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## VISIBLE CHEMICAL LASERS

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1.        Introduction

For many years the potential utility of chemical lasers operating in the visible region of the spectrum has been obvious. The use of chemical fuels would eliminate the need for massive electrical power supplies, and visible light propagates with minimal diffraction spreading through the atmosphere. Much effort has been expended in trying to develop visible chemical lasers in the United States. After reaching an unsuccessful climax of activity in the mid-seventies, work on chemical lasers subsided to a low level. The recent development by the Air Force Weapons Laboratory of the oxygen-iodine laser operating at 1.31  $\mu$  in the near infrared has stimulated renewed interest in the feasibility of visible chemical lasers.

In the spring of 1980 DARPA requested that JASON review the present status of research on visible chemical lasers. During the summer of 1980 a JASON committee spoke to a number of scientists with interests in areas related to visible chemical lasers. This report summarizes the most interesting ideas encountered during the summer. The committee found that excellent work is being carried out at several laboratories. The prospects for visible chemical lasers seem guardedly hopeful, although many key questions remain unanswered and no avenues of research seem so likely to succeed that a major increase in the research effort is warranted.

The lessons of the oxygen-iodine laser have not been lost on the community and much work has been devoted toward finding other systems which

have similar favorable characteristics. The useful electronic energy of the oxygen iodine lasers is generated because the ground state of the oxygen molecule is a spin triplet while most chemical reactions which produce oxygen molecules proceed along a singlet potential energy surface. Because the nuclear charge of the oxygen atom is relatively small, electronic spin is quite a good quantum number and the low-lying singlet states of the  $O_2$  molecule are extremely metastable, even in solution. Thus, adequate time is available for the oxygen metastable molecules to transfer their energy to atomic iodine which has a sufficiently short radiative lifetime and a sufficiently narrow emission linewidth to lase on the fine structure transition  $^2P_{1/2} \rightarrow ^2P_{3/2}$ . The same spin-selection rule which makes  $O_2(^1\Delta)$  molecules so metastable also makes it impossible for the  $O_2$  molecule to lase on the transition  $^1\Delta \rightarrow ^3\Sigma$  to the ground state. Even if the radiative transition were not so highly forbidden, the broad linewidth of the transition in molecular oxygen, which results from the large number of occupied vibration-rotation levels in the upper state,  $^1\Delta$ , of the metastable molecule and the large number of vibration-rotation levels to which lasing is allowed by the Franck-Condon principle, lead to a very broad stimulated emission linewidth and a correspondingly low gain.

The nitrogen halide molecules, in particular NF which is isoelectronic to  $O_2$ , have received a great deal of attention. Nitrogen halides have  $^1\Delta$  and  $^1\Sigma$  metastable states like  $O_2$ ; they can be generated by chemical reactions similar to those which produce metastable  $O_2$ ; and atoms, e.g., bismuth, can be found which have energy levels

resonant with metastable NF . One should not be blinded to other possibilities by the success of the oxygen-iodine laser. Good work on chemically excited metal oxides and metal atoms is being pursued at the Air Force Weapons Laboratory. Interesting work on vibrational to electronic energy transfer is proceeding at Calspan. Excellent computational resources are available, for example, at the National Bureau of Standards where the group headed by M. Krauss has had much successful experience in calculating key molecular parameters.

After evaluating the information received during the summer, the JASON committee reached the following conclusions:

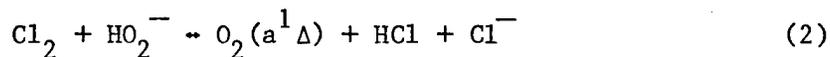
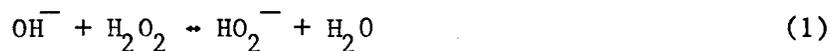
- A. Visible chemical lasers cannot be ruled out on the basis of any known scientific laws, and indeed the success of the oxygen-iodine laser gives encouragement that other chemical lasers at still shorter wavelength may be found.
- B. There is no obvious area which, if heavily funded, would very likely lead to new visible chemical lasers. Thus, no large new program on visible chemical lasers can be justified at this time.
- C. There are a few good ideas for new visible chemical lasers; for example, the work on NF at Aerospace, the work on metal oxides at the Air Force Weapons Laboratory, and the work on CO-NO at Calspan. Modest support of work in areas like these would be a good investment, since it would encourage continued awareness of DOD needs for visible chemical lasers.
- D. It would not be in the best interests of the DOD to have work on new visible chemical lasers stop completely. The history of

the oxygen-iodine laser at the Air Force Weapons Laboratory shows the wisdom of long-term funding of good but slowly maturing new ideas.

## 2. The Oxygen-Iodine Laser

The  $O_2$ -I electronic transition chemical laser was developed at the Air Force Weapons Laboratory and is the only such laser in existence. At a wavelength of 1.31  $\mu$  it is not quite "visible," but presents many of the same problems faced by any electronic transition chemical laser. That it works at all is seemingly miraculous, for it depends on a number of fortunate reaction rates.

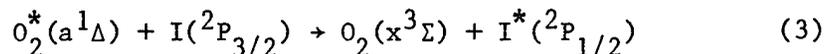
Energy is stored by the first excited state of  $O_2(a^1\Delta)$ . This highly metastable state has a radiative lifetime of about 45 minutes, essentially infinite. It is also nearly immune to deactivation on many surfaces and in most collisions and may flow through pipes almost as if it were a stable gas. It may be produced in an alkaline solution of  $H_2O_2$  by the addition of  $Cl_2$  in the following reactions:



The second reaction has a quantum yield near 100%, presumably because all species have zero spin. Spin conservation then prevents the formation of ground state  $O_2(x^3\Sigma)$  in reaction (2).

Aqueous solutions are messy things, in which spin conservation may not be exact, so  $O_2(a^1\Delta)$  may be de-excited. The de-excitation rate has been measured, and is quite slow, with a time constant of about 2  $\mu$  sec. If  $Cl_2$  gas is bubbled through the alkali-peroxide solution then reaction (2) will take place in solution near the surface of the bubbles.  $O_2(a^1\Delta)$  may diffuse back into the bubbles and be convected out of the liquid. Quantum yields for the production of  $O_2(a^1\Delta)$  of 40% have been reported, and a metastable density of 0.3 torr ( $10^{16} \text{ cm}^{-3}$ ) has been measured in the gas phase above the solution.

Figure 1 shows the relevant energy levels.  $O_2(a^1\Delta)$  is resonant with the first excited state ( $^2P_{1/2}$ ) in the I atom, so the reaction



occurs rapidly. The spontaneous radiative decay of excited I is slow (the lifetime is about 0.1 second for this magnetic dipole transition), so it is possible to pump an inversion in I atoms with a reasonable density of metastable  $O_2$ , even though the lower lasing level in I is the ground state.

Iodine is ordinarily diatomic, and some energy is required to break up diatomic iodine molecules into iodine atoms. Fortunately (and fortuitously) the following reactions dissociate molecular  $I_2$ :

