Ultrafast X-ray Auger Probing of photoexcited molecular dynamics

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Molecules can efficiently and selectively convert light energy into other degrees of freedom. Disentangling the underlying ultrafast motion of electrons and nuclei of the photoexcited molecule presents a challenge to current spectroscopic approaches. We explore the photoexcited dynamics by an interaction with an ultrafast x-ray pulse creating a highly localized core hole which decays via Auger emission. We discover that the Auger spectrum as a function of photoexcitation – x-ray pulse delay contains valuable information about the nuclear and electronic degrees of freedom from an element specific point of view. For the nucleobase thymine, the oxygen Auger spectrum shifts towards high kinetic energies, resulting from a particular C-O bond stretch in the $\pi\pi$ * photoexcited state. A subsequent shift of the Auger spectrum towards lower kinetic energies displays the electronic relaxation of the initial photoexcited state within 200 fs. Ab-initio simulations reinforce our interpretation and indicate an electronic decay to the $n\pi$ * state.

Some molecules have the ability to selectively and efficiently convert light into other forms of energy like heat and charge separation, or store it in altered chemical bonds. These processes often require transitions between the multiple electronic states of the molecule, proceeding through violations of the Born-Oppenheimer approximation (BOA) (1). The BOA allows the separation of electronic and nuclear degrees of freedom and is an important tool for the prediction of molecular properties. Non-BOA transitions between different electronic states pose challenges to theory and experiment; they are difficult to model, they proceed on an ultrafast timescale, and prominently occur at so called conical intersections (CIs) of electronic potential

energy surfaces (2-4)(see Fig. 1a). The theory of non-BOA dynamics has advanced significantly over the last two decades, but challenges in the simulation of photoexcited electronic structure and non-BOA dynamics persist, even for the high level methods employed in isolated molecules (4-6). Experiments on non-BOA dynamics in isolated molecules typically use ultrafast optical pulses for probing molecular dynamics, utilizing transitions between mostly delocalized electrons (7, 8, 9). Here we show that element and site specific probing by soft x-ray pulses in combination with Auger electron detection can resolve non-BOA processes in isolated molecules, even for cases that are not easily detected by traditional ultrafast experiments. We performed a delayed ultrafast x-ray Auger probe (DUXAP) investigation of photoinduced non-BOA dynamics in thymine at the LINAC coherent light source (LCLS). We selectively probe the initial elongation of a C-O bond after molecular photoexcitation which is displayed in a shift of the Auger spectrum to higher kinetic energies. From a subsequent shift to lower kinetic energies we deduce an initial photoexcited state lifetime of 200 fs. Our results demonstrate that DUXAP is able to distinguish between nuclear relaxation and non-BOA electronic transitions. DUXAP is applicable to very dilute targets and therefore complements the method of ultrafast soft x-ray absorption spectroscopy, which is ideally suited for condensed phase high density targets (10, 11).

In our experiment, performed at the LCLS, the soft x-ray (SXR) probe pulse ionizes a highly localized oxygen 1s electron after the molecule has been excited by an ultrashort ultraviolet (UV) pulse which has changed the valence electronic occupation (see Fig 1b). The core-ionized state promptly decays to a dicationic state by filling the core hole with a valence electron and emitting an Auger electron (see Fig. 1). The Auger electron kinetic energy is analyzed in a spectrometer as a function of pump-probe delay (see methods). This new DUXAP method has several compelling advantages for elucidating non-BOA dynamics: First, soft x-rays with energies of several eV above the absorption edge are capable of core-ionizing the molecule at any nuclear geometry. Thus the signal strength does not decrease due to reduced Franck-Condon overlap upon vibrational relaxation. The latter can be problematic in other ultrafast pump-probe spectroscopies using optical pulses. Second, the core electron binding energies as well as the Auger kinetic energies differ vastly for different elements and sites within a molecule. This allows us to observe the nuclear as well as the electronic dynamics of the molecule from a highly local point of view. Similar to infrared spectroscopy we can monitor the motion of certain bonds within the molecule, but in addition we obtain information on the molecular electronic state. Third, as we will show here, the nuclear and electronic relaxation cause distinct transient shifts in the Auger spectra, aiding the interpretation. Importantly, Auger spectra are insensitive to the strong spectral fluctuations that are typical in self amplified spontaneous emission (SASE) x-ray free electron laser sources, which are currently the most common ultrashort soft x-ray laser sources (12).

The difficulties of resolving excited state molecular dynamics through pump-probe experiments are illustrated using a sketch of potential energy surfaces along a one dimensional reaction coordinate in fig. 1a. A wavepacket, which is launched in the Franck-Condon region of a neutral photoexcited state (blue), follows potential gradients and immediately starts to relax along a nuclear coordinate. It reaches regions with CIs that connect to other electronic states (red and black), offering an ultrafast electronic relaxation route. Along the path from the Franck-Condon to the CI region other features, such as reaction barriers, may be encountered. Distinguishing the ultrafast nuclear relaxation on the initially photoexcited state from electronic relaxation presents

a challenge to the interpretation of ultrafast measurements with optical pulses, because both can lead to a transient signal decay.

This prototypical difficulty is exemplified with the case of the nucleobase thymine. Thymine shows an electronic relaxation process out of the photoexcited $\pi\pi^*$ state (blue). This relaxation contributes to the protection of DNA from damaging ultraviolet-induced dimerization (13, 14). Previous time-resolved ion (15,16,17) and photoelectron measurements (18) in isolated molecules aimed at attributing a time constant to the electronic relaxation. They all showed a very short, ~100 fs, decay constant followed by additional 5-7 ps decay (15-18). The time constants are generally consistent with calculations of the potential energy surface (19,20,21,23). However, the assignment of the transients to electronic or nuclear relaxation varies among theoretical approaches, as it depends strongly on the reaction path and reaction barrier in the $\pi\pi^*$ state which is particularly sensitive to the chosen quantum chemical details. Approaches based on linear interpolation (21) or minimal energy paths (22) predict a barrierless and thus very fast decay to the electronic ground state not involving any C-O bond stretch. This suggests an interpretation of fastest time constant as electronic relaxation. A second, so called indirect path (23) was suggested to compete with the direct ultrafast electronic relaxation to the ground state. The full dynamics simulation (19) predicts an initial ultrafast nuclear relaxation into the $\pi\pi^*$ state minimum involving the C(4)-C(8) stretch. The population is then trapped for picoseconds behind a reaction barrier. These results have been extended to much longer timescales stating that molecular population transfers into the $n\pi^*$ state with a picoseconds time constant (20). This suggests an interpretation of the 100 fs constant as a nuclear relaxation. The thymine photochemistry clearly represents a difficult case for theory and experiment, motivating further ultrafast experimental studies. The SXR pulses used in our investigation are capable of coreionizing the molecule in any nuclear geometry and thus the integrated Auger signal persists upon nuclear relaxation on the $\pi\pi^*$ state. Moreover, we will show that Auger spectroscopy allows for experimental separation of electronic and nuclear relaxation. Nuclear relaxation on $\pi\pi^*$ includes a elongation of the C(4)-C(8) bond close to the methyl group (see Fig. 2), which is intuitively clear from the π^* orbital shape having a node on this C-O bond (see Fig. 1 b orbital scheme). We will show that this elongation results in a blueshift of x-ray induced Auger spectra. In contrast, electronic relaxation from the $\pi\pi^*$ state to the $n\pi^*$ or the ground state manifests itself as a shift towards lower kinetic energies (see below).

