ELECTRONIC SUPPORTING INFORMATION

# 2-THIOURACIL INTERSYSTEM CROSSING PHOTODYNAMICS STUDIED BY WAVELENGTH-DEPENDENT PHOTOELECTRON AND TRANSIENT ABSORPTION SPECTROSCOPIES

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## 1. Time-Resolved Photoionization Spectroscopy

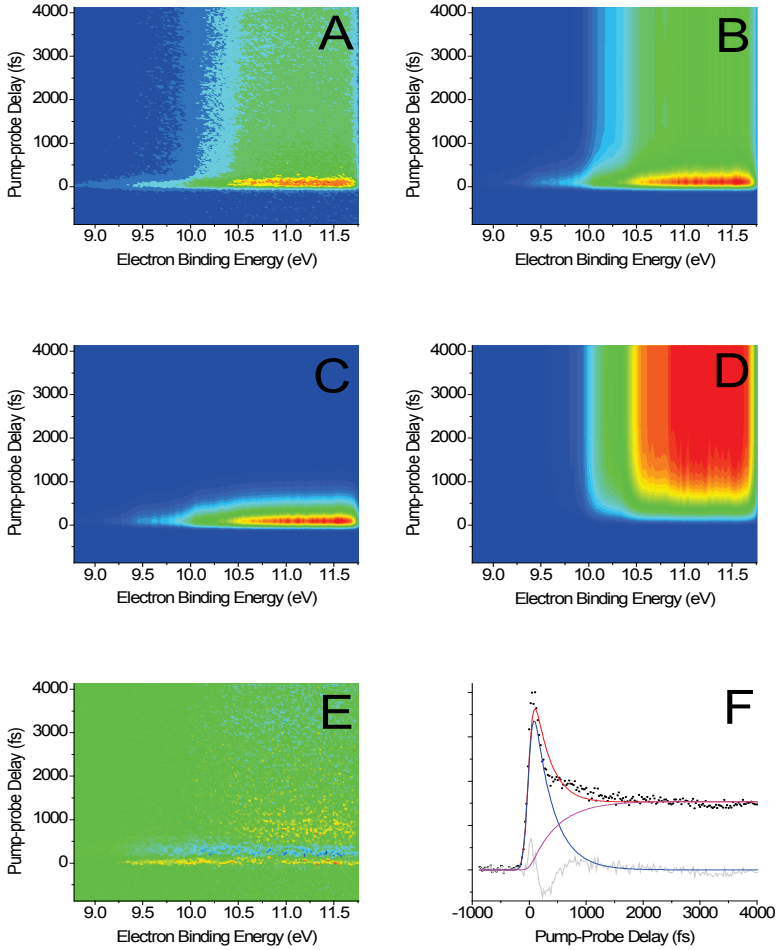


**Figure S1:** 2D fit of the 291.5 nm data with only two time constants. (A) raw data. (B) total fit (=C+D). (C) fast component of fit. (D) slow component of fit. (E) residuals (=A-B). (F) integrated data (black dots), fits (red, blue, magenta), and residuals (grey).
As can be seen from the residuals, fitting the data with only two time constants is not adequate, and three time constants are needed.

## 2. Transient Absorption Spectroscopy

The kinetic model used in the 2D fits of the experimental data is based on the standard sequential equation for a three-component system (Capellos, C.; Bielski, B. H. J. Kinetic Systems, Wiley Interscience, New York, 1973), with rate constants $k_1$, $k_2$, and $k_3$, and associated amplitudes of $\sigma_A$, $\sigma_B$, and $\sigma_C$, respectively. The rate law is convoluted with the instrument response function of our setup (IRF; see below).
The explicit equations can be written easily with the Gauss-convoluted exponential:

$$\Phi_{k,\beta}(t) = \int_0^{+\infty} e^{-kx} e^{-\frac{(x-t)^2}{\beta}} \frac{1}{\sqrt{\beta\pi}} dx = \frac{1}{2} e^{-kt} e^{\frac{\beta k^2}{4}} \left(1 + \mathrm{erf}\left(\frac{t}{\sqrt{\beta}} - \frac{\sqrt{\beta}k}{2}\right)\right),$$

