

For these reasons, we would prefer to think that a vibrational or electronic excitation of the nitrogen molecule takes place in the gas phase, by inelastic collisions with electrons, prior to adsorption. The vibrational quantum of nitrogen being $0.29 \text{ V} (= 2,359 \text{ cm}^{-1})$ one should admit the molecules are in their 3rd or 4th vibrational level, the thermal energy being only about 0.04 V . A possible process for this vibrational excitation is the formation of a negative transitory N_2^- ion, loosing its electron and afterwards getting vibrationally excited. This may occur in the particular case of nitrogen as has been shown by Schulz⁷.

The other possibility is an electronic excitation by the electron beam; this happens for higher electron energies, and Schulz⁷ has distinguished the formation of $A^2\Sigma_u^+$, $a \Pi_g$ and $C^2\Pi_u$ excited states at approximately 8, 10 and 12 V. There is no way for the moment of deciding what state might be concerned here, but it may be pointed out that the first excited electronic states of nitrogen correspond to an electron jump into either a $\pi_y^* 2p$, $a\pi_z^* 2p$ or a $\sigma^* 2p$ orbital; these are all antibonding and should bring an increase of nuclear distance, resulting in a more polarizable and more easily adsorbed molecule.

Finally, the curve reported by Marmet and Morrison shows a hump about 1.2 V above threshold and it may be significant that the first excited state $A^2\Pi_u$ of the N_2^+ ion is also situated some $1.15\text{--}1.21 \text{ V}$ above the ground $X^2\Sigma_g^+$ state⁸.

To conclude, the anomalies observed may be explained on the assumption of excited states of ions taking part in the charge exchange process on the surface, after vibrational or electronic excitation of the nitrogen molecule in the gas phase by electron collisions. Experiments of charge exchange between nitrogen and water by Lindholm's ion bombardment technique should also prove useful in explaining these phenomena.

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Luminescence from the H—O₂ Reaction

THE spectrum of the HO₂ radical is of considerable importance and several unsuccessful attempts have been made to record it. The HO₂ radical has one more electron than the HNO molecule, which has an electronic transition at 7600 \AA (ref. 1), and consideration of the molecular orbitals of HO₂ suggests that this radical should have a very similar electronic transition to that of HNO (ref. 2). The HNO spectrum was first obtained in absorption during flash photolysis experiments¹, but has more recently been observed in emission in the chemiluminescent reaction of hydrogen atoms with NO (ref. 3). The similarity of the bond dissociation energies of H—NO (49 kcal/mole)³ and H—O₂ (46 kcal/mole)⁴ suggests that hydrogen atoms might give a chemiluminescent reaction with oxygen, despite previous failures to find any electronic emission from this reaction.

Hydrogen atoms were produced by the dissociation of commercial hydrogen in two Wood's tubes and pumped through two side-arms on opposite sides of a reaction vessel 3.5 cm in diameter and 35 cm long connected directly to a 150 l./min rotary pump. Commercial oxygen

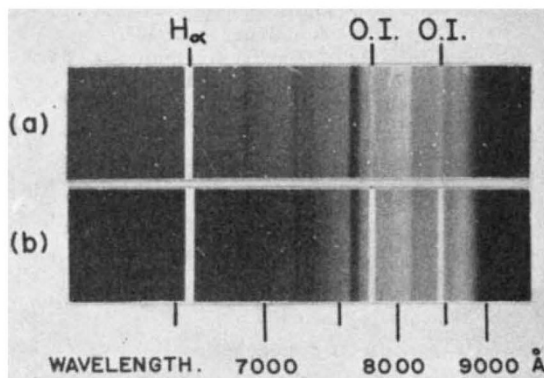


Fig. 1. The spectrum emitted in the reaction of hydrogen atoms with oxygen

was introduced through a third side-arm situated between the hydrogen inlets. The vessel was screened from direct light from the discharges, and mounted end-on directly in front of the slit of a Hilger 'Wave-length' spectrograph with $f/10$ glass optics and a focal length of 30 cm. The spectrum shown in Fig. 1 was photographed on hypersensitized Kodak II.N (I.R.E.R.) plates in 30 min, using a 100μ slit-width, and a partial pressure of each reactant of about 0.5 mm mercury. No visible glow was apparent. The intensity of the spectrum was extremely variable, and the relative intensity of hydrogen and oxygen atomic lines, due to partial entry of the discharge region into the reaction vessel, was also very variable, as shown by the comparison between the spectra in Fig. 1a and b, which were taken under almost identical conditions. However, the intensity distribution within the spectrum was reproducible. The erratic behaviour suggests that a trace impurity may be important in the production of the spectrum, either because the impurity supplies the excited molecules, or because the impurity (water ?) acts as a catalyst in the production of the excited molecules.

The reaction between hydrogen atoms and ozone leads to the emission of near infra-red vibration-rotation bands of OH (ref. 5), and H₂O emits near infra-red vibration-rotation bands in the flame of oxygen burning in an atmosphere of hydrogen⁶. However, both these systems are of red-degraded bands, and their wave-lengths do not agree with those of the spectrum in Fig. 1, which shows prominent violet-degraded heads at $6853, 7149, 7562$ and 8103 \AA ($\pm 10 \text{ \AA}$). The coarse rotational structure of the HNO bands is violet degraded, due to an opening out of the HNO angle on electronic excitation, and a similar behaviour is to be expected for HO₂. Thus, although there is no proof of the carrier of the observed spectrum, it seems possible that this is the spectrum of the HO₂ radical.

A new reaction vessel is being built to accommodate a set of multiple reflexion mirrors, and it is hoped to obtain sufficient intensity for a higher resolution study of this spectrum.

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