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ENERGY TRANSFER REACTIONS OF EXCITED ATOMS AND MOLECULES.(U)  
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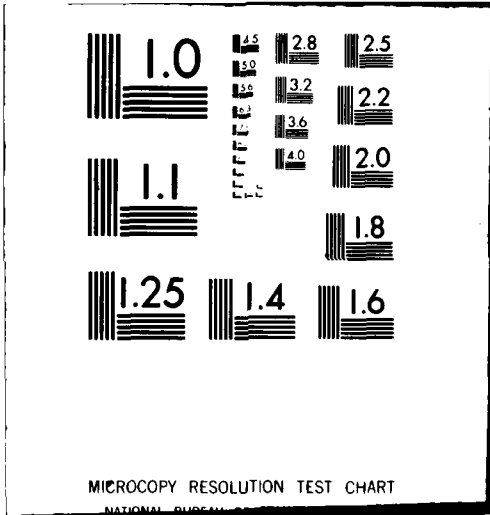
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REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER 19) 14708.4-L	2. GOVT ACCESSION NO. 18) ARD L AD-A089203	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) 6) Energy Transfer Reactions of Excited Atoms and Molecules.		5. TYPE OF REPORT & PERIOD COVERED 9) Final Report 16 May 77 - 15 May 80
7. AUTHOR(s) 10) Tom G. Slinger		8. CONTRACT OR GRANT NUMBER(s) 15) DAAG29-77-C-0018
9. PERFORMING ORGANIZATION NAME AND ADDRESS SRI International Menlo Park, CA 94025 12) 35 L		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 14) SRI-MP-80-84
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709 11) 38		12. REPORT DATE Jul 80
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES 27
16. DISTRIBUTION STATEMENT (of this report)  Approved for public release; distribution unlimited.		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)  NA		
18. SUPPLEMENTARY NOTES The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)  energy transfer                      molecules                      quenching excitation                            atoms metastable state                    nitric oxide oxygen                                    photodissociation		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Five main areas have been investigated: (1) observations of the three metastable states of O <sub>2</sub> <sup>-</sup> with excitation energies between 4 and 5 eV have been made in after-glow systems, (2) a new energy transfer process has been discovered in the NO molecule, (3) using the H <sub>2</sub> laser, direct observations were made of o(D) radiation at 6300 Å from O <sub>2</sub> <sup>-</sup> photodissociation, (4) the product channels for the quenching  (1D)		

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# **ENERGY TRANSFER REACTIONS OF EXCITED ATOMS AND MOLECULES**

**Final Report  
Covering the Period May 1977 through May 1980**

**MP 80-87**

**July 28, 1980**

**By: Tom G. Slanger**

**Prepared for:  
U.S. ARMY RESEARCH OFFICE  
P.O. Box 12211  
Research Triangle Park, North Carolina 27709**

**Contract DAAG 29-77-C-0018**

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**Approved by:**

**D. C. Lorents, Director  
Molecular Physics Laboratory**

**P. J. Jorgensen, Vice President  
Physical and Life Sciences**

## ABSTRACT

Five main areas have been investigated during the term of this contract.

First, observations of the three metastable states of  $O_2$  with excitation energies between 4 and 5 eV have been made in afterglow systems. Three electronic transitions new to gas phase laboratory emission spectroscopy have been reported, and the first set of vibrational constants for  $O_2(a^1\Delta_g)$  based on observation of an extended array of vibrational levels has been obtained. With the aid of the laboratory spectra, these various transitions have now been identified in the terrestrial and Venusian atmospheres.

Second, a new energy transfer process has been discovered in the NO molecule. Direct pumping of NO to the  $B'^2\Delta$  state with 1600 Å radiation from an  $H_2$  laser, when carried out in the presence of  $N_2$ , leads to electronic excitation of  $N_2$ . The  $N_2(A^3\Sigma_u^+)$  state is ultimately generated, and the energy flow is then reversed, with the NO removing this energy and radiating it. This process may be useful in photolytic  $N_2(A^3\Sigma_u^+)$  generation. Unidentified bands, most likely belonging to an NO transition, appear around 4000 Å when NO is pumped at 1600 Å. It is important to establish their identity.

Third, using the  $H_2$  laser, we have been able to directly observe  $O(^1D)$  radiation at 6300 Å from  $O_2$  photodissociation. This has enabled us to settle a controversy over the rate coefficient for the reaction  $O(^1D) + H_2O \rightarrow OH + OH$ , a critical reaction in stratospheric chemistry.

Fourth, the product channels for the quenching of  $O(^1S)$  by  $O(^3P)$  have been investigated. Our present conclusion is that  $O(^3P)$  ground state oxygen atoms are produced, and that the process therefore releases

4.2 eV translational energy. It will be a challenge for theoreticians to explain these conclusions based on current potential curve calculations.

Fifth, quenching of  $O(^1S)$  by the species in an oxygen-helium afterglow gives convincing evidence that the most important quenching molecule is  $O_2(a^1\Delta_g)$ , with a rate coefficient of approximately gas kinetic collision frequency. It is thus desirable to reconsider a number of earlier studies in afterglow systems, and also to determine the effect of such a large rate coefficient on  $O(^1S)$  studies in the mesosphere and in aurorae.

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## INTRODUCTION

A variety of tasks have been performed under the present contract, generally directed toward the elucidation of some aspect of atmospheric photochemistry.

Primary interest has revolved around the interactions between the various electronic states of the oxygen atom and molecule. The question of the source of  $O(^1S)$  in the lower thermosphere is a problem of long standing, and our group at SRI has been studying this issue for a number of years.<sup>1-3</sup> At present, it is felt that the  $O(^1S)$  is excited by transfer from an electronically excited  $O_2$  molecule; consequently, a large part of our work has been devoted to studying the higher excited states of  $O_2$ ,  $A^3\Sigma_u^+$ ,  $A'^3\Delta_u$ , and  $c^1\Sigma_u^-$ , which have sufficient energy to excite  $O(^3P)$  to  $O(^1S)$ .

Apart from the question of the mechanism of  $O(^1S)$  excitation, the study of the excited  $O_2$  states coincidentally got a significant boost just as this contract commenced, when the Russian Venera 9 and 10 spacecraft observed emission in the Venus atmosphere<sup>4</sup> that was subsequently identified<sup>5</sup> as originating from the  $c^1\Sigma_u^- \rightarrow X^3\Sigma_g^-$  transition in  $O_2$ . With the support from ARO, we were then immediately able to begin investigating the mechanism of the excitation; although the  $c^1\Sigma_u^-$  state was virtually unknown in laboratory experiments, it was a beacon in the Venus nightglow.

It soon became evident that the  $O_2$  states in question could be easily produced in laboratory afterglows; it is astounding, in fact, that the various new transitions observed had not been thoroughly studied during the last several decades. After it had been shown that, apart from the  $c^1\Sigma_u^- \rightarrow X^3\Sigma_g^-$  transition, three new  $O_2$  band systems could be

observed in the  $O_2$  afterglows, close perusals were made of existing spectra that had appeared in the literature during the last 30 years.<sup>6-8</sup> It then became clear that the strongest of the new systems ( $A'^3\Delta_u \rightarrow a^1\Delta_g$ ) had actually been noted in previous laboratory spectra, without being identified. Furthermore, this same transition was observed in the Venera spectra,<sup>4</sup> although it was weak. A recently received preprint from the Russian workers<sup>9</sup> identifies the second of the three new transitions,  $c^1\Sigma_u^- \rightarrow a^1\Delta_g$ , in the Venera spectra, and we have recently demonstrated for the first time that the  $c^1\Sigma_g^- \rightarrow X^3\Sigma_g^-$  band system, so intense in the Venus atmosphere, can also be seen in the terrestrial nightglow.

