Ultrafast Competitive Relaxation Pathways of the Pterin Chromophore

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Introduction:

Pterins are a class of biomolecules found in every biological system from archae to humans.[1] Their bioreactivity include photoreception in plants and amino acid metabolism.[2-3] However, they are also photo-active[4-5] and have been suspected of initiating photosensitized damage of skin cells following UVA light absorption. To improve the understanding of the photoreactivity of the pterins in general, the relaxation dynamics of the freebase core chromophore, pterin, were determined.[6]

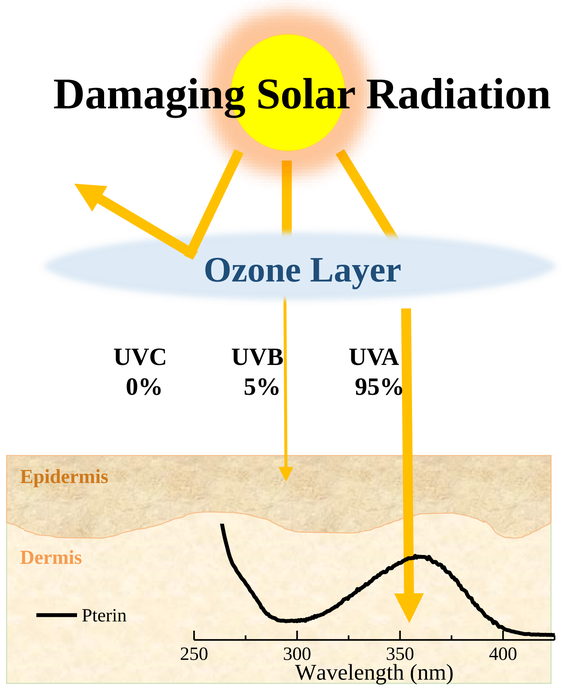


Figure 1. Solar UV radiation through ozone layer and skin corresponding to absorption spectrum of pterin.

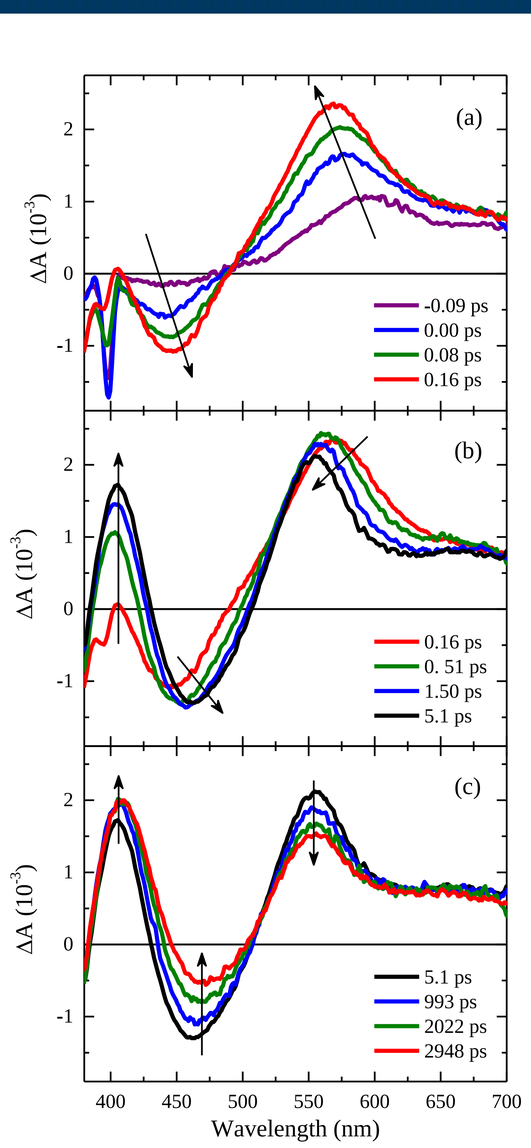
Methods: Transient Absorption Spectroscopy

This method uses a pump pulse (ca. 200fs, 1mW, 350 nm) to excite a sample and a broadband white-light pulse to probe the excited-state species hence it is known as a pump-probe technique. Changing the probe distance controls the time delay enabling precise temporal resolution. All experiments were on identical solutions of ca. 600 μM of pterin in 10.5 pH borate buffer.

