Gaining insights into different bioactivity mechanisms by DFT modeling of *soda-lime phospho-silicate* glasses

Enrico Berardo

NIS COLLOQUIUM, TORINO, 28-29 NOVEMBER 2013

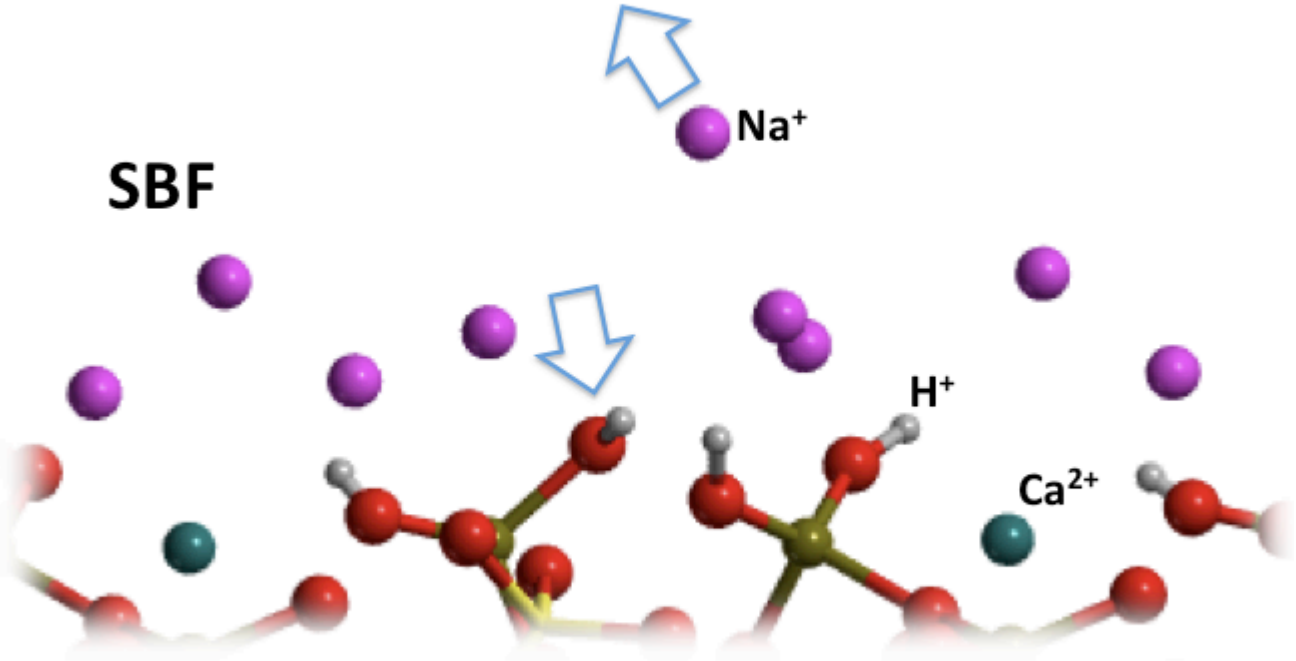
BIOACTIVE GLASSES

SiO_2 46% Na_2O 24.4% CaO 26.9% P_2O_5 2.5%

45S5 ®BIOGLASS

Prof. Larry Hench

1969



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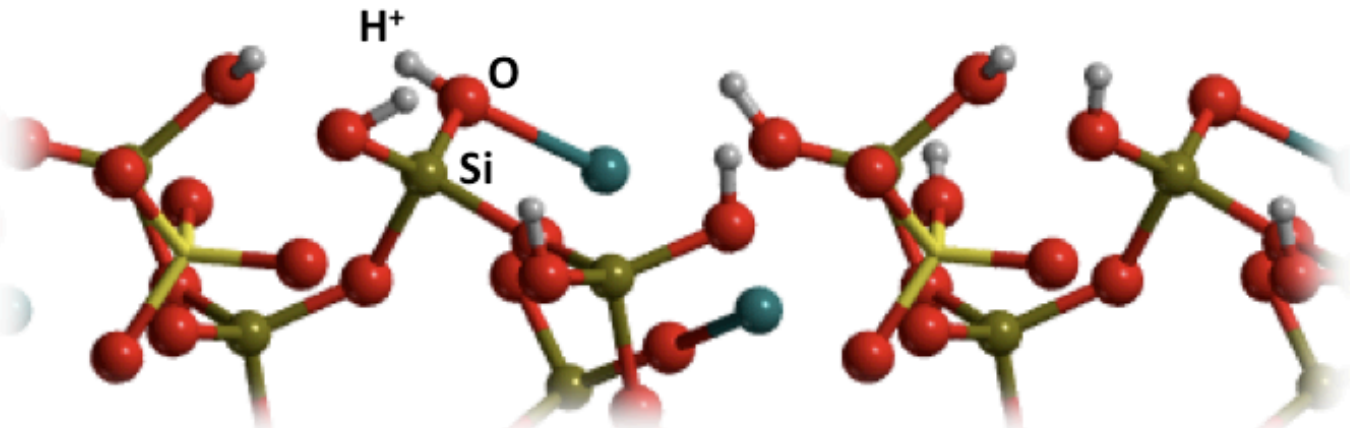
SBF



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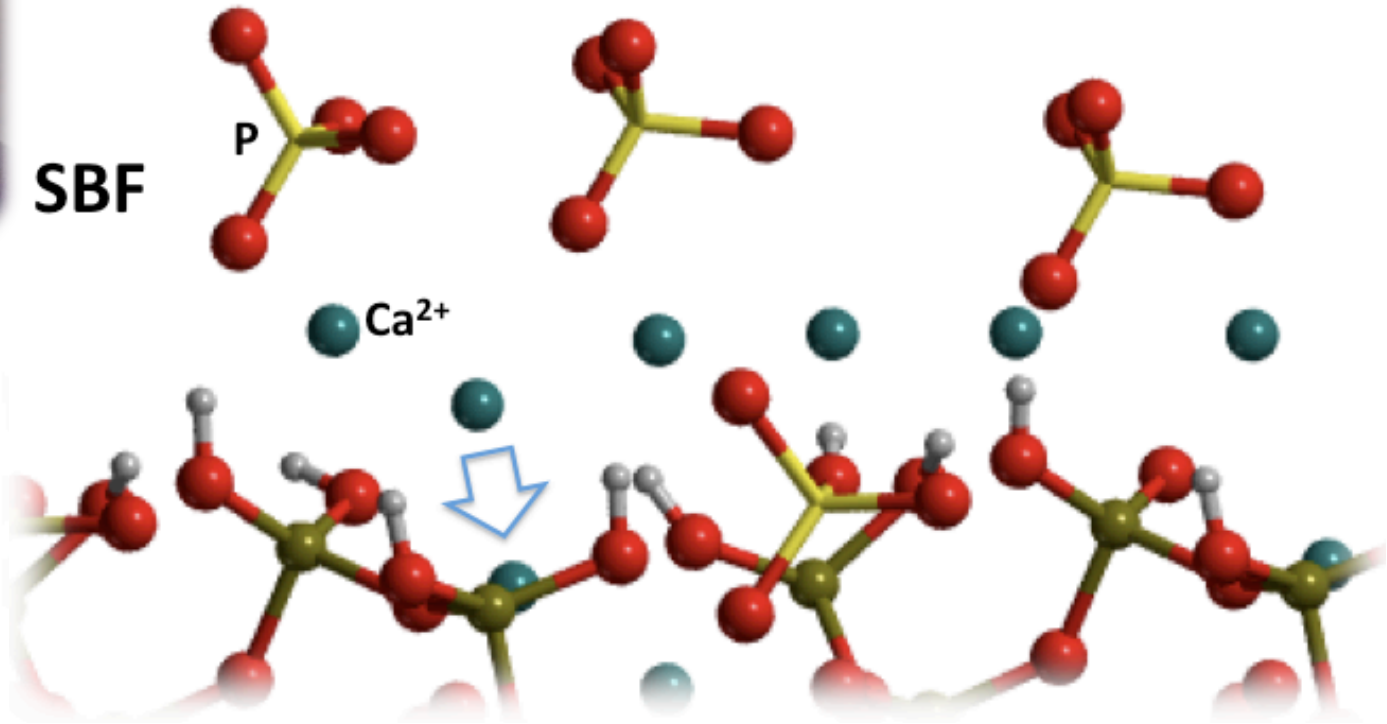
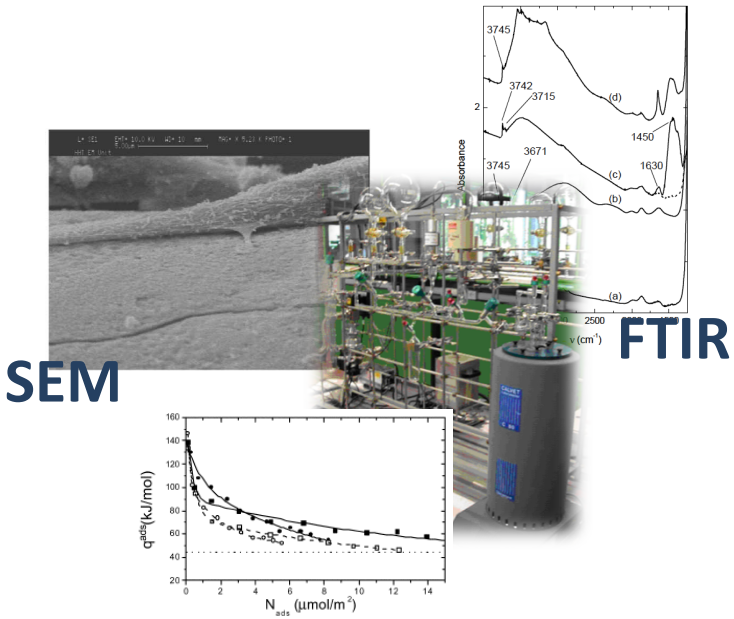


Open questions



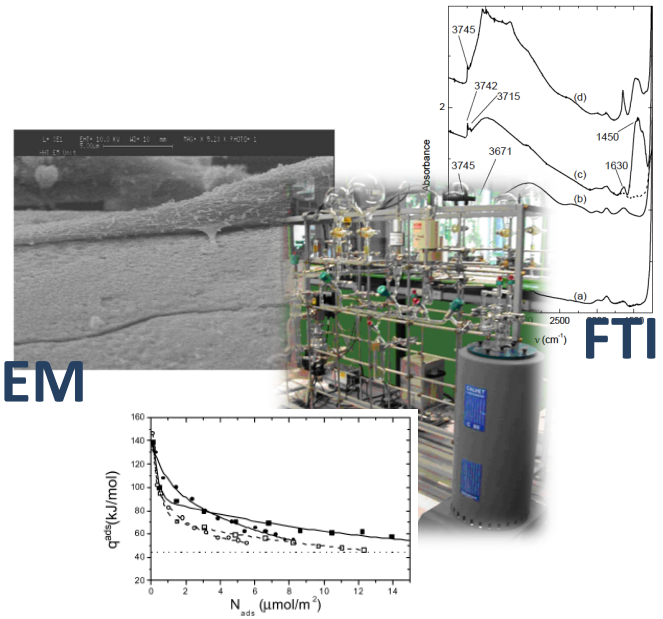
FTIR

SEM

Micro-calorimetry

- What is the role of Na^+ ions
- How P_2O_5 affects bioactivity
- First steps of Hench's mechanism

