Stepwise microhydration of biomolecular building blocks: size-induced segregration and proton-induced charge transfer

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Radiation damage in (isolated) biomolecules

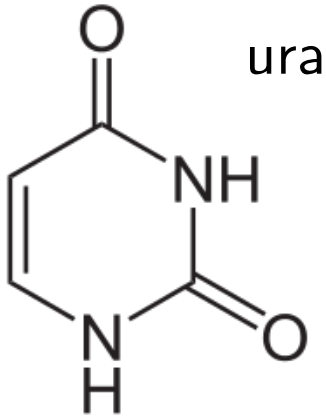
General context of radiation damage:

- Fundamentally important to understand the interaction between biomolecular compounds and high energy photons, electrons, ions or atoms that can subsequently cause decay of biological medium;
- Also relevant in prebiotic chemistry as a possible mechanism to trigger chemical reactions and produce more complex edifices from elementary building blocks

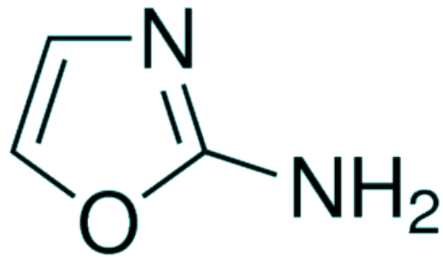
Charge transfer induced by collision with a charged particle is an important decay channel

Isolated studies offer a convenient framework to *disentangle the intrinsic effects* from those due to the environment
$\Longrightarrow$Here we aim at bridging the gap towards condensed phase studies by addressing the case of microhydrated biomolecules

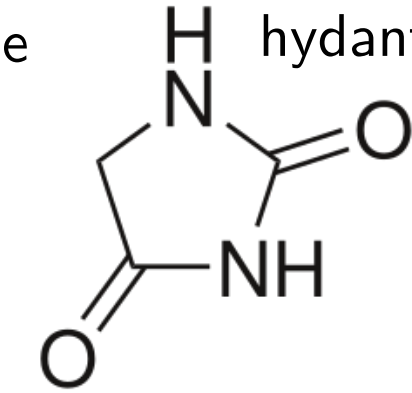
Systems of interest



uracil



2-aminooxazole



hydantoin

are involved as nucleobases or as intermediates in their synthesis or in the formation of polypeptides. Particularly relevant in astrochemistry

Our goals: computationally investigate the structure and reactivity in microhydrated form

