

Supplementary Information for

Production of Singlet Oxygen by the Reaction of Non-Basic Hydrogen Peroxide with Chlorine Gas

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CONTENTS

Measurement of the yield of O ₂ (¹ Δ) by spontaneous Raman scattering method	S2
Methods for estimating [HO ₂ ⁻] and PH Value in H ₂ O ₂ solutions	S4
Figure S1. Interference of Cl ₂ fluorescence with SRS spectrum in nBHP-2 experiment	S8
Figure S2. Interference of Cl ₂ fluorescence with SRS spectrum in nBHP-3 experiment	S8
Figure S3. Interference of Cl ₂ fluorescence with SRS spectrum in nBHP-4 experiment	S9
Figure S4. Cl ₂ fluorescence-eliminated SRS spectrum in nBHP-4 experiment	S9
Gaussian Calculations	S10
References	S11

Measurement of the Yield of O₂(¹Δ) by spontaneous Raman scattering method

The yield of O₂(¹Δ), Y_Δ, is defined as the fraction of O₂(¹Δ) in total O₂ gas,

$$Y_{\Delta} = \frac{[\text{O}_2(^1\Delta)]}{[\text{O}_2(^1\Delta)] + [\text{O}_2(^3\Sigma)]} \quad (1)$$

where [O₂(¹Δ)] and [O₂(³Σ)] denote the concentration of singlet oxygen and ground state oxygen respectively. In 1998, Gyls *et al.*^{1,2} developed a spontaneous Raman scattering (SRS) method for the measurement of the yield of O₂(¹Δ). The principle is as follows. When an O₂(¹Δ) gas flow is excited by a laser beam, the produced SRS intensities of O₂(¹Δ) and O₂(³Σ), I_{RΔ} and I_{RΣ}, can be expressed as

$$\begin{aligned} I_{R\Delta} &= \sigma_{\Delta} \cdot [\text{O}_2(^1\Delta)] \cdot I \\ I_{R\Sigma} &= \sigma_{\Sigma} \cdot [\text{O}_2(^3\Sigma)] \cdot I \end{aligned} \quad (2)$$

where σ_Δ and σ_Σ denote the Raman cross-section of O₂(¹Δ) and O₂(³Σ) respectively (the subscript Δ and Σ hereinafter are referred to O₂(¹Δ) and O₂(³Σ) respectively), and I is the laser intensity. According to Eqs.(1)-(2), the final formula used to calculate the yield of O₂(¹Δ) can be written as

$$Y_{\Delta} = \frac{I_{R\Delta}}{I_{R\Delta} + (\sigma_{\Delta}/\sigma_{\Sigma})I_{R\Sigma}} = \frac{I_{R\Delta}}{I_{R\Delta} + \theta \cdot I_{R\Sigma}} \quad (3)$$

where the Raman cross-sectional ratio θ=σ_Δ/σ_Σ, and has been measured to be 0.45–0.03 at 527 nm (frequency-doubled YLF laser),² and is expected to be close to that at 532 nm (frequency-doubled YAG laser) because of the closeness of the wavelengths.

Obviously, according to Eq.(3) the relative error of Y_Δ can be expressed as

$$\left| \frac{dY_{\Delta}}{Y_{\Delta}} \right| = (1 - Y_{\Delta}) \cdot \left[\left| \frac{d\theta}{\theta} \right| + \left| \frac{dI_{R\Delta}}{I_{R\Delta}} \right| + \left| \frac{dI_{R\Sigma}}{I_{R\Sigma}} \right| \right] \quad (4)$$

In practice, the I_{RΔ} and I_{RΣ} in Eq.(3) were replaced respectively by the peak areas of O₂(¹Δ) and O₂(³Σ) in a SRS spectrum, and the $\left| \frac{dI_{R\Delta}}{I_{R\Delta}} \right|$ and $\left| \frac{dI_{R\Sigma}}{I_{R\Sigma}} \right|$, the relative errors of I_{RΔ} and I_{RΣ} in Eq.(4) were replaced respectively by the reciprocals of the signal-to-noise

ratios of $O_2(^1\Delta)$ and $O_2(^3\Sigma)$ in a SRS spectrum.

