5th Workshop of the Italian Astrobiology Society
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Nucleic Acid Components adsorbed on mineral surfaces: A test bed for searching signs of life on Mars

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SCUOLA NORMALE SUPERIORE PISA

INAF - Arcetri

Mars Exploration

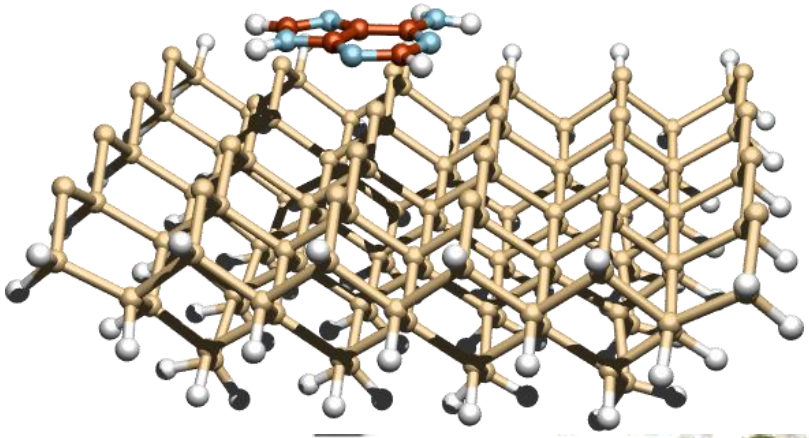
Mars Exploration: Laboratory Simulations

INTRODUCTION

Spectroscopic studies of the effects of UV radiation on biomolecules in heterogeneous environments: Relevance of the Research

- **Prebiotic chemistry**

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

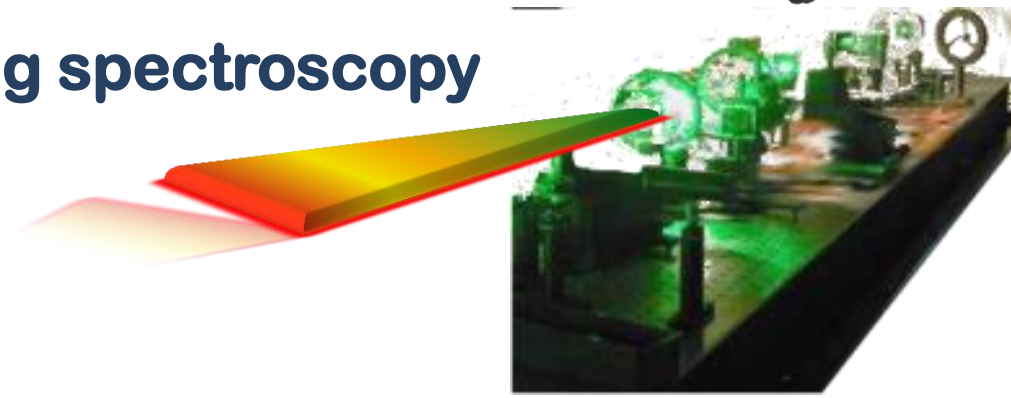


- **Life detection**

Identification of potential **biomarkers**

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

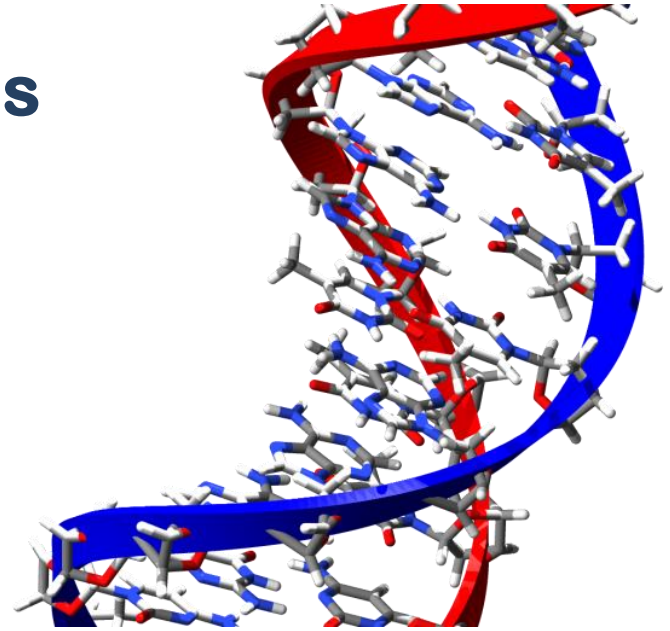
Detection of **organic compounds in space**

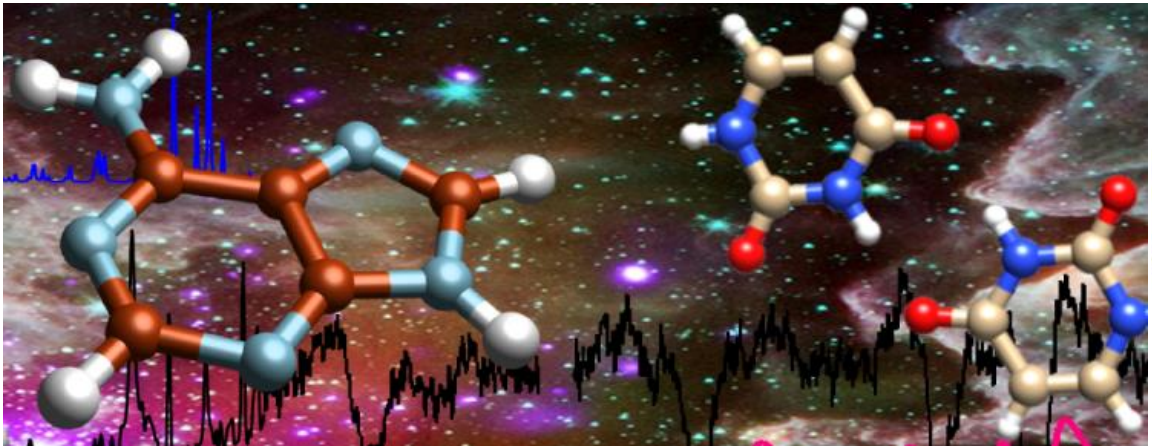


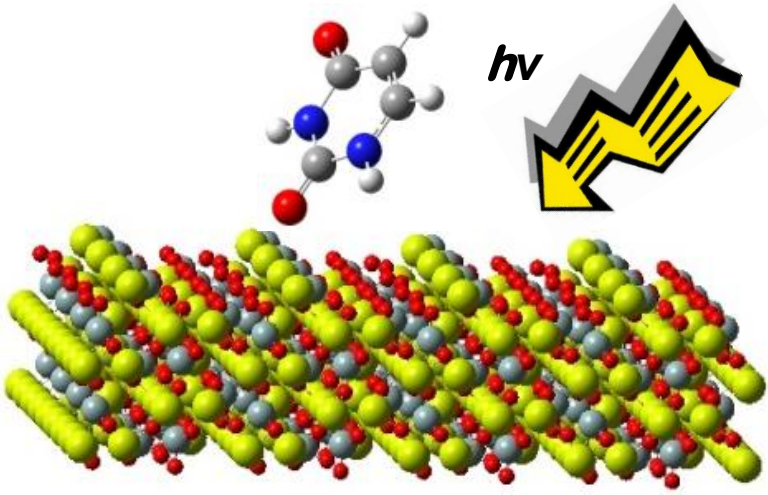
Nucleobases: Relevance of the Research

Coding components of nucleic acids

- **Biomarkers** of **extant life**
- Study of the **origin of life**
- **Preservation** of **biological matter** under space conditions

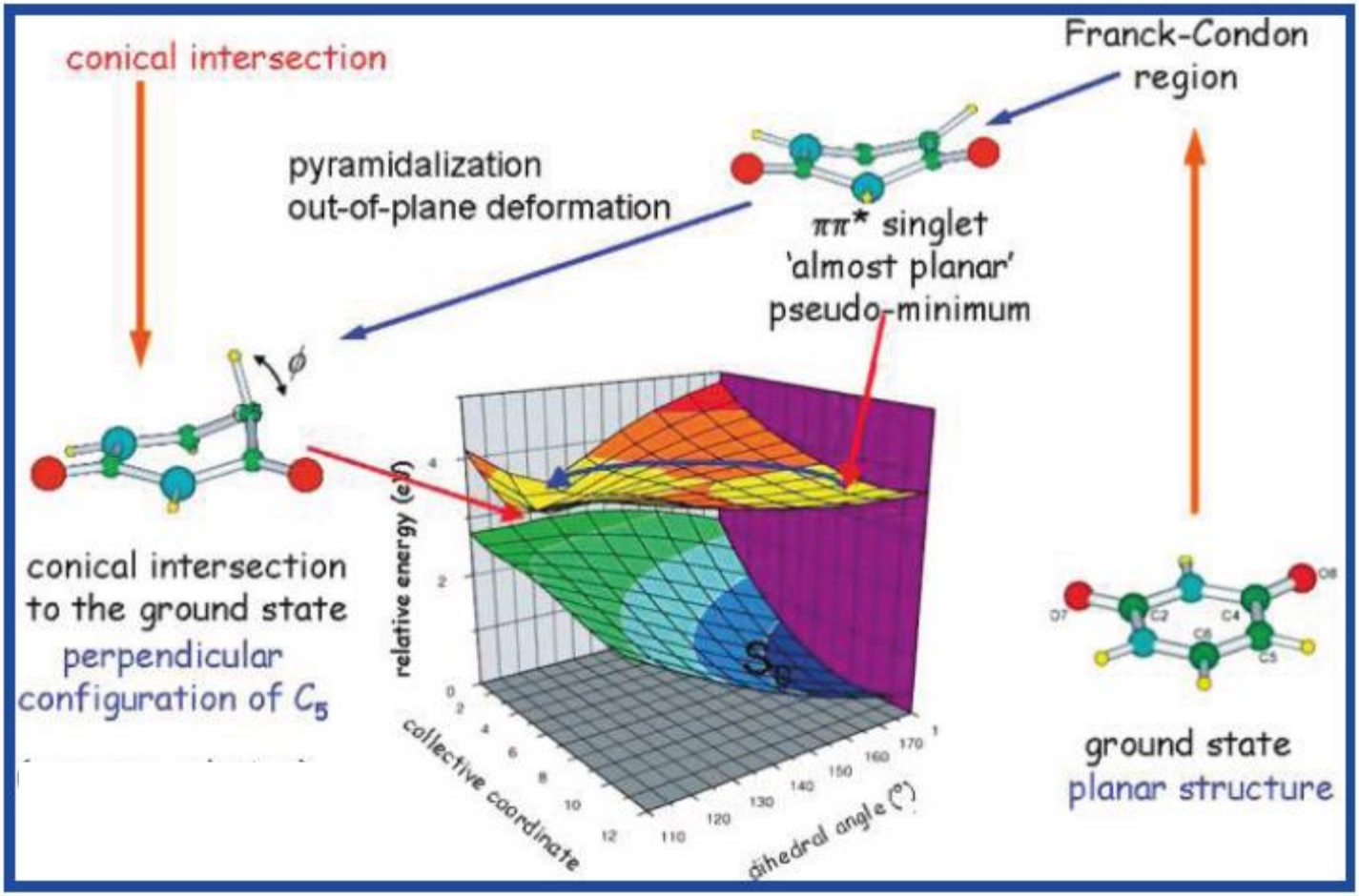






Nucleobases: Relevance of the Research

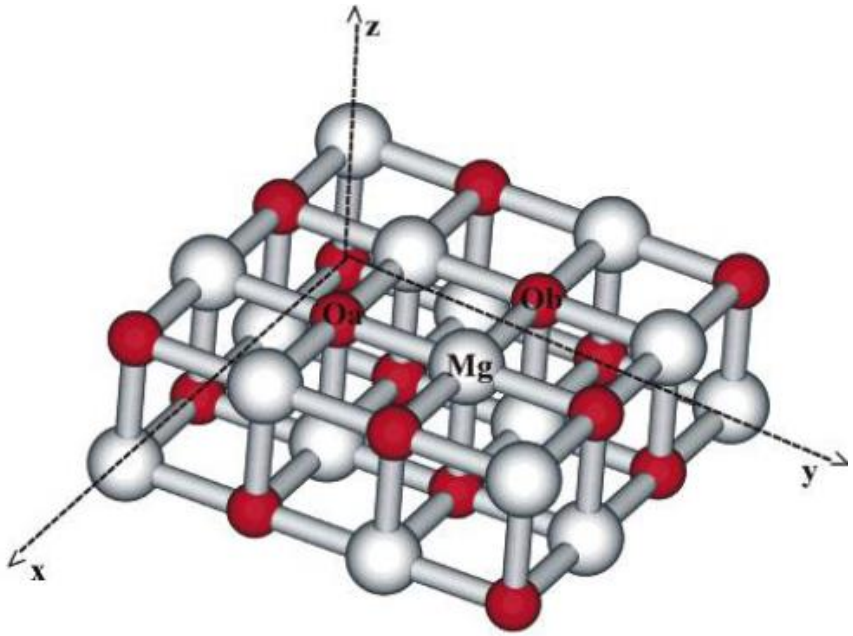
Nucleobases might have played a critical role at the dawn of life due to their photoprotective properties



