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**THE POSSIBILITY OF A HIGH-ENERGY-STORAGE
VISIBLE LASER ON THE AURORAL LINE OF OXYGEN**

J. R. Murray
C. K. Rhodes

September 12, 1973

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THE POSSIBILITY OF A HIGH-ENERGY-STORAGE VISIBLE LASER ON THE AURORAL LINE OF OXYGEN

Abstract

The auroral line of oxygen at 5577 Å has properties which may make it useful for a high energy storage, short pulse, visible gas laser. Reactions and kinetics which would affect the operation of an

auroral line laser are reviewed. A kinetic model of a possible laser using photolytic decomposition of N_2O by krypton excimer radiation is described. Other possible excitation mechanisms are discussed.

I. Introduction

Laser fusion requires a laser with at least kilojoules of energy storage that can generate high intensity subnanosecond pulses.¹ This requirement puts three general restrictions on potential laser devices for this application:

(1) The stimulated emission cross section must be low enough that super-fluorescence and other parasitic processes do not depopulate the upper state in a large amplifier, yet large enough that the saturation flux for a subnanosecond pulse is less than the optical breakdown threshold of the active medium. This condition requires that the stimulated emission cross section be near 10^{-20} cm^2 .

(2) The wavelength of the laser should be short, yet not so short that two-photon absorption to the intrinsic conduction band will be possible in convenient optical materials.

(3) Storage of energy at high excited state densities (a few hundred or thousand

joules per liter) is desirable to minimize the bulk of the laser.

This memorandum presents the 5577 Å auroral line of atomic oxygen as an interesting candidate for such a laser. The stimulated emission cross section for this transition, assuming a 300°K Doppler-broadened line, is $\sim 9 \times 10^{-20} \text{ cm}^2$. This leads to a saturation energy flux of 4 J/cm^2 , a value within the limits of technology for mirrors and windows for a subnanosecond pulse. The oxygen 1S_0 state also has a low probability of deactivation on collision with a variety of collision partners, including the important case of a second excited $O(^1S_0)$ atom, leading to a prediction of high density energy storage on a microsecond time scale or longer. Furthermore, since this energy is stored in a single atomic state, it is available for efficient picosecond pulse extraction.

Section II of this report discusses the properties of the auroral line and the atomic states involved. Section III discusses possible mechanisms for producing a large density of $O(^1S_0)$ atoms. Section IV presents a conceptual design for an auroral line laser based on the photolysis of N_2O with electron-beam-generated Kr_2^* continuum radiation, and Section V discusses a possible laser in

an $Ar + O_2$, CO_2 discharge. Section VI summarizes the information on presently unknown processes and rates which will be required to properly evaluate the potential of this transition as a high energy storage, short pulse laser device. Appendix A discusses a problem in high intensity photolysis, and Appendix B presents some preliminary results on the kinetics of a laser active medium produced by N_2O photolysis.

II. Properties of the Auroral Line of Oxygen and the Oxygen Metastable Singlet States

A. THE FREE ATOM

Figure 1 shows a level diagram of the three states in the $2p^4$ electron configuration of the oxygen atom.²⁻⁵ States of the

Fig. 1. Energy levels of the $2p^4$ configuration of atomic oxygen.

$2p^3 3s$ and higher configurations lie 5 eV or more above the 1S_0 state and interact very little with this configuration. Both the 1S_0 and the 1D_2 state are radiatively metastable in the dipole approximation, but all of the possible "forbidden" higher-order lines have been detected and are labeled in the figure. The importance of these lines in atmospheric and astrophysical phenomena has led to the common names shown. The "auroral" green line is in fact the most prominent atomic line in the night sky emission from the atmosphere and the largest contributor to the luminosity of most auroral displays.⁶

Table 1 shows the rate of reaction or deactivation of the 1S_0 and 1D_2 states with various molecules, giving a measure of the ability of these states to survive collisions in a gas. Note that the 1S_0 state is highly resistant to deactivation in collisions with a wide variety of gas molecules and that the 1D_2 state is much less stable. As an example, if excited oxygen atoms are produced in otherwise pure molecular nitrogen at one atmosphere

Table 1. Rate constants for or deactivation of the metastable singlet states of oxygen at $\sim 300^\circ\text{K}$.^a (See also Tables 3-9.)

	$\text{O}(^1\text{S}_0)$ $\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$	$\text{O}(^1\text{D}_2)$ $\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$
N_2	$< 5 \times 10^{-17}(\text{b})$	5.5×10^{-11}
$\text{N}(^4\text{S})$	$\leq 10^{-12}(\text{c})$	
O_2	$2 \times 10^{-13}(\text{d})$	7.5×10^{-11}
$\text{O}(^3\text{P})$	$2 \times 10^{-13}; 7.5 \times 10^{-12}(\text{e})$	
O_3	$6 \times 10^{-10}(\text{f})$	5.0×10^{-10}
NO	4×10^{-10}	2.1×10^{-10}
N_2O	1.5×10^{-11}	2.2×10^{-10}
CO_2	$4 \times 10^{-13}(\text{g})$	2.2×10^{-10}
CO	9.4×10^{-14}	7.5×10^{-11}
H_2	1×10^{-15}	2.9×10^{-11}
H_2O	4×10^{-10}	3.5×10^{-10}
C_2H_4	$\sim 10^{-10}$	$2 \times 10^{-11}(\text{h})$
He	$< 4 \times 10^{-19}(\text{i})$	10^{-15}
Ar	$5.2 \times 10^{-18}(\text{i})$	1×10^{-12}
Xe	6.7×10^{-15}	10^{-10}

^aData from Ref. 7 for $\text{O}(^1\text{S}_0)$ and Ref. 8 for $\text{O}(^1\text{D})$ unless otherwise indicated.

^bSee Ref. 9.

^cSee Ref. 10.

^dTemperature dependence: $4 \times 10^{-12} e^{-1730/RT}$ (see Ref. 9,11).

^eSee Ref. 10,12. Theoretical temperature dependence: $10^{-11} e^{-500 \pm 300/RT}$ (Ref. 13).

^fSee Ref. 14.

^gTemperature dependence: $3.3 \times 10^{-11} e^{-2630/RT}$ (see Ref. 9).

^hSee Ref. 7.

ⁱSee Ref. 3.

pressure, the $1/e$ decay time for the $^1\text{S}_0$ state will be longer than $\sim 800 \mu\text{sec}$ while for the $^1\text{D}_2$ state the decay time will be some five orders of magnitude less or $\sim 2 \text{ nsec}$. One may, therefore, maintain an inverted population on the auroral transition for some microseconds in nitrogen or in a variety of other gases if the concentration of rapidly reacting

molecules such as H_2O or NO is carefully controlled.

Another important collision property of an excited atom is its rate of reaction on collision with a second excited atom, since this rate sets an upper bound on the density of excited atoms which can be maintained. For the collision between $^1\text{S}_0$ oxygen atoms there are in principle two channels available for deactivation, the excitation transfer

and molecular formation

The available energy for two colliding $^1\text{S}_0$ atoms is 8.34 eV, while the nearest higher excited state of the oxygen atom is at 9.12 eV, giving an energy defect of some 0.78 eV for excitation transfer. This argues that the excitation transfer rate will be negligible at any reasonable gas temperature. Theoretical treatments of molecular formation in a collision between two $\text{O}(^1\text{S}_0)$ atoms indicate that this is also a very unlikely process.¹⁵ Two $\text{O}(^1\text{S}_0)$ atoms collide on a repulsive surface which does not cross any lower energy bound state surface of the oxygen molecule or ion at energies up to $\sim 3 \text{ eV}$, far above thermal energies. There are no quantitative data available to confirm these predictions, but it appears from the information presently available that upper-laser-level excited-state collisions will

have a negligible influence on the kinetics of an auroral line laser, unlike, for example, the Xe_2^+ excimer laser.

The stimulated emission cross section for the auroral transition is evaluated from the usual expression for line strength:

$$\sigma(\nu) = \frac{\lambda^2}{8\pi\tau_R} h(\nu) = Sh(\nu) \quad (4)$$

where τ_R is the radiative lifetime and $h(\nu)$ is the lineshape of the transition. For a Doppler broadened line

$$h(\nu) = \frac{1}{\sqrt{\pi}\gamma} \exp\left[-\frac{(\nu - \nu_0)^2}{\gamma^2}\right] \quad (5)$$

where

$$\gamma = \frac{\nu_0}{c} \sqrt{\frac{2kT}{m}} = \frac{\bar{\nu}}{\lambda}$$

and $\sigma(\nu_0)$ at line center and 300°K is $9 \times 10^{-20} \text{ cm}^2$. Collision broadening, which lowers $\sigma(\nu_0)$, has not been taken into account here. The cross section in a practical amplifier is likely to be less than $9 \times 10^{-20} \text{ cm}^2$ by perhaps an order of magnitude.

The saturation energy of an amplifier is given by $h\nu/\sigma$ assuming no pumping or relaxation during the light pulse. This gives $\sim 4 \text{ J/cm}^2$ for the 5577 Å transition Doppler broadened at 300°K. The effects of level degeneracy in the 1D_2 level, although they may be expected to influence the saturation behavior, have been ignored in this simplified treatment.

B. OXYGEN EXCIMERS

Oxygen in the 1S_0 and 1D states forms excimer molecules with the rare gases,

N_2 , and probably other molecules.^{7,16-18} Analysis¹⁷ of excimer band spectra of XeO indicates that these excimers have the structure shown in Fig. 2. The state correlating to $\text{O}(^1S_0)$ is weakly bound ($\sim 0.06 \text{ eV}$ for XeO), while the $\text{O}(^1D_2)$ state is more tightly bound ($\sim 0.34 \text{ eV}$). The state correlating to $\text{O}(^3P)$ is repulsive and crosses the $\text{O}(^1D_2)$ state, leading to rapid nonradiative decay.¹³ Laser oscillation has been seen in a similar situation in NO .¹⁹ The states do not look promising for laser oscillation in XeO or similar excimers, however. The kinetic data for deactivation of $\text{O}(^1S_0)$ (by, for example,

Fig. 2. Part of the semiquantitative potential energy diagram (Morse potentials) for some low-lying states of XeO . Positioning of the $^3\Pi$, $^1\Delta$, and $^1\Pi$ states is arbitrary. Reprinted with permission from Chemical Reviews (Ref. 7). Copyright by American Chemical Society.

Xe or N₂) indicates a slow rate of formation combined with a fast radiative lifetime, so that it is difficult to generate a high density of the excited excimer species.

Note that the excimer radiation is blue-shifted here, since the [Xe - O(¹D₂)] complex is more tightly bound than [Xe - O(¹S₀)].

The rates for collision-stimulated radiation from excimer formation and for

the closely associated collision broadening of the auroral transition are not well understood. One measurement of collision broadening in argon extrapolates to a width of ~3 times the Doppler width at one atmosphere pressure, which is rather low and hard to reconcile with the excimer radiation seen²⁰ from Ar-O. Much more information is needed on these effects.

III. Populating the ¹S₀ State of Atomic Oxygen

Many reactions produce O(¹S₀). For most of these there is insufficient information available to determine whether the production is efficient and can operate at the high excited state densities which a compact laser will require. The simplest and, therefore, best understood source of O(¹S₀) is the photolysis of simple molecules such as CO₂, N₂O, and O₂. Most of this discussion will concern these photolytic sources, but first we list other energy transfer mechanisms known to produce O(¹S₀).

