

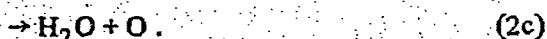
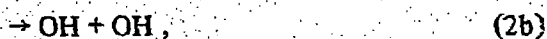
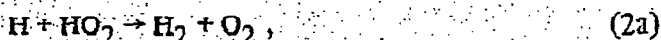
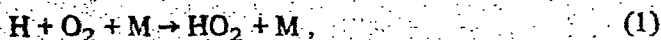
EXCITED STATE FORMATION IN THE H + O₂ SYSTEM

D.J. GIACHARDI, G.W. HARRIS and R.P. WAYNE

Physical Chemistry Laboratory, Oxford University, Oxford, OX1 3QZ, UK

This paper describes emission in the near-infrared, produced in a mixture containing atomic hydrogen (or deuterium) and molecular oxygen. The bands observed are ascribed to the formation of O₂(¹Σ_g⁺), of electronically and vibrationally excited HO₂, and perhaps O₂(¹Δ_g), in the reaction system. Possible excitation mechanisms are presented.

The gas phase reaction between atomic hydrogen and molecular oxygen has been the subject of many investigations. Attention has mainly been directed at the rate of disappearance of H, monitored, for example, by resonance fluorescence [1,2], optical absorption [3] or the chemiluminescent reaction with nitric oxide [4]; or at the emission spectrum of hydroxyl produced in the system [5], the time-variant concentrations of H, OH and O being monitored by ESR [6] or, together with HO₂, by mass spectrometry [7]. The reaction is commonly supposed to produce the hydroperoxyl radical, HO₂, which then reacts further with H atoms



We have observed chemiluminescence of a type not previously reported from the H + O₂ system. Our observations are made at short contact time; other experimental arrangements have generally not distinguished between emission produced at different reaction times. It will be shown that this chemiluminescence is most probably attributable to vibrationally and electronically excited HO₂ and to O₂(¹Σ_g⁺).

HO₂ has been detected spectroscopically in the gas phase by UV absorption [8], IR absorption [9], laser

magnetic resonance [10], mass spectrometry [7], and IR emission [11,12]. In the last case the HO₂ was excited by near-resonant energy-transfer from O₂(¹Δ_g), the ground state HO₂ being an intermediate product in an O atom/olefin/O₂ system. O₂(¹Σ_g⁺) has been observed by its emission at 762 nm as a product of the energy pooling reaction of O₂(¹Δ_g) [13], and of the energy transfer process between O(¹D) and O₂, either in the vacuum UV photolysis of O₂ [14], or in the UV photolysis of O₃/O₂ mixtures [15].

A hydrogen/argon mixture (about 1% H₂ in Ar at a total pressure of about 1.5 torr) was passed through a 2450 MHz discharge into a tube 36 mm in diameter and 80 cm long. Luminescence observations were made in a widened section of the flow tube, 56 mm in diameter. A side arm entered the widened section at right-angles to the flow and molecular oxygen could be added through it. Typically the partial pressure of O₂ was 0.5 torr. Flow velocities of the order of 1.6 m s⁻¹ were maintained by an Edwards ES150 pump and pressures were measured by a capacitance manometer (MKS Baratron 145 AH-10).

Immediately downstream of the point of entry of the side arm, the flow tube was viewed by two chopper-monochromator-detector assemblies mounted at right angles to each other and to the direction of the flow. One detector was an EMI 9558 QB photomultiplier used for the visible to near infrared region, and the other was an RCA 6904A germanium photodiode used to cover the 1.0–1.6 μm region. PM pulses were processed using a synchronous up/down

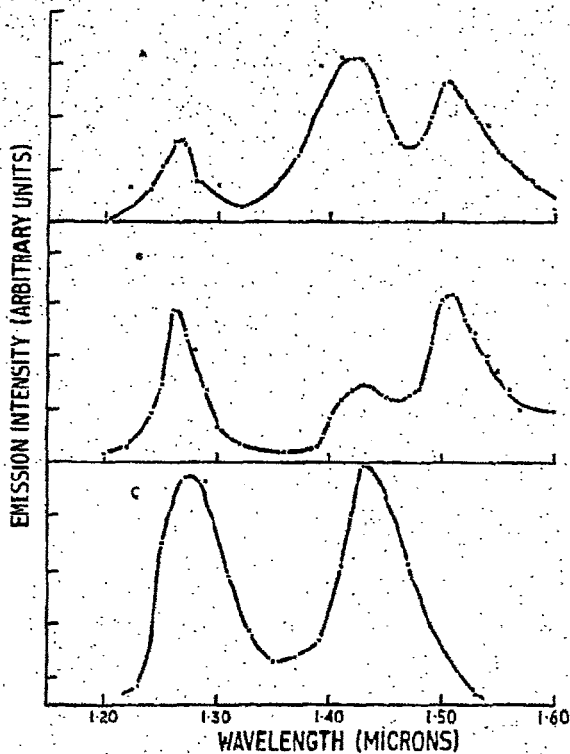


Fig. 1. Spectrograms obtained in the spectral region 1.00–1.60 μm , (a) H in Ar added to O_2 introduced at the sidearm; (b) O_2 and Ar passed through a discharge and added to ethylene introduced at the sidearm; (c) D in Ar added to O_2 introduced at the sidearm.

counter and photodiode signals by a (Princeton JB4) phase-sensitive detector.