Computational methodology

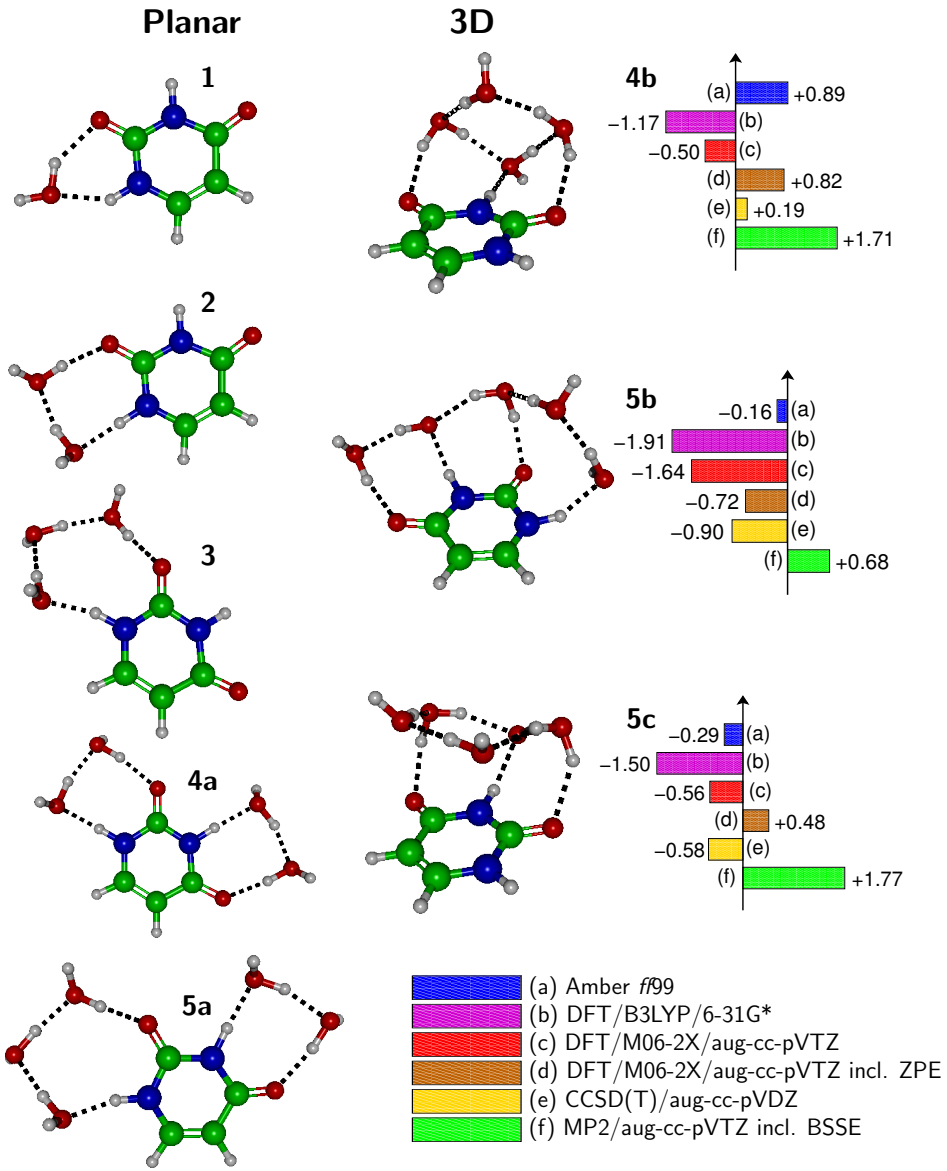
- → Search for stable structures at zero temperature;
- → Evaluate the possible role of temperature;
- → Evaluate the propensity for experiencing charge transfer upon collision with an impinging proton

Structural search

- Force field exploration of potential energy surface (replica-exchange MD)
- Local refinement at quantum chemical level

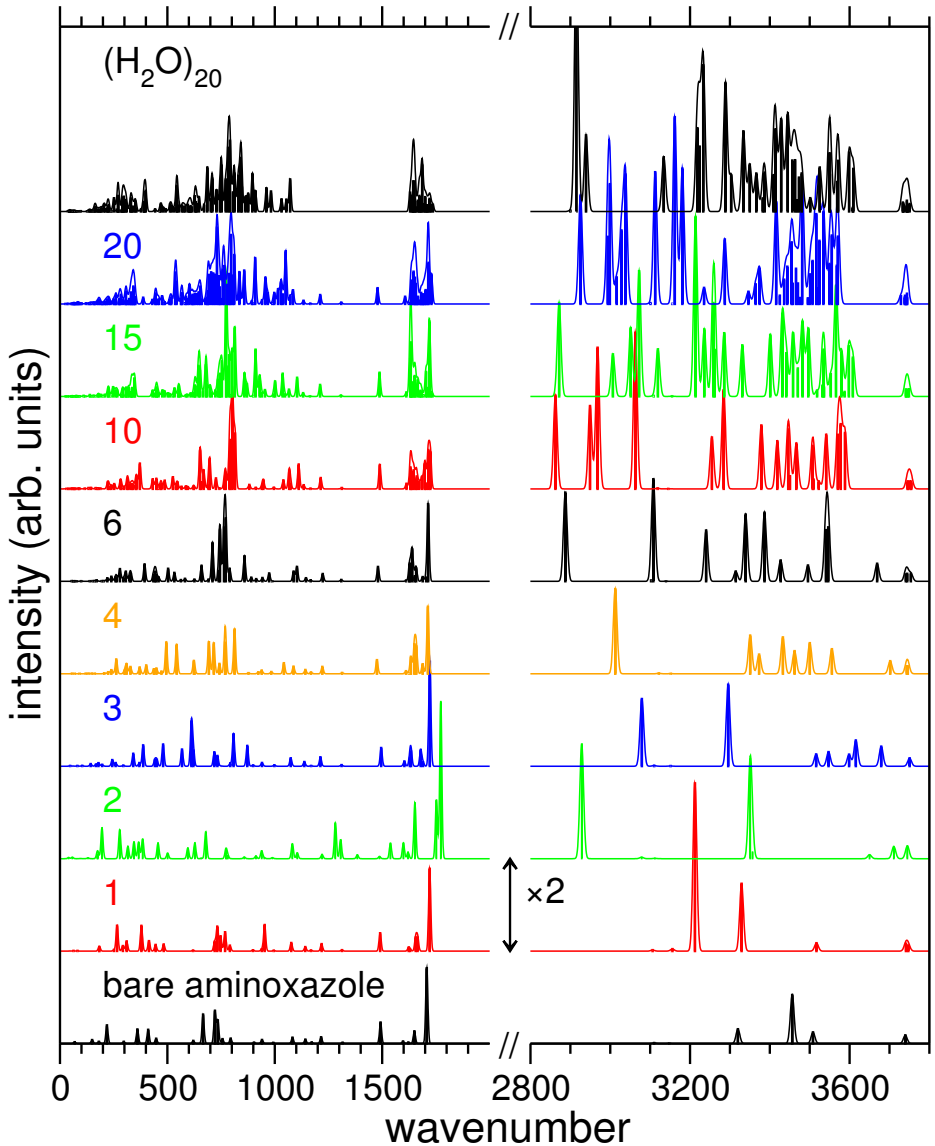
→ Amber *ff*99 and DFT/M06-2X/AVTZ found to agree reasonably well