Figure 2 shows a comparison of experimental (free electron laser with synchrotron data) and simulated oxygen Auger 1s electron spectra for thymine in the electronic ground state. The theoretical analysis is described in the SI. The high level algebraic diagrammatic construction (ADC(2)) (24, 25) method simulates the observed features well. For excited states, the ADC(2) method is unfeasible, and we developed a lower level approach based on the complex Kohn (26) and configuration interaction singles method (27) (CK-CIS). To further simplify our approach, we concentrate only on the strongest Auger transitions (shown as lines), which are broadened by spectrometer and lifetime limitations. Although the CK-CIS method is expected to be less accurate than ADC(2), it has the advantage of providing access to features of the photoexcited state Auger decay. The molecular valence orbitals which are strongly localized at the coreionized oxygen site dominate the Auger decay features calculated with the ADC(2) and CK-CIS methods (Tables SI1 and SI2). This is the underlying basis of Auger decay element sensitivity.

The change of the Auger spectrum following ultraviolet excitation is shown as difference spectra in Fig. 3a as a function of pump-probe delay. The subtraction of unexcited spectra from UV excited spectra reveals the change between the unexcited and excited molecule (see method section). Figure 3b shows the integrated signal in the kinetic energy intervals (I,II,III) for different delays. The fastest features are a decrease in region II accompanied by a rise in region I. This reflects a shift of the whole Auger band towards higher Auger kinetic energies due to the UV excitation. The immediate appearance of this modulation in regions I and II reflect the creation of a wave packet in the $\pi\pi^*$ excited state by the ultraviolet pulse.

The immediate blueshift of the Auger spectrum after photoexcitation is connected to nuclear relaxation dynamics. As pointed out above, probing the oxygen Auger decay gives us the advantage of monitoring nuclear and electronic dynamics of bonds in the vicinity of oxygen atoms, which are two C-O bonds for thymine. A stretch in these bonds leads to a blueshift in the Auger spectrum. This can be understood from electrostatic considerations with the help of Fig. 1a. The final states in the Auger decay with two valence holes (dicationic states given in grey) are strongly repulsive due to some unscreened nuclear repulsion. They have lower bond strength and therefore a lowered electronic energy for increasing C-O bond lengths (see Fig. 1a). Thus the energy difference between the core-ionized state and the very repulsive dicationic final state increases along the CO stretch which increases with the reaction coordinate. This effect leads to a blueshifted Auger spectrum. In order to resolve the C-O bond motion in time as a continuous shift, a better time resolution would be required. This argument is supported by CK-CIS simulations, as shown in Figure 4a and b depicting Auger spectra for the ground state, the $\pi\pi^*$ state at the Franck-Condon, and $\pi\pi^*$ minimum geometries. The $\pi\pi^*$ state at the Franck-Condon geometry is slightly shifted blue with respect to the ground state and an even larger shift occurs at the $\pi\pi^*$ minimum. The CK-CIS Auger spectrum can be separated according to which of the oxygen atoms was core-excited. Remarkably, only the spectrum arising from O(8) (thin solid blue) shows major changes upon excited state relaxation. The O(7) (dashed blue line) spectrum is rather static since the C(2)-O(7) bond does not change as a consequence of photoexcitation. The C(4)-O(8) bond elongates by 15% as the molecule changes from the Franck-Condon nuclear geometry to the $\pi\pi^*$ state minimum (19, 20). This fast nuclear relaxation results in a large Auger blueshift comparable to the shift observed in the experimental difference spectrum measured for 75 fs delay (Fig. 4e). This confirms that nuclear relaxation including the C(4)-O(8) elongation out of the Frank-Condon region leads to a consistent shift towards higher kinetic energies, just as qualitatively expected from experimental considerations.

We observe a decrease in region I with a 200 fs time constant together with a rise in region III, indicating a spectral shift towards lower Auger kinetic energies. This is contrary to the nuclear relaxation trend described above. The observed experimental shift therefore disagrees with further nuclear relaxation and indicates an *electronic relaxation*. This fast electronic decay of the $\pi\pi^*$ state *must occur unimpeded by any significant reaction barrier* within the relaxation path. We cannot exclude that potential maxima exist on the side of the path and are circumvented by the molecular wavepacket. These barriers however cannot be directly measured via population trapping.

We now concentrate on the interpretation of the signal in region III in terms of product states. A return of photoexcited population to the vibrationally hot ground state as well as population of the dark $n\pi^*$ state is possible and was controversially discussed in the theoretical literature (19-23). The simulated $n\pi^*$ spectrum (red line, Fig. 4c) shows a shift of its maximum into spectral region III, in agreement with our experimental observations (the shift is consistent for different nuclear geometries, see Fig. SI8). The simulated hot ground state spectrum in fig. 4d shows a rather symmetric broadening due to the sampling over different nuclear geometries (see Fig. SI6 for further discussion). Furthermore, its modulation is shallow compared to that in the electronically excited states, which points at low sensitivity of our experiment towards this state. We point out that the hot ground state was sampled with a reduced set of geometries due to the computational effort associated with the chosen algebraic diagrammatic construction (ADC(2)) method. Based on the comparison of our experimental data with these preliminary theoretical results, we attribute the increase in region III to the population of the $n\pi^*$ state.

