

Characteristics of Premixed, Laminar CO/N₂O Flames

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Several properties are studied of fuel-rich ($\text{CO/N}_2\text{O} = 1.5/1$) and stoichiometric ($\text{CO/N}_2\text{O} = 1/1$) carbon monoxide/nitrous oxide flames with varying water content up to 10%. Flame temperatures, ranging from 2680 to 2860°K, are measured with the line-reversal method, and compared with calculated adiabatic values. Excess concentrations of H and OH radicals are determined by the LiOH/Li method; the ratios $[\text{H}]/[\text{H}_2\text{O}]$ appear to exceed their (calculated) equilibrium values by a factor 1.5 to 3.0, even after 10 msec rise time of the flame gases. Burning velocities of the various mixtures, estimated from the height of the combustion cones, range from 30 to 75 cm/sec and are markedly dependent on the water content of the mixture. The absolute spectral intensity of the (quasi) continuous emission of the burnt gases was measured and was found to have the same dependence on CO and O concentrations as in CO/air flames. Electron concentrations of 10^9 to 10^{10} cm⁻³, measured with a HF resonance method, are tentatively attributed to (thermal) ionization of NO.

Introduction

This paper deals with some properties of a number of carbon monoxide/nitrous oxide flames at one atmosphere, with varying fuel-oxidant mixtures and varying amounts of water vapor. We used these flames in the determination of the dissociation energies of the alkaline earth monoxides and monohydroxides MO and MOH ($M \approx \text{Ca, Sr or Ba}$) [1, 2]. For this determination, a laminar, homogeneous high-temperature flame with low, variable hydrogen content was required. To this end, the CO/N₂O system was found to be satisfactory because of its low burning velocity, when compared to the CO/O₂ system.

In contrast to the acetylene/nitrous oxide flame, which is widely used now in analytical flame spectroscopy [3], the properties and analytical possibilities of the CO/N₂O flame have been but little explored. Palmer and Seery [4] have given a qualitative description of the chlorine inhibition of CO/N₂O flames. Simpson and Linnett [5] have determined the burning velocities of CO/N₂O mixtures diluted with nitrogen; these authors have used unburnt mixtures with only 15 and 25% N₂O. Van Wouterghien and Van Tiggelen [6] have measured the burning velocities of stoichiometric and fuel-rich CO/N₂O flames.

The properties of CO/N₂O flames make them useful for those applications where an intermediate temperature between that of the C₂H₂/air flame and the C₂H₂/N₂O flame is required. Moreover, for elements that may form hydroxides, the degree of atomization is expected to be better in the CO/N₂O flame than in flames burning with C₂H₂ or H₂ of comparable temperature on account of the low water content of the former [7].

In this paper, the determination of the flame temperature and of the ratio of the partial pressures of the flame species H and H₂O will be emphasized. This ratio is involved in the compound formation of the alkaline earth metals [1, 2]. Some preliminary results concerning the burning velocities, the spectral emission characteristics and the ionization of the metal-free flame gases will be reported here, too.

Experimental Arrangement

The apparatus used is a conventional setup for flame-spectrometric measurements. The supply gases CO and N₂O are obtained from commercially available cylinders, their purity is stated by the manufacturer to exceed 99.9%, with nitrogen being the major impurity. The unburnt mixture contains less than 0.05% hydrogen, either as H₂ or

in compounds. The circular, Meker type burner head supports two concentric cylindrical flames, only the inner flame (diameter 14 mm) contains the nebulized metal salt solutions, the outer flame (outer diameter 31 mm) shields the inner flame against contamination from the surrounding air. The oxidant gas of both the inner and outer flame passes a nebulizer, that for the outer flame is fed with distilled water only, the other with the metal salt solution to be investigated. Both ("perspex") nebulizers are immersed in a water bath the temperature of which controls the supply of water vapor to the flame. The tubings from the nebulizers to the burner are wrapped in heating elements to prevent condensation of water vapor. Height adjustment of the burner with respect to the optical axis can be performed over a 70 mm range. The light emitted by the flame passes a 50 Hz chopper and a simple Leiss prism monochromator and is detected by an EMI photomultiplier, type 9558, coupled to an ac amplifier with synchronous rectifier. Output signals can be read from a dc μ A meter, or a 1 V pen recorder.