Open questions



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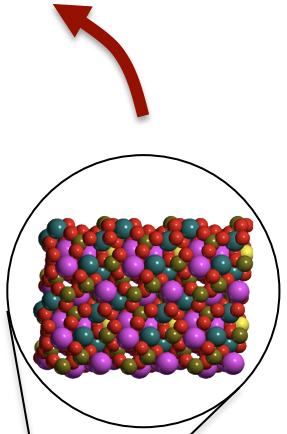
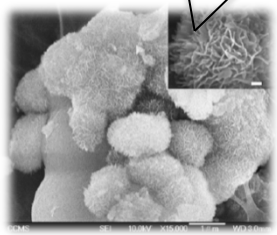


MOLECULAR MODELLING

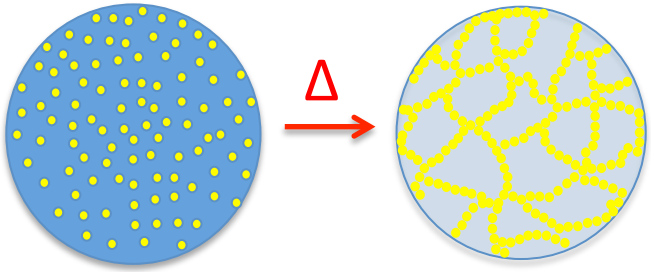


What is the origin of the bioactivity?

BIOACTIVITY

Melt-Quench

SOL-GEL



45S5		77S
46%	SiO_2	80%
27%	CaO	16%
2.6%	P_2O_5	4%
24%	NaO	--

Multilevel **MM/QM** approach for bioglasses

- **Amorphous**
- **Unknown structure**

ATOMS with **RANDOM** positions in **UNIT CELL**, to reproduce the **CORRECT** glass **COMPOSITION**

Interatomic potentials

Curtin University of Technology GULP

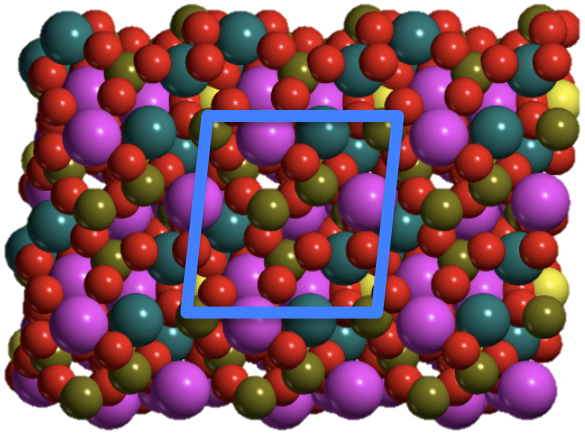
The General Utility Lattice Program, J.D. Gale and A.L. Rohl, *Mol. Simul.*, 29, 291 (2003)

Molecular **D**ynamics are used to **MELT** the system, which is then **COOLED** down in order to simulate a **MELT-QUENCH** process

CRYSTAL a computational tool for solid state chemistry and physics

DENSITY FUNCTIONAL THEORY **(DFT)** – **PBE** XC-potential

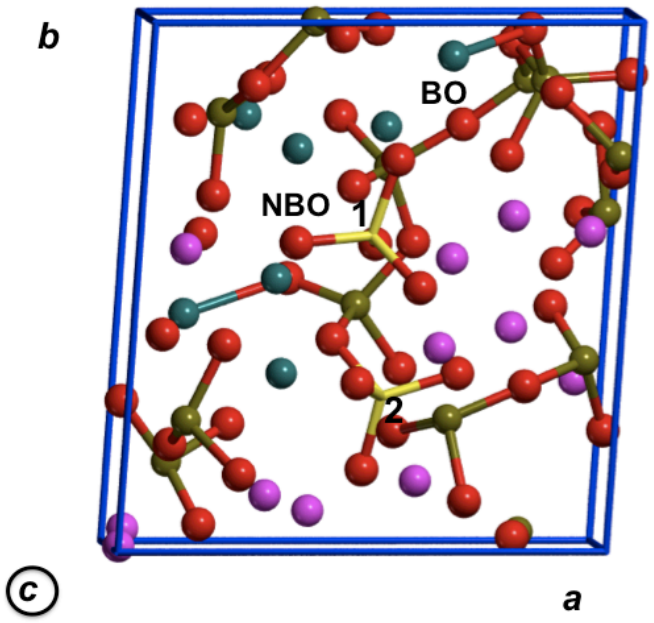
The generated structure is then **RELAXED** through a **Q**uantum **M**echanical approach

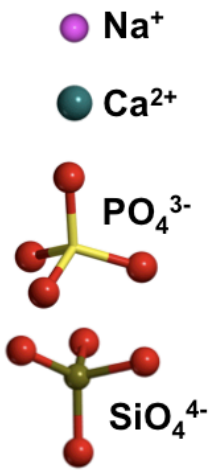


Bulk properties of the two models

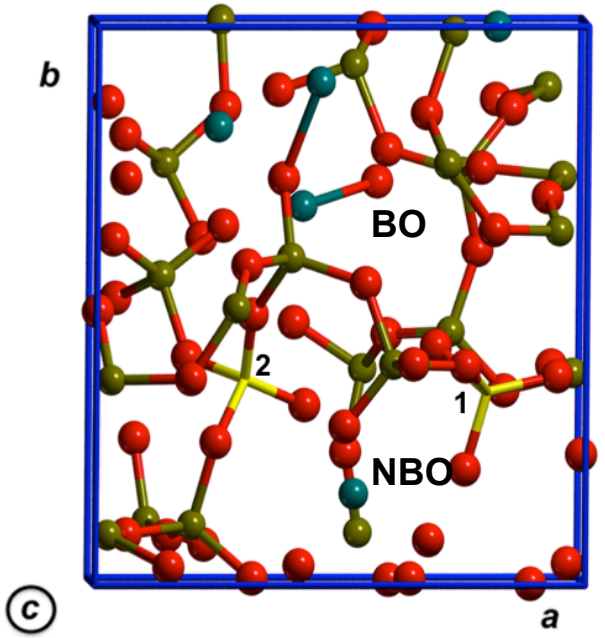
Bioglass	SiO_2	P_2O_5	CaO	Na_2O
45S5	48.1	3.7	22.2	25.9
77S	77.7	3.7	18.5	0

45S5





77S



78 atoms

80 atoms

Bulk properties of the two models

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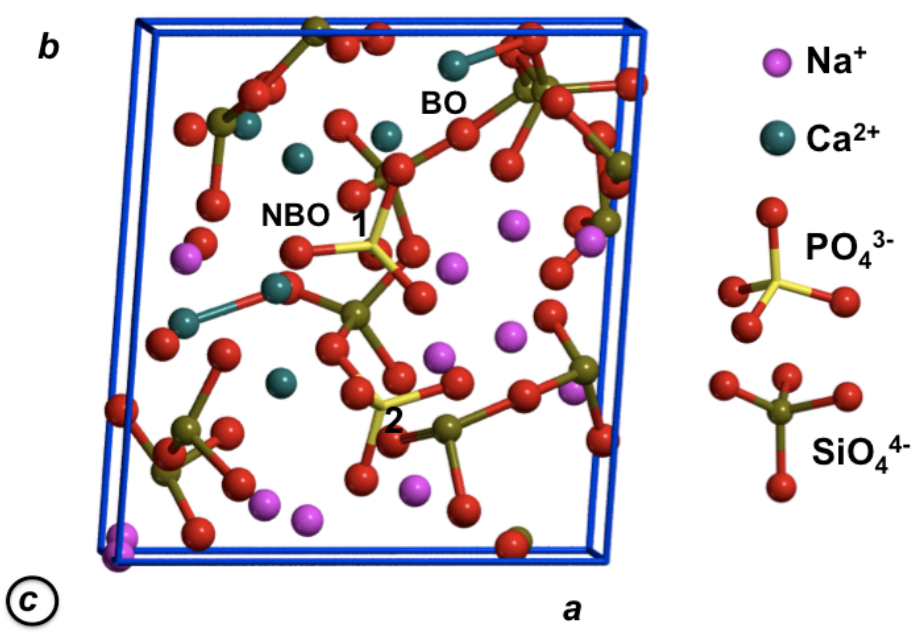
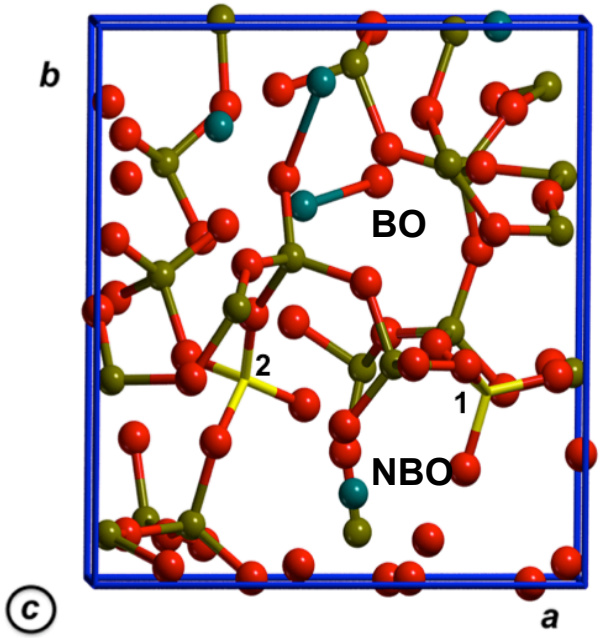