However, as shown in Figures S1-S3, the SRS of $O_2(^1\Delta)$ and $O_2(^3\Sigma)$ is often interfered with the fluorescence of residual Cl_2 resulted from the incomplete reaction of Cl_2 with H_2O_2 , and the yield of $O_2(^1\Delta)$ can not directly be calculated out by Eq.(3). The method for eliminating fluorescence interference from SRS spectrum has been proposed by Wolga³ in 1978 and is as follows. A polarizer is inserted between the sample and the spectrograph. When the polarization directions of the laser and the polarizer are parallel (//) to each other, the total light intensity detected, $I_{t//}$, is

$$I_{t//} = I_{R//} + I_{F//} \quad (5a)$$

and when perpendicular (^), the total light intensity detected becomes $I_{t\perp}$ (note that the acquisition times for $I_{t//}$ and $I_{t\perp}$ are strictly equal),

$$I_{t\perp} = I_{R\perp} + I_{F\perp} \quad (5b)$$

In Eq.(5), I_R and I_F are the intensity of SRS and fluorescence respectively. Given the fact that Raman radiation is always strongly polarized while fluorescence is essentially non-polarized and $I_{F//} = I_{F\perp}$ in a gaseous medium, the fluorescence will be eliminated from the SRS spectrum and Eq.(6) be obtained when Eq.(5a) is subtracted by Eq.(5b).

$$I_{t//} - I_{t\perp} = I_{R//} - I_{R\perp} \quad (6)$$

Basing on the above Wolga's method,³ we further suggested⁴ that the total intensity of Raman scattering, I_R , be expressed as

$$I_R = I_{R//} + I_{R\perp} = \frac{(1+\rho)}{(1-\rho)}(I_{t//} - I_{t\perp}) \quad (7)$$

where $\rho = I_{R\perp}/I_{R//}$, is depolarization ratio, and Eq.(3) is then changed as follows

$$Y_{\Delta} = \frac{(I_{t//} - I_{t\perp})_{\Delta}}{(I_{t//} - I_{t\perp})_{\Delta} + \theta' \cdot (I_{t//} - I_{t\perp})_{\Sigma}} \quad (8)$$

$$\theta' = \frac{1+\rho_{\Sigma}}{1-\rho_{\Sigma}} \left(\frac{1+\rho_{\Delta}}{1-\rho_{\Delta}} \right)^{-1} \cdot \theta$$

In Eq.(7) the values of ρ_{Σ} and ρ_{Δ} have been estimated by us⁴ to be $\rho_{\Sigma}=0.067$ and $\rho_{\Delta}=0.05$, and then $\theta' = 0.47$, very close to the value of θ (0.45) used in Eqs.(3-4). Therefore, Eqs.(3-4) still hold for the fluorescence-eliminated SRS spectrum except that the I_R term is needed to be substituted by the $(I_{\parallel} - I_{\perp})$.

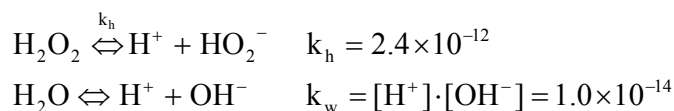
In BHP (KO₂H) and nBHP-1 (C₅H₅N) experiments in which the fluorescence of residual Cl₂ had not yet obviously interfere with the SRS spectrum of O₂(¹Δ) and O₂(³Σ) (see A and B in Figure 1), the yield of O₂(¹Δ) and its relative error were directly calculated out by Eqs.(3-4). While in nBHP-2 (CH₃COONH₄), nBHP-3 (HCOONH₄) and nBHP-4 (NH₄F) experiments in which the SRS spectrum of O₂(¹Δ) and O₂(³Σ) had been overwhelmed by the fluorescence of residual Cl₂ (see Figures S1-S3), $(I_{\parallel} - I_{\perp})$, the fluorescence-eliminated SRS intensity is first obtained and then Eqs.(3-4) are applied.

