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EXPERIMENTAL INVESTIGATIONS AND GAIN MEASUREMENTS OF ALKALINE EARTH CATALYZED N₂O + CO FLAMES

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Introduction

Dry N₂O-CO flames can be efficiently catalyzed by a metal atom induced chain reaction.¹ In the case of catalysis by Mg, Ca or Sr atoms the resultant chemiluminescence contains banded molecular emissions which are not seen in conventional metal oxidation flames.² The 372 nm band of MgO identified as the ³Δ→³Π system³ is characteristic of the new features obtained from metal oxidation flames upon addition of CO. Also in Ca and Sr catalyzed N₂O-CO flames very similar appearing bands arise at 550 and 595 nm respectively. These features have been previously observed in arcs⁴ and have been tentatively assigned to polyatomic oxides,⁵ however, more recent studies⁶ including isotopic displacement⁷ have shown at least for the 372 nm band that the carrier is MgO. The basis for the early assignment was the complex rotational structure that was observed, which however is also understandable in terms of the ³Δ→³Π assignment. Slightly to the red of the narrow MgO, CaO and SrO (³Δ→³Π) bands in each case lies a broader and more complex structure lying at about 380, 620 or 665 nm in Mg, Ca or Sr catalyzed N₂O-CO flames respectively.

Assignments

The bands are very close to and overlapping the metal monohydroxide flame bands but are distinct from them. Reference flames were produced by burning the metal vapor in either N₂O or H₂O and mixing the reacted products with discharged nitrogen in a flow system. The resultant

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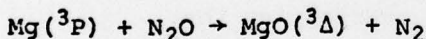
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chemiluminescence was characteristic of the metal oxides when N₂O was used as the oxidizer and was identical in appearance to the metal-N₂O-CO flame emissions, whereas when H₂O was used as the oxidizer the emission induced by transfer from nitrogen was of a distinctly different origin and was identical to the well known monohydroxide flame bands characteristic of wet N₂O-CO flames.⁸

The new bands, which are characteristic of arc sources, are efficiently produced with photon yields (per metal atom) lying in the range of 1-6% and are assigned by analogy to the known MgO systems⁹ to the ³Δ→³Π system (narrow bands) and the ¹Δ→¹Π and ¹Σ⁻→¹Π systems (broad bands). The new bands which characterize the metal-N₂O-CO flames are also strongly produced at higher density in the supersonic transient flow of a shock tube driven reactor.¹⁰

Chemical Excitation

An interesting feature of the metal-N₂O-CO flames is that the ³Δ state lies too high (≈30 000 cm⁻¹) to be directly populated by the metal-oxidation step alone, therefore an efficient multistep chain reaction must lead to the metal oxide excitation. Correlation arguments¹¹ would tend to support a mechanism by which oxidation of electronically excited metal atoms (in the metastable ³P state) leads to population of the metal oxide ³Δ state by an exothermic reaction. Such a mechanism would be possible because the metal-N₂O-CO flames are also characterized by a high density and efficient production of excited metal atoms.¹² Therefore to determine if the mechanism responsible for the new chemiluminescence was the oxidation of excited metal atoms according to the reaction



both the intensities of Mg(³P₁ → ¹S₀) and MgO(³Δ → ³Π) chemiluminescence were monitored as functions of the N₂O concentration. At low pressures and low oxidant density it was found that the ratio of molecular to atomic chemiluminescence was proportional to the N₂O flow into the reactor.

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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The addition of CO to alkaline earth-N ₂ O flames in a fast flow low pressure reactor has resulted in the observation of banded molecular emissions which are not seen in conventional alkaline earth oxidation flames. These bands are assigned to the ³ Δ→ ³ Π, Δ→Π, and ¹ Σ→ ¹ Π systems in CaO and SrO. A white light gain measuring procedure was developed to probe for gain/absorption in these flames, and preliminary (absorptive) results are given. | | |

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Gain Measurements The potential for development of such systems as possible visible chemical lasers rests in the fact that the transitions which are excited are part of a three level radiative cascade and that the upper state is sufficiently excited to produce a useable gain coefficient if the intermediate level can be depopulated either radiatively or by quenching. To assess whether the pumping or relaxation of the states is favorable to the maintenance of population inversion, gain measurements have been employed. The technique which was employed makes use of the sensitivity of an optically resonant cavity to internal sources of gain or absorption. Furthermore, since the banded structures to be studied are characterized by very dense rotational packing⁴⁻⁶ it was possible to employ without serious loss a white light probe (quartz halogen lamp) to measure the changes in overall transmissivity of the optical cavity upon modulation of the flame source within it. As shown in the figure, the flame was oriented transversely to the axis of the optical cavity. The light source, appropriately filtered was chopped at a high frequency (~ 1 KHz) and directed through the cavity. The metal-N₂O-CO flame was modulated at 5 Hz in an on-off fashion by a solenoid valve that controlled the flow of the carrier gas which entrained the vaporized metal atoms within a heated crucible, while the N₂O-CO flow was continuous. An alternative scheme which modulated the N₂O-CO flow with a continuous flux of metal atoms was found to yield incomplete modulation of the flame thereby causing erroneous results.

