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BY A PULSED DYE-LASER.

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THE RESONANCE FLUORESCENCE OF BO_2
EXCITED BY A PULSED DYE-LASER

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By

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* * * * *

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I wish to dedicate this
dissertation to my wife Patty

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CHAPTER I. INTRODUCTION

The study of the gas phase spectra of small polyatomic molecules has received considerable attention during the past few years. Expressions which characterize the energy levels and interactions in these molecules, such as vibrational anharmonicity and spin-orbit interactions, are analogous to those developed earlier for diatomic molecules. In addition, however, there are a number of interactions for polyatomic molecules which are not possible for diatomic molecules. The Renner-Teller effect and Fermi resonance are two such examples. The presence of these interactions along with spin-orbit coupling has significant effects on the spectrum of the linear symmetric molecule, BO_2 . Despite the fact that the energy levels and spectra of BO_2 have been characterized fairly extensively (1-6), these interactions result in some continued ambiguity in the classification of vibrational energy levels. The purpose of the present study is to provide results of a new type of experimental data for BO_2 which help remove some of these ambiguities, and therefore permits a more meaningful test of existing theories for linear triatomic molecules.

Experimental observations of related systems by which to test such theories have been based upon the electronic absorption and emission spectra of molecules such as NCO (7,8) and CO_2^+ (9-14). In understanding the above mentioned effects it becomes essential to have firmly

established vibrational assignments for transitions involving all interacting levels. Rotational analysis may provide the necessary confirmation of vibrational assignments, but it requires considerable effort, and it is not possible in some cases because of low intensity or overlapping structure. The electronic spectrum of BO_2 is a prime example where these difficulties have been encountered in the vibrational analysis. In view of this, and the fact that this molecule has been of considerable interest in our laboratory over the past few years, the electronic spectrum of BO_2 was studied in this work using laser-excited fluorescence.

Laser-excited fluorescence is a technique whereby a molecule is selectively excited by absorption of laser light to particular vibrational-rotational levels of an excited electronic state. If the pressure is low enough so that the time between collisions is long compared to the fluorescence lifetime, minimizing loss of energy through collisions, the molecule emits a series of lines corresponding to transitions from the common upper state to lower state levels in accord with the appropriate selection rules.

In studying the electronic spectrum of BO_2 by laser-excited fluorescence, vibrational assignments can be made with less ambiguity than those obtained by conventional techniques of absorption and emission, particularly in dense, badly-overlapped spectral regions. Furthermore, this technique is extremely valuable in revealing information about high-lying vibrational levels in the ground state, previously inaccessible using conventional techniques of absorption spectroscopy. Observations of emission spectra, which would contain this information,

usually involve the necessity of increasing the effective temperature of the sample. This results in larger Doppler widths and more complex overlapping spectral features. In addition to the reduction of vibrational structure complications, laser-excited fluorescence also results in a considerable decrease of overlapping rotational structure. The vibrational features therefore, are often easier to recognize than the corresponding features in conventional emission spectra. Consequently, laser-excited fluorescence should yield band heads in the electronic spectrum of BO_2 which had not been reported previously. Therefore, the objective of this work was to obtain and analyze laser-excited fluorescence spectra of BO_2 and thereby accomplish the following:

- 1) Assign previously unassigned band heads observed in the electronic spectrum of BO_2 .
- 2) Confirm the assignment of band heads previously given.
- 3) Establish energies for $^2\Pi$ and possibly $^2\Delta$ vibronic levels in the ground state of $^{11}\text{BO}_2$.
- 4) Resolve discrepancies in previous assignments.
- 5) Test the theoretical treatment given by Hougen (15) for Fermi resonance in linear triatomic molecules in $^2\Pi$ electronic states.
- 6) Improve molecular constants in the ground and first excited states of $^{11}\text{BO}_2$.
- 7) Provide a foundation for future laser-excited fluorescence experiments on BO_2 and other transient species employing single rotation line excitation.