We now compare the measured time constants and our interpretation to literature data of the thymine model system. Short decay constants on the order of 100 fs have been documented in the optical pump-probe literature (15, 16, 18) and were interpreted either as nuclear relaxation on the $\pi\pi^*$ state or electronic relaxation out of this state. 151618The soft x-ray experiments described here distinguish between nuclear and electronic relaxation and we can interpret the 200 fs decrease in region I as an electronic reduction of the $\pi\pi^*$ population. The fast decay of a majority of the $\pi\pi^*$ state population is in agreement with some previous theoretical calculations of the $\pi\pi^*$ potential energy surface (21-23). We are not able to resolve the 100 fs process observed in optical experiments but it is most likely hidden in the blueshift due to nuclear relaxation out of the $\pi\pi^*$ Franck-Condon window. Several simulations point towards the hot ground state as a product of few 100 fs electronic relaxation (21,22,23), which was confirmed in liquid phase (28). Due to reduced Auger sensitivity to this state, we abstain from a statement. Our experimental transients together with Auger simulations of the $n\pi^*$ state however point towards a 200-300 fs filling of the $n\pi^*$ state. Dynamical simulations predict a several ps timescale (19,20) for this process and the discrepancy might originate from an overestimated reaction barrier (21,23). In order to show excited state fluorescence as measured in liquid phase according to ref. (29), some molecular population must be trapped behind a reaction barrier, but we assume that our experimental signal to noise ratio is not good enough to deduce such detailed information.

In summary, we have demonstrated a new method for accessing the photoinduced dynamics on excited states of isolated molecules. The DUXAP technique is particularly well suited to distinguish ultrafast nuclear and electronic relaxation with high local sensitivity. A particular advantage of the DUXAP method lies in different spectral features for nuclear and electronic relaxation which allows a new perspective on dynamics. We have found a 200 fs electronic relaxation of a majority of the photoexcited $\pi\pi^*$ state in thymine, and thus conclude that under the conditions in this experiment the majority of the excited state population is not efficiently trapped by an excited state reaction barrier as previously suggested. Tuning the x-ray wavewlenght into the resonance region could result in site specific resolution of molecular dynamics in the future. The DUXAP method is ideal for dilute quantum systems, and complements the now established method of ultrafast soft x-ray absorption spectroscopy applicable to high density targets (10, 11). The method makes optimal use of x-rays sources with

short pulse duration and high fluence. Such sources are now available due to the development of free electron lasers such as LCLS (30), FLASH (31) and SACLA (32).

Methods:

Our experiments are performed at the LCLS at SLAC National Accelerator Laboratory and at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory. At LCLS, our experiment took place in the high field physics (HFP) chamber of the Atomic, Molecular and Optical science instrument (33). Molecules evaporated by a 140 deg C hot oven were guided to the photon interaction region through a 900 micron diameter, 40 mm long capillary. Measurements on the beam ex-situ gave an estimated sample density of 10¹¹ molecules/cm³ at the exit of the capillary and a molecular beam opening angle in the range of 10 degrees. The background pressure was in the 10⁻⁹ mbar range, corresponding to particle densities that are 3-4 orders of magnitude below the thymine density in the interaction region. The molecules were first irradiated by a UV pulse of 266 nm wavelength having a duration of 70 fs. After a time delay in the femtosecond to picosecond domain, the photoexcited molecules were exposed to a soft x-ray pulse with a photon energy of 565 eV and an estimated duration from 50 to 80 fs. The SXR pulses had a spectral jitter and bandwidth of about 0.25-0.5%. The Auger measurements were not sensitive to the spectral jitter. The relative delay between UV and SXR pulses also jittered from shot to shot, giving at best a temporal resolution near 250 fs. We dramatically increase our temporal resolution to 70 fs by characterizing the jitter with a single shot, x-ray optical cross-correlator that measures and re-sorts the shots according to delay (34). The UV pump pulse was focused to a ~70 micron spot, estimated from a microscope image of a YAG screen in the interaction region. The x-rays were focused more tightly than the UV. The energy of the UV pulses and the x-ray pulses were chosen to avoid nonlinear effects. This was checked by observing the spectra during a systematic scan of both pulse energies independently. Since the multiphoton UV excitation lead to molecular fragmentation, it was easy to confirm the low excitation limit. The SXR pulse creates 1s core holes in carbon, nitrogen and oxygen inside the molecule according to their relative absorption cross sections. The photoelectrons were discarded, since their energy fluctuated strongly with the LCLS spectral jitter. Instead we analyzed the Auger electrons around 500 eV kinetic energy, which are exclusively ejected by an O 1s core hole decay. The electrons were funneled towards a 2 m long flight tube by a strong permanent magnet. They encounter a retardation of 470 V and hit an MCP detector to measure their time of flight (TOF) which is then converted to kinetic energy. The spectrometer was designed as a magnetic bottle (35); however we turned the solenoid in the flight tube off to increase the spectral resolution. The presence of the permanent magnet provided a high spatial sensitivity on the intersection region between the pump and probe pulse. With this setup we were able to distinguish lines spaced by 2 eV in the Xe-MNN-Auger spectrum (36), which also served as our calibration standard. The polarizations of the UV and SXR pulses were aligned with the flight tube symmetry axis.

Assuming a fraction f of the molecules were excited by the UV pulse, the difference signal is given as Signal(UV_{on})-Signal(UV_{off})=Signal_{GS}(1-f)+Signal_{ES}f-Signal_{GS}=f(Signal_{ES}-Signal_{GS}), where the subscripts *GS* and *ES* refer to the ground and photoexcited molecular states,

respectively. The Signal(UV_{on}) and Signal(UV_{off}) spectra are the mean of the single shot spectra that fall into a selected delay interval; the error is the standard error of this mean.

At the ALS, we used beamline 8 to record Auger spectra of unexcited molecules at variable photon energies for N, C and O core hole decay. The kinetic energy of the Auger spectra was measured with a hemispherical analyzer whose axis was aligned to 56 deg with respect to the soft x-ray polarization. The molecules were evaporated at similar temperatures to the LCLS experiments into a gas cell flanged onto the analyzer.