A. SOURCES OF O(¹S₀) IN THE ATMOSPHERE⁶

Since the auroral line is the brightest atomic line in the night sky, it is useful to consider its sources. A number of mechanisms for producing O(¹S₀) have been proposed, not all of which are quantitatively understood. Photolysis of O₂ and collision with N₂(A³Σ) are discussed in sections IIIB and IIIC respectively. Of the others, those which are thought to be most important are listed below.

Three Body Recombination:

	Rate Constants *		
	N ₂ Buffer (Ref. 12)	Ar Buffer (Ref. 12) (Ref. 10)	
(a) O + O + O → O ₂ + O(¹ S ₀)	1.5 × 10 ⁻³⁴	1.5 × 10 ⁻³⁴	4.8 × 10 ⁻³³
(b) N + N + O → N ₂ + O(¹ S ₀) (1+5P) × 10 ⁻³³		2 × 10 ⁻³²	1.3 × 10 ⁻³⁰
(c) N + O + O → NO + O(¹ S ₀) 3 × 10 ⁻³³		3 × 10 ⁻³³	2.6 × 10 ⁻³¹

(6)

* k with buffer at p Torr, 300°K (cm⁶ sec⁻¹).

The three body recombination "Chapman mechanism" is one of the earliest proposed sources. Its importance has been the subject of considerable controversy, with most recent interpretations tending to the affirmative. For the present application it does not look too promising. Reaction a requires a high density of $O(^3P)$ leading to rapid deactivation of $O(^1S_0)$, while reactions b and c must compete with $N + O + M \rightarrow NO + M$ ($k \sim 10^{-32} \text{ cm}^6 \text{ sec}^{-1}$). This consumes atomic oxygen and generates NO, which quenches $O(^1S_0)$ very efficiently. The efficiency of transfer of electrical to chemical to $O(^1S_0)$ stored energy is also low.

Electron Collision:²¹

The theoretical cross section²² for electron excitation of ground state oxygen to the $O(^1S_0)$ level shows a broad peak at $\sim 6 \text{ eV}$ with a maximum of $2 \times 10^{-18} \text{ cm}^2$. This is an order of magnitude lower than the cross section for excitation of the $O(^1D_2)$ level. Further calculations²³ indicate that each electron of $\sim 9 \text{ eV}$ coming to rest in a weakly ionized gas of O atoms produces $\sim 0.2 O(^1S_0)$ states and $\sim 2 O(^1D)$ states. The $O(^1S_0)$ production is therefore very inefficient.

Electron collision excitation is spin forbidden for both of these excitations.

Dissociative Recombination:

The total cross section for dissociative recombination²⁴ is $\sim 2.1 \times 10^{-7} \text{ cm}^2$. The cross-section for production of $O(^3P)$ is 2.1×10^{-7} , $O(^1D)$ 1.9×10^{-7} , $O(^1S_0)$ 2.1×10^{-8} . Airglow observations²⁵ confirm the relative values of these rates and imply that reaction (8) is about five times as probable as reaction (9). The large production of $O(^1D)$ and low efficiency for $O(^1S_0)$ argue against this reaction for the present application.

Dissociative Excitation:

This reaction has not been thoroughly studied, but should be similar to photolytic results. The cross section to produce $O(^1S_0)$ might be as high as 10^{-16} cm^2 to explain some auroral observations,²⁶ but is not known and is unlikely to be so large.²⁷ An energy transfer of at least 9 eV is required.

B. PHOTOLYTIC PRODUCTION OF $O(^1S_0)$

Light absorption by a molecule involves an unambiguous energy change, unlike electronic or molecular collision processes. Also there are fewer bodies leaving the reaction complex after a photolytic reaction (at the very least the photon has disappeared) so the number of allowed channels for the reaction products is reduced. Photolytic reactions are, therefore, more specific than electronic or

molecular collisional reactions and reactions with a high yield of $O(^1S_0)$ are more easily identified and studied. Photolytic reactions have a disadvantage; photons, rather than easily produced energetic electrons or molecules, must be generated to carry the energy to the reactants. The additional energy transfer reaction required to generate the photons will add engineering complications and may reduce the overall efficiency. A similar transfer of electrical energy to intermediates to final excited state is required for a gas discharge device, however, so it is by no means certain which will be the most efficient.

Fig. 3. Photolysis of CO_2 in argon at ~ 1100 Å.
a. Yield of $O(^1S_0)$ vs wavelength.²⁹
b. Absorption coefficient of CO_2 vs wavelength.³⁰

We discuss below photolytic reactions in which the production of $O(^1S_0)$ has been demonstrated and also certain reactions which have not been thoroughly investigated but are potential sources of $O(^1S_0)$.

The photolysis of O_2 to yield $O(^1S_0)$ is energetically allowed for wavelengths < 1340 Å and is thought to be one source of $O(^1S_0)$ in the upper atmosphere.²⁸ $O(^1S_0)$ will be produced from 1340 Å to the ionization threshold at 1028 Å, a region²⁹ containing many diffuse bands with absorption coefficients ranging from a few tenths to a few hundred per centimeter-atmosphere. The quantum yield of $O(^1S_0)$ is unknown but appears¹⁶ to be rather low, ~ 0.03 at 1216 Å. The competing $O(^1D) + O(^1D)$ channel is very close to $O(^1S_0) + O(^3P)$ in energy, but is spin forbidden and should be weak. This does not seem to agree with the low photolytic yield. Deactivation of $O(^1S_0)$ by O_2 is moderately slow (Table 1: $k \sim 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$), and by $O(^3P)$ is moderately fast ($k \sim 7 \times 10^{-12}$).

$O(^1S_0)$ production is energetically allowed for wavelengths less than 1286 Å. The quantum yield in the region 1080 Å - 1150 Å is 0.75 ± 0.25 and is thought³⁰ to be unity, as shown in Fig. 3. Another measurement¹⁶ of $O(^1S_0)$ production from CO_2 at 1165 Å gives ≤ 0.07 , which is rather lower than measured by Lawrence³⁰ though the scatter in the data could allow such a discrepancy. In this region³¹ CO_2 absorbs in many overlapping bands with an absorption which is always greater than $200 \text{ cm}^{-1} \text{ atm}^{-1}$. The quantum yield

decreases below 1080 Å because of increasing competition from the reaction $\text{CO}_2 + h\nu \rightarrow \text{CO}(a^3\pi) + \text{O}(^3\text{P})$; $\text{CO}(a^3\pi) \rightarrow \text{CO}(x^1\Sigma) + h\nu$ (Cameron band phosphorescence). There are theoretical reasons to believe^{32,33} that the reaction $\text{CO}(a^3\pi) + \text{O}(^3\text{P}) \rightarrow \text{CO}(x, v=0) + \text{O}(^1\text{S}_0)$ has a large cross-section, so not all of the energy deposited in $\text{CO}(a^3\pi)$ will be lost. There are no experimental results on $\text{O}(^1\text{S}_0)$ yield, but the total quenching rate for the $\text{CO}(a) + \text{O}(^3\text{P})$ reaction has been measured³³ to be $2 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$.

A semi-empirical theoretical treatment^{32,34} of the electronic states of CO_2 indicates that absorption near 1100 Å is the strongly allowed $X^1\Sigma_g^+ \rightarrow ^1\Sigma_u^+$ (Fig. 4). This theoretical result is not in conflict with a quantum yield near 100% for $\text{O}(^1\text{S}_0)$ near 1100 Å, though the curve crossings show a possible reaction path $^1\Sigma_u^+ \rightarrow ^1\Sigma_u^- \rightarrow ^1\Pi_g$ for production of $\text{O}(^1\text{D})$ similar to that seen in N_2O . These curves are not precisely known, making such predictions rather vague.

Deactivation of $\text{O}(^1\text{S}_0)$ by CO and CO_2 is moderately slow (Table 1: $k \sim 10^{-13} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$) and for CO probably proceeds as $^1\Sigma_u^+ \rightarrow ^1\Sigma_u^- \rightarrow ^1\Pi_g$ to yield $\text{CO}(x) + \text{O}(^1\text{D})$.

The peak yields of $\text{O}(^1\text{S}_0)$ from CO_2 are at wavelengths for which lithium fluoride absorption is increasing to 10-30%. This argues that a high energy photolytic source may be difficult or impossible to construct.³⁵ Photolysis with argon atomic resonance radiation or collision transfer from the argon atomic metastable states would fall into the appropriate region for efficient production of $\text{O}(^1\text{S}_0)$, suggesting that a discharge in argon with added CO_2 could be an intense source of $\text{O}(^1\text{S}_0)$ if conditions can be arranged to excite these

atomic levels efficiently. Such excitation has been detected and is discussed in III C.

The production of $\text{O}(^1\text{S}_0)$ in N_2O photolysis is energetically allowed for wavelengths shorter than ~2100 Å, but it has been demonstrated only at 1470 Å and shorter wavelengths. For this discussion we shall focus on the N_2O absorption continuum near 1450 Å shown in Fig. 5. The largest detected N_2O photolysis yield of $\text{O}(^1\text{S}_0)$ comes from this continuum,³⁶ though yields have not been carefully measured elsewhere.

The studies of N_2O photolysis^{16,36,37} in the 1450 Å continuum imply, in summary, that the competing reaction channels proceed as shown in Table 2. Results for photolysis at several other wavelengths are also shown. The $\text{O}(^1\text{S}_0)$ yield is determined by fluorescence of the auroral line. Other yields are found by analyses of reaction products. The rather complex chemistry involved makes these yields somewhat less certain.

A theoretical semi-empirical calculation^{33,41,42} of the potential energy surfaces for the singlet states of NN-O and N-NO appears in Fig. 6. The 1450 Å, 8.5 eV band probably correlates with the $2^1\Sigma^+$, $1^1\Pi$, and $2^1\Pi$ dissociative states which fall theoretically at 7.5 to 9.5 eV; such an error is within the expected precision of the calculation. These diagrams predict a large abundance of $\text{O}(^1\text{S}_0)$ and $\text{N}_2(A^3\Sigma)$ from the $2^1\Sigma^+$ and $2^1\Pi$ states respectively, a large abundance of $\text{O}(^1\text{D})$ from the $1^1\Pi$ or from non-adiabatic processes through curve crossings in the energy surfaces, and a

Fig. 4. Singlet states of CO_2 below 12 eV.³¹ The vertical lines indicate the Franck-Condon region of the ground state. The energies are qualitative (Ref. 32).

fairly large abundance of $\text{N}(^2\text{D})$ from the dissociative $^1\Pi$ absorptions correlating to it. Triplet states (spin forbidden reactions) are omitted from Table 2.

Other Photolytic Sources of $\text{O}(^1\text{S}_0)$

There are other potential $\text{O}(^1\text{S}_0)$ sources which have not been investigated. Deactivation rates for $\text{O}(^1\text{S}_0)$ in collision with

Fig. 5. N₂O photodissociation continua at 1450 Å and 1275 Å, with superposed emission continua (dashed lines) for (a) Kr₂⁺ and (b) Ar₂⁺.

radicals such as SO and ClO which might be produced in such reactions are also unknown. A few possibilities are:

$\text{ClO}_2 + h\nu \rightarrow \text{ClO} + \text{O}(^1\text{S}_0)$ —This reaction is energetically allowed for $\lambda \leq 1860$ Å. Photolysis at $\sim 3750 - 3100$ Å yields O(³P) with high quantum efficiency (~ 1).⁴³ The reaction $\text{ClO}_2 + \text{O}(^3\text{P}) \rightarrow \text{ClO} + \text{O}_2$ is known to be very fast⁴⁴ and may also efficiently quench O(¹S₀).

