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I Spectrographic and Spectrometric Data of Project Firefly 1960.

II Spectrographic Studies of the Formation of Molecular Complexes between the Rare Gases and Elements which Have Low-Lying Metastable States.

III A Recording Interferometer for Determining the Temperature of Cesium Clouds Released in the Upper Atmosphere by Measuring Spectral Line Widths.

BY C. DEWEY COOPER
Department of Physics
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Athens, Ga.

Final Report
Contract No. AF 19(604)6163
30 December 1961

Prepared for
GEOPHYSICS RESEARCH DIRECTORATE
AIR FORCE CAMBRIDGE RESEARCH CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
BEDFORD, MASSACHUSETTS
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FINAL REPORT

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ABSTRACT

I. Spectrographic and Spectrometric Data of Firefly 1960 Releases.

Spectral data are presented for cesium and sodium releases in the upper atmosphere. The detection of the $A^2\Sigma \rightarrow X^2\Sigma$ transition of $A10$ shows that $A10$ is a by-product of the chemical release. Relative intensity data are discussed and a slitless spectrograph is proposed for future releases where low light levels are expected.

II. Spectrographic Studies of the Formation of Molecular Complexes between the Rare Gases and Elements which Have Low-Lying Metastable States.

A reprint "Visible Spectra of XeO and KrO" is included. An investigation of the spectra in the neighborhood of the "forbidden" Mg 4571A and Ca 6573A lines revealed no continua or bands when the elements were excited in the presence of argon with pressures as high as 6 atmospheres. The resonant lines (Mg 2852A and Ca 4227A) show asymmetric broadening.

The investigation of the spectrum of CO in an atmosphere of argon revealed an unassigned band around 3080A and unreported bands of the Fourth Positive system. Also, the forbidden lines of carbon 2964A ($5S_2 \rightarrow 3P_1$) and 2967A ($5S_2 \rightarrow 3P_2$) are observed as very intense lines.
III. A Recording Interferometer for Determining the Temperature of Cesium Clouds Released in the Upper Atmosphere by Measuring Spectral Line Widths.

The practical design of a recording interferometer is presented for measuring the line width of the Cs 4555A and Cs 4593A lines whenever they are emitted by cesium clouds in the upper atmosphere. The instrument uses 10 cm aperture quartz plates which are flat to within 1/37 λ as the components of a Fabry-Perot etalon. Line profiles are to be obtained by sweeping the interference pattern across a grid in front of a photomultiplier. The hfs of the cesium lines has been resolved with this instrument; but additional improvements are needed before satisfactory field-type operations will be possible.
OBJECTIVES

The objectives of this research have been the following:

I. To provide equipment and personnel in the field to make spectrographic studies of Firefly releases.

II. To perform spectrographic studies of the formation of molecular complexes between atmospheric gases and elements which have low-lying metastable states such as barium and calcium.

III. To investigate the spectral line broadening of cesium lines as a method of determining the temperature of cesium clouds which are placed in the upper atmosphere.

The main body of this report is divided into three sections with one section being devoted to each of the above objectives.

I. Spectrographic and Spectrometric Data of Firefly Releases.

EXPERIMENTAL PROCEDURE

Spectrographic coverage for a series of chemical releases in the upper atmosphere was provided in an effort to help identify the atomic or molecular species which were actually released or formed by a reaction with ambient species of the atmosphere. The following spectrographs were used in the visible region: A slit type spectrograph using a 600 grooves/mm blazed grating, an f/1.8 camera lens, and a 50 micron slit; an auroral type spectrograph utilizing a 600 groove/mm blazed grating, an f/0.8 Schmidt type camera lens, and an adjustable slit; and a slitless
spectrograph(1) composed of a blazed transmission grating with 600 grooves/mm, an f/1.1, 50 mm lens and a 35 mm Eyemo movie camera. This camera was used to record 4 frames per second for a minute after each firing. Several of the releases were observed with the prototype of the spectrometer(2) used by Fastie in the rocket observations of auroras [Fastie, Crosswhite, and Markham, 1961]. With this spectrometer the spectra between 4000A and 6000A were recorded every 12 seconds. Telescopic lenses were used to image the released chemical clouds on the slit of the spectrographs, and auxiliary telescopes were used for tracking purposes.

EXPERIMENTAL RESULTS

A. Spectra Obtained with Slit-Type Spectrographs.

The spectra which were recorded by slit spectrographs for alkali element releases are recorded in Table I. In this table the first four columns give the rocket code name, date, release time, and release altitude, respectively. An x in the remaining columns indicates the presence of the particular wavelength at the top of the column. For the sake of brevity the code name given in Table I will be used as the means of identifying the different releases discussed in this paper. The appearance

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(1) This slitless spectrograph was constructed and operated by the Georgia Tech Research Institute under contract AF 19(604)5467. The experimental data was analysed jointly under contract AF 19(604)5467 and AF 19(604)6163.

