1st Italian Workshop on Astrochemistry
Prebiotic Chemistry in Space

INSPECTING THE ROLE OF MINERALS IN PREBIOTIC PROCESSES AND SPACE-LIKE CONDITIONS

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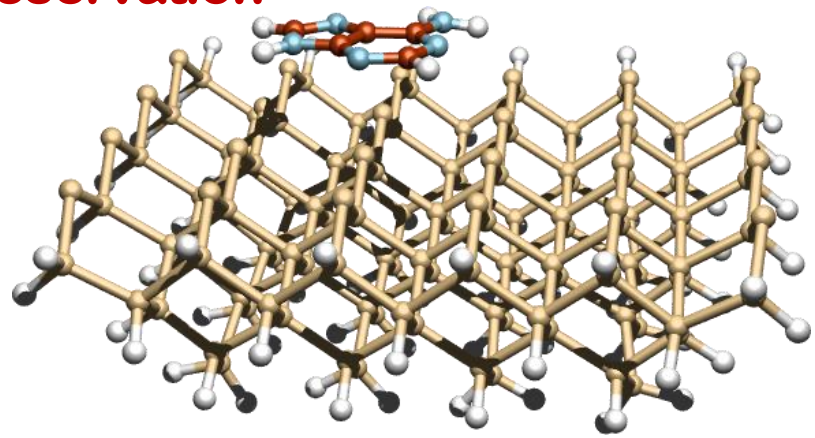
March 11, 2016 · Palazzo Strozzi, Firenze

Relevance of the Research

- **Prebiotic chemistry**

Role of **minerals** in the **transformation/preservation of biomolecules**

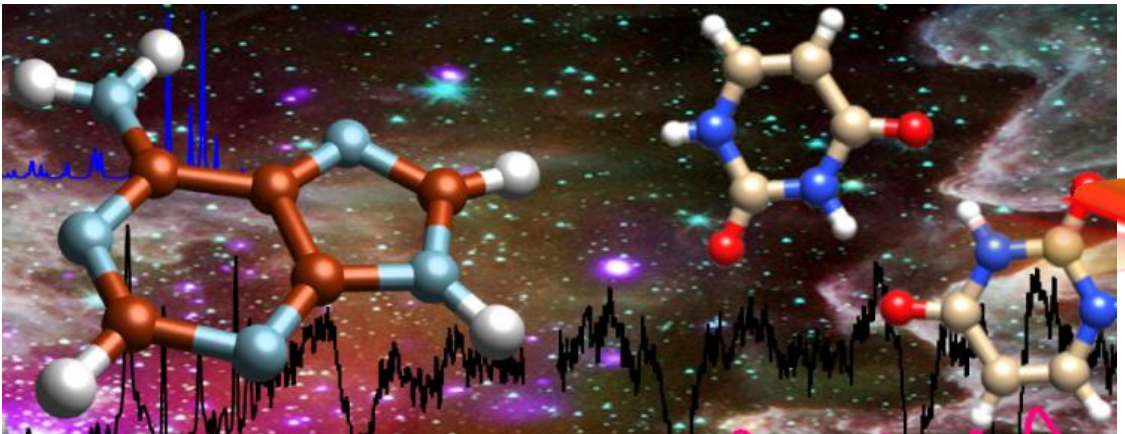


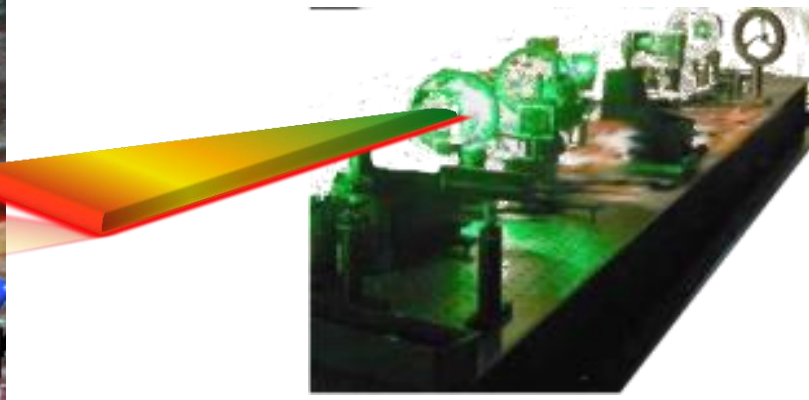
- **Life detection**

Identification of potential **biomarkers**

- ***In situ* and remote sensing spectroscopy**

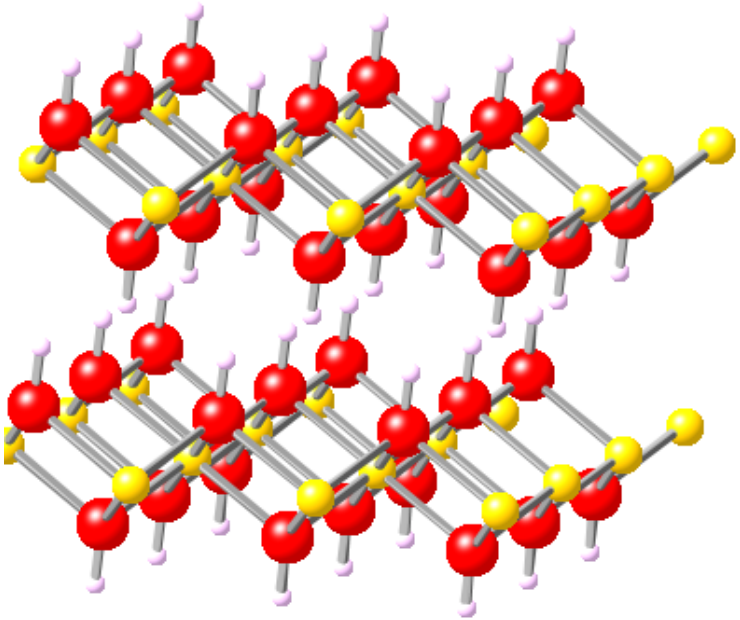
Detection of **organic compounds in space**



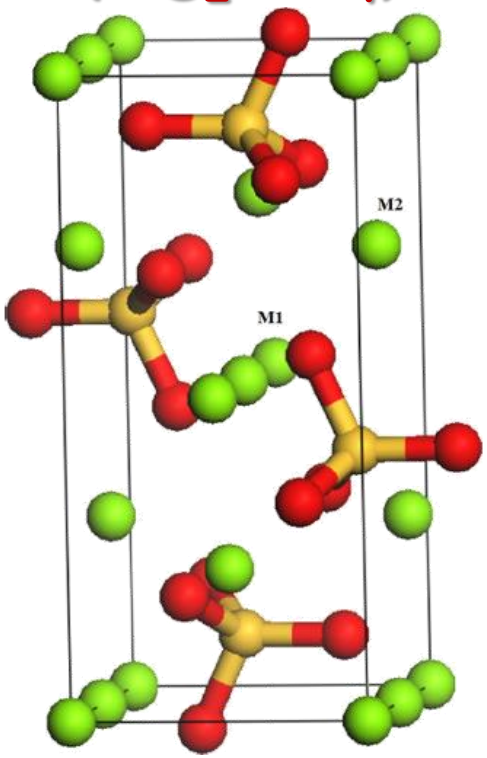


Minerals: Metal Oxides, Hydroxides and Silicates

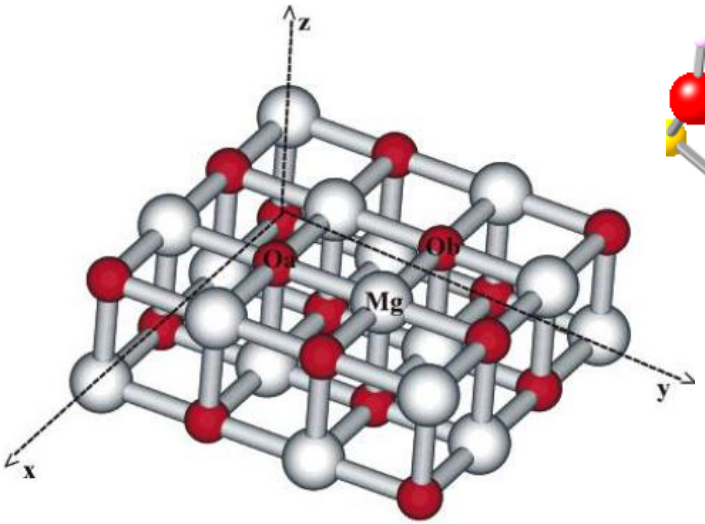
Magnesium Hydroxide, Brucite ($Mg(OH)_2$)



Forsterite (Mg_2SiO_4)



Magnesium oxide (MgO)



Hazen & Sverjenski *Cold Spring Harbor Perspectives in Biology* **2010**; Holm *Geobiology* **2012**; Fornaro et al. *International Journal of Astrobiology* **2013**; Fornaro et al. *Icarus* **2013**; Estrada et al. *Geochim et Cosmochim Acta* **2015**.

INTRODUCTION

Interaction of Nucleic Acid Components with Mg-containing Minerals in two different Astrobiologically Relevant Environments:

1. Serpentinite-hosted Hydrothermal Vents

Lost City Hydrothermal Field

SERPENTINIZATION

$$(Mg,Fe)_2SiO_4 + H_2O + C \dashrightarrow Mg_3SiO_5(OH)_4 + Mg(OH)_2 + Fe_3O_4 + H_2 + CH_4 + C_2–C_5$$

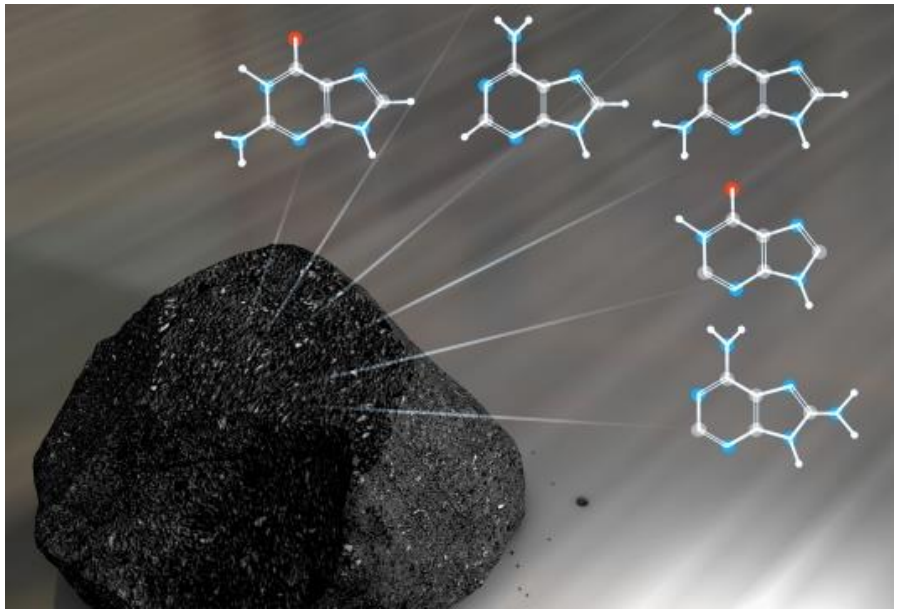
- ✓ **Disequilibria, redox gradient potentially catalyze formation of prebiotic molecules**
- ✓ **Lower temperatures typical of the Lost City hydrothermal fluids favor biosynthesis**

Holm et al. *Geochem Trans* **2006**; Shock and Canovas *Geofluids* **2010**; Holm *Geobiology* **2012**; Estrada et al. *Geochim et Cosmochim Acta* **2015**.

