Semi-Annual Report No. 3

# RESEARCH ON METASTABLE SPECIES IN ATOMIC AND MOLECULAR BEAMS PRODUCED BY CHARGE TRANSFER Tasks I, II, and III

RESEARCH

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By: J. R. PETERSON G. BLACK

SRI Project PAU-5962

Approved: C. J. COOK, EXECUTIVE DIRECTOR Physics & Chemical Physics Laboratory

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SYNOPS IS

- i -13 Two types of experiments are being used to study collisions between metastable species and ground state atoms and molecules. One type involves fast beams (energies between 150 and 1000 eV) containing excited particles, and is aimed at developing methods of detecting these species, as well as measuring cross sections for their collisional deexcitation. Studies of the detection and deexcitation of He 2<sup>1</sup>S and 2<sup>3</sup>S metastables are reported; the techniques developed for these studies are expected to be used for atmospheric species. The other type of experiment involves the production of metastables by rf excitation and photodissociation of low pressure gases. The mechanisms and rates of energy transfer between many excited and ground state species of particular importance in the upper atmosphere have been examined. Deactivation of  $O(\frac{1}{2}D)$ ,  $O(\frac{1}{2}S)$ ,  $O_{2}(b_{+}^{1}\Sigma)$ , and  $N_{2}(A_{+}^{3}\Sigma)$  is discussed here. Another phase of our program has involved field measurements of emissions from Ba-Sr releases in the upper atmosphere. ()

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#### INTRODUCTION

The need for information on the behavior of excited species in the earth's upper atmosphere has been widely recognized in recent years. These species play important roles in the energy balance of the ionosphere, in the behavior of the excited wakes of vehicles reentering the atmosphere, and in the highly disturbed upper atmosphere after nuclear explosions.

For the past several years, experiments have been carried out at Stanford Research Institute to examine collisions involving excited species. We report here on three tasks sponsored by ARPA through ARO. In Task I, beam methods have been developed to study energy transfer processes of metastable excited atoms and molecules in collisions with ground state species. In Task II, flowing afterglow techniques and pulsed photolysis methods involving optical detection of photolysis fragments are used to study exothermic energy transfer reactions in excited atmospheric gases.

A third Task has been concerned with optical measurements of the radiation from clouds of barium after their release, or generation, at high altitudes in field tests.

Progress in each of these tasks is described in this report. Task I has been carried out by M. Hollstein, J. R. Sheridan, D. C. Lorents, and J. R. Peterson. Tasks II and III were carried out by G. Black, T. G. Slanger, G. A. St. John, R. Sharpless, and R. A. Young.

#### I BEAM STUDIES OF EXCITED SPECIES

The problem of producing excitation in beams was solved in our early studies. We found<sup>1</sup> that charge transfer cross sections were quite large for reactions in which the electron is captured into an excited state if the reaction was nearly resonant, i.e., the collision involved little change in total internal energy of the system. On the other hand, satisfactory methods of detecting the excited beams are more elusive than the production. Our attempts to use secondary electron emission were unsuccessful because of the great dependence of the secondary emission efficiency on the surface conditions of the detector.

We turned to ionizing collisions between the fast metastable atoms and the molecules or atoms in a gas to yield a detecting signal. If the excitation energy of the metastable is greater than the ionization energy of the gas species, then Penning ionization can occur, even at very low relative energies. This process can lead to an efficient detector of metastables, although it cannot distinguish between two states of similar excitation energy in a beam. On the other hand, even if the excitation energy is insufficient to ionize a species by the Penning process, collisional ionization may still occur in collisions which use some of the kinetic energy of the fast metastables to supply the additional energy required. If the cross sections for collisional ionization by metastables

are considerably larger than those for ionization by ground state particles, then the ionization can still be used to indicate the presence of metastables in a beam. The discrimination against ground state particles in the beam will decrease as the beam energy increases to high values (at least several keV).

