Magnetically Induced Enhancement and Quenching of the Chemiluminescence from OH Radicals [$A^2\Sigma^+ \rightarrow X^2\Pi$ (0–0)] in Hydrogen–Oxygen Flames

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Whether the chemiluminescence of OH radicals in hydrogen–oxygen flames is magnetically enhanced or quenched is found to depend on the combustion conditions, as well as the rotational quantum number (K') of the $A^2\Sigma^+$ state, and the F_1, F_2 components.

Recently, the emission intensities of such combustion reaction intermediates as OH,[1,2] HPO and SnH[3] have been found to be influenced by an external magnetic field under atmospheric pressure. The hydroxyl radical, OH, is one of the most important intermediates in combustion processes. The emission intensity from the F_1 component of the rotational levels (especially $K' = 4,5,6$) of the $A^2\Sigma^+$ state of OH was enhanced by *ca.* 30% at 1.8 T in propane–oxygen flames, while no magnetic field effect was observed for the F_2 ones.[1,2] Such magnetically induced enhancement of the emission as observed in OH has never been observed before. However, magnetically induced quenching was observed in the fluorescence of several gaseous molecules, I_2, CS_2, NO_2 and carbonyls,[4] and explained by the enhancement of the radiationless transition from the emitting state by a magnetic field. This explanation cannot be applicable to the magnetically induced enhancement of the OH emission, the lifetime of which is about 1 ns in flames.[5] We report here magnetically induced enhancement and quenching of each rovibrational band of the OH (A → X) emission in hydrogen–oxygen flames. Such a magnetic field effect on luminescence has never previously been observed.

The experimental apparatus was described in detail in our previous paper.[3] Premixed hydrogen and nitrogen were passed through the central nozzle of a quartz burner (bore diameter 6 mm), while premixed oxygen and nitrogen flowed through the outer ring (bore diameter 16 mm). The resulting laminar flame was enclosed in a quartz tube. Diffusion flames were studied instead of premixed ones because of the possibility of backfiring. The burner was set in the gap of a magnet (Nihon Komitsu Laboratory NPS 60TS). The flame chemiluminescence was measured using a monochromator (Nihon Bunko CT50) and a photon counter (AMINCO).

The spectral shapes in the OH chemiluminescence were not changed by a magnetic field below 1.4 T at the present resolution ($\delta\lambda = 0.08$ nm). Therefore, their Zeeman effects were negligibly small. The rotational structure was well resolved for some of the components, while the majority of the lines were blended. The magnetically induced change of the emission intensities of the well resolved lines was measured by changing the magnetic field strength (H) from 0 to 1.4 T. A magnetic field effect was measured for the following combustion conditions: hydrogen (1840 ml min^{-1}) flowed through the central nozzle of the quartz burner, while the premixed oxygen (1440 ml min^{-1}) and nitrogen (640 ml min^{-1}) flowed through the outer, ring condition (*a*). The emission intensity ratios (I_H/I_0), observed for the band $P_1(5)$ and $P_2(5)$ in (*a*), are plotted in Fig. 1(*a*). Here, I_H and I_0 are the emission intensities at $H = H$ and 0 T, respectively. The I_H/I_0 ratio of the $P_1(5)$ peak increased simply with increasing H, and attained a value of 1.43 ± 0.01 at 1.4 T. The peak $P_2(5)$ showed similar behaviour, though the induced increase at 1.4 T (1.13 ± 0.01) was much smaller than that for $P_1(5)$. In Fig. 2(*a*), the I_H/I_0 ratio at 1.4 T is plotted against the rotational quantum number (K') of the $A^2\Sigma^+$ state. In the

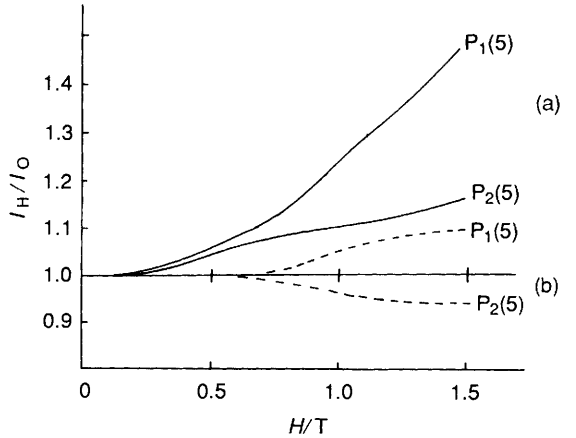

Fig. 1 Magnetic field dependence of the ratio I_H/I_0 for the peak $P_1(5)$ and $P_2(5)$. (*a*) condition (*a*), (*b*) condition (*b*)

