

Supporting Information for:
Reactivities of Singlet Oxygen: Open-Shell or Closed-Shell?

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Contents:

Computational Details

Methodology

Supporting Table S1

Supporting Figures S2 - S5

Computational Details

The complete active space self-consistent field (CASSCF)^[1-2] and multi-reference configuration interaction with single and double excitations (MR-CISD)^[3-4] calculations were computed using Molpro2012 package,^[5] and four low-lying states are used for the state average calculation. Since the self-interaction error was pathological in the oxygen molecule, the M06-HF functional^[6-7] with 100% of HF exchange term was used in all the MSDFT calculations. MSDFT calculations were performed using our local modified GAMESS2009 with cc-pVTZ basis set. The geometries were optimized relative to the ground state at B3LYP/6-31G(d) level using Gaussian09 package.^[8]

Methodology

In Figure 1, the energy levels for four low-lying states ($^3\Sigma_g^-$, $^1\Delta_g$ and $^1\Sigma_g^+$) of the oxygen molecule are illustrated with the O-O σ bond along the z direction. The determinants with the angular momentum of $S_z=0$ can be divided into two groups. The determinants on the left panel in which two π orbitals are half filled with opposite spins are named

as open-shell determinants (OS Det. with A_2 symmetry in C_{2v} point group). The determinants on the right side belonging to the second group are called closed-shell determinants (CS Det. with A_1 symmetry) in which two electrons occupy the same π orbital. Thus, using MSDFT, four spin-adapted configuration state functions (CSFs) of oxygen molecule in Figure 1 were constructed as followed,

$$|\Psi[T_0^{os}]\rangle = N_{T_0}^{os} [\hat{A} \{ \phi_{\pi_x}^1 \phi_{\pi_y}^{-1} \} - \hat{A} \{ \phi_{\pi_x}^{-1} \phi_{\pi_y}^1 \}] \quad (S1a)$$

$$|\Psi[S_1^{os}]\rangle = N_{S_1}^{os} [\hat{A} \{ \phi_{\pi_x}^1 \phi_{\pi_y}^{-1} \} + \hat{A} \{ \phi_{\pi_x}^{-1} \phi_{\pi_y}^1 \}] \quad (S1b)$$

$$|\Psi[S_1^{cs}]\rangle = N_{S_1}^{cs} [\hat{A} \{ \phi_{\pi_x}^2 \phi_{\pi_y}^0 \} - \hat{A} \{ \phi_{\pi_x}^0 \phi_{\pi_y}^2 \}] \quad (S1c)$$

$$|\Psi[S_2^{cs}]\rangle = N_{S_2}^{cs} [\hat{A} \{ \phi_{\pi_x}^2 \phi_{\pi_y}^0 \} + \hat{A} \{ \phi_{\pi_x}^0 \phi_{\pi_y}^2 \}] \quad (S1d)$$

where $N_{T_0}^{os}$, $N_{S_1}^{os}$, $N_{S_1}^{cs}$, and $N_{S_2}^{cs}$ are normalization factors, and \hat{A} is the anti-symmetric operator, the subscripts π_x^* and π_y^* denote anti-bonded π orbitals along x and y directions, and the superscripts 1 and -1 refer to the single occupations by an electron with α and β spin, respectively.

In Figure 2, π_x^* and π_y^* denote the oxygen orbitals and π_{AN} and π_{AN}^* are the bonded and anti-bonded π orbitals located on anthracene, for the final state, the oxygen π_x^* orbital mixes with the anthracene's π orbital while the oxygen π_y^* orbital does not change. Based on MSDFT, the initial diabatic states were constructed by the combination of open-shell and closed-shell singlet oxygen with the AN singlet ground state wave functions, which can be simplified to $^1(OS)$ and $^1(CS)$,

$$|\Omega[^1(OS)]\rangle = N_{AN}^{os} [\hat{A} \{ \phi_{\pi_x}^1 \phi_{\pi_y}^{-1} \phi_{\pi_{AN}}^2 \} + \hat{A} \{ \phi_{\pi_x}^{-1} \phi_{\pi_y}^1 \phi_{\pi_{AN}}^2 \}] \quad (S2a)$$

