Photoelectron Spectra of 2-Thiouracil, 4-Thiouracil and 2,4-Dithiouracil

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Ground- and excited-state UV photoelectron spectra of thiouracils (2-thiouracil, 4-thiouracil and 2,4-dithiouracil) have been simulated using multireference configuration interaction calculations and Dyson norms as measure for the photoionization intensity. Except for a constant shift, the calculated spectrum of 2-thiouracil agrees very well with experiment, while no experimental spectra are available for the two other compounds. For all three molecules, the photoelectron spectra show distinct bands due to ionization of the sulphur and oxygen lone pairs and the pyrimidine $\pi$ system. The excited-state photoelectron spectra of 2-thiouracil show bands at much lower energies than in the ground state spectrum, allowing to monitor the excited-state population in time-resolved UV photoelectron spectroscopy (TRPES) experiments. However, the results also reveal that single-photon ionization probe schemes alone will not allow monitoring all photodynamic processes existing in 2-thiouracil. Especially, due to overlapping bands of singlet and triplet states the clear observation of intersystem crossing will be hampered.

I. INTRODUCTION

Thionucleobases, which are nucleobase analogues where one or more oxygen atoms have been substituted by sulphur, play an important role in molecular biology and pharmacology. They are, e.g., contained in natural t-RNA and RNA, as well as for pharmaceutical purposes such as photosensitizers for photodynamic therapy or antithyroid drugs. Besides their occurrence in biological environments and wide applicability, thiobases have received a lot of attention due to their remarkably different photophysics in comparison to canonical nucleobases. Despite their similar structure, the presence of a thiacarbonyl group results in a red-shift of the UV absorption spectrum and an increase of intersystem crossing. These differences have prompted a large number of studies with focus on their electronic structure and excited-state dynamics, both from the theoretical and experimental points of view, in particular by means of transient absorption spectroscopy.

Among thiobases, the series of thiouracils, i.e., 2-thiouracil (2TU), 4-thiouracil (4TU) and 2,4-dithiouracil (DTU), are particularly interesting. Under experimental conditions, all three compounds exist only in their oxothione or dithione tautomeric form (see Fig. 1). The UV absorption spectra of 4TU and DTU have been analysed extensively; the absorption spectrum is slightly red-shifted compared to uracil and shows signs of a low-lying dark $n\pi^*$ state. The UV absorption spectra of 4TU and DTU are considerably red-shifted compared to 2TU, but their general excited-state behaviour appears to be not much different from the one of 2TU: all three molecules show sub-picosecond intersystem crossing after excitation to the first absorption band. In contrast to the UV absorption spectra, not much has been reported on the photoelectron spectra of thiouracils. The main interest in this respect has been laid on the anions of these compounds, because ionizing radiation creates anions on the way to single and double strand breaks in DNA. A single study on the tautomerism of 2TU and its methyl derivates contains a static He(I) photoelectron spectrum of neutral 2TU.

Also, up to our knowledge, no time-resolved photoelectron spectroscopy (TRPES) has been reported for these molecules, even though this methodology has been extensively applied to study the excited-state dynamics of the canonical nucleobases (see, e.g., Ref. 31 for a list of these experiments) and a small number of nucleobase analogous. TRPES has a number of advantages with respect to other spectroscopic techniques, e.g., it allows to study the excited-state dynamics in the gas phase, while methods like transient absorption spectroscopy usually measure solvated compounds. Furthermore, due to very different selection rules for photoionization compared to absorption, in TRPES it is possible to probe dark states, which is very useful to elucidate the

FIG. 1. Structures of (a) 2-thiouracil (2TU), (b) 4-thiouracil (4TU) and (c) 2,4-dithiouracil (DTU), with numbering of the ring atoms. Hydrogen atoms attached to carbons are omitted.

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photophysical intermediates of these compounds. Such knowledge can be particularly relevant for thiouracils, helping to promote the use and eventual functionalization of thiobases with phototherapeutic aims.

