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FLAME OPTIMIZATION FOR THE SPECTROSCOPIC ANALYSIS OF  
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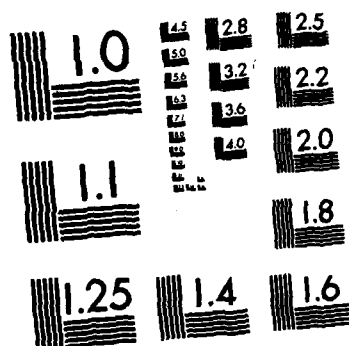
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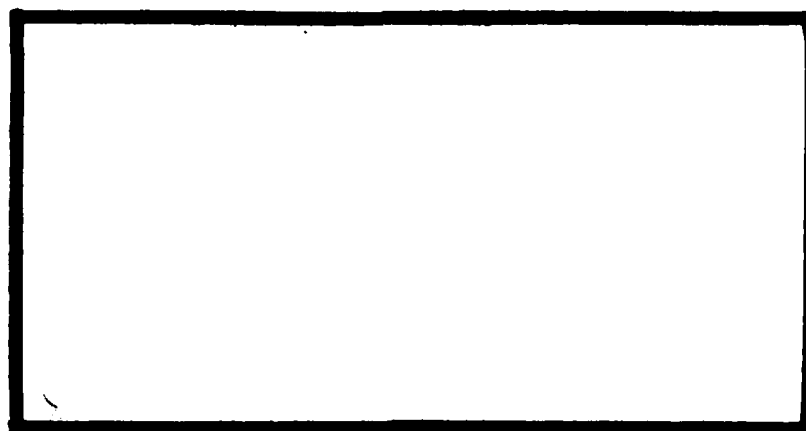


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FLAME OPTIMIZATION FOR THE  
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CHEMILUMINESCENCE FROM LEAD OXIDE

THESIS

AFIT/GEP/PH/82D-9

John W. Glessner  
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CHEMILUMINESCENCE FROM LEAD OXIDE

THESIS

Presented to the Faculty of the School of Engineering  
of the Air Force Institute of Technology

Air University

in Partial Fulfillment of the  
Requirements for the Degree of  
Master of Science

by

John W. Glessner, B.S.

1Lt

USAF

Graduate Engineering Physics

December 1982

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## Preface

This research is part of an ongoing effort at AFIT to develop the capability and expertise to perform spectroscopy of diatomic metal oxides using a flow tube reactor. I am glad to be a part of this effort, and I am proud of my contribution to it. I have found this thesis to be a tremendous learning experience.

I wish to thank Dr. Ernest Dorko, my advisor, for his guidance during preparation of the manuscript. I wish to extend my appreciation to the personnel of the AFIT Machine Shop, especially Mr. Ron Ruley and Mr. Carl Short for their interest in this thesis and their fast and excellent work in making components for the flow tube. I also thank Captain Robert Hartley for many stimulating discussions of matters dealing with my thesis that helped me solve problems and reach new ones. Most of all, I thank my wife and companion, Rosemarie, for her never-ending support, understanding, and love.

John W. Glessner

(This thesis was typed by Sharon Gabriel)

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### Abstract

A flow tube reactor was used to produce a chemiluminescent flame by the reaction of lead vapor with oxygen. The flow tube geometry, furnace design, and reactant mixing has been optimized to produce maximum flame emission for extended periods of time. Reaction chemistry was found to be sensitive to specific reactant mixing technique. A mass balance of 98% allowed the flux of lead into the reaction area to be determined to be approximately  $3 \times 10^{18}$  atoms/cm<sup>2</sup>sec. The lead oxide chemiluminescent flame, whose temperature was measured to be 175° C, was spectroscopically analyzed using a Jarrel-Ash 0.5 m monochrometer with a photomultiplier tube detector. Measurements of the B-X, A-X, and a-X transitions led to the determination of the following spectroscopic constants (in cm<sup>-1</sup>).

| <u>State</u> | <u>T<sub>e</sub></u> | <u><math>\bar{w}_e</math></u> | <u><math>\bar{w}_e x_e</math></u> |
|--------------|----------------------|-------------------------------|-----------------------------------|
| B            | 22296.9              | 495.8                         | 2.22                              |
| A            | 19851.4              | 453.7                         | 2.05                              |
| a            | 16025.9              | 483.1                         | 2.81                              |
| X            | 0                    | 719.3                         | 3.49                              |

FLAME OPTIMIZATION FOR THE  
SPECTROSCOPIC ANALYSIS OF THE  
CHEMILUMINESCENCE FROM LEAD OXIDE

I. Introduction

Background

A thorough spectroscopic study of lead oxide (PbO) chemiluminescence is a necessary prerequisite before PbO can be considered as a candidate molecule for a chemical electronic transition laser. Researchers at the Air Force Institute of Technology (AFIT) are currently alone in studying the PbO chemiluminescent spectra. At AFIT, Snyder used a flow tube reactor built by Koym (Ref 1) to study the flame emission produced by the oxidation of lead with nitrous oxide and oxygen (Ref 2). Snyder was able to obtain low resolution spectra using a 0.25 meter monochrometer with 0.5 mm slit widths. To better analyze the PbO molecule, higher resolution spectra are desirable. Obtaining higher resolution spectra requires narrow monochrometer slit widths. For a given flame intensity, as slit width is reduced for increased resolution, signal strength is reduced. Recording a spectrum using narrow slit widths demands high detectivity or bright flame emission or both. Maximizing PbO flame emission forms the basis for this thesis.

### Problem

The purpose of this thesis was to optimize the performance of a flow tube reactor to maximize PbO chemiluminescent flame emission. Additionally, spectra of emissions produced by the reaction



where PbO is produced in electronically excited state which were required to provide baseline spectra for the electronic transitions. Finally, spectroscopic constants were to be calculated for the electronic states of PbO from the data.

### Approach

Furnace designs and oxidizer mixing techniques were varied to achieve maximum flame emission. Spectroscopy was performed conventionally using a 0.5 meter monochrometer. Least squares analysis of spectroscopic data was used to obtain spectroscopic constants for the PbO molecule.

## II. Theory

### Introduction

This section will develop some background to understand the spectroscopy of PbO. After a discussion of the spectroscopy of diatomic molecules, a detailed analysis of the correlation between the excited states of the PbO molecule and its constituent atoms will be presented. Next, the reaction exothermicities of lead oxidation reactions will be discussed. Then a literature review of earlier work on PbO spectroscopy will be presented.

### Spectroscopy

The energy state of a diatomic molecule can be analyzed using the Born-Oppenheimer Approximation (Ref 3):

$$E = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}} \quad (2)$$

The energies of the transitions follow the Bohr-Einstein Law (Ref 4:1):

$$\Delta E = h\nu = hc\bar{\nu} \quad (3)$$

When this result is linked to the Born-Oppenheimer Approximation, the result is

$$\bar{\nu} = \bar{\nu}_{\text{electronic}} + \bar{\nu}_{\text{vibrational}} + \bar{\nu}_{\text{rotational}} \quad (4)$$

An electronic transition possesses a vibrational course structure and a rotational fine structure because

$$\bar{\nu}_e \approx 10^3 \bar{\nu}_v \approx 10^6 \bar{\nu}_r \quad (5)$$

Except in high resolution work, the rotational energy changes are neglected, so that the analysis of the vibrational spectrum of the molecule can be performed.

A vibrating diatomic molecule acts as an anharmonic oscillator, which can be represented by the Morse potential energy curve. Its vibrating energy, by this model, is

$$E(v) = hcw_e(v+\frac{1}{2}) - hcw_e x_e(v+\frac{1}{2})^2 + hcw_e y_e(v+\frac{1}{2})^3 + \dots \quad (6)$$

where  $v$  is the vibrational quantum number,  $hcw_e$  equals the vibrational energy  $h\nu$ , and  $x_e$  and  $y_e$  are the anharmonicity constants (Ref 3). The energies of all possible transitions between different vibrational levels of the electronic states can be obtained by use of the equation

$$\begin{aligned} \bar{\nu}(v', v'') &= T'_e + w'_e(v'+\frac{1}{2}) - w'_e x'_e(v'+\frac{1}{2}) + \dots \\ &\quad - w''_e(v''+\frac{1}{2}) + w''_e x''_e(v''+\frac{1}{2}) + \dots \quad (7) \end{aligned}$$

where  $T_e$  is the difference between ground state energies of the two electronic states,  $v'$  is the upper state quantum number, and  $v''$  is the lower state quantum number (Ref 5:151). The selection rule for transitions of this type is (Ref 3)

$$v' - v'' = \Delta v = 0, \pm 1, \pm 2, \dots \quad (8)$$

Transitions can be grouped into families called progressions and series. Transitions from the same upper state to different lower states represent a  $v''$  progression. Likewise,  $v'$  progressions exist. A series consists of transitions where the vibrational quantum number is the same in both the upper and lower electronic states. Figure 1 shows examples of progressions and series.

All the possible vibrational transitions between two energy levels are arranged in a Deslandres Table (Ref 5:40), schematically shown in Figure 2. The  $v'$  progressions form columns,  $v''$  progressions form rows, and series form the main diagonal. When the energy of the transitions are assigned to the proper  $(v', v'')$  transition, the columns formed by the energy differences between successive pairs in a row will be equal, and the rows formed by successive pairs in a column will be equal, within experimental error limits (Ref 4:122). This correspondence gives a good check on the accuracy of the transition assignments.

Although there is basically no selection rule for the vibrational transitions discussed here, not all transitions

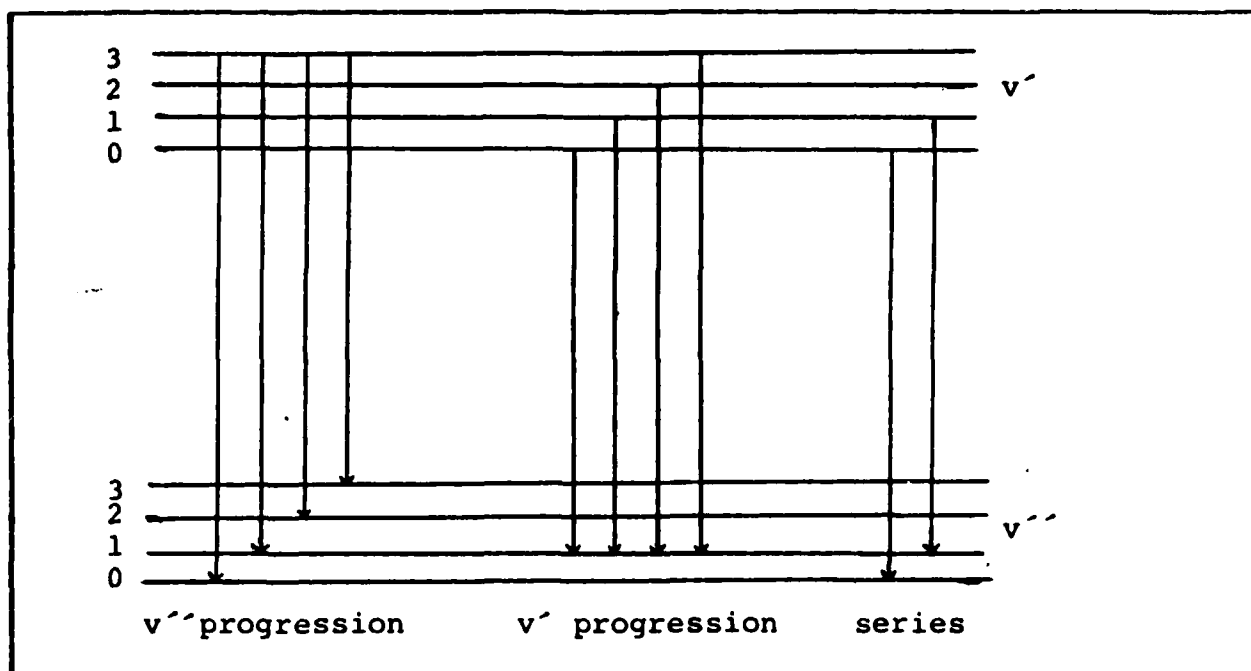


Figure 1. Progressions and Series

|        | $v''$ |       |       |       |       |           |
|--------|-------|-------|-------|-------|-------|-----------|
|        | 0     | 1     | 2     | 3     | 4     | 5         |
| 0      | (0,0) | (0,1) | (0,2) | (0,3) | (0,4) | (0,5) ... |
| 1      | (1,0) | (1,1) | (1,2) | (1,3) | (1,4) | (1,5) ... |
| 2      | (2,0) | (2,1) | (2,2) | (2,3) | (2,4) | (2,5) ... |
| 3      | (3,0) | (3,1) | (3,2) | (3,3) | (3,4) | (3,5) ... |
| $v'$ 4 | (4,0) | (4,1) | (4,2) | (4,3) | (4,4) | (4,5) ... |
| 5      | (5,0) | (5,1) | (5,2) | (5,3) | (5,4) | (5,5) ... |
| 6      | (6,0) | (6,1) | (6,2) | (6,3) | (6,4) | (6,5) ... |
| 7      | (7,0) | (7,1) | (7,2) | (7,3) | (7,4) | (7,5) ... |
| 8      | (8,0) | (8,1) | (8,2) | (8,3) | (8,4) | (8,5) ... |

Figure 2. Deslandres Table (Ref 5:40)

are observed and not all observed transitions are of equal intensity. These observations can be explained by considering the relative positions of the potential energy curves for the two states in question, and by considering the Frank-Condon Principle. The Frank-Condon Principle states that an electronic transition occurs so rapidly that the vibrating molecule does not change its internuclear distance or its momentum during the transition (Ref 3). This, on the potential energy curves shown in Figure 3, means the molecule executes a "vertical" transition to the lower state. While doing so, the molecule maintains constant internuclear spacing. Hence, not all transitions have equal probability. In Figure 3, the  $v' = 0$  to  $v'' = 0,1$  set of transitions has a very low probability of occurrence. In a spectrum, it is expected that the intensities of the vibrational bands will vary and some bands may be missing altogether.

Mathematically, the Frank-Condon Principle gives the overlap integral of the wave functions of the two states. The following development is taken from References 4 and 5. The emission intensity of a transition is given by

$$I_{nm} = N_n h c \bar{\nu}_{nm} A_{nm} \quad (9)$$

where

$I_{nm}$  = intensity of the n to m transition

$N_n$  = population of the upper state n

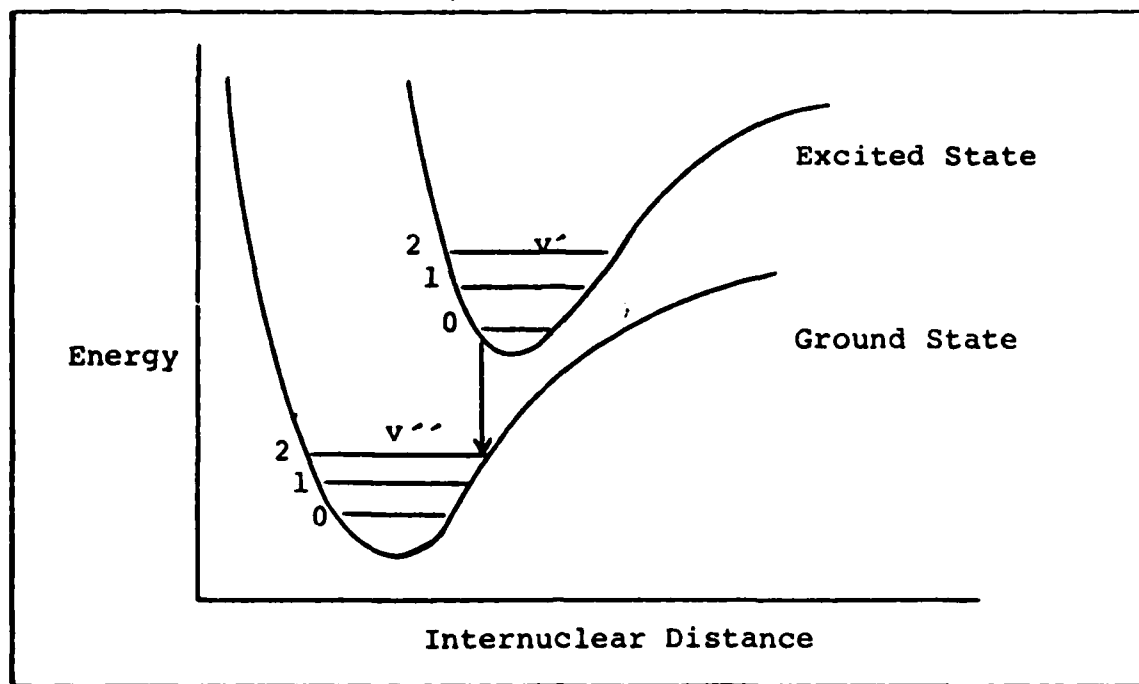


Figure 3. Frank-Condon Principle

$$hc\bar{\nu}_{nm} = \text{energy of emitted photon}$$

$$A_{nm} = \text{probability of transition}$$

The probability of a transition, or Einstein's A coefficient, is given by

$$A_{nm} = \frac{64\pi^4\bar{\nu}_{nm}^3}{3h} |\vec{R}_{nm}|^2 \quad (10)$$

where

$$\vec{R}_{nm} = \int \psi_n^* \vec{M} \psi_m dt \quad (11)$$

and  $\vec{M}$  is the electric dipole moment.

The wave functions are separable as part electronic and part vibrational,

$$\Psi = \psi_e \psi_v = \psi_e(r, R) \psi_v(R) \quad (12)$$

where  $R$  is the internuclear distance and  $r$  is nuclear coordinates. The electric dipole moment can be modeled as part electronic and part nuclear,

$$\vec{M} = \vec{M}_e + \vec{M}_R = M_e(r) + M_n(R) \quad (13)$$

Thus, substituting Eqs (12) and (13) into Eq (11) gives

$$\vec{R}_{nm} = \int \psi_e^{n*} \psi_v^{n*} M_e \psi_e^m \psi_v^m dt + \int \psi_e^{n*} \psi_v^{n*} M_n \psi_e^m \psi_v^m dt \quad (14)$$

or, rearranging

$$\vec{R}_{nm} = \int (\int \psi_e^{n*} M_e \psi_e^m dr) \psi_v^{n*} \psi_v^m dR + \int \psi_e^{n*} \psi_e^m dr \int \psi_v^{n*} M_n \psi_v^m dR \quad (15)$$

But  $\int \psi_e^{n*} \psi_e^m dr = 0$  if  $n \neq m$  since the  $\psi$ 's are orthogonal.

Define  $\int \psi_e^{n*} M_e \psi_e^m dr \equiv R_e(R)$  as the electronic transition moment. Then  $\vec{R}_{nm}$  is simply

$$\vec{R}_{nm} = \int R_e(R) \psi_n^* \psi_m dR \quad (16)$$

By the Frank-Condon Principle, the  $R$  dependence of  $R_e(R)$

is weak, so that during a transition

$$R_e(R) \approx \text{constant} \equiv \bar{R}_r \quad (17)$$

Then

$$\bar{R}_{nm} = \bar{R}_e \int \psi_n^* \psi_m dR \quad (18)$$

where the integral is called the wavefunction overlap integral. Finally, the intensity of a transition is given as

$$I_{nm} = \frac{N_n 64\pi^4 \bar{\nu}^4}{3} \bar{R}_e^2 \left| \int \psi_n^* \psi_m dR \right|^2 \quad (19)$$

From this it is shown that the intensity is proportional to the upper state population and the overlap integral.

In addition to predicting transition intensities, the Frank-Condon Principle also predicts an intensity maximum at a  $v''$  value that is determined by the relative position of the minima of the two potential energy curves (Ref 5:197). This can be seen with the aid of Figure 4. During vibration, the molecule spends more time at the turning points of the motion. Therefore, there are two  $v''$  values for which the probability of the transition from a given  $v'$  is a maximum, those for which the overlap integral is also a maximum. One of these is at small  $v''$ , the second at a larger  $v''$ .

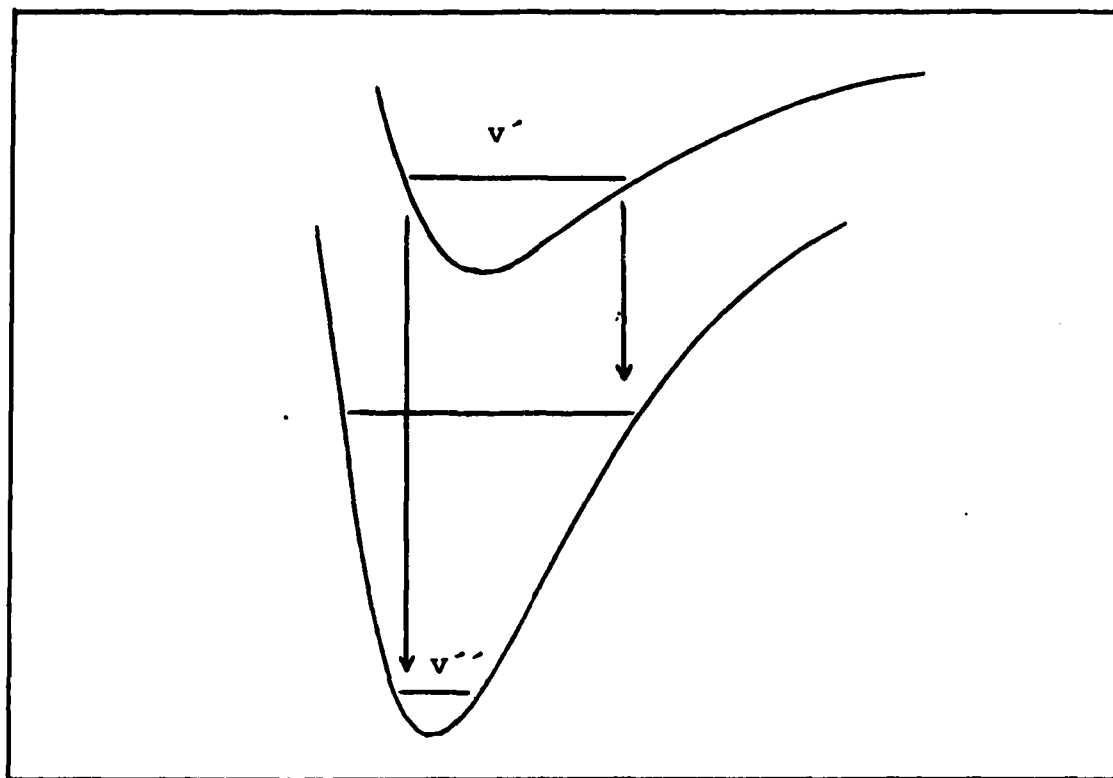


Figure 4. Transition Intensity Maxima (Ref 5:197)

If the intensity of the bands is plotted on a Deslandres Table, the most intense bands form a parabolic curve whose axis is the principle diagonal. This curve is called the Condon parabola (Ref 5:198). The width of the Condon parabola increases with increasing internuclear separation between the upper and lower states. Generally, the wider the Condon parabola, the greater will be the number of bands that appear in the band system. Also, the Condon parabola will develop only when a large number of successive vibrational levels of the upper state are about equally populated (Ref 5:198).

