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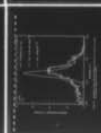
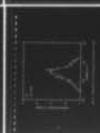
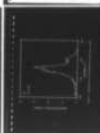
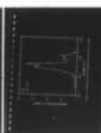
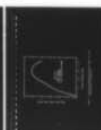
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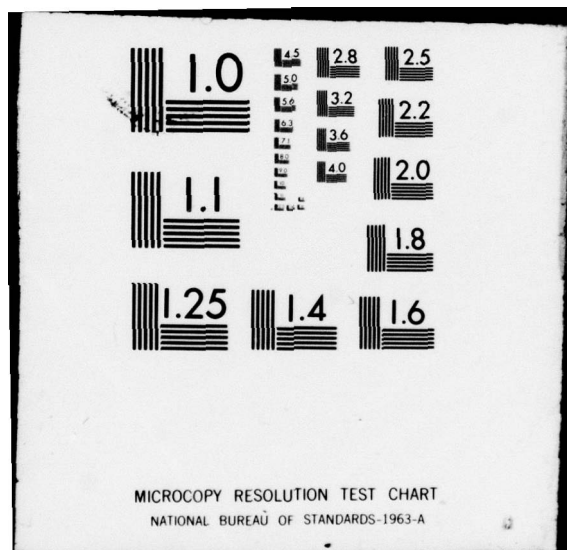
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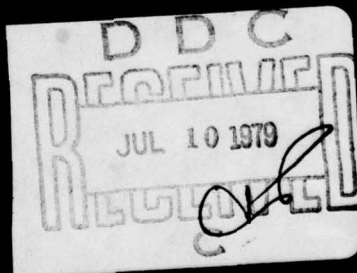
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QUANTITATIVE SPECTROSCOPIC STUDIES OF BORON OXIDES  
AND FLUORIDES

(Annual Report)

By

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Prepared for

Air Force Office of Scientific Research  
Directorate of Chemical Sciences  
Bolling Air Force Base, DC 20332

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# TABLE OF CONTENTS

| <u>Section</u>                                           | <u>Page</u> |
|----------------------------------------------------------|-------------|
| ABSTRACT . . . . .                                       | iii         |
| 1 INTRODUCTION . . . . .                                 | 1           |
| 2 STATUS OF APPARATUS DEVELOPMENT . . . . .              | 2           |
| 3 MEASUREMENT OF $\nu_3$ BAND OF $\text{BF}_3$ . . . . . | 8           |
| 4 SUMMARY . . . . .                                      | 15          |
| 5 PUBLICATIONS AND PRESENTATIONS . . . . .               | 16          |
| 6 REFERENCES . . . . .                                   | 17          |

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# ABSTRACT

The objective of this study is the measurement of the infrared absorption coefficients and absorption line spacings of several boron compounds in the gas phase over the temperature range of 300 to 1500K. In particular, the species of interest are  $\text{BF}_3$ ,  $\text{BF}$ ,  $\text{OBF}$ ,  $\text{BO}_2$ , and  $\text{HBO}_2$ . In the past year, the following technical progress was made. The high temperature flow reactor was developed to the point where it ran reliably at temperatures up to 1500K. The optical system was tested and operated at its design specifications. The flow reactor was interfaced to the molecular beam quadrupole mass spectrometer. A prototype discharge flow system for producing the IR active species of interest was tested. Finally, the absorption coefficients of the  $\nu_3$  band of  $\text{BF}_3$  have been measured from approximately 300 to 1500K.

## 1. INTRODUCTION

The objective of the present research program is the performance of quantitative spectroscopic measurements on a number of boron oxides, fluorides, and oxy-fluorides. The measurement program is designed to produce results which are suitable for use in infrared radiation band models<sup>(1)</sup>, and, therefore, the infrared absorption measurements will be performed at high spectral resolution, as well as at low spectral resolution. This will permit the determination of the two band model parameters, the average absorption coefficient and the fine structure parameter<sup>(1)</sup>. In addition, the measurements will be performed within the temperature range of 300-1500°K. At present, it is anticipated that measurements will be performed on the species  $\text{BF}_3$ ,  $\text{BF}$ ,  $\text{OBF}$ ,  $\text{HBO}_2$ , and  $\text{BO}_2$ . These species must be produced in high temperature reactions, with the exception of  $\text{BF}_3$  which is a commercially available gas.

A conceptual diagram of the experimental apparatus is shown in Figure 1. The species of interest are produced by reaction in, or introduced into, a variable temperature flow reactor. Then, the flow is passed through an analysis region in which a multi-pass absorption cell (White cell)<sup>(2)</sup> is mounted perpendicular to the flow direction. Finally, a portion of the flow is sampled by a molecular beam mass spectrometer before being exhausted to a large mechanical vacuum pump. Since the number density of the absorbing species is measured in-situ by the mass spectrometer, one can obtain absolute values for the absorption coefficients without assuming that the reactive species in the flow tube have achieved local thermodynamic equilibrium.

The remainder of this report is organized as follows: The status of the apparatus development will be discussed in Section 2. The measurements of the IR absorption coefficients of the  $\nu_3$  band of  $\text{BF}_3$  will be described in Section 3. The present status of the contractual effort will be summarized in Section 4. Finally, the publications and presentations supported by this contract will be enumerated in Section 5.