$$|\Omega[^1(CS)]\rangle = N_{AN1}^{cs} [\hat{A} \{ \phi_{\pi_x}^2 \phi_{\pi_y}^0 \phi_{\pi_{AN}}^2 \}] + N_{AN2}^{cs} [\hat{A} \{ \phi_{\pi_x}^0 \phi_{\pi_y}^2 \phi_{\pi_{AN}}^2 \}] \quad (S2b)$$

another diabatic state with charge transfer between oxygen and AN, $^1(CT)$, was defined to introduce electron delocalization to the final product state,

$$\begin{aligned}
|\Omega[{}^1(CT)]\rangle &= N_{AN1}^{CT} \left[\hat{A} \left\{ \phi_{O_2^+}^1 \phi_{AN^-}^{-1} \right\} + \hat{A} \left\{ \phi_{O_2^+}^{-1} \phi_{AN^-}^1 \right\} \right] + N_{AN2}^{CT} \left[\hat{A} \left\{ \phi_{O_2^-}^1 \phi_{AN^+}^{-1} \right\} + \hat{A} \left\{ \phi_{O_2^-}^{-1} \phi_{AN^+}^1 \right\} \right] \\
&\quad (S2c)
\end{aligned}$$

In equations S2, the subscripts 0 and 2 denote the number of occupied electrons and 1 and -1 means an electron with α and β spin, respectively.

In Figure 3, π_{CM} and π_{CM}^* are the bonded and anti-bonded π orbitals located on carotenoid. Similar to above cycloaddition reaction in equation S2, two degenerate diabatic initial states, ${}^1(S_1^{OS}S_0^{CM})$ and ${}^1(S_1^{CS}S_0^{CM})$, were constructed as follows:

$$|\Omega[{}^1(S_1^{OS}S_0^{CM})]\rangle = N_{CM}^{OS} \left[\hat{A} \left\{ \phi_{\pi_x^*}^1 \phi_{\pi_y^*}^{-1} \phi_{\pi_{CM}}^2 \right\} + \hat{A} \left\{ \phi_{\pi_x^*}^{-1} \phi_{\pi_y^*}^1 \phi_{\pi_{CM}}^2 \right\} \right] \quad (S3a)$$

$$|\Omega[{}^1(S_1^{CS}S_0^{CM})]\rangle = N_{CM1}^{CS} \left[\hat{A} \left\{ \phi_{\pi_x^*}^2 \phi_{\pi_y^*}^0 \phi_{\pi_{CM}}^2 \right\} \right] + N_{CM2}^{CS} \left[\hat{A} \left\{ \phi_{\pi_x^*}^0 \phi_{\pi_y^*}^2 \phi_{\pi_{CM}}^2 \right\} \right] \quad (S3b)$$

The final diabatic state is the combination of two triplet states and there are 6 possible determinants in $S_z=0$ space. The combination of these determinants can generate 6 spin-adapted configurations (1 quintet, 3 triplets and 2 singlets), only the lowest spin-adapted singlet configurations contributed importantly to the singlet oxygen energy transfer pathway. To this end, the final state configuration ${}^1(T_0^{OS}T_1^{CM})$ was constructed as

$$|\Omega[{}^1(T_0^{OS}T_1^{CM})]\rangle = N_{CM}^{TT} \left[\Psi(T_1 T_{-1}) + \Psi(T_{-1} T_1) + \Psi(T_0 T_0) \right] \quad (3c)$$

where the subscripts 1, 0 and -1 indicate the component of spin angular momentum of $\alpha\alpha$, $\alpha\beta$ and $\beta\beta$, respectively, and basis determinants are

$$|\Psi(T_1 T_{-1})\rangle = \hat{A} \left\{ \phi_{\pi_x^*}^1 \phi_{\pi_y^*}^1 \phi_{\pi_{CM}}^{-1} \phi_{\pi_{CM}^*}^{-1} \right\} \quad (3c-1)$$