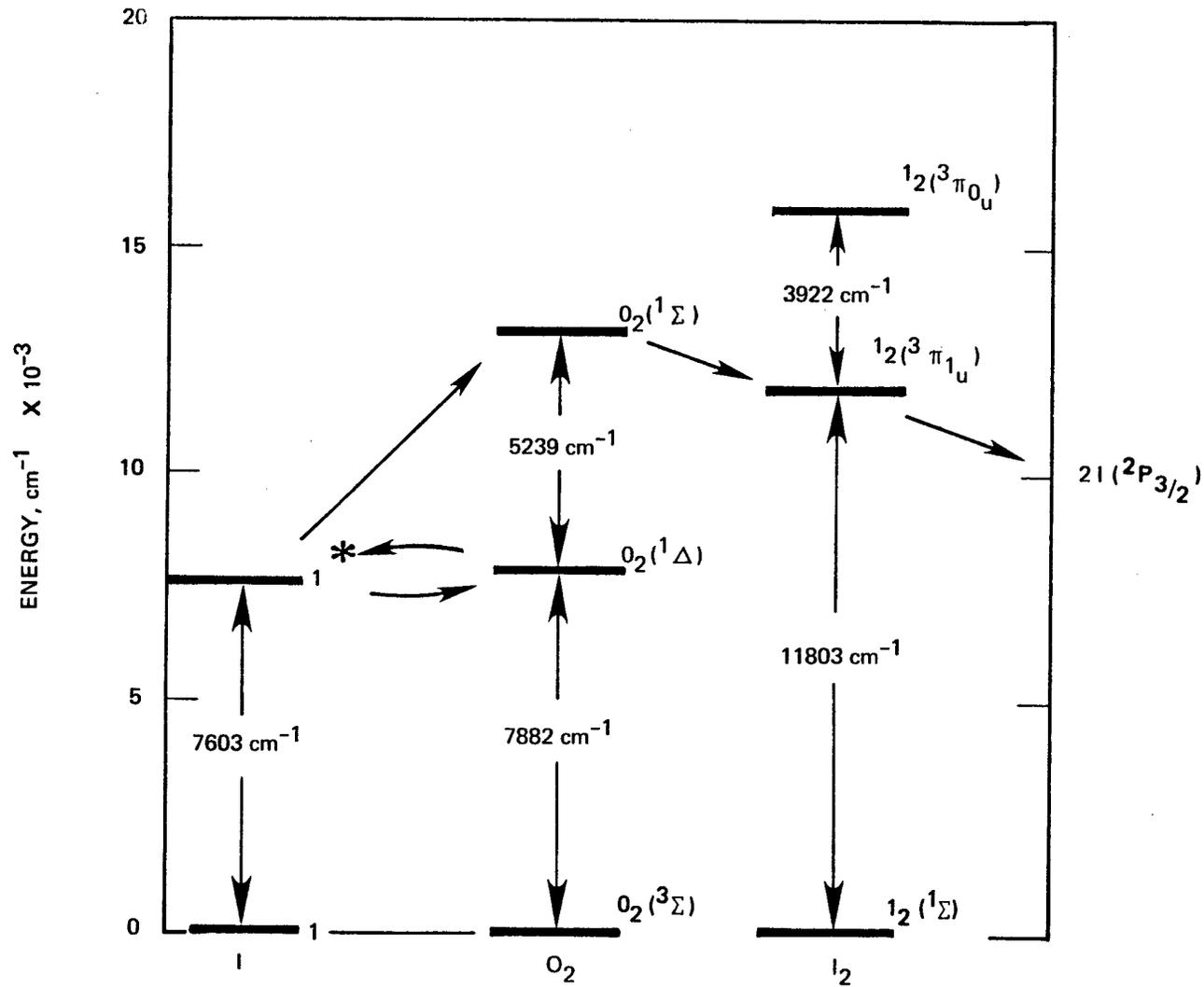
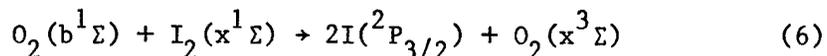
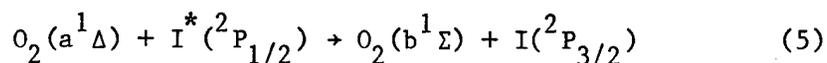
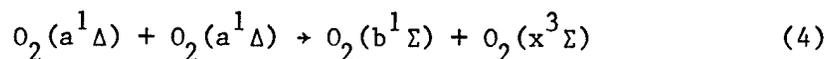


Figure 1 Energy levels of Oxygen and Iodine (Avizonis, AFWL)

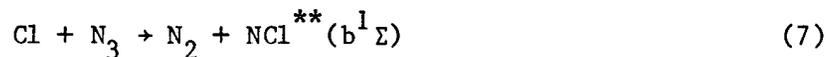


Reaction (4) is spin-forbidden and slow, while (5) depends on the low density of  $I^*$ . The highly excited  $O_2(b^1\Sigma)$  generated through either pathway can dissociate  $I_2$ .

The rates of these reactions, and others necessary for the understanding of gas phase kinetics of  $O_2$ ,  $I_2$ , and  $I$  are well measured. The aqueous chemistry is less well understood, but well enough to use it as a "black box" source of  $O_2(a^1\Delta)$ .

### 3. Nitrogen Halides

Nitrogen halides, like  $NF$ , are isoelectronic to  $O_2$  and they have the same metastable  $^1\Delta$  and  $^1\Sigma$  states as  $O_2$ . It is possible to produce excited states of nitrogen halides in a variety of different reactions. In Section 5 on azides we discuss reactions like



and



It is also possible to produce excited NF in the reaction



Reaction (9) is of particular interest because it is known to produce  $\text{NF}^*$  with high efficiency. It may also be adaptable to the large scale combustor technology used in the HF laser.

$\text{NF}_2$  is readily produced by the thermal decomposition of  $\text{N}_2\text{F}_4$ , a chemical which may be purchased commercially.

Figure 2 shows the lower potential curves of NF. The  $a^1\Delta$  state has a spontaneous radiative lifetime of over a second. If it did emit a photon its wavelength would be 8740 Å, but because of the extremely small oscillator strength of this transition, its stimulated emission cross-section is insignificant and it cannot lase. The same is true for  $\text{O}_2(a^1\Delta)$  (NF and  $\text{O}_2$  are isoelectronic, and the electronic states correspond closely), but this metastable state is still useful, for it can be used to pump the I atomic laser.  $\text{NF}(a^1\Delta)$  carries more energy than the corresponding state in  $\text{O}_2$  so one might hope to couple its energy to an atomic species which can lase at a shorter wavelength. Fortunately, it is resonant with the first excited state of  $\text{Bi}(^2D_{3/2}^0)$ . If the pumping rate is high enough, it might be possible to invert Bi atoms and to produce a laser at 8760 Å, in close analogy to the atomic I laser at 1.31 μ.