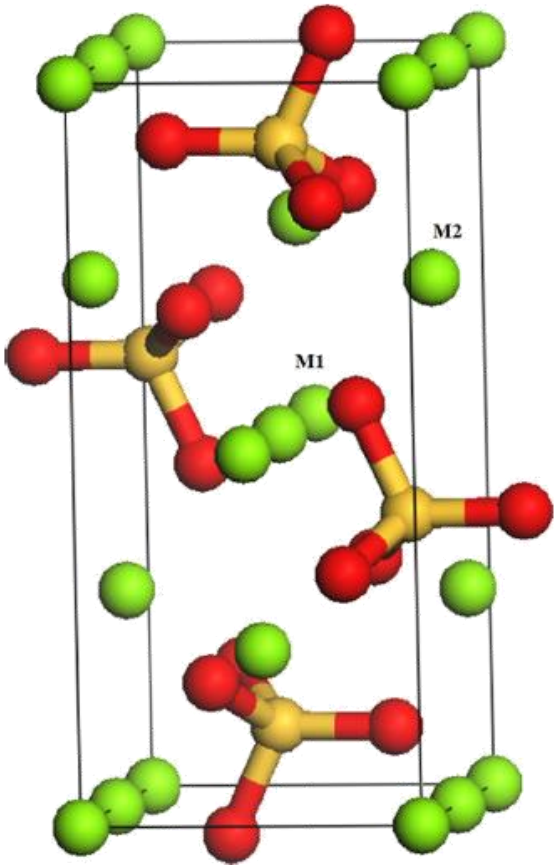
Gustavsson, T. *et al.*, *J. Am. Chem. Soc.* **2006**, *128*, 607–619;
Gustavsson, T.; Improta, R.; Markovitsi, D. *J. Phys. Chem. Lett.* **2010**, *1*, 2025–2030.

Minerals: Metal Oxides and Silicates

Magnesium oxide (MgO)



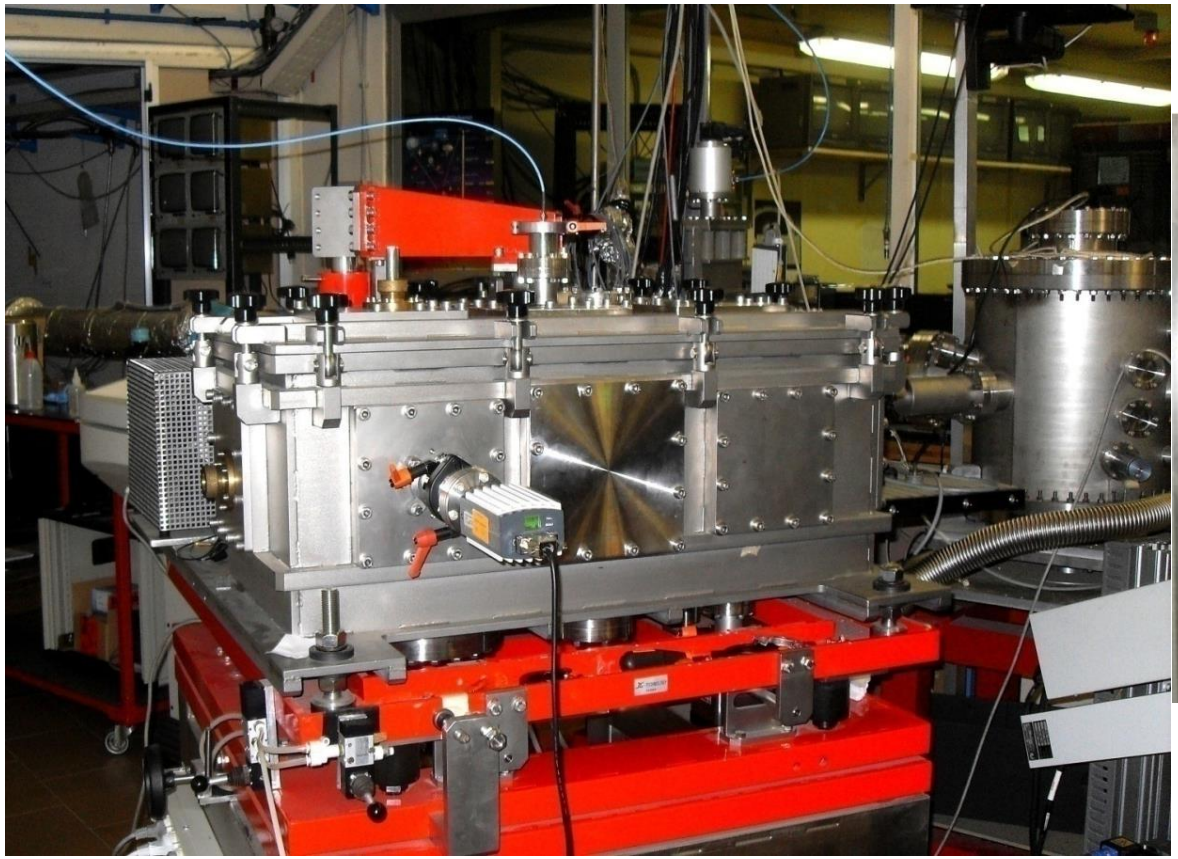
Forsterite (Mg_2SiO_4)

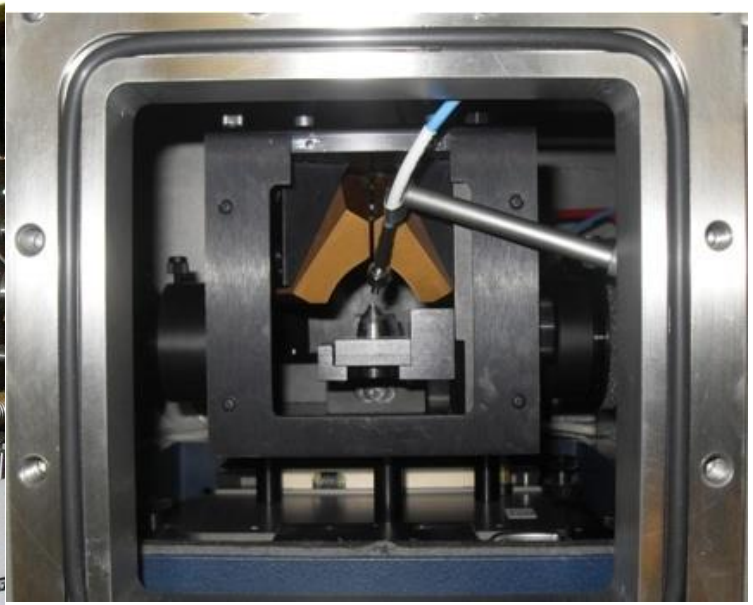


UV IRRADIATION EXPERIMENTS

Photostability of nucleobases adsorbed on Magnesium Oxide and Forsterite

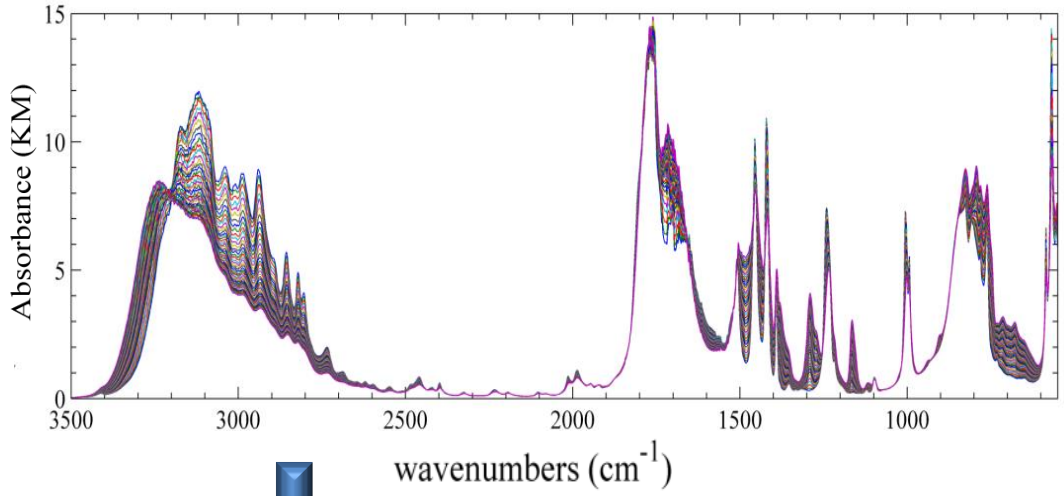
FTIR spectroscopic *in-situ* analysis during UV irradiation in vacuum
Biconical diffuse reflectance spectra acquisition technique (**DRIFTS**)
UV source Mercury-Xenon lamp 500 W, 185-2000 nm





