Nature of the red emission in the chemical oxygen iodine laser system

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Intense red emission peaking at 703 nm is observed when a heated metal wire is placed downstream of an \(\text{O}_2\left(^1\Delta_u\right)\) generator used in the chemical oxygen iodine laser (COIL) system. The \(\text{O}_2\left(^1\Delta_u\right)\) is produced by bubbling \(\text{Cl}_2\) through an alkaline solution of \(\text{H}_2\text{O}_2\). Evidence is presented that strong red emission requires the presence of both \(\text{O}_2\left(^1\Delta_u\right)\) and \(\text{Cl}_2\) in contact with a heated metal surface. Several metals have been used. The red emission spectrum is independent of the metal and the intensity is strongest for copper.

1. Introduction

Beginning with the pioneering work of Kasper and Pimentel \([1]\) in 1964, there has been much interest in the production of chemical lasers, particularly those operating in the visible. Presently, the shortest-wavelength high-energy chemical laser is the chemical oxygen iodine laser (COIL), operating at 1.315 \(\mu\text{m}\) on the \(^2P_{1/2} \rightarrow ^2P_{3/2}\) transition in atomic iodine \([2,3]\). The excited iodine atoms are produced by resonant energy transfer from \(\text{O}_2\left(^1\Delta_u\right)\), which is generated by the overall reaction

\[
\text{Cl}_2(g) + \text{H}_2\text{O}_2(\ell) + 2\text{KOH}(\ell) \\
\rightarrow \text{O}_2\left(^1\Delta_u\right) + 2\text{KCl} + 2\text{H}_2\text{O}.
\]

Recently, Yoshida et al. \([4]\) reported a new visible chemical laser using a subsonic COIL system. They claimed that "so-called dimol emission of singlet oxygen could be enormously intensified" by injecting iodine vapor downstream of the \(\text{O}_2\left(^1\Delta_u\right)\) reactor. The emission was attributed to \(\text{O}_2\left(^1\Delta_u\right)\cdot\text{O}_2\left(^1\Delta_u\right) \rightarrow \text{O}_2\left(^3\Sigma_g^-, v = 0\right) + \text{O}_2\left(^3\Sigma_g^+, v = 1\right)\). A gain of 2.8\% was measured at 703 nm \([5]\). However, the red emission did not show the two characteristic bands of dimol emission at 634 and 703 nm \([6]\). Most recently, Yoshida, Tokuda and Shimizu \([7]\) have revised their assignment of the emitter to be a stable excited \(\text{O}_4\) molecule. Moreover, they report that injection of iodine is unnecessary to initiate the intense red glow. Instead, heating of the \(\text{O}_2\left(^1\Delta_u\right)\) metal inlet (Al or Cu) suffices. Stimulated by these results we have undertaken a simple study of what conditions affect the appearance and intensity of the 703 nm red emission.

2. Experimental

Fig. 1 shows the experimental apparatus. The \(\text{O}_2\left(^1\Delta_u\right)\) molecules were generated by bubbling \(\text{Cl}_2\) through a plexiglass cylinder, 150 mm in diameter and 300 mm high, containing an aqueous solution of \(\text{H}_2\text{O}_2\) and \(\text{KOH}\). For each experiment, 500 ml of 50\% \(\text{H}_2\text{O}_2\) (Fischer) was mixed with 350 ml of 50\% \(\text{KOH}\) (Fischer). The \(\text{Cl}_2\) (Matheson, 99.9\% purity) at a flow rate of 1.5 mmol s\(^{-1}\) bubbled through six plexiglass tubes (10 mm in diameter) having many small holes (0.5 mm in diameter) on their sides. During an experiment the temperature of the solution was \(-10^\circ\text{C}\) and the pressure of the gas above the generator was about 1.8 Torr. The resulting stream of gas passed through a trap cooled by dry ice and ethanol \((-78^\circ\text{C})\) to remove water vapor.