Under low resolution, a vibrational spectrum consists of a series of broad bands. The banded structure is due to

the non-resolved rotational transitions within the vibrational transition. The bands have a sharply defined edge, called the band head, where the intensity drops rapidly to a minimum. On the other side of the band peak, the intensity drops off slowly; this is called shading. The band head is usually very close to the band origin. The band origin corresponds to the transition between two rotationless states (Ref 5:112). When the band origin is not resolved, the band head is used in its place as the energy of that transition.

#### Correlation of Atomic States

The valence electronic configuration for lead is  $6s^2 6p^2$ . The  $p^2$  equivalent electrons ( $l = 1$ ,  $s = \frac{1}{2}$ ) give rise to 15 distinct energy states (Ref 4:38). These states are listed for both LS coupling and jj coupling in Table I. The state of highest multiplicity has the lowest energy, and the state of lowest J has the lowest energy (Ref 3). A correlation diagram for the  $p^2$  equivalent electrons is shown in Figure 5.

The emission lines of lead have been measured (Ref 4:45). They are shown in Table II. The splitting of the triplet P state denotes jj coupling, but this is far from pure jj coupling because the  $^3P$  multiplets are still grouped together and distinct from the  $^1S$  and  $^1D$  states (Ref 4:46).

The valence configuration for oxygen is  $2s^2 2p^4$ . The  $p^4$  electrons fill one orbital and half fill two others. This situation can be analyzed as two half filled orbitals; i.e.,

| <u>LS Coupling</u> | <u>jj Coupling</u> | <u>States</u> |
|--------------------|--------------------|---------------|
| $^1D_2$            | $J = 2$            | 5             |
| $^1S_0$            | $J = 0$            | 1             |
| $^3P_2$            | $J = 2$            | 5             |
| $^3P_1$            | $J = 1$            | 3             |
| $^3P_0$            | $J = 0$            | 1             |

Table I. Valence Electron States of Lead

| <u>Line</u> | <u>Energy</u><br><u>(cm<sup>-1</sup>)</u> | <u>Wavelength</u><br><u>(Å)</u> |
|-------------|-------------------------------------------|---------------------------------|
| $^1S_0$     | 29466                                     | 3393                            |
| $^1D_2$     | 21457                                     | 4660                            |
| $^3P_2$     | 10650                                     | 9389                            |
| $^3P_1$     | 7819                                      | 12789                           |
| $^3P_0$     | 0                                         | --                              |

Table II. Emission Lines of Lead (Ref 4:45)

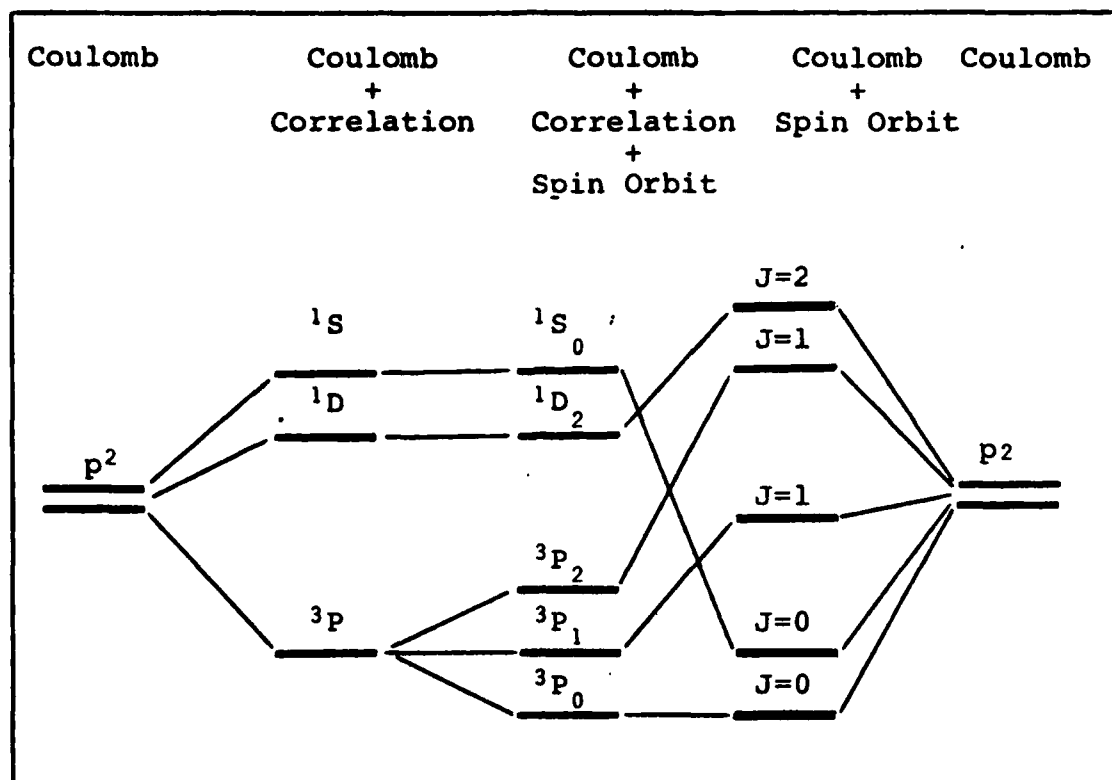


Figure 5. Energy Correlation Diagram (Ref 4:44)

the  $p^2$  configuration of lead. But in a case where the valence band is more than half full, the highest  $J$  values have the lowest energy (Ref 1). Hence, oxygen's  $p^2$  configuration has the energy splitting as shown in Figure 6.

#### Correlation of Molecular States

Molecular orbitals can be modeled as a linear combination of atomic orbitals (Ref 4:76). With this in mind, the valence electrons of lead and oxygen give rise to the ground state correlation diagram for lead shown in Figure 7. From Figure 7 it is evident that PbO is triply bonded. Using Mulliken's

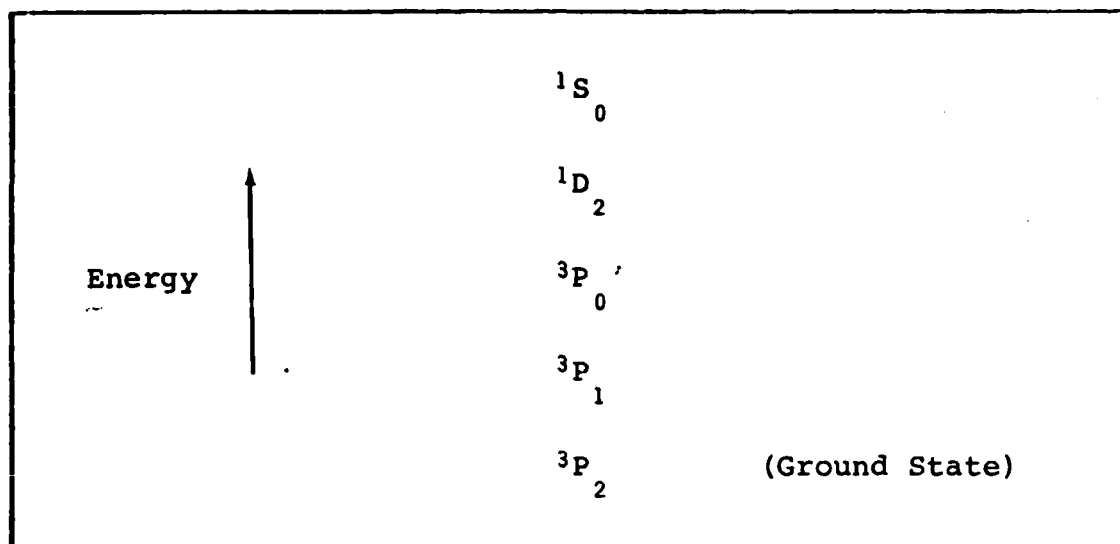


Figure 6. Valence Electron States of Oxygen

notation (Ref 5:452), the ground state electronic configuration is denoted

$$[\text{KKLMNO}] (\text{Z}\sigma)^2 (\text{Y}\sigma)^2 (\text{W}\pi)^4 (\text{X}\sigma)^2 \quad \text{or} \quad \sigma^2 \pi^4 \quad (20)$$

The first two excited states of PbO have the electronic configuration  $\pi^3 \pi^1$  and  $\sigma^1 \pi^1$ . In the  $\pi^3 \pi^1$  state, a  $\pi$  bonding electron is excited to a  $\pi$  antibonding orbital. In the  $\sigma^1 \pi^1$  state, a  $\sigma$  electron is excited to a  $\pi$  antibonding orbital.

#### Correlation Between Atomic and Molecular States

The correlations between atomic and molecular spectroscopic states arise by coupling angular momenta so that the

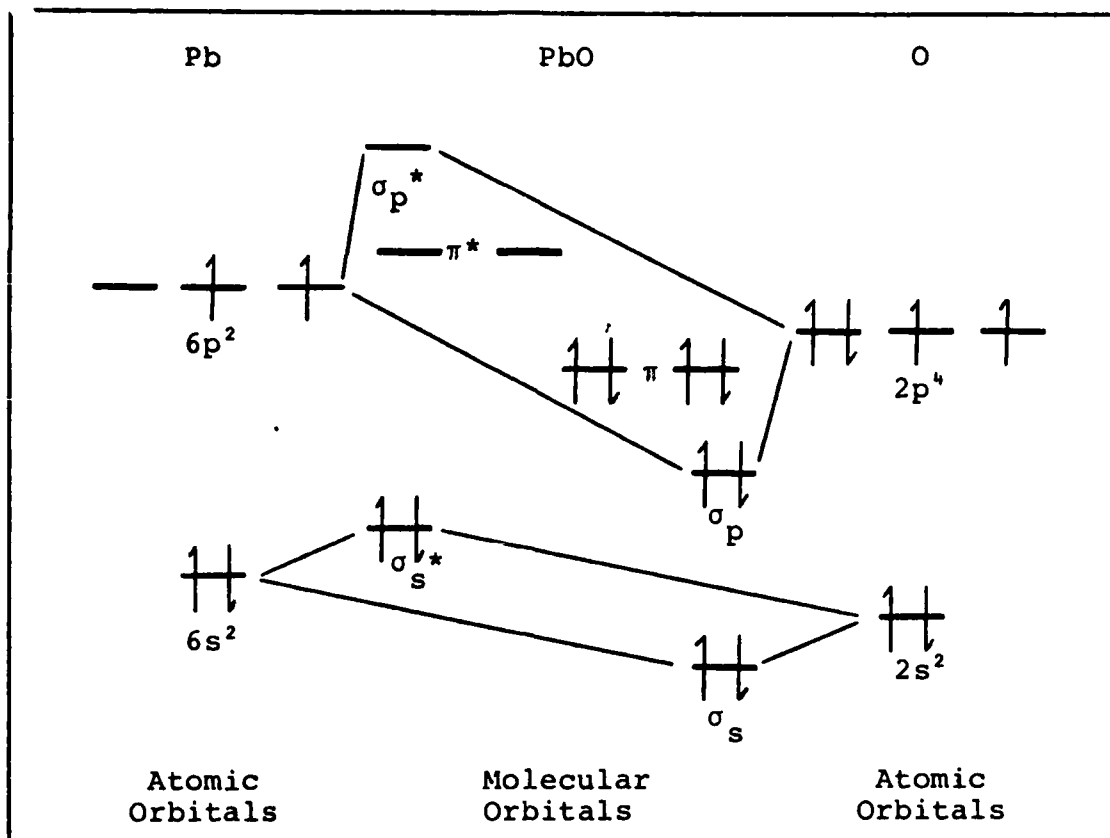


Figure 7. Orbital Correlation for PbO

total atomic angular momentum equals the total molecular angular momentum. This correlation is shown in Table III. The first column lists the electronic configuration of PbO for the ground state and the first two excited states. The next two columns list the spectroscopic states derived from the electronic states for the different coupling cases, Hund's case a and c. The fourth column gives the correlation between Hund's case a and c. The final column gives the spectroscopic state notation for observed excited states.

The selection rules of transition for Hund's case a and case c coupling cases are different. Therefore, the allowed

| Electronic Configuration | Hund's Case a        | Hund's Case c         | Correlation                          | State         |
|--------------------------|----------------------|-----------------------|--------------------------------------|---------------|
| $\sigma^2 \pi^4$         | ${}^1\Sigma_0^+$     | $0^+$                 | ${}^1\Sigma_0^+ \leftrightarrow 0^+$ | X<br>(ground) |
| $\pi^3 \pi^1$            | ${}^1\Sigma_0^+$     | $0^+,$                | ${}^1\Sigma_0^+ \leftrightarrow 0^+$ | E             |
|                          | ${}^1\Delta_2$       | $2^\pm$               | Not Observed                         |               |
|                          | ${}^1\Sigma_0^-$     | $0^-$                 | Not Observed                         |               |
|                          | ${}^3\Sigma_{1,0}^-$ | $0, 1^\pm$            | ${}^1\Sigma_0^+ \leftrightarrow 0^+$ | C             |
|                          |                      |                       | ${}^3\Sigma_1^- \leftrightarrow 1$   | C'            |
|                          | ${}^3\Sigma_{1,0}^+$ | $0, 1^\pm$            | ${}^3\Sigma_0^+ \leftrightarrow 0^-$ | b             |
|                          |                      |                       | ${}^3\Sigma_1^+ \leftrightarrow 1$   | a             |
| $\sigma^1 \pi^1$         | ${}^3\Delta_{3,2,1}$ | $2^\pm, 1^\pm$        | --                                   | --            |
|                          | ${}^1\Pi_1$          | $1^+$                 | ${}^1\Pi \leftrightarrow 1$          | D             |
|                          | ${}^3\Pi_{0,1,2}$    | $0^\pm, 1^\pm, 2^\pm$ | ${}^1\Pi_1 \leftrightarrow 1$        | B             |
|                          |                      |                       | ${}^3\Pi_0 \leftrightarrow 0^+$      | A             |
|                          |                      |                       |                                      |               |

Table III. Spectroscopic Correlation

and forbidden transitions will vary according to which coupling scheme is followed. The experimentally observed spectra of PbO indicate that PbO is more accurately described by Case c coupling

(Ref 6:454). The selection rule for electronic transitions for Hund's case c are  $\Delta\Omega = 0, \pm 1$  with  $0^+ \nleftrightarrow 0^-$  (Ref 5:244). The b-X transition is forbidden in case c coupling. This transition is characterized by weak emission intensity, and has been observed by Oldenborg (Ref 7), Kurylo (Ref 8), and others.

A tabulation of the energies of the various states of PbO obtained from spectroscopic studies by many workers is shown in Table IV.

| State | Energy<br>( $\text{cm}^{-1}$ ) | Reference |
|-------|--------------------------------|-----------|
| X     | 0                              | 9         |
| a     | 16024.9                        | 8         |
| b     | 16315                          | 10        |
| A     | 19862.3                        | 10        |
| B     | 22289                          | 10        |
| C     | 23820                          | 10        |
| C'    | 24947                          | 10        |
| D     | 30194                          | 10        |
| E     | 34455                          | 10        |

Table IV. Excited State Energies (Refs 8,9,10)

### Reaction Exothermicities

The heats of formation for various forms of lead, lead oxide and oxidizers are shown in Table V.

| <u>Substance</u> | <u><math>\Delta H_f</math> (Kcal/mole)</u> | <u>Reference</u> |
|------------------|--------------------------------------------|------------------|
| Pb               | 0                                          | 11               |
| Pb(g)            | +46.34                                     | 11               |
| PbO              | -52.07                                     | 11               |
| PbO(g)           | +11.48                                     | 12               |
| O                | +54.56                                     | 11               |
| O <sub>2</sub>   | 0                                          | 11               |
| O <sub>3</sub>   | +34.0                                      | 12               |
| N <sub>2</sub> O | +19.49                                     | 11               |

Table V. Heats of Formation  
(Refs 11,12)

Using this information, the exothermicities of various reactions can be calculated. These are shown in Figure 8.

Figure 9 compares these reaction exothermicities with the excited state energies of PbO. This comparison roughly indicates which excited states will be populated by a given reaction. But the reaction exothermicity is an average value, so that a given reaction can still populate electronic states that are higher in energy than the exothermicity of that reaction.

| Reaction                                           | Exothermicity |                     |
|----------------------------------------------------|---------------|---------------------|
|                                                    | (Kcal/m)      | (cm <sup>-1</sup> ) |
| Pb(g) + $\frac{1}{2}$ O <sub>2</sub> → PbO(g)      | -34.86        | 12195.3             |
| Pb(g) + N <sub>2</sub> O → PbO(g) + N <sub>2</sub> | -54.35        | 19013.4             |
| Pb(g) + O <sub>3</sub> → PbO(g) + O <sub>2</sub>   | -68.86        | 24089.7             |
| Pb(g) + O → PbO(g)                                 | -94.42        | 33031.5             |
| Pb(g) + $\frac{1}{2}$ O <sub>2</sub> → PbO         | -98.41        | 34427.4             |

Figure 8. Reaction Exothermicities

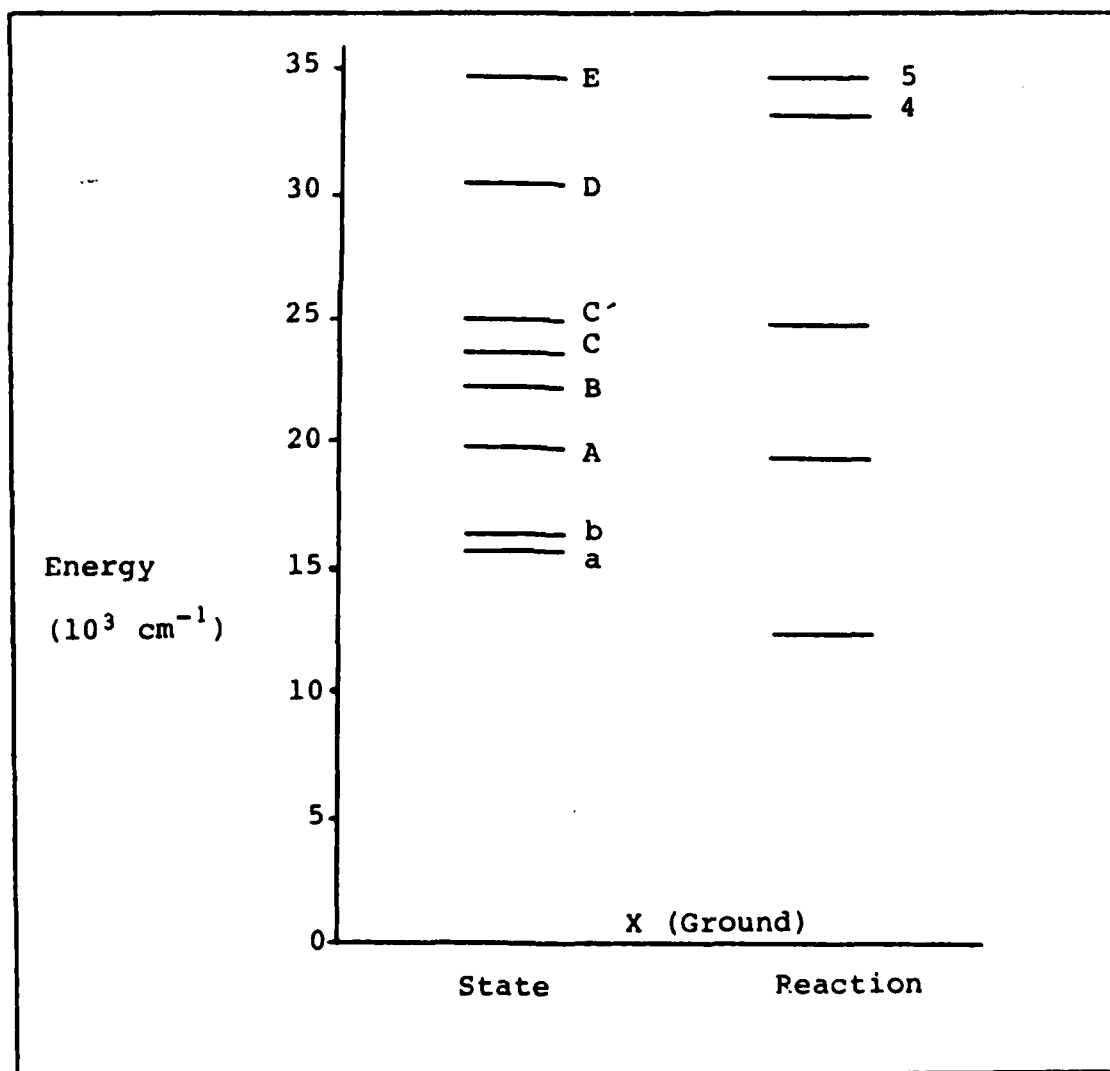


Figure 9. PbO States and Exothermicities

Finally, Table VI lists the color and decomposition temperatures of various lead oxides. This information will be useful when analyzing flow tube deposits.

| <u>Substance</u>               | <u>Color</u> | <u>Decomposition (°C)</u> |
|--------------------------------|--------------|---------------------------|
| PbO                            | Yellow       | 888                       |
| PbO <sub>2</sub>               | Bronze       | 290                       |
| Pb <sub>2</sub> O              | Black        | ---                       |
| Pb <sub>2</sub> O <sub>3</sub> | Orange       | 360                       |
| Pb <sub>3</sub> O <sub>4</sub> | Red          | 500                       |

Table VI. Oxides of Lead (Ref 11)

#### Literature Review

The PbO molecule has been extensively studied since the early 1900's. To observe the band spectra, early researchers used lead chloride gas flames or lead chloride carbon arcs. Subsequently, high resolution absorption and emission studies identified at least six band systems, all of which terminated on the ground state (Ref 7:284).

Among the most recent workers, Oldenborg, Dickson, and Zare (Ref 7) studied the spectrum obtained during the reaction between Pb and O<sub>3</sub>. They identified 49 bands of the a-X system and six bands of the forbidden b-X system. Using pulsed laser excitation, radiant lifetimes of three states were measured with the result

A-X             $\tau = 3.74 \text{ } \mu\text{sec}$

B-X             $\tau = 2.58 \text{ } \mu\text{sec}$

a-X             $\tau > 10 \text{ } \mu\text{sec}$

Kurylo, Brauch, Abramowitz, and Krauss (Ref 8) also studied the spectrum resulting from the reaction between Pb and  $\text{O}_3$ . These researchers observed transitions from the a, b, A, and B states to the ground state. They reported greater intensity of the b-X bands than earlier workers.

Linton and Broida (Ref 9) performed an extensive study of the PbO emission during the reaction of Pb with different oxidizers. They used various oxidizer pressures and temperatures as well. Reactions of Pb with  $\text{N}_2\text{O}$ ,  $\text{O}_3$ ,  $\text{O}_2$ , and O were used to generate PbO emission. The  $\text{O}_2$  reaction resulted in weak flames and severe system fouling which precluded an extensive study of emissions from that reaction.

Linton and Broida extensively studied the emissions from the decay from the a and A states. They also observed transitions from the B, C, and C' states. Atomic oxygen as an oxidizer gave bright flames, with ozone giving the brightest.

They analyzed their data using intensity ratio plots. The ratio of intensity of spectral lines at different oxidizer pressures was plotted as a function of the energy of the lines. The semi-log graph allowed population level comparisons to easily be made between experimental data and theoretical

Boltzman distribution. Their data showed for the  $\text{Pb} + \text{N}_2\text{O}$  reaction, as the oxidizer pressure varied from 3.4 to 34 Torr, the most intense emission shifted from the blue to the red; i.e., the emission from the a state was increased relative to the emission from the A and B states.

