Paper Presentation

Tryptophan-to-heme electron transfer in ferrous myoglobins

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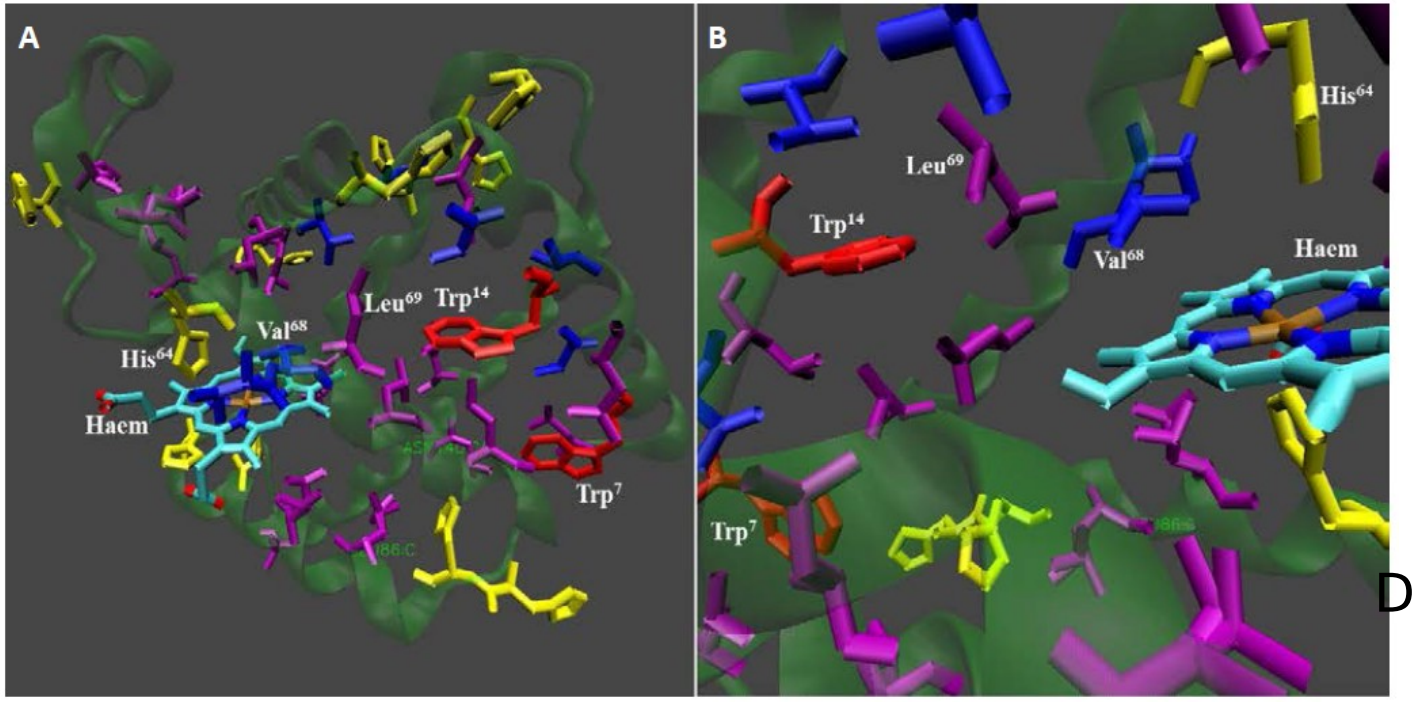

Debasmita Ghos
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Introduction

❖Electron transfer plays a fundamental role in many biological systems ranging from photosynthetic proteins to iron–sulfur, copper, and heme proteins.

❖It was demonstrated that electron transfer can be used to produce from heme proteins in situ drugs with antimalarial activity and it might have a role in protein folding.

❖ In general, electron transfer in proteins can occur over long distances (>10 Å) by hopping through different residues.

❖ Tryptophan (Trp) also acts as a phototriggered electron donor, e.g., in DNA repair by photolyase and in cryptochromes.

❖When no obvious electron acceptors are present, excited Trp or (*Trp) still displays shorter lifetimes than its nanosecond decay times in solution. This is due to its strong tendency to act as an electron donor, undergoing electron transfer toward the protein's backbone as in the case of apo-myoglobin mutants.

n this paper

❖ They demonstrated the occurrence of Trp to heme electron transfer (ET) in ferrous myoglobins by ultrafast UV spectroscopy.