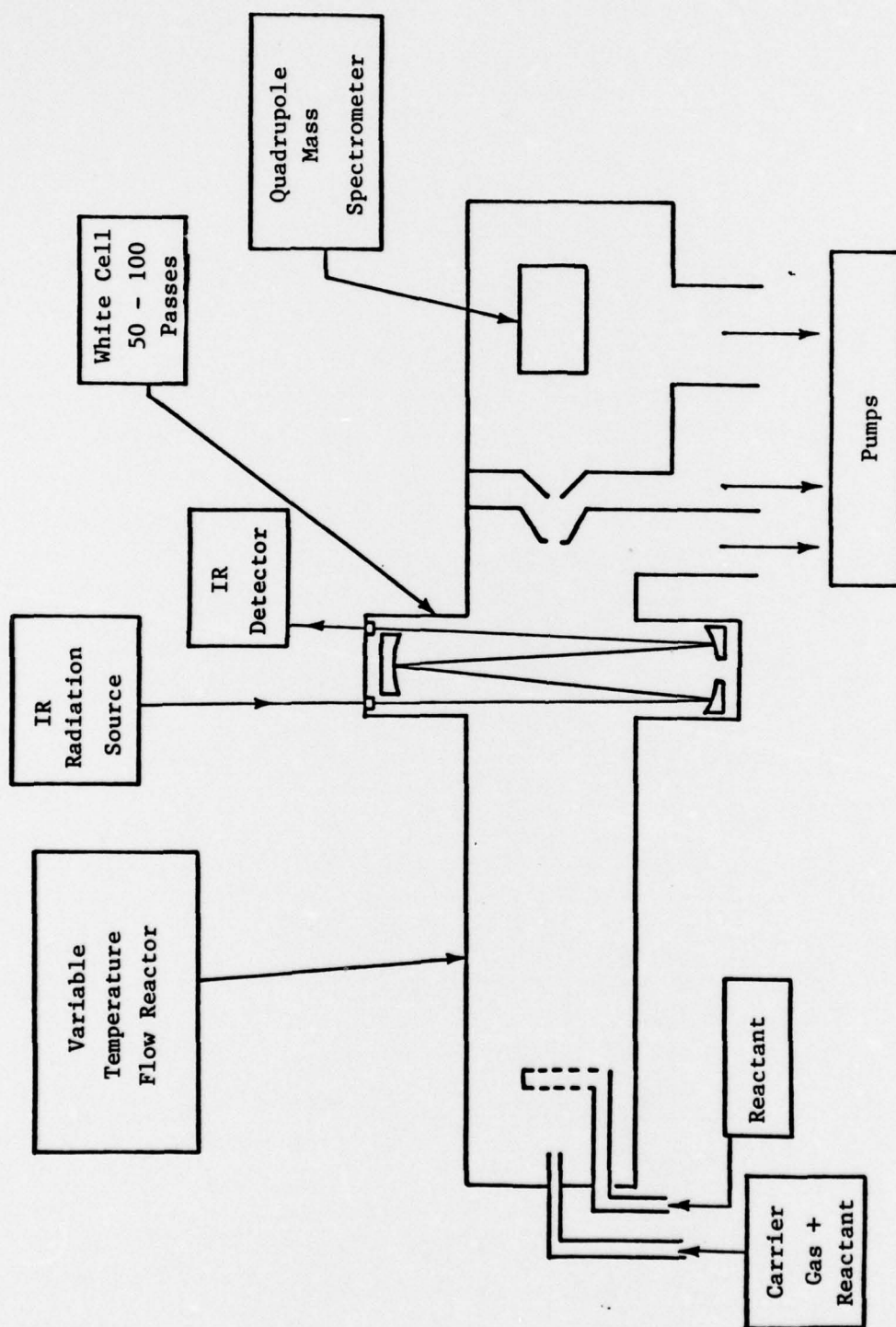


Figure 1. Conceptual Diagram of Flow Reactor/Infrared Spectrometer

## 2. STATUS OF APPARATUS DEVELOPMENT

This section will describe the present status of the development of the experimental apparatus. In our previous Annual Report<sup>(3)</sup> we discussed, in some detail, the design of the high temperature flow reactor, the IR optical system, and the fluid mechanical (wall-less) confinement of the flow of the IR active species in the analysis region. For the sake of brevity, these discussions will not be repeated here. Rather, we shall focus on the development of the apparatus that has occurred during the past year.

To date, all of the major subsystems have been operated satisfactorily, either individually or in combination with others. The set of subsystems of the complete apparatus is composed of: the high temperature flow reactor, the IR optical system (double beam spectrometer), the molecular beam mass spectrometer, and the discharge flow system. The status of each of these subsystems will now be discussed below.

The complete high temperature flow reactor was described in the previous Annual Report under this contract.<sup>(3)</sup> In practice, the flow reactor, as described in that report, proved to be soundly designed. During the performance of the measurements on  $\text{BF}_3$ , some problems were encountered in the use of the apparatus, including electrical breakdown (at high temperature and low pressure) from the heater arrays. However, these minor deficiencies were corrected, and the flow reactor now operates reliably between 300 and 1500°K. In addition, the fluid mechanical confinement of the flow of IR active species<sup>(3)</sup> appears to behave in the predicted manner with no evidence for recirculation of IR active species in the White cell. In summary, the flow reactor subsystem may be described as fully operational. This flow reactor is an advance in the state-of-the-art in that it now offers a unique capability for the study of the infrared spectra of high temperature species.

The IR optical system is also fully operational. For the  $\text{BF}_3$  measurements the double beam spectrometer was set up to cover the 4 to 8  $\mu\text{m}$  spectral region

with a spectral resolution of approximately  $0.02 \mu\text{m}$ . (The spectral resolution can, of course, be improved with a resultant loss in sensitivity.) The sensitivity of the optical system is limited by the detector noise. For a signal to noise ratio of 2, this corresponds to a minimum detectable number density of  $\text{BF}_3$  at  $300^\circ\text{K}$  in the flow tube of approximately  $3 \times 10^{13}$  molecules/ $\text{cm}^3$ . Thus, in order to study the other boron containing molecules of interest to this investigation, it will be necessary to produce species number densities in the flow reactor in excess of  $10^{14}$  molecules/ $\text{cm}^3$ . The one exception to this statement is for the molecule  $\text{BF}$  which will be studied with the use of a tunable diode laser and, therefore, at an increased sensitivity of 2 to 3 orders of magnitude (compared to the low spectral resolution measurements).