$\text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O}(^1\text{S}_0)$ —Photolysis of ozone is energetically allowed for $\lambda \leq 2400$ Å. Photolysis at ~ 2480 Å yields⁴⁵ O₂(¹Δ_g, ¹Σ_g⁺) + O(¹D). Photolysis at 1216 Å shows a yield ≤ 0.03 .⁴⁶ O(¹S₀) reacts rapidly with O₃,¹⁴ $k \sim 6 \times 10^{-10}$ cm³ sec⁻¹. An absorption spectrum⁴⁷ shows many diffuse bands below 2400 Å with absorption from 10 to 200 cm⁻¹ atm⁻¹.

$\text{SO}_2 + h\nu \rightarrow \text{SO} + \text{O}(^1\text{S}_0)$ —Photolysis of SO₂ is energetically allowed for $\lambda \leq 1260$ Å. Such wavelengths are shorter

Table 2. Abundance of N₂O photolysis products at various wavelengths, %.^a

N ₂ O + hν →	1849 Å	1470 Å	1236 Å	1216 Å	1165 Å
N ₂ (x) + O(¹ S ₀)		50 ± 10	strong ~88 present also N ₂ (B)	(40 ± 20)x Φ(1236 Å)	(40 ± 30)x Φ(1236 Å)
N ₂ (x) + O(¹ D)	99	≤55; (~40)			
N ₂ (A) + O(³ P)		8 ± 2		present	present
NO + N(² D)	≤1	2 ± 2 (≥0.03)	~12		
Reference	38	35, 39	16, 39, 40	16	16

^aThis table assumes that spin conservation is strictly obeyed. If it is not, O(³P) and N atom yields may change.

than would be desirable for a practical source.

$\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}(^1\text{S}_0)$ —This reaction is energetically allowed for $\lambda \leq 1720 \text{ \AA}$. Reaction of $\text{O}(^1\text{S}_0)$ with NO and NO_2 is very fast, which is undesirable. The yield of $\text{O}(^1\text{S}_0)$ at $1470 \text{ \AA}$ is ≤ 0.1 .¹⁶

C. PRODUCTION OF $\text{O}(^1\text{S}_0)$ IN MOLECULAR COLLISION PROCESSES IN A GAS DISCHARGE

Auroral line emission has been seen from discharges containing a small oxygen impurity in nitrogen, rare gases, or nitrogen-rare-gas mixtures. The auroral line is often one of the most intense lines in such systems. Experiments that show copious auroral emission range from α particle⁴⁸ and electron¹⁷ radiolysis to Tesla-coil excitation of an ordinary incandescent light bulb.⁴⁹ Very little is known about the efficiency of conversion of electron energy to $\text{O}(^1\text{S}_0)$ population or about the reactions of $\text{O}(^1\text{S}_0)$ with ions and electrons, though some rather indirect evidence³ indicates that electron deactivation is slow. Also, very little is known about the competing production of $\text{O}(^1\text{D})$, since radiation from this state is usually undetectably weak. Kinetic absorption spectroscopy of $\text{O}(^1\text{D})$ is difficult because of interference from molecular absorptions at the appropriate wavelengths ($1152.13 \text{ \AA}$, $999.9 \text{ \AA}$). Kinetic spectroscopy of $\text{O}(^1\text{S}_0)$ has been attempted, but the results were not precise.⁴

We discuss here possible $\text{O}(^1\text{S}_0)$ sources from well-known energetic species in "active nitrogen"⁵⁰ or rare gas discharges. Dissociative recombination and direct electron excitation mechanisms

Fig. 6. Qualitative dissociation curves for the singlet states of N_2O : a. along the NN-O^{33} dissociation path, b. along the ON-N^{33} dissociation path.

The vertical lines denote the approximate Franck-Condon region of the ground state. Reprinted by permission of Journal of Chemical Physics (Ref. 41).

have been discussed under IIIA in connection with their possible atmospheric role. This list does not, of course, exhaust the possibilities.

Reactions with Ionic Species

Dondes, Harteck, and Kunz⁴⁸ have analyzed $O(^1S_0)$ production mechanisms in ^{210}Po α -particle radiolysis of nitrogen at atmospheric pressure containing ~100 ppm oxygen. They make two important observations:

- a) When an electric field is applied to drift ions rapidly out of the acceptance angle of the photodetector, the auroral line intensity is greatly reduced. The principal $O(^1S_0)$ production mechanism must, therefore, involve an ion and must proceed relatively slowly at this density of excitation, implying that the ion reacts with a species present in small concentration or in a slow reaction with a large activation energy.
- b) Emission is enhanced by about a factor of three by chilling the cell to liquid oxygen temperature (90°K). This could be from freezing out impurities or from an increase in the population of weakly bound excimer complexes such as $[(N_2 - O(^1S_0))]$ which have shorter radiative lifetimes than $O(^1S_0)$ and are therefore less affected by non-radiative decay processes. In fact it is completely explained by the temperature dependence, unknown at the time of this work, of the deactivation of $O(^1S_0)$ by collisions with O_2 . If one assumes that the rate constant for deactivation by N_2 plus impurities is $1.5 \times 10^{-17} \text{ cm}^3 \text{ sec}^{-1}$, and is temperature independent, then the measured^{9,11} O_2 deactivation T dependence gives a factor of three increase in the $O(^1S_0)$

nonradiative decay lifetime at 90°K. Such a deactivation rate is not in conflict with reported values for rather clean nitrogen gas. The conclusion of Dondes, et al., that reactions with a significant activation energy are excluded from the kinetic chain producing $O(^1S_0)$ still stands, so the ionic reaction must be with a species of low concentration.

The major primary reactions in N_2 radiolysis by α particles are thought to be

Subsequent reactions will redistribute the energy in the system to give all of the species N_2 , N_2^+ , N , N^+ , NO , NO^+ , O_2 , O , O^- , O^+ , O_2^- , O_2^+ , leading to a rather complex set of possible kinetic chains for $O(^1S_0)$ production. At higher pressures N_4^+ and other complex ions will also appear.

The most probable kinetic chain of the present experiment terminates in the reaction

This is estimated to have a rate constant of $\sim 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$. This terminal reaction is chosen to fit the observation that an increase in the concentration of O_2 above ~300 ppm quenches the auroral emission, suggesting that reactions involving oxygen ions are not involved. The oxygen ion concentration and, hence, $O(^1S_0)$ formation rate will be proportional to O_2 concentration while $O(^1S_0)$ lifetime

will be inversely proportional to O_2 concentration, suggesting that auroral line emission is independent of O_2 concentration for a process involving oxygen ions. The accumulation of NO at higher oxygen concentrations may also be important, however, since NO is an extremely efficient quencher of $O(^1S_0)$. Careful study of the dependence of NO concentration and auroral line fluorescence intensity on O_2 concentration and time might give somewhat more convincing arguments for or against this analysis. The accumulation of NO or some competing ion might be enough to explain the quenching, making it unnecessary to exclude oxygen ion reactions.

Other possible ion reactions of low activation energy which could produce $O(^1S_0)$ are

The slow ionic transfer step might also be higher in the kinetic chain.

This short discussion indicates the great complexity of discharges and some of the problems involved in determining unambiguous kinetic chains. Also, it should be noted that other mechanisms may be involved at high densities of excitation.

Molecular Nitrogen Metastable $N_2(A^3\Sigma)$

The metastable $N_2(A^3\Sigma)$ is produced in large quantity in a nitrogen discharge⁵⁰ and the reaction

has a rate constant $k = 3 - 10 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$, of which greater than 5% is $O(^1S_0)$ as detected by auroral line fluorescence.⁵¹ (The $O(^1S_0)$ may be subjected to considerable collisional deactivation in this experiment.) This may be understood from the theoretical interaction surfaces in Fig. 6 which show $N_2(A^3\Sigma)$ and $O(^3P)$ colliding on a weakly repulsive surface which crosses the $^1\Sigma^+$ state correlating with $O(^1S_0) + N_2(x)$. Subsequent curve crossings in the $^1\Sigma^+$ can take the system to states yielding $O(^1D)$. Collisions along a $^3\Pi$ surface (not shown) can produce $O(^3P)$, and atom exchange reactions may produce $NO + N(^2D)$. Qualitatively speaking the yields should be similar to those in the photolysis of N_2O at $\sim 1500 \text{ \AA}$ except for the relaxation of selection rules. The reaction $NO(V \geq 4) + N(^4S) \rightarrow N_2 + O(^1S_0)$ has also been proposed⁵² as a source for $O(^1S_0)$.

Rare Gas Metastables, Excimers, and Resonance Radiation

A source of $O(^1S_0)$ in discharges through rare gas-oxygen mixtures may be processes such as collisions with rare gas metastables or excimers:

which are energetically allowed. The products and rates of most of these reactions are unknown but should bear some similarity to the results of photolysis with comparable energies except for the relaxation of spin selection rules. The results⁵³ of a discharge experiment in $\text{He} + \text{O}_2$ have been interpreted as

with an overall rate constant $\sim 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$ to explain the behavior of the $\text{O}(^1\text{D})$ concentration. The behavior of the $\text{O}(^1\text{D})$ emission seems to support this analysis, but it should be noted that the helium metastable is rather low in energy for this process; it can only barely excite a dissociation level of $\text{O}_2^+(b)$ (see Fig. 7 based on the work of Schaefer and Harris¹⁵ and Gilmore⁵⁴).

$\text{O}(^1\text{S}_0)$ may also arise directly from photolysis by rare gas resonance radiation and other ultraviolet lines in the discharge. Corney and Williams³ assume that production of $\text{O}(^1\text{S}_0)$ in low pressure rare gas discharges is by electron collision with atomic oxygen.

The $\text{CO}_2 + \text{Ar}(^1\text{P}_1, ^3\text{P}_{2,1,0})$ reaction may be an efficient source of $\text{O}(^1\text{S}_0)$ in discharges. The yield of $\text{O}(^1\text{S}_0)$ from CO_2 photolysis near 1100 Å is $\sim 100\%$, as discussed in III C. Photolysis at such a short wavelength presents technical problems as discussed there. Collision transfer from excited molecules in radiatively trapped or metastable states near 1100 Å may be a more practical mechanism for the decomposition. The four levels of the $3p^5 4s$ configuration of atomic argon lie at the proper energy for efficient transfer into the high-yield region for $\text{O}(^1\text{S}_0)$ production from CO_2 reported by Lawrence.³⁰

Figure 4 shows the relative positions of these energy levels. The reaction $\text{Ar}(^1\text{P}_1) + \text{CO}_2(^1\Sigma) \rightarrow \text{Ar}(^1\text{S}_0) + \text{CO}(^1\Sigma) + \text{O}(^1\text{S}_0)$ is spin allowed and is expected to have a fast rate, while the reaction with the argon triplet states $\text{Ar}(^3\text{P}_{2,1,0}) + \text{CO}(^1\Sigma) \rightarrow \text{CO}(^1\Sigma) + \text{O}(^1\text{S}_0) + \text{Ar}(^1\text{S}_0)$ is spin forbidden if total spin is a good quantum number. Taylor and Setzer,⁵⁵ and also Starr⁵⁶ have investigated the $\text{CO}_2 - \text{Ar}(^3\text{P}_{0,2})$ metastable reaction. They find a large yield of $\text{CO}(a^3\Pi) + \text{O}(^3\text{P})$ and significant yield of $\text{CO}(X^1\Sigma) + \text{O}(^1\text{S}_0)$. Starr finds that the intensity of the auroral line fluorescence is 10-20% of the $\text{CO}(a^3\Pi - X^1\Sigma)$ Cameron band phosphorescence. If we assume a radiative lifetime^{57,58} of 7 msec for $\text{CO}(a^3\Pi)$ and a 2×10^{-10} deactivation rate with the background $\sim 10^{14} \text{ cm}^{-3}$ concentration of CO_2 , the $\text{O}(^1\text{S}_0)$ production rate in the reaction zone was about 2 to 5% of the $\text{CO}(a^3\Pi)$ production rate. The experimental apparatus would have to be analyzed much more carefully before one could put much confidence in this rate, but it is probably safe to say that $\text{O}(^1\text{S}_0)$ production is

1-10% of $\text{CO}(a^3\Pi)$ production. The fraction of energy transfer collisions that produce bound states of CO_2 (which may then radiate or cross to states yielding $\text{CO}(x^1\Sigma) + \text{O}(^3\text{P})$) was not determined in these experiments. The reaction rate constant was also not determined. Collisions similar to this⁵⁹ are estimated to have rates which are some significant fraction of the gas kinetic collision rate, or $k \sim 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$.