Brom and Beattie (Ref 6) used a tunable dye laser to analyze the rotational structure of the a state. The rotational structure contained P, Q, and R branches.

Snyder (Ref 2) studied the chemiluminescent flames from the reaction of Pb with  $\text{N}_2\text{O}$  and  $\text{O}_2$  at various oxidizer pressures. Emissions were observed from the a, b, A, B, and D states. The a state was generally the most intense, while the b state was the weakest. The severe fouling problems encountered by Linton and Broida with the  $\text{Pb} + \text{O}_2$  reaction were not encountered. Significant enhancement of emission from the A and B states was noted at 0.4 Torr of  $\text{O}_2$  in the  $\text{Pb} + \text{O}_2$  reaction. This was the first report of this low pressure enhancement.

To generate PbO flames for analysis, later researchers have boiled lead in an evacuated chamber, then mixed the lead vapor with an oxidizer. Oldenberg et al used a beam gas apparatus called LABSTAR (Ref 7:284-285). They boiled their lead in a crucible made of graphite.

Kurylo et al boiled lead in an alumina crucible and entrained the lead vapor with an inert carrier gas (Ref 8:168). They allowed the oxidizer gas to flow past the optical windows

to reduce contamination by reaction products. Snyder tried this technique, but it increased the severity of the contamination (Ref 2:25).

Both Linton and Broida and Brom and Beattie reference West et al when discussing their apparatus. Brom and Beattie used carrier gas flow rates and crucible mass losses to estimate the number density of lead in the reaction area as  $10^{13} - 10^{14}$  atoms/cm<sup>3</sup> (Ref 6:446).

West, Bradford, Eversole, and Jones (Ref 13) describe flow systems for the production of diatomic metal oxides and halides. They reported on furnace designs for different operating temperatures, some simple oxidizer mixing schemes, and on metal condensation problems. They do not discuss using lead as a sample metal.

Koym (Ref 1) built a flow tube reactor, but was unable to observe PbO spectra because of severe window contamination. Snyder (Ref 2) used this flow tube and did observe spectra. It was a highly modified version of this flow system that was used for this thesis.

### III. Experimental Apparatus and Procedures

#### Introduction

This chapter describes the experimental equipment and procedures used during this thesis. System modifications will be discussed in detail. Flame optimization and mass deposition experiments will be described.

#### Flow Tube Reactor

The flow tube reactor system used during this thesis is shown schematically in Figure 10. A photograph of the apparatus is shown in Appendix A. This section explains Figure 10 in detail. The experimental system can be analyzed as three interconnected subsystems:

- (1) Flow tube and furnace
- (2) Optical train
- (3) Detection and recording.

Each of these subsystems will be discussed in turn. A detailed discussion of the vacuum system is given in Reference 1 and will not be repeated here.

Flow Tube and Furnace. The flow tube and furnace used for this thesis is a highly modified version of the one previously used at AFIT (Refs 1, 2). The flow tube is made of 3-inch ID stainless steel (Alloy Products). Sections of the tube are connected by means of flanges fastened with heavy duty clamps. Vacuum tightness is ensured at the flanges by O-ring seals.

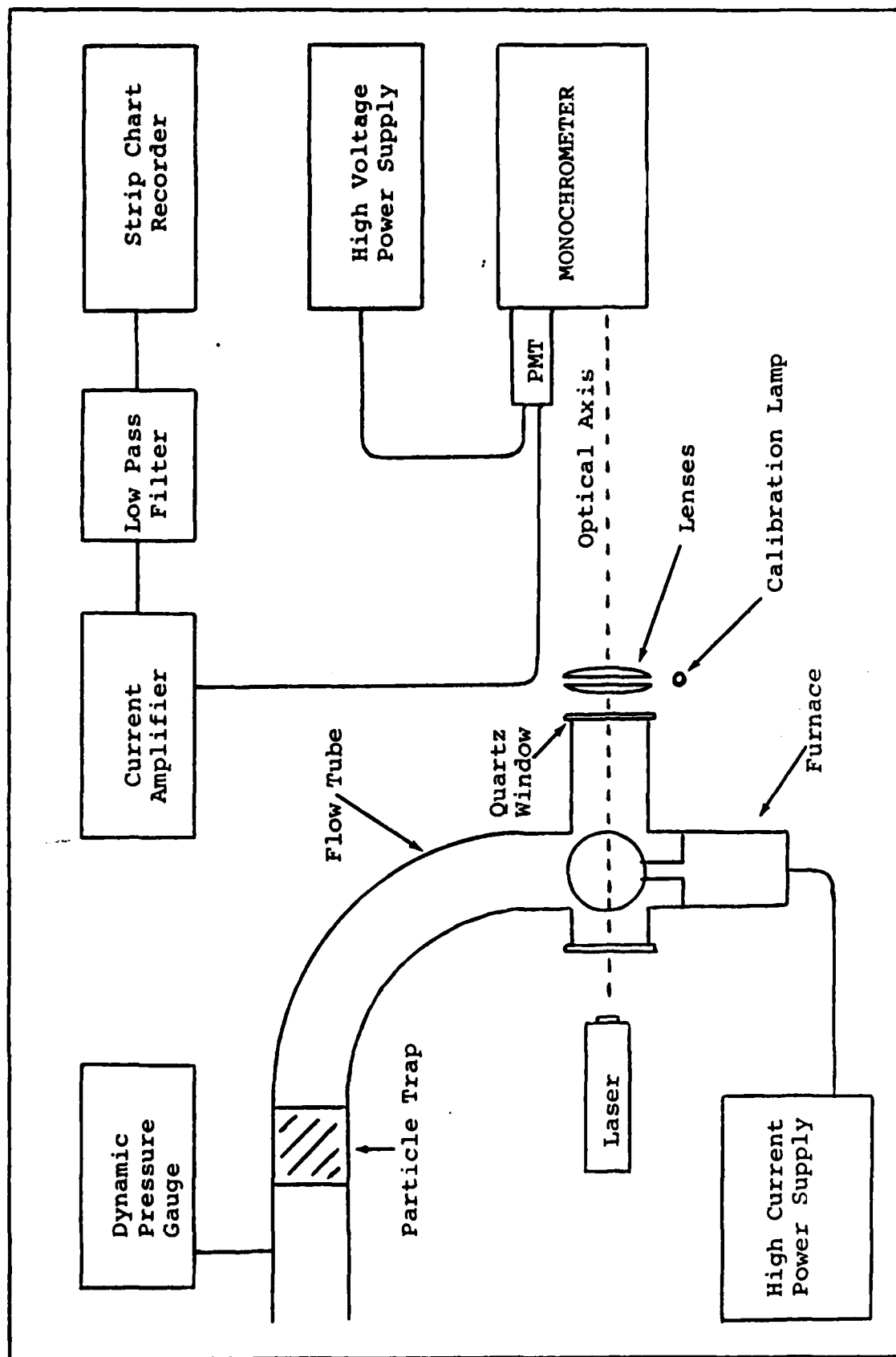


Figure 10. Experimental System

The current flow tube geometry was recommended by Snyder (Ref 2:52). Figure 11 shows the flow tube geometry which Snyder used and the geometry used in the current study.

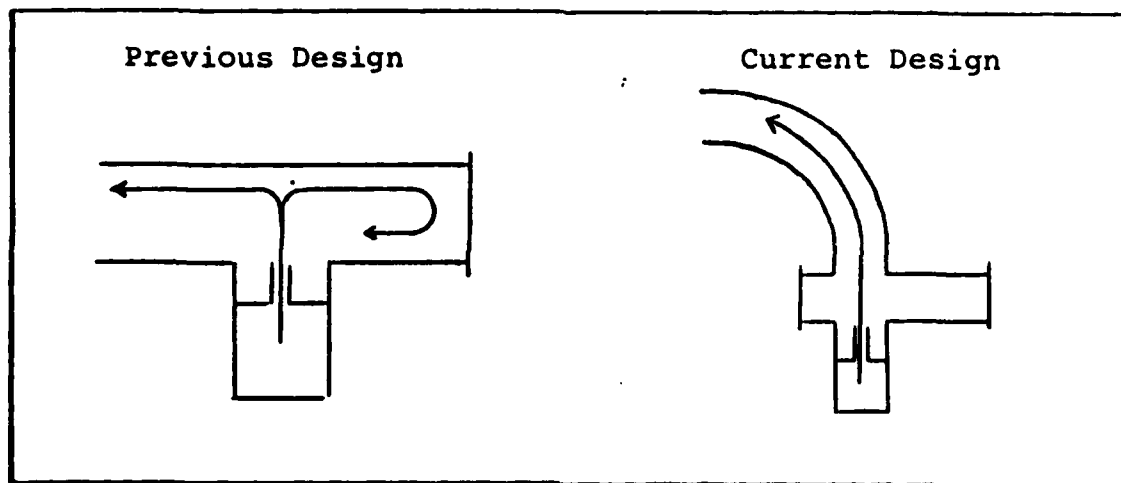


Figure 11. Flow Tube Geometries

In the previous design, reaction products would hit the top of the tube and spread throughout the tube. This recirculation of reaction products resulted in contamination of the quartz window. The current design allows the reaction products to flow efficiently to the vacuum system, with no abrupt corners. This one change greatly reduces window contamination by the reaction products.

Each port of the flow tube cross is 3.5 inches from the geometric center. A 4-inch flow tube extension was used on the port facing the monochrometer. This decreased window contamination further by forcing the reaction products to travel much farther in order to deposit. A glass wool particle trap prevented ingestion of reaction products by the vacuum system.

Dynamic pressures in the flow tube were measured downstream of the particle trap with a MKS Baratron 77 pressure meter.

The furnace and chimney assembly is shown in Figure 12. A photograph of this assembly is given in Appendix A. It attached to the lower port of the flow tube cross. Granular lead (Fisher Scientific Company) was resistively heated in a 1-inch diameter by 1-inch tall alumina crucible (R.D. Mathis Company). A tungsten wire basket heater (R.D. Mathis Company) held the crucible. The heater wire was insulated with asbestos to improve heating efficiency. The heater leads were attached to brass electrodes. The electrodes were electrically insulated from the flow tube by Teflon Swage lock fittings (Nacon Industries, Tustin CA). These Teflon fittings are a three-piece device that, when secured, give a vacuum tight seal. Water flowing through copper coils, wrapped around the electrode supports, cools the electrodes.

With the furnace design used by Snyder, the electrodes were cooled by using a water filled chamber at the base of the furnace (Ref 2:23). During operation with this furnace, dissolved salts in the water would corrode the silver solder joints where the gas inlet and electrodes penetrated the chamber. This corrosion, coupled with the thermal stresses involved during operation, would lead to water leaks at these joints. By switching to the cooling coil scheme, this problem was eliminated.

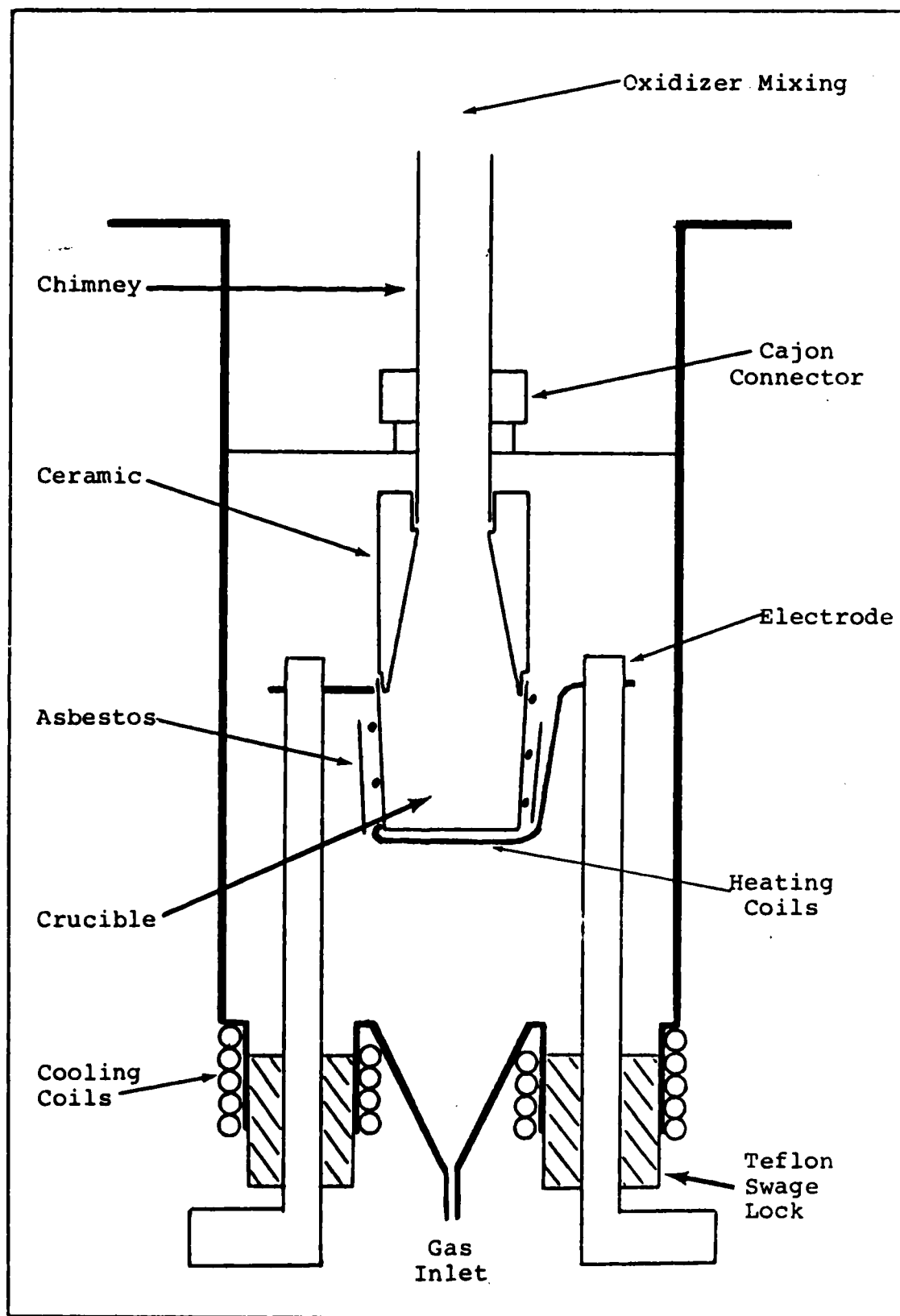


Figure 12. Furnace Chamber

Argon gas was introduced into the furnace chamber to entrain lead vapor and transport it to the reaction area via the chimney. The chimney was made of a thin-walled 0.5-inch OD stainless steel tube. A precisely machined glass ceramic transition section linked the crucible to the chimney. The glass ceramic was manufactured by the Corning Glass Works. It is sold under the trade name MACOR. For the current project, it was purchased from Astro Met Associates, Inc., 9974 Springfield Pike, Cincinnati OH 45215. This ceramic is machineable and useful up to temperatures of 1200° C.

The glass ceramic was machined to loosely fit between the chimney and crucible (see Figure 13). The loose fit was to prevent thermally induced stresses between the different materials at operating temperature. Four tangential slots, approximately 1/16 in wide and 1/8 in deep, were cut into the ceramic at the bottom to allow carrier gas to enter the crucible and mix with the lead vapor.

The chimney was held in place by a 0.5-inch ID Cajon connector (replacing the conventional O-ring with an aluminum one). This arrangement allowed easy replacement of badly lead-coated chimneys and adjustment of chimney position.

When the mixture of carrier gas and lead vapor reached the reaction area, it was mixed with oxygen to produce a flame. Oxidizer mixing will be discussed in a later section.

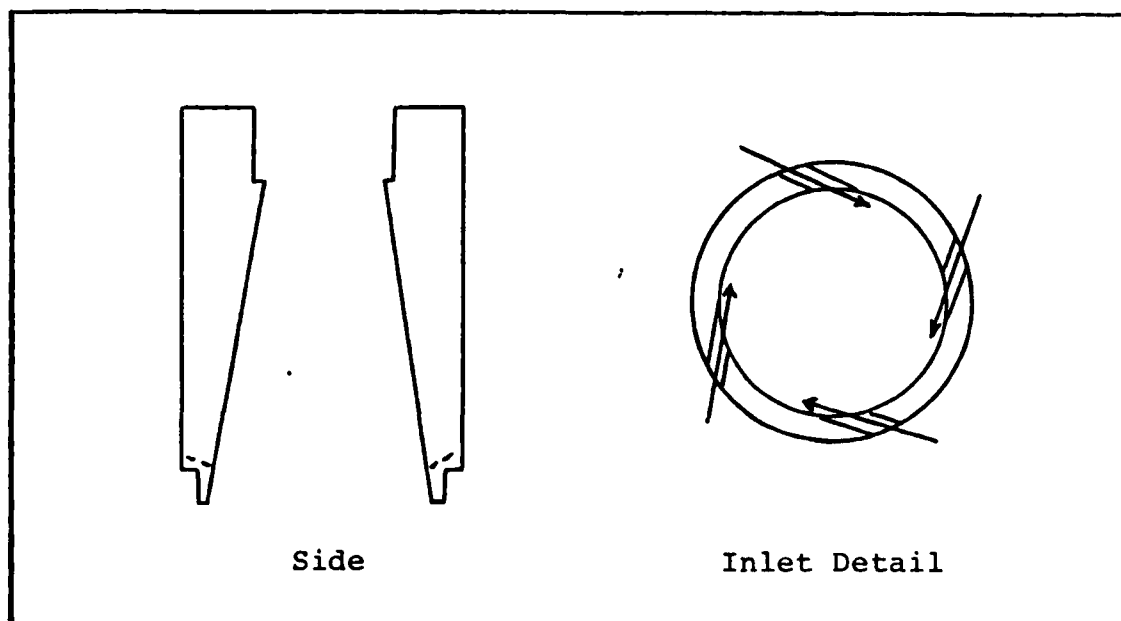


Figure 13. Ceramic Transition Section

Optical Train. The light from the PbO flame is spectrally focused onto the photomultiplier by the optical train. A 3-inch diameter planar-convex lens of 25 cm focal length was used to collect the light from the flame. A 3-inch diameter planar-convex lens of 50 cm focal length was used to focus the light onto the entrance slit of the monochromometer. The monochromometer was positioned 75 cm from the flame region. A Jarrel-Ash 0.5 Meter Ebert Mount Monochromometer was used. This instrument has curved slits and an 1180 groove/mm grating blazed at  $5000 \text{ \AA}$ . The slits can be varied in width from  $5 \text{ }\mu\text{m}$  to  $200 \text{ }\mu\text{m}$ . Dispersion at the exit slit is  $16 \text{ \AA/mm}$  with a maximum resolution of  $0.2 \text{ \AA}$  in first order. Scanning speeds are variable from  $2 \text{ \AA/min}$  to  $500 \text{ \AA/min}$ . The optical train was aligned using a Spectra Physics 2mW Helium-Neon laser.

Detection and Recording. The heart of the detection and recording system is the photomultiplier tube (PMT). An RCA 7265 PMT was used. Unfortunately, this PMT has a low signal-to-noise ratio (S/N) at the low light levels encountered during this thesis. To reduce noise, a liquid nitrogen cooled cold finger was used. The cold finger was made from a strip of copper 1/16 by 1 1/2 inches. It was wrapped around the PMT housing and dipped into a Dewar vessel filled with liquid nitrogen. The PMT was biased with a Keithley 244 High Voltage Power Supply.

The signal from the PMT was fed into a Keithley 427 Current Amplifier via a redundantly shielded coaxial cable. The double shielding reduced stray noise pickup (Ref 14:35). From the current amplifier, the signal was fed into a low-pass filter. This filter design is shown in Figure 14. This design allows the rise time constant to be varied from 1 msec to 1 sec.

From the filter, the signal was fed to a Sargent SR Recorder. The recorder is a strip chart type. The available horizontal scanning speeds are 2, 1, or 1/2 inch/min. Originally, the vertical sensitivity was fixed at 1 mV full scale. Vertical sensitivity of the recorder is controlled by one resistor within its circuitry. This resistor was replaced by a rotary switch with 8 resistor values giving full scale ranges from 1 mV to 100 mV. This greatly improved the utility and flexibility of the recorder.

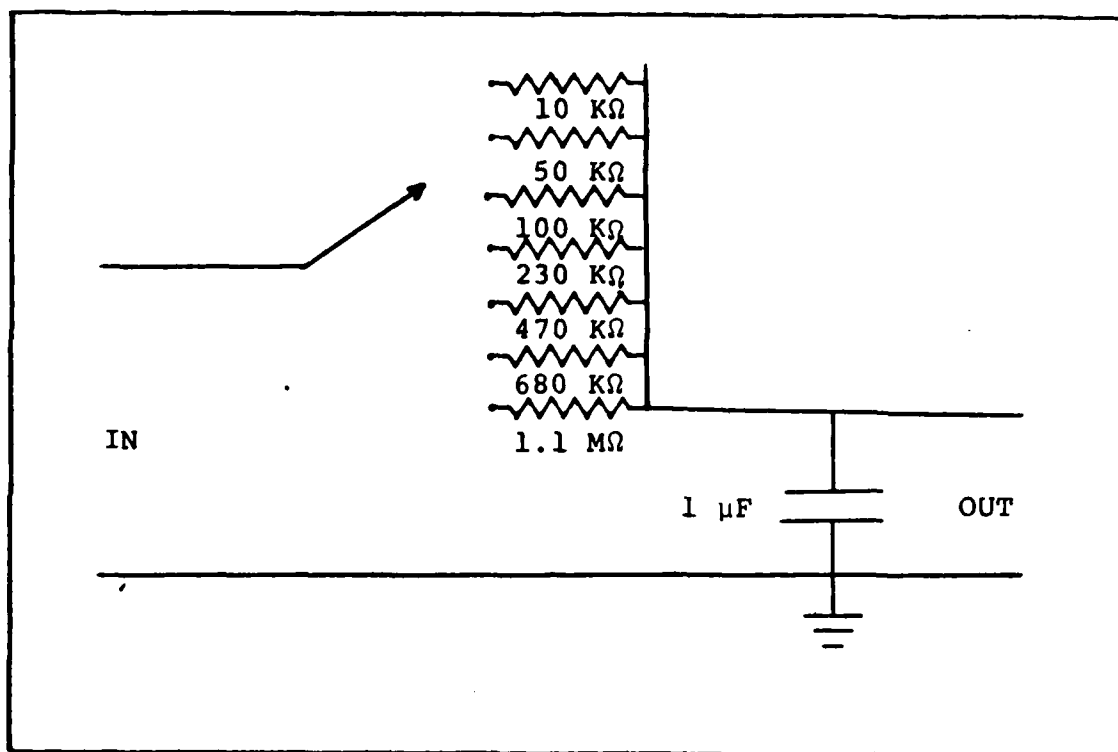


Figure 14. Low Pass Filter

### Operational Procedures

This section will cover procedures unique to this thesis. Start-up and shut-down procedures are given in Reference 1. General operating procedures are given in Reference 2. Neither of these procedures will be repeated here.