The molecular beam mass spectrometer is an existing instrument which has been reconfigured for use in the present investigation. Since the mass spectrometer had originally been set up to sample atmospheric pressure flames,<sup>(4)</sup> it was necessary to construct a new sampling nozzle and skimmer in order to optimize the performance at the anticipated operating pressures in the flow reactor of 1 - 10 torr. The sampling nozzle orifice is now 0.036", the skimmer orifice is 0.040", and the nozzle to skimmer distance is 0.475". In order to test this new configuration, a variable pressure of argon gas was placed in the flow tube and the mass spectrometer signal was recorded as a function of pressure. The result is shown in Figure 2. The signal is seen to increase monotonically with source pressure to a peak around 25 - 30 torr, above which it decreases. This is the behavior that one would expect for a properly designed supersonic molecular beam sampling system.<sup>(5)</sup> The operating regime for the present configuration extends up to approximately 20 torr. (Above that pressure, skimmer interference and scattering degrade the quality of the molecular beam.) Thus, it has been demonstrated that the molecular beam mass spectrometer will operate, as required, in the pressure regime of interest to the present experimental investigation.

A prototype of the discharge source that will be used to generate the boron containing species of interest has been assembled and tested. The heart of the flow system is shown in Figure 3. The discharge source is of a rather traditional

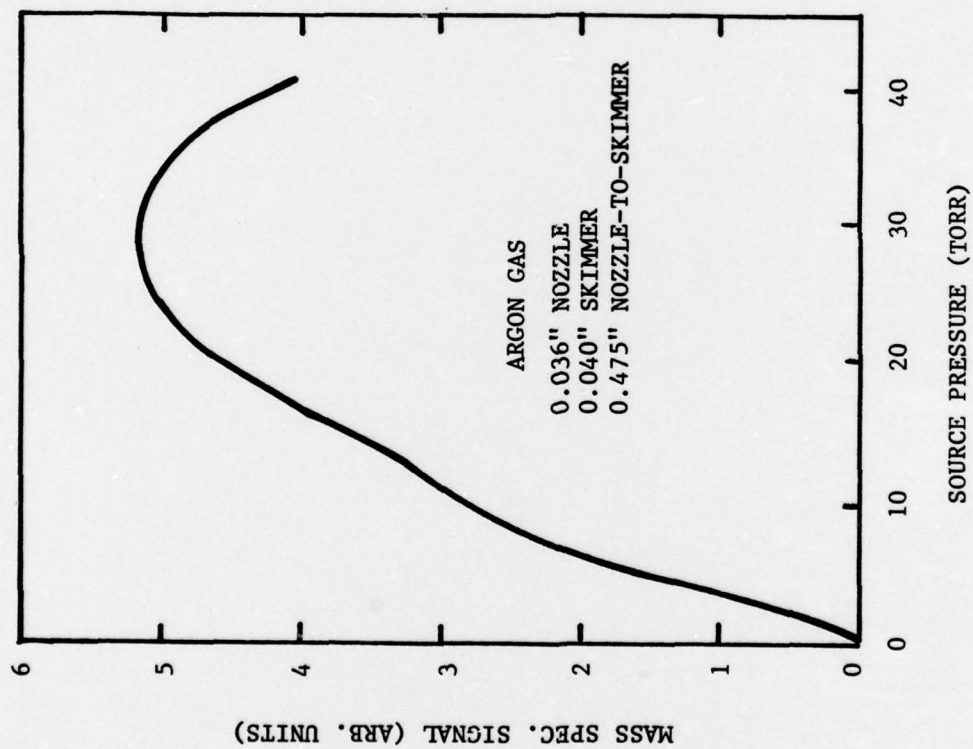


Figure 2. Molecular Beam Mass Spectrometer Signal vs. Flow Tube Pressure for Argon Gas.