However, it should be pointed out that even with the use of Wolga's method, the SRS spectrum for nBHP-4 could not anyway be separated from the Cl₂ fluorescence background (see Figure S3-S4) due to the low Cl₂+(nBHP-4) reaction efficiency, hence the yield of O₂(¹Δ) was unable to be measured in the case of nBHP-4.

Methods for estimating [HO₂⁻] and PH Value in H₂O₂ Solutions

In this section, all the dissociation constants of acids are cited from Ref. [5].

Basic Hydrogen Peroxide (BHP) Solution. The acid-base equilibriums are



The equation of charge conservation may be written as

$$[\text{H}^+] + [\text{K}^+] = [\text{HO}_2^-] + \text{OH}^- \quad (9.1)$$

The [K⁺] should equal C_{KO₂H}, the initial concentration of KO₂H (6.6M here).

$$[\text{K}^+] = C_{\text{KO}_2\text{H}} \quad (9.2)$$

$[\text{HO}_2^-]$ can be expressed as

$$[\text{HO}_2^-] = \alpha_{\text{HO}_2^-} \times (C_{\text{H}_2\text{O}_2} + C_{\text{KO}_2\text{H}}) \quad (9.3)$$

where $C_{\text{H}_2\text{O}_2}$ is the initial concentration of H_2O_2 (2.4M here), $(C_{\text{H}_2\text{O}_2} + C_{\text{KO}_2\text{H}})$ represents the apparent concentration of H_2O_2 , i.e. the total concentration of H_2O_2 in all forms, and $\alpha_{\text{HO}_2^-}$ is the fraction of HO_2^- in total H_2O_2 , and can be expressed as

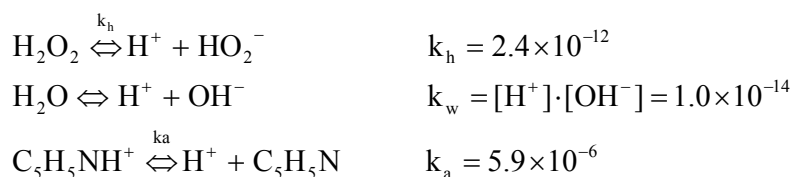
$$\alpha_{\text{HO}_2^-} = \frac{[\text{HO}_2^-]}{C_{\text{H}_2\text{O}_2} + C_{\text{KO}_2\text{H}}} = \frac{k_h}{k_h + [\text{H}^+]} \quad (9.4)$$

The water ionic product is a constant (1.0×10^{-14} at 25°C) as

$$[\text{H}^+] \cdot [\text{OH}^-] = k_w \quad (9.5)$$

$[\text{H}^+]$, $[\text{K}^+]$, $\alpha_{\text{HO}_2^-}$, $[\text{HO}_2^-]$, and $[\text{OH}^-]$ can be solved out from Eqs.(9.1-9.5), and then the PH value, $-\log([\text{H}^+])$, can be obtained.

C₅H₅N - Dissolved Hydrogen Peroxide Solution. The acid-base equilibriums are



The proton balance equation can be written as

$$[\text{H}^+] + [\text{C}_5\text{H}_5\text{NH}^+] = [\text{HO}_2^-] + \text{OH}^- \quad (10.1)$$

And it is evident that

$$[\text{C}_5\text{H}_5\text{NH}^+] = \alpha_{\text{C}_5\text{H}_5\text{NH}^+} \times C_{\text{C}_5\text{H}_5\text{N}} \quad (10.2)$$

$$\alpha_{\text{C}_5\text{H}_5\text{NH}^+} = \frac{[\text{C}_5\text{H}_5\text{NH}^+]}{C_{\text{C}_5\text{H}_5\text{N}}} = \frac{[\text{H}^+]}{k_a + [\text{H}^+]} \quad (10.3)$$

$$[\text{HO}_2^-] = \alpha_{\text{HO}_2^-} \times C_{\text{H}_2\text{O}_2} \quad (10.4)$$