CHAPTER II. HISTORICAL BACKGROUND

Spectra associated with the bright green emission from boron flames and arcs were reported as early as 1873 by Salet (16). However, it was not until the study of Kaskan and Millikan (17) in 1960 that the source of the emitter was identified as BO_2 . Johns (1) shortly thereafter confirmed this with a detailed analysis of the spectra generated by flash photolysis of mixtures of $^n\text{BCl}_3$ (n for natural isotopic abundance) and O_2 . Spectra recorded in this study extended from 3964 Å to 6429 Å, and were assigned to two transitions of BO_2 : the $\tilde{\text{A}}^2\Pi_u - \tilde{\text{X}}^2\Pi_g$ transition, designated the $\tilde{\text{A}} - \tilde{\text{X}}$ system, and the $\tilde{\text{B}}^2\Sigma_u^+ - \tilde{\text{X}}^2\Pi_g$ transition, designated the $\tilde{\text{B}} - \tilde{\text{X}}$ system. Rotational analyses of several bands involving $^2\Pi$ and $^2\Sigma$ vibronic levels were important in confirming vibrational assignments in this study.

Snowden (2) studied the emission spectrum of $^n\text{BO}_2$ to obtain more information about the ground state. In his studies BO_2 spectra were generated by heating a 1:1 mixture of KBF_4 and B_2O_3 and passing the vapor produced through an electrodeless (microwave) discharge. Snowden analyzed the rotational structure of several bands and observed many new bands involving transitions to excited vibronic levels in the ground state; however, more than ninety such bands were not assigned.

More recently, Dymek (3) produced $^{10}\text{BO}_2$ in mixtures of $^{10}\text{BCl}_3$ and O_2 in a transverse discharge cell. The absorption spectrum was

recorded, and a large number of bands in the $\tilde{A} - \tilde{X}$ system of $^{10}\text{BO}_2$ were assigned, including a few bands previously misassigned to $^{11}\text{BO}_2$. In addition, Dymek successfully employed Hougen's Fermi resonance treatment (15) in calculating the energies of levels involved in the (100-020) Fermi diads in both the $\tilde{A}$ and $\tilde{X}$ states $^{10}\text{BO}_2$. Molecular constants used in these calculations were obtained by applying isotopic relations to constants reported for $^{11}\text{BO}_2$. The agreement obtained between predicted and observed energies was taken as support for both the constants and the method of calculation.

Russell et al. have given a preliminary report (5) and, more recently, a detailed analysis (6) of the molecular fluorescence spectrum of BO_2 excited by several lines of an argon-ion laser. Their observations and subsequent analysis resulted in the assignment of a wide range of vibrational states ($v_1 = 0-5$, $v_2 = 1-10$, $v_3 = 0-2$) in Σ , Δ (for $^{10}\text{BO}_2$) and Φ vibronic levels of the ground state. All laser-excited fluorescence studies of BO_2 (4-6), however, relied on accidental coincidences with argon-ion laser lines, and were therefore severely limited in the range of levels that could be populated in the $\tilde{A}$ state. The results reported in this work, on the other hand, were obtained from fluorescence of BO_2 excited by a tunable dye laser. This tunability has permitted the observation of transitions involving selected vibrational energy levels in the ground state ($\tilde{X}^2\Pi_g$), as well as the first excited state ($\tilde{A}^2\Pi_u$) of BO_2 . Vibrational energy levels of BO_2 requiring further analysis, such as the Π and Δ levels of $^{11}\text{BO}_2$ in both electronic states, could therefore be studied using this type of excitation.

Bryson (18) has calculated band head frequencies for a large number of transitions in the $\tilde{A}$ and $\tilde{X}$ electronic states of six isotopic species of BO_2 concurrent with the fluorescence studies carried out in this work. These calculations were based upon Hougen's Fermi resonance treatment (15), and were extremely useful in the vibrational analysis as well as in the determination of spectral regions in which to observe laser-excited fluorescence.

CHAPTER III. EXPERIMENTAL

A. Introduction

The earliest resonance fluorescence studies made use of atomic emission lines as the excitation source (19). One of the most widely known examples of this technique is the excitation of I_2 by the 5461 Å Hg line resulting in a progression of closely spaced rotational doublets. In this and a few other cases atomic emission sources produced valuable data. However, the number of wavelengths available by this approach was extremely limited. The advent of lasers with intense, coherent, monochromatic, and in some cases tunable outputs, greatly extended the applicability and versatility of resonance fluorescence techniques. Such experiments can be categorized into two broad classes according to the excitation source employed: experiments using fixed frequency lasers, such as those reported in studies (4-6, 20-29), and experiments employing tunable dye lasers (30-42). Lasers employed in these experiments can be further classified as continuous wave (cw) or pulsed systems. Both fixed frequency and tunable cw lasers offer a number of advantages over their pulsed counterparts: higher average powers; easier visual alignment of the fluorescence cell and related optics with the spectrometer; fluorescence signals with improved signal-to-noise ratio; lower levels of high-frequency electrical noise in some cases; and the possibility of employing photographic rather than photoelectric detection. Photographic detection is desirable from