(2) We are grateful to Mr. Tom Markham of Air Force Cambridge Research Laboratories for making this instrument available.
Table I

Observed Spectra Firefly 1960

<table>
<thead>
<tr>
<th>Rocket Code Name</th>
<th>Date</th>
<th>Release Hr CST</th>
<th>Release Altitude Km</th>
<th>Na</th>
<th>Cs</th>
<th>Cs</th>
<th>Cs</th>
<th>Cs</th>
<th>Cs</th>
<th>Al0 Bands</th>
<th>Solar Scatter</th>
<th>Other Lines</th>
</tr>
</thead>
<tbody>
<tr>
<td>Margie</td>
<td>8/13</td>
<td>0437</td>
<td>74</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Marie</td>
<td>8/9</td>
<td>0438</td>
<td>82</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>Lola</td>
<td>8/15</td>
<td>0438</td>
<td>83</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>Peggy</td>
<td>8/16</td>
<td>0442</td>
<td>103</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>Olive</td>
<td>8/18</td>
<td>0442</td>
<td>106</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jennie</td>
<td>8/10</td>
<td>0437</td>
<td>109</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Susan</td>
<td>8/17</td>
<td>0442</td>
<td>114</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dolly</td>
<td>7/27</td>
<td>0421</td>
<td>115</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Li 6708</td>
</tr>
<tr>
<td>Betsy</td>
<td>8/88</td>
<td>0416</td>
<td>108</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
of the A10 bands confirms an earlier assignment of a band at 4850Å to A10 [Cooper 1959]. In this series of experiments a total of eight A10 bands have been observed. Spectrograms and additional details of the results may be found in the Firefly 1960 report [Cooper 1960].

B. Spectra Obtained with a Slitless Spectrograph.

For the releases above 100 km the slitless camera spectrograph recorded the cesium 4555Å and 4593Å spectral lines on the burst frame for the Olive release only. Other releases in this altitude region showed only as a continuum on the burst spectrograms. Below 100 km the rockets Margie and Lola provided both a continuum and many lines or bands on the burst spectrograms. For Lola these same lines were present on the 1/4 to 1/2 second (time after burst) exposure. Even though the zero order was not recorded on the frame, it was possible to measure the lines relative to the prominent cesium and sodium lines. The measured lines or bands for Lola are included in Table II where the wavelength measurements are accurate to within ±20Å and the intensities are given on an arbitrary scale. The wavelengths between 5256Å and 3943Å in Table II were also observed for the Margie release. The spectral region for wavelengths greater than 5300Å was not recorded for Margie with the slitless spectrograph.

C. Spectra Obtained with a Recording Photometer.

The spectrometer recorded the same visible spectra which were photographed with the slit spectrographs on most
Table II
Wavelengths for the Lola (83 km)
Release as Recorded by the Slitless Spectrograph

<table>
<thead>
<tr>
<th>Measured λ(A)</th>
<th>Intensities</th>
<th>Assignments</th>
<th>Measured λ(A)</th>
<th>Intensities</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>6017</td>
<td>30</td>
<td>6035Cs</td>
<td>4940*</td>
<td>10</td>
<td>4888A10</td>
</tr>
<tr>
<td>5907</td>
<td>5</td>
<td></td>
<td>4830</td>
<td></td>
<td>4842A10</td>
</tr>
<tr>
<td>5890</td>
<td>30</td>
<td>5890Na</td>
<td>4770*</td>
<td>5</td>
<td>4736A10</td>
</tr>
<tr>
<td>5839</td>
<td>30</td>
<td>5845Cs</td>
<td>4620</td>
<td></td>
<td>4648A10</td>
</tr>
<tr>
<td>5778</td>
<td>10</td>
<td></td>
<td>4591</td>
<td>10</td>
<td>4593Cs</td>
</tr>
<tr>
<td>5738</td>
<td>5</td>
<td>5746Cs</td>
<td>4558</td>
<td>10</td>
<td>4555Cs</td>
</tr>
<tr>
<td>5661</td>
<td>15</td>
<td>5664Cs</td>
<td>4122</td>
<td>5</td>
<td>4119Cs</td>
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<td>5632</td>
<td>15</td>
<td>5635Cs</td>
<td>4087</td>
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<td>4081Cs</td>
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<td>5475</td>
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<td>5466Cs</td>
<td>4032</td>
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<td>4035Cs</td>
</tr>
<tr>
<td>5409</td>
<td>10</td>
<td>5414Cs</td>
<td>3960</td>
<td>30</td>
<td>3961A1</td>
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<tr>
<td>5350</td>
<td>10</td>
<td>5350Cs</td>
<td>3943</td>
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<td>3944A1</td>
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<td>5256</td>
<td>5</td>
<td>5257Cs</td>
<td>3873</td>
<td>5</td>
<td>3876Cs</td>
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<tr>
<td>5230*</td>
<td>5</td>
<td>5161A10</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>5070</td>
<td></td>
<td>5102A10</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Band covers region between the bracketed values.
of the releases. A detailed report of these results are included because they have not been included in technical reports. The spectrometer traces which were obtained are separated into two groups: The low altitude releases below 100 km and those above 100 km.