The production of $\text{O}(^1\text{S}_0)$ in these experiments suggests that spin is in fact not a good quantum number in the $\text{CO}_2 - \text{Ar}^*$ collision complex. The results might also be explained by production of $\text{Ar}(^1\text{P}_1)$ in a process such as $\text{Ar}(^3\text{P}_{2,0}) + \text{Ar}(^1\text{S}_0) \rightarrow \text{Ar}(^1\text{P}_1) + \text{Ar}(^1\text{S}_0)$ followed by collision of $\text{Ar}(^1\text{P}_1)$ with CO_2 and a spin allowed decomposition to yield $\text{O}(^1\text{S}_0)$ or by radiative decay of $\text{Ar}(^1\text{P}_1)$ giving a photon which photolyses CO_2 to yield $\text{O}(^1\text{S}_0)$. The reaction to produce $\text{Ar}(^1\text{P}_1)$ is 850 cm^{-1} endothermic ($\sim 4 \text{ kT}$) so this is unlikely. Radiatively trapped $\text{Ar}(^1\text{P}_1)$ atoms could possibly be present in the reaction zone though the experiments were designed to eliminate them. An excited state collision process such as $\text{Ar}(^3\text{P}_{2,0})$

$+ \text{Ar}(^3\text{P}_{2,0}) \rightarrow \text{Ar}^+ + e + \text{Ar}(^1\text{S}_0)$ followed by recombination to give $\text{Ar}(^1\text{P}_1)$ is unlikely since no emissions from argon ion levels were detected. Note that the $\text{CO}(a^3\Pi) + \text{O}(^3\text{P})$ collision has a high probability^{32, 33} for transfer to give $\text{CO}(x) + \text{O}(^1\text{S}_0)$, so that the $\text{CO}(a)$ state production also contributes to $\text{O}(^1\text{S}_0)$ production.

The $\text{Xe}(^3\text{P}_{2,0}) + \text{N}_2\text{O}$ reaction is similar in principle to the $\text{Ar}(^3\text{P}_{2,0}) + \text{CO}_2$ reaction but there is an apparent conflict in the results of the two experiments.⁶⁰ No auroral line fluorescence is detected in the N_2O reaction. There is a weak continuum emission which may be N_2O ($\text{A}^3\Sigma^- \rightarrow \text{X}^1\Sigma^+$) and some decomposition to $\text{N}_2(\text{A}^3\Sigma) + \text{O}(^3\text{P})$. Since the N_2O was present at pressures from 0.3 to 10 Torr and is known to quench $\text{O}(^1\text{S}_0)$ with a rate $\sim 1.1 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$, the negative result for $\text{O}(^1\text{S}_0)$ may be explained by rapid quenching of $\text{O}(^1\text{S}_0)$ under these conditions (collision lifetime $\sim 0.3\text{-}8 \mu\text{sec}$ compared to $\sim 20 \text{ msec}$ in Starr's experiment⁵⁶ on CO_2) which could have reduced the auroral line signal to an undetectable level. $\text{Kr}_2^* - \text{N}_2\text{O}$ is another candidate for collision transfer, and for this process no information is available.

IV. A Possible Auroral Line Laser Using Photolysis of N_2O with Kr_2^* Continuum Radiation

Figure 5 shows the Kr_2^* excimer emission continuum superposed on the N_2O $1450 \text{ \AA}$ absorption continuum which shows a high yield of $\text{O}(^1\text{S}_0)$. The overlap is good, implying that a Kr_2^* source will couple very well to the N_2O absorption. To optimize such a device we must have an efficient

source of Kr_2^* radiation, an active medium chosen to maximize the auroral line inversion, and a physical design which couples the Kr_2^* radiation to the N_2O efficiently. Each of these points will be briefly discussed in the following sections.

Note that the Ar_2^* emission continuum couples efficiently to the N_2O 1280 Å continuum. This absorption also has a high yield of $\text{O}(^1\text{S}_0)$ and may be suitable for $\text{O}(^1\text{S}_0)$ production, though the yields are not well known. The larger absorption coefficient in the 1280 Å continuum is an advantage since it simplifies the design for efficient coupling between lamp and absorber. The Xe_2^* continuum likewise couples to an 1850 Å continuum, but this yields $\text{O}(^1\text{D})$.³⁸

A. EFFICIENT GENERATION OF Kr_2^* EXCIMER RADIATION

At low densities of excitation in high pressure krypton the Kr_2^* continuum at 1450 Å is produced efficiently in a kinetic scheme depicted in Fig. 8. Kinetic models have been developed by George and Rhodes⁶¹ and also Lorents and Olson.⁶² The principal nonradiative loss of Kr_2^* is excited state collisions of Kr_2^* excimers which feed energy back into Kr^+ and Kr_2^+ . Each such collision converts one excimer to kinetic energy in the gas and returns the other to an ion state, thus lengthening the time spent in the kinetic chain so that diffusion and other such non-radiative losses become more significant. The kinetic model predicts that these losses become important at an excitation density of $10^{15} - 10^{16} \text{ Kr}_2^* \text{ cm}^{-3}$ for an assumed 20-nsec Kr_2^* radiative lifetime. However, the pressure of the background gas should be high since the three-body reactions which form Kr_2^+ and Kr_2^* must be as rapid as possible to reduce diffusive losses and the risetime of the fluorescence. Collision-induced absorption does not appear to be a problem in krypton, but in the similar argon and

xenon systems it is apparently quite large.

Jortner, et al.,⁶³ measure an efficiency of 10-100% for radiolysing particle energy transfer to excimer fluorescence from rare gas excimers at low densities of excitation and Huber, et al.,⁶⁴ measure ~30%. For the case of krypton a simple argument based on the known energy deposition per ion pair⁶⁵ predicts a maximum efficiency of ~35% if only the

Fig. 8. Energy transfer chain for the generation of Kr_2^* excimer radiation by electron beam radiolysis (simplified).

ionic chain of Fig. 8 leads to excimer radiation, or 45-50% if the highly excited atoms which are produced at about one-third the ion production rate also enter the chain.

Kr_2^* lasers to date⁶⁶ have been operated at excited state densities one or two orders of magnitude higher than 10^{16} and show correspondingly low efficiency.

At an excited state density of 2×10^{16} and with an assumed 20-nsec radiative lifetime for Kr_2^* , the radiant flux into 4π is 10^{24} photons per cubic centimeter of Kr_2^* lamp active volume per second, or a radiance of $\sim 1.4 \text{ MW cm}^{-3}$. Presumably such a lamp will have a structure similar to the plasma cathode electron beam devices used for preionization of $\text{CO}_2 - \text{N}_2 - \text{He}$ lasers⁶⁷ (but with somewhat higher current) and will have an excitation pulse length of some few microseconds. If one crudely estimates a practical range of 5 cm in 2-3 atm of krypton for 200 keV electrons and assumes $\sim 30\%$ conversion of electron energy to Kr_2^* radiation, the electron beam current through the foil window in a two-dimensional simple gun will be $\sim 100 \text{ A cm}^{-2}$. The details of such a device will not be treated here. Other primary energies and krypton gas pressures might be chosen to simplify the design of a lamp of this type. It may also be necessary to operate at substantially lower excited state densities in order to get high efficiency in the Kr_2^* fluorescence. Some careful modeling and experimental verifications will be required before a Kr_2^* lamp can be well characterized.

B. KINETIC EQUATIONS DESCRIBING A LASER ACTIVE MEDIUM PRODUCED BY PHOTOLYSIS OF N_2O IN THE 1450 Å CONTINUUM

The model to be developed here will be suitable for a laser medium containing N_2O at an initial particle density up to $\sim 10^{18} \text{ cm}^{-3}$ in a buffer of nitrogen plus helium at up to $\sim 10^{20} \text{ cm}^{-3}$. The buffer is used to thermalize hot atoms from the photolytic reaction and as a heat sink to prevent a drastic temperature rise. It also serves to deactivate $\text{O}(^1\text{D})$ rapidly.

Molecular nitrogen will be restricted to a maximum pressure of one atmosphere ($2.4 \times 10^{19} \text{ cm}^{-3}$) to avoid stimulated Raman oscillation on the N_2 vibration: stimulated Raman processes involving the vibrations or rotations of molecular constituents could be a very important parasitic loss mechanism in a laser amplifier such as that proposed here.

Tables 3-9 present a collection of bimolecular and a few important trimolecular reactions which govern the kinetics of an $\text{N}_2\text{O}-\text{N}_2-\text{He}$ mixture after photolysis. Reactions are numbered in the order of appearance. Reactions that reappear in subsequent tables retain their original numbers. The collection is fairly complete, though it omits the possible production of species such as O_3 and $\text{N}(^2\text{P})$ which may be formed in very small concentration and will react rapidly with the species of higher concentration. Obviously, some of these reactions will be insignificant in a gas mixture chosen for the best laser properties: for example, $\text{O}(^1\text{D})$ is deactivated so rapidly in one atmosphere of N_2 that nearly all of the $\text{O}(^1\text{D})$ produced in the primary photolysis will enter the kinetic chain as $\text{O}(^3\text{P})$.

Table 3. Energy transfer processes in a photolysed N_2O - N_2 -He mixture: $O(^1S_0)$ destruction.