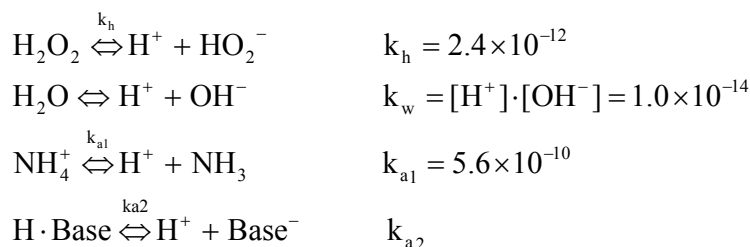
$$\alpha_{\text{HO}_2^-} = \frac{[\text{HO}_2^-]}{C_{\text{H}_2\text{O}_2}} = \frac{k_h}{k_h + [\text{H}^+]} \quad (10.5)$$

$$[\text{H}^+] \cdot [\text{OH}^-] = k_w \quad (10.6)$$

In Eqs.(10.1-10.6), $\alpha_{\text{C}_5\text{H}_5\text{NH}^+}$ is the fraction of $\text{C}_5\text{H}_5\text{NH}^+$ in total $\text{C}_5\text{H}_5\text{N}$, $C_{\text{C}_5\text{H}_5\text{N}}$ and $C_{\text{H}_2\text{O}_2}$ are the initial concentrations of $\text{C}_5\text{H}_5\text{N}$ and H_2O_2 respectively, and are both 9.0M here. $[\text{H}^+]$, $[\text{C}_5\text{H}_5\text{NH}^+]$, $[\text{HO}_2^-]$, $[\text{OH}^-]$, $\alpha_{\text{C}_5\text{H}_5\text{NH}^+}$ and $\alpha_{\text{HO}_2^-}$ can be solved out from Eqs.(10.1-10.6), and then the PH value, $-\log([\text{H}^+])$, can be obtained.

CH₃COONH₄, H₃COONH₄, and NH₄F Dissolved Hydrogen Peroxide Solutions.

The acid-base equilibriums for these solutions are



where Base^- represents CH_3COO^- , HCOO^- or F^- , and k_{a2} equals 1.75×10^{-5} (CH_3COOH), 1.8×10^{-4} (HCOOH) or 6.3×10^{-4} (HF).

The proton balance equation may be written as

$$[\text{H}^+] + [\text{H} \cdot \text{Base}] = [\text{NH}_3] + [\text{HO}_2^-] + \text{OH}^- \quad (11.1)$$

And it is evident that

$$[\text{H} \cdot \text{Base}] = \alpha_{\text{H} \cdot \text{Base}} \times C_s \quad (11.2)$$

$$\alpha_{\text{H} \cdot \text{Base}} = \frac{[\text{H} \cdot \text{Base}]}{C_s} = \frac{[\text{H}^+]}{k_{a2} + [\text{H}^+]} \quad (11.3)$$

$$[\text{NH}_3] = \alpha_{\text{NH}_3} \times C_s \quad (11.4)$$

$$\alpha_{\text{NH}_3} = \frac{[\text{NH}_3]}{C_s} = \frac{k_{a1}}{k_{a1} + [\text{H}^+]} \quad (11.5)$$