The time dependence of the cavity transmission as sensed by the monochromator and PMT detector depends on the two modulation sources and the optical interaction between them. Absorption or stimulated emission processes within the flame act as a low frequency amplitude modulator of the high frequency carrier generated by the lamp and chopper. The resultant intermodulation products can then be detected and processed electronically as shown to

determine the gain or loss coefficient. In general prefiltering of the white light probe is necessary to prevent unwanted photoluminescence responses, however, for the systems studied here, no such effect was detected when the light source and chopper were moved so as to illuminate the intracavity flame from the side. Experimental checks were included to show that no unintentional intermodulation products were generated by the detector or the following electronics and that spontaneous emission (chemiluminescence) was discriminated against as a possible alias for gain or absorption by the signal processor. The system response was shown to be due only to physical processes in the flame itself which were interactive with the external light source but only in a colinear geometry between the source, cavity, flame and detector. The most difficult problem was to ensure that the flame was totally modulated, as otherwise the difference between two levels of absorption could be mistaken for gain if the modulation were incomplete and the flame chemistry were adjusted into a region where the absorption was decreasing with increasing reactant density. The system noise level as obtained with a cavity formed by two 1% transmitting dielectric mirrors, a cooled low noise RCA 4832 PMT and 3 sec data integration was more than adequate for the observation of gain or absorption related to transitions between excited states of the molecules, although resolution was practically limited to ~ 2 nm.

The preliminary results show absorption on all the $^3\Delta \rightarrow ^3\Pi$ and $^1\Delta + ^1\Sigma^- \rightarrow ^1\Pi$ transitions of CaO and SrO, therefore it must be concluded that either the radiative lifetimes and/or branching ratios for pumping into the various energy levels are unfavorable for lasing. However, with substantial metal flows a regime has been encountered in which increasing the CO content of the flames results in a simultaneous increase of the chemiluminescence and a decrease of the absorption. Therefore, the effects of quenching may upon sufficient scaling and variation of the flame parameters lead to a condition

of optical gain suitable for a laser. Also the possible addition of a selective quencher to the flame could have the same result. These possibilities are now being explored by means of the modulated gain measurement technique. Data typical of Ca-N₂O-CO flames are shown in Fig. 2.

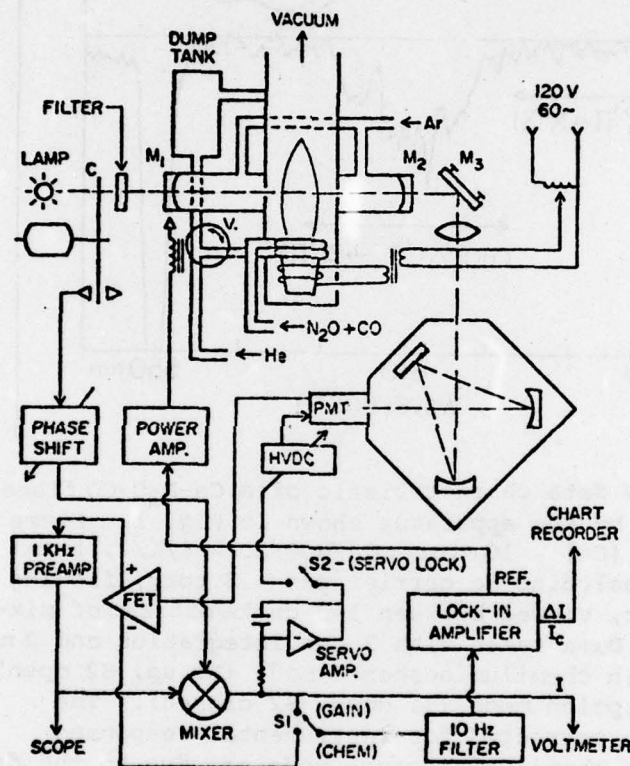


Fig. 1: Experimental arrangement for measurement of gain or absorption of intracavity modulated flame.

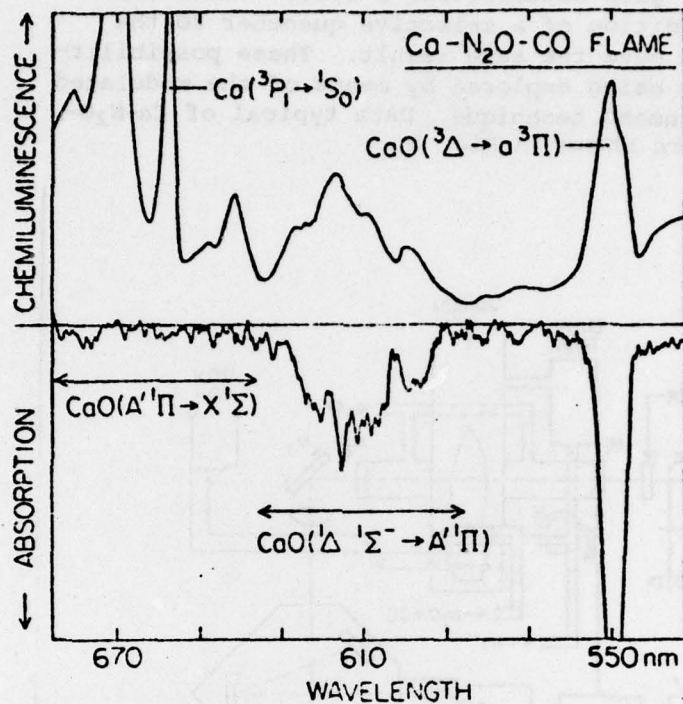


Fig. 2: Raw data characteristic of a Ca-N₂O-CO flame as obtained by the apparatus shown in Fig. 1. Flame parameters, [Ca] ~ 10.mtorr, Ca/N₂O/CO ~ 1/1/2, total pressure, including He carrier gas ~ 3 torr, flowing at 200 m/sec, viewed between 1-3 cm downstream of mixing point. Data taken with 3 sec integration and 2 nm resolution in chemiluminescence mode (S1 up, S2 open) and in absorption mode (S1 down, S2 closed). The data are not corrected for instrumental responses which in the chemiluminescence mode are due to the detector, whereas in the absorption mode the only wavelength dependent factor is the cavity finesse which is broadly peaked at 600 nm.

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