Supplementary Information for

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

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S1
Measurement of the Yield of $O_2(1^\Delta)$ by spontaneous Raman scattering method

The yield of $O_2(1^\Delta)$, $Y_\Delta$, is defined as the fraction of $O_2(1^\Delta)$ in total $O_2$ gas,

$$Y_\Delta = \frac{[O_2(1^\Delta)]}{[O_2(1^\Delta)]+[O_2(3^{3}\Sigma)]}.$$

where $[O_2(1^\Delta)]$ and $[O_2(3^{3}\Sigma)]$ denote the concentration of singlet oxygen and ground state oxygen respectively. In 1998, Gylys et al.\textsuperscript{1,2} developed a spontaneous Raman scattering (SRS) method for the measurement of the yield of $O_2(1^\Delta)$. The principal is as follows.

When an $O_2(1^\Delta)$ gas flow is excited by a laser beam, the produced SRS intensities of $O_2(1^\Delta)$ and $O_2(3^{3}\Sigma)$, $I_{RA}$ and $I_{RE}$, can be expressed as

$$I_{RA} = \sigma_\Delta \cdot [O_2(1^\Delta)] \cdot I, \quad I_{RE} = \sigma_\Sigma \cdot [O_2(3^{3}\Sigma)] \cdot I$$

where $\sigma_\Delta$ and $\sigma_\Sigma$ denote the Raman cross-section of $O_2(1^\Delta)$ and $O_2(3^{3}\Sigma)$ respectively (the subscript $\Delta$ and $\Sigma$ hereinafter are referred to $O_2(1^\Delta)$ and $O_2(3^{3}\Sigma)$ respectively), and $I$ is the laser intensity. According to Eqs.(1)-(2), the final formula used to calculate the yield of $O_2(1^\Delta)$ can be written as

$$Y_\Delta = \frac{I_{RA}}{I_{RA} + (\sigma_\Delta / \sigma_\Sigma)I_{RE}} = \frac{I_{RA}}{I_{RA} + \theta \cdot I_{RE}}$$

where the Raman cross-sectional ratio $\theta = \sigma_\Delta / \sigma_\Sigma$, and has been measured to be $0.45 \pm 0.03$ at 527 nm (frequency-doubled YLF laser),\textsuperscript{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 $Y_\Delta$ can be expressed as

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

In practice, the $I_{RA}$ and $I_{RE}$ in Eq.(3) were replaced respectively by the peak areas of $O_2(1^\Delta)$ and $O_2(3^{3}\Sigma)$ in a SRS spectrum, and the $\left| \frac{dI_{RA}}{I_{RA}} \right|$ and $\left| \frac{dI_{RE}}{I_{RE}} \right|$, the relative errors of $I_{RA}$ and $I_{RE}$ 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$_2$O$_2$, 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 Wolga\(^3\) 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, \(I_{//}\), is

\[ I_{//} = I_{R//} + I_{F//} \]  

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

\[ I_{\perp} = I_{R\perp} + I_{F\perp} \]  

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).

\[ I_{//} - I_{\perp} = I_{R//} - I_{R\perp} \]  

Basing on the above Wolga’s method\(^3\), we further suggested\(^4\) that the total intensity of Raman scattering, \(I_R\), be expressed as

\[ I_R = I_{R//} + I_{R\perp} = \frac{(1 + \rho)}{(1 - \rho)} (I_{//} - I_{\perp}) \]  

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

\[ Y_{\Delta} = \frac{(I_{//} - I_{\perp})_{\Delta}}{(I_{//} - I_{\perp})_{\Delta} + \theta' \cdot (I_{//} - I_{\perp})_{\Sigma}} \]

\[ \theta' = \frac{1 + \rho_{\Sigma} \left( 1 + \rho_{\Delta} \right)^{-1}}{1 - \rho_{\Sigma} \left( 1 - \rho_{\Delta} \right)} \cdot \theta \]
In Eq.(7) the values of $\rho_\Sigma$ and $\rho_\Delta$ have been estimated by us \(^4\) to be $\rho_\Sigma=0.067$ and $\rho_\Delta=0.05$, and then $\theta'=0.47$, very close to the value of $\theta$ (0.45) used in Eqs.(3-4). Therefore, Eqs.(3-4) still hold for the fluorescence-eliminated SRS spectrum except that the $I_\parallel$ term is needed to be substituted by the $(I_\parallel-I_\perp)$.