INTRODUCTION

Interaction of Nucleic Acid Components with Mg-containing Minerals in two different Astrobiologically Relevant Environments:

2. High UV Irradiation and Space-like Environments



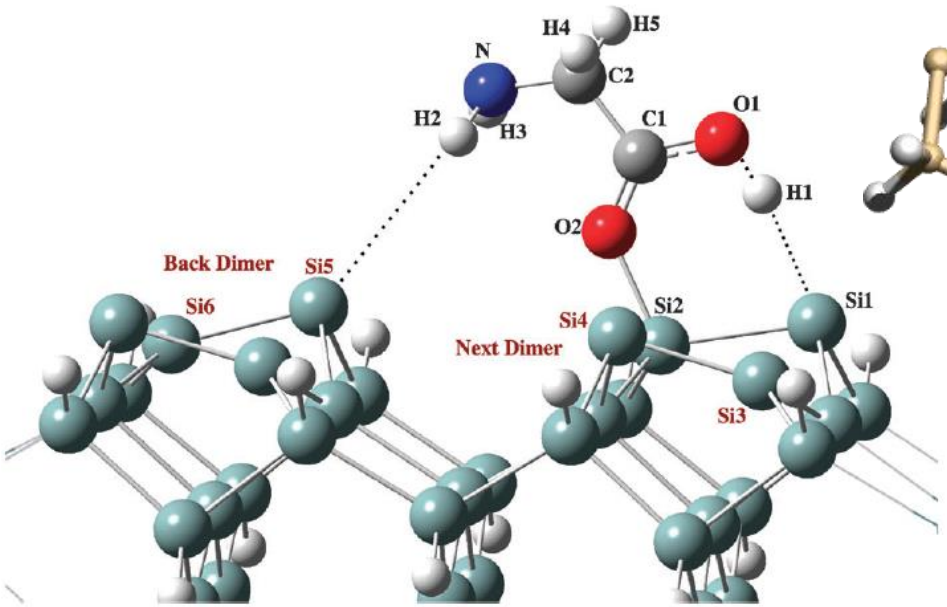
Magnesium oxide (MgO);

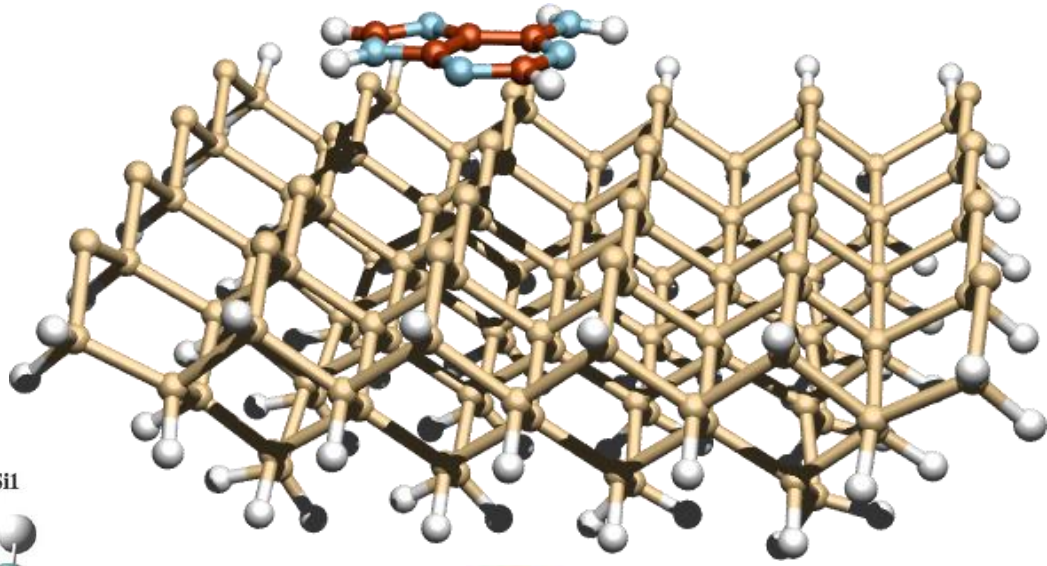
Forsterite (Mg_2SiO_4)…

Weinbruch et al. *Meteoritics & Planetary Science* **2000**; Barber and Scott *PNAS* **2002**; Messenger et al. *Science* **2005**; Ming et al. *Journal of Geophysical Research* **2006**; Chevrier and Mathé *Planetary and Space Science* **2007**; Poteet et al. *The Astrophysical Journal Letters* **2011**.

1. SERPENTINITE-HOSTED HYDROTHERMAL MINERALS

BINDING MECHANISM OF "BUILDING BLOCKS OF LIFE" TO MINERALS, STABILITY AND REACTIVITY UNDER PREBIOTIC CONDITIONS





CARNEGIE INSTITUTION FOR SCIENCE

GEOPHYSICAL LABORATORY–CARNEGIE INSTITUTION OF WASHINGTON

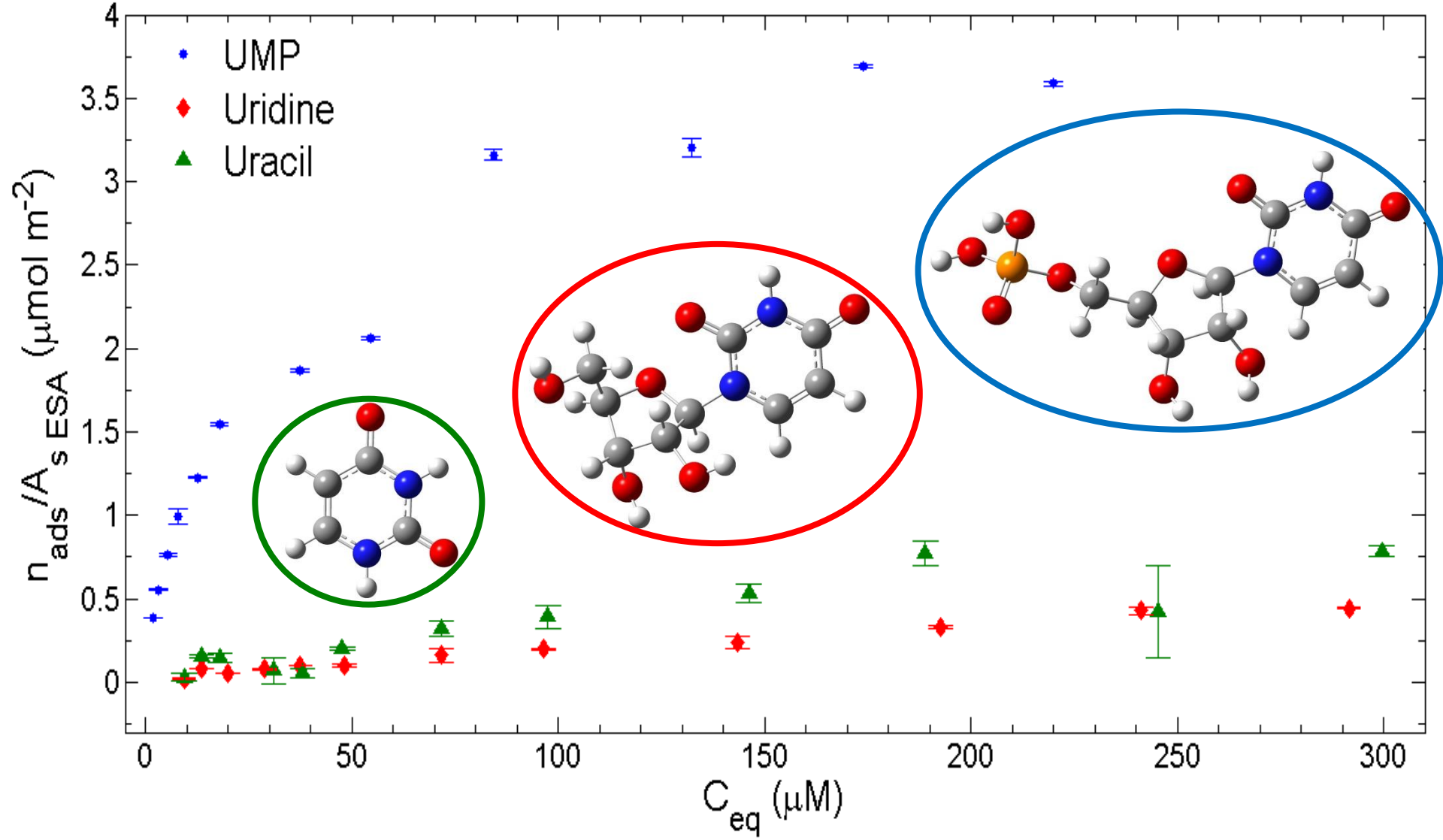
Thermodynamics of Adsorption of Nucleic Acids Components on Brucite in Water

- **Equilibrium Adsorption Isotherms at room temperature**

- **Quantitative Thermodynamic Characterization of the adsorption data with the Extended Triple-Layer Model (ETLM) (computer code GEOSURF)**

Sverjensky D.A. & Sahai N. *Geochimica et Cosmochimica Acta* **1996**,*60*(20), 3773-3797. Sahai N. & Sverjensky D.A. *Computers & Geosciences* **1998**,*24*(9), 853-873. Sverjenski D.A. *Geochimica et Cosmochimica Acta* **2003**,*67*(1),17-28. Sverjenski D.A. & Fukushi K. *Geochimica et Cosmochimica Acta* **2006**,*70*(15),3778-3802.

Adsorption of Uracil, Uridine and UMP on Brucite in Water

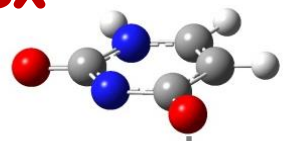


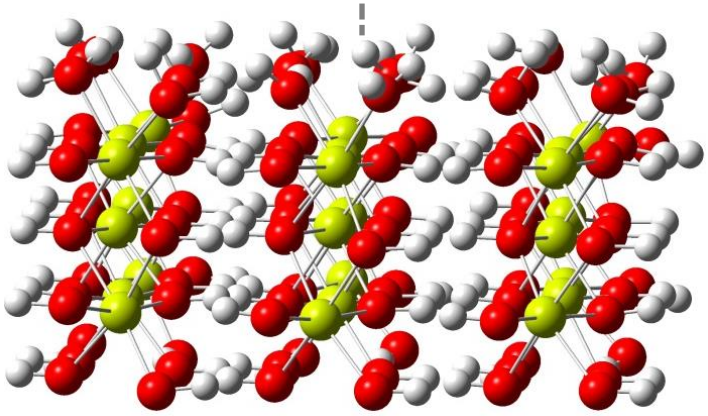
Ribose not involved in the adsorption (only weak outer-sphere interactions)
Strong interactions via Phosphate group

