METAL OXIDE STUDIES

General Electric Company
Space Science Lab.

Sponsored by
Defense Advanced Research Projects Agency
ARPA Order No. 1649

Approved for public release; distribution unlimited.

The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the Defense Advanced Research Projects Agency or the U. S. Government.

Reproduced by
NATIONAL TECHNICAL INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151

Rome Air Development Center
Air Force Systems Command
Griffiss Air Force Base, New York
When US Government drawings, specifications, or other data are used for any purpose other than a definitely related government procurement operation, the government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded, by implication or otherwise, as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.
Emission and absorption spectra over mixtures of liquid uranium-urania have been obtained using the carbon-tube furnace facility. In the temperature range of approximately 2100°C to 2400°C a complex system of bands has been observed in the region of 4800 Å to 7000 Å. The wavelength region from 5900 Å to 6000 Å is especially noteworthy since it contains a very intense highly dense band system. By comparison with the temperature coefficient of a known uranium line it was shown that the most intense feature in this region was due to either UO or UO₂. No complete analysis has been carried out, however, preliminary indications from the complexity of the spectra points to UO₂ as the most likely species giving rise to the observed spectra.

Flame studies have been initiated using UF₆ seeded into cyanogen/oxygen and hydrogen/nitrous oxide flames. Spectra of these flames have been observed and are completely different in nature from the furnace results. The flame spectra appear to be continuous with no line structure evident. The predominant uranium species in these flames should be the higher oxides, e.g. UO₃, rather than U, UO, or UO₂. Further work is continuing.

The oscillator strength of the (0, 0) and the (1, 1) band of the E₁Σ⁺ → X₁Σ⁻ transition in ThO has been obtained. The spectra were observed in absorption over mixtures of liquid thorium-thoria and total absorption measurements of several rotational lines in the band were carried out. From a knowledge of the vapor pressure of ThO at various temperatures a curve growth was constructed and the oscillator strength obtained. f₀,₀ was found to be approximately 0.08. From the relative intensity of the (1, 1) band head to the (0, 0) head, f₁,₁ was found to be approximately 0.06. Further work is continuing on other bands for ThO.
<table>
<thead>
<tr>
<th>KEY WORDS</th>
<th>LINK A</th>
<th>LINK B</th>
<th>LINK C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ROLE</td>
<td>WT</td>
<td>ROLE</td>
</tr>
<tr>
<td>Uranium oxides</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thorium oxide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spectra</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oscillator strengths</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
METAL OXIDE STUDIES

Dr. Milton J. Linevsky

Contractor: General Electric Co., Space Science Lab
Contract Number: F30602-69-C-0380
Effective Date of Contract: 1 July 1969
Contract Expiration Date: 31 December 1972
Amount of Contract: $264,725.00
Program Code Number: 2E20

Principal Investigator: Dr. Milton J. Linovsky
Phone: 215 962-3495

Project Engineer: Joseph J. Simons
Phone: 315 330-3451

Approved for public release; distribution unlimited.

This research was supported by the Defense Advanced Research Projects Agency of the Department of Defense and was monitored by Joseph J. Simons, RADC (OCSE), GAFB, NY 13440 under Contract F30602-69-C-0380.
FOREWORD

This study is being performed at General Electric Company, Space Sciences Laboratory, King of Prussia, Pa., 19406, for the Advanced Research Projects Agency, Washington, D. C., Rome Air Development Center Griffiss Air Force Base, New York, is monitoring the study for ARPA, under Contract F30602-69-C-0380, Project 1649. Mr. Joseph J. Simons (OCSE) is the RADC Project Engineer.

Distribution of this report is limited by the Mutual Security Act of 1949.

This technical report has been reviewed and is approved.

PUBLICATION REVIEW

This technical report has been reviewed and is approved.

[Signature]

RADC Project Engineer
SUMMARY

Emission and absorption spectra over mixtures of liquid uranium-urania have been obtained using the carbon-tube furnace facility. In the temperature range of approximately 2100°C to 2400°C a complex system of bands has been observed in the region of 4800 Å to 7000 Å. The wavelength region from 5900 Å to 6000 Å is especially noteworthy since it contains a very intense highly dense band system. By comparison with the temperature coefficient of a known uranium line it was shown that the most intense feature in this region was due to either UO or UO₂. No complete analysis has been carried out, however, preliminary indications from the complexity of the spectra points to UO₂ as the most likely species giving rise to the observed spectra.