Addition of O_2 to a flow of H atoms in argon led to emission both in the spectral region 1.20–1.60 μm (see fig. 1a) and near 762 nm (fig. 2). No other spectral features were detected in the ranges 450–800 nm and 1.0–1.6 μm . The IR emission consisted of a band at $1.265 \pm 0.01 \mu\text{m}$, and an imperfectly resolved pair of bands at $1.430 \pm 0.01 \mu\text{m}$ and $1.510 \pm 0.01 \mu\text{m}$. These bands correspond to those observed by Becker et al. [11,12] in their O atom/olefin/ $\text{O}_2/\text{O}_2(^1\Delta_g)$ system and, for comparison, fig. 1b is a spectrogram obtained in our apparatus by adding ethylene through the sidearm to a flow of oxygen and argon which had been passed through a microwave discharge.

Mason and Dixon [16] observed band heads at 685, 715, 756 and 810 nm in an apparently similar system and assigned these transitions to an excited

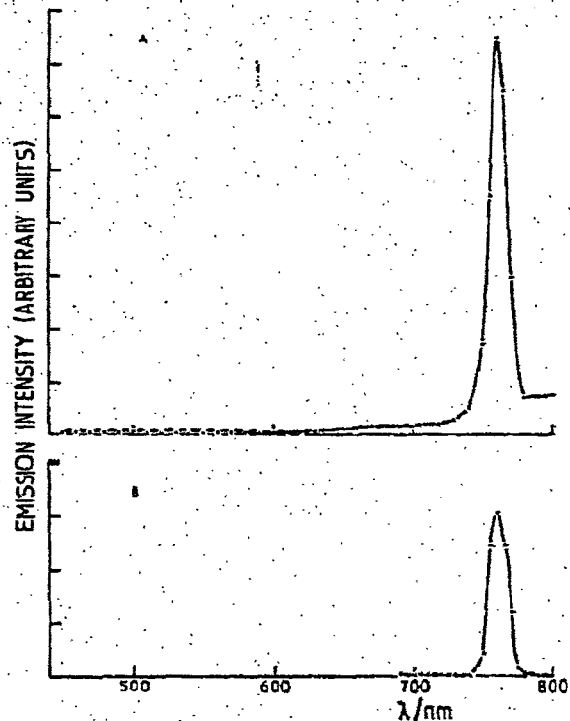


Fig. 2. Spectrograms obtained in the spectral region 450–800 nm, (a) H in Ar added to O_2 introduced at the sidearm; (b) molecular oxygen passed through a discharge and then through an HgO ring to remove O atoms.

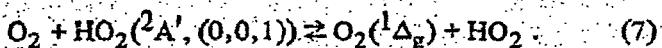
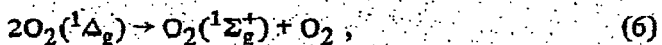
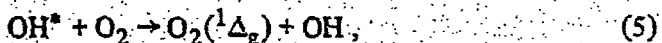
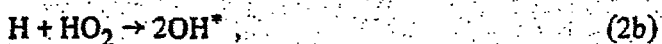
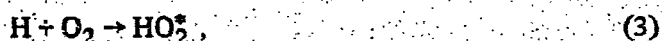
state of HO_2 . We did not observe these bands; moreover the spectra published in ref. [16] show no evidence of an emission at 762 nm.

We make the tentative assignment that the 1.43 μm band is due to the $\text{HO}_2(^2A'(0,0,0) \rightarrow ^2A''(0,0,0))$ transition and the 1.51 μm band to the $\text{HO}_2(^2A''(2,0,0) \rightarrow ^2A''(0,0,0))$ transition. The band at $1.265 \pm 0.01 \mu\text{m}$ could be due either to $\text{O}_2(^1\Delta_g, v=0 \rightarrow ^3\Sigma_g^-, v=0)$ or to $\text{HO}_2(^2A'(0,0,1) \rightarrow ^2A''(0,0,0))$ or to both. The 762 nm line is likely to be the $\text{O}_2(^1\Sigma_g^+, v=0 \rightarrow ^3\Sigma_g^-, v=0)$ transition, but could also be the (9 \rightarrow 4) vibrational transition of OH in the electronic ground state which would be indistinguishable at our resolution.

As a diagnostic test, the experiment was repeated using D_2 instead of H_2 . Under these circumstances, the 1.51 μm line disappeared and the 1.265 μm and 1.43 μm lines were unaffected. Fig. 1c is a spectrogram

obtained in the D/Ar/O₂ system. These changes are in accord with the observations of both Becker et al. [12] and Hunziker and Wendt [9], and are consistent with the assignments given above. The (9 → 4) transition of OD occurs at 942 nm. However, the emission at 762 nm was still observed in the D/Ar/O₂ system. No other spectral features were observed although several other OH and OD transitions fall within the regions we scanned. We therefore conclude that the 762 nm line is due to the presence of O₂(¹Σ_g⁺).

The following elementary processes are amongst those possible in the system:



HO₂^{*} signifies some undefined excited state of HO₂; HO₂[‡] signifies the emitting states (²A', (0,0,1; 0,0,0) and ²A''(2,0,0)); OH* is the vibrationally excited electronic ground state.

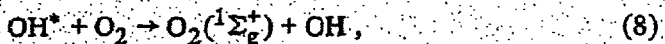
Possible excitation mechanisms which would explain the observations would be

(a) reactions (3), (4a), (4b);

(b) reactions (3), (2b), (5), (6), (4a);

(c) reactions (3), (4a), (7), (6).

We exclude the process



since the total exothermicity of (2b) can only produce

(in a single OH) OH* up to v = 4, which lies below the excitation energy of O₂(¹Σ_g⁺).

The present data are insufficient to distinguish between these or other excitation processes. Further diagnostic experiments are currently being conducted.

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