# Near-infrared emission in a chemically excited oxygen system

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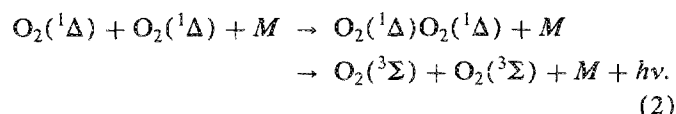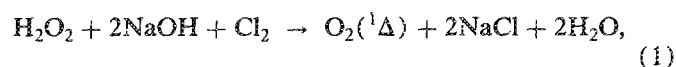# Near-infrared emission in a chemically excited oxygen system

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Near-infrared emission has been observed in a chemically generated singlet oxygen system. Spectrum peaks observed at 1090, 1275, and 1550 nm appear to correspond to $O_2(^1\Delta)O_2(^3\Sigma)$ dimer transitions to ground state accompanied by vibrational changes. The experimental result suggests that the previously observed visible emission which accompanies the present infrared emission is also due to an excited oxygen dimer. The possibility of lasing at the infrared wavelengths is discussed.

Recently we observed a new visible emission spectrum from chemically produced singlet oxygen.[1] The new spectrum interested us not only because it was new but also it showed laser gain[2] and laser oscillation like behaviors.[3] In Refs. 1–3, we assumed that the new emission was from excited oxygen dimers $O_2(^1\Delta)O_2(^1\Delta)$ produced by the following chemical reactions:

$$H_2O_2 + 2NaOH + Cl_2 \rightarrow O_2(^1\Delta) + 2NaCl + 2H_2O, \tag{1}$$

$$O_2(^1\Delta) + O_2(^1\Delta) + M \rightarrow O_2(^1\Delta)O_2(^1\Delta) + M$$
$$\rightarrow O_2(^3\Sigma) + O_2(^3\Sigma) + M + h\nu. \tag{2}$$

The biggest reason for this assumption was that the visible emission was always accompanied by near-infrared emission whose spectrum peaks seemed to correspond to already known transitions of another electronic state oxygen dimer $O_2(^1\Delta)O_2(^3\Sigma)$.[4]

$$O_2(^1\Delta)O_2(^3\Sigma) \rightarrow O_2(^3\Sigma) + O_2(^3\Sigma) + h\nu. \tag{3}$$
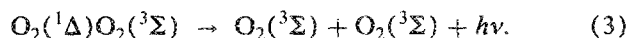
In this letter we report on the infrared emission. If the above assumption is correct, this is the first observation of chemically produced $O_2(^1\Delta)O_2(^3\Sigma)$ state oxygen dimer, to our knowledge. In addition, we observed emission from the $v = 1$ vibrational level of this electronic state, which D. L. Huestis *et al.* did not observe in their laser excited emission experiment.[4] We will further elaborate on the experimental results in this letter.

The experimental arrangement for the present investigation is described in Ref. 1. Briefly, the experimental system is made up of a flow system and a diagnostic system. The flow system is a remodeled version of our chemical oxygen iodine laser (COIL),[5] which consists of an excited oxygen generator, a water vapor trap, and a laser head. The only difference from the COIL system is that we replaced the iodine injector with an electrical heater. Empirically we know that it is essential to heat $O_2(^1\Delta)$ flow to produce the emission.[1]

The diagnostic system consists of a PbS detector with a band pass filter centered at 1270 nm, a Si detector with a band pass filter centered at 705 nm, and a data acquisition system. We used these detectors to compare the visible and infrared emissions. A monochromator was used to measure the infrared spectrum. The light passing through the monochromator was detected by another PbS detector whose output signal was transferred to a lock-in amplifier and then to a pen-recorder.

Figure 1 compares time historical intensity variations of the visible emission at 705 nm and the infrared at 1270 nm. Those wavelengths correspond to the spectrum peaks which give the maximum intensities in the respective spectral regions. We varied the intensities by adjusting operational parameters such as temperature or flow rate. The time historical traces of the two emissions are seen to be quite similar to each other. At least, peaks and valleys of both wavelengths correspond in time to each other. This suggests that the two electronic states, namely $O_2(^1\Delta)O_2(^1\Delta)$ and $O_2(^1\Delta)O_2(^3\Sigma)$, are either formed by a common catalytic process or one of the states is an intermediate product of the other. We need further investigations to conclude such possibilities.

In spite of the similarity in the time historical trace, the relation between the two signals in the intensity amplitude is not constant; in the first and third envelopes appearing in Fig. 1, the visible signal is larger than the infrared signal, whereas the situation is reversed in the second enveloped. This eliminates the possibility that what we observed by the visible and infrared detectors were different spectral regions of the same transition.

It may seem that the 1270 nm emission is due to $O_2(^1\Delta)$ monomer rather than $O_2(^1\Delta)O_2(^3\Sigma)$ dimer. But this possibility is eliminated because the intensity of 1270 nm emission observed along with the visible emission is an order of magnitude higher than the $O_2(^1\Delta)$ monomer emission we normally observe by the same detector with the same arrangement under nonheating conditions, i.e., conditions under which the visible emission is not observed. Such an increase in the 1270 nm intensity is most plausibly explained by the existence of the $O_2(^1\Delta)O_2(^3\Sigma)$ state because in the form of such a dimer, the electrical forbiddenness of the $O_2(^1\Delta)$ transition to ground state is relaxed. In fact, the observed emission spectrum suggests a vibrational structure of a stable $O_2(^1\Delta)O_2(^3\Sigma)$ dimer as discussed below.

