Supporting Information

Quenching of Singlet Oxygen by Carotenoids via Ultrafast Super-exchange Dynamics

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Rotation of π_g* orbitals of O$_2$

There is arbitrariness in the rotation of the degenerate π_g* orbitals (π_y* and π_z*) along the bond axis of isolated O$_2$. The ^{1}O$_2$ ($^1\Delta_g$) CASSCF wavefunction with 45-degree rotated π_g* orbitals is equivalent to the ^{1}O$_2$ ($^1\Delta_g$') wavefunction, and vice versa, as shown below.

The 45 and −45 degree rotated π_g* orbitals are expressed with the original π_y* and π_z* orbitals as follows.

$$\pi_{45}^* = \frac{1}{\sqrt{2}}\pi_x^* + \frac{1}{\sqrt{2}}\pi_y^* , \quad \pi_{-45}^* = \frac{1}{\sqrt{2}}\pi_x^* - \frac{1}{\sqrt{2}}\pi_y^*$$

In the $^1\Delta_g$ configuration, either π_{45}* or π_{-45}* orbital is occupied by two electrons (electrons 1 and 2).

$$
\begin{aligned}
^1\Delta_g &= \frac{1}{\sqrt{2}}\pi_{45}^*(1)\pi_{45}^*(2) - \frac{1}{\sqrt{2}}\pi_{-45}^*(1)\pi_{-45}^*(2) \\
&= \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}\pi_x^*(1) + \frac{1}{\sqrt{2}}\pi_y^*(1)\right]\left[\frac{1}{\sqrt{2}}\pi_x^*(2) + \frac{1}{\sqrt{2}}\pi_y^*(2)\right] - \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}\pi_x^*(1) - \frac{1}{\sqrt{2}}\pi_y^*(1)\right]\left[\frac{1}{\sqrt{2}}\pi_x^*(2) - \frac{1}{\sqrt{2}}\pi_y^*(2)\right] \\
&= \frac{1}{\sqrt{2}}\left[\frac{1}{2}\pi_x^*(1)\pi_x^*(2) + \frac{1}{2}\pi_x^*(1)\pi_y^*(2) + \frac{1}{2}\pi_y^*(1)\pi_x^*(2) + \frac{1}{2}\pi_y^*(1)\pi_y^*(2)\right] \\
&\quad - \frac{1}{\sqrt{2}}\left[\frac{1}{2}\pi_x^*(1)\pi_x^*(2) - \frac{1}{2}\pi_x^*(1)\pi_y^*(2) - \frac{1}{2}\pi_y^*(1)\pi_x^*(2) + \frac{1}{2}\pi_y^*(1)\pi_y^*(2)\right] \\
&= \frac{1}{\sqrt{2}}\left[\pi_x^*(1)\pi_y^*(2) + \pi_y^*(1)\pi_x^*(2)\right]
\end{aligned}
$$

^{1}O$_2$ $\left(^1\Delta_g\right)$ $\qquad$ ^{1}O$_2$ $\left(^1\Delta_g'\right)$

The final expression corresponds to the $^1\Delta_g$' configuration consisting of the original π_y* and π_z* orbitals, where the respective orbitals are occupied by one electron.