Adsorption of Uracil on Brucite in Water

Monodentate Outer-Sphere Surface Complex

$SOH + HU = SOH_2^+\_U^-$ $\Delta\Psi_r = +\Psi_0 - \Psi_\beta$; logK=2.8

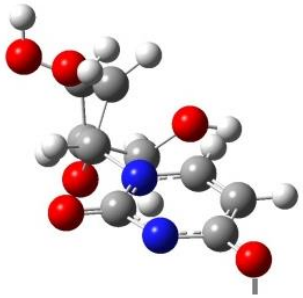


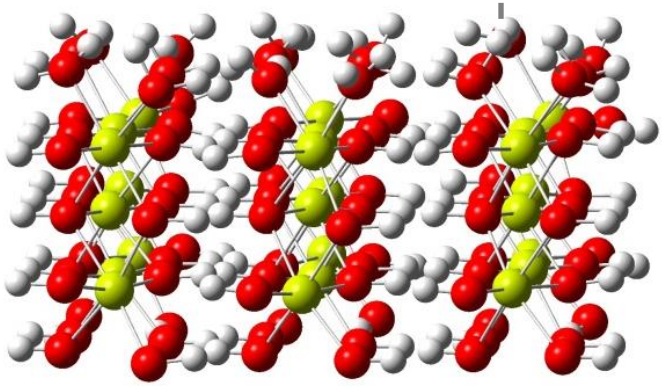


Adsorption of Uridine on Brucite in Water

Monodentate Outer-Sphere Surface Complex

$SOH + HUD = SOH_2^+\_UD^-$ $\Delta\Psi_r = +\Psi_0 - \Psi_\beta$; logK=2.75



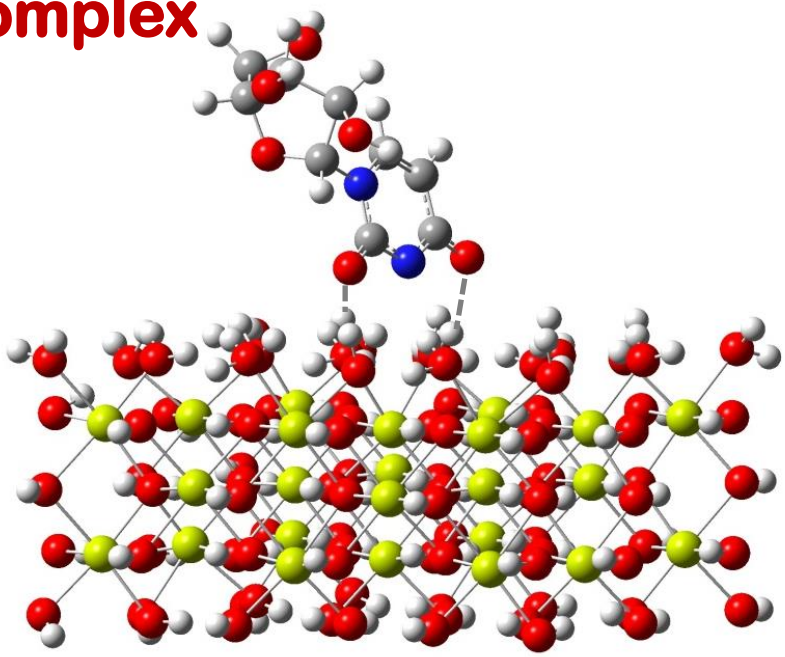


Adsorption of Uridine on Brucite in Water

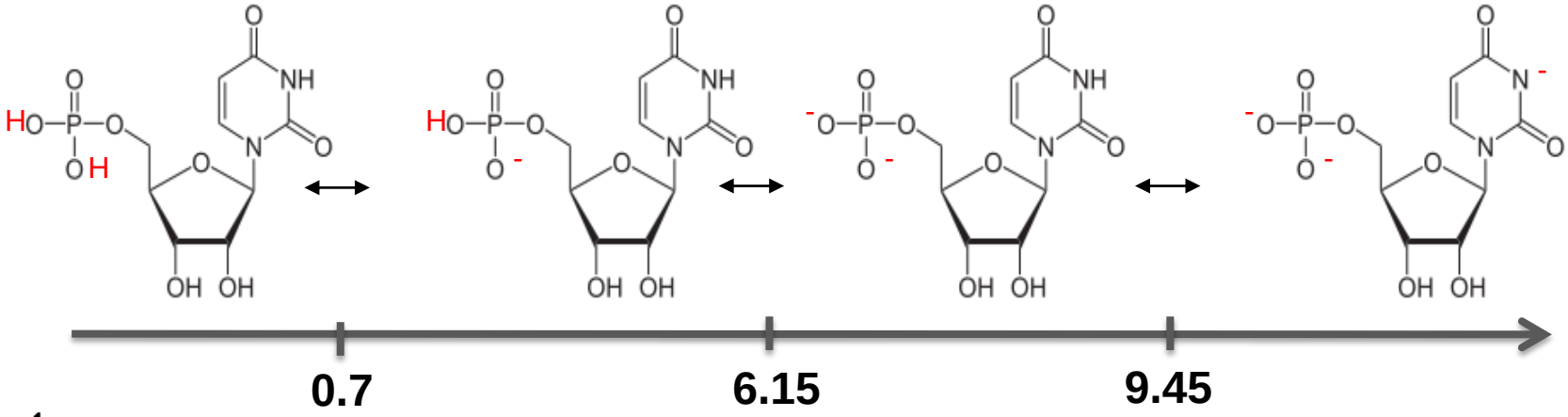
Bidentate Outer-Sphere Surface Complex

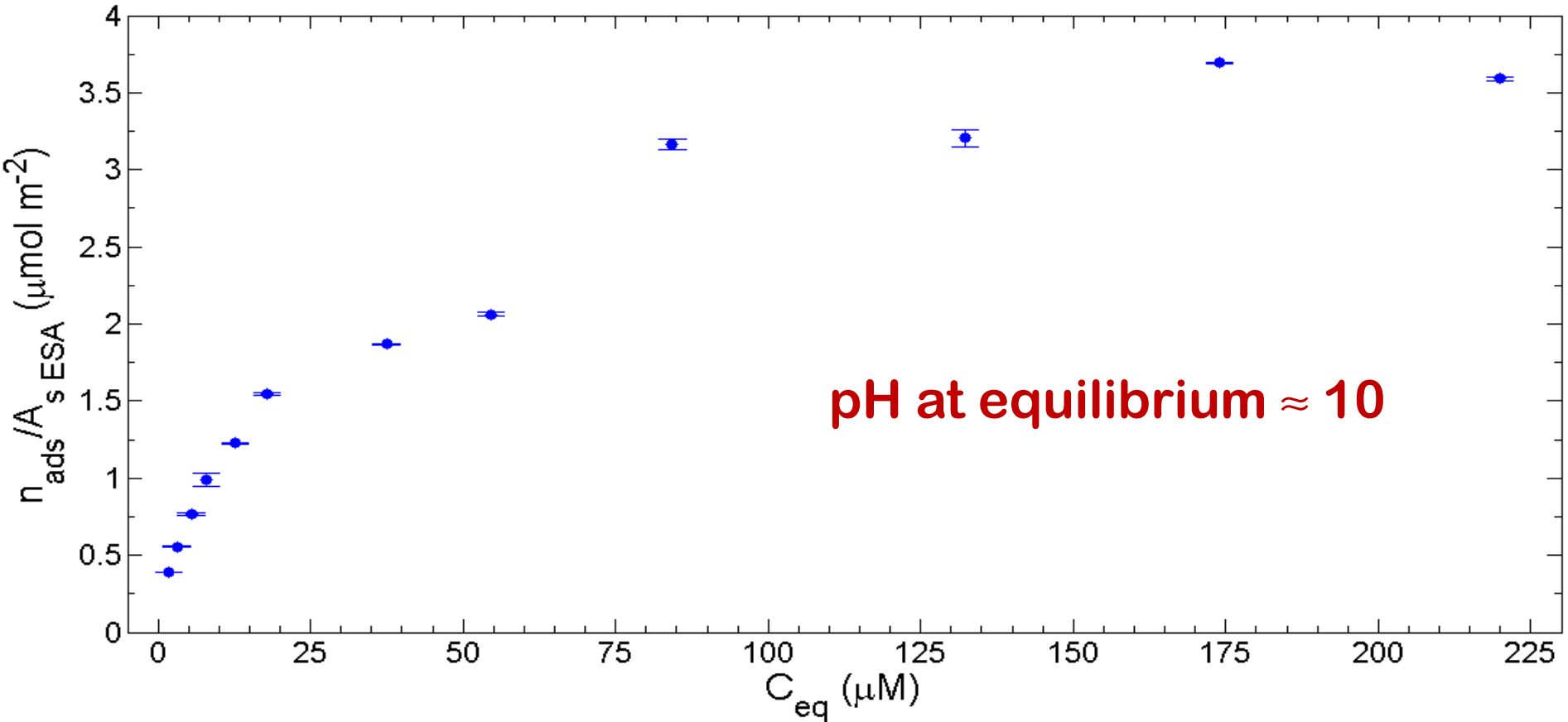
$$2\ SOH + H^+ + HUD = (SOH_2^+)_2\_UD^-$$

$$\Delta\Psi_r = +2\Psi_0 - \Psi_\beta;\ \log K = 16.2$$



Adsorption of UMP on Brucite in Water

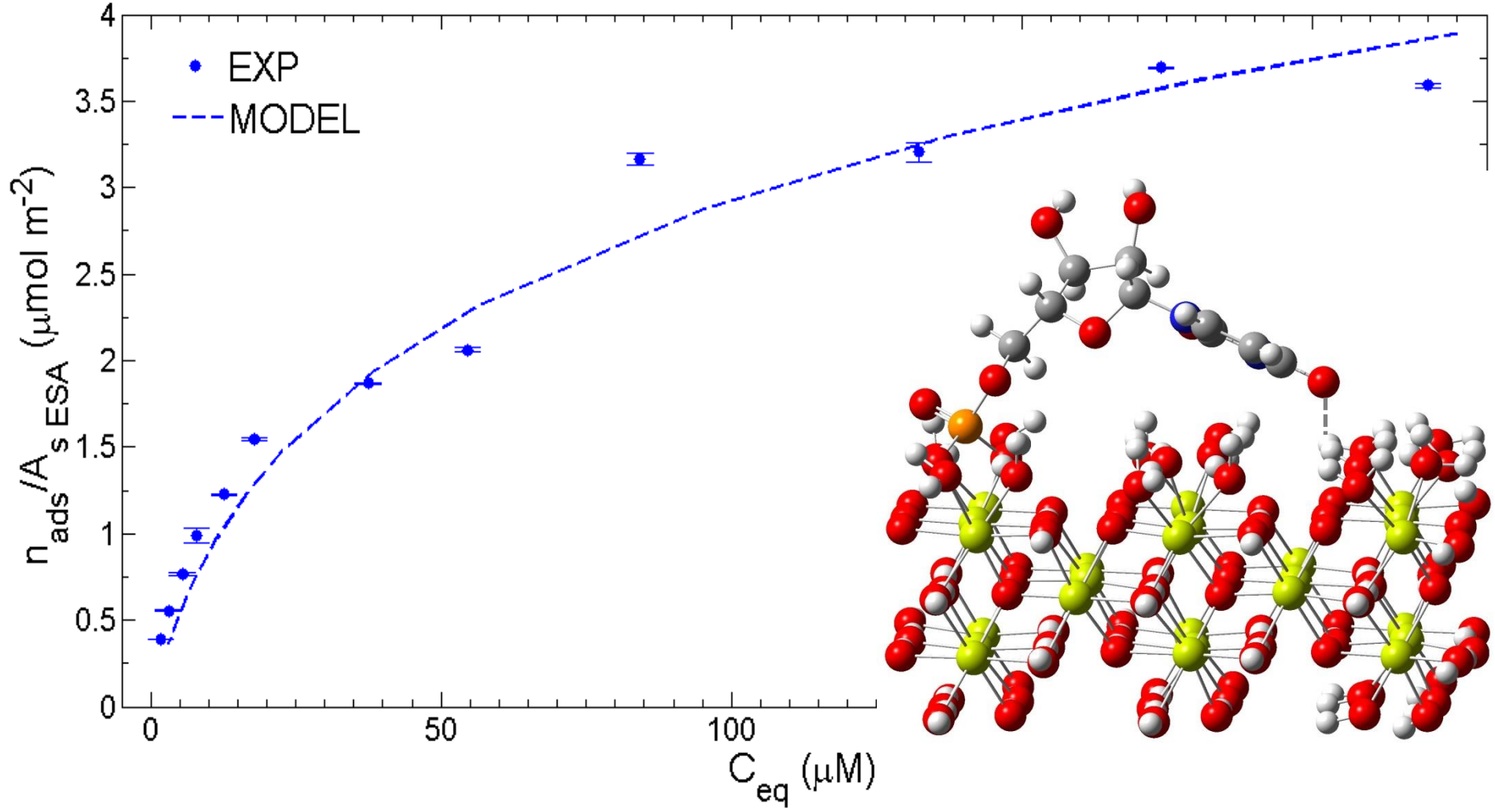




Adsorption of UMP on Brucite in Water

Tridentate with 2 Inner-Sphere Linkages and 1 Hydrogen Bond

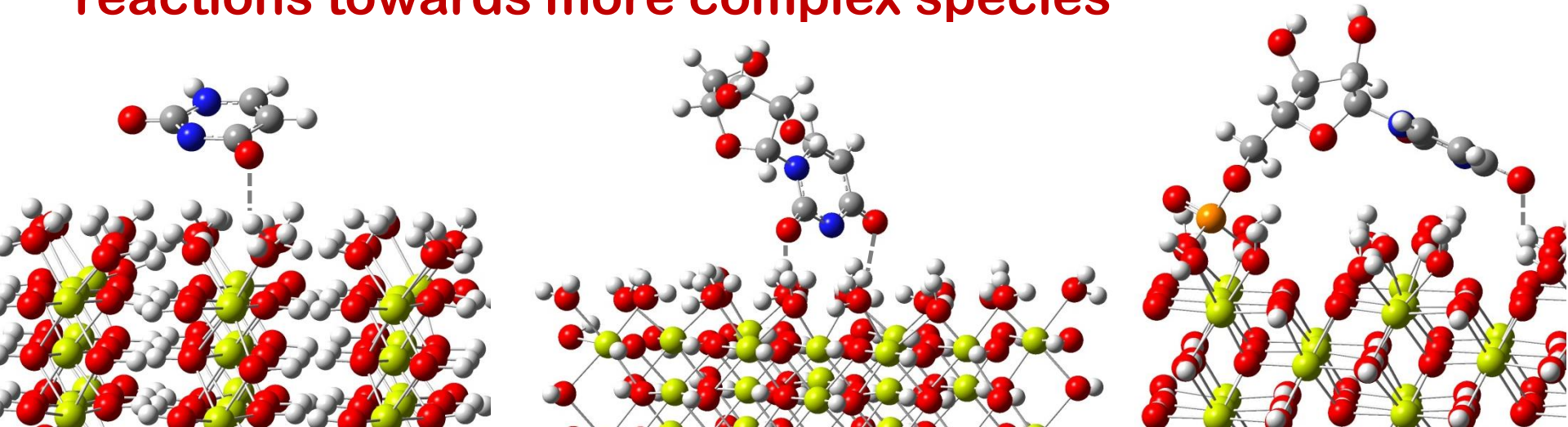
3 SOH + H_3UMP = $(SOH_2^+)\_S_2UMP^-$ + 2 H_2O $\Delta\Psi_r=+\Psi_0-\Psi_\beta$; logK=23.75



