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Quenching of NO_2 Continuum by NO, H_2O & CH_4

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The K/A ratio, where K is the quenching rate coefficient of NO_2 continuum by NO H_2O and CH_4 and A is the transition probability of NO_2 continuum has been measured using flowing afterglow method The obtained values are 3 1 1 8 and 5 3 $\times 10^{-16}$ cm^3 for quenching by NO H_2O and CH_4, respectively

Different investigators have measured the concentrations of NO in the earth's middle atmospheric region (20-40 km) and the obtained values are of the order of 10^9-10^{10} cm^{-3} (Ref 1, 2) Its formation and destruction processes in the middle atmosphere has been extensively studied[3] The continuum state of NO_2 may be produced in earth's atmosphere due to the absorption of solar radiations by NO_2. Quenching of this continuum state by N_2, O_2, Ar, CO_2 and NH_3 has already been studied[4,5] However, the quenching rate coefficients of this continuum state by NO, H_2O and CH_4, which are some of the minor constituents of earth's atmosphere[3], have not yet been measured Thus, the study of these quenching processes may be important from atmospheric point of view.

The quenching processes may be studied by different methods such as, flowing afterglow, fast absorption spectrophotometry, discharge shock tube, flash-photolysis, etc methods But due to the simple experimental technique and high accuracy of results of flowing afterglow method, it can be used to study the quenching processes In this communication the quenching of NO_2 continuum $[A(^2B_1) \rightarrow X^2A_1]$ by NO, H_2O and CH_4 has been investigated by using the flowing afterglow method

The experimental system used for the present investigation has been described in detail in various papers[6,7] The NO_2 continuum was obtained in the afterglow of microwave discharge of N_2 and O_2 mixture introduced in the reaction chamber through one-needle valve The intensity of the continuum was studied for different mixing ratios ($[N_2]/[O_2] < 1$, $[N_2]/[O_2] > 1$ and $[N_2]/[O_2] = 1$) and maximum intensity was obtained for equal mixing ratios of N_2 and O_2 at 200 mtorr This continuum was then quenched by different quenchers (NO, H_2O and CH_4) introduced into the reaction chamber through another needle valve The substances N_2, O_2 and CH_4 were obtained directly from UHP cylinders (IOL, minimum purity 99 999%) and double distilled water was used for H_2O The gas NO was obtained from cylinder (minimum purity 99 9%) which was then thoroughly outgassed and vacuum distilled from 90-77K

For quenching studies one strong line of NO_2 continuum $[A(^2B_1) \rightarrow X^2A_1)]$ was picked by the Ebert monochromator set at 5300 Å with 2 mm slit width Radiation through the monochromator was allowed to fall on photomultiplier tube RCAIP 28 which was operated by a highly stabilized power supply (ECIL, H218) Several sets of observations were taken on the intensity variation with the partial pressures of the quenching gases The variations of intensity with the partial pressures of NO, H_2 and CH_4 were obtained in terms of photoelectric current and are presented in Fig. 1. It was found that the maximum intensity of the

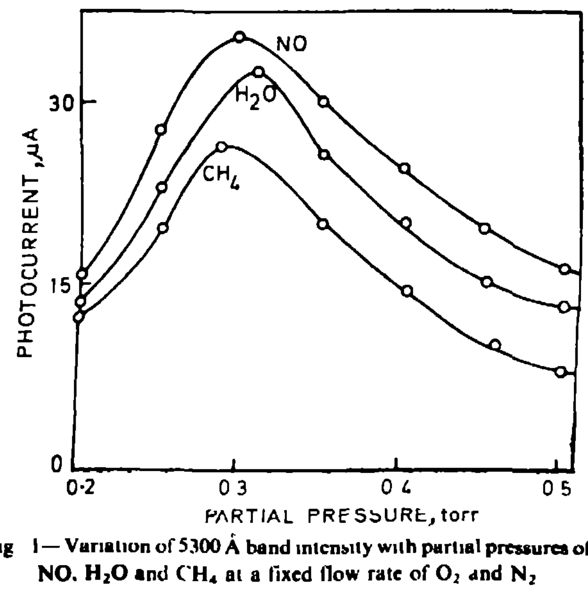

Fig 1—Variation of 5300 Å band intensity with partial pressures of NO, H_2O and CH_4 at a fixed flow rate of O_2 and N_2

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Table 1—Experimental K/A Values for Quenching of NO_2 Continuum

Quencher	K/A 10^{-16} cm^3
NO	3 1
H_2O	1 8
CH_4	5 3

quenching processes occurs at 0.3, 0.31, and 0 29 torr partial pressures of the quenchers, NO, H_2O and CH_4, respectively The intensity then decreased very rapidly with the further increase of the partial pressures of the quenchers (Fig 1) The quenching processes may be written as follows.

$$NO_2(A^2B_1)+NO \rightarrow NO_2(X^2A_1)+NO' \quad \dots (1)$$

$$NO_2(A^2B_1)+H_2O \rightarrow NO_2(X^2A_1)+H_2O' \quad \dots (2)$$

$$NO_2(A^2B_1)+CH_4 \rightarrow NO_2(X^2A_1)+CH_4' \quad \dots (3)$$

where prime denotes some excited state other than ground state of the molecules From different curves of Fig 1 the rate coefficients (K) of the above quenching processes may be measured following the method of Ghosh[8] and the obtained K/A values, where A is the transition probability of NO_2 continuum, are presented in Table 1

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