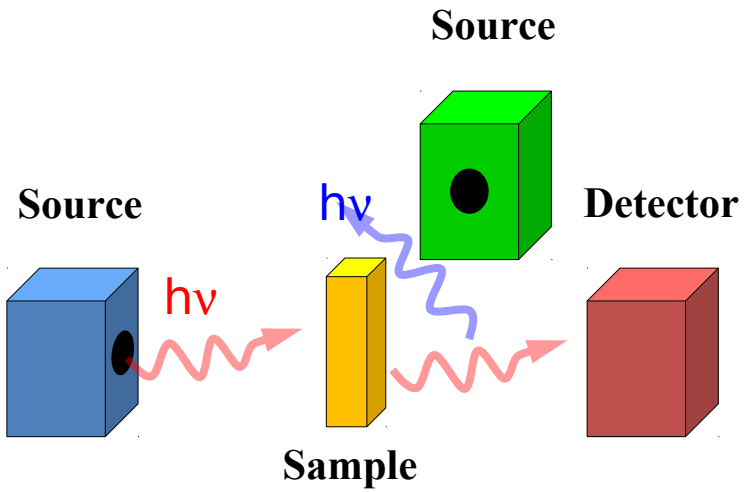
❖ The ET gives rise to the theoretically predicted, low-valence Fe(II)(porph●−) anion radical, which we observe for the first time to our knowledge under physiological conditions.

❖These results highlight the generality of Trp–porphyrin electron transfer events in heme proteins and question the systematic use of Trp fluorescence in FRET studies of protein dynamics.

❑ The invariance of *Trp decay times in ferric and ferrous Mbs suggests that similar electron transfer processes may also occur in ferrous Mbs. In this event, questions arise as to
(i) whether a formally FeI heme is formed.
(ii) whether the electron localizes on the porphyrin ring or even on the ligand that binds to the Fe ion.

