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The effect of methylation on the intersystem crossing dynamics of 2-thiouracil: Time-resolved photoelectron spectroscopy of 2-thiothymine

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Abstract: The ultrafast internal conversion (IC) and intersystem crossing (ISC) dynamics of 2-thiouracil (2TU) and 2-thiothymine (2TT) are studied with time-resolved photoelectron spectroscopy (TRPES) to investigate the effect of methylation on the deactivation mechanism.

1. Introduction

Structurally modified nucleobases, such as thiouracils, where an oxygen atom in uracil is replaced by sulfur, have been observed to undergo fast and efficient ISC from the lowest singlet excited state, $S_1(n\pi^*)$, to the triplet manifold along a sulfur out-of-plane coordinate [1]. TRPES studies on a series of thiouracils [2-5] have shown that minor changes such as the position and degree of thionation profoundly alter the subsequent triplet state dynamics. Specifically, in the case of 2TU ISC back to the ground state (GS) occurs on a picosecond timescale, while in 4-thiouracil and 2,4-dithiouracil population remains trapped in the lowest triplet excited state. These differences in the ISC behavior were attributed to intricate details of the triplet state potential energy topography as well as spin-orbit couplings (SOC) at T_1/GS crossing points. Ab initio calculations identified two minima on the lowest triplet state with boat-like ($T_{1\ \mathrm{boat}}$) and sulfur-out-of-plane ($T_{1\ \mathrm{op\text{-}S}}$) geometries (Fig.1 (b)). The triplet dynamics are therefore governed by factors such as the relative energies of the minima, the barrier height separating them, and the accessibility of T_1/GS crossing points from each minimum. The 2TT TRPES study presented here further interrogates the triplet state topography and deactivation coordinates in thiouracil derivatives. Methylation provides a sensitive probe of barriers along a pathway that involves displacements of the methyl substituent and will manifest itself in slower triplet dynamics. As such, it provides insight into the role of the boat-like minimum in the excited state deactivation mechanism of thio- and methyl-substituted uracils.

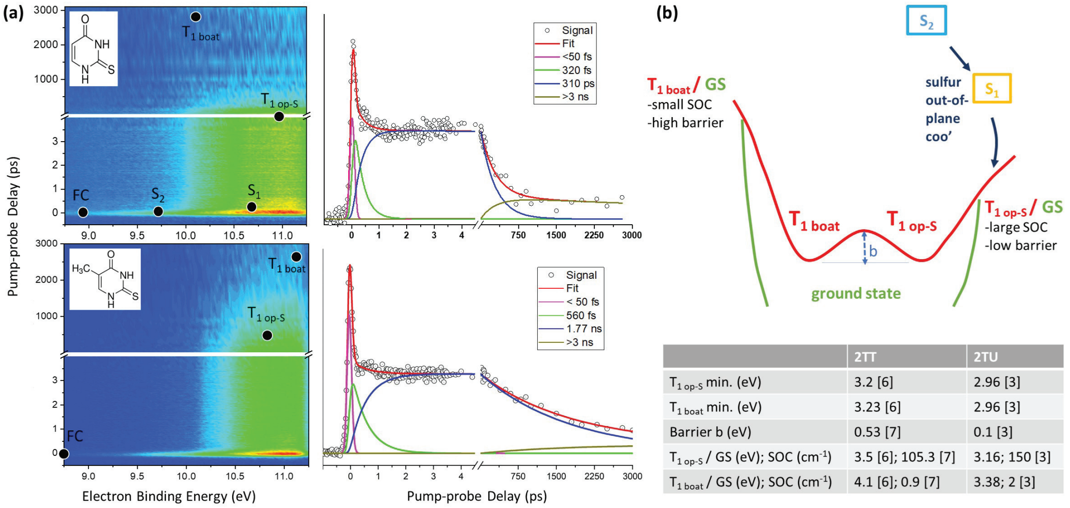
2. Experimental Details

The TRPES apparatus consists of an amplified ultrafast laser system and a magnetic bottle photoelectron spectrometer which have been described in detail elsewhere [2-5]. A continuous molecular beam of either 2TT or 2TU is intersected by the pump (300nm) and time-delayed probe (330nm) pulses in the ionization region of the spectrometer. The molecules undergo a 1+2' excitation-ionization process and photoelectron kinetic energies are recorded at different pump-probe delays to acquire a time-resolved photoelectron spectrum. The TRPES in Fig. 1 (a) are plotted in terms of electron binding energy (eBE), i.e. the measured electron kinetic energies subtracted from the total photon energy, for easy comparison to calculated ionization potentials along the relaxation path [2] which are represented as black dots superimposed on the TRPES colormaps. These take into account an additional shift due to vibrational energy gain during electronic relaxation which is transferred to the cation upon ionization. TRPES are recorded over a pump-probe delay range of 3ns to, at least partially, capture the slower triplet state dynamics.

