Transient X-ray Absorption Spectral Fingerprints of the S₁ Dark State in Uracil

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Supporting Information

ABSTRACT: Low-lying dark nπ* states play an important role in many photophysical and photochemical processes of organic chromophores. Transient X-ray absorption spectroscopy (TXAS) provides a powerful technique for probing the dynamics of valence states by exciting the electrons into high-lying core excited states. We employ multiconfigurational self-consistent field calculations to investigate the TXAS of uracil along its nonradiative photodecay pathways. An open issue is whether dark nπ* state S₁ (n is the lone pair localized on an oxygen atom) is accessible when bright ππ* state S₀ is selectively excited. Vertical core excitations were calculated along the potential energy surfaces of the three lowest states, S₅−S₃, interpolated between two minima and two minimum-energy conical intersections. Computed TXAS data from the C, N, and O K edges show distinct spectral fingerprints of the dark state in all spectral regimes. At the O 1s edge, the nπ* state has a very strong absorption at 526−527 eV, while at the C (N) 1s edge, by contrast, there is almost zero (very weak) absorption at 279−282 eV (397−398 eV). All K-edge spectra can be used to sensitively detect the dark states. Our proposed O 1s feature has already been observed in a recent TXAS experiment with thymine. Natural transition orbital analysis is used to interpret all dominant features of the three lowest-valence states along the reaction coordinate and reveal some important valence fine-structure information from the core excitation.

The ultraviolet (UV) photochemistry of nucleobases has attracted intensive theoretical and experimental attention in the past several decades. A detailed understanding of ultrafast photochemistry is fundamentally important to reveal the DNA/RNA photodamage and photoprotection mechanisms¹−⁴ and essential for many applications to organic chromophores, such as photosynthesis, photocatalysis, and coherent control of reactions.⁵ The low-lying optically dark nπ* states, where n is a lone pair orbital localized on oxygen, play a key role in the photophysics. Open issues regarding the deactivation mechanism after UV absorption include whether the dark state is accessible in the pyrimidine bases (uracil, thymine, and cytosine).¹−¹¹ Low-lying dark nπ* states play important roles in many common organic chromophores with heteroatoms (e.g., pyrazine,¹² acetylene,¹³ and azobenzene¹⁷). Sensitive spectral fingerprints that distinguish different nuclear structures and electronic states are called for.

Pump-probe transient X-ray absorption spectroscopy (TXAS) provides a powerful tool for monitoring photoinduced dynamics.¹⁸−²⁵ The technique uses X-ray free-electron laser (XFEL), high harmonic generation (HHG), and synchrotron sources. Recently, TXAS based on XFEL has been employed to study the photochemistry in nucleobase thymine.¹⁴ There is growing interest in probing the photodynamics in gas phase small molecules (thymine,¹⁴,²⁶ CF₄,²⁷ CH₃Cl,²⁸ CF₄ and SF₆,²⁹ acetylene,³⁰ 1,3-cyclohexadiene,³¹,³² NO₂,³³ acetylace-tone,³⁶ and furfural²⁸) owing to the development of experimental technologies, whereby TXAS,²⁸,²⁹,³¹,³⁴ and related time-resolved Auger¹³ and photoelectron spectroscopies (TRPES),¹⁶,³³ and electron diffraction²⁷,³² had been used. More elaborate ultrafast nonlinear X-ray spectroscopies beyond pump–probe spectroscopy are gradually becoming possible.³⁵,³⁶

Despite extensive experimental effort, the interpretation of TXAS signals is still a challenge. Most theoretical approaches are based on quantum mechanical studies of discrete structures (see, e.g., refs 14, 17, 28, 34, and 37), and the dynamics is obtained by fitting the intensity of a specific peak, often in conjunction with semiempirical rate equations or kinetic models. The current work provides a new interpretive framework by quantifying important spectroscopic signatures for the low-lying dark states.
models. Discrete models provide an inexpensive practical way to study the photodynamics. However, some intermediate steps may be missed by the measurement time resolution, and sometimes different kinetic models have been proposed for the same reaction. A continuous picture can provide more information. For a dissociation along a single bond, TXAS of CF$_4$ was calculated along the CF$_4$ - F bond distance. Quantum dynamics can provide a continuous picture for TXAS but at a greater computational cost. Simulating transient spectroscopy is far more difficult than steady state. For trajectory-based methods, longer dynamics requires more trajectories to represent the wavepacket (sampled configuration spaces of different trajectories become farther apart). Direct solution of the time-dependent Schrödinger equation avoids this problem (propagation on a single trajectory). The method is accurate but numerically expensive and applied to only di- and triatomic molecules.

