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Title: Ultrafast laser-assisted photoprotection mechanism in the adenine cation

Attosecond pulses have become a mature tool for tracking in real time nuclear and electronic degrees of freedom in systems with increasing complexity [1]. Our particular interest is the ultrafast response of DNA building blocks upon irradiation, from which emerge photostability and bond breaking.

Through time-resolved photo-fragmentation measurements, we demonstrate a laser-assisted photoprotection scheme in the adenine nucleobase [2]. Surprisingly, a path to retain the molecule structurally intact arises when a near infrared (NIR) pulse is sent precisely 2.3 fs following ionization by an isolated attosecond XUV pulse. Without the properly timed NIR, the singly or doubly photoionized adenine mainly dissociates, as confirmed by TDDFT simulations. Rate equations and ab-initio many-body time-dependent calculations based on Green's function associate this characteristic 2.3 fs time delay to the population of a specific shake-up state after XUV ionization, driving the electronic density away from the molecular plane. Further numerical simulations show that depletion of this shake-up state by the NIR pulse accounts for internal energy removal from the molecule and leads to a stable dication.

[1] Calegari F. *et al.,* Science **346**, 336 (2014)
[2] Månsson E. P. *et al.,* Science (in preparation)