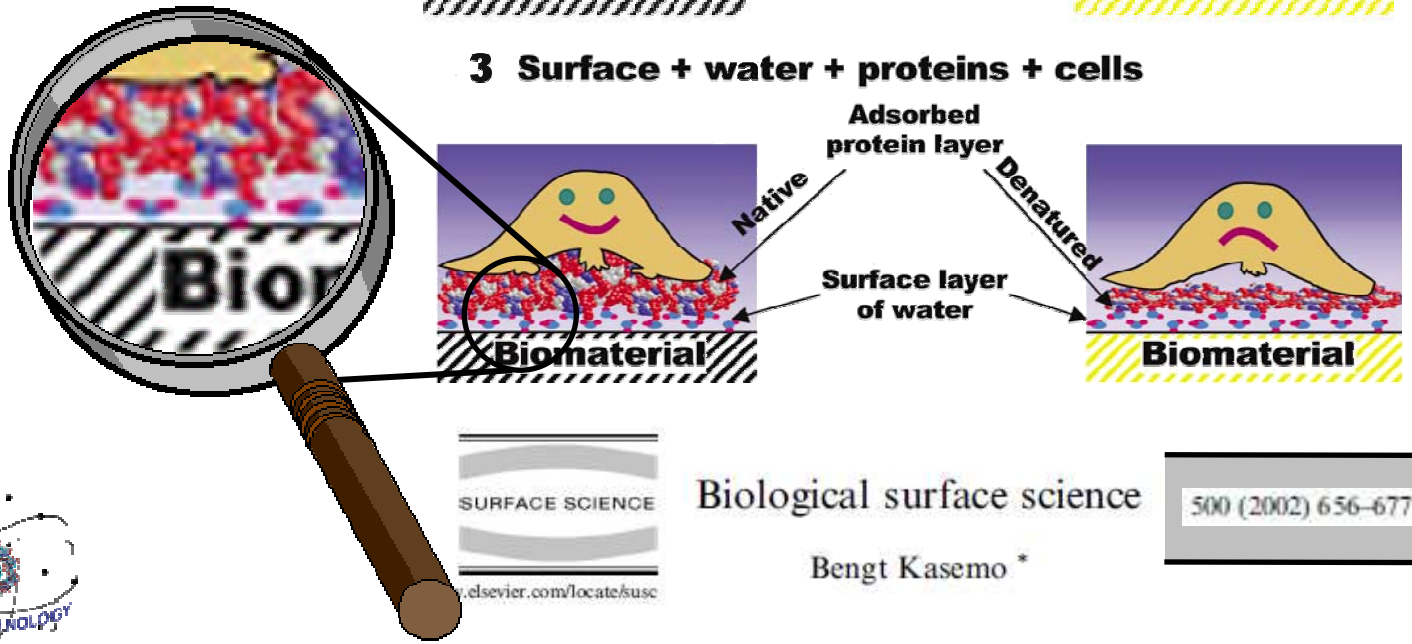
Different bonding orientations and bonding strengths

2 Surface + water + proteins

Native or denatured confirmation



3 Surface + water + proteins + cells



SURFACE SCIENCE

www.elsevier.com/locate/susc

Biological surface science

Bengt Kasemo *

500 (2002) 656–677

NANOTECHNOLOGY Summer School

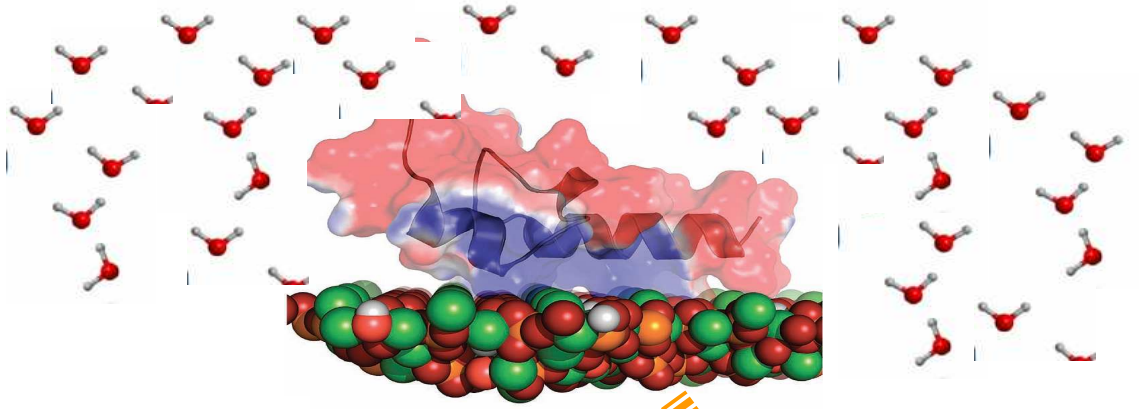
nis Università di Torino

Biomaterial surfaces, water, biomolecules

complex

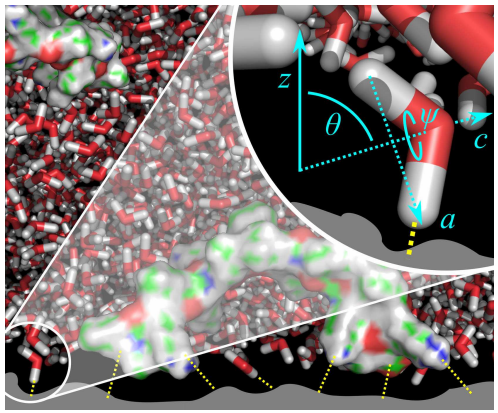
heavy (QM)

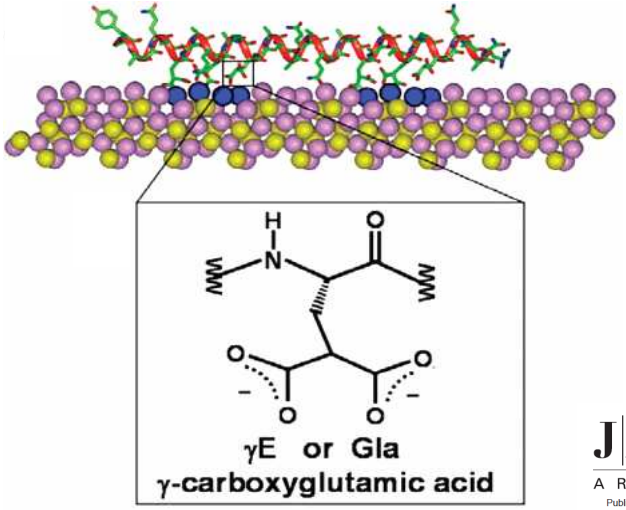
…..



biomaterial/water

biomaterial/biomolecules (small)





Water structure at solid surfaces and its implications for biomolecule adsorption

Kailash C. Jena and Dennis K. Hore

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J|A|C|S ARTICLES

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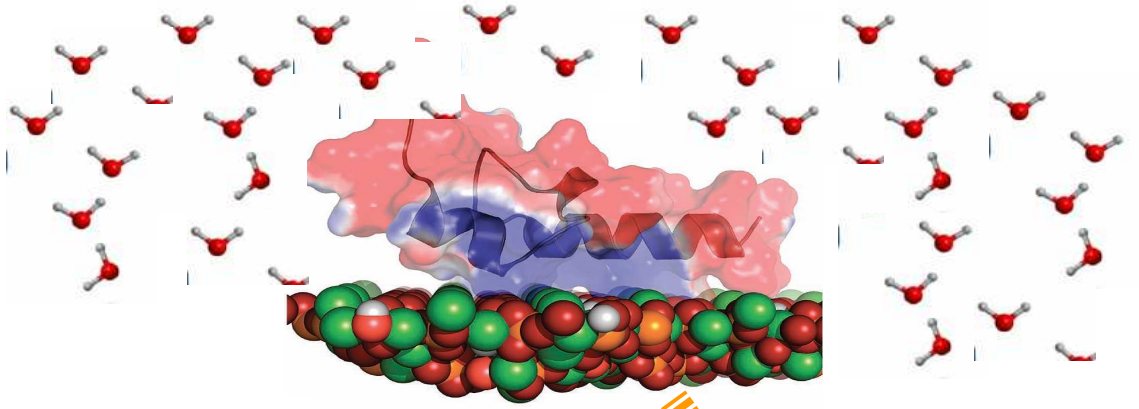

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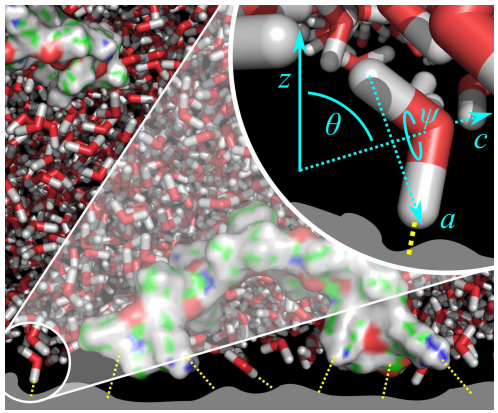

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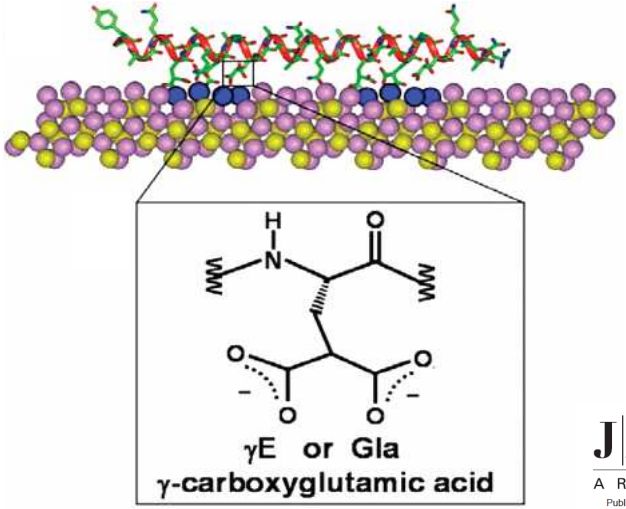