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Fig. 1a) Sketch illustrating general features of photoexcited molecular states. After a light-induced electronic transition, a nuclear wavepacket is driven by gradients in the potential energy

surface (blue) towards regions containing conical intersections (CIs), allowing for ultrafast electronic transitions to lower electronic states (red, black) under violation of the Born-Oppenheimer approximation. The electronic relaxation of photoexcited population can be intercepted by reaction barriers between the initial photoexcited reaction coordinate and CI region. For the particular case of thymine, the UV excitation (pump) pulse excites a wave packet on the $\pi\pi^*$ state and CIs connect to $n\pi^*$ and ground state (GS). The topology of the $\pi\pi^*$ state controls the speed of electronic relaxation and the height of the sketched barrier is currently a matter of debate. The soft x-ray probing is shown by a transition to core ionized molecular potential energy surfaces, from which the Auger decay proceeds to a manifold of dicationic states. The potential energy difference between core ionized and dicationic state determines the kinetic energy of the Auger electron. b) DUXAP (delayed ultrafast x-ray induced Auger probing) scheme applied to thymine photoprotection. The images on the left side show the π n and π^* molecular valence orbitals. The oxygen 1s orbitals, in which the core hole can be created, are highly localized at one of the marked two oxygen sites. The π and n orbitals are both doubly occupied in the ground state configuration. The UV pump pulse promotes an electron from a π orbital to a π^* orbital, giving rise to the chemically reactive $\pi\pi^*$ state. We probe the electronic valence state by a delayed soft x-ray (SXR) probe pulse creating a core hole and inducing Auger decay. The emitted Auger electrons carry information about the valence electronic state at the core hole position (oxygen in our case).

Figure 2



Fig. 2: Comparison of experimental and theoretical ground state Auger spectra for thymine. The green and yellow curves are data taken at the advanced light source (ALS) synchrotron and the LCLS free electron laser, respectively, and are offset in intensity from the theory. The magnetic bottle spectrometer employed for the FEL measurements used a retardation voltage of 470 eV leading to a reduction in transmission for the lower kinetic energy range until about 487 eV. The ADC(2) calculations (blue) as well as the CK-CIS simulations (black) are explained in the SI, they reproduce the essential features of the experiment and are in agreement. The lines from the CK-CIS calculations are shown by sticks reflecting the Auger rate from distinct valence orbitals that have a large spatial overlap with the oxygen 1s core orbitals. The sticks for the O(7) atom (red) and the O(8) atom (blue) produce similar Auger spectra (see also Table SI1-2). The inset shows the molecular geometry with the number convention used for its atoms.



Fig.3 a) Difference Auger spectra with and without UV excitation as function of Auger electron kinetic energy and time delay between UV pump and soft x-ray probe pulse, color code: blue: UV induces less Auger decay, red: UV induces more Auger decay. The kinetic energy axis is divided in three ranges I (506-513 eV), II (497-503 eV), and III (485-495 eV). A time resolution around 70 fs has been achieved by single shot delay measurements (34)and subsequent resorting of our data. Note the non-equidistant time intervals. The bottom part shows difference spectra at two different delays marked by the arrows (75 fs dashed blue and 465 fs solid red). (b) Integrations over kinetic energy range in a) scaled by a factor as given in the legend. The grey lines show the fit described in the SI.





Fig. 4: Calculated Auger decay spectra using the CK-CIS method (see SI) for the ground state GS, the $n\pi^*$ and $\pi\pi^*$ (a-c), states (see tables SI1-6 for more information on prominent Auger decay features). (a)The ground state Auger decay is calculated at its minimum energy geometry and corresponds to the Auger decay of a non-UV excited molecule. (b) The $\pi\pi^*$ state is evaluated at the Frank Condon geometry and the $\pi\pi^*$ minimum geometry according to (19). While the spectrum of O(7) does not shift with respect to the ground state the O(8) spectrum shifts blue in the $\pi\pi^*$ minimum because of the C(4)-O(8) stretch. (c) The simulation predicts a redshift for $n\pi^*$ states, which once more is only due to the O(8) spectrum. Other geometries on the respective state confirm the trend (see fig. SI8). The vibrationally hot electronic ground state in (d) calculated by the ADC(2) method via averaging different nuclear geometries (see Fig. SI7 and discussion) broadens the Auger spectrum with respect to the the ADC(2) simulation of the "cold" ground state for reference. (e) Experimental difference spectra cut at two different times from Fig. 2b indicating a shift toward higher kinetic energy at early times and lower kinetic energies later.

Supplementary Material

Theoretical Methods

The calculation of the Auger spectra is composed of two steps. In a first step, we calculate the rate of the Auger decay. The integrated rates over all dicationic channels are normalized to one. Since the fluorescence decay cannot compete with Auger decay rates, close to one Auger electron is emitted per core hole. In a second step, we evaluate the energy of this particular decay. The kinetic energy of the Auger electron is determined by the energy difference between the core excited state (having a 1s electron missing) and a dicationic state, in which two valence electrons are removed and the core hole is filled (see Fig. 1).

The Auger spectra of the ground state molecule, at its equilibrium geometry and at some vibrationally hot ground state geometries (Fig. 3b) are computed by the second-order Algebraic Diagrammatic Construction, ADC(2), method (24, 25). This yields the spectrum of double ionization energies, which are then subtracted from the core ionization potential to obtain the Auger electron energies. The intensities of the Auger transitions are estimated by a two-hole population analysis of the ADC(2) eigenvectors, according to the method outlined previously(37). It is important to note here, that no exact Auger matrix element as discussed below is calculated, but only the two valence hole density at the core hole position is analyzed. Spectra such as that in Fig. 2 are then obtained by Gaussian broadening of the discrete lines. The calculations have been performed using the cc-pVDZ basis set (38).