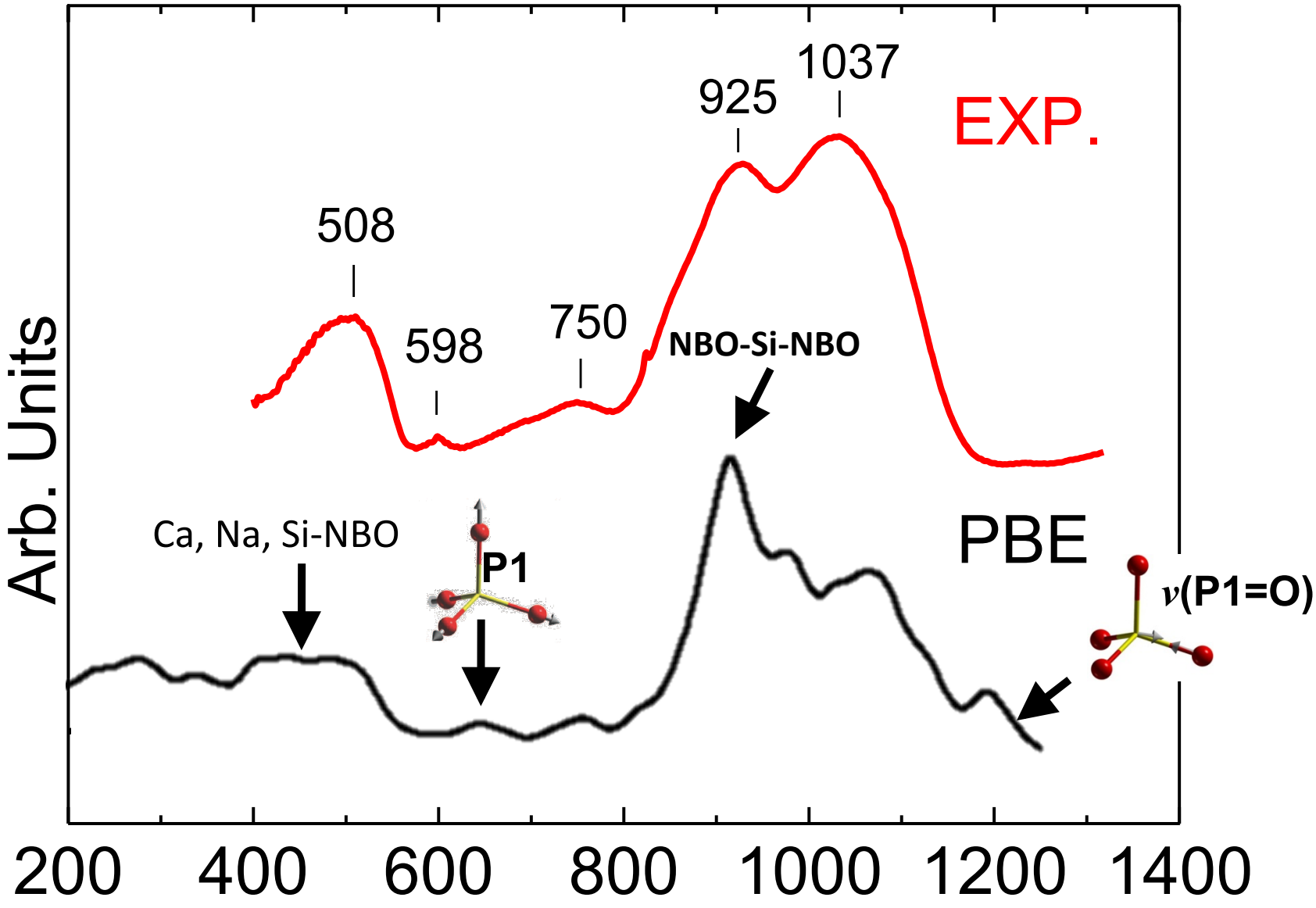
δ (g/cm³)	**2.82** (2.72)
E_{gap} (eV)	4.40

77S

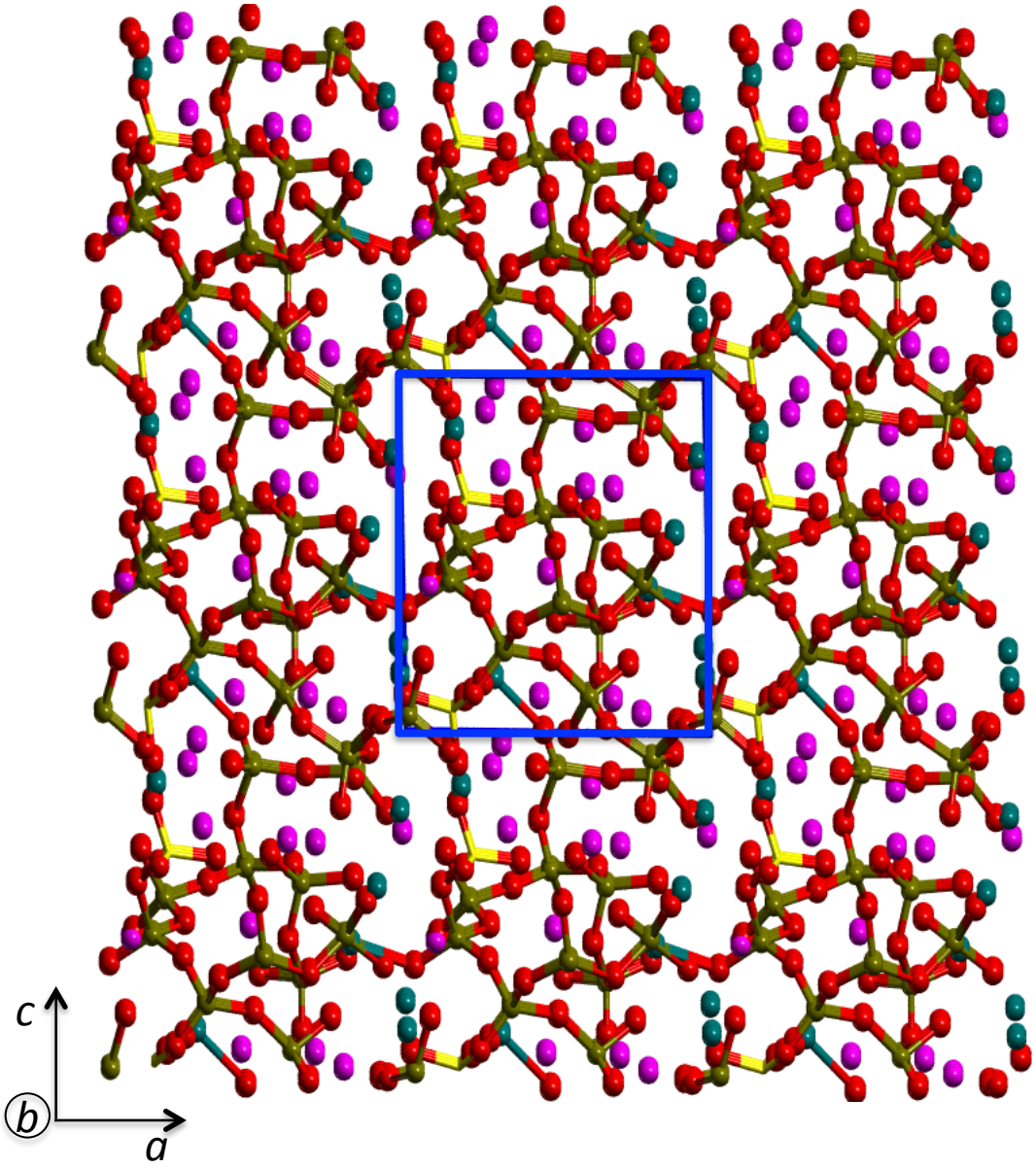


δ (g/cm³)	**2.55** (2.39)
E_{gap} (eV)	4.12

Vibrational properties of 45S5 ®Bioglass



Surface generation - Methodology



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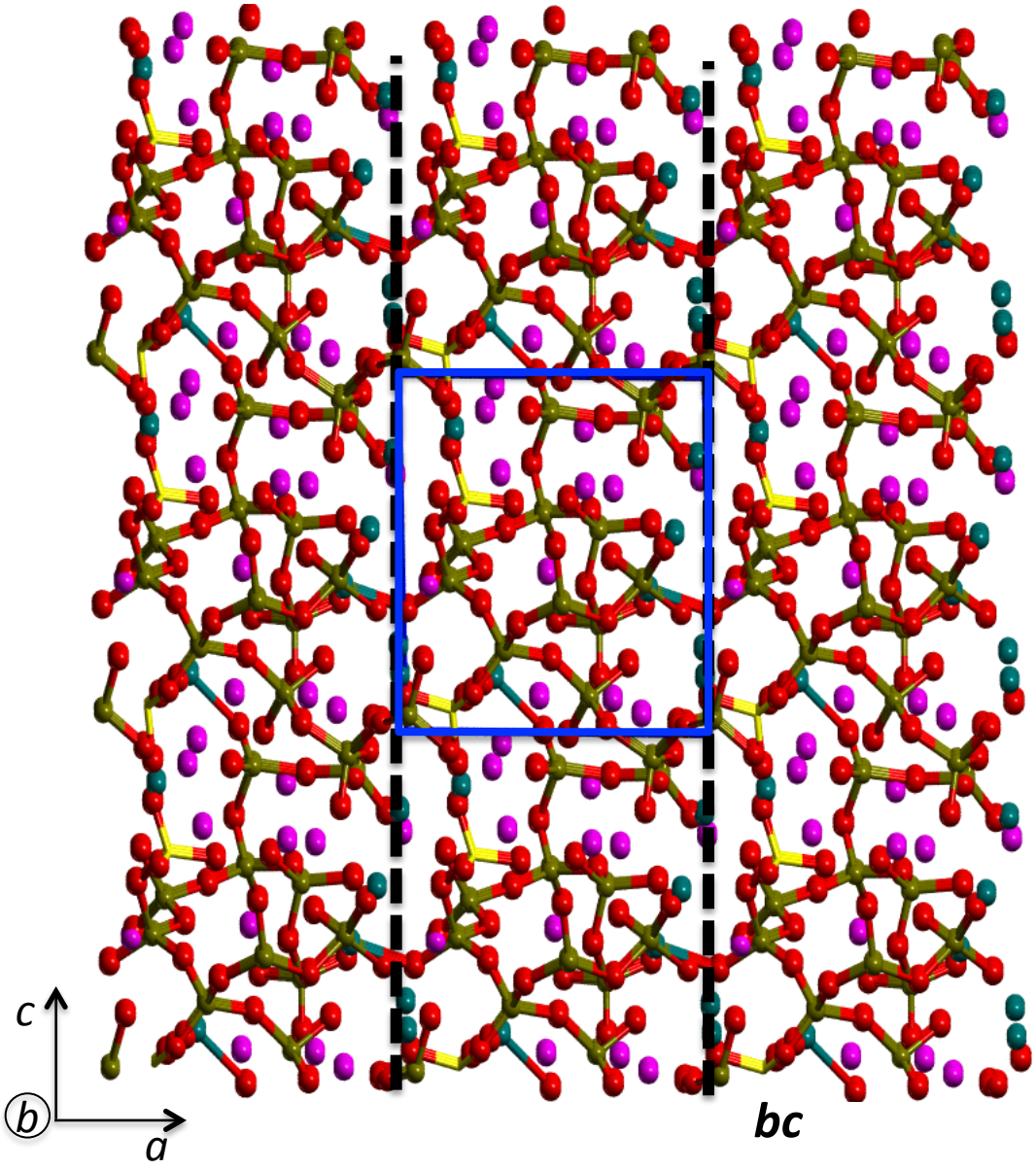