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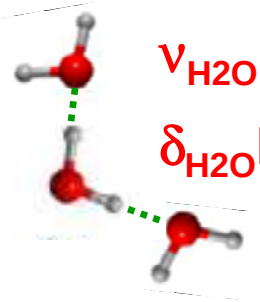
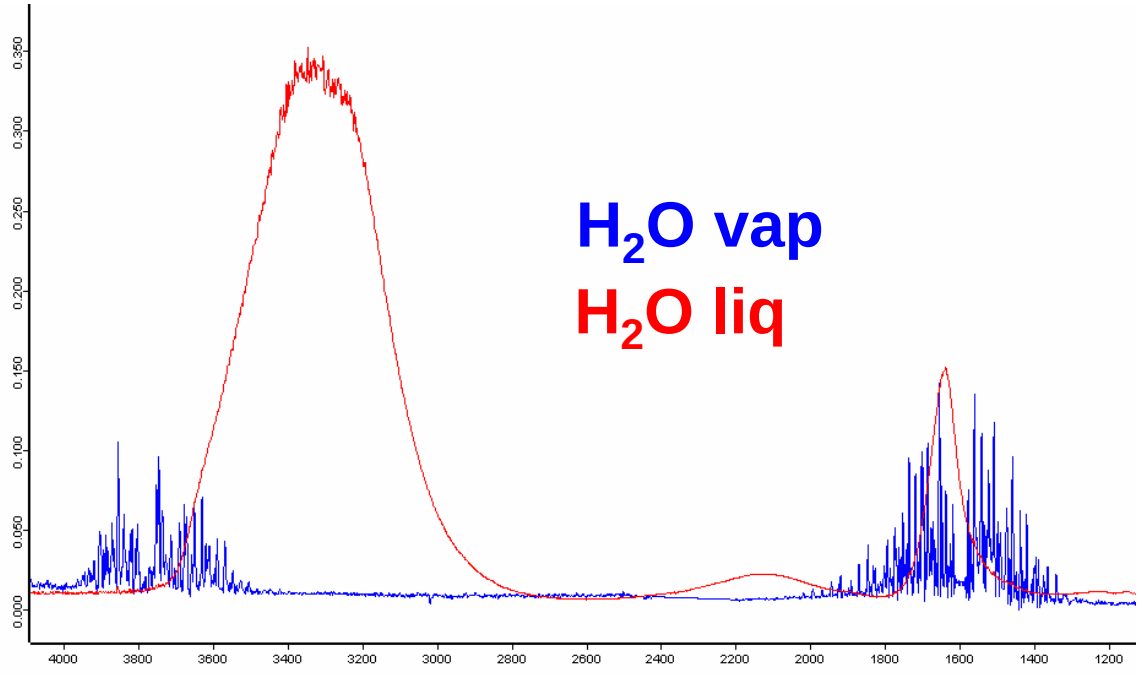
Probing H_2O interactions by IR

from H_2O-$(H_2O)_n$



$\nu_{H2O}HB < \nu_{H2O}$ free

$\delta_{H2O}HB > \delta_{H2O}$ free



H_2O vap

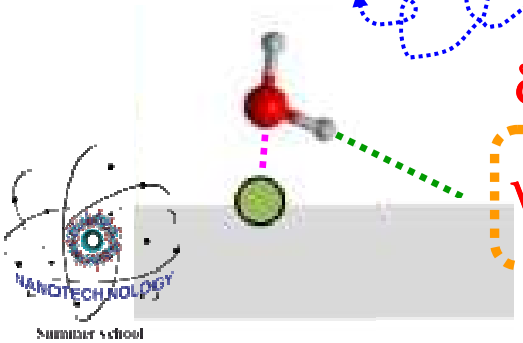
H_2O liq

to H_2O – surface….

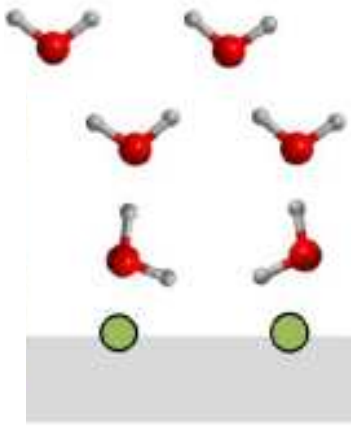
$\delta_{H2O}HB < \delta_{H2O}$ free

$\delta_{H2O}HB > \delta_{H2O}$ free

$\nu_{H2O}HB < \nu_{H2O}$ free

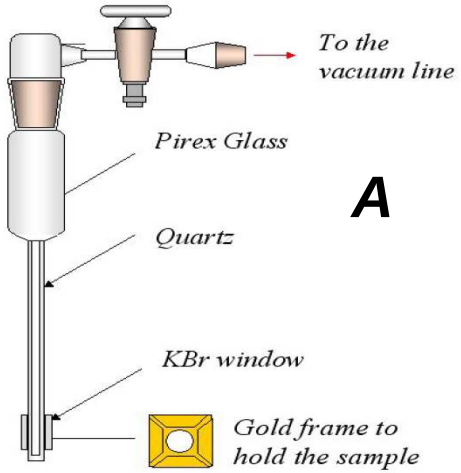


….to H_2O-H_2O on a surface

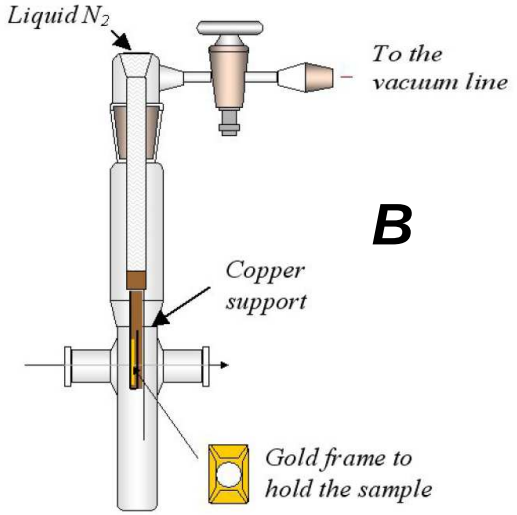


Università di Torino

Water adsorption/desorption in controlled and model conditions

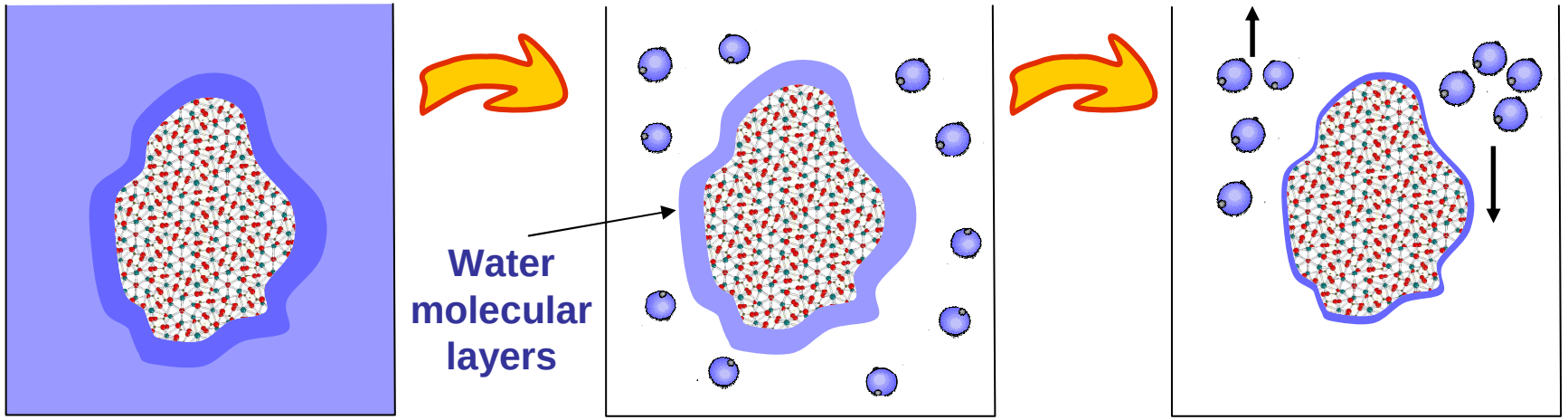


A



B

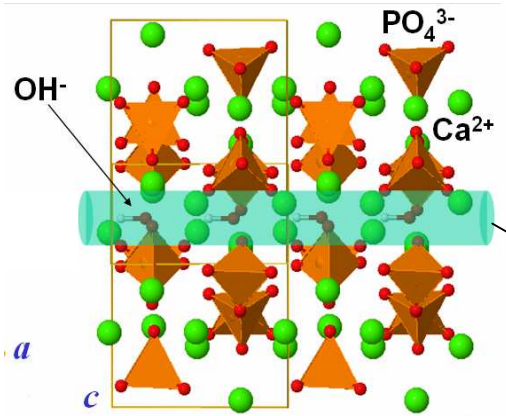
outgassing/readsorption



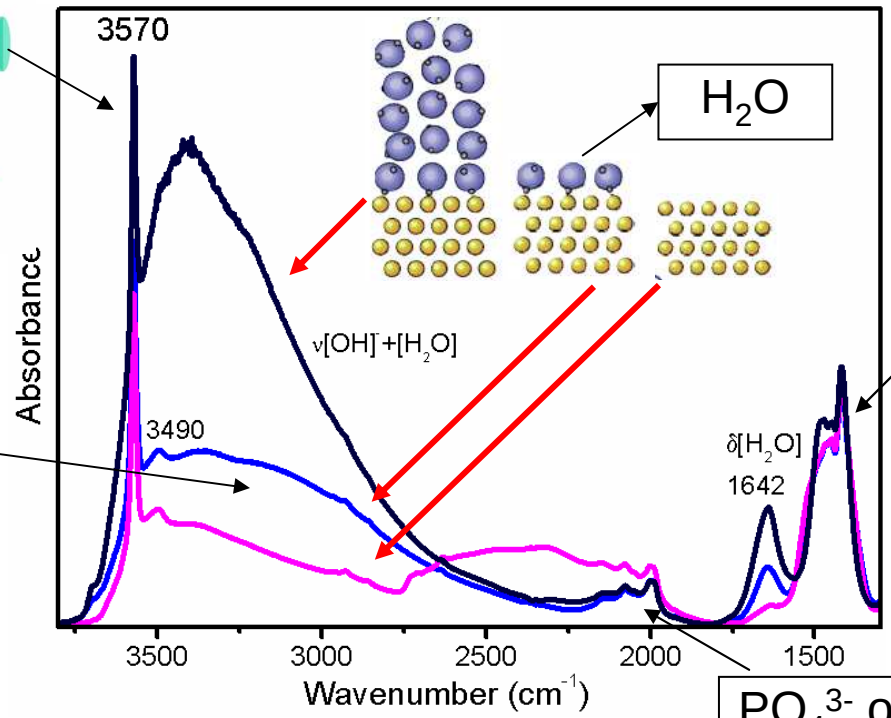
Nano-particles in water

control of the amount of adsorbed H_2O

Water at the surface of HA-am and HA-Cry: general overview



- w.v.p
- outgassing at b.t. for 40 min
- exchange with D_2O & outgassing at b.t. for 40 min



HA outg. at b.t. :
ca 4.0 H_2O nm^{-2}
0.5 OH nm^2
(MG, IR, SSA_{BET})

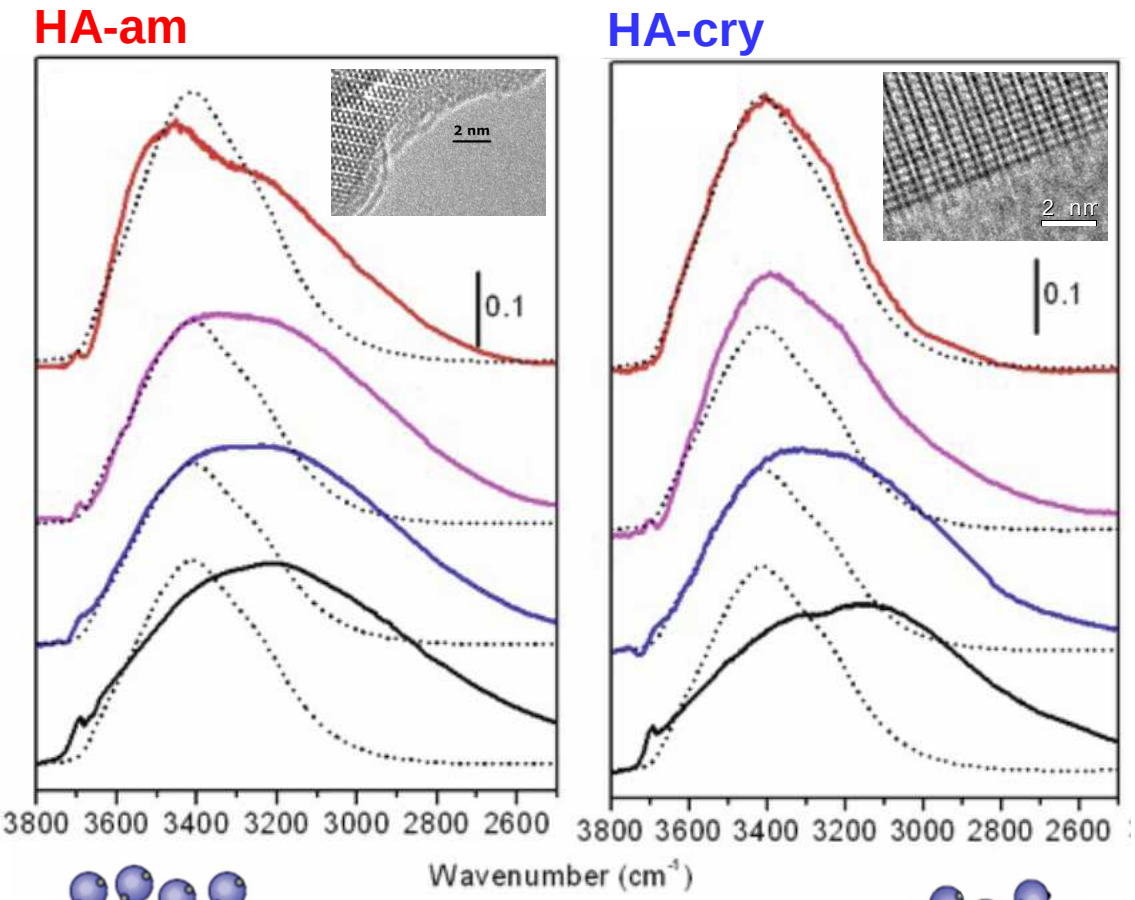
CO_3^{2-} substituting PO_4^{3-} and OH^-