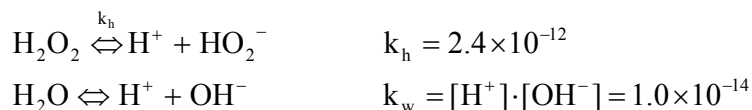
$$[\text{HO}_2^-] = \alpha_{\text{HO}_2^-} \times C_{\text{H}_2\text{O}_2} \quad (11.6)$$

$$\alpha_{\text{HO}_2^-} = \frac{[\text{HO}_2^-]}{C_{\text{H}_2\text{O}_2}} = \frac{k_h}{k_h + [\text{H}^+]} \quad (11.7)$$

$$[\text{H}^+] \cdot [\text{OH}^-] = k_w \quad (11.8)$$

In Eqs.(11.1-11.8), $\alpha_{\text{H-Base}}$ is the fraction of H-Base^- in total Base^- , C_S is the initial concentration of the salt $\text{CH}_3\text{COONH}_4$, H_3COONH_4 , or NH_4F (9.0M here). $[\text{H}^+]$, $[\text{H} \cdot \text{Base}]$, $[\text{NH}_3]$, $[\text{HO}_2^-]$, $[\text{OH}^-]$, $\alpha_{\text{H-Base}}$, α_{NH_3} and $\alpha_{\text{HO}_2^-}$ can be solved out from Eqs.(11.1-11.8), and then the PH value, $-\log([\text{H}^+])$, can be obtained.

$\text{H}_2\text{O}_2 - \text{H}_2\text{O}$ System. The $\text{H}_2\text{O}_2 - \text{H}_2\text{O}$ system consists of H_2O_2 and H_2O only, and the acid-base equilibriums are



And evidently,

$$[\text{H}^+] = [\text{HO}_2^-] + [\text{OH}^-] \quad (\text{The proton balance equation}) \quad (12.1)$$

$$[\text{HO}_2^-] = \alpha_{\text{HO}_2^-} \times C_{\text{H}_2\text{O}_2} \quad (12.2)$$

$$\alpha_{\text{HO}_2^-} = \frac{[\text{HO}_2^-]}{C_{\text{H}_2\text{O}_2}} = \frac{k_h}{k_h + [\text{H}^+]} \quad (12.3)$$

$$[\text{H}^+] \cdot [\text{OH}^-] = k_w \quad (12.4)$$

From Eqs.(12.1-12.4), $[\text{H}^+]$, $[\text{HO}_2^-]$, $[\text{OH}^-]$ and $\alpha_{\text{HO}_2^-}$ can be solved out, and then the PH value, $-\log([\text{H}^+])$, can be obtained.

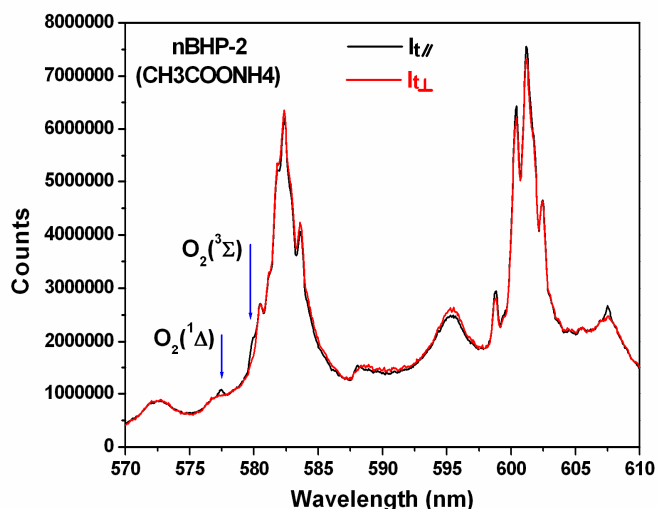


Figure S1. Interference of Cl₂ fluorescence with SRS spectrum in nBHP-2 experiment. Where $I_{t//}$ and $I_{t\perp}$ is the spectrum obtained when the polarization directions of the laser and the polarizer are parallel ($//$) and perpendicular (\perp) to each other respectively, and the expected peak positions of the Raman scattering of O₂(¹Δ) and O₂(³Σ) are indicated by the arrows.