	Note	$k(\text{cm}^3 \text{sec}^{-1})$
1. $N_2 + O(^1S_0) \rightarrow N_2 O(^1D)$	a	$<5 \times 10^{-17}$
2. $He + O(^1S_0) \rightarrow He + O(^1D)$	a	$<4 \times 10^{-19}$
3. $N_2O + O(^1S_0) \xrightarrow{2} N_2 + O_2$	b	1.6×10^{-11}
4. $NO + O(^1S_0) \xrightarrow{2} NO + O(^1D)$	c	5×10^{-10}
5. $NO + O(^1S_0) \xrightarrow{2} NO_2$		$(1.5[N_2] + [He]) 10^{-31}$
6. $O(^3P) + O(^1S_0) \rightarrow O(^1D) + O(^1D)$	d	7.5×10^{-12}
7. $O(^1D) + O(^1S_0) \rightarrow \text{no reaction}$	e	
8. $O(^1S) + O(^1S_0) \rightarrow \text{no reaction}$	e	
9. $N(^2D) + O(^1S_0) \xrightarrow{2} NO$	f	$([N_2] + 0.35[He]) \times 10^{-32} \leq 10^{-12}?$
10. $N(^4S) + O(^1S_0) \xrightarrow{2} NO$	f	$([N_2] + 0.35[He]) \times 10^{-32}?$
11. $NO_2 + O(^1S_0) \xrightarrow{2} NO + O_2$	g	5×10^{-10}
12. $O_2 + O(^1S_0) \xrightarrow{2} O_2 + O(^1D)$	h	5×10^{-11}
13. $N_2(A^3\Sigma) + O(^1S_0) \xrightarrow{2} N_2(A^3\Sigma) + O(^3P)$	i	$10^{-11}?$

^aThis may be $O(^1D)$ or $O(^3P)$. Nitrogen-oxygen and rare-gas-oxygen complexes are known to radiate intense excimer bands near 5577 Å;^{17,18} $O(^1D)$ is assumed for this reason and because it is the worst case for the present purpose. The effect on the kinetics is small since $O(^1D)$ is rapidly converted to $O(^3P)$. Rate constants are from Ref. 3 and 9. The rate for He is estimated from the result for Ne; He is known to have a smaller rate constant.¹⁶

^bThe reaction to yield $N_2 + O_2$ is adiabatically connected to states of $N_2O + O(^1S_0)$ while $2NO$ is not.⁷ The reaction may also yield $N_2O + O(^1D, ^3P)$. Rate constants Ref. 7.

^cA correlation diagram indicates that this state is connected to $N(^2D) + O_2(^1\Delta_g)$, an endothermic reaction.⁷ Assume NO_2 is formed at the three body rate for $NO + O(^3P)$ (Ref. 68) and $O(^1D) + N_2$ is formed at the rate given by low pressure experiments.

^d $O(^1D) + O(^1D)$ is assumed because this surface is near $O(^3P) + O(^1S)$ and exothermic.¹³ The rate constant is from Ref. 10. Three body recombination is neglected (note e).

^eThese collisions occur on repulsive surfaces which do not cross bound states at any reasonable translational energy. There are no experimental results. Three body recombination such as the "Chapman Mechanism" discussed in III A ($k \sim 10^{-30} - 10^{-34} \text{ cm}^6 \text{sec}^{-1}$) is neglected.

^fThe rate constant is assumed equal to that for three body recombination of ground state atoms (Ref. 7), although there is no experimental evidence. The reaction is relatively unimportant in the present system. See also Ref. 10.

^gThe products are assumed to be $NO + O_2$, which is highly exothermic. The rate constant is from Ref. 7. There are no experimental results.

^hPhysical deactivation of $O(^1S_0)$ and excitation transfer from $O(^1D)$ are expected.⁷ $O_2(b^1\Sigma_g)$ has been observed in the $O(^1D)$ reaction. The rate constants are from Refs. 7 and 69.

ⁱAssume that, on collision with an excited atom, $N_2(A)$ goes to a higher electronic state of N_2 and decays rapidly by radiation back to $N_2(A)$. The atom goes to the ground state. This neglects those molecules which go into a singlet state and radiate to the ground state. There is some discussion of $N_2(A)$ deactivation in Ref. 39, but no results to support this assumption. Further assume that the reaction rate is equal to the measured rate for $N_2(A) + O(^3P)$.

Table 4. Energy transfer processes in a photolysed N_2O - N_2 -He mixture: $O(^1D)$ destruction.

	Note	$k(\text{cm}^3 \text{ sec}^{-1})$
14. $N_2 + O(^1D) \rightarrow N_2 + O(^3P)$	a	5.5×10^{-11}
15. $He + O(^1D) \rightarrow He + O(^3P)$	a	10^{-15}
16. $N_2O + O(^1D) \rightarrow N_2 + O_2$	b	1.1×10^{-10}
17. $\rightarrow NO + NO$		1.1×10^{-10}
18. $NO + O(^1D) \rightarrow NO + O(^3P)$	c	2.1×10^{-10}
19. $\rightarrow NO_2$		$(1.5[N_2] + [He]) \times 10^{-31}$
20. $O(^3P) + O(^1D) \rightarrow \text{no reaction}$	d	
21. $O(^1D) + O(^1D) \rightarrow \text{no reaction}$	e	
7. $O(^1S_0) + O(^1D) \rightarrow \text{no reaction}$	d	
22. $N(^2D) + O(^1D) \rightarrow NO$	f	$[N_2] + 0.35[He] \times 10^{-32}$
23. $N(^4S) + O(^1D) \rightarrow NO$	f	$[N_2] + 0.35[He] \times 10^{-32}$
24. $NO_2 + O(^1D) \rightarrow NO + O_2$	g	4×10^{-10}
25. $O_2 + O(^1D) \rightarrow O_2(a, b) + O(^3P)$	h	7.5×10^{-11}
26. $N_2(A^3\Sigma) + O(^1D) \rightarrow N_2(A^3\Sigma) + O(^3P)$	i	10^{-11}

^a $N_2 + O(^1D)$ collide in states of $N_2 - O$ which permit rapid deactivation to vibrationally excited nitrogen or translational energy. The rate constants are from Refs. 7, 8, and 68. $He + O(^1D)$ is expected to relax via a curve crossing to $O(^3P)$ as discussed for $Xe + O(^1D)$ in Ref. 7.

^bDiscussed in Ref. 7.

^cSee Table 3 note c. The argument here is similar.

^dSee Table 3 note e.

^eReaction to yield $O(^3P) + O(^1S_0)$ is endothermic and is neglected (see Table 3 note d). Three-body recombination is neglected (see Table 3 note e).

^fSee Table 3 note f.

^gSee Table 3 note g.

^hSee Table 3 note h.

ⁱSee Table 3 note i.

Table 5. Energy transfer processes in a photolysed N_2O-N_2 -He mixture: $O(^3P)$ destruction.

	Note	$k(\text{cm}^3 \text{sec}^{-1})$
27. $N_2 + O(^3P) \rightarrow$ no reaction		
28. $He + O(^3P) \rightarrow$ no reaction		
29. $N_2O + O(^3P) \rightarrow$ products	a	10^{-17} (no reaction)
30. $NO + O(^3P) \rightarrow NO_2$	b	$(1.5[N_2] + [He]) \times 10^{-31}$
31. $O(^3P) + O(^3P) \rightarrow$ no reaction	c	
20. $O(^1D) + O(^3P) \rightarrow$ no reaction	c	
6. $O(^1S_0) + O(^3P) \rightarrow O(^1D) + O(^1D)$	d	7.5×10^{-12}
32. $N(^2D) + O(^3P) \rightarrow NO$	e	$([N_2] + 0.35[He]) \times 10^{-32}$?
33. $N(^4S) + O(^3P) \rightarrow NO$	f	$[N_2] + 0.35[He] \times 10^{-32}$
34. $NO_2 + O(^3P) \rightarrow NO + O_2$	g	2×10^{-12}
35. $O + O(^3P) \rightarrow$ no reaction		
36. $N_2(A^3\Sigma) + O(^3P) \rightarrow O(^1S) + N_2$	h	5×10^{-12}
37. $O(^1D) + N_2$		5×10^{-12}

^aThe rate estimate is from Ref. 70.

^bMeasured rate of Ref. 66. There may be a non-radiative channel also; this is neglected.

^cSee Table 3 note e.

^dSee Table 3 note d.

^eSee Table 3 note f.

^fThree body recombination is $\sim 10^{-32}$ with N_2 and $\sim 3.5 \times 10^{-33}$ with He.⁷¹ There is a weak two-body radiative recombination, $k \sim 5 \times 10^{-17} \text{ cm}^3 \text{sec}^{-1}$, which is negligible at the high densities of interest here.

^gReaction to yield $NO + O_2$ is assumed. The rate constant is $> 2 \times 10^{-12}$ from Ref. 70.

^hThe product is at least 5% $O(^1S_0)$ (see III B). Assume 50% $O(^1S_0)$ 50% $O(^1D)$ and the total rate of Ref. 50. See also Ref. 49, pp. 104, and references listed there.

Table 6. Energy transfer processes in a photolysed N_2O-N_2 -He mixture: $N(^2D)$ destruction.

	Note	$k(\text{cm}^3 \text{sec}^{-1})$
38. $N_2 + N(^2D) \rightarrow N_2 + N(^4S)$	a	$<6 \times 10^{-15}$
39. $He + N(^2D) \rightarrow N_2 + N(^4S)$	a	$<2 \times 10^{-16}$
40. $N_2O + N(^2D) \rightarrow N_2 + NO$	b	3×10^{-12}
41. $NO + N(^2D) \rightarrow N_2 + O(^3P)$	b	1.8×10^{-10}
32. $O(^3P) + N(^2D) \rightarrow NO$	c	$([N_2] + 0.35[He]) \times 10^{-32} ?$
22. $O(^1D) + N(^2D) \rightarrow NO$	c	$([N_2] + 0.35[He]) \times 10^{-32} ?$
9. $O(^1S_0) + N(^2D) \rightarrow NO$	c	$([N_2] + 0.35[He]) \times 10^{-32} ?$
42. $N(^2D) + N(^2D) \xrightarrow{?}$ no reaction	d	
43. $N(^4S) + N(^2D) \xrightarrow{?}$ no reaction	d	
44. $NO_2 + N(^2D) \rightarrow N_2O + O(^3P)$	e	$4 \times 10^{-11} ?$
45. $\quad \quad \quad \rightarrow NO + NO$		$3 \times 10^{-11} ?$
46. $O_2 + N(^2D) \rightarrow NO + O(^3P)$	f	$10^{-11} ?$
47. $N_2(A^3\Sigma) + N(^2D) \xrightarrow{?} N_2(A) + N(^4S)$	g	$10^{-11} ?$

^aRate constants are from Ref. 7 and 72. Physical deactivation assumed from results of Ref. 72.

^bRate constants from Ref. 7 and 72. Chemical reaction indicated by the results of Ref. 72.

^cSee Table 3 note f.

^dPresumably, this will be a slow three-body reaction. Some possible slow two-body reactions are discussed in Ref. 50, pp. 153ff. The reaction is neglected here. $N_2O + N(^4S) < 2 \times 10^{-16}$, Ref. 70 and Ref. 50, pp. 396. $N_2 + NO$ is spin forbidden.

^eThe reaction is "fast" and is assumed to have a gas kinetic cross-section. $N_2O + O$ the principal product (43%), but there is also $2NO$ (33%), $N_2 + O_2$ (10%), $N_2 + 2O$ (13%). See Ref. 50, pp. 399-400 and listed references. The rate for $N(^2D)$ is assumed equal to that for $N(^4S)$. The two minor products are neglected, but NO is retained because of its importance for $O(^1S_0)$ deactivation.

^fThe rate for $N(^4S) + O_2$ has been measured. (Ref. 50, pp. 482). $N(^2D)$ is assumed to overcome the 7 kcal activation energy and react faster.

^gSee Table 3 note i.

Table 7. Energy transfer processes in a photolysed N_2O - N_2 -He mixture: $N(^4S)$ destruction.

