# Ultrafast laser-assisted stabilization of ionized adenine

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**Abstract:** A NIR pulse following attosecond XUV-photoionization at specific time delay can prevent irreparable damage of adenine. We identify the stabilizing mechanism in electronic correlation driven charge migration away from the molecular plane.

Photostability and radiation damage in DNA building blocks have a fundamental role in living organism as they dictate the response, for example, to the exposure to ultraviolet sunlight and high-energy ionizing radiation used in some cancer therapies [1]. The complexity of these molecules makes it challenging to understand under which conditions ionization leads to bond-breakage. Much of the tissue damage from radiation therapy is caused by secondary electrons carrying an energy similar to what can be deposited onto nucleobases with extreme ultraviolet (XUV) attosecond pulses[2,3]. In this energy range, the charge dynamics following photoionization is strongly affected by electronic correlation. In our combined experimental and theoretical investigation we show how electronic correlation can open pathways to molecular stabilization.

Here we present a time-resolved study of photo-fragmentation following ionization by an isolated attosecond XUV pulse (20–35 eV) of the nucleobase adenine, one of the building blocks of DNA. The most intriguing experimental finding is that doubly ionized adenine can be stabilized by a NIR pulse delayed by 2–3 fs from the XUV, as shown by our time-delay resolved mass spectra in Fig. 1a. Without the properly timed NIR pulse, the singly or doubly photoionized adenine mainly undergoes fragmentation, as confirmed by theoretical simulations based on Time-Dependent Density Functional Theory combined with Ehrenfest dynamics investigations.

We explain the need for a delay between NIR and XUV pulses as the time it takes for electronic correlation to bring the molecule into a state where the NIR pulse is able to remove excess energy through photoionization and hence stabilize the molecule (Fig. 1b). We obtain qualitatively agreeing time scales from a simple Fermi's golden rule approach and from ab-initio many-body time-dependent dynamics based on Green's function theory. We identify the relevant mechanism as a shake-up process to an excited state with a delocalised electronic distribution (Fig. 1c), enhancing the cross section for NIR photoionization, from which 2-NIR-photon ionization is energetically feasible. In summary we found that it is possible to stabilize an excited nucleobase ion against fragmentation by sending a NIR-pulse after a delay characteristic of the shake-up charge migration process.

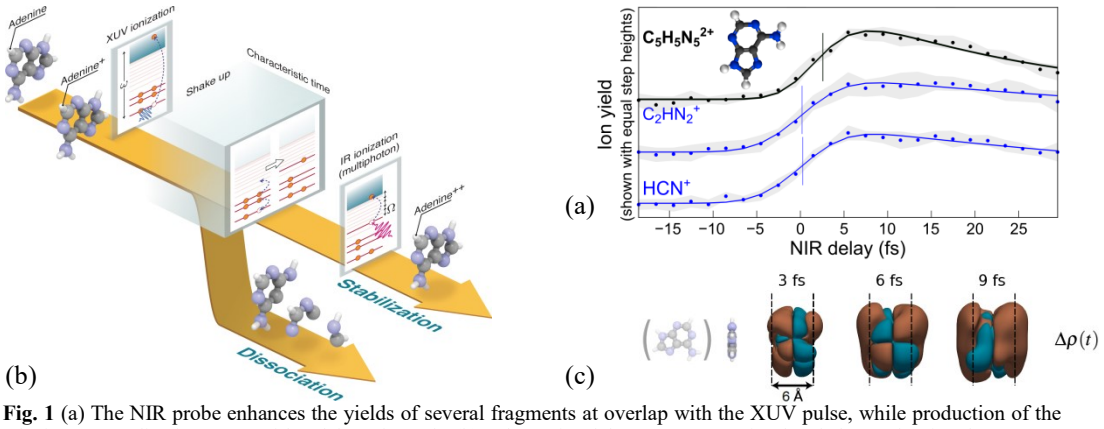


**Fig. 1** (a) The NIR probe enhances the yields of several fragments at overlap with the XUV pulse, while production of the adenine parent dication starts with a delay of 2–3 fs. (b) Schematic of the process. (c) Simulated charge density changes.

## References

[1] M. K. Shukla & J. Leszczynski (Eds.), *Radiation Induced Molecular Phenomena in Nucleic Acids* (Springer, 2008).

[2] F. Calegari et al. *Ultrafast electron dynamics in phenylalanine initiated by attosecond pulses*, Science **346**, 336 (2014).

[3] E. P. Månsson et al. *Ultrafast Dynamics in the DNA Building Blocks Thymidine and Thymine Initiated By Ionizing Radiation*, Phys. Chem. Chem. Phys. **19**, 19815 (2017).