Alignment. The optical train was aligned with the flow tube using a HeNe laser. First, the laser was solidly positioned so that its beam passed through the center of the flame region of the flow tube. This was accomplished by placing pinholes at the center of each end of the flow tube cross. The laser was aligned so that the beam passed through the two pinholes. With

the laser on, the monochrometer was aligned along the beam axis by watching the position of the laser spot on the entrance slit and the reflection of that laser spot. The monochrometer was positioned so that the laser beam impinged directly on the center of the entrance slit and simultaneously reflected back on itself. The two lenses were mounted back-to-back in the same lens holder. The lenses were positioned so that the laser spot fell directly on the center of the entrance slit and all reflections fell back upon the original beam. The PMT was rigidly mounted to the exit slit, so no alignment was needed. As long as the laser was not disturbed, its beam defined the optical axis. The other optical elements were quickly and easily realigned following the above procedure.

Calibration. Spectra were calibrated using Oriel Pen Lamp Calibration Sources. Mercury, neon, and argon sources were used. The pen lamps were mounted adjacent to the lenses. The lamps were covered with black paper to form a sheath. Pinholes in the paper sheath allowed just enough light to pass through so that the calibration peaks remained on scale during a spectral scan. The number of pinholes varied with the strength of the particular calibration peak. The entire set of lamps was turned on prior to a scan to eliminate noise spikes. The lamps were covered with a second sheath, which was removed momentarily when the wavelength counter on the monochrometer approached the desired calibration peak. Additionally, calibration using the well defined band origins of the  $a(3,1)$  and  $a(4,1)$  bands was used (Ref 6).

Signal-to-Noise. The noise encountered with the electronic equipment was determined to originate with the PMT itself. To reduce the thermal noise, the PMT was cooled with a cold finger (as described earlier). When cooling the PMT in this crude manner, a delicate balance had to be maintained between noise reduction and internal water vapor condensation. With too little cooling, the noise is higher than it need be. With too much cooling, water vapor will condense within the high voltage base. If this occurs, sporadic short circuits will occur, causing wild PMT output behavior. The size of the cold finger is critical to achieve this balance.

A search for the operating region of the PMT yielding the highest S/N was conducted. Using the 5461 Å line of mercury as the source, the PMT high voltage was varied and the ratio of the calibration peak signal to the average noise peak-to-peak signal was recorded and measured. The mercury source was positioned where the flame would be and attenuated using a neutral density filter with  $10^6$  times attenuation. This better simulated the PbO flame. A plot of the S/N versus PMT high voltage is shown in Figure 15. This plot shows that the optimum operating voltage is 1400 V.

Resolution. Although this monochromometer is capable of resolution to 0.2 Å, this resolution was not achieved during the current work. To allow maximum signal, the widest slits were used (200 μm). Using the  $10^6$  times attenuated signal from the yellow doublet of mercury (5780 Å), it was determined that,

when using 200  $\mu\text{m}$  slit widths and 50  $\text{\AA}/\text{min}$  scan speed, the resolution was 7  $\text{\AA}$  FWHM.

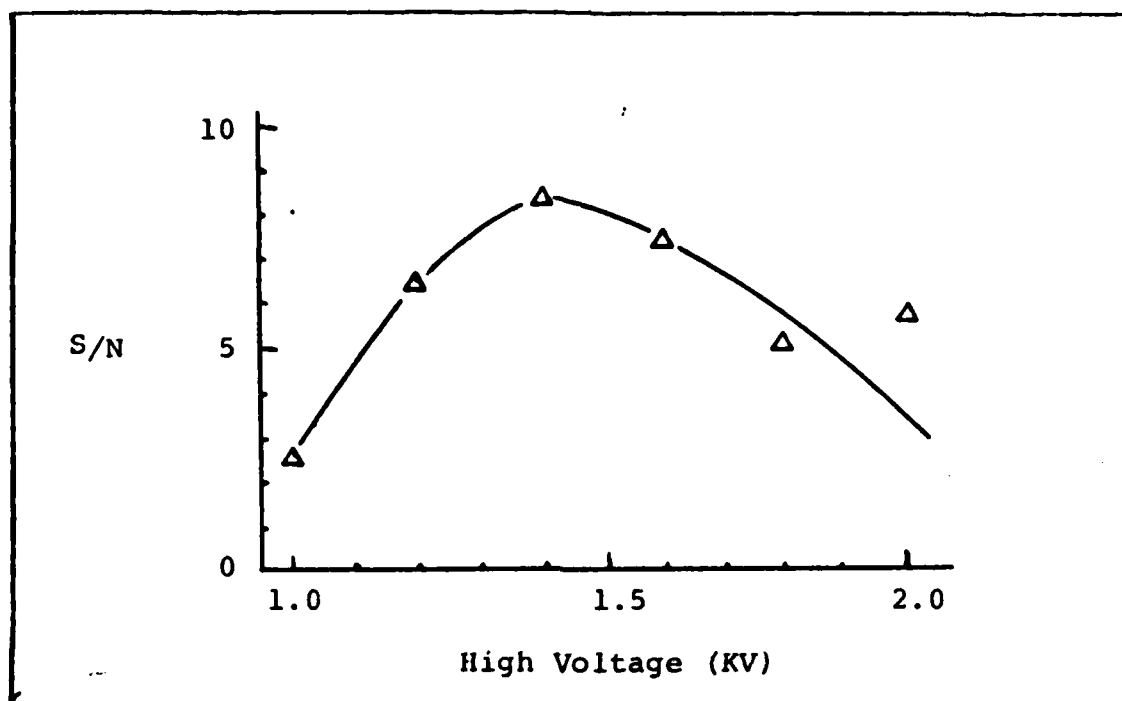


Figure 15. Signal-to-Noise Optimization

#### Flame Optimization

Maximizing chemiluminescent flame emission is another way to increase the S/N. Bright PbO flames require sufficient lead vapor throughput to the reaction area and good mixing of the metal vapor with the oxidizer. Experiments were carried out to maximize flame emission with respect to these two areas.

There is little detailed information on flame optimization in flow tube reactors in the literature. Some material is given by West et al (Ref 13). He reports that maximum emission occurs with compact flames, and that compact flames are

generated by high oxidizer flow rates. West also reported that a good flow of metal vapor to the reaction area is obtained if excess vaporization of metal for a given carrier gas flow rate is not attempted. If the evaporation is too fast, the carrier gas cannot effectively entrain a significant fraction of the metal vapor, and much of it will condense before reaching the reaction area.

During this thesis, areas of investigation to improve flame emission included furnace design and oxidizer mixing techniques. Five furnace designs were tried. They are shown in Table VII. The first design was that used by Snyder (Ref 2). The second uses a large, solid chimney cone with a carrier gas inlet ring around the base of the cone. The third design is a variation of the first one, with a carrier gas inlet cone. The fourth design uses a ceramic transition section between the crucible and the chimney proper. The final design is similar to the fourth, with tangential slots cut into the ceramic.

Seven oxidizer mixing configurations were tried. They are shown in Table VIII. The first two are the ring design used by Snyder. In the first, the gas jets angle up  $20^\circ$ , and in the second, down  $20^\circ$ . The third design is a tube with a hole in it. The remaining designs clamp to the top of the chimney. The fourth design is a half cylinder manifold, 1 inch tall, with 24 holes in it to give a "bed-of-nails" type oxidizer flow. The last three designs are short manifolds with four gas inlets. The difference lies in the angle of the holes with respect to the

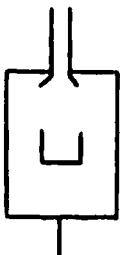
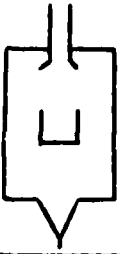
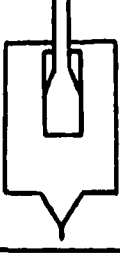
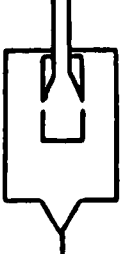
| <u>DESIGN</u>                                                                                | <u>DESCRIPTION</u>                                                               |
|----------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------|
| <p>A</p>    | <p>Baseline System<br/>Used by Snyder<br/>Collar on Chimney Base</p>             |
| <p>B</p>    | <p>Large, Solid Chimney Cone<br/>Carrier Gas Inlet Ring<br/>Around Cone</p>      |
| <p>C</p>   | <p>Baseline System with Carrier<br/>Gas Inlet Cone Attached</p>                  |
| <p>D</p>  | <p>Ceramic Transition Section<br/>Loose Fitting</p>                              |
| <p>E</p>  | <p>Ceramic Transition Section<br/>Four Tangential Slots Cut<br/>into Ceramic</p> |

Table VII. Furnace Designs

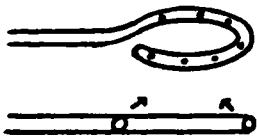
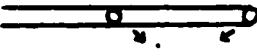
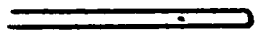
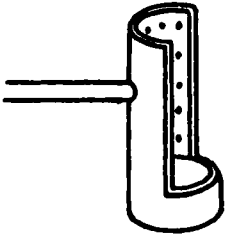
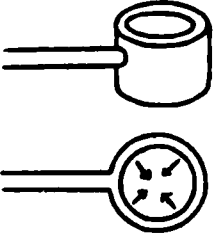
| CONFIGURATION                                                                                | DESCRIPTION                                                                                |
|----------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------|
| <p>1</p>    | <p>Standard Oxidizer Ring<br/>Used by Snyder<br/>Gas Jets up 20°</p>                       |
| <p>2</p>    | <p>Inverted Ring<br/>Gas Jet Down 20°</p>                                                  |
| <p>3</p>    | <p>Straight Tube with One Hole</p>                                                         |
| <p>4</p>   | <p>Half Cylinder Manifold<br/>24 Gas Jets Aimed at Center<br/>Attaches to Chimney Top</p>  |
| <p>5</p>  | <p>Short Manifold<br/>Gas Jets up 20°<br/>Straight in Flow<br/>Attaches to Chimney Top</p> |
| <p>6</p>  | <p>Like Above, but<br/>Tangential Flow</p>                                                 |
| <p>7</p>  | <p>Like Above, but<br/>Part Tangential Flow,<br/>Part Straight in Flow</p>                 |

Table VIII. Oxidizer Mixing Configurations

axis of the chimney. For the three designs, they are: straight in, tangential, and half-way between those two extremes.

An additional experiment varied the heating efficiency of the furnace. In this experiment, various amounts of asbestos insulation were wrapped around the heating coils. The effect of this modification on lead throughput and operating power requirements was observed.

Also, flame and crucible temperature experiments were carried out. Alumel-chromel and iron-constantan thermocouples were placed in the crucible and in the flame region. Readings were taken using a Honeywell Potentiometer, Model 2733. Conversion to temperature was done using standard tables from Reference 11.

#### Mass Deposition

Snyder reported lead vapor densities in the flow tube during operation to be in the order of  $10^{14}$  atoms/cm<sup>3</sup>, (Ref 2:28), but he does not say where or how he arrived at that value. Brom and Beattie reported number densities on the order of  $10^{13}$  -  $10^{13}$  atoms/cm<sup>3</sup> (Ref 6:446). An attempt was made to justify Snyder's claim.

An aluminum foil covered microscope slide was suspended over the chimney by an oxidizer ring. Furnace designs A and E from Table VII were used. All runs were made at 2 Torr pressure of Argon.

An additional aluminum foil sleeve was slipped over the foil covered slides for some runs. This sleeve covered just the area over the oxidizer ring. By this procedure, deposition directly over the chimney was compared to that occurring in regions of the flow tube away from the chimney.

The procedure was to run the furnace for different operating times. In this way, a value for steady state deposition could be determined by subtracting the values of the deposits from samples of different run times. The crucible was weighed before and after a series of runs to determine the amount of mass removed from the crucible. When using Furnace E, it was possible to obtain a mass balance because the ceramic and chimney could also be weighed. From these experiments, the flux of lead into the reaction region was determined.

#### IV. Results and Discussion

##### Introduction

This chapter is presented in four parts. In the first part, the results of the flame optimization experiments are given. The next section presents the findings of the mass deposition experiments. In the third part, assignments of spectral lines are made and compared to theoretical values. Finally, the spectroscopic constants obtained from data from this thesis and Snyder's work are presented and compared to each other and to published literature values.

##### Flame Optimization

Three elements were varied in order to optimize emission from the flame. They are: furnace design, oxidizer mixing technique, and heating coil insulation. Each element will be discussed in order. Finally, the results of the thermocouple experiments will be presented.

Furnace Design. The furnace designs used in the optimization study, along with the results of the experiments with the furnaces, are shown in Table IX. Snyder (Ref 2) used a furnace based on the design shown in part A of Table IX. Snyder reported that the collar on the chimney greatly improved lead throughput to the reaction area and improved flame emission (Ref 2:25). During operation, however, lead deposits built up on the collar.

Additional buildup of lead occurred on the top plate of the furnace chamber in such a location as to indicate that a recirculation zone was created by the collar. Lead continued to be deposited in this region by recirculation of the carrier gas and lead vapor mixture within the chamber. Clearly, recirculation within the chamber was shown to be undesirable.

Furnace design B was developed to eliminate upper chamber recirculation. Additionally, the upper gas jets were designed to prevent lead plating of the upper cone. In operation, however, lead heavily plated the upper chamber walls regardless of gas flow from the upper gas jets. If the lower gas inlet was shut off, lead would severely coat the entire furnace chamber and no flame could be detected when operating in this mode.

Furnace B was made with a solid upper chamber. This large mass of steel has considerable heat capacity. Even when the furnace is boiling lead, the upper chamber surface is relatively cool. The lead vapor will deposit on a cool surface more readily than a hot one. It was this effect that led to the poor results. The upper gas jets failed to draw lead vapor into the chimney because they were too far from the crucible ( $\sim \frac{1}{2}$  inch). This furnace was not considered useful for optimization purposes.

Furnace C was a modification of Furnace A. It was designed with the hope of improving gas flow within the chamber. The gas inlet cone was meant to reduce the recirculation zone

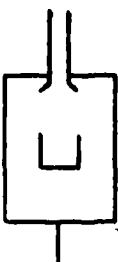
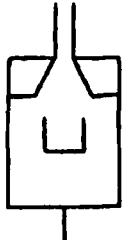
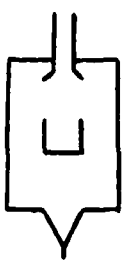
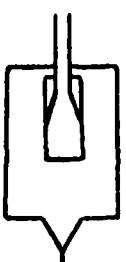
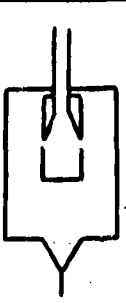
| <u>DESIGN</u>                                                                                | <u>RESULT</u>                                                                                                  |
|----------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------|
| <p>A</p>    | <p>Lead Deposits on Collar</p> <p>Lead Deposits in Chamber</p> <p>Poor Gas Flow</p> <p>Recirculation Zones</p> |
| <p>B</p>    | <p>Bad Lead Plating in Upper Chamber</p> <p>Little Lead Throughput</p>                                         |
| <p>C</p>   | <p>Improved Gas Flow</p> <p>Lead Deposits in Chamber</p> <p>Improved Lead Throughput</p>                       |
| <p>D</p>  | <p>Poor Lead Vapor Entrainment</p> <p>Large Lead Condensation Beads</p> <p>Little Lead Throughput</p>          |
| <p>E</p>  | <p>Excellent Lead Vapor Entrainment</p> <p>Good Lead Throughput</p>                                            |

Figure IX. Furnace Design Result Summary

present when a gas stream abruptly expands between two different tube diameters (Ref 1:14). Results indicate that this design did improve lead throughput into the reaction area. Lead plating within the furnace chamber was still occurring. It was observed that Furnace C produced its best flame at 0.5 Torr of Ar, while with Furnace A optimization occurred at 2 Torr of Ar.

Furnace D was designed to prevent lead from plating within the furnace chamber by containing the lead vapor more efficiently. The chamber plating problem was eliminated, but the loose fit of the ceramic transition section did not allow carrier gas to effectively entrain the lead vapor. Even at 10 Torr of Ar, PbO flames were weak because little lead reached the reaction area. Also, large lead condensation beads formed on the inside of the ceramic and chimney. This was another indication that the carrier gas was not effectively entraining the lead vapor (Ref 13:166).

Furnace E provided easy access of the carrier gas to the lead vapor via tangential slots in the ceramic section. The slots were cut tangentially and angled down to deliberately swirl the carrier gas and force it to mix with the boiling lead. This swirling and mixing action was viewed by keeping the carrier gas flow on after the furnace was turned off. The lead would solidify in the same pattern it had while it was boiling. The result was a spinning centrifuge type pattern in the crucible. The carrier gas jets definitely did spin the

boiling lead and swirl with the lead vapor. The number and size of condensation beads on the upper ceramic walls was drastically reduced with this configuration. Good flames were observed at 2-4 Torr of Ar.

Oxidizer Mixing. The results of the oxidizer mixing studies are shown in Table X. The key to signal optimization from the flame is to produce the brightest flame possible within the optical viewing region. This optimization is a function of good mixing of lead vapor with the oxidizer. Tall flames that persist well beyond the viewing region indicate poor mixing.

The standard oxidizer ring configuration produced tall, uniform flames of moderate brightness. If the oxidizer pressure was too high for the given carrier gas flow, the flame was badly distorted as the individual jets of oxidizer gas penetrated the lead vapor column giving fingers of flame. During normal operation, the oxidizer ring became coated with a fine, yellow deposit. This indicated extensive  $PbO$  formation in the flame.

In the first attempt to improve mixing, the oxidizer ring was inverted. This configuration resulted in a slightly brighter flame than with the standard ring configuration. The inverted ring configuration gave better mixing because of colliding gas flows. After use, the ring was coated with yellow, orange, and red deposits. The additional orange and red deposits were not present on the standard ring configuration.

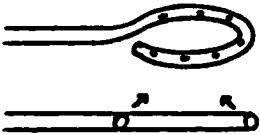
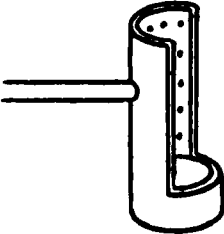
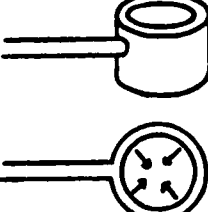
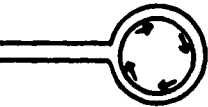
| CONFIGURATION                                                                                | RESULT                                                                                                                     |
|----------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------|
| <p>1</p>    | <p>Tall, Uniform Flames</p> <p>Moderate Intensity</p> <p>Yellow Deposit (PbO)</p>                                          |
| <p>2</p>    | <p>Tall, Uniform Flames</p> <p>Slightly Brighter Flames than No.1</p>                                                      |
| <p>3</p>    | <p>Tall, Uniform Flames</p> <p>Moderate Intensity</p>                                                                      |
| <p>4</p>   | <p>Poor Flames</p> <p>Reflected Glowing Heating Coils</p>                                                                  |
| <p>5</p>  | <p>Short, Bright Flames</p> <p>Some Flame Flicker with 3" Flame</p> <p>Yellow Deposit (PbO)</p>                            |
| <p>6</p>  | <p>Tall, Uniform Flames</p> <p>Brightest Region 2-6" from Manifold</p> <p>Orange Deposit (Pb<sub>2</sub>O<sub>3</sub>)</p> |
| <p>7</p>  | <p>Short, Good Flames</p> <p>A Little Flicker</p> <p>Mostly Yellow Deposit (PbO)</p>                                       |

Table X. Oxidizer Mixing Configuration Result Summary

The orange and red deposits are an indication of  $\text{Pb}_2\text{O}_3$  and  $\text{Pb}_3\text{O}_4$  formation in the flame region. The formation of these deposits with the inverted ring seems to indicate that higher oxides of lead can be formed using energetic oxidizer mixing techniques.

Configuration No. 3 of Table X was the only one which led to direct disturbance of the flow of gases coming from the chimney. The results were unimpressive, with tall flames similar to the standard ring configuration. Again, some orange and red deposits formed near the outlet hole for the oxidizer.

Configuration No. 4 represented a radical change from previous concepts. The cylindrical bed-of-nails approach was to introduce more oxygen over a larger area to create a bright flame. Unfortunately, the orange glow from the tungsten heating coil was brilliantly reflected into the flame region by this configuration. This reflection was so intense that it prevented the viewing of any flame emission. This oxidizer mixing configuration was not considered practical for optimization purposes.

The next three designs are short manifolds with four gas jet inlets placed  $90^\circ$  apart. In No. 5, these holes directed the oxidizer to the center of the chimney. The result of this design was a short, bright flame. The flame was brightest where the four jets collided. Some flame flicker was present with the flame extending to the top of the viewing region only. After use, the interior of the manifold was coated with a fine

yellow deposit. This deposit indicates PbO formation within the flame.

The manifold with tangential inlets (No. 6) produced good, uniform flames that were tall with no flicker. The brightest region of emission extended from 2 to 6 inches upstream from the manifold. This was the only design to show such a phenomenon. This behavior can be explained as follows. The lead vapor and carrier gas mixture coming from the chimney is a radially diffusing column of gas. The oxygen coming from the tangential manifold is a radially diffusing cylinder of gas. The best mixing of these two gas flows occurs when they diffuse into each other. From the results of this experiment, this occurs from 2 to 6 inches from the manifold. After use, the interior of the manifold was found to contain a bright orange deposit, indicating extensive formation of  $\text{Pb}_2\text{O}_3$ .

Design No. 7 gave results somewhat between that of design No. 5 and design No. 6. Flame optimization occurred with a 2-inch flame having a little flame flicker. After use, the interior of the manifold was found to have an orange-tinted yellow deposit. This indicated extensive PbO formation with some  $\text{Pb}_2\text{O}_3$  formation in the flame region.