PO_4^{3-} overtones & combinations

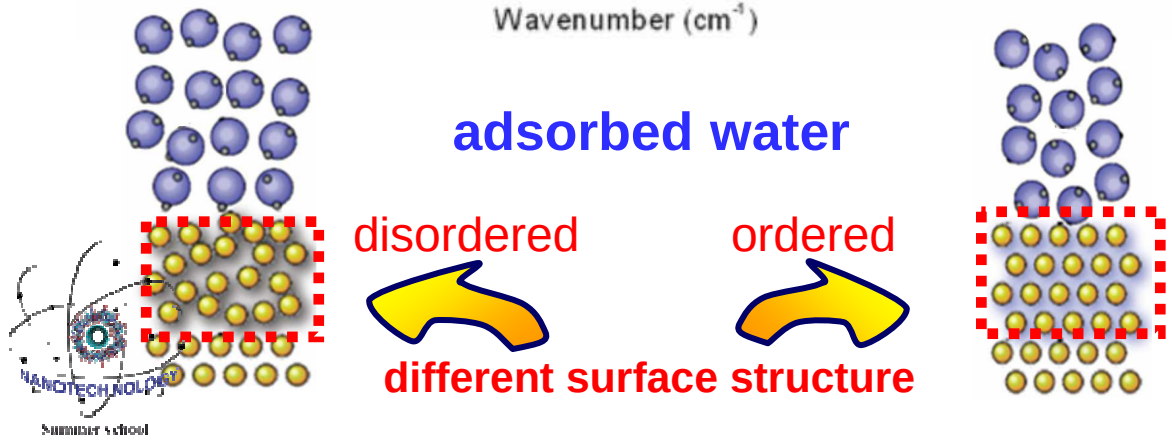
- **parallel microgravimetric experiments: number of H_2O molecules adsorbed;**
- **measure of the SSA (m^2/g); estimation of number Ca^{2+} ions/nm^2**

intensity IR H_2O bands number of H_2O/nm^2

Water at the surface of HA-am and HA-Cry: structural insights



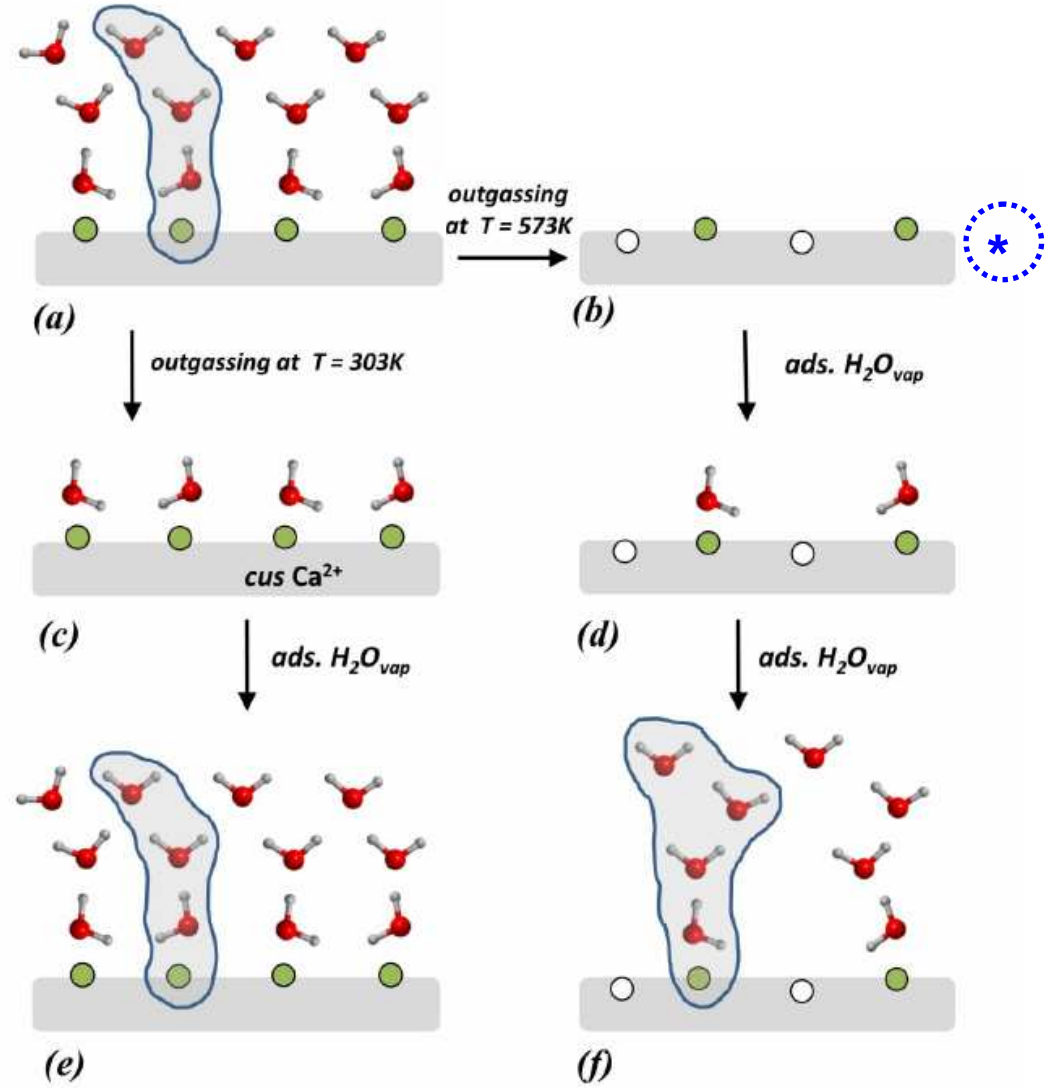
	HA-am		HA-cry	
	$\Delta\nu(H_2O)$	FWHM $\nu(H_2O)$	$\Delta\nu(H_2O)$	FWHM $\nu(H_2O)$
Liquid water	0	400	0	400
4th layer	0	580	0	400
3rd layer	120	650	0	500
2nd layer	250	720	200	680
1st layer	300	780	280	760



- **No differences** for the first hydration layer (H_2O molecules in direct interaction with surface cations);
- **Significant differences** in the structure of water overlayers (up to 4 water layers).

V. Bolis, Y. Sakhno et al.,

Water molecules on hydroxyapatite

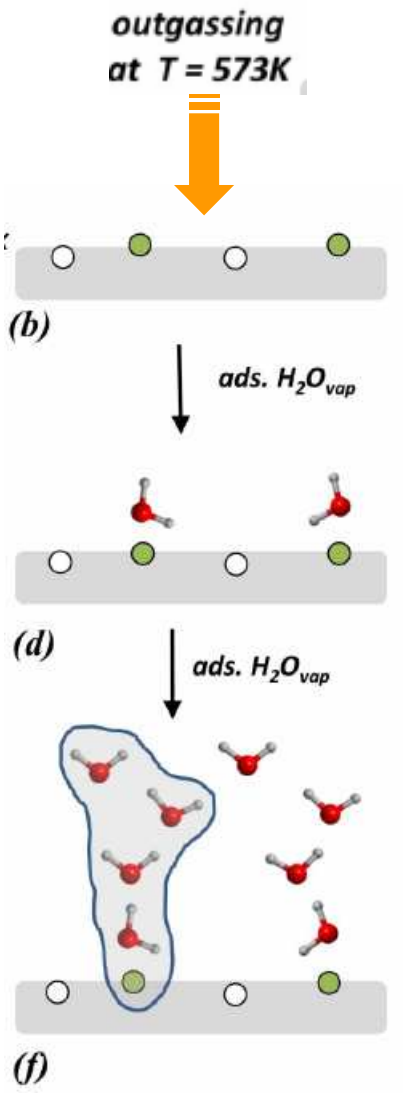


* Surface Hydration and Cationic Sites of Nanohydroxyapatites with Amorphous or Crystalline Surfaces: A Comparative Study

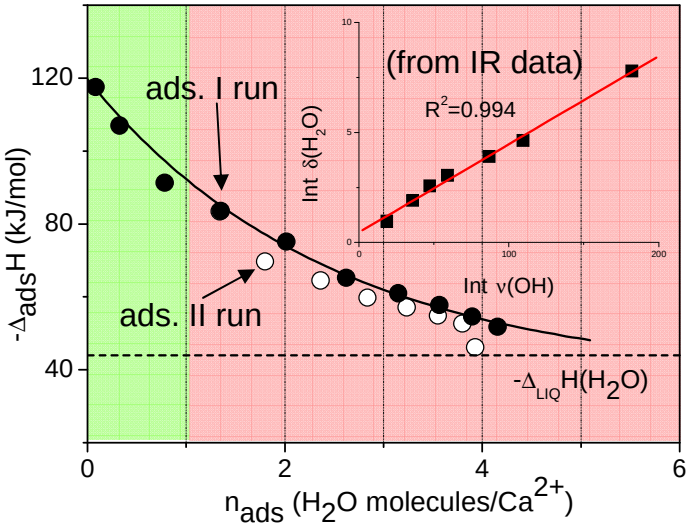
Yuriy Sakhno,[†] Luca Bertinetti,[†] Michele Iafisco,[‡,§] Anna Tampieri,[∥] Norberto Roveri,[‡] and Gianmario Martra*[,†]

J. Phys. Chem. C **2010**, *114*, 16640–16648

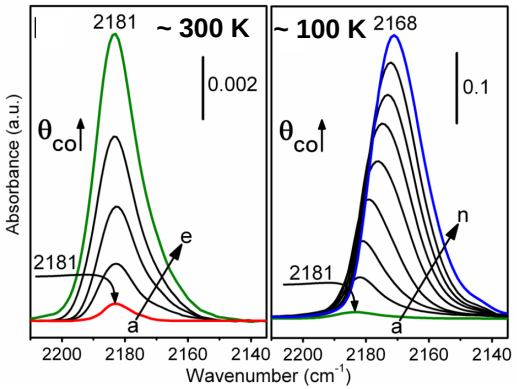
Water molecules on hydroxyapatite: energetic & structural features