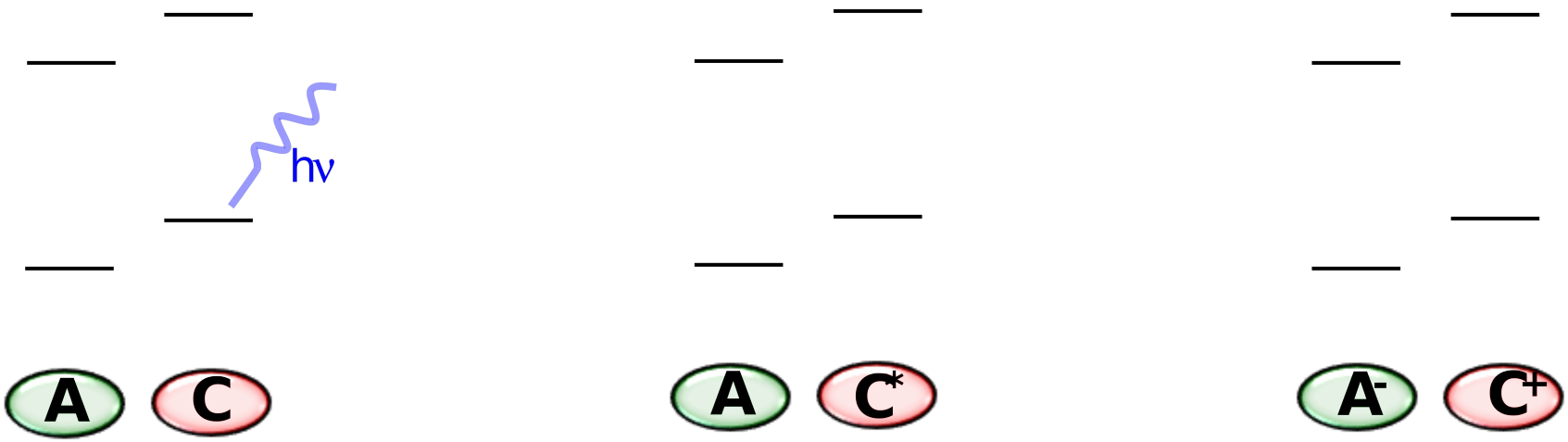
Transient Absorption Spectroscopy

Instrumental Set-up



Transient Absorption Spectroscopy

Electron Transfer Dynamics



esults and discussion

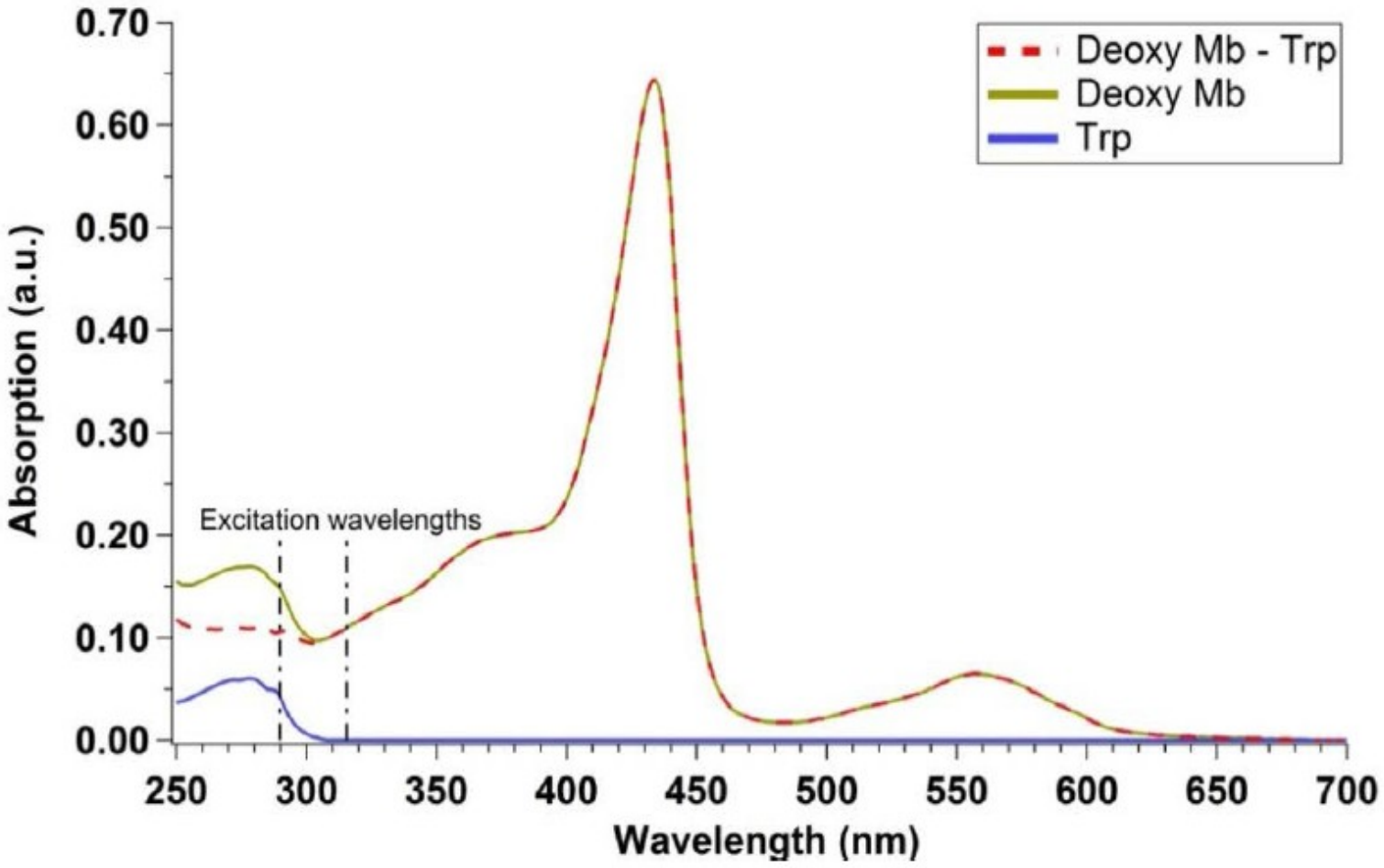


Figure 1: Static spectra of deoxy-Mb 0.27 mM (solid yellow line), Trp in water 0.54 mM (solid blue line) and difference between deoxy-Mb and Trp spectra (dotted red).