Thus, using the production of slow ions as a signal of the relative content of metastables in the beam, we were able to measure cross sections for the deexcitation of a beam as it traversed a gas. Deexcitation cross sections were measured for He<sup>\*</sup> in N<sub>2</sub>, Ar, and C<sub>2</sub>H<sub>2</sub>, and for Ar<sup>\*</sup> in C<sub>2</sub>H<sub>2</sub>. These studies were made fairly easy by the relatively high detection efficiency due to Penning ionization. For He<sup>\*</sup> in He and Ar<sup>\*</sup> in Ar, however, the low ion yields of collisional ionization, coupled with smaller excitation cross sections, made the experiments more difficult and the results less certain. These measurements were all discussed in the last report.<sup>2</sup>

Results of the first group of experiments were unambiguous, and they are currently being prepared for publication. Considerable effort has been made to improve the less reliable He<sup>\*</sup> + He and Ar<sup>\*</sup> + Ar data. Work during the past six months has been concentrated on the He<sup>\*</sup> + He system. First, attempts were made to improve the measurements which detected the collisional ionization as a signal. These studies were followed by a new technique which detected collisionally excited optical radiation, and which is yielding considerably improved results. These studies will be discussed separately.

## A. Determining Deexcitation Cross Sections by Detecting Ionization

This method of measurement is described in Semi-Annual Report No. 2. In brief, slow ions, produced in collisions between excited beam atoms and the target gas, are collected in each of three collection cells of equal length along the beam path. Deexcitation cross sections are obtained from the ratios of the slow ion currents in different cells. The measurement of the deexcitation of a beam, using collisional ionization to indicate the presence of excited states in the beam, suffers mainly from the low ionization cross sections at low beam energies and

from lack of discrimination against ground state ions at high energies. These facts, coupled with a rather small deexcitation cross section, made the measurements subject to error from background effects, and beam instabilities, and to other systematic errors such as small differences in the slow ion collection efficiencies of the three cells. Particularly in the low and high extremes of the energy range, the computed cross sections often showed some systematic dependence on the target gas pressure. Several modifications to the apparatus were made to eliminate possible errors, and the data gradually became more consistent. The "best" results are shown, along with the optical results, in Fig. 1.

#### B. Measurements Using Optical Techniques

Because of the difficulties connected with the ionization method of monitoring the excited beam intensity in the He<sup>\*</sup> + He deexcitation measurements, it was decided to attempt a different detection scheme. During the course of our work last year, we had the opportunity to use an image intensifier spectrograph to analyze the light emitted in the beam region of the target chamber for several combinations of excited beams and target gases. This spectrograph was about fifty times more sensitive than the fast, but conventional, grating spectrograph that had been used in our earlier studies of charge transfer induced excitation<sup>3</sup> and had been tried unsuccessfully on this apparatus.

Both the 5876Å and 6678Å HeI lines (from the 3<sup>3</sup>D and 3<sup>1</sup>D states, respectively) appeared whenever the metastable helium beam traversed any gas. No emission was observed when a ground state He beam (obtained from He<sup>+</sup> + He charge transfer) traversed tiese gases. Thus, these emissions could be used to monitor the presence of He<sup>\*</sup> metastables, and a relative measure of the intensity of the light emitted from two positions on the beam path, separated by a known length, could yield deexcitation cross sections.

## 1. Method and Apparatus

An apparatus capable of performing these measurements was constructed and mounted in the target chamber, as shown in Figure 2. Two identical



FIG. 1 DEEXCITATION CROSS SECTIONS FOR He<sup>\*</sup> + He COLLISIONS. Results of ionization technique follow dashed line; data points are from singlet and triplet optical transitions. Theoretical results of Evans and Lane for He 2<sup>3</sup>S excitation transfer are given, however [added in proof] the energy scale is in error by a factor of two: their results are for center of mass energies.



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front surface mirrors, at  $135^{\circ}$  and  $45^{\circ}$  to the beam direction, sample the light at two locations separated by a distance of 16 cm. Centered between these mirrors is a third, slightly larger mirror that can be rotated between two extreme orientations in which it directs the light from either sampling mirror vertically through a quartz lens and quartz window in the vacuum wall, then through an interference optical filter and into a freon-cooled photomultiplier tube. The focal length of the lens is such that the image of the atom beam is somewhat out of focus at the phototube, to avoid adverse effects due to local irregularities in the sensitivity of the photocathode.