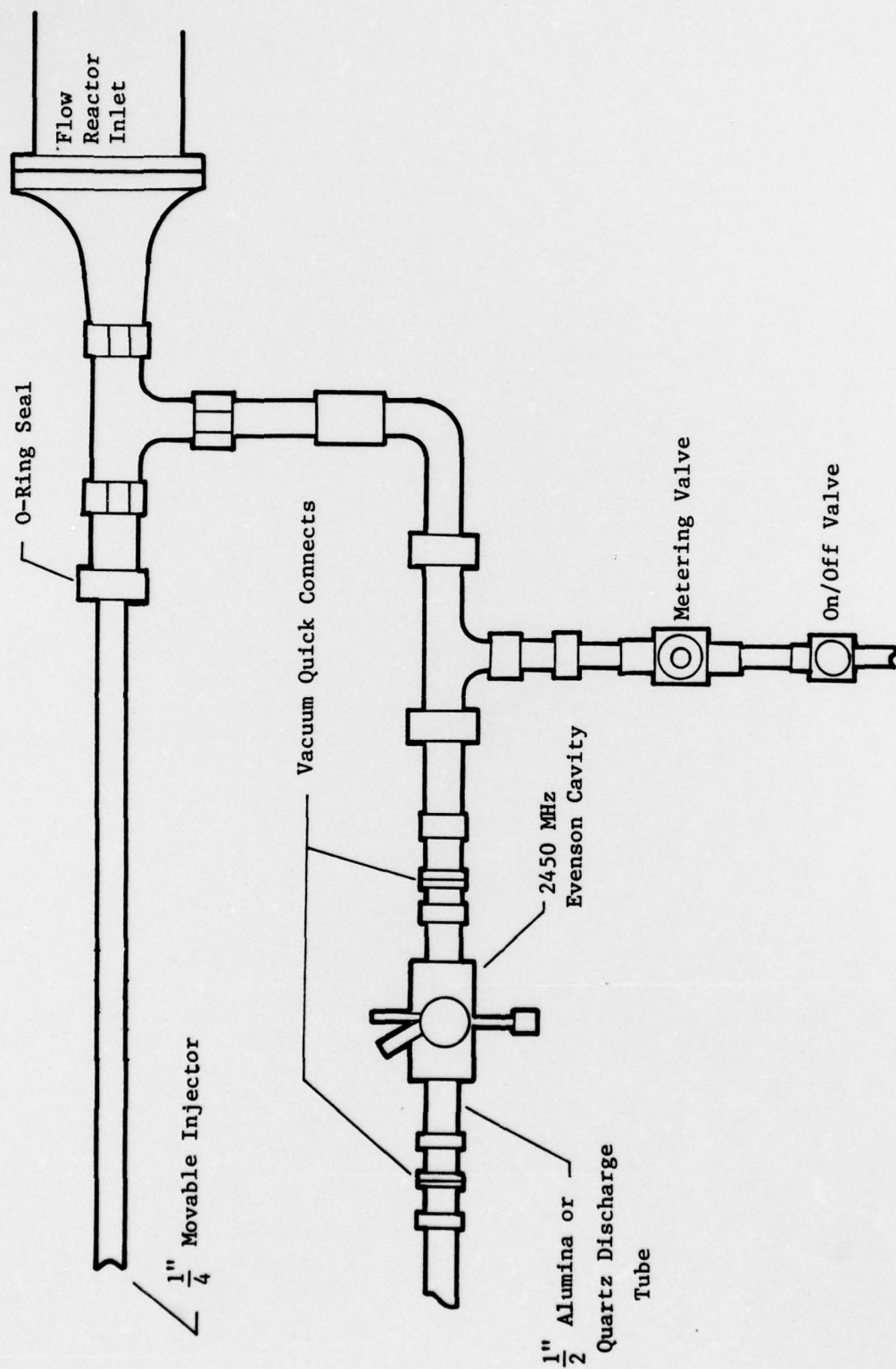


Figure 3. Discharge Source for Flow Reactor.

design. However, the system is designed so that an improved configuration discharge cavity<sup>(6)</sup> can be used in place of the almost universally used Evenson cavity.<sup>(7)</sup> The advantage of the new cavity design is that discharges can be maintained at pressures of up to an atmosphere, whereas Evenson cavities are only usable at pressures up to 10 or perhaps 20 torr. Thus, it may be possible to use a high pressure discharge in the new cavity to generate larger number densities of boron containing species in the flow reactor. This would help to insure the success of the present measurement program.

### 3. MEASUREMENT OF $\nu_3$ BAND OF $\text{BF}_3$

During the past year we have measured the absorption coefficients for the  $\nu_3$  band of  $\text{BF}_3$  at five temperatures between  $300^\circ\text{K}$  and  $1500^\circ\text{K}$ . The only other existing measurements are those of McKean<sup>(8)</sup> at room temperature and some recent measurements by Peterson<sup>(9)</sup> and Boyer<sup>(10)</sup> at about  $2400^\circ\text{K}$ .

The present results are shown in Figures 4 - 8. (Preliminary results were presented in Ref. 11.) For the convenience of the reader, the data points have been connected by straight lines. At  $290^\circ\text{K}$  the features due to the two boron isotopes ( $^{11}\text{B}$  at  $1454\text{ cm}^{-1}$  and  $^{10}\text{B}$  at  $1510\text{ cm}^{-1}$ ) are clearly resolved. As the temperature increases the spectral features become broader, and the apparent peaks shift to longer wavelengths. Finally, at  $1440^\circ\text{K}$  the absorption features have coalesced into a single broad band.

An initial comparison of the data at  $1150^\circ\text{K}$  with two existing band models<sup>(12,13)</sup> is shown in Figure 9. From the figure it is evident that Bernstein's band model<sup>(12)</sup> provides a considerably better representation of the data than that of Slack and Ludwig.<sup>(13)</sup> In the near future, these experimental results will be submitted for publication as a journal article, along with an updated version of the Bernstein band model that will be modified in order to account for the newly available data. Therefore, a more detailed discussion of these data will not be undertaken at this time.

