Supplementary Information: Formation and Stabilization of Ground and Excited State Singlet $O_2$ upon Recombination of $^{3}P$ Oxygen on Amorphous Solid Water

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S1 Methods

The simulation system consists of an equilibrated cubic box of amorphous solid water with dimension $31 \times 31 \times 31 \, \text{Å}^3$ containing 1000 TIP3P water molecules, and two oxygen atoms, see Figure 1. The time step in all simulations was $\Delta t = 0.1 \, \text{fs}$ which ensures conservation of total energy also during the recombination dynamics. All bonds involving hydrogen atoms were constrained using SHAKE$^2$ and the non-bonded cutoff was at 13 Å. Initial conditions were generated from an existing, equilibrated ASW structure$^{3,4}$ by adding two oxygen atoms, minimizing the system, heating it for 5 ps to 50 K and equilibrating for 10 ps. Data (energies, coordinates and velocities) are saved every 1,000 steps. This was followed by production simulations of various lengths, as indicated throughout this work.
All simulations are performed using the CHARMM program\textsuperscript{5} modified for reactive MD simulations\textsuperscript{6,7} and potential energy surfaces for O\textsubscript{2} based on reproducing kernels.\textsuperscript{8,9} For treating nonadiabatic transitions a surface hopping scheme based on the Landau Zener formalism is used, see below. Three electronic states for O\textsubscript{2} are considered: the ground state (\(X^3\Sigma^-\)) and the next two electronically excited states (\(a^1\Delta_g\) and \(b^1\Sigma^+_g\)) based on earlier calculations at the MRCI/aug-cc-pVTZ level of theory\textsuperscript{10} which were accurately represented as a reproducing kernel Hilbert space (see Figure S2a).\textsuperscript{8,9} The spin orbit coupling (SOC) matrix elements involving the \(3\Sigma^-_g\) and \(1\Sigma^+_g\) states were recomputed at the MRCI/aug-cc-pVTZ level of theory and can be compared with previous works at the CI/cc-pVTZ\textsuperscript{11} and CASSCF/CASPT2/5s4p3d2f atomic natural orbital basis set\textsuperscript{12} levels of theory, see Figure S2b. Because the \(a^1\Delta_g\) and the \(b^1\Sigma^+_g\) states do not cross (see inset Figure S2) and the nonadiabatic coupling (NAC) matrix element between the two states is zero, transitions between these two states will not be included.

In the gas phase all transitions between the \(3\Sigma^-_g\), \(1\Delta_g\) and \(1\Sigma^+_g\) states are strictly forbidden. Transitions from the ground state to the two excited states are spin-forbidden\textsuperscript{13} and Laporte rule,\textsuperscript{14} because all states have \(g\) symmetry. Due to the second rule, transitions between \(a^1\Delta_g\) and \(b^1\Sigma^+_g\) are also forbidden. However, because the reaction occurs on the ASW surface, no symmetry rules apply for allowed transitions. This is similar to the fact that \(Q\)–branches for diatomics in liquids and high pressure fluids become allowed due to symmetry breaking induced by the environment,\textsuperscript{15} whereas such \(\Delta J = 0\) transitions are forbidden in free space.\textsuperscript{16}

For the nonadiabatic transitions the trajectory surface hopping (TSH) method\textsuperscript{17} within the Landau-Zener (LZ)\textsuperscript{18,19} formalism was used. The implementation follows earlier work\textsuperscript{20,21} for which the transition probability \(P_{LZ}^{i\rightarrow k}\) from state \(j\) to \(k\) is

\[
P_{LZ}^{i\rightarrow k} = \exp \left( -\frac{2\pi}{\hbar} \left( \frac{(\Delta H_{jk})^2}{\nabla(\Delta E_{jk})} \right) \right) 
\]  

(S1)
The transition probability depends on the gradient of the energy difference $\vec{\nabla}(\Delta E_{jk})$ between states $j$ and $k$, the coupling $\Delta H_{jk}$, which is the conformationally dependent spin orbit matrix element, and the velocity of the center of mass $\dot{\vec{R}}$ at the transition.

The trajectories are started from a given initial electronic state $j$ and the electronic state is followed along the trajectory. Close to a crossing between the present state $j$ and a neighboring state $k$, $P_{LZ}^{j\rightarrow k}$ is calculated and compared with a random number $\xi \in [0, 1]$. If $P_{LZ}^{j\rightarrow k} \geq \xi$ a transition from state $j$ to state $k$ occurs. To ensure conservation of the total energy and total angular momentum, a momentum correction

$$p' = p - \frac{\hat{n}M^{-1}p}{\hat{n}M^{-1}\hat{n}} \left[ 1 - \left( 1 - 2\Delta E \frac{\hat{n}M^{-1}\hat{n}}{(\hat{n}M^{-1}p)^2} \right)^{1/2} \right],$$  \hspace{1cm} (S2)$$

is applied\textsuperscript{22} where $p$ and $p'$ are the momenta before and after the hop and $M$ is the mass matrix and $\hat{n}$ is the unit vector along the velocity direction.

