# Fragmentation of protonated hydrated uracil clusters

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## Motivations

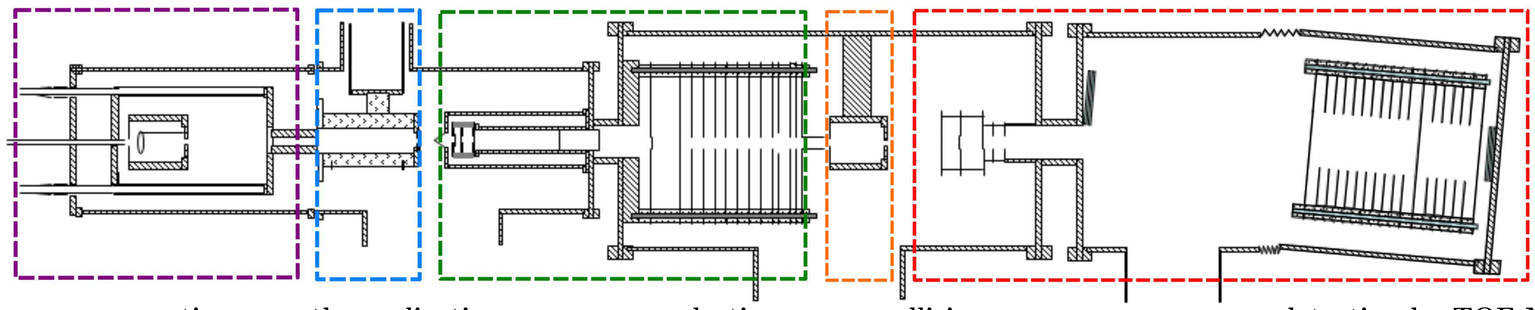
**Uracil (U):** $C_4H_4N_2O_2$

- one of the four bases in ribonucleic acid
- biological relevance
- extensively studied under CID

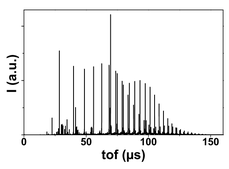
**Hydrated Uracil:** $(H_2O)_nUH^+$, n=1-11;

- water = natural medium of biomolecules
- few experiments
- mostly theoretical studies so far

## Experimental setup



- **gas aggregation source**




- **thermalization**

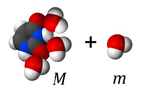
$25\ \mathrm{K} \leq T \leq 293\ \mathrm{K}$

- **mass-selection, energy focusing and slowing-down**

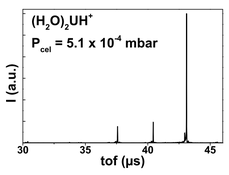
$33\ \mathrm{eV} \leq E_{lab} \leq 113\ \mathrm{eV}$


- **collisions**

$$E_{cm} = E_{lab}\frac{m}{m+M} + \frac{3}{2}k_B T_{cel}\frac{M}{m+M} \backsim \frac{E_{lab}}{size}$$

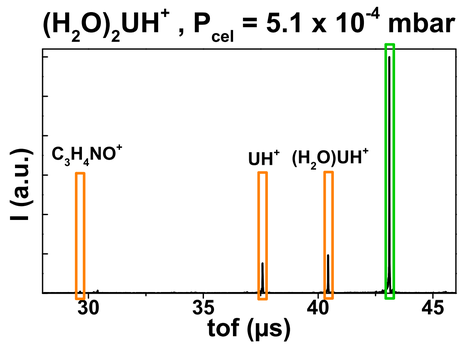



- **detection by TOF-MS**




## Measurement method

**Fragmentation Mass Spectrum:**



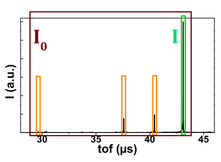

The number of collisions in the collision cell varies approximately from 0.6 for $UH^+$ to 1.2 for $(H_2O)_{11}UH^+$.

**Branching Ratio:**
for a fragment of mass $m$

$$BR = \frac{number\ of\ fragment\ of\ mass\ m}{total\ number\ of\ fragments}$$

**Fragmentation cross-section:**

$$\sigma_{frag} = -\frac{v_{cluster}}{\overline{v_{rel}}}\frac{ln\,(I/I_0)}{\rho L}$$




with $v_{cluster}$ : velocity of the cluster
$\overline{v_{rel}}$ : mean relative velocity between the molecule and the cluster
$\rho$ : density of the vapour in the collision cell
$L$ : length of the collision cell

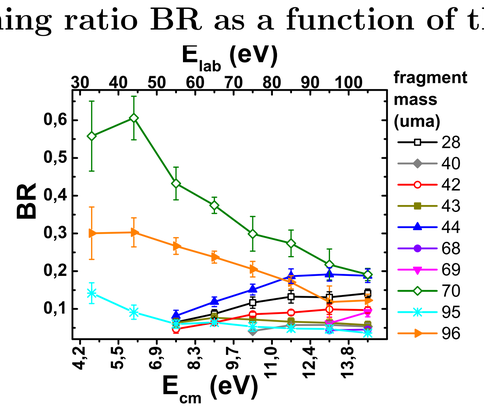
**Geometrical fragmentation cross-section:**

$$\sigma_{geo} = \pi\left(\left[n \cdot r_w^3 + r_U^3\right]^{1/3} + r_{vap}\right)^2$$

with $n$ : number of water molecules in the cluster
$r_w$ : molecular radius of a water molecule (2 Å)
$r_{vap}$ : molecular radius of the molecule of the vapor, water here
$r_U$ : molecular radius of the uracil molecule (3.2 Å)