Flame Temperatures

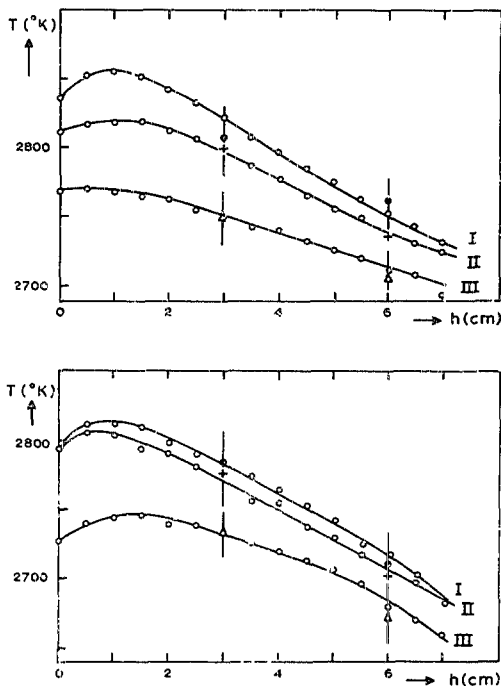
For reasons to be discussed in Ref. 2, the optimum mixing ratio of CO and N_2O for the determination of the dissociation energies of MO and MOH, is between 1:1 and 1:1. So two flames were studied, one with 3.60 l/min CO and 2.40 l/min N_2O the other with 2.40 l/min for both CO and N_2O . These gas supplies refer to the inner flame only, the outer shielding flame consumed 13.6 l/min CO and 9.1 l/min N_2O (fuel-rich flame), and 9.1 l/min for both CO and N_2O (stoichiometric flame). The precision of the gas supply adjustment is better than 3%. The water (vapor + droplets) flow into the inner flame, measured with a $CaCl_2$ trap, was expressed in liters of vapor/min, for spray temperatures of 0, 22 and 64°C this water supply (as vapor) was 0.035, 0.058 and 0.550 l/min respectively, with a precision of 10%. These amounts appear to correspond roughly to the saturation pressure of the water vapor at the temperature of the water bath.

All flame temperatures were measured with the visual sodium D-lines reversal method. We used a small tungsten strip lamp designed for microprojection (Philips) as a background light source. It

takes 17 A at 6 V under normal conditions, but in order to produce the intensities required for our purpose, currents of 21 A were used for short periods. The slight blackening of the glass bulb at these increased temperatures was taken into account in the calibration. Before and after measuring the flame temperatures the lamp was calibrated pyrometrically at the Precision Calibrations Division of this laboratory, readings differed by no more than 10°K.

Line reversal temperatures were measured at two heights in the flame, namely 3 and 6 cm above the burner, corresponding to about 4.5 and 9.0 msec rise time respectively in the fuel-rich flame, and to 5.5 and 11.0 msec in the stoichiometric flame. Relative measurements of $\exp(-E_{Na}/kT)$ (E_{Na} is the excitation energy of the Na D-doublet and T is the local flame temperature) were performed by spraying solutions of 10 mg/l Na (+ excess cesium to suppress ionization), and recording the Na emission signal as a function of flame height (0 to 7 cm above the burner). The relative variation in T derived from these relative emission measurements was fitted to the absolute line reversal data, while it was assumed that the Na atom concentration did not vary with the height in the cylindrical flame. The resultant temperature curves are presented in Figs. 1 and 2.

The temperature curves as given in these figures show two distinct parts: (i) a rise in temperature from the burner top to about 1 or 1.5 cm flame height, and (ii) a gradual temperature decrease from 1 or 1.5 cm to larger heights. Part (i) may be due to the relatively slow, so-called "afterburning" of carbon monoxide with excess oxygen atoms [8]. This afterburning is a well-known feature of carbon monoxide/air flames and apparently the same phenomenon occurs with nitrous oxide as the oxidant. In the latter flame, a slow reduction of N_2O might also contribute to the afterburning effect. The energy released by recombination of CO and excess O may contribute to an increase in flame temperature (see Figs. 1 and 2), to the flame radiation [9] and to the (chemi) excitation and (chemi) ionization of metal atoms added to the flame [9, 10]. Along with the disequilibrium of the oxygen atoms there are also excess concentrations, relative to the equilibrium values, of H atoms and probably of OH radicals (see below).