Flame studies have been initiated using UF₆ seeded into cyanogen/oxygen and hydrogen/nitrous oxide flames. Spectra of these flames have been observed and are completely different in nature from the furnace results. The flame spectra appear to be continuous with no line structure evident. The predominant uranium species in these flames should be the higher oxides, e.g. UO₃, rather than U, UO, or UO₂. Further work is continuing.

The oscillator strength of the (0, 0) and the (1, 1) band of the E¹Σ⁻→ X¹Σ⁺ transition in ThO has been obtained. The spectra were observed in absorption over mixtures of liquid thorium-thoria and total absorption measurements of several rotational lines in the band were carried out. From a knowledge of the vapor pressure of ThO at various temperatures, a curve of growth was constructed and the oscillator strength obtained. f₀,0 was found to be approximately 0.08. From the relative intensity of the (1, 1) band head to the (0, 0) head, f₁,₁ was found to be approximately 0.06. Further work is continuing on other bands for ThO.
## TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. URANIUM OXIDES</td>
<td>3</td>
</tr>
<tr>
<td>1. Furnace Studies</td>
<td>3</td>
</tr>
<tr>
<td>2. Flame Studies</td>
<td>8</td>
</tr>
<tr>
<td>III. THORIUM OXIDE</td>
<td>11</td>
</tr>
<tr>
<td>1. Furnace Studies-Oscillator Strengths</td>
<td>11</td>
</tr>
<tr>
<td>IV. DISCUSSIONS AND RECOMMENDATIONS</td>
<td>18</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENT</td>
<td>19</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>20</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>v</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>v</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1</td>
<td>Uranium Oxide Spectra - Low Resolution</td>
<td>4</td>
</tr>
<tr>
<td>Figure 2</td>
<td>Uranium Oxide Spectra - Moderate Resolution</td>
<td>5</td>
</tr>
<tr>
<td>Figure 3</td>
<td>Absorption Intensity 5915A UI vs 5935A Feature</td>
<td>7</td>
</tr>
<tr>
<td>Figure 4</td>
<td>Flame Spectra UF$_6$ Seeded C$_2$N$_2$/O$_2$ Flame</td>
<td>10</td>
</tr>
<tr>
<td>Figure 5</td>
<td>ThO Absorption Spectrum E$^1\Sigma$ - X$^1\Sigma$</td>
<td>13</td>
</tr>
<tr>
<td>Figure 6</td>
<td>Curve of Growth for ThO E$^1\Sigma$ - X$^1\Sigma$</td>
<td>17</td>
</tr>
</tbody>
</table>

LIST OF TABLES

<table>
<thead>
<tr>
<th>Table I</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table I</td>
<td>Total Absorption Measurement for ThO E$^1\Sigma$ - X$^1\Sigma$ (0, 0)</td>
<td>14</td>
</tr>
</tbody>
</table>
I. INTRODUCTION

This report describes a continuation of an experimental study aimed at obtaining information relevant to several ARPA programs. Of particular concern is the evaluation of the importance of certain metal oxides to Project Ivy Owl.

The objectives of the past six months' efforts were: 1) to perform spectroscopic studies on the uranium/uranium oxide system in an attempt to obtain in a controlled manner the absorption spectrum of UO and to further the understanding of U/O spectroscopy and 2) attempt to obtain oscillation strength information on various transitions in the electronic spectrum of ThO.