	Note	$k(\text{cm}^3 \text{ sec}^{-1})$
48. $N_2 + N(^4S) \rightarrow \text{no reaction}$	a	
49. $\text{He} + N(^4S) \rightarrow \text{no reaction}$	a	
50. $N_2O + N(^4S) \xrightarrow{?} N_2 + \text{NO}$	a	$< 2 \times 10^{-16}$
51. $\text{NO} + N(^4S) \rightarrow N_2 + O(^3P)$	b	2×10^{-11}
33. $O(^3P) + N(^4S) \rightarrow \text{NO}$	c	$([N_2] + 0.35[\text{He}]) \times 10^{-32}$
23. $O(^1D) + N(^4S) \xrightarrow{?} \text{NO}$	d	$([N_2] + 0.35[\text{He}]) \times 10^{-32} ?$
10. $O(^1S_0) + N(^4S) \xrightarrow{?} \text{NO}$	d	$([N_2] + 0.35[\text{He}]) \times 10^{-32} ?$
43. $N(^2D) + N(^4S) \rightarrow \text{no reaction}$	a	
52. $N(^4S) + N(^4S) \rightarrow \text{no reaction}$	a	
53. $\text{NO}_2 + N(^4S) \xrightarrow{?} N_2O + O$	e	4×10^{-11}
54. $\quad \quad \quad \rightarrow \text{NO} + \text{NO}$		3×10^{-11}
55. $\text{O}_2 + N(^4S) \rightarrow \text{NO} + O(^3P)$	f	3×10^{-17}
56. $N_2(A^3\Sigma) + N(^4S) \rightarrow N_2 + N(^4S)$	g	5×10^{-11}

^aSee Table 6 note d.

^bThe reaction is "very fast" and assumed to be at a gas kinetic rate. See Ref. 50, pp. 382ff and Table 6 note b.

^cSee Table 5 note f.

^dSee Table 3 note f.

^eSee Table 6 note e.

^fSee Table 6 note f.

^gThe rate of $N_2(A)$ destruction is measured in Ref. 73. The products are assumed from an argument in Ref. 50, pp. 102.

Table 8. Energy transfer processes in a photolysed N_2O-N_2 -He mixture: $N_2(A^3\Sigma)$ destruction.

	Note	$k(\text{cm}^3 \text{ sec}^{-1})$
57. $N_2 + N_2(A) \rightarrow N_2 + N_2$	a	$<10^{-17}$
58. $\text{He} + N_2(A) \rightarrow \text{He} + N_2$	a	$<10^{-17}$
59. $N_2O + N_2(A) \xrightarrow{?} N_2 + N_2O$	b	6.1×10^{-12}
60. $\text{NO} + N_2(A) \rightarrow \text{NO} + N_2$	c	8×10^{-11}
36. $\text{O}(^3P) + N_2(A) \rightarrow \text{O}(^1S_0) + N_2$	d	$5 \times 10^{-12} ?$
37. $\quad \quad \quad \rightarrow \text{O}(^1D) + N_2$		$5 \times 10^{-12} ?$
56. $\text{N}(^4S) + N_2(A) \rightarrow N_2 + \text{N}(^4S)$	e	5×10^{-11}
61. $\text{NO}_2 + N_2(A) \xrightarrow{?} \text{products}$	f	$10^{-10} ?$
62. $\text{O}_2 + N_2(A) \rightarrow N_2 + \text{O}_2$	a	3.6×10^{-12}
63. $N_2(A) + N_2(A) \rightarrow N_2(A) + N_2$	g	$3-10 \times 10^{-10} ?$

^aThe rates are measured in Refs. 39 and 74.

^bThe rate is measured in Refs. 39 and 74. $N_2 + N_2 + \text{O}$ is assumed; however, there may be other products. See also Ref. 50.

^cThe rate is from Refs. 39 and 74. Excitation transfer to $\text{NO}(A)$ and subsequent radiative decay is assumed.

^dSee Table 5 note h.

^eSee Table 7 note g

^fThe reaction is assumed to be fast. The yields have not been studied.

^gThe rate constant is from Refs. 39 and 74. The reaction is to $N_2 + N_2(B, C,)$ which rapidly decays to $N_2(A)$ by radiation.

Table 9. Energy transfer processes in a photolysed N_2O-N_2 -He mixture: photolytic N_2O destruction.

	$k(\text{cm}^3 \text{ sec}^{-1})$
64. $N_2O + h\nu \rightarrow N_2 + \text{O}(^1S)$	4.8×10^{-8}
65. $\quad \quad \quad \rightarrow N_2 + \text{O}(^1D)$	3.8×10^{-8}
66. $\quad \quad \quad \rightarrow N_2(A) + \text{O}(^3P)$	7.7×10^{-9}
67. $\quad \quad \quad \rightarrow \text{NO} + \text{N}(^2D)$	1.9×10^{-9}

Products and rate constants are poorly known for many of these reactions, indicated by question marks in the tables. Fortunately, the principal reactions have been studied in some detail. Reasonable assumptions have been made for unknown products and rate constants, as discussed in the appropriate footnotes.

A comparison of the results of different experiments indicates that the rate constants in Tables 3-9 in the range $\sim 10^{-14} - 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$ are accurate within about a factor of two. Slow rates such as the $\text{O}(^1\text{S}_0)$ deactivation with N_2 and He are less well known, since a $\sim 10^{-18}$ rate is highly sensitive to minute impurities of fast quenchers such as H_2O and NO. The constants listed for such rates are the best recent measurements and are an upper bound on the actual rates. They are representative of the rates which may be expected in a very clean system with some few parts per million residual impurities.

Some of the reaction rates are known to be temperature dependent; that is, to have a significant activation energy. This dependence has been neglected and all rates in the table are for room temperature reactions. The temperature of the active medium will be treated in a rather crude fashion in this preliminary model by assuming that 6.5 eV is immediately converted to heat in the gas for each 8.5 eV photon absorbed. Later more precise models will have to keep track of the gas temperature while proceeding through the kinetic chain. Since the rate constants have been assumed to be temperature independent for this initial model, the gas temperature does not affect the kinetics, but in a more detailed model it will.

Photolytic decomposition of N_2O is treated in Table 9. Photons are absorbed by N_2O according to

$$\frac{d\rho_{\text{N}_2\text{O}}}{dt} = \rho_P \rho_{\text{N}_2\text{O}} S \int_{-\infty}^{\infty} h(\nu) g(\nu) d\nu$$

$$= \rho_P \rho_{\text{N}_2\text{O}} k \quad (29)$$

where ρ_P and $\rho_{\text{N}_2\text{O}}$ are the density of photons and N_2O molecules per cubic centimeter, $h(\nu)$ and $g(\nu)$ are the line-shapes of the Kr_2^* continuum and N_2O absorption, and S is the line strength of the N_2O absorption. The equivalent rate constant in $\text{cm}^3 \text{ sec}^{-1}$ is k . The Kr_2^* continuum is centered at $1460 \text{ \AA}$ and has a $1/e$ halfwidth of $\sim 70 \text{ \AA}$, while the N_2O continuum is centered at $1450 \text{ \AA}$ and has a $1/e$ halfwidth of $\sim 45 \text{ \AA}$, as seen in Fig. 4: and Fig. 4 also implies that $S g(\nu \text{ peak})$ is $6 \times 10^{-18} \text{ cm}^2$. Assuming these values and Gaussian lineshapes for $h(\nu)$ and $g(\nu)$ leads to a total rate constant for absorption of Kr_2^* continuum photons by N_2O of $k \approx 9.6 \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$. The photolysis is presumed to proceed with unit quantum efficiency and with fractional yields as shown for photolysis at $1470 \text{ \AA}$ in Table 2.

There will be some secondary photolytic decomposition of reaction products such as NO_2 , O_2 and possibly NO in the active medium. This will be neglected in the model.

This set of equations makes possible a rough evaluation of the population inversion density and lifetime of the auroral green line in the model laser for various initial conditions. Such an evaluation is currently in progress.

C. QUALITATIVE ANALYSIS OF THE KINETICS IN THE MODEL LASER

A survey of the reactions in Tables 3-9 shows four species present in large concentration after the primary photolytic step which have $O(^1S_0)$ quenching rates on the order of $10^{-12} - 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$. These products, N_2O , NO , $O(^3P)$, and possibly $N_2(A)$, will be the principal destroyers of $O(^1S)$. The relative importance of these deactivators can be qualitatively compared with a simplified model for the photolytic decomposition;

in which $O(^1D)$ is immediately deactivated to $O(^3P)$ and all other secondary reactions are ignored. With F as the fraction of N_2O decomposed and C the initial concentration of N_2O the deactivation rate for $O(^1S_0)$ is (using the rates of Tables 3-9)

$$\frac{1}{\tau O(^1S_0)} \cdot \frac{1}{C} = \begin{array}{ll} 3.6 \times 10^{-12} F & O(^3P) \\ 8 \times 10^{-12} F & NO \\ 0.8 \times 10^{-12} F & N_2(A) \\ 1.5 \times 10^{-11} (1-F) & N_2O \\ 1.25 \times 10^{-11} F + 1.5 \times 10^{-11} (1-F) & \text{Total} \end{array} \quad (31)$$

Thus the rate constant for $O(^1S_0)$ deactivation is predicted to be $\sim 1.3 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$ and is not strongly dependent on the fractional decomposition of N_2O . The concentration of $O(^1S_0)$ is proportional to the fractional decomposition, however, so this decomposition should be as large as possible. There are important secondary reactions such as the very fast $N + NO$

$\rightarrow N_2 + O$ which will reduce the deactivation rate for the first few microseconds of the experiment and secondary production of NO , NO_2 , and other species which will become important somewhat later in time and increase the deactivation rate. The simplified model crudely predicts a lifetime $\sim 8 \mu\text{sec}$ for the $O(^1S_0)$ in a demonstration laser with $10^{16} \text{ N}_2\text{O}/\text{cm}^3$ photolysed $\sim 100\%$ to yield $\sim 5 \times 10^{15} O(^1S_0)/\text{cm}^3$. Such a laser might have a small signal gain of 10% in 1 to 10 meters (depending on the unknown pressure broadening coefficient) and store an energy of 1 to 2 Joules per liter with 13 Joules per liter of Kr_2^* pump radiation. The appropriate rates are sufficiently well known to provide some confidence in the performance of an active medium with energy storage at this level. Higher energy storage and longer inversion lifetimes would be desirable, though not essential, for a practical amplifier.

The following discussion considers each of the principal deactivators to assess what rates and products are poorly known, and to determine what might be done to reduce the quenching rate of $O(^1S_0)$ in a laser using photolysis of N_2O as a source of $O(^1S_0)$.

NO

The NO molecule, with a deactivation rate of $4 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$, is the most effective deactivator of $O(^1S_0)$ among the primary photolytic products. NO has another undesirable property which will begin to affect the kinetics if the $O(^1S_0)$ concentration is maintained for any time longer than a few microseconds: it is an efficient catalyst for the destruction of atomic oxygen in the catalytic chain

$$\times 4 \times 10^{-11} \text{ (1 atm N}_2 + 1 \text{ atm He) (32)}$$

There are also secondary sources of NO in the system such as $\text{O}(^1\text{D}) + \text{N}_2\text{O} \rightarrow 2\text{NO}$.

The yield of NO from photolysis in the 1450 Å continuum is poorly known (Table 2); there is also some very qualitative evidence to suggest that it is a function of wavelength within the continuum. Present results show a yield of 0.02 ± 0.02 and $\geq 3 \times 10^{-4}$.