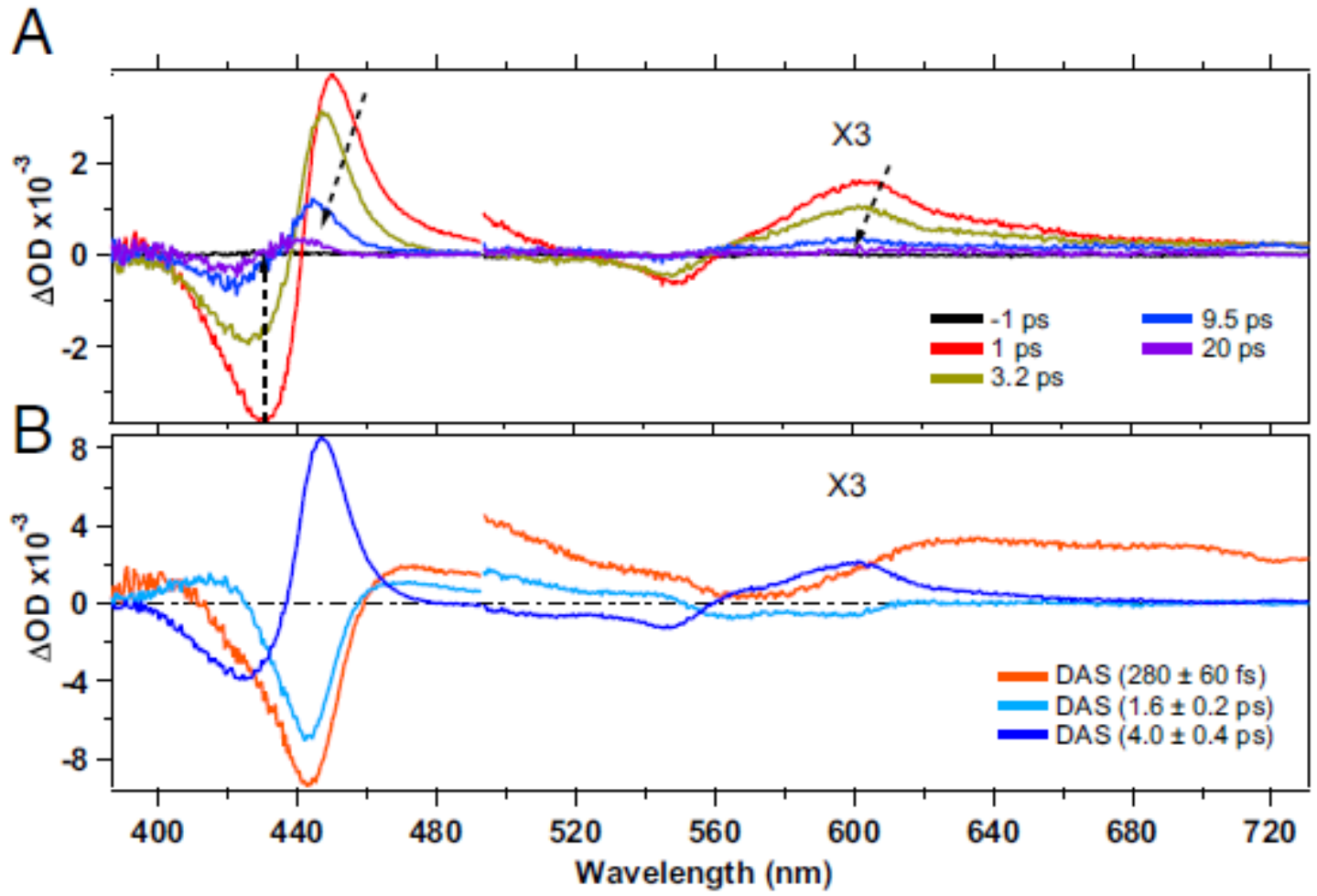


Fig. 2. (A) Transient absorption spectra at selected pump–probe delays of deoxy-Mb upon 315-nm photoexcitation. (B) Decay-associated spectra of the timescales obtained by an SVD analysis. The regions from 500 nm to 730 nm have been multiplied by 3.