To calculate the Auger spectra of excited electronic states, we pursue a different strategy outlined in the following. The Fermi Golden rule expression for the total Auger decay rate of the initial core-hole state F_0 into a final state with outgoing momentum **k** for the Auger electron $\Upsilon_{\mathbf{k}}^{(-)}$, which is energy normalized, is

$$G = \frac{2\rho}{\hbar} \int \left| \left\langle \Upsilon_{\mathbf{k}}^{(-)} \middle| \sum_{i \neq j} \frac{e^2}{r_{ij}} \middle| F_0 \right\rangle \right|^2 dW_{\mathbf{k}} \quad (1)$$

where dW_k is the solid angle of the Auger electron. We compute the rates using single determinant wavefunctions for both states, and we assume that the relaxation effects do not appreciably affect the transition rates so that the spin orbitals that do not participate in the transition are the same in the initial and final state functions. Such assumption was used with success, and Siegbahn and Zähringer have given a detailed derivation of the Auger decay rate expressions (39, 40). Here we follow their treatment and compute the decay rates with Coulomb and Exchange matrix elements of the two-electron repulsion operator,

$$J_{nn'}^{c\mathbf{k}} = \left\langle j_{c}(1)j_{\mathbf{k}}^{(-)}(2) \left| \frac{e^{2}}{r_{12}} \right| j_{v}(1)j_{v'}(2) \right\rangle$$

$$K_{nn'}^{c\mathbf{k}} = \left\langle j_{c}(1)j_{\mathbf{k}}^{(-)}(2) \left| \frac{e^{2}}{r_{12}} \right| j_{v'}(1)j_{v}(2) \right\rangle$$
(2)

where j_c is the core molecular orbital and j_v and j_v are the valence molecular orbitals. The continuum orbital for the Auger electron, $j_{\mathbf{k}_i}^{(-)}$, is computed using the electron-molecule scattering wavefunction obtained with the complex-Kohn method (26) at the static level of theory. There are two cases that must be considered. In the first case, the Auger electron and the electron that repopulates the core hole come from the same molecular orbital. The decay rate is then given by

$$G = \frac{2\rho}{\hbar} \int \left| J_{nn}^{ck} \right|^2 dW_k.$$
 (3)

In the second case, the two electrons are from different molecular orbitals, which results in an expression that depends on the spin multiplicity of the bound part of the final state wavefunction. If the residual ion of the final state is singlet coupled, the decay rate is

$$G = \frac{2\rho}{\hbar} \int \frac{1}{2} \left| J_{nn'}^{c\mathbf{k}} + K_{nn'}^{c\mathbf{k}} \right|^2 dW_{\mathbf{k}}.$$
(4)

Finally, if the residual ion of the final state is triplet coupled, and the decay process involves two different valence molecular orbitals, the rate is

$$G = \frac{2\rho}{\hbar} \int \frac{3}{2} \left| J_{nn'}^{ck} - K_{nn'}^{ck} \right|^2 dW_k.$$
(5)

We are interested in the Auger decay rates of thymine in excited states, which can involve decay transitions from open shell valence molecular orbitals. Here we follow McGuire's (41) treatment. If there are n_i electrons in a shell that could contain n_0 electrons, and if one of the n_i electrons are involved in the transition we reduce the full-shell decay rate by n_i/n_0 . If two of the n_i valence electrons are involved in the process we reduce the full-shell rate by $n_i(n_i-1)/n_0(n_0-1)$.

The Auger decay rates presented here are obtained using the electron-molecule scattering wavefunction obtained by the complex-Kohn method. The final state wavefunction for production of ions in a specific state g_0 and with final angular momentum l_0m_0 is written as

$$\Upsilon_{g_0 l_0 m_0}^{-} = \mathop{\text{ad}}_{lm} A \Big(C_g(\mathbf{r}_1, ..., \mathbf{r}_{N-1}) F_{glm g_0 l_0 m_0}^{-}(\mathbf{r}_N) \Big)$$
(6)

where g labels the final ionic target states C_g , $F_{glmg_0l_0m_0}^-$ are the channel functions that describe the Auger electron, and A is the antisymmetrization operator. In the present application, only one ionic target state is included, that being the final dication state. Note that in Eq. 1 we use a combined index **k** to describe $g_0 l_0 m_0$. In the Kohn method, the channel functions are further expanded, in the molecular frame, as

$$F_{glmg_{0}l_{0}m_{0}}^{-}(\mathbf{r}) = \mathop{a}_{i}^{a} c_{i}^{glmg_{0}l_{0}m_{0}} f_{i}(\mathbf{r}) + \mathop{a}_{lm}^{a} [f_{lm}(k,r)d_{ll_{0}}d_{mm_{0}}d_{GG_{0}}^{-} + T_{ll_{0}mm_{0}}^{gg_{0}}h_{lm}^{-}(k,r)]Y_{lm}(\hat{\mathbf{r}}) / k^{1/2}r,$$
(7)

where the $f_i(\mathbf{r})$ are a set of square-integrable (Cartesian Gaussian) functions, Y_{lm} is a normalized spherical harmonic, k are channel momenta, and the $f_{lm}(k,r)$ and $h_{lm}^-(k,r)$ are numerical continuum functions that behave asymptotically as regular and incoming partial-wave Coulomb functions, respectively (42). The coefficients $T_{ll_0 m m_0}^{GG_0}$ are the T-matrix elements. Auger rates in the molecular frame can be constructed from the matrix elements

$$I_{g_0 l_0 m_0} = \left\langle \left\langle \Upsilon_{g_0 l_0 m_0}^{-} \middle| \underset{i^{1} j}{\overset{\circ}{\mathbf{r}_{ij}}} \middle| \mathbf{F}_0 \right\rangle = \\ \underset{i^{1} j}{\overset{\circ}{\mathbf{o}}} \left\langle \Upsilon_{g_0 l_0 m_0}^{-} (\mathbf{r}_1, ..., \mathbf{r}_N) \frac{e^2}{r_{ij}} \mathbf{F}_0 (\mathbf{r}_1, ..., \mathbf{r}_N) d\mathbf{r}_1, ..., d\mathbf{r}_N \right\rangle$$
(8)

The desired Auger decay rates are obtained using Eqs.(3)-(5), and the total Auger rate for a particular final state is

$$G = \frac{2\rho}{\hbar} \mathop{\rm alphi}_{l_0 m_0} \left| I_{g_0 l_0 m_0} \right|^2.$$
(9)

The scattering calculations were carried out using Dunning's double-zeta basis (43). Numerical continuum functions up to $l_{max} = 15$ are included. Note that the decay rates are computed using molecular orbitals from a Hartree-Fock calculation on the neutral thymine, and we use the same set of molecular orbitals to compute the decay rates of the excited states. We assume that the relaxation effects are not important because our Auger electron spectrum is constructed from the transitions that are intense. Howat has pointed out that the orbital relaxation and correlation effects are only important for the case of relatively weak Auger transitions (44).