Results:

Time-resolved spectra documenting all mechanistic transitions on pterin from initial through full ground-state recovery are shown in Figure 2. The ground state is recovered by three processes (τ_3,[4] τ_4 and τ_5), indicating three photophysically active states are formed which all decay to recover the ground state. These have been characterized as a $S_l(\pi\pi^*)$ (Figure 2c-d; τ_3), $T_1(\pi\pi^*)$ (Figures 2 and 3; τ_4) and neutral radical (Figures 2e, 3 and 4), respectively.

Fluorescence is observed immediately (Figure 2a) and so the fluorescent S_1 state must be the initially excited, and part of the population must transfer to the triplet manifold during vibrational cooling (indicated by symmetric spectral shifting). The receiver T_2 state is believed to be capable of hydrogen abstraction to generate the neutral radical species, which will compete with internal conversion to the T_1 state. All of this happens within 5 ps of excitation.



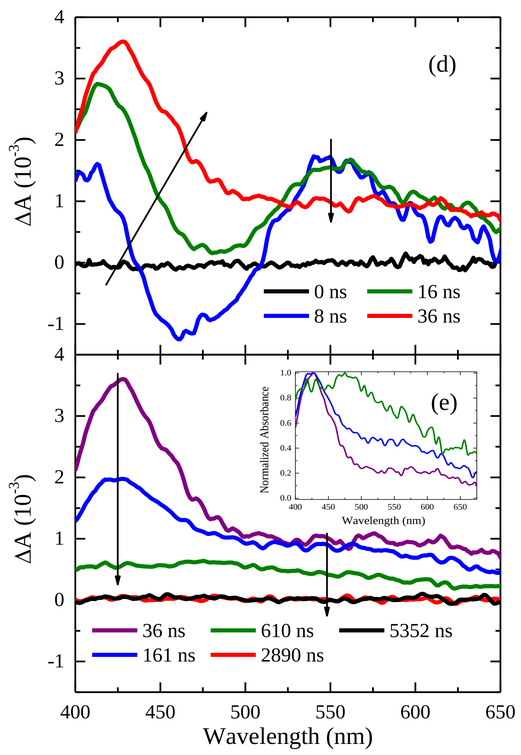


Figure 2.
Time-resolved spectra for pterin in borate buffer (pH 10.5) following 350 nm excitation. Ultrafast dynamics (left) and ground state recovery (top) normalized spectra in inset. Figure modified from reference 6.