Summary

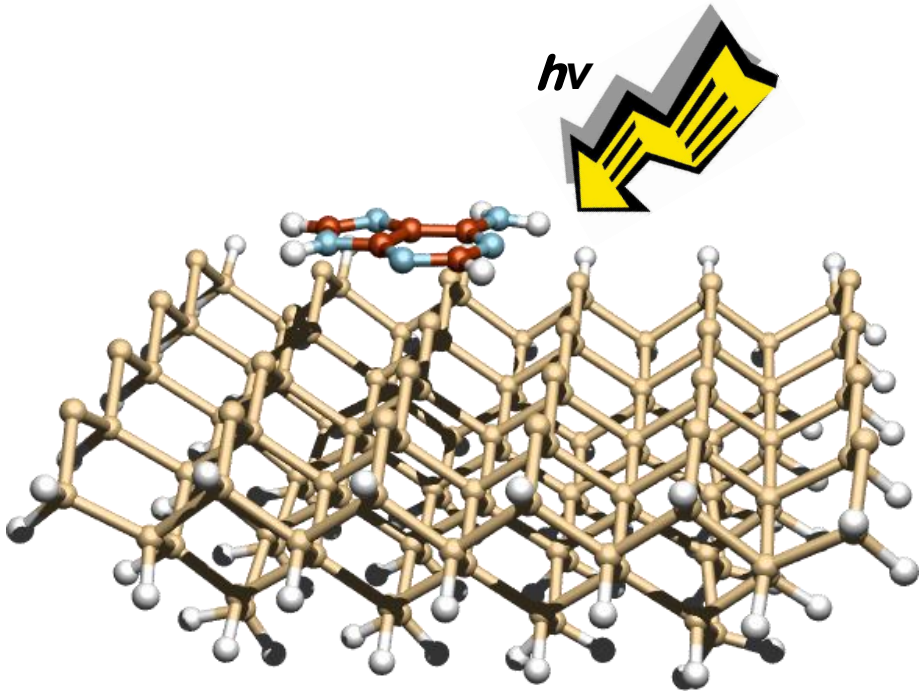
- Brucite selectively adsorbs nucleic acid components from dilute aqueous environments, suggesting a role in concentrating biomolecules in prebiotic conditions

- Brucite surface induces well-defined orientations of the molecules through specific molecule-mineral interactions, suggesting a role in assisting prebiotic self-organization, increasing molecular complexity and promoting chemical reactions towards more complex species



2. HIGH UV IRRADIATION AND SPACE-LIKE ENVIRONMENTS

UV IRRADIATION OF "BUILDING BLOCKS OF LIFE" ADSORBED ON MINERALS

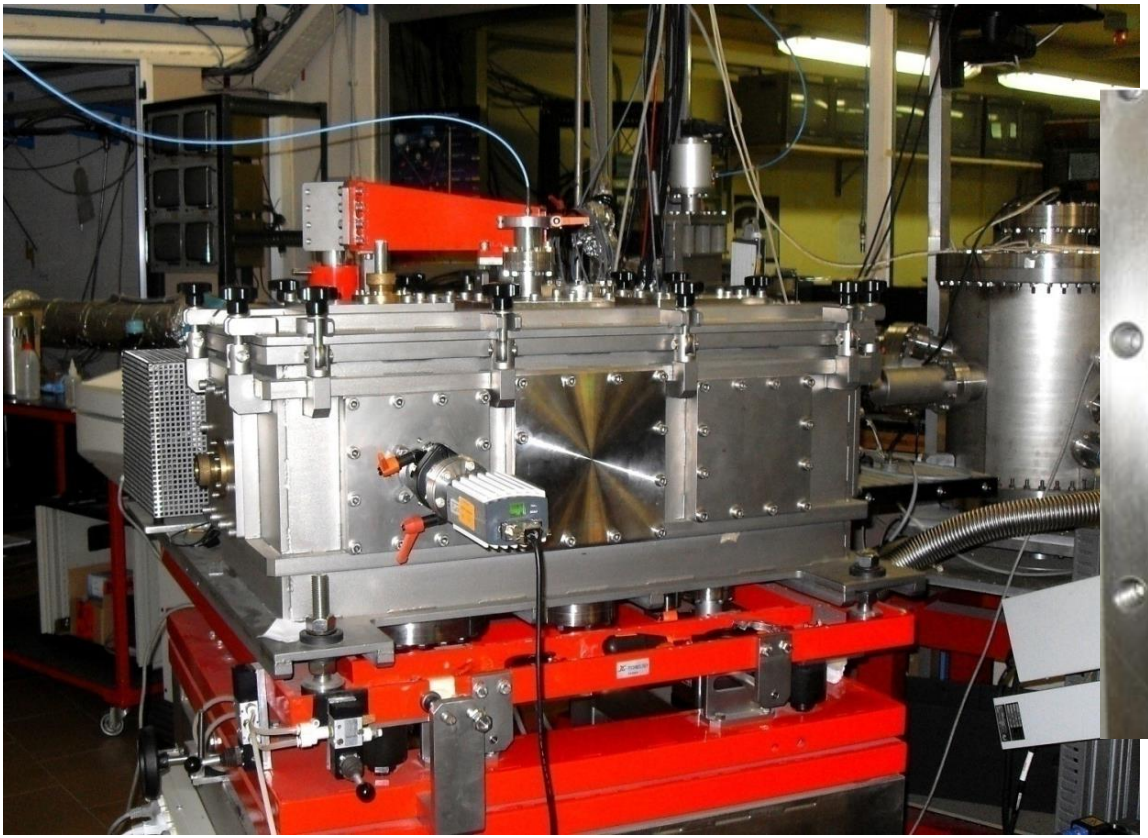


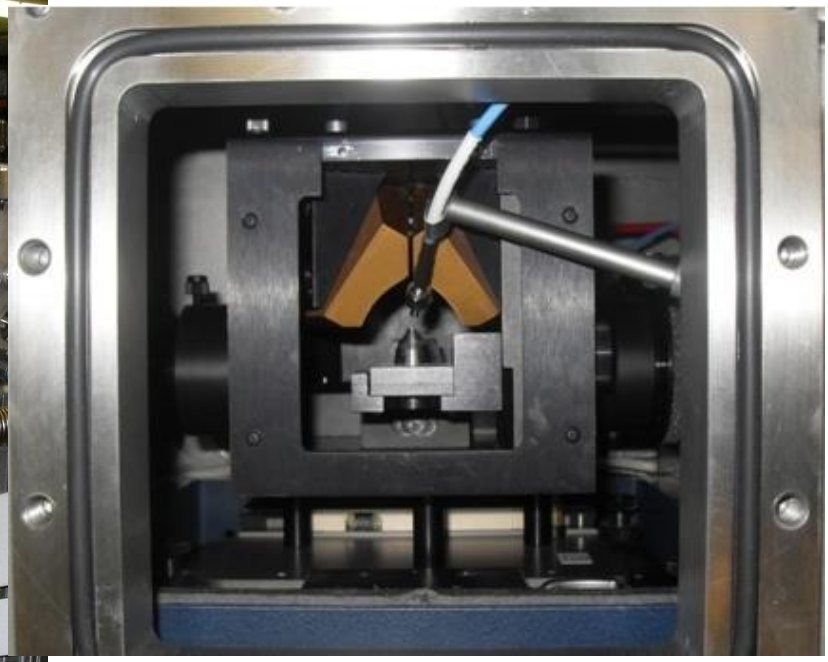
INAF – Astrophysical Observatory of Arcetri

INFN – Laboratori Nazionali di Frascati

Experimental Setup

FTIR spectroscopic *in situ* analysis during UV irradiation in vacuum; Biconical diffuse reflectance spectra acquisition technique (DRIFTS); UV source Mercury-Xenon lamp 500 W, 185-2000 nm

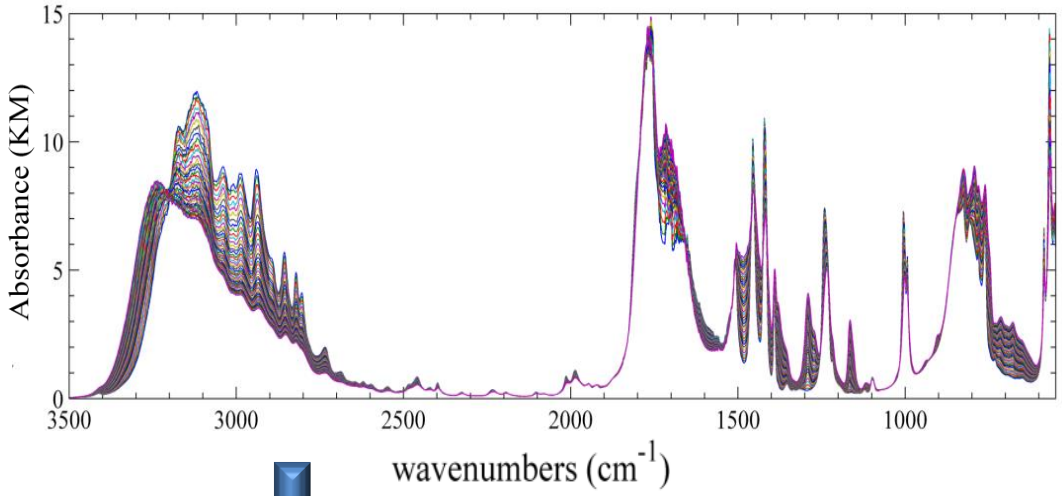




Fornaro, T.; Brucato, J. R.; Pace, E.; Guidi, M. C.; Branciamore, S.; Pucci, A. *Icarus* **2013**, *226*(1), 1068-1085.

UV IRRADIATION EXPERIMENTS

UV degradation kinetics



$$N(t)/N_0 = Be^{-\beta t} + c$$

$N(t)/N_0$ fraction of unaltered molecules
β degradation rate
B fraction of interacting molecules
c fraction of non-interacting molecules

$$t_{1/2} = \ln 2 / \beta$$

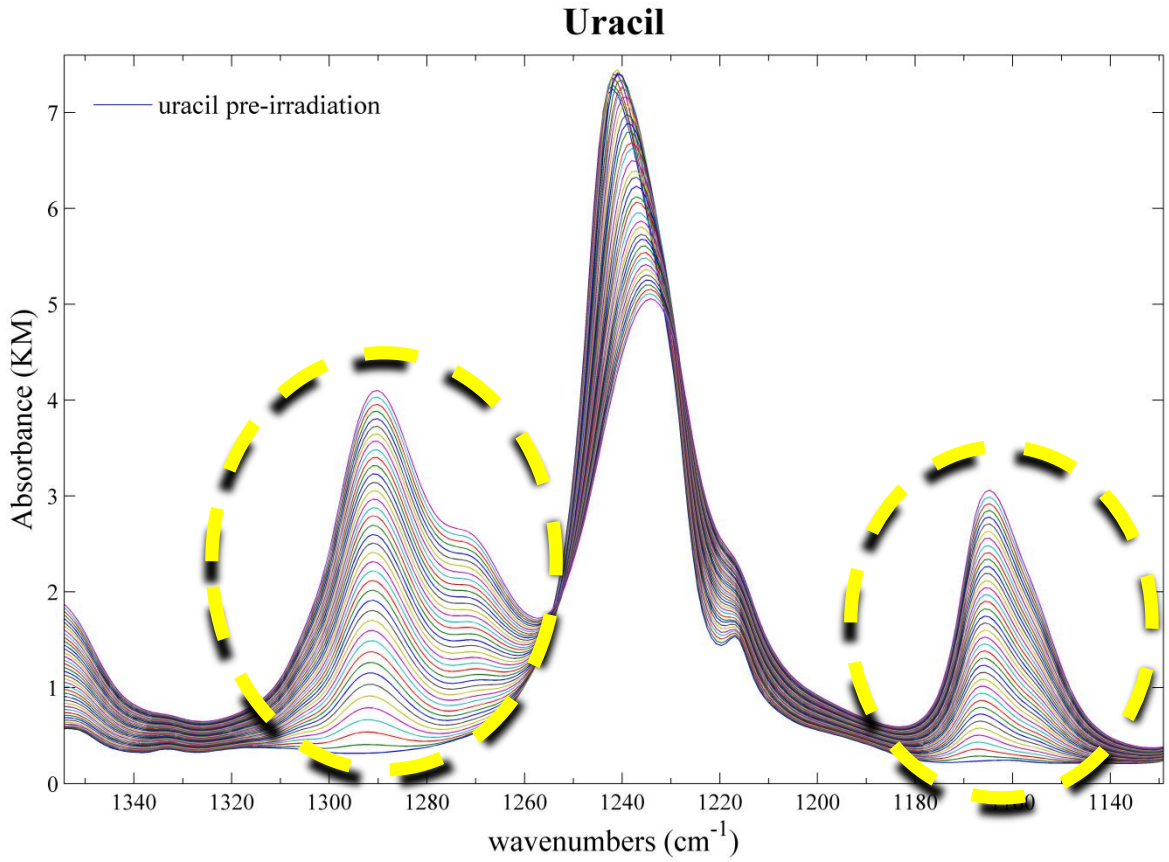
$$\beta = \sigma \Phi_{tot} / A_0$$

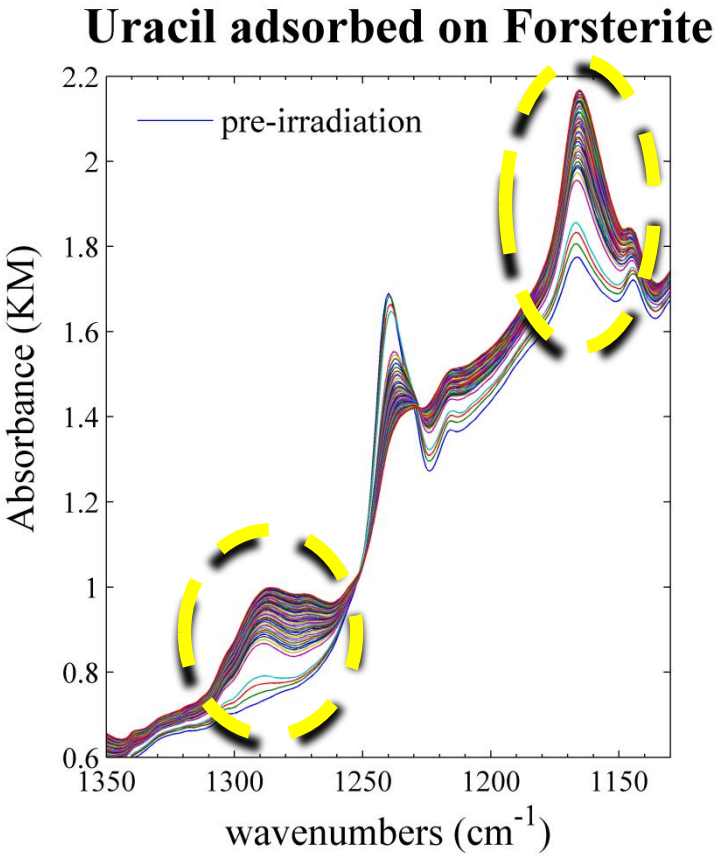
$t_{1/2}$ half-lifetime
σ UV destruction cross section
Φ_{tot} total focused incident UV flux
A_0 sample irradiated area

- **Cytosine** and **hypoxanthine** have a greater photostability
- For **adenine** and especially **uracil** degradation was observed both pure and adsorbed onto MgO and forsterite
- **Minerals** make degradation faster and more probable

Fornaro, T.; Brucato, J. R.; Pace, E.; Guidi, M. C.; Branciamore, S.; Pucci, A. *Icarus* **2013**, *226*(1), 1068-1085.

