

Understanding the formation of metastable furan dication in collisions with ions

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Synopsis This work relies on complementary theoretical and experimental studies of the processes induced by ion-furan collisions. Results of the Molecular Dynamics simulations and exploration of the energy profiles combined with coincidence mass spectrometry provide complete picture of the fragmentation of furan dication.

The main aim of this work is to investigate and understand the fragmentation processes of a furan dication induced by ion collisions with complementary theoretical methodology and experimental technique. The furan molecule has been chosen as a target due to its model structure that can be seen as an elementary analogue of deoxyribose, fundamental component of the DNA backbone chain. Depending on the charge state, the furan molecule is expected to dissociate in various ways [1].

Our theoretical approach consists of *ab initio* Molecular Dynamics describing the evolution of the system following deposition of the energy, and exploration of the Potential Energy Surface (PES) studied at high level of theory. Therefore, the dynamical and energetical considerations of the studied process are expected to create a complete picture of the fragmentation mechanism.

Results of the dynamics simulations lead to the observation of four different processes: isomerization, skeleton fragmentation, H⁺/H₂⁺ loss and H/H₂ loss. Total occurrence of the most abundant channels varies depending on the energy deposited to the system (from 5 to 30 eV). More insight into three- and four-body fragmentation processes is obtained by investigation of the order of events occurring as the trajectory progresses. Therefore, average time scales of sequential events leading to the major channels are also estimated.

Calculated fragmentation pathways, presenting minima and transition states, indicate stability of intermediate structures leading to chan-

nels with many fragments. Investigation of the PES and MD suggests that fragmentation of the furan dication follows a dissociation path with one channel clearly distinguished as most probable and producing fragments of formyl cation (CHO⁺) and cyclopropenyl cation (C₃H₃⁺).

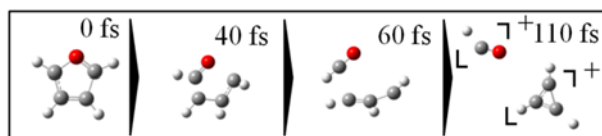


Figure 1. Snapshots of the dynamical simulation.

In order to support theoretical results, coincidence time-of-flight (TOF) mass spectrometry has been employed to study the interaction of 46 keV O⁶⁺ ions with neutral furan. Measured relative intensities of the coincident ion pairs are in good agreement with calculated energy barriers of the lowest-energy pathways. Geometrical parameters of the measured correlation islands in the fragment-fragment map indicate the mechanism of a specific dissociation channel. Long tail in the TOF mass spectrum points out to slow charge separation associated with the production of a metastable furan dication. This feature can be explained by the properties of the calculated PES.

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References

- [1] Erdmann E *et al* 2018 *J. Phys. Chem. A.* **122** 4153

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