The \(\text{O}_2\left(^1\Delta_u\right)\) stream enters an optical cavity, 300
mm long by 200 mm wide by 45 mm high. The stream enters this cavity through four inlet ports (20 mm in diameter) and exists through three outlet ports (20 mm in diameter), which are pumped by two mechanical pumps. Each pump is protected by a liquid nitrogen trap, which removes residual chlorine gas. The pumping rate was about 30 l/s. Some Teflon cylinders (6 mm in diameter) were placed in the cavity to make the flow rate as uniform as possible. A metal wire in the form of a coil was placed inside the optical cavity perpendicular to the stream. This coil having 6-8 turns per cm could be resistively heated during the experiment by a dc power supply attached to a variable transformer.

Two windows (2" in diameter) are attached to the optical cavity downstream of the coil of metal wire. In addition, the body of the cavity is constructed from plexiglass, allowing direct observation from above.

3. Results and discussion

When the Cl₂ gas is allowed to flow into the O₂(1Δg) generator but the wire coil is not heated, a faint red glow fills the optical cavity. This emission is thought to be dimol emission involving the collisions between two O₂(1Δg) molecules [6]. Upon heating the wire to about 600±50°C, as measured by a thermocouple, there is a strong enhancement of the red emission. This enhancement often is short-lived, lasting only for seconds. Increased heating does not restore the emission process, and the wires cannot be successfully reused. This enhancement takes place both upstream and downstream from the heated coil. The upstream region extends only 1-2 cm, while the downstream region is 15-20 cm long.

The following metals were tried: W, Ni, stainless steel, Pt, nichrome, Cu, and tin-coated Cu. Of these, only Cu and Sn-coated Cu gave enhanced emission that lasts for as long as there is O₂(1Δg) generation. In addition, Cu and Sn-coated Cu gave the most intense emission (2000 times stronger than the background dimol emission) and could be reused. Evidently, the surfaces of the other metals become "poisoned". Different coil geometries were tried, but there is no particular distinction based on wire diameter or turns per centimeter. The results of many different runs are collected in table 1. Yoshida, Tokuda and Shimizu [7] also found that heated Cu and Al enhanced the red emission, the Cu being stronger by about a factor of ten that the Al. After the intense red glow has been initiated by heating the copper wire to 600±50°C, an increase in the temperature of the wire coil has no significant effect on the intensity of the red emission.

A low-resolution emission spectrum was recorded using an optical multichannel analyzer (PAR OMA-1205A with OMA-1205D detector) attached to a 0.25 m polychromator. A 300 mm focal length lens gathers the light through one of the windows in the optical cavity and images it on the slits of the polychromator. Fig. 2 presents the resulting spectra along with the detector response curve. This spectrum is basically identical (after correction for the
Table 1
Red emission (703 nm) under different experimental conditions. The first entry is for the gradual heating of the wire coil to 600°C during $O_2(^1\Delta_g)$ generation; the second entry is for heating of the wire coil to 600°C prior to $O_2(^1\Delta_g)$ generation.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Enhancement factor compared to dimol emission background</th>
<th>Emission duration (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>15</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>2</td>
</tr>
<tr>
<td>stainless steel</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>2</td>
</tr>
<tr>
<td>W</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>2</td>
</tr>
<tr>
<td>Pt</td>
<td>15</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>4</td>
</tr>
<tr>
<td>Nichrome *</td>
<td>25</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>5</td>
</tr>
<tr>
<td>Cu</td>
<td>100</td>
<td>no limit</td>
</tr>
<tr>
<td></td>
<td>1500</td>
<td>no limit</td>
</tr>
<tr>
<td>Sn-coated Cu</td>
<td>150</td>
<td>no limit</td>
</tr>
<tr>
<td></td>
<td>2500</td>
<td>no limit</td>
</tr>
</tbody>
</table>


We attempted to observe laser action by replacing the two windows in the optical cavity by pair of 1 m concave mirrors. These mirrors have a broad-band dielectric coating (100 nm fwhm), centered at 703 nm (99.8% reflectivity, CVI). These mirrors enclose an effective laser medium 30 cm long. The mirrors are aligned with a HeNe laser. A photomultiplier (RCA 7265) was placed in front of one of the mirrors and fitted with a red bandpass filter centered at 700 nm (20 nm fwhm). A photodiode was placed so that it viewed the red glow perpendicular to the cavity axis. Using a two-pen chart recorder, measurements were made of the photomultiplier signal referenced to the photodiode signal when the laser cavity was aligned and unaligned. No significant differences were ever recorded, which indicates that there is no lasing action.