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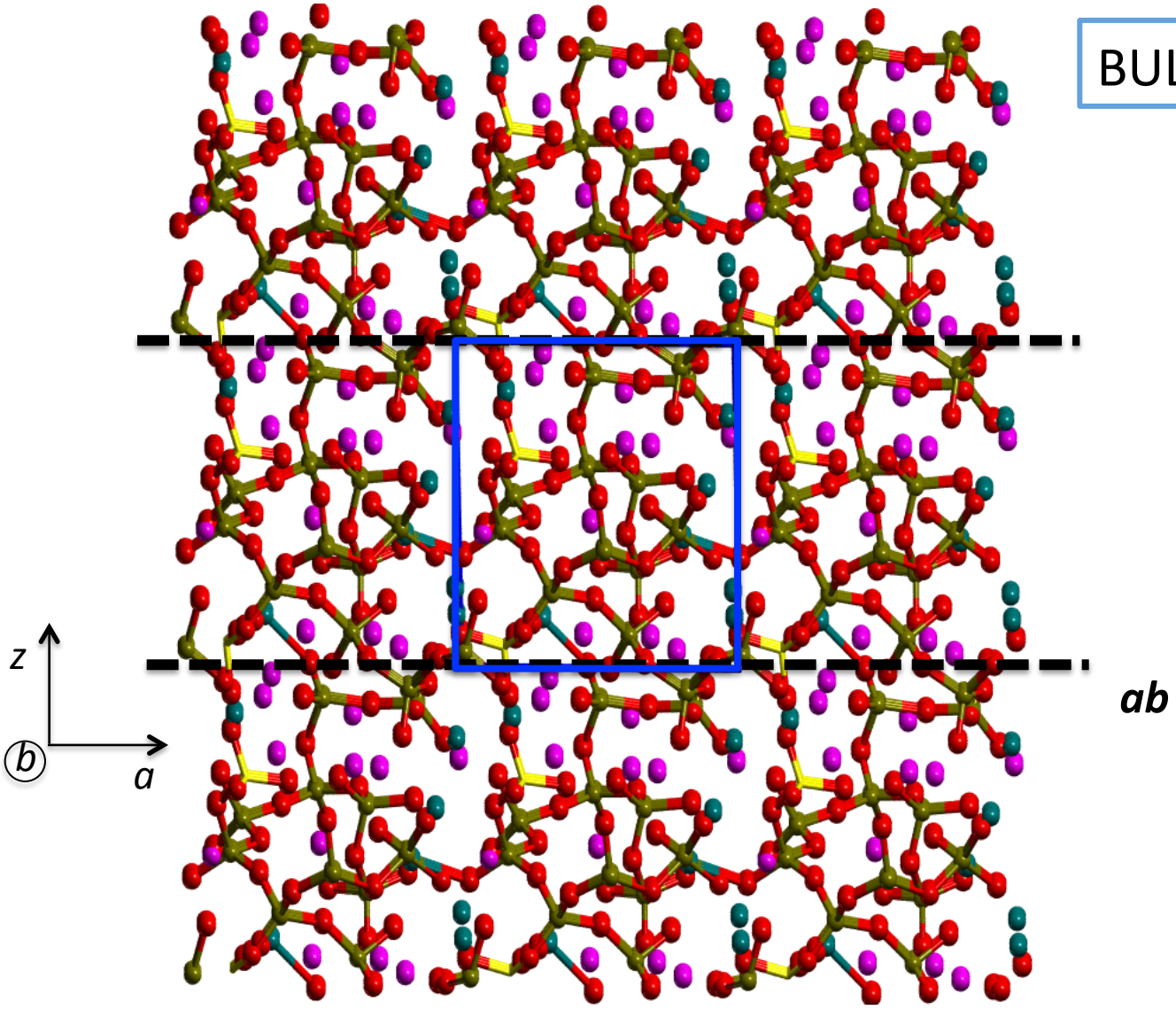

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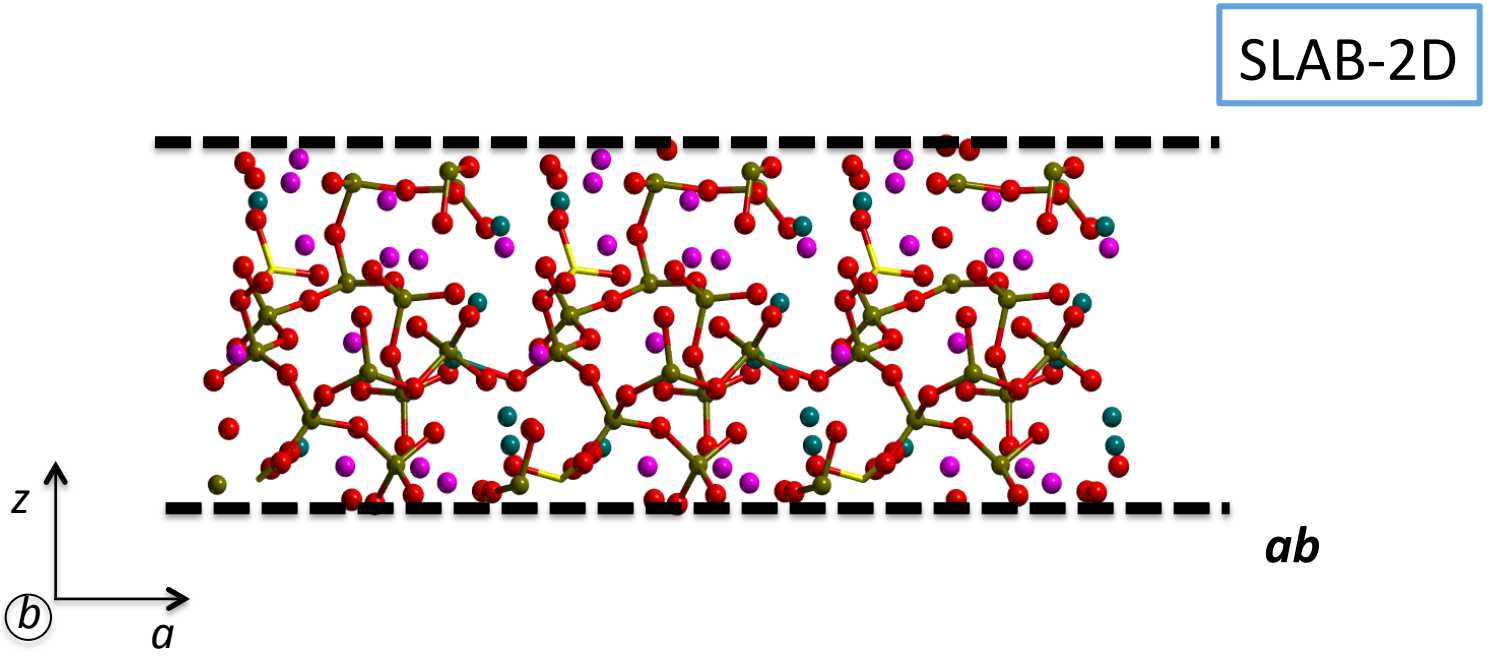

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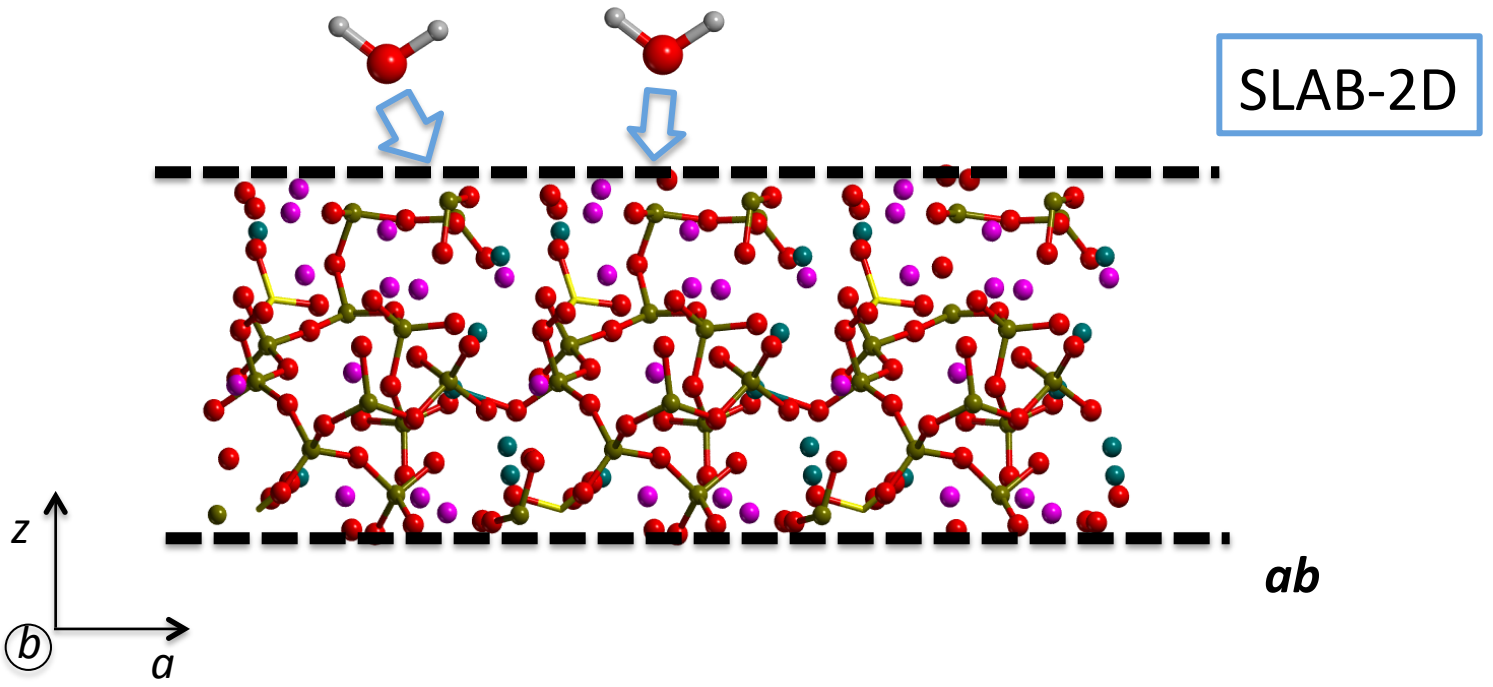