Attempts to obtain characteristic band spectra of UO have been for the most part unsuccessful (Ref. 1 - 3). Indeed only the results of Gatterer (Ref. 1) on arc discharges between uranium electrodes have indicated any discrete-like spectra due to uranium containing species. The studies in seeded flames (Ref. 2) and by laser vaporization "blow-off" (Ref. 3) have yielded at best what appears to be continuum-like spectra in the visible and near u.v. Based on existing thermodynamic information for the species UO, UO₂, and UO₃ (see Ackermann et al Ref. 4 and DeMaria et al Ref. 5), it can be shown that in the temperature range of several thousand degrees, at equilibrium, under conditions similar to those encountered in flames and possibly in blow-off experiments, the predominant vapor species is the highest oxide, i.e. UO₃. Therefore, it is not surprising to find that flames and laser blow-off plumes have yielded little information concerning the spectroscopy of UO or UO₂. In order to favor the existence of these lower oxides a more reducing environment must be established. In the study reported by Ackermann et al (Ref. 4), the predominant molecular vapor species over mixtures of uranium and uranium oxide was found to be UO and UO₂. Similarly these species were observed in the mass spectrometric investigation by DeMaria et al (Ref. 5), on the vaporization from mixtures of uranium and aluminum oxide. In the former study, for example, at 2000°C the partial pressures of UO and UO₂ in equilibrium with urania - liquid
uranium was found to be approximately $5 \times 10^{-6}$ atm. and $6 \times 10^{-7}$ atm. respectively. It is interesting to note that the corresponding partial pressure of O-atoms was found to be less than $10^{-13}$ atm. Clearly in order to produce spectroscopically significant qualities of UO and/or UO$_2$ oxygen must be excluded from the system.

In the present study the carbon - tube furnace facility was used to generate molecular uranium oxide species under conditions very similar to those reported above. In this fashion spectra both in absorption and emission have been obtained which are line-like in nature and most likely due to UO or UO$_2$. No complete analysis has yet been carried out. Preliminary indications point to UO$_2$ as the principle species observed.

Seeded flame studies have also been initiated in order to investigate the radiative properties of higher oxide species. These studies have just gotten underway and the results are preliminary. The nature of the emission thus far observed is completely different from that seen in the furnace.

In the case of ThO, the spectroscopy of this molecule appears to be fairly well understood and many transitions have been assigned (see a recent review by Wentink and Spindler Ref. 6). However, no absolute intensity data have been reported on any of these transitions. Again the carbon - tube furnace was used to generate a known concentration of ThO in the gas phase and subsequent absorption measurements on the $E^1\Sigma - \chi^1\Sigma$ transition allowed the determination of the oscillation strengths for the (0, 0) and (1, 1) bands.
II. URANIUM OXIDES

1. Furnace Studies

The carbon tube furnace facility has been described in detail elsewhere (Ref. 7). Approximately equal amounts of powdered uranium metal and uranium dioxide (obtained from the K and K Laboratories) were thoroughly mixed and loaded into a tantalum boat contained in a tantalum-lined cylindrical carbon cell. The inside length of the cell was approximately 4 1/2 inches. Tantalum lined carbon end pieces with 1/4 inch openings were fitted into the ends of the cell and served to allow light to pass through the cell. The cell was placed in the center of the carbon tube furnace and thoroughly degassed under vacuum at approximately 1500°C. After several hours of degassing, helium gas (O₂ impurities removed by passing over red-hot titanium metal) was admitted to the furnace to a pressure of 1 atm. The furnace temperature was gradually raised and spectral observations were made both in absorption and emission using the 2 meter Bausch and Lomb dual grating spectrograph.

At approximately 2000°C the onset of a complex system of bands was observed. Under relatively low resolution these bands appeared to be diffused in nature and extended from approximately 4800 Å to 7000 Å. A very intense line like feature at 5935 Å is especially evident. In addition, a great many uranium I lines are seen and have been identified by comparison with reported spectra (Ref. 8 and 9). The nominal plate dispersion was approximately 8 Å/mm. Similarly, spectra have also been observed at higher resolution in the 2nd order of the 30,000 line/inch grating. The nominal plate dispersion was approximately 2 Å/mm. In this case those features especially in the 5900 Å to 6000 Å region which previously appeared diffuse in nature now are seen to be line-like with many close lying lines throughout. In Figure 1 is shown a typical absorption spectrum at relatively low resolution in the spectral region of approximately 5000 Å to 6900 Å. This spectrum was obtained using a high pressure Xenon arc as a source and the cell temperature was approximately 2300°C. (The uranium oxide spectrum is the upper dark lined spectra while the lower white lined
Figure 1. Uranium Oxide Spectra - Low Resolution
spectrum is an iron comparison. The abrupt change in shading at approximately 6067 Å is not real. Uranium I lines have been identified. The corresponding absorption spectrum obtained at higher resolution in the 5900 Å to 6000 Å region is shown in Figure 2. Wavelength identification of significant uranium oxide features is included in this spectrum. The densely packed line structure should be noted.