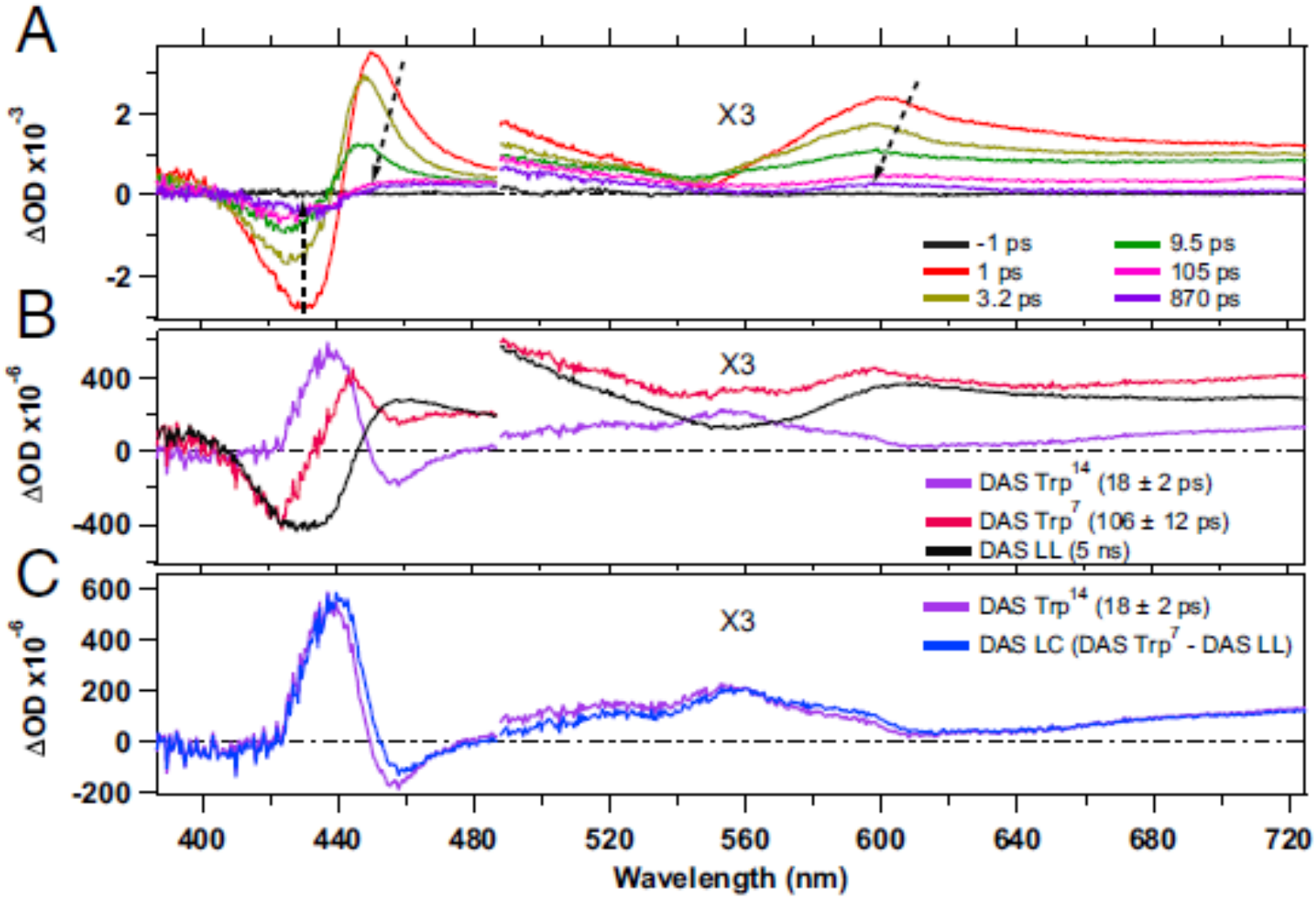


Fig. 3. (A) Transient absorption spectra, at selected pump–probe delays, of deoxy-Mb upon 290-nm photoexcitation. (B) DASs obtained by SVD analysis. (C) Comparison of the Trp14 DAS with the linear combination DAS LC = –LL DAS + DAS Trp7. The regions above 500 nm are multiplied by 3.