With this in mind, in this paper we report theoretical UV-photoelectron spectra 2TU, 4TU, and DTU from the ground state equilibrium geometries. We describe the character of the various ionization source orbitals and how thio-substitution influences the number, intensity, and position of the bands in the low-energy spectra. For 2TU, we also explore the photoelectron spectra from the neutral excited states at the Frank-Condon region as well as around the stationary points on the potential energy surface of the lowest excited singlet and triplet states, complementing our recent study on the relaxation and intersystem crossing mechanism after UV irradiation of this molecule. While we do not report time-resolved photoelectron spectra here, the spectra at the stationary points indicate that single-photon UV-TRPES alone probably cannot discern the different deactivation pathways, in particular intersystem crossing, of photoexcited 2TU and should be complemented by some other method to probe the excited-state population.

II. METHODS

A. Theory

An efficient way to calculate static ground or excited-state UV-photoelectron spectra is to employ Dyson norms as a measure of the ionization intensities. In the case of single-photon ionization, the norms of Dyson orbitals have been shown to be a good approximation for relative ionization probabilities. An excellent introduction into the description of photoionization using Dyson orbitals can be found in references 37–39, so here we only provide a brief overview.

In the following, we describe transitions from a neutral source state \( i \) to an ionic state \( \alpha \) as the ionization channel \( i \rightarrow \alpha \). The corresponding Dyson orbital \( |\phi_{i,\alpha}^D\rangle \), which can be thought of as the wavefunction of the electron to be detached, is defined as

\[
|\phi_{i,\alpha}^D\rangle := \sqrt{n} \langle \Theta_{n+1,\alpha}^{(n-1)} | \Psi_{\text{src},i}^{(n)} \rangle_{(n-1)},
\]

with the \( n \)-electron source wavefunction \( |\Psi_{\text{src},i}^{(n)}\rangle \), as well as the \( (n-1) \)-electron ionic wavefunction \( |\Theta_{n+1,\alpha}^{(n-1)}\rangle \). The subscript \( (n-1) \) of the bra ket indicates integration over \( n-1 \) electrons. As a measure for the relative ionization yield \( W_{i,\alpha} \) we use an expression analogous to the oscillator strength, where the Dyson norm is scaled with the energy difference \( \Delta E_{i,\alpha} \) between the \( n \)-electron source state \( i \) and the \( (n-1) \)-electron state \( \alpha \):

\[
W_{i,\alpha} \propto \Delta E_{i,\alpha} \langle \phi_{i,\alpha}^D | \phi_{i,\alpha}^D \rangle.
\]

We do not explicitly consider the continuum wavefunction \( \chi_{\alpha}^p \) for the calculation of the intensities here.

In the case of wavefunctions of the configuration interaction (CI) type expanded in Slater determinants with orthonormal spin orbitals \( \theta_{a,r} \) and \( \psi_{b,s} \):

\[
|\Theta_{n+1,\alpha}^{(n-1)}\rangle = \sum_a c_{\text{ion},\alpha,a} |\Theta_{n+1,\alpha,a}\rangle,
\]

\[
|\Theta_{n+1,\alpha,a}\rangle = \frac{1}{\sqrt{(n-1)!}} \langle \theta_{a,1} \cdots \theta_{a,r} \cdots \theta_{a,(n-1)} \rangle,
\]

\[
|\Psi_{\text{src},i}^{(n)}\rangle = \sum_b c_{\text{src},i,b} |\Psi_{\text{src},i,b}\rangle,
\]

\[
|\Psi_{\text{src},i,b}\rangle = \frac{1}{\sqrt{n!}} |\psi_{b,1} \cdots \psi_{b,s} \cdots \psi_{b,n}\rangle,
\]

the total Dyson orbital is the sum of the overlaps of all Slater determinant pairs (indices \( a, b \)) weighted with the product of their CI coefficients

\[
|\phi_{i,\alpha}^D\rangle_{\text{CI}} = \sum_a \sum_b c_{\text{ion},\alpha,a} c_{\text{src},i,b} |\phi_{i,\alpha}^D\rangle_{a,b}.
\]

