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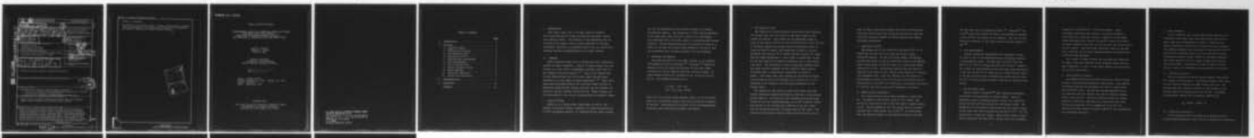

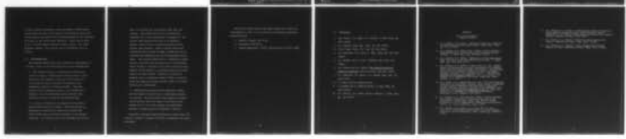

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Alkaline earth catalyzed N_2O-CO flames have been studied as potential electronic transition chemical lasers. The addition of CO to the $M+N_2O$ flames, where M=Mg, Ca, and Sr, has been shown to efficiently produce the respective metastable alkaline earth (^3P) atoms. These flames have been further shown to exhibit enhanced MO($A \rightarrow X$) photon yields as well as new MO band systems in the chemiluminescence spectra. The mechanism of these reactions has been elucidated and information has been gained regarding

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the identity of the reservoir state. Results of spectroscopic assignments and gain measurements on the alkaline earth oxide bands are reported as are results of transfer and excimer formation studies.

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FINAL SCIENTIFIC REPORT

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David J. Benard
Warren D. Slafer
Paul H. Lee

Quantum Institute
University of California
Santa Barbara, California 93106

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I. INTRODUCTION

This report deals with a two year study of alkaline earth catalyzed N_2O-CO flames as potential electronic transition chemical lasers. The details of the experiments and the analysis of the results have all been published in the open literature, therefore, we summarize herein only the significant findings and make recommendations as to future efforts.

II. FINDINGS

Metal oxidation flames such as Ba+N_2O have been intensively studied as laser candidates. Central to these studies lies the concept of a long lived or metastable reservoir state that is the adiabatic reactions product.(1) Many of the results that we have obtained deal with this state, which was previously sensed by us in CO_2 energy transfer experiments.(2) These early experiments provided evidence for efficient energy storage in chemically generated MgO (Mg+N_2O reaction) and for chemical reaction of the MgO reservoir state with CO. These findings set the background for our initial investigations of M-N_2O-CO flames.

1. M-N_2O-CO Flames

Adding CO to a M+N_2O flame, where M=Mg, Ca and Sr, had several interesting effects, including (1) efficient production of M(^3P) metastable species, (2) enhanced MO(A→X) photon yields and (3) the appearance of new MO band systems in the chemiluminescence spectra. The production of $M(^3P)$ species appeared to be essentially 100% efficient; however, the metastables once generated were, of course, subject to quenching and further reaction. The MO photon yields were increased by as much as a factor of 40 (MgO, B→X system) upon addition of CO and in this way an absolute SrO, A→X photon yield of 22% was obtained.

2. Mechanism of Reaction

The gases N_2O and CO do not react rapidly at low pressure and temperature unless catalyzed.$^{(3)}$ Fennimore$^{(4)}$ found that catalysis by Na was rapid and resulted in efficient chemiexcitation of the Na atoms to the first excited p-state. We found similar results for catalysis by Mg, Ca and Sr but not for Ba. The mechanism appears to be

$$M + N_2O \rightarrow MO^{+} + N_2$$
$$MO^{+} + CO \rightarrow CO_2 + M^{*}(^3P)$$

where MO^{+} is the metal oxide reservoir state, since the second step is an endothermic reaction for ground state MO to produce M^* species. Coproduction of CO_2 with M^* was also demonstrated using CO_2 laser induced fluorescence techniques.

3. The Reservoir State

The identity of the MO reservoir state was of much interest. Our results show that this state is much more stable in the lighter MO species. This result can be understood simply in terms of the energy overlap of the MO emitting states with the heat of reaction; whereas the Mg-N_2O reaction exoergicity fails to reach the MgO($B^1\Sigma$ state), the Ba+N_2O heat release is in good resonance with the BaO $a^3\Pi$, $^1\Pi$ states and the emitting $A^1\Sigma$ state. Thus BaO chemiluminescence is very bright in comparison to MgO, but the MgO retains its chemical excitation over a much longer time scale. The efficiency of the M* generation suggests that the M+N_2O reaction produces the MO^+ reservoir state with an efficiency that is essentially independent of molecular weight. This means that laser schemes can profitably be based on Mg flames as well as Ba systems, thus allowing one to take advantage of the superior volitilization properties of the lighter metal.