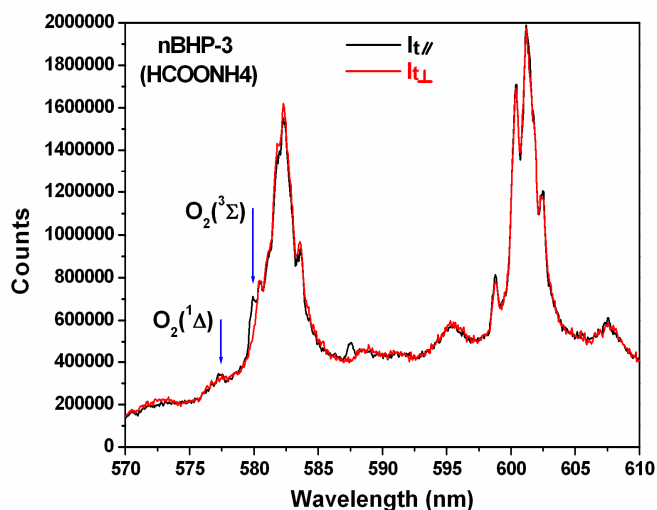


Figure S2. Interference of Cl₂ fluorescence with SRS spectrum in nBHP-3 experiment. Where $I_{t//}$ and $I_{t\perp}$ is the spectrum obtained when the polarization directions of the laser and the polarizer are parallel ($//$) and perpendicular (\perp) to each other respectively, and the expected peak positions of the Raman scattering of O₂(¹Δ) and O₂(³Σ) are indicated by the arrows.

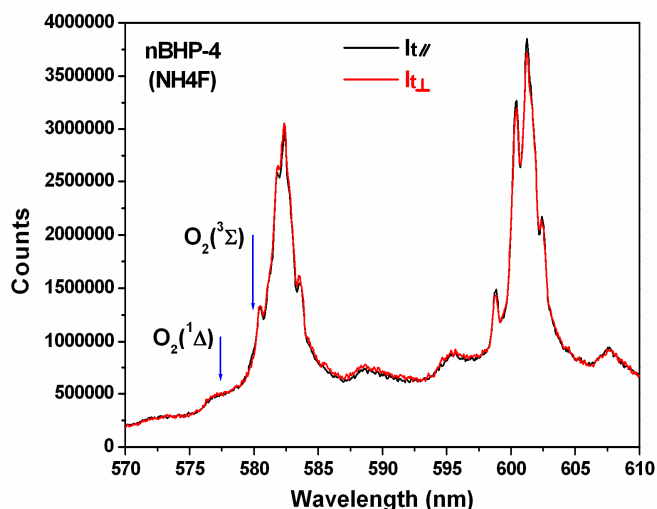


Figure S3. Interference of Cl_2 fluorescence with SRS spectrum in nBHP-4 experiment. Where I_{\parallel} and I_{\perp} is the spectrum obtained when the polarization directions of the laser and the polarizer are parallel (\parallel) and perpendicular (\perp) to each other respectively, and the expected peak positions of the Raman scattering of $O_2(^1\Delta)$ and $O_2(^3\Sigma)$ are indicated by the arrows.

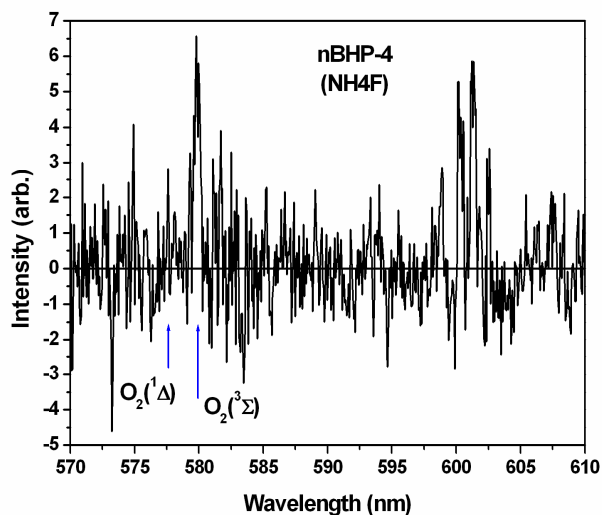


Figure S4. Cl_2 fluorescence-eliminated SRS spectrum in nBHP-4 experiment, separated from Figure S4. Where the Raman scattering of $O_2(^1\Delta)$ and $O_2(^3\Sigma)$ is too weak to be distinguished out of the noise, and the expected peak positions of the Raman scattering of $O_2(^1\Delta)$ and $O_2(^3\Sigma)$ are indicated by the arrows.