These spectra were also observed photometrically using a Spex 1500 monochromator both in absorption and emission. An EMI 9558, S-20 photomultiplier and P. A. R. lock-in amplifier and chopper were used to monitor and record the spectrum. In order to help determine the nature of the carrier of the strong feature at 5935 Å, the temperature dependence of the absorption centered at 5935 Å relative to the strong uranium I line at 5915 Å was carried out. Ackermann et al (Ref. 4) have given the following observed heats of vaporization of U, UO and UO$_2$ from mixtures of urania-liquid uranium: 116, 123, and 138 kcal/mole respectively. The uranium I line at 5915 Å involves the ground state and, if the feature at 5935 Å also involves the ground states of either UO or UO$_2$, then from the above heats of vaporization it is expected that the two features will have the same temperature dependency within approximately 20%. This is fully borne out by the results of the photometric measurements made on these features. A log-log plot of the quantity $T \log \frac{I_0}{I}$ for 5915 Å (UI) against that for the unknown features at 5935 Å ($T \log \frac{I_0}{I}$ is proportional to the vapor pressure) yields a straight line whose slope is $1 \pm 0.2$. This is shown in Figure 3. Therefore, it must be concluded that the strong feature at 5935 Å is due to the uranium oxide UO or UO$_2$. It is not possible from the temperature dependency to decide which oxide gives rise to the observed spectra.

Attempts to carry out a vibrational analysis of the spectra shown in Figures 1 and 2 have met with very limited success. Abramowitz (Ref. 10) using matrix isolation techniques, has reported the vibrational spacing for supposedly ground state U$^{16}$O to be 776 cm$^{-1}$. A matrix shift of approximately 10% to 15% for this molecule would not be unreasonable. Therefore, a vibrational spacing of approximately 800 ± 100 cm$^{-1}$ would be expected to be reflected in the spectra given in
Figure 3. Absorption Intensity 5915 A UI vs 5935 A Feature

SLOPE = 1 ± 0.2
Figure 1 and 2. No progression with this spacing is observed. On the other hand, if UO$_2$ is the carrier of the observed spectra, progressions in both the symmetric stretching mode, $\nu_1$, and the bending mode $\nu_2$ should be evident. Abramowitz (Ref. 10) has also reported a value of approximately 81 cm$^{-1}$ for $\nu_2$ and a value of 874 cm$^{-1}$ for one of the stretching modes in U$^{16}$O$_2$. These frequencies again being observed in argon matrices. From an examination of the spectra reported here especially that given in Figure 2, it is possible to pick out a progression of bands that could possibly correspond to the bending mode spacing (i.e. 60 cm$^{-1}$ to 90 cm$^{-1}$). Another progression in this spectrum appears to have a spacing around 400 cm$^{-1}$. This could conceivably correspond to the spacing due to a progression in $\nu_1$. At the present time it has not been possible to carry out a complete vibrational analysis. However, it is felt that UO$_2$ is most likely responsible for the observed spectra.

2. Flame Studies

A preliminary investigation of uranium oxide spectra in high temperature flames has been initiated. Uranium hexafluoride has been seeded in small quantities into cyanogen-oxygen and nitrous oxide-hydrogen flames burned at atmospheric pressure. The addition of UF$_6$ has been found to give rise to relatively strong continuous radiation in the wavelength region from about 2000 $\mu$m to at least 8000 $\mu$m. Extension of these measurements to the infrared region are currently planned.

Nitrous oxide - hydrogen and cyanogen - oxygen flames were supported on a water cooled Meker type burner. Gases were individually metered and premixed before entering the burner chamber. Small quantities of UF$_6$, approximately 5% in argon, were introduced into the unburned gases, spectra were taken of both the seeded and unseeded flames and the contribution to radiation by uranium species obtained by difference. Spectroscopic measurements in the flame were made in a volume element approximately 3 cm above the burner top (reaction zone) where the flame gases are in thermodynamic equilibrium. Spectra were obtained using an EG&G 580 series spectral radiometer equipped with both UV and visible gratings, and also with
a Bausch and Lomb 2 meter grating spectrograph.