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

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

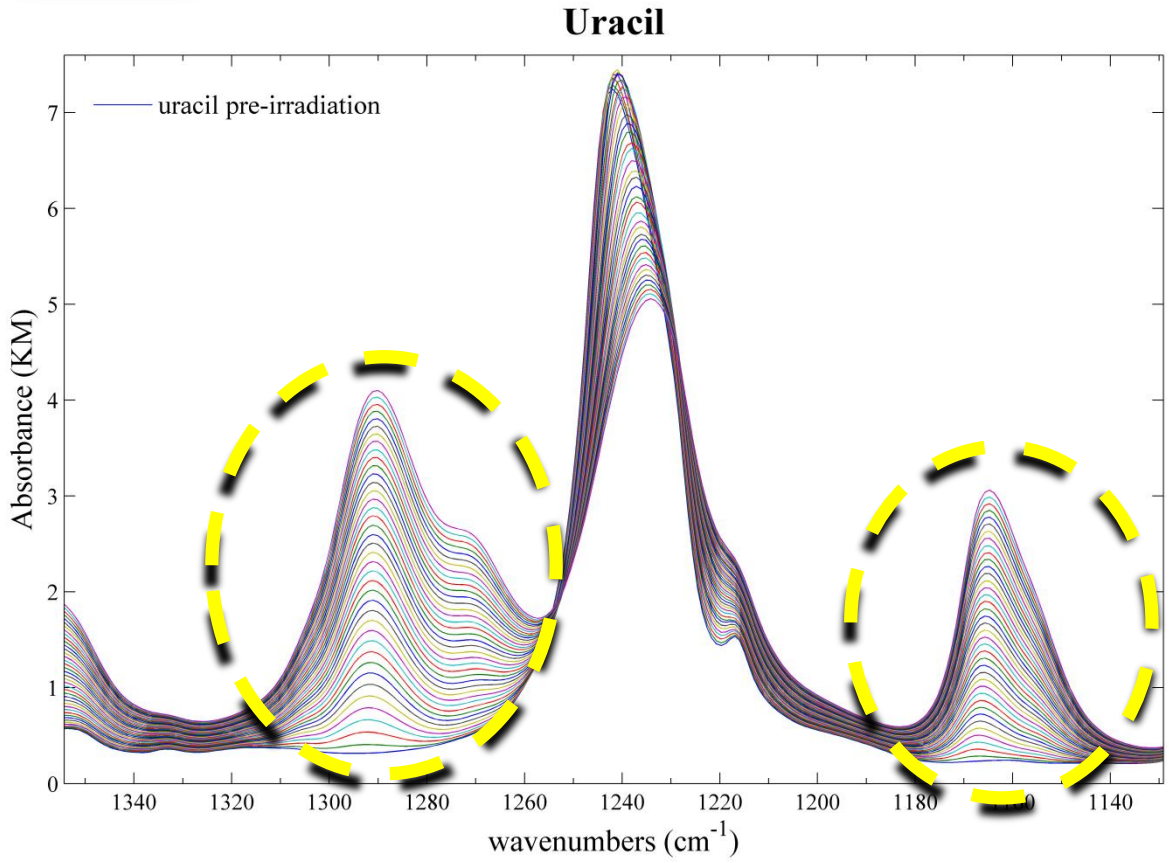
$$\beta = \sigma \Phi_{tot} / A_0$$

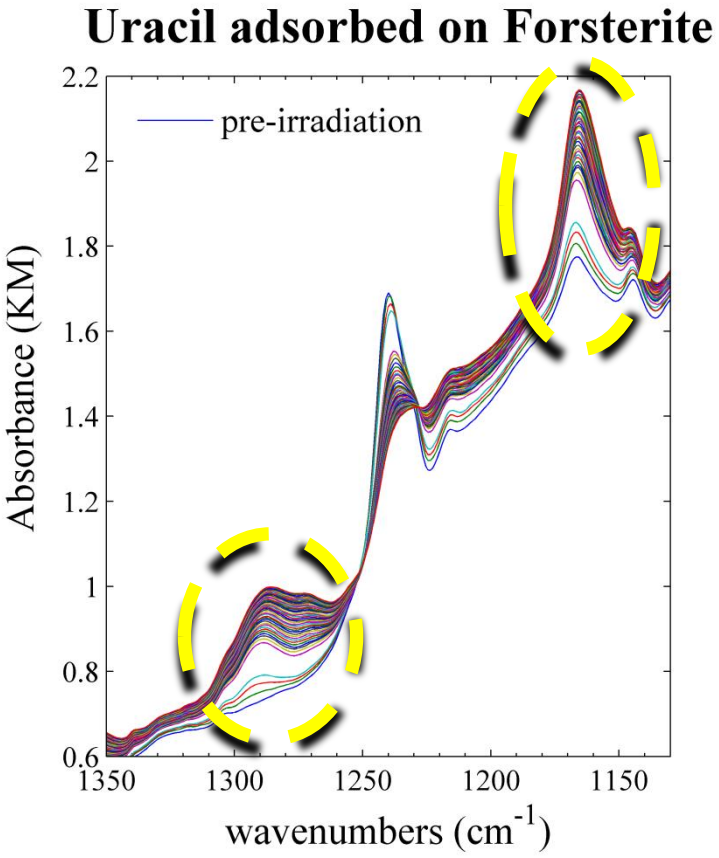
$t_{1/2}$ half-lifetime
σ UV destruction cross section
Φ_{tot} total focused incident UV flux
A_0 sample irradiated area

- **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. et al. *Icarus* **2013**, *226*, 1068-1085.

Photoproducts marker bands

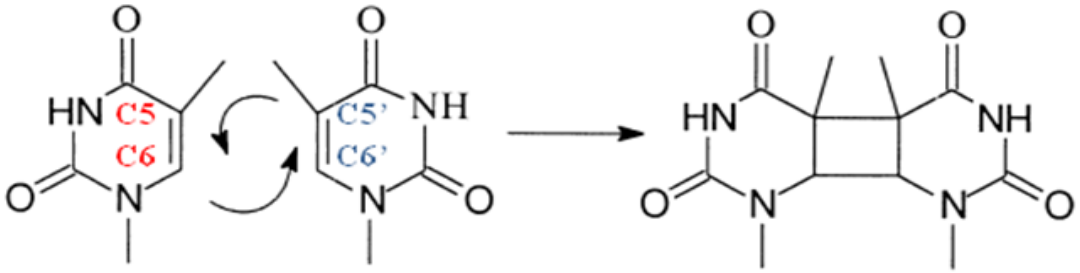


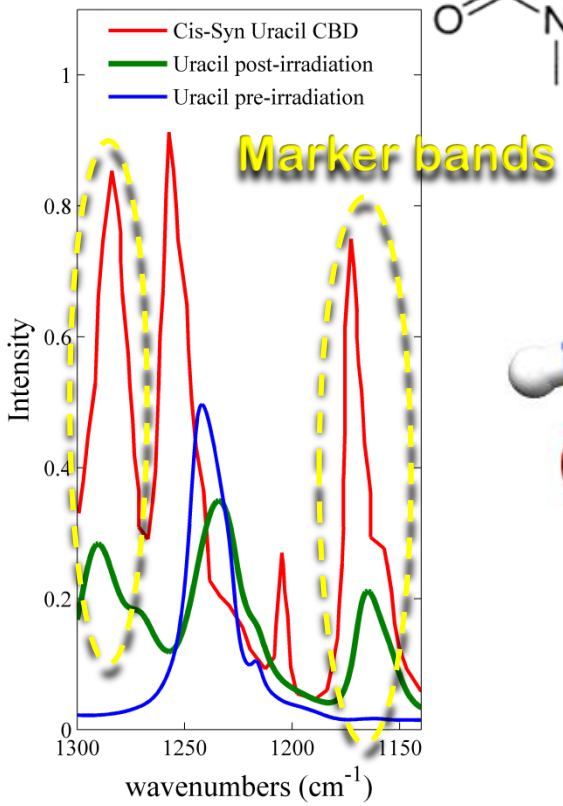


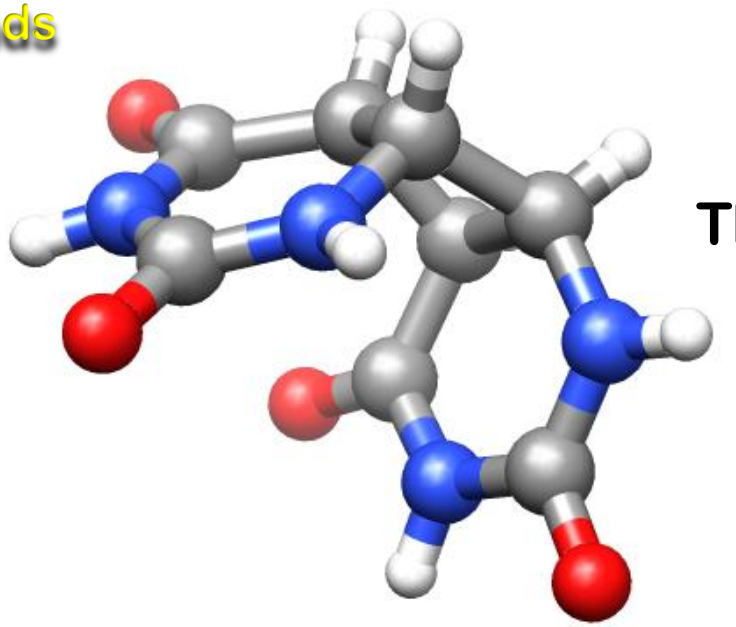
Fornaro, T.; Brucato, J.R.; Pace, E.; Cestelli Guidi, M.; Branciamore, S.; Pucci, A. *Icarus* **2013**, *226*, 1068-1085.

Proposed Photoproducts

[2+2] Photocycloaddition







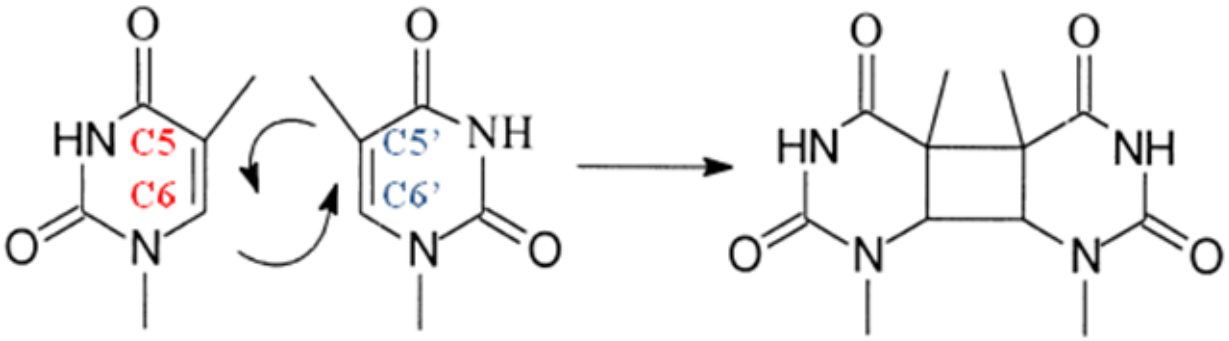
The main photoproduct:

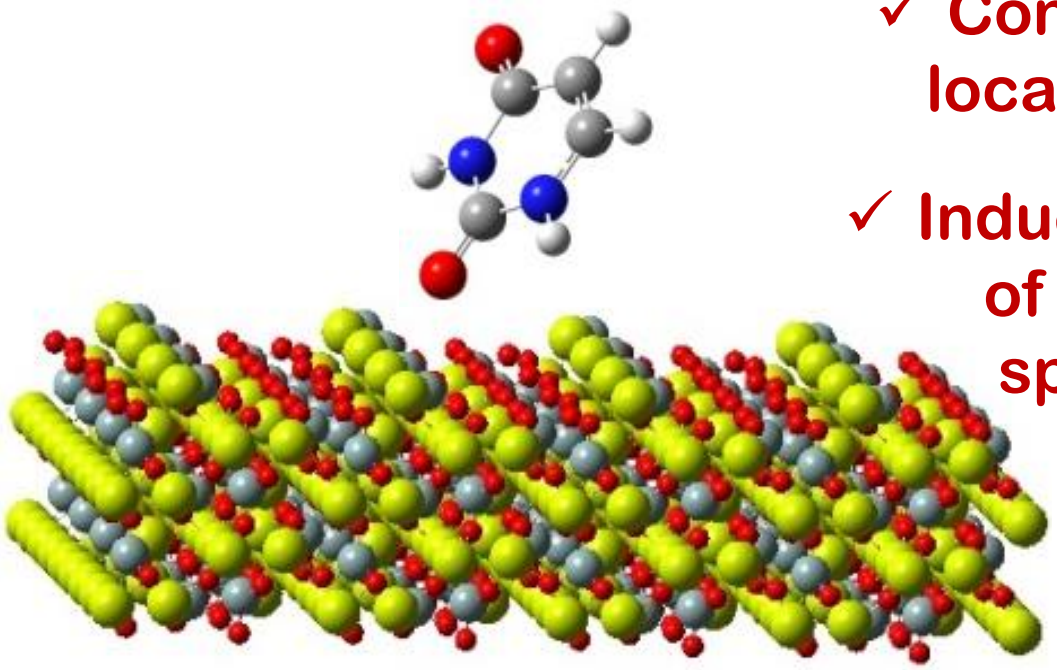
Cis-syn cyclobutane dimer (CBD)