$$|\Psi(T_{-1} T_1)\rangle = \hat{A} \left\{ \phi_{\pi_x^*}^{-1} \phi_{\pi_y^*}^{-1} \phi_{\pi_{CM}}^1 \phi_{\pi_{CM}^*}^1 \right\} \quad (3c-2)$$

$$\begin{aligned}
|\Psi(T_0 T_0)\rangle &= N_1 \left[\hat{A} \left\{ \phi_{\pi_x^*}^{-1} \phi_{\pi_y^*}^1 \phi_{\pi_{CM}}^{-1} \phi_{\pi_{CM}^*}^1 \right\} - \hat{A} \left\{ \phi_{\pi_x^*}^1 \phi_{\pi_y^*}^{-1} \phi_{\pi_{CM}}^{-1} \phi_{\pi_{CM}^*}^1 \right\} \right] + N_2 \left[\hat{A} \left\{ \phi_{\pi_x^*}^{-1} \phi_{\pi_y^*}^1 \phi_{\pi_{CM}}^1 \phi_{\pi_{CM}^*}^1 \right\} \right] \\
&\quad (3c-3)
\end{aligned}$$

where the super- and sub- scripts have the same meanings with the previous definition in equation S2.

In the case of $S_z = 0$, there are four determinants that could form four electronic states

with one triplet state and three singlet states as shown in Figure S1. The triplet state with $S_z = 0$ is characterized as the combination of two open shell determinants,

$$\Psi^T(|1,0\rangle) = \frac{\sqrt{2}}{2}(\Psi_{12}^{OS} - \Psi_{12}^{OS}) \quad (\text{S4})$$

On the other hand, in triplet state with $S_z = 1$, there is only one determinant, $\Psi^T(|1,0\rangle) = \Psi_{12}^T$, and MSDFT reduces to KS-DFT. Because $T_0^{OS} = E^T(|1,0\rangle) = E^T(|1,1\rangle)$, the coupling in MSDFT between two open shell determinants can be rigorous defined as,

$$E_{OS}^{TDF} = T_0^{OS} - E_{12}^{OS} \quad (\text{S5})$$

However, an exact expression for the coupling between two close-shell determinants (Ψ_{11}^{CS} and Ψ_{22}^{CS}) is not available. Thus, we introduce the following scaling factor to approximately define this coupling,

$$\frac{E_{CS}^{HF} + \Delta V^{HF} + E_{OS}^{HF}}{(H_{11}^{CS} + H_{22}^{CS})/2 - H_{12}^{OS}} = \frac{E_{CS}^{TDF} + \Delta V^{DFT} + E_{OS}^{TDF}}{(E_{11}^{CS} + E_{22}^{CS})/2 - E_{12}^{OS}} = k \quad (\text{S6})$$

where the superscript ‘HF’ denote the energies are computed using WFT, and H_{11}^{CS} , H_{22}^{CS} and H_{12}^{OS} are the determinant wave function energies using Kohn-Sham orbitals. ΔV^{DFT} (or ΔV^{HF}) describes the energy splitting between two nondegenerate close-shell determinants that could be exactly obtained from the 2×2 secular equation. As shown in Figure S1, this scaling factor restricts the energy splitting between two close-shell and open-shell determinants obtained from MSDFT to the CASSCF one. Thus, the coupling between close-shell determinants can be expressed as,

$$E_{CS}^{TDF} = k[(E_{11}^{CS} + E_{22}^{CS})/2 - E_{12}^{OS}] - \Delta V^{DFT} - E_{OS}^{TDF} \quad (\text{S7})$$

Obviously, when $k = 1$, two singlet states that are obtained from two open-shell and close-shell determinants, respectively, are degenerate, such as oxygen molecule, in this case, equation (S7) is well defined for the coupling between two close-shell determinants.

