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Infrared Emission Spectra of CO_2 in the Explosion Reaction of CO and O_2 Using a Rapid-Scan Spectrometer

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Synopsis. The infrared emission spectra of CO_2 were observed by means of a rapid-scan infrared spectrometer during the explosion of CO–O_2 in a cylindrical vessel. The R-branch band heads of 001-000 and 011-010 were detected. The time dependences of the emission intensities of these band heads, $\nu_1+\nu_3$, and $2\nu_2+\nu_3$, were studied.

It is well known that infrared emissions due to CO_2 are observed in a CO–air flame; past studies have been reviewed by Gaydon.1) However, there have been very few studies of the CO_2 emission spectra in the explosion of a CO–O_2 mixture by means of a rapid-scan spectrometer other than those by Bullock *et al.*2,3) As previously reported,4) we constructed a new rapid-scan spectrometer which had a better resolving power than that of Bullock. This paper will be concerned with the detailed spectra and the time dependence of each band after the explosion.

The rapid-scan infrared spectrometer was constructed by modifying a Shimadzu IRG-27 apparatus which is equipped with an oscillating mirror and a PbSe detector. The details of the optics and electronic circuits for synchronization have been described elsewhere.4) The scan time was 10 ms. The scan rate was 125 cm^{-1}/ms at 3000 cm^{-1} and 12 cm^{-1}/ms at 500 cm^{-1}. The time interval of the repetition was 20 ms. The observed resolving power was 15 cm^{-1} at 3000 cm^{-1}, with the slit width of 700 μm.

The explosion was provoked by a spark discharge. A pyrex cylindrical vessel of 70 mmϕ and 40 cm long was used for the reaction. The vessel had electrodes at one end and an optical window 12 cm away from the electrodes. The CO and O_2 were passed through a liquid nitrogen trap before they were used. The total pressure was 225—350 mmHg. All the spectra were recorded at the slit width of 500 μm.

Some typical emission spectra after the explosion are shown in Figs. 1(a) and (b). In Fig. 1(a), well-resolved R-branch band heads due to the 001-000 and 011-010 transitions are observed at 2401 and 2389 cm^{-1} respectively. The bands in the band-head region are very similar to those in the spectrum obtained in the stationary flames of CO and O_2 by Benedict.5) Two absorption bands are observed. One is the self absorption of CO_2 at around 2350 cm^{-1}, while the other is the absorption due to unreacted CO at around 2150 cm^{-1}. The band shape of CO seems very broad because the linearity of the sweeping time with the wave number is not established beyond 7.5 ms, as has been described in a previous report.4) The emission band maximum of the CO_2 fundamental seems to be at around 2280 cm^{-1} immediately after the explosion. The rise and decay of this band maximum was more rapid compared with the other bands.

As is shown in Fig. 1(b), broad emission bands at 3480 cm^{-1} and a shoulder at 3700 cm^{-1} are observed. The weak, fine structures observed of these bands are considered to be due to the absorption of the H_2O in the optical path. The 3480 cm^{-1} and 3700 cm^{-1} bands were assigned to the 021-000 and 101-000 transitions respectively. When 5 mmHg of H_2O are added, the explosion proceeds vigorously, as is well known. The emission spectra are shown in Figs. 2(a) and (b). Again, bands similar to those seen in Fig. 1 appeared, but the emission intensity of each band, especially that at 2280 cm^{-1}, were very much higher than in a dry mixture at the initial stage.

The time dependences of the combination bands and the fundamental band heads are plotted in Figs. 3 and 4. In the explosion shown in Fig. 3, the time for the flame fromt to run across the optical window was estimated to be less than 10 ms. The rise time of the emission to the peak intensity in Fig. 3 is 70—80 ms, which is much longer than the value given above, and CO was found to decrease during the emission rise. These facts suggest that the emission-rising process is caused by the combustion occurring after the flame front has passed and that the emission-decay

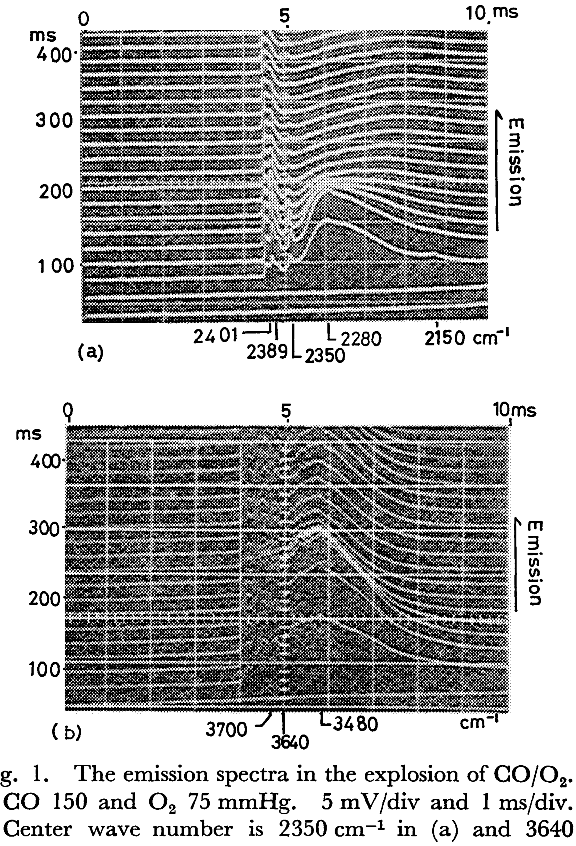

Fig. 1. The emission spectra in the explosion of CO/O_2. CO 150 and O_2 75 mmHg. 5 mV/div and 1 ms/div. Center wave number is 2350 cm^{-1} in (a) and 3640 cm^{-1} in (b). The spectra were recorded with the slit width of 300 μm in (a).