$\text{O}(^3\text{P})$

Ground state oxygen atoms quench $\text{O}(^1\text{S}_0)$ at a rate measured to be $7.5 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$ in a recent experiment¹⁰ and $\sim 2 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$ in older work.¹² Experimental difficulties make these values less accurate than the quenching rates measured for stable molecules. The lower value would significantly increase the lifetime of $\text{O}(^1\text{S}_0)$ in N_2O photolysis. A theoretical calculation¹³ of the deactivation by $\text{O}(^3\text{P})$ predicts an activation energy of $\sim 750 \text{ cal/mole}$. Assuming a simple Arrhenius expression for the reaction rate, the ratio of the reaction rate at 300°K to that at 120°K is $e^{E_a/400}$ where E_a is the activation energy in calories per mole. This gives about a factor of six decrease in the $\text{O}(^3\text{P})$ deactivation rate at 120°K (for which the vapor pressure of N_2O is 0.5 Torr). If the theoretical results are compared to experimental data, the activation energy may be as low as 200 cal/mole, for which the rate at 120°K is decreased by a factor of 1.6.

Unfortunately, there is little chance of such an activation energy for the NO reaction, since this reaction seems to occur at every collision for $T \sim 300^\circ\text{K}$. A recent measurement⁷⁵ verifies the lack of activation energy.

N_2O

As for $\text{O}(^3\text{P})$, the $\text{N}_2\text{O} + \text{O}(^1\text{S}_0)$ reaction may have an activation energy large enough to affect the deactivation rate in a chilled system. No measurements are available.

$\text{N}_2(\text{A}^3\Sigma)$

The $\text{N}_2(\text{A}^3\Sigma) + \text{O}(^1\text{S}_0) \rightarrow (\text{products})$ rate has not been measured. It has been assumed to be some significant fraction of the gas kinetic collision rate since $\text{N}_2(\text{A}) + \text{O}(^1\text{S}) \rightarrow \text{N}_2(\text{B}) + \text{O}(^1\text{D}, ^3\text{P})$ is energetically allowed. This rate will be very difficult to measure, but it can be estimated from molecular orbital theory.

D. COUPLING A Kr_2^* LAMP TO AN N_2O ACTIVE MEDIUM

The integrated absorption cross-section for Kr_2^* radiation on N_2O is $\sim 3 \times 10^{-18} \text{ cm}^2$, so that the 1/e distance for absorption in a 10^{16} cm^{-3} N_2O concentration is $\sim 30 \text{ cm}$. The path length in the laser active medium for Kr_2^* radiation must be at least two absorption lengths for efficient absorption. Thus a practically sized feasibility demonstration laser will require multiple reflection of the Kr_2^* radiation through the active volume for high efficiency.

High reflectances are not easily obtained at 1460 Å for near perpendicular incidence. Highly polished aluminum coated with MgF_2 without the usual Al_2O_3

oxidation layer is suitable, but fabrication will be difficult and expensive.

Reflection at grazing incidence can be quite efficient even for highly absorbing materials.⁷⁶ The reflection coefficient for a ray incident at a small angle α to a flat surface is

$$= 1 - \frac{2(n^2 + 1)}{n^2 - 1} \alpha \quad (34)$$

where α is the angle between the ray and the surface and n is the index of refraction of the denser medium. (The refractive index of the gas is assumed to be 1.) The (for example) aluminum pipe which encloses the laser active medium must still be highly polished on the inside surface, but the effect of an Al_2O_3 oxidation layer will be reduced.

The propagation distance for the Kr_2^* radiation in the laser active medium may be much greater than an absorption length. A high intensity photolytic pulse bleaches the N_2O absorption, making the laser active medium behave as a saturable absorber to the Kr_2^* radiation. This point is discussed in more detail in Appendix A.

E. MEASURING THE AURORAL LINE INVERSION IN A SMALL SCALE EXPERIMENT

A demonstration of an auroral line oscillator will require a gain length of $\sim 1 - 10$ meters at $5 \times 10^{15} \text{ O}(^1\text{S}_0)$ density. It would be desirable to verify the in-

version and gain of the medium before undertaking such a large scale experiment. In a practical system one may wish to use the auroral line only as an amplifier in any case and generate the initial pulse in a dye laser locked to the auroral transition.

Intercavity measurement in a CW dye laser is an extremely sensitive probe of small gains and losses. An absorption of $\sim 10^{-7}$ and gain of $\sim 3 \times 10^{-4}$ have been measured in such an experiment.⁷⁷ The sensitivity of the technique becomes arbitrarily large near the threshold for oscillation of the dye laser, within limits imposed by mechanical stability and dye laser pump stability.

For a cell 10 cm long with $5 \times 10^{-20} \text{ cm}^2$ optical cross-section on the auroral line and an inversion of $3 \times 10^{15} \text{ cm}^{-3}$, the gain in a round trip through the cell is 3×10^{-3} . This should be easily detectable in an intracavity dye laser experiment, though some very careful evaluations of dye laser stability near threshold and of various losses induced by firing the Kr_2^* lamp (e.g., refraction by optical inhomogeneities from shock waves) will be required before quantitative gain measurements are possible. Appendix B discusses some preliminary results on kinetic modeling of experimental conditions which give an excited state density near $3 \times 10^{15} \text{ cm}^{-3}$.

V. Production of $O(^1S_0)$ in Rare Gas Discharges with CO_2 and O_2

A. Ar- CO_2

The argon atomic 4s levels lie at the proper energy for efficient production of $O(^1S_0)$ from CO_2 by photolysis or collision transfer as discussed in Section III. From known rates we may determine rough limits on the locus of efficient $O(^1S_0)$ production in an Ar- CO_2 discharge.

Figure 9 shows the energy transfer chain in an Ar- CO_2 discharge. The production of $O(^1S_0)$, or large concentrations of any other electronically excited species, requires a large concentration of electrons with energies above 10-20 eV. Dissociative recombination processes such as the Ar_2^* ion recombination are electron energy

dependent and have a maximum cross section at near zero energy.⁷⁸ These conditions suggest that a radiolytic discharge is more suitable than a conventional glow discharge for producing high densities of electronically excited species. A radiolytic discharge contains a large population of cold electrons as well as fast primary and secondary particles. A glow discharge typically has a Maxwell-Boltzmann distribution of electron energies peaking at a few eV and thus satisfies neither of these conditions very well.⁷⁹

Table 10 lists the important reactions in the kinetic chain leading to $O(^1S_0)$ and the competing channels. CO_2 , Ar, and electron concentration must be adjusted

Table 10. Reactions important for $O(^1S_0)$ production in an Ar- CO_2 discharge.

$Ar^+ + Ar + Ar \rightarrow Ar_2^+ + Ar$	a	$4 \times 10^{-31} \text{ cm}^6 \text{ sec}^{-1}$
$Ar^+ + CO_2 \rightarrow CO_2^+ + Ar$	a	$8 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$
$Ar_2^+ + e \rightarrow Ar + Ar^*$	b	$7 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$
$CO_2^+ + e \rightarrow CO(a^3\Pi) + O$	c	$4 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$
$Ar^* + Ar + Ar \rightarrow Ar_2^* + Ar$	d	$1.5 \times 10^{-32} \text{ cm}^6 \text{ sec}^{-1}$
$Ar^*(^4S) + CO_2 \rightarrow CO(a^3\Pi) + O + Ar$	e	$5 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1} ?$
$\quad \quad \quad \rightarrow CO(X) + O(^1S_0) + Ar$		
$Ar(^1P_1) \rightarrow Ar + h\nu$	f	$5 \times 10^8 \text{ sec}^{-1}$
$Ar(^3P_1) \rightarrow Ar + h\nu$	f	$1.5 \times 10^8 \text{ sec}^{-1}$

^aRef. 80.

^bRef. 78. $Ar^+ + e + m$ is neglected.

^cRef. 78, Ref. 57, 100% yield $CO(a^3\Pi)$ assumed.

^dRef. 81.

^eRef. 55, 56. The rate constant is assumed to be near gas kinetic.

^fRef. 82.

Fig. 9. Energy transfer in an Ar-CO₂ discharge (simplified).

to favor the production and rapid recombination of Ar_2^+ , to suppress formation of CO_2^+ , and to favor $\text{Ar}(^1\text{P}_1, ^3\text{P}_1)$ radiation and absorption by CO_2 or Ar^+-CO_2 collisions over the formation of Ar_2^* . Some

Ar_2^* radiation will be energetic enough to produce $\text{O}(^1\text{S}_0)$ in CO_2 photolysis, but most of it will lead to $\text{O}(^1\text{D})$ production.

The formation of Ar_2^+ proceeds faster than charge exchange of Ar^+ on CO_2 for

$$\frac{[\text{CO}_2]}{[\text{Ar}]^2} < 5 \times 10^{-22} \quad (35)$$

Charge exchange of Ar_2^+ on CO_2 can be neglected provided that the electron concentration is $> 10^{-2}$ of the CO_2 concentration, which is assumed. $\text{Ar}^+ - \text{CO}_2$ transfer collisions, assuming a 5×10^{-11} rate, will be faster than Ar_2^+ formation for

$$\frac{[\text{CO}_2]}{[\text{Ar}]^2} > 3 \times 10^{-22} \quad (36)$$

For an oversimplified but qualitatively correct model of Ar resonance radiation transfer to CO_2 one may assume an infinite medium and equal absorption cross-sections for the ground state argon atom and CO_2 . The transfer rate to CO_2 is then

$$\frac{[\text{CO}_2]}{[\text{Ar}] + [\text{CO}_2]} \quad (37)$$

times the radiative rate of the appropriate level, and this transfer must be faster than the Ar_2^+ formation.

Argon atomic resonance radiation will also be suppressed by electron collisions which relax the atom to the $^3\text{P}_2$ lowest level of the 4s configuration. The $^3\text{P}_1 - ^3\text{P}_0$ relaxation is fast in neon, with a cross-section near 10^{-14} cm^2 for very low energy electrons giving a rate constant near $10^{-8} \text{ cm}^3 \text{ sec}^{-1}$. The $^1\text{P}_1$ relaxation rate is not known but is probably comparable. If one assumes a 10^{-8} rate for the unknown deactivation in argon then radiative transfer from $\text{Ar}(^1\text{P}_1)$ to CO_2 will proceed faster than electron deactivation to a metastable level for

$$\frac{[\text{CO}_2]}{[\text{CO}_2] + [\text{Ar}]} > 2 \times 10^{-17} [e]. \quad (38)$$

Figure 10 summarizes these conditions. The locus of efficient $\text{O}(^1\text{S}_0)$ production lies at low CO_2 , Ar, and electron densities, indicating that a simple CO_2 -Ar discharge such as this will probably not be useful for the present purpose. However, since many of the rate constants (and even processes) in such discharges are not well known, it might be useful to verify these predictions experimentally.

B. He, Ne- CO_2

The Ar- CO_2 discharge production scheme suffers from conflicting requirements of high and low CO_2 density and high and low electron density. There is some possibility that such conflicting

Fig. 10. Locus of efficient $\text{O}(^1\text{S}_0)$ production in an Ar- CO_2 discharge. a-a. Ar_2^+ forms faster than CO_2 ; b-b. $\text{Ar}^+ - \text{CO}_2$ faster than Ar_2^+ formation; c-c. $\text{Ar}(^3\text{P}_1)$ radiates faster than Ar_2^+ formation; d-d. $\text{Ar}(^1\text{P}_1)$ radiates faster than Ar_2^+ formation; e-e. $\text{Ar}(^1\text{P}_1)$ radiates faster than electron deactivation (important only for radiative transfer)

requirements could be eliminated in an excitation scheme based on dissociative recombination of electronically excited O_2 or some other molecule, but there is very little information available to evaluate this process. High O_2 and e densities are favored here.