Let the total light collection efficiency along the path observed by mirror 1 vary as  $c_1 f_1(x)$  as a function of the distance x along the beam axis ( $c_1$  is a constant accounting for solid angle effects, the transition probability of the emission, the excitation cross section, quantum efficiency of the detector, transmission losses, and for possible mirror inefficiency or misalignments that do not affect the x dependence). Let the front edge of mirror 1 be at x = a; then the light intensity observed by it will be given by

$$I_{1} = N_{0}^{n} \exp(-nQa)c_{1} \int_{1}^{1} \exp(-nQx)f_{1}(x) dx$$
 (1)

where  $N_0$  is the flux of metastables at x = 0 in the target gas of number density n and Q is the deexcitation cross section. Similarly, the light observed with mirror 2 is

$$I_{2} = N_{0}n \exp - [nQ(a + d)]c_{2} \int_{2} \exp (-nQx)f_{2}(x) dx$$
 (2)

and

$$I_{1}/I_{2} = \exp(nQd)\alpha R(nQ)$$
(3)

where

 $\alpha = c_1/c_2$ , d is the distance between the mirrors, R = F\_1/F\_2

and

$$F_{i}(nQ) = \int exp(-nQx)f_{i}(x) dx$$

Thus

$$Q = \frac{1}{nd} \left( ln \frac{I_1}{I_2} - ln \alpha R \right) . \qquad (4)$$

The functions  $f_1$  and  $f_2$  are actually mirror images of each other and are, in principle, symmetric about the midpoint of the two mirrors. They have been computed from the geometry using a Monte Carlo method, and have also been determined experimentally by measuring the optical signal from a thin slit light source as a function of its position along the beam axis. Results from the two methods agree very well. Although  $f_1$  and  $f_2$  are not similar functions displaced by d, they are sufficiently alike that  $R \approx 1$ over the range of nQ of interest experimentally. For very large values of nQ such that the exponential varies considerably over the region observed by one mirror, R will depend on nQ and Q can be obtained from an iterative computer fit to Eq. (4) for data taken over a range of nQ. This has been done; however, we have generally been able to use (4) with R = 1. Actually, even  $\alpha$  is very close to unity (within 5%). Assuming R doesn't vary greatly with n, a plot of  $ln(I_1/I_2)$  against n gives a straight line with slope equal to Qd and intercept equal to  $\ln \alpha$  R. It can be used to obtain Q when  $\alpha$  and/or R deviate significantly from unity.

# 2. Results

Although there is still some uncertainty in the data for  $He^{+}$  + He, they indicate cross sections that are different by almost a factor of two depending on whether light from the singlet or triplet states is monitored.

The preliminary results are shown in Fig. 1 (along with the ionization data) for measurements using the 6678 Å  $(3^{1}D-2^{1}P)$  and 5876 Å  $(2^{3}D-2^{3}P)$  emissions. These results are consistent with spin conservation in the excitation, so that the triplet light comes only from collisions involving the  $2^{3}S$  metastables in the beam, and the singlet light comes only from excitation of the  $2^{1}S$  metastables. No other excited states are in the beam in any significant quantities.

The collisions producing the observed light, let us say for the triplet case, are probably of two types:

$$He(2^{3}S) + He(1^{1}S) \rightarrow He(3^{3}P) + He(1^{1}S) \text{ or}$$
  
 $He(2^{3}S) + He(1^{1}S) \rightarrow He(1^{1}S) + He(3^{3}P)$ .

Similar equations can be written for the singlet radiation. Spinconserving collisions such as

$$\operatorname{He}(2^{3}S) + \operatorname{He}(1^{1}S) \xrightarrow{\rightarrow} \operatorname{He}(2^{3}S) + \operatorname{He}(3^{1}D)$$