One additional oxidizer mixing configuration was tried. The final configuration (No. 8) combined the standard oxidizer ring of No. 1 and the straight flow manifold of No. 5. The arrangement used is shown in Figure 16. This configuration

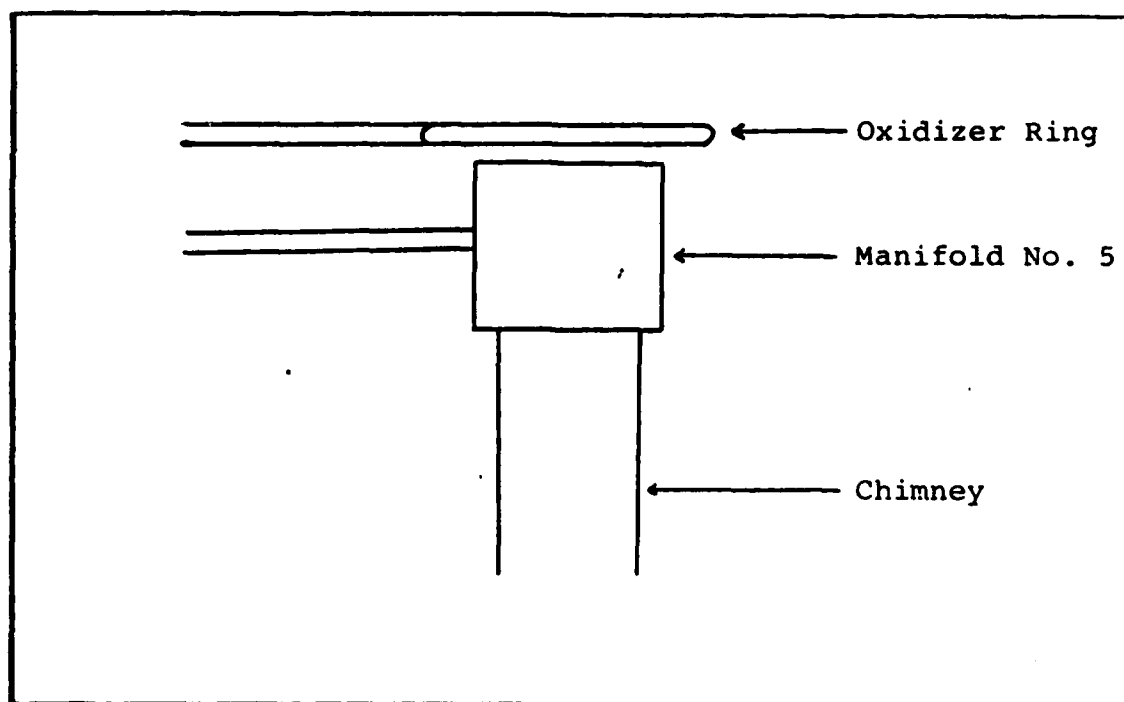


Figure 16. Optimum Oxidizer Mixing Configuration

produced the best overall flame. The flame just filled the viewing area, had little flicker, and was bright and uniform. After operating with this configuration for 90 minutes, there was very little window contamination present. The oxidizer ring may have acted as a gas curtain preventing the reaction products from diffusing throughout the flow tube.

Asbestos Insulation. During normal operation of the furnace, the crucible sits in the tungsten basket heater and the heater wires are uncovered within the furnace chamber. For the heater to boil lead in this configuration required 12-15 volts at 1000 watts. These operating conditions are at the tolerance limit of the heater wires and brass electrodes. An experiment

was initiated to increase heater component longevity by reducing the power required to boil lead by improving lead heating efficiency.

Wrapping the heater wires with insulation was the chosen approach to improve heater efficiency. Asbestos ribbon,  $\frac{1}{2}$  and 1 inches wide, was selected as the insulation. The result of using either ribbon size was to greatly improve heating efficiency. An asbestos wrapped heater could boil lead using 9-10 volts at 500 watts. Both ribbon samples gave the same results. When using insulation over the heater wires, the voltage to the wires should not exceed 10 volts at 500 watts. In excess of this limit, using furnace design A of Table VII, it was noticed that the molten lead had splattered within the furnace chamber. This was an indication of excessive, violent boiling of the lead.

The use of insulation around the heater coil had a drastic impact on the rate of lead boiloff from the crucible. Operating with furnace configuration A using normal carrier gas pressures ( $\sim$  2-4 Torr) and using insulation, it was found that a crucible initially full of lead would have its entire contents boiled off within 45 to 60 minutes. When operating without insulation, normal boil-off time is about three hours. Obviously, using insulation around the heating coils allows the experimenter a greater control of the rate of lead boil-off.

While operating the flow tube with insulation over the heating coil, and in a fast lead boil-off mode, the viewing

windows fogged completely opaque in about ten minutes. Later examination revealed a thick black coating in the flow tube. This black deposit was an indication of extensive  $Pb_2O$  formation. Obviously, a great amount of lead throughput to the reaction area was met by an insufficient amount of oxygen or insufficient mixing. The resulting chemical reactions were lead rich. When operating under these conditions, no oxidizer mixing configuration was found sufficient to reduce  $Pb_2O$  formation in favor of  $PbO$  formation.

Thermocouple Experiments. The thermocouple experiments were initiated to measure the temperature of the lead vapor as it was boiled off from the crucible and the temperature of the  $PbO$  flame. The results are presented in Table XI. Published literature values for the temperature of the crucible range between  $750^{\circ} C$  and  $1000^{\circ} C$  (Ref 6:446, 7:285, 9:398). The lead vapor temperature reported here compares favorably with this temperature range. The flame temperature has not been previously reported in the literature. The cooling effect of the carrier gas on the metal vapor, as pointed out by West et al (Ref 13:164), is clearly evident by these results. The lead vapor cooled by about  $700^{\circ} C$  while traveling from the crucible to the flame region (about four inches).

| <u>THERMOCOUPLE</u> | <u>LOCATION</u>              | <u>TEMPERATURE</u> |
|---------------------|------------------------------|--------------------|
| Iron-Constantan     | Directly<br>over<br>Crucible | 890° C             |
| Chromel-Alumel      | Flame<br>Region              | 175° C             |

Table XI. Thermocouple Experiment Results

#### Mass Deposition

The mass deposition experiments were initiated to determine the number density of lead present in the reaction area during normal flow tube operation. An experiment using furnace design E of Table VII gave the most detailed information regarding the history of lead vapor leaving the crucible. This configuration allowed the weights of all important components to be taken for a determination of a mass balance. The results of this experiment are shown in Table XII. The mass balance achieved was 98%. The 2% of lead unaccounted for represents the deposit of lead on the flow tube itself. It is noteworthy that only 36% of the mass lost by the crucible actually made it to the reaction area. The deposit within the chimney accounted for 42% of the mass lost by the crucible.

The flux of lead in the reaction area is given by

| Item                                                                                                 | Mass Change (gr)     |
|------------------------------------------------------------------------------------------------------|----------------------|
| Crucible                                                                                             | - 5.2671 $\equiv$ -A |
| Ceramic                                                                                              | 1.1809               |
| Chimney                                                                                              | 2.1911               |
| Oxidizer Ring                                                                                        | 0.2521               |
| Glass Wool                                                                                           | 1.0936               |
| Slide A<br>(start-up)                                                                                | 0.0427               |
| Slide B<br>(start-up + 10 min)                                                                       | 0.1355               |
| Slide C<br>(start-up + 20 min)                                                                       | 0.2683               |
| Total Mass Collected                                                                                 | 5.1642 $\equiv$ B    |
| Total for Ceramic<br>and Chimney                                                                     | 3.3720 $\equiv$ C    |
| Total for Slide A, B, C                                                                              | 1.8951 $\equiv$ D    |
| Mass Deposited in 10 min<br>(Slide C - Slide B)                                                      | 0.1326 $\equiv$ m    |
| Mass Balance ( $\frac{B}{A}$ )                                                                       | 98%                  |
| Percentage of Mass that<br>Made It Up the Chimney<br>( $\frac{A-C}{A}$ )                             | 36%                  |
| Percentage of Mass that<br>Made It Up the Chimney<br>That Deposited on Slides<br>( $\frac{D}{A-C}$ ) | 23.6% $\equiv$ P     |

Table XII. Mass Balance Results

$$\Gamma = \frac{1}{P} \cdot \frac{m}{tA} \cdot \frac{N}{M} \quad (21)$$

where

$$\begin{aligned} P &= \text{flux correction} &= 0.236 \\ m &= \text{mass deposited} &= 0.1326 \text{ gr} \\ t &= \text{time of deposit} &= 600 \text{ sec} \\ A &= \text{area of chimney} &= 0.95 \text{ cm}^2 \\ N &= \text{Avagadro's number} &= 6 \times 10^{23} \text{ atoms/mole} \\ M &= \text{molecular weight} &= 209 \text{ gr/mole} \end{aligned}$$

Using the above values in Eq (21), yields for the flux

$$\Gamma = 2.8 \times 10^{18} \frac{\text{atoms}}{\text{cm}^2\text{-sec}} \quad (22)$$

The number density of lead in the reaction area is given by

$$n = \Gamma/v \quad (23)$$

where  $v$  is the gas flow velocity. The flow velocity must be subsonic because shock waves have never been observed during operation. As a reasonable estimate, assume the flow velocity is half the speed of sound. Using this value for  $v$  in Eq (23) and using the value for flux from Eq (22) in Eq (23) yields the number density of

$$n = 2 \times 10^{14} \frac{\text{atoms}}{\text{cm}^3} \quad (24)$$

Snyder's unsubstantiated claim of number densities of the order of  $10^{14}$  (Ref 2:28) are now justified assuming the value in Eq (24) is a valid estimate.

As mentioned in earlier sections, Brom and Beattie reported number densities as  $10^{13} - 10^{14}$  (Ref 6:446). They used gas flow rate measurements and crucible mass loss to arrive at their value. The current work compares favorably to their value. The confidence of the value arrived in the current work is based upon the confidence of the estimate of the flow velocity.

An additional experiment was performed to further characterize the flow of lead into the reaction area. Furnace design A of Table VII was used. The results are presented in Table XIII. A significant result was that very little deposits formed on the microscope slide, outside of the sleeve area (directly over the chimney). This means that the lead flow velocity is fairly fast, leaving little time for the lead vapor to diffuse, and that the lead flow is well collimated. The results of this experiment offer support to the velocity estimate made earlier.

An unusual result of this additional experiment was the formation of lead spikes on the microscope slides. Photographs of these formations are shown in Appendix A. These formations

| SLIDE                                          | A      | B         | C      |
|------------------------------------------------|--------|-----------|--------|
| Runtime (min)                                  | 5      | 10        | 15     |
| Deposit on Sleeve (gr)                         | 0.1140 | 0.2221    | 0.2908 |
| Deposit on Slide (gr)                          | 0.0002 | 0.0023    | 0.0001 |
| Total Deposit (gr)                             | 0.1142 | 0.2244    | 0.2909 |
| <u>Deposit on Slide</u><br>Total Deposit (%)   | 0.2    | 1         | 0.03   |
| <hr/>                                          |        |           |        |
| Total Mass Deposited                           |        | 0.6296 gr |        |
| Total Mass Lost by Crucible                    |        | 4.0305 gr |        |
| <u>Mass Deposited</u><br>Mass Lost by Crucible |        | 16%       |        |

Table XIII. Mass Deposition Results

may be a gas dynamic flow phenomenon. As the laminar flow of carrier gas and lead vapor strike the microscope slide, the center of impact is a stagnation point. Lead deposits may readily build up there. The deposit may grow back along the central streamline, fed by lead vapor diffusing toward the cool deposit. The central streamlines would be the most stable location for such a growth within the flow field. The irregular formation at the end of the spike of Slide C would tend to violate this hypothesis. The reason for its particular formation remains to be determined.

## spectra

Spectra were recorded at various scan speeds and strip chart recorder speeds to give linear dispersions from 10 to 100 Å/cm. Spectra were observed from 4000-7500 Å. Figures 17 through 19 show representative spectra recorded during this work. The vibrational band structure is evident in the spectra. The rotational structure is shaded toward the red region of the spectrum. Due to a small S/N obtained with the RCA 7265 PMT, the rotational fine structure could not be distinguished from noise. However, bandhead assignments could be made with a good degree of certainty.

Four spectral runs were analyzed to determine bandheads. Table XIV lists the linear dispersion and the reading resolution for each of these spectra. All spectra were recorded using 200 µm slit widths for maximum signal strength.

Assignments of the observed bandheads from the spectra were made with the aid of a Deslandres Table. The Deslandres Table was calculated using spectroscopic constants reported in the literature. A computer program, called SEARCH, was developed to search the Deslandres Table for close matches between data and Table values. This program is reproduced in Appendix B.

In making assignments, if it happened that more than one calculated value closely corresponded to the observed bandhead, additional information was used to help make the correct assignment. The observed bandheads and their assignments as reported

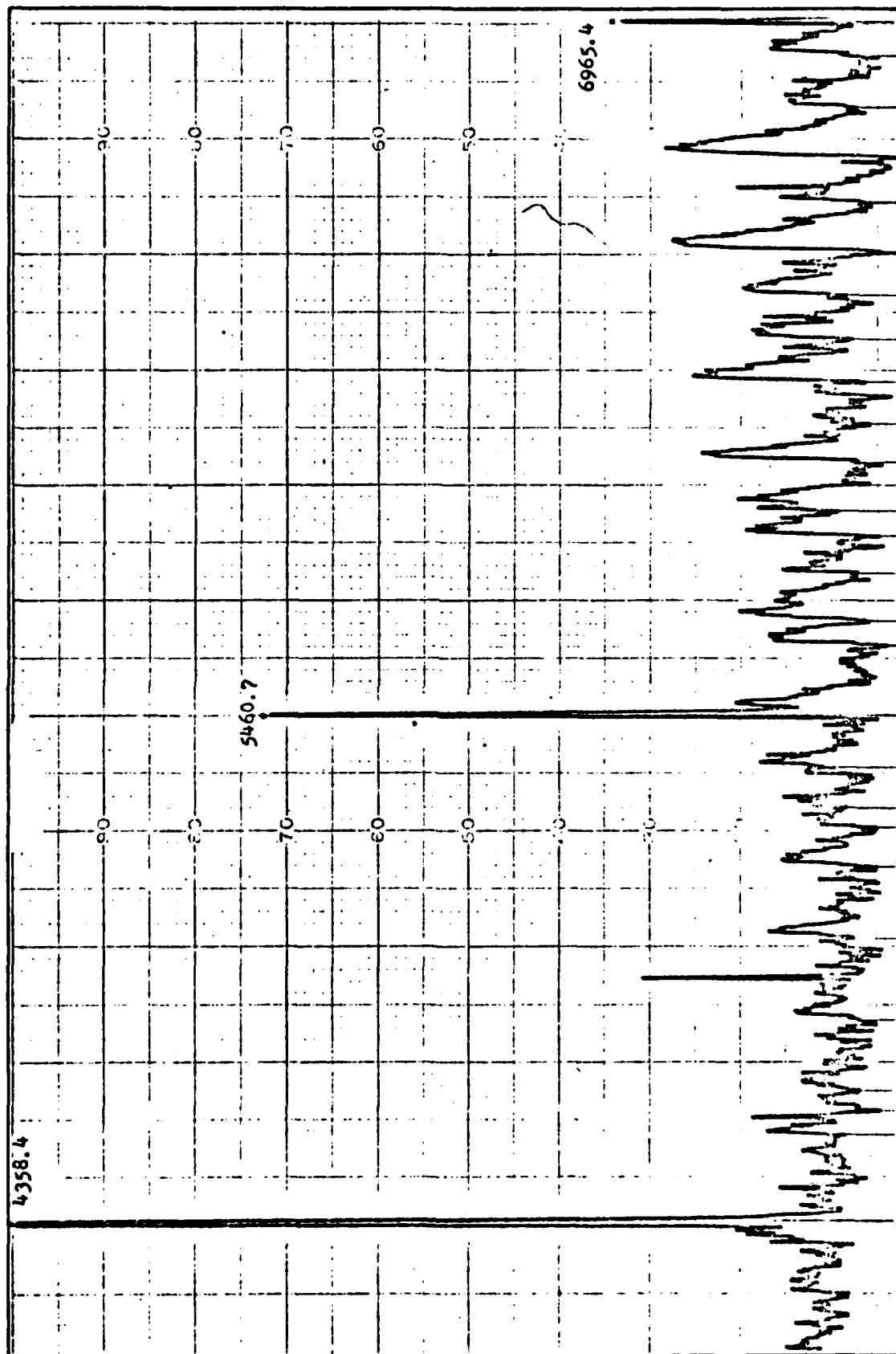


Figure 17. Low Dispersion Spectrum

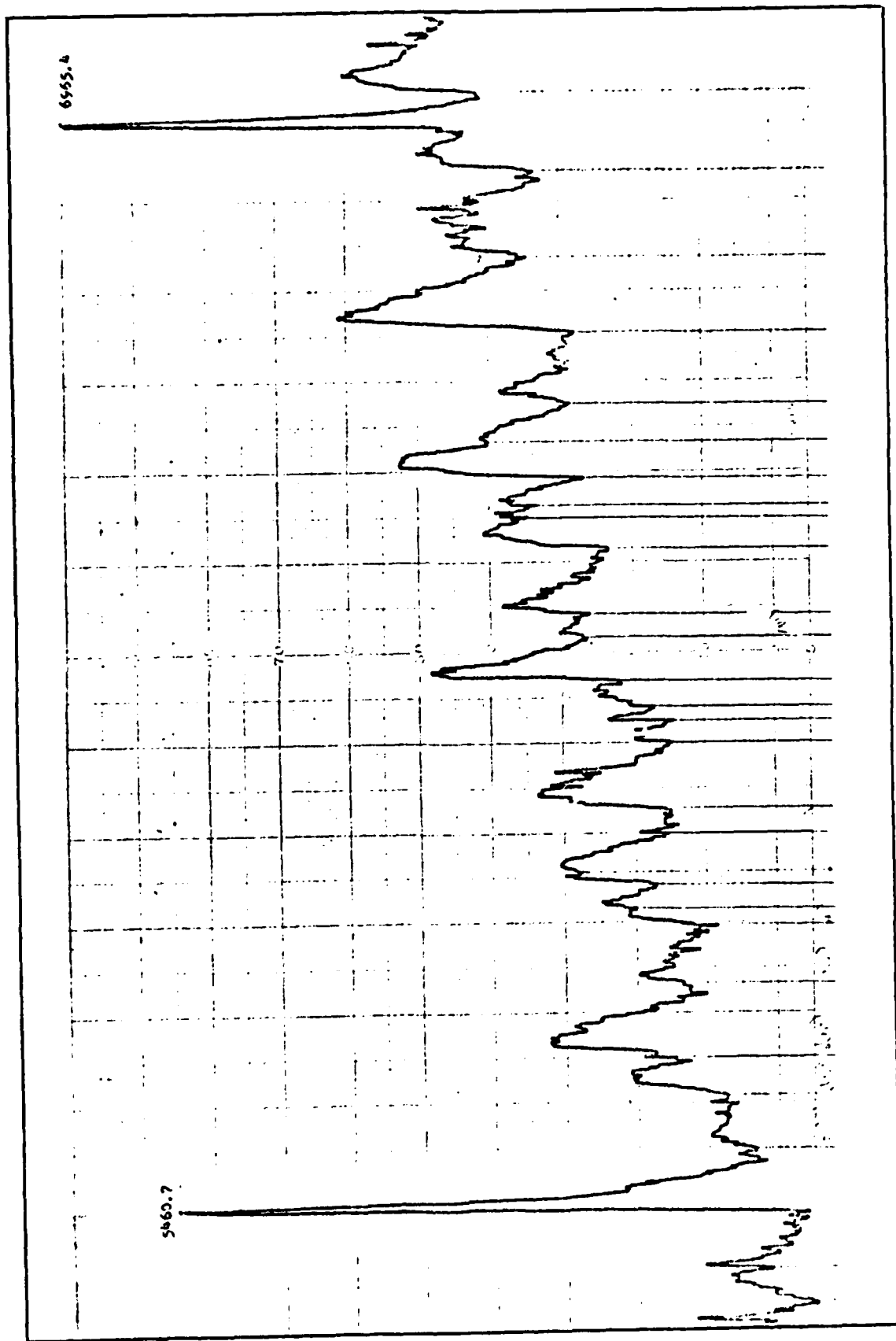


Figure 18. Moderate Dispersion Spectrum

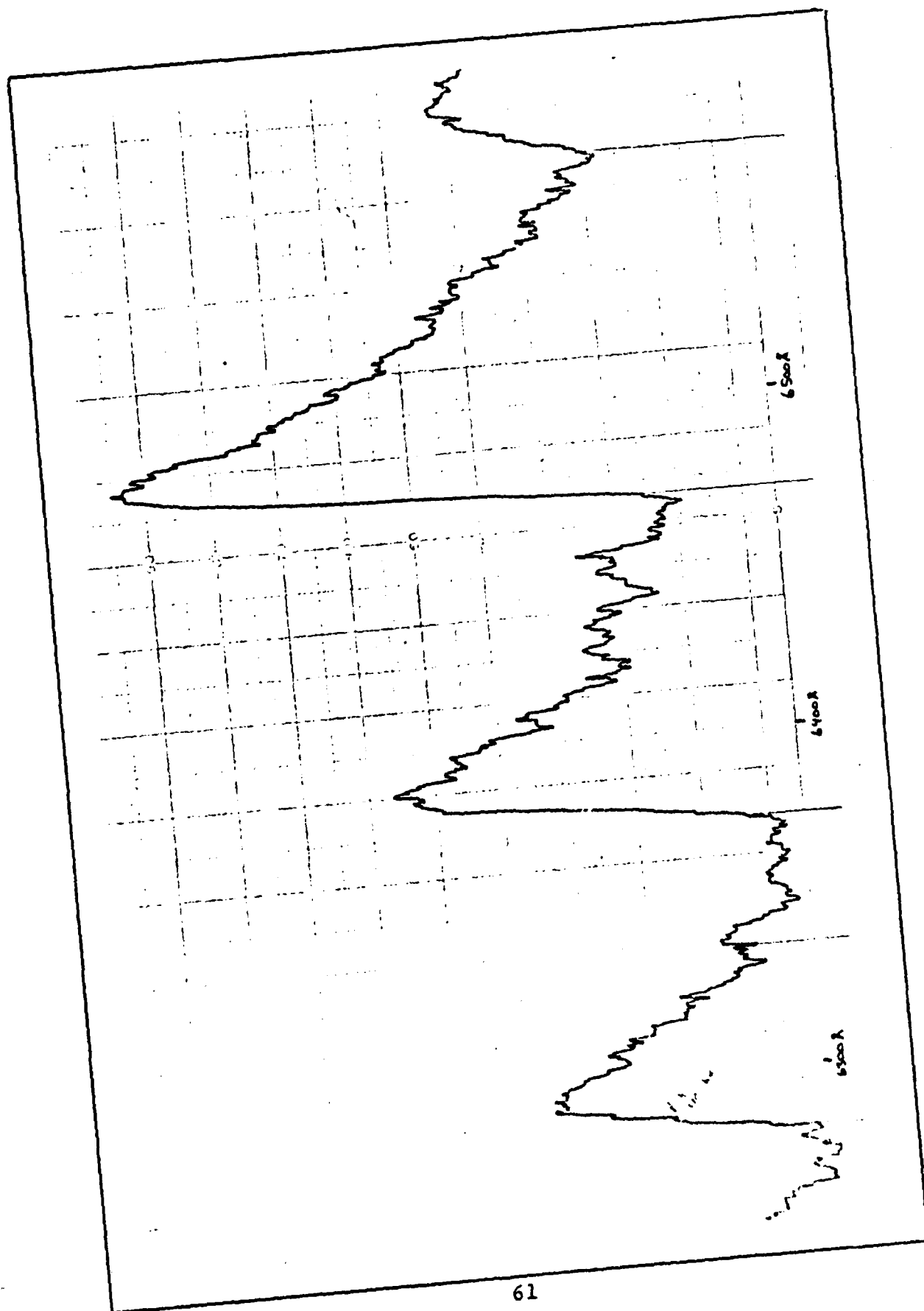


Figure 19. High Dispersion Spectrum

in the literature were used to assist in making the assignments. Assignments were made which would continue a progression or sequence where the other bands of the progression or sequence were assigned unambiguously.

| Spectrum | Linear<br>Dispersion<br>(Å/cm) | Reading<br>Resolution<br>(Å) |
|----------|--------------------------------|------------------------------|
| 1        | 100                            | 15                           |
| 2        | 50                             | 7.5                          |
| 3        | 40                             | 6                            |
| 4        | 10                             | 2.5                          |

Table XIV. Dispersion and Resolution of Spectra

Observed bandheads and assignments for all four spectral runs are presented in Appendix C. The Deslandres Table values for the transitions are listed, as well as the difference between the observed and calculated wavelengths. Spectrum No. 4 represents the highest dispersion spectrum recorded. The observed bandheads and assignments for Spectrum No. 4 are presented in Table XV.

