IX.—*The Infra-red Emission Spectra of Flames in Nitrous Oxide.*

By Charles Reynolds Bailey and Kun-Hou Lih.

The combustion of certain gases in an atmosphere of nitrous oxide has been described by Barratt (*Proc. Roy. Soc.*, 1920, *A*, **98**, 40), Dixon and Higgins (*Fuel*, 1926, **6**, 232) and others. Reiss (*Z. physikal. Chem.*, 1911, **76**, 560) and Reiss and Waldbauer (*ibid.*, 1913, **85**, 62) have also utilised nitric oxide as the supporting atmosphere. All these authors have been struck by the characteristic appearance of the flames, their enlarged size, the increased illumination, and the numerous zones. Reiss showed ammonia, hydrogen cyanide, and formaldehyde to be present in the interconal space, and Barratt obtained spectroscopic evidence of the water vapour, ammonia, and cyanogen bands under the appropriate conditions. The ready decomposition of nitrous oxide at temperatures above 700° has justified the assumption that, as far as the end products are concerned, the combustible gas burns in the oxygen furnished by this decomposition. Our examination of such flames by infra-red spectroscopy supports the assumption in general, but we have obtained evidence of a striking anomaly in the case of the hydrogen flame.

EXPERIMENTAL.

Apparatus.—A Hilger constant-deviation spectrometer (type D 42), fitted with a rock-salt prism, was used in conjunction with a thermopile–galvanometer combination. The galvanometer was of the Downing pattern (*J. Sci. Inst.*, 1926, **3**, 331) and was protected from magnetic disturbances by a mu-metal shield (A. V. Hill, *ibid.*, p. 335). Mechanical interference was largely eliminated by supporting the instrument on a large wooden block resting on a brick pillar let into the ground, and the inertia of the whole was greatly increased by the use of the soft-iron shields associated with the Paschen instrument. The sensitivity was of the order of $2{\cdot}5 \times 10^{-10}$ amp. per mm. deflexion at a scale distance of 1 metre. The work was carried out in a constant-temperature room with double walls; the spectrometer was enclosed in a felt-covered box of which the thermal capacity was increased by means of a large stoppered bottle full of water: the temperature of the enclosure was checked at intervals and found to be constant at 18°. The drum was manipulated from a distance and read by means of a telescope. The instability of zero due to the adiabatic compression and expansion of the atmosphere was reduced to a minimum by coupling a similar thermopile in an opposed sense to the recording instrument inside the case. The gases were burned in a cupboard and viewed by the spectrometer through parallel slits in two large pieces of tin plate, local heating in the box thus being prevented. The work was carried out between the hours of 11 p.m. and 5 a.m.

The spectrometer was calibrated in the following manner: The instrument was set on the sodium lines 0·5893 μ, very narrow slits being used; this setting gave concordant results on bench marks in the further infra-red with those obtained by using the helium line 0·588 μ. As a check on the drum graduations, additional maxima were determined: these included the helium bands at 1·08 and 2·06 μ from a gaseous discharge lamp fitted with a quartz window, and the water vapour emission bands at 2·81, 5·32, and 6·60 μ from a hydrogen flame in air, as determined by Paschen (*Ann. Physik*, 1894, **53**, 334). With these precautions, the carbon dioxide maximum in the Bunsen flame was obtained at 4·46 μ : the generally accepted value of 4·40 μ is probably too low, but inasmuch as the drum, in the type of instrument used, is engraved with reference to values of the refractive index of rock-salt uncorrected for temperature changes, too much stress cannot be placed on this. With a slit width of 0·25 mm. for both collimator and thermopile, the average deflexion for this maximum at 1·5 metres scale distance was 50 cm. The value of the slit width in terms of range of spectrum varies over the region examined and is indicated by hatched lines above the curves; the separate maxima are uncorrected for slit width.

The gases were burned at a 4-mm. silica jet in a vessel of Pyrex glass of the form shown in Fig. 1, the window A being of rock-salt. This shape of tube was chosen in order to avoid emission from the heated walls, and for the same reason the tip of the silica jet was kept below the level of the window.