Photoproducts marker bands

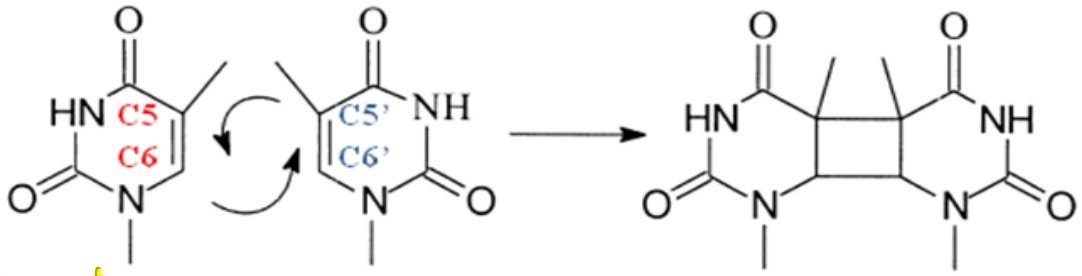


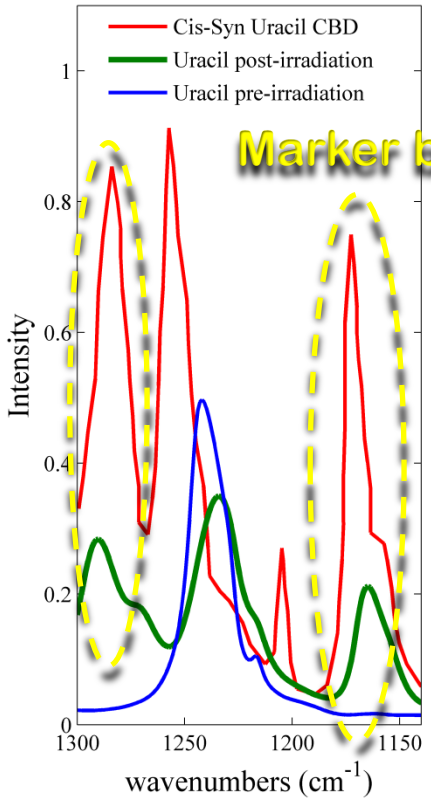


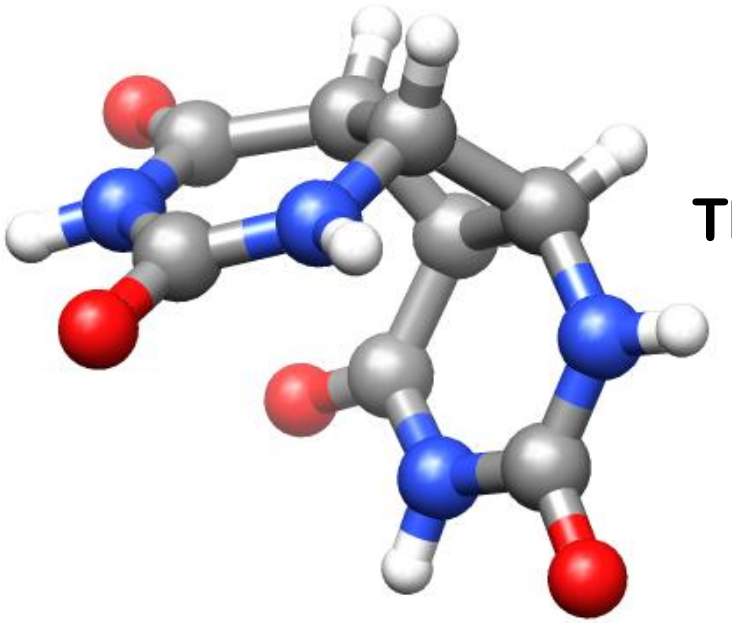
Fornaro, T.; Brucato, J. R.; Pace, E.; Guidi, M. C.; Branciamore, S.; Pucci, A. *Icarus* **2013**, *226*(1), 1068-1085.

Proposed Photoproducts

[2+2] Photocycloaddition







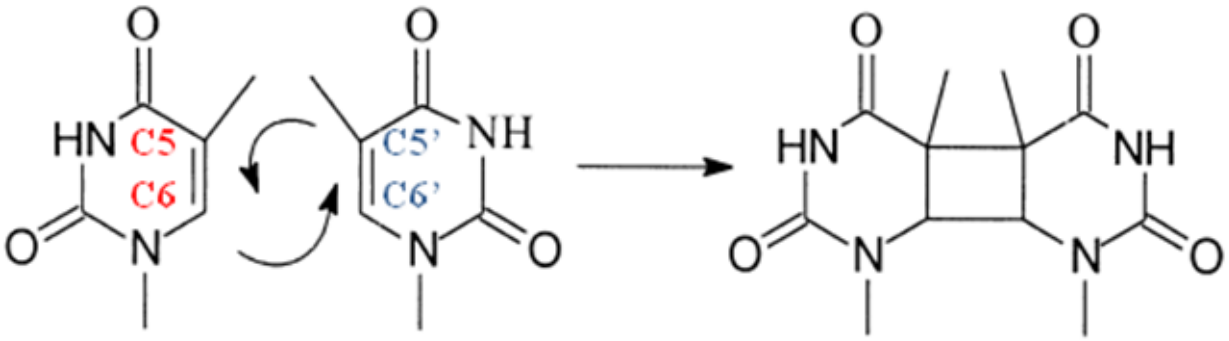
The main photoproduct:

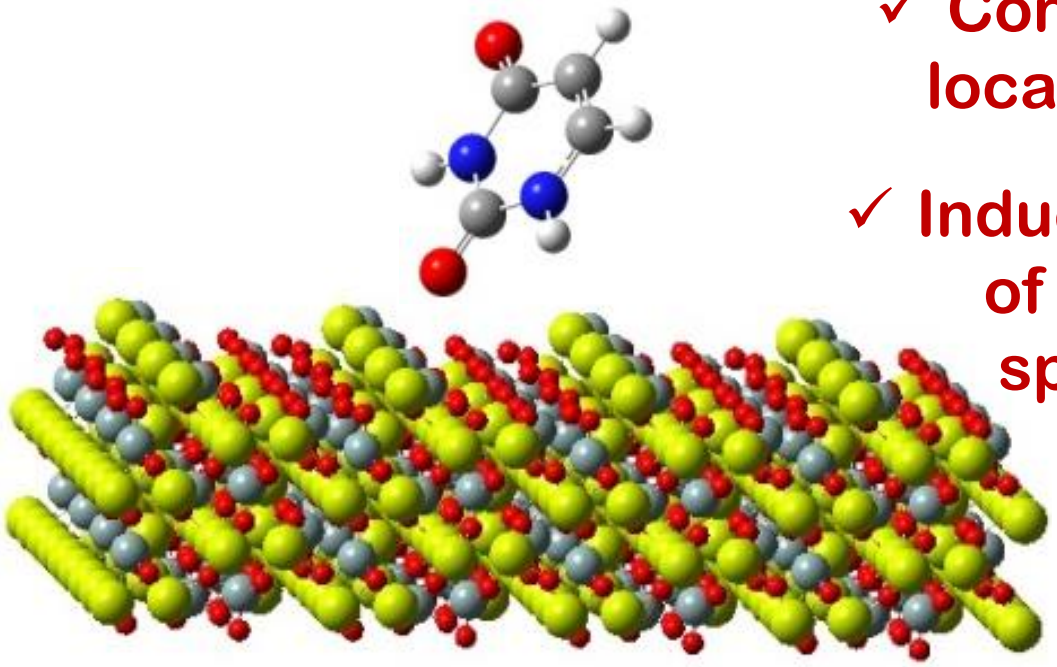
Cis-syn cyclobutane dimer (CBD)

Varghese, A.J. *Biochemistry* **1971**, *10* (23), 4283-4290; Shetlar, M.D.; Basus, V.J. *Photochemistry and Photobiology* **2011**, *87* (1), 82-102.

Catalytic Effect of Forsterite

[2+2] Photocycloaddition

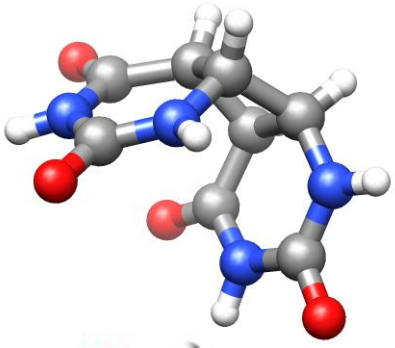




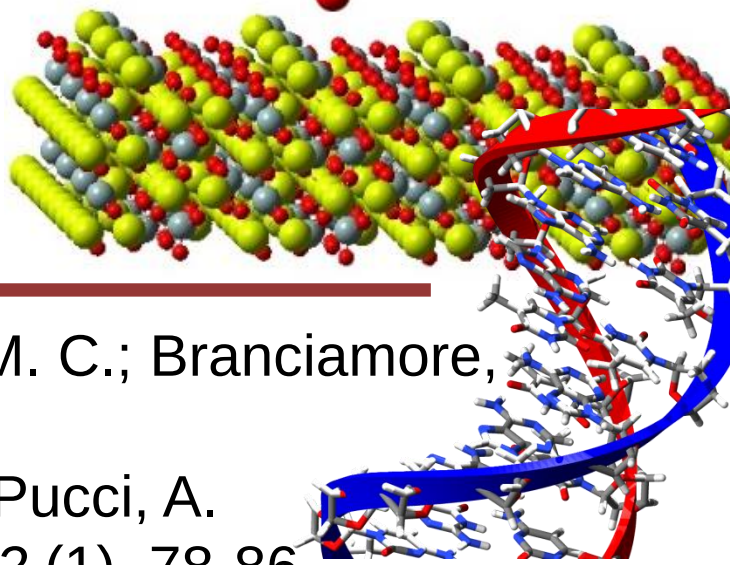
- ✓ Concentrates molecules on a local scale through adsorption
- ✓ Induces the correct orientation of reactive groups through specific molecule-mineral interactions

Summary

- **Uracil is the most photoreactive, probably forming cyclobutane dimers**



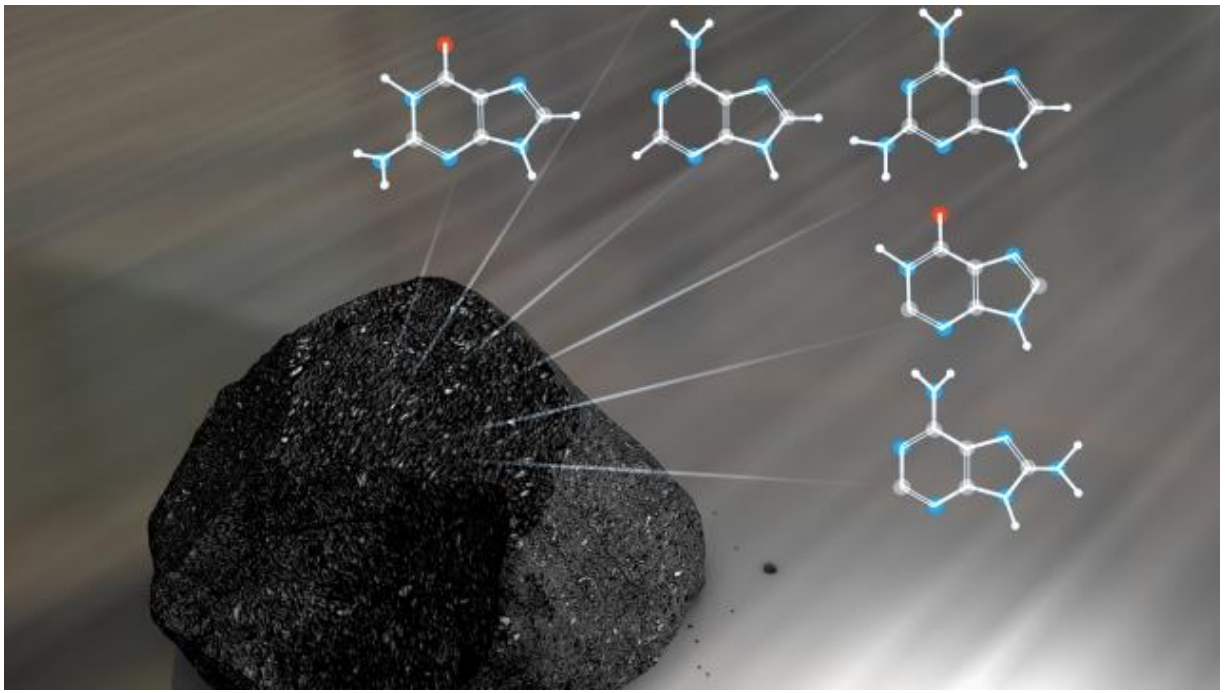
- **MgO and Forsterite have no protective effect, instead they may be catalytic potentially triggering chemical processes towards complex species**



Fornaro, T.; Brucato, J. R.; Pace, E.; Guidi, M. C.; Branciamore, S.; Pucci, A. *Icarus* **2013**, *226*, 1068-1085.
Fornaro T.; Brucato, J. R.; Branciamore, S.; Pucci, A. *International Journal of Astrobiology* **2013**, *12* (1), 78-86.