H_2O on HA:
enthalpy of adsorption



IR of adsorbed CO



ΔnCO= 42 cm^{-1}; $-\Delta_{ads}$ H ~ 45 kJ/mol

Ca^{2+}_{cus}: moderate Lewis acid strength

strong H_2O – Ca^{2+}_{cus} interaction

strong H_2O – H_2O interaction

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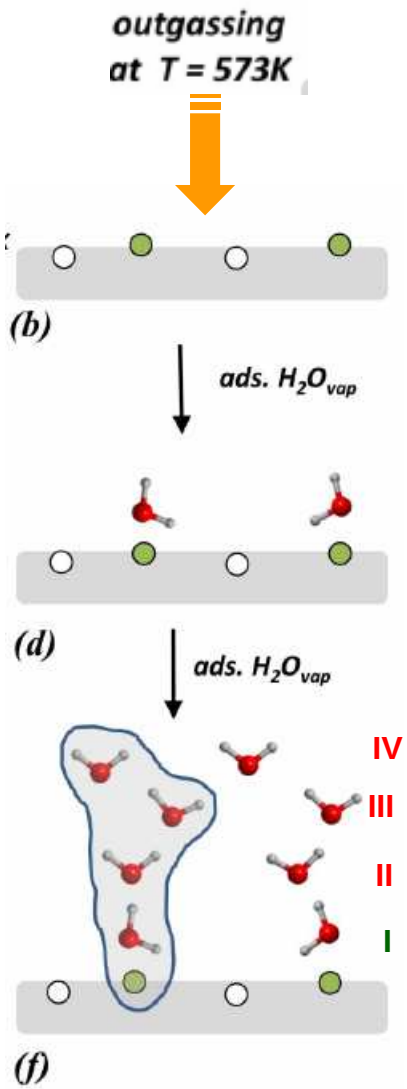
Water molecules on hydroxyapatite: energetic & structural features



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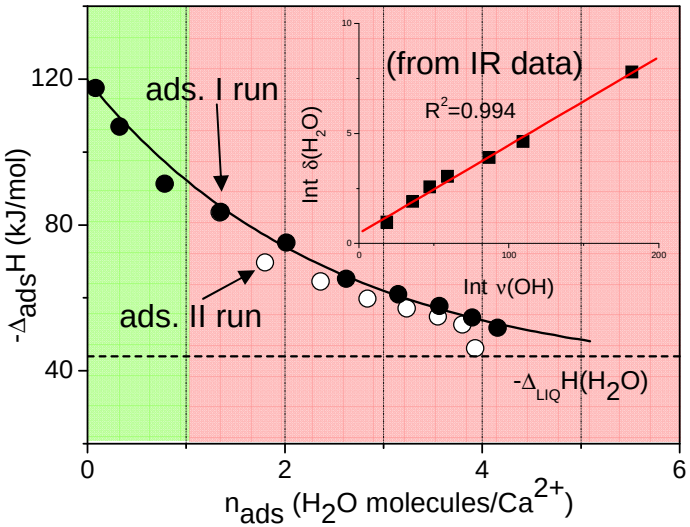

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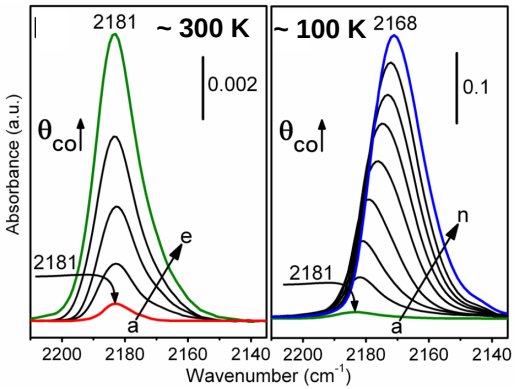

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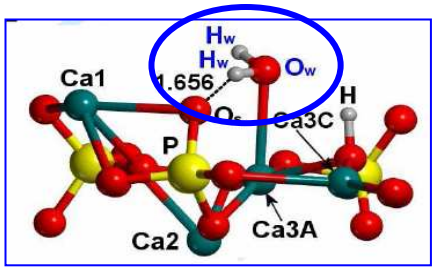
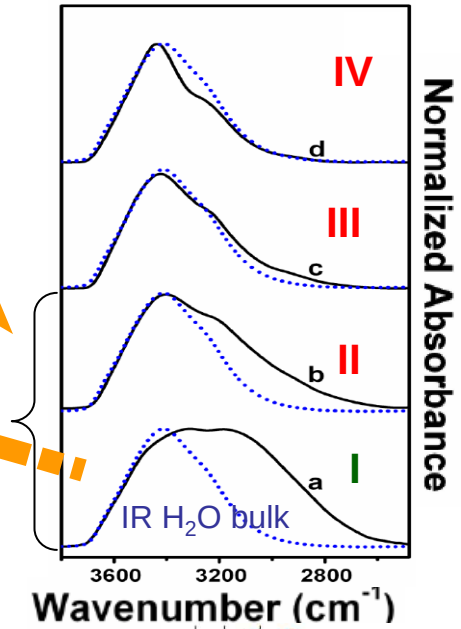


H_2O on HA: IR



Coordination chemistry of Ca sites at the surface of nanosized hydroxyapatite: interaction with H_2O and CO

Vera Bolis,[a] Claudia Busco,[a] Gianmario Martra,[b] Luca Bertinetti,[b] Yuriy Sakhno,[b] Piero Ugliengo,[b] Fabio Chiatti,[b] Marta Corno,[b] Norberto Roveri.[c]

Phil. Trans. R. Soc. A, 370 (2012) 1313-1336

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heavy (QM)

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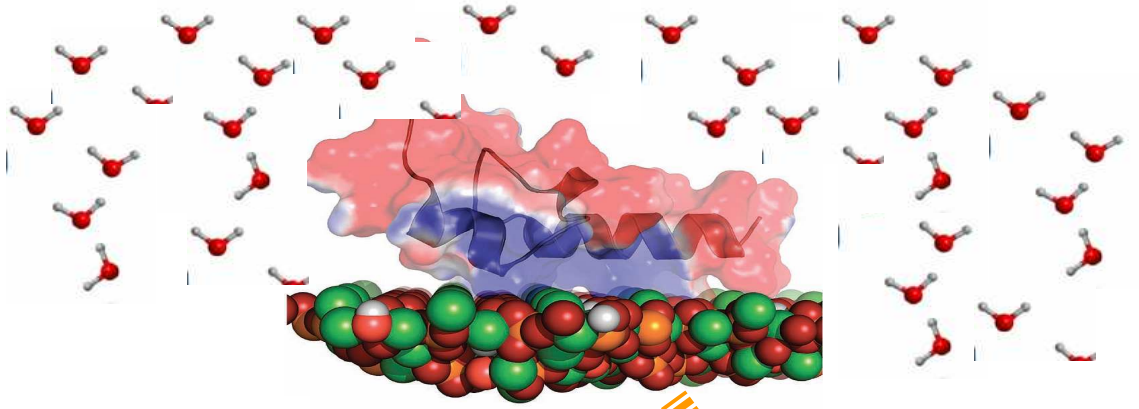
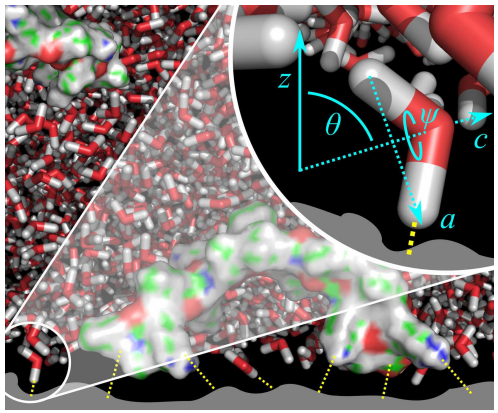
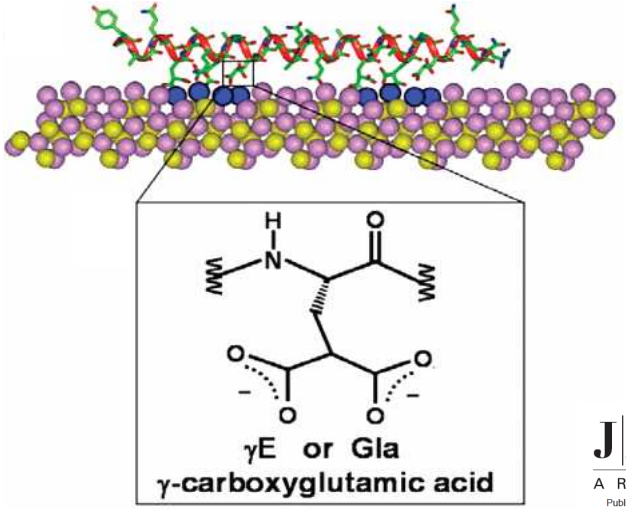


biomaterial/water



biomaterial/biomolecules (small)



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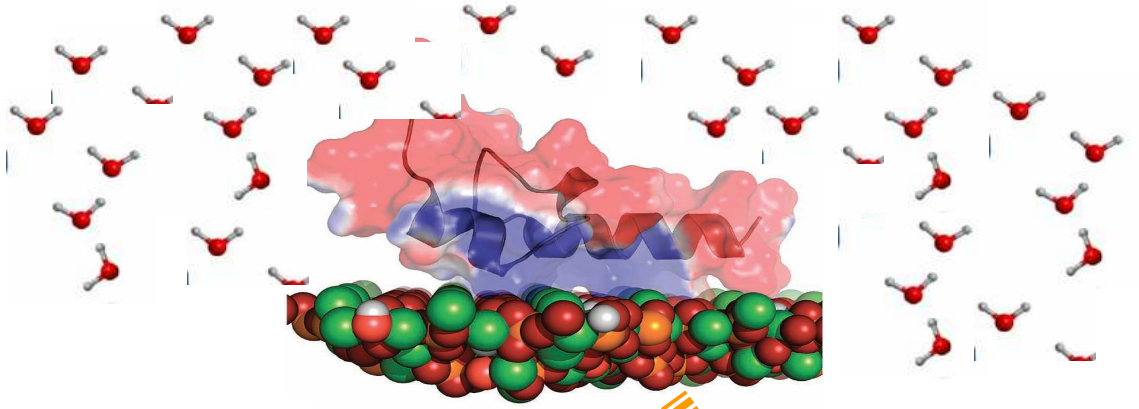

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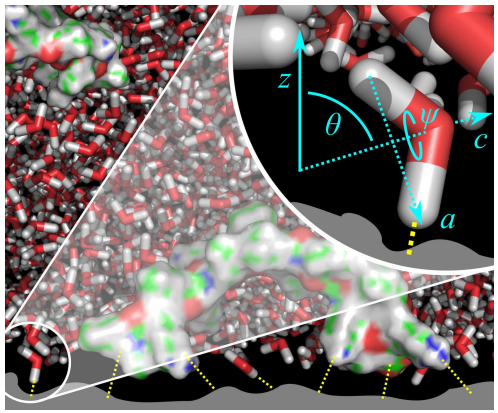

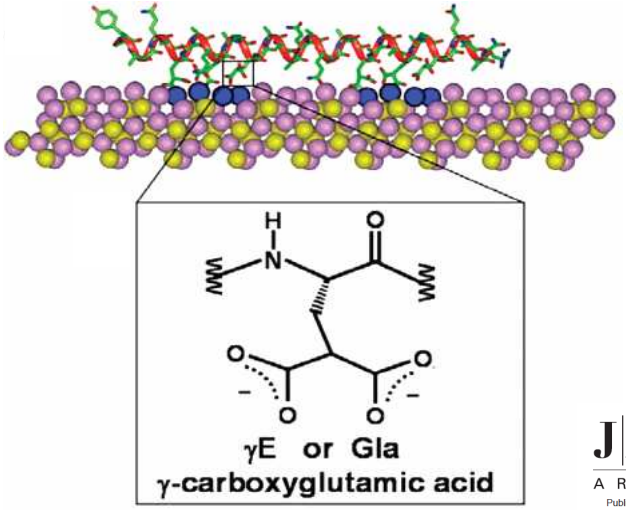

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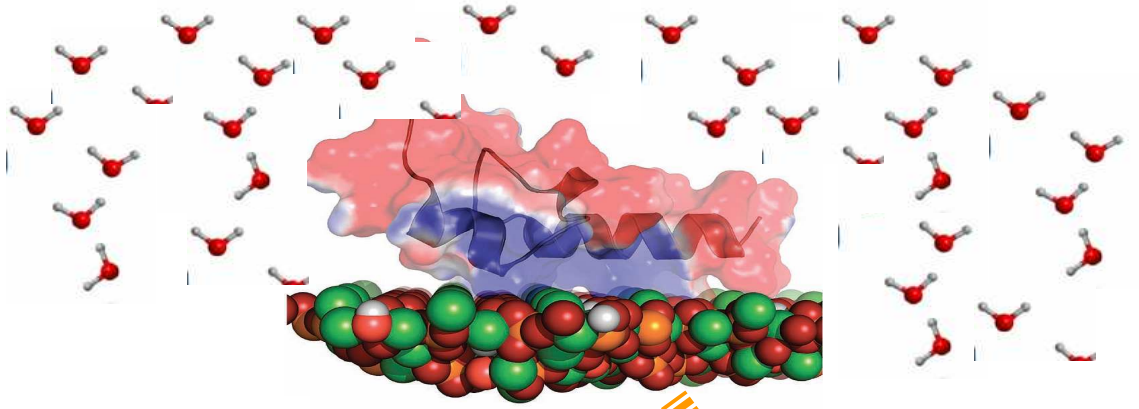