## Bare Uracil Fragmentation : $UH^+$

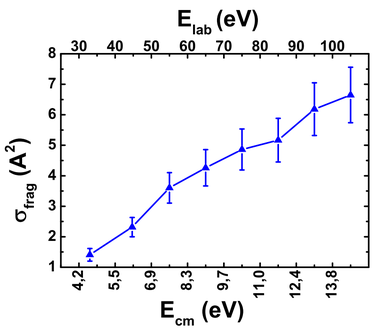
**Branching ratio BR as a function of the energy:**




**Elucidation of the fragments:**
from the CID of stable isotope labeled uracil in Nelson and McCloskey [1] and Molina *et al* [2]

| mass | fragment | ref |
|---|---|---|
| 96 | $UH^+ - NH_3$ (loss of ammonia) | 1 |
| 95 | $UH^+ - H_2O$ (loss of water) | 1 |
| 70 | $UH^+ - HNCO$ or $UH^+ - NCOH$ loss of isocyanic or cyanic acid | 1 |
| 69 | $UH^+ - HNCO - H$ ? | |
| 68 | $UH^+ - NH_3 - CO$ | 1 |
| 44 | $HNCOH^+$ | 2 |
| 43 | $HNCOH^+ - H$ or $UH^+ - HNCO - HCN$ | 2 or 1 |
| 42 | $UH^+ - HNCO - CO$ | 2 |
| 40 | $UH^+ - NH_3 - CO - HCN$ from 96 | 2 |
| 28 | $HNCH^+$ | 2 |

**Total fragmentation cross-section as a function of the energy:**

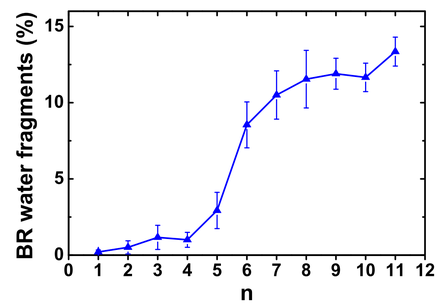



- We see an increase of the fragmentation cross-section with the collision energy;
- The experimental fragmentation cross-section is well below the geometrical one which is 85 Å;
- We have not reached the maximum of total fragmentation cross-section.

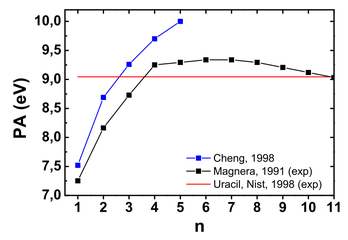
## Hydrated Uracil Fragmentation $(H_2O)_nUH^+$

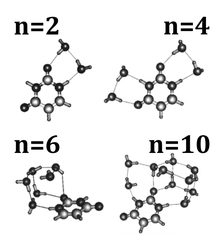
The energy is kept constant in the center-of-mass frame : $E_{cm}$ =6.2 eV

**Ratio between all the water fragments over the total number of fragments as a function of the number of water molecules in the mixed cluster:**

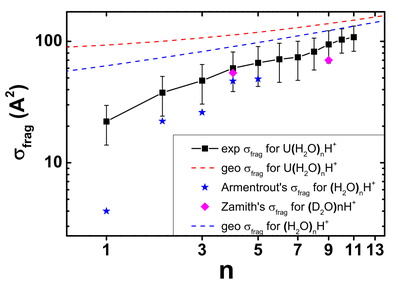



- Up to about n = 5 the fragments essentially keep the uracil molecule whereas above this size the proportion of fragments containing only water molecules increases;
- Attributed to a combined effect of the water clusters proton affinity increasing with size [3, 4] and structure change [5]




**Fragmentation cross-section as a function of the number of water molecules:**

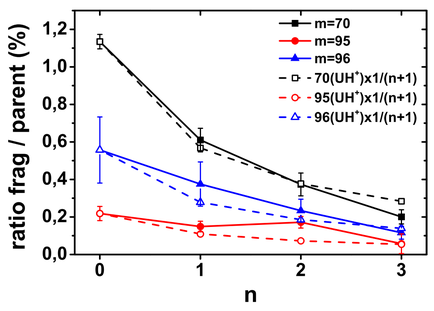



The fragmentation cross-section increases with the number of molecules in the cluster. They are close the geometrical one for the bigger sizes. They have the same order of magnitude as those already measured by our team[6] for deuterated water and by Armentrout's team [7].

## Bare Uracil Fragmentation in Hydrated Clusters

For the smallest hydrated clusters (n=1-3) we still observe some fragmentation of the uracil molecule.

**Evolution of the ratio between the fragment of mass m and the parent cluster:**




- Simple hypothesis: the collision probability for each constituant of the cluster decreases as:

$$1/size\ of\ the\ cluster$$

- Observation that the ratios of each uracil fragments follow this trend;
- There is no protective effect of water on the uracil molecule for those small clusters.

## Conclusions

- Observation of the bare protonated uracil fragmentation and of the energy thresholds for the different fragment appearance;
- Indirect observation of the proton affinity between the uracil molecule and water clusters and of a structure change;
- Measures of the total fragmentation cross-sections;

## References:

1. Nelson and McCloskey, *Am. Soc. Mass Spectrom.*, **5** 339-349 (1994)
2. Molina *et al J. Mass. Spectrom.*, **2015**, *50*, 1340-1351
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4. http://webbook.nist.gov on the 16/02/2016
5. Gadre *et al J. Phys. Chem. A*, **2000**, *104*, 8976-8982
6. Zamith *et al J. Chem. Phys.*, **2012**, *136*, 214301
7. Dalleska *et al J. Am. Chem. Soc.*, **1993**, *115*, 12125-12131

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