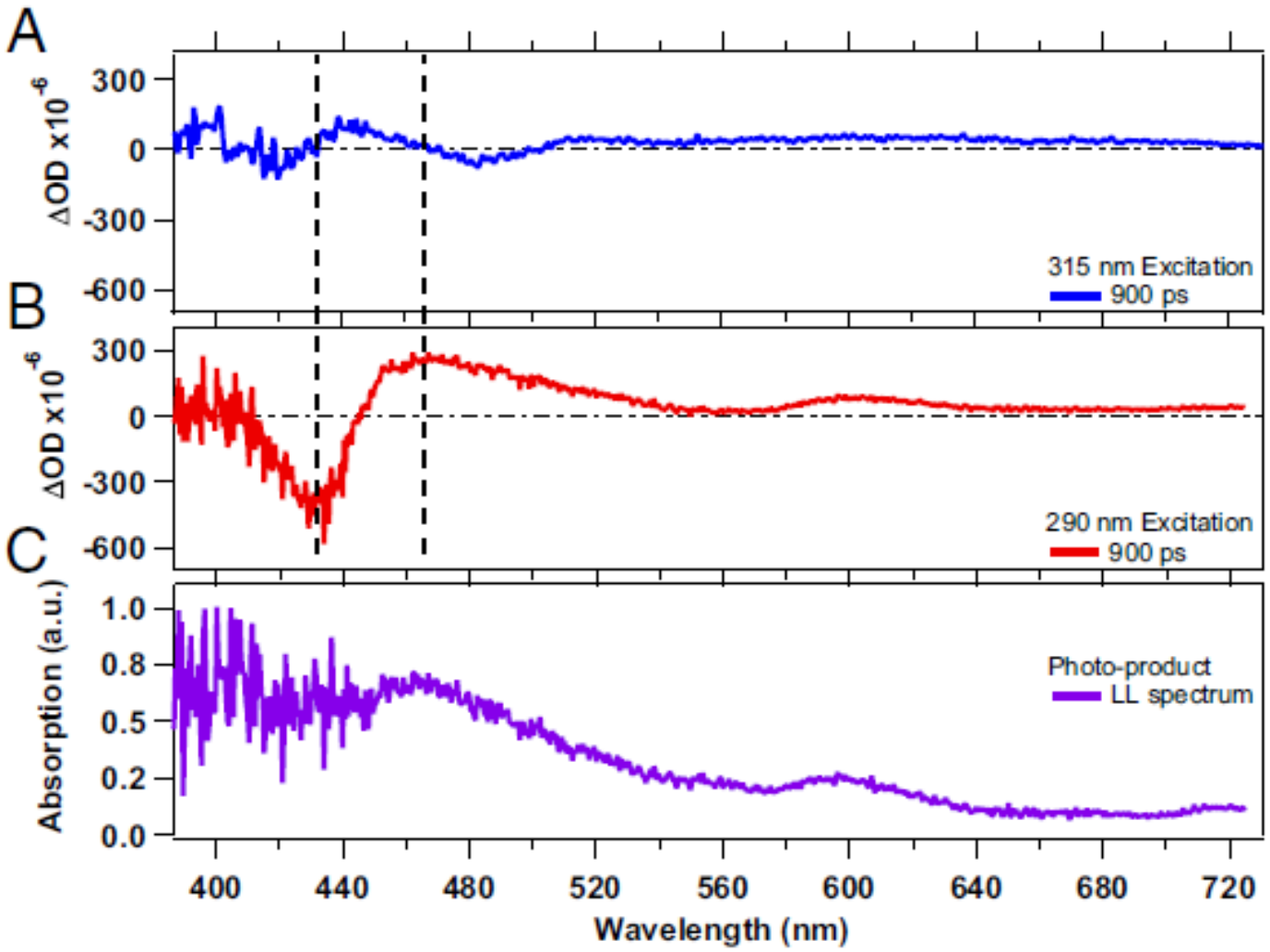
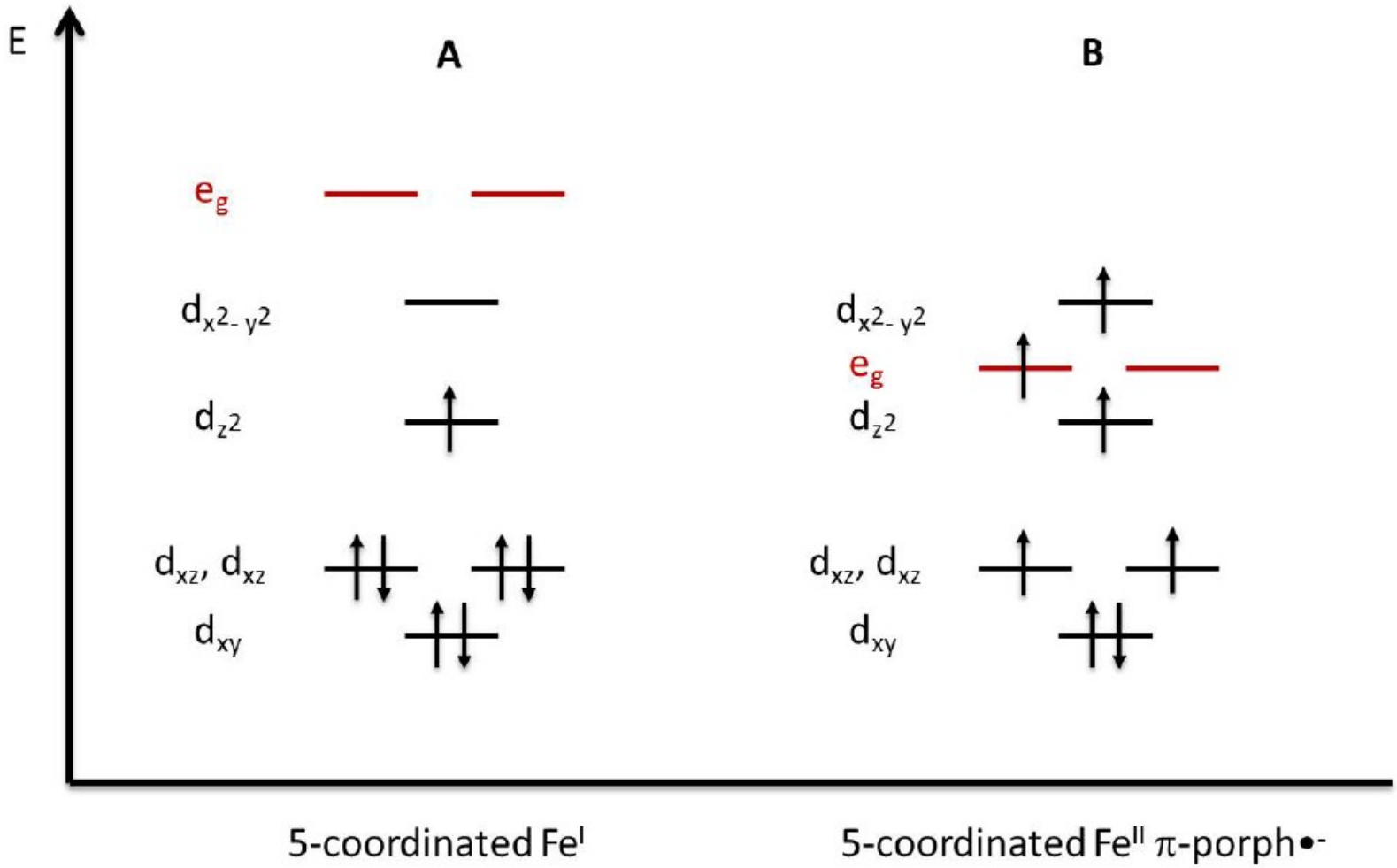


Fig. 4. Comparison of transient spectra of deoxy-Mb at 900 ps pump–probe delay time, obtained upon 315-nm (A) and 290-nm (B) excitation. C reports the spectrum of the LL photoproduct obtained by subtracting the bleach contribution from the LL transient shown in B.



Scheme S1: Schematic representation of relative metal and porphyrin orbital energies for penta-coordinated FeI (A) and penta-coordinated FeII porphyrin π-anion radical (B). The Fe d-orbitals are in black while the eg orbitals of the porphyrin are in red. Reproduced from ref. (1) .

Summary

- Femtosecond UV-visible transient absorption experiments were performed on deoxy-Mb for excitation wavelengths near 300 nm.

- They reveal the formation of a long-lived photoproduct, which results from a *Trp14-to-heme electron transfer with a quantum yield of ~30%. This species is an FeII–porphyrin π-anion radical that has a lifetime exceeding our measurement window of 1 ns.

- In studies of protein dynamics the fluorescence decay of *Trp is not only for the FRET, parallel electron transfer pathways may also contribute to its quenching.

Future direction

Au@BSA cluster can be studied by femtosecond absorption spectra to see whether any transient species is formed or not which is responsible for the fluorescence quenching.

Thank You