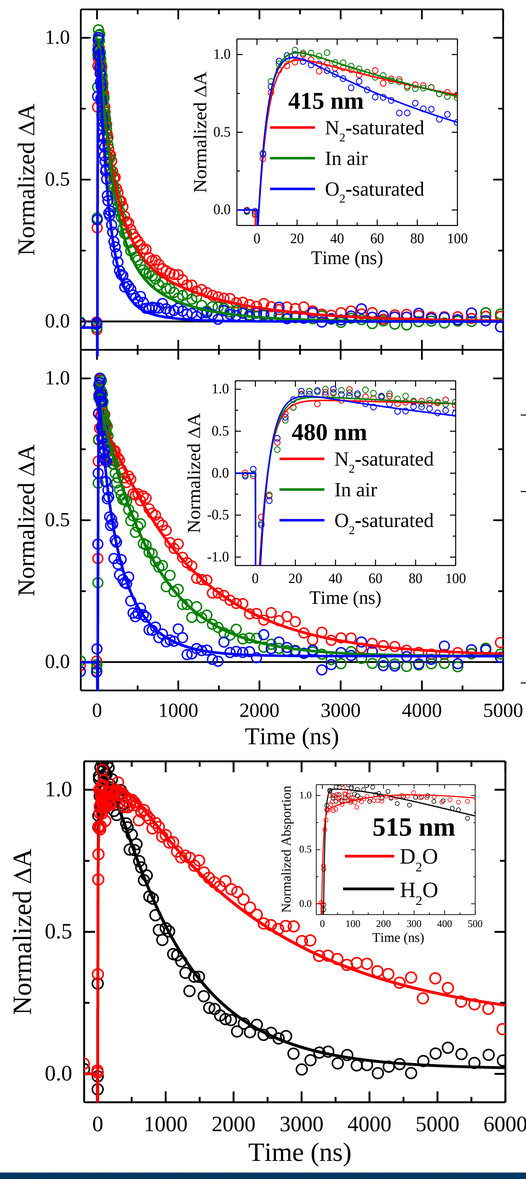


Figure 3.
Kinetic traces and mathematical fits for pterin with variable concentrations of molecular oxygen. The decay rates of both long-lived species shown in Figure 3e (τ_4 and τ_5) are inversely proportional to molecular oxygen concentration. Triplet species and radical species are known to be quenched by molecular oxygen. Figure taken from reference 6.

Table 1: Pterin Electronic Lifetimes in Ambient Conditions

τ_1	0.161 ± 0.006 ps
τ_2	1.61 ± 0.03 ps
τ_3	5000 ps (held)
τ_4	170 ± 20 ns
τ_5	670 ± 50 ns

Figure 4.
Kinetic traces and mathematical fits for pterin in aqueous buffer (black) and deuterated buffer (red). The species associated with τ_5 exhibits a normal kinetic isotope effect (k_h/k_d = 2) indicating a hydrogen transfer of some kind. Given the known reactivity[5] and oxygen quenching (Figure 3) this is most likely a neutral radical generated by hydrogen abstraction. Figure taken from reference 6.

Conclusion:

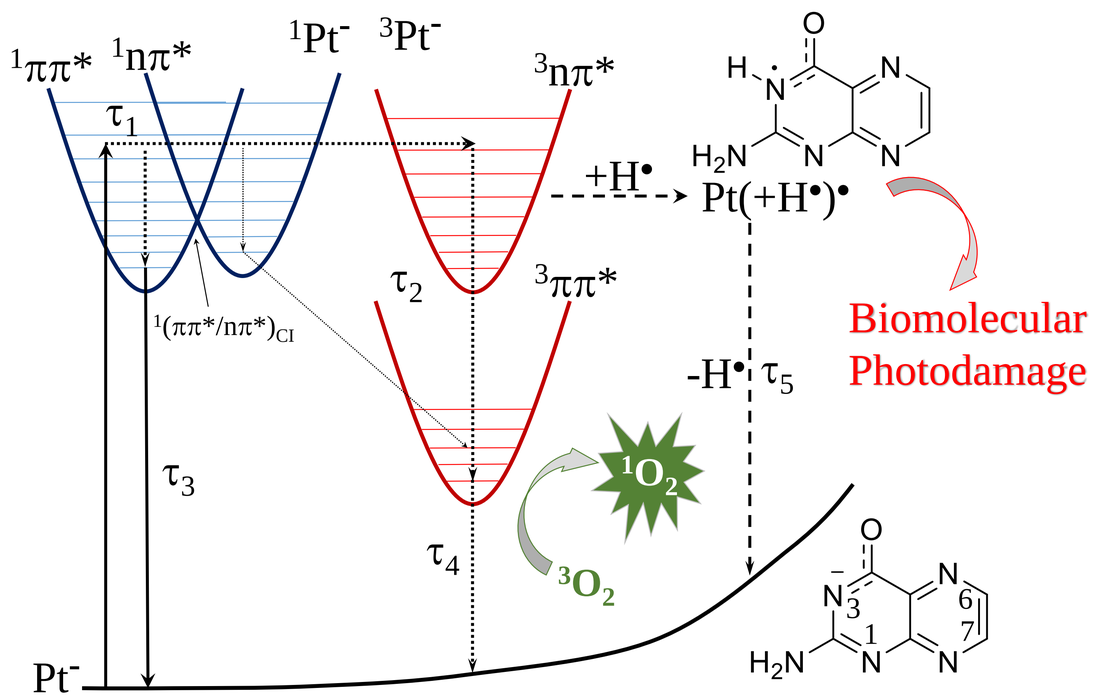


Figure 5. Proposed electronic relaxation mechanism for anionic pterin, showing ultrafast population of all photophysically active states and their pathways to the ground state. Figure modified from ref. 6.

Acknowledgements and References:

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