Currently, we are in the process of demonstrating that these three states of  $O_2$  may play a very important role in stratospheric chemistry, quite apart from their possible interactions with  $O(^3P)$  in the higher atmosphere.

Another aspect of interpreting the  $O(^1S)$  observations in the lower thermosphere has to do with the  $O(^1S)$  loss processes. Quenching by  $O(^3P)$  is accepted as the most important of these,<sup>2</sup> but there is an interesting disagreement in experimental and calculated<sup>10</sup> rate coefficients for this process, by three orders of magnitude. We felt that the best contribution we could make to resolving this controversy was to measure the products of the interaction; if they disagreed with those used in the calculations, then there would be less reason to doubt the experimental conclusions.

From the  $O_2$  afterglow spectra, we already had information relevant to  $O(^1S)$  losses, namely, that one species in the  $O_2$ -He afterglow is extremely efficient in quenching  $O(^1S)$ . Considerable effort was put into identifying this particle, because of its possible interfering effects both in laboratory  $O(^1S)$  studies and in atmospheric observations. We concluded that the probability is high that it is  $O_2(a^1\Delta_g)$ ; because this molecule is found in high concentration in many systems, it would

be beneficial to reevaluate the decay kinetics of  $O(^1S)$  in laboratory studies and in atmospheric models.

The  $H_2$  laser, although having an unimpressive  $5 \mu\text{J}/\text{pulse}$  output, has the capability of making heretofore unsuccessful experiments practical. With this laser we have made the first direct time-resolved measurements on  $O(^1D)$  production from  $O_2$  photodissociation,<sup>11</sup> and were able to respond immediately to a problem that arose at the Fall meeting of the AGU in 1978. A difference of a factor of two existed in the two best sources of rate data<sup>12,13</sup> for the reaction of  $O(^1D)$  with  $H_2O$ . Since this reaction is the principal stratospheric source of OH, a resolution of this issue was critical. We were able to perform the experiment in one day, and return to the meeting to report on it. Since  $O(^1D)$  is perhaps the single most important atom in stratospheric and mesospheric chemistry, such a simple and direct way of studying it is of great utility.

The irradiation of NO by the  $1600 \text{ \AA}$   $H_2$  laser output has also led to interesting results. There appears to be a strong resonance with a particular nondissociative state of NO that makes it possible to observe new energy transfer effects involving  $N_2$ . Although the spectroscopy of NO is now believed to be well understood, collisional effects involving the states lying above 6 eV are complex, and accessing these states with a  $1600 \text{ \AA}$  photon is a convenient way of energizing the system. Apart from the energy transfer studies, the laser excitation generates a series of double-headed bands at  $\sim 4000 \text{ \AA}$ , and these bands do not correlate with any known NO transitions. Thus, continuation of these studies is important.

## TECHNICAL PROGRAM

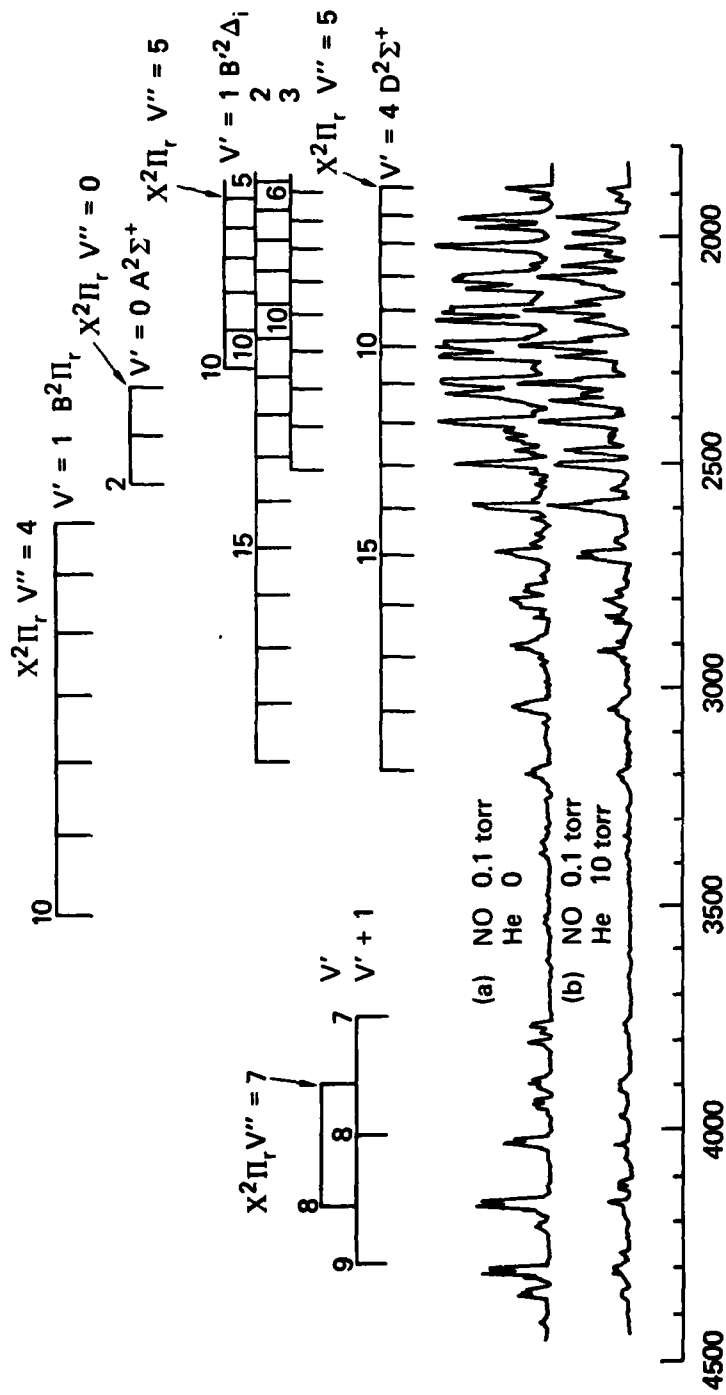
In this section, we start with the details of work not yet published, while abstracts of the published work are given at the end.