To this end, the contribution of one Slater determinant pair \( |\Theta_{n+1,\alpha,a}\rangle \) and \( |\Psi_{\text{src},i,b}\rangle \) can be rewritten in terms of the molecular spin-orbitals of the source wavefunction, \( |\psi_{b,s}\rangle \), and the annihilation operator, \( \hat{a}_s \), for the \( s \)-th occupied source-spin space orbital, \( |\psi_{b,s}\rangle \):

\[
|\phi_{i,\alpha}^D\rangle_{a,b} = \sqrt{n} \langle \Theta_{n+1,\alpha,a} | \Psi_{\text{src},i,b}^{(n)} \rangle_{(n-1)}
\]

\[
= \sqrt{n} \sum_{s,\text{occ}} |\Theta_{n+1,\alpha,a} \hat{a}_s |\Psi_{\text{src},i,b}^{(n)} \rangle_{(n-1)} |\psi_{b,s}\rangle.
\]

The overlap \( \langle \Theta_{n+1,\alpha,a} | \hat{a}_s |\Psi_{\text{src},i,b}^{(n)} \rangle_{(n-1)} \) can be then obtained as a matrix determinant over appropriate molecular orbital overlap integrals.

B. Computational Details

The source and ionic wavefunctions have been calculated with the quantum-chemistry package COLUMBUS 7.0 [40,41] using atomic integrals from MOLCAS 8.0 [42]. The cc-pVDZ basis set was used in all calculations. Neutral and ionic wavefunctions were computed on the relaxation and intersystem crossing mechanism after UV irradiation of these compounds. Such photophysical intermediates of these compounds have been shown to be a good approximation for relative ionization probabilities.
neutral and ionized states employed a SA(4S+4T) and SA(10D+10Q) averaging protocol, respectively.

In the MRCIS calculation, the active orbitals of the preceding CASSCF have been used as reference space, restricting the references to configurations with at most two electrons in the three antibonding π* orbitals. In the MRCIS procedure, 12 orbitals for 2TU and 4TU and 16 orbitals for DTU were kept frozen. A total of 12 doublet and quartet (if applicable) states were computed on the MRCIS level of theory. This level of theory cannot accurately describe singlet and triplet excitation energies due to a deficiency of dynamic correlation (see below). However, having all important ionization source orbitals in the reference space ensures an adequate description of the lower ionized states.

Using the so-obtained wavefunctions, Dyson norms have been calculated to estimate photoionization probabilities. To reduce the computational cost, the CI vectors were truncated by removing the configuration state functions with the smallest absolute coefficients until the remaining wavefunction has a norm of 0.97. A careful inspection showed that this procedure strongly reduces the computational costs of the Dyson norms without significant deterioration of the results.

Finally, photoelectron spectra have been calculated from the S0 minimum and, in case of 2TU also from the S1 and T1 minima, optimized at the MRCIS level of theory specified above. In order to simulate vibrational broadening, for each compound 200 geometries were sampled randomly from a Wigner distribution based on frequencies obtained at the MRCIS level of theory. For each geometry, the Dyson norms for all applicable pairs of states were computed using the molecular orbital coefficients and CI vectors from the corresponding quantum-chemistry calculations. Spectra were calculated as a sum over Gaussians centered at the excitation energies and height proportional to W in equation (2). A full width at half maximum of 0.2 eV was chosen for the purpose of obtaining a smoothed spectrum from the calculated number of geometries. The photoelectron spectrum of the ground state of 2TU was normalized to a maximum signal of one, and the same normalization factor was then used for all other spectra (Note that all spectra were calculated with the same number of geometries and the same full width at half maximum). The generation of photoelectron spectra has been performed using tools from the development version of the SHARC molecular dynamics suite.46–48