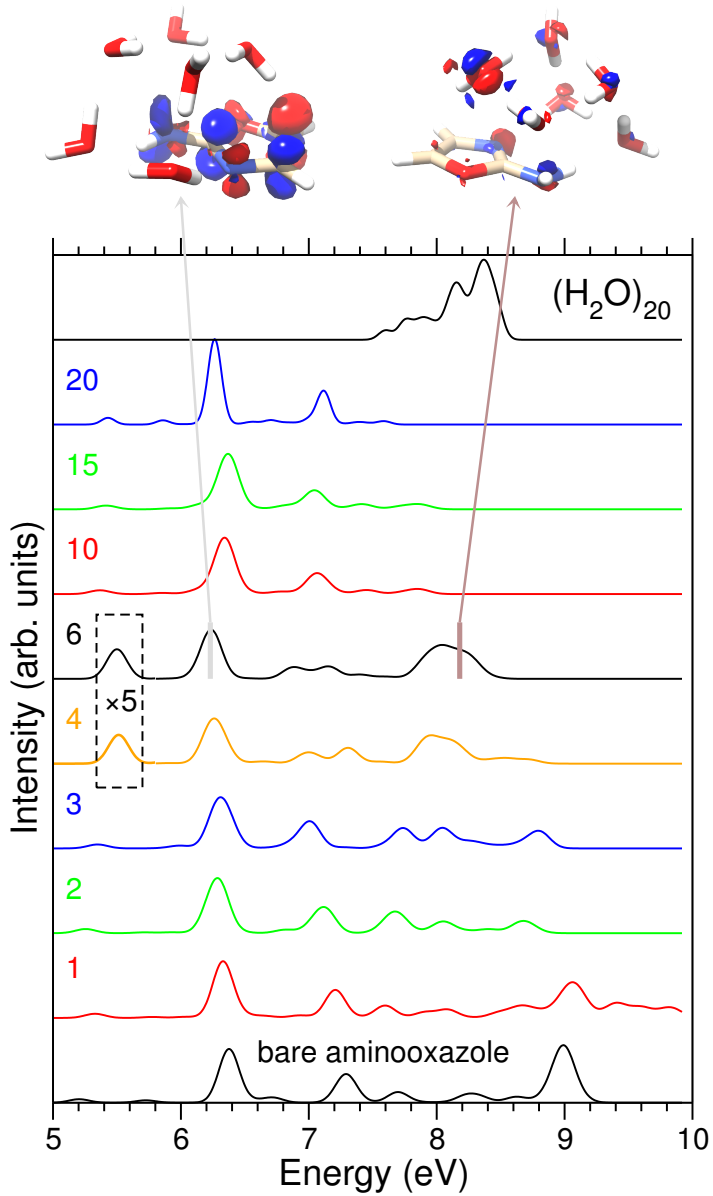
- In the case of uracil, *size-induced segregation* from planar to 3D hydration patterns:



Spectroscopic characterization: IR and UV

Case of aminooxazole:

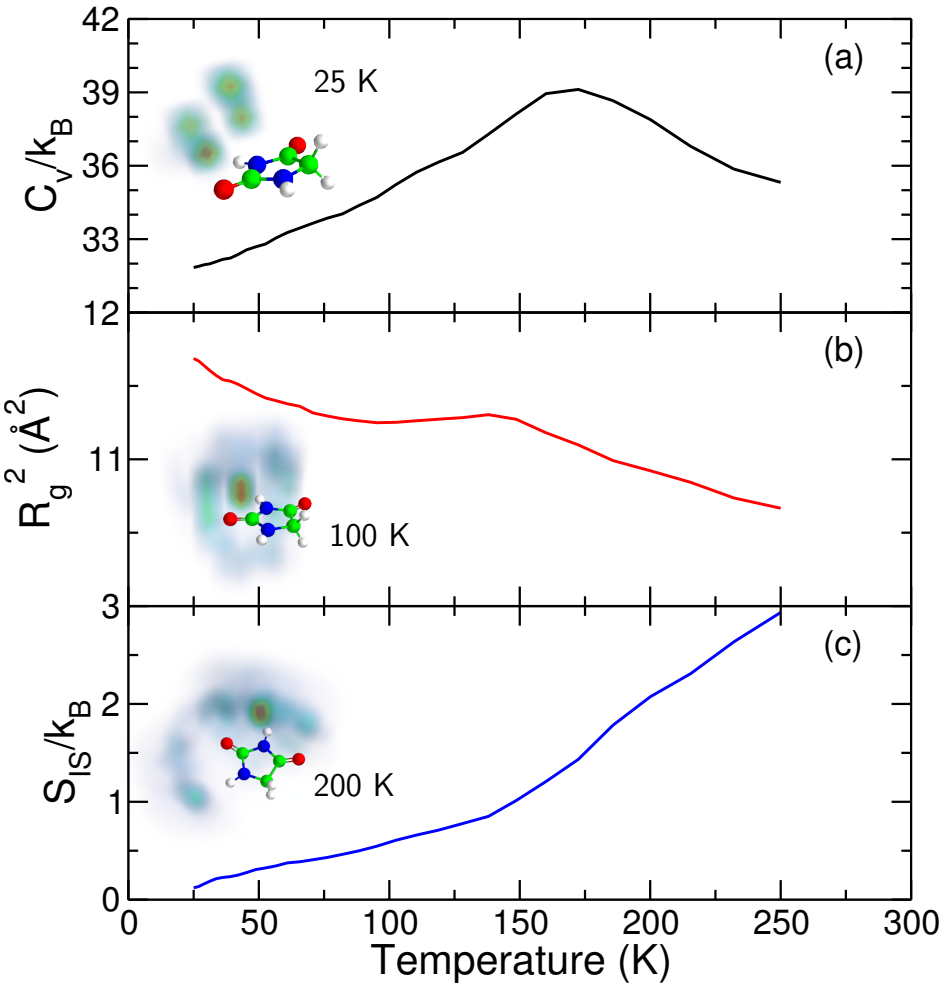




Finite-temperature behavior

- Statistical analysis of REMD data
- evaluation of heat capacity, gyration radius and inherent structures entropy