### Unpublished Work

#### NO Excitation by 1600 Å Laser Photolysis

The H<sub>2</sub> laser generates photons in the 1540-1610 Å wavelength region (7.70-8.50 eV) that can excite NO to the B'<sup>2</sup>Δ<sub>1</sub> (v ≤ 4), D<sup>2</sup>Σ<sup>+</sup> (v ≤ 5), E<sup>2</sup>Σ<sup>+</sup> (v ≤ 1), F<sup>2</sup>Δ (v = 0), and H<sup>2</sup>Σ<sup>+</sup> (v = 0) states. The emission spectra from the laser excitation of 0.1 torr pure NO and a mixture of 0.1 torr NO and 10 torr He are shown in Fig. 1(a) and (b), respectively. In pure NO [Fig. 1(a)], most of the spectrum in the ultraviolet region is identified as the B'<sup>2</sup>Δ<sub>1</sub> (v' = 2,3) and D<sup>2</sup>Σ<sup>+</sup> (v' = 4) → X<sup>2</sup>Π<sub>r</sub>(v'') systems, with minor contributions from the A<sup>2</sup>Σ<sup>+</sup> (v' = 1) and B<sup>2</sup>Π (v' = 1) → X<sup>2</sup>Π<sub>r</sub>(v'') systems. Emission is also observed in the near ultraviolet region (3700-4400 Å), for which the origins are not known. The vibrational spacing can be fit by either the X<sup>2</sup>Π<sub>r</sub> or the a<sup>4</sup>Π state. As an example shown in Fig. 1(a), the lower state for these bands is fit by the vibrational levels of the X<sup>2</sup>Π state. In this case, the upper state has an energy very close to the a<sup>4</sup>Π state, but the vibrational spacing is about 160 cm<sup>-1</sup> smaller than the a<sup>4</sup>Π (v=0 and 1) spacing of 990 cm<sup>-1</sup>. The doublet structure is characteristic of several NO transitions, but identification of these bands will require further study.

When 10 torr of He was added to NO, the emission intensities from the B'<sup>2</sup>Δ<sub>1</sub> (v' = 2 and 3) vibrational levels decrease and the emission bands from the B'<sup>2</sup>Δ<sub>1</sub> (v = 1) level appear as shown in Fig. 1(b). This result can be interpreted as vibrational relaxation of the B'<sup>2</sup>Δ<sub>1</sub> (v = 2 and 3)



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FIGURE 1 EMISSION SPECTRA FROM H<sub>2</sub> LASER EXCITATION OF GAS MIXTURES

levels by He. Also shown in Fig. 1(b), the near ultraviolet bands disappear when 10 torr He is added. This result implies that either the excited states are quenched by He or the mechanism for the production of these excited states does not occur in the presence of He. When He is added, the  $A^2\Sigma^+ (v' = 0) \rightarrow X^2\Pi_r (v'')$  emission becomes prominent. The NO ( $A^2\Sigma^+$ ) species is produced, at least in part, by a secondary process,  $E^2\Sigma^+ (v' = 0) \rightarrow A^2\Sigma^+ (v'' = 0)$  radiation. The emission from this transition at 5980 and 6025 Å has been observed.

The decay of the total UV emission from NO has two components with time constants of 5  $\mu$ s and 44  $\mu$ s, as shown in Fig. 2(a). When  $N_2$  is added, both the decay time and emission intensity increase as shown in Fig. 2(b) - (d). The increase of decay time is a consequence of the formation of the  $N_2(A^3\Sigma_u^+)$  metastable. The NO state initially excited by the  $H_2$  laser transfers its energy to  $N_2$ , forming the  $A^3\Sigma_u^+$  state, probably after cascading from a higher  $N_2$  state. Then the energy flows back to NO, exciting the  $A^2\Sigma^+$  state and giving NO ( $\gamma$ ) band emission. The  $N_2(A^3\Sigma_u^+)$  species is confirmed as the intermediate by measuring the emission quenching rate constants by NO and  $O_2$ . Values of  $7.6 \times 10^{-11}$   $cm^3/sec$  and  $4.9 \times 10^{-12}$   $cm^3/sec$  for NO and  $O_2$ , respectively, were found, and these agree with the  $N_2(A^3\Sigma_u^+)$  quenching rate constants existing in the literature.<sup>14</sup>

The increase in emission intensity as a result of  $N_2$  addition is shown in Fig. 3(a), which is the difference of the curves shown in Fig. 2(a) and (b). The additional emission intensity shows a build-up period, which indicates that it is produced by a secondary process. The build-up time can be obtained by extending the decay curve at long decay times to the short decay time region and taking the difference of the extended and observed intensities as shown in Fig. 3(b). The build-up time obtained from Fig. 3(b) is 45  $\mu$ s, which agrees very well with the long decay time of NO emission of 44  $\mu$ s as shown in Fig. 2(a).