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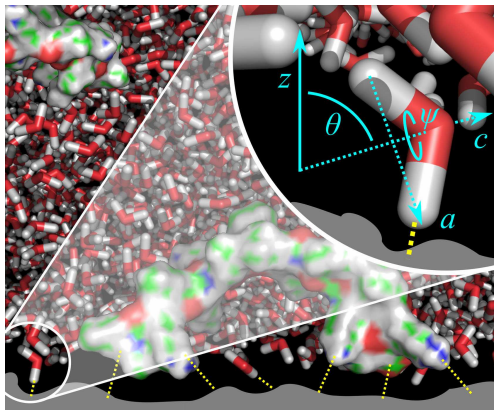

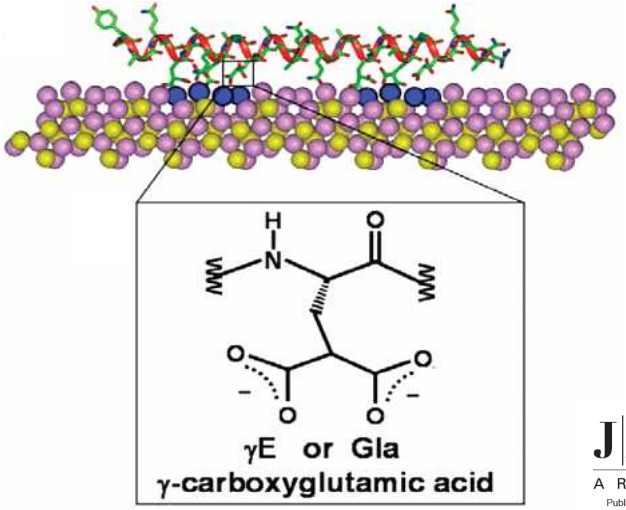

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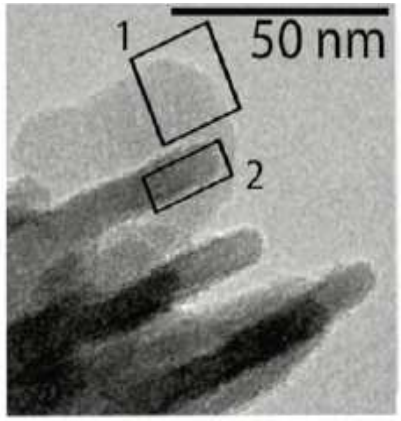
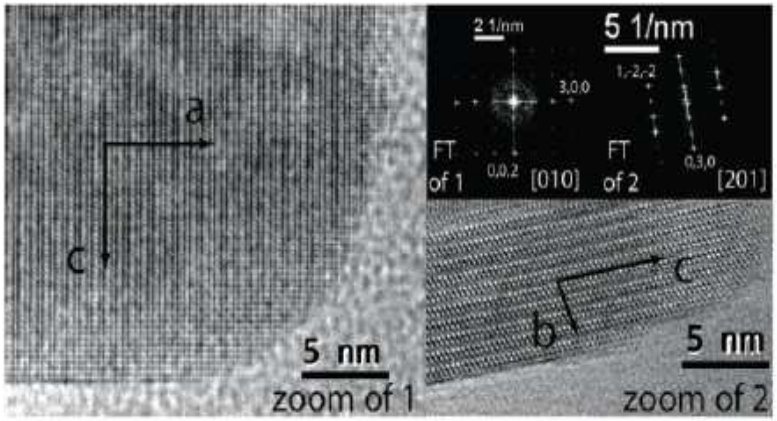
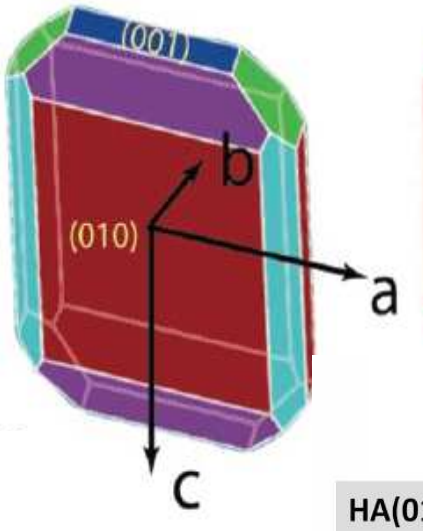
Material: nano-HA with well defined surfaces

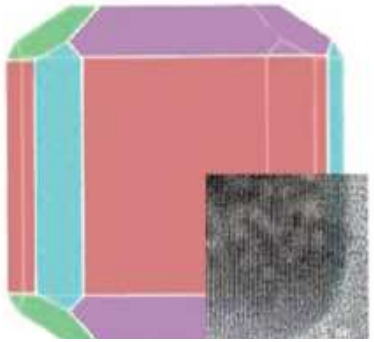
surface structure: experiments & modeling

(Prof. P. Ugliengo)



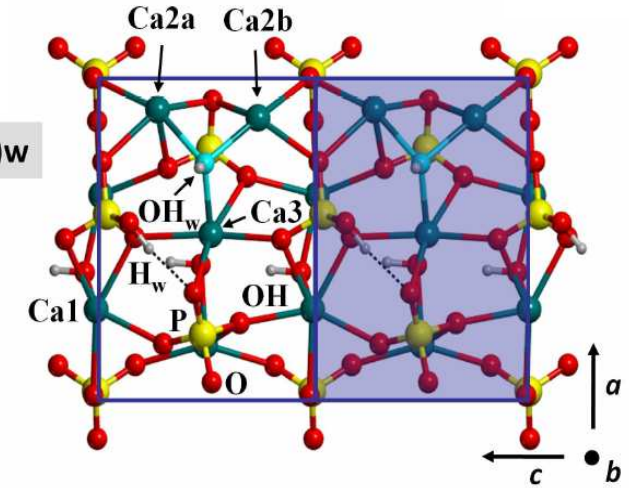




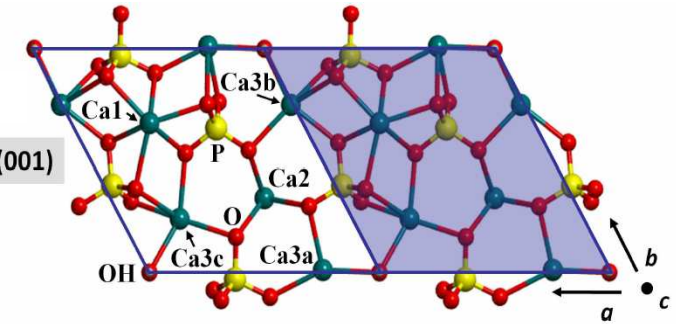


B3LYP/6-31G(d,p)
with CRYSTAL06 code

HA(010)w



HA(001)



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nis Università di Torino

Gly on HA: a step toward a surface science model for biology

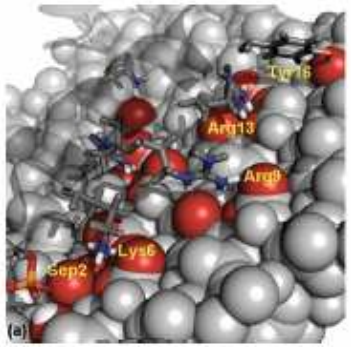
state-of-the-art

JACS ARTICLES

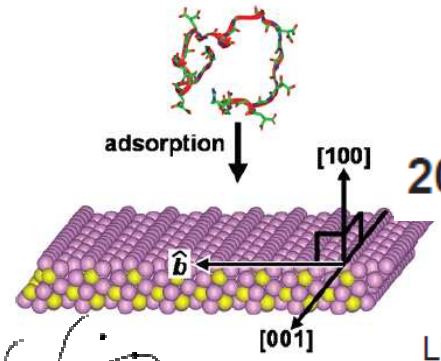
. **2007**, *129*, 13713−13722

Structure Prediction of Protein−Solid Surface Interactions Reveals a Molecular Recognition Motif of Statherin for Hydroxyapatite

Kosta Makrodimitris,† David L. Masica,‡ Eric T. Kim,§ and Jeffrey J. Gray



- **no identification of experimental surfaces**
- **MM, DM:**
  - **FFs accuracy**
  - **occurrence of chemical reactions?**



2007, *129*, 5281−5287

Hydroxyapatite Surface-Induced Peptide Folding

Lisa A. Capriotti, Thomas P. Beebe, Jr., and Joel P. Schneider*

our targets

1) **nano HA with defined surfaces**
2) **adsoprtion of biomolecules in highly controlled conditions**
3) **in-situ spectroscopy (IR)**
4) **first principle QM**

simple biomolecule: glycine

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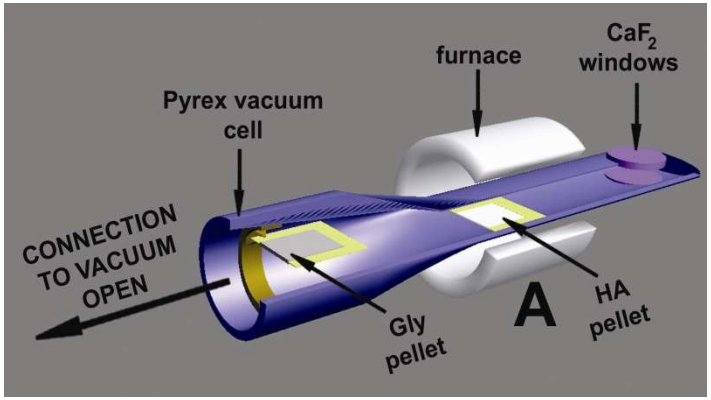
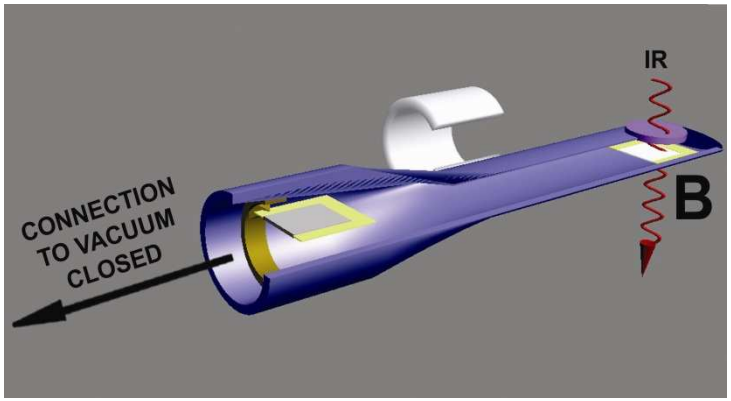
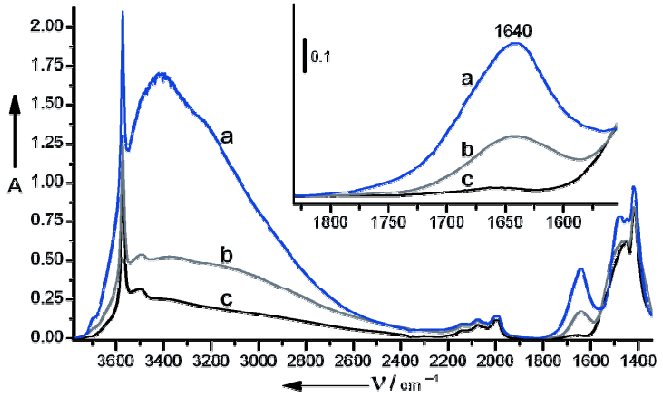
Glycine adsorption in controlled and model conditions