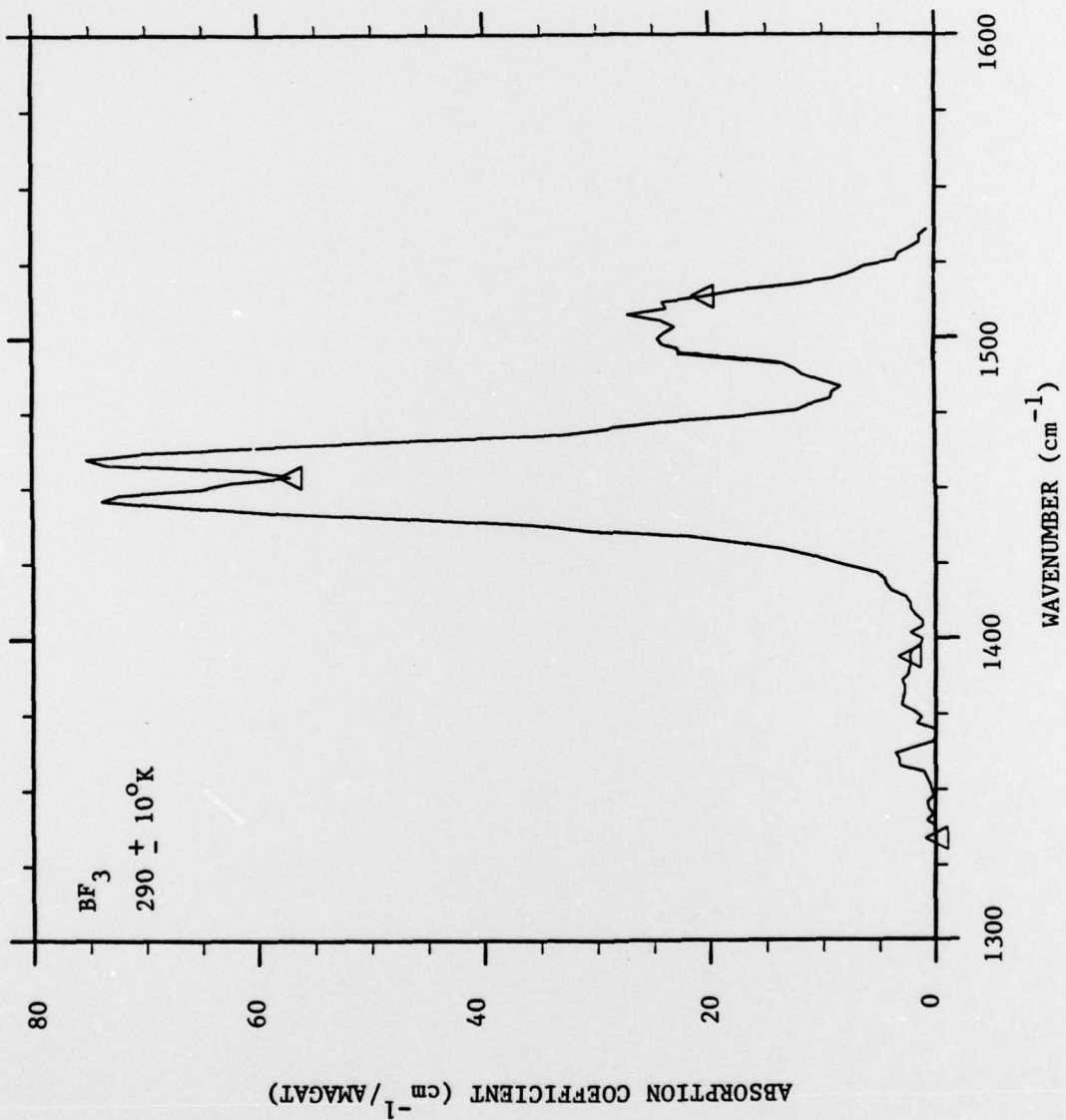


Figure 4. Measured BF<sub>3</sub> 6.9 μm Band Absorption Coefficients at 290°K.