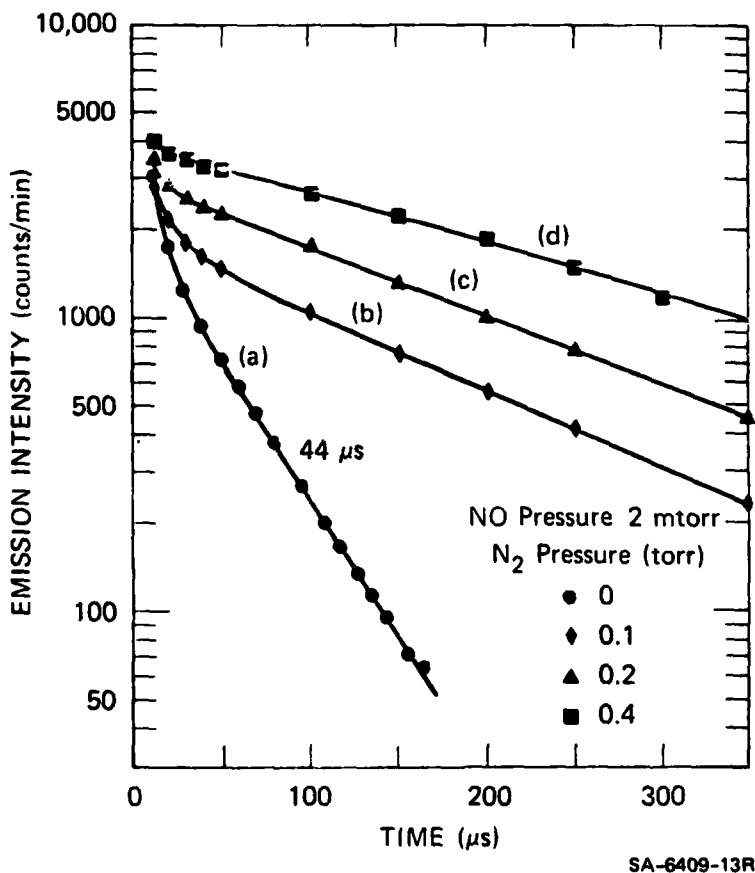


FIGURE 2 TIME DECAY OF EMISSION INTENSITIES FOR VARIOUS N<sub>2</sub> PRESSURES

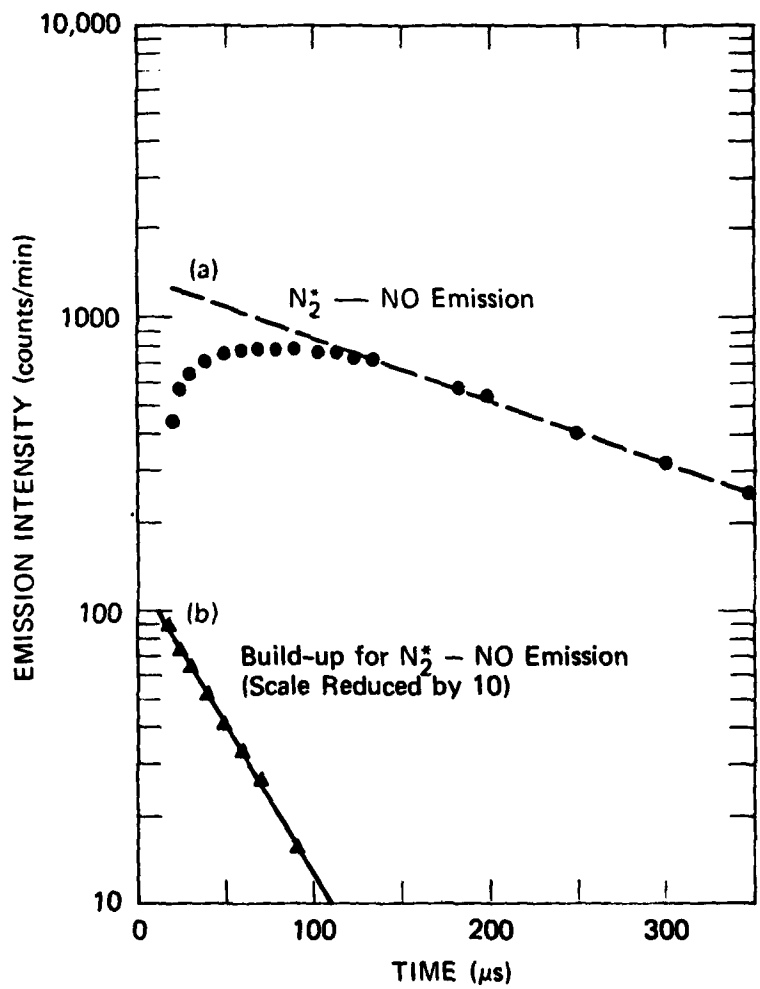


FIGURE 3 TIME DEVELOPMENT OF EMISSION INTENSITY RESULTING FROM  $\text{N}_2$  ADDITION TO  $\text{NO}$

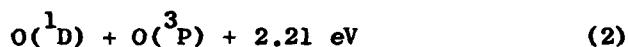
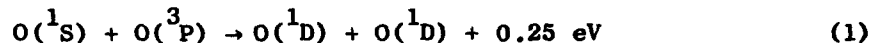
These results indicate that  $N_2(A^3\Sigma_u^+)$  is produced by energy transfer from a long-lived NO excited state, which is not the initially produced  $B'^2\Delta$  state, since that state has a lifetime of 100 ns.<sup>15</sup> This long-lived state is not identified, but since no known NO states have radiative lifetimes longer than 5  $\mu$ s, we conjecture that the unobserved  $^2\Phi_1$  state may be involved.

This double energy transfer process between NO and  $N_2$  has previously been observed when the initial NO states have been  $B^2\Pi(v=9)$ <sup>16</sup> and  $D^2\Sigma^+(v=0)$ ;<sup>17</sup> thus, it seems to be a generalized phenomenon. However, the unusually long NO emission lifetime that we see following the initial excitation demands an explanation; it would certainly be worthwhile to determine if it actually does involve the  $^2\Phi_1$  state, which has previously been sought by many investigators.

#### The $O(^1S) + O(^3P)$ Reaction

This reaction has proven to be one of the most interesting studied under the present contract, and has led us into a number of unexpected areas. The rationale behind the work was that a large discrepancy exists between the experimental rate coefficient for  $O(^1S)$  quenching by  $O(^3P)$  [ $k_{300} = 2 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ ] and the calculated rate coefficient<sup>10</sup> ( $2 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ ). The three experimental values<sup>2,18,19</sup> agree within a factor of two, and even artificial aurorae experiments<sup>20</sup> give values of  $k \approx 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ ; hence, it is surprising that ab initio calculations show such marked disagreement. If the fault lies with the calculations, it is important to know whether it is due to errors in calculations of potential curves, inadequate understanding of the relevant interaction, or other factors. If the error is in the experiments, then the fault common to the various determinations must be identified.

Our approach has been to determine the product channel for the reaction:

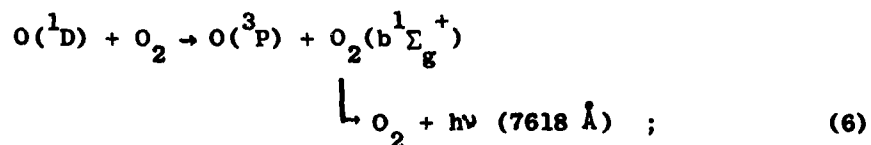


The calculations<sup>10</sup> identified the channel giving two  $\text{O}({}^1\text{D})$  atoms as the only important one; thus our experiment was designed to test this point. If this deduction is incorrect, then the calculations are based on false premises, and there is then no reason to doubt the experimental values. Thus, it was necessary for the experiment to differentiate between reactions producing two, one, and zero  $\text{O}({}^1\text{D})$  atoms.

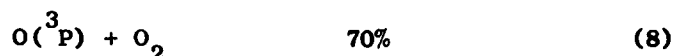
The experiment requires (1) a modulated  $\text{O}({}^1\text{S})$  source, (2) an  $\text{O}({}^3\text{P})$  source, and (3) an  $\text{O}({}^1\text{D})$  detection scheme. The  $\text{O}({}^1\text{S})$  source is the dissociation of  $\text{N}_2\text{O}$  by a 1304 Å oxygen atom resonance lamp. Both the absorption cross section and quantum yield for this process are very high.<sup>21</sup> Upon quenching by  $\text{N}_2\text{O}$ ,  $\text{O}({}^1\text{S})$  undergoes electronic deactivation via<sup>22</sup>



Although the 1304 Å  $\text{O}({}^1\text{S})$  yield is 90%, the secondary  $\text{O}({}^1\text{D})$  yield is a third of this value, and can thus be used as a calibration standard. In such a system,  $\text{O}({}^1\text{D})$  cannot be directly detected because its radiative lifetime is 150 s, but the addition of  $\text{O}_2$  to the gas mixture results in the reaction



This radiation is readily observed, and has been shown to be a reliable  $O(^1D)$  monitor.<sup>11</sup> Furthermore, the reaction



gives the same  $O(^1D)$  yield<sup>23</sup> as reaction (4); hence, in terms of an  $O(^1D)$  standard production source, it is immaterial whether  $N_2O$  or  $O_2$  deactivates the  $O(^1S)$ .

This experiment entails photolyzing an  $N_2O-O_2$ -He mixtures, which generates 0.3  $O(^1D)$  atoms for every absorbed photon, and then efficiently converts the  $O(^1D)$  to radiating  $O_2(b^1\Sigma_g^+)$ . The next step is to add  $O(^3P)$  to the system; if it quenches all the  $O(^1S)$ , the  $O(^1D)$  quantum yield will either increase to 2, to 1, or will drop to zero, depending on whether the  $O(^1S)$  quenching channel is reaction (1), (2), or (3). Thus, in the ideal case, the 7618 Å signal will increase by a factor of six or three, or will vanish.

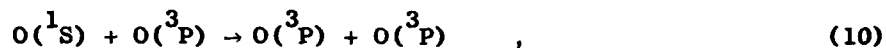
The  $O(^3P)$  atoms are generated by titrating the products of an  $N_2$ -He microwave discharge with NO, to the point where all N atoms have been converted to O atoms,



Because of various system constraints, it is not possible to quench all the  $O(^1S)$  by  $O(^3P)$ ; at best, half is quenched. In that case, the expectations for the three channels, reactions (1), (2), and (3), are that the 7618 Å signal will quadruple, double, or halve. These possibilities are thus well differentiated. The only requirement is that the  $O(^1S)-O(^3P)$  interaction involve only a single channel.