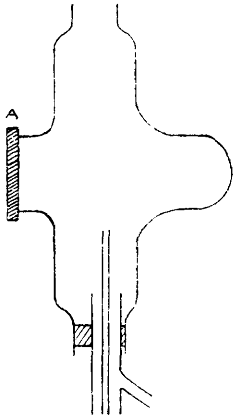


FIG. 1.

Results and Discussion.

The normal spectrum derived from a flame in the infra-red is that of the resultants and not of the reactants. The gases studied in the present research include hydrogen, carbon monoxide, and coal gas; consequently the anticipated spectra are those of water vapour and carbon dioxide. This experimental fact may be due to the condition that generally the supporting atmosphere consists of oxygen or air, both of which are non-polar and without a characteristic infra-red spectrum. If the conditions were reversed and, say, oxygen burnt in an atmosphere of carbon monoxide, it might be possible by thermal stimulation to obtain an emission spectrum from both reactants and resultants. It will be seen that in the case of hydrogen burning in nitrous oxide we have been able to obtain a spectrum which will admit of the above suggestion as a partial explanation.

Two methods were adopted for burning the gases : in one the gases were premixed with nitrous oxide in a Y-tube, and in the other the combustible gas was burned in an atmosphere of nitrous oxide. Hydrogen and nitrous oxide were obtained from cylinders, and carbon monoxide was prepared by the action of warm sulphuric acid on formic acid; the gases were roughly dried by passing over a long column of phosphoric oxide. Observations of the energy curves were made at intervals of 0·1 μ, except in the neighbourhood of each peak maximum, for which the interval was 0·05 μ, or less; the process adopted was to make each reading a difference observation by the use of a shutter.

Carbon monoxide. The same spectrum is obtained whether the gas is premixed with nitrous oxide or burned in the supporting atmosphere, and is the normal carbon dioxide emission spectrum shown in Fig. 2. The higher temperature of the flame produces shifts in the position of the bands and a characteristic decrease in the ratio of their relative intensities (compare Garner and Johnson, *Phil. Mag.*, 1927, **3**, 97). The data are summarised in Table I, which includes the corresponding absorption values as determined by Schaefer and Philipps (*Z. Physik*, 1926, **36**, 641). The intensities are assumed to be roughly measured by the galvanometer throw for the peak maximum.

FIG. 2.

Carbon monoxide burning in nitrous oxide.

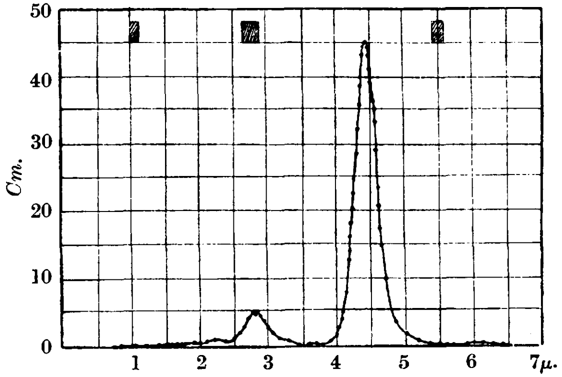


TABLE I.

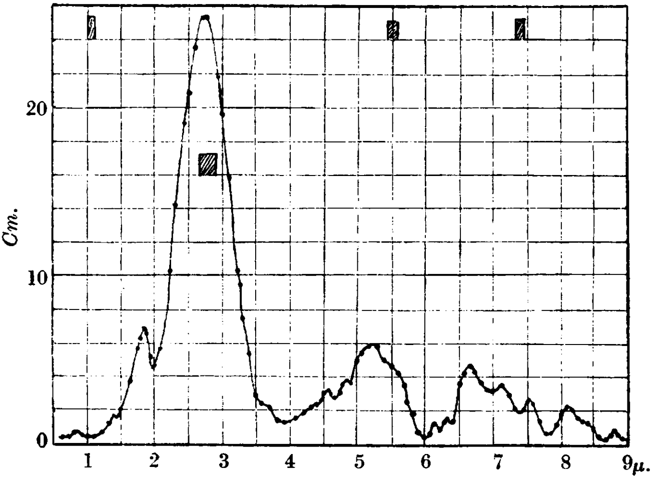
	Wave-length.		Ratio of intensities,
	(1).	(2).	(2)/(1).
Emission in air	2·84 μ	4·46 μ	10·1
,, N_2O	2·88	4·50	9·0
Absorption	2·72	4·25	28·5

Coal gas. Here again the spectra obtained in both cases are the normal water vapour and carbon dioxide emission curves superimposed, but with slight shifts in the position of the maxima. A detailed consideration of these is therefore omitted.