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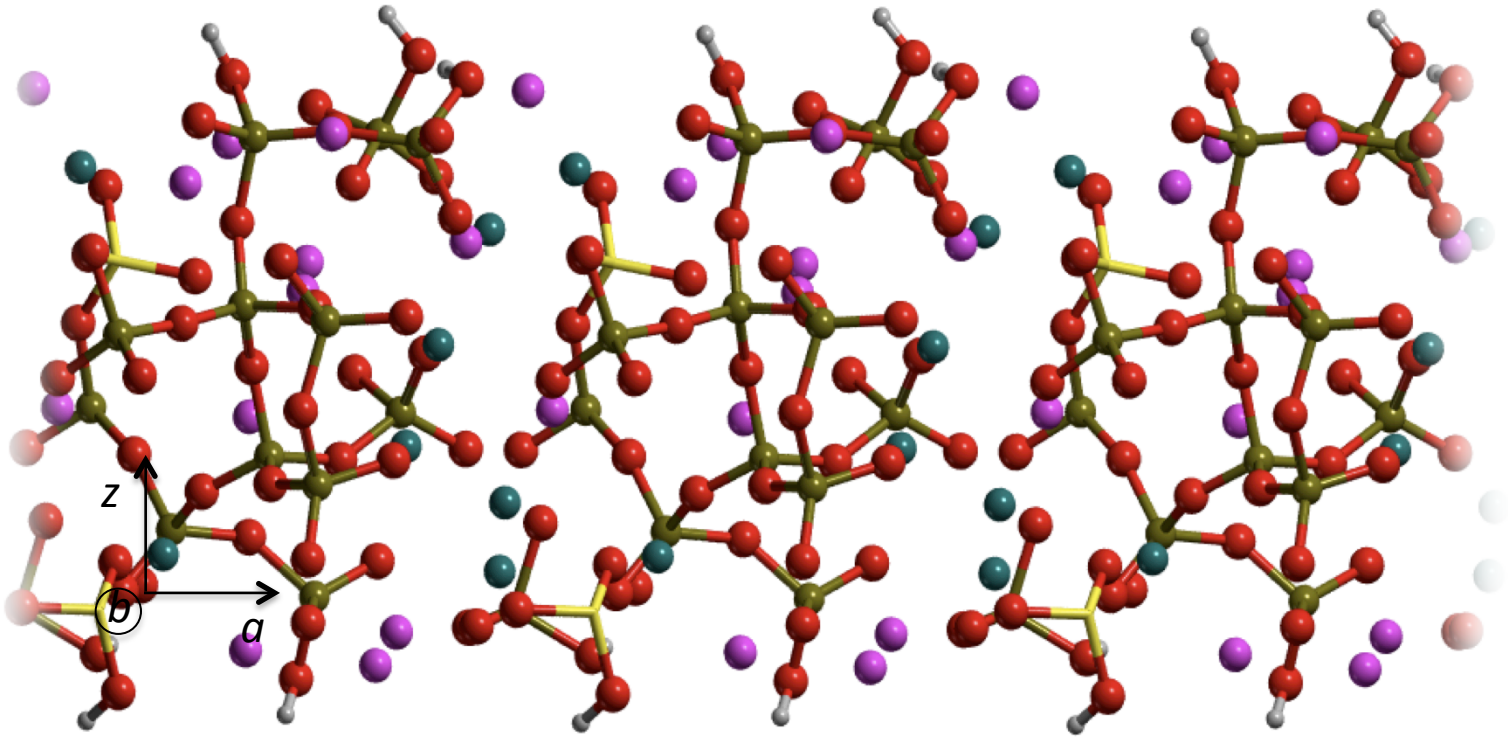
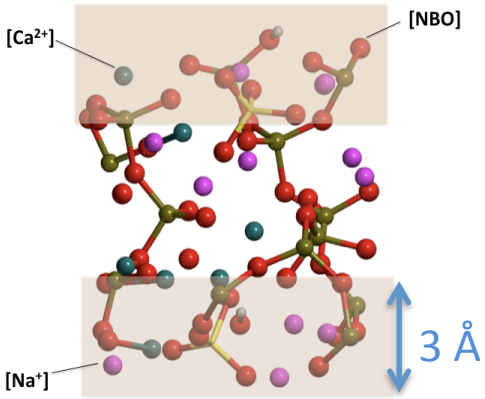


Exposed Ions and surface energy

$$\frac{E_{form}}{H_2O} = \frac{E_{slab} - [(n \times E_{H2O}) + E_{Bulk}]}{n}$$



Surface chemical species	45S5			77S		
	ab	*ac*	*bc*	*ab*	*ac*	*bc*
[Na^+]	17.3	24	9.4	--	--	--
[Ca^{2+}]	3.5	6.8	9.4	0	9.7	12.2
[NBO]	34.6	54.8	31.5	3.1	12.9	12.2
E_{form} (kJ/mol)/H_2O	172.0	458.4	124.5	-7.8	5.2	25.9

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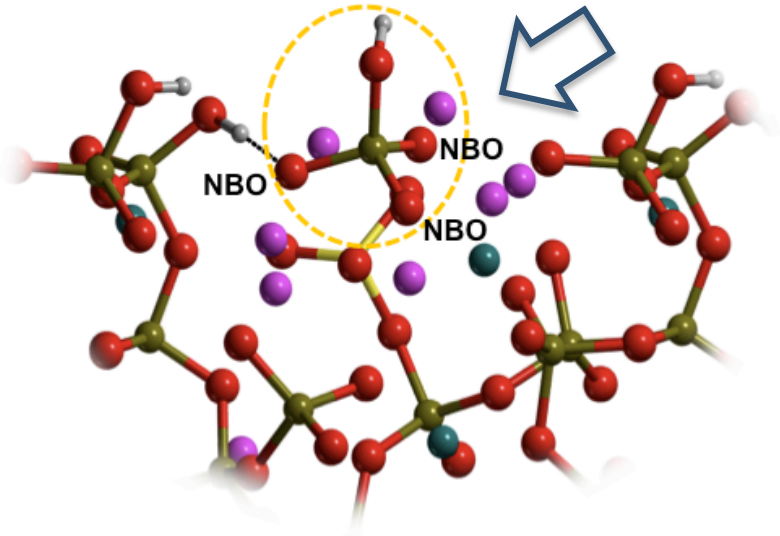
Surface species

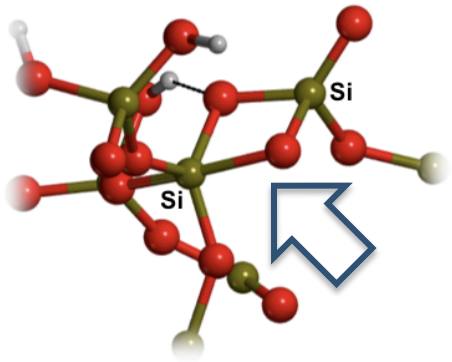
45S5

- Orthosilicate group (***ab*** surface)



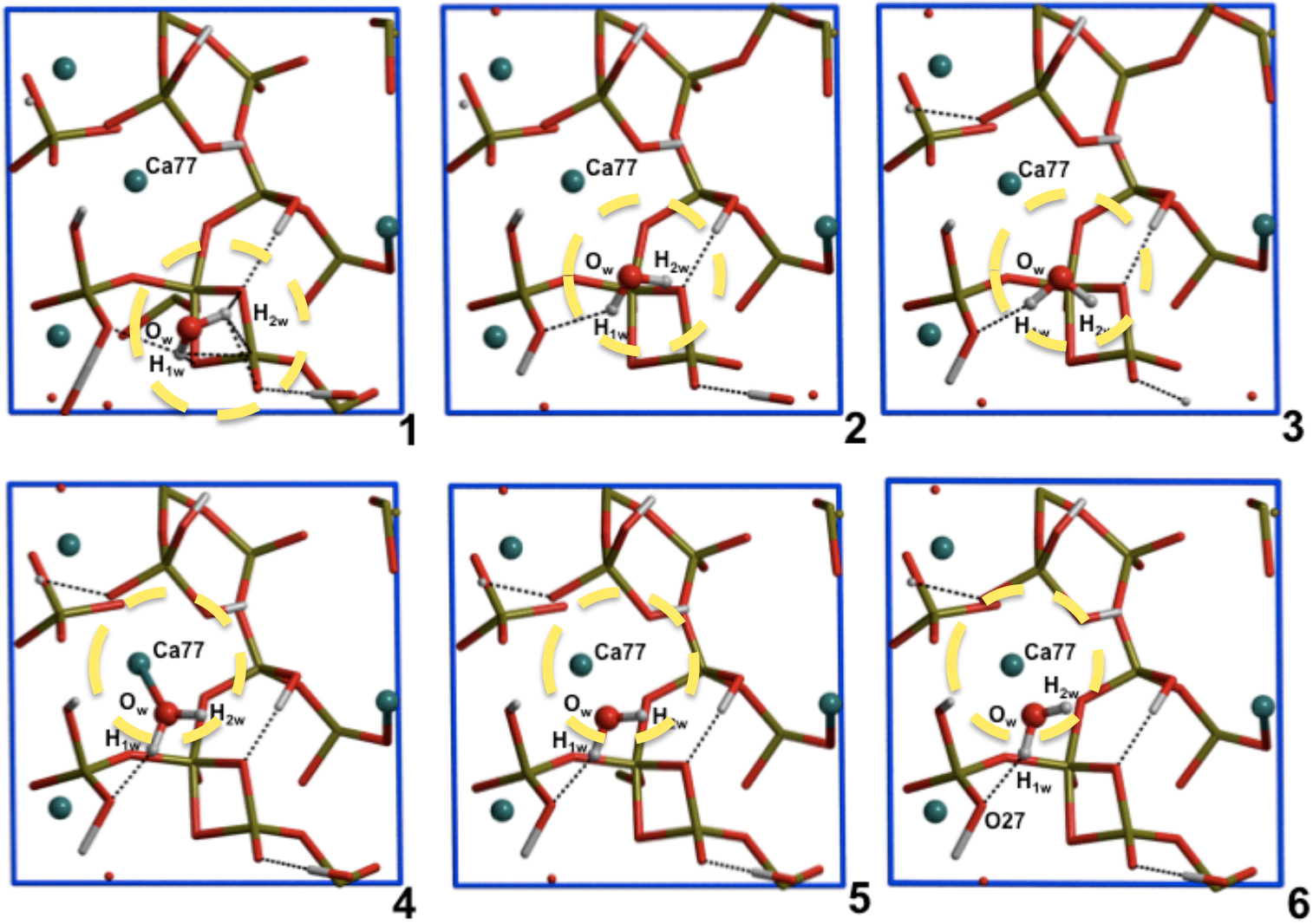
77S

- **2M** RING (***ac*** surface)



What is the role of rings on the surface?