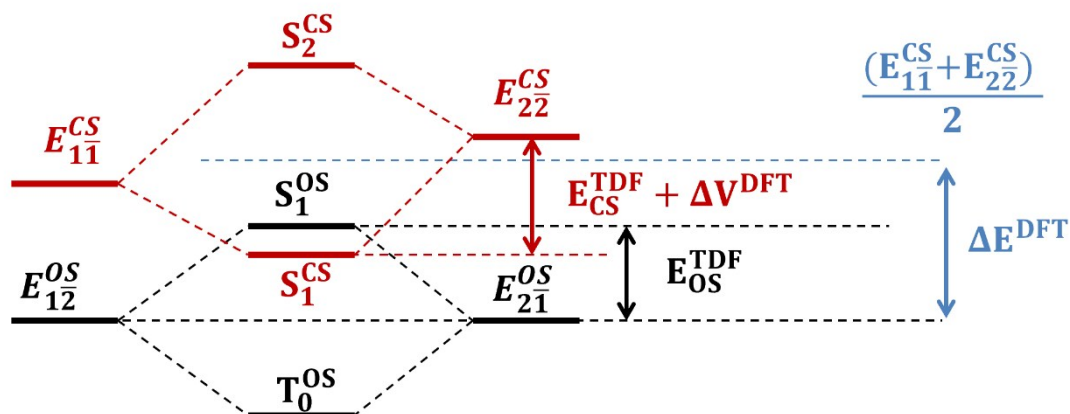


Figure S1: The electronic couplings and energy splitting for the determinants with $S_z = 0$ in a minimal active space, (2,2). E_{CS}^{TDF} and E_{OS}^{TDF} are the couplings between two close-shell determinants and two open-shell determinants, respectively. E_{12}^{OS} , E_{11}^{CS} , E_{21}^{OS} and E_{22}^{CS} , are the configuration energies of each determinant.

Equations S5, S6 and S7 are used to compute the diabatic couplings in MSDFT. Based on these equations. Equation S5 is introduced to give a correct energy degeneracy of the three components in triplet state. Equations S6 and S7 suggest that the coupling between two closed-shell configurations is inversely proportional to the one of two open-shell configurations. Thus, for oxygen molecule, the stronger coupling term of the closed-shell diabatic states means that the coupling term from the open-shell diabatic states will be weak. For the real cases, the initial and final diabatic states are constructed by the wavefunctions of both oxygen and substrate, although the couplings are affected by the overlap of substrate wavefunction, the inversely-proportional relationship according to equation S6 and S7 could be approximately conserved, but the amplitudes of these couplings are still needed to be computed using diabatic wavefunctions

Supporting Table S1

Table S1: The absolute energies (in a.u.) for the low-lying states of oxygen molecules computed using CASSCF(2,2), CASSCF(12,8), MRCI(2,2), MRCI(12,8) and MSDFT at cc-pVTZ level. The M06-HF functional is used for MSDFT calculation. All calculations were computed using the same geometry with $R(\text{O-O})=1.208 \text{ \AA}$.

	$^3\Sigma_g^-$	$^1\Delta_g(A_2)$	$^1\Delta_g(A_1)$	$^1\Sigma_g^+$

MSDFT	-150.33609981	-150.29304805	-150.29304805	-150.27381953
CASSCF(2,2)	-149.65212250	-149.60527531	-149.60527531	-149.55842812
MRCI(2,2)	-150.07686050	-150.03708426	-150.03631495	-150.00625799
CASSCF(12,8)	-149.75701363	-149.72173039	-149.72173039	-149.70209105
MRCI(12,8)	-150.10256167	-150.06656401	-150.06614959	-150.04266721