Figure 4 shows typical wavelength distributions of the uranium species emission in a cyanogen oxygen flame having a calculated adiabatic flame temperature of about 3900°K. The continuum emission from somewhat cooler burning UF$_6$ seeded nitrous oxide/hydrogen flames (T $\approx$ 2900°K) was similar to that in the cyanogen oxygen flames. In both types of flames the continuum is observed to have intensity maximum at about 3500 and 5900 Å and an apparent short wavelength cut off at about 2200 Å.

In separate experiments, equivalent or greater flows of COF$_2$ were substituted for the UF$_6$/Ar mixtures seeded into the cyanogen oxygen flames. Absence of enhanced continuum emission in these experiments indicated that fluorine atom radiative recombination was not responsible for the continuum observed upon UF$_6$ addition. Uranium seeding into the cyanogen oxygen flame by entrainment of sprayed droplets of aqueous uranyl nitrate solution into unburned gas flows resulted in a spectrum similar to that observed with UF$_6$ but at reduced intensity. On the basis of these experiments it was concluded that the continuous emission originated from a uranium oxide species.

Detailed examination of the emission in the wavelength region 5600 - 6100 Å using the Bausch and Lomb spectrograph revealed that the radiation was truly continuous. Unlike the spectra observed in the furnace, discrete line structure could not be observed at high resolution.

As has been indicated previously, UO$_3$ is expected to be the major uranium oxide species present in the flames. Therefore, it is not surprising to find that the flame spectra are completely different from those observed in the furnace where U, UO and UO$_2$ are the major uranium containing species. At the present time, the processes leading to the observed continuum are unknown. However it is felt that the species involved may include UO$_3$ or more complex oxides and since these species may be important in disturbed environments, a more thorough study of the flame spectra is warranted.
FUEL/O₂ = 0.78
T = 3968°K

Figure 4. Flame Spectra UF₆ Seeded C₂N₂/O₂ Flame
III. **THORIUM OXIDE**

1. Furnace Studies - Oscillator Strengths

ThO is characterized by extensive band spectra throughout the visible and near infrared regions. The analyses of several of these systems are fairly complete and the understanding of the ThO spectroscopy as compared to UO appears to be well in hand, (Ref. 6, 11). No absolute intensity data have been reported on any transitions for ThO. In light of the importance of ThO and the lack of intensity measurements for this molecule an experimental study was undertaken to obtain intensity information. The technique used was entirely analogous to that employed in the BaO study recently carried out in this laboratory (Ref. 12). Known partial pressures of ThO were generated by heating a mixture of liquid thorium and thoria to various temperatures.

Total absorption measurements were made on several rotational lines in the $E^1\Sigma \rightarrow X^1\Sigma$ system and the oscillator strengths for ThO (0,0) and (1,1) bands deduced. It should be noted that various electronic band systems have been observed in this study in absorption and it is anticipated that other electronic systems of ThO will be investigated in the near future.

In a fashion similar to that used in the uranium oxide studies, the carbon tube furnace was used to vaporize a mixture of liquid thorium-thoria so as to generate a known concentration of ThO. A mixture of equal amounts of thorium metal and thoria were loaded into a tantalum lined cylindrical carbon cell. The cell was 4½ inches long and had tantalum lined carbon and end pieces with ¼ inch openings. The cell was degassed at approximately 1500°C under vacuum then pressurized to 1 atm. helium. Spectra were observed with the 2 meter B&L spectrograph and the Spex 1500 spectrometer.

It was found that the intensity of the bands slowly decreased with time at constant temperature. Apparently there is a decrease in the activity of thorium metal because of its slow solution into the thoria. Therefore, all quantitative measurements
were made as quickly as possible using a fresh mixture of thorium/thoria for each
determination and with the B&L spectrograph rather than the scanning spectrometer.

A conventional optical arrangement was employed. This consisted of a 150-w
Osram high pressure xenon light source whose beam was collimated and allowed to
pass through the furnace. The beam was then focused to allow diaphragming out of
unwanted light from the hot furnace walls and then refocused on to the slit of the
spectrograph with a cylindrical quartz lens. A rotating step sector was used to cal-
ibrate each photographic plate so that relative intensity measurements could be made.
10 µm slits were used with the 30,000 line/inch grating in the 1st order which gave a
nominal plate dispersion of approximately 4Å/mm. Estman Kodak type III-F plates
were used to photograph the spectra. Optical densities were recorded directly with
a Joyce-Loebl double beam microdensitometer.