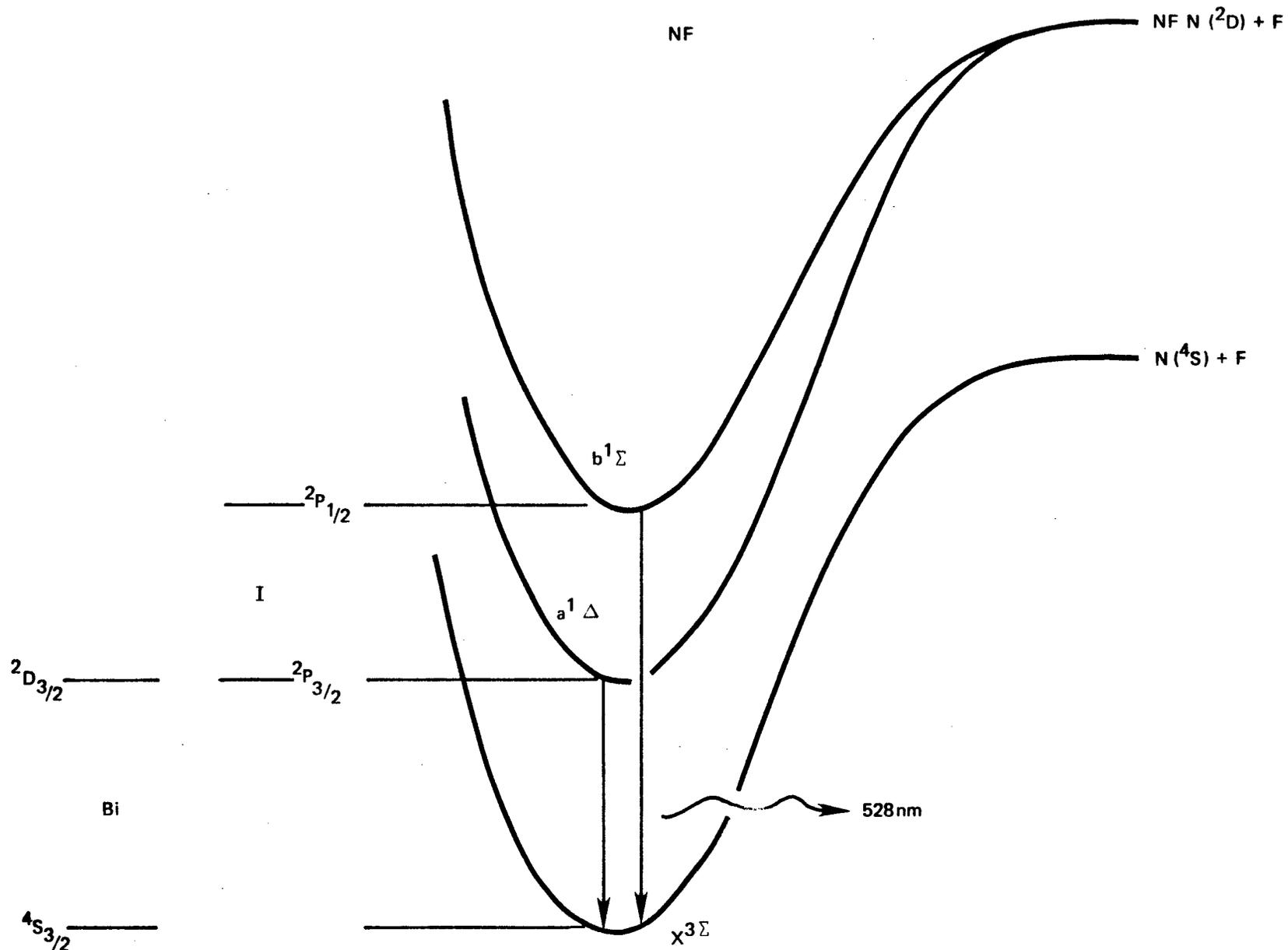


Figure 2 Energy levels of the NF molecule and the bismuth atom. Energy levels of the iodine atom are shown for comparison. (Warren, Aerospace)

In one respect the  $O_2^*$  and  $NF^*$  generators are quite different;  $O_2^*$  is produced in aqueous solution, while the more reactive fluorine compounds which produce  $NF^*$  must be handled in the gas phase. Reaction (9) requires H atoms which are hard to obtain. Fortunately, it may be possible to regenerate them, using them only as a catalyst, with the following reactions



In this way reactions (9), (10), and (11) react  $H_2$  and  $NF_2$  to produce  $N_2F_2$ , HF and energy in the form of excited Bi atoms. Such a laser system would not be purely chemical because a certain number of H or F atoms are needed to initiate the cycle, and replenish losses. These atoms may be supplied by flash-lamp or excimer laser photolysis of  $NF_2$  or by a discharge in  $NF_3$ . If the losses of monatomic species are small, then the amount of electrical or photon energy required is small, and the laser system is almost entirely chemical. Alternatively, F atoms may be supplied chemically from the reaction between  $H_2$  and  $NF_3$  in a continuously reacting system.

Fig. 3 shows two conceptual designs of NF-Bi laser systems presented by the group at Aerospace, led by W. Warren. They hope that it will be possible to apply the nozzle and flow hydrodynamic technology developed for HF lasers. Fig. 3a shows a concept for a pulsed laser in

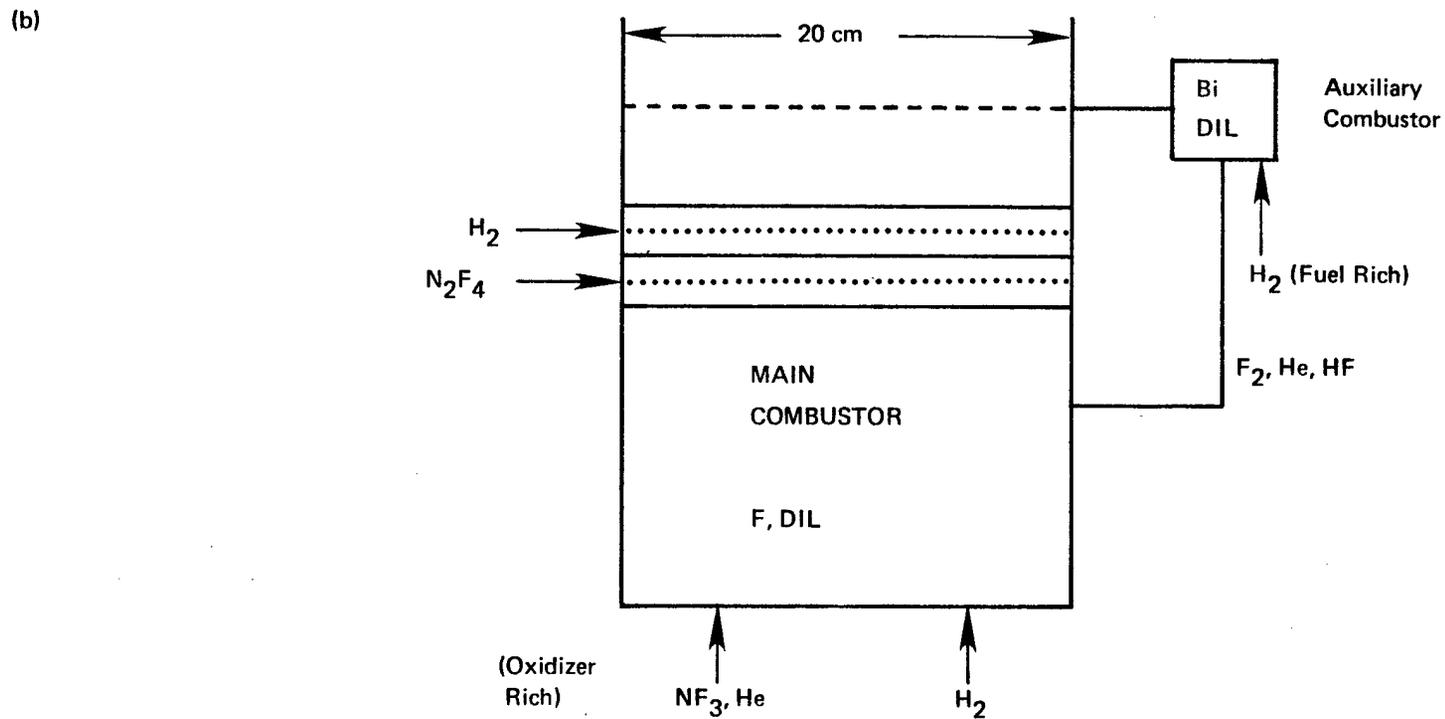
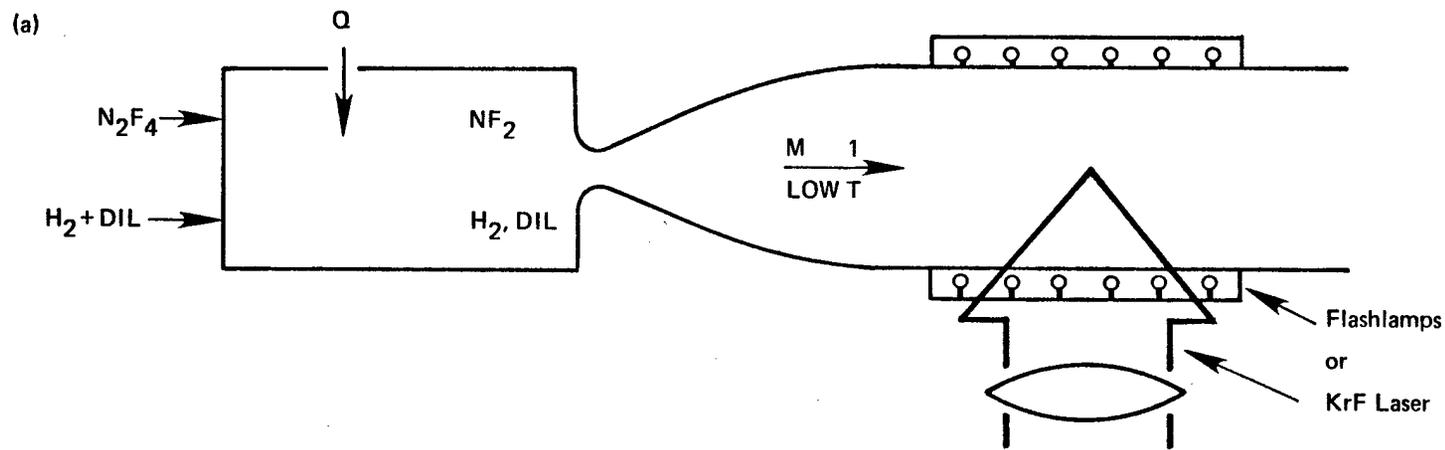
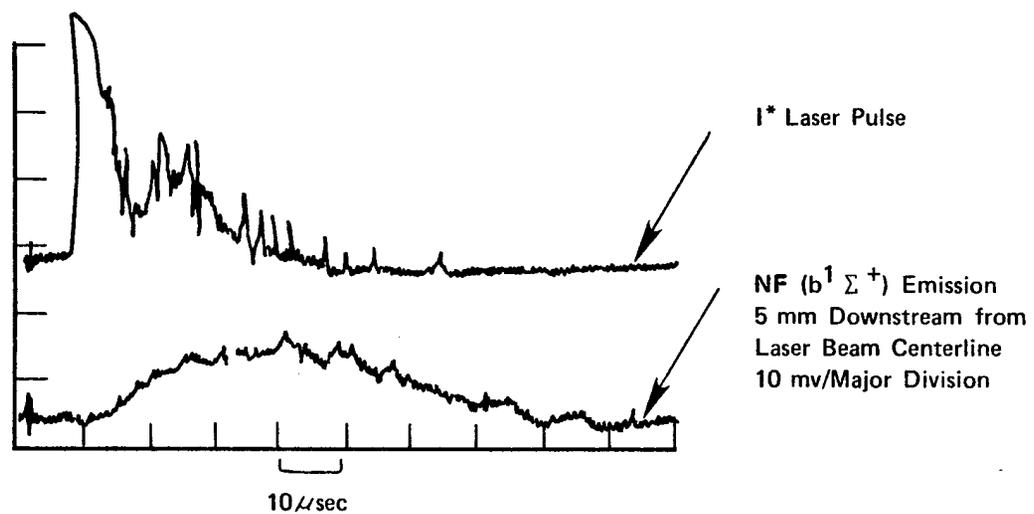