To learn more about the identity of the emitter responsible for the 703 nm band, several experiments were carried out. First, Cl₂ gas was passed through the system but the $H_2O_2$/KOH solution was removed. No red emission is observed whether or not the coil is heated. Next, we explore whether an electrical discharge was occurring. We varied the voltage drop (0.5–1.0 V) across the heated copper coil but found no difference, provided the wire was maintained at the same temperature. We also replaced the dry ice and ethanol coldbath by a liquid nitrogen trap. This removes residual Cl₂ but does not remove the $O_2(^1\Delta_g)$, which can be detected by the faint dimol emission. Under this condition, only dimol emission appears whether or not the Cu coil is heated. We then injected some Cl₂ gas downstream from the liquid nitrogen coldtrap but upstream from the heated coil. This caused enhanced red emission. Hence, we conclude that three factors must be present for the production of the strong red emission, first reported by Yoshida et al. [4,5,7]: $O_2(^1\Delta_g)$ molecules and Cl₂ must both be in contact with the heated metal surface.

The role of the metal surface is unclear. Sharpless and Slanger [8] have investigated the quenching of $O_2(^1\Delta_g)$ on a variety of metal surfaces. They find that
the most rapid deactivation occurs with Ag and Cu, whereas W, for example, causes almost no quenching. It seems very likely that the copper surface is converted quantitatively to copper oxide. We found that the exposed surface is black in appearance. We attempted to replace the Cu coil with a flow of Cl atoms, generated by a microwave discharge, but no enhancement of the red emission was observed, again emphasizing the importance of the metal surface in initiating the formation of the emitter.

What role Cl₂ plays is also a mystery at present. It is possible that it helps to refresh the surface because of the volatility of the copper chlorides. Perhaps this explains why other metals are easily poisoned. We cannot exclude the possibility that chlorine becomes incorporated in the emitter. We replaced the injection of Cl₂ by Br₂ downstream of the liquid nitrogen cold trap. However, Br₂ quenches the red emission, indicating that Cl₂ is necessary for its observation.

If the emitter is formed only on the surface of the coil and then escapes into the gas phase, we might expect the intensity would fall off exponentially with the distance from the coil. We made a crude spatial mapping of the red emission downstream from the coil using the OMA system without the polychromator. We find at low Cl₂ partial pressures in the optical cavity a slight increase of the intensity away from the coil, followed by a slow decrease. These measurements suggest that the reaction responsible for the generation of the strong red emission does not occur exclusively on the metal surface or that some other species generated on the metal surface acts to quench the emitter.

We presently do not know the identity of the emitter but believe it does not contain a metal atom and may contain oxygen and/or chlorine. Clearly, our results demonstrate the importance of Cl₂ in the \( \text{O}_2(\Delta_g) \) feed stream, a conclusion apparently also reached by Zhuang et al. [9]. This is in contradiction to the work of Yoshida, Tokuda and Shimizu [7] who state that unreacted Cl₂ coming from the singlet oxygen generator is not related to the emission they observed.

Whatever is the identity of the emitter, it seems that surface-catalyzed reactions are responsible for initiating its creation and that the presence of Cl₂ is necessary as well as \( \text{O}_2(\Delta_g) \). We attempted to increase the partial pressure of Cl₂ by increasing the Cl₂ flow rate through the singlet oxygen generator. As the Cl₂ partial pressure increases in the optical cavity the intense red emission becomes more localized about the heated coil, suggesting that excess Cl₂ quenches the emitter.

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**References**