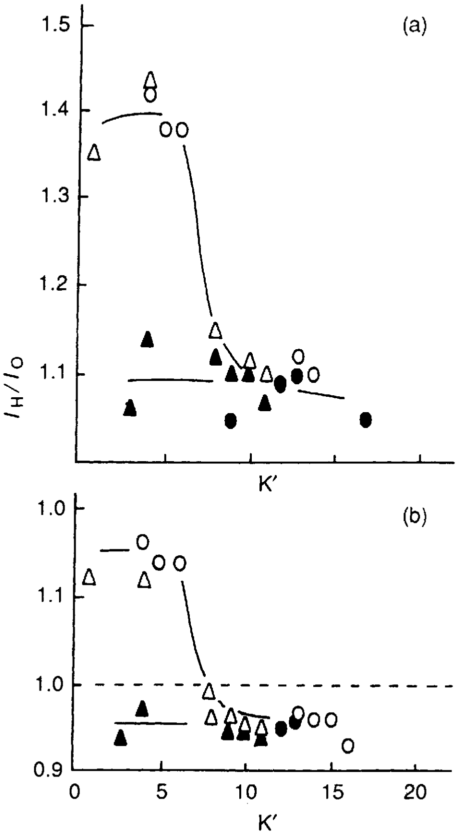

Fig. 2 Dependence of the ratio I_H/I_0 on the rotational quantum number K' of the $A^2\Sigma^+$ state observed for (*a*) condition (*a*) and (*b*) (*b*). The rotational intensities are P_1 (△), P_2 (▲), Q_1 (○) and Q_2 (●) respectively

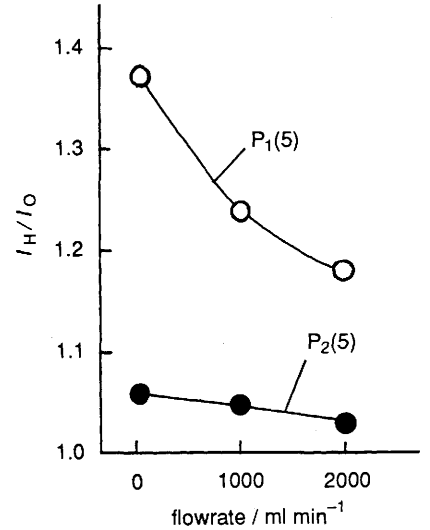

Fig. 3 Dependence of the ratio I_H/I_0 on the flow rate of nitrogen for the peaks $P_1(5)$ and $P_2(5)$

present combustion conditions, both the F_1 and F_2 components were found to increase in the presence of a magnetic field. As clearly seen in Fig. 2(*a*), large magnetic field effects on I_H/I_0 were observed for the F_1 sublevels with $I \le K' \le 6$. The I_H/I_0 ratio of the F_1 levels attained a maximum (*ca.* 1.4) around $K' = 4$, and decreased sharply at high rotational quantum numbers (about 1.1). However, the I_H/I_0 ratio of F_2 components was less sensitive to the K' number, and attained a value of 1.1.

The magnetically induced change was found to depend on the flow rates of the supplied gases. The I_H/I_0 ratio showed different behaviour in the following combustion conditions (*b*). Premixed hydrogen (1000 ml min^{-1}) and nitrogen (180 ml min^{-1}) flowed through the central nozzle, while premixed oxygen (550 ml min^{7}) and nitrogen (770 ml min^{-1}) passed through the outer ring. In Fig. 1(*b*), the I_H/I_0 ratios for the $P_1(5)$ and $P_2(5)$ bands in condition (*b*) are also plotted against H. The I_H/I_0 ratio of the $P_1(5)$ peak showed no magnetic field effect below 0.7 T beyond the experimental error (±2%), but increased at >0.7 T, attaining a value of 1.10 ± 0.02 at 1.4 T. However, the $P_2(5)$ peak showed magnetically induced quenching of the emission intensity. The I_H/I_0 ratio of this band showed no magnetic field effect below 0.6 T, and decreased >0.6 T, attaining a value of 0.94 ± 0.02 at 1.4 T. The K' dependence of the F_1 components observed in condition (*b*) was found to be similar to that observed in (*a*), although the maximum value, 1.15 T, was much smaller than that in (*a*) [Fig. 2(*b*)]. Interestingly, magnetically induced quenching was observed for the F_1 bands at high rotational numbers and for all of the F_2 bands (*ca.* 0.95).

Fig. 3 also shows the dependence of magnetically induced change ($H = 1.4$ T) on combustion conditions. Here, the flow rate of nitrogen was varied, keeping the flow rate of oxygen (2000 ml min^{-1}) and hydrogen (1000 ml min^{-1}) constant. As the flow rate of nitrogen increased from 0 to 2000 ml min^{-1}, lowering the flame temperature, the I_H/I_0 ratios of the $P_1(5)$ and $P_2(5)$ were observed to decrease.

In the present study, whether the OH emission was magnetically enhanced or quenched was found to be related in a complicated way to combustion conditions, as well as K' numbers and spin components (F_1 or F_2). This magnetic field effect shows quite different features from the magnetically induced quenching of the fluorescence of gaseous molecules. Therefore, we have to consider the possibility of a magnetic field to affect chemical reactions. The increase of H_2–O_2 reactions on the SnO_2 surface by applying a strong magnetic field[6] also suggests this mechanism. Further study will be necessary to elucidate the mechanism of this magnetic field effect.

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