Supporting Figures S2 - S5

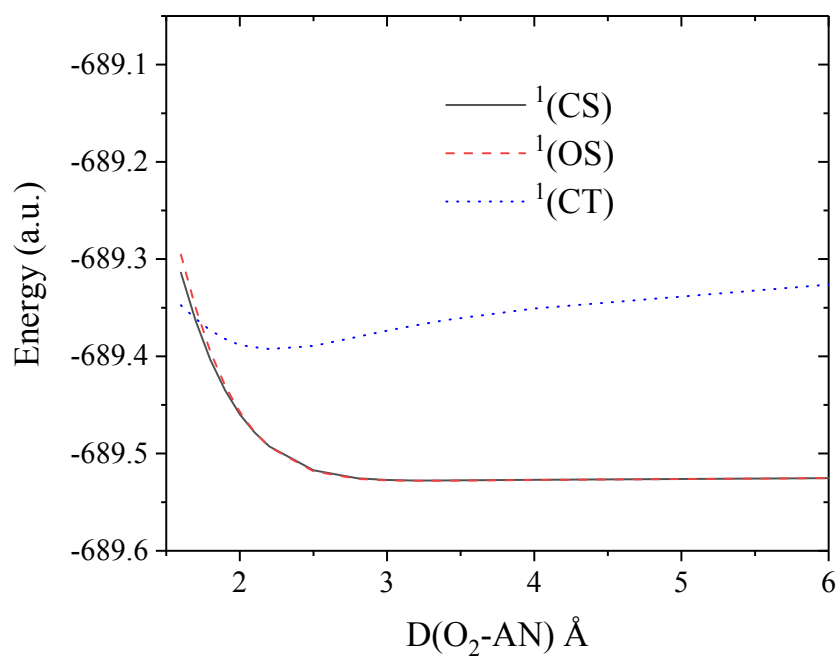


Figure S2: The diabatic potential energy curves (in a.u.) for $^1(\text{CS})$, $^1(\text{OS})$ and $^1(\text{CT})$ as a function of $\text{O}_2\text{-AN}$ distance.

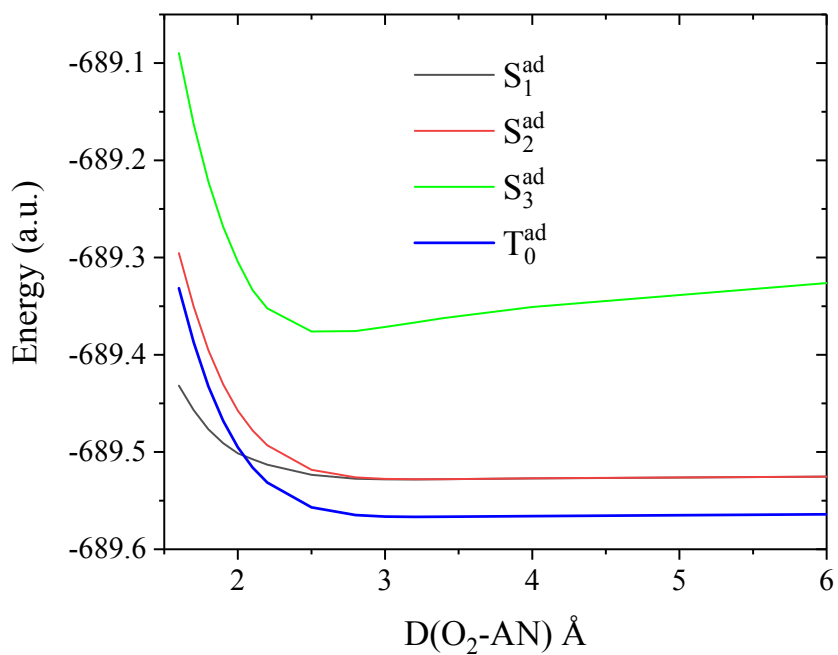


Figure S3: The potential energy curves (in a.u.) for the adiabatic states of S_1^{ad} , S_2^{ad} , S_3^{ad} and T_0^{ad} as a function of $\text{O}_2\text{-AN}$ distance.