Spectra of the $E^1\Sigma \rightarrow X^1\Sigma$ system was recorded at temperatures between
2180°C to 2345°C. A typical spectrum is shown in Figure 5. Indicated in this figure
are the rotational lines selected for quantitative total absorption determinations.
These were chosen on the basis of being least overlapped by other features. The
total absorption i.e.

$$\int_{0}^{\infty} \frac{I_0 - I}{I_0} \, d\nu$$

(where I is the intensity at a frequency, $\nu$, along a line profile,) were determined
directly from the microdensitometer traces. These results at various temperatures
are given in Table 1.

Assuming optically thin conditions, the total absorption, $A$, is given by (see
Ref. 13)

$$A = \frac{\pi e^2}{mc} Nf \ell \quad \text{(1)}$$

$$= 2.654 \times 10^{-2} Nf \ell$$

where $\ell$ is the path length, $e$ and $m$ the charge and mass of the electron, $N$, the
concentrations in molecules/cc of absorbers and $f$ the oscillator strength of
TABLE I

TOTAL ABSORPTION MEASUREMENT FOR THO

\[ E^{1\Sigma} \rightarrow X^{1\Sigma} (0,0) \]

<table>
<thead>
<tr>
<th>TEMPERATURE (^{0}\text{K})</th>
<th>( P(45) )</th>
<th>( P(46) )</th>
<th>( P(47) )</th>
<th>( P(48) )</th>
<th>( P(62) )</th>
<th>( P(63) )</th>
<th>( P(64) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2607</td>
<td>1.72</td>
<td>1.72</td>
<td>2.11</td>
<td>1.87</td>
<td>1.91</td>
<td>1.91</td>
<td>2.04</td>
</tr>
<tr>
<td>2520</td>
<td>1.01</td>
<td>1.06</td>
<td>1.05</td>
<td>1.24</td>
<td>1.10</td>
<td>1.10</td>
<td>1.16</td>
</tr>
<tr>
<td>2453</td>
<td>0.93</td>
<td>0.91</td>
<td>0.80</td>
<td>0.78</td>
<td>0.90</td>
<td>--</td>
<td>0.90</td>
</tr>
<tr>
<td>2503</td>
<td>1.22</td>
<td>1.09</td>
<td>1.11</td>
<td>1.28</td>
<td>1.34</td>
<td>1.44</td>
<td>1.39</td>
</tr>
<tr>
<td>2618</td>
<td>2.25</td>
<td>1.99</td>
<td>2.51</td>
<td>2.45</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>2562</td>
<td>1.35</td>
<td>1.33</td>
<td>1.34</td>
<td>1.51</td>
<td>1.75</td>
<td>1.53</td>
<td>1.54</td>
</tr>
</tbody>
</table>
the individual rotational line. The rotational line oscillator strengths are related
to the so-called band oscillator strength by:

\[ f_{\text{line}} = f_{\text{band}} \frac{S_j}{2j + 1} \]  \hspace{1cm} (2)

where \( S_j \) is the rotational line strength and \( j \) the rotational quantum number. The
number of absorbers in any rotational level of the ground state is given by:

\[ N = N_T (2j + 1) e^{-F_j/kT}/Q \]  \hspace{1cm} (3)

where \( N_T \) is the total concentration of molecules, \( F_j \) is the rotational energy of
the absorbing state and \( Q \) is the partition function. Substituting (3) and (2) into
(1) gives:

\[ A = 2.654 \times 10^{-2} f_{\text{band}} t N_T S_j e^{-F_j/kT}/Q \]  \hspace{1cm} (4)

or

\[ A = 2.654 \times 10^{-2} f_{\text{band}} t N_{j \nu} \]  \hspace{1cm} (5)

where

\[ N_{j \nu} = N_T S_j e^{-F_j/kT} \]  \hspace{1cm} (6)

The quantity \( N_T \) was obtained from measured vapor pressures of ThO over mixtures
of liquid thorium/thoria. Several sets of vapor pressure data for ThO are available
in the literature. In the present case an average of the vapor pressure data reported
by Darnell and McCollum (Ref. 14) and by Ackermann, Rauh and Thorn (Ref. 15) was
used to derive values of \( N_T \). Differences up to a factor of four between these two
sets of data were encountered. Therefore, the derived \( N_T \) values could be in error
by this amount. The partition function, \( Q \), at the various temperatures was calcul-
ated from the free energy functions given by Brewer and Rosenblatt (Ref. 16) while
the rotational energy levels for ground state ThO were taken from the observed
spectrum given by Edvinsson et al (Ref. 15). \( S_j \) for a \( ^1\Sigma \rightarrow ^1\Sigma \) transition is
given by (Ref. 17):

\[ S_j = J + 1 \text{ for R} \]  \hspace{1cm} (7)

\[ S_j = J \text{ for P} \]  \hspace{1cm} (8)
\( \ell \) was taken to be 11.4 cm.

