Abstract. Nucleobases absorb strongly in the ultraviolet region, leading to molecular excitation into reactive states. The molecules avoid the photoreactions by funnelling the electronic energy into less reactive states on an ultrafast timescale via non-Born-Oppenheimer dynamics. Current theory on the nucleobase thymine discusses two conflicting pathways for the photoprotective dynamics. We present our first results of our free electron laser based UV-pump soft x-ray-probe study of the photoprotection mechanism of thymine. We use the high spatial sensitivity of the Auger electrons emitted after the soft x-ray pulse induced core ionization. Our transient spetra show two timescales on the order of 200 fs and 5 ps, in agreement with previous (all UV) ultrafast experiments. The timescales appear at different Auger kinetic energies which will help us to decipher the molecular dynamics.

Although nucleobases absorb strongly in the near ultraviolet region transmitted by the Earth’s atmosphere, the UV excitation surprisingly does not lead to photoinduced chemistry or damage of the base molecules. Theory and previous experiments indicate that the photoprotection of the nucleobases proceeds via fast (femtoseconds to picoseconds) non-adiabatic transitions [1,2]. Even for isolated nucleobases the understanding of the non-Born-Oppenheimer approximation (non-BOA) dynamics is currently controversial. Past experiments rely heavily on simulations to interpret the observed timescales and depending on the level of ab-initio approximations, different timescales are predicted.

The UV light excites an electron from the \( \pi \) orbital (see Fig. 1) to the initially unoccupied \( \pi^* \) orbital. This \( \pi \pi^* \) (one electron in \( \pi \) one in \( \pi^* \)) state is highly reactive. To avoid photoinduced reactions, non-Born-Oppenheimer dynamics funnels the electronic population down to the ground state on a fast timescale. The first step is a radiationless transition in which the hole in the \( \pi \) orbital is filled by the electron from the \( n \) orbital, leading to the \( n\pi^* \) state. For thymine, theoretical models predict either a
few picoseconds [3] or 100 fs [4,5] for this process, depending on the ab-initio approximations made. Current experiments contain both timescales and an unambiguous interpretation is not possible at the moment.

![Fig. 1: Valence orbitals of thymine – oxygen atoms are marked by the arrows. A UV fs pulse excites electronic population from the π to a π* orbital. The molecule is reactive in this so called ππ* state. Non-Born-Oppenheimer dynamics is responsible for the first photoprotection step, in which a lone pair electron (n orbital) is funneled into the π orbital (leading to the nπ* state). The timescale for this process is currently a matter of debate. The x-ray probe pulse ionizes the K shell. We observe the kinetic energy of the Auger electrons from the oxygen K-edge decay (site specific probe). The Auger spectrum with UV excitation contains transient features. Their peak strength and position as a function of delay contains all the information on the photoprotection path.](image)

We conducted an experiment at the Linac Coherent Light Source (LCLS) free electron laser to get a more direct insight into the transient valence occupation during photoprotection via element sensitive Auger spectroscopy. Using soft x-ray transitions for probing molecular electronic processes has the advantage of element sensitivity and increased electronic sensitivity to certain valence orbitals. We used an ultrashort UV laser pulse to initiate the photoprotection mechanism in thymine (see Fig 1). The soft x-ray pulse from LCLS acted as a probe by generating photo- and Auger electrons. We tuned the LCLS to 565 eV photon energy, which is about 25 eV above the oxygen K edge. Calculations of Auger rates confirmed that Auger electrons emitted from the oxygen atoms in the photoexcited base are very sensitive to the population of the lone pair orbital (n in Fig. 1), which is strongly localized at the oxygen atoms (see n orbital in Fig.1). The jitter between the UV laser pump and SXR probe pulse was measured for every shot via a transient reflection [6]. We then resorted our data according to this jitter leading to relative delay accuracy below 100 fs.

The main Auger band of Thymine in its ground state is about 20 eV wide and peaked around 500 eV. Fig. 2 shows the effects of UV excitation on a transient Auger spectrum. We plot the difference of Auger spectra with UV on and off normalized on the sum of Auger spectra with UV on and off for each time delay. Depending on spectral region and time delay, we observe either a loss in Auger signal (dark) or newly created signal due to UV irradiation (light). The main Auger band at 500 eV bleaches in its upper half from about 500 eV on. We attribute this to UV induced depopulation of the ground state (about 10%), which weakens the main Auger band. Furthermore, we observe a UV induced transient increase in the Auger decay. For early delays around 0-100 fs, new Auger features appear between 505 and 510 eV kinetic energy. The features have a very fast decay time of about 200 fs. Moreover a 2 eV redshift of the 510 nm peak can be observed with a ~5ps time constant. We
have evidence from resonant Auger spectroscopy at the synchrotron (ALS Berkeley Natl. Lab) that the kinetic energies above 500 eV display the Auger decay of photoexcited states of thymine.

We are currently working on a more detailed attribution of Auger channels to valence states which will open the chance to shed new light onto the UV photoprotection mechanism. In particular we are simulating the kinetic energy and strength of the Auger decay for the $\pi\pi^*$, $n\pi^*$ and vibrationally hot ground state geometries. While the 200 fs transient decay in the Auger signal points towards a very fast non-BOA dynamics, it is too early to draw definite conclusions on the exact electronic dynamics.

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References