Figs 1 and 2. The temperature of the fuel-rich (Fig 1) and the stoichiometric (Fig 2) CO/N₂O flames as a function of height in the flame are shown. The curves I, II and III correspond to different spray-chamber temperatures (that is, to different H₂O supplies) of 0, 22 and 64°C, respectively. At the heights 3 and 6 cm the temperatures measured by the visual line-reversal method are indicated by ●, + and Δ respectively. The points ○ refer to the relative T value obtained by measuring the emission of the Na D -lines which is proportional to the Boltzmann factor $\exp(-E_{Na}/kT)$, as a function of height.

The second, downward sloping part of the temperature curve is explained by the cooling effect caused by the emission of (mainly infrared) radiation. This cooling effect starts right above the burner top, but in the first few cm it is (over) compensated by the afterburning effect. Thanks to the fairly straight shape of this part of the curve, linear extrapolation of the temperature to zero flame height seems justified, yielding an "experi-

mental maximum temperature" which has been corrected for afterburning and cooling by radiation. This maximum temperature is compared with the adiabatic flame temperature calculated from the flow rates and the initial temperature (70°C) of the input gases. The uncertainty in the experimental data will not be smaller than 20°K owing to the error in the extrapolation to zero flame height. The actual temperatures used in the calcu-

TABLE I
Calculated (Adiabatic) and Measured Flame Temperatures^a

No.	Flame CO/N ₂ O/H ₂ O (l/min)	Flame temperature °K	
		Calculated	Experimental
1	3.60/2.40/0.035	2895	2896 ± 20
2	2.40/2.40/0.035	2897	2846
3	3.60/2.40/0.038	2886	2854
4	2.40/2.40/0.058	288	2837
5	3.60/2.40/0.550	2796	2788
6	2.40/2.40/0.550	2778	2774

^aCorrected for radiation losses and afterburning

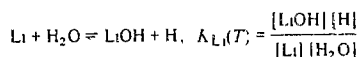
lation of the flame gas composition are believed to be correct within 15°K. The adiabatic temperatures calculated with thermodynamic data given in the JANAF tables [11], are estimated to be correct within 5°K.

The difference between adiabatic and experimental maximum temperature, amounting at most to about 50°K, may be due to a number of effects discussed in detail by Snelleman [12], among which heat losses to the burner head may be dominant.

The Ratio $[H]/[H_2O]$

The existence of free radical (H, OH and O) concentrations larger than the equilibrium values in the flame region a few msec downstream from the primary reaction zone is a well-known phenomenon in $H_2/O_2/N_2$ and $C_2H_2/C_2/N_2$ flames (for reviews on this subject see e.g. [9, 13, and 14]). The carbon monoxide flame exhibits non-equilibrium effects through its "afterburning," causing an initial rise in temperature shortly after passing the primary combustion zone. It is assumed that in this region of the $CO/O_2/N_2$ flame excess oxygen atoms recombine relatively slowly with CO molecules until equilibrium concentrations have settled. Excess H and/or OH radicals downstream of the primary combustion zone have not been reported until now, although the important role of the OH radicals in the overall combustion process of $CO + O_2$ has been recognized and verified experimentally [15]. In view of the importance of a correct knowledge of the ratio $[H]/[H_2O]$ in connection with hydroxide forma-

tion of the alkaline earth metals in the flame [12], this ratio was determined in the various $CO/N_2/O_2$ flames with the Li/LiOH method, first described by Eulewicz et al. [16]. In this method (see also [17]) the ratio $\phi_{Li} \equiv [LiOH]/[Li]$ in the flame is determined by comparing the resonance-line intensities of lithium and sodium under conditions where self-absorption and ionization are negligible. From the values of ϕ_{Li} and of the equilibrium constant $K_{Li}(T)$ of the (partial) equilibrium



the actual ratio $[H]/[H_2O]$ can be determined. The molecular constants of LiOH, required for the determination of $K_{Li}(T)$, were taken from Ref. 18. The dissociation energy of LiOH was assumed to be 4.55 eV [19].