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

Catalytic Effect of Forsterite

[2+2] Photocycloaddition

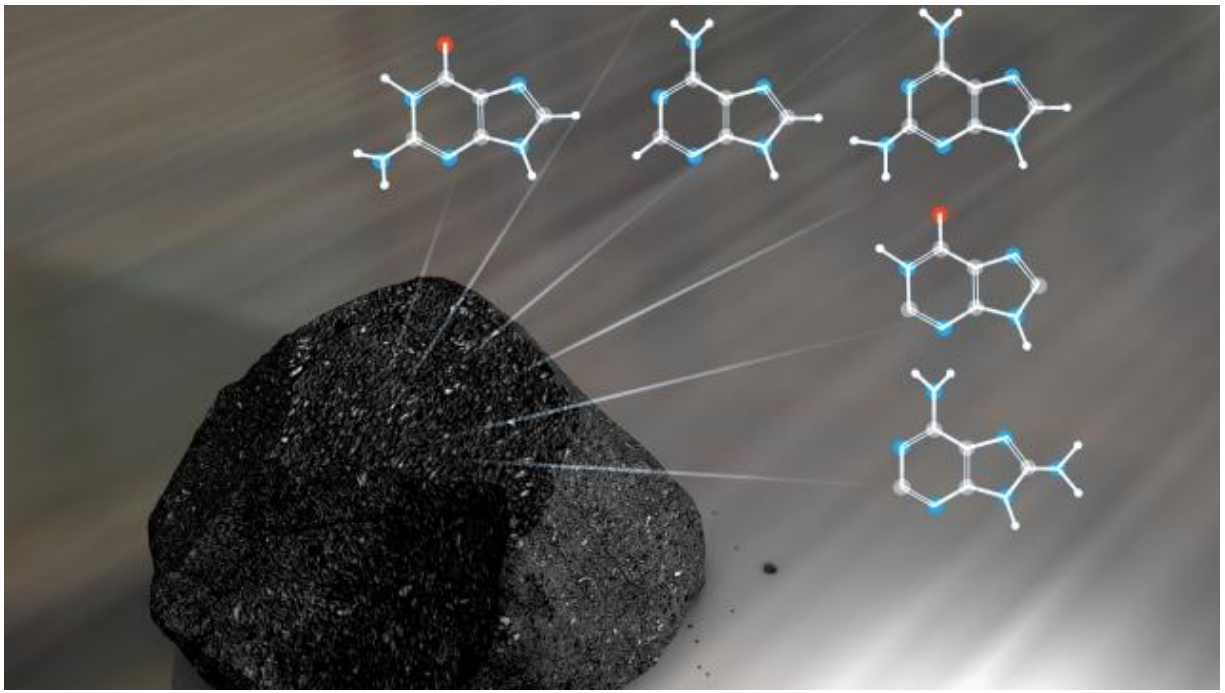




- ✓ Concentrates molecules on a local scale through adsorption
- ✓ Induces the correct orientation of reactive groups through specific molecule-mineral interactions

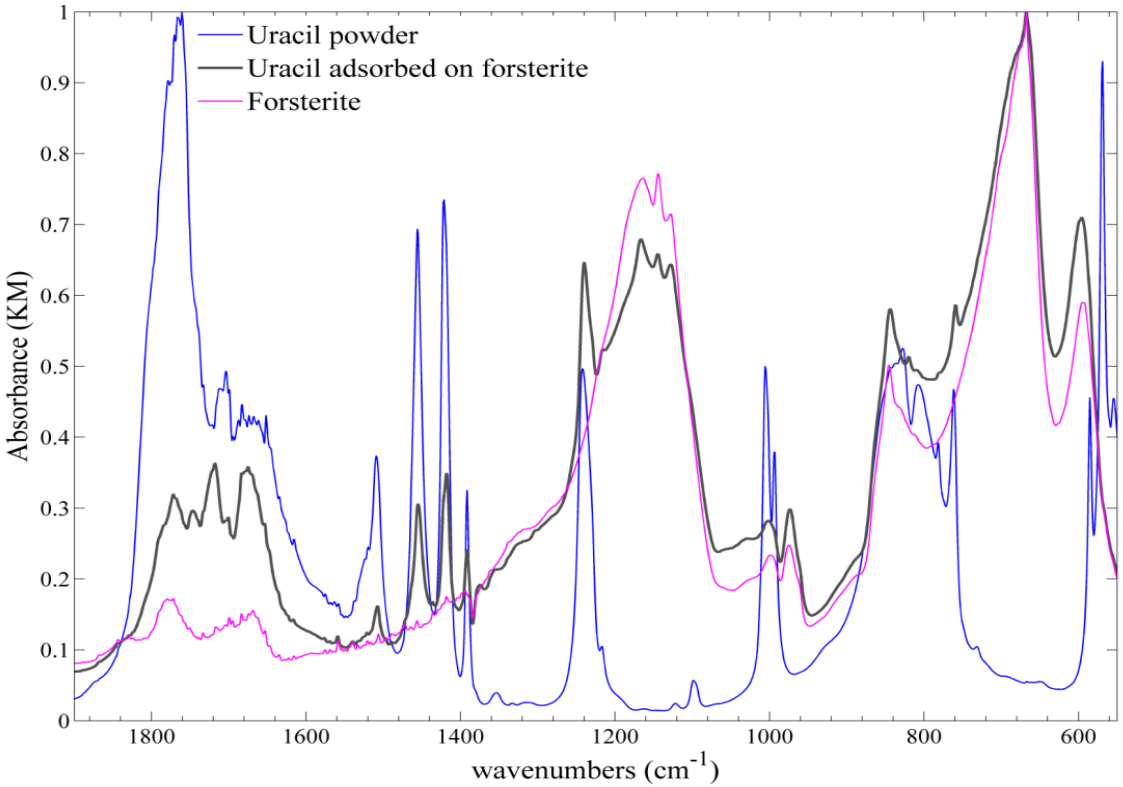
Open Questions

- 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

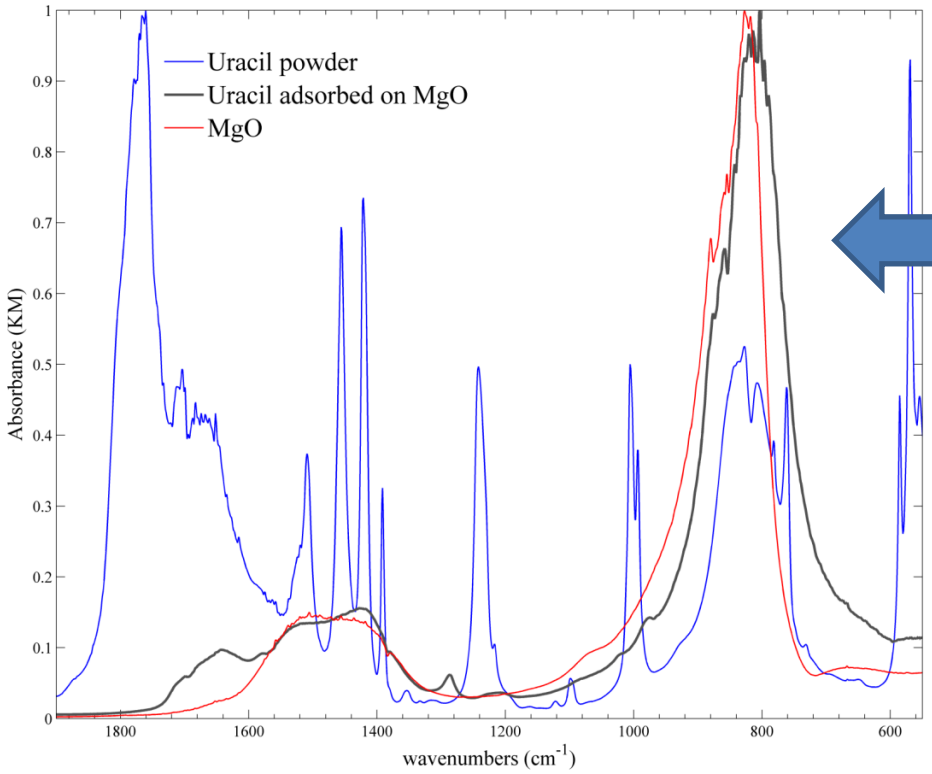
- Which are the causes of the different behavior of nucleobases in the presence of UV radiation?
- Which is the photochemistry of the degradation process at a mechanistic level?



Need of a correct interpretation of the spectroscopic features

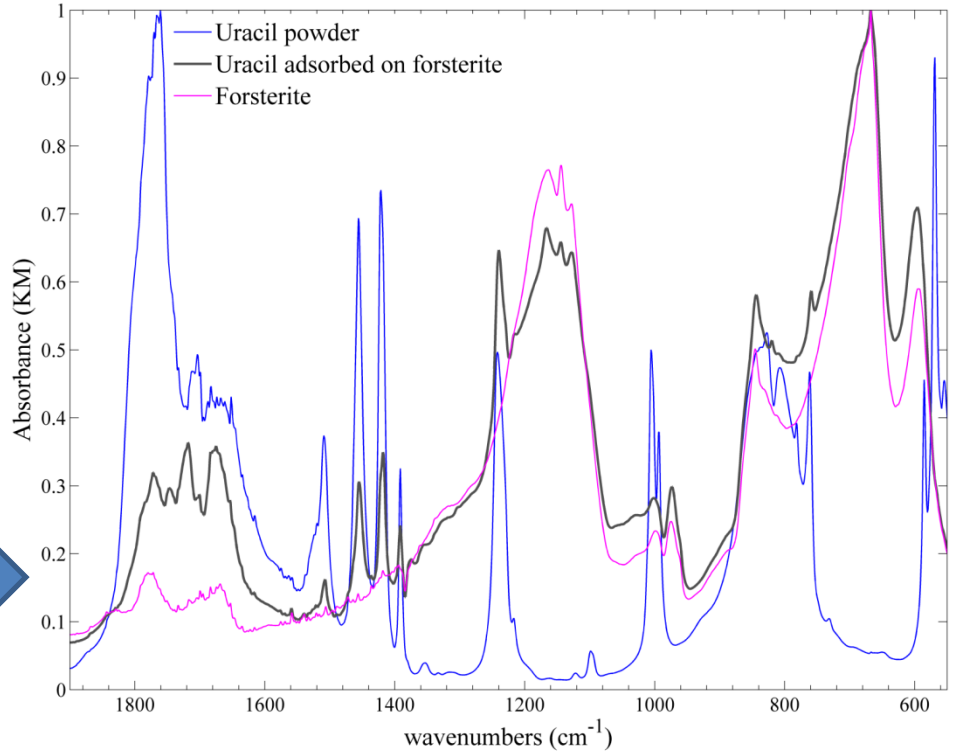
INTERPRETATION OF IR SPECTRA

IR-spectroscopy studies of nucleobase-mineral complexes

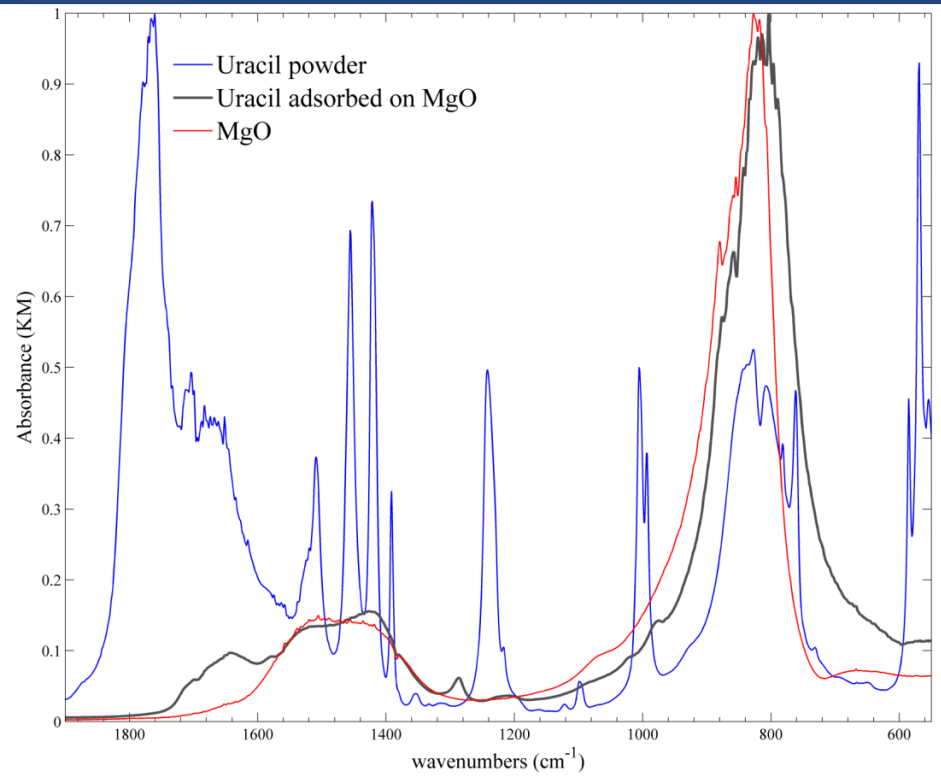


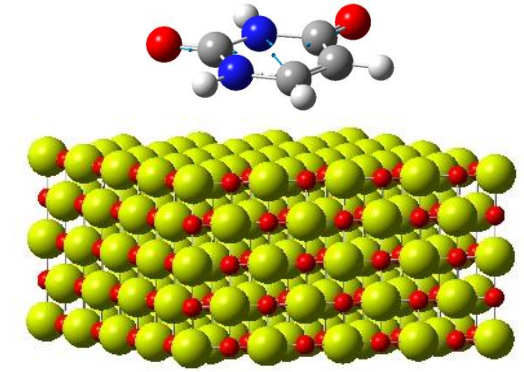
Uracil adsorbed on MgO
IR bands are NOT observed