Open Questions

- What are the causes of the different behavior of nucleobases in the presence of UV radiation?
- What is the photochemistry of the degradation process at a mechanistic level?



Open Questions

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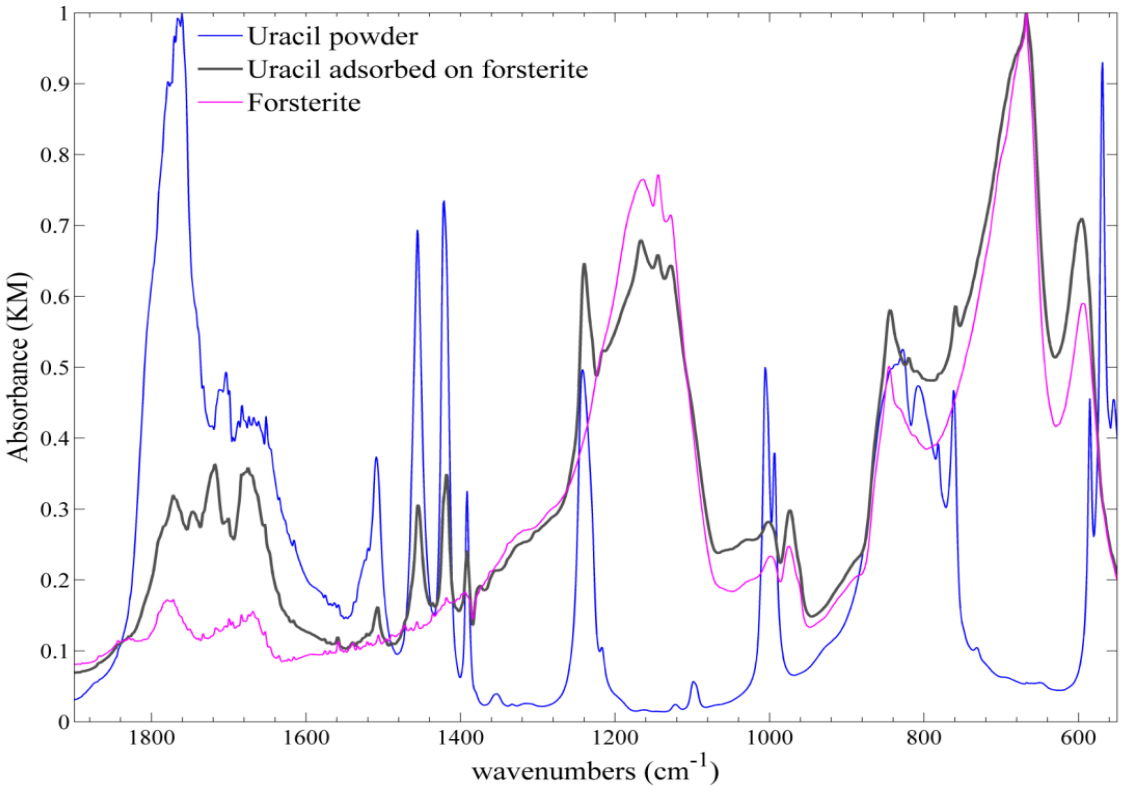
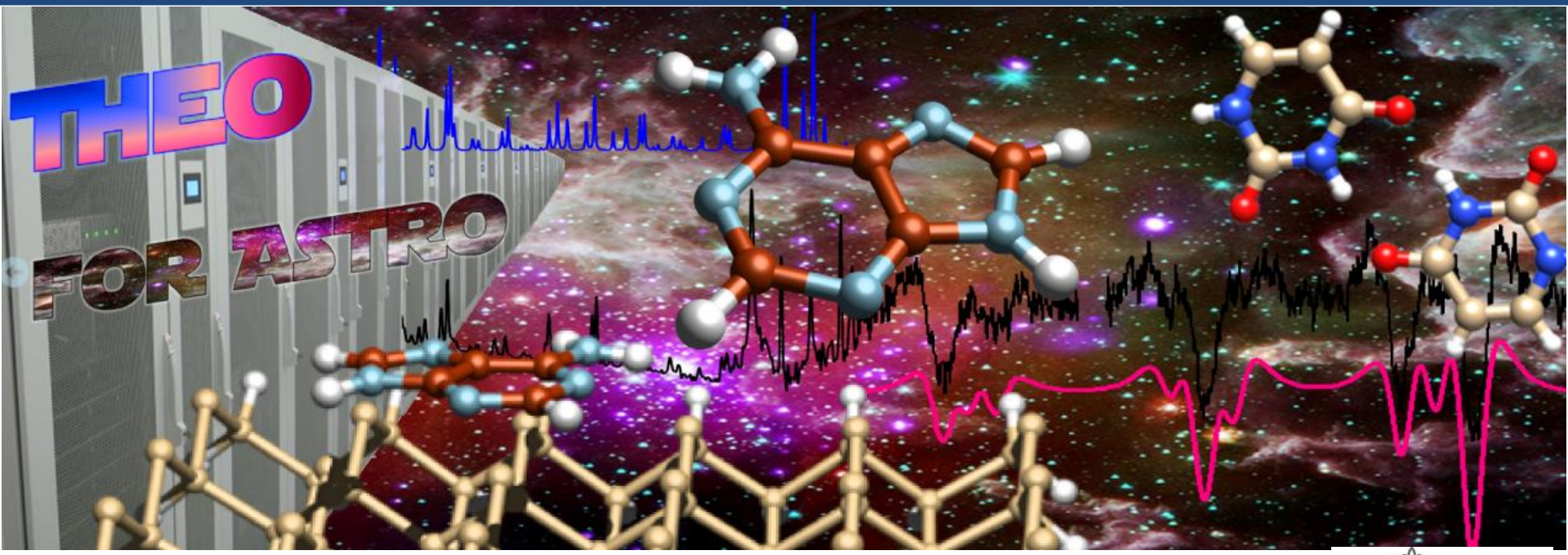


Need of a correct interpretation of the spectroscopic features

COMPUTATIONAL SPECTROSCOPY

Development of a computational procedure based on quantum mechanical anharmonic computations of vibrational frequencies and IR intensities

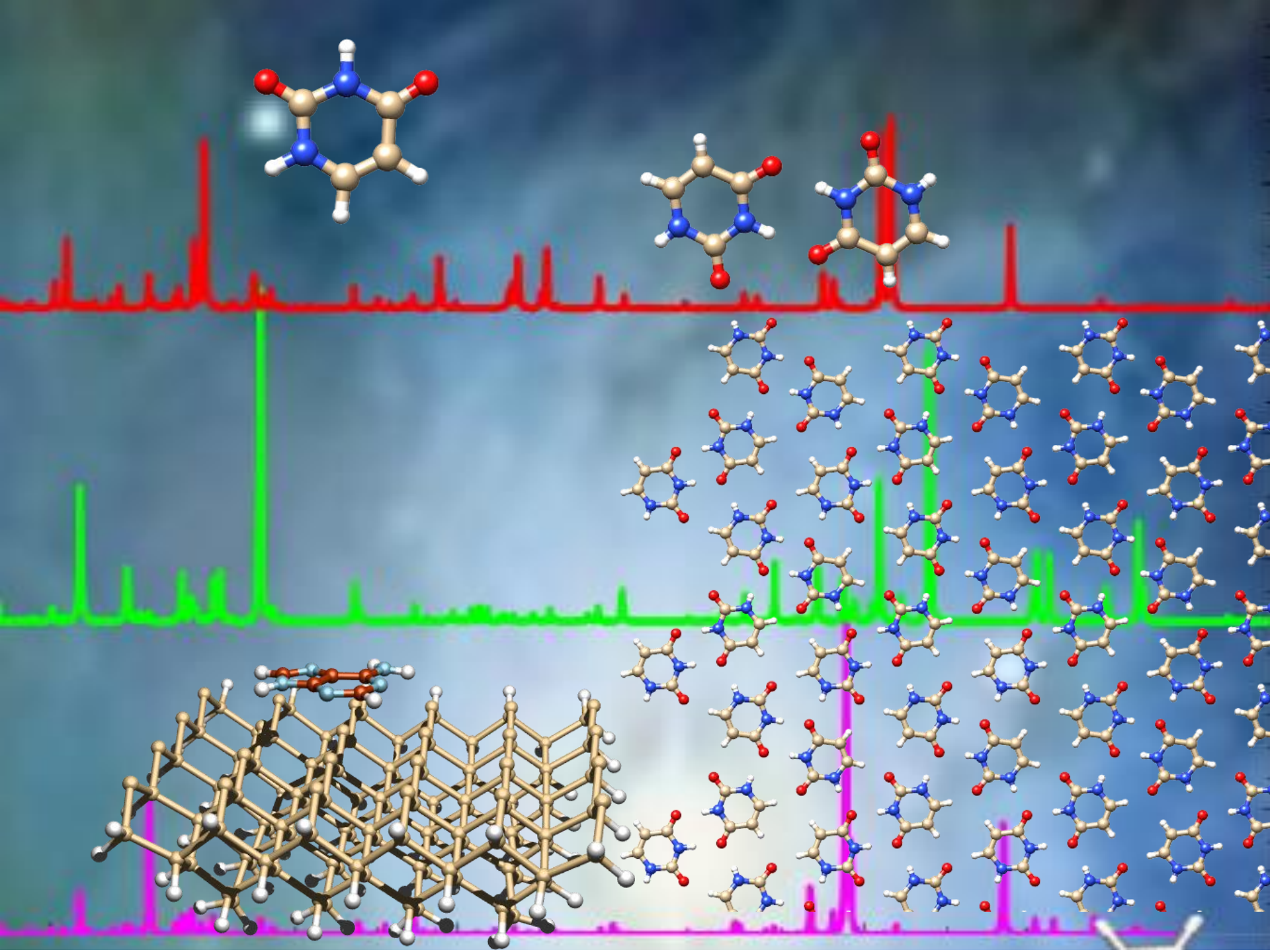


HPC 3D LAB DREAMS

DREAMS

Dedicated Research Environment for Advanced Modeling and Simulation

SCUOLA NORMALE SUPERIORE



Methods

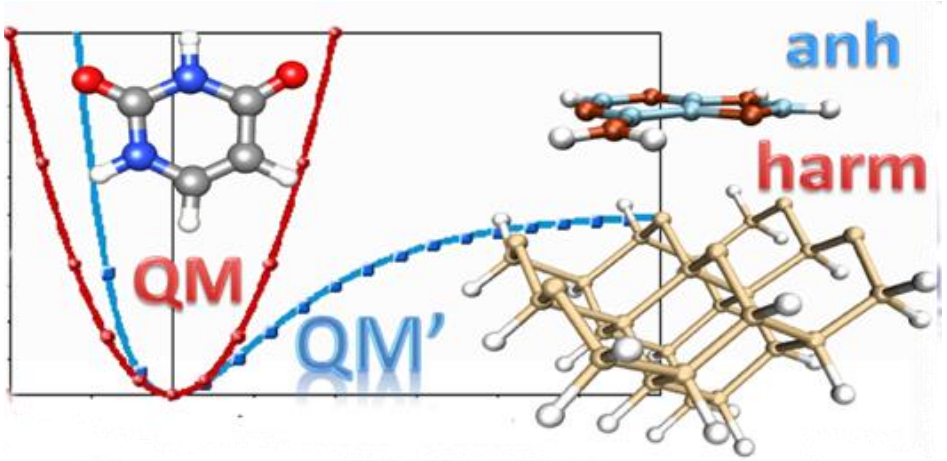
Dispersion-corrected Density Functional Theory methods