The results are clear-cut. When  $O(^3P)$  is added in a sufficient amount (several mtorr) to quench one half the  $O(^1S)$ , the 7618 Å signal

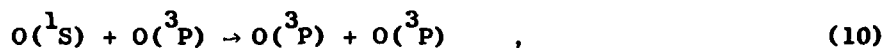
is halved. This indicates that no  $O(^1D)$  is produced in the quenching process and thus the reaction is



with the entire 4.2 eV electronic energy going into translation. Thus, the calculations, based as they are on  $O(^1D) + O(^1D)$  as the products, appear to be incorrect, and use of the experimental value of  $2 \times 10^{-11}$   $\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$  is indicated. Reaction (10) conserves spin, which reaction (1) does not, a factor that makes the  $^3P + ^3P$  channel more plausible.

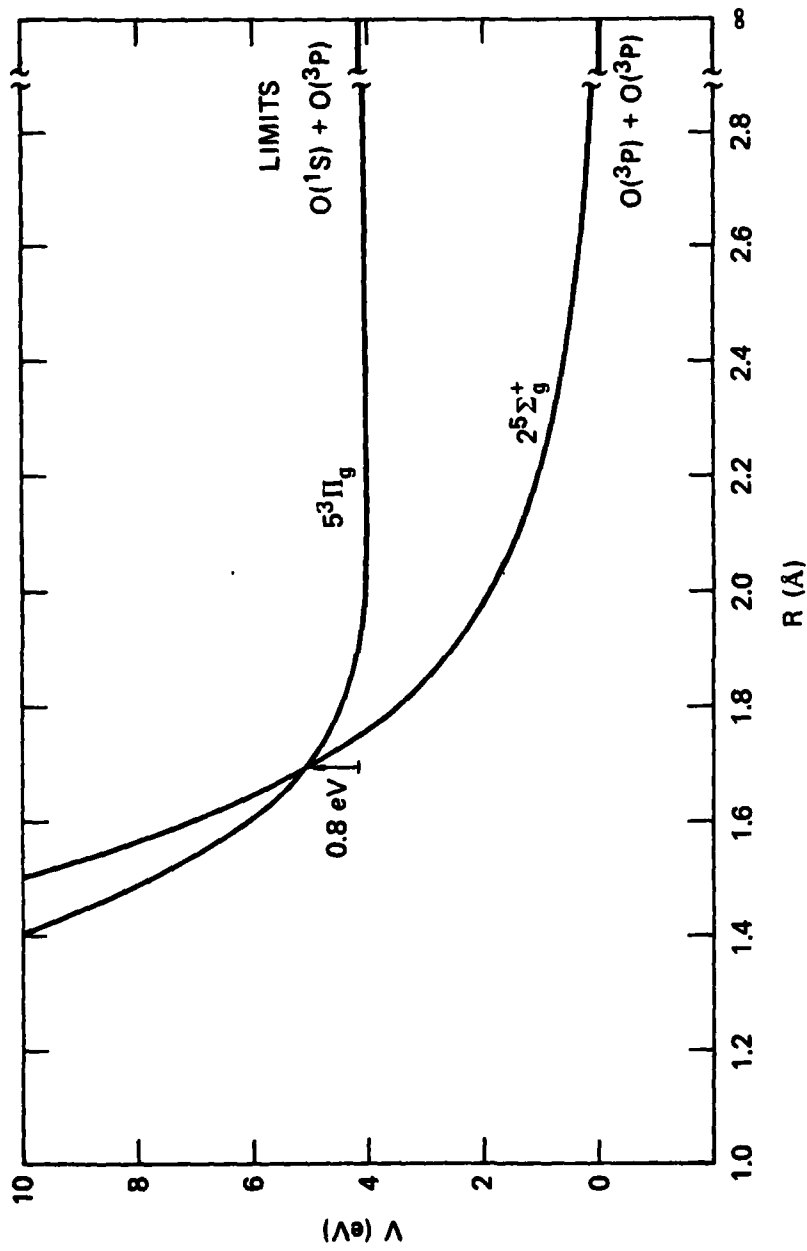
If the deactivation proceeds by this pathway, then a mechanism must be proposed by which the  $O_2$  molecule can pass from  $O(^1S) + O(^3P)$  to  $O(^3P) + O(^3P)$  limits. The most accurate  $O_2$  potential energy curves are those published by Saxon and Liu,<sup>24</sup> and it is evident that to obtain a pair of potentials that approach each other sufficiently closely to result in significant interaction, we must select the most attractive potential coming from the  $O(^1S) + O(^3P)$  limits, and the most repulsive one coming from  $O(^3P) + O(^3P)$  limits. These correspond to the  $5^3\Pi_g$  and  $2^5\Sigma_g^+$  states, respectively, and are shown in Figure 4. The strongest interaction would be at the intersection, which lies 0.8 eV above the available  $O(^1S) + O(^3P)$  energy, and is unaccessible, since the measured activation energy<sup>2</sup> is only 0.075 eV. Therefore, if our experimental determination of the product channel is correct, we would conclude that the potential curve calculations are inaccurate to the extent that the crossing must lie lower; that is, either the  $5^5\Sigma_g^+$  curve is steeper or the  $3^3\Pi_g$  curve is more attractive. We thus find that the  $O(^1S) + O(^3P)$  interaction, which we initially investigated for strictly aeronomic motives, now has an impact on ab initio potential curve calculations; it is hoped that the results will lead to an improved understanding of the interactions between  $O_2$  states which are generally inaccessible to study.

is halved. This indicates that no  $O(^1D)$  is produced in the quenching process and thus the reaction is



with the entire 4.2 eV electronic energy going into translation. Thus, the calculations, based as they are on  $O(^1D) + O(^1D)$  as the products, appear to be incorrect, and use of the experimental value of  $2 \times 10^{-11}$   $\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  is indicated. Reaction (10) conserves spin, which reaction (1) does not, a factor that makes the  $^3P + ^3P$  channel more plausible.

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FIGURE 4  $5^3\Pi_g$  AND  $2^5\Sigma_g^+$  POTENTIAL ENERGY CURVES



While this work was in progress, a very relevant problem arose. Since the work of Young and Black,<sup>1</sup> it has been known that  $O(^1S)$  is generated in a stream of  $O(^3P)$  and  $N_2$ . That is, an NO-titrated  $N_2$  afterglow shows strong 5577 Å emission. There is an extensive body of literature relating these observations to the 5577 Å emission seen in the terrestrial nightglow,<sup>3,25-27</sup> and it is generally assumed that the mechanism for  $O(^1S)$  production, not yet fully understood, is the same in the two cases.

Recent work at SRI has concentrated on generating excited states of  $O_2$  in oxygen atom afterglow systems.<sup>28</sup> The atoms can be generated either in an  $O_2$ -He afterglow or in an NO-titrated  $N_2$ -He afterglow; for similar  $O(^3P)$  densities, the  $O_2$  emissions are similar. However, the 5577 Å  $O(^1S)$  emission is seen only in the titrated  $N_2$  system; in the  $O_2$ -He afterglow it is indiscernible. As the  $O(^1S)$  is certainly generated in a manner utilizing the atom recombination energy as the ultimate source of the 4.2 eV electronic excitation energy, it is reasonable to expect that for equal  $O(^3P)$  densities, the  $O(^1S)$  production rate is the same in the two afterglow systems. Therefore, the lack of observation of  $O(^1S)$  in the  $O_2$ -He system must indicate an  $O(^1S)$  loss rate much greater than in the titrated  $N_2$  system.

