



# STUDYING THE REACTIVITY OF URACIL IN THE GAS PHASE: STATISTICAL vs. NON-STATISTICAL APPROACH

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# STUDYING THE REACTIVITY OF URACIL IN THE GAS PHASE: STATISTICAL vs. NON-STATISTICAL APPROACH

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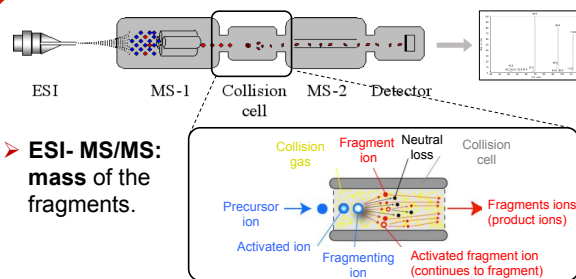
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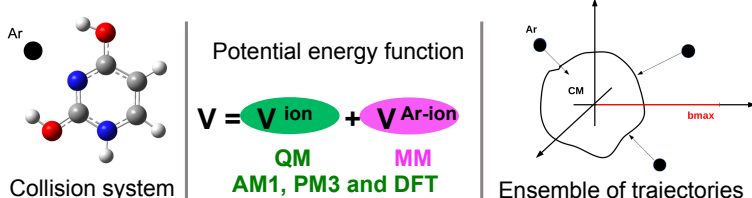
## INTRODUCTION

- Studying the reactivity of biomolecules in the gas phase allows to get rid of the effects of the environment: **intrinsic properties of the molecule**.
- System: **Uracil in DNA has cytotoxic and mutagenic potential**.
- Our AIM**
- Explain non-statistical and statistical reactivity of protonated Uracil in the gas phase and obtain predictive MS-MS spectra.



## ESI- MS/MS: mass of the fragments.

## QM-MM CHEMICAL DYNAMICS SIMULATIONS <sup>[1]</sup>: non-statistical mechanisms

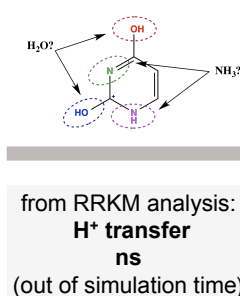
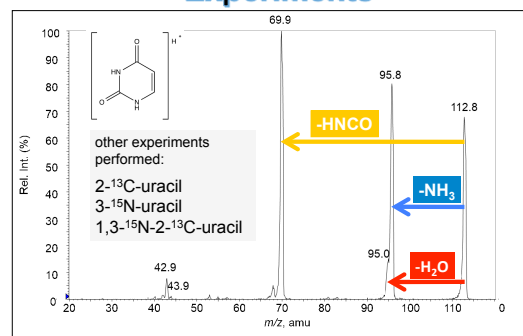


## RRKM and KINETIC MONTE CARLO (KMC) SIMULATIONS : statistical reactivity.

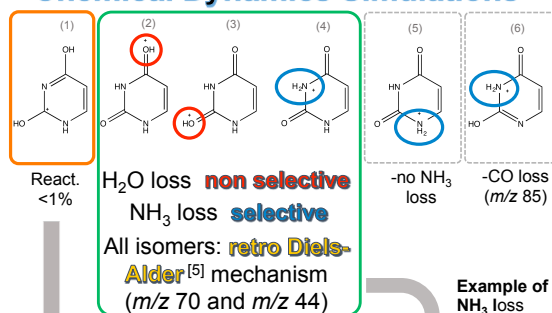
- For trajectories that did not react before IVR (intramolecular vibrational relaxation) takes place but have enough energy to react later on.
- Following automatic protocol<sup>[3]</sup> to find all fragmentation pathways, **TSs** and **minima**. Then this is used as input for RRKM and KMC simulations.

## RESULTS

### Experiments

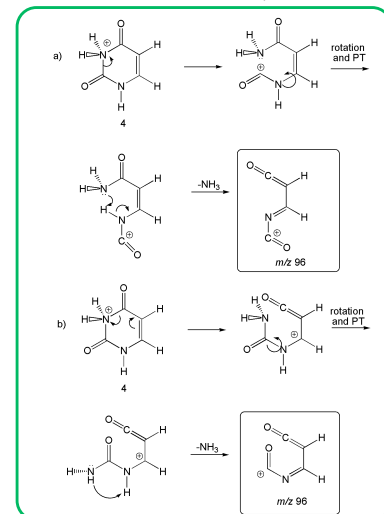
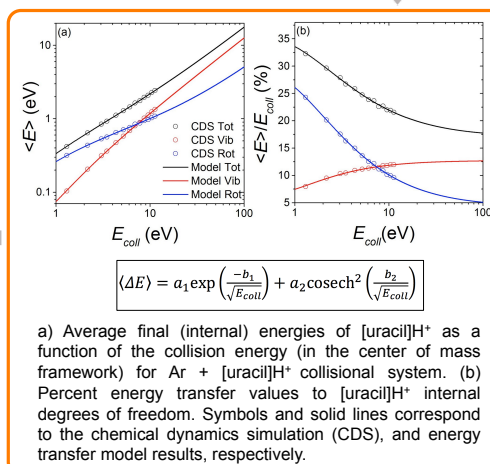
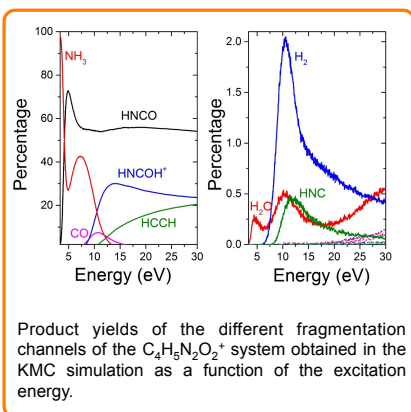


### Chemical Dynamics Simulations<sup>[2]</sup>



Example of  $\text{NH}_3$  loss mechanism for isomer 4.

## RRKM and KMC



## CONCLUSIONS

- As suggested by experiments,  $m/z$  70 is obtained by a retro Diels-Alder (rDA) mechanism.
- rDA reaction does not follow the minimum energy path along the reaction coordinate, while stepwise mechanisms do. In experiments, both mechanisms can co-exist.
- Initial protonation state of the ion plays a crucial role in determining the fragmentation pathway.
- $\text{NH}_3$  loss is a selective reaction, while  $\text{H}_2\text{O}$  loss it is not.

Refs.

- [1] Hase et al. JPCA (1999)
- [2] Rossich Molina et al. J. Mass Spectrom. (2015)
- [3] Martinez Nuñez. Phys. Chem. Chem. Phys. (2015)
- [4] Diels and Alder. Chemische Berichte. (1929)