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# STUDY OF CHEMILUMINESCENCE BY MEANS OF CROSSED BEAMS: NITRIC OXIDE — HYDROGEN ATOM SYSTEM

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NO-H chemiluminescence was studied by crossed molecular beams. Anomalously bright light emissions have been observed with low temperature NO beams. It is considered that the chemiluminescence is caused by the $^1A''$—$^1A'$ transition of HNO formed by the two-body collisions between NO dimers and H atoms. The apparent activation energy and the radiation cross section are estimated to be about -2.8 kcal/mole, and about $2\times10^{-18}$ cm$^2$ for 6000–8300 Å, respectively.

Cashion and Polanyi have shown that emission bands of HNO can be detected in chemiluminescence of H atoms with nitric oxide[1)]. Clement and Ramsey have studied the emission spectrum[2)]. For the emission mechanism Clyne and Thrush have proposed the apparent second order reaction involving the three-body recombination,

$$H + NO + M \longrightarrow HNO^*(^1A'') + M$$
$$HNO^*(^1A'') \longrightarrow HNO(^1A') + h\nu$$

which is analogous to that for O atoms with nitric oxide[3)]. In this paper, the chemiluminescent reaction of H atoms with nitric oxide has been studied using crossed molecular beams, which exclude the occurrence of three-body collisions. The following processes,

$$H + (NO)_2 \longrightarrow HNO^* + NO$$
$$HNO^* \longrightarrow HNO + h\nu$$

were assumed to explain the anomalously bright emission as in the case of the previous paper[4)].

## EXPERIMENTAL

The experimental apparatus as in the previous paper was used with a little improvement. H atomic beam was formed by passing $H_2$ gas through a microwave cavity (2450 MHz) and effusing from a glass tube of ca. 0.5 mm diameter and ca. 5 mm length and collimated into a beam by a slit of 0.5 mm width.

Two types of NO molecular beam sources were used. One of them was made of pyrex glass and the same as in the previous paper, and the other was made of copper metal. With both sources the beams were formed by effusing NO through a glass tube of ca. 0.5 mm diameter and ca. 5 mm length and collimated by a slit of 1 mm width. From the former source, the low temperature NO molecular beams of short duration were formed by evaporating solid NO as described previously. From the latter source, low temperature stationary beams of NO were formed. The temperature of the source

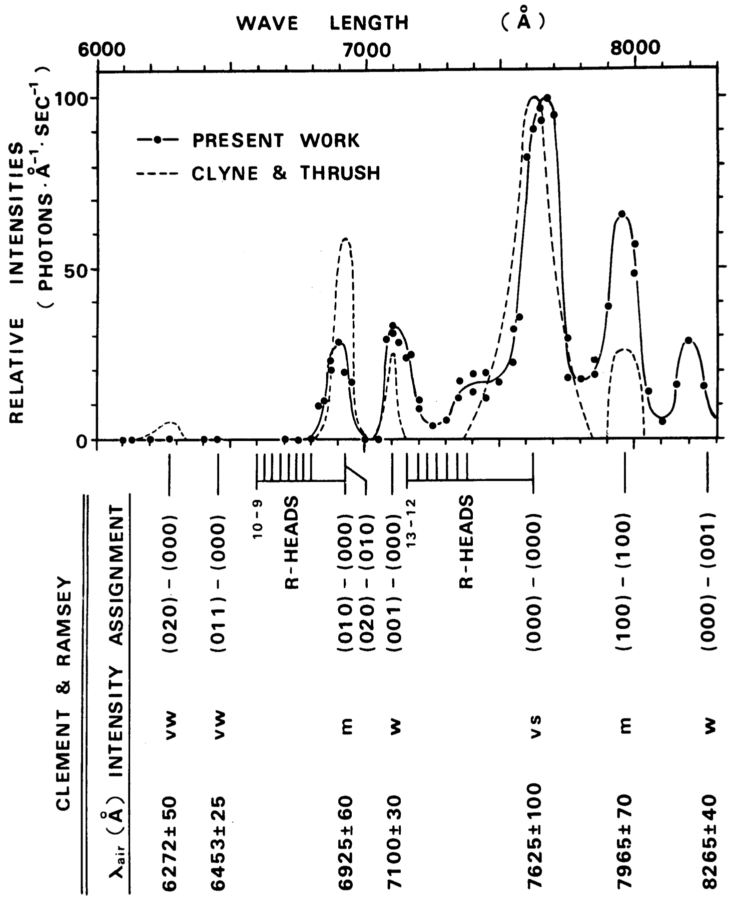

Fig. 1. Spectrum of the chemiluminescence.