The results concerning $[H]/[H_2O]$ are summarized in Table 2 together with the calculated equilibrium values. The slight influence of the correction for the formation of NaOH is also shown in the table. The dissociation energy of $NaOH \rightarrow Na + OH$ was assumed to be 3.47 eV according to Cotton and Jenkins [18]. From a consideration of all possible sources of error, it is estimated that the experimental $[H]/[H_2O]$ ratios may have a maximum error of about 40%. The greater part of this error (35%) is due to the uncertainty in the constants used in the calculation of $K_{Li}(T)$, but this is a retrievable systematic

error. The uncertainty in the ratio of $[H]/[H_2O]$ at height $h = 1$ cm to $[H]/[H_2O]$ at $h = 6$ cm amounts to about 15%.

It can be seen from Table 2 that (i) the actual ratio $[H]/[H_2O]$ is larger than the equilibrium value in all cases; (ii) the deviations are relatively larger at the greater height in the flame, or in other words, it appears that the ratio $[H]/[H_2O]$ measured at the heights 1 and 6 cm varies hardly, whereas the equilibrium ratio $[H]_{eq}/[H_2O]_{eq}$ decreases strongly with height in the flame. This behavior of $[H]/[H_2O]$ with height contrasts with that in C_2H_2 and H_2 /air flames [9].

An additional experimental check on the measured behavior of $[H]/[H_2O]$ with height in the flame is the measurement of the OH radical concentration at different heights. It is assumed that the ratio $[H]/[OH]$ at any height in the flame is fully determined by the partial equilibrium $CO + OH \rightleftharpoons CO_2 + H$ (equilibrium constant K_1), which is known to be of primary importance in the combustion processes in carbon monoxide flames (see e.g., [8] and the literature cited there), then this ratio can be written as

$$\frac{[H]}{[OH]} = K_1 \frac{[CO]}{[CO_2]}$$

Since CO and CO₂ are major species in the burnt gases, and since afterburning effects are small for

heights $h \geq 1$ cm (see also Ref. 1, thesis), it can be concluded that the actual ratio $[CO]/[CO_2]$ in this flame region, virtually, equals the equilibrium ratio $[CO]_{eq}/[CO_2]_{eq}$, and by consequence the ratio $[H]/[OH]$ will be equal to the equilibrium ratio $[H]_{eq}/[OH]_{eq}$. Detailed calculations of the afterburning effect show that the actual CO concentration might exceed its equilibrium value by at most 2.5% for $h \geq 1$ cm (see Ref. 1, thesis). The four hydrogen containing compounds of importance in our flames (H_2O , H_2 , H and OH) are mutually linked by the partial equilibrium $H + H_2O \rightleftharpoons OH + H_2$ (with equilibrium constant K_2 [20]). Since the partial pressures of these four species are all of the same order of magnitude (about 5×10^{-3} atm), deviations of H and OH radical concentrations from their equilibrium values will produce deviations in the separate H_2 and H_2O concentrations too but the relation $[H_2]/[H_2O] = K_2 [H]/[OH]$ will still hold. Then, as a consequence of the relation $[H]/[OH] = [H]_{eq}/[OH]_{eq}$, stated above, the ratio $[H_2]/[H_2O]$ will also equal its equilibrium value $[H_2]_{eq}/[H_2O]_{eq}$. These two relations together with the measured ratio $[H]/[H_2O]$ and the mass balance for the hydrogen atoms, allow us to calculate the actual partial pressures of the four species H , OH , H_2O and H_2 , at the heights 1 and 6 cm in all our flames. From these results the ratio $[OH]_{h=1}/[OH]_{h=6}$ were calculated and compared

TABLE 2
Experimental and (Calculated) Equilibrium Values for $[H]/[H_2O]$

Flame nr	h cm	ϕ_{L1}	$([H]/[H_2O])_{exp}$		$([H]/[H_2O])_{eq}$
			Without corr for NaOH	With corr for NaOH	
1	1	0.82	0.95	0.91	0.75
	6	0.83	0.83	0.80	0.41
2	1	1.16	0.64	0.61	0.43
	6	1.35	0.50	0.48	0.23
3	1	1.12	0.67	0.64	0.43
	6	0.98	0.71	0.68	0.29
4	1	1.62	0.46	0.44	0.29
	6	1.17	0.47	0.35	0.17
5	1	2.28	0.31	0.29	0.099
	6	3.36	0.20	0.18	0.074
6	1	4.67	0.15	0.14	0.064
	6	3.63	0.18	0.17	0.045