the standpoint that it does not require prior knowledge of the frequencies at which fluorescence features are expected, thus precluding the possibility of not recording unexpected fluorescence features. Furthermore, because all features are recorded simultaneously, relative intensities by photographic detection may be more meaningful, especially in cases where experimental conditions change during the experiment. Photographic detection using pulsed systems is often impractical due to the extremely long exposure times required. Despite these factors, there are a few advantages in using pulsed lasers in resonance fluorescence experiments: pulsed systems can be constructed typically for one-tenth the cost of cw systems, they are generally more durable, and most importantly, they can achieve outputs at shorter wavelengths where only the most expensive cw systems can operate. In this work, these three factors were of prime importance in selecting a pulsed nitrogen laser-pumped-dye laser as the excitation source. Such a system also offers the advantage of versatility; future experiments such as time-resolved and two-photon spectroscopy can be carried out without major modifications to the laser system.

B. The Nitrogen Laser and Dye Laser Systems

A pulsed nitrogen laser was constructed utilizing a modified version of the design reported by Schenck and Metcalf (43). In this design, similar to the one described by Harrington and Malmstadt (44), the laser channel is formed by two aluminum bars in which grooves were milled to accommodate tempered plate glass (6 mm thick, 8 cm wide and 1.3 m long). (Refer to Figures 1 and 2.) The high voltage electrode

is a band-saw blade (14 teeth/inch) which is press-fitted into a slot milled in one of the aluminum bars. Nitrogen enters the laser channel through a 3 mm hole in the lower aluminum plate (ground) and exits at the other end through a similar hole. A low inductance storage capacitor (Tobe-Deutschmann model ESC-302, 0.01 μF , 20 kV) is charged to 10-15 kV through a 250 k Ω current-limiting resistor. A trigger pulse is sent to the gate of a hydrogen thyratron (Amperex 6279/5C22), placing the thyratron in a conducting mode and thereby effectively grounding the positive side of the floating storage capacitor to which it is attached. The charge on the storage capacitor is dumped into twenty Sprague door-knob capacitors (400 pF, 30 kV) spaced evenly along the laser channel and mounted on the high voltage bar. Each capacitor is connected to the ground aluminum bar by short flexible copper wire (14 AWG) as illustrated in Fig. 1. A discharge in the nitrogen gas occurs resulting in a superradiant emission near 3371 Å from both ends of the laser channel. A mirror at the rear of the laser channel nearly doubles the peak power of the nitrogen laser (≈ 100 to 200 kW) by directing the beam back through the discharge and out the front end. The above configuration is useful in eliminating capacitor failure associated with mechanical stress during the discharge (45). The durability of this laser is excellent; no appreciable degradation in performance could be detected after approximately 4×10^6 pulses.

The output of the nitrogen laser is focused into a dye cell by a 15 cm focal length spherical quartz lens. The dye cell was machined from a stainless steel block to which three quartz windows were sealed, one input and two antireflective-coated side windows. The dye cell, a

75% reflective output mirror, a beam expanding telescope (Tropel model 280-50, magnification of 33) and an 1800 line/mm grating (PTR optics model TF-26) form the dye laser cavity as shown in Fig. 3. This system provided tunability throughout the region 4890 to 5470 Å* with bandwidths of 0.4 Å. Typical peak output powers from the dye laser have been roughly estimated at around 1000 watts.

C. The Fluorescence Cell and Detection System

The output of the dye laser was focused into a region in a fluorescence cell where BO_2 was generated by mixing BCl_3 with the products of a microwave discharge in O_2 at a total pressure of a few torr, as shown in Fig. 4. The reaction products were pumped away by liquid nitrogen traps and a single stage rotary pump (33.4 l/min. free air capacity). The fluorescence perpendicular to the path of the laser beam was collected with a 5.5 cm focal length Mamiya Sekor lens (f/1.8) and focused onto the slit of a 1-m Jarrell-Ash spectrometer (f/8.7) equipped with an EMI 6256S photomultiplier. The collecting lens was placed about 7 cm in front of the fluorescence cell and about 26 cm from the entrance slit of the spectrometer, a distance determined by the necessity of matching solid angles. Slit widths corresponding to a resolution of 0.5 cm^{-1} to 2.3 cm^{-1} at $20\,000 \text{ cm}^{-1}$ were used primarily. The spectrometer was calibrated with an iron hollow cathode lamp giving an overall estimated accuracy of 1 cm^{-1} . Output signals from the photomultiplier tube were processed by a preamplifier (PAR model 115) and boxcar integrator (PAR model 160), triggered by the nitrogen laser

* Actually this system can provide a considerably larger range of wavelengths, but they were not used in the present study.