III. RESULTS AND DISCUSSION

A. Photoelectron spectra of 2TU, 4TU and DTU

The photoelectron spectrum of 2TU computed from the electronic ground state is compared to the experimental one of Katritzky et al.,26 in Figure 2. As can be seen, there is a shift of +1.7 eV towards lower binding energies (as used here, the vertical energy difference between the neutral source state and the ionic state under consideration) with respect to the experimental values. This shift originates from the lack of size extensivity49 of MRCIS and the difference in the number of correlated electrons in neutral and ionized wavefunctions. However, the peak separations and relative peak heights in the simulated spectrum agree nicely with the experimental data, particularly at low energies, showing that the method predicts the energetic spacing of the ionic states and the relative intensities correctly. For higher binding energies the experimental spectrum shows a very broad band starting at ≈ 11 eV, which could not be reproduced by our calculations. We assume that this band originates either from ionization to higher-lying excited doublet states or from ionization from σ orbitals, both effects not well described by our simulation. An extension of the simulated energy range to higher doublet states with the present level of theory is not expected to yield better results because already in the present calculations the highest states (D9−11) are strongly mixed and have large contributions of double excitations within the reference space. Since the description of higher-lying states would require a much more accurate electronic structure method, which is out of the scope of this paper, the analysis following in the next sections focuses on the lower part of the spectrum.

The simulated photoelectron spectra of the neutral ground states of all three compounds are presented in Figure 3, together with the contributing signals of the ionization channels (D9−D11). While 2TU and 4TU both show three groups of signals, the spectrum of DTU is characterized by only two bands. The band lowest in energy (≈ 8 eV – 10 eV) is common to all three compounds but it is more intense in DTU than in the other two molecules due to the different composition of the bands. Only the D9 and D11 ionization channels contribute to the first band of 2TU and 4TU, whereas D9−D3 compose the first band of DTU. The next band higher in energy, centered around 10 eV is only present for 2TU and 4TU
The dyson orbitals of the S atoms can be seen, the for the relevant ionization channels present in Figure 3. As can be seen, the n and π orbitals of the sulphur atom are the dominant contributions to the Dyson orbitals of the Sₐ → Dₙₙ orbitals and the π orbitals of oxygen. The different extent of mixing of the oxygen π orbital with pyrimidine π orbitals explains the differently shaped bands in 2TU and 4TU. Since there is no oxygen in DTU, it is apparent that this second band around 10 eV binding energy is missing in this compound. Finally, the signals in the high-energy range (> 12 eV) contain the contributions of ionization from the π orbitals of the pyrimidine ring. The binding energy for electrons involved in a bond is naturally higher than for the lone pairs. The density of doublet states is very high in this energy region and many states show no significant intensity. For DTU only the D₁₀ yields substantial ionization probability. Hence, we assume that this band is only partially described by our calculations.

The simulated spectra show that the three compounds, 2TU, 4TU and DTU could certainly be discriminated on the basis of their photoelectron spectra. DTU is clearly marked by the intensity of the sulphur-ionization band and the absence of an oxygen-ionization band. In contrast, 2TU and 4TU show distinctly different shapes of the band arising from ionization of oxygen-localized orbitals.

### B. Excited-state photoelectron spectra of 2TU

Using the same set of geometries as for the 2TU S₀ photoelectron spectrum, the excited-state (source states S₁ and S₂) photoelectron spectra have been calculated (see Figure 5). The character of the neutral excited states at the equilibrium geometry is listed in Table I, together with vertical excitations energies and oscillator strengths, calculated at the MRCIS level of theory and compared to our recently published CASPT2 results. Irrespective of the level of theory, the order of the states is the same and the S₁ state is an nπ⁺ excitation while the S₂ is a ππ⁺ state. In both states, an electron is excited from an orbital located at the sulphur atom and promoted to a π⁺ orbital on the pyrimidine ring. Quantitatively, one can see that the excitation energies are described too high at the MRCIS level of theory, more so for the ππ⁺ state. As this would lead to systematically too low binding energies in the simulation of photoelectron spectra with excited states as ionization source, an additional shift of +0.5 eV (towards higher binding energies) for the S₁ spectrum and +0.77 eV for the S₂ one was introduced.