TABLE 3
Ratios of OH Radical Concentrations at Heights 1 and 6 cm, Obtained
by Three Different Methods

Flame no.	$[\text{OH}]_{h=1}/[\text{OH}]_{h=6}$		
	Bi-absorption measurement	From $[\text{H}]/[\text{H}_2\text{O}]$	From calculated equilibrium values
1	$1.00 \pm 20\%$	$0.96 \pm 10\%$	1.25
2	0.92	0.96	1.20
3	0.93	0.90	1.21
4	1.04	0.78	1.22
5	0.99	1.34	1.20
6	1.10	0.77	1.18

with the corresponding ratios determined from relative OH absorption measurements. These absorption measurements were carried out with a bismuth hollow cathode lamp as a background source [21], emitting the 7667.72 Å line. This radiation is partly absorbed by two different rotational transitions of the (0,0) band of the $^2\Sigma^+ - ^2\Pi$ system of the OH radical; these transitions are ($K'' = 10, J'' = 9\frac{1}{2} \rightarrow K' = 11, J' = 10\frac{1}{2}$) and ($K'' = 9, J'' = 8\frac{1}{2} \rightarrow K' = 10, J' = 9\frac{1}{2}$). It should be noted that in these measurements the absorption of both the inner and the outer flame is observed, as secondary combustion at the greater flame height might enhance the OH concentration in the outer flame regions; a slightly too low value for $[\text{OH}]_{h=1}/[\text{OH}]_{h=6}$ might result.

In Table 3 the ratios $[\text{OH}]_{h=1}/[\text{OH}]_{h=6}$, derived from the absorption measurements as well as from the measured $[\text{H}]/[\text{H}_2\text{O}]$ ratios, are collected, while the equilibrium ratios are also presented for flames no. 1, 2 and 3. The agreement between the experimental values in columns 2 and 3 is satisfactory. In Refs. 1 and 2 evidence is presented that the measured $[\text{H}]/[\text{H}_2\text{O}]$ ratio at $h = 6$ cm in flame no. 5 is somewhat too low, yielding, by consequence, a too high ratio $[\text{OH}]_{h=1}/[\text{OH}]_{h=6}$ in this flame. Considering the deviations between the experimental $[\text{OH}]$ ratios, it seems safer to assume a probable accidental error of 20% in the measured $[\text{H}]/[\text{H}_2\text{O}]$ ratios than the *a priori* calculated accidental error of 10%.

The behavior of excess $[\text{H}]/[\text{H}_2\text{O}]$ with height in the flame is typically different from what might be expected by comparison with $\text{C}_2\text{H}_2/\text{air}$ and

H_2/air flames. The values found here have been used in the evaluation of the alkaline earth dissociation energies $D_0(\text{MO})$ and $D_0(\text{MOH})$, described in Refs. 1 and 2.

Burning Velocities of the $\text{CO}/\text{N}_2\text{O}/\text{H}_2\text{O}$ Mixtures

The noticeable variation of the height of the primary combustion cones with varying water supply to the flame and the complete blowoff when all traces of water are removed from the tubes and burner house, made it clear that for the $\text{CO}/\text{N}_2\text{O}$ flame, like for the $\text{CO}/\text{O}_2/\text{N}_2$ flame, the burning velocity is primarily determined by the water content in the mixture. In order to compare our observations with available data from the literature, estimates of the burning velocity were derived as a function of water content from the top height and basis diameter of the combustion cones and the flow velocity of the unburnt mixture through the burner ports. Although this method, as discussed by Gaydon and Wolfhard [22], may yield absolute burning velocities that are too high—owing to the neglect of the detailed flame structure at the base of the cone—it is believed that the ratios of the burning velocities thus obtained for different water contents are correct within about 15%.