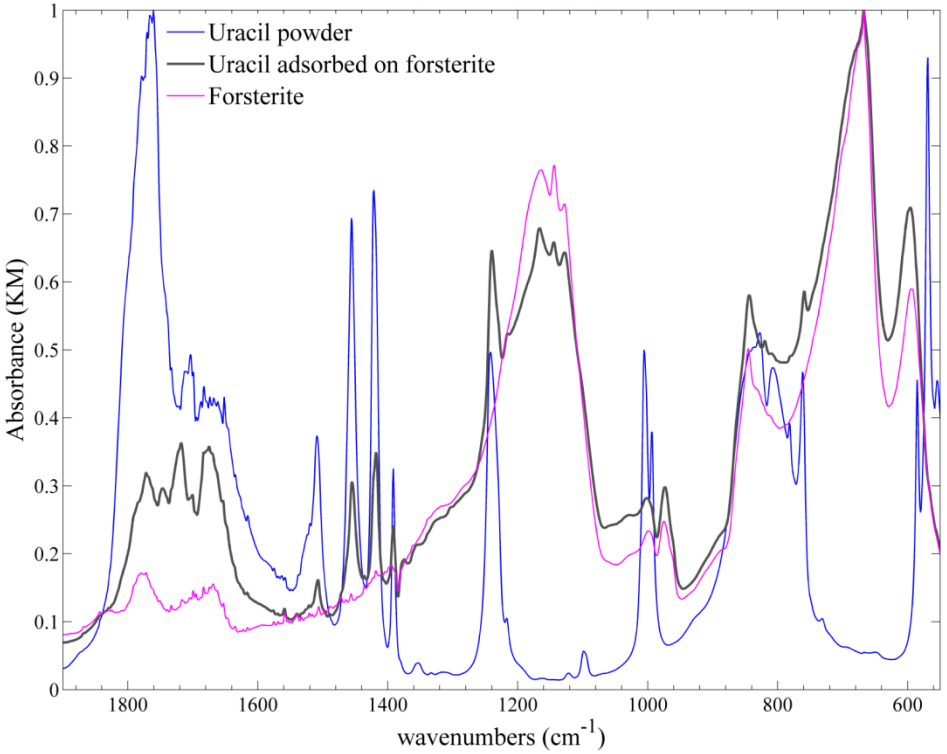
Uracil adsorbed on Forsterite
Detectable IR bands

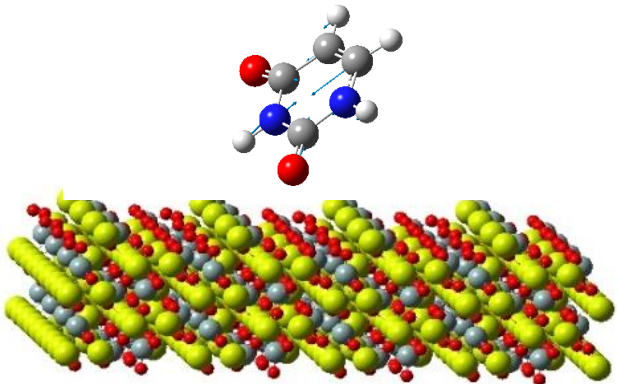


IR-spectroscopy studies of nucleobase-mineral complexes

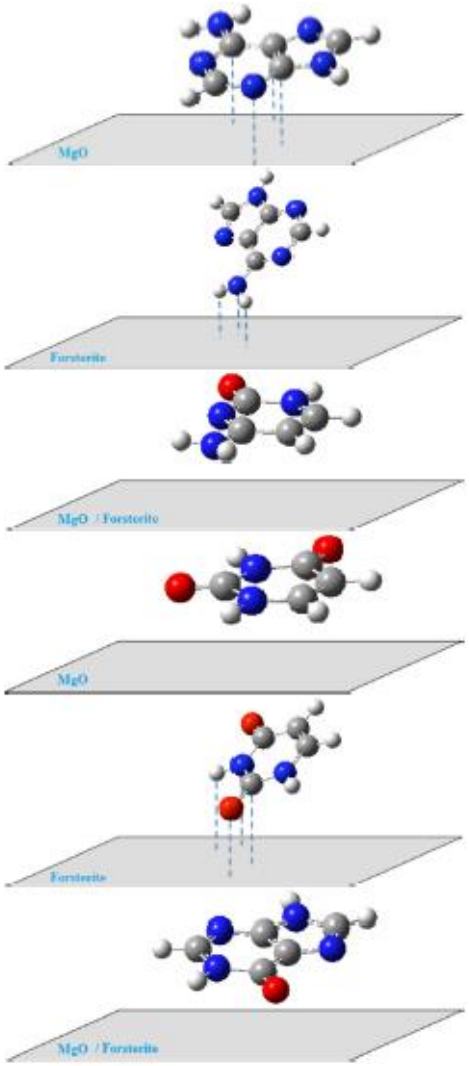








Proposed geometrical arrangements of nucleobases on MgO and Forsterite



Adenine on MgO
Interaction with the $N_3C_4C_5C_6$ part of the molecule in a distorted nearly planar arrangement

Adenine on forsterite
Interaction with the NH_2 group in a tilted arrangement

Cytosine on MgO and forsterite
Face-to-face configuration

Uracil on MgO
Face-to-face configuration

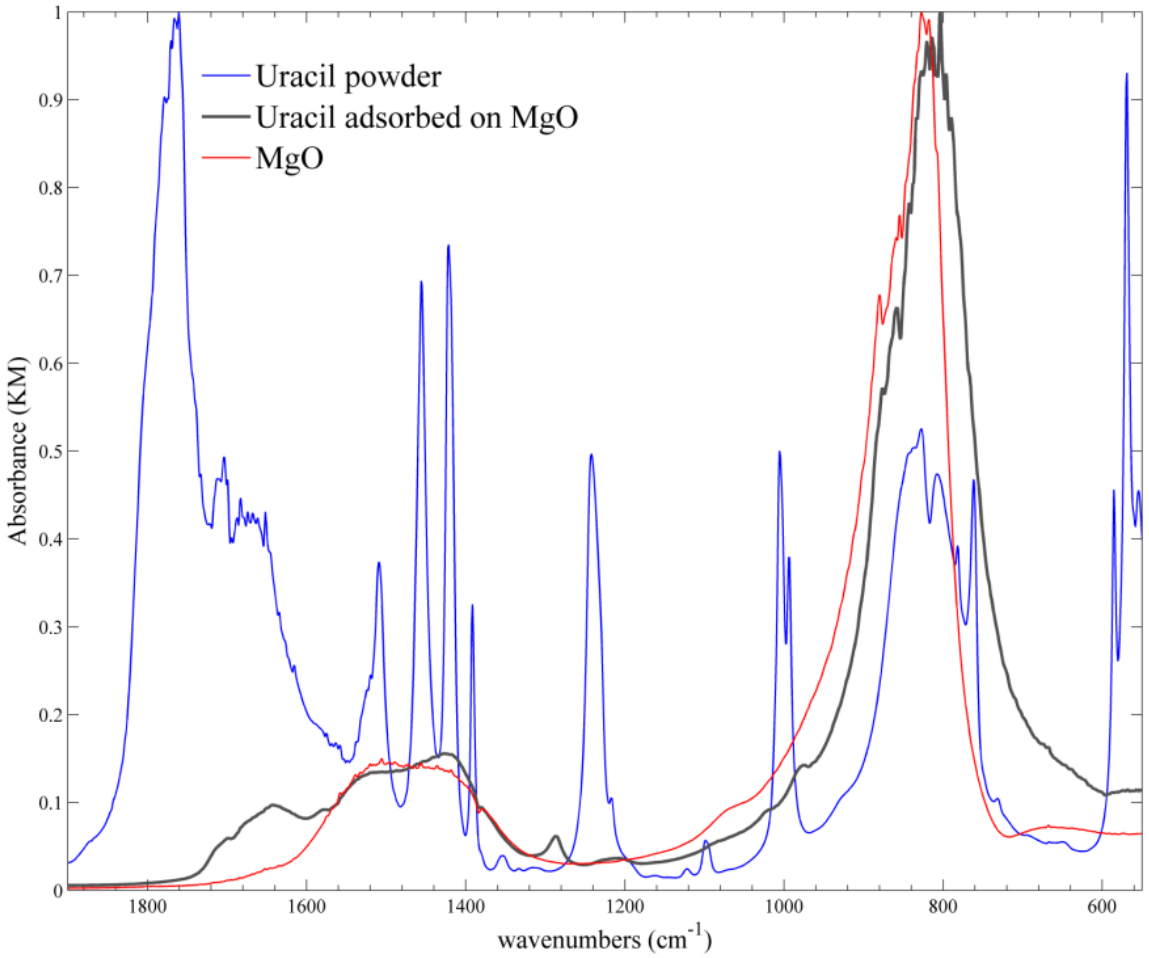
Uracil on forsterite
Interaction with the C_2=O and N_3H groups in a tilted arrangement

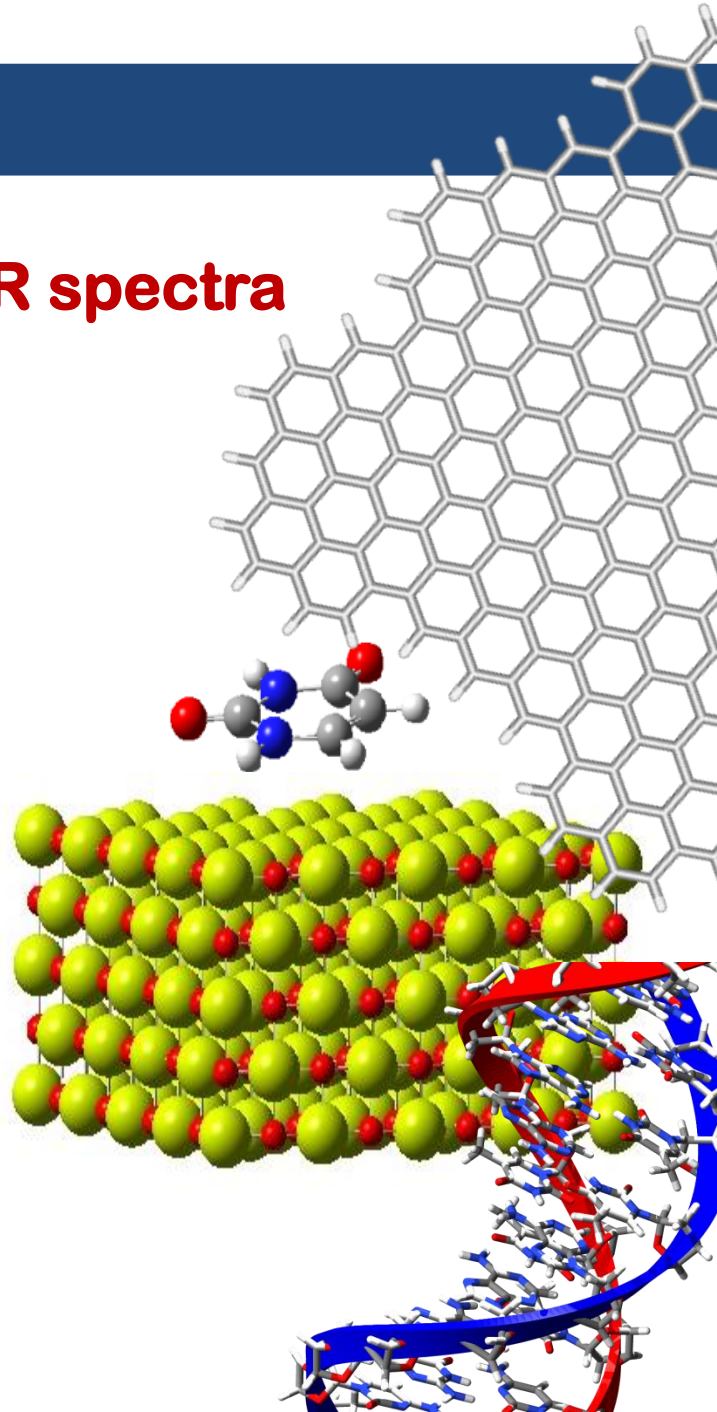
Hypoxanthine on MgO and forsterite
Face-to-face configuration