The identity of the reservoir state was sought after and initial quenching experiments tended to indicate a vibrationally excited species. We found that the continuum emitted by M+N_2O flames was not the chemiluminescence of the MO^+ reservoir state, even though it was quenched upon addition of CO, but rather that the continuum derived its energy from the MO^+ state. The carrier of this feature remains unknown but may be polyatomic, such as $(MO)_2$, which would explain the lack of spectroscopic structure and the fact that energy pooling must be involved, since the continuum extends to photon energies well beyond the $M+N_2O$ exoergicity.

4. Reactions of $M(^3P)$

The primary end of the chemically generated $M(^3P)$ in our flames was to react again with N_2O and produce highly excited MO species. In the case of Mg flames, the Mg^*+N_2O reaction was shown to lead by correlation rules to the $MgO(^3\Delta)$ state, which decays to the $a^3\Pi$ state in a narrow band system centered at 372 nm. The Mg^*+N_2O reaction was also found to populate the B state as well, which is not expected if correlation arguments hold. This may, however, be the result of a non-adiabatic process, since the Mg^*+N_2O reaction may also go adiabatically to $MgO(a^3\Pi)$ with sufficient vibrational excitation to transfer into the B state upon subsequent collisions.

5. Spectroscopic Assignments

The results with Ca and Sr were analogous to those with Mg. The bands of CaO and SrO, known as "arc bands", were excited by reactions of Ca* or Sr* with N_2O in flames containing CO. The assignment of the "arc bands" has been largely confused with "flame bands" due to MOH.(5) We established that the systems present in the $M+N_2O+CO$ flames are not MOH nor are they $(MO)_2$, as though by Gaydon.(6) Eckstrom(7) and Field(8) have also studied the 550 nm band system we assigned to CaO $(^3\Delta \rightarrow a^3\Pi)$ and concur in our findings. The CaO and SrO bands are analogous to the known ultraviolet band systems of MgO.(9)

6. Gain Measurements

Several diagnostic measurements were employed to assay for gain on any of the chemiluminescent transitions inherent in the $M\text{-}N_2O\text{-}CO$ flames. We found that the $M(^3P_1 \rightarrow {}^1S_0)$ and $MO(^3\Delta, {}^1\Delta + {}^1\Sigma^- \rightarrow a^3\Pi, {}^1\Pi)$ transitions were not inverted. However, as a result of these efforts we did find very large populations in the CaO and SrO $a^3\Pi, {}^1\Pi$ states and we further showed, based on the way in which these concentrations varied with CO, that the $a^3\Pi, {}^1\Pi$ states were not the MO^+ reservoir or energy pooling states.

7. The MO Ground State

Harris, Revelli and Wicke(10) have reported anomalously low $BaO(X^1\Sigma)$ concentrations in $Ba+N_2O$ flames. Using an absorption probe we obtained similar results for $Ca+N_2O$ and $Sr+N_2O$ and confirmed the results for the $Ba+N_2O$ flames. The absorptions on the $MO(A \leftarrow X)$ transitions were two orders of magnitude lower than those recorded for the $MO(^3\Delta, {}^1\Delta + {}^1\Sigma^- \leftarrow a^3\Pi, {}^1\Pi)$ transitions in identical flames. These results imply a rapid removal mechanism for the $MO(X^1\Sigma)$ ground state and a probable inversion of the MO($a^3\Pi, {}^1\Pi \rightarrow X^1\Sigma$) band systems. These forbidden transitions are, however, too weak to produce a laser based on a molecular species. Adding CO to the M+N_2O flames decreased still further the MO($X^1\Sigma$) ground state while initially enhancing (at least for CaO and SrO) the concentration of the A states. Had this trend continued, which was not the case, inversion of the strong chemiluminescent A→X transitions could have been obtained.

As a result of these studies, we concluded that there are no useful inversions inherent in the M+N_2O+CO flames and that laser potential, if any, in such flame systems lies with their use as M(^3P) generators.

