

Energy Flow Between Pyrimidines and Water Triggered by Low Energy Electrons

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Synopsis Substituted pyrimidines form a base of several cancer chemotherapeutics. Their effective dissociation by low energy electrons was identified to be a source of their radiosensitizing properties in combined chemo-radiation treatments. Here we combine experiment and theory to explore the energetics of the low energy electron interaction with these molecules in a solution. Novel approach enables estimation of the total energy flow between pyrimidines and water.

We present the results of experiments with molecular beams of microhydrated pyrimidines uracil, 5-Fluorouracil and 5-Bromouracil. Microhydrated pyrimidines are prepared by recently described gas humidification technique [1]. The molecules interact with low energy 1.5 eV or 70 eV electrons and reaction products are analyzed by the means of negative or positive ion mass spectrometry, respectively. Control over the hydration process enables the change of hydration level of the neutral microhydrated pyrimidines in molecular beam. The combination of two different ionization techniques with theory then allows us to estimate absolute energy flow from pyrimidines to water after electron attachment and electron ionization.

In a good agreement with the interpretation of our previous work on uracil and thymine [1], water reduces the dissociation of pyrimidines by caging of the dissociation products. The energy transferred to the cage is released by evaporation of individual water molecules. Number of evaporated molecules can be used to estimate the total energy transferred to the solvent. In our experiment, number of evaporated water molecules is not measured directly but estimated from the comparison of positive and negative ion mass spectra.

The amount of energy transferred to the solvent after electron attachment copies the trend of rising electron affinity of the pyrimidines from uracil to 5-bromouracil. On the other side, the energy transferred to the solvent after electron ionization is nearly constant. On the basis of our previous studies with pure water clusters [2] one can expect that after the ionization, the energy transferred to solvent should be high. However, the experiments show that it is actually low and comparable to the energy transferred to the solvent after electron attachment

to 5-bromouracil. This indicates that stable cluster cations are formed only after ionization of pyrimidines within the cluster, while ionization of water results in prompt fragmentation and possible pyrimidine dissociation after proton transfer reaction.

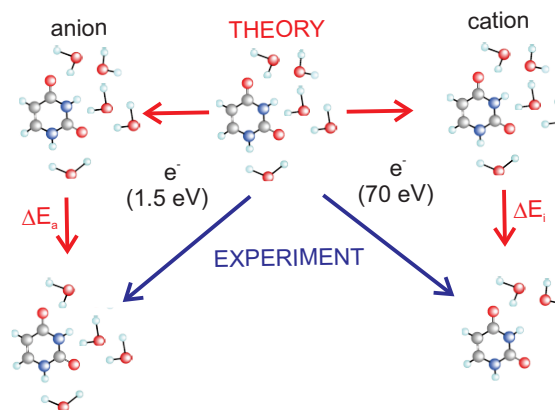


Figure 1. Sketch of the present approach. Experiment provides information about distributions of microhydrated cations and anions formed after electron ionization and electron attachment, respectively. Theory is then used to estimate the amount of energy needed to evaporate the water molecules as observed for electron attachment (ΔE_a) and electron ionization (ΔE_i). Experiments with different pyrimidines and at different level of hydration were done to validate the approach.

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References

- [1] J. Kočíšek *et al.* 2016 *J. Phys. Chem. Lett.* **7** 3401
- [2] J. Lengyel *et al.* 2014 *Chem. Phys. Lett.* **612** 256

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