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Molecular dynamics of photodissociation: towards more complex systems

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Synopsis We present a combined experimental and theoretical study of the photodissociation of thiophene molecule using energy-resolved electron-ion-ion coincidence technique and self-consistent charge density functional tight-binding theory combined with a statistical approach. The observed complex molecular dynamics with many internal-energy-dependent fragmentation pathways is successfully described by the theoretical simulations.

Following the dynamics of molecular reactions as they proceed has been a topic of keen interest for chemists as well as physicists, from both the fundamental and applied points of view. Unimolecular reactions that follow the deposition of energy into the system by photoabsorption is a particular category that has recently spurred significant theoretical and experimental efforts [1,2]. Despite of active studies, our understanding of the molecular dynamics in radiation-induced reactions is still very limited, particularly when it comes to medium- and large-sized systems.

Here, we present a combined experimental and theoretical study of thiophene molecule – a ring structure of 9 atoms. We employed energy-resolved electron-ion-ion coincidence (PEPIPICO) technique using synchrotron radiation at MAX-lab, Sweden and observed the molecular fragmentation pathways depending on the amount of the internal energy deposited into the molecule during the sulphur 2p photoionization and the subsequent Auger relaxation processes.

Theoretical simulations were performed by using the semi-empirical self-consistent charge density functional tight-binding (SCC-DFTB) method. By running thousands of these simulations, the variability of the initial conditions encountered in the experiment were taken into account, including the systematic dependencies on the internal energy.

Our chosen molecule exhibits a rich pattern of molecular dynamics with numerous ring rupture processes accompanied by hydrogen migration and/or ejection (see Figure 1). Both the ring ruptures and the hydrogen dynamics are highly internal-energy-dependent and the branching ratios into all available dissociation pathways show major variations: in experiment as a func-

tion of the Auger electron kinetic energy and in simulations as a function of the initial total vibrational energy of the molecule.

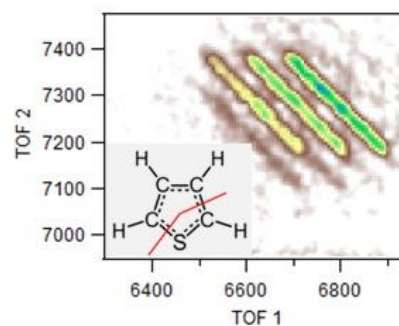


Figure 1. A small region of the PEPIPICO map following S 2p photoionization and Auger decay in thiophene. Illustration shows the ring bond ruptures and the sequence of patterns is due to additional ejection of hydrogen(s).

This study demonstrates that a computationally feasible theoretical model can successfully reproduce the complex dissociation pattern and its energy-dependent variations in a medium-sized molecule. The approach can be extended to larger systems in future.

References

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