To generate our spectrum, we first computed the decay rates for all possible transitions using single determinant initial and final state wavefunctions. We then computed the Auger electron energies for the final dication states, whose transition intensities were above some given threshold. Finally, we lowered the threshold until enough final states are considered in our calculation and the spectrum was converged to a graphical accuracy. The Auger electron energies were determined by configuration interaction singles (CIS) method. For the core-hole states, we started with a reference ion configuration with a single vacancy in the oxygen 1*s* orbital. We then performed a CIS calculation, keeping the oxygen 1*s* occupancy either one or zero. The dication energies are computed in a similar manner. We started with a reference dication configuration that gives rise to intense Auger transition, and we then performed a CIS

calculation keeping the occupation of the desired valence orbitals to be one or zero. Note that O1s, N1s and C1s orbitals are kept frozen in this calculation. This approach produced a ground state spectrum that closely resembled the experimental spectrum. To give better agreement with the ADC(2) calculation and the experiment, we have red shifted the spectrum by 1.7 eV (see fig. 2). We also note that all our decay rates are computed at a constant kinetic energy of the continuum electron that being 500 eV. Since the kinetic energy of the electron is large, the decay rates are insensitive to minor changes in the energy. To confirm our prediction, we have computed the ground state Auger decay rate of thymine at the Franck-Condon geometry that involve valence MOs 22a and 31a at various energies. In the energy from 485-515 eV, the rate only varied by 5%. Lastly, there are two oxygen atoms in the molecule and the experiment does not distinguish which atom the photoelectron is being ejected from; thus, we present the spectra that are summed over the two oxygen components. Both electrons contribute equally, as can be deduced from near edge absorption spectra (45). The total decay rates of thymine in its ground state at its equilibrium geometry computed using the aforementioned procedure agree with those obtained using the ADC(2) method (see Fig. 2).

The experiment tracks the nuclear wavepacket dynamics on the ground and excited state surfaces of thymine. We concentrated on the canonical tautomer of thymine, all other tautomers have negligible excitation at our sample temperatures (17). Thus, we computed the Auger decay rates of neutral thymine in various electronic states (ground (π^2) n π^* and $\pi\pi^*$ states) at key geometries previously determined by Hudock et al. (19) that included Franck-Condon, $n\pi^*$ and $\pi\pi^*$ minimum geometries. We are also interested in the "hot ground state spectrum" since the wavepacket created on the $\pi\pi^*$ state can return to the ground state surface with excess energy. To compute such a spectrum we generated the positions and momenta of our initial nuclear wavepacket from a Boltzmann distribution at a constant temperature. The normal modes and the vibrational frequencies of neutral thymine at the Franck-Condon geometry, which were used to obtain such a distribution, were first computed using the HF/6-31G* method. Since there is no standard way to generate a "hot ground state" trajectory, here we chose to distribute 4.5 eV of extra thermal energy equally into seven vibrational modes with high intensity for transition. Finally, we set the temperature for other vibrational modes to zero Kelvin and obtained the initial condition. We then ran a classical trajectory for 800 fs on the potential energy surface computed using the HF/6-31G* method and randomly picked four geometries from the dynamical calculation to compute the averaged Auger electron spectrum. More points will be calculated for future publications, however the ADC(2) method requires a lot of calculation time. We have chosen to use the ADC(2) method to compute the "hot ground state" spectrum since we are interested in weak Auger decay transitions that give rise to shifts in the spectrum compared to the ground state spectrum at the Franck-Condon geometry (see the Analysis section for more detail).

Analysis

We now give a detailed analysis of our Auger electron spectra computed with the complex-Kohn/CIS method. In table SI1 we present the Auger decay rates of ground state thymine at the Franck-Condon geometry following oxygen 1s ionization. Note that we only show the transitions that give rise to intense peaks in the spectra. We also labeled the two valence molecular orbitals that are involved in such intense transitions. We present the orbital energies

and the sum of Mulliken populations for each basis function located on the desired oxygen atom for relevant MOs in table SI2. The calculation is conducted in C_1 symmetry because nuclear motion breaks the Cs symmetry of the molecule. When the oxygen core-hole is created on O(8), which is located closer to the methyl group, the valence MOs that give rise to intense peaks are 22a, 24a and 31a, and they have large electron population located on O(8) (see table SI2). On the other hand, when the core-hole is created on O(7), the valence MOs 22a, 23a and 30a give intense transitions, and they have large electron population located on O(7). This observation strengthens our argument that the Auger decay in a selected energy window displays highly local properties of the valence electronic states. These transitions give rise to a broad peak centered around 500 eV. Note that we have red shifted our spectra by 1.7 eV to give better agreement with the ADC(2) method.

Table SI1. We present the relative normalized Auger decay rates and the electron kinetic energy of ground state thymine at the Franck-Condon geometry following oxygen 1s ionization. We show only the intense transitions for both Oxygen atoms. We also labeled the valence MOs that participate in such transitions. They are canonical Hartree-Fock orbitals obtained using Dunning's double-zeta basis (DZP).

O(8)	KE	MOs	Rate	O(7)	KE(e	MOs	Rate
	(eV)		(relative)		V)		(relative)
	493.1	22a, 24a	0.64		491.7	22a, 23a	0.41
	496.3	24a	0.42		494.8	23 <i>a</i>	0.49
	500.8	22a, 31a	0.66		500.1	23a, 30a	1.00
	502.4	24a, 31a	0.45		500.6	22a, 30a	0.45
	505.9	31 <i>a</i>	0.33		503.3	30 <i>a</i>	0.60

Table. SI2. We present the orbital energies and the sum of Mulliken populations for each basis function located on the desired Oxygen atom for selected MOs of ground state thymine at the Franck-Condon geometry. They are canonical Hartree-Fock orbitals obtained using Dunning's double-zeta basis (DZP).