→ temperature-induced changes in hydration layer



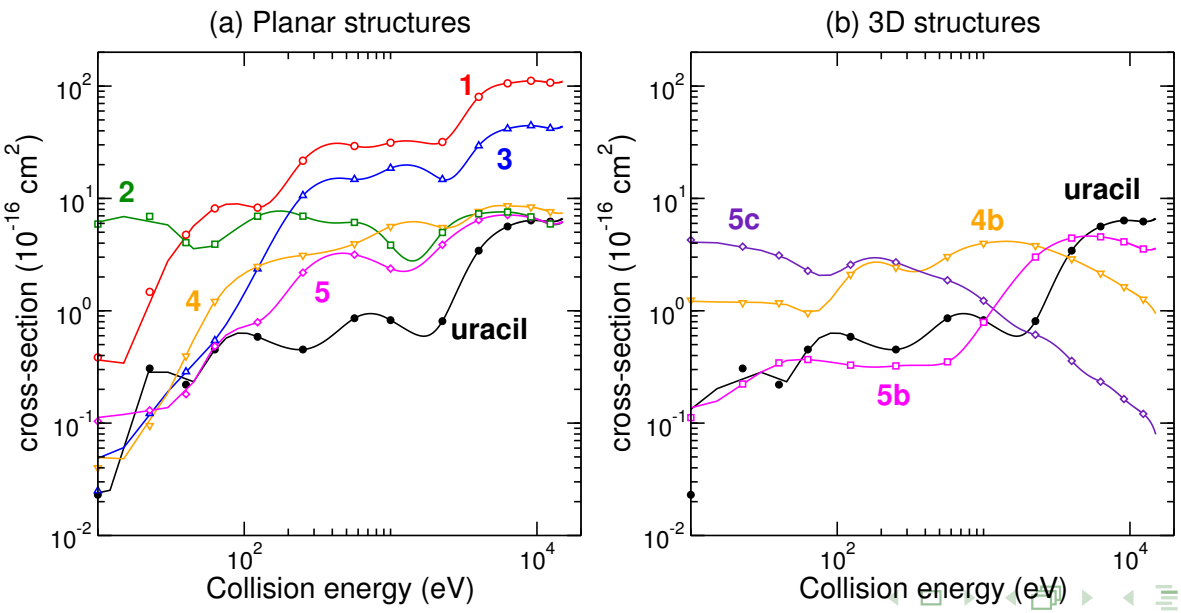
- In hydantoin with 4 waters, *entropy-driven reverse segregation* where planar solvation is favored again
- [*very similar behavior in uracil@*$(H_2O)_4$]

Proton-induced charge transfer

Charge transfer cross sections theoretically determined assuming

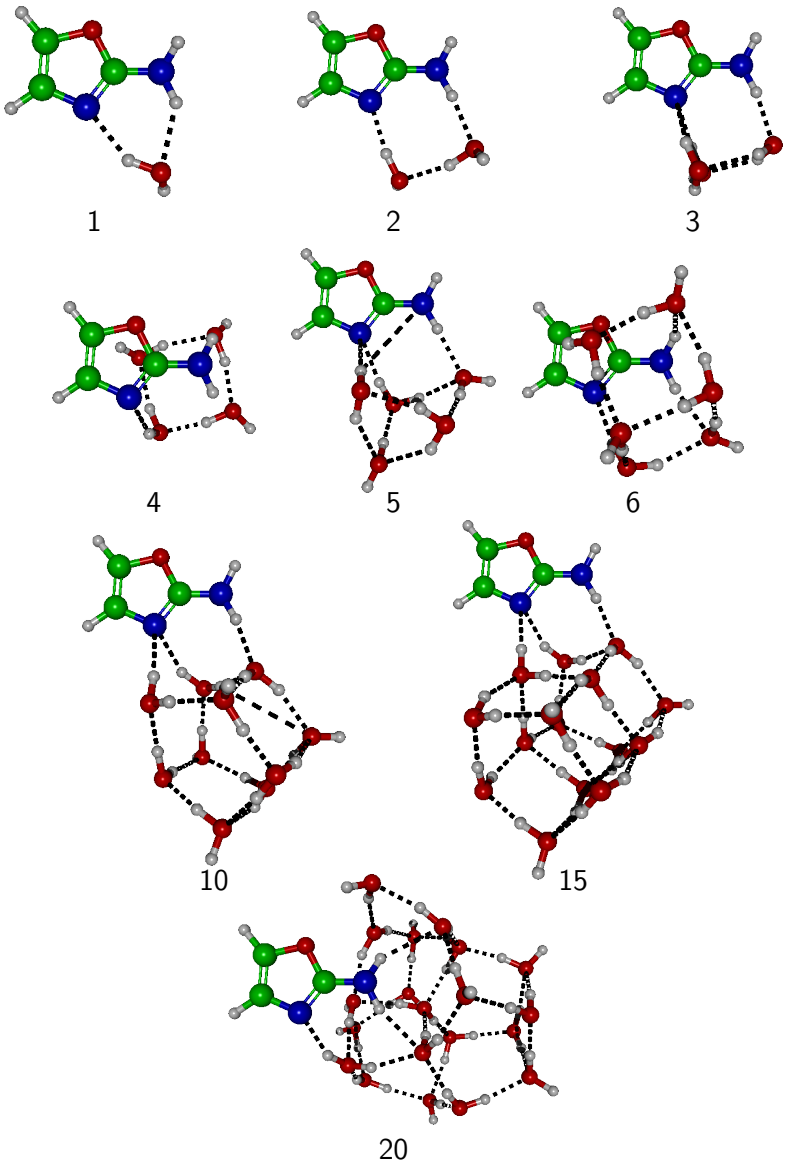
- a one-dimensional reaction coordinate with the proton colliding towards the target center of mass;
- sudden approximation: at collision energies in the keV range, vibrational motion is frozen;
- semiclassical treatment of the collision dynamics with energy surfaces determined using state-averaged CASSCF