Figure 7 shows an energy level diagram of O_2 and O_2^+ . Several of the many theoretical repulsive curves of the oxygen molecule have been added to the figure, with infinite separation energy limits adjusted to agree with the experimental values. Ab-initio calculations of the type used to predict these surfaces tend to give repulsive curves which are somewhat more repulsive than the actual molecular states, so the actual repulsive states plotted here probably lie lower in energy by up to a volt or so at $1.5 \text{ \AA}$ than the theoretical curves. If the $1\Sigma^+ VII$ curve correlating to $O(^1S_0) + O(^1S_0)$ crosses a bound state of the O_2^+ ion (e.g., $b^4\Sigma_g^-$ or $\tilde{B}^2\Sigma_g^-$) and dissociative recombination of O_2^+ takes place faster than

the radiative lifetime of this state, there will be a high probability that the O atoms will move apart along the curve correlating to $2 O(^1S_0)$. There will be competing dissociative channels from any other dissociative curves which cross the bound state, and this competition may be so severe that the process is useless for $O(^1S_0)$ excitation; the states are not sufficiently well known to make possible a clear decision. If the theoretical curves in Fig. 7 are accurate, the process is clearly not favored, since dissociative curves correlating to states formed from $O(^3P)$ and $O(^1D)$ lie much nearer the minima of the ion state potential wells than the $1\Sigma_g^+ VII$ curve.

Ne^+ charge transfer and He^* Penning ionization collisions with O_2 lie at the appropriate energy for excitation of the b and B states.

If one assumes the rates of Table 11, dissociative recombination of excited states of O_2^+ is favored over competing processes in the locus shown in Fig. 11.

Fig. 11. Locus for efficient dissociative recombination of electronically excited O_2^+ in a Ne- O_2 discharge.

- a-a. $Ne^+ \rightarrow O_2^+$ faster than Ne_2^+ formation
- b-b. $O_2^+ + e$ faster than collisional relaxation
- c-c. $O_2 < 1\% \text{ Ne}$
- d-d. $O_2 < 10\% \text{ Ne}$
- e. $O_2^+ + e$ faster than radiative relaxation

Table 11. Reactions important for potential $O(^1S_0)$ production in a Ne + O_2 discharge.

$Ne^+ + Ne + Ne \rightarrow Ne_2^+ + Ne$	a	$7 \times 10^{-32} \text{ cm}^6 \text{ sec}^{-1}$
$Ne_2^+ + e \rightarrow Ne^* + Ne$	b	$2 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$
$Ne^+ + O_2 \rightarrow O_2^{++} + Ne$	c	$10^{-16} \text{ cm}^3 \text{ sec}^{-1}$
$O_2^{++} + e \rightarrow O + O$	d	$3 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$
$O_2^{++} \rightarrow O_2^+(X)$	e	10^9 sec^{-1}
$O_2^{++} + (Ne, O_2) \rightarrow O_2^+ + (Ne, O_2)$	f	$10^{-11} \text{ cm}^3 \text{ sec}^{-1} ?$

^aRef. 80.

^bRef. 78.

^cAssumed equal to rates for reactions such as $CO^+ + O_2$, $N_2^+ + O_2$, $Ar^+ + O_2$ (Ref. 80).

^dAssumed equal to the ion ground state recombination rate of Ref. 78.

^eAssumed 10^{-9} sec lifetime.

^fAssumed collisional deactivation.

VI. Summary

The auroral line of oxygen has properties which suggest its suitability as a high energy storage visible laser. Production of $O(^1S)$ in the photolytic decomposition of N_2O is the only source of $O(^1S)$ which is characterized well enough for serious consideration at the present time. The information presently available indicates that a laser with a few joules per liter energy storage and a few microseconds inversion lifetime is feasible with $O(^1S)$ formed by photolysis of N_2O with Kr_2^* radiation, and that better performance could be achieved if poisons such as NO and $O(^3P)$ can be suppressed. There are other possible efficient sources of $O(^1S)$ which need more investigation.

Research at present should address the following unknowns:

- Collision broadening of the auroral line - required for accurate predictions of gain.
- Deactivation of $O(^1S_0)$ in excited-state collision with itself, $N_2(A)$,

$CO(a)$ and other excited species in potential laser active media.

- Temperature dependence of reaction rates of $O(^1S_0)$ with constituents of a laser active medium (such as N_2O and $O(^3P)$).
- Detailed information on the production of $O(^1S_0)$, and of poisons such as NO, from photolysis of N_2O or other $O(^1S_0)$ sources at various wavelengths.
- Efficiency of production of Kr_2^* and Ar_2^* excimer radiation at low densities of excitation.
- Careful evaluation of possible $O(^1S_0)$ production mechanisms in discharges and photolytic sources other than N_2O .
- Measurement of $O(^1S_0)$ densities and lifetimes in $Kr_2^* - N_2O$ photolysis.
- More detailed and precise modeling of laser active media for an auroral line laser.

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duction from dissociative recombination of electronically excited ions. M. Krauss and W. Braun of NBS also brought to our attention that an auroral line laser has been independently suggested there.

The chemical kinetics code used in the more detailed analysis of an N_2O active medium was originally written by J. Creighton of LLL and is being modified and extended for the present purpose by W. L. Morgan.

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Appendix A

HIGH INTENSITY PHOTOLYSIS OF AN OPTICALLY THICK MEDIUM

Photolysis of an optically thick medium is exactly equivalent to the bleaching of a saturable absorber,* except that in the case of photolysis the situation is simplified: spontaneous emission rates and other relaxation rates back to the initial state are zero. A high intensity photolytic experiment will therefore show the pulse steepening effects and the reduced velocity of front propagation that occur in other saturable absorbers, and these effects must be taken into account when modeling these experiments.

There is a limiting case of saturable absorption, soluble in closed form, which displays the important features of the problem. Assume that the optical absorption cross section of the absorbing molecule is so large that the absorption length in the absorbing medium is effectively zero. Also assume a plane wave propagating through the absorber in one dimension with a photon flux of $n(t)$ photons per square centimeter per second. At time t the wave will have bleached a distance x_0 into the absorber given by

$$x_0(t) = \frac{1}{\rho} \int_0^t n(t) dt \quad (\text{A-1})$$

where ρ is the density of absorbing

molecules per cubic centimeter.[†] For this ideal case the photon flux at time t is $n(t)$ for $0 \leq x \leq x_0(t)$ and is zero for $x \geq x_0(t)$.

The velocity of propagation of the photolytic bleaching front is

$$\frac{\partial x_0(t)}{\partial t} = \frac{n(t)}{\rho}. \quad (\text{A-2})$$

This velocity can be $\ll c$, giving a propagation delay. In this ideal model the pulse rise time becomes infinitely short since the transmission at a point x is either zero or one.

A real saturable absorber with a finite absorption length will show similar behavior. There will be a finite transition region of length approximately equal to the absorption length $1/\rho\sigma$ which propagates at a velocity near $n(t)/\rho$, and the transmitted pulse will have a rise time which can be crudely approximated by the time required for the bleaching wave to travel one absorption length.

The saturable absorption of a laser active medium produced by high intensity photolysis has several important effects, both good and bad from our point of view. Turning first to the bad effects, note that there will be a large release of thermal energy at the position of the bleaching front as it travels through the active medium. If the front is steep, the energy release can drive a hydrodynamic shock front with all the attendant undesirable

* A recent review of theoretical and experimental results on saturable absorbers is contained in A. Zunger and K. Bar-Eli, *J. Chem. Phys.* 57, 3558 (1972); and in K. W. Smith and L. Allen, *Opt. Commun.* 8, 166 (1973).

[†] There is an implicit assumption that $\partial x_0(t)/\partial t \ll X/C$ where X is the length of the absorber. This allows the retarded time to be omitted since $n(t) = n[t - (X/C)]$.

optical inhomogeneities. To avoid driving a shock, the velocity of propagation of the bleaching front must be much faster than the velocity of propagation of a shock front driven by the energy release in the transition region. The velocity of sound in a gas is typically $0.1-1 \text{ km sec}^{-1}$, so if we make the fairly reasonable assumption that the thermal energy release in any practical photolytic laser medium is only sufficient to drive shocks $\leq$ Mach 10, the bleaching front propagation velocity must be $\geq \sim 10 \text{ km sec}^{-1}$ to complete the photolysis before the medium can respond by forming a shock front. If the velocity of bleaching front propagation were much less than the shock velocity the coupling

would also be small, but sonic disturbances could be generated. Although sonic disturbances affect optical homogeneity less seriously than shock fronts, it would be desirable to avoid them.

On the other hand, the high absorption cross sections and saturable absorption of the laser active medium can be very useful. They make it possible to photolyse large volumes of active material to nearly 100% decomposition very uniformly. The photolysing light will need fewer reflections through the active medium than for a weak absorption such as that used in the photolytic iodine laser. Hence less energy will be lost to the mechanical structure and other unwanted absorptions.

Appendix B

PRELIMINARY RESULTS OF A MORE DETAILED KINETIC MODEL FOR N_2O PHOTOLYSIS

Figures B-1 and B-2 show some preliminary predictions of the behavior of a model laser active medium evolving in accordance with a simplified set of the reactions of Tables 3-9. (The model is, however, much more detailed than that of Sect. IV.C.) A 10^{16} cm^{-3} concentration of N_2O in a 10^{19} cm^{-3} (300 Torr) background of N_2 is photolysed with a photon density of $5 \times 10^{12} \text{ photons cm}^{-3}$ at peak (a flux of $1.5 \times 10^{23} \text{ photons cm}^{-2} \text{ sec}^{-1}$). This is the flux from a Kr_2^* lamp with an optical depth of 1.5 cm behind each cm^2 of window area, assuming 10% of the total Kr_2^* radiation passes through the window. A Kr_2^* radiance of $10^{24} \text{ photons cm}^{-3} \text{ sec}^{-1}$ is assumed as discussed in Sect. IV.A.

The Kr_2^* radiative pulse rises in 100 nsec to its peak value and then has a constant photon flux to 5 μsec , at which time it terminates. The $O(^1S)$ concentration in the active medium peaks at 27% of the initial N_2O concentration 3.5 μsec into the photolytic pulse. This run assumes N_2O photolysis yields as given in Table 2 for 1470 Å (2% NO, 8% $N_2(A^3\Sigma)$, 50% $O(^1S_0)$, 40% $O(^1D)$). The model used here does not include the photolytic pulse propagation effects of Appendix A, and is appropriate for an optically thin active medium. The bleaching front propagation velocity for this case is $\sim 150 \text{ km/sec}$.

The inversion reaches 25% of the initial N_2O concentration 2 μsec after the arrival of the photolysing pulse. If the volume nearest the photolysis lamp window has been illuminated for 5 μsec and the most

Fig. B-1. Some products of photolysis of N_2O in N_2 - a simplified set of reactions as a test case.

Fig. B-2. Some participants in photolysis of N_2O in N_2 - a simplified set of reactions as a test case.

distant point of the laser volume for 2 μ sec (to assure uniform inversion density), then the maximum propagation depth for the photolytic radiation is about 45 cm.

Since the transition region is of dimensions comparable to this for a 10^{16} cm⁻³ concentration of N₂O (30 cm), the actual propagation depth will be somewhat larger.