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The Ultraviolet Absorption Bands Ascribed to HNO_2

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Attention is drawn to the similarity of a series of absorption bands obtained by Melvin and Wulf as the results of experiments at normal temperatures with a $\text{NO}-\text{NO}_2-\text{H}_2\text{O}$ medium and by Bone and Newitt from the explosion of a $\text{CO}-\text{H}_2\text{O}-\text{NO}$ medium at high pressures. The formation of these bands in explosion experiments at atmospheric pressure and in static flames is described and evidence is brought forward which suggests that they may be due to the enhancement of certain bands of the normal NO_2 absorption spectrum.

OUR attention has been drawn by Professor Kondratjew to two papers¹ in which the ultraviolet absorption of a $\text{NO}-\text{NO}_2-\text{H}_2\text{O}$ medium is described and discussed. They find that mixtures of NO and NO_2 containing small amounts of water give rise to a group of bands in the near ultraviolet, lying in the same region, but not resembling, the longer wave-length NO_2 absorption. From the results of their experiments they suggest the possibility of the enhancement of certain of the NO_2 bands, but conclude that the probable carrier of the bands is the HONO molecule.

The series of bands given in Table I of their second paper appears to be identical with that described by one of us and W. A. Bone,² and obtained from the explosion of a $\text{CO}-\text{N}_2\text{O}-\text{NO}$ mixture at high pressures. We have since obtained the same spectrum from explosions at atmospheric pressure and from stationary flames of CO burning in various media containing N_2O and NO ; and since the combustion method throws some light upon the origin of the bands, it may be of interest if we describe very briefly the conditions under which they are formed.

The radiation emitted by a gas explosion at atmospheric or high pressure may be conveniently examined in an apparatus of the form shown diagrammatically in Fig. 1. A massive cylindrical, steel, explosion vessel E , 1 meter long and 3 cm bore, is fitted with two conical quartz windows W_1 and W_2 and two ignition plugs Y_1 and Y_2 . Gases from a number of storage cylinders C_1 , C_2 , etc., can be admitted

separately to E , their respective partial pressures being indicated by a standard pressure gauge G . V_1-V_3 are valves for controlling the supply of gas. Before entering the vessel E the gases may, if so desired, be passed through a steel drying tube D containing freshly distilled phosphorus pentoxide. The vessel itself also may be heated and any water vapor removed by evacuation. In the ordinary way the gaseous mixtures are ignited at the end Y_1 nearest the spectroscope so that the radiation from the flame traverses a column of the hot products of combustion before reaching the window W_1 ; alternatively it may be ignited at Y_2 the radiation then only traversing a column of unburnt gas.

The apparatus employed in the stationary flame experiments is shown in Fig. 2, which is self-explanatory.

EXPERIMENTAL

(1) The spectrum given by the explosion of an equimolecular $\text{CO}-\text{N}_2\text{O}$ mixture at a pressure of several atmospheres is continuous, extending on an ordinary unsensitized plate down to about 3100Å. It shows none of the characteristic OH

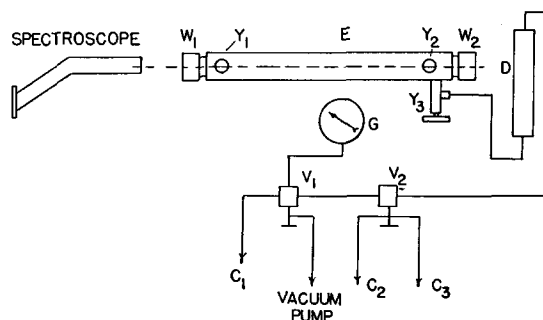


FIG. 1.

¹ E. H. Melvin and O. R. Wulf, *Phys. Rev.* **38**, 2294 (1931); *J. Chem. Phys.* **3**, 755 (1935).

² *Proc. Roy. Soc.* **115**, 41 (1927).

bands and little or no sign of the faint banded structure of the spectrum of CO burning in air or oxygen at atmospheric pressure.³

(2) By the addition of NO to the above mixture a series of regularly distributed absorption bands in the region 4000–3000Å are superposed on the continuous CO–N₂O spectrum; there are no OH bands and no trace of the ordinary absorption spectrum of NO₂. The bands are broad and ill-defined, but the regularity of their distribution is clearly shown on the negatives.

(3) When Exp. (2) is repeated at atmospheric pressure (some ten separate explosions being necessary to obtain a comparable intensity), the same spectrum is obtained together with the 3064Å OH bands and the ordinary absorption spectrum of NO₂.

(4) The addition of up to 1 percent of hydrogen to the CO–N₂O–NO mixture has no appreciable effect upon the intensity of the spectrum, but careful drying of the gases causes a slight diminution.

(5) The spectra obtained from the stationary flames of CO burning in N₂O and from a mixture of CO and NO in equal proportions burning in N₂O are similar to those obtained in Exps. (3) and (4).

(6) Careful drying of the gases or the addition of up to 1 percent of hydrogen has little effect upon the intensity.