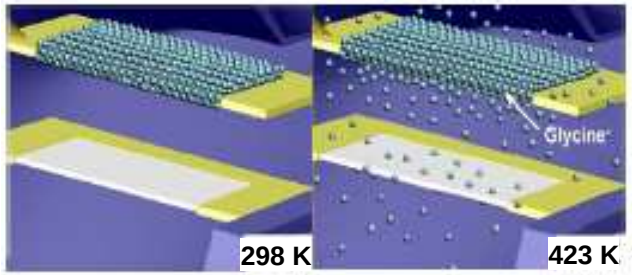


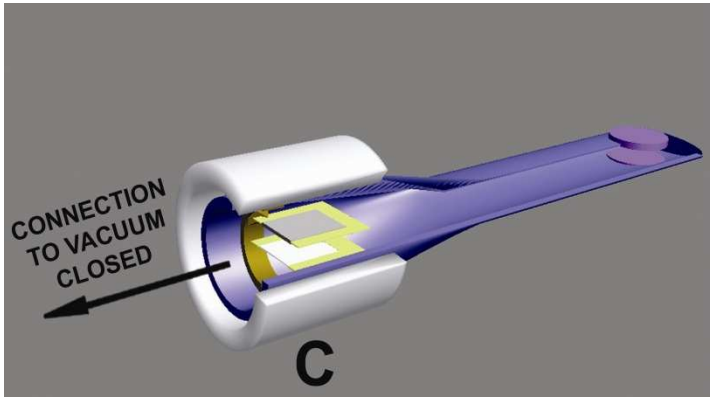
HA outg. at r.t. : ca 4.0 H_2O nm^{-2}
0.5 OH nm^2

HA outg. At 150 ℃. : ca 0.6 H_2O nm^{-2}
0.5 OH nm^2









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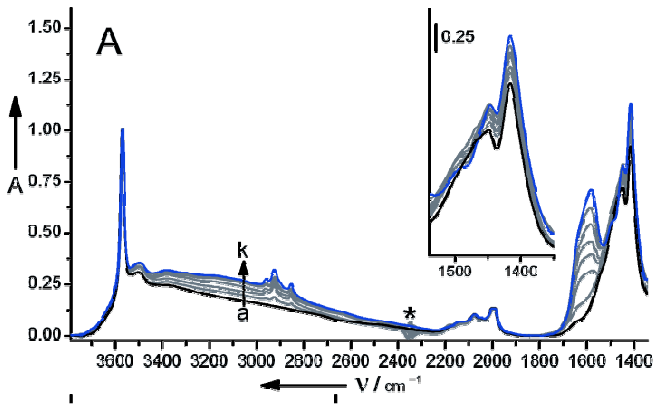
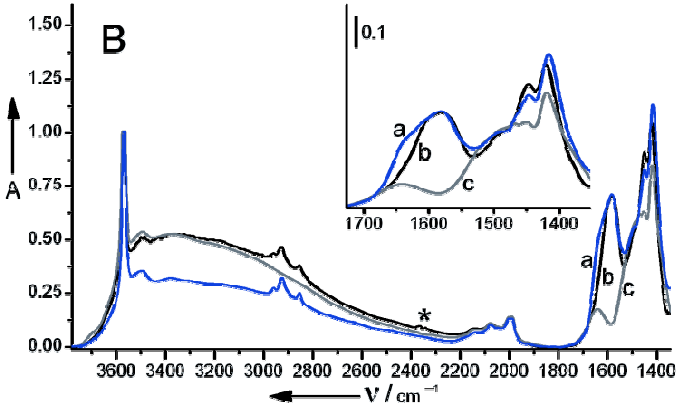
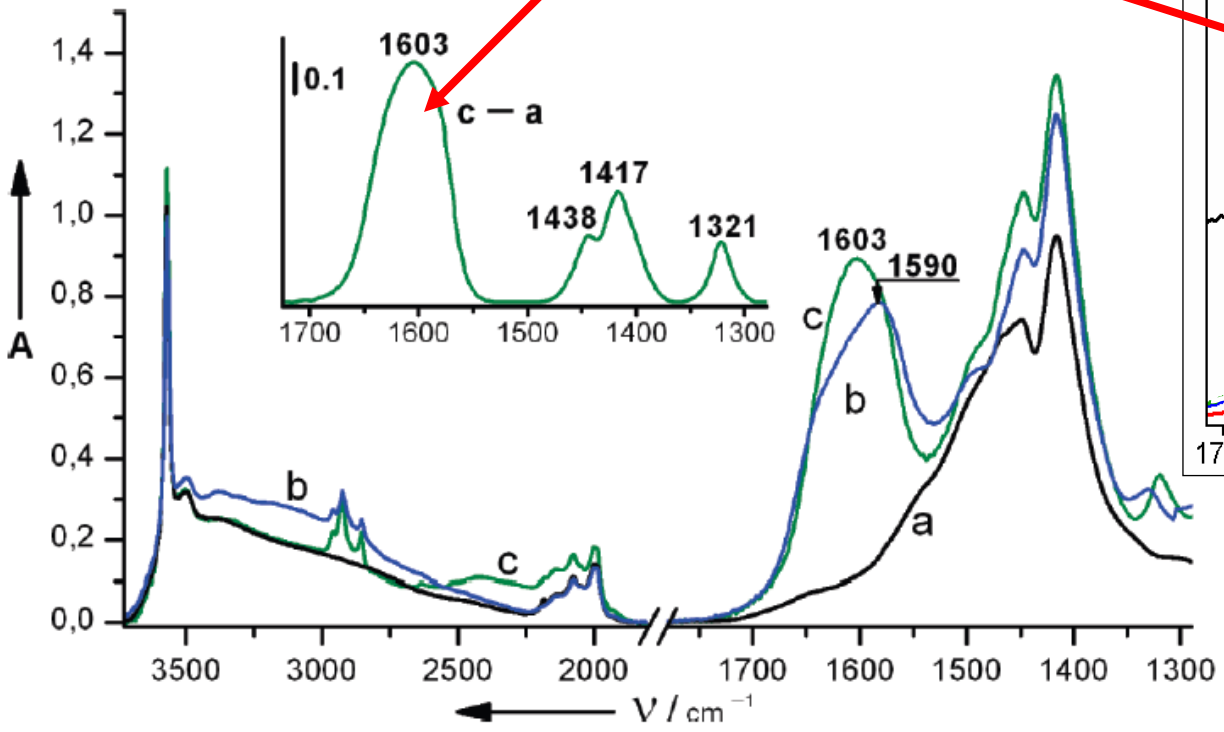
Glycine adsorption in controlled and model conditions

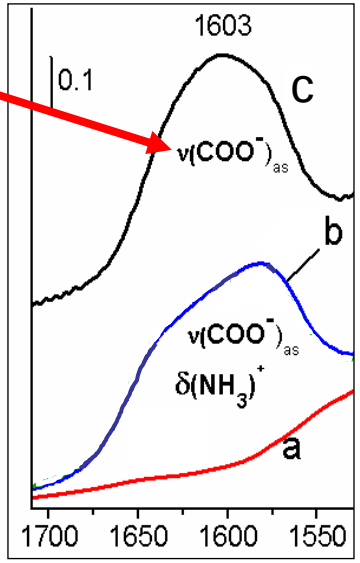


- step-wise adsorption procedure
- control of the adsorbed amount



more than 1 component

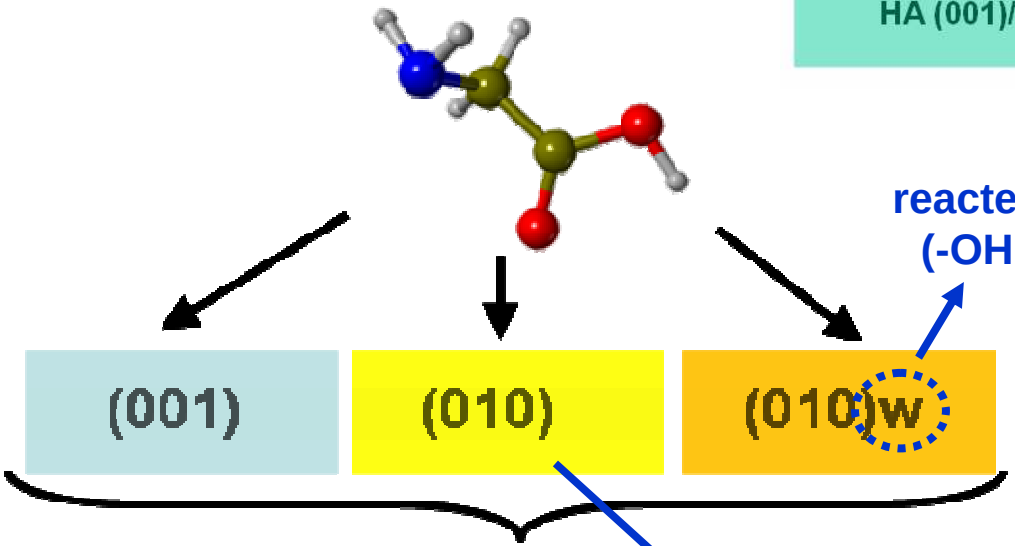




Chemisorption of Gly on HA: QM calculations

B3LYP/6-31G(d,p)

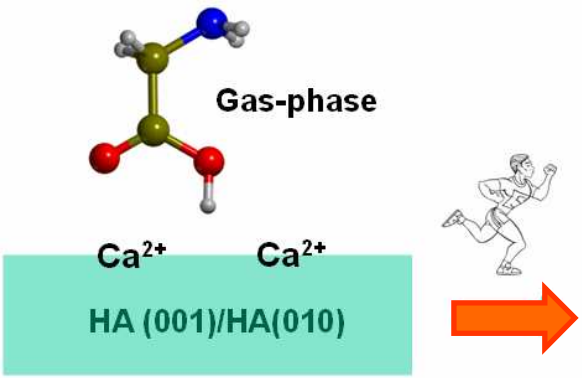
CRYSTAL09

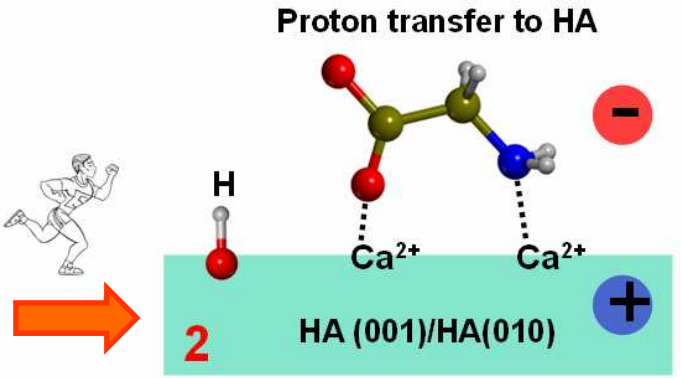


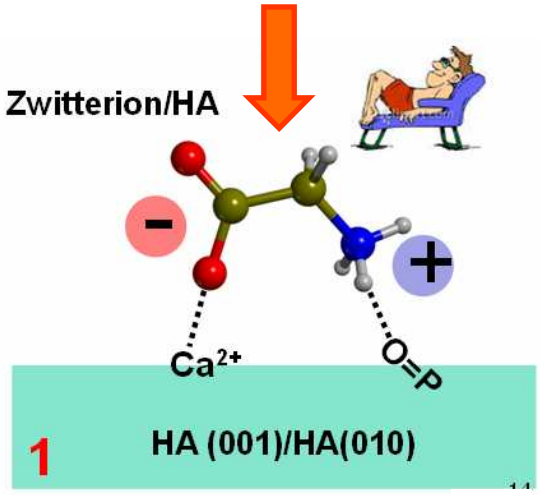
reacted with water
(-OH formation)