would produce the observed singlet light from the 2<sup>3</sup>S atoms in the beam. However, these require 23 eV excitation as compared to about 2 eV in the first two reactions, and probably do not contribute effectively to the 6678 Å signal. More work is still needed to confirm this spin-conservation speculation; however, if it is true, the cross sections from the singlet light are those for the deexcitation of the singlet state, etc. This may be a very useful detection scheme for subsequent experiments. It already offers a clear advantage over the ionization technique in allowing us to compare our results with some recent unpublished computations by Evans and Lane.<sup>4</sup> They are making the first real attempt at a good quantum mechanical calculation involving realistic wave functions and computed interatomic potentials, and have some results for the excitation transfer cross sections between the 2°S state and ground state He for energies less than 500 eV. The solid curve in Fig. 1 represents their results. The comparison with our preliminary data is amazingly good--within about 10% over the energy range covered. This is well within the accuracy of our

measurements, but the close agreement may be fortuitous. We have used the  $3889 \text{ \AA} (3^3\text{P}-2^3\text{S})$  line to measure the triplet deexcitation cross sections. The results indicate generally larger cross sections than were obtained from the 5876 Å line. The reason for this is not yet understood, but some transmission of 3965 Å light from the  $4^1\text{P}-2^1\text{S}$  transition may be responsible for shifting the apparent cross section to values intermediate between the pure singlet and triplet cases. Further study is required to determine the actual cause.

## C. Other Studies

The same apparatus has also been used during this period to measure molecular lifetimes. Lifetime measurements are important because of their direct relationship to optical emission and absorption coefficients which play a strong role in determining the behavior of the air plasmas associated with atmospheric nuclear explosions and vehicle reentry phenomena. This work was carried out under a small contract from Air Force Weapons Laboratories. For some time we have anticipated using the near-resonant charge transfer collisions to produce excited beams in desired states for the purpose of determining their lifetimes. This is accomplished by observing the spatial decay of the pertinent optical radiation as the fast excited beams with known speeds travel away from the exciting collision region. Very successful measurements<sup>5</sup> were made on several bands of the N<sub>2</sub> first positive system, and measurements were made on the N<sub>2</sub><sup>+</sup> Meinel bands, yielding the first reliable values for this system.

# D. Future Work

With the behavior and reliability of the optical detection system now established, we plan to undertake shortly a series of studies on the deexcitation of the  $A^{3}\Sigma_{u}^{+}$  state of N<sub>2</sub>. This will be produced by electron capture by N<sub>2</sub><sup>+</sup> in NO, and will be detected by observing the NO Y-bands that are excited by energy transfer from the A state to NO.<sup>6</sup> It is likely that similar emissions excited by collisions of N<sub>2</sub>( $A^{3}\Sigma_{u}^{+}$ ) with other species than NO, such as the 2537 Å from energy transfer to Hg,<sup>7</sup> can be used for studies of deexcitation cross sections in these other gases. The studies performed under Tasks II will be very useful in this respect.

### II ENERGY TRANSFER AND OPTICAL EXCITATION

The atomic and molecular species that constitute the upper atmosphere have many low lying metastable excited states. Energy can be deposited in the upper atmosphere either by the natural means of solar and cosmic radiation absorption or by such means as nuclear explosions and missile penetrations. This energy will result in significant populations of the metastable states of the atmospheric constituents. The long radiative lifetimes of these states make energy transfer a particularly likely mode for their deactivation. The energy acceptor may then radiate energy in making a transition back to its ground state. Observations of this radiated energy, together with an understanding of the appropriate energy transfer processes, provide a measure of both the total energy and the means by which that energy was deposited in the upper atmosphere.

Four metastable species of particular interest in excitation of the upper atmosphere,  $O_2(b^1\Sigma)$ ,  $O(^1D)$ ,  $O(^1S)$ , and  $N_2(A^3\Sigma)$ , have been produced and their collisional deactivation, and the consequences of this deactivation, have been studied in considerable detail.

#### A. Methods of Approach

Two experimental approaches are being successfully pursued. In one approach called, for convenience, the rf excitation experiment, highly purified gas at low pressure flows past several inlets (in a glass system), through a 5-liter quartz rf excitation bulb, through a l-liter chemiluminescence observation bulb, and finally to a l-liter/sec mechanical vacuum pump.