Figure 1
End View of N₂ Laser Channel

Figure 1

Figure 2**Nitrogen Laser**

1. Storage capacitor
2. Doorknob capacitor
3. Thyatron

Figure 2

Figure 3
Dye Laser Cavity

Figure 3

Figure 4

 $\text{BCl}_3\text{-O}_2$ Inlet and Exhaust System

Dimensions of nozzle at the $\text{BCl}_3\text{-O}_2$ mixing region

5 mm ID O_2 port

7 mm OD O_2 port

11 mm ID BCl_3 port

Excitation region

2 mm from the exhaust port

8 mm from the O_2 port

Figure 4

trigger generator. Integrated signals from the boxcar were then directed into a strip chart recorder. A complete diagram of the entire experimental apparatus is shown in Fig. 5.

D. Laser-Excited Fluorescence Spectra of BO_2

Prior to initiating a fluorescence experiment a number of preliminary procedures were carried out. First, the output of the dye laser, appropriately attenuated, was directed into the spectrometer and was tuned to a selected absorption band head. This process was of further importance in establishing proper experimental recording conditions such as boxcar settings, scan rate, laser repetition rate, strip chart recorder speed and photomultiplier biasing voltage. A typical set of such conditions is given in Table 1. Once the desired laser frequency was obtained, the fluorescence cell was positioned and properly aligned by translating it in three directions such that scattered laser light off the tip of a copper wire (placed along the axis of, and 8 mm from the end of the O_2 port) was incident on the entrance slit of the spectrometer. The copper wire was removed and the vacuum-flow system was carefully connected. The entire system was then evacuated for at least four hours to achieve a background pressure of 10^{-3} torr or less measured with a Hastings thermocouple gauge. At this point the fluorescence experiment was ready to be initiated.

The input offsets on both the preamplifier and boxcar integrator were adjusted to achieve a stable baseline with the nitrogen laser operating at five to ten pulses a second but blocked off at the dye cell. Once this was accomplished the obstruction in front of the dye

Figure 5
Block Diagram of Experimental Apparatus

Figure 5

cell was removed, and the output of the dye laser was once again focused into the discharge region. A Matheson flow meter in line with an O_2 tank was then opened allowing O_2 (industrial grade) to enter the flow system. Using an air-cooled microwave cavity, a stable discharge was established by adjusting the O_2 flow rate. A Hoke needle valve was opened to allow BCl_3 (obtained from Matheson Chemical Company) to enter the system and mix with the products of the discharge in O_2 in the excitation region. This resulted in a bright green emission flame indicating the formation of BO_2 in the excited state. At this point the O_2 and BCl_3 flow rates were adjusted so as to optimize the resulting fluorescence signal by monitoring the boxcar output at a predetermined frequency (usually the frequency of the P lines associated with the band head being pumped). It is important to note that in this process the BCl_3 flow rate was kept to a minimum in order to avoid premature termination of an experiment due to clogged traps and/or B_2O_3 deposits on the laser entrance and fluorescence observation windows. It was also important in this regard to avoid a spreading flame due to an improper BCl_3 - O_2 mixture. Experiments as long as five hours could be run by carefully aligning the exhaust port shown in Fig. 4, by adjusting the flow rates so as to obtain a compact emission flame, and by using total pressures (measured with a buffer manometer described in detail by Dymek (3)) less than two torr. Increasing the total pressure to 6 torr, which was sometimes necessary to obtain appreciable fluorescence from weaker transitions, greatly reduced the duration of the experiment, often to less than two hours.