In order to assess the role of quantum effects on the nuclear dynamics, time-dependent wave packet (WP) simulations were carried out for the two state model (see below), including the $X^3\Sigma_g^-$ and $b^1\Sigma_g^+$ states. For this, the time-dependent Schrödinger equation is\textsuperscript{23–25}

$$\begin{pmatrix} \psi_1(r; t) \\ \psi_2(r; t) \end{pmatrix} = e^{-iHt/\hbar} \begin{pmatrix} \psi_1(r; 0) \\ \psi_2(r; 0) \end{pmatrix}$$  \hspace{1cm} (S3)$$

where the Hamiltonian $H$ is

$$\hat{H} = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} + \begin{pmatrix} V_{11}(r) & V_{12}(r) \\ V_{21}(r) & V_{22}(r) \end{pmatrix}$$  \hspace{1cm} (S4)$$

where $\mu$ is the reduced mass of the system, $V_{11}$, $V_{22}$ are the diabatic potential energies and $V_{12} = V_{21}$ is the geometry-dependent coupling matrix element between two states.
The initial wave packet is a (complex-valued) Gaussian function

$$
\psi_0(r) = (1/2\pi\sigma^2)^{1/4} \exp[-1/(2\sigma^2)(r - r_0)^2] \exp[ip_0(r - r_0)], \quad (S5)
$$

where $\sigma$ is the width parameter, $r_0$ and $p_0$ are the initial position and momentum of the wavepacket, respectively. The time-dependent wave function is propagated on the coupled $X^3\Sigma_g^+$ and $b^1\Sigma_g^+$ potentials using the split-operator method. Fast Fourier transformation (FFT) is used to calculate the double differentiation $\frac{\partial^2}{\partial r^2}$ of the wave function. A sine damping function is multiplied to the wave function at the grid boundary to avoid reflection. The state population can then be calculated as the expectation value of the projection operator

$$
P_2(t) = \left\langle \begin{pmatrix} \psi_1(x; t) \\ \psi_2(x; t) \end{pmatrix} \left| \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \right| \begin{pmatrix} \psi_1(x; t) \\ \psi_2(x; t) \end{pmatrix} \right\rangle \quad (S6)
$$

and $P_1(t) = 1 - P_2(t)$. 


Figure S1: Top panel: Time evolution of the interatomic distance between two oxygen atoms for the simulation inside the cavity. The first time that the bound state is reached, at 103.5 ps, it suddenly dissociates due the collision of the molecule with one of the TIP3P hydrogen water. A similar situation happens near the formation time (around 670 ps). Both are shown in the graph by a blue star. Bottom panel: kinetic energy for the dioxygen system. The bound state can be recognized by the peak in kinetic energy at 103.5 ps and at 670 ps (shown with a blue star). The transition between $^1\Sigma^+_g$ and $^3\Sigma^+_g$ is observed between 720 ps and 750 ps and is characterized by the $\sim$40 kcal/mol energy increase. This energy corresponds to the energy difference between the two states. A color code here is applied in order to distinguish the three different states: the green line represents the unbound state, the red one the time interval where the triplet region is explored and the black is used when O$_2$ lays in the singlet state.
Figure S2: Panel A: Potential energy curves for the $X^3\Sigma_g^-$, $a^1\Delta_g$ and the $b^1\Sigma_g^+$ states (black, red and green, respectively) with the crossing region enlarged in the inset. Panel B: SOC between the $^3\Sigma_g^-$ and $^1\Sigma_g^+$ states from the literature (blue\textsuperscript{11} and violet\textsuperscript{12}) and the SOC calculated in the present work (orange). The differences can be explained by the difference in methodologies and basis set between used in the different calculations. Asymptotically, the SOC approaches twice the value of O $^3P$, which is 74.182 cm\textsuperscript{-1} for a single oxygen atom in its ground state.
Figure S3: Probability distribution for $\tau_c$. The average is $47.4 \pm 11.7$ fs. This corresponds to approximately one transition every two vibrational periods.
Figure S4: Relaxation of the O$_2$ bond length during two independent 8 ns simulation with the two states models for two simulations. Transitions are observed only in the initial steps of the simulations corresponding to the overlap between the time series and the crossing point between the two states (2.209 Å, red line). The green line represents the moving average of the time series over 0.2 ps time interval. The signatures between 4 ns and 4.5 ns are collisional re-excitation of the diatomic due to collisions with the surface.
Figure S5: Probability distributions of the interatomic distance within the transition between the $a^1\Delta_g$ and the $X^3\Sigma_g^-$ (B), $b^3\Sigma_g^-$ and the $X^3\Sigma_g^-$ (A) for an ensemble of simulations. In the first case the interval is localized around $2.097 \pm 0.003$ Å and in the second case around $2.209 \pm 0.003$ Å.
Figure S6: The time distribution for the three $\tau_{LZ}$ for the O$_2$ recombination from b$^3\Sigma_g^-$, in red simulations that from the initial $X^3\Sigma_g^-$ state leads to final $b^1\Sigma_g^+$ state, in green simulations that have $X^3\Sigma_g^-$ as initial and final state. The black line is the sum of the two previous sets.
Figure S7: Computed spin orbit coupling between $X^3\Sigma_g^-$ and $a^1\Delta_g$. The function is discontinuous, with values different from 0, only in the crossing regions. The two atoms are in the $^3P$ state.
Figure S8: State dynamics for four different simulations during the $\tau_{LZ}$ interval. All simulations start from the $X^3\Sigma_g^-$ state (red dot).

Figure S9: Population on each state as a function of time.
Figure S10: Fourier transform of the initial wave packet on $X^3\Sigma_g^-$ state as a function of energy. The initial wave packet is a Gaussian function defined in Eq. 5 and $g(k) = \frac{\sqrt{2\pi}}{(2\pi)^{1/4}}\exp[-\sigma^2(k-p_0)^2]\exp(ir_0k)$, where, $k = \sqrt{2\mu E}$ and $p_0 = \sqrt{2\mu E_0}$.

Figure S11: Kinetic model for multiple crossing. Left: 2-state model, right: 3-state model. Here, $k$s are the probabilities for the transition from one state to another.
References