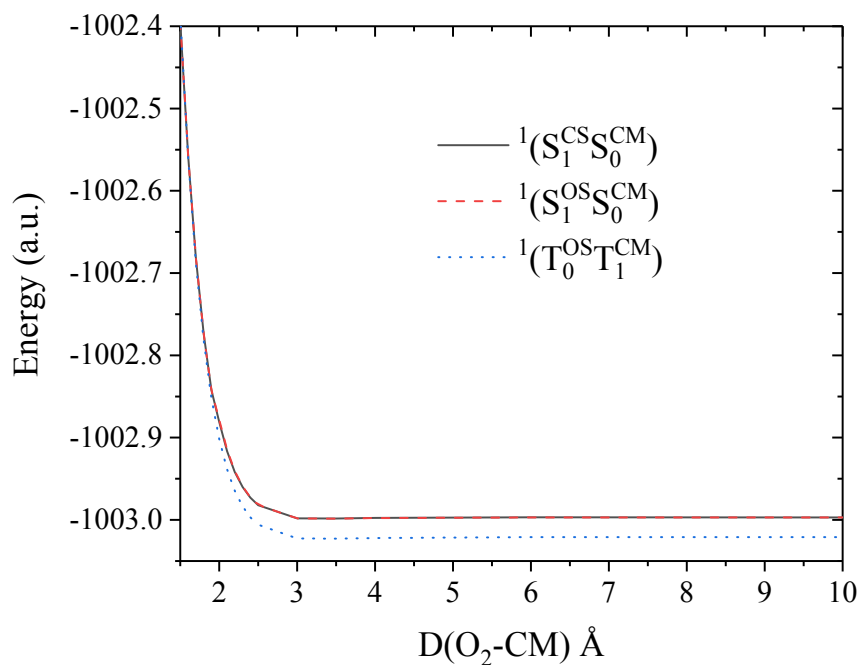


Figure S4: The diabatic potential energy curves (in a.u.) for ${}^1(S_1^{\text{CS}}S_0^{\text{CM}})$, ${}^1(S_1^{\text{OS}}S_0^{\text{CM}})$ and ${}^1(T_0^{\text{OS}}T_1^{\text{CM}})$ as a function of $\text{O}_2\text{-CM}$ distance.

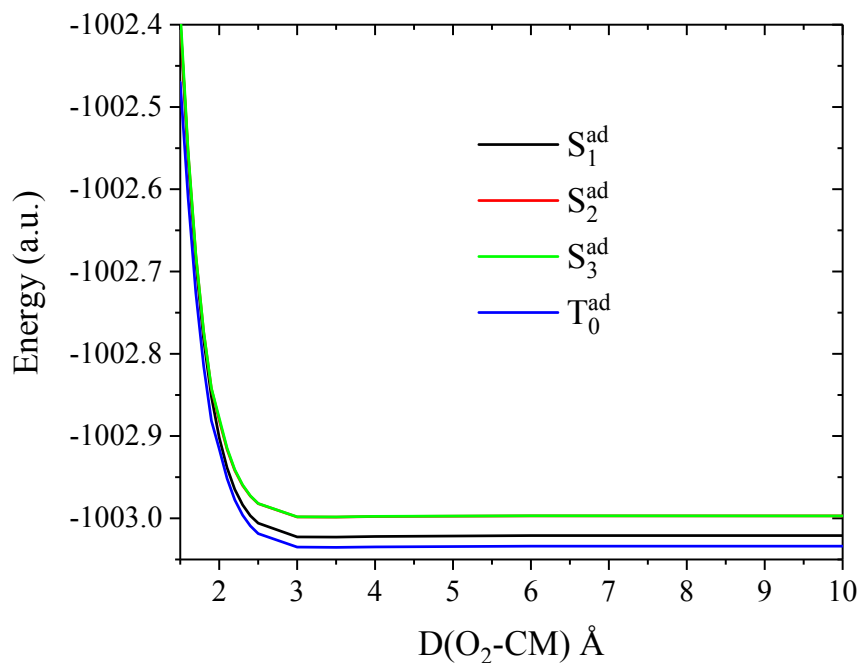


Figure S5: The potential energy curves (in a.u.) for the adiabatic states of S_1^{ad} , S_2^{ad} , S_3^{ad} and T_0^{ad} as a function of $\text{O}_2\text{-CM}$ distance

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