3. Results and Discussion

Fig. 1 (a) shows the TRPES of 2TU (top) and 2TT (bottom) following photoexcitation to their optically bright, singlet excited state of $\pi\pi^*$ character, $S_2(\pi\pi^*)$. The TRPES of 2TT closely resembles 2TU indicating that both share the same, general deactivation mechanism. The minimum energy pathway for 2TU has been characterized by detailed ab initio calculations and the first step involves IC to $S_1(n\pi^*)$ via a conical intersection in the vicinity of the $S_2(\pi\pi^*)$ minimum [2]. The shift in the photoelectron spectrum toward higher eBE within the first few picoseconds following excitation is associated with an increase in ionization potential during this IC process. As labelled, the black dots correspond to vertical ionization in the Franck-Condon (FC) region and from the S_2 and S_1 state minima. Subsequent ISC through a crossing point in the vicinity of the $S_1(n\pi^*)$ minimum populates the triplet manifold. The lowest triplet state, $T_1(\pi\pi^*)$, is characterized by two minima, $T_{1\ \mathrm{op\text{-}S}}$ and $T_{1\ \mathrm{boat}}$, separated by a barrier, b, and the corresponding black dots indicate ab initio ionization energies from these points [2].

The decay dynamics of both molecules are adequately described by a fitting function consisting of four sequential exponential decays convoluted with the Gaussian instrument response function. The time traces of the integrated photoelectron signal, the total fit and the four contributions are plotted in Fig. 1 (a, right), and the extracted time constants are provided in the legend. The four time constants are attributed to $S_2 \rightarrow S_1$ IC (τ_1), ISC to the triplet manifold (τ_2), and the triplet state dynamics associated with $T_{1\ \text{op-S}}$ (τ_3) and $T_{1\ \text{boat}}$ (τ_4). The IC and ISC time constants, τ_1 and τ_2, of 2TT and 2TU are similar and therefore confirm a mechanism along the sulfur out-of-plane coordinate with only minimal distortion of the ring. After population of T_1, the system equilibrates between the two minima, $T_{1\ \text{op-S}}$ and $T_{1\ \text{boat}}$, which involves sampling of coordinates along out-of-plane distortions of the ring and surmounting the barrier, b. Displacement of the additional methyl group and a larger barrier in the case of 2TT, results in significantly slower triplet dynamics as observed clearly in τ_3. Eventually, ISC back to the GS favors the $T_{1\text{op-S}}$/GS crossing point with larger SOC and lower access energy. Trapping in the $T_{1\ \text{boat}}$ minimum and a subsequent two-step process to access $T_{1\text{op-S}}$/GS is characterized by τ_4 but exceeds the time window of our experiment.



	2TT	2TU
$T_{1\ \text{op-S}}$ min. (eV)	3.2 [6]	2.96 [3]
$T_{1\ \text{boat}}$ min. (eV)	3.23 [6]	2.96 [3]
Barrier b (eV)	0.53 [7]	0.1 [3]
$T_{1\ \text{op-S}}$ / GS (eV); SOC (cm^{-1})	3.5 [6]; 105.3 [7]	3.16; 150 [3]
$T_{1\ \text{boat}}$ / GS (eV); SOC (cm^{-1})	4.1 [6]; 0.9 [7]	3.38; 2 [3]

Fig. 1: (a) TRPES and corresponding timetraces of 2TU (top) and 2TT (bottom). An error of approx. 20% is estimated for the extracted time constants. (b) Schematic of IC and ISC pathway based on ab initio calculations in Refs [3,6,7].

4. Conclusions

This TRPES study presents the first measurements of the photophysics of 2TT in the gas phase and, through comparison to 2TU, provides insight into the dynamics of the lowest triplet state, T_1. The experimental observations concur in the ab initio mechanism pictured in Fig. 1(b). While the deactivation dynamics of 2-TU and 2-TT follow a generally similar pathway, $S_2(\pi\pi^*) \rightarrow S_1(n\pi^*) \rightarrow$triplet manifold, involving primarily coordinates with a sulfur out-of-plane displacement, methylation significantly alters the T_1 dynamics. This observation confirms an equilibration of population across both T_1 minima, which requires an out-of-plane ring distortion, and results in extended (> 3ns) trapping in $T_{1\ \text{boat}}$ and considerably different ISC times from $T_{1\ \text{op-S}}$ back to GS (310ps 2TU vs. 1.77ns 2TT).

5. Acknowledgement

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6. References

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