Figure 3 Photolytic (a) and chemical (b) sources of  $NF(a^1\Delta)$  molecules for chemical pumping of lasing atoms, e.g., Bismuth. (Warren, Aerospace)

which external sources of heat and light are required (to dissociate  $N_2F_4$  and photolyse  $NF_2$ ), while Fig. 3b is an entirely chemical system, more suitable to a CW laser in which chemical reactions provide both the necessary heat and the F atoms.

The near infrared NF-Bi laser would be a substantial improvement in wavelength over  $O_2-I$ , but still shorter wavelengths are desirable. The energy difference between the  $NF(a^1\Delta)$  and  $b^1\Sigma$  states is almost exactly resonant with the excitation of  $O_2(a^1\Delta)$  or the I atom. Thus, it may be possible to use energy pooling reactions between excited states of  $O_2$ , I, and NF to produce  $NF(b^1\Sigma)$ , and to use the energetic  $NF(b^1\Sigma)$  molecules to make a green laser. The Aerospace group has demonstrated that it is possible to use the light of an I laser to excite the  $NF(b)$  state from the a state. Fig. 4 shows the evidence. The resulting apparatus is complex but not necessarily impractical. It would be desirable to transfer the excitation chemically, but we do not know how to do this; the direct reaction between excited NF and  $O_2$  is spin forbidden (though that between NF and I is allowed), and various destructive side reactions are also possible in such a complex mixture.  $NF(b^1\Sigma)$  might be used to make a laser directly, for it is less metastable than the a state and has a larger stimulated emission cross-section, or it too might be used as a storage medium to couple energy into some other suitable species.

The NF-Bi laser concept builds on the established chemistry of the  $O_2-I$  laser system and on the gas-dynamic technology established in



**Figure 4** Demonstration of  $I^* + NF(a^1 \Delta) \rightarrow I + NF(b^1 \Sigma^+)$ . Transfer at System Concentration level. The  $NF(b^1 \Sigma)$  molecules could serve as the upper state or as a chemical pump for a green chemical laser. (Warren, Aerospace).

HF lasers. The basic reactions are reasonably well understood, at least qualitatively. This was one of the few areas considered worthy of further work by the Huestis memorandum<sup>1</sup> in 1976. The use of  $NF(a^1\Delta)$  to pump Bi atoms is a possible solution to the problem of the insignificant gain of  $NF(a^1\Delta)$  itself. Unfortunately, quantitative kinetic information is scarce, and may be the limiting factor in further development. The utility of the  $NF(b^1\Sigma)$  state is more speculative but certainly is a worthwhile subject for basic research.

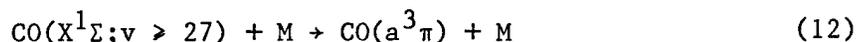
#### 4. Carbon Monoxide-Nitric Oxide

Interesting work on mixtures of CO and NO is being carried on at Calspan by W. Rich and co-workers. The CO-NO system is not really a chemical laser, because it is pumped by a CO laser. However, it is worth briefly considering because it involves a process, vibrational to electronic energy conversion, which may be of importance in some chemical laser systems. Many exothermic chemical reactions produce vibrational, instead of electronic, excitation, so it is important to see if vibrational energy can be used to make an electronic transition chemical laser. For example, the very exothermic reaction  $2N_3 \rightarrow 3N_2$  may feed all of its released energy into vibration.

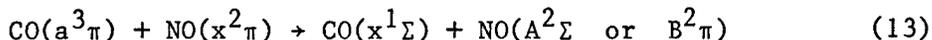
If the vibrational laser levels of CO vibration are pumped by the radiation of a CO laser, a series of nearly resonant energy exchange processes pumps a significant number of CO molecules into very high vibrational states. Coupling of vibrational to transitional motion is very weak, and the energy exchange processes are slightly exothermic, so that

the reverse processes cannot proceed if the transitional temperature is low. Fig. 5 shows the level diagrams of CO and NO. Infrared emission spectra have established that CO molecules are pumped up to vibrational levels with  $v \gtrsim 30$ ; a small amount of He gas, as shown by the horizontal dashed lines, provides some vibration-translation relaxation and reduces the degree of excitation.

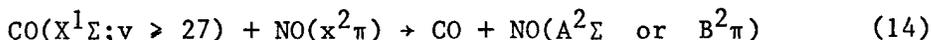
If NO is added to this highly vibrationally excited gas of CO, its  $\beta$  and  $\gamma$  emission bands are seen, and are shown in Fig. 6. The mechanism is not clear. One possibility is



followed by



but (12) is slow unless M has non-zero spin. Another possibility is



NO(A) cannot make a laser, but NO(B) might, if vibrational relaxation of NO( $x^2\pi$ ) is fast enough. Preliminary estimates (by Rich, of Calspan, who also did this experimental work) suggests that gains will be uncomfortably small. The subject is still worth pursuing as a basic research problem, for the kinetics are interesting and (aside from CO vibrational pumping) not understood.