The spectrophotometer traces of these clouds are difficult to interpret for at least two reasons. First, the scattered sunlight was much greater than expected and in many instances the recorder pen was driven off scale. Second, the peaks or absorptions which occur are not repeated and often appear several minutes after a release. This leads one to suspect that instrumental errors may be present.

a. Margie - 74 km height.

Margie, the lowest release, formed a white cloud that produced strong solar scatter and possibly some emission and absorption. Representative traces are given on page 9. The labeling on these traces as well as the other traces has the meanings given below. The B trace depicts the background just before the firing of the specified rocket. The B-16 and B-15.5 labels are special traces which were obtained of sky background at release time plus 16 and 15.5 minutes. All other traces are labeled with numerals to represent the number of the spectrometer trace following release time. Each trace required 12 seconds. Then trace number 2 was recorded between 12 and 24 seconds after release time and
trace number 6 between 60 and 72 seconds after release.

Traces 2, 5, and 6 show strong solar scatter with possible emission superimposed; however, measured peak positions do not repeat from trace to trace and one is inclined to attribute these variations to fluctuations produced by picking up different positions of the cloud as it drifts.

b. Marie - 82 km height.

Marie proved to be a strong scatterer of sunlight, but initially at least two discrete emissions were observed. Evidently the cloud was not in the field of view on trace 1 (See page 11). However, two strong lines or narrow band emissions appear on the second trace. The strongest of these is sodium at 5893A and the other one is found at 5360A. A plausible assignment of the 5360A radiation has not been obtained. Regrettably, the next three traces are off scale and a measure of the duration of this signal is not available.

Traces 6 and 7 shown in Fig. 2 for Marie, were obtained on a less sensitive scale than trace 2. Trace 6 shows emission peaks, but all successive traces show only solar scatter as is depicted by trace 7. The emission peak at 4850A can be A10. The other peak in trace 6 appears to have two components, one at 5200A and the other at 5255A. These peaks have not been assigned.

c. Lola - 83 km height.

Representative traces for the Lola release are given
on page 12. A hump is seen on trace 1 as the cloud enters the field of view. Then on trace 2 and 3 the pen is run off scale (see trace 2). Trace 5 was on scale and appears to show only solar scatter.

Traces 11 and 17 show unusual absorptions which are not repeated. It is believed that these resulted from instrumental errors or possible from absorption by low lying clouds.

2. Spectra of PEC Releases above 100 km.

Resonant line radiation from sodium and cesium were observed for Peggy, Olive, Jeannie, Susan and Betsy. Resonant scattering of the $A^2\Sigma \rightarrow X^2\Sigma$ bands of $A_10$ were observed for Jeannie and Susan.

a. Peggy - 103 km.

The white cloud which resulted from the release was tracked with the spectrometer and very weak sodium and cesium lines were observed for 50 seconds. Solar scatter from the cloud was high.

b. Olive - 106 km.

Weak cesium and sodium lines were observed for one minute before the recorder chart drive jammed. Solar scatter from the cloud was high during this period.

c. Jeannie - 109 km; Susan - 114 km.

Representative traces for Jeannie and Susan are shown on page 14. Strong resonant radiations from sodium, cesium, and $A_10$ were observed for both of these releases. The intensity measurements, on an arbitrary scale, for
these radiations are recorded in Table III. Corrections have been included for background radiation and the S11 response of the E.M.I. 9565B photomultiplier. The intensities of lines and bands may be compared since the total area under the curve was used instead of the peak intensities. Column one of this table provides the trace number for each 12-second trace. Intensity values are given in the next three columns for the combined cesium blue lines, the AlO bands, and the sodium yellow lines. Column five shows the ratio of the peak intensities of the 4555A and 4593A cesium lines.

**DISCUSSION**

The appearance of AlO as one of the release gases is definitely confirmed by the appearance of its spectrum on some of the burst releases and by the identification of the 0.0;0.1;1.0;1.1;2.1;2.2;2.3 and 3.2 bands of the A $^2\Sigma \rightarrow X ^2\Sigma$ transition which are observed due to the resonant scattering of sunlight. The method by which AlO is produced is not certain. Both AlO and Al spectra were observed on spectrograms of some of the initial bursts (see Table II). In addition, the AlO content in some of the clouds appears to fluctuate with time following the burst. This fact can be verified by a study of the intensity measurements given in Table III. The AlO radiation for the Jeannie release fails to show any intensity fluctuations with time, but the AlO intensity for the Susan release shows a very definite decrease between 50
Table III
Spectrometer Intensities of Radiations From Jeannie and Susan Releases.