with $\beta = (\mathrm{FWHM})^2/(4 \ln 2)$ and FWHM the full-width-at-half-maximum of the instrument response function, as:

$$x(t,\lambda) =$$
$$\sigma_A(\lambda)\left[\Phi_{k_1,\beta}(t)\right] + \sigma_B(\lambda)\left[\frac{k_1}{k_2-k_1}\Phi_{k_1,\beta}(t) - \frac{k_1}{k_2-k_1}\Phi_{k_2,\beta}(t)\right] + \sigma_C(\lambda)\left[-\frac{k_2k_3}{k_1^2+(k_2-k_1)k_3-k_1k_2}\Phi_{k_1,\beta}(t) + \frac{k_1k_3}{k_2^2-(k_2-k_1)k_3-k_1k_2}\Phi_{k_2,\beta}(t) + \frac{k_1k_2}{k_3^2-(k_1+k_2)k_3+k_1k_2}\Phi_{k_3,\beta}(t)\right].$$

Here, $k_1$, $k_2$, were globally fitted during data analysis, while $k_3$ was held at a large value of ca. $10^3$ $sec^{-1}$ in order to provide the constant offset. The wavelength-dependent fitting parameters $\sigma_A$, $\sigma_B$, and $\sigma_C$ are the decay-associated spectra for the three elementary steps of our kinetic model. In particular, $\sigma_C$ is identical to the excited-state absorption spectrum of the $T_1$ state.

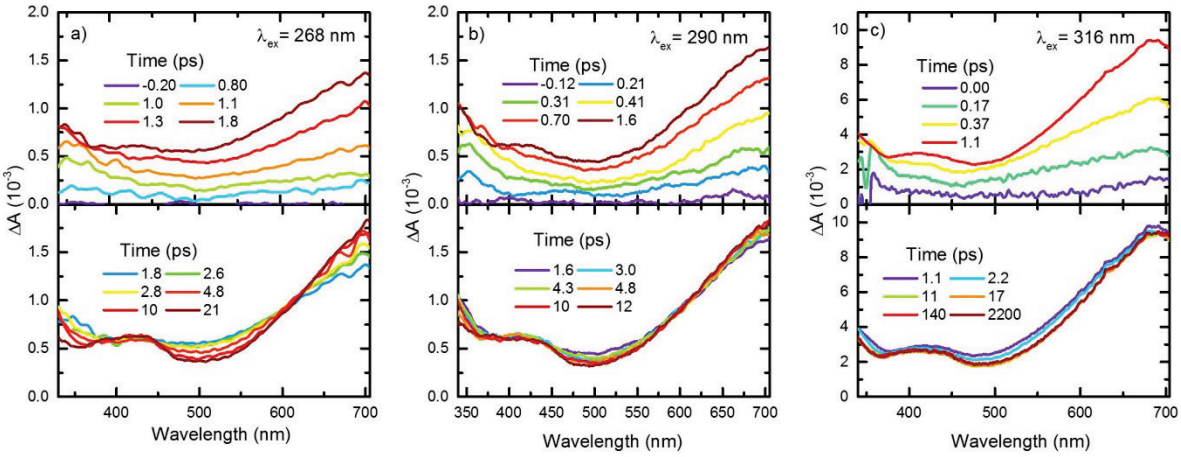


**Figure S2**: Transient absorption spectra of 2tUra in acetonitrile following excitation at (a) 268, (b) 290, and (c) 316 nm from sub-picosecond to picosecond time delays.