Table 1
Typical Experimental Conditions

<u>Laser</u>		<u>Spectrometer</u>	
input voltage	13-15 kV	slits	20-125 μ
repetition rate	7-10 pps	photomultiplier voltage	-1400 V
N ₂ gas pressure	$\approx$ 20 torr	preamplifier gain	x 10
		scan rate	2 cm ⁻¹ /min.
		chart speed	0.5 inch/min.
<u>Boxcar Integrator Settings</u>			
aperture time	50 ns	duty factor	(50 ns)(7 pps) = 3.5×10^{-7}
time base	2 μ s	retention switch	on
time constant (NR)	0.1 μ s	prefilter	off
time constant (HR)	1 μ s	input sensitivity	100 mv full scale
stretch time	30 μ s	initial delay	4%

Increased fluorescence signals were often observed by carefully adjusting the output wavelength of the dye laser during a fluorescence experiment. This clearly demonstrated that the signals were not caused by electrical noise or background emission from BO_2 or other species formed in the discharge. This was further demonstrated by periodically blocking the output of the dye laser and watching the signal disappear. The possibility of observing fluorescence from other species produced in the discharge is discussed at length in Section VB.

Resonance fluorescence spectra were recorded by scanning the Jarrell-Ash spectrometer toward longer wavelengths than the laser in order to detect band heads corresponding to emission in a manifold of vibronic levels in the ground state. The spectral regions scanned were determined prior to initiating each fluorescence experiment, and were based upon prior determinations of ground state energies and the preliminary transition frequency calculations of Bryson (18). (Refer to Section VB.) In some cases the corresponding P branch features were scanned as well.

E. Data Reduction

The center frequency of each fluorescence peak was determined with the aid of a frequency marker built into the strip chart recorder using the appropriate scan and chart speeds. These measurements were then converted to vacuum wavenumbers using the appropriate spectrometer calibration for the spectral region of interest. The calibrations were determined or checked before each fluorescence experiment. If a broad peak was observed, the lower and upper limits were recorded

in addition to the center frequency. Where possible, band head frequencies determined in this manner were compared with band heads observed in high resolution emission and absorption spectra recorded on a 3.4 m-Ebert spectrograph. Although the precision of measuring features on these plates was definitely less than 0.5 cm^{-1} , there were some cases where the appearance of the band head was very questionable, thus resulting in an uncertain correlation with features observed in fluorescence. The band head frequency determinations therefore, have uncertainties larger than 0.5 cm^{-1} . Conservative estimates typically place this uncertainty at about $\pm 2 \text{ cm}^{-1}$.

CHAPTER IV. THEORETICAL

It has long been established that light absorbed or emitted by ions, atoms and molecules causes transitions to take place between energy levels. Scientists using spectroscopy have been able to test theoretical models which are used to describe the energy levels involved in these transitions. In this chapter the quantitative expressions derived from the theoretical models as applied to the BO_2 molecule will be presented. This discussion, however, will only be a cursory presentation, and the reader is therefore referred to a series of books by Herzberg (46-48) for a more detailed presentation of the general theory and to Ph.D. dissertations by Dymek (3) and Snowden (2) for additional information on BO_2 .

Molecular energy levels can be characterized by three types of motion: electronic, vibrational and rotational. In calculating these energy levels one must simultaneously consider all three motions for a rigorous treatment of the problem. However, a useful approximation first introduced by Born and Oppenheimer (49) can be made. In this approximation the nuclei are considered to be stationary compared to the lighter and faster moving electrons. The nuclear kinetic energy terms in the Hamiltonian can thereby be separated from the other terms allowing the electronic energy to be determined. As will be seen in Section B of this chapter, this approximation breaks down in polyatomic

molecules due to the interaction of electronic and vibrational angular momentum, and results in quantitative expressions which are considerably more complex than those derived using the Born-Oppenheimer approximation. Other examples of breakdowns in this approximation are discussed in an excellent review article by Hougen (50).

A. Electronic Structure

In this section the classification of the electronic states between which transitions occur will be discussed. In polyatomic molecules as in diatomic molecules, the nature of the ground and low-lying excited electronic states can be determined by the addition of electrons to a fixed nuclear frame, obtaining various electron configurations. In this approach molecular orbitals are formed from appropriate linear combinations of atomic orbitals, designated LCAO MO's. Correlation diagrams are then constructed in which the molecular orbitals are correlated to orbitals from the corresponding united atoms at one extreme and the separated atom at the other. In this manner the relative energies of the molecular orbitals may be estimated in a qualitative way. A more complete discussion of this approach as well as other methods of "building-up" molecules are detailed by Herzberg (46,48).