B3LYP-D3 / SNSD(N07D) (Semi-empirical dispersion correction)

Simulation of anharmonic IR spectra

Generalized second-order vibrational perturbation (GVPT2) model approach

$$E_\upsilon = \chi_0 + \sum_i \omega_i \left(\upsilon_i + \frac{1}{2}\right) + \sum_i \sum_{j<i} \chi_{ij} \left(\upsilon_i + \frac{1}{2}\right)\left(\upsilon_j + \frac{1}{2}\right)$$



Suite of programs: GAUSSIAN

Grimme, S. *et al. J. Chem. Phys.* **2010**, *132*, 154104.
Barone, V. *J. Chem. Phys.* **2005**, *122*, 014108.
Bloino, J.; Barone, V. *J. Chem. Phys*. **2012**, *136*, 124108.
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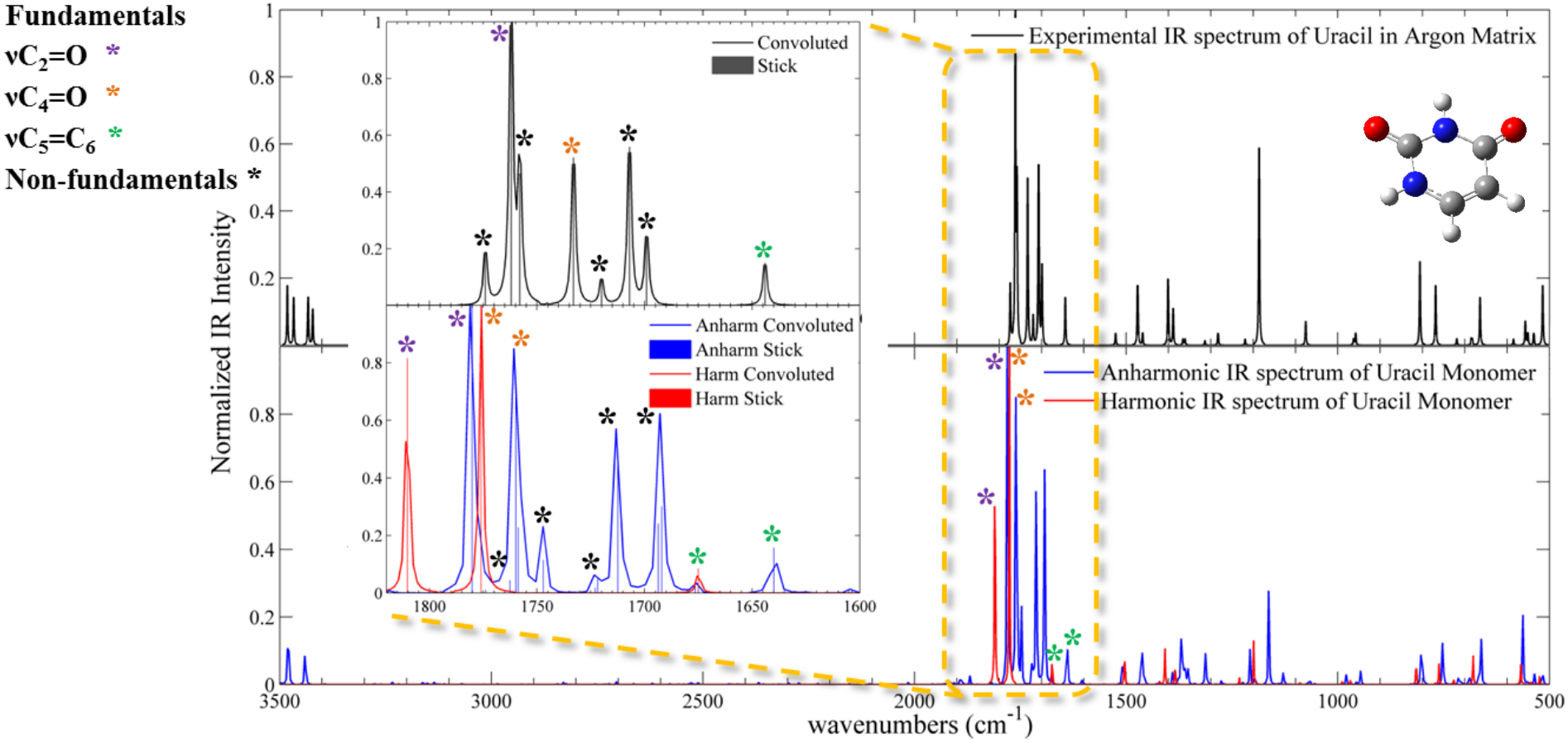
Simulation of anharmonic IR spectra: Uracil

B3LYP-D3/N07D + GVPT2 APPROACH



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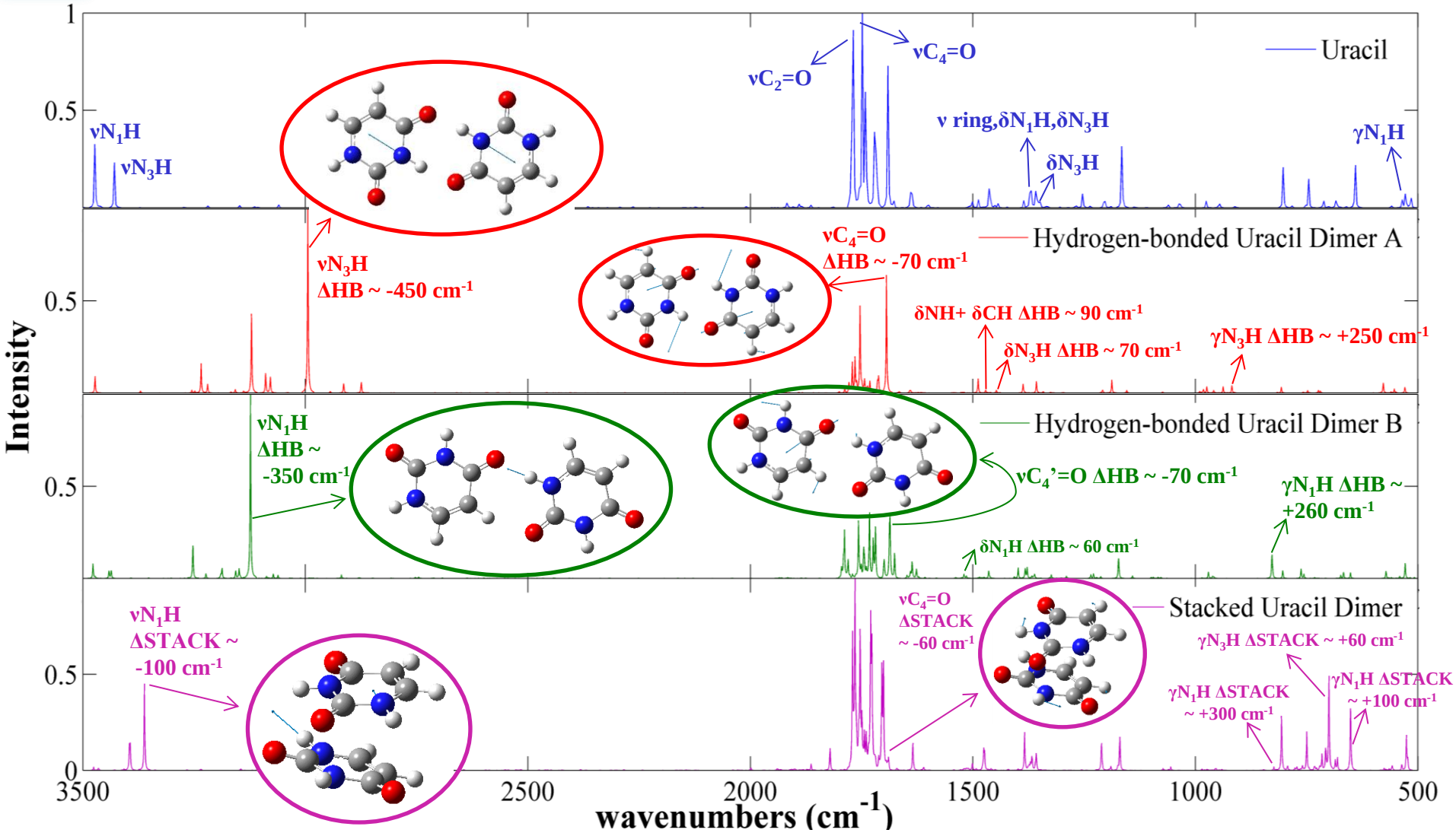
Effects of intermolecular interactions: Uracil Dimers



Fornaro, T.; Biczysko, M.; Monti, S.; Barone, V. *Phys. Chem. Chem. Phys.* **2014**, *16*, 10112-10128.
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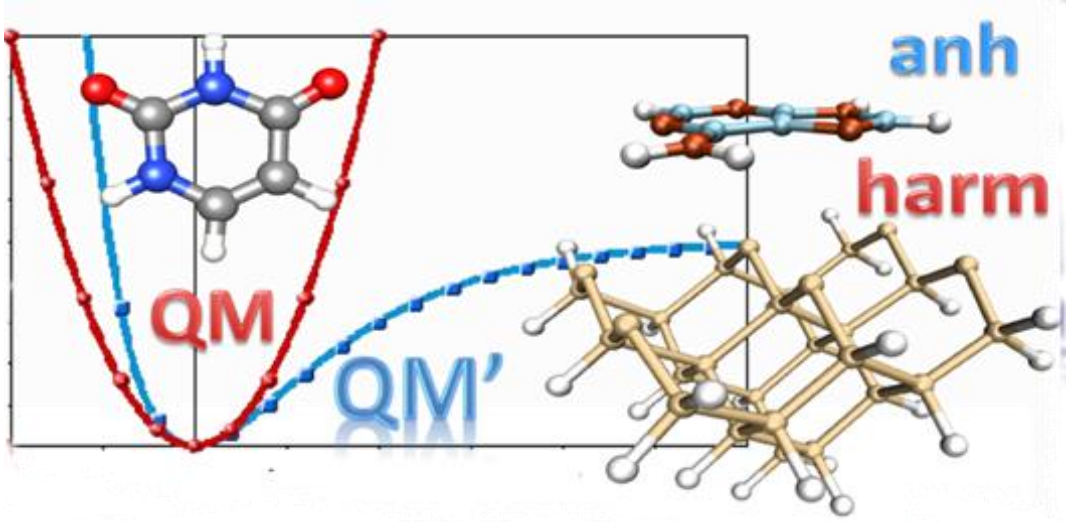
Development of feasible protocols for large systems: Uracil in the Solid State

Hybrid Model: B3LYP-D3/N07D:DFTBA

$$E_\upsilon = \chi_0 + \sum_i \omega_i \left(\upsilon_i + \frac{1}{2}\right) + \sum_i \sum_{j<i} \chi_{ij} \left(\upsilon_i + \frac{1}{2}\right)\left(\upsilon_j + \frac{1}{2}\right)$$



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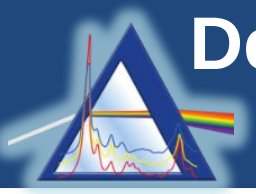


Development of feasible protocols for large systems: Uracil in the Solid State

Reduced dimensionality (RD)-VPT2: B3LYP-D3/N07D

-Set of M "active" normal modes for which anharmonic frequencies are evaluated (i)

-Couplings with other (harmonic) modes (j,k)

Differences wrt FULL VPT2:

-ONLY some limited number of cubic force constants (terms including only j and k indices) are not evaluated

-Important ONLY if j,k and i are coupled

$$4\chi_{ij} = k_{iijj} - \frac{2\omega_i {k_{iij}}^2}{4{\omega_i}^2 - {\omega_j}^2} - \frac{2\omega_j {k_{ijj}}^2}{4{\omega_j}^2 - {\omega_i}^2} - \frac{k_{iii}k_{ijj}}{\omega_i} - \frac{k_{jjj}k_{iij}}{\omega_j}$$
$$+ \sum_{\substack{k=1 \\ k\neq i,j}}^{N} \left[\frac{2\omega_k({\omega_i}^2 + {\omega_j}^2 - {\omega_k}^2){k_{ijk}}^2}{\Delta_{ijk}} - \frac{k_{iik}k_{jjk}}{\omega_k} \right] + \frac{4({\omega_i}^2 + {\omega_j}^2)}{\omega_i\omega_j} \sum_{\tau=x,y,z} B_e^{\tau} \left(\zeta_{ij}^{\tau}\right)^2$$

Selection of "active modes" based on nature of the vibrations and energy range

Barone, V. et al. *Int. J. Quant. Chem.* **2012**, *112*, 2185. Barone, V.; Biczysko, M.; Bloino, J. *Phys. Chem. Chem. Phys.* **2014**, *16*, 1759–1787.