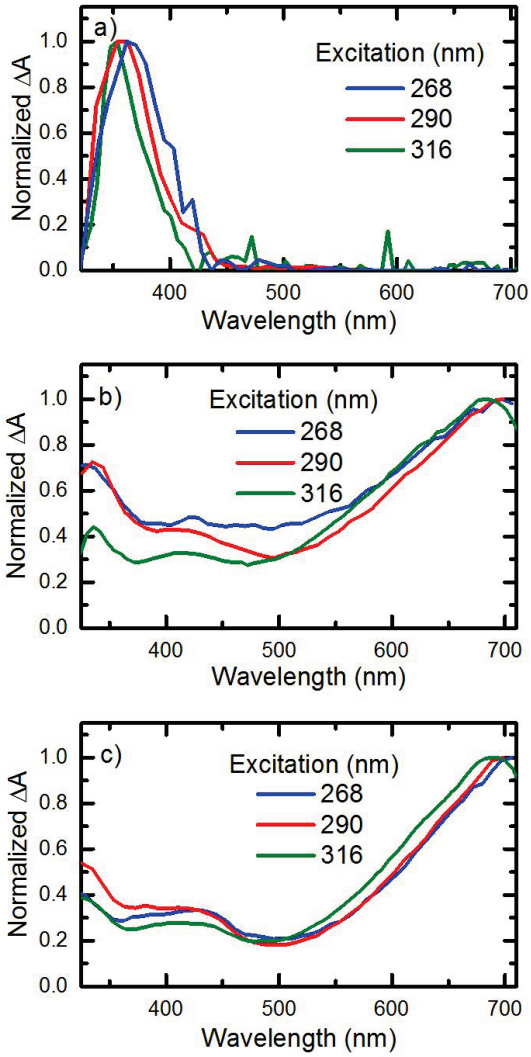


**Figure S3**: Normalized (a) first, (b) second, and (c) third decay-associated spectra of 2-thiouracil in acetonitrile depending on excitation wavelength.

## 3. Simulated Transient Absorption Spectra

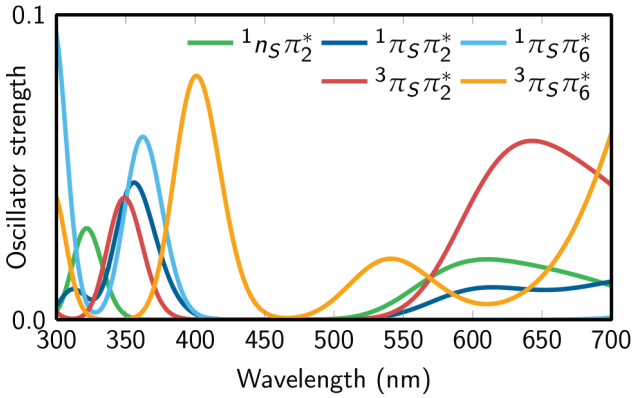


**Figure S4**: Simulated transient absorption spectra of the different excited states of 2-thiouracil. Each spectrum was computed from a single-point calculation at the optimized geometry of the respective state, followed by Gaussian convolution. The computations were performed with MS(12)-CASPT2(14,11)/ANO-RCC-VTZP, DKH, standard IPEA.

## 4. Optimized Coordinates of Critical Points of 2-Thiouracil

The following coordinates are the result of the optimizations of the $T_1$ minima and $T_1/S_0$ crossing points, as presented in Figure 7 of the main manuscript.

```
12
3piSpi2* Min E = -737.27190143
N    0.043698 -0.022638  1.372425
C   -0.017694 -0.036710 -0.025577
N    1.245076  0.157333 -0.619321
C    2.503673  0.086702 -0.007897
C    2.428229 -0.045845  1.450905
C    1.206398 -0.077732  2.079260
S   -1.361649  1.007045 -0.640853
O    3.532457  0.155490 -0.671816
H   -0.850131 -0.079504  1.852382
H    1.262992  0.228927 -1.635379
H    3.358950 -0.087269  2.016322
H    1.098410 -0.158609  3.163545

12
3pi5pi6* Min E = -737.27196482
N    0.330818  0.101655  1.428815
C    0.196229  0.217418  0.072377
N    1.385230  0.295036 -0.649083
C    2.655140 -0.100091 -0.154593
C    2.693684 -0.280491  1.281980
C    1.505186 -0.067608  2.087439
S   -1.350086  0.349424 -0.642552
O    3.598763 -0.246410 -0.928516
H   -0.547226  0.148566  1.943941
H    1.293519  0.307623 -1.663537
H    3.645754 -0.549522  1.740793
H    1.467029 -0.134223  3.173654
```