The electron configurations for the three lowest electronic states of the linear symmetric BO_2 molecule can be built-up using the approach indicated above. BO_2 has 21 electrons which occupy the orbitals indicated below from left to right in order of increasing energy. The orbitals indicated by K's are 1s atomic orbitals for boron and each of the oxygen atoms. They are not influenced by molecule formation.

$$(K)^2 (K)^2 (K)^2 (3\sigma_g)^2 (2\sigma_u)^2 (4\sigma_g)^2 (3\sigma_u)^2 (1\pi_u)^4 (1\pi_g)^3 \quad (1)$$

$$(K)^2 (K)^2 (K)^2 (3\sigma_g)^2 (2\sigma_u)^2 (4\sigma_g)^2 (3\sigma_u)^2 (1\pi_u)^3 (1\pi_g)^4 \quad (2)$$

$$(K)^2 (K)^2 (K)^2 (3\sigma_g)^2 (2\sigma_u)^2 (4\sigma_g)^2 (3\sigma_u)^1 (1\pi_u)^4 (1\pi_g)^4 \quad (3)$$

As in diatomic molecules, the molecular orbitals for linear polyatomic molecules are designated as σ , π , δ . . . orbitals corresponding to a value of λ , the quantum number indicating the electronic orbital angular momentum about the internuclear axis, equal to 0, ± 1 , ± 2 . . . , respectively. The molecular orbitals for BO_2 are further classified by subscripts g or u denoting that the wavefunctions remain unchanged or change sign, respectively, upon inversion through a center of symmetry. Obviously asymmetric molecules such as NCO cannot have this classification.

The rules for generating molecular term symbols given by Herzberg (46) provide a convenient method of classifying electronic states:

$$(2S + 1) \Lambda_{g \text{ or } u} .$$

Lower case symbols refer to individual electronic symmetries while upper case symbols refer to the overall symmetry of the particular electronic configuration. In this general form S is the total electron spin; Λ , analogous to λ for the one-electron molecule, is the total orbital angular momentum about the internuclear axis; and the subscripts g and u now represent the parity of the electronic state with respect to inversion through a center of symmetry. As an additional specification, the term symbol is often prefixed by an $\tilde{X}$, $\tilde{A}$, $\tilde{B}$, to indicate respectively, the ground state; the first and the second excited states of the same

multiplicity ($2S+1$ value). The three lowest electronic states of BO_2 indicated by (1) - (3) can therefore be conveniently represented by $\tilde{X}^2\Pi_g$, $\tilde{A}^2\Pi_u$, and $\tilde{B}^2\Sigma_u$, respectively. Two important features of these states should be noted. First, for Π electronic states, as in all states with $\Lambda > 0$, there are two possible values for Λ , ± 1 in this case. It is this feature which is responsible in part for the coupling between electronic motion and other types of motion in the BO_2 molecule. Secondly, the electron spin multiplicity of 2 gives rise to an interaction between the electron spin angular momentum and orbital angular momentum called spin-orbit interaction. These two effects will be discussed in more detail in the following sections.

B. Vibrations

In a linear triatomic molecule such as BO_2 the complex vibrational motions can be described in terms of $3N - 5 = 4$ ($N=3$) normal modes of vibration: a symmetric stretch whose frequency is given by ν_1 , two degenerate bending vibrations, ν_2 , and an antisymmetric stretch, ν_3 . Displacement vector diagrams illustrating these modes, which are identical to those of CO_2 , appear in many sources, and will not be reproduced here. In the absence of interactions between electronic and vibrational motions (vibronic coupling) and spin-orbit coupling, the total energy, T_{ev} in units of cm^{-1} , of a non-rotating linear triatomic molecule is given by

$$T_{\text{ev}} = T_e + G(\nu_1, \nu_2, \nu_3) , \quad (4)$$

where T_e is the pure electronic energy at the minimum of the potential

well for a given electronic state and $G(v_1, v_2, v_3)$ is given by

$$G(v_1, v_2, v_3) = \omega_1(v_1 + 1/2) + \omega_2(v_2 + 1) + \omega_3(v_3 + 1/2) \quad (5)$$

$$+ \sum_{i=1}^3 \sum_{k \geq i} x_{ik} (v_i + d_i/2) (v_k + d_k/2) + g_{22} l_2^2 .$$

In this equation ω_1 , ω_2 and ω_3 are the classical vibrational frequencies (ν/c) of the symmetric, bending and antisymmetric modes, respectively; x_{ik} and g_{22} are anharmonicity constants; d_i and d_k are the degeneracies of the i^{th} and k^{th} vibrational modes which are excited to quanta v_i and v_k ; and l_2 is the quantum number associated with the angular momentum of the degenerate bending vibrations. The significance of l will be discussed in greater detail shortly.