8. Energy Transfer Studies

We attempted briefly and without success to observe energy transfer from chemi-excited MgO to iodine atoms. Much greater success was achieved by introducing Ca into a flowing afterglow of Mg(^3P) atoms. The Mg* was rapidly quenched and the Ca atoms were excited, despite the lack of resonance between atomic energy levels. The Mg-Ca transfer system was further studied by electrical discharge in a mixed metal heat pipe. Evidence was obtained for the pumping of Ca by Mg*, but deleterious energy pooling reactions (Mg*+Ca*) were responsible for preventing inversion.

9. Metal Hydrides

We also observed very intense MgH and CaH emission in RF discharged metal vapor heat pipes where trace impurities of water vapor had contaminated the sample. Electrical-to-optical conversion efficiencies as high as 5% were measured. The probable mechanism was excitation of the metals to the ^3P state by the discharge, which is a very efficient process, followed by resonant energy transfer to the metal hydrides which then decay by a set of highly allowed transitions to the ground state. The potential curves of MgH or CaH are, however, such as to discourage any possibility of inversion.

10. Bimetallic Molecules

We also attempted to observe energy transfer from $Mg(^3P)$ to K atoms in the afterglow. The nearly resonant K(5s) state was not excited although the K(4p) energy level was. The molecule KMg was, however, observed to form rapidly in the excited state with efficiencies of up to 20%. Subsequent investigations showed that the pumping reaction was

$$K_2 + Mg(^3P) \rightarrow KMg^* + K.$$

11. Bound-Free Transitions

It was speculated that KMg might be an excimer and that the KMg chemiluminescence might consist of bound-free transitions.

A laser induced fluorescence study disclosed a weakly bound ground state but due to the shape of the potential curves the excited state was found to decay predominantely to the dissociative part of the ground state potential. Hence KMg is shown to be a "Van der Waals" molecule similar to Ca_2. For laser purposes, however, this species can be considered to be an excimer.

III. RECOMMENDATIONS

The $M+N_2O+CO$ system shows high promise for development as a chemical laser if the following goals can be accomplished.

1. The $M+N_2O+CO$ flame as a generator of M* must be scaled to supply a sufficient M* flow to power a laser system and the quenching lifetime of the M* must be long enough to allow efficient M* generation and subsequent reaction or energy transfer. This may likely occur in supersonic flows. Our studies were subsonic, thus back diffusion mixed reactants and products and lead to rapid M* quenching by N_2O.

2. A means of extracting the energy in M* by stimulated emission has to be found. This could occur by supplying a reactant that selectively attacks the $M(^1S)$ ground state, by energy transfer, or by excimer formation. Our studies have only scratched the surface

here, but already one interesting lead, KMg, has emerged. KMg itself may not be an interesting candidate due to the unfortunate overlapping of the $K_2(B \rightarrow X)$ band system which acts as an absorber. However, this is not an essential feature of this excimer type molecule. Hence, similar bound-free transitions may be found in RbMg or NaMg that do not coincide with absorption by the corresponding alkali dimer. The scaling properties of a chemically pumped excimer laser are very favorable due to the probable short radiative lifetime of the laser transition which imparts a high immunity to quenching once the excited species has been formed. Therefore it should be possible given an adequate supply of Mg* to pressure scale the chemically pumped excimer laser to a satisfactory gain coefficient.

3. Compatability between the M* generation scheme and the method of extraction by stimulated emission is required. This may entail some chemical considerations and may favor one means of extraction over another but it is in fact largely an engineering problem in staged injection supersonic reactors.

Therefore, continued experimentation in these areas (M* scaling, transfer, excimers and $M(^1S)$ scavenging) are highly warranted.

The kind of laser system that might emerge as a result of developments in this field would have the following desirable characteristics.

1. Specific Energy ~400 kJ/lb
2. Wavelength 450-750 nm
3. Plenum Temperature ~1200°C (boiling point of Mg @ 1ATM)

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APPENDIX

List of Publications
(AFOSR 76-2959)

1. D.J. Benard, W.D. Slafer, "Efficient Chemical Production of Metastable Alkaline Earth Atoms," Chem. Phys. Lett. 43, 69-72 (1976).

2. D.J. Benard, W.D. Slafer and J. Hecht, "Chain Reaction Chemiluminescence of Alkaline Earth Catalyzed N_2O-CO Flames," J. Chem. Phys. 66, 1012-1016 (1977).

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