Gaussian Calculations

Gaussian calculations were performed by using Gaussian03 program.⁶ The Route Section input parameter is “#opt freq b3lyp/6-31+g(d,p) scrf=(solvent=water) geom=connectivity”, and the Spin multiplicity is “1”. The input geometries for the calculated species are listed in Table 1S. The resulted optimized geometries and the charge distributions for HOOH, Cl-Cl, [HOOH...Cl-Cl] and [HOO⁻-Cl-Cl] are shown in Figure 4.

Table 1S. The input geometries and the energy results from the calculations

Species	Input geometry	Energy results (Hartree-Fork)
Cl ₂	Cl B1 1.98000000 Cl 1 B1	-920.3543376
HOH	O B1 0.95840000 H 1 B1 B2 0.96000000 H 1 B2 2 A1 A1 104.45000000	-76.4484363
HOOH	O B1 0.96000000 A2 100.00000000 H 1 B1 B2 1.48000000 D1 111.50000000 O 1 B2 2 A1 B3 0.96000000 H 3 B3 1 A2 2 D1 A1 100.00000000	-151.579444
[HOH Cl- Cl]	O B1 0.96000000 A2 110.11775945 H 1 B1 B2 0.96000000 A3 110.11775945 H 1 B2 2 A1 B3 1.65000000 D1 -120.45367159 Cl 1 B3 2 A2 3 D1 B4 3.63000000 D2 -120.45367159 Cl 1 B4 2 A3 3 D2 A1 109.50000006	-996.8082014
[HOOH Cl- Cl]	O B1 0.99505392 A2 101.14597691 H 1 B1 B2 1.45054355 A3 110.00880127 O 1 B2 2 A1 B3 0.99260790 A4 110.75285873 H 3 B3 1 A2 2 D1 B4 2.53531358 D1 111.02684643 Cl 1 B4 3 A3 4 D2 B5 4.62081074 D2 -138.43057729 Cl 1 B5 3 A4 4 D3 A1 101.83784163 D3 -138.21874323	-1071.937958
[HOO ⁻ - Cl Cl]	O B1 1.46009246 A2 105.46689451 O 1 B1 B2 0.98662074 A3 105.46689451 H 2 B2 1 A1 B3 1.65000000 D1 121.55171848 Cl 1 B3 2 A2 3 D1 B4 3.63000000 D2 121.55171848 Cl 1 B4 2 A3 3 D2 A1 100.17403771	-1071.5031257

Based on the energy results listed in Table 1S, the interaction energy between H₂O and Cl₂, $E_{\text{H}_2\text{O}-\text{Cl}_2}$, and the interaction energy between H₂O₂ and Cl₂, $E_{\text{H}_2\text{O}_2-\text{Cl}_2}$, can be calculated out as follows.

$$E_{\text{H}_2\text{O}-\text{Cl}_2} = E_{\text{H}_2\text{O}} + E_{\text{Cl}_2} - E_{[\text{HOH}\cdots\text{Cl}-\text{Cl}]^*} = 3.4 \text{ kcal/mol}$$

$$E_{\text{H}_2\text{O}_2-\text{Cl}_2} = E_{\text{H}_2\text{O}_2} + E_{\text{Cl}_2} - E_{[\text{HOOH}\cdots\text{Cl}-\text{Cl}]^*} = 2.6 \text{ kcal/mol}$$

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