Hydrogen. When the two gases are premixed, the normal emission spectrum of water vapour is obtained; the energy curve is given in Fig. 3, and may be compared with that given by Paschen (*loc. cit.*) for the hydrogen flame in air. The flame, however, is complex and possesses at least five zones.

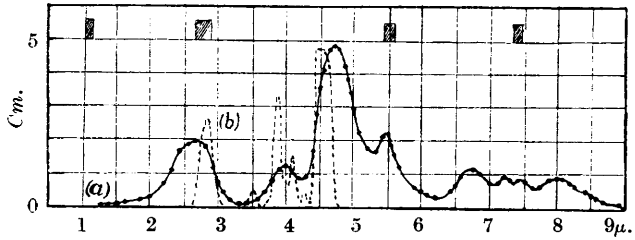
FIG. 3.

Hydrogen premixed with nitrous oxide.



If, now, the hydrogen is burned at the jet (see Fig. 1) in a supporting atmosphere of nitrous oxide, a very different spectrum appears and is shown in Fig. 4, curve (*a*). For the analysis of this, we must refer (i) to the absorption spectrum of nitrous oxide as determined

FIG. 4.



(a) —·—·—·— *Hydrogen burning in an atmosphere of nitrous oxide.*
(b) .... *Absorption spectrum of nitrous oxide (Warburg and Leithäuser).*

by Warburg and Leithäuser (*Ann. Physik*, 1909, **28**, 313), whose results are given in Fig. 4, curve (*b*), the chief maximum at 4·47 μ having been afterwards resolved into a Bjerrum doublet by von Bahr (*Verh. deut. physikal. Ges.*, 1913, **15**, 710); and (ii) to the emission and absorption curves for water vapour as given by Paschen (*loc. cit.*) and Hettner (*Ann. Physik*, 1918, **55**, 476). The data for the outstanding peaks (in μ) of the spectra involved are collected in Table II.

TABLE II.

Emission	Hydrogen in N_2O	2·76	4·00	4·75	—	5·49	6·75	7·50	8·00
	Hydrogen in air	2·75	—	—	5·32	—	6·70	7·50	8·10
Absorption	Water vapour	2·66	—	—	5·95	—	6·51	7·45	8·20
	Nitrous oxide	2·88	3·89 4·05	4·47	—	—	—	—	—

The following deductions can be made concerning the new spectrum : (1) the broad band at 2·76 μ may be attributed to a combination of the respective water vapour and nitrous oxide bands; (2) the band at 4·00 μ is the emission analogue of the nitrous oxide absorption bands at 3·89 and 4·05 μ, the dispersion of rock-salt in this region being insufficient to separate these; (3) nitrous oxide has a powerful absorption band at 4·47 μ; it seems reasonable to ascribe the emission band at 4·75 μ to this substance, the shift in position with increase in temperature being of the order obtained with carbon dioxide; (4) the appearance of a maximum at 5·49 μ may be due to absorption by hot water vapour at 5·32 μ; and finally (5) the peaks from 6·5 to 9·0 μ present most of the characteristics of the water-vapour spectrum, but upon this another spectrum is imposed which, with the resolution available, is indistinguishable.

The new spectrum does not occur with carbon monoxide, or with coal gas in either mode of burning, and it is absent in the case of hydrogen premixed with nitrous oxide. Its production may therefore be attributed to some form of stimulation by the burning hydrogen molecules, and, since it does not appear in the coal-gas flame, it is probably inhibited by carbon monoxide and hence the excitement is not merely thermal.

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