+ co-adsorbed H_2O (W)

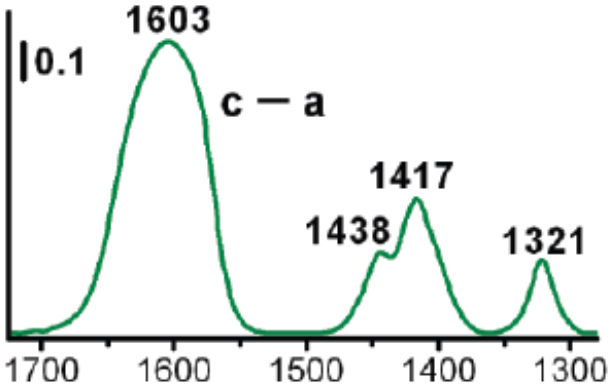
for each adduct:
optimum structure
IR spectrum



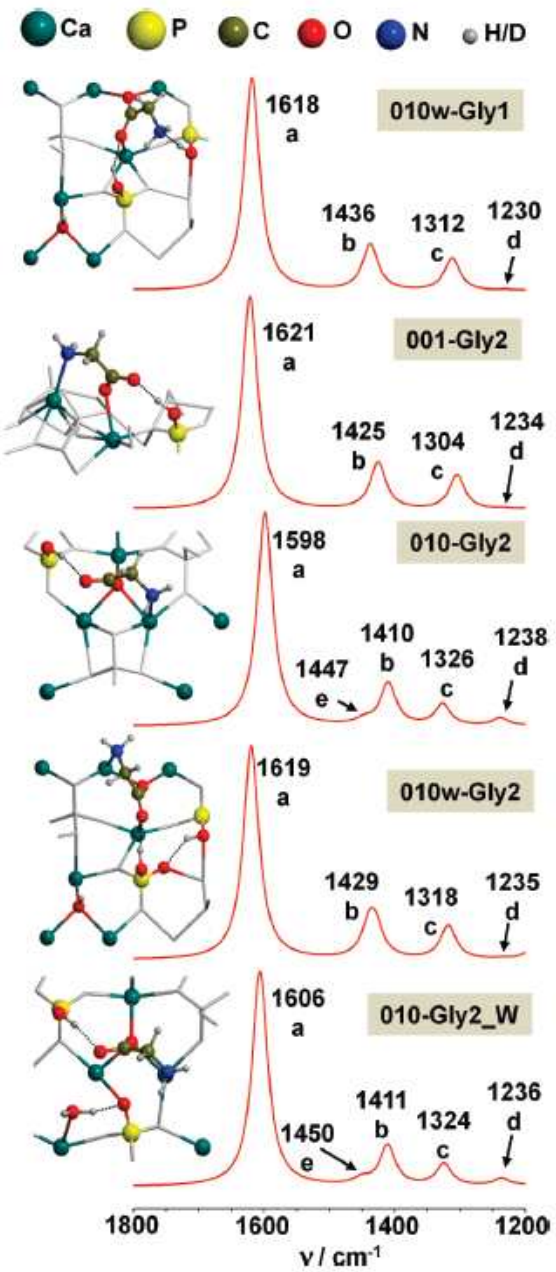




Exp & Calc IR spectra: selection of structures



how many spectral combinations?



Assignments

a: $\nu(COO^-)a$

b: $\nu(COO^-)s + \delta(CCH)$

c: $\nu(COO^-)s + \delta(CCH)$

d: $\gamma(CH_2)$

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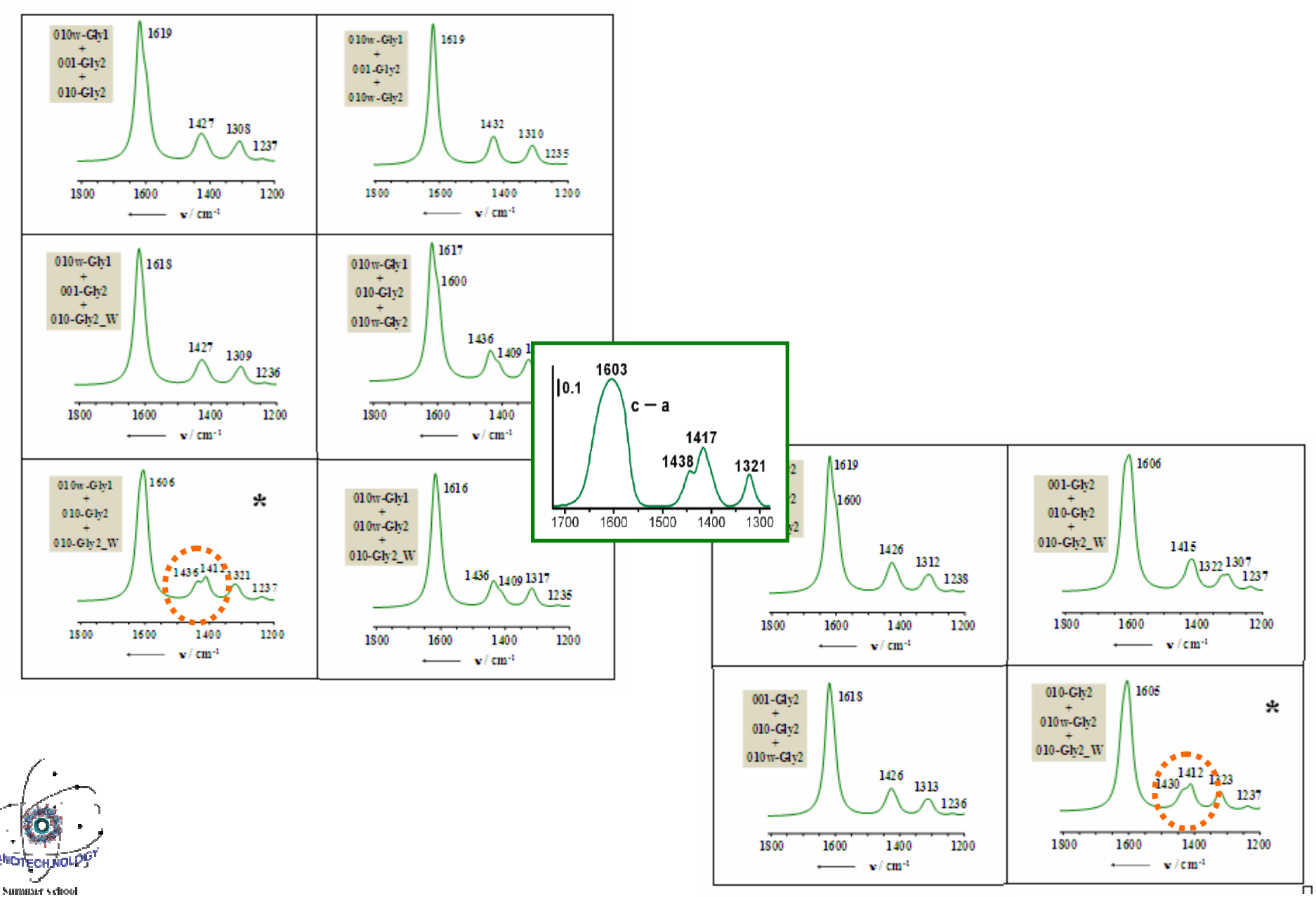
Exp & Calc IR spectra: combination of structures



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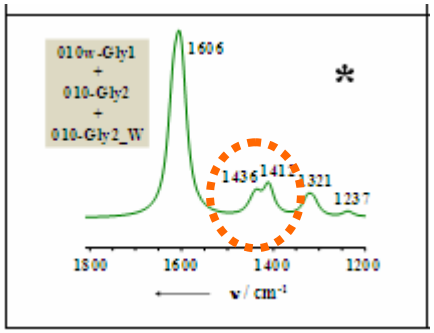
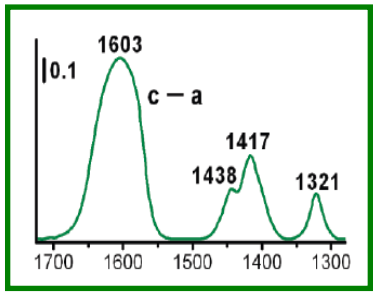
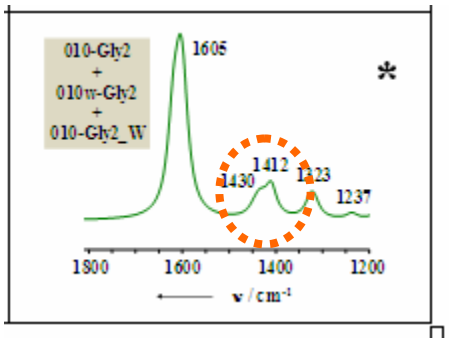
Exp & Calc IR spectra: combination of structures







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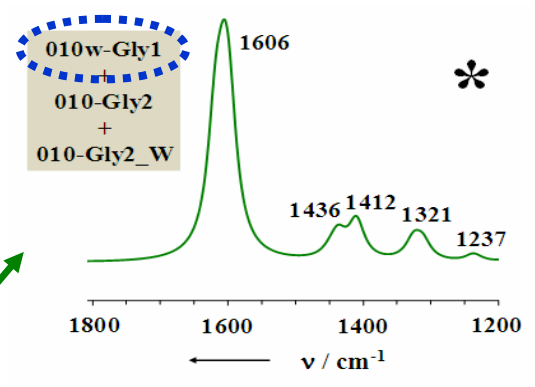
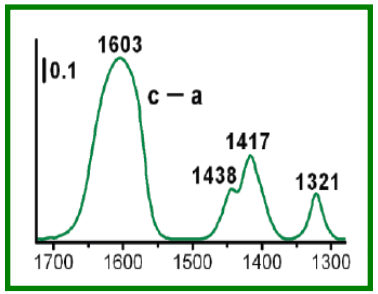
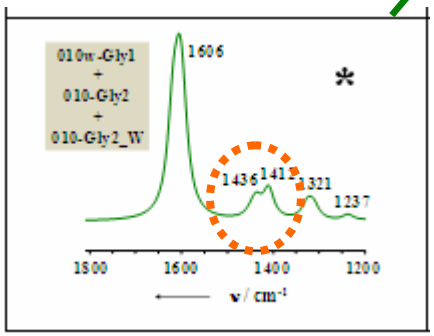
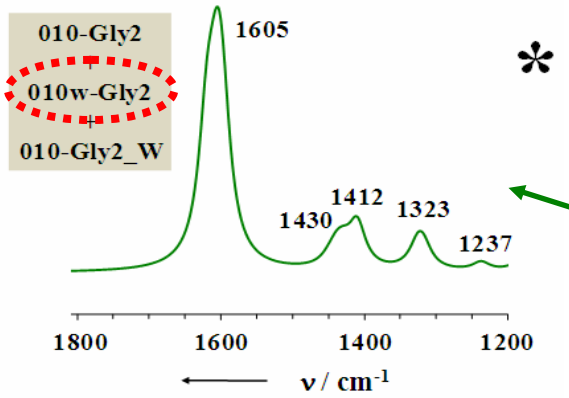
Exp & Calc IR spectra: combination of structures