Nonadiabatic molecular dynamics (NAMD) with time-dependent density functional theory (TDDFT) was used to model the TXAS of 1,3-cyclohexadiene. Had computed TXAS and Auger spectra of CO with multi-configurational time-dependent Hartree (MCTDH). A trajectory-based version of MCTDH was developed and recently applied to study the TXAS of CFCF$_4$ and H$_2$O. Related time-resolved Auger and X-ray/electron diffraction signals were simulated by using the multiple spawning method and simulated X-ray Raman signals by NAMD.

In this work, we use snapshots of the potential energy surfaces (PESs) to simulate TXAS signals along the reaction pathways. The simplest RNA base, uracil (C$_4$H$_4$N$_2$O$_2$), was chosen as a model system, to verify the ability of the TXAS at the C, N, and O K edges to probe the dark states along its nonradiative photodecay pathways. Vertical core excitations were calculated along the PESs of the three lowest valence states. For the deactivation mechanism of uracil, there is an open issue about whether n$\pi^*$ state S$_2$ is selectively excited. Figure 1a (bottom) sketches the PESs of S$_0$ - S$_2$ interpolated between two minima and two minimum-energy Conls (Figure 1b and Figure S1). The PESs were computed at the complete-active-space self-consistent field (CASSCF) level for the three states. Starting in S$_0$, the system evolves to the S$_2$/S$_1$ Conl. It may decay directly to the ground state via the S$_1$/S$_0$ Conl (direct pathway) or undergo additional thermalization near the minimum of n$\pi^*$ state S$_1$ (indirect pathway). A sensitive probe of the n$\pi^*$ excited state is required to pinpoint the mechanism.

Vertical core excitations were calculated for each interpolated structure along the reaction coordinate at the restricted-active-space SCF (RASSCF) level. To investigate the C, N, and O K edges, individual calculations were performed for each of the eight heavy atoms. Figure 1a (top) displays the PESs of the lowest core excited states (e$_1$). e$_1$ plays an important role in probing the excited-state absorption (ESA). This is because they contain information about the valence hole (Figure 1c and Figure S2) that captures the character of the initial valence excited state. The underlying photophysics is that filling the valence hole (an n or $\pi$ orbital) by the core electron costs the least photon energy, i.e., e$_1$ (Figures 1d). As expected, we found that core excited states have a much higher density of states than valence states and that PESs of e$_1$ are better separated in energy from higher-lying states along the entire reaction coordinate (Figure S3).

We have used the natural transition orbitals (NTOs) to provide a compact visual picture of the transition. Mathematically, they are obtained by singular-value decomposition of the spin-summed transition density matrix, and the multiconfigurational transitions are approximately expressed as excitation involving a few NTO pairs (from hole to particle NTOs). The change in electronic structure can be visualized by evolution of the hole and particle orbitals. For n$\pi^*$ and $\pi\pi^*$ valence states, they exhibit different features (Figure 1c and Figure S2). The S$_1$ hole is always localized on O$_5$, while the S$_2$ hole is more delocalized (around C$_3$ = C$_4$ or C$_1$ = C$_2$). For the latter, analysis based on discrete structures does not clearly track the excited-state evolution, and interpolation was performed to obtain a continuous, smooth picture of the evolution. With respect to core excitations, the NTO analysis verified the physical picture for the excited-state absorption shown in Figures 1d, because we found a high degree of similarity of the dominant hole orbital for the S$_1$ state S$_1$ - S$_0$. The particle orbital for the S$_1$ - S$_0$ core excitation (j = 1 or 2) (Figure S4).

Figures 2–4 display the computed TXAS for both the direct and indirect deactivation mechanisms at O, N, and C K edges, respectively. Detailed atom-specific contributions and NTO analysis for dominant peaks are provided in Figures S6–S14. All important features for valence fine structures at critical points are summarized in Figure S5.

We first verified the accuracy of RASSCF simulations by comparing them with steady-state experimental spectra. RASSCF had been well documented for core excitations.
and successfully applied to model X-ray spectroscopy of furan in the photoinduced reaction. We found good agreement at all K edges [Figure S5 and Figure 5 (top)]. In the C (O) π* edges, the experimental π* peaks, in increasing energies, correspond to C5, C6, C4, and C2 (O8 and O7) 1s absorption to e1. The order is the same as that of the PESs (see Figure 1a). In the N 1s edge, the N1 and N3 excitations are mixed together. Agreement with experiment verified the accuracy of our simulations, and the uniform shift for calibration (−4.0, −4.45, and −3.5 eV for C, N, and O edges, respectively) was further extended to calibrate all valence−core absorption at each edge.

