

SUPPLEMENTAL INFORMATION

INTERNAL CONVERSION AND INTERSYSTEM CROSSING PATHWAYS IN UV
EXCITED, ISOLATED URACILS AND THEIR IMPLICATIONS IN PREBIOTIC
CHEMISTRY

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1. Mass spectrum and parent dynamics for 2-thiouracil

Time-resolved ion yield (TR-IY) spectra of 2-thiouracil were recorded under similar molecular beam conditions as the time-resolved photoelectron spectra (TR-PES) presented in the main manuscript. While the TR-IY spectra provide no additional information regarding the 2-thiouracil photodynamics they serve as confirmation that our TR-PES data originates from the intact parent molecule. Fig. 1 displays the mass spectrum of 2-thiouracil which was obtained by integrating the TR-IY spectrum over all pump-probe delays. The 2-thiouracil parent peak and fragmentation into primarily 69 and 70 amu are observed. Experimental work by Giuliano *et al.*¹ showed no signs of decomposition of 2-thiouracil inside their heated nozzle and we therefore exclude this process as a potential source of fragments in our experiment. Overall, there is close resemblance of the fragmentation pattern in Fig. 1 to the mass spectrum obtained by electron impact ionization² and we therefore conclude that the smaller mass peaks are likely related to dissociation in the cation rather than excited state dynamics. Similar fragmentation was also observed in strong field ionization experiments by Matsika *et al.*³ for uracil and these authors also assign the fragments to dissociation in the cationic state. Additionally, a sequential exponential decay fit to the 2-thiouracil parent time trace reveals time constants of <100 fs, 825 fs, and 195 ps in good agreement with the values obtained from the TR-PES data (see Table 1 of main manuscript) which provides further evidence that the latter is indeed associated with the 2-thiouracil parent.

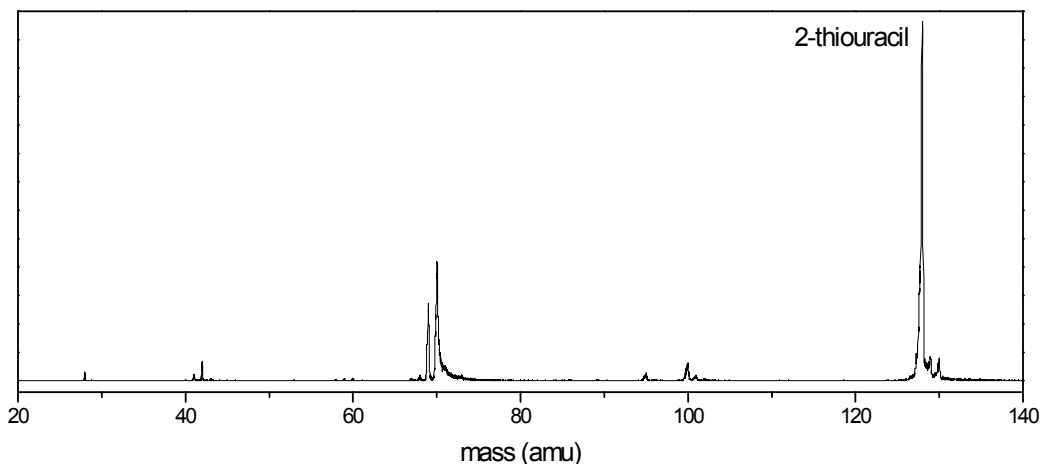


Fig. 1: Mass spectrum of 2-thiouracil recorded at 290 nm excitation and 330 nm two-photon probe.

2. Triplet to ground state pathway for uracil

Fig. 2 shows an interpolation scan for uracil from the T_1 ($^3\pi\pi^*$) minimum to the T_1/S_0 crossing point which are separated only by a small barrier of 0.4 eV. The spin orbit coupling amounts to about 1-2 cm^{-1} along this path.

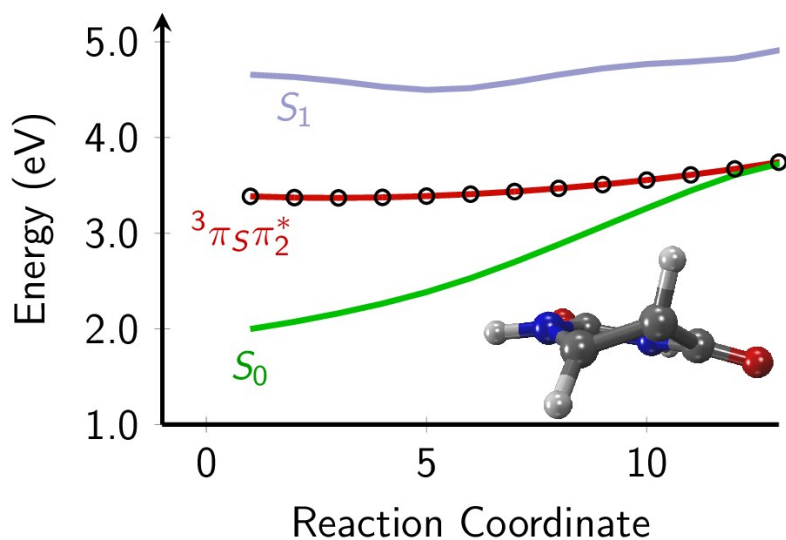


Fig. 2: Linear interpolation scan from the T_1 minimum of uracil to a T_1/S_0 crossing at the MS-CASPT2(12,9)/cc-pVDZ level of theory. The geometry at the crossing point is shown in the lower right corner and the coordinates are provided below in Section 3 of the Supplemental Information.

3. Optimized T_1/S_0 crossing geometries for 2-thiouracil and uracil

The optimized T_1/S_0 crossing geometries for 2-thiouracil and uracil are shown as insets in Fig. 4 of the main manuscript and Fig. 2 of the Supplemental Information, respectively, and the corresponding coordinates are given below.

a) Coordinates for 2-thiouracil at MS-CASPT2(12,9)/cc-pVDZ level of theory

N	0.110764	0.592043	0.711809
C	0.334242	0.778230	-0.700286
N	1.721131	0.700995	-0.981351
C	2.701728	0.059270	-0.241738
C	2.264411	-0.311988	1.128480
C	1.017597	-0.005829	1.558045
S	-0.800179	-0.584335	-1.186654
O	3.842635	-0.115883	-0.655474
H	-0.804957	0.869298	1.062249
H	2.001942	0.942030	-1.929861
H	2.995877	-0.782838	1.786124
H	0.668428	-0.185368	2.579557

b) Coordinates for uracil at the MS-CASPT2(12,9)/cc-pVDZ level of theory

C	0.793848	-0.399875	-1.126498
C	1.427767	0.219737	0.019086
C	-0.739308	0.029791	-1.305434
C	-0.691358	0.037597	1.215969
N	0.710933	0.014271	1.196307
N	-1.290999	0.129958	-0.044052
O	-1.269568	0.211080	-2.353037
O	-1.341201	0.025583	2.241935
H	-2.294810	0.291802	-0.017371
H	2.056874	1.112348	-0.077703
H	0.819411	-1.495664	-1.265237
H	1.128156	0.221489	2.099405

References

- ¹ B. M. Giuliano, V. Feyer, K. C. Prince, M. Coreno, L. Evangelisti, S. Melandri, W. Caminati, *J. Phys. Chem. A*, 2010, **114**, 12725-12730.
- ² NIST chemistry webbook
- ³ S. Matsika, M. Spanner, M. Kotur and T. C. Weinacht, *J. Phys. Chem. A*, 2013, **117**, 12796-12801.