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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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INTRODUCTION

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
INTRODUCTION

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

Magnesium oxide (MgO)

Forsterite (Mg$_2$SiO$_4$)
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 degradation kinetics

\[ \frac{N(t)}{N_0} = B e^{-\beta t} + c \]

- \( \frac{N(t)}{N_0} \) fraction of unaltered molecules
- \( \beta \) degradation rate
- \( B \) fraction of interacting molecules
- \( c \) fraction of non-interacting molecules

- \( t_{1/2} = \ln(2) / \beta \)
- \( \beta = \sigma \Phi_{\text{tot}} / A_0 \)
- \( t_{1/2} \) half-lifetime
- \( \sigma \) UV destruction cross section
- \( \Phi_{\text{tot}} \) 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

INTERPRETATION OF EXPERIMENTAL DATA

Photoproducts marker bands

Proposed Photoprodusts

[2+2] Photocycloaddition

The main photoproduct: Cis-syn cyclobutane dimer (CBD)

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**?
Uracil adsorbed on MgO
IR bands are NOT observed

Uracil adsorbed on Forsterite
Detectable IR bands
INTERPRETATION OF IR SPECTRA

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$_3$H groups in a tilted arrangement

**Hypoxanthine on MgO and forsterite**
Face-to-face configuration

Problems

Scarcity of bands in the IR spectra
Problems

High complexity of experimental IR spectra
Goal:
Development of a computational procedure based on quantum mechanical anharmonic computations of vibrational frequencies and IR intensities

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

\[
E_v = \chi_0 + \sum_i \omega_i \left( \nu_i + \frac{1}{2} \right) + \sum_i \sum_{j<i} \chi_{ij} \left( \nu_i + \frac{1}{2} \right) \left( \nu_j + \frac{1}{2} \right)
\]

Suite of programs: **GAUSSIAN**\(^e\)

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\(\text{\textsuperscript{e}}\) Frisch, M. J. \textit{et al.}, Gaussian 09 Revision D.01, 2013, Gaussian Inc. Wallingford CT 2009.
Computational Spectroscopy: Monomers

**Fundamentals**
- $\nu C_2=O$
- $\nu C_4=O$
- $\nu C_5=C_6$

**Non-fundamentals**
- $\delta N_1H$
- $\delta N_3H$
- $\gamma N_1H$

**Experimental IR spectrum of Uracil in Argon Matrix**
- Stick
- Convolved

**Theoretical IR spectrum of Uracil Monomer**
- Stick
- Convolved

- B3LYP-D3 Anharmonic IR spectrum of Uracil Monomer
- $\nu C_2=O$
- $\nu C_4=O$
- $\nu \text{ring, } \delta N_1H, \delta N_3H$
- $\delta N_3H$
- $\gamma N_1H$

**Computational Studies**
COMPUTATIONAL STUDIES

Effects of intermolecular interactions: Dimers

**Experimental data:**

<table>
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<tr>
<th>Assign</th>
<th>( \nu ) Uracil in Argon</th>
<th>( \Delta \nu ) Solid Uracil</th>
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<tbody>
<tr>
<td>( \nu N1H )</td>
<td>3482</td>
<td>-376</td>
</tr>
<tr>
<td>( \nu N3H )</td>
<td>3433</td>
<td>-433</td>
</tr>
<tr>
<td>( \nu C5H )</td>
<td>3130</td>
<td>-42</td>
</tr>
<tr>
<td>( \nu C2=O )</td>
<td>1762</td>
<td>-1</td>
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<tr>
<td>( \nu C4=O )</td>
<td>1733</td>
<td>-81</td>
</tr>
<tr>
<td>( \nu C5C6 )</td>
<td>1644</td>
<td>-28</td>
</tr>
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</table>

**RD – VPT2 scheme:** 15 selected modes

<table>
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<th>( \Delta \nu )</th>
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<tbody>
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<td></td>
<td>( u )</td>
<td>( u2a )</td>
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<tr>
<td>( \nu N1H )</td>
<td>3473</td>
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<td>-62</td>
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<td>( \nu C5C6 )</td>
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UV IRRADIATION EXPERIMENTS

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

**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.

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