

# NIR-assisted stabilization of adenine following ionization by XUV attosecond pulses

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**Abstract:** A stable dication of adenine is produced for short positive NIR delays after photoionization by an isolated attosecond pulse. This delay (2.3 fs) is explained as the time required for a shake-up process to occur.

## 1. Introduction

Ionizing radiation causes mutations and irreparable damage to DNA. However, nucleobases also exhibits relatively high inherent photo-stability. The complexity of these molecules makes it a challenging task to elucidate in detail all the physical mechanisms activated by ionization including fragmentation, internal energy dissipation and electronic correlation effects.

As recently shown, access to the time scale immediately following ionization of a bio-chemically relevant molecule can be gained using an extreme ultraviolet (XUV) attosecond pump in combination with a near-infrared (NIR) few-femtosecond probe [1, 2]. Moreover, attosecond pulses can be produced in the 20–40 eV energy range, which is highly relevant for the biological context. This is indeed the typical energy of the secondary electrons that - by impacting with DNA - represent the main source of indirect damage following tissue irradiation [3]. Ionization with 20–40 eV energy is often accompanied by the transition of an outer shell electron to an unoccupied state by a shake-up mechanism. It has been demonstrated that the population of such shake-up states can be probed with attosecond time resolution [4]. However, so far this investigation has been only limited to atoms and small molecules.

Here we present a time-resolved study of photo-fragmentation of the nucleobase adenine, one of the key building blocks of DNA, following ionization by an XUV attosecond pulse. Our most intriguing observation is that a stable dication of the parent molecule can be produced if (and only if) the probing NIR pulse is very briefly delayed from the XUV pulse. Our experimental and theoretical findings indicate that this short delay corresponds to the time required for a shake-up process to occur.

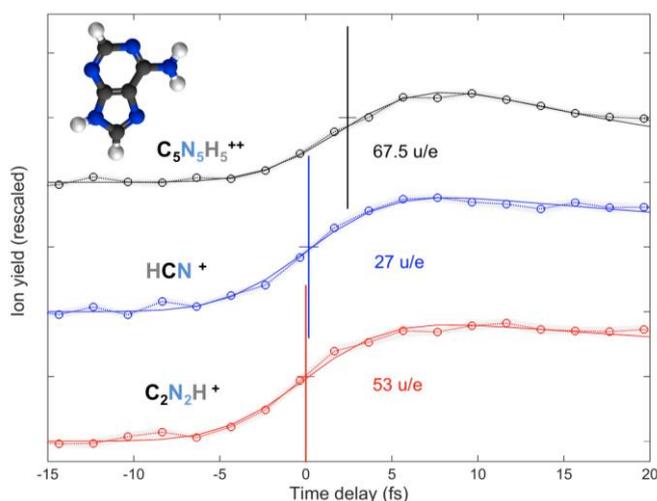


Fig. 1. Time dependent yield for fragments 27, 53 and 67.5 u/e. The yield is fitted by a step function with exponential decay, convoluted with a Gaussian.

## 2. Results and discussion

In our experiment, ionization of adenine was initiated by isolated sub-300-as pulses with photon energies between 17 eV and 40 eV, and subsequently probed by sub-4-fs, waveform-controlled NIR pulses. Adenine was evaporated and carried to the laser interaction region by a buffer gas. The produced ions were then collected using a VMI spectrometer operated in the ion time-of-flight mode as a function of the XUV-pump NIR-probe delay. The time dependent yield of many fragments displays a clear step-like increase, in some cases followed by a rapid decay. Figure 1 shows the partial ion yield for fragments 27, 53 and 67.5 u/e as a function of the pump-probe delay. By fitting the time-dependent signal we find that the formation of the dication of the parent (67.5 u/e) is delayed compared to the other cationic fragments by about 2.3 fs. It is worth noting that no stable dication of the parent is observed in the XUV-only signal, or in the combined XUV+NIR signal when the XUV is below 17 eV.

Theoretical calculations based on the Time-Dependent Density Functional Theory (TDDFT) indicate that ionization of adenine by XUV pulses inevitably leads to dissociation. This implies that the sub-sequent creation of a stable parent dication requires energy relaxation of the system. As depicted in Figure 2, energy dissipation occurs via ionization of a shake-up state by the NIR probe pulse. The measured delay of 2.3 fs thus corresponds to the time required for the shake-up process to occur.

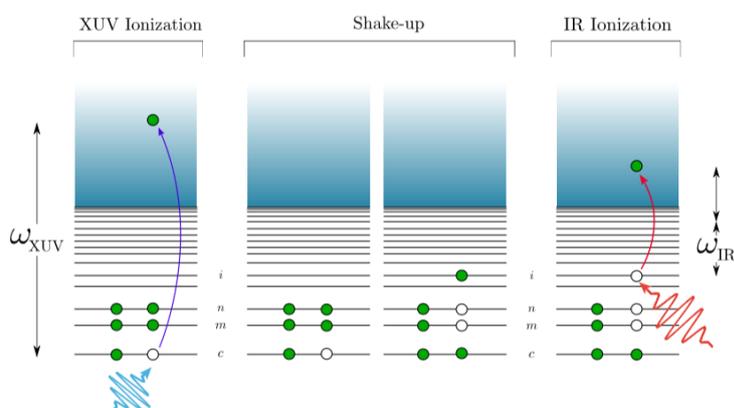


Fig. 2. Scheme of the NIR-assisted stabilization process of ionized adenine: i) an XUV pulse ionizes the molecule, ii) a shake-up process occurs in 2.3 fs and finally iii) a few NIR photons are absorbed to ionize a second electron and stabilize the molecule.

## 3. Conclusions

In summary, we have used attosecond time resolved mass-spectrometry to address photoionization of adenine. Two key contributions are presented. First, we show that a stable dication of the parent can be observed 2.3 fs after zero time delay. This delay has been interpreted as the intrinsic time for shake-up. Second, we demonstrated that a NIR-probe pulse can be sent at a controlled time delay to ionize the shake-up electron and stabilize the molecule.

## 4. References

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