<table>
<thead>
<tr>
<th>Trace Number</th>
<th>Jeannie</th>
<th>Susan</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trace Number</td>
<td>Cs $\text{Na}_{4555+}$</td>
<td>Al $\text{Na}_{4555+}^2$</td>
</tr>
<tr>
<td>1</td>
<td>9</td>
<td>23</td>
</tr>
<tr>
<td>2</td>
<td>13</td>
<td>7</td>
</tr>
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<td>3</td>
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<tr>
<td>4</td>
<td>13</td>
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<tr>
<td>5</td>
<td>13</td>
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</tr>
<tr>
<td>6</td>
<td>13</td>
<td>1</td>
</tr>
<tr>
<td>7</td>
<td>13</td>
<td>1</td>
</tr>
<tr>
<td>8</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>13</td>
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</tr>
<tr>
<td>10</td>
<td>13</td>
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</tr>
<tr>
<td>11</td>
<td>10</td>
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<td>14</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>13</td>
<td></td>
</tr>
</tbody>
</table>
70 seconds after release followed by an increase which returns it to the original level for approximately 2 minutes. This fluctuation of the Al radiation with no change in the cesium or sodium radiation represents a change in the total number of Al molecules in the field of view. The presence of Al in the initial burst probably results from the high temperature dissociation of Al₂O₃ which is the stable oxide resulting from the CsNO₃ and Al reaction. The variation in the amount of Al in the main cloud may result from a reaction of vaporized aluminum with ambient oxygen, a further dissociation of Al₂O₃, or a partial separation of Al from Cs and Na in the cloud. Existing experimental data are insufficient to permit a choice between these possible explanations.

Ideally, one would like to determine the density of the cesium atoms as a function of time by studying the intensity ratio of the 4555Å and 4593Å cesium lines [Blamont, Lory, and Courtès 1960]. Theoretically, for an optically thin cloud, k₁ ≪ 1, the intensity ratio should be 4 to 1. Our intensity measurements show considerable fluctuations from trace to trace and therefore the errors in such density measurements would render such data useless. Undoubtedly, the intensity fluctuations result primarily from the viewing of different portions of the cloud for the various traces. The measurements do indicate that after about 3 minutes the cloud can be considered as an optically thin cloud for the cesium blue lines.
Spectra of the releases at the time of burst showed continua except for Olive and the low altitude releases, Margie, and Lola, where line spectra were observed. These spectra for Margie and Lola have been assigned to cesium, sodium, aluminum, and A1O as shown in Table II. Poor resolution, which is inherent in slitless spectrograms, leaves some doubt about the assignment of a few of the observed lines to cesium.

Several very faint lines which were observed for the Jeannie and Peggy releases are recorded in Table I. Of these lines only the 5845A, 6305A and 6360A lines have been assigned. Apparently the 5845A is a cesium line, and as reported earlier [Cooper 1960] the other two are believed to be the oxygen red lines at 6300A and 6363A. This assignment is strengthened by similar observations by Blamont and co-workers [Blamont, Hieblot and Selzer, 1961].

PROPOSALS FOR THE FUTURE

A study of the experimental data has prompted the following proposals.

A. Use of A1O to Determine the Temperature of the Upper Atmosphere.

Now that A1O can be produced in the upper atmosphere it provides a means of measuring the temperature at the point of release. The simplest approach, from the spectral point of view, would use the sun as a source and observe the high-dispersion-absorption spectrum of A1O. Then if the A1O
cloud is not too dense, so that multiple scattering is not an important factor, the intensity distribution of the rotational lines is directly related to temperature. The altitude can be determined by an accompanying electron cloud.

With this experiment the difficult task will be the placing of the A10 between the observer and the sun. However, such a problem should be solvable using a rocket which seeks the sun using an infra-red detector.


The intensity of scattered light from artificial clouds of cesium in the upper atmosphere has a complicated dependence on the optical density of the cloud. The specific dependence has been determined assuming a plane layer of radiating atoms such as is needed for the twilight flash of sodium. Numerous references to this work may be found in Chamberlain's [1961] book. Attempts have been made toward solving this problem for rectangular-shaped clouds [Blamont, Lory, and Courtés 1960]. In the special case of cesium clouds let us center our attention on the 4555A and 4593A radiations. For optically thin clouds their intensity ratio for resonant scattering should be 4:1; however, in clouds which are dense enough to scatter all of the 4593A radiation then the intensity ratio should be 1:1. If the problem can be solved theoretically for a spherical cloud, then measurements of the relative intensities of the 4555A and 4593A radiations will give the
optical density of the cesium as a function of time. The measurements of the relative intensities of the two cesium blue lines can be obtained most reliably by the use of cameras and filters. (The spectrometer used in the research reported herein may give ambiguous data because of the inhomogeneity of the cloud and the narrow field of view of the spectrometer). It is suggested that three cameras be used to record the clouds with a narrow band filter for the two lines and another narrow filter for a region close by the blue lines so as to give a measure of the continuum in this region. With careful development and standardization an excellent measurement of the relative intensities of the lines could be obtained for any portion of the cloud.

c. Spectrograph for Recording Luminescent Cloud of Low Intensity and Short Duration.