MOs	Orbital energy	Mulliken Population	
	(eV)	O(7)	O(8)
$34a (\pi^*)$ LUMO	5.398	0	0
33 <i>а</i> (<i>π</i>) НОМО	-8.306	0.151	0.151
$32a(\pi_1)$	-11.452	0.454	0.565
31 <i>a</i> (<i>n</i>)	-11.488	0.292	1.183
$30a(n_1)$	-12.491	1.263	0.221
24 <i>a</i>	-16.030	0.093	0.656
23 <i>a</i>	-16.940	1.263	0.163
22 <i>a</i>	-17.835	0.329	0.713

The selected Auger decay rates of thymine in $\pi\pi^*$ electronic state, computed at the $\pi\pi^*$ minimum geometry, are shown in table SI3. Similar to table SI1 we show the intense transitions, electron kinetic energy and the valence MOs that participate in the process. In contrast to the ground state spectrum at Franck-Condon geometry, the intense O(8) decay transitions are now located around 506 eV, which explains the blue shifted difference signal observed in the experiment immediately following UV excitation. In table SI4 we present the orbital energies and the sum of Mulliken population on the Oxygen atoms for selected MOs computed at the $\pi\pi^*$ minimum geometry. MOs 25*a*, 28*a*, 31*a* and 32*a* are important for the O(8) transitions. MOs 22*a*, 23*a* and 30*a* have large population on O(7) atom, and they give rise to major features in the O(7) spectrum.

O(8)	KE	MOs	Rate	O(7)	KE(eV)	MOs	Rate
	(eV)		(relative)				(relative)
	500.6	25a, 28a	0.41		496.2	22a, 23a	0.63
	505.5	25a, 32a	0.90		500.4	22a, 30a	1.00
	506.7	28a, 32a	0.62		501.7	23a, 30a	0.66
	506.8	28a, 31a	0.43		504.3	30 <i>a</i>	0.69

Table SI3. As in table. SI1, for $\pi\pi^*$ thymine at the $\pi\pi^*$ minimum geometry.

Table. SI4. As in table. SI2, for $\pi\pi^*$ thymine at the $\pi\pi^*$ minimum geometry.

MOs	Orbital energy	Mulliken Populatio	
	(eV)	O(7)	O(8)
34 <i>a</i> (<i>π</i> *) LUMO	3.083	0	0
33 <i>a</i> (<i>π</i>) НОМО	-7.876	0.084	0.457
32 <i>a</i> (<i>n</i>)	-10.547	0.073	1.685
$31a(\pi_1)$	-10.592	0.327	0.783
$30a(n_1)$	-12.523	1.330	0.152
28 <i>a</i>	-13.855	0.055	0.367
25 <i>a</i>	-15.116	0.036	0.351
24 <i>a</i>	-15.805	0.071	0.052
23 <i>a</i>	-16.958	0.741	0.053
22 <i>a</i>	-17.631	0.803	0.123

In table SI5 we present the selected Auger decay rates of thymine in $n\pi^*$ electronic state, computed at the $n\pi^*$ minimum geometry. Once again we show the intense transitions, electron kinetic energy and the valence MOs that participate in the process. In table SI6 we present the orbital energies and the sum of Mulliken population on the Oxygen atoms for selected MOs computed at this geometry. In the O(8) spectrum MOs 25*a*, 28*a* and 32*a* are involved in the intense transitions and they have relatively large electron population located on that particular oxygen atom. Furthermore, those intense transitions are located at slightly lower kinetic energy

than the Ground state spectrum computed at the Franck-Condon geometry. Thus, they give an overall red shift in the spectrum (see Fig.3a of the main text). MOs 22a, 23a and 30a are important in the O(7) spectrum, and particularly MOs 23a and 30a have large electron population located around the O(7) atom.

O(8)	KE	MOs	Rate	O(7)	KE(eV)	MOs	Rate
	(eV)		(relative)				(relative
)
	495.7	25a, 28a	0.50		494.5	22a, 23a	0.62
	497.7	25a, 32a	0.81		501.7	22a, 30a	0.76
	498.4	28a, 32a	0.86		502.7	23a, 30a	1.00
	507.8	31 <i>a</i> , 33 <i>a</i>	0.40		504.8	30 <i>a</i>	0.56

Table SI5. As in table S1, for $n\pi^*$ thymine at the $n\pi^*$ minimum geometry.

Table. SI6. As in table. S2, for $n\pi^*$ thymine at the $n\pi^*$ minimum geometry.

MOs	Orbital energy	Mulliken Populatio	
	(eV)	O(7)	O(8)
$34a (\pi^*)$ LUMO	5.749	0	0
33 <i>a</i> (<i>π</i>) НОМО	-8.381	0.078	0.551
32 <i>a</i> (<i>n</i>)	-10.701	0.099	1.645
$31a(\pi_1)$	-10.727	0.397	0.639
$30a(n_1)$	-12.604	1.361	0.173
28 <i>a</i>	-14.070	0.116	0.440
25 <i>a</i>	-15.310	0.045	0.451
24 <i>a</i>	-15.799	0.091	0.035
23 <i>a</i>	-17.152	0.961	0.037
22 <i>a</i>	-17.862	0.534	0.139

Now we show the Auger electron spectra of the ground state thymine at one of the representative geometries determined by the dynamical calculation for the vibrationally hot ground state (see main text for details) in Fig. SI7. We plot the "hot" O(8) and O(7) spectra, in Fig.SI7c and Fig.SI7d, respectively. For comparison we have plotted the "cold" ground state spectra computed at the Franck-Condon geometry in Fig.SI7a (O(8)) and Fig.SI7b (O(7)). The difference spectrum, which has been summed over both oxygen components, is shown in Fig.SI7e. Here the spectra are computed using the ADC(2) method. Clearly, in one of the hot ground state spectra the main band at 500 eV extends to lower electron kinetic energy for both oxygen atoms, and this gives rise to the ~490 eV peak in the experimental difference plot. However, there is no single Auger decay channel that explains such a shift (see the sticks in Fig.

SI7), and the red shift results from the contribution of many weak transitions, located around \sim 490 eV, that are different at the two geometries. Thus, to predict this shift it was crucial to use the ADC(2) method that gives a very good description of electron correlation effects in the Auger decay transition; thus, accurate description of weak Auger decay transitions. In Fig.SI7f we plot the difference spectrum at another one of the representative geometries determined by the dynamical calculation. This spectrum shows a blue shift. Thus, by averaging the ground spectra computed at various geometries along the trajectory, the overall spectrum broadens and the peak maximum located around 500 eV goes down. This leads to a broadened difference spectrum.



Fig. SI7. The O(8) (a) and O(7) (b) Auger electron spectra of ground state thymine computed at the Franck-Condon geometry. Also shown are the O(8) (c) and O(7) (d) Auger electron spectra computed at one of the representative geometries determined by the dynamical calculation. (e) The difference spectrum at one of the representative geometries. Note that we have summed over both oxygen components. (f) The difference spectrum at another one of the representative geometries. Once again the spectrum has been summed over the two oxygen components. All spectra are computed using the ADC(2) method.