- Water in interaction with a **2M** ring (*ac* surface):



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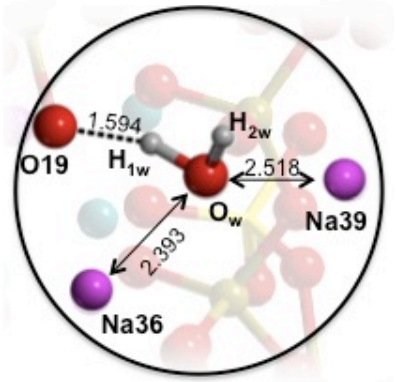
Water as a probe: 45S5 and 77S surfaces

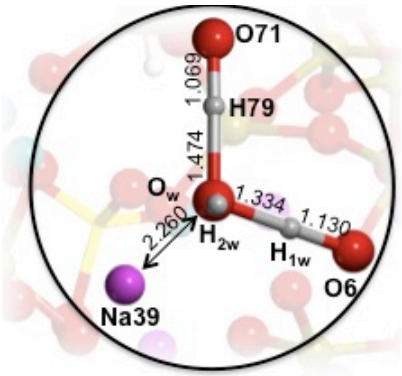
- One water molecule in interaction with **45S5** surfaces (energies in kJ/mol):

ab Surface



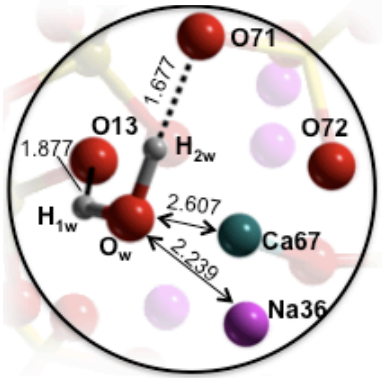
74

ac Surface



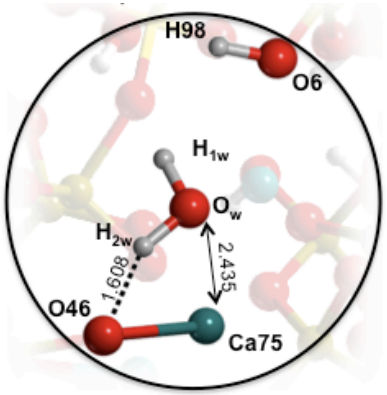
90

bc Surface



110

- One water molecule in interaction with **77S** surfaces:



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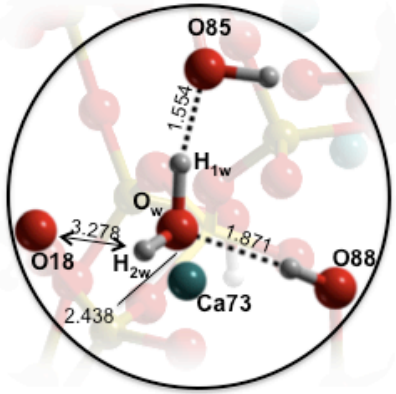

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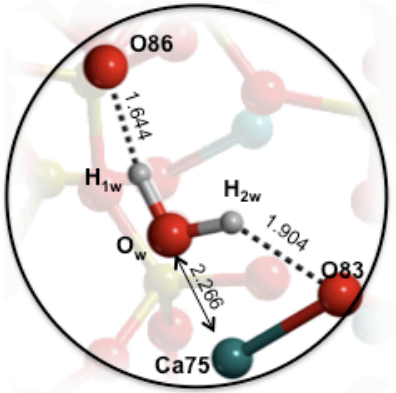

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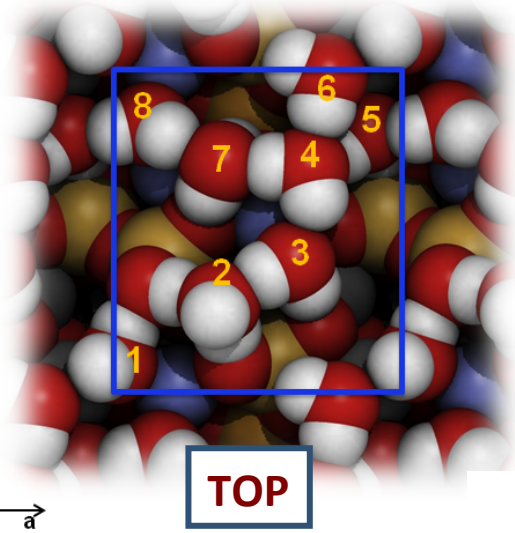
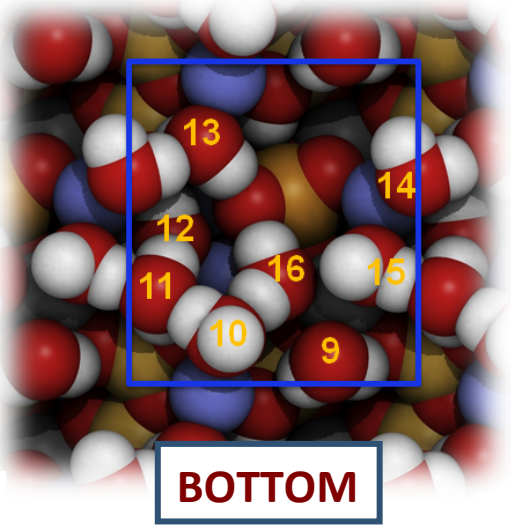
Effect of a monolayer of waters





Average interaction

Surface	n° H_2O	BE^C
45S5 *ab*	17	72.2
45S5 *ac*	16	71.5
45S5 *bc*	15	62.6
77S *ab*	16	60.2
77S *ac*	17	67.8
77S *bc*	16	64.3

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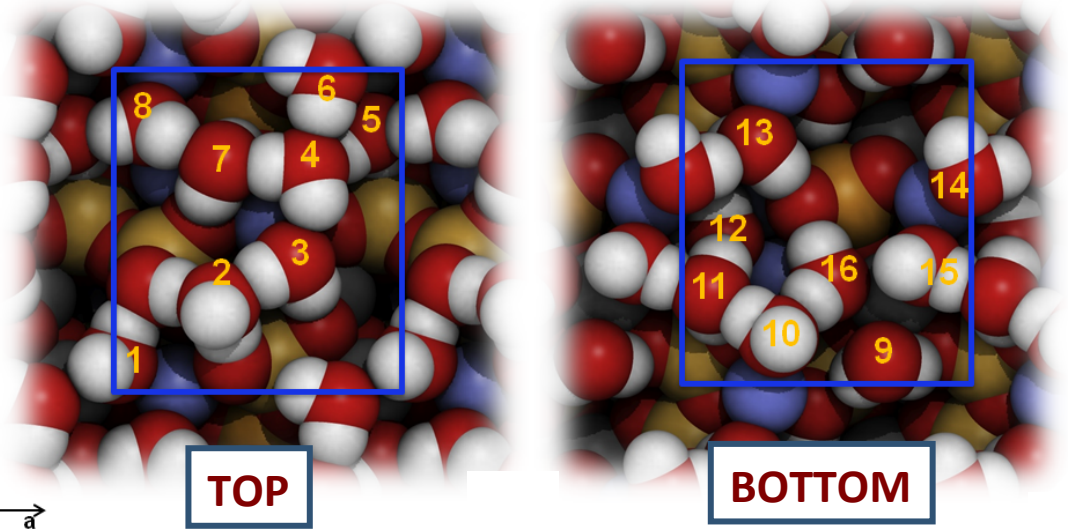
Cerruti, M.; Magnacca, G.; Bolis, V.; Morterra, C.; *J. Mater. Chem.*, 2003, **13**, 1279

Effect of a monolayer of waters



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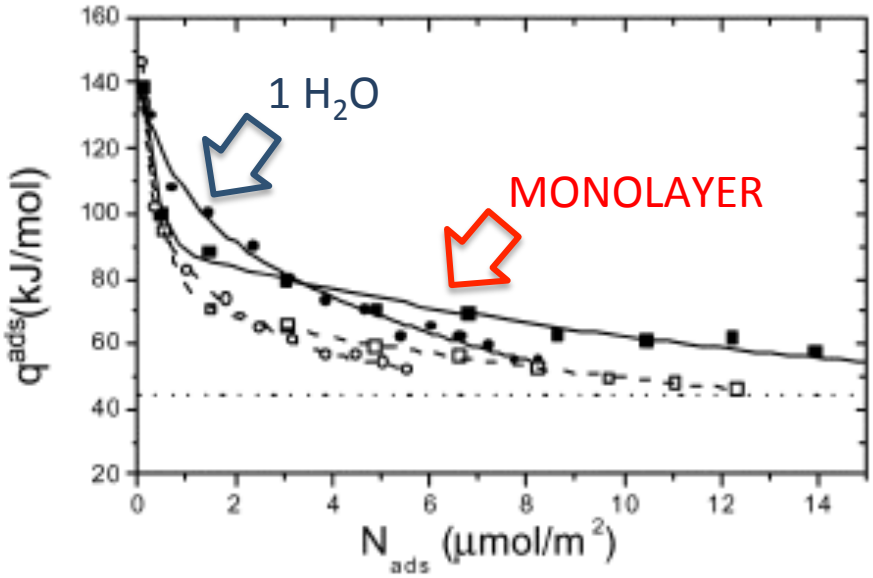

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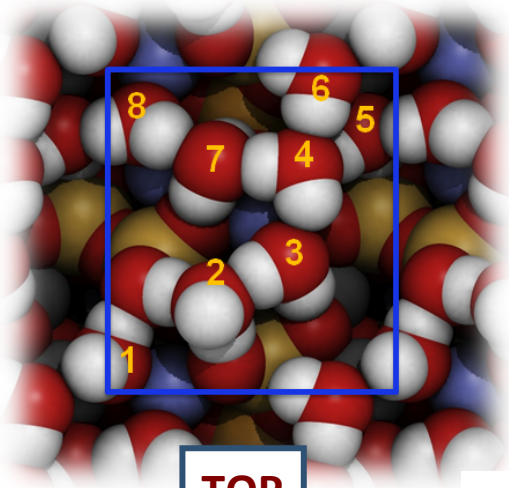
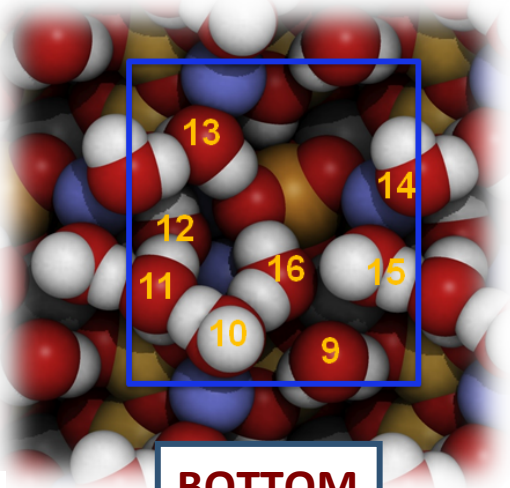
Effect of a monolayer of waters

For two 45S5 surfaces we observed the **splitting of a water molecule** during relaxation