In the discussion of vibrations thus far, we have neglected vibronic and spin-orbit couplings. The name vibronic is given to those electronic and vibrational energy levels involved in a breakdown of the Born-Oppenheimer approximation. Renner (51), using an idea introduced by Teller, first quantitatively described the interaction between electronic and nuclear motions in a linear triatomic molecule. The splitting of vibrational levels arising from this interaction has since been labeled the Renner-Teller effect. In the BO_2 molecule, as in some other triatomic molecules, this interaction is large and is responsible in part for the complexity of its electronic spectra (spectra in which electronic, vibrational and rotational transitions may occur). Vibronic coupling in BO_2 involves the doubly degenerate bending vibrations, ν_2 , which take place in orthogonal planes. The superposition of these two

motions can be viewed as an effective rotation about the internuclear axis, with an associated vibrational angular momentum of magnitude $\ell\hbar$, where $|\ell| = v_2, v_2 - 2, \dots, 1$ or 0 and $\hbar$ is Plank's constant divided by 2π . As the molecule bends the nuclear charges set up a field which perturbs the electronic motion, thus effectively coupling the electronic and vibrational motions. This interaction can conveniently be treated by a coupling between the total electronic orbital angular momentum and the vibrational angular momentum. In the absence of molecular rotation, components of these angular momenta along the internuclear axis, $\Lambda\hbar$ and $\ell\hbar$, can be added vectorially to give $K\hbar$, the vibronic angular momentum along this axis excluding electron spin, where

$$K = \Lambda + \ell^* . \quad (6)$$

If the total electronic spin angular momentum, S , is strongly coupled with the total electronic orbital angular momentum, $\Omega\hbar$ must be specified instead of $\Lambda\hbar$, where

$$\Omega = \Lambda + \Sigma . \quad (7)$$

In this expression Σ is the quantum number designating the component of spin along the linear axis, and for BO_2 can take on values of $\pm 1/2$. The resultant of Ω and ℓ , called P , is the quantum number associated with the vibronic angular momentum along the internuclear axis including electronic spin,

* In this expression as well as in expression (7) and (8) the symbols Λ , ℓ , Σ , K and P represent signed numbers, i.e., both positive and negative values which correspond to the two different directions of the angular momenta along the linear axis.

$$P = \Omega + \ell = \Lambda + \ell + \Sigma = K + \Sigma . \quad (8)$$

To illustrate the various ways in which the quantum numbers associated with the coupled momenta may be combined, consider a linear triatomic molecule in a $^2\Pi$ electronic state characterized by the quantum numbers $v_1, v_2 = 4, v_3; \Lambda = \pm 1; \ell = \pm 4, \pm 2, 0$ and $\Sigma = \pm 1/2$. By systematic combination of these quantum numbers the following table is generated.

Table 2
Generation of Vibronic Species

Λ	ℓ	Σ	K	P	Species
+1	+4	+1/2	5	11/2	$^2H_{11/2} (04^4_0)$
+1	-4	+1/2	-3	-5/2	$^2\Phi_{5/2} (04^4_0)$
-1	+4	+1/2	3	7/2	$^2\Phi_{7/2} (04^4_0)$
-1	-4	+1/2	-5	-9/2	$^2H_{9/2} (04^4_0)$
+1	+2	+1/2	3	7/2	$^2\Phi_{7/2} (04^2_0)$
+1	-2	+1/2	-1	-1/2	$^2\Pi_{1/2} (04^2_0)$
-1	+2	+1/2	1	3/2	$^2\Pi_{3/2} (04^2_0)$
-1	-2	+1/2	-3	-5/2	$^2\Phi_{5/2} (04^2_0)$
+1	0	+1/2	1	3/2	$^2\Pi_{3/2} (04^0_0)$
-1	0	+1/2	-1	-1/2	$^2\Pi_{1/2} (04^0_0)$

In generating this table it is important to note that the ten vibronic species indicated all originate from the single 040 vibrational level in the absence of the Renner-Teller effect and spin-orbit coupling. It is not difficult therefore, to understand why the electronic spectrum

of BO_2 and other polyatomic molecules exhibit such complexity. The vibronic species indicated in this diagram are designated by the following general form:*

$$(2S+1)_{K_P}(\nu_1, \nu_2^{\ell}, \nu_3)$$

where $\Sigma, \Pi, \Delta, \Phi, \Gamma, H \dots$ vibronic levels correspond with K equal to 0, 1, 2, 3, 4, 5 . . . , respectively. In addition, each of the levels, other than those for $K = 0$, are doubly degenerate since the same ten species can be generated by reversing the signs of Λ, ℓ and Σ . This degeneracy (P-type doublets), however, will be split when the finer interaction between vibronic and rotational motion is taken into account.