The unburnt mixture for each central flame passes 19 burner ports of 0.8 mm diameter each. It is assumed that the flow velocity is uniform over the entire cross section of each port and that the flame front is a geometrical cone, the basis of which equals the burner port aperture. The measured top height of the cones yields the cone

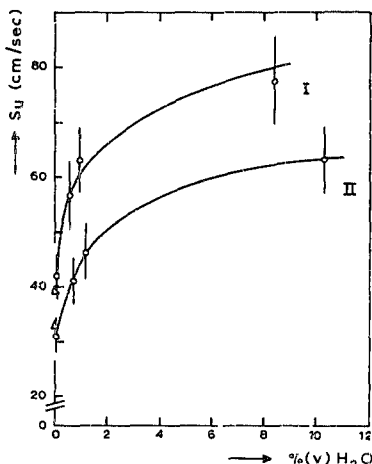


Fig. 3 The burning velocity S_u of the CO/N₂O/H₂O flames is plotted vs the fraction (in volume %) of H₂O vapor in the unburnt mixture. The curves I and II refer to the fuel-rich and stoichiometric flame, respectively. Points Δ have been measured by Van Wouterghem and Van Tiggelen [6].

half-angle α which relates the burning velocity S_u with the flow velocity v_0 according to $S_u = v_0 \sin \alpha$. The results for both gas-mixture strengths and the various fractions of water vapor in the unburnt mixture, are given in Fig. 3. The measurements at "zero" volume % of water vapor correspond to the cone heights measured about one hour after stopping all water supply to the flame, while maintaining the CO and N₂O flows in order to dry the walls of the spray chambers and the tubes to the burner thoroughly. Under this condition the upper limit of the water content in the stoichiometric flame amounts to about 0.05%. In some cases the flame tended to blow off.

Van Wouterghem and Van Tiggelen [6] have measured the burning velocities of CO/N₂O mixtures at 1 atm containing 0.2% (by volume) H₂ at most. They have found $S_u = 33.5$ cm/sec for the stoichiometric flame ($T = 2650^\circ\text{K}$) and $S_u = 39$ cm/sec for a flame with CO:N₂O = 1.5:1 ($T = 2615^\circ\text{K}$). There is a good agreement between our data and theirs, within the limits set by the accidental error of about 10%. The strong depen-

dence of the burning velocity on the water content in our CO/N₂O flames is comparable to that of CO/air flames [8], pointing to the great importance of H-containing radicals in the combustion mechanism. The burning velocity of "dry" CO/O₂/N₂ flames [15] is of the same order of magnitude as that for our CO/N₂O flames, which means that the same burner head can be safely used for both types of flame.

Emission Spectrum of the Metal-Free Flame

The spectrum emitted by the interconal gases of the metal-free CO/N₂O flames studied here exhibits the well-known features of the CO/O₂/N₂ flame, i.e., a (quasi) continuous emission ranging from the near ultraviolet to the green region in the spectrum, superimposed by a very weak banded structure, and (even in the almost "dry" flames) a strong OH emission from 3064 Å to about 3200 Å. These characteristics were found by us with a "SPEX" 3/4-m Czerny-Turner scanning spectrometer with a bandpass of 0.4 Å.

The absolute spectral intensity of the background (quasi) continuum was measured and compared with calculations based upon data given by Zeegers [9]. According to this author the spectral intensity of the metal-free CO/O₂/N₂ flame, apart from the OH emission, can be empirically described by $I_\lambda = a_\lambda [\text{CO}][\text{O}] + c_\lambda \exp(-hc/\lambda kT) [\text{CO}_2]$, where $[\text{O}]$ may be in equilibrium or not. These two terms represent the contribution of the radiative recombination of CO and O, and of the thermal quasicontinuous emission of the CO₂ molecules, respectively. The λ -dependent coefficients a_λ and c_λ have been found by Zeegers to be independent of temperature in the range from 2000 to 2400°K.

For $\lambda = 4500, 4000$ and 3600 Å and at a height of 3.3 cm (where afterburning effects may be neglected) the emission of the fuel-rich and the stoichiometric CO/N₂O flame (sprayer temperature 0°C) was measured in absolute value by calibration against a standard tungsten-strip lamp (see Table 4). The accuracy of our experimental values amounts to about 15%. Table 4 also shows the intensities calculated from the values of a_λ and c_λ taken from Ref. 9 and from the equilibrium concentrations of the relevant species (details of the calculation of the equilibrium composition of the burnt gases are given in Ref. 1, thesis).