TOP



BOTTOM

Average interaction

Surface	n° H_2O	BE^c
45S5 *ab*	17	72.2
45S5 *ac*	16	71.5
45S5 *bc*	15	62.6
77S *ab*	16	60.2
77S *ac*	17	67.8
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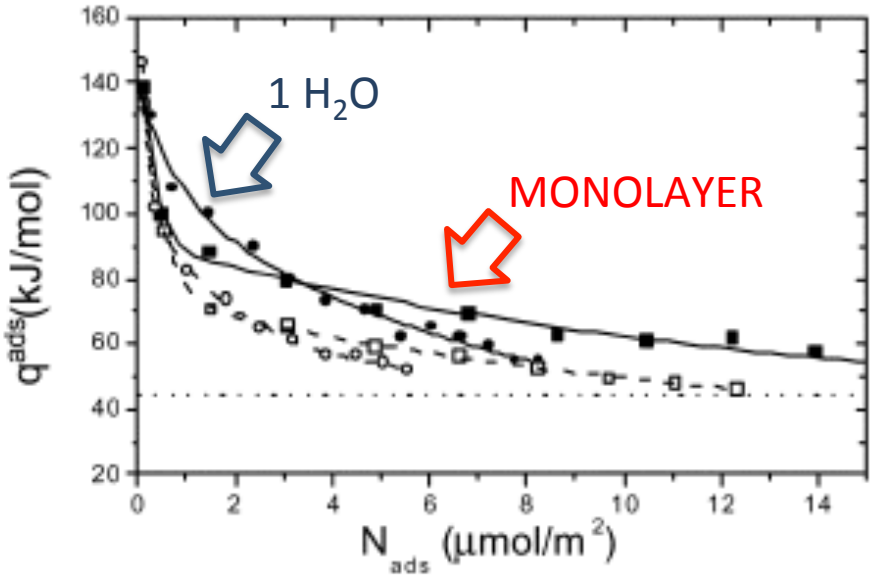

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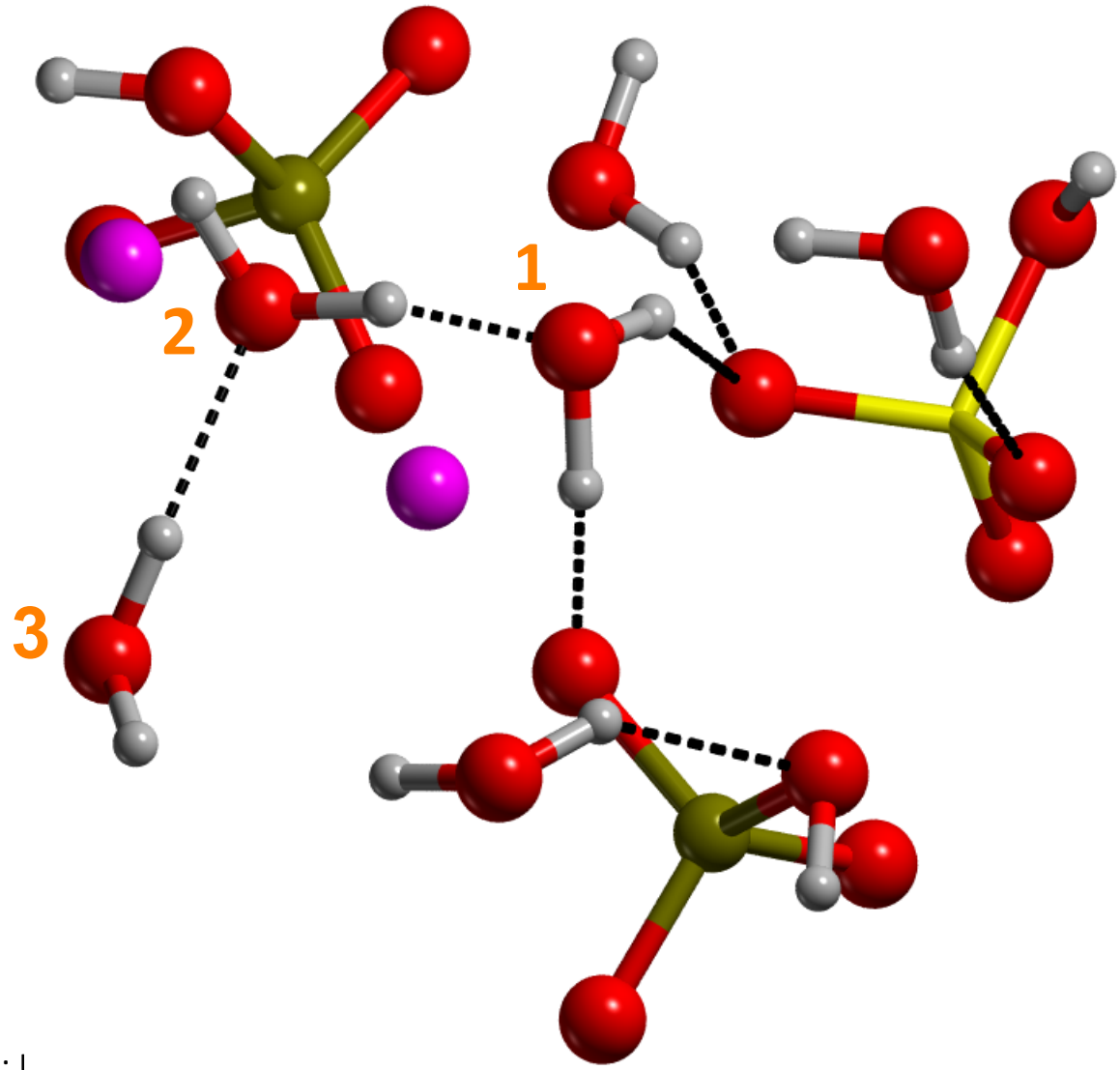
Water splitting process on *ab* surface

45S5 ®BIOGLASS



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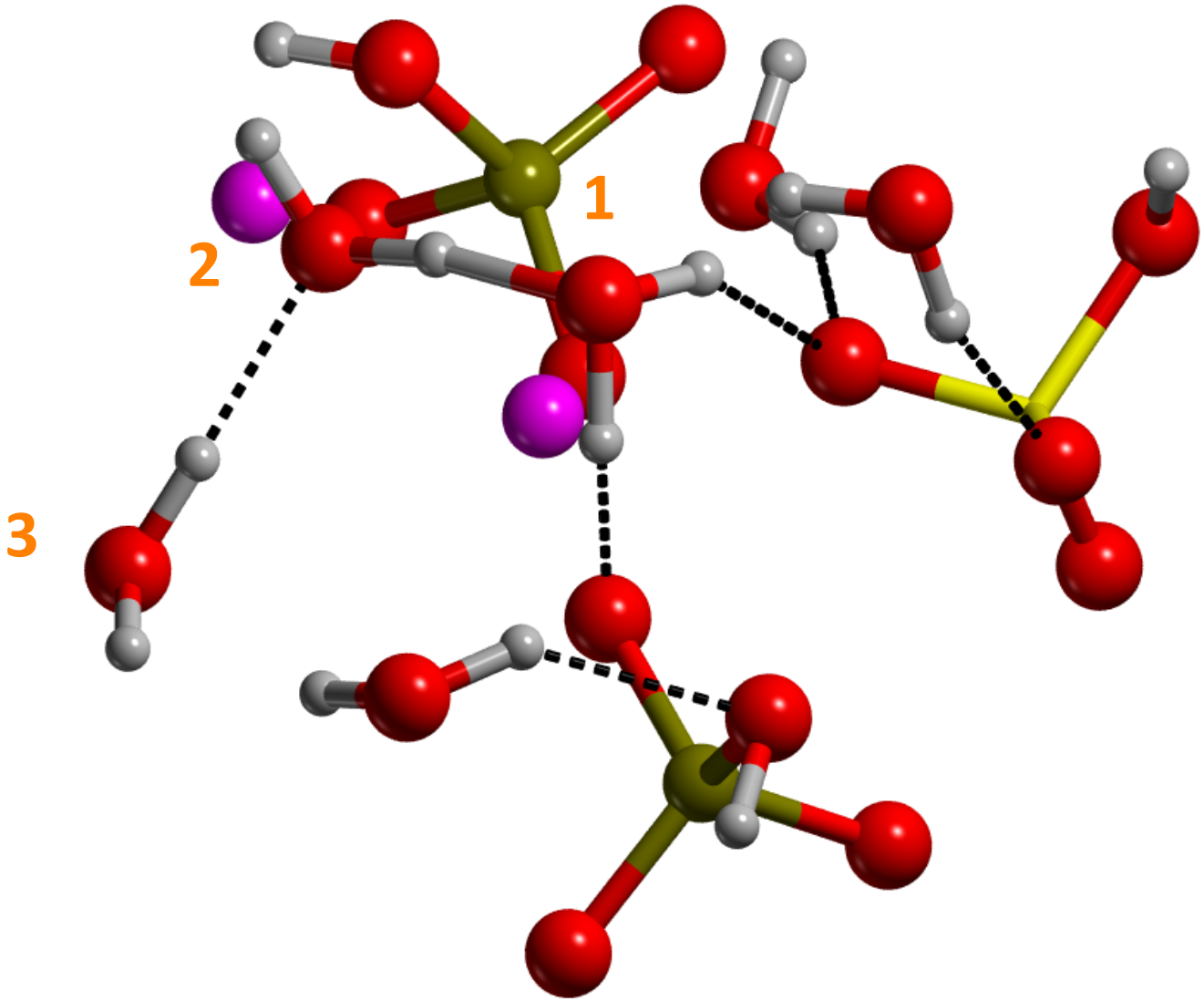