A Deslandres Table was prepared with the observed band-head values which were assigned to the a-X system. This table is shown as Table XVI. Energy differences between adjacent transitions are shown in parentheses. The rows formed by the

| Observed (Å) | Calculated (Å) | Obs - Cal (Å) | Assignment |
|--------------|----------------|---------------|------------|
| 5226.6       | 5225.0         | 1.6           | a(7,0)     |
| 5351.2       | 5350.0         | 1.2           | a(6,0)     |
| 5481.6       | 5482.6         | -1.0          | a(5,0)     |
| 5621.8       | 5623.5         | -1.7          | a(4,0)     |
| 5708.4       | 5706.0         | 2.4           | a(5,1)     |
| 5773.2       | 5773.5         | -0.3          | a(3,0)     |
| 5858.6       | 5858.6         | 0.0           | a(4,1)     |
| 5932.1       | 5933.4         | -1.3          | a(2,0)     |
| 6021.3       | 6021.3         | 0.0           | a(3,1)     |
| 6102.6       | 6104.3         | -1.7          | a(1,0)     |
| 6195.7       | 6195.9         | -0.2          | a(2,1)     |
| 6288.4       | 6287.2         | 1.2           | a(0,0)     |
| 6380.5       | 6382.4         | -1.9          | a(1,1)     |
| 6477.7       | 6479.6         | -1.9          | a(2,2)     |
| 6580.2       | 6582.6         | -2.4          | a(0,1)     |
| 6681.1       | 6683.9         | -2.8          | a(1,2)     |
| 6785.9       | 6787.4         | -1.5          | a(2,3)     |
| 6902.4       | 6903.8         | -1.4          | a(0,2)     |
| 7010.0       | 7011.9         | -1.9          | a(1,3)     |
| 7254.0       | 7254.3         | -0.3          | a(0,3)     |
| 7370.4       | 7369.8         | 0.6           | a(1,4)     |
| 7640.0       | 7638.1         | 1.9           | a(0,4)     |
| 5031.4       | 5032.4         | -1.0          | b(10,1)    |

Table XV. Observed PbO Bandheads and Their Assignments from Spectrum No. 4

| Observed (Å) | Calculated (Å) | Obs - Cal (Å) | Assignment |
|--------------|----------------|---------------|------------|
| 4560.6       | 4559.6         | 1.0           | A(5,0)     |
| 4958.0       | 4958.4         | -0.4          | A(1,0)     |
| 5260.4       | 5260.4         | 0.0           | A(0,1)     |
| 5463.1       | 5463.7         | -0.6          | A(0,2)     |
| 5677.1       | 5681.0         | -3.9          | A(0,3)     |
| 5913.4       | 5913.9         | -0.5          | A(0,4)     |
| 6163.7       | 6163.9         | -0.2          | A(0,5)     |
| 6256.0       | 6254.8         | 1.2           | A(1,6)     |
| 6342.4       | 6345.9         | -3.5          | A(2,7)     |
| 4230.9       | 4230.0         | -0.9          | B(3,0)     |
| 4316.1       | 4319.4         | -3.3          | B(2,0)     |
| 4411.6       | 4412.6         | -1.0          | B(1,0)     |
| 4661.9       | 4660.0         | 1.9           | B(0,1)     |
| 4819.1       | 4818.8         | 0.3           | B(0,2)     |
| 4988.0       | 4987.1         | 0.9           | B(0,3)     |
| 5038.8       | 5038.4         | 0.4           | B(1,4)     |
| 5139.0       | 5138.6         | 0.4           | B(3,6)     |
| 5281.7       | 5221.8         | -0.1          | B(6,9)     |
| 5329.1       | 5327.2         | 1.9           | B(7,10)    |

Table XV. Observed PbO Bandheads and Their Assignments from Spectrum No. 4  
(Continued)

| $v'$ | $v''$          |                |                |                |
|------|----------------|----------------|----------------|----------------|
|      | 0              | 1              | 2              | 3              |
| 0    | 15902<br>(484) | 15197<br>(476) | 14488<br>(480) | 13786<br>(479) |
| 1    | 16386<br>(471) | 15673<br>(467) | 14968<br>(470) | 14265<br>(471) |
| 2    | 16857<br>(464) | 16140<br>(468) | 15438<br>(702) | 14736<br>(702) |
| 3    | 17321<br>(468) | 16608<br>(461) |                |                |
| 4    | 17789<br>(454) | 17069<br>(449) |                |                |
| 5    | 18243<br>(444) | 17518          |                |                |
| 6    | 18687<br>(446) |                |                |                |
| 7    | 19133          |                |                |                |

NOTE: Values are in  $\text{cm}^{-1}$

Table XVI. Deslandres Table from Observed Bandheads of the a-X System

energy differences of the columns and the columns formed by the energy differences of the rows agree within experimental error. This correspondence supports the correctness of the assignments.

Relative intensities of the bands of the a-X system were calculated. The values were uncorrected for PMT response and grating response. Intensities were measured from the band peak to the point where the signal began to rise from the baseline. These differences were then normalized relative to the most intense band (the (1,2) band). Finally, the relative intensities for each band were calculated by dividing the normalized intensity by the sum of all the normalized intensities. This value can be compared, at least qualitatively, with Frank-Condon factors. Only qualitative comparison is possible since, in the present work, not all bands have been observed. The results of these calculations are in Table XVII.

The relative intensities of Table XVII were arranged in a Deslandres Table shown in Table XVIII. The values were arranged in this way to display the Condon parabola (Ref 5: 197). The values of Table XVIII were normalized to 10. This was done to allow easy comparison with a similar table prepared by Oldenberg et al (Ref 7:288).

There is a qualitative agreement between the two sets of results. From Table XVIII, the Condon parabola is made up of the transitions: (4,0), (2,1), (1,2), (1,3), (1,4). From

| Band                                                            | Normalized Intensity <sup>a</sup> | Relative Intensity <sup>b</sup> |
|-----------------------------------------------------------------|-----------------------------------|---------------------------------|
| (7,0)                                                           | 0.165                             | 0.018                           |
| (6,0)                                                           | 0.231                             | 0.025                           |
| (5,0)                                                           | 0.330                             | 0.036                           |
| (4,0)                                                           | 0.385                             | 0.042                           |
| (3,0)                                                           | 0.352                             | 0.039                           |
| (2,0)                                                           | 0.154                             | 0.017                           |
| (1,0)                                                           | 0.165                             | 0.018                           |
| (0,0)                                                           | 0.440                             | 0.048                           |
| (5,1)                                                           | 0.110                             | 0.012                           |
| (4,1)                                                           | 0.484                             | 0.053                           |
| (3,1)                                                           | 0.660                             | 0.072                           |
| (2,1)                                                           | 0.725                             | 0.080                           |
| (1,1)                                                           | 0.550                             | 0.060                           |
| (0,1)                                                           | 0.231                             | 0.025                           |
| (2,2)                                                           | 0.857                             | 0.094                           |
| (1,2)                                                           | 1.000                             | 0.110                           |
| (0,2)                                                           | 0.429                             | 0.047                           |
| (2,3)                                                           | 0.330                             | 0.036                           |
| (1,3)                                                           | 0.747                             | 0.082                           |
| (0,3)                                                           | 0.220                             | 0.024                           |
| (1,4)                                                           | 0.220                             | 0.024                           |
| (0,4)                                                           | 0.330                             | 0.036                           |
| <sup>a</sup> Intensity of (1,2) band is defined as 1.000        |                                   |                                 |
| <sup>b</sup> Normalized intensity/Sum of normalized intensities |                                   |                                 |

Table XVII. Relative Intensities of the a-X System

|   | $v''$ |     |      |     |     |
|---|-------|-----|------|-----|-----|
|   | 0     | 1   | 2    | 3   | 4   |
| 0 | 4.4   | 2.3 | 4.3  | 2.2 | 3.3 |
| 1 | 1.7   | 5.5 | 10.0 | 7.5 | 2.7 |
| 2 | 1.5   | 7.3 | 8.6  | 3.3 |     |
| 3 | 3.5   | 6.6 |      |     |     |
| 4 | 3.9   | 4.8 |      |     |     |
| 5 | 3.3   | 1.1 |      |     |     |
| 6 | 2.3   |     |      |     |     |
| 7 | 1.7   |     |      |     |     |

Table XVIII. Relative Intensity Deslandres  
Table of the a-X System

the table Oldenberg reports, the Condon parabola is made up of the transitions: (6,0), (3,1), (2,2), (1,3).

Differences are most likely due to the differences in the detector response, since no correction was made in either case. A major discrepancy is that Oldenberg's table is missing the (0,0), (0,1), (0,2), (1,0), and (1,1) transitions altogether. The reason for this is unclear, since in the current work these transitions were fairly intense.

The Condon parabola of Table XVIII is fairly wide. This observation indicates that a large separation exists between the potential energy curves corresponding to the a and X states. Using this deduction, the Frank-Condon principle, and the

transitions of the Condon parabola, a schematic representation of the most likely relative positions of the potential energy curves for the a and X states can be made. This representation is shown in Figure 20. Figure 20 also shows some of the transitions belonging to the Condon parabola and some vibrational probability distributions.

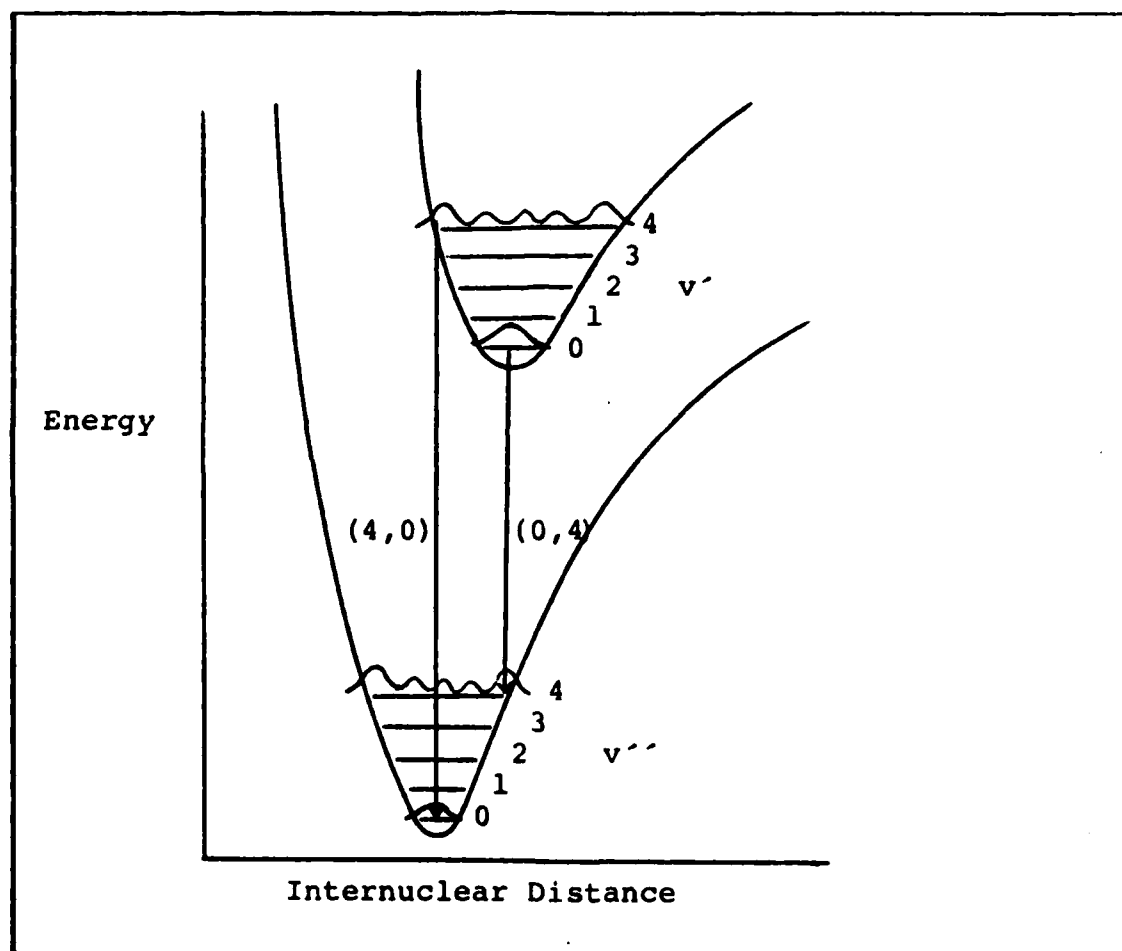


Figure 20. Potential Energy Curves of the a and X States of PbO

The recording of good spectra was frustrated by the low signal-to-noise ratio of the RCA 7265 PMT. Even with cooling, the S/N was never better than 15. The PMT degraded during the course of the thesis, ending up with a S/N of about 3. The reason for this performance is unclear, since this is the same PMT used by Snyder. Attempts to use other 7265 PMTs resulted in even poorer performance.

### Spectroscopic Constants

Spectroscopic constants for different states of the PbO molecule were calculated from observed bandheads and assignments. A computer program which employed a linear least squares routine was used to calculate the constants. Using Eq (7), the constants were calculated for the quadratic case and the cubic case. The programs which were written are called SPECT5 and SPECT7, respectively, and are reproduced in Appendix B.

The constants calculated from the band assignments of spectrum No. 4 are shown in Table XIX. In addition, Snyder's data (Ref 2:36-39) from the emission from the reaction  $\text{Pb} + \text{O}_2$  were used to calculate spectroscopic constants. These values are also reported in Table XIX. The ground state constants were calculated by a weighted average arrangement. The weighting factors were the number of bands for each data set. Table XIX also presents published values for the constants. Bloomenthal's work (Ref 15) was used for the B state constants. Linton and Broida's work (Ref 9) was used for the

| Source                                                                   | State | $T_e$ ( $\text{cm}^{-1}$ ) | $\bar{w}_e$ ( $\text{cm}^{-1}$ ) | $\bar{w}_e x_e$ ( $\text{cm}^{-1}$ ) |
|--------------------------------------------------------------------------|-------|----------------------------|----------------------------------|--------------------------------------|
| Present Work                                                             | B     | 22296.9 (0.03)             | 495.8 (-0.1)                     | 2.22 (-4.7)                          |
|                                                                          | A     | 19851.4 (-0.06)            | 453.7 (2.1)                      | 2.05 (280)                           |
|                                                                          | a     | 16025.9 (-0.006)           | 483.1 (0.33)                     | 2.81 (14.7)                          |
|                                                                          | X     | 0                          | 719.3 (-0.24)                    | 3.49 (-1.4)                          |
| Snyder <sup>a</sup><br>(Ref 2)                                           | B     | 22292.3 (0.01)             | 483.1 (-2.7)                     | -1.07 (-54)                          |
|                                                                          | A     | 19863.9 (0.007)            | 446.4 (0.47)                     | 0.48 (-11)                           |
|                                                                          | a     | 16026.0 (0.007)            | 484.6 (0.64)                     | 2.97 (21)                            |
|                                                                          | X     | 0                          | 723.0 (0.28)                     | 3.74 (5.6)                           |
| Bloomenthal<br>(Ref 15)                                                  | B     | 22289.9                    | 496.3                            | 2.33                                 |
|                                                                          | A     | 19862.6                    | 444.3                            | 0.54                                 |
| (Ref 9)                                                                  | a     | 16024.9                    | 481.5                            | 2.45                                 |
|                                                                          | X     | 0                          | 721.0                            | 3.54                                 |
| <sup>a</sup> Using emission from the reaction $\text{Pb} + \text{O}_2$ . |       |                            |                                  |                                      |

Table XIX. Spectroscopic Constants for  $\text{PbO}^b$

<sup>b</sup> The constants were calculated by a linear least squares analysis of the data. The percent differences between those results and the constants reported by Bloomenthal (Ref 15) and Linton and Broida (Ref 9) are in parentheses.

A, a, and X state constants. The percent difference between the calculated values and the published values are given in parentheses beside the values of the constants.

The comparison between the values obtained in the present work and Snyder's work with the values reported in the literature shows good correspondence. Most of the calculated values are within one percent of the published values. Differences of greater than one percent occur for the  $\bar{w}_e x_e$  values. This is so because a large enough data set was not available to get good correspondence for these higher order constants. For example, consider the A state values. In the present work, these constants were based on calculations from only nine bands. The A state constants from Snyder's work were based on 13 bands. Table XIX shows that, for the A state, Snyder's data gave constants of closer correspondence to the published values than did the current work.

The general good correspondence between the values in Table XIX is strong evidence to support the correctness of the assignments. In this regard, it was found that, during the calculations, if one band was not properly assigned, it would lead to a significant change in the values of the calculated constants.

Constants calculated for the assignments of the spectral runs Nos. 1, 2, 3, and 4, using both SPECT5 and SPECT7, are shown in Appendix D. Additionally, analysis of all of Snyder's data (Ref 2:36-39) was performed using both SPECT5 and SPECT7.

The results of these calculations are shown in Appendix E.

Overall, the values for the constants shown in Appendices D and E are in fair agreement with the literature values. Some values are quite close to, while others are far from, the literature values. In Appendix E, the constants calculated from the data from the reaction  $\text{Pb} + \text{O}_2$  are generally better than those from the  $\text{Pb} + \text{N}_2\text{O}$  reaction. This observation can be explained by Snyder's observation that the emission from the  $\text{Pb} + \text{O}_2$  reaction was brighter than the emission from the  $\text{Pb} + \text{N}_2\text{O}$  reaction (Ref 2:32). With a bright flame emission, the bandheads can be determined more accurately. This will lead to accurate assignments, then to accurate spectroscopic constants.

When comparing spectra, the current work observed fewer bands, but at higher resolution, than Snyder's work. A comparison of the calculated constants shows the current work in marginally better agreement with published values than constants from Snyder's data. The comparison is far from conclusive. This comparison suggests that a trade-off may exist between resolution and the number of bands observed for precisely determining spectroscopic constants. There may exist an optimum resolution/number of bands observed combination that yields the most precise constants. The validity of this hypothesis remains to be determined.

## V. Conclusions and Recommendations

### Conclusions

A gas flow tube reactor has been used to generate chemiluminescent flames from the reaction  $\text{Pb} + \text{O}_2$ . The flow tube geometry has been selected for vacuum flow efficiency and reduced reaction product recirculation. The flame has been optimized for maximum emission intensity by varying the furnace design and oxidizer mixing configurations. A "closed system" crucible and chimney arrangement resulted in excellent mixing and entrainment of the lead vapor by the carrier gas. An oxidizer ring over a straight flow oxidizer manifold produced the optimum short, bright flame emission. Heater coil insulation was used to double the lead heating efficiency. Different oxides of lead were formed by different oxidizer mixing configurations. The reaction chemistry is, therefore, sensitive to the reactant mixing technique. A mass balance of 98% was achieved. The flux of lead vapor into the reaction region was determined to be  $2.8 \times 10^{18}$  atoms/cm<sup>2</sup>sec at 2 Torr pressure of Argon carrier gas. The temperature of the PbO flame was measured to be 175° C.

Emission was observed from the a, b, A, and B states of PbO. Spectra were recorded at higher resolution and far greater linear dispersion than previously at AFIT. Assignments of the observed bandheads of the B-X, A-X, and a-X

transitions led to the following spectroscopic constants (in  $\text{cm}^{-1}$ ).

| State | $T_e$   | $\bar{w}_e$ | $\bar{w}_e x_e$ |
|-------|---------|-------------|-----------------|
| B     | 22296.9 | 495.8       | 2.22            |
| A     | 19851.4 | 453.7       | 2.05            |
| a     | 16025.9 | 483.1       | 2.81            |
| X     | 0       | 719.3       | 3.49            |

The spectroscopic constants calculated from this work compare favorably to published values. The emission intensities of observed a-X transitions were measured and relative intensities calculated and prepared in a Deslandres Table format to display the Condon parabola. The Condon parabola was observed to consist of the transitions (4,0), (2,1), (1,2), (1,3), and (0,4).

### Recommendations

Reaction Chemistry. The reaction chemistry was observed to be sensitive to the reactant mixing technique. The effect, if any, that the reactant mixing technique (hence, reaction chemistry) has on the emission spectra should be observed and explained (if possible).

Excited Gases. Excited gases, such as atomic O,  $\text{O}_2(^1\Delta)$ , and active  $\text{N}_2$  should be introduced to the flame region to determine if any of these enhance emission from particular electronic states.

Furnace Design. The furnace design shown in Figure 21 should be built. This design will greatly simplify the furnace and reduce the distance from the crucible to the reaction region. This should reduce the amount of lead vapor which condenses before reaching the reaction area.

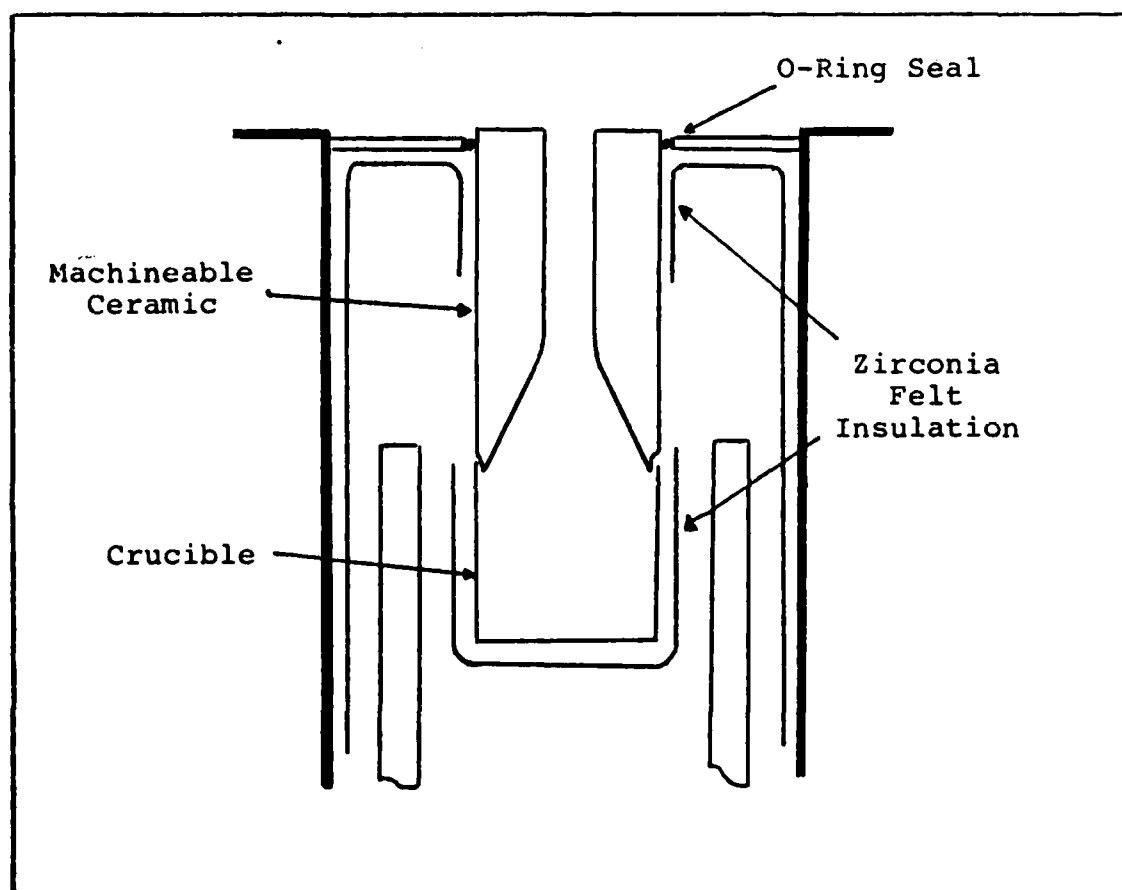


Figure 21. Proposed Furnace

Gas Curtain. The oxidizer mixing configuration should allow the oxidizer gas to flow freely, parallel to the lead vapor flow, to act as a gas curtain to further prevent reaction product contamination of the optical windows.