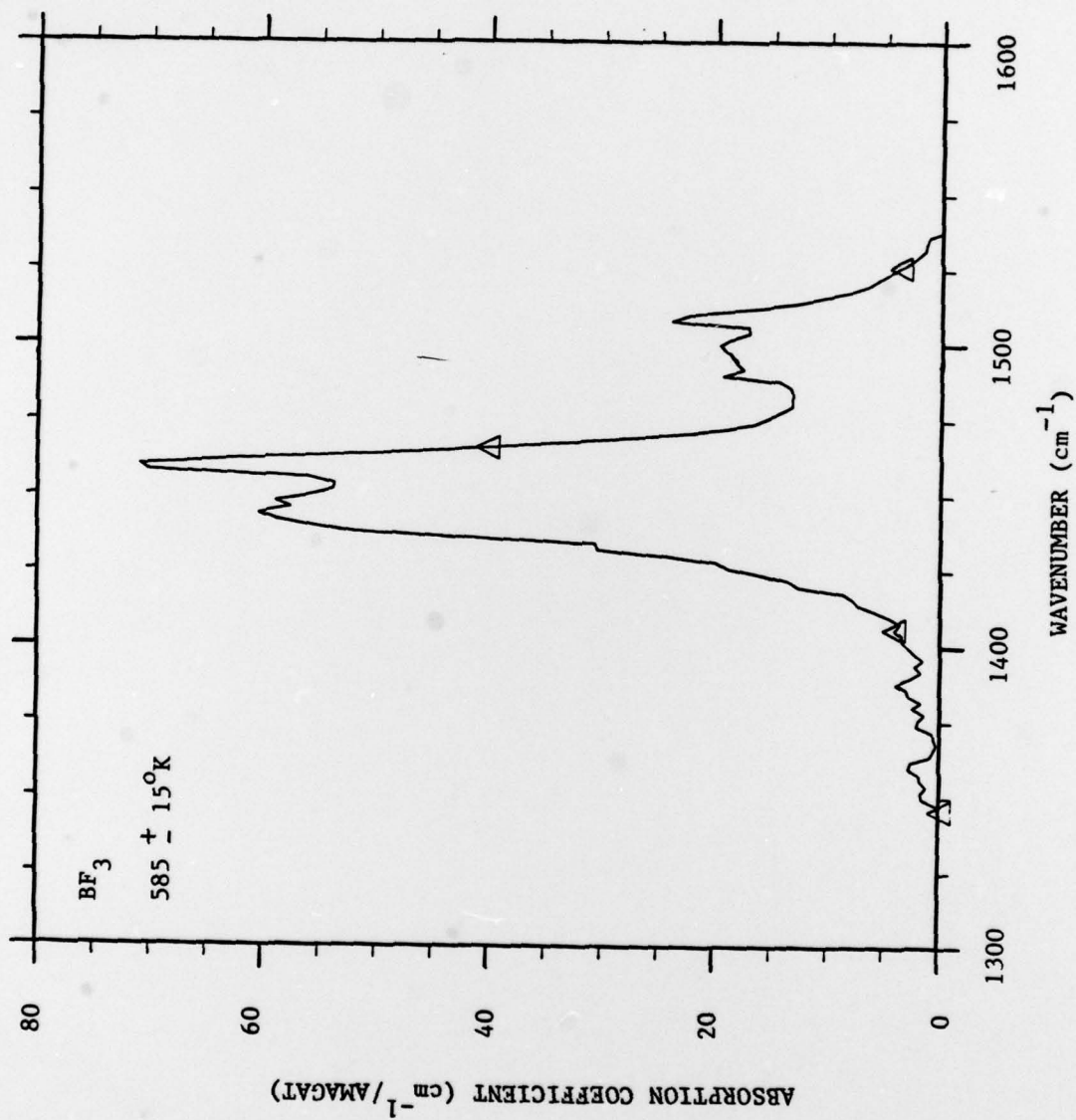


Figure 5. Measured BF<sub>3</sub> 6.9 μm Band Absorption Coefficients at 585°K

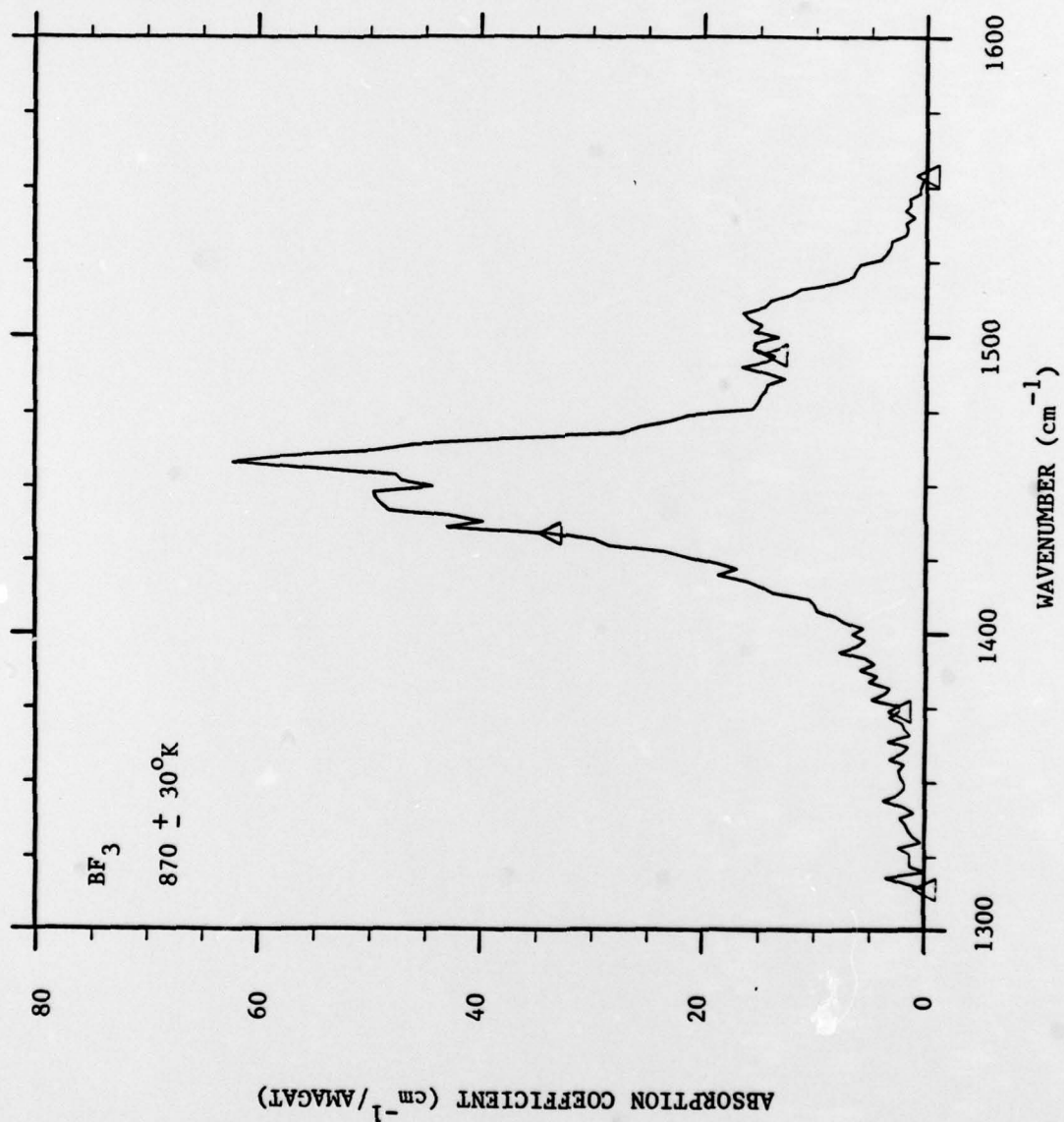


Figure 6. Measured BF<sub>3</sub> 6.9 μm Band Absorption Coefficients at 870°K.