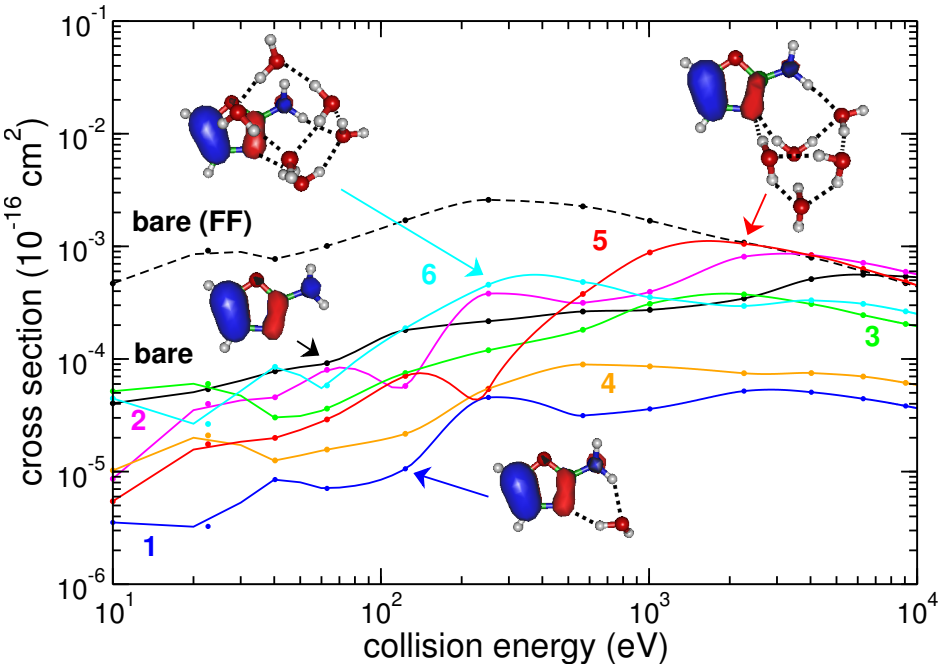
Case of uracil: solvent arrangement plays a strong role!