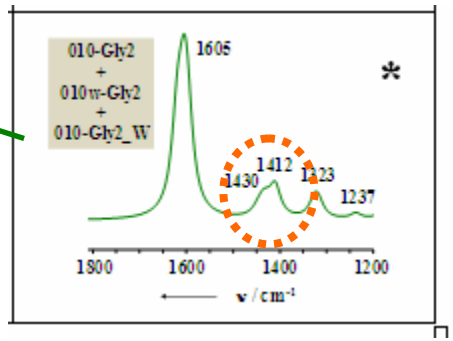






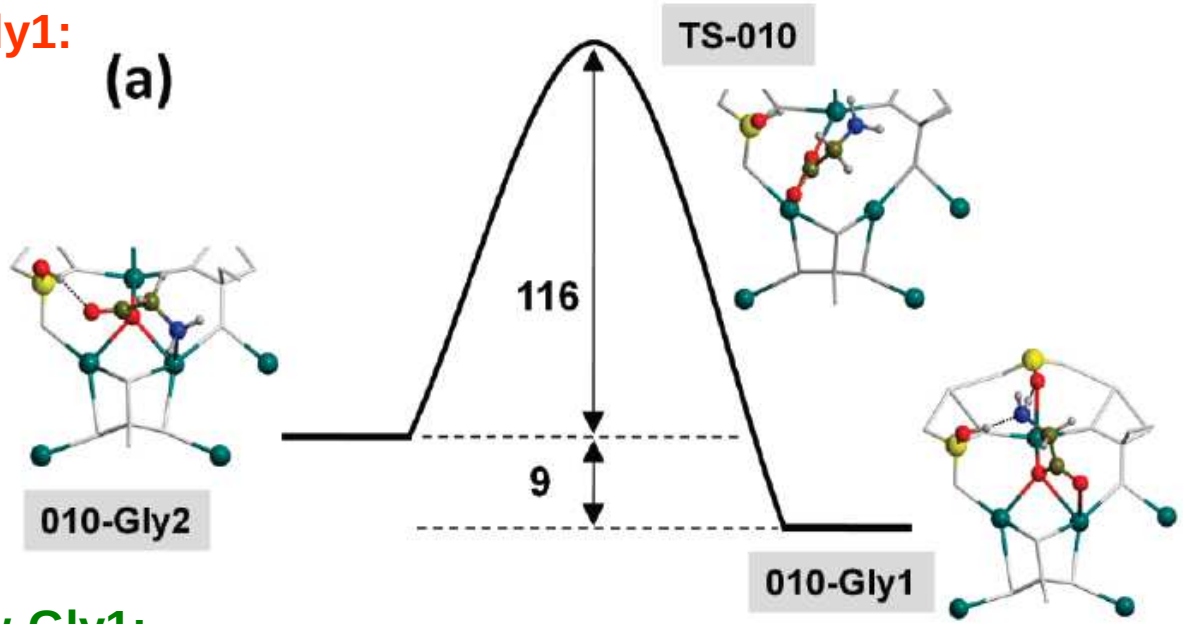
010w-Gly1 vs 010w-Gly2

energetic features

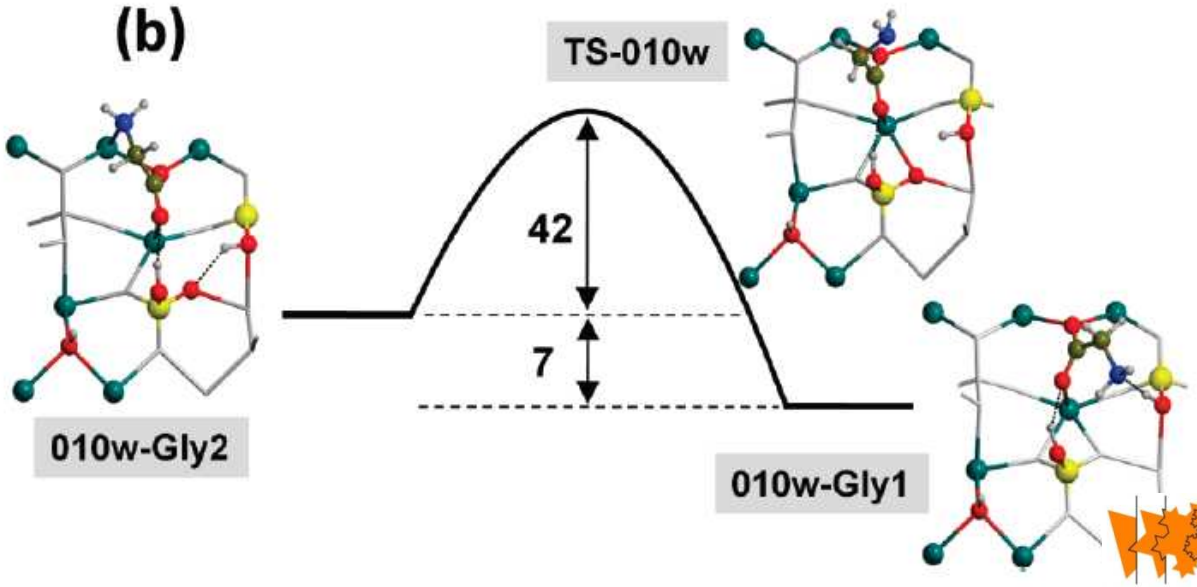


PES of alternative structures

010-Gly2 → 010-Gly1: breaking of COO^-••• D-OP Ca ••• N



010w-Gly2 → 010w-Gly1: breaking of Ca ••• N



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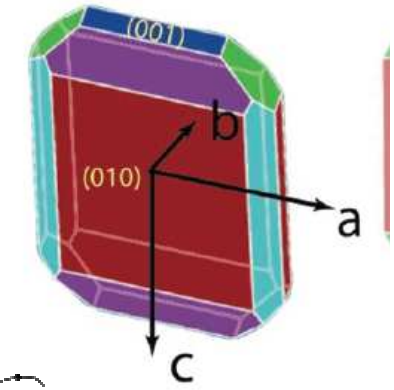
Recognition of components in the Exp spectrum

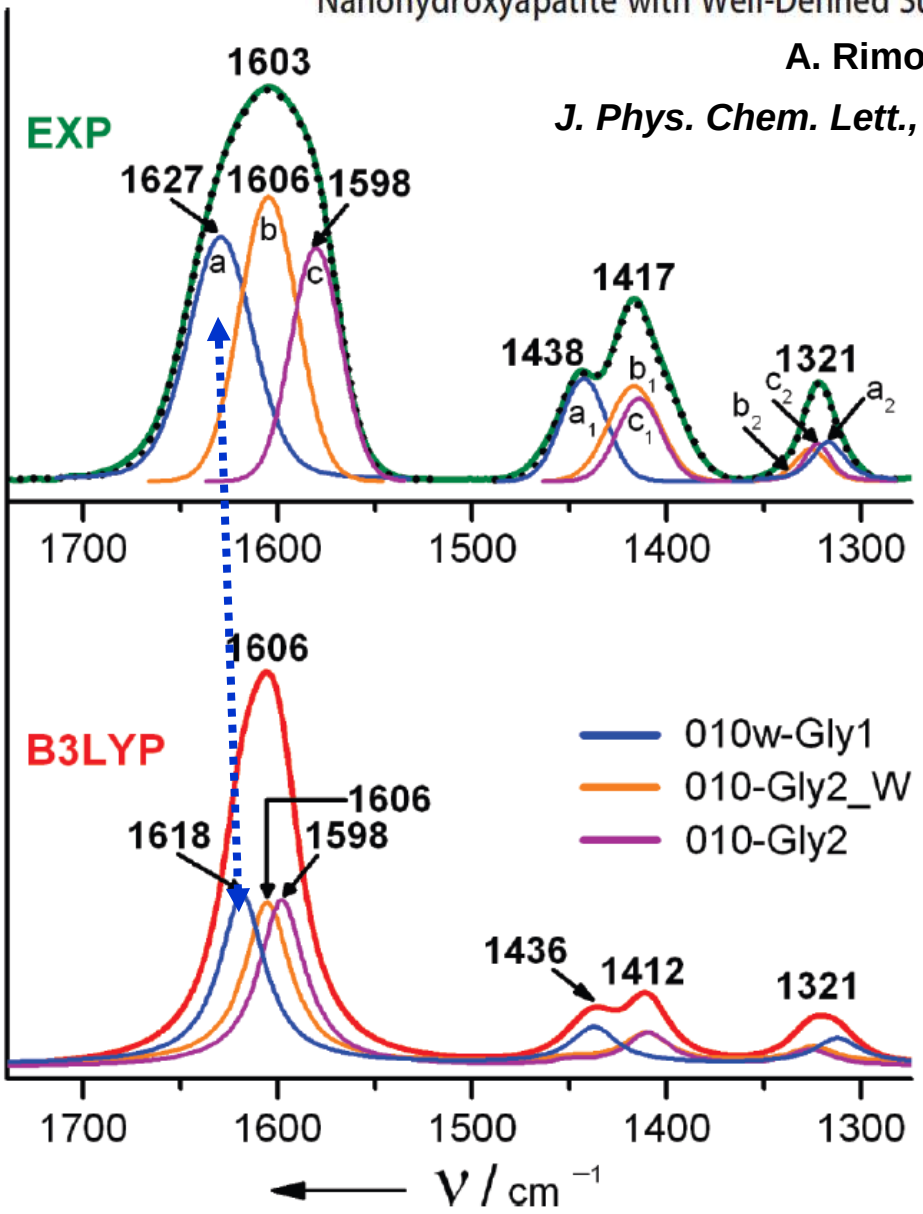
Toward a Surface Science Model for Biology: Glycine Adsorption on Nanohydroxyapatite with Well-Defined Surfaces

A. Rimola, Y. Sakhno et al.

J. Phys. Chem. Lett., 2 (2011) 1390-1394

+ minor contributions from other species on less abundant different terminations





Conclusions on Gly on HA

well-shaped nano-HA

in situ IR

QM

precise description of the Gly-surface interaction

selected, simplified, model conditions

extension to more complex systems:
- other aminoacids
- oligopeptides
- water

General conclusion

A precise investigation of surface sites and of their interaction with molecules is a puzzling task, but it can be achieved

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General conclusion

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➡ ***"God made the bulk,***
the surface,
and populated the surface"
(adapted from Genesys)

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General conclusion

A precise investigation of surface sites and of their interaction with molecules is a puzzling task, but it can be achieved

➡ ***"God made the bulk; the surface was invented by the devil"***
(attributed to Wolfgang Pauli)

…but molecules & spectroscopy can help
surface chemists to enjoy life

➡ ***"God made the bulk,***
the surface,
and populated the surface"
(adapted from Genesys)

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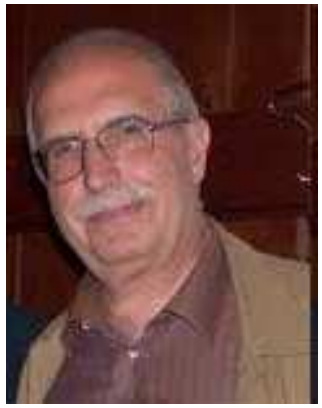
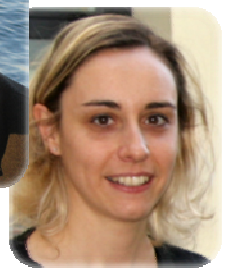
Acknowledgments



S. Coluccia
(mentor)

Y. Sakhno

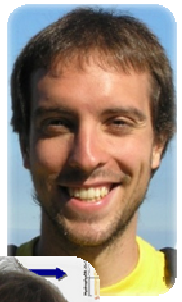
V. Bolis



C. Busco
(*Univ. Piemonte Orientale*)
calorimetry

modeling

P. Ugliengo



A. Rimola

M. Corno

L. Bertinetti