Ionization of an electron which has been excited into an antibonding orbital (e.g., π⁺) requires lower energy than to eject electrons in bonding orbitals. Consequently, the Dyson orbitals (Figure 6) for the first ionizations (S₁ → D₁ and S₂ → D₀) are very similar to the π⁺ orbitals occupied in the S₁ and S₂ states. The second band arises mostly from ionization of the π orbital located at the

![Diagram](https://via.placeholder.com/150)

**Figure 3.** Computed S₀-photoelectron spectra for 2TU, 4TU and DTU with individual contributions of the first 12 ionization channels (D₀-D₁₁). “S”, “O” and “Pyr” labels indicate predominant ionization from orbitals on sulphur, oxygen and the pyrimidine ring respectively. All spectra have been shifted by +1.7 eV (off-setting the shift shown in Figure 2).

| State | Geometry | This work | CASPT2(16,12) |
|-------|----------|-----------|--------------|
| S₁ (nSπ⁺) | S₀ min | 4.27 (0.00) | 3.77 (0.00) |
| S₂ (πSπ⁺) | S₀ min | 5.92 (0.29) | 4.25 (0.35) |
| S₁ (nSπ⁺) | S₁ min | 3.79 | 3.45 |
| T₁ (πSπ⁺) | T₁ “boat” min | 3.36 | 3.35 |
| T₁ (πSπ⁺) | T₁ “pyr.” min | 3.43 | 3.21 |

**Table I.** Calculated vertical excitation energies (eV) and oscillator strengths (in parentheses) of S₁ and S₂ and relative energies of S₁/T₁ minima of 2TU at the MRCIS and CASPT2 levels of theory, the latter taken from Ref. 13.
C_5 = C_6 bond.

The first band of each spectrum (Figure 5) is in the region of 4 eV – 6 eV and thus more than 2 eV separated from the onset of the S_0 spectrum and from the next band in the excited-state spectra. Judging from the simulated spectra it should be possible to obtain a clear signal from the lowest ionization channels of the excited singlet states without interference of the ground state signal using probe laser energies of 6 eV – 8 eV. This allows for experimental studies using photoelectron spectroscopy to selectively track excited states. Furthermore, the spectra in Figure 5 show that S_1 and S_2 are distinguishable in the Frank-Condon region, but it is expected that during the dynamics after excitation their spectra will broaden and shift independently and hence might not be separable when moving away from the Franck-Condon point.

An important application of photoelectron spec-
The UV-photoelectron spectra of three thio-analogues of uracil, 2-thiouracil (2TU), 4-thiouracil (4TU) and 2,4-dithiouracil (DTU) have been simulated using Dyson norms as a measure for the relative ionization probabilities of the different ionization channels. In all three molecules, the respective first band of the photoelectron spectra is mainly due to ionization from the $n$ and $\pi$ orbitals on oxygen, while for all three compounds the highest calculated band is related to the pyrimidine $\pi$ system. These two (DTU) or three (2TU, 4TU) bands are well separated.

In the monosubstituted thiouracils (2TU and 4TU) the position of the substitution has some effect on the band shape. With reasonably good resolution in the energy domain, we predict that the two molecules could be discerned mainly by the shape of the bands that originate from ionization from the oxygen orbitals at around 10 eV binding energy. The photoelectron spectrum of DTU is easily distinguishable from the other compounds since it lacks the band from the oxygen-orbital ionization completely and in return it shows an intense double peak from the ionization out of orbitals located on the sulphur atoms.

An inspection of the excited-state photoelectron spectra from the $S_1$ and $S_2$ states of 2TU shows that the excited states can be detected without being disturbed by the ground state signal. Furthermore, the photoelectron spectra of 2TU simulated at the relevant $S_1$ and $T_1$ minima show strong overlap and very similar intensity. Hence, experimental pump-probe UV-TRPES using single-photon ionization alone might not be able to track the populations of the different excited singlet and triplet states and therefore intersystem crossing could be opaque to this methodology. However, other experimental techniques like multi-photon ionization might still be able to detect a signature from intersystem crossing.

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