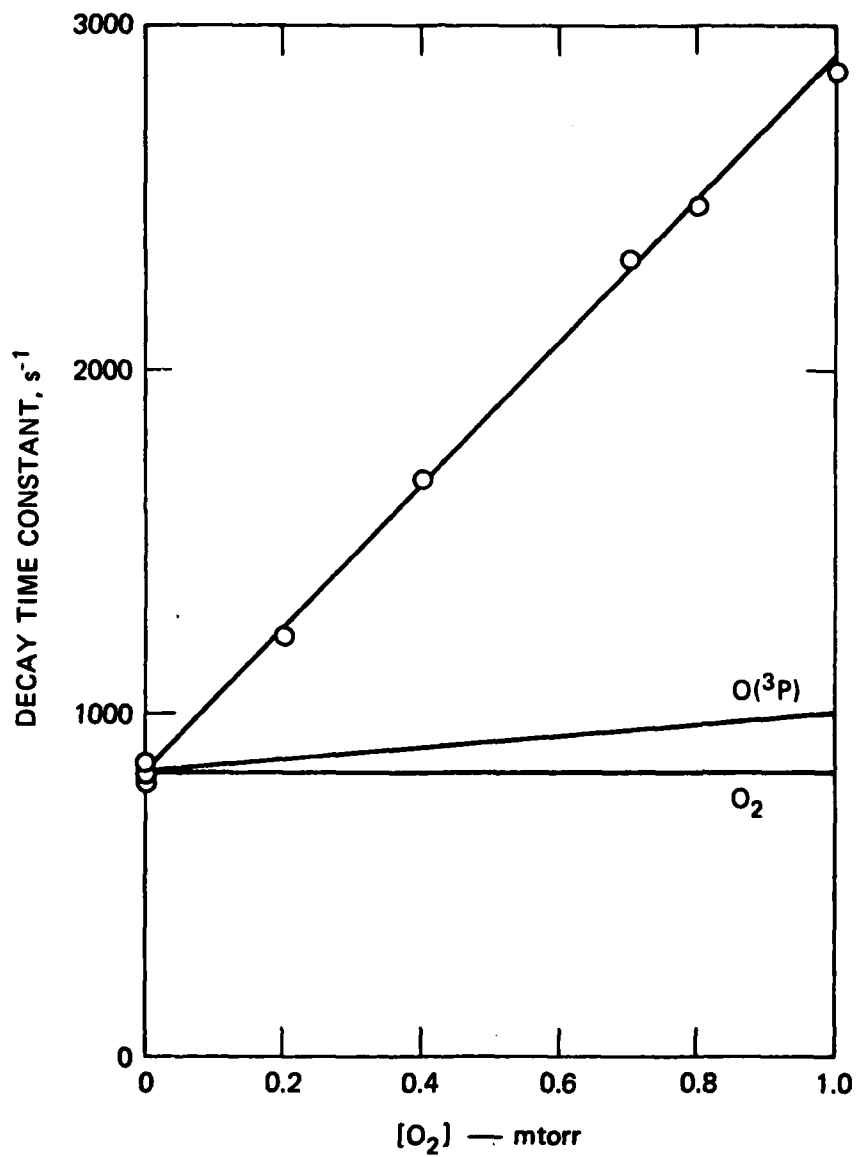
It is generally assumed that the principal  $O(^1S)$  quencher in such systems is  $O(^3P)$ , but clearly this is not true in the  $O_2$ -He afterglow. What then is the quencher, and how can we be sure that it is not also present, to a lesser extent, in the titrated  $N_2$  system?

The problem was approached using the same apparatus described above, but instead of looking at 7618 Å radiation, we observed the 5577 Å emission. A low concentration (1.5-3 mtorr) of  $N_2O$  was photolyzed at 1304 Å, in a modulated mode, and the decay rate of the  $O(^1S)$  was obtained, in a helium buffer. Upstream from the photolysis bulb, in the helium line, a microwave discharge was turned on, and as long as pure helium

flowed through the line, the decay rate of  $O(^1S)$  in the bulb was unaffected. Then a minute quantity of  $O_2$  was added above the discharge.

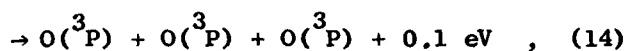
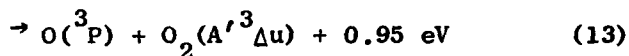
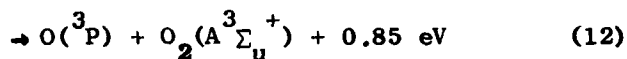
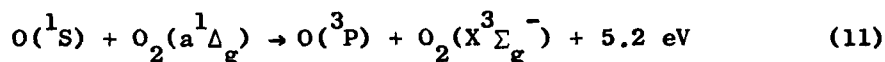
Figure 5 shows the effect on the  $O(^1S)$  decay rate, and also shows the effect attributable to  $O(^1S)$  quenching by both  $O_2$  and  $O(^3P)$ . The  $O(^3P)$  line is drawn based on a measured efficiency of  $O_2$  dissociation under these conditions, corresponding to  $[O(^3P)]/[O_2] = 0.3$  (i.e., 15% dissociation). The observed initial slope of the plot of reciprocal decay time versus  $[O_2]$  is thus 300 times steeper than expected for  $O_2$  and 14 times steeper than expected for  $O(^3P)$ . Furthermore, the slope is equal to  $1 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  based on  $[O_2]$ . Since any quenching rate coefficient for  $O(^1S)$  is unlikely to be greater than  $5 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  ( $O_3$  and  $H_2O$  have such values),<sup>29,30</sup> we can say that the concentration of the quencher cannot be less than 20% of the  $O_2$ . This is a very large fraction, but there is one species that is expected at this level in an  $O_2$ -He afterglow--namely  $O_2(a^1\Delta_g)$ , the first excited state of  $O_2$ .

$O_2(a^1\Delta_g)$  radiates to the ground state at  $1.27 \mu_m$ , an inconvenient wavelength for observation. It is known to be extraordinarily stable for an excited state. Quenching by stable atoms and molecules is extremely slow,<sup>31</sup> always  $< 10^{-15} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ , and wall deactivation is also ineffective,<sup>31</sup> so that the state is transported great distances in flow systems. Work carried out by Ogawa and Ogawa<sup>32</sup> to measure the  $O_2(a^1\Delta_g)$  absorption spectrum established that it is a simple matter to reach  $O_2(a)/O_2(X)$  ratios of 0.2 at low  $O_2$  pressures, as has been reported by others.<sup>33</sup> For the submicron levels used in the present study, the  $O_2(a)/O_2(X)$  ratio may well be much larger than 0.2; hence it would seem that for the sum of the following reactions



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FIGURE 5 O(<sup>1</sup>S) DECAY TIME CONSTANT VERSUS [O<sub>2</sub>]  
 [N<sub>2</sub>O] = 1.5 mtorr  
 [He] = 3 torr



a rate coefficient of  $(3 \pm 1) \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  is indicated. Other possible pathways are excluded since the earlier work on the  $O(^1S) + O(^3P)$  quenching channel had shown that when the  $O(^3P)$  came from an  $O_2$ -He afterglow (as also in the titrated  $N_2$  afterglow), no  $O_2(b^1\Sigma^+)$  or  $O(^1D)$  was formed. On the basis of spin, we can then exclude  $O_2(c^1\Sigma_u^-)$  as a product, and the above four reactions are the remaining possibilities.