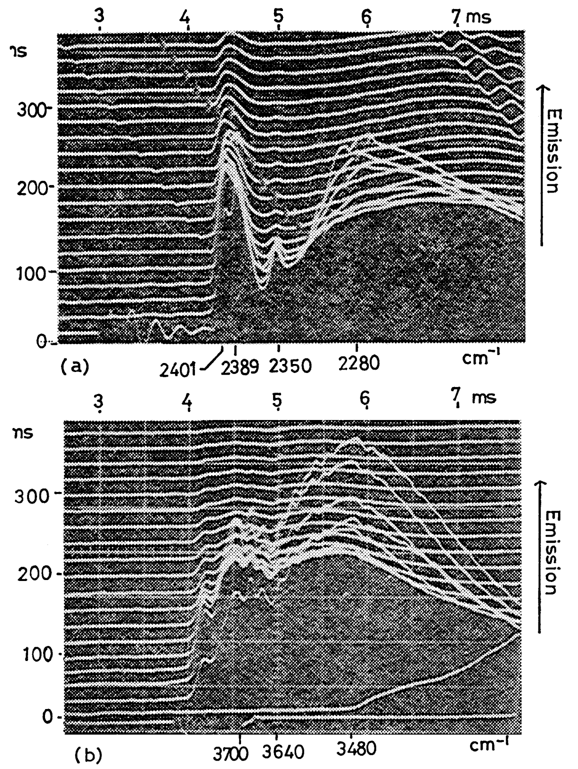

Fig. 2. The emission spectra in the explosion of $CO/O_2/H_2O$. CO 150, O_2 75 and H_2O 5 mmHg. 5 mV/div and 0.5 ms/div. The center wave number are the same as in Fig. 1.

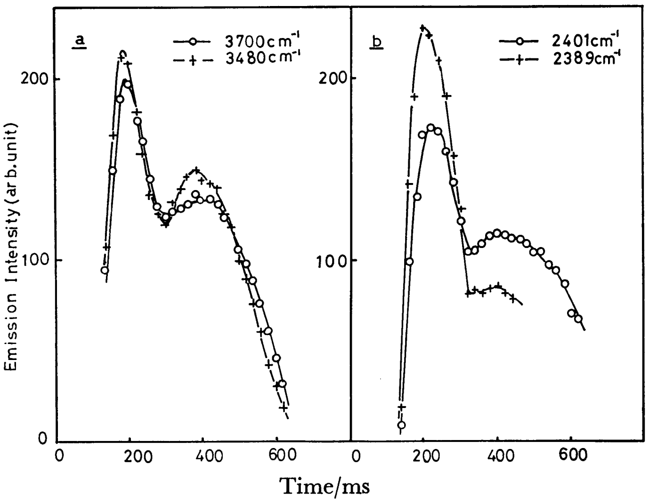

Fig. 3. Time dependence of the emission intensity in the explosion of CO/O_2.

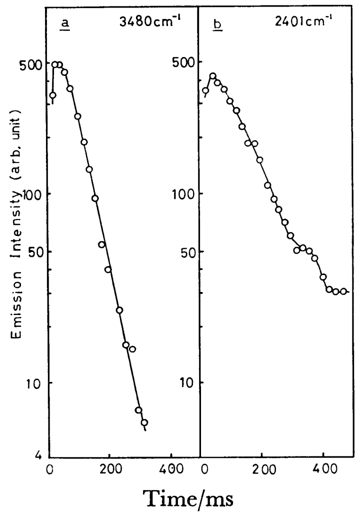

Fig. 4. Time dependence of the emission intensity in the explosion of $CO/O_2/H_2O$.

process is the cooling process. It may be seen in Fig. 3(a) that the rises and decays of the two combination bands are similar. On the other hand, in the band-head region, as is shown in Fig. 3(b), the rise times of the 001 band and the 011 band are about the same, but the decay of the 011 band is faster than that of the 001 band. Then the intensities of the two bands are reversed after 300 ms. In H_2O-added mixtures, the rise and the decay of the emission bands are considerably increased. In this case, the reversing of the intensities in the band-head region occurred early, at 60 ms, as is shown in Fig. 2(a). "Afterglows" appeared during the emission-decay process, as is shown in Fig. 3. Bullock had already observed the "afterglows," but only in the self-absorption region. However, in this experiment they were observed in the combination bands and band heads, and not in the region of the absorption or on the low-frequency side of the emission. Figure 4 indicates that the combination band decayed faster than the fundamental band head. Such differences in the decay rate were observed also when excess O_2 or N_2 was added to $CO-O_2$ stoichiometric mixtures. In the O_2-rich mixtures, the decay rates of the combination bands and the two band heads increased to about an equal extent, but when 20 mmHg of N_2 was added, only those of the band heads increased. It should be pointed out that different time dependences were observed between the two band heads and between the band heads and the combination bands in the cooling process, although the reason for this is not clear.

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References

1) A. G. Gaydon, "The Spectroscopy of Flames," Chapman and Hall, London (1974), p. 221.

2) B. W. Bullock and S. Silverman, *J. Opt. Soc. Am.*, **40**, 608 (1950).

3) B. W. Bullock, G. A. Hornbeck, and S. Silverman, *J. Chem. Phys.*, **18**, 1114 (1950).

4) M. Tanaka, S. Nagasaka, S. Sawamura, and M. Katayama, *Nippon Kagaku Kaishi*, **1978**, 1322.

5) W. S. Benedict, R. C. Herman, and S. Silverman, *J. Chem. Phys.*, **19**, 1352 (1952).