In BHP (KO\(_2\)H) and nBHP-1 (C\(_3\)H\(_5\)N) experiments in which the fluorescence of residual Cl\(_2\) had not yet obviously interfere with the SRS spectrum of O\(_2\)(\(^1\Delta\)) and O\(_2\)(\(^3\Sigma\)) (see A and B in Figure 1), the yield of O\(_2\)(\(^1\Delta\)) and its relative error were directly calculated out by Eqs.(3-4). While in nBHP-2 (CH\(_3\)COONH\(_4\)), nBHP-3 (HCOONH\(_4\)) and nBHP-4 (NH\(_4\)F) experiments in which the SRS spectrum of O\(_2\)(\(^1\Delta\)) and O\(_2\)(\(^3\Sigma\)) had been overwhelmed by the fluorescence of residual Cl\(_2\) (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 Cl\(_2\) fluorescence background (see Figure S3-S4) due to the low Cl\(_2\)+(nBHP-4) reaction efficiency, hence the yield of O\(_2\)(\(^1\Delta\)) was unable to be measured in the case of nBHP-4.

**Methods for estimating [HO\(_2\)^−] and PH Value in H\(_2\)O\(_2\) 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

\[
\begin{align*}
\text{H}_2\text{O}_2 & \rightleftharpoons \text{H}^+ + \text{HO}_2^- \\
\text{H}_2\text{O} & \rightleftharpoons \text{H}^+ + \text{OH}^- \\
\end{align*}
\]

The reaction rate is $k_h = 2.4 \times 10^{-12}$

The equation of charge conservation may be written as

\[
[H^+] + [K^+] = [\text{HO}_2^-] + \text{OH}^- \tag{9.1}
\]

The $[K^+]$ should equal $C_{\text{KO}_2\text{H}}$, the initial concentration of KO\(_2\)H (6.6M here).

\[
[K^+] = C_{\text{KO}_2\text{H}} \tag{9.2}
\]
[\text{HO}_2^-] \text{ can be expressed as}

\begin{equation}
[\text{HO}_2^-] = \alpha_{\text{HO}_2^-} \times (C_{\text{H}_2\text{O}_2} + C_{\text{K}_2\text{O}_2\text{H}})
\end{equation}

(9.3)

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

\begin{equation}
\alpha_{\text{HO}_2^-} = \frac{[\text{HO}_2^-]}{C_{\text{H}_2\text{O}_2} + C_{\text{K}_2\text{O}_2\text{H}}} = \frac{k_h}{k_h + [\text{H}^+]} 
\end{equation}

(9.4)

The water ionic product is a constant \((1.0 \times 10^{-14} \text{ at } 25^\circ\text{C})\) as

\begin{equation}
[\text{H}^+] \times [\text{OH}^-] = k_w 
\end{equation}

(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.

\text{C}_3\text{H}_5\text{N} - \text{Dissolved Hydrogen Peroxide Solution.} The acid-base equilibriums are

\begin{align*}
\text{H}_2\text{O}_2 & \rightleftharpoons \text{H}^+ + \text{HO}_2^- & k_h = 2.4 \times 10^{-12} \\
\text{H}_2\text{O} & \rightleftharpoons \text{H}^+ + \text{OH}^- & k_w = [\text{H}^+] \times [\text{OH}^-] = 1.0 \times 10^{-14} \\
\text{C}_3\text{H}_5\text{NH}^+ & \rightleftharpoons \text{H}^+ + \text{C}_3\text{H}_5\text{N} & k_a = 5.9 \times 10^{-6}
\end{align*}

The proton balance equation can be written as

\begin{equation}
[\text{H}^+] + [\text{C}_3\text{H}_5\text{NH}^+] = [\text{HO}_2^-] + \text{OH}^- 
\end{equation}

(10.1)