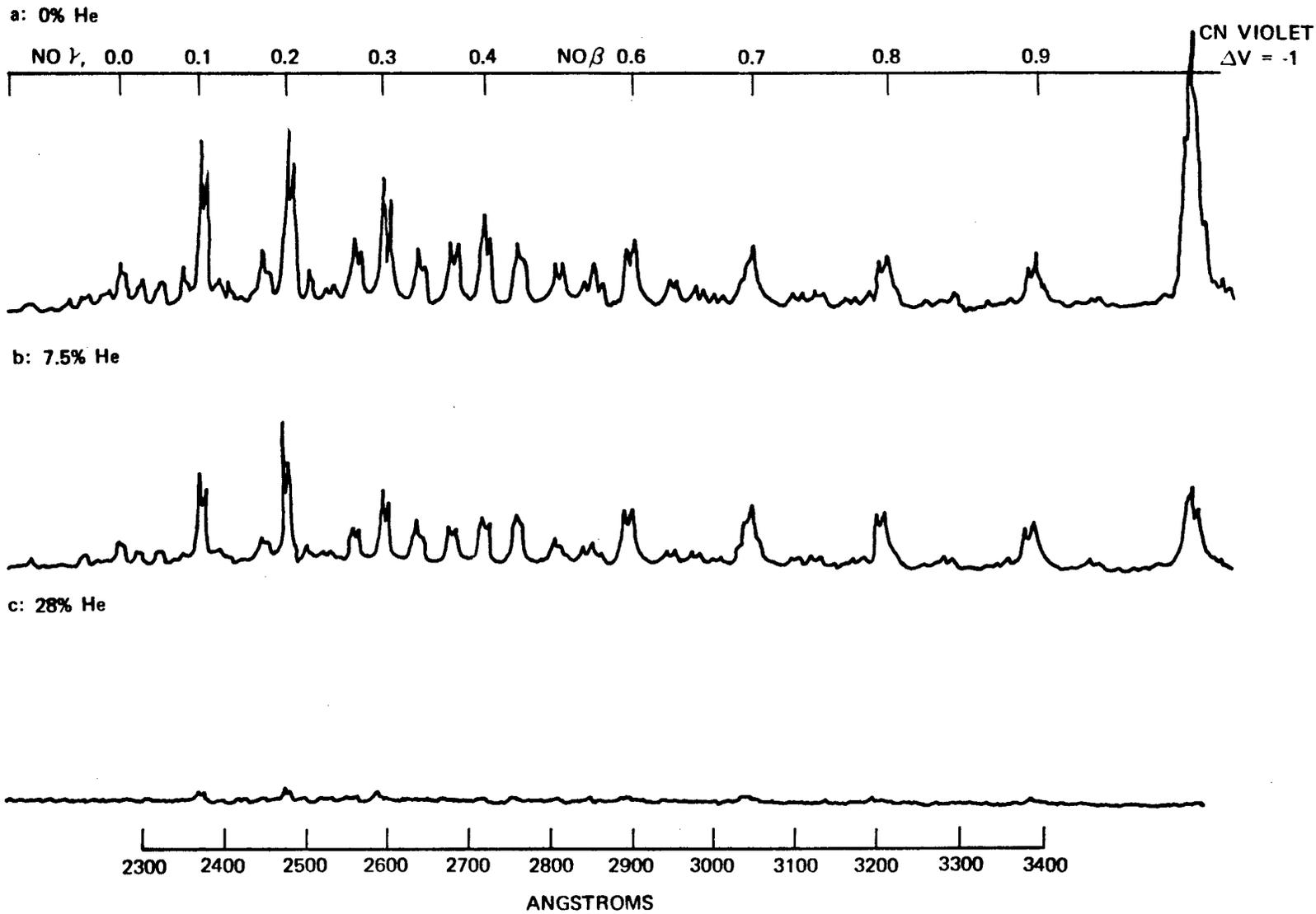


Figure 6 No  $\beta$  and  $\gamma$  emission spectra for several He concentrations in mixtures of He, CO and NO pumped by a CO laser. (Rich, Calspan)

5. Azides

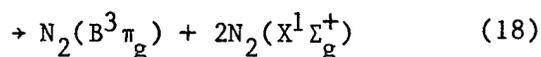
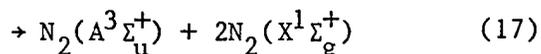
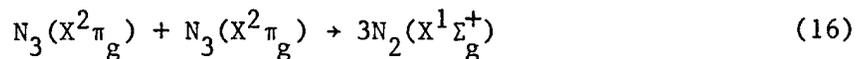
The azide radical,  $N_3$ , and its compounds are natural candidates for making a visible chemical laser. Nitrogen atoms are most stable when bound into ordinary  $N_2$  molecules with strong triple bonds; its dissociation energy of 9.8 eV makes  $N_2$  among the most strongly bound molecules in existence. The reaction



releases 8.8 eV if all species are in their ground states. There is enough energy available from reordering the nitrogen atoms in azide radicals to make a visible, or even an ultraviolet laser. Despite all this stored potential energy, many azide compounds are quite stable, readily obtained, and safely handled. These include ionic azides like  $NaN_3$ . Covalent azides may be generated in the laboratory. Some azides, like  $Pb(N_3)_2$ , are explosive, of course.

Having a strongly exothermic chemical reaction is far from sufficient for making a laser. It is necessary to create electronically excited atoms or molecules from this energy, and to produce an inversion with sufficient net gain. Ray Taylor reported on some experiments he performed at Physical Sciences, Inc. By heating  $NaN_3$  a steady flow of  $N_3$  radicals is obtained (verified by observing NO chemiluminescence if O atoms are introduced); the Na vapor which is also produced condenses on the walls of the apparatus. Flowing inert carrier gas carries the  $N_3$  through the experimental apparatus.

If a sufficiently high density of  $N_3$  is obtained the following chemical reactions may take place:



There is no a priori way to determine the branching ratio of these reactions. Contrary to the published statement of Piper, Krech, and Taylor, all these reactions are spin-allowed. The A and B states are excited above the ground state by 6.3 and 7.4 eV respectively (for zero vibrational quantum number). The B state rapidly radiatively decays to the A state. The A state is metastable because LS coupling is an excellent approximation for such low Z atoms, and it is of different multiplicity from the only state (X) to which it can decay. If it is produced in sufficient quantity  $N_2(A^3\Sigma_u^+)$  may be very useful, because it stores energy which might be transferred to some lasing species. (It is highly unlikely that  $N_2(A)$  itself could lase because its transition is so forbidden and is broadened by vibrational and rotational structure and because of the unavoidable presence of large quantities of ground state  $N_2$ ).

Having created a sufficient density of  $N_3$ , one must try to determine the relative branching ratios into reactions (16), (17), and

(18), or at least the rate of the useful reactions (17) and (18). One might measure the density in state A using its absorption spectrum. This has not been done, and the only evidence available to us comes from Taylor's search for the emission of radiation in the B to A transition, known as the first positive band  $N_2(1^+)$ . If detected, this would imply that reaction (18) is taking place. The evidence is shown in Fig. 7. Taylor suggests that the broad emission in the red is  $N_2(1^+)$ , and indicates the expected position of various vibrational sequences above the curve. We are quite skeptical, for the shape of the curve is not that of familiar band spectra, nor does it even correspond to the expected sequences. We have not seen a confirmed spectrum of  $N_2(1^+)$  with this appearance. The unidentified band in the blue (and another, not shown, in the ultraviolet) seem to imply contamination, and force us to conclude that the case for any production of electronically excited  $N_2$  is unproven. There is no doubt that excited  $NO(A^2\Sigma^+)$  may be produced, but this is of no interest for making a laser because of its rapid allowed decay to the ground state. If  $NO(B^2\Sigma\pi)$  is produced it may be of more interest, because it decays to excited vibrational levels of the ground state.