The gas is excited by a pulsed, high impedance (Tesla type) 150-kc/sec oscillator and is observed with a filtered photomultiplier and two monochromators with photomultiplier detection. Steady state data (i.e., spectral scans, or variations of light intensity with power or with the concentration of an additive) are recorded. Transient data (i.e., the build-up and decay of intensity as the excitation is turned on and off) are stored digitally in a 1024-channel data accumulator. After sufficient repetitive cycles have occurred, the information is read out and photographed on an oscilloscope.

The second experimental program uses vacuum ultraviolet light to photodissociate simple molecules into excited fragments of atmospheric interest. The photolysis vessel is constructed as a double Wood's horn; one horn faces the photolysis lamp, the second faces a quartz observation window. The outside of the bulb is thoroughly blackened to reduce the amount of light from the photolysis lamp that can be scattered through the observation window. The bulb is part of a conventional flow apparatus that has a mechanical vacuum pump with a volume capacity of ~2 liter/sec. The residence time of the gas in the photolysis vessel is about 1 sec.

Microwave-powered rare gas resonant light sources have been used for these experiments. The photon energies available range from 8.4 to 11.6 ev depending on the gas used. The excited fragments produced are monitored by emission spectroscopy using image tube spectrographs to cover the UV and visible regions and then using a filter-photomultiplier combination to isolate the emission feature of particular interest.

A very recent development in our photolysis program has been the use of pulsed photolysis lamps. The circuit to pulse the lamps is shown in Fig. 3. As in the rf excitation experiments, steady state data can be recorded or transient data can be stored in a signal accumulator. In the latter mode, after a few thousand cycles, the time history of the emission signal is displayed on an oscilloscope. A schematic of the apparatus for doing this is shown in Fig. 4.

#### B. Results

### 1. RF Excitation Experiments

These experiments have proved very successful, and the rates of energy transfer reactions involving  $N_2(A^3\Sigma)$  and  $O_2(b^1\Sigma)$  have been , determined. Quenching rates for  $O({}^1S)$  could not be determined, as it was found that quenching rates for the 5577 Å emission of  $O({}^1S)$  were



FIG. 3 RF OSCILLATOR CIRCUIT (~300 MHz) USED FOR EITHER PULSED OR CONTINUOUS OPERATION OF THE LIGHT SOURCE

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FIG. 4 SCHEMATIC DIAGRAM OF THE INTEGRATION SYSTEM USEL FOR EMISSION DECAY MEASUREMENTS

essentially identical to those for  $N_2(A^3\Sigma)$ , indicating that  $O({}^3P)$  is excited to  $O({}^1S)$  by energy transfer from  $N_2(A^3\Sigma)$  and that  $O({}^1S)$ , in the absence of excitation, would decay more rapidly than observed. This work has been incorporated in articles submitted to the Journal of Chemical Physics.<sup>8,9</sup> It also forms part of an article submitted to Science.<sup>10</sup>

2. Photolysis Experiments

a. O<sub>2</sub> Photolysis Giving  $O({}^{1}D)$ . Oxygen photolysis at 1470 Å has been found to be a convenient source of  $O({}^{1}D)$ . Although the radiative lifetime of  $O({}^{1}D)$  is too long for this atom to be conveniently studied by its emission at 6300 Å, an emission technique has been developed whereby relative  $O({}^{1}D)$  quenching and reaction rate constants can be ascertained. The technique involves measuring the ground state O atom production rate by the chemiluminescent association of NO and  $O({}^{3}P)$ . As the rate depends in part on the rate at which  $O({}^{1}D)$  is quenched to  $O({}^{3}P)$ , competitive quenching experiments enable relative quenching and reaction rates to be measured for  $O({}^{1}D)$ . Other considerations make it

possible to put the rates on an absolute basis, and the values obtained are all very high. All gases measured (other than the rare gases) give rates faster than 4  $\times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> sec<sup>-1</sup>. This work will soon appear in the Journal of Chemical Physics.<sup>11</sup>