Slit-type spectrographs necessarily limit the amount of light that may be used to produce a photographic image and the necessity for producing an image of the cloud on the entrance slit of the instrument severely limits the field of view. Because of this limitation it is difficult to obtain spectral information from a cloud of short duration using a slit-type instrument. A slitless spectrograph overcomes the above objection and may be used where the spectral source is a small distant one. Such an instrument produces separate images of the cloud for different spectral regions and the resolution depends only on the
number of grooves/mm of the diffraction grating. An instrument which uses a transmission grating is limited to a grating of 600 grooves/mm; however, if a reflection grating is used, 1800 grooves/mm gratings are available which will give a dispersion, and in this case a resolution, which is 3 times better than that provided by the transmission type. On the basis of these facts, an instrument using the following components is recommended for future point or trial release shots: An f/0.87 lens with a 76 mm focal length and a 30 degree field of view; an 1800 grooves/mm blazed grating with a (102 x 102)mm² ruled area, and a 70 mm recording film system. Such an instrument is under construction at the present time.

II Spectrographic Studies of the Formation of Molecular Complexes between the Rare Gases and Elements which Have Low-Lying States.


B. Spectra of Calcium and Magnesium in an Atmosphere of the Rare Gases.

The formation of weakly bound molecules of ArO, KrO, and XeO when oxygen is in the metastable \(^1S_0\) state prompted a spectroscopic investigation for the existence of similar molecules involving the rare gases and calcium
or magnesium. Both magnesium and calcium have $^3P$ states which are metastable relative to their $^1S_0$ ground states. Indeed, earlier studies of mercury by Oldenberg [1928], Kuhn [1932], and Preston [1937] have shown the existence of diffuse maxima near the 2537Å ($^3P_1 \rightarrow ^1S_0$) line of mercury when an electrical discharge is maintained in a mixture of mercury and the rare gases. These spectra indicate the existence of weakly bound Hg($^3P_1$) Ar($^1S_0$) molecules.

The present study utilized two different types of discharge tubes. An electrodeless tube [Cooper and Lichtenstein 1958] was used with quartz walls for pressures up to an atmosphere. This entire cell was heated to between 500°C and 600°C to maintain a sufficient vapor pressure of the calcium or magnesium. An arc discharge tube using the above elements as electrodes was used with rare gas pressures of 1, 4, and 6 atmospheres.

Spectra were obtained in the neighborhood of the Mg 4571Å ($^3P_1 \rightarrow ^1S_0$) and the Ca 6573Å ($^3P_1 \rightarrow ^1S_0$) lines using argon pressures up to 6 atmospheres. The intensities of these lines were increased relative to the allowed lines at the higher pressures, but the lines remained sharp and no diffuse bands or continua were observed.

Even though these experiments failed to show appreciable broadening for the lines originating from metastable levels, the resonant lines (Mg 2852Å and Ca 4227Å) show considerable broadening with definite asymmetric
shifts to longer wavelengths. Qualitatively, these shifts are very similar to those observed in absorption spectra [Ch'en and Takeo, 1957]. The quantitative study of the broadening of these lines has not been completed.

C. Spectra Obtained with Mixtures of Carbon Monoxide and Argon.

In an earlier experiment with oxygen and argon using an electrodeless discharge tube [Cooper and Lichtenstein 1958] the Triplet band system of CO was observed. The mechanism of exciting the levels that give rise to the Triplet system is of interest since these levels are metastable relative to the ground state. Experiments were initiated to explore the excitation mechanism of the observed spectra. Using essentially the same experimental arrangement as was employed for O₂ and Ar mentioned above, small quantities of oxygen and carbon monoxide along with an atmosphere of argon were admitted into an ozonizer type discharge tube and excited by a 4 Mc/sec exciter. In the first experiment a glass discharge tube was used and approximately 10 parts per million of both O₂ and CO were added to the argon. The spectra observed with this mixture were as follows: Triplet system of CO, Third Positive system of N₂, and an unassigned band system around 3080Å. A photograph of this unassigned band is shown in Plate IA and the measured wavelengths are given in Table IV. The bands heads are fairly distinct and are shaded toward shorter wavelengths.
Plate I

(A) (0,2) Third Positive CO

(B) Carbon 2967 A 2965 A

- 3086.3 A
- 3076.5
- 3085.2 A
- 3040.2 A
- 3022.7 A

(0,1) Third Positive CO
Table IV

Wavelengths of Band Heads in the Unassigned System

<table>
<thead>
<tr>
<th>Wavelengths</th>
</tr>
</thead>
<tbody>
<tr>
<td>3088.57 A</td>
</tr>
<tr>
<td>3086.33</td>
</tr>
<tr>
<td>3083.84</td>
</tr>
<tr>
<td>3081.50</td>
</tr>
<tr>
<td>3078.98</td>
</tr>
<tr>
<td>3076.51</td>
</tr>
<tr>
<td>3075.31</td>
</tr>
<tr>
<td>3072.31</td>
</tr>
<tr>
<td>3070.33</td>
</tr>
<tr>
<td>3068.29</td>
</tr>
<tr>
<td>3060.84</td>
</tr>
<tr>
<td>3058.21</td>
</tr>
<tr>
<td>3042.66</td>
</tr>
<tr>
<td>3040.24</td>
</tr>
<tr>
<td>3022.4</td>
</tr>
</tbody>
</table>

A group of ten band heads which are separated by about 24 cm\(^{-1}\) form the most intense band group of the system. Beyond this group toward shorter wavelengths the bands appear in pairs with a separation of about 26 cm\(^{-1}\). All of the observed bands of this system lie between the 0,1 and 0,2 bands of the Third Positive System of CO, which were observed along with the unknown bands. Several attempts to obtain this new band system using a quartz discharge tube have failed; therefore, the ultraviolet extent of the spectrum has not been determined. At the present time the band remains unassigned.

