Short Communication

H$_2$(E,F) photosensitized reaction of NO with hydrogen atoms

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A persistent emission feature at 336 nm has been found during experiments in which 193 nm ArF laser radiation was directed into a cell containing partially dissociated hydrogen from a microwave discharge. Light emitted at right angles to the laser beam was detected using a McPherson model 218 monochromator in combination with an EMI type 9813QB photomultiplier and a PAR model 160 boxcar integrator. The laser was a Lumonics model 861-T operating at a repetition frequency of 35 Hz with a pulse energy of approximately 100 mJ, and the 336 nm emission was observed both with and without a lens to focus the light in the viewing region. The intensity observed with the lens was about twice as strong as that obtained in its absence.

The spectrum of the emission (Fig. 1) shows the well-known and highly characteristic A $^3\Pi_i \rightarrow$ X $^3\Sigma^-$ bands of NH [1] with an intense line-like Q branch of the (0, 0) band at 336.0 nm, weak unresolved P and R branch structure and overlapping (1, 1) and (2, 2) Q branches at 337 nm. This result initially posed a problem since the bands were observed strongly with only H$_2$ and H flowing through the cell. The addition of small flows of N$_2$ or N$_2$O (which was present for other reasons) caused the emission intensity to decrease, and it was finally concluded that the reaction involved traces of NO$_2$ which had been used in a previous series of experiments
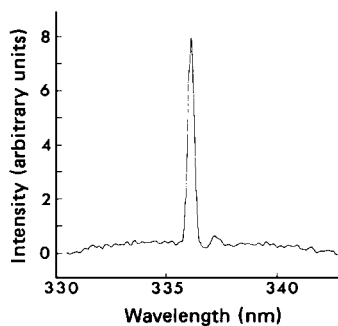

Fig. 1. Spectrum observed during irradiation of partially dissociated H$_2$ using an ArF laser: resolution, about 0.4 nm (full width at half-maximum); cell pressure, 1 Torr.

in the same apparatus and which was slowly diffusing from solution in the Teflon keys of greaseless stopcocks. In the presence of excess hydrogen atoms, NO_2 is rapidly converted to NO and, as shown in Fig. 2, the addition of a small amount of NO to the gas stream caused the NH emission intensity to increase. The minimum concentration of NO required to produce detectable NH emission was estimated to be 5×10^{10} molecules cm^{-3} in H_2 at 1 Torr, or about 2 ppm, under conditions where the H_2 was about 5% dissociated to atoms.
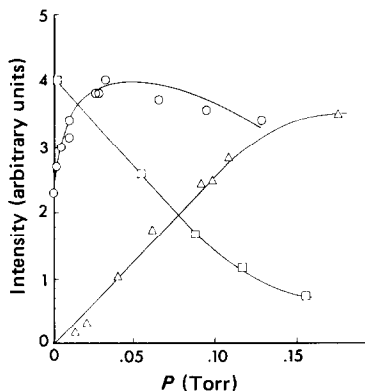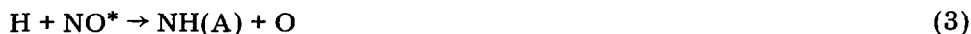

Fig. 2. Variation in the NH emission intensity with reactant partial pressure: $\bigcirc$, [NO]; $\triangle$, [H] calculated by assuming 90% dissociation of H_2 in a large excess of argon carrier; $\square$, 0.1 $[H_2]$.

Also shown in Fig. 2 is the dependence of the 336 nm emission intensity on the partial pressures of atomic and molecular hydrogen. At low hydrogen atom concentrations the intensity was proportional to [H]. To determine the dependence on $[H_2]$, hydrogen atoms were generated by a microwave discharge in a stream of argon containing 1% or less of H_2, such that the degree of dissociation of the H_2 was expected to be close to 100%, and additional hydrogen was added after the discharge. The minimum partial pressure of molecular hydrogen which could be attained in this way while still observing the NH emission was approximately 10^{-3} Torr. The intensity decreased with increasing $[H_2]$, even when the H_2 pressure was very low.

With NO entering the cell at a flow rate corresponding to maximum NH intensity, low resolution scans of the emission spectrum showed the presence of the $(0, v'')$ progression of the NO γ bands between 220 and 300 nm [1], individual bands having at most 0.5% of the intensity of the 336 nm peak, together with a weak feature near 305 nm (about 0.25% of the 336 nm intensity) which was tentatively attributed to the 306.4 nm band of OH on the grounds that it was observed only when hydrogen atoms were present.

The intensity of 336 nm emission was proportional to the square of the average laser power (the slope of the logarithmic plot is 1.96 ± 0.27 where

the stated uncertainty corresponds to 95% confidence limits from Student's t test). Two-photon absorption of ArF radiation by molecular hydrogen results in population of the double-minimum E,F state which is very strongly quenched by ground state H_2 (rate constant, 2.1×10^{-9} cm^3 molecule^{-1} s^{-1}) to the C $^1\Pi_u$ state [2]. The radiative lifetime of the C state is about 1 ns, which is a factor of 100 less than that of the E,F state [3]. The observed effect of varying $[H_2]$ on the NH emission intensity implies that it is the E,F state rather than the C state which is involved in the emission process. Hence we are led to the mechanism

$$H_2(X) + 2h\nu(193 \text{ nm}) \rightarrow H_2(E,F) \tag{1}$$

$$H_2(E,F) + NO(X) \rightarrow H_2 + NO^* \tag{2}$$

$$H + NO^* \rightarrow NH(A) + O \tag{3}$$

where the electronic states of the products of reaction (2) are unknown. NO has a number of suitable Rydberg states which might undergo reaction (3); a complete range of such states up to and beyond the ionization limit could be populated by reaction (2). An attempt was made to detect the $H_2(E,F \rightarrow C)$ emission bands between 700 and 750 nm, using an EMI 9558Q photomultiplier and a Corning 7-69 filter, with a view to measuring quenching by NO, but the intensity was too low. The observed NO γ band emission may be accounted for by cascading from unobserved higher states of NO, while the very weak OH emission is presumably the result of an alternative reaction channel for process (3). The extent to which reaction (3) favours excited NH over excited OH as a product seems quite remarkable.

1 R. W. B. Pearse and A. G. Gaydon, *The Identification of Molecular Spectra*, Chapman and Hall, London, 4th edn., 1976.
2 D. J. Kligler, J. Bokor and C. K. Rhodes, *Phys. Rev. A*, *21* (1980) 607.
3 D. J. Kligler and C. K. Rhodes, *Phys. Rev. Lett.*, *40* (1978) 309.