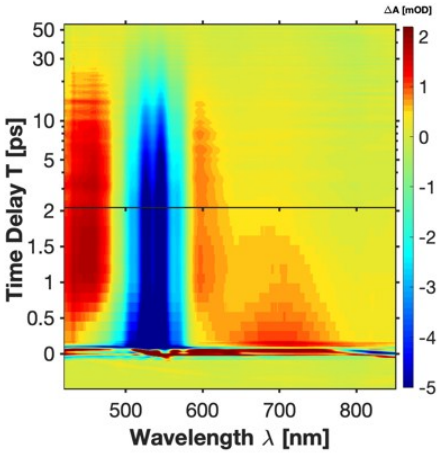
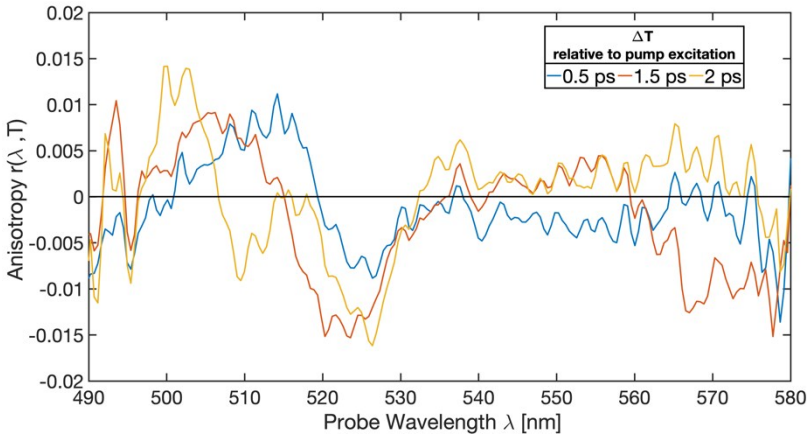
# Supplementary Information

## The elusive dynamics of aqueous permanganate photochemistry

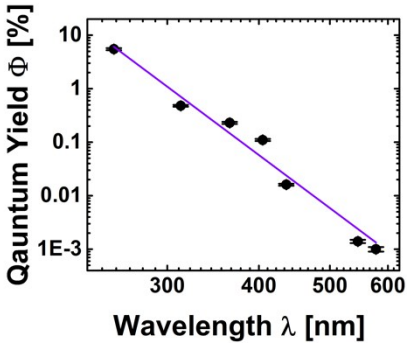
Omer S. Haggag, Partha Malakar, Pavel Pokhilko (USC), John F. Stanton (University of Florida), Anna I. Krylov (USC), and Sanford Ruhman



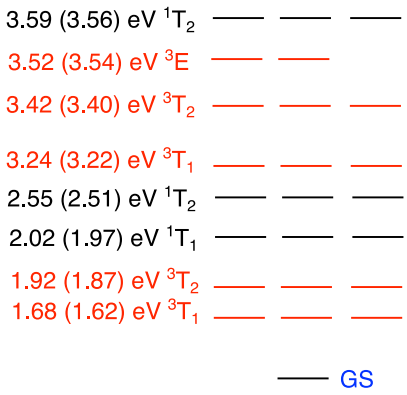

**S1.** Transient absorption data of aqueous permanganate pumped at 680 nm (pump 2). As seen, the obtained TA data is similar to the data obtained by pumping at 545 nm.




**S2.** Anisotropy spectrum at different delay times relative to pump excitation. No significant anisotropy is observed.




**S3.** The quantum yield of photoproduct formation ( ) as a function of CW excitation energy of aqueous permanganate. Based on data obtained from Zimmerman's work on the photochemistry of aqueous permanganate[1]




**S4.** Comparison of EOM-EE-CCSD excitation energies with aug-cc-pVTZ/cc-pV(T+d)Z and 6-31+G* (in *parenthesis*) basis sets. wB97X-D/aug-cc-pVTZ/cc-pV(T+d)Z geometry was used in both cases.

Ground state, optimized with wB97X-D/aug-cc-pVTZ/cc-pV(T+d)Z.
Nuclear Repulsion Energy = 345.28139051 hartrees
$molecule
-1 1
O 0.0000000000 -1.2950348696 0.9163894295
Mn 0.0000000000 0.0000000000 0.0000000000
O 0.0000000000 1.2950348696 0.9163894295
O 1.2950348696 0.0000000000 -0.9163894295
O -1.2950348696 0.0000000000 -0.9163894295
$end

Lowest triplet state, optimized with EOM-EE-CCSD/aug-cc-pVTZ/cc-pV(T+d)Z

Nuclear Repulsion Energy = 336.01764397 hartrees
$molecule
-1 1
O -1.3647696715 0.0000000000 -0.9489525273
Mn 0.0000000000 0.0000000000 -0.1549118897
O 1.3647696715 0.0000000000 -0.9489525273
O 0.0000000000 1.0524377450 1.1872245272
O 0.0000000000 -1.0524377450 1.1872245272
$end

Lowest component of JT-distorted singlet state, optimized with EOM-EE-CCSD/aug-cc-pVTZ/cc-pV(T+d)Z
Nuclear Repulsion Energy = 336.21246872 hartrees
$molecule
-1 1
O -1.3529233114 0.0000000000 -0.9668696001
Mn 0.0000000000 0.0000000000 -0.1461383945
O 1.3529233114 0.0000000000 -0.9668696001
O 0.0000000000 1.0476536534 1.1914485400
O 0.0000000000 -1.0476536534 1.1914485400
$end

MECP between the ground state and the lowest triplet state, found with EOM-EE-CCSD/aug-cc-pVTZ/cc-pV(T+d)Z
Nuclear Repulsion Energy = 337.82991430 hartrees
$molecule
-1 1
O -1.3638720088 0.0000000000 -0.9226054744
Mn 0.0000000000 0.0000000000 -0.1241032705
O 1.3638720088 0.0000000000 -0.9226054744
O 0.0000000000 1.1379559579 1.1053666016
O 0.0000000000 -1.1379559579 1.1053666016
$end

(1) Zimmerman, G. Photochemical Decomposition of Aqueous Permanganate Ion. *The Journal of Chemical Physics* **1955**, *23* (5), 825. https://doi.org/10.1063/1.1742130.