It may be possible to use the energy stored in the azide radical to create metastable electronically excited species other than  $N_2$ . Although these don't have as much energy as excited  $N_2$ , they usually have about 2eV, enough to suggest that a red or near-IR laser might be possible. Possibly the simplest and most direct scheme is to photolyse a covalent azide such as  $ClN_3$ . This couldn't lead to a completely chemical laser, because of the need for photons but is worth considering, even if

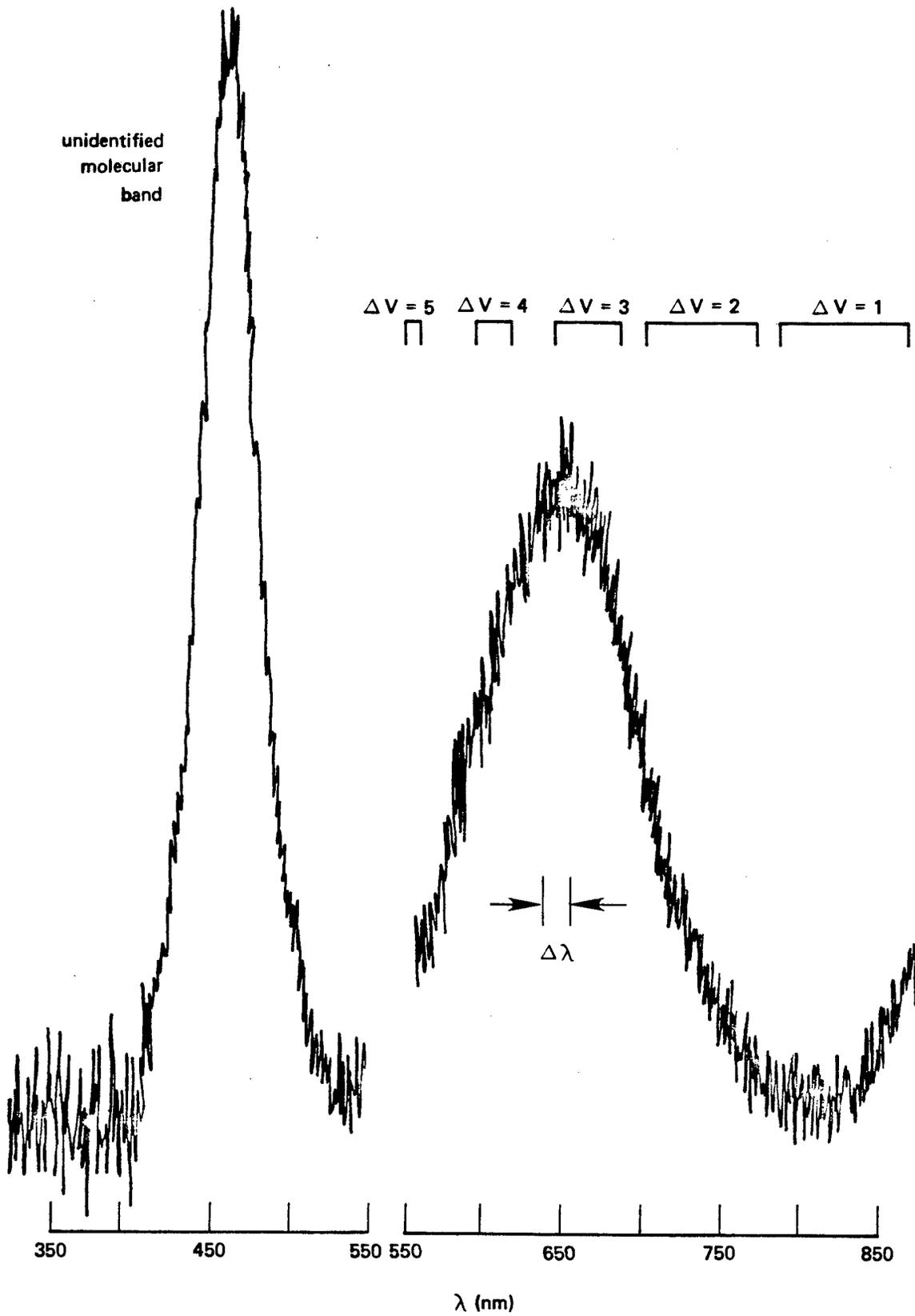
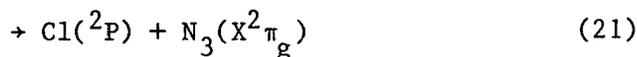
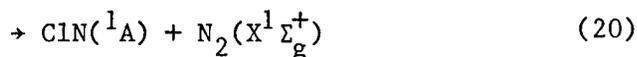
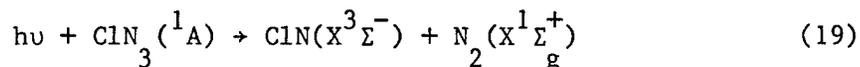


Figure 7 Radiation from gas containing  $N_3$ . Vibrational sequences expected for  $N_2(1^+)$  etc. are shown. (Taylor)

only as an experiment in kinetics. The easiest bond to break is the one between  $N_2$  and the rest of the molecule; this generally requires less than 1 eV, while detaching the  $N_3$  from the Cl requires 1.6 eV, and substantially more if other atoms or radicals are substituted for the Cl. One may consider three types of reactions:

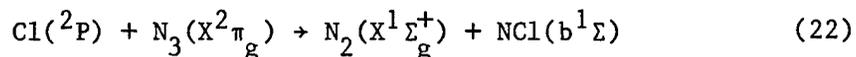


Reaction (19) requires the least energy, but has a negligible cross-section because it is spin-forbidden. Reaction (20) is allowed and requires less than 2eV;  $ClN(^1A)$  refers to all low-lying singlet states. The last reaction is useless and a parasitic loss of photons but has a higher threshold than (20). Therefore, efficient production of metastable singlet  $ClN$  is promising via reaction (20). One might consider using either a single UV photon (the  $ClN_3$  absorption is insignificant for wavelengths longer than 3000 Å) or many infrared laser photons to accomplish this.

Taylor attempted to produce the  $b^1\Sigma^+$  state of  $ClN$  via flash-lamp induced reaction (20). This state has lifetime of a few ms to radiative decay to the ground state. This is shorter than the lifetimes of metastable states in lighter molecules (  $NF$  and  $O_2$  , for example), because of the higher  $Z$  of  $Cl$  but still long enough to permit coupling

the energy to some lasing species; spontaneous fluorescence should be detectable. The lowest vibrational state stores 1.86 eV, so  $\text{ClN}(b^1\Sigma^+)$  fluoresces in the red (0-0 is near  $6650 \text{ \AA}$ ). Taylor was not able to find convincing evidence of this fluorescence.

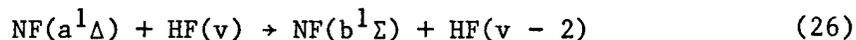
More promising may be attempts to produce metastable  $\text{NCl}$  and related compounds chemically. There are a number of ways of doing this, but here we consider only processes based on azides. One may consider two series of reactions. The first proceeds through the azide radical.



$\text{N}_3$  may be made thermally by decomposition of  $\text{NaN}_3$ , or chemically:



A possible alternative is



Reactions (24) and (25) can only produce excited  $\text{NF}$  because of spin conservation.

Bob Kuhn at Rockwell Science Center has observed the red bands of  $\text{NCl}(b^1\Sigma) \rightarrow (X^3\Sigma)$  from reactions (22) and (26) (see Fig. 8).

Metastable  $\text{O}_2(a^1\Delta)$  has been successful in pumping the I atomic laser. For that reason analogous species like NF and  $\text{NCl}(a^1\Delta)$  are of interest as are other metastables like  $(b^1\Sigma)$ . It is possible to consider lasing either in the nitrogen halide molecule or in an atom (such as Bi) to which excitation is transferred. NF(a) is too metastable to lase itself, but other states or species are not ruled out. Azide reactions are one way of producing them, but must compete with alternative chemical processes.

In summary, azides are worth investigating as candidate fuels for visible chemical lasers. At present their reaction kinetics are almost entirely unknown and must be considered a problem in basic research. The first step which should be taken is to measure the rates of their reactions. It is important that the effort to make these measurements have sufficient support and duration to carry the work to its conclusion. An effort like Taylor's, which is terminated when a few tantalizing hints have been observed, is wasted.

## 6. Magnesium-Calcium

Dr. D. Benard at AFWL has reported building a chemical flame generator for metastable Mg atoms in the lowest excited  $^3P$  state. He would like to use these metastable atoms, each containing 2.7 eV, to excite Ca atoms. The excited  $\text{Mg}(^3P)$  is energetically resonant with  $\text{Ca}(^1D)$ .