In Fig.SI8a we present the $\pi\pi^*$ spectra of thymine computed at the Franck-Condon, $\pi\pi^*$ minimum and $\pi\pi^*$ transition state geometries. The spectra shown are summed over both oxygen atom contributions. For comparison, the ground state spectrum at the FC geometry is also shown in the figure. The $\pi\pi^*$ spectrum at FC geometry is already slightly blueshifted compared to the ground state. The C(4)-O(8) distance at the FC geometry is 1.206 Ang. As the bond stretches to 1.355 Ang in the $\pi\pi^*$ minimum, the spectrum experiences an even stronger blueshift, as explained in the main text. The transition state (barrier in Fig.1) has a C-O elongation of 1.273

Ang, in between the FC and minimum. This still leads to a blueshift compared to the FC geometry. The 1 d sketch of a reaction coordinate in Fig. 1 does not completely grasp the multidimensional potential landscape; the C-O bond increases towards the minimum and then gets reduced at the transition state. Figure 8 in ref. (19) displays this geometry change much better. Both, the $\pi\pi^*$ spectra at $\pi\pi^*$ minimum and $\pi\pi^*$ transition state geometries are shifted to higher kinetic energies. This supports our intuitive argument that *nuclear relaxation* to larger bond distances shifts the Auger electrons towards higher kinetic energies.



Fig. SI8.a) The $\pi\pi^*$ Auger electron spectra of thymine computed at the Franck-Condon, $\pi\pi^*$ minimum and $\pi\pi^*$ transition state geometries. The spectra shown are summed over both oxygen atom contributions. For comparison we also present the ground state spectrum computed at the Franck-Condon geometry. **b)** The $n\pi^*$ Auger electron spectra of thymine computed at the Franck-Condon, $n\pi^*$ minimum and $\pi\pi^*$ minimum geometries. The spectra shown are summed over both oxygen atom contributions. For comparison we also present the ground state spectrum computed at the Franck-Condon, $n\pi^*$ minimum and $\pi\pi^*$ minimum geometries. The spectra shown are summed over both oxygen atom contributions. For comparison we also present the ground state spectrum computed at the Franck-Condon geometry.

The $n\pi^*$ spectra of thymine computed at the Franck-Condon, $n\pi^*$ minimum and $\pi\pi^*$ minimum geometries are shown in Fig.SI8b. The ground state spectrum at the FC geometry is also shown. In contrast to the ground state and $\pi\pi^*$ spectra, the peaks in the $n\pi^*$ spectra extends to lower kinetic energy, and the rise in low kinetic energy region (region III) observed in the experimental difference spectrum (see Fig.3c) could indicate a population transfer from $\pi\pi^*$ to $n\pi^*$ state.

Exponential fit details

Due to the large number of electrons collected in each shot in the experiment, much of the interesting region in our time of flight traces has a significant degree of electron pileup, such that we could not reliably use constant fraction discrimination or an equivalent method to count electron hits. To estimate the error in our measurements we implemented a bootstrap resampling routine as follows. We randomly select N electron spectra with replacement from the set electron spectra for one time delay, where N is the total number of spectra lying at the chosen delay. The mean is calculated from this random sample. This process is iterated and is used to populate a histogram of the mean spectral amplitude for each electron kinetic energy. The

standard deviation is calculated from the histogram as an estimate of the standard error of the mean.

We fit our data to the convolution of a molecular response function with a Gaussian given by the crosscorrelation between the UV pump and x-ray probe pulses (46). Decreasing signals have a molecular response function of the form

$$M(t) = \begin{cases} 0 & t < t_0 \\ A \exp\left[-\frac{t-t_0}{\tau}\right] & t > t_0 \end{cases}$$

whereas the molecular response for increasing signals are modeled by

$$M(t) = \begin{cases} 0 & t < t_0 \\ A\left(1 - \exp\left[-\frac{t - t_0}{\tau}\right]\right) & t > t_0. \end{cases}$$

In the above equations t is time, t_0 denotes the start of the exponential decay, τ is the 1/e decay time, and A is the amplitude of the exponential for t=t₀ (t>> τ) for decreasing (increasing) signals. The Gaussian cross-correlation is given by

$$F(t) = \exp\left[-\frac{t^2}{2 \sigma_{cc}^2}\right]$$

where σ_{cc} is the cross correlation width for the pump and probe pulses and is related to the full width half maximum (FWHM) by

$$\sigma_{cc} = \frac{\text{FWHM}}{2\sqrt{2 \ln 2}}.$$

The convolution of molecular response with the Gaussian gives a fitting model

$$S(t) = A \sqrt{\frac{\pi}{2}} \sigma_{cc} \left\{ \exp\left[\frac{\sigma_{cc}^2}{2\tau^2} - \frac{t - t_0}{\tau}\right] \operatorname{erfc}\left[\frac{1}{\sqrt{2}}\left(\frac{\sigma_{cc}}{\tau} - \frac{t - t_0}{\sigma_{cc}}\right)\right] \right\}$$

for decreasing signals, and for increasing signals

$$S(t) = A \sqrt{\frac{\pi}{2}} \sigma_{cc} \left\{ \left(1 + \operatorname{erf}\left[\frac{t - t_0}{\sqrt{2} \sigma_{cc}}\right] \right) - \exp\left[\frac{\sigma_{cc}^2}{2 \tau^2} - \frac{t - t_0}{\tau}\right] \operatorname{erfc}\left[\frac{1}{\sqrt{2}}\left(\frac{\sigma_{cc}}{\tau} - \frac{t - t_0}{\sigma_{cc}}\right)\right] \right\}$$

Here erf (x) and erfc(x) are the error function and complimentary error function, respectively. Using a least squares routine the model above was fit to the transients in the integrated spectral regions given in the table below. In the experiment the full width half maximum of the pump an probe pulses are estimated to be 70 fs and 50 fs, respectively. This gives a cross correlation FWHM of ~90 fs, which was used for the width of the Gaussian cross-correlation. The fit results in region I give a decay with τ of (180 ± 20)fs, in region II we observe a rise with $\tau = (260 \pm 40)$ fs.