Flow Velocity. The flow velocity should be measured so that, with flux calculations, the number density of lead vapor within the reaction region can be determined. The simplest approach is to use a flow meter to measure carrier gas flow.

Resolution. A detector of high detectivity, low noise should be obtained and used to exploit the resolution capability of the 0.5 m monochrometer. With such a detector, a trade-off study showing the effect of spectral resolution versus number of bands observed on the calculation of spectroscopic constants could be performed.

## Bibliography

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## APPENDIX A

### Photographs

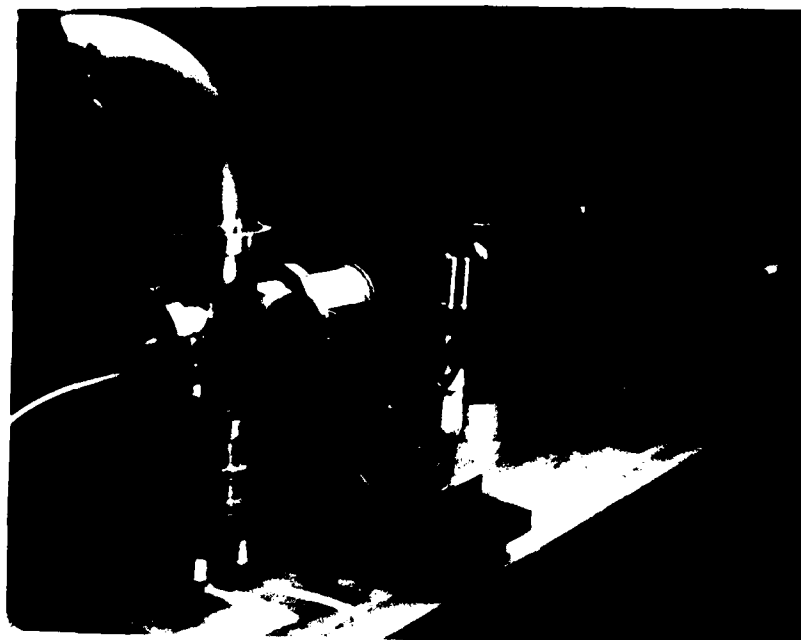


Figure A-1. Experimental Setup

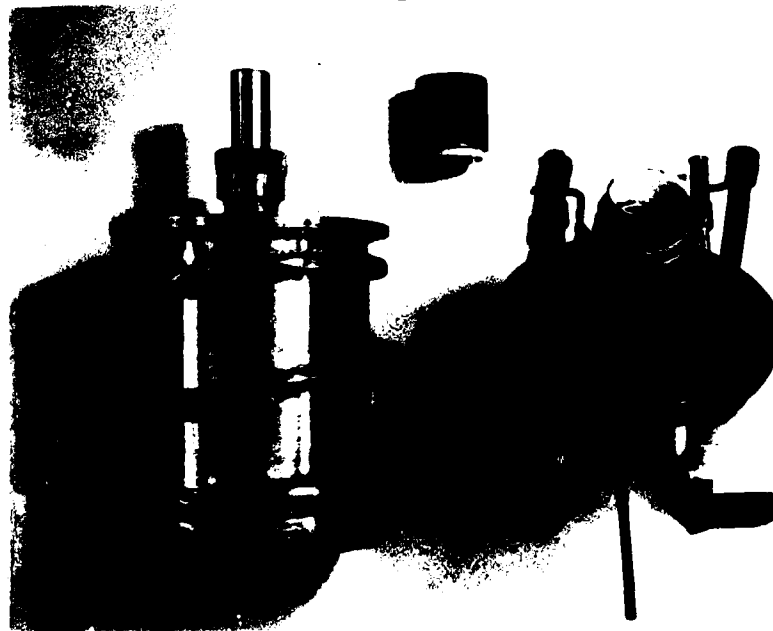


Figure A-2. Furnace

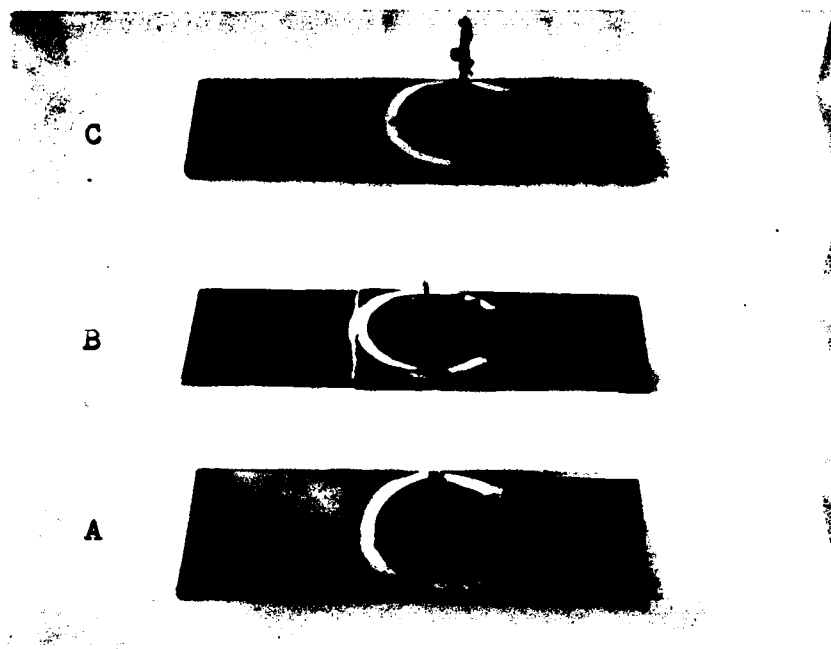


Figure A-3. Deposit on Slides

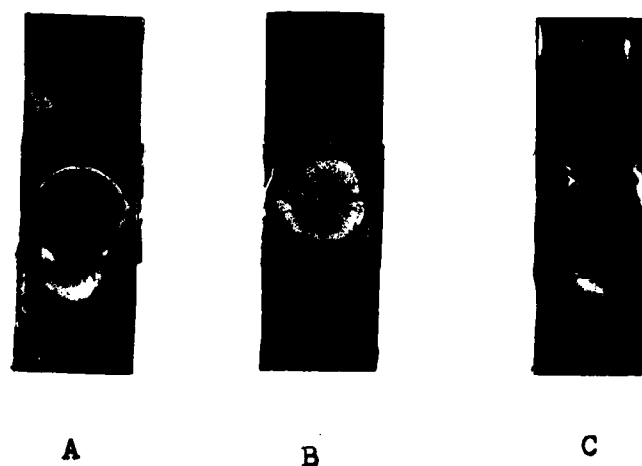


Figure A-4. Deposit Pattern on Slides

## SEARCH

```
C
C      ** THIS PROGRAM MATCHES SPECTRAL LINES **
C      ** TO THOSE FROM A DESLANTERS TABLE **
C      ** MUST UPDATE FOR EACH DATA RUN **
C      ** USE /EXCLAMATION/= /DATA POINTS/,A **
C      ** ALSO, MAY WANT TO CHANGE SEARCH RANGE**
C      ** OR TABLE CONSTANTS **
C
REAL WL(2),WL12(8,21,21),TE1(3),WE1(3),WEXE1(3)
REAL WE2(8),WEXE2(9),DELTA,MW,JWL
CHARACTER TR(4)*2,SOURCE*25

C
C      ** INITIALIZE
C
M=2
DELTA=10.
SOURCE='GLESSNE?'
DATA (TR(I),I=1,5)/'SA','SB','','A','','B','','C','','CP','','D','','E'/

C
C      ** SMALL A-X TRANSITION,LINTON&BROIDA
C
DATA TE1(1),WE1(1),WEXE1(1)/15324.0,461.5,2.45/
DATA WE2(1),WEXE2(1)/720.97,3.54/

C
C      ** SMALL B-X TRANSITION,KURYLO,ETAL
C
DATA TE1(2),WE1(2),WEXE1(2)/15315.0,441.0,0.0/
DATA WE2(2),WEXE2(2)/721.45,3.54/

C
C      ** LARGE A-X TRANSITION,SUCHARD
C
DATA TE1(3),WE1(3),WEXE1(3)/19352.3,444.2,0.46/
DATA WE2(3),WEXE2(3)/721.45,3.54/

C
C      ** LARGE B-X TRANSITION,SUCHARD
C
DATA TE1(4),WE1(4),WEXE1(4)/22297.0,487.0,0.00/
DATA WE2(4),WEXE2(4)/721.46,3.54/

C
C      ** LARGE C-X TRANSITION,SUCHARD
C
DATA TE1(5),WE1(5),WEXE1(5)/23320.0,532.0,3.0/
DATA WE2(5),WEXE2(5)/721.45,3.54/

C
C      ** LARGE C'-X TRANSITION,SUCHARD
C
DATA TE1(6),WE1(6),WEXE1(6)/24347.0,474.0,3.0/
DATA WE2(6),WEXE2(6)/721.45,3.54/

C
C      ** LARGE D-X TRANSITION,SUCHARD
C
DATA TE1(7),WE1(7),WEXE1(7)/30134.0,533.4,2.0/
DATA WE2(7),WEXE2(7)/721.45,3.54/

C
C      ** LARGE E-X TRANSITION,SUCHARD
```

# SEARCH (Continued)

```

DATA TE1(8),WE1(8),WX1(8)/34455.0,454.1,6.85/
DATA WE2(8),WX2(8)/721.46,3.54/

C
C  ** INPUT RAW DATA
C
DO 10 L=1,M
  READ*,WL(L)
10 CONTINUE

C
C  ** CALCULATE DESLANTERS TABLE
C
DO 20 I=1,6
  DO 30 J=1,21
    DO 40 K=1,21
      WW=TE1(I)+WL1(I)*(J-.5)-WE1(I)*(J-.5)**2-W 2(I)*(K-.5)+
      WEK2(I)*(K-.5)**2
      WW=(10**8)/WW
      WL12(I,J,K)=(FLOAT(INT(10.*WW+.5)))/10.
40 CONTINUE
30 CONTINUE
20 CONTINUE

C
C  ** PRINT OUT HEADING
C
PRINT*,*
PRINT*,*   DESLANTERS TABLE SEARCH*
PRINT*,*
PRINT*,*   DATA IS FROM *,SOURCE
PRINT*,*
PRINT*,*DATA WL   TABLE WL   DIFF. TRANS*
PRINT*,*

C
C  ** SEARCH THE TABLE FOR MATCHES
C
DO 50 L=1,M
  PRINT*,*
  PRINT*,WL(L)
  DO 60 I=1,8
    DO 70 J=1,21
      DO 80 K=1,21
        IJ=J-1
        IK=K-1
        DWL=WL(L)-WL12(I,J,K)
        IF(DWL.LT.0.0) GO TO 100
        DWL=(FLOAT(INT(10.*DWL+.5)))/10.
        GO TO 90
100 DWL=(FLOAT(INT(10.*DWL-.5)))/10.
90 IF(ABS(DWL).LE.DELTA) PRINT*,*   *,WL12(I,J,K),
C   *,DWL,*   *,IR(I),*(*,IJ,*(*,IK,*
80 CONTINUE
70 CONTINUE
60 CONTINUE
50 CONTINUE

C
STOP
END

```

# SEARCH, Sample Output

## DESLANTERS TABLE SEARCH

DATA IS FROM GLESSNER

DATA WL    TABLE WL    DIFF    TRANS

3456.7

|        |      |          |
|--------|------|----------|
| 3465.8 | -9.1 | B(18,3)  |
| 3456.3 | .4   | C(14,2)  |
| 3466.2 | -9.5 | C(19,5)  |
| 3447.2 | 9.5  | CP(9,0)  |
| 3463.6 | -6.9 | CP(12,2) |
| 3448.6 | 8.1  | CP(14,3) |
| 3460.3 | -3.6 | CP(19,6) |
| 3450.8 | 5.9  | D(6,6)   |
| 3459.1 | -2.4 | D(10,9)  |
| 3448.6 | 8.1  | D(13,11) |
| 3463.7 | -7.  | D(17,14) |
| 3459.2 | -2.5 | D(20,16) |
| 3446.8 | 9.9  | E(2,9)   |
| 3453.6 | -1.9 | E(5,11)  |
| 3447.7 | 9.   | E(7,12)  |
| 3449.9 | 6.8  | E(13,15) |
| 3462.2 | -5.5 | E(15,16) |
| 3455.9 | .8   | E(18,17) |

4567.8

|        |      |           |
|--------|------|-----------|
| 4561.9 | 5.9  | SA(17,2)  |
| 4564.4 | 3.4  | SB(13,0)  |
| 4559.6 | 8.2  | A(5,0)    |
| 4563.2 | 4.6  | A(13,5)   |
| 4575.7 | -7.9 | A(16,7)   |
| 4565.  | 2.8  | H(8,6)    |
| 4573.1 | -5.3 | B(12,8)   |
| 4567.8 | 0.   | H(16,12)  |
| 4565.9 | 1.9  | C(6,7)    |
| 4566.7 | 1.1  | CP(4,7)   |
| 4566.7 | 1.1  | CP(19,17) |
| 4568.6 | -0.8 | D(1,13)   |
| 4571.8 | -4.  | D(7,18)   |

# SPECT5

```

1      PROGRAM SPECT5
2
3      C
4      C
5      C
6      C
7      C
8      C
9      C
10     C
11     C
12     C
13     C
14     C
15     C
16     C
17     C
18     C
19     C
20     C
21     C
22     C
23     C
24     C
25     C
26     C
27     C
28     C
29     C
30     C
31     C
32     C
33     C
34     C
35     C
36     C
37     C
38     C
39     C
40     C
41     C
42     C
43     C
44     C
45     C
46     C
47     C
48     C
49     C
50     C
51     C
52     C
53     C
54     C
55     C
56     C
57     C
58     C
59     C
60     C
61     C
62     C
63     C
64     C
65     C

      ** THIS PROGRAM CALCULATES FIVE CONSTANTS
      ** MUST UPDATE PROGRAM FOR EACH DATA RUN
      ** USE /EXCLAMATION/= /NUMBER OF DATA POINTS/,A

      INTEGER IA,M,N,KBASIS,IP(5),IER,IVP(22),IVDP(22)
      REAL A(22,5),H(22),TOL,X(5),H(5),WL(22)
      CHARACTER EXST=*,REF=25

      ** INITIALIZE

      M=22
      IA=22
      N=5
      TOL=0.0
      KBASIS=0

      ** INPUT RAW DATA
      ** FIRST CARD, EXCITED STATE DESIGNATION
      ** SECOND CARD, REFERENCE SOURCE OF DATA
      ** OTHER CARDS, WAVELENGTH, VP, VDP

      READ*,EXST
      READ*,REF
      DO 10 I=1,M
      READ*,WL(I),IVP(I),IVDP(I)
      CONTINUE
10
      ** REFINE THE RAW DATA

      DO 20 I=1,M
      A(I,1)=1.0
      A(I,2)=IVP(I)+0.5
      A(I,3)=(-1)*((IVP(I)+0.5)**2)
      A(I,4)=(-1)*((IVDP(I)+0.5)
      A(I,5)=((IVDP(I)+0.5)**2
      B(I)=(10**8)/WL(I)
      CONTINUE
20

      ** PERFORM THE LEAST SQUARES FIT

      CALL LLSQF(A,IA,M,N,B,TOL,KBASIS,X,M,IP,IER)

      ** OUTPUT THE CONSTANTS

      PRINT*,*
      PRINT*,THE CONSTANTS ARE FOR THE *,EXST,*,X TRANSITION,*
      PRINT*,*
      PRINT*,THE SOURCE OF DATA IS *,REF
      PRINT*,*
      PRINT*,TE = *,X(1)
      PRINT*,*
      PRINT*,WE1 = *,X(2)
      PRINT*,*
      PRINT*,WEK1 = *,X(3)
      PRINT*,*
      PRINT*,WE2 = *,X(4)
      PRINT*,*
      PRINT*,WEK2 = *,X(5)
      PRINT*,*

      STOP
      END

```

# SPECT7

```

1      PROGRAM SPECT7
2      C
3      C ** THIS PROGRAM CALCULATES SEVEN CONSTANTS
4      C
5      C ** MUST UPDATE PROGRAM FOR EACH DATA RUN
6      C ** USE /EXCLAMATION/= /NUMBER OF DATA POINTS/,A
7      C
8      INTEGER IA,M,N,KBASIS,IP(7),IER,I,VP(21),IVDP(21)
9      REAL A(21,7),H(21),TOL,K(7),H(1),H(21)
10     CHARACTER EXST=*,REF=25
11     C
12     C ** INITIALIZE
13     C
14     M=21
15     A=21
16     I=7
17     TOL=0.0
18     KBASIS=0
19     C
20     C ** INPUT RAW DATA
21     C ** FIRST CARD, EXCITED STATE DESIGNATION
22     C ** SECOND CARD, REFERENCE SOURCE OF DATA
23     C ** OTHER CARDS, WAVELENGTH, VP, VDP
24     C
25     READ*,EXST
26     READ*,REF
27     DO 10 I=1,M
28     READ*,WL(I),IVP(I),IVDP(I)
29     CONTINUE
30     10 C
31     C ** REFINE THE RAW DATA
32     C
33     DO 20 I=1,M
34     A(I,1)=1.0
35     A(I,2)=IVP(I)*0.5
36     A(I,3)=(-1)*((IVP(I)+0.5)**2)
37     A(I,4)=(IVP(I)+0.5)**3
38     A(I,5)=(-1)*(IVDP(I)+0.5)
39     A(I,6)=(IVDP(I)+0.5)**2
40     A(I,7)=(-1)*((IVDP(I)+0.5)**3)
41     B(I)=(10**6)/WL(I)
42     20 CONTINUE
43     C
44     C ** PERFORM THE LEAST SQUARES FIT
45     C
46     CALL LLSQF(A,IA,M,N,B,TOL,KBASIS,X,H,IP,IER)
47     C
48     C ** OUTPUT THE CONSTANTS
49     C
50     PRINT*,*
51     PRINT*,THESE CONSTANTS ARE FOR THE *,EXST, *-X TRANSITION*
52     PRINT*,*
53     PRINT*,THE SOURCE OF DATA IS *,REF
54     PRINT*,*
55     PRINT*,WL = *,X(1)
56     PRINT*,*
57     PRINT*,WL1 = *,X(2)
58     PRINT*,*
59     PRINT*,WLX1 = *,X(3)
60     PRINT*,*
61     PRINT*,WLX1 = *,X(4)
62     PRINT*,*
63     PRINT*,WE2 = *,X(5)
64     PRINT*,*
65     PRINT*,WE12 = *,X(6)
66     PRINT*,*
67     PRINT*,WE12 = *,X(7)
68     PRINT*,*
69     C
70     STOP
71     END

```

AD-A124 825

FLAME OPTIMIZATION FOR THE SPECTROSCOPIC ANALYSIS OF  
THE CHEMILUMINESCENC. (U) AIR FORCE INST OF TECH  
WRIGHT-PATTERSON AFB OH SCHOOL OF ENGI.. J W GLESSNER  
DEC 82 AFIT/GEP/PH/82D-9 F/G 7/4

2/2

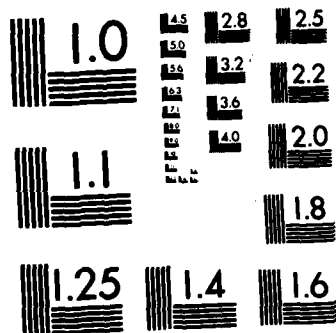
UNCLASSIFIED

NL

END

FILMED

DTIC



MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A

## SPECT5, Sample Output

THESE CONSTANTS ARE FOR THE SMALL A -X TRANSITION  
THE SOURCE OF DATA IS GLESSNER

TE = 16040.9221431  
MA1 = 484.8036943299  
WEXE1 = 3.712001233678  
WE2 = 713.9666652484  
WEXE2 = .1016451640755

## SPECT7, Sample Output

THESE CONSTANTS ARE FOR THE SMALL A -X TRANSITION  
THE SOURCE OF DATA IS GLESSNER

TE = 15002.394245-3  
ME1 = 484.4665944769  
WEXE1 = 3.634202278047  
WEY11 = .002470106566421  
WE2 = 713.9631841629  
WEXE2 = 1.67759507310  
WEY22 = .22776734466 5

# APPENDIX C

## Observed Bandheads and Assignments

| <u>Observed</u> (Å) | <u>Calculated</u> (Å) | <u>Obs - Cal</u> (Å) | <u>Assignments</u> |
|---------------------|-----------------------|----------------------|--------------------|
| 4545                | 4543.9                | 1.1                  | B(4,3)             |
| 4598                | 4601.9                | - 3.9                | B(2,2)             |
| 4642                | 4647.1                | - 5.1                | B(3,3)             |
| 4797                | 4801.8                | - 4.8                | B(3,4)             |
| 4973                | 4980.1                | - 7.1                | B(7,8)             |
| 5127                | 5128.0                | - 1.0                | A(9,6)             |
| 5215                | 5218.8                | - 3.8                | B(1,5)             |
| 5265                | 5271.0                | - 6.0                | B(2,6)             |
| 5612                | 5614.6                | - 2.2                | B(1,7)             |
| 5662                | 5670.6                | - 8.6                | B(2,8)             |
| 5766                | 5773.5                | - 7.5                | a(3,0)             |
| 5848                | 5858.6                | -10.6                | a(4,1)             |
| 6008                | 6021.3                | -13.3                | a(3,1)             |
| 6093                | 6104.3                | -11.3                | a(1,0)             |
| 6155                | 6163.9                | - 8.9                | A(0,5)             |
| 6183                | 6195.9                | -12.9                | a(2,1)             |
| 6275                | 6287.2                | -12.2                | a(0,0)             |
| 6371                | 6382.4                | -11.4                | a(1,1)             |
| 6464                | 6479.6                | -15.6                | a(2,2)             |
| 6574                | 6582.6                | - 8.6                | a(0,1)             |
| 6672                | 6683.9                | -11.9                | a(1,2)             |
| 6780                | 6787.4                | - 7.4                | a(2,3)             |
| 6892                | 6893.1                | - 1.1                | a(3,4)             |