b. N20 Photolysis. The active species produced in N<sub>2</sub>O photolysis are O(<sup>1</sup>D), O(<sup>1</sup>S), N<sub>2</sub>(A<sup>3</sup> $\Sigma$ ), N<sub>2</sub>(B<sup>3</sup> $\Pi$ ), and N(<sup>2</sup>D). A complete analysis of the quantum yields of excited species formed with 1470 Å radiation has been made and will be published in the Journal of Chemical Physics.<sup>12</sup> At shorter wavelengths, quenching measurements on the N<sub>2</sub> lst positive emission, the upper state of which is N<sub>2</sub>(B<sup>3</sup> $\Pi$ ), permit evaluation of quenching rate coefficients for N<sub>2</sub>(B<sup>3</sup> $\Pi$ ). Because of the previously investigated energy transfer from N<sub>2</sub>(A<sup>3</sup> $\Sigma$ ) to NO, resulting in excitation of NO to the emitting A<sup>2</sup> $\Sigma$  state (γ-bands), it has also been possible to measure quenching coefficients for N<sub>2</sub>(A<sup>3</sup> $\Sigma$ ). A paper covering energy transfer from these two states of N<sub>2</sub> is presently in press.

Observation of the 5577 Å emission from  $O({}^{1}S)$  has enabled us to make relative measurements of  $O({}^{1}S)$  quenching rate coefficients. Photolysis of CO<sub>2</sub> with an argon resonance lamp (1048 + 1067 Å) was also used to produce  $O({}^{1}S)$ . Results with the two sources of  $O({}^{1}S)$  were identical. This rules out secondary processes [e.g.,  $N_{2}(A^{3}\Sigma) + O({}^{3}P) \rightarrow O({}^{1}S) + N_{2}({}^{1}\Sigma)$ ] as a major source of  $O({}^{1}S)$  in our experiments and confirms that the quenching does indeed pertain to  $O({}^{1}S)$ . The work will appear in a future issue of the Journal of Chemical Physics.<sup>14</sup>

c. <u>Other Photolysis Experiments</u>. The emission observed from CO excited by 1470 Å irradiation was found to involve various triplet transitions. The system was investigated and it was found possible, by means of xenon photosensitization, to compare the effects of transferring equal amounts of energy by radiative and collisional processes. It was determined that excitation by radiation results in fluorescence principally from  $CO(d^3\Delta)_{\nu=7}$ , whereas collisional excitation produces fluorescence from various vibrational levels of the a'  ${}^3\Sigma$ ,  $d^3\Delta$ , and  $e^3\Sigma$  states. The work has been published.<sup>15</sup>

Photolysis of a number of simple gases has been carried out, using all the available resonance lamps, to see what excited fragments could

be produced and their emission detected. With the high sensitivity available with image tube spectroscopy, previously undetected emissions were observed with  $N_2^{0}$ , CO, CO<sub>2</sub>, and NO. A summary of this survey work has been published.<sup>16</sup>

d. <u>Pulsed Photolysis</u>. The photolysis work so far described has used continuous microwave excited UV resonance lamps as the photolysis sources. Quenching rate coefficients were always measured relatively, since it was never possible to measure the pertinent loss processes absolutely. The apparatus shown in Figs. 3 and 4 enables absolute quenching rates to be measured from the decay time of the emission between pulses. So far, this has been done for  $O({}^{1}S)$  with various quenching gases. Evaluation of the decay curves has shown that, after accounting for quenching and diffusion effects, there is a residual lifetime of 3 msec. This is either the radiative lifetime (which would be in marked disagreement with the 1 sec calculation of Garstang<sup>17</sup>) or the lifetime due to residual impurity quenching. Experiments are underway to resolve these alternatives.

Another species of interest is  $O_2(b^1\Sigma)$ , the source of the  $O_2$  atmospheric bands in the airglow. Certain aspects of its formation and destruction are not understood, and we feel that emission decay measurements, coupled with our previous studies, should shed light on this problem.

Energy transfer from  $N(^{2}D)$ , produced in  $N_{2}O$  photolysis at 1470 Å, will also be studied. In this case, direct detection of  $N(^{2}D)$  in emission is impossible because of its very long radiative lifetime (26 hours). In  $N_{2}O$ , the observed  $\beta$ -band emission is believed to result from the reactions

$$N(^{2}D) + N_{2}O \rightarrow NO(B^{2}\Pi) + N_{2}$$
  
 $NO(B^{2}\Pi) \rightarrow NO(X^{2}\Pi) + hv(\beta-bands)$ 

We have already demonstrated that the decay lifetime of the  $\beta$ -band emission is much longer than the radiative lifetime (2.5  $\times$  10<sup>-6</sup> sec) of

 $NO(B^2\Pi)$ . The measured lifetime must therefore be that of a precursor. Experiments to prove our conjecture that  $N(^2D)$  is the precursor and to determine the rate coefficients for its quenching by atmospheric constituents will be undertaken.