The dark nπ* S1 state shows clear signatures at all K-edge spectra, which indicates thermalization in S1 (among geometries i−iii) can be sensitively detected. In the O 1s edge, a strong peak appears at 526−527 eV (in Figure 2c, see the purple frame), coming from S1 → e1 (O8) excitation. NTO analysis interpreted it as mainly O8 1s to nO8 resonance (Figure 5 and Figure S6). The valence hole in nO8 is thus filled by the excited core electron. The large oscillator strength is a result of the dipole selection rule. The transition dipole moments ⟨1s|r|2p⟩ are large when the 1s and 2p orbitals are localized on the same atom (r is the position operator). The N and C 1s-edge spectra show the reverse side of this principle, where 1s and 2p are localized on different atoms. At the N 1s (C 1s) edge, the trap in S1 exhibits very weak (almost zero) resonance at 397−398 eV (279−282 eV) (in Figures 3c and 4c, see the purple frame). The transitions from N1 and C3 1s to corresponding e1 states are responsible for these weak absorption. Our results show that all edges can be used to sensitively probe low-lying nπ* dark states and can be applied to distinguish different reaction mechanisms related to such states. Our O 1s feature had already been observed in a recent TXAS experiment of thymine. It is worth noting that for excitations from other nonequivalent centers, the same physical picture (filling the nO valence hole always leads to the lowest core excited state) persists, but their oscillator strengths are too low to be visible in the spectra.

The higher-energy region of the S1 absorption spectra represents a normal 1s → π* absorption. The O 1s-edge spectra show the simplest patterns, and the second peak at 532.5 eV arises from O2 1s excitations to higher-lying core states. In the N 1s edge, the three strong peaks between 400 and 405 eV are all attributed to mixed contributions from N1 and N3 excitations (Figure S7). The C 1s spectra generally show four peaks between 282 and 288 eV and can roughly be interpreted as C6, C5, C4, and C2 contributions, while a mixture of C4 and C2 oscillations happens in some structures, which generates an enhanced strong peak at 289 eV (Figure S8). Note that the C6 and C5 peaks are reversed here compared to the S0 absorption. This indicates the difference in ground-state absorption (GSA) and excited-state absorption. These π* orbitals are distributed around the C=O, C=C, and C−N bonds. Among these edges, the O 1s excitations are the most...
Many weak peaks appear near the ground-state geometry. This correlation effects can lower the selectivity of core excitations through transitions (Figure S10) and C 1s-edge (Figure S11) spectra. Figures 2−4 shows patterns more complex than those of S2. Many weak peaks appear near the ground-state geometry. This indicates that the π valence hole (delocalized over a few atoms) can lower the selectivity of core excitations through correlation effects. The low-energy regimes of spectra are attributed to excitations filling the π valence holes (Figures S5). Such absorption can be very strong [395−397 eV, N 1s edge (Figure 3)], very weak [277−279 eV, C 1s edge (Figure 4)], or comparable to other normal 1s → π* transitions [524−526 eV, O 1s edge (Figure 2)]. They are also sensitive to small structural changes (geometries i−iii), which can be related to the delocalized feature of the valence hole orbital. Figures S9−S11 illustrate the NTO particle orbitals for such core excitations at geometries i−iii. The π features can alter among C≡C, C==O, and C−N bonds, consistent with the evolution of valence hole orbitals (Figure S2). The S2 absorption shows additional multiconfigurational features compared to S1 absorption. The relevant core excited states filling the π valence hole are not limited to e1, but also include other higher-lying states, as observed in the N 1s-edge (Figure S10) and C 1s-edge (Figure S11) spectra.

Figure 5. Valence fine structure of C 1s, N 1s, and O 1s TXAS at critical points along the indirect pathway (recaptured from Figures 2c−4c). For ESA from S1 and S2, those transitions filling the valence holes are labeled as follows: 1s → nO8 (purple) and 1s → π (blue).

Signatures for the dark nO8,π state are shaded in purple for emphasis. At geometry iv, 1s → 2p (C5) transitions are specially labeled (gray). All unlabeled TXAS peaks stand for normal 1s → π* transitions. Note that passages through CoIns (iii and iv) lead to evident spectral changes. The top portion shows steady-state experimental XAS (black) compared with the computed S0 absorption at geometry i.

localized (at the C5=O2 bond), and N 1s excitations are the most delocalized.