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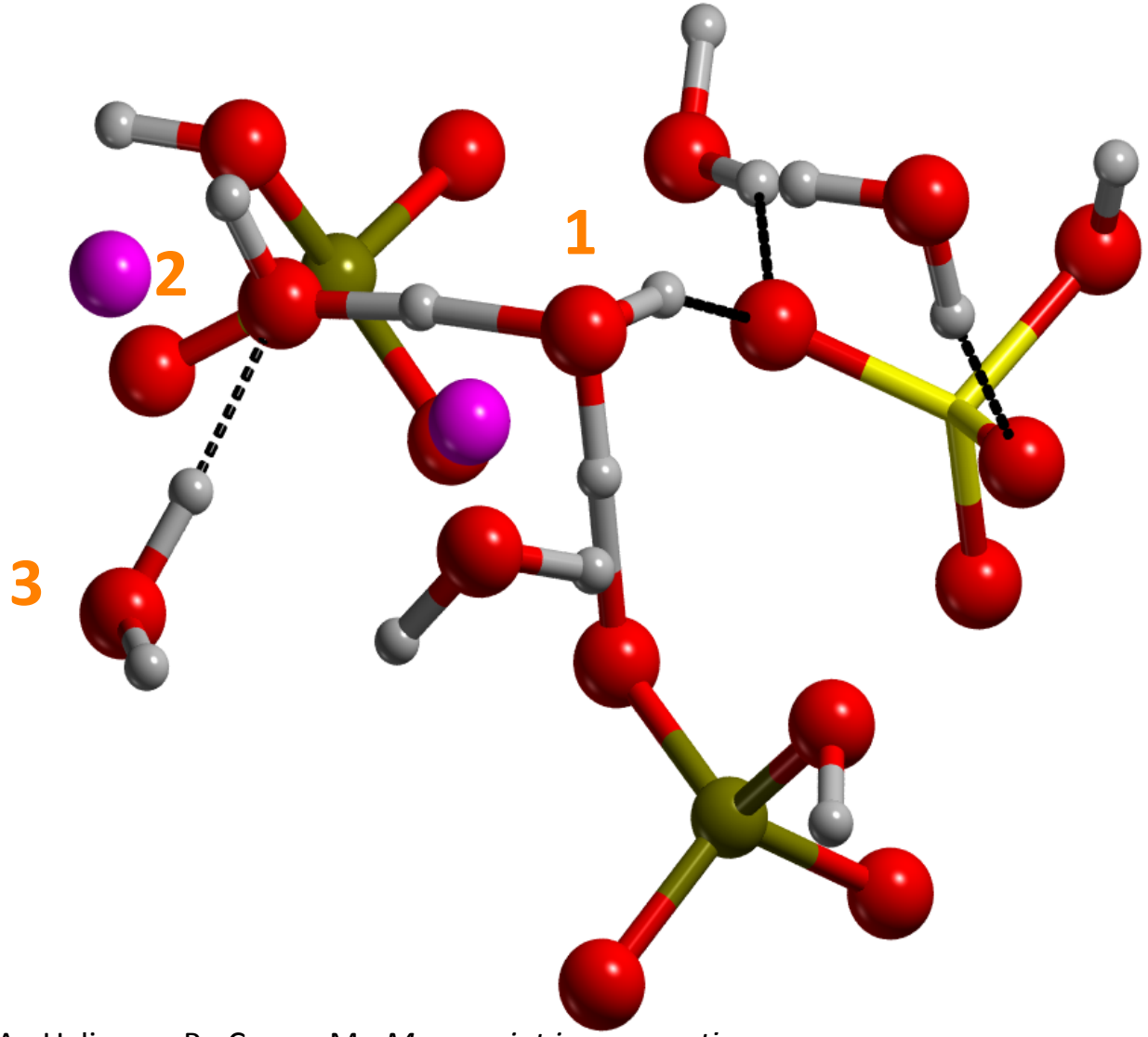

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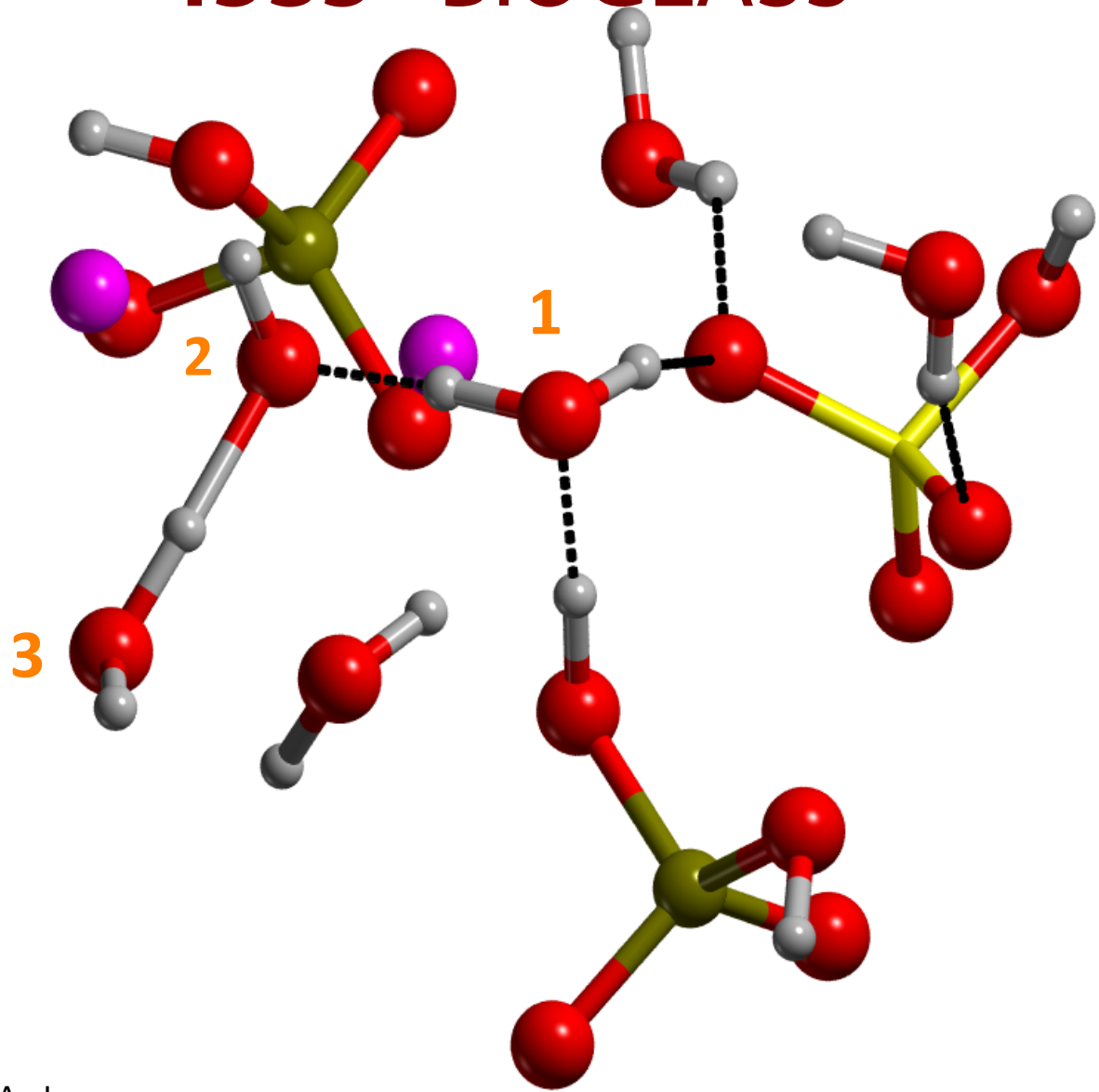

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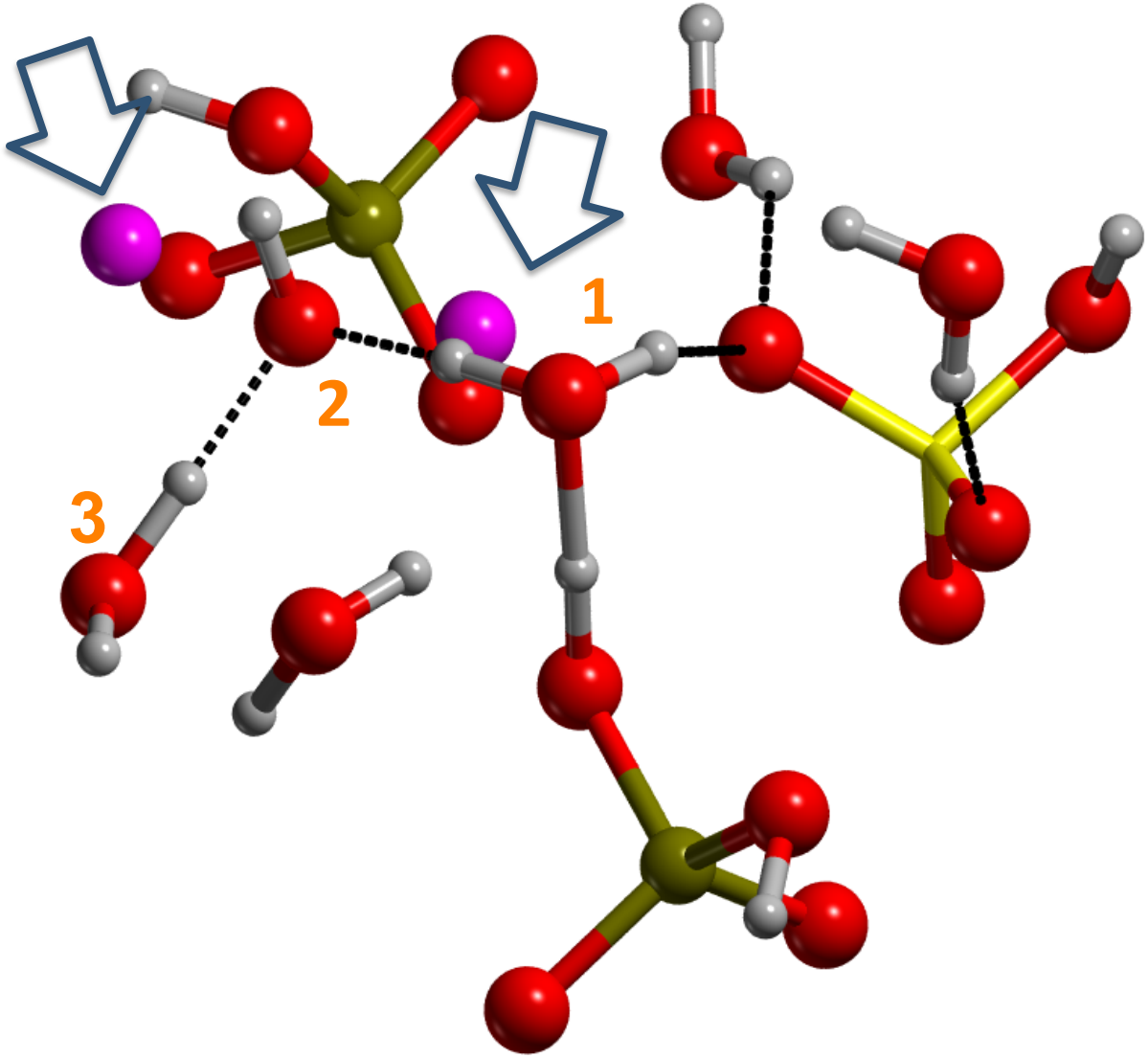

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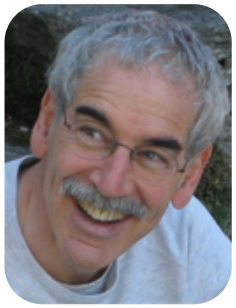
ACKNOWLEDGEMENTS

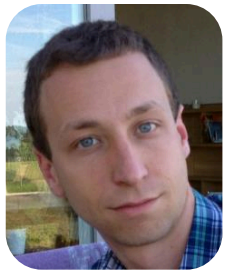


P. Ugliengo
Università di Torino

M. Corno
Università di Torino

A. Pedone
Università di Modena e Reggio Emilia

A. Tilocca
University College London



M. Delle Piane
Università di Torino

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