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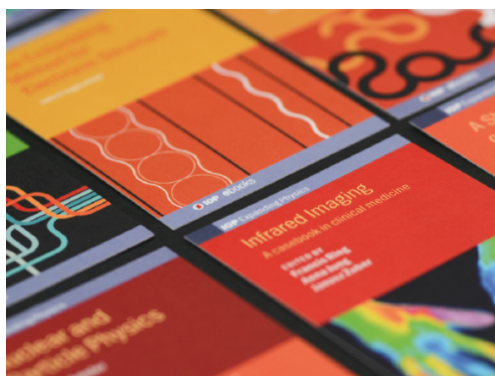
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Delayed relaxation of highly excited naphthalene cations

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Synopsis The efficiency of energy transfer in ultrafast electronic relaxation of molecules depends strongly on the complex interplay between electronic and nuclear motion. In this study we use wavelength-selected XUV pulses to induce relaxation dynamics of highly excited cationic states of naphthalene. Surprisingly, the observed relaxation lifetimes increase with the cationic excitation energy. We propose that this is a manifestation of a quantum mechanical population trapping that leads to delayed relaxation of molecules in the regions with a high density of excited states.

Relaxation of highly excited electronic states of large molecules follows a complex web of potential energy surfaces and involves transitions through many conical intersections. These dynamics pose a formidable challenge for modern quantum chemistry tools and therefore call for extensive experimental investigations. The complexity of the spectroscopic picture suggests that time-domain methods may bring insights, which are hard or impossible to reach using energy-domain tools only.

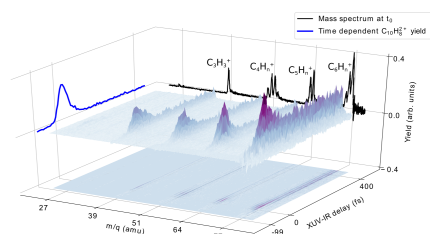


Figure 1. Fragment ion and di-cation yields for naphthalene molecules ionized by the XUV and IR pulses as a function of the time delay between the pulses.

The ultrafast XUV sources developed in the recent decades offer a perfect tool to study highly excited molecules, in particular, highly excited cations created upon photoionization with sufficiently large photon energy. Recently, XUV pulses produced by the method of high order harmonic generation were used to prepare highly excited cations of polyaromatic hydrocarbon molecules (PAH) [1, 2]. Surprisingly, it was

observed that relaxation times of the states close to the double-ionization threshold increase both with the size of the molecule and with the energy of the excited state.

The above-mentioned experiments were carried out with broadband XUV sources exciting a broad range of cationic states without control over the excitation. Here we report time-resolved experiments on naphthalene molecules using an XUV time-delay-compensating monochromator beamline which delivers wavelength-selected XUV pulses and was previously used to study relaxation dynamics of highly excited nitrogen cations [3]. We record fragment ion and di-cation yields in a pump-probe XUV-IR configuration (see Figure 1) and observe that electronic states with higher excitation energy relax slower despite of having more total energy deposited into the molecule.

The striking similarity between our results and those of Refs [1, 2] leads us to formulating a conjecture, that relaxation of highly excited PAH molecules, which are known to very efficiently proceed towards the electronic ground state, exhibits the quantum mechanical effect of trapping and timescale separation, due to the large density of excited states and the low number of relaxation channels.

References

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- [2] Marciniak A *et al* 2019 *Nat. Comm.* **10** 337
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