Table C-1. Observed PbO Bandheads and Their Assignments for Spectrum No. 1

| <u>Observed (Å)</u> | <u>Calculated (Å)</u> | <u>Obs - Cal (Å)</u> | <u>Assignments</u> |
|---------------------|-----------------------|----------------------|--------------------|
| 4192                | 4182.4                | - 0.4                | C(3,2)             |
| 4275                | 4270.7                | 4.3                  | B(4,1)             |
| 4306                | 4319.4                | -13.4                | B(2,0)             |
| 4396                | 4403.7                | - 7.7                | B(4,2)             |
| 4447                | 4445.1                | 1.9                  | B(5,3)             |
| 4477                | 4485.8                | - 8.8                | B(6,4)             |
| 4496                | 4500.7                | - 4.7                | B(3,2)             |
| 4543                | 4543.9                | - 0.9                | B(4,3)             |
| 4640                | 4647.1                | - 7.1                | B(3,3)             |
| 4696                | 4707.9                | -11.9                | B(1,2)             |
| 4743                | 4755.1                | -12.1                | B(2,3)             |
| 4803                | 4801.8                | 1.2                  | B(3,4)             |
| 4850                | 4847.7                | 2.3                  | B(4,5)             |
| 4975                | 4980.1                | - 5.1                | B(7,8)             |
| 5018                | 5012.6                | 5.4                  | B(4,6)             |
| 5125                | 5128.8                | - 3.0                | A(9,6)             |
| 5215                | 5218.8                | - 3.8                | B(1,5)             |
| 5273                | 5271.0                | 2.0                  | B(2,6)             |
| 5325                | 5322.4                | 2.6                  | B(3,7)             |
| 5373                | 5372.6                | 0.4                  | B(4,8)             |
| 5539                | 5541.5                | - 2.5                | A(1,3)             |
| 5613                | 5614.6                | - 1.6                | B(1,7)             |
| 5667                | 5670.6                | 3.6                  | B(2,8)             |
| 5770                | 5773.5                | - 3.5                | a(3,0)             |

Table C-2. Observed PbO Bandheads and Their Assignments for Spectrum No. 2

| <u>Observed (Å)</u> | <u>Calculated (Å)</u> | <u>Obs - Cal (Å)</u> | <u>Assignments</u> |
|---------------------|-----------------------|----------------------|--------------------|
| 5851                | 5858.6                | - 7.6                | a(4,1)             |
| 5907                | 5896.6                | 10.4                 | b(5,2)             |
| 5926                | 5933.4                | - 7.4                | a(2,0)             |
| 5979                | 5988.2                | - 9.2                | b(6,3)             |
| 6015                | 6021.3                | - 6.3                | a(3,1)             |
| 6106                | 6104.3                | 1.7                  | a(1,0)             |
| 6156                | 6163.9                | - 7.9                | A(0,5)             |
| 6191                | 6195.9                | - 4.9                | a(2,1)             |
| 6252                | 6254.8                | - 2.8                | A(1,6)             |
| 6283                | 6287.2                | - 4.2                | a(0,0)             |
| 6375                | 6382.4                | - 7.4                | a(1,1)             |
| 6417                | 6424.5                | - 7.5                | b(5,4)             |
| 6436                | 6433.2                | 2.8                  | A(0,6)             |
| 6473                | 6479.6                | - 4.6                | a(2,2)             |
| 6524                | 6529.2                | - 5.2                | A(1,7)             |
| 6576                | 6582.6                | - 6.6                | a(0,1)             |
| 6675                | 6683.9                | - 8.9                | A(1,2)             |
| 6780                | 6787.4                | - 7.4                | a(2,3)             |
| 6900                | 6893.1                | 6.9                  | a(3,4)             |
| 7010                | 7011.9                | - 1.9                | a(1,3)             |
| 7250                | 7254.3                | - 4.3                | A(2,10)            |

Table C-2. Observed PbO Bandheads and Their  
Assignments for Spectrum No. 2  
(Continued)

| <u>Observed (Å)</u> | <u>Calculated (Å)</u> | <u>Obs - Cal (Å)</u> | <u>Assignments</u> |
|---------------------|-----------------------|----------------------|--------------------|
| 5604.8              | 5614.6                | - 9.8                | B(1,7)             |
| 5670.6              | 5670.6                | 0.0                  | B(2,8)             |
| 5806.4              | 5790.1                | 15.3                 | a(6,2)             |
| 5846.4              | 5858.6                | -12.2                | a(4,1)             |
| 5959.6              | 5958.0                | 1.6                  | b(3,1)             |
| 6013.1              | 6021.3                | - 8.2                | a(3,1)             |
| 6104.5              | 6104.3                | 0.2                  | a(1,0)             |
| 6154.8              | 6193.9                | - 9.1                | A(0,5)             |
| 6186.9              | 6195.9                | - 9.0                | a(2,1)             |
| 6250.7              | 6254.8                | - 4.1                | A(1,6)             |
| 6281.9              | 6287.2                | - 5.3                | a(0,0)             |
| 6371.4              | 6382.4                | - 9.0                | a(1,1)             |
| 6430.2              | 6433.2                | - 3.0                | A(0,6)             |
| 6468.4              | 6479.6                | -11.2                | a(2,2)             |
| 6526.7              | 6529.2                | - 2.5                | A(1,7)             |
| 6582.1              | 6582.6                | - 0.5                | a(0,1)             |
| 6642.7              | 6636.5                | 6.2                  | b(10,8)            |
| 6674.0              | 6683.9                | - 9.9                | a(1,2)             |
| 6777.3              | 6787.4                | -10.1                | a(2,3)             |
| 6898.5              | 6893.1                | 5.4                  | a(3,4)             |
| 7003.0              | 7011.9                | - 8.9                | a(1,3)             |
| 7139.6              | 7146.3                | - 6.7                | A(1,9)             |

Table C-3. Observed PbO Bandheads and Their Assignments for Spectrum No. 3

| <u>Observed (<math>\text{\AA}</math>)</u> | <u>Calculated (<math>\text{\AA}</math>)</u> | <u>Obs - Cal (<math>\text{\AA}</math>)</u> | <u>Assignments</u> |
|-------------------------------------------|---------------------------------------------|--------------------------------------------|--------------------|
| 4230.9                                    | 4230.0                                      | -0.9                                       | B(3,0)             |
| 4316.1                                    | 4319.4                                      | -3.3                                       | B(2,0)             |
| 4411.6                                    | 4412.6                                      | -1.0                                       | B(1,0)             |
| 4560.6                                    | 4559.6                                      | 1.0                                        | A(5,0)             |
| 4661.9                                    | 4660.0                                      | 1.9                                        | B(0,1)             |
| 4819.1                                    | 4818.8                                      | 0.3                                        | B(0,2)             |
| 4958.0                                    | 4958.4                                      | -0.4                                       | A(1,0)             |
| 4988.0                                    | 4987.1                                      | 0.9                                        | B(0,3)             |
| 5031.4                                    | 5032.4                                      | -1.0                                       | b(10,1)            |
| 5038.8                                    | 5038.4                                      | 0.4                                        | B(1,4)             |
| 5139.0                                    | 5138.4                                      | 0.4                                        | B(3,6)             |
| 5226.6                                    | 5225.0                                      | 1.6                                        | a(7,0)             |
| 5260.4                                    | 5260.4                                      | 0.0                                        | A(0,1)             |
| 5281.7                                    | 5281.8                                      | -0.1                                       | B(6,9)             |
| 5329.1                                    | 5327.2                                      | 1.9                                        | B(7,10)            |
| 5351.2                                    | 5350.0                                      | 1.2                                        | a(6,0)             |
| 5463.1                                    | 5463.7                                      | -0.6                                       | A(0,2)             |
| 5481.6                                    | 5482.6                                      | -1.0                                       | a(5,0)             |
| 5621.8                                    | 5623.4                                      | -1.7                                       | a(4,0)             |
| 5677.1                                    | 5681.0                                      | -3.9                                       | A(3,0)             |
| 5708.4                                    | 5706.0                                      | 2.4                                        | a(5,1)             |
| 5773.2                                    | 5773.5                                      | -0.3                                       | a(3,0)             |
| 5858.6                                    | 5858.6                                      | 0.0                                        | a(4,1)             |
| 5913.4                                    | 5913.9                                      | -0.5                                       | A(0,4)             |
| 5932.1                                    | 5933.4                                      | -1.3                                       | a(2,0)             |

Table C-4. Observed PbO Bandheads and Their Assignments for Spectrum No. 4

| <u>Observed (<math>\text{\AA}</math>)</u> | <u>Calculated (<math>\text{\AA}</math>)</u> | <u>Obs - Cal (<math>\text{\AA}</math>)</u> | <u>Assignments</u> |
|-------------------------------------------|---------------------------------------------|--------------------------------------------|--------------------|
| 6021.3                                    | 6021.3                                      | 0.0                                        | a(3,1)             |
| 6102.6                                    | 6104.3                                      | -1.7                                       | a(1,0)             |
| 6163.7                                    | 6163.9                                      | -0.2                                       | A(0,5)             |
| 6195.7                                    | 6195.9                                      | -0.2                                       | a(2,1)             |
| 6256.0                                    | 6254.8                                      | 1.2                                        | A(1,6)             |
| 6288.4                                    | 6287.2                                      | 1.2                                        | a(0,0)             |
| 6342.4                                    | 6345.9                                      | -3.5                                       | A(2,7)             |
| 6380.5                                    | 6382.4                                      | -1.9                                       | a(1,1)             |
| 6477.7                                    | 6479.6                                      | -1.9                                       | a(2,2)             |
| 6580.2                                    | 6582.6                                      | -2.4                                       | a(0,1)             |
| 6681.1                                    | 6683.9                                      | -2.8                                       | a(1,2)             |
| 6785.9                                    | 6787.4                                      | -1.5                                       | a(2,3)             |
| 6902.4                                    | 6903.8                                      | -1.4                                       | a(0,2)             |
| 7010.0                                    | 7011.9                                      | -1.9                                       | a(1,3)             |
| 7254.0                                    | 7254.3                                      | -0.3                                       | a(0,3)             |
| 7370.4                                    | 7369.8                                      | 0.6                                        | a(1,4)             |
| 7640.0                                    | 7638.1                                      | 1.9                                        | a(0,4)             |

Table C-4. Observed PbO Bandheads and Their  
Assignments for Spectrum No. 4  
(Continued)

# APPENDIX D

## Calculated Spectroscopic Constants

| <u>Transition</u> | <u>Constant</u> | <u>SPECT5</u> | <u>SPECT7</u> |
|-------------------|-----------------|---------------|---------------|
| a-X               | $T_e'$          | 16040.9       | 16042.4       |
|                   | $w_e'$          | 488.8         | 488.5         |
|                   | $w_e x_e'$      | 3.712         | 3.638         |
|                   | $w_e y_e'$      | ---           | 0.003         |
|                   | $w_e''$         | 711.0         | 713.9         |
|                   | $w_e x_e''$     | 0.102         | 1.678         |
|                   | $w_e y_e''$     | ---           | 0.226         |
| <hr/>             |                 |               |               |
| B-X               | $T_e'$          | 22309.0       | 22054.0       |
|                   | $w_e'$          | 491.3         | 609.4         |
|                   | $w_e x_e'$      | 0.226         | 35.48         |
|                   | $w_e y_e'$      | ---           | 2.887         |
|                   | $w_e''$         | 727.0         | 633.8         |
|                   | $w_e x_e''$     | 4.203         | -13.10        |
|                   | $w_e y_e''$     | ---           | -0.970        |

NOTE: Values are in  $\text{cm}^{-1}$

Table D-1. Spectroscopic Constants Calculated from the Band Assignments of Spectrum No. 1

| <u>Transition</u> | <u>Constant</u> | <u>SPECT5</u> | <u>SPECT7</u> |
|-------------------|-----------------|---------------|---------------|
| a-X               | $T_e'$          | 16022.2       | 16037.3       |
|                   | $w_e'$          | 482.6         | 467.1         |
|                   | $w_{e x_e}'$    | 2.376         | -4.730        |
|                   | $w_{e y_e}'$    | ---           | -0.885        |
|                   | $w_e''$         | 701.3         | 719.7         |
|                   | $w_{e x_e}''$   | -1.498        | 8.905         |
|                   | $w_{e y_e}''$   | ---           | 1.546         |
| A-X               | $T_e'$          | 19869.9       | 18248.4       |
|                   | $w_e'$          | 447.2         | 1418.7        |
|                   | $w_{e x_e}'$    | 0.705         | 559.7         |
|                   | $w_{e y_e}'$    | ---           | 48.48         |
|                   | $w_e''$         | 721.5         | -1.370        |
|                   | $w_{e x_e}''$   | 3.495         | -126.9        |
|                   | $w_{e y_e}''$   | ---           | -7.530        |
| B-X               | $T_e'$          | 22415.6       | 22324.1       |
|                   | $w_e'$          | 453.3         | 519.6         |
|                   | $w_{e x_e}'$    | -4.086        | 13.57         |
|                   | $w_{e y_e}'$    | ---           | 1.366         |
|                   | $w_e''$         | 735.6         | 714.6         |
|                   | $w_{e x_e}''$   | 4.284         | -0.596        |
|                   | $w_{e y_e}''$   | ---           | -0.320        |

NOTE: Values are in  $\text{cm}^{-1}$

Table D-2. Spectroscopic Constants Calculated from the Band Assignments of Spectrum No. 2

| <u>Transition</u> | <u>Constant</u> | <u>SPECT5</u>         | <u>SPECT7</u> |
|-------------------|-----------------|-----------------------|---------------|
| a-X               | $T_e'$          | 16012.4               | 16026.9       |
|                   | $w_e'$          | 491.0                 | 496.1         |
|                   | $w_{e'e}^{x'}$  | 3.535                 | 6.767         |
|                   | $w_{e'e}^{y'}$  | ---                   | 0.595         |
|                   | $w_e''$         | 697.0                 | 734.3         |
|                   | $w_{e'e}^{x''}$ | -2.387                | 16.81         |
|                   | $w_{e'e}^{y''}$ | ---                   | 2.693         |
| A-X               | $T_e'$          | $-1.8 \times 10^{14}$ | 20423.2       |
|                   | $w_e'$          | $4.8 \times 10^{14}$  | 446.6         |
|                   | $w_{e'e}^{x'}$  | $2.4 \times 10^{14}$  | 0             |
|                   | $w_{e'e}^{y'}$  | ---                   | 0             |
|                   | $w_e''$         | 775.7                 | 917.9         |
|                   | $w_{e'e}^{x''}$ | 6.974                 | 26.1          |
|                   | $w_{e'e}^{y''}$ | ---                   | 0.84          |

NOTE: All values in  $\text{cm}^{-1}$

Table D-3. Spectroscopic Constants Calculated from the Band Assignments of Spectrum No. 3

| <u>Transition</u> | <u>Constant</u> | <u>SPECT5</u> | <u>SPECT7</u> |
|-------------------|-----------------|---------------|---------------|
| a-X               | $T_e'$          | 16025.9       | 16028.3       |
|                   | $w_e'$          | 483.1         | 485.0         |
|                   | $w_{e'e}^{x'}$  | 2.81          | 3.46          |
|                   | $w_{e'e}^{y'}$  | ---           | 0.056         |
|                   | $w_e''$         | 179.6         | 728.1         |
|                   | $w_{e'e}^{x''}$ | 3.07          | 7.52          |
|                   | $w_{e'e}^{y''}$ | ---           | 0.624         |
| A-X               | $T_e'$          | 19851.4       | 19860.9       |
|                   | $w_e'$          | 453.7         | 410.0         |
|                   | $w_{e'e}^{x'}$  | 2.05          | -27.89        |
|                   | $w_{e'e}^{y'}$  | ---           | -4.069        |
|                   | $w_e''$         | 715.9         | 712.9         |
|                   | $w_{e'e}^{x''}$ | 2.80          | 3.11          |
|                   | $w_{e'e}^{y''}$ | ---           | 0.137         |
| B-X               | $T_e'$          | 22296.9       | 22261.1       |
|                   | $w_e'$          | 495.8         | 509.7         |
|                   | $w_{e'e}^{x'}$  | 2.22          | 1.99          |
|                   | $w_{e'e}^{y'}$  | ---           | -0.733        |
|                   | $w_e''$         | 731.7         | 697.9         |
|                   | $w_{e'e}^{x''}$ | 5.06          | -5.708        |
|                   | $w_{e'e}^{y''}$ | ---           | -0.917        |

NOTE: All values are in  $\text{cm}^{-1}$

Table D-4. Spectroscopic Constants Calculated from the Band Assignments of Spectrum No. 4

## APPENDIX E

Calculated Spectroscopic Constants Using Snyder's Data<sup>a</sup>

| <u>Transition</u> | <u>Constant</u> | <u>SPECT5</u> | <u>SPECT7</u>         |
|-------------------|-----------------|---------------|-----------------------|
| a-X               | $T_e'$          | 16786.0       | 16902.0               |
|                   | $w_e'$          | 339.3         | 665.0                 |
|                   | $w_{ex_e}'$     | -1.857        | 87.89                 |
|                   | $w_{ey_e}'$     | ---           | 6.034                 |
|                   | $w_e''$         | 1041.6        | 1557.3                |
|                   | $w_{ex_e}''$    | 54.57         | 202.9                 |
|                   | $w_{ey_e}''$    | ---           | 10.51                 |
| A-X               | $T_e'$          | 19832.5       | 19811.8               |
|                   | $w_e'$          | 457.9         | 466.0                 |
|                   | $w_{ex_e}'$     | 2.259         | 4.60                  |
|                   | $w_{ey_e}'$     | ---           | 0.184                 |
|                   | $w_e''$         | 714.1         | 699.2                 |
|                   | $w_{ex_e}''$    | 2.879         | -0.598                |
|                   | $w_{ey_e}''$    | ---           | -0.212                |
| B-X               | $T_e'$          | 22271.0       | $3.2 \times 10^{14}$  |
|                   | $w_e'$          | 517.1         | $-9.5 \times 10^{14}$ |
|                   | $w_{ex_e}'$     | 6.435         | $-6.8 \times 10^{14}$ |
|                   | $w_{ey_e}'$     | ---           | $-1.2 \times 10^{14}$ |
|                   | $w_e''$         | 721.0         | 348.0                 |
|                   | $w_{ex_e}''$    | 3.158         | -126.0                |
|                   | $w_{ey_e}''$    | ---           | -13.94                |

NOTE: All values are in  $\text{cm}^{-1}$

Table E-1. Spectroscopic Assignments Calculated from the Band Assignments of the Pb + N<sub>2</sub>O Reaction from Snyder<sup>a</sup>Reference 2

| <u>Transition</u> | <u>Constant</u> | <u>SPECT5</u> | <u>SPECT7</u> |
|-------------------|-----------------|---------------|---------------|
| a-X               | $T_e'$          | 16026.0       | 16028.2       |
|                   | $w_e'$          | 484.6         | 482.2         |
|                   | $w_{e'}^{x'}$   | 2.971         | 2.147         |
|                   | $w_{e'}^{y'}$   | ---           | -0.074        |
|                   | $w_e''$         | 723.0         | 723.7         |
|                   | $w_{e''}^{x''}$ | 3.713         | 3.906         |
|                   | $w_{e''}^{y''}$ | ---           | 0.015         |
| A-X               | $T_e'$          | 19863.9       | 19866.2       |
|                   | $w_e'$          | 446.4         | 445.9         |
|                   | $w_{e'}^{x'}$   | 0.479         | 0.128         |
|                   | $w_{e'}^{y'}$   | ---           | -0.048        |
|                   | $w_e''$         | 724.9         | 728.5         |
|                   | $w_{e''}^{x''}$ | 4.013         | 5.244         |
|                   | $w_{e''}^{y''}$ | ---           | 0.107         |
| B-X               | $T_e'$          | 22292.3       | 22290.4       |
|                   | $w_e'$          | 483.1         | 476.2         |
|                   | $w_{e'}^{x'}$   | -1.068        | -5.373        |
|                   | $w_{e'}^{y'}$   | ---           | -0.643        |
|                   | $w_e''$         | 721.3         | 714.6         |
|                   | $w_{e''}^{x''}$ | 3.533         | 1.533         |
|                   | $w_{e''}^{y''}$ | ---           | -0.151        |

NOTE: All values in  $\text{cm}^{-1}$

Table F-2. Spectroscopic Constants Calculated from the Band Assignments of the Pb + O<sub>2</sub> Reaction from Snyder

| <u>Transition</u> | <u>Constant</u> | <u>SPECT5</u> | <u>SPECT7</u> |
|-------------------|-----------------|---------------|---------------|
| D-X               | $T_e'$          | 29906.0       | 30318.3       |
|                   | $w_e'$          | 490.1         | 481.9         |
|                   | $w_e x_e'$      | -16.53        | -29.35        |
|                   | $w_e y_e'$      | ---           | -2.869        |
|                   | $w_e''$         | 606.2         | 887.0         |
|                   | $w_e x_e''$     | -8.325        | 49.15         |
|                   | $w_e y_e''$     | ---           | 3.686         |

Table E-2. Spectroscopic Constants Calculated from the Band Assignments of the Pb + O<sub>2</sub> Reaction from Snyder (Continued)

| <u>Transition</u>                        | <u>Constant</u> | <u>SPECT5</u> | <u>SPECT7</u> |
|------------------------------------------|-----------------|---------------|---------------|
| b-X                                      | $T_e'$          | 16313.3       | 16323.3       |
|                                          | $w_e'$          | 437.8         | 423.3         |
|                                          | $w_e x_e'$      | -0.233        | -5.807        |
|                                          | $w_e y_e'$      | ---           | -0.441        |
|                                          | $w_e''$         | 715.8         | 731.9         |
|                                          | $w_e x_e''$     | 2.939         | 8.158         |
|                                          | $w_e y_e''$     | ---           | 0.413         |
| NOTE: All values are in cm <sup>-1</sup> |                 |               |               |

Table E-3. Spectroscopic Constants Calculated from the Band Assignments of the b-X System from Snyder

### Vita

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| 19. KEY WORDS (Continue on reverse side if necessary and identify by block number)<br>Flow Tube Reactor<br>Lead Oxide<br>Spectroscopy                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                      |                                                                |
| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number)<br>A flow tube reactor was used to produce a chemiluminescent flame by the reaction of lead vapor with oxygen. The flow tube geometry, furnace design, and reactant mixing has been optimized to produce maximum flame emission for extended periods of time. Reaction chemistry was found to be sensitive to specific reactant mixing technique. A mass balance of 98% allowed the flux of lead into the reaction area to be determined to be approximately $3 \times 10^{18}$ atoms/cm <sup>2</sup> sec. The lead oxide chemiluminescent flame, whose temperature was<br>(Continued on Reverse) |                                      |                                                                |

BLOCK 20: Abstract (cont'd)

measured to be 175° C, was spectroscopically analyzed using a Jarrel-Ash 0.5 m monochrometer with a photomultiplier tube detector. Measurements of the B-X, A-X, and a-X transitions led to the determination of the following spectroscopic constants (in  $\text{cm}^{-1}$ ).

| <u>State</u> | <u><math>T_e</math></u> | <u><math>\bar{w}_e</math></u> | <u><math>\bar{w}_e x_e</math></u> |
|--------------|-------------------------|-------------------------------|-----------------------------------|
| B            | 22296.9                 | 495.8                         | 2.22                              |
| A            | 19851.4                 | 453.7                         | 2.05                              |
| a            | 16025.9                 | 483.1                         | 2.81                              |
| X            | 0                       | 719.3                         | 3.49                              |

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