

Supplementary Material: Tautomerisation of thymine using ultraviolet light

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Details of fitting procedures

When fitting the XPS core levels, we have first and foremost tried to implement the requirement that the number of distinct components matches that of the thymine molecule, i.e. five C atoms, two N atoms and two O atoms giving rise to matching numbers of components. Furthermore, we assume that the width of each component will be the same for each element, i.e. that the C1s region should consist of 5 components of similar width. The position of each component, and its height are free parameters in the fit, as is the single, common value for the width. No further *a priori* assumptions are used unless fitting in the manner is not satisfactory.

For example, in the case of the ‘as deposited’ thymine C1s, the fit converges on the

solution that two of the components are at the same energy (C4 and C5). An identical fit would have been produced with 4 components, but this component would have to be larger (i.e. representing C4+C5). It is therefore a result of the fit that we discover C4 and C5 to have a very similar energy and not an *a priori* assumption.

In the case of the ‘as deposited’ thymine O1s, this procedure is not satisfactory. The calculations indicate that O1 and O2 are very close in energy, but an additional (broader) component is found at larger binding energy. This additional component matches well with a small amount of contamination, presumably water, and is seen to increase with exposure time. In this case we are forced to use the *a priori* assumption that O1 and O2 form a common peak.

In the case of the ‘as deposited’ thymine N1s, the two component fit converges on the solution that N1 and N2 are at very similar energy (in agreement with the calculations). Whilst the fit has converged upon this solution without an *a priori* assumption, fitting two components to a single peak is bound to produce such a result. Furthermore, the energy separation found by fitting has a large uncertainty since it can be partially traded for a change in component width. Nonetheless, the point of this fit is to demonstrate that if the N1s peak contains two components (as we expect), then their energy separation must be small.

To summarise, using the assumption that the number of components in the XPS measurements should match the number of distinct atoms in the thymine molecule, we are able to make a satisfactory fit to all of the core levels, with the exception of those in which contamination (or other species) are present.

Substrate core levels

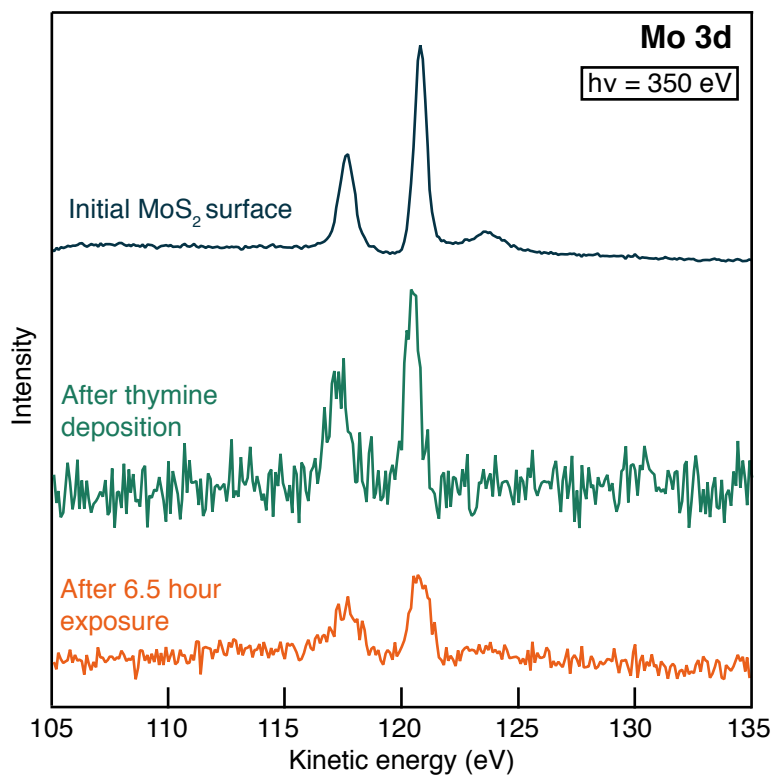


Figure S1: Mo 3d core level collected at a photon energy of 350 eV from the clean surface, after deposition and after irradiation. After deposition, the intensity is strongly attenuated, so the scaling has been increased accordingly. Except for the attenuation, and a small shift, there is no significant change in the core level during the experiment – indicating that there is no substrate reaction or damage to the substrate due to the 6.5h exposure to zero order synchrotron light.

NEXAFS

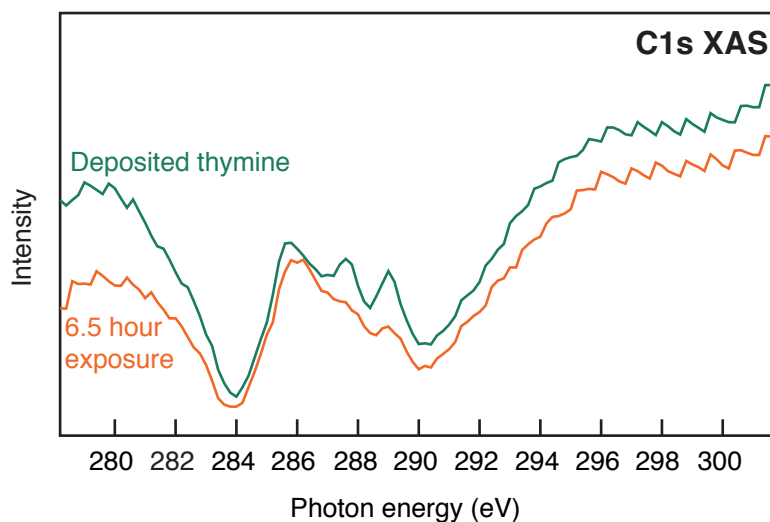


Figure S2: Carbon K-edge NEXAFS. After exposure, the features become less pronounced, but appear otherwise unchanged. No significant shift is seen. This indicates that the structure of the molecule has not changed significantly as a result of the exposure. [Note: the ‘pre edge’ intensity at photon energy <284 eV is an artefact of the strongly decreasing beamline flux]