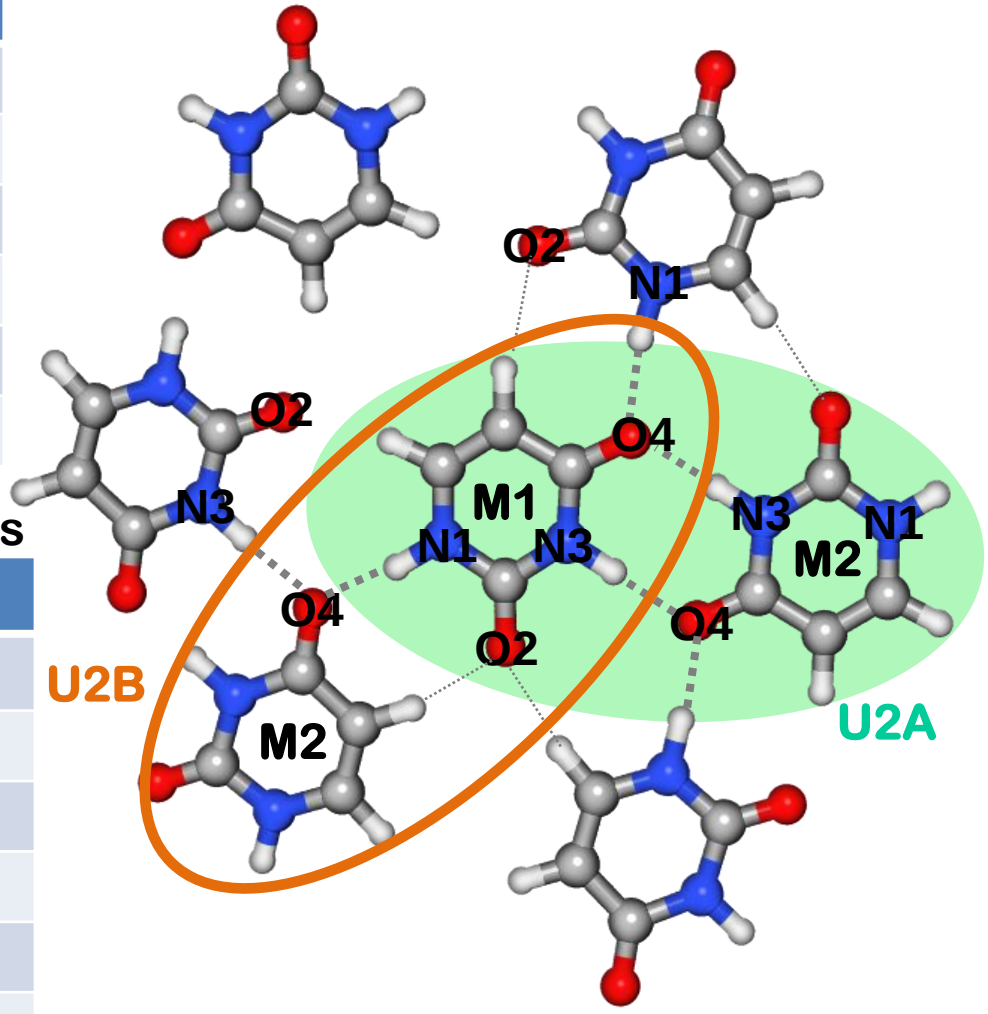
Effects of intermolecular interactions

Experimental data:

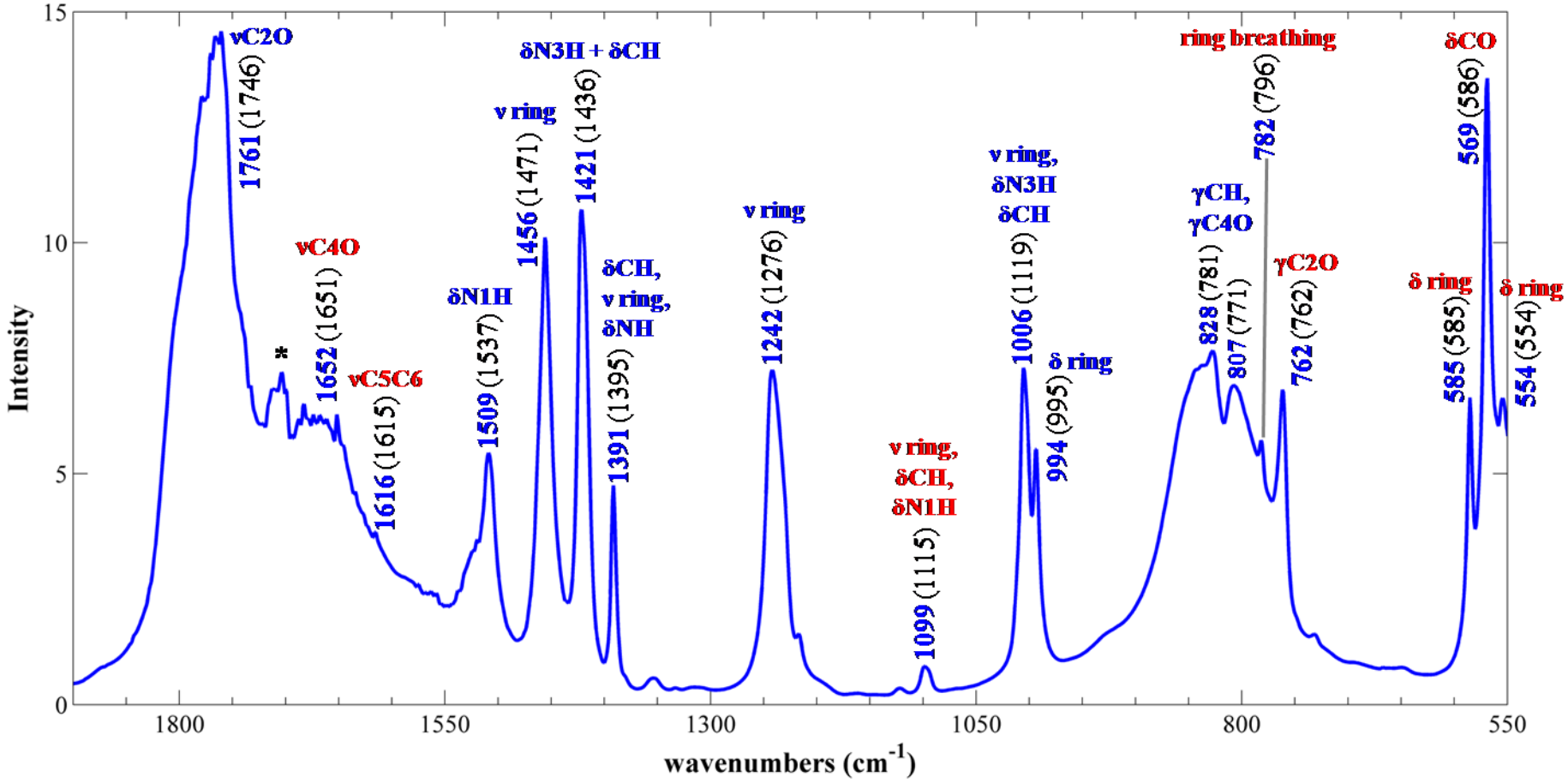
assign	ν Uracil in Argon	Δν Solid Uracil
νN1H	3482	**-376**
νN3H	3433	**-433**
νC5H	3130	-42
νC2=O	1762	-1
νC4=O	1733	**-81**
νC5C6	1644	-28

RD –VPT2 scheme: 15 selected modes

assign	ν	Δν		
	U	U2A	U2B	U7
νN1H	3473	3	-351 (M1)	-399
νN3H	3430	-450	10	-393
νC5H	3109	20	-35	-40
νC2=O	1770	18	9	-24
νC4=O	1749	-62	-55 (M2)	-98
νC5C6	1638	-9	0	-23



Assignments of the Experimental Spectrum



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Summary

- A **reliable** and **feasible** computational protocol for **simulating the IR spectra of quite large systems at anharmonic level** has been developed, combining the **hybrid B3LYP-D3/N07D:DFTBA** approach with the **RD-VPT2** one

- Such a protocol has prepared the ground for further studies of biomolecules adsorbed on minerals

Fornaro, T.; Carnimeo, I.; Biczysko, M. *J. Phys. Chem. A* **2015**, *119* (21), 5313–5326.
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TAKE-HOME MESSAGES…

Abiogenesis = set of processes that led to emergence of life from inorganic matter on early Earth and potentially on other planets

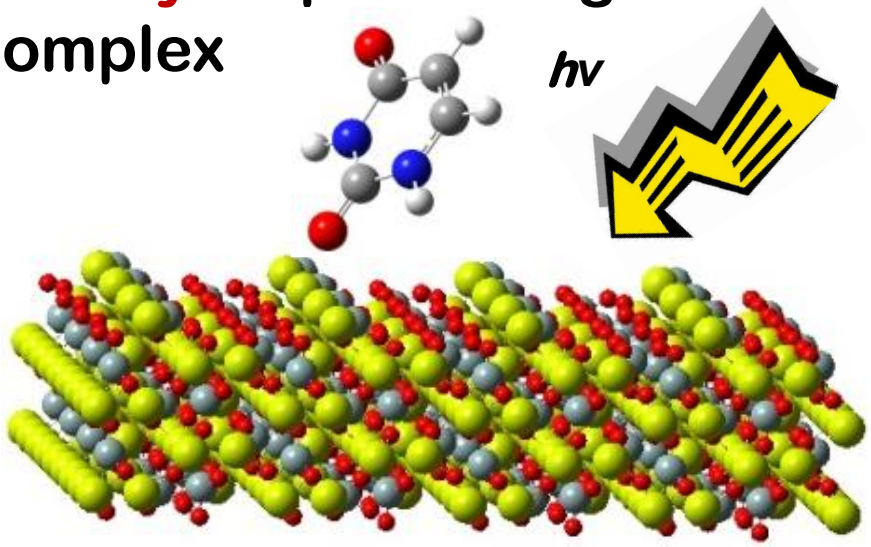
→ Crucial transition from inanimate matter to biological systems probably occurred through **selection**, **concentration** and **organization of organic precursors**, yielding to the essential macromolecules of life

TAKE-HOME MESSAGES…

Our results:

- Mineral surfaces have the ability to selectively adsorb and concentrate organic molecules on a local scale, removing key organics from aqueous environments, promoting self-organization through specific molecule- mineral interactions

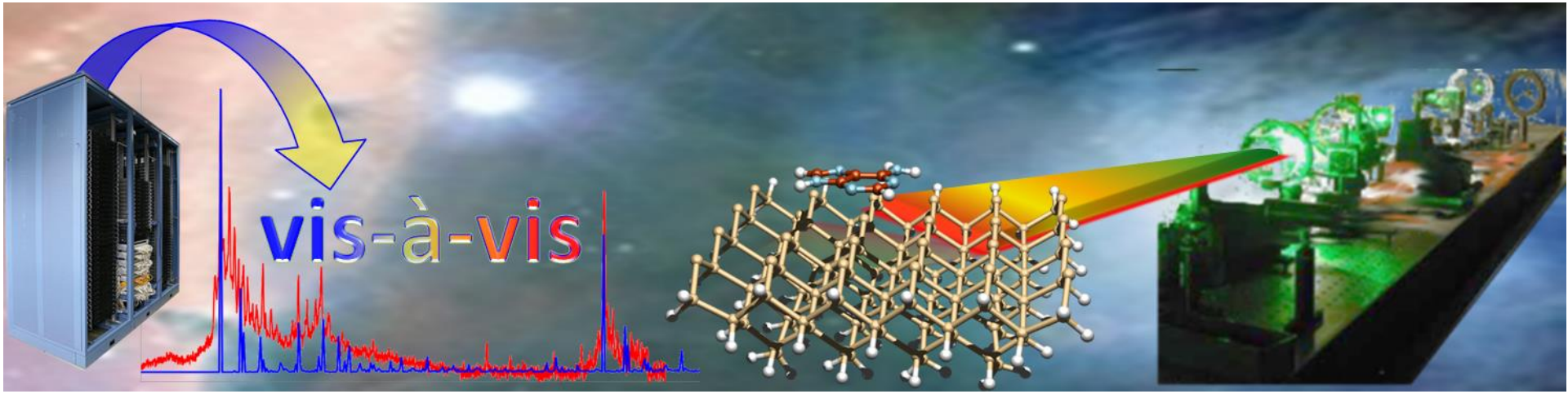
- Minerals can act as photocatalysts promoting reactions towards more complex species



TAKE-HOME MESSAGES…

The study of abiogenesis is an overwhelming task due to the huge amount of possible reactive pathways, the complexity of the involved heterogeneous systems, the extreme environmental conditions which need to be taken into account

- Spectroscopic methods can be employed to investigate a variety of properties and processes occurring in the prebiotic systems
- *In silico* modeling is a useful tool in order to unravel the intricate experimental data for molecular systems of increasing size and complexity



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