And it is evident that

\begin{align*}
[\text{C}_3\text{H}_5\text{NH}^+] &= \alpha_{\text{C}_3\text{H}_5\text{NH}^+} \times C_{\text{C}_3\text{H}_5\text{N}} \\
\alpha_{\text{C}_3\text{H}_5\text{NH}^+} &= \frac{[\text{C}_3\text{H}_5\text{NH}^+]}{C_{\text{C}_3\text{H}_5\text{N}}} = \frac{[\text{H}^+]}{k_a + [\text{H}^+]} \\
[\text{HO}_2^-] &= \alpha_{\text{HO}_2^-} \times C_{\text{H}_2\text{O}_2} \\
\alpha_{\text{HO}_2^-} &= \frac{[\text{HO}_2^-]}{C_{\text{H}_2\text{O}_2}} = \frac{k_h}{k_h + [\text{H}^+]} 
\end{align*}

(10.2-10.5)
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 $\text{C}_5\text{H}_5\text{N}$, $\text{C}_{\text{C}_5\text{H}_5\text{N}}$ and $\text{C}_{\text{H}_2\text{O}_2}$ are the initial concentrations of $\text{C}_5\text{H}_5\text{N}$ and $\text{H}_2\text{O}_2$ 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.

**CH$_3$COONH$_4$, H$_3$COONH$_4$, and NH$_4$F Dissolved Hydrogen Peroxide Solutions.**

The acid-base equilibriums for these solutions are

\[
\begin{align*}
\text{H}_2\text{O}_2 & \rightleftharpoons \text{H}^+ + \text{HO}_2^- & k_a &= 2.4 \times 10^{-12} \\
\text{H}_2\text{O} & \rightleftharpoons \text{H}^+ + \text{OH}^- & k_w &= [\text{H}^+] \cdot [\text{OH}^-] = 1.0 \times 10^{-14} \\
\text{NH}_2^+ & \rightleftharpoons \text{H}^+ + \text{NH}_3 & k_{a1} &= 5.6 \times 10^{-10} \\
\text{H} \cdot \text{Base} & \rightleftharpoons \text{H}^+ + \text{Base}^- & k_{a2} &= \\
\end{align*}
\]

where Base$^-$ represents CH$_3$COO$^-$, HCOO$^-$ or F$^-$, and $k_{a2}$ equals $1.75 \times 10^{-5}$ (CH$_3$COOH), $1.8 \times 10^{-4}$ (HCOOH) or $6.3 \times 10^{-4}$ (HF).

The proton balance equation may be written as

\[
[\text{H}^+] + [\text{H} \cdot \text{Base}] = [\text{NH}_3] + [\text{HO}_2^-] + \text{OH}^- 
\]

(11.1)

And it is evident that

\[
[\text{H} \cdot \text{Base}] = \alpha_{\text{H} \cdot \text{Base}} \times C_S 
\]

(11.2)

\[
\alpha_{\text{H} \cdot \text{Base}} = \frac{[\text{H} \cdot \text{Base}]}{C_S} = \frac{[\text{H}^+]}{k_{a2} + [\text{H}^+]}
\]

(11.3)

\[
[\text{NH}_3] = \alpha_{\text{NH}_3} \times C_S
\]

(11.4)

\[
\alpha_{\text{NH}_3} = \frac{[\text{NH}_3]}{C_S} = \frac{k_{a1}}{k_{a1} + [\text{H}^+]}
\]

(11.5)

\[
[\text{HO}_2^-] = \alpha_{\text{HO}_2^-} \times C_{\text{H}_2\text{O}_2}
\]

(11.6)
\[ \alpha_{\text{H}_2\text{O}_2^{-}} = \frac{[\text{HO}_2^-]}{C_{\text{H}_2\text{O}_2}} = \frac{k_h}{k_h + [\text{H}^+]} \]  \hfill (11.7)

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

In Eqs.(11.1-11.8), \( \alpha_{\text{H-Base}} \) is the fraction of H\text{-Base} in total Base\(^-\), \( C_S \) is the initial concentration of the salt CH\(_3\)COONH\(_4\), H\(_3\)COONH\(_4\), or NH\(_4\)F (9.0M here). [H\(^+\)], [H\cdotBase], [NH\(_3\)], [HO\(_2^-\)], [OH\(^-\)], \( \alpha_{\text{H-Base}} \), \( \alpha_{\text{NH}_3} \) 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.