The spectra which were obtained with the quartz tube proved to be interesting even though the 3080 A bands were missing. The observed spectra may be classified in two categories: (A) Spectra when no impurities were observed, and (B) Spectra showing OH as an impurity.

In category (A) the following spectra were observed: The Triplet system, Third-Positive and 5B bands, and the Fourth Positive group of CO; the Swan system and a few bands of the Desladres-D'Azambuja's system of \(C_2\) the 5577 A line of oxygen and the carbon arc line at 2478 A. New bands of the Fourth Positive system which have not been reported
previously were observed. The measured wavelengths of these bands are recorded in Table V along with values which were computed by a formula given by Read [1934].

Table V

<table>
<thead>
<tr>
<th>ν'</th>
<th>ν''</th>
<th>λobs (A)</th>
<th>λcalc (A)</th>
<th>ν'</th>
<th>ν''</th>
<th>λobs (A)</th>
<th>λcalc (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>21</td>
<td>2523.70</td>
<td>2524.46</td>
<td>10</td>
<td>23</td>
<td>2832.12</td>
<td>2833.28</td>
</tr>
<tr>
<td>13</td>
<td>23</td>
<td>2590.00</td>
<td>2590.66</td>
<td>11</td>
<td>24</td>
<td>2866.13</td>
<td>2867.11</td>
</tr>
<tr>
<td>8</td>
<td>20</td>
<td>2649.78</td>
<td>2650.60</td>
<td>15</td>
<td>27</td>
<td>2891.93</td>
<td>2892.88</td>
</tr>
<tr>
<td>9</td>
<td>21</td>
<td>2679.77</td>
<td>2680.61</td>
<td>12</td>
<td>25</td>
<td>2901.66</td>
<td>2902.63</td>
</tr>
<tr>
<td>10</td>
<td>22</td>
<td>2711.22</td>
<td>2712.01</td>
<td>10</td>
<td>24</td>
<td>2962.72</td>
<td>2963.70</td>
</tr>
<tr>
<td>14</td>
<td>25</td>
<td>2734.86</td>
<td>2735.83</td>
<td>17</td>
<td>29</td>
<td>2977.80</td>
<td>2978.28</td>
</tr>
<tr>
<td>11</td>
<td>23</td>
<td>2744.03</td>
<td>2744.89</td>
<td>15</td>
<td>28</td>
<td>3018.99</td>
<td>3019.78</td>
</tr>
<tr>
<td>12</td>
<td>24</td>
<td>2778.39</td>
<td>2779.30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*These bands are partially covered by the Third Positive bands of CO.

When the same mixture of gases used to obtain the spectra of category (A) was excited at liquid air temperature, only the Swan bands of C₂ and the little known but very interesting 2964A (5S₂ → 3P₁) and 2967A (5S₂ → 3P₂) lines of carbon were observed. These lines will be discussed further in the next paragraph.

In category (B) the spectra showed that a small amount of OH was present in the discharge. In these spectra the Triplet system of CO and the Swan bands of C₂ were observed but no bands of the singlet systems of CO were observed. In the ultraviolet region two very intense lines were observed at 2964A and 2967A. These lines were reported earlier by Shenstone [1947] to be due to the (2s2p³)⁵S₂ → (2s² 2p²)⁴P₁,₂ transitions of carbon. The ⁵S₂ state is the tetravalent state of carbon. As may be seen
on Plate IB these lines are the only ones which appear under these experimental conditions, all other carbon lines are absent.

The appearance of the $^5S_2 \rightarrow ^3P_{1,2}$ carbon lines poses the problem of how the $^5S_2$ state gets excited. The production of the $^1S_0$ metastable level in an oxygen and argon mixture was explained as being due to a resonant transfer of energy from the $^3P_1 (11.5 \text{ ev})$ metastable state of argon to the dissociation of O$_2$ into O ($^1D_2$) and O ($^1S_0$). Such an explanation cannot be used for the production of C ($^5S_2$) from CO because the dissociation energy of CO alone is 11.1 ev. Also, a transfer of energy from the O ($^1S_0$) state to the C ($^5S_2$) state can be ruled out by the spin selection rule even though the two states have almost the same energy. The most likely method of producing the metastable oxygen and carbon now appears to be due to the production of a large number of free electrons in the discharge with 4 to 5 ev of energy. Possibly there is a tie-in between the excitation of metastable carbon ($^5S_2$) and the metastable upper state of the triplet system of CO. This investigation has not been completed.

III A Recording Interferometer for Determining the Temperature of Cesium Clouds Released in the Upper Atmosphere by Measuring Spectral Line Widths.