Additional details of calculations

The following section contains the atomic co-ordinates of the optimised thymine, enol-tautomer and photo-dimer. The table captions give further details, including the minimised energy (per molecule).

Table S1: Thymine geometry in Å. CCSD energy is computed to be -453.18599 a.u. and MP2 energy is computed to be -453.14819 a.u. in aug-cc-pVDZ basis.

| | X | Y | Z |
|---|----------|----------|----------|
| C | -1.63321 | 0.04259 | -0.00005 |
| C | 0.75695 | 0.83836 | -0.00009 |
| C | 1.19786 | -0.57130 | -0.00003 |
| C | 0.23997 | -1.54316 | -0.00005 |
| C | 2.68171 | -0.85098 | 0.00016 |
| N | -0.64148 | 1.02146 | -0.00065 |
| N | -1.12187 | -1.25093 | -0.00021 |
| O | -2.83526 | 0.29190 | 0.00048 |
| O | 1.51178 | 1.81047 | 0.00025 |
| H | -0.97342 | 1.98347 | -0.00022 |
| H | 0.48688 | -2.60874 | 0.00001 |
| H | -1.81526 | -1.99007 | 0.00047 |
| H | 3.15888 | -0.40278 | -0.88843 |
| H | 3.15871 | -0.40246 | 0.88868 |
| H | 2.87209 | -1.93758 | 0.00051 |

Table S2: Tautomer geometry in Å. CCSD energy is computed to -453.15734 a.u., and MP2 energy is computed to be -453.12104 a.u. in aug-cc-pVDZ basis.

| | X | Y | Z |
|---|----------|----------|----------|
| C | 1.54494 | -0.18895 | -0.00001 |
| C | -0.65574 | 0.90779 | 0.00017 |
| C | -1.19279 | -0.44337 | -0.00001 |
| C | -0.30576 | -1.50030 | -0.00006 |
| C | -2.68768 | -0.60502 | -0.00011 |
| N | 0.76233 | 0.93457 | 0.00006 |
| N | 1.07460 | -1.40441 | -0.00002 |
| O | 2.89574 | -0.03284 | -0.00010 |
| O | -1.28932 | 1.96971 | -0.00008 |
| H | 1.16367 | 1.87133 | -0.00003 |
| H | -0.68860 | -2.52591 | -0.00014 |
| H | -3.12652 | -0.11916 | 0.88565 |
| H | -3.12643 | -0.11892 | -0.88579 |
| H | -2.96201 | -1.67015 | -0.00027 |
| H | 3.13056 | 0.90679 | -0.00006 |

Table S3: Thymine dimer geometry in Å. MP2 energy is computed to be -906.02614 a.u. in aug-cc-pVDZ basis.

| | X | Y | Z |
|---|----------|----------|----------|
| O | 2.21966 | -2.14007 | 0.46930 |
| O | -2.22006 | -2.13992 | -0.46888 |
| O | 3.62870 | 2.14610 | -0.00918 |
| O | -3.62861 | 2.14648 | 0.00866 |
| N | 1.56534 | 1.61953 | -0.88751 |
| N | -1.56528 | 1.61989 | 0.88704 |
| N | 2.71357 | 0.08920 | 0.44790 |
| N | -2.71366 | 0.08943 | -0.44807 |
| C | 0.58475 | -0.68317 | -0.53838 |
| C | -0.58495 | -0.68299 | 0.53843 |
| C | 0.37075 | 0.84302 | -0.68703 |
| C | -0.37078 | 0.84320 | 0.68675 |
| C | 0.45921 | -1.55407 | -1.78181 |
| C | -0.45950 | -1.55363 | 1.78205 |
| C | 1.89917 | -1.00370 | 0.15652 |
| C | -1.89943 | -1.00352 | -0.15637 |
| C | 2.69755 | 1.37215 | -0.14482 |
| C | -2.69745 | 1.37255 | 0.14428 |
| H | -0.33784 | 1.05055 | -1.50426 |
| H | 0.33782 | 1.05083 | 1.50393 |
| H | 1.30784 | -1.35693 | -2.45796 |
| H | 0.47005 | -2.61741 | -1.50216 |
| H | -0.47477 | -1.34147 | -2.32226 |
| H | -1.30811 | -1.35624 | 2.45817 |
| H | -0.47048 | -2.61702 | 1.50263 |
| H | 0.47451 | -1.34102 | 2.32244 |
| H | 1.48732 | 2.58693 | -1.18949 |
| H | -1.48717 | 2.58732 | 1.18891 |
| H | 3.60567 | -0.14183 | 0.88568 |
| H | -3.60582 | -0.14161 | -0.88575 |