RESULTS AND DISCUSSION

In Table I the wave-lengths, wave numbers in air, and intensities are recorded. The wave-lengths were measured by comparison with an ivory scale, the spectrum of iron furnishing the necessary standards. As already mentioned the bands are in many cases broad and ill-defined and the measurements are, therefore, subject to a probable error of 5Å units. The intensities are rough estimates on a scale of 3 for the brightest band and 0 for bands which are just visible. The wave-lengths are given in two columns, the first including all the bands visible on the spectrum of the high pressure explosion experiment (2), and the second, a few additional intense bands which appear in the spectra of

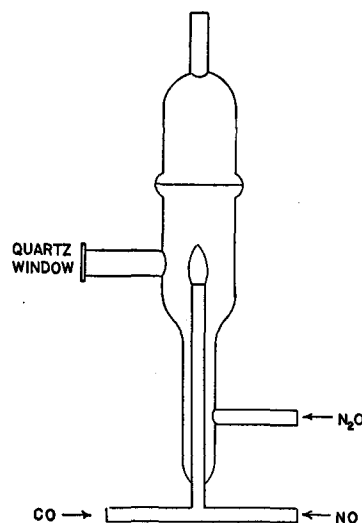


FIG. 2.

Exps. (3)–(6) and probably form part of the same system. It will be noted that the actual values differ, in some cases, from those given in the original paper by Bone and Newitt, because of better definition in the later experiments.

On account of the approximate character of the wave numbers the regularity of the distribution of the bands is not as clearly demonstrable as could be desired; nevertheless, the following partial analysis (Table II) may serve to indicate that the bands are distributed roughly in accordance with the general laws governing the

TABLE I.

WAVE-LENGTHS		WAVE NUMBERS	INTENSITY
HIGH PRESSURE EXPLOSION	LOW PRESSURE EXPLOSION AND FLAMES		
3845		26008	1
	3800	26316	0
	3764	26567	1
3726		26838	2
3680		27173	3
3656		27352	1
	3615	27662	0
3575		27972	0
3545		28209	3
3513		28465	1
	3485	28694	1
3440		29070	0
3418		29257	3
3390		29498	1
	3330	30030	0
3305		30257	0
3270		30581	1
3202		31230	0
3183		31417	0

³ Weston, Proc. Roy. Soc. A109, 176, 523 (1925).

TABLE II. *Structure of the band spectrum.*

31417(0) 836	30581(1) 1083	29498(1) 1033	28465(1) 1113	27352(1) 1036	26316(0)
187	324	241	256	179	308
31230(0) 973	30257(0) 1000	29257(3) 1048	28209(3) 1036	27173(3) 1165	26008(1)
	227	187	237	335	
	30030(0) 960	29070(0) 1098	27972(0) 1134	26838(2)	
		376	310	271	
		28694(1) 1032	27662(0) 1095	26567(1)	

structure of band spectra; and the differences in the columns and rows are as nearly equal as can be expected. The heavy line serves to demarcate the additional bands which appear only in the low pressure explosion and flame spectra.

Melvin and Wulf have shown (reference 1) that under their experimental conditions the intensities of the bands depend upon the partial pressures of the three constituents NO, NO₂ and H₂O and upon temperature, and they conclude that the molecule HONO, or a polymer, acts as the band carrier. Our results, on the other hand, do not entirely support this view. In none of our experiments was NO₂ present initially although small quantities would undoubtedly be formed as the result of the thermal decomposition of any excess of N₂O present in the system.⁴ Furthermore, water vapor was present only in traces, not exceeding 0.1 percent by volume, in the high pressure experiments and in the low pressure explosion and flame experiments with specially dried gases; in the latter experiments, indeed, the gases were so dry that considerable difficulty was experienced in getting them to ignite with an electric spark or heated platinum wire. In spite of the absence of any considerable quantities of water vapor, however, the greatest intensity was obtained in the explosion experiment (2), at 9 atmospheres pressure, and the addition of up to 1 percent of hydrogen to the combustible gases caused very little variation in the intensity.

It would appear, therefore, that water vapor and/or hydrogen are not essential to the formation of the bands but that, under the conditions of our experiments, they are always associated

with the presence of nitric oxide and the hot products of the thermal decomposition of nitrous oxide.

If the results from the explosion experiments (1), (2) and (3) are compared, it will be noted that in (1) and (2) there is no indication of the ordinary NO₂ absorption spectrum although the cold products of the explosion contain appreciable quantities of the gas, while in (3) the NO₂ bands are quite distinct. In both (2) and (3) the bands attributed to HONO are present. The temperature of the explosion flame of a CO-N₂O-NO medium exceeds 2000°C, but whereas in the low pressure experiment the products cool almost instantly to the temperature of their environment, in the high pressure explosion the rate of cooling is much slower and the flame is probably able to traverse the whole length of the vessel before the products have cooled to a temperature at which the NO₂ molecule is thermally stable. The radiation from the burning carbon monoxide, therefore, in the one case traverses a medium containing NO and NO₂ in partial thermal equilibrium, and in the other a medium containing NO and an NO-O complex which might be regarded as a transition complex or as predissociated NO₂.

This would support the view that the origin of the spectrum is the selective enhancement of certain of the NO₂ absorption bands due to a combination of temperature and the presence of a high concentration of one of the products of its dissociation, namely nitric oxide. The additional bands found in the low pressure experiments, and separately listed in Table I, might then be assigned to NO₂ in the stable state, their intensities being increased by the particular environmental conditions.

⁴ Carlton-Sutton, Ambler and Wyn Williams, *Phys. Soc.* 48, 189 (1936).