12
3piSpi2*/S0 MXP E = -737.264750 & -737.264729
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

12
3pipi6*/S0 MXP E = -737.2563852 & -737.2562901
N  0.050358 -0.427434  1.064587
C  0.003138  0.146932 -0.186338
N  1.173959  0.789226 -0.582670
C  2.470517  0.524308 -0.098639
C  2.393640 -0.411798  1.065001
C  1.176499 -0.289082  1.882728
S -1.356086  0.104642 -1.152858
O  3.456910  0.987237 -0.641035
H -0.861793 -0.701907  1.432539
H  1.126198  1.253296 -1.490387
H  2.839983 -1.401656  0.899329
H  1.086437  0.323206  2.788386

12
3pipi6* Min (PCM) E = -737.291848
  N       0.325724      0.086320     -1.432357
  C       0.191527      0.228631     -0.079391
  N       1.355127      0.055182      0.675665
  C       2.646527     -0.112386      0.157765
  C       2.705931     -0.224149     -1.281066
  C       1.490366     -0.147988     -2.078009
  S      -1.320554      0.574477      0.649014
  O       3.617351     -0.160356      0.927000
  H      -0.546212      0.169631     -1.980376
  H       1.276379      0.202772      1.687831
  H       3.681920     -0.384216     -1.765806
  H       1.449954     -0.246540     -3.170987

12
3pipi2* Min (PCM) E = -737.288828
  N       0.037575     -0.057834      1.356396
  C      -0.022725     -0.066783     -0.046430
  N       1.257452      0.127738     -0.632591
  C       2.493405      0.085234     -0.015504
  C       2.416658     -0.023053      1.442510
  C       1.191640     -0.075967      2.068170
  S      -1.311468      1.103949     -0.538083
  O       3.542154      0.156714     -0.669584
  H      -0.861469     -0.142975      1.852306
  H       1.286200      0.197654     -1.657714
  H       3.344619     -0.037506      2.019449
  H       1.076369     -0.139982      3.155072

12
3pipi6*/S0 MXP (PCM) E = -737.2739803 & -737.2740132

| | | | |
|---|---|---|---|
| N | 0.036752 | -0.314752 | 1.104200 |
| C | 0.023775 | 0.094237 | -0.207170 |
| N | 1.201543 | 0.732040 | -0.633713 |
| C | 2.476364 | 0.564323 | -0.092279 |
| C | 2.395731 | -0.409111 | 1.043180 |
| C | 1.184601 | -0.230749 | 1.867209 |
| S | -1.326869 | -0.029496 | -1.180423 |
| O | 3.465670 | 1.114307 | -0.555891 |
| H | -0.878050 | -0.579942 | 1.502822 |
| H | 1.135587 | 1.231272 | -1.532466 |
| H | 2.719360 | -1.445007 | 0.778966 |
| H | 1.125300 | 0.169851 | 2.886206 |

12
3pipi2*/S0 MXP (PCM) E = -737.278369 & -737.278357

| | | | |
|---|---|---|---|
| N | 0.090455 | 0.523956 | -0.705459 |
| C | 0.333020 | 0.861513 | 0.658248 |
| N | 1.712593 | 0.655966 | 0.971235 |
| C | 2.698556 | 0.024177 | 0.236299 |
| C | 2.303953 | -0.279571 | -1.149215 |
| C | 1.027489 | -0.004094 | -1.575116 |
| S | -0.822215 | -0.479860 | 1.318011 |
| O | 3.822507 | -0.196664 | 0.700441 |
| H | -0.845243 | 0.751455 | -1.071057 |
| H | 1.998729 | 0.934664 | 1.916275 |
| H | 3.051584 | -0.699102 | -1.826243 |
| H | 0.682192 | -0.136816 | -2.604319 |