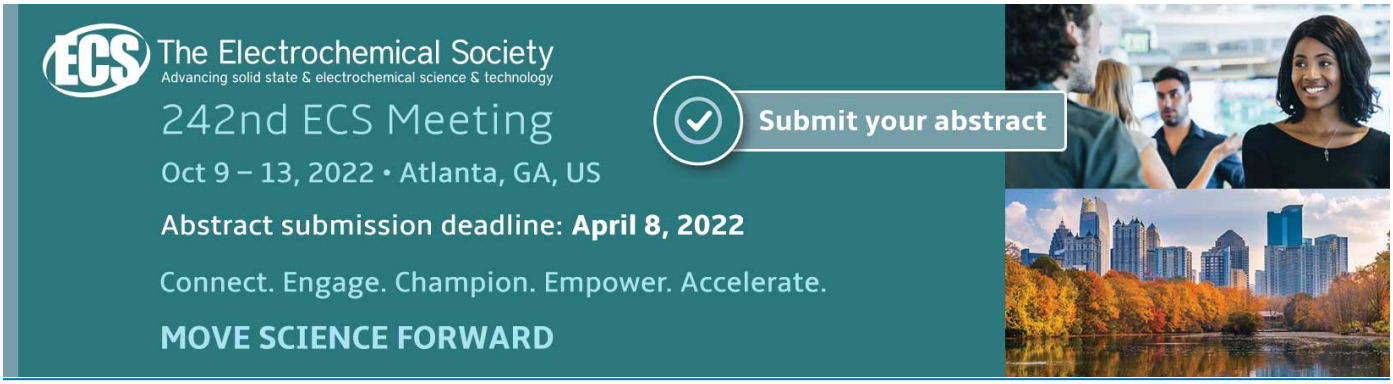
Halogen loss induced by electron collisions in halouracils at low energies



Halogen loss induced by electron collisions in halouracils at low energies

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Synopsis We employed both eletronic scattering techniques and *ab initio* quantum dynamics to study electron-driven reactions in halouracils at low energies. Particularly, it was addressed halogen dissociation and H-loss probabilities in anionic 5-BrU and 5-IU. Besides, we also propose a model of how to include auto-ionization probabilities during the dynamics.

Dynamics of transient negative ions (TNI's) is a subject of different complexities. The formation of such systems begina when an electron attaches to a closed-shell neutral molecule in its ground electronic state, though being related to the formation of resonances. The dynamics triggered by the formation of resonant states could decay to different channels, but in either case the auto-detachment process is one of the possible outcomes.

In this context, radiosensitizers like 5-halouracils constitute an interesting group for studying dissociative electron attachment (DEA), so it has been shown they might decay to different dissociative channels under low-energy ($0 \sim 3$ eV) electron collisions[1]. From previous theoretical works[2], both anionic 5-BrU and 5-IU present a set of low-lying anionic states. In the case of 5-BrU we observe one valence π_1^* state, a σ_{CBr}^* antibonding resonance and a π_2^* resonance at energies -0.30 eV, 0.78 eV and 1.50 eV. Theoretical predictions rely on the most significant dissociation mechanism to be the electron attachment on π_2^* state followed by a π^*/σ^* coupling/crossing.

Combining Schwinger multichannel (SMC) method for describing resonances with *ab initio* multiple spawning (AIMS) methodology[3] we have approached TNI's dynamics as a photochemical reaction of the anion species (Fig. 1). We also have implemented the auto-ionization probability during the dynamics *a posteriori*.

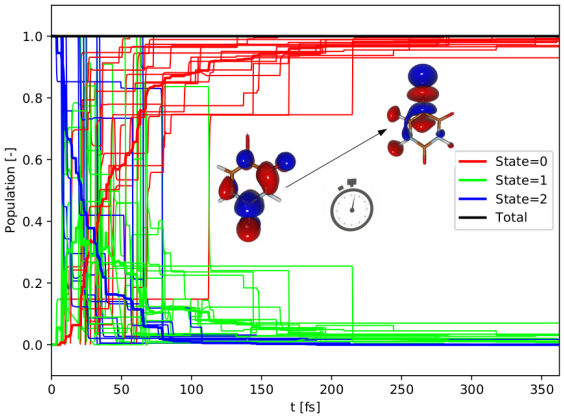

Figure 1: Population of the involved electronic states for 122 trajectories obtained for anionic 5-BrU. Thinner lines represent distinct initial conditions while thicker lines represent the average over all trajectories at each time.

The present work has been leading us to a clearer comprehension of different features, like the dissociative mechanisms induced by low-energy electron attachments, the presence and absence of distinct signals in DEA experiments and the role of the auto-ionization probabily.

References

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