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

Problems

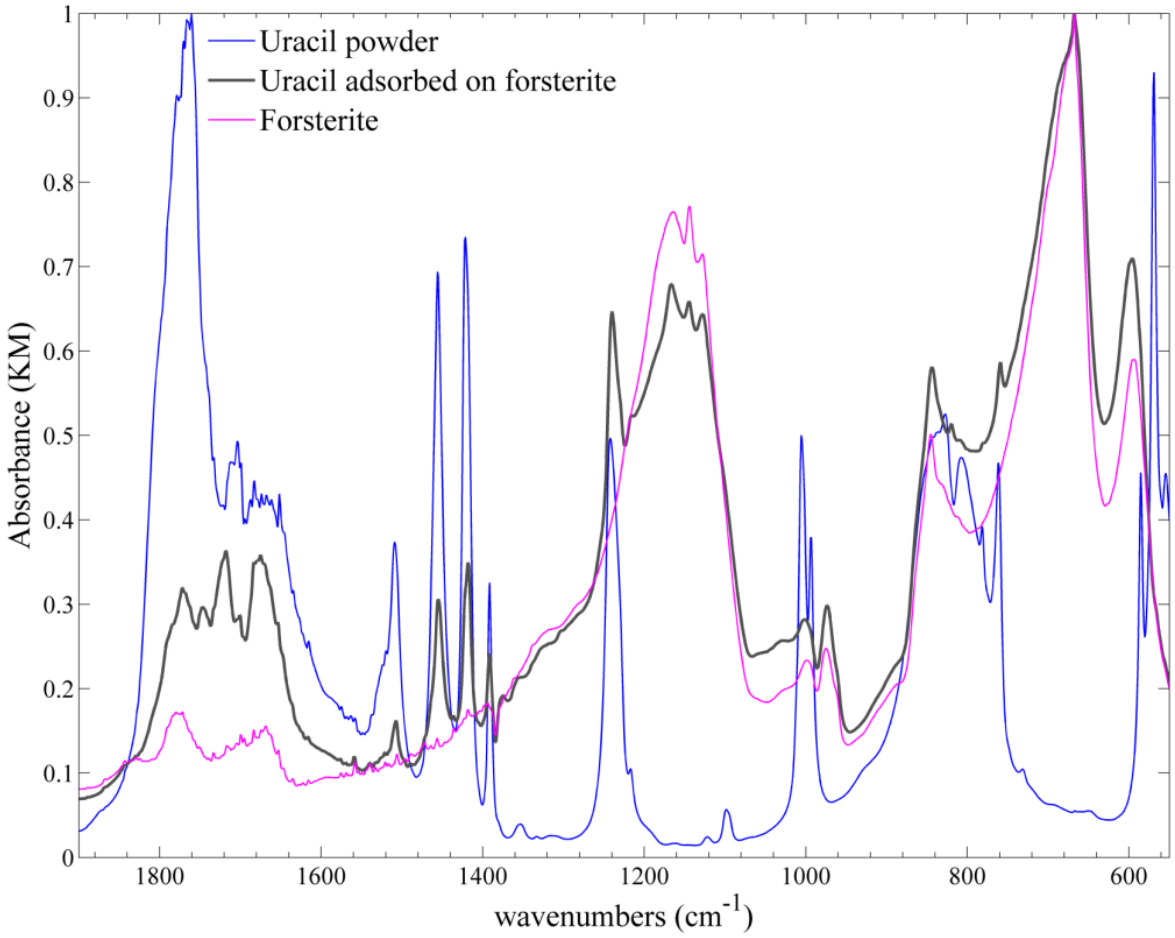
Scarcity of bands in the IR spectra

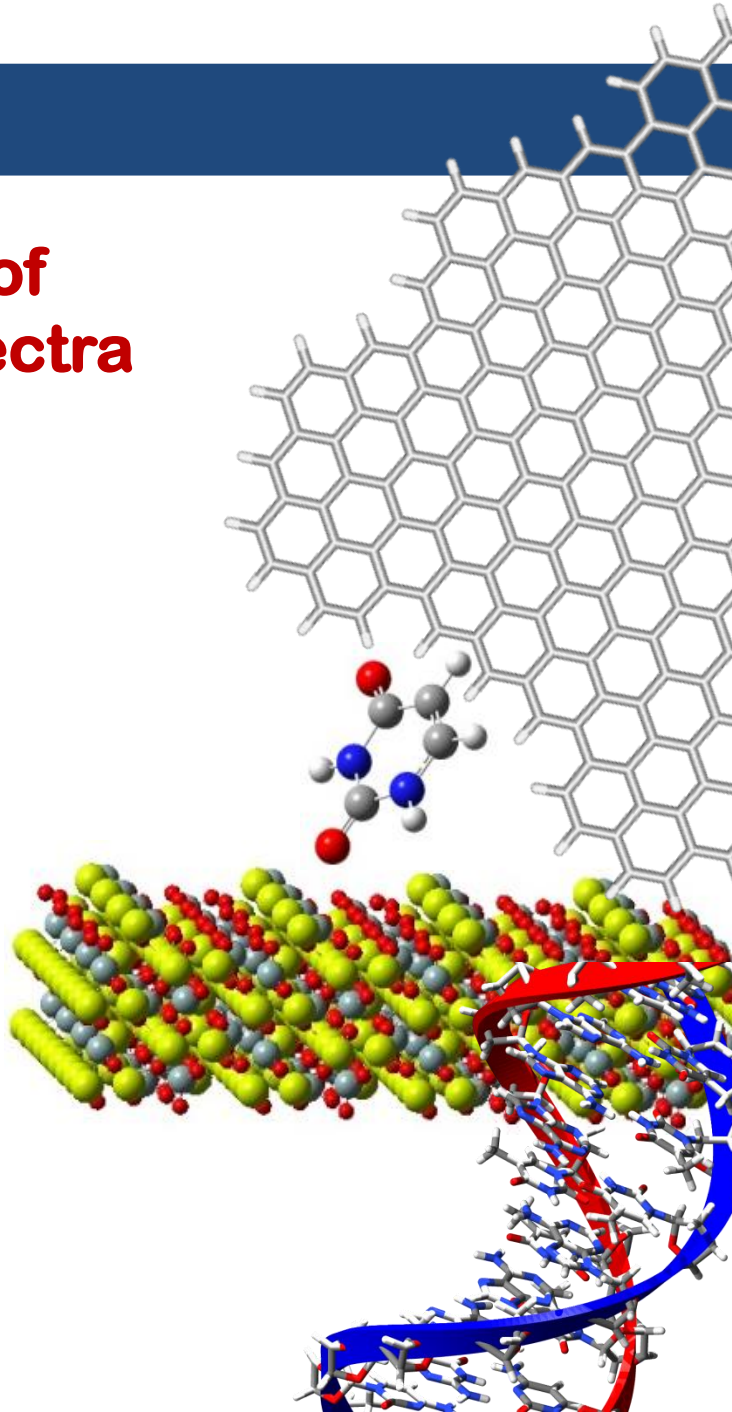




Problems

High complexity of experimental IR spectra

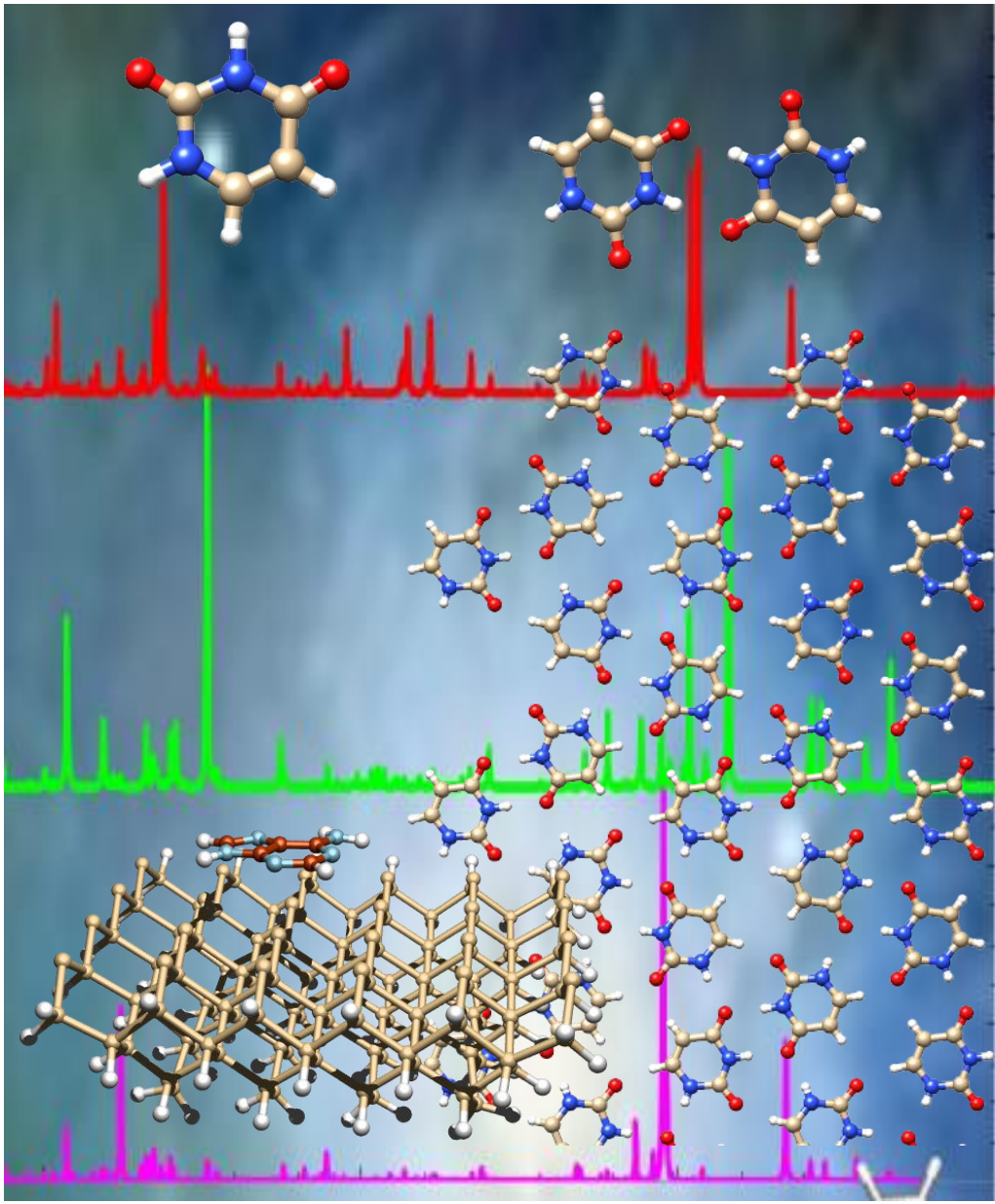




Computational Spectroscopy

Goal:

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



Fornaro, T.; Biczysko, M.; Monti, S.; Barone, V. *Phys. Chem. Chem. Phys.* **2014**, *16*, 10112-10128.