**H\(_2\)O\(_2\) - H\(_2\)O System.** The H\(_2\)O\(_2\) - H\(_2\)O system consists of H\(_2\)O\(_2\) and H\(_2\)O only, and the acid-base equilibriums are

\[ \text{H}_2\text{O}_2 \rightleftharpoons \text{H}^+ + \text{HO}_2^- \quad k_h = 2.4 \times 10^{-12} \]

\[ \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \quad k_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14} \]

And evidently,

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

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

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

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

From Eqs.(12.1-12.4), [H\(^+\)], [HO\(_2^-\)], [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 $I_{∥}$ and $I_{⊥}$ is the spectrum obtained when the polarization directions of the laser and the polarizer are parallel (∥) and perpendicular (⊥) 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 S2. Interference of Cl₂ fluorescence with SRS spectrum in nBHP-3 experiment. Where $I_{∥}$ and $I_{⊥}$ is the spectrum obtained when the polarization directions of the laser and the polarizer are parallel (∥) and perpendicular (⊥) 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 S3.** Interference of Cl₂ fluorescence with SRS spectrum in nBHP-4 experiment. Where \( I_{//} \) and \( I_{\perp} \) 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 \( O_2(^1\Delta) \) and \( O_2(^3\Sigma) \) are indicated by the arrows.

**Figure S4.** Cl₂ 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. 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]∪ and [HOO⁻−Cl◊◊◊Cl]∪ are shown in Figure 4.

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

<table>
<thead>
<tr>
<th>Species</th>
<th>Input geometry</th>
<th>Energy results (Hartree-Fork)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl₂</td>
<td>Cl Cl</td>
<td>B1 1.98000000</td>
</tr>
<tr>
<td>HOH</td>
<td>O H</td>
<td>B1 0.95840000</td>
</tr>
<tr>
<td></td>
<td>H 1 B1</td>
<td>A1 104.45000000</td>
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<tr>
<td></td>
<td>H 1 B2 2 A1</td>
<td>A2 100.00000000</td>
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<td>O H</td>
<td>B1 0.96000000</td>
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<tr>
<td></td>
<td>H 1 B1</td>
<td>A2 100.00000000</td>
</tr>
<tr>
<td></td>
<td>O 1 B2 2 A1</td>
<td>A3 110.11775945</td>
</tr>
<tr>
<td></td>
<td>H 3 B3 1 A2 2 D1</td>
<td>A4 110.11775945</td>
</tr>
<tr>
<td>[HOH◊◊◊Cl⁻⁻⁻Cl]∪</td>
<td>O H</td>
<td>B1 0.96000000</td>
</tr>
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<td></td>
<td>H 1 B1</td>
<td>A2 110.11775945</td>
</tr>
<tr>
<td></td>
<td>O 1 B2 2 A1</td>
<td>A3 110.11775945</td>
</tr>
<tr>
<td></td>
<td>H 3 B3 1 A2 2 D1</td>
<td>A4 110.11775945</td>
</tr>
<tr>
<td></td>
<td>Cl 1 B3 2 A2 3 D1</td>
<td>A5 110.11775945</td>
</tr>
<tr>
<td></td>
<td>Cl 1 B4 2 A3 3 D2</td>
<td>A6 110.11775945</td>
</tr>
<tr>
<td>[HOOH◊◊◊Cl⁻⁻⁻Cl]∪</td>
<td>O H</td>
<td>B1 0.96000000</td>
</tr>
<tr>
<td></td>
<td>H 1 B1</td>
<td>A2 110.11775945</td>
</tr>
<tr>
<td></td>
<td>O 1 B2 2 A1</td>
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<td>H 3 B3 1 A2 2 D1</td>
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<td>Cl 1 B3 2 A2 3 D1</td>
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</tr>
<tr>
<td></td>
<td>Cl 1 B4 2 A3 3 D2</td>
<td>A6 110.11775945</td>
</tr>
</tbody>
</table>

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.

$$E_{\text{H}_2\text{O}-\text{Cl}_2} = E_{\text{H}_2\text{O}} + E_{\text{Cl}_2} - E_{[\text{HOOH◊◊◊Cl}]} = 3.4 \text{ kcal/mol}$$

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