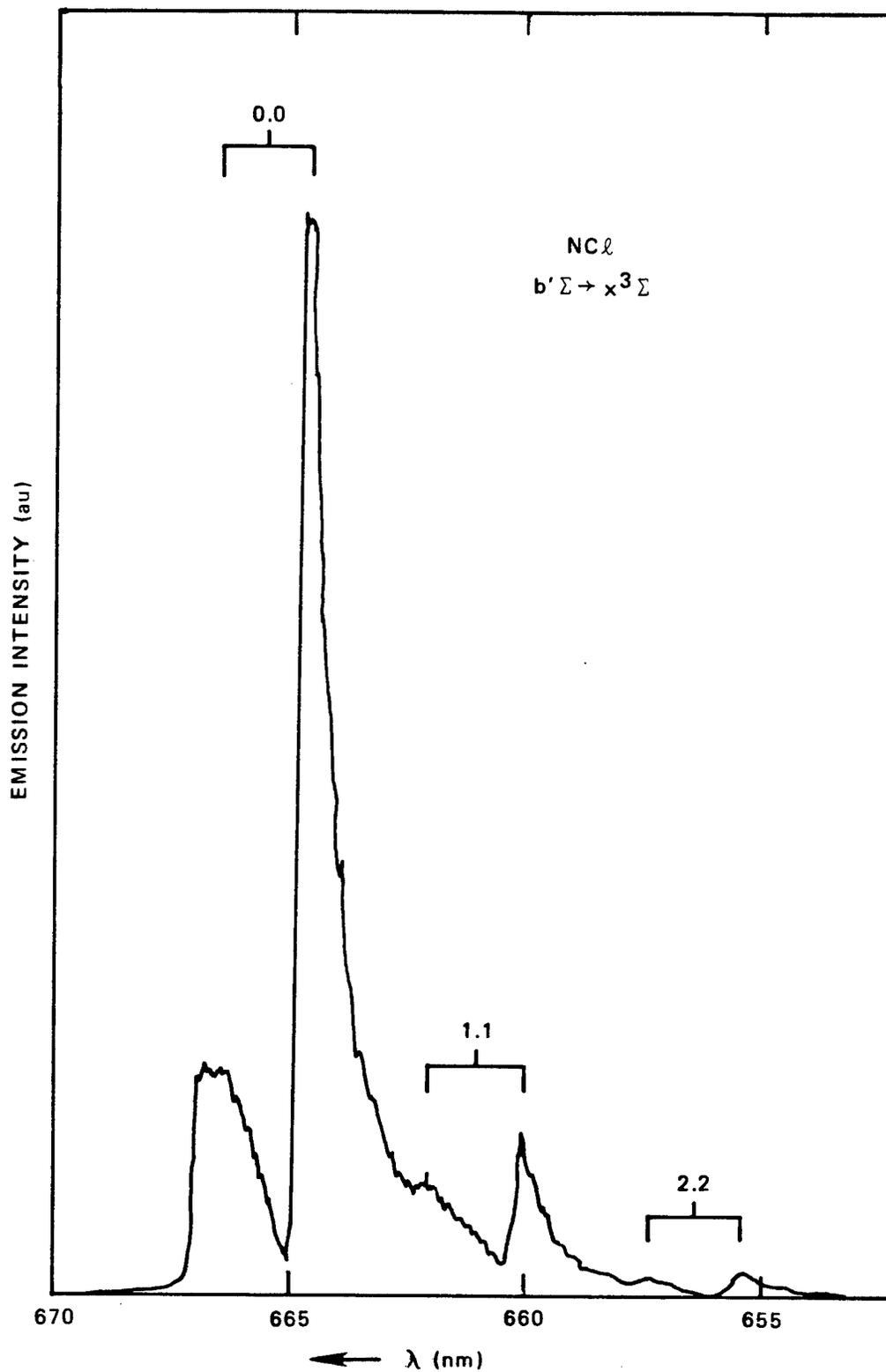


Figure 8 The red bands of the transition  $\text{NC1}(b'\Sigma) \rightarrow \text{NC1}(x^3\Sigma)$  produced by azide chemistry. (Kuhn, Rockwell)

After the latter is collisionally de-excited to the  $^3D$  state, which radiatively decays to the  $^3P$  state, he hopes to invert the  $^3P$  states of Ca with respect to the  $^1S$  ground state. Although forbidden, this last transition has enough oscillator strength ( $A = 2600 \text{ s}^{-1}$ ) to make significant gain possible if an inversion can be obtained. This is in contrast to molecular forbidden transitions which have their limited stimulated emission cross-section spread over a broad vibrational and rotational structure.

Benard reports the formation of  $\text{Mg}(^3P)$  in a  $\text{Mg-N}_2\text{O-CO}$  flame. His evidence, shown in Fig. 9, is persuasive. Unfortunately, the mechanism is obscure. He suggests reactions:



The  $^+$  denotes a vibrationally excited species. In reaction (28) all species, except  $\text{Mg}^*$ , are singlets;  $\text{Mg}^*$  is a triplet. This ought to make the rate of (28) small, while the production of ground state Mg should be rapid. An analogous series of reactions producing  $\text{Na}^*$  is known to proceed, but that is expected because both  $\text{NaO}$  and  $\text{Na}^*$  are doublets.

By introducing Ca vapor into the gas flow containing Mg, transfer of excitation is hoped for.

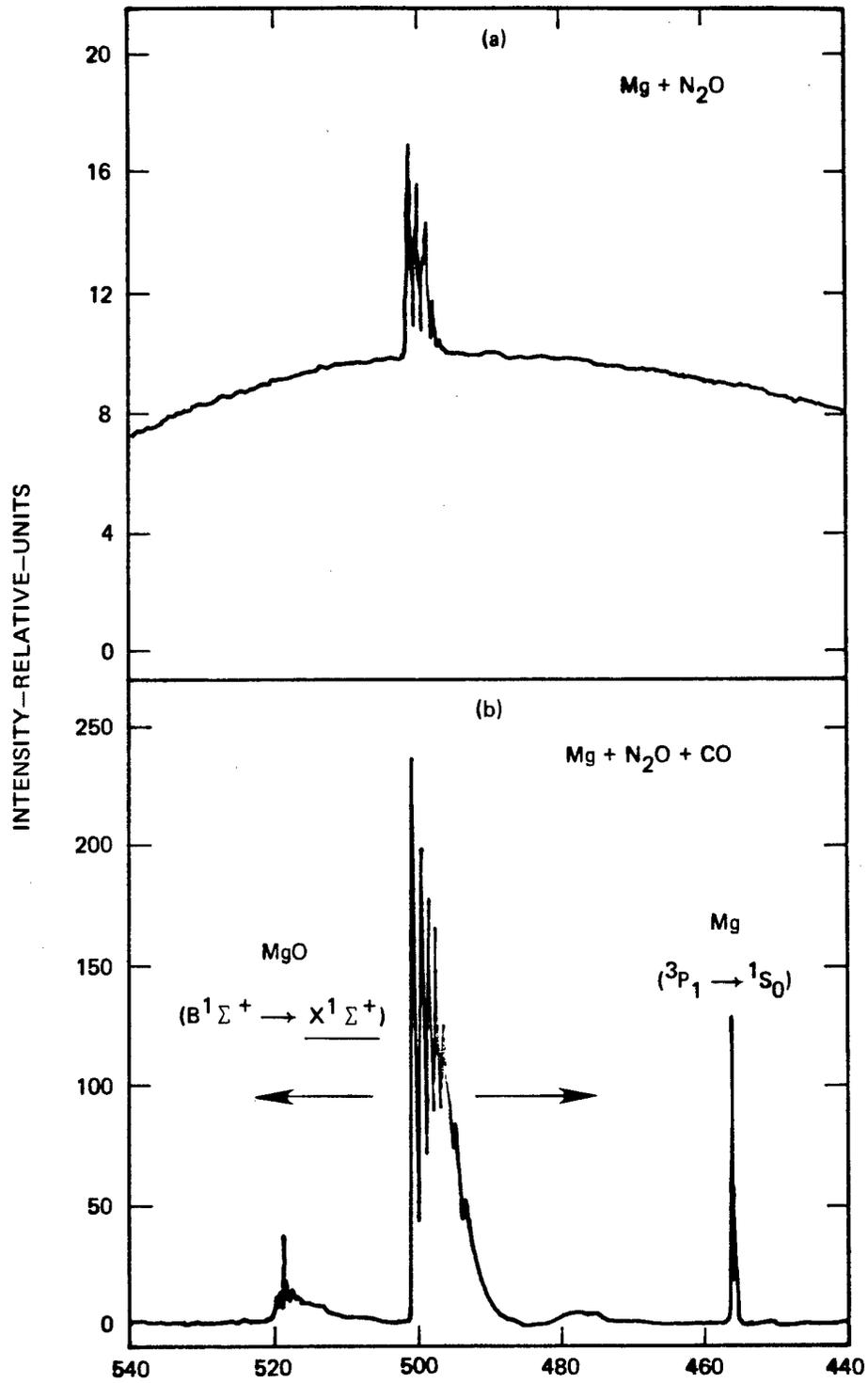
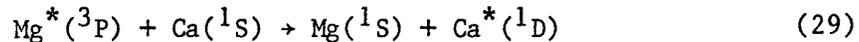