Fornaro, T.; Carnimeo, I. *Reference Module in Chemistry, Molecular Sciences and Chemical Engineering* **2014**, DOI: 10.1016/B978-0-12-409547-2.11025-X.

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

Fornaro, T.; Burini, D.; Biczysko, M.; Barone, V. *J. Phys. Chem.* **2015**, *119* (18), 4224–4236.

Computational Spectroscopy: Methods

Dispersion-corrected Density Functional Theory methods

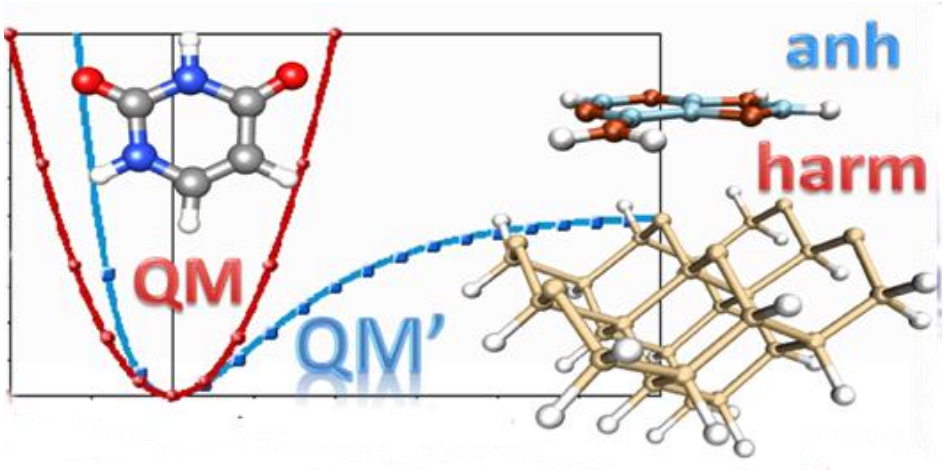
- **B3LYP-D3/SNSD**[a] (Semi-empirical dispersion correction)

Simulation of anharmonic IR spectra

- Generalized second-order vibrational perturbation (**GVPT2**)[b,c,d] model approach

Fully anharmonic calculation of frequencies and intensities

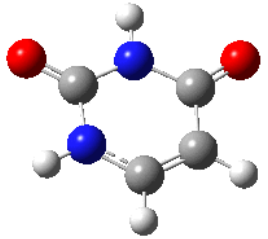
$$E_\upsilon = \chi_0 + \sum_i \omega_i \left(\upsilon_i + \frac{1}{2}\right) + \sum_i \sum_{j<i} \chi_{ij} \left(\upsilon_i + \frac{1}{2}\right)\left(\upsilon_j + \frac{1}{2}\right)$$

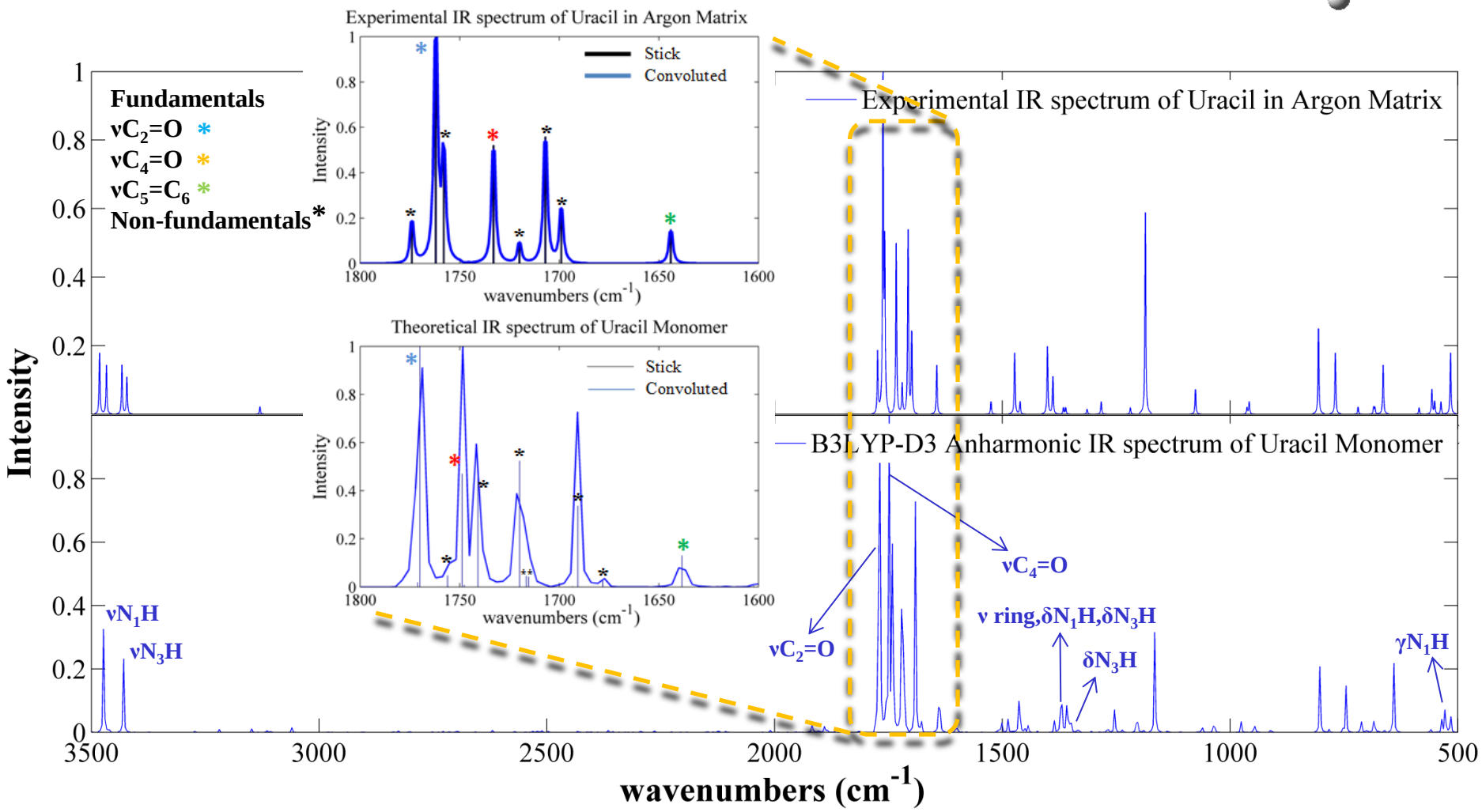


Suite of programs: GAUSSIAN[e]

[a] Grimme, S. *et al. J. Chem. Phys.* **2010**, *132*, 154104.
[b] Barone, V. *J. Chem. Phys.* **2005**, *122*, 014108.
[c] Bloino, J.; Barone, V. *J. Chem. Phys*. **2012**, *136*, 124108.
[d] Bloino, J.; Biczysko , M.; Barone, V. *J. Chem. Theory Comput.* **2012**, *8* (3), 1015–1036.
[e] Frisch, M. J. *et al.*, Gaussian 09 Revision D.01, 2013, Gaussian Inc. Wallingford CT 2009.

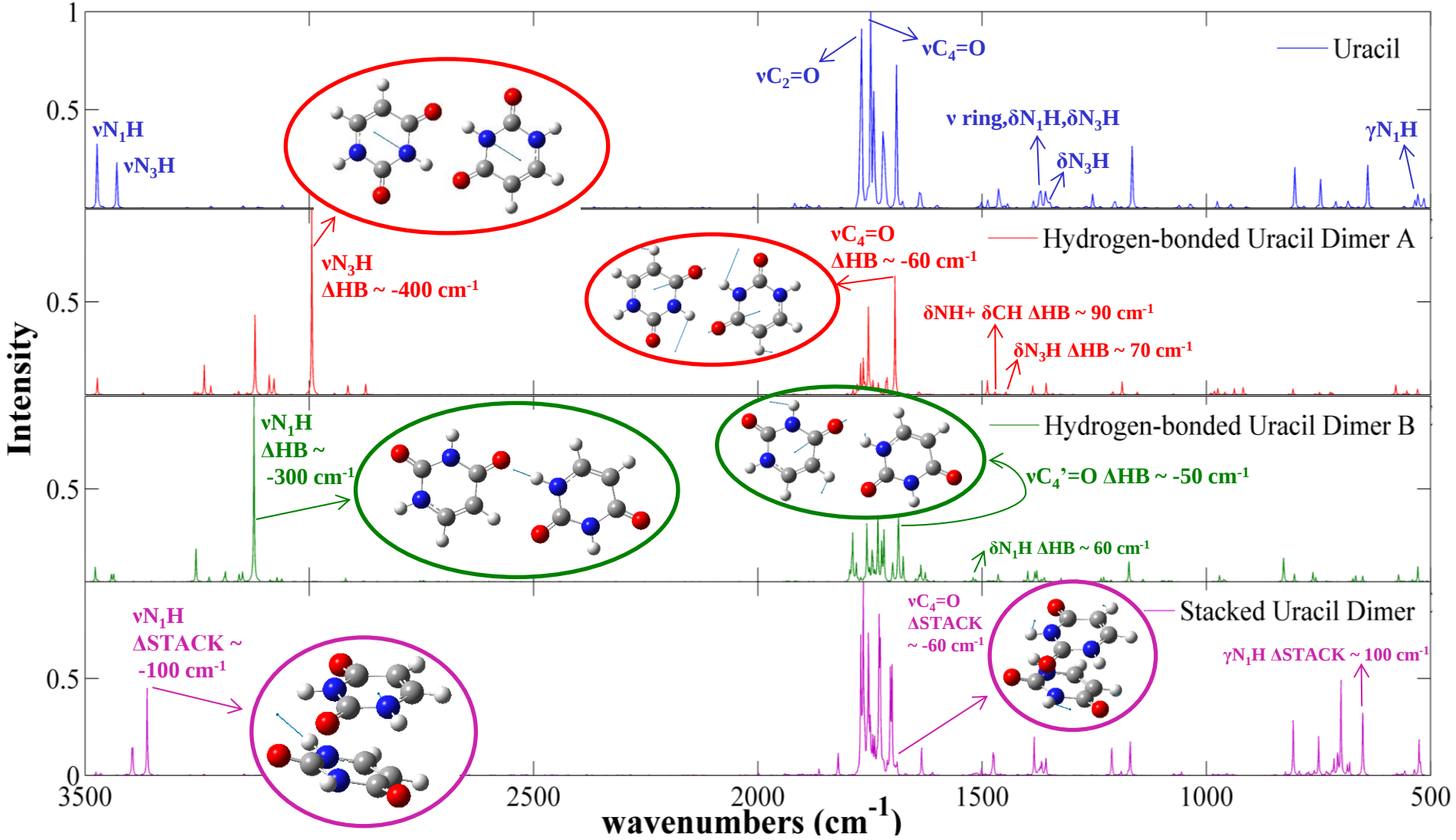
Computational Spectroscopy: Monomers





Fornaro, T.; Biczysko, M.; Monti, S.; Barone, V. *Phys. Chem. Chem. Phys.* **2014**, *16*, 10112-10128.

Effects of intermolecular interactions: Dimers



Fornaro, T.; Burini, D.; Biczysko, M.; Barone, V. *J. Phys. Chem.* **2015**, *119* (18), 4224–4236.