In passing, we must consider two other species that could conceivably be involved--ozone and vibrationally excited  $O_2$ . Ozone can be excluded because (a) its formation rate at submicron  $O_2$  levels is too slow, and (b) addition of substantial amounts of  $O_2$  below the discharge, which would certainly accelerate any three-body ozone generation, has no effect on the  $O(^1S)$  loss rate. The active species is created only in the discharge. As for  $O_2(\text{vib})$ , Ogawa and Ogawa<sup>32</sup> looked for it in the system where they saw up to 20%  $O_2(a^1\Delta_g)$  and failed to detect any Schumann-Runge absorption.  $O_2(\text{vib})$  would be rapidly quenched by  $O(^3P)$  and would be deactivated on the walls, and it is quite unrealistic to expect to find it, 0.5 sec after the discharge, at concentration levels exceeding 20% of the  $O_2$ .

By elimination we have concluded that in an  $O_2$ -He afterglow, the 5577 Å emission from  $O(^1S)$  is suppressed by quenching by  $O_2(a^1\Delta_g)$ . However, it is possible that in the titrated  $N_2$  system where we measure the quenching of  $O(^1S)$  by  $O(^3P)$ , the quencher might be  $O_2(a^1\Delta_g)$  with a concentration proportional to  $O(^3P)$ . Then all our conclusions about product channel identifications would be wrong, and the ab initio calculations could well be right.

The situation is in fact ambiguous. We have shown that the  $O(^1S)-O(^3P)$  quenching data is pressure-independent. In an  $O(^3P)-N_2$  stream, homogeneous production of  $O_2(a^1\Delta_g)$  would come from three-body recombination,  $O + O + M \rightarrow O_2(a) + M$ . Pressure-independence suggests that  $O_2(a^1\Delta_g)$  made in this manner is insufficient to compete with  $O(^3P)$  for the  $O(^1S)$ . However, we cannot be certain about heterogeneous processes. We know that  $O(^3P)$  recombines on the walls between the titration point and the cell. What  $O_2$  state is formed? We claim that the  $O(^1S)-O(^3P)$  rate coefficient is  $2 \times 10^{-11}$  and the  $O(^1S)-O_2(a^1\Delta_g)$  rate coefficient is  $3 \times 10^{-10}$ ; if half of the  $O(^3P)$  atoms are lost on the way to the cell, and 10% of the recombination leads to  $O_2(a^1\Delta_g)$  production, then half the observed quenching effect would be due to  $O_2(a^1\Delta_g)$ . We know that surface recombination leads to  $O_2$  excited states in some circumstances. Kenner and Ogryzlo<sup>34</sup> are currently studying the  $O_2(A^3\Sigma_u^+)$  state, using recombination of atoms on a metal surface as their source. Generation of the  $O_2(a^1\Delta_g)$  state in a similar manner has not been studied, but cannot be excluded in the system under consideration. The fact that three laboratories<sup>2,18,19</sup> have obtained similar  $O(^1S)-O(^3P)$  rate coefficients is encouraging, but the problem will not be entirely solved without direct observations on  $O_2(a^1\Delta_g)$ . Alternatively, we hope to perform measurements on the  $O(^1S)-O(^3P)$  system in a titrated  $N_2$  afterglow in which the atoms are removed by a mercuric oxide film in the course of the experiment. If the  $O(^1S)$  decay rate then remains constant, the atoms are not the quencher; if the decay rate decreases upon atom removal, the quenching species is presumably  $O(^3P)$ .

Finally, the aeronomic implications of the fast  $O(^1S)-O_2(a^1\Delta_g)$  reaction need discussion. For the reaction to be a significant  $O(^1S)$  loss mechanism, say at the 10% level, the  $O_2(a^1\Delta_g)$  concentration needs to be  $4 \times 10^8 \text{ cm}^{-3}$  (which gives a loss rate of 10% of the  $O(^1S)$  radiative rate). Model profiles<sup>35</sup> of the atmospheric  $O_2(a^1\Delta_g)$  density show values

at 95 km, the peak 5577 Å emission altitude, of  $2 \times 10^9 \text{ cm}^{-3}$ , indicating that  $\text{O}(^1\text{S})$  quenching by  $\text{O}_2(^1\Delta_g)$  is substantial. This is a process never previously considered. Since considerable work has been performed to explain the  $\text{O}(^1\text{S})$  atmospheric profiles through either the Barth or Chapman mechanisms, it is now essential that a close look be given to the existence of this new  $\text{O}(^1\text{S})$  quenching process, and its effect on the current models.

The effect of the  $\text{O}(^1\text{S})-\text{O}_2(^1\Delta_g)$  reaction is expected to be much greater in aurorae, where the localized  $\text{O}_2(^1\Delta_g)$  density may reach  $10^{11} \text{ cm}^{-3}$ . In this case,  $\text{O}(^1\text{S})$  quenching will be completely dominated by  $\text{O}_2(^1\Delta_g)$ , and all studies that have related  $\text{O}(^1\text{S})$  emission intensities in aurorae to other processes [electron quenching, radiation,  $\text{O}(^3\text{P})$  quenching] must be reevaluated.

It is clear that the existence of this enormously efficient quenching process has not been considered previously in lab experiments or in atmospheric experiments and observations. Even the mesospheric artificial aurorae experiments (PRECEDE),<sup>20</sup> in which the decay of  $\text{O}(^1\text{S})$  excited by an electron beam has been interpreted as quenching by background  $\text{O}(^3\text{P})$ , may require reinterpretation, since quenching by  $\text{O}_2(^1\Delta_g)$  simultaneously produced by electron impact is now a possibility. In fact, analysis of the data from the PRECEDE experiment leads to a rate coefficient for  $\text{O}(^1\text{S})$  quenching by  $\text{O}_2$  that is three times the laboratory value. This would be expected if 0.1% of the  $\text{O}_2$  in the electron beam had been converted to  $\text{O}_2(^1\Delta_g)$ .

In summary, we have established that:

- (1) There is an extremely efficient quencher of  $\text{O}(^1\text{S})$  in an  $\text{O}_2$ -He afterglow.
- (2) This quencher does not appear to be  $\text{O}(^3\text{P})$ ,  $\text{O}_2(\text{vib})$ , or  $\text{O}_3$ , and by elimination is most likely  $\text{O}_2(^1\Delta_g)$ . The  $\text{O}(^1\text{S})$  quenching rate coefficient is deduced to be  $(3 \pm 1) \times 10^{-10}$

$\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ , by far the largest value reported for any  $\text{O}_2(a^1\Delta_g)$  reaction.