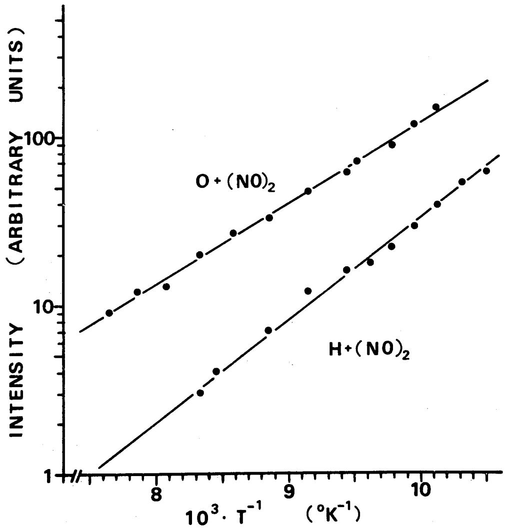

Fig. 2. Dependence of the total emission intensity (uncorrected) on the temperature of the NO beam source.

was controled by liquid nitrogen and air stream.

Emission spectrum was observed by a grating monochromater CT-25 of Japan spectroscopic Co. at low resolution with a photomultiplier R374 of Hamamatsu TV. Co. The spectral relative sensitivity was calibrated with a standard lamp in the same optical system. Another photomultiplier MS-9S of Toshiba Co. was used to monitor the changing intensities of radiations. The wave length of monitored radiation was limited above 6900 Å by a colored glass filter V-R69 of Toshiba Kasei Co. The total intensities of radiations were measured with the photomultiplier R374 through a colored glass filter V-R67.

## RESULTS AND DISCUSSION

The light emission from two-body collisions between H and NO at room temperature could not be observed by the crossed molecular beams. However, anomalously bright light emissions have been observed with the low temperature NO beams. Similar bright light emissions have been observed near the liquid nitrogen cooled surfaces in the molecular beam chamber.

The emission spectrum is shown in Figure 1. The intensity is normalized to a value of 100 photons emitted per Ångstrom unit per second at 7625 Å band. Although the position of each band agrees with the results of Clement and Ramsey, the intensity distribution differs somewhat from that obtained by other authors. Similar intensity distribution has been obtained using interference filters of KL-70 to 80 of Toshiba Kasei Co. Weak bands at 6272 Å and 6453 Å described in the above papers have not been observed.

Dependence of the total emission intensities on temperatures of NO beam source is shown in Figure 2. From the inclination of the plots the apparent activation energy of Arrhenius equation ( $I=Ae^{-E/RT}$ ) is estimated to be $E = -2.8$ kcal/mole. Similar observation with O atoms gave the value of $E = -2.2$ kcal/mole. The difference of these value can not be explained at present without more precise examination of the experimental condition.

The heat of formation of the reaction,

$$2NO \rightleftarrows (NO)_2$$

have been estimated as $\Delta H = 2.62$ kcal/mole and 1.49 kcal/mole by Guggenheim$^{5)}$ and Scot$^{6)}$, respectively, from the deviation of the second virial coefficient of nitric oxide from that of monomer at low temperatures. Dinerman and Ewing obtained the value of $\Delta H = 2.45$ kcal/mole from the infrared absorption of NO dimers at low temperatures$^{7)}$.

These values show that the chemiluminescence and the dimerization of NO have a similar temperature dependence. Therefore, it is very probable that the chemiluminescence is due to two-body collisions between H or O atoms and NO dimers as is shown below.

$$2NO \rightleftarrows (NO)_2$$
$$H + (NO)_2 \longrightarrow HNO^* + NO$$
$$HNO^* \longrightarrow HNO + h\nu$$

Assuming this process and using the dimerization constant K of Guggenheim$^{5)}$; i.e., $\ln(K/\mathrm{atm}) = -15.44+1320°\mathrm{K}/T$ and a presumed H concentration of 50 %, the radiation cross section for H atom and NO dimer is estimated to be $\sigma \approx 2 \times 10^{-18}$ cm$^2$ for 6000 – 8300 Å.

From the agreement of band positions with the results of other authors, the emitting process is considered to be $^1A'' — ^1A'$ transition of HNO.

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