Figure 2 shows the observed infrared emission spectrum. The three peaks appearing at 1090, 1275, and 1550 nm seem to correspond to the $O_2(^1\Delta)O_2(^3\Sigma)$ dimer transitions to ground state accompanied by the vibrational changes of $v = 1$ to $v = 0$, $v = 0$ to $v = 0$, and $v = 0$ to $v = 1$, respectively. Of these three transitions, those from the $v = 0$
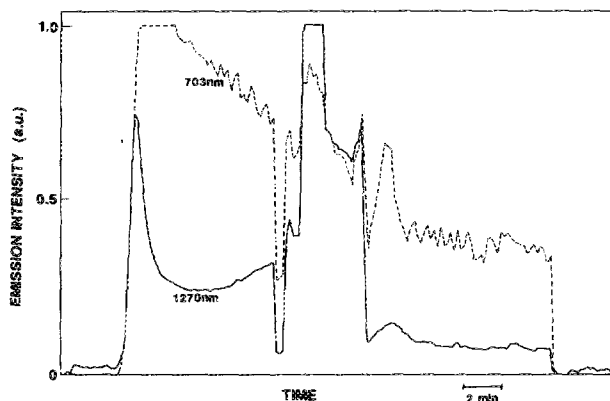
FIG. 1. Time historical traces of the infrared and visible emissions. The solid line represents the intensity at 1270 nm, while the dashed line represents that at 705 nm. The plateaus appearing at the top are due to saturation of the detectors.

upper level have previously been observed by Huestis et al.[4] in their laser excited emission experiment. They excited liquid oxygen by 1060 nm Nd:glass laser and observed the so-called cooperative emission where two oxygen molecules emit a photon in a cooperative way, resulting in the wavelength corresponding to the sum energy of the two molecules. In such a cooperative process, it is said that a short-lived Van der Waals type complex is formed.[6] In spite of that the absorption of 1060 nm can give $O_2(^1\Delta)$ in the $v=1$ state, they did not observe emission from the $v=1$ state. They have concluded that this is because the $v=1$ level of $O_2(^1\Delta)$ is rapidly quenched to the $v=0$ level by
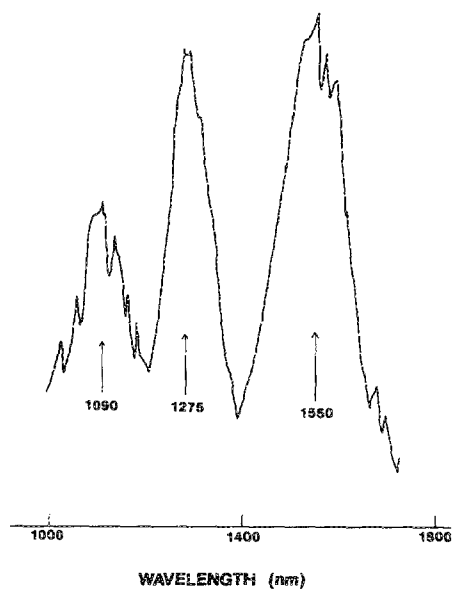


FIG. 2. Observed infrared emission spectrum.

V-V or E-E exchange with ground-state oxygen, even if the $v=1$ state is the major product of the laser excitation. Then, the fact that we observed $v=1$ to $v=0$ emission together with the $v=0$ to $v=0$ and $v=1$ transitions suggests that the emitting species in our system is different from the Van der Waals type complex, and would rather be a more stable dimer whose $v=1$ state would not be quenched so easily. Such a stable dimer seems to be formed through a three-body process. This assumption is consistent with our previous observation of the visible emission from the $O_2(^1\Delta)O_2(^1\Delta)$ state, in which we observed the dimer emission intensity had cubic dependence on the $O_2(^1\Delta)$ partial pressure.[1]

If this assumption is correct, the production rate of the dimer should be treated as a three-body collisional process rather than the two-body process as Huestis considered. The most intriguing consequence of this is that the present $O_2(^1\Delta)O_2(^3\Sigma)$ system has a chance to give reasonably high laser gain:

$$g = \frac{\lambda^2 A}{4d\omega} k[O_2]^2[M]\tau \cong 3\times 10^{-3}\,\text{cm}^{-1} \quad \text{at 1 Torr,}$$

(4)

where $g$ is the gain coefficient, $\lambda$ is the wavelength, $A$ is the Einstein's coefficient, $k$ is the three-body rate coefficient, $M$ is the third body, $\tau$ is the radiative lifetime of the upper state, and $d\omega$ is the spectral width. In this evaluation, we neglected the lower state population and all the quenching processes for the upper state, and employed a typical three-body rate coefficient of $10^{-30}$ cm$^3$/molecule s. The estimated gain coefficient is three orders of magnitude higher than Huestis's estimation at 1 Torr if the same spectral width is assumed.

In conclusion, we have observed infrared emission in a chemically excited oxygen flow. Judging from peaks of the emission spectrum, the $O_2(^1\Delta)O_2(^3\Sigma)$ dimer seems most plausible as the species responsible for the observed emission. The time historical trace of the near-infrared emission intensity is quite similar to that of the visible emission simultaneously observed in the same chemical system. These results suggest that $O_2(^1\Delta)O^2(^1\Delta)$ dimer is responsible for the visible emission as we discussed previously.[1]

We would like to thank Dr. W. E. McDermott for his helpful discussion.

[1] S. Yoshida, T. Tokuda, and K. Shimizu, Appl. Phys. Lett. 55, 2707 (1989).
[2] S. Yoshida, M. Taniwaki, T. Sawano, K. Shimizu, and T. Fujioka, Jpn. J. Appl. Phys. 28, L831 (1989).
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