- (3) The quenching of  $\text{O}(^1\text{S})$  by  $\text{O}(^3\text{P})$  appears to proceed by the  $\text{O}(^3\text{P}) + \text{O}(^3\text{P})$  channel, releasing 4.2 eV as translational energy. This pathway is contrary to that used in ab initio calculations of the system. These conclusions are based on the assumption that in an NO-tritrated  $\text{N}_2$ -He afterglow,  $\text{O}(^3\text{P})$  is the only active species. If this assumption is proved wrong, and it turns out that small amounts of  $\text{O}_2(a^1\Delta_g)$  are in fact produced by surface recombination, then what we have established is that  $\text{O}(^1\text{S})$  quenching by  $\text{O}_2(a^1\Delta_g)$  produces neither  $\text{O}(^1\text{D})$  nor  $\text{O}_2(b^1\Sigma_g^+)$ .
- (4) The rapid rate of  $\text{O}(^1\text{S})$  quenching by  $\text{O}_2(a^1\Delta_g)$ , when substantiated by more direct measurements, will necessitate a reevaluation of current atmospheric models of mesospheric processes, and particularly of auroral processes, involving  $\text{O}(^1\text{S})$ .

#### Publications

Listed below are the publications, together with their abstracts, resulting from work performed under this contract.

- (1) "Metastable Oxygen Emission Bands"  
T. G. Slanger  
*Science*, **202**, 751 (1978).

Recombination of ground-state oxygen atoms populates six different bound electronic states of molecular oxygen. Of the six optical transitions expected between the three upper states at 4 to 4.5 electron volts and the two lowest states, five have been observed in the afterglow of a conventional helium-oxygen microwave discharge in both  $^{16}\text{O}_2$  and  $^{18}\text{O}_2$ ,

three of them for the first time in gas-phase spectra. Generation of these emissions from oxygen atoms in a system free of molecular oxygen establishes that atom recombination is the production mechanism.

- (2) "Generation of  $O_2(c^1\Sigma_u^-, C^3\Delta_u, \text{ and } A^3\Sigma_u^+)$  from Oxygen Atom Recombination"

T. G. Slanger

J. Chem. Phys. 69, 4779 (1978).

The spectrum produced in the afterglow of an  $O_2$ -He discharge has been studied between 4000 and 8000 Å. Until recently, only the  $O_2(A^3\Sigma_u^+ \rightarrow X^3\Sigma_g^-)$  emission bands had been observed in this region. The work of Lawrence et al. established that, under the appropriate conditions, the  $O_2(c^1\Sigma_u^- \rightarrow X^3\Sigma_g^-)$  system could also be observed. We were able to duplicate their results, and in addition we have discovered three  $O_2$  band systems not previously seen in gas phase laboratory spectra. These systems are  $C^3\Delta_u \rightarrow a^1\Delta_g$ ,  $C^3\Delta_u \rightarrow X^3\Sigma_g^-$ , and  $c^1\Sigma_u^- \rightarrow a^1\Delta_g$  and were positively identified by isotopic substitution experiments. The O-v" progression in the C-a system is the first gas phase spectrum involving a large range of the higher vibrational levels in the  $a^1\Delta_g$  state. Analysis of the system establishes a new set of  $a^1\Delta_g$  vibrational constants:  $\omega_e = 1510.23 \pm 0.34 \text{ cm}^{-1}$ , and  $\omega_e x_e = 13.368 \pm 0.12 \text{ cm}^{-1}$ . The C-a system involves only the  $\Omega = 1$  spin component of the  $C^3\Delta_u$  state. The  $C^3\Delta_u \rightarrow X^3\Sigma_g^-$  system, on the other hand, radiates mainly through the  $\Omega = 2$  component. By combining the present data on the  $C^3\Delta_u$  ( $v = 0$ ) level, the absorption measurements of Herzberg on the  $v = 5$  and  $v = 6$  levels, the known dissociation energy, and the high-pressure bands measured by Herman and by Finkelburg and Steiner, we have established vibrational constants for the  $C^3\Delta_u$  state. These are  $\omega_e = 803.5 \pm 1.0 \text{ cm}^{-1}$ ,



$\omega_e x_e = 8.18 \pm 0.13 \text{ cm}^{-1}$ , and  $\omega_e y_e = 0.872 \pm 0.006 \text{ cm}^{-1}$ . From data existing in the literature, combined where necessary with the present measurements, we have estimated radiative lifetimes for the three  $\text{O}_2$  metastable states that we observed. From the band strength data of Hasson et al., one may calculate  $\tau = 250\text{-}160$  msec for  $\text{A}^3\Sigma_u^+$  ( $v = 0\text{-}6$ ), and deduce an estimate of  $\tau = 25\text{-}50$  sec for  $\text{c}^1\Sigma_u^-$  ( $v = 0\text{-}10$ ). For  $\text{C}^3\Delta_u$  ( $\Omega = 1$ ,  $v = 0\text{-}6$ ), the estimated lifetime is 5-50 sec, and for  $\text{C}^3\Delta_u$  ( $\Omega = 2$ ,  $v = 6$ ), the estimated lifetime is 10-100 sec. The  $\text{O}_2$  spectra have been produced not only in  $\text{O}_2$ -He afterglows, but also in NO-titrated  $\text{N}_2$ -He afterglows (i.e., in an  $\text{O}_2$ -free environment), proving that the source of excited  $\text{O}_2$  molecules is oxygen atom recombination. The results are pertinent to  $\text{O}_2$  emissions in the terrestrial and Venusian air glows, and to combustion processes.

- (3) "Atmospheric OH Production--The  $\text{O}(\text{}^1\text{D}) + \text{H}_2\text{O}$  Reaction Rate"  
 L. C. Lee and T. G. Slanger  
 Geophysical Research Letters, 6, 165 (1979).

Successful modeling of the chemistry of the troposphere and stratosphere requires accurate knowledge of the production rate of the OH molecule, since it occupies a central position in a number of chemical cycles. The reaction between  $\text{O}(\text{}^1\text{D})$  and  $\text{H}_2\text{O}$  is believed to be the principal primary OH source, and an evaluation of the literature shows a discrepancy of about a factor of two between two of the most recent rate coefficients for this reaction. We have generated  $\text{O}(\text{}^1\text{D})$  from pulsed 1600 Å photolysis of  $\text{O}_2$ , and observed the 6300 Å  $\text{O}(\text{}^1\text{D}) \rightarrow \text{}^3\text{P}$  transition. The rate coefficient for  $\text{H}_2\text{O}$  quenching of  $\text{O}(\text{}^1\text{D})$  has been directly determined, and found to be  $(2.6 \pm 0.5) \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  at 300°K, in good agreement with the measurements of Streit, Howard, Schmeltekopf, Davidson, and Schiff.

#### MEETING PRESENTATIONS

"The  $O(^1D) + H_2O$  Reaction Rate Coefficient," report informally presented at American Geophysical Union Fall Meeting, San Francisco, December 1978.

"Spectra of  $O_2$  Metastables," G.E.S.E.M. Meeting, Meudon, France, May 1979.

"The Terrestrial Nightglow at 2500-4500 Å," AGU Fall Meeting, San Francisco, December 1979.

"Spectral Composition of the 2500-4500 Å Terrestrial Nightglow," 14th Informal Conference on Photochemistry, Newport Beach, CA., April 1980.

"The  $A^3\Sigma_u^+$ ,  $A'^3\Delta_u$ , and  $c^1\Sigma_u^-$  States of  $O_2$  in the Laboratory and in Planetary Airglows," 35th Symposium on Molecular Spectroscopy, Columbus, Ohio, June 1980.

**SCIENTIFIC CONTRIBUTORS**

**Contributors to the research performed under this contract were:**

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