INTRODUCTION

A spectral line, free from hyperfine structure, is of finite width due to four distinct processes commonly
referred to as: natural broadening, the Doppler effect, pressure broadening, and the Stark effect. In general the natural width of a spectrum line is much smaller than the Doppler width. Since the cesium cloud is not electrically excited and in regions of low pressure, both the Stark effect and pressure broadening are negligible. Therefore any measured broadening of the Cs 4555 radiation resulting from resonant scattering of sunlight from optically thin cesium clouds in the upper atmosphere will be predominately due to the Doppler effect.

One method for the determination of upper atmosphere temperatures is to measure the Doppler width of the Cs 4555 line with a high-resolution instrument such as the Fabry-Perot interferometer. The Doppler width is proportional to the square-root of the absolute temperature and inversely proportional to the square-root of the atomic mass of the emitting atom.

Cesium atoms ejected from rocket flights at twilight produce a visible cloud capable of being tracked with the portable photoelectric Fabry-Perot interferometer. The Cs 4555A or Cs 4593A radiations can be isolated by using narrow-band interference filters and then passed through a Fabry-Perot etalon followed by a long focal length lens to produce circular fringe patterns. An aperture can be used in the focal plane of the lens to allow only the light flux from a small portion of one of the fringes to pass through for measurement. The flux passing through this aperture can be recorded using a photomultiplier and appropriate accessories.
The order of the etalon may be linearly changed by varying the air density between the plates causing the circular fringes to expand or contract. The light flux from different portions of the central fringe will be recorded as a result of this scanning process. Once instrument parameters are determined one can extract from the recording (line profile) the half-intensity width and temperature.

EXPERIMENTAL PROCEDURE

The major components of the recording interferometer are described below.

1. Fabry-Perot etalon.

The Fabry-Perot etalon used for this project consists essentially of two quartz plates with surfaces optically flat to within 1/37 of a wavelength over a 10 cm aperture. The inner surfaces are coated with five layers of dielectric films giving a reflectivity of approximately 0.9 at 4555A. The absorption is not more than .01%. The plates themselves are made slightly prismatic to avoid disturbing effects due to reflections at the outer uncoated surfaces. The plates are separated by a fixed spacer consisting of three optically worked studs so that the planes defined by the studs are as nearly parallel as possible. Fine adjustments can be made by varying the spring pressure which holds the plates against the projecting studs. At present, two spacers are available permitting a plate separation of 1.25 cm and 2.50 cm thereby providing orders of interference of 54880 and 109760, respectively.

Two other related characteristics of the Fabry-Perot
etalon which are important in the present research problem is the finesse and the transparence of the etalon. The finesse is a measure of the sharpness of the fringes which increase with reflectivity. For a reflectivity of 0.9 the finesse is approximately 30. The transparence or peak-transmission appears in the ratio of transmitted to incident intensity when absorption due to the dielectric coatings are considered. For a given reflectivity, the effect of absorption is to diminish the intensity of the transmitted radiation by a factor called the transparence or peak-transmission. For an absorption of 0.01% and 0.9 reflectivity, the peak-transmission is 0.81. The peak-transmission is found to decrease with increasing finesse. Thus high values of both peak-transmission and finesse (or contrast factor) are incompatible requirements.

It should be noted that there is an upper limit of fringe sharpness which cannot be exceeded whatever the reflectivity of the coatings. This value of finesse depends on the form and magnitude of the departure from plane parallelism. That is, in general the plate separation always varies over the aperture. Plate imperfections are more pronounced at higher values of reflectivity.

Finally, a word about the resolving power and spectral range of the Fabry-Perot etalon. The resolving power depends on two quantities, the order of interference and the reflectivity (or finesse) of the etalon plates. The range of wavelengths which can be examined without one order overlapping the next must be greater than the line width at half-
intensity. The wavelength difference corresponding to a displacement of one order is called the spectral range. The spectral range is inversely proportional to the plate separation, so that an increase of resolving power obtained by increasing the plate separation is accomplished by a proportionate reduction of the spectral range. The resolving power is important because the theoretical half-widths of the interference patterns must be less than the half-width of the lines to be observed and the hyperfine structure of the line should be resolved. The ground state, $^2S_{1/2}$ of cesium consists of two levels separated by 0.3066 cm\(^{-1}\) which gives rise to this same wave number separation between the two hfs components of both the 4555A and 4593A lines. Assuming the temperatures given for the ARDC model atmosphere, the temperatures between 85 km and 150 km will be between 1650 K and 10000 K. The corresponding half-widths for cesium lines due to Doppler broadening is computed to be 0.0174 cm\(^{-1}\) and 0.0430 cm\(^{-1}\), respectively. The Fabry-Perot interferometer with a reflectivity of 0.9 and plate separation of 1.25 cm and 2.50 cm will have resolving powers of 1.63 \times 10^6 and 3.27 \times 10^6, respectively. Thus a doublet with a minimum separation of 0.0134 cm\(^{-1}\) should be resolved for the 1.25 cm plate separation and the corresponding wave number difference for the 2.50 cm spacer should be 0.0067 cm\(^{-1}\). This resolution is more than ample to resolve the hfs. In fact, since the free spectral range for the 2.50 cm spacer is 0.2 cm\(^{-1}\), the m\(^{th}\) order of interference for the $\lambda_2$ component of the doublet will fall about half way between
the m-1 and m-2 orders for $\lambda_1$. Consequently, the spectral range available for observation of line broadening is 0.1 cm$^{-1}$. This spectral range should be greater than twice the maximum half-width to be measured, or 0.086 cm$^{-1}$ in this case, to prevent overlapping of the interference fringes. Thus a plate separation much greater than 2.50 cm would not be usable. Also, it should be noted that a separation much less than 1.25 cm would not be practical if a line half-width of 0.017 cm$^{-1}$ (low temperature value) is to be measured. The final choice between the 1.25 cm and 2.50 cm spacers will depend upon the experimental data to be obtained from a temperature-controlled cesium lamp. The minimum acceptable resolving power will be used since the light flux which reaches the detector is decreased when the resolving power is increased.