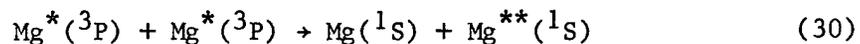
Figure 9 Observation of  $\text{Mg}(^3p)$  in  $\text{Mg}-\text{N}_2\text{O}$  flame. (Benard, AFWL)



Even though this reaction is energetically resonant (the right hand side has  $21850 \text{ cm}^{-1}$ , and the left hand side between  $21850 \text{ cm}^{-1}$  and  $21911 \text{ cm}^{-1}$ , depending on  $J$ ) it is spin forbidden. As a result we find the reported rate constant of  $3 \times 10^{-11} \text{ cm}^3/\text{sec}$  surprisingly large.

Benard then depends on collisional relaxation from  $^1\text{D}$  to  $^3\text{D}$ ; at a wavelength near  $7\mu$  the forbidden radiative decay is very slow. After this the excited atoms rapidly decay to  $^3\text{P}$ , which is supposed to be inverted with respect to the ground  $^1\text{S}$  state, producing a  $6572 \text{ \AA}$  laser. See Fig. 10.

A number of other processes may occur, interfering with desired processes. For example



The excited  $^1\text{S}$  has  $43503 \text{ cm}^{-1}$ , which compares to a range due to fine structure of  $43701 \text{ cm}^{-1}$  to  $43822 \text{ cm}^{-1}$  on the left hand side. The resonance is close and the reaction is spin-allowed. If this reaction occurs the excitation energy is lost in the rapid allowed radiation of photons at  $11832 \text{ \AA}$  and  $2853 \text{ \AA}$ , which should be readily detectable. Similar reactions between two excited Ca atoms should be possible; a number of highly excited Ca states are nearly resonant, and will rapidly decay

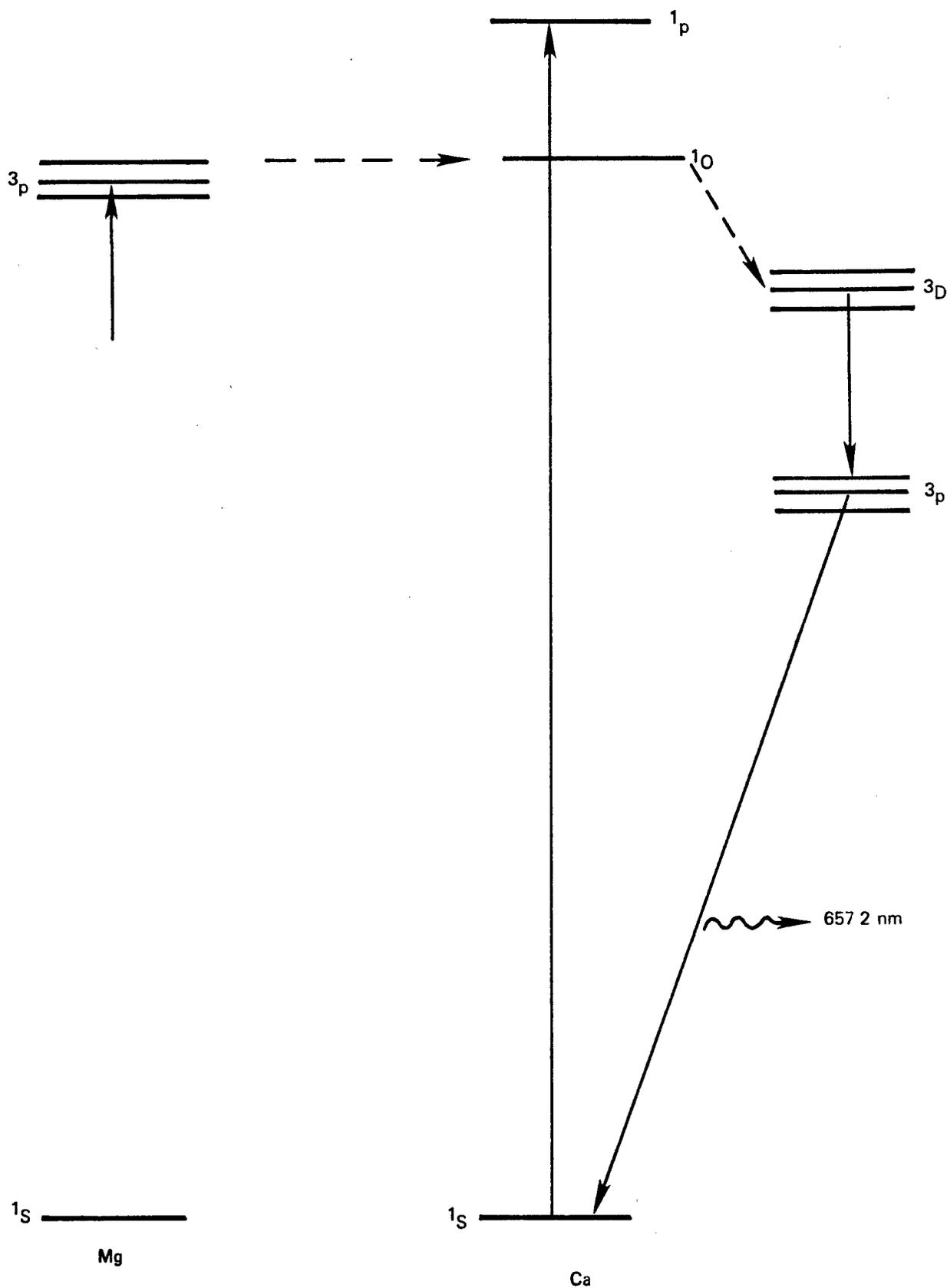


Figure 10 Hypothetical Mg-Ca Energy Flow. (Benard, AFWL)

radiatively. Reactions between excited Ca and excited Mg are also possible. Finally, one must also consider de-excitation of excited Ca and Mg in collisions with other species, such as the noble gases used as buffer gases in these systems. Benard presented a table of Ca de-excitation rate coefficients. He reported that the coefficients for He and Ne were identical to 5%, and only a factor of 3 less than that for Xe. We are skeptical because of the strong variation in polarizability among the noble gases and of a similar variation in the strength of coupling between  $\vec{L}$  and  $\vec{S}$ .

We found the reported results on Mg-Ca systems quite interesting. There are a number of things we don't understand. That does not prove them wrong, but means that a much greater effort is needed to understand them. Very careful experimental work should be done to be sure that the kinetics are occurring as suggested and not through some very different pathway. Without such an understanding, it is not possible to proceed beyond the stage of basic research.

#### REFERENCE

1. Eckstrom, D., S. Edelstein and D. Huestis. Stanford Research Institute Memorandum, May 27, 1976.

#### ACKNOWLEDGEMENTS

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Prof. C. Rhodes	University of Illinois in Chicago	July 8, 1980
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