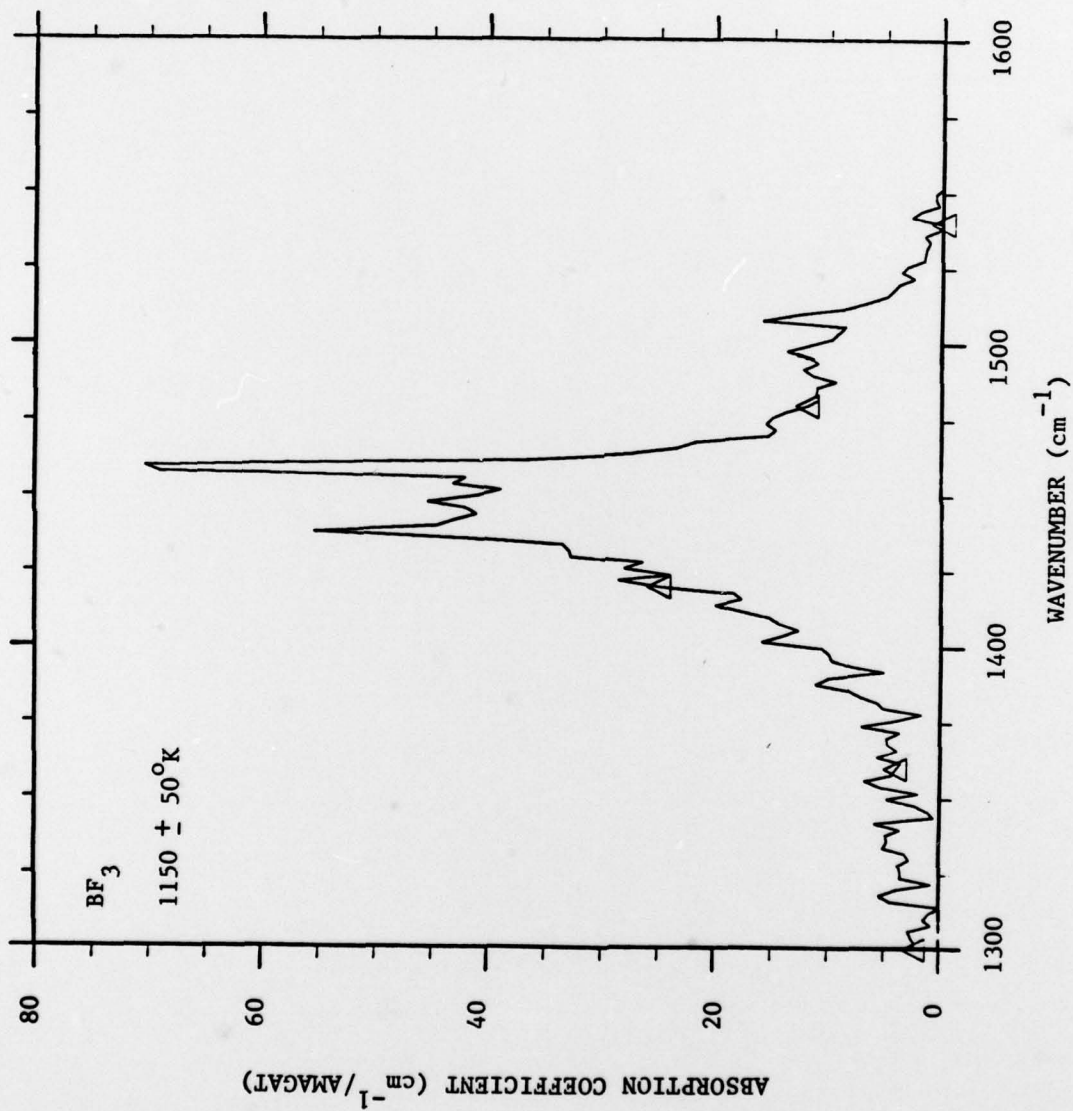


Figure 7. Measured  $\text{BF}_3$  6.9  $\mu\text{m}$  Band Absorption Coefficients at  $1150^\circ\text{K}$ .

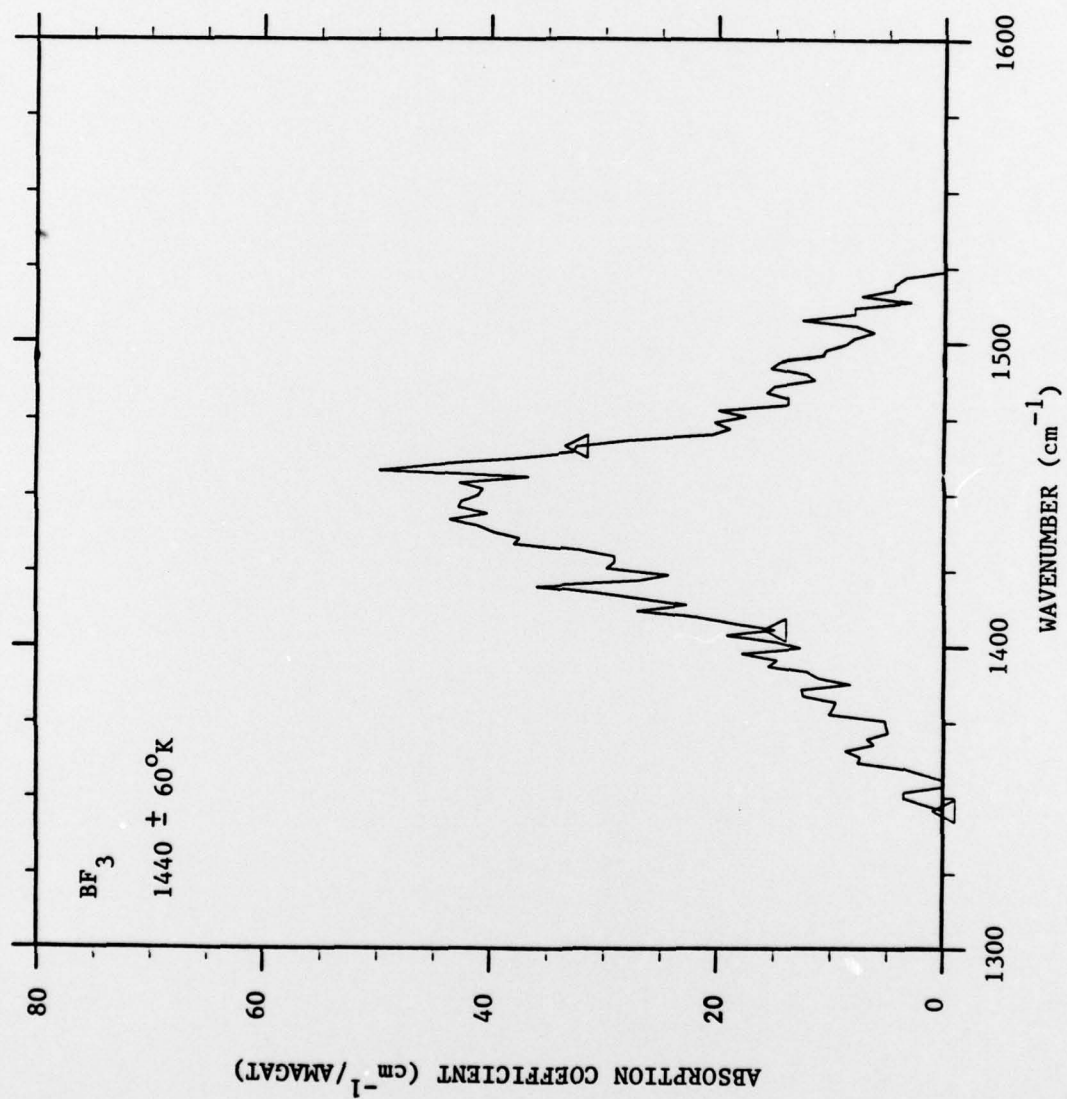


Figure 8. Measured BF<sub>3</sub> 6.9 μm Band Absorption Coefficients at 1440°K.