Proton-induced charge transfer

Microhydration of 2-aminooxazole



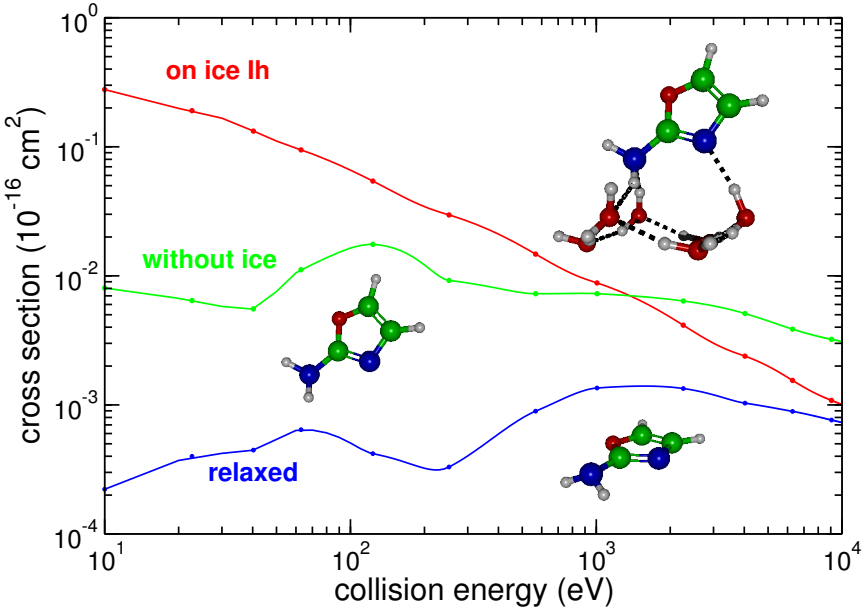


2-aminooxazole is mostly hydrophobic

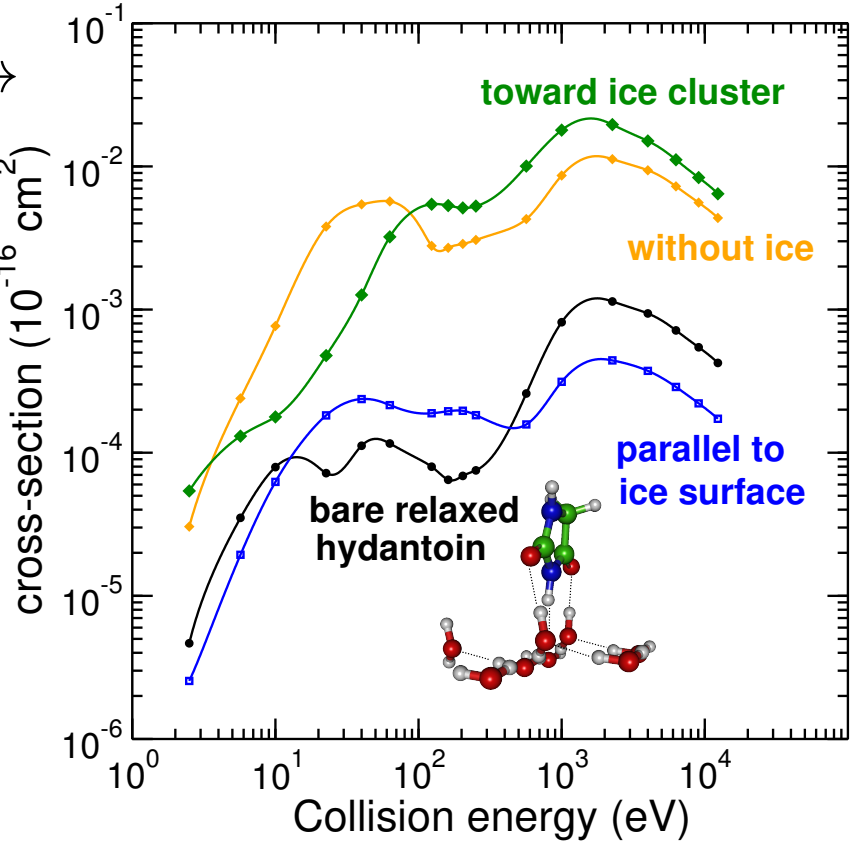
→much weaker effect of microhydration on reactivity

Molecules adsorbed on ice surfaces

Aminooxazole



Hydantoin→



Water surface *restricted to a basic (hexagonal) unit of Ih ice*

→ in aminooxazole, strong effects due to the interaction with the icy substrate;

→ in hydantoin, much weaker but anisotropic effects

Thank you for your attention!

Further reading

Nanohydration of uracil: emergence of three-dimensional structures and proton-induced charge transfer, M.-C. Bacchus-Montabonel and F. Calvo, Phys. Chem. Chem. Phys. 17, 9629 (2015)

Stepwise hydration of 2-aminooxazole: theoretical insight into the structure, finite temperature behavior and proton-induced charge transfer, F. Calvo, M.-C. Bacchus-Montabonel, and C. Clavaguéra, J. Phys. Chem. A 120, 2380 (2016)

Size-induced segregation in the stepwise microhydration of hydantoin and its role in proton-induced charge transfer, F. Calvo and M.-C. Bacchus-Montabonel, J. Phys. Chem. A 122, 1634 (2018)