A plot of \( I \) vs the quantity \( 2.654 \times 10^{-2} \ell N_{jV} \) (equation 5) is shown in Figure 6. Although a great deal of scatter is evident a relatively good straight line can be placed through the points and the origin. The slope of this line yields directly the band oscillator strength \( f_{0,0} = 0.08 \).

The oscillator strength for the corresponding (1,1) band in the \( E^1\Sigma \Rightarrow X^1\Sigma \) system was estimated from the relative intensities of the (1,1) band at 6146.42 Å to that of the (0,0) band at 6121.43 Å and the ratio of populations in the first vibrational state to that of the ground state, i.e.

\[
\frac{f_{1,1}}{f_{0,0}} = \frac{I_{1,1}}{I_{0,0}} \times \frac{N_0}{N_1}
\]  

(9)

\( N_0/N_1 \) was calculated using the spectroscopic constants of Edvinsson (Ref. 5). \( f_{1,1} \) was found to be approximately equal to 0.06. The ratio \( f_{0,0}/f_{1,1} \) compares favorably with the ratio of the corresponding Frank Condon factors, i.e. \( g_{0,0}/g_{1,1} \), as obtained from a recent report by Wentink and Spindler (Ref. 6).

\[
f_{0,0}/f_{1,1} = 1.33
\]

\[
g_{0,0}/g_{1,1} = 1.36
\]

As mentioned earlier the largest source of error in these determinations is most likely due to the uncertainty in the vapor pressures of ThO. Based on two sets of results this error could be as large as a factor of four. Until more reliable vapor pressure information becomes available, this uncertainty must be retained.
Figure 6. Curve of Growth for ThO $E^1\Sigma \rightarrow X^1\Sigma$

CURVE of GROWTH
For
THO $E'^\Sigma \rightarrow X'^\Sigma (0,0)$

$A\sec^{-1} \times 10^{-9}$

$2.654 \times 10^{-2} \ln N_{uv} \times 10^{-10}$

$P_{45}$

$P_{46}$

$P_{47}$

$P_{48}$

$P_{62}$

$P_{63}$

$P_{64}$
IV. DISCUSSIONS AND RECOMMENDATIONS

It has been possible using the carbon tube furnace and strong reducing environments to obtain discrete spectra for either UO or UO$_2$. These spectra appear to be the best available to date.

It has been tentatively concluded, based on gross vibrational structure, that these spectra are most likely due to UO$_2$ rather than UO. The extreme complexity of the spectra is further evidence for the carrier being polyatomic rather than diatomic. The question as to the electronic spectrum of UO still remains unanswered. A technique similar to that used by Edvinsson et al (Ref. 15) for generating ThO spectra, viz. microwave discharge through a mixture of uranium and iodine in a neon carrier gas has been attempted with negative results. It is anticipated that during the next reporting period, excitation of UO spectra by microwave discharges through various UF$_6$ mixtures will be attempted. Work will continue on the interpretation of the furnace spectra.

It is felt that the results of the flame studies, initiated during the latter half of this reporting period, can be significant to the interests of Ivy Owl. Up until now only UO and UO$_2$ were being considered as important neutral species. Clearly when appreciable quantities of oxygen are also present, higher oxides such as UO$_3$ must also be considered. Further work on the seeded flames is being carried out.

It appears that reliable results on the oscillator strengths of various electronic transitions for ThO can be obtained from absorption measurements using the carbon tube furnace. Although the system presently studied is perhaps one of the simplest in the ThO spectra, extension to other transition should be quite feasible. It is anticipated that several other bands systems for ThO will be investigated.
ACKNOWLEDGEMENT

The author would like to express his appreciation to Dr. Ralph Carabetta for his able assistance with the flame measurements.
REFERENCES