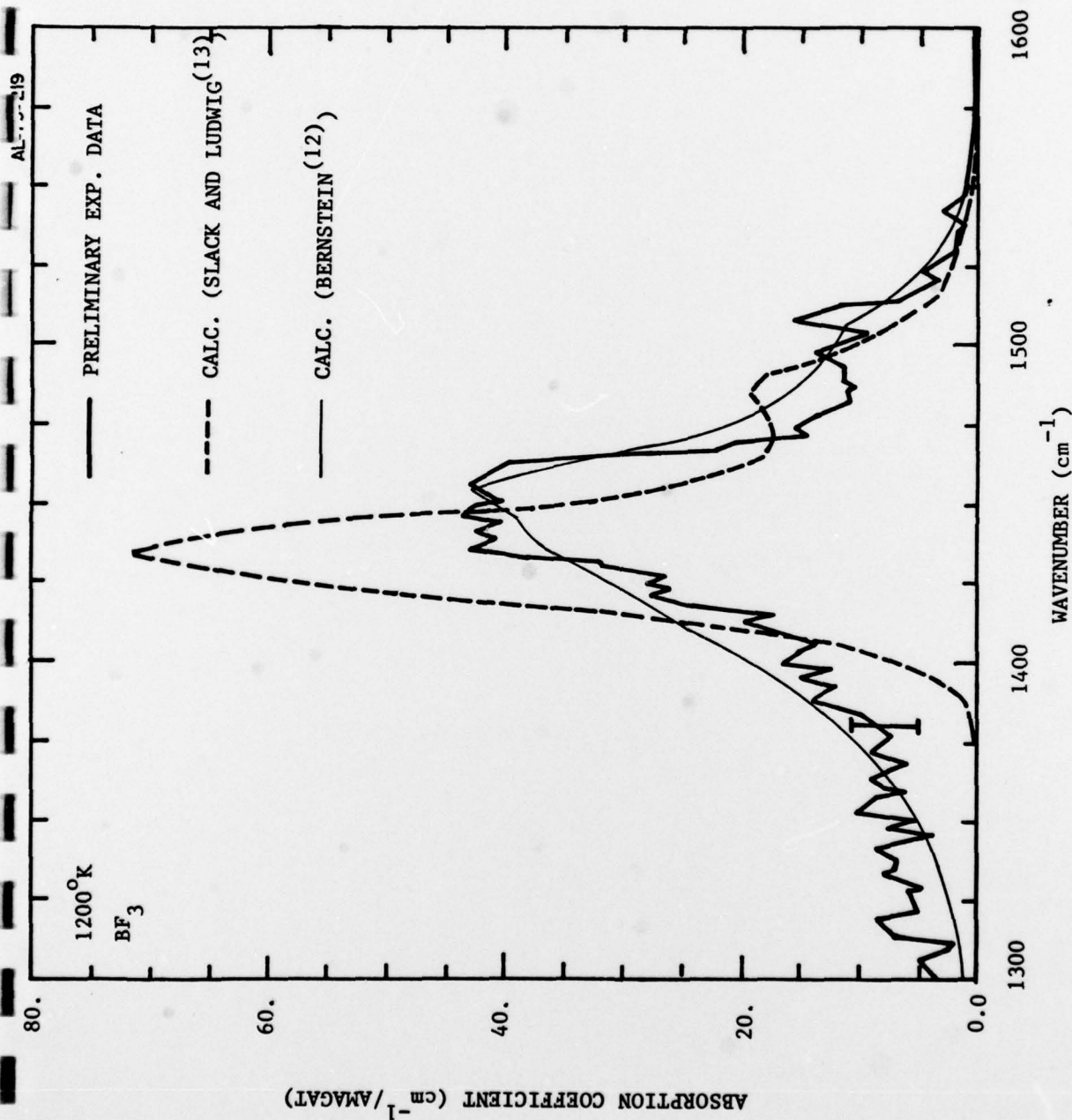


Figure 9. Comparison of Data and Band Model Calculations for BF<sub>3</sub> 6.9  $\mu$ m Band at a Nominal Temperature of 1200°K.

#### 4. SUMMARY

The present status of the contractual effort may be summarized as follows: The construction of the apparatus has been essentially completed, and the spectral absorption coefficients of  $\text{BF}_3$  have been measured between  $300^\circ\text{K}$  and  $1500^\circ\text{K}$ . The major remaining task is the measurement of the absorption coefficients of  $\text{OBF}$ ,  $\text{BO}_2$ ,  $\text{HBO}_2$ , and  $\text{BF}_2$ .

Of the above molecules, the first three will be studied at low spectral resolution. The success of these measurements will depend on the successful production of adequate number densities of these species in the flow tube. Thus, the initial work in the current contract year will be concerned with the optimization of the conditions for the production of these species in the discharge flow reactor. Then the absorption measurements will be performed on  $\text{OBF}$ ,  $\text{BO}_2$ , and  $\text{HBO}_2$ .

On the other hand, since  $\text{BF}$  will be studied at high spectral resolution with the use of a tunable diode laser, (with greatly increased sensitivity), there will be no problem in producing adequate number densities of  $\text{BF}$  in the flow tube. Accordingly, we plan to perform the measurements on  $\text{BF}$  after the more difficult low spectral resolution measurements have been performed on the other species.

## 5. PUBLICATIONS AND PRESENTATIONS

In the past year, the following paper was presented. It will be published by the National Bureau of Standards in a book covering the symposium proceedings.

Gersh, M.E., and Kolb, C.E., "Infrared Spectral Measurements of Species in a High Temperature Flow Tube," Presented at 10th Materials Research Symposium on Characterization of High Temperature Vapors and Gases, Gaithersburg, MD., 1978.

In addition, the following three manuscripts are in preparation (with anticipated authors, titles, and journals):

Gersh, M.E., and Bernstein, L.S., "The  $\nu_3$  Band of  $\text{BF}_3$ : Measured Absorption Coefficients and Band Model Comparisons" may be submitted to the Journal of Chemical Physics or the Journal of Molecular Spectroscopy.

Gersh, M.E., "Fluid Mechanical Simulation as an Aid to the Design of Fast Flow Reactors" will probably be submitted to the Journal of Physical Chemistry.

Gersh, M.E., "Design of a High Temperature Flow Reactor for Measuring Infrared Absorption Coefficients of Transient Species" will be submitted to the Review of Scientific Instruments.

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5. Gersh, M.E., "Measurement of the Energy Dependence of the Reaction Cross Section for  $K + CH_3I \rightarrow KI + CH_3$  from 0.1 to 1 eV (c.m.) using a New Crossed Molecular Beam Scattering Apparatus", Ph.D. Thesis, U. of Wisconsin, Madison (1971).
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11. Gersh, M.E., and Kolb, C.E., "Infrared Spectral Measurements of Species in a High Temperature Flow Tube", Presented at 10th Materials Research Symposium on Characterization of High Temperature Vapors and Gases, Gaithersburg, MD (1978).

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12. Bernstein, L.S., Aerodyne Research, Inc., Private Communication (1979).
13. Slack, M. and Ludwig, C., "Plume Data Analysis of Advanced Propellants: Volume II Appendix", Report No. AFRPL-TR-78-4, Air Force Rocket Propulsion Laboratory, Edwards AFB, CA (1978).

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