TABLE 4
Spectral intensities of Background Continuum of Two CO/N₂O Flames,
Measured and Calculated from the Literature Data (in quanta/cm²s Å)

Wavelength, Å	Fuel-rich $T = 2815^\circ\text{K}$		Stoichiometric $T = 2775^\circ\text{K}$	
	Exp.	Calc.	Exp.	Calc.
4500	3.3×10^{12}	4.2×10^{12}	3.4×10^{12}	3.2×10^{12}
4000	4.4×10^{12}	6.8×10^{12}	4.6×10^{12}	5.2×10^{12}
3600	2.6×10^{12}	7.6×10^{12}	2.7×10^{12}	5.8×10^{12}

According to Ref. 9 the uncertainties in a_λ amount to 25%, c_λ is believed to be correct within a factor of 2.5. In all cases studied here, the first term in I_λ containing a_λ exceeds about four times the term containing c_λ , so the uncertainty in the calculated values of I_λ is about 30%. Within these error limits the calculated and experimental values for both flames at $\lambda = 4500$ and 4000 Å are in agreement. The deviations found at $\lambda = 3600$ Å might be explained by a possible temperature dependence of a_λ above 2400°K , assuming that this dependence is stronger for $\lambda = 3600$ Å than for the other wavelengths investigated.

Gavdon [8] has compared the spectra of CO/O₂ and CO/N₂O flames and found a "slightly different" distribution of intensity in the continuum. No evidence for the presence of the NO + O continuum, reported in Refs. 8 and 23, was obtained in our flames. If the NO + O continuum, extending from 4000 Å to the red, it would play a noticeable part in our flames, the absolute spectral intensities at $\lambda = 4000$ Å and $\lambda = 4500$ Å would be larger than the calculated values, especially so for the stoichiometric flame.

Ionization in the Metal-Free CO/N₂O Flames

The order of magnitude of the free electron concentration in the metal-free CO/N₂O flames was investigated with the HF resonance method developed by Borgers [24] and compared with the calculated thermal ionization of NO (ionization potential 9.25 V [25]).

In the HF resonance method the flame under test forms a part of the dielectric of a parallel-plate condenser, which is shunted by an inductance. Under the conditions of our experiment, the bandwidth of this resonant LC circuit is a linear function of the concentration of free electrons

present in the flame. The circuit was tuned at a frequency of 23 MHz and calibrated by supplying a known amount of electrons into the flame while observing the subsequent increase in width of the resonance peak. Cesium is a useful electron donor as it is, virtually, fully ionized at the temperatures of the CO/N₂O flame. The total Cs concentration in the fuel-rich CO/N₂O flame was determined to be 1.8×10^9 cm⁻³ for a 10 mg/l Cs-salt solution by calibration of the sprayer performance with the curve-of-growth method [10]. By comparing the increase in bandwidth of the LC circuit when the fuel-rich flame without Cs and with 1.8×10^9 cm⁻³ Cs ions, respectively, was placed between the condenser plates, the concentration of free electrons in the metal-free flame was found to be of the order of 2×10^9 cm⁻³. This figure is an average value referring to a height interval extending from 3 to 5 cm above the flame base, the diameter of the condenser plates being 20 mm. In this comparison the effect of the partial suppression of the (thermal) NO ionization by the electrons originating from the Cs ionization was taken into account. Also allowance was made for the fact that Cs was present in the inner flame only, whereas NO was present in both the inner flame and outer flame mantle (see for details Ref. 1, thesis). The experimental figure is uncertain by at least a factor of 2, as the temperature and thus the electron concentration in the outer flame mantle may not be uniform. Also the inhomogeneity of the electric field between the circular condenser plates introduces an uncertainty, since the diameter of the plates was of similar magnitude as their mutual distance. It was checked by observation of the residual Na D-line emission that ionization of Na-impurity atoms did not play a major role.

From the value of the ionization constant for

NO at $T = 2780^\circ\text{K}$ ($2.1 \times 10^{13} \text{ cm}^{-3} \pm 30\%$) and the NO-equilibrium concentration in the flame considered ($2.4 \times 10^{16} \text{ cm}^{-3}$), the thermal electron concentration in the metal-free flame was calculated to be $7.1 \times 10^9 \text{ cm}^{-3}$ ($\pm 30\%$).

Comparing this calculated thermal electron concentration with the rough experimental value found above, we may conclude that the order of magnitude of the ionization found in the metal-free, fuel-rich CO/N₂O flame can be accounted for by thermal ionization of the NO molecules.

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(Received August 1971, revised version
received April 1972)