Excited-state absorption from bright ππ* state S2 (bottom of Figures 2−4) shows patterns more complex than those of S1. Many weak peaks appear near the ground-state geometry. This indicates that the π valence hole (delocalized over a few atoms) can lower the selectivity of core excitations through correlation effects. The low-energy regimes of spectra are attributed to excitations filling the π valence holes (Figures S5). Such absorption can be very strong [395−397 eV, N 1s edge (Figure 3)], very weak [277−279 eV, C 1s edge (Figure 4)], or comparable to other normal 1s → π* transitions [524−526 eV, O 1s edge (Figure 2)]. They are also sensitive to small structural changes (geometries i−iii), which can be related to the delocalized feature of the valence hole orbital. Figures S9−S11 illustrate the NTO particle orbitals for such core excitations at geometries i−iii. The π features can alter among C≡C, C==O, and C−N bonds, consistent with the evolution of valence hole orbitals (Figure S2). The S2 absorption shows additional multiconfigurational features compared to S1 absorption. The relevant core excited states filling the π valence hole are not limited to e1, but also include other higher-lying states, as observed in the N 1s-edge (Figure S10) and C 1s-edge (Figure S11) spectra.

Photochemical reactions involve complex PESs, and it is possible to have a valence hole even in the S0 state. This information can be probed by GSA, as reflected in the particle NTO for transitions from S0. For example, at geometry iv, the particle orbital for both S0 → S1 and S0 → S2 transitions is the 2p orbital at C4 (see the particle orbital in Figure S2). It indicates a valence hole in 2p (C4) in the S0 state, which was not explicitly mentioned in early studies. This is consistent with the large geometrical change around C4 at geometry iv (Figure S1), and this CoIn is termed C4-puckered CoIn in the literature.10 The NTO analysis has been widely used for ground-state geometries and much less for conical intersections.39 This CoIn had been denoted as ππ*/gs or ππ*/cs (gs for ground state and closed shell, respectively) CoIn. Our NTO shows that the S0 state at geometry iv is more likely to have an open-shell character in a single-electron approximation. This 2p (C4) valence hole in S0 can be further verified by core excitations from S0. As shown in Figures S12−S14 and summarized in Figure S5, all NTO analysis for GSA shows evident absorption from 1s (O8 weak; N1,3, weak; C2,4,5, strong) to the 2p (C3) orbital. By contrast, the S1 state near geometry iv acts more like a closed shell (i.e., no evident valence hole), as all core excitation gives normal 1s → π* transitions (Figure S15). In addition, normal 1s → π* transitions also dominate the S0 absorption at geometries i−iii (Figures S12−S14).

In summary, we have computed the C, N, and O K-edge transient X-ray absorption spectra (TXAS) of uracil along its photodecay pathways. Vertical core excitations were calculated over potential energy surfaces of lowest valence states S0−S2 along interpolated collective coordinates. We have demonstrated that TXAS at all K edges can provide a sensitive probe for the low-lying ππ* dark states for two different reasons. When the 1s orbital of the excited atom coincides with the localized lone pair orbital n, a strong resonance fingerprint appears; when they are on two sites, a weak or almost "flat"
profile can also be used as an evident signature. For uracil, nO, π* state S1 has strong O 1s absorption at 526–527 eV and almost zero (very weak) C 1s (N 1s) absorption at 279–282 eV (397–398 eV). Our simulation provides the valence fine structure of core excitations and a continuous picture of uracil TXAS. For excited states with a delocalized feature (e.g., π π* state of uracil), it is not evident to draw a smooth picture from results of discrete structures. By using the NTOs to characterize all valence-valence and valence-core excitations along the entire reaction pathways, we demonstrated the physical picture for excited- and ground-state absorption and emphasize the importance of the lowest core excited state (e1).

The new i→ii path in either valence PESs (Figure S16d) or spectra (Figure S16e) and does not affect our conclusions.

**COMPUTATIONAL METHODS**

Three-state-averaged CASSCF methods are used to compute S1–S3. The active space consists of 10 electrons in 8 orbitals, including 4 4s and 3 π* orbitals and 1 lone pair orbital on O8 (Figure S17). C, N, and O 1s core excitations are simulated along the reaction pathways at the RASSCF(12, 1/8/0) level, where in parentheses are the number of electrons and the numbers of active orbitals in RAS1/RAS2/RAS3 space, respectively. For a review of RASSCF for core-state calculations, see ref 52. Twenty states are calculated for state averaging to cover several electronvolts for spectral usage. The excited core orbital was set in RAS1 with fixed occupation 1. The aug-cc-pVDZ basis set is used. The electronic structure was determined by using the Molpro package, and spectra and NTOs were simulated by our in-house code MCNOX.

**RELATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.9b02692.

Optimized geometries, NTO orbital evolution of valence states, vertical core potential energy surfaces with more

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**Notes**

The authors declare no competing financial interest.

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