2. Filter and Lens System.

The Cs 4555A and 4593A radiation will be isolated from the other light by placing interference filters in front of the Fabry-Perot etalon. Since it is necessary to have the etalon in an airtight chamber the interference filters also serve as a window for the incident radiation. Both the Cs 4555A and Cs 4593A interference filters have a peak transmittance between 45% to 50% at their respective wavelengths. Their bands pass at half-width does not exceed 15Å. The filters have a 4 in. usable aperture.

The quasi-monochromatic light reaching the etalon plates is brought to focus on a circular aperture centered on the optical axis with a f/2.5, 12 in. focal length lens. The flux passing through this aperture is received by a
second lens, (f/2.5, 3 in. focal length), which projects the light onto the photocathode of a 1P21 tube.


The scanning of the fringe system is achieved by linearly varying the pressure in the etalon gap. This is accomplished by the back-and-forth motion of a piston operated by a motor-driven linear-displacement cam. The pressure change caused by the change in volume is approximately 5 cm of Hg. This pressure variation is sufficient for sweeping two complete orders of interference. Hence, with a cam speed of 12 rpm the rate of sweeping is 24 fringe patterns per minute. This scanning speed allows a study of any rapidly changing temperature variation which might occur in the cesium cloud.

Pressure variations within the airtight chamber are measured with a reluctance pressure transducer, the output being fed into a recorder.

4. Radiation Detection.

On the basis of previous reports involving the detection of extremely low light levels the RCA 1P21 9-stage photomultiplier seems most favorable. This tube is selected primarily because of its spectral response and low dark current. Because the small photocurrents involved are of the same order of magnitude as the dark current, a refrigerant will be used. The output of the photomultiplier is amplified and fed into an automatic recorder.

5. Instrument Width.

One cannot obtain an accurate measure of the source width and the corresponding temperature from the recorded
fringe profile alone. The fringe profile will consist of the true source broadening plus instrument broadening. The instrument width will be determined experimentally using the known width of the 4358A line of Hg 198.

As part of the interferometer calibration, profiles of the cesium lines will be obtained from a temperature-controlled cesium lamp. The results of these data will determine whether it will be more accurate to obtain the temperature from the half-width measurements or from a matching of complete line profiles with those obtained at a known temperature.

6. Comparison of Li and Cs for Temperature Determination.

Since the Doppler broadening of a spectral line in wave numbers is inversely proportional to both the wavelength and the square root of the atomic weight of the element involved, it is easy to show that over a given temperature range the Doppler broadening for lithium (6707A) is about 3 times greater than that for cesium (4555A). Thus the measurements of the Li line half-width should provide more accurate temperature measurements. However, practical problems arise whenever photomultiplier detecting of the 6707A line is considered. Even the tri-alkali cathode surfaces are only 1/3 as sensitive to the 6700A radiation as they are to radiation at 4500A. Still more important, the dark current on the best tri-alkali photomultipliers is a factor of 10 higher than that available on the 1P21 tube. Consequently, the intensity of the Cs 4555A line can be about 30 times weaker than the 6700A line and still
be detected. Then the chances of obtaining enough light to record from an optically thin Cs cloud is better than from a Li cloud. If the density of the Li cloud is increased to too high a value, then multiple absorption and emission within the cloud will alter the line shape. If the experimental data show that the interferometer has more than adequate sensitivity for the Cs lines then it would be advisable to change the optics of the instruments for observation of the Li 6700A line.

7. Experimental Results.

For the purpose of testing the instrument we have prepared a low pressure cesium source which is excited by microwaves. At present we have been successful in resolving the splitting in both the cesium 4555A and 4593A lines. However, details of the line width has been hampered by unexpected noise. Tests show that this undesirable noise cannot be assigned to either dark current or amplifier noise. The present hypothesis is that this noise is due to air-turbulence between the etalon plates causing a variational effect during the scanning process. This possibility is presently under investigation.
REFERENCES

Blamont, J. E., J. Hiéblot and E. Selzer, Compt. rend. 252, 3317(1961).


Kuhn, H. and O. Oldenberg, Phys. Rev. 41, 72(1932).

Oldenberg, O., Z. Physik 47, 184(1928).


Read, D. N., Phys. Rev. 46, 571(1934).

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