The pulsed photolysis lamp will also be used to determine the rate coefficients for energy transfer reactions involving  $N_2(A^3\Sigma)$  (using  $N_2^{\ 0}$  photolysis at 1470 Å as its source). These measurements should confirm the rate coefficients obtained when the  $N_2(A^3\Sigma)$  was excited by pulsed rf excitation of molecular nitrogen.

e. <u>Resonance Lamp Development</u>. In the  $O({}^{1}D)$  studies, the concentration of O atoms was measured by monitoring their chemiluminescent reaction with NO. Thus, NO was present in all the measurements. This was of little concern except when  $CO_{2}$  was quenching  $O({}^{1}D)$ . This is an important reaction because of its application to the chemistry of the atmospheres of Mars and Venus. The large discrepancy between our measurements and those of Noxon<sup>18</sup> for  $CO_{2}$  may be due to the presence of NO in our system. It is felt that  $CO_{3}$  is a possible product of the  $CO_{2}-O({}^{1}D)$  interaction, and widely different quenching rate coefficients obtained in the presence and absence of NO may indicate interaction between NO and  $CO_{3}$ . To determine  $O({}^{3}P)$  concentrations, in the absence of NO, a lamp is being developed to emit a sharp 1304 Å oxygen resonance line. This will enable  $O({}^{3}P)$  concentration to be determined by resonance line absorption or scattering.

# III FIELD OBSERVATIONS OF UPPER ATMOSPHERIC RELEASES

The objective of the work reported here is to obtain spectra of radiation associated with high altitude release of barium and strontium. The experiment was conducted during the nights of October 3 and 4, 1967; the rockets carrying the release material were launched from the Wallops Island range, and the optical equipment was set up at Langley Air Force Base.

Spectra were recorded with two instruments: a transmission spectrograph system employing an image intensifier tube and a spectrograph employing all reflecting optics for use in the ultraviolet region of the spectrum. Both instruments were modified for use on this project. These modifications have been described in a previous report.<sup>2</sup>

Figure 5 shows the emission of the cloud almost 24 minutes after release. Emission by ionized barium and no detectable emission by neutral



FIG. 5 SPECTRUM OBTAINED WITH IMAGE TUBE SPECTROGRAPH IN 10-sec EXPOSURE BEGINNING 1406 sec AFTER Ba-Sr RELEASE

barium or strontium characterize this late stage of the release. Wavelength calibration is provided by the airglow emissions of  $O(^{1}S)$  and  $O(^{1}D)$  at 5577 and 6300 Å, respectively, and by the HgI emission (presumably of terrestrial origin) at 5461, 5777, and 5790 Å (the latter two wavelengths constituting an unresolved doublet).

Figure 6 shows the build-up and decay of the emission of neutral strontium during the first two minutes after a Ba-Sr release. The decay of the emission of neutral strontium is followed out to 5 minu<sup>+</sup> is in Fig. 7, which also shows the characteristics of the development and decay of the 4554 Å emission of ionized barium.

These results serve to confirm that the SRI spectrographs can monitor the emission features of a Ba-Sr cloud from the first few seconds after release to the very late stages (30 minutes and longer) when the emission intensities are comparable with the airglow background.

Benefiting from the experience gained in the above experiments, we obtained much more spectrographic data on the subsequent Ba-Sr releases at Arecibo (Secede I). This work was done for ARPA under Contract F 30602-68-C-0076, and a Technical Report No. 1 (Classified Secret-RD) has been written.



FIG. 6 RELATIVE INTENSITY OF 4607Å EMISSION OF SrI vs. TIME



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FIG. 7 RELATIVE INTENSITIES OF 4607Å EMISSION OF SrI AND 4554Å EMISSION OF Ball vs. TIME

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