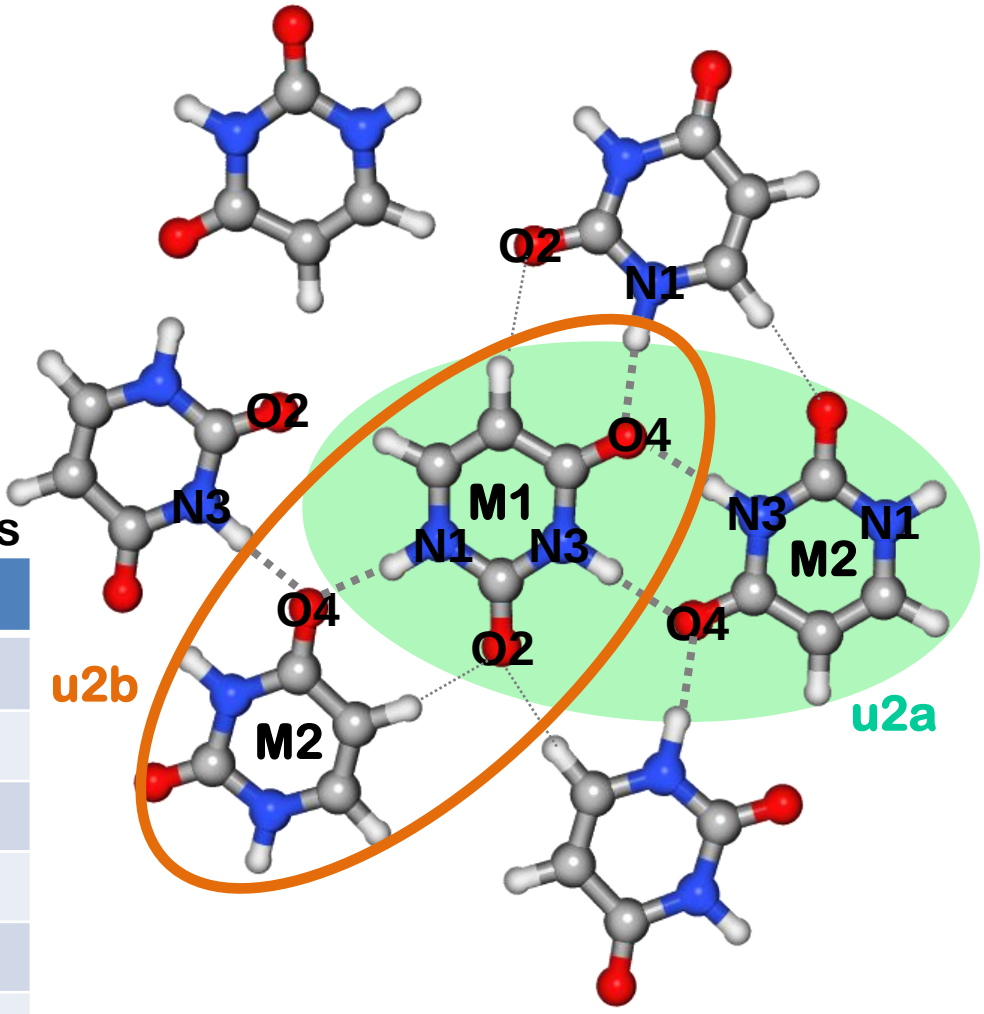
Modeling Solid Uracil: Heptamer unit

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

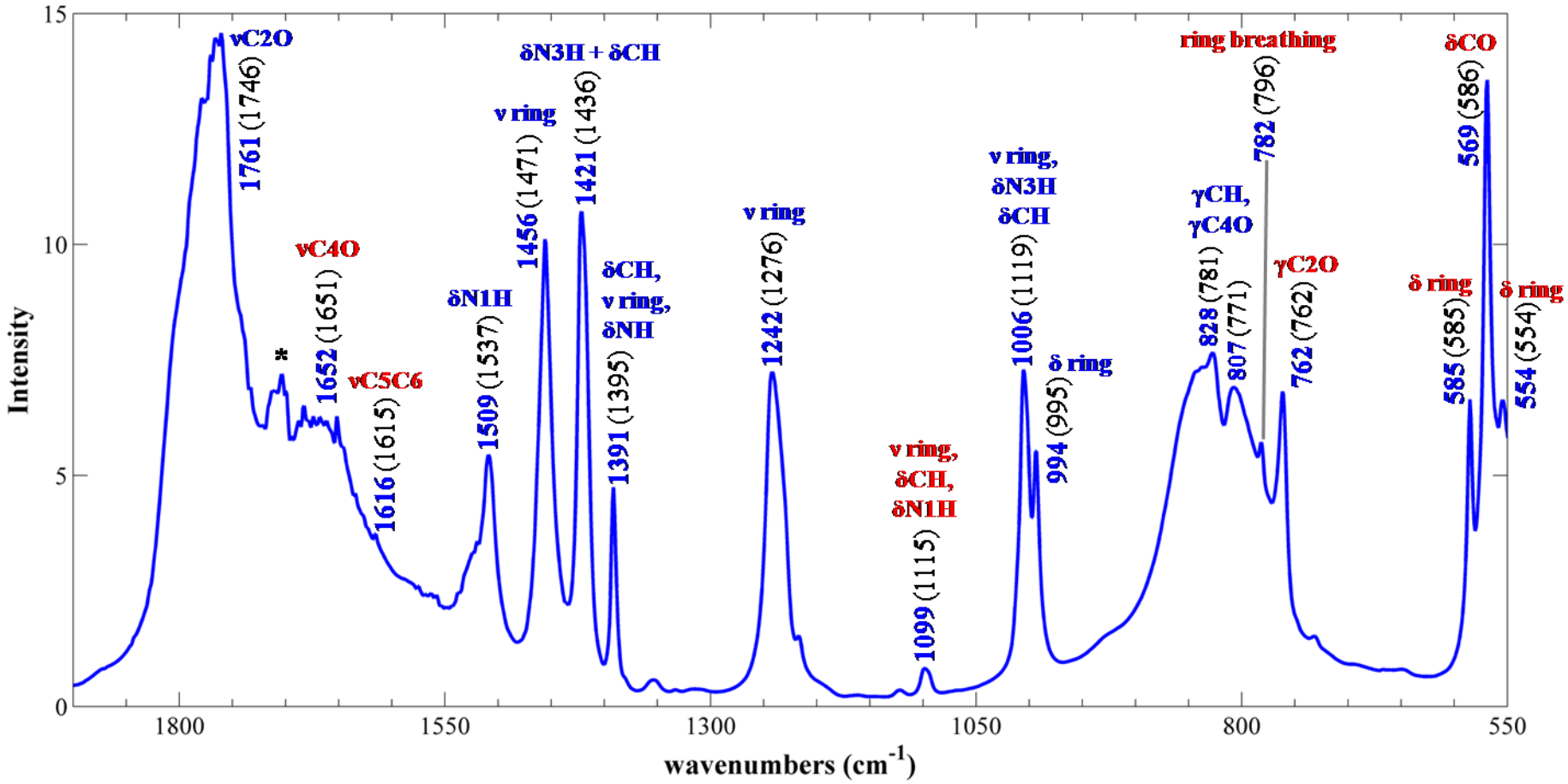
RD –VPT2 scheme: 15 selected modes

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



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

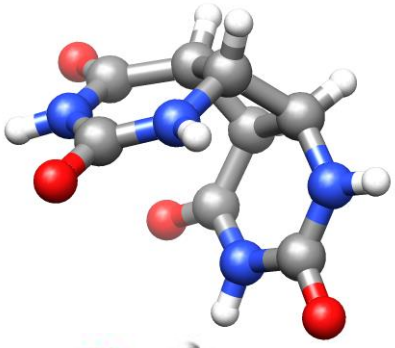
Assignments of the Experimental Spectrum



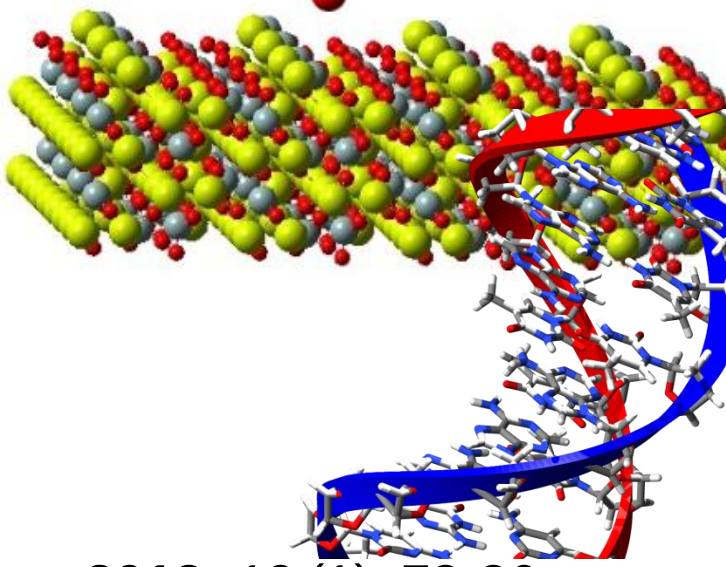
Fornaro, T. et al. *Icarus* **2013**, *226*, 1068 – 1085.
Fornaro, T.; Carnimeo, I.; Biczysko, M. *J. Phys. Chem. A* **2015**, *119* (21), 5313–5326.

Conclusions

- **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. et al. *Icarus* **2013**, *226*, 1068-1085.
Fornaro T. et al. *International Journal of Astrobiology* **2013**, *12* (1), 78-86.

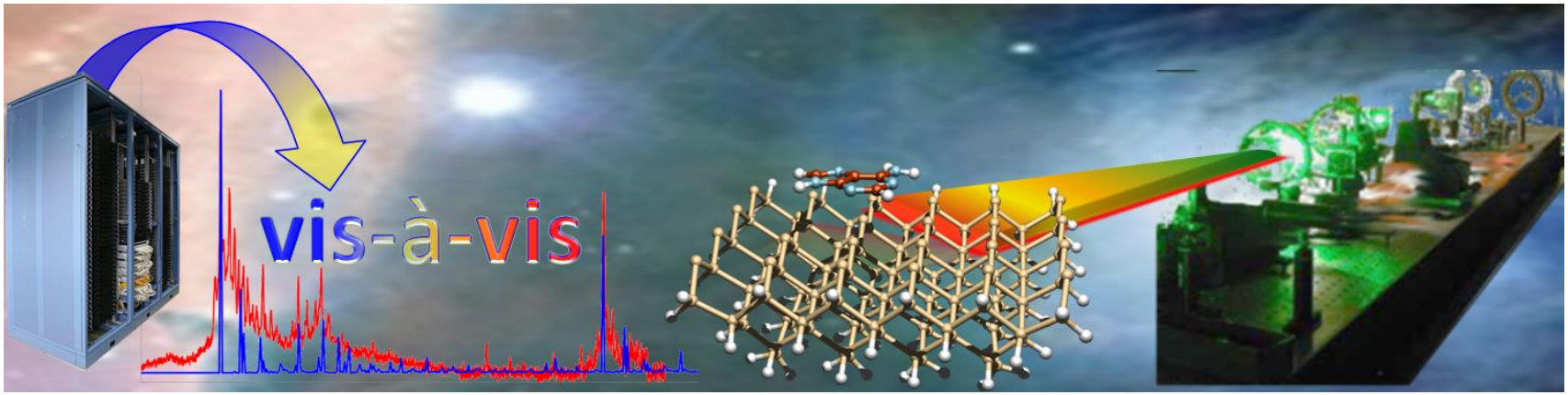
Conclusions

IR spectroscopy analysis:

Important shifts of the vibrational frequencies and changes of the IR intensities of specific functional groups due to intermolecular interactions are observed;

Assignments based on gas-phase data could be misleading;

Computational spectroscopy approaches pave a way for the analysis of experimental data of nucleobases complexes.



Fornaro T. et al. *J. Phys. Chem. A* **2015**, *119* (21), 5313–5326; Fornaro T. et al. *J. Phys. Chem.* **2015**, *119* (18), 4224–4236; Fornaro T. & Carnimeo I. *Reference Module in Chemistry, Molecular Sciences and Chemical Engineering* **2014**; Fornaro T. et al. *Phys. Chem. Chem. Phys.* **2014**, *16*, 10112-10128.

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