The theory of the Renner-Teller effect was first developed for linear triatomic molecules in which the interaction between electronic and vibrational motions was assumed to be small. Pople and Longuet-Higgins (52) extended the theory for the interpretation of the spectrum of the nonlinear NH_2 molecule in which a strong interaction was observed. Subsequently, Pople (53) modified this treatment to obtain expressions which included the effects of both the Renner-Teller interaction and spin-orbit coupling. In this approach it was assumed that the two interactions were of the same order of magnitude but less than ν_2 , the bending vibrational frequency. The vibronic expressions

* In this equation and those which follow the symbols S, Λ, ℓ, K, P are to be given only positive values in accordance with the usual convention.

derived by Pople, and corrected by Hougen (54), for a linear triatomic molecule in a ${}^2\Pi$ electronic state are as follows:

For levels in which $K = v_2 + 1$,

$$G(v_2, K, \pm 1/2) = \omega_2(v_2+1) \pm (1/2)A_{\text{eff}} - (1/8)\epsilon^2\omega_2 K(K+1) \quad (9)$$

where the $\pm 1/2$ designates the two values of Σ , A_{eff} is an effective spin-orbit coupling constant given by $A_{\text{eff}} = A[1 - (1/8)\epsilon^2 K(K+1)]$ and ϵ is a dimensionless constant called the Renner parameter; however, some authors designate $\epsilon\omega_2$ as the Renner parameter.

For levels in which $K < v_2 + 1$,

$$G^+(v_2, K, \pm 1/2) = \omega_2[1 - (1/8)\epsilon^2](v_2+1) + (1/2)A^* \mp \frac{\epsilon^2 A \omega_2 K(v_2+1)}{8A^*} \quad (10)$$

and

$$G^-(v_2, K, \pm 1/2) = \omega_2[1 - (1/8)\epsilon^2](v_2+1) - (1/2)A^* \pm \frac{\epsilon^2 A \omega_2 K(v_2+1)}{8A^*}, \quad (11)$$

where A^* is given by

$$A^* = \left[A_{\text{eff}}^2 + \epsilon^2 \omega_2^2 [(v_2+1)^2 - K^2] \right]^{1/2}, \quad (12)$$

and in the case when $K = v_2 + 1$, A^* becomes A_{eff} .

The expression for levels in which $K = 0$ (Σ levels) can easily be derived from (10) and (11).

The total vibronic energy can now be obtained by substituting the appropriate vibronic expression for $G(v_2, K, \pm 1/2)$ into Eq. (5) for $\omega_2(v_2+1)$; the total energy of a non-rotating linear triatomic molecule then becomes

$$T_{ev} = T_e + G(v_2, K, \pm 1/2) + G(v_1, v_3) . \quad (13)$$

Figure 6 illustrates the relative positions of the energy levels of BO_2 associated with 0, 1 and 2 quanta of excitation in the bending mode. The actual relative positions of these levels, however, are somewhat different from those indicated due to another perturbation called Fermi resonance. This will be discussed in detail later. In region (B) of this figure only the Renner-Teller effect is taken into account. The vibronic levels are symmetrically displaced from the unperturbed energy levels indicated in region (A) by the factor $(1/2)\epsilon\omega_2[(v_2+1)^2 - K^2]^{1/2}$. However, when second-order effects are taken into account there is a slight asymmetric shift downward by the factor $C' = -(v_2+1)(v_2+2)\epsilon^2\omega_2/8$ for levels in which $K = v_2 + 1$ and by the factor $C = -(v_2+1)\epsilon^2\omega_2/8$ for all other levels. In region (C) both the Renner-Teller effect and spin-orbit coupling are simultaneously considered, causing states of the same symmetry to mix and repel one another. There are four levels for which $0 < K < v_2 + 1$, and in accordance with a negative spin-orbit coupling constant for BO_2 , components with the largest P value (${}^2\Pi_{3/2}$) exhibit the greatest interaction. These levels are therefore furthest from the center of the group. The two levels for which $K = v_2 + 1$ occur in the center of each group with different symmetries, and therefore do not interact one another. In addition, they are inverted in accordance with the negative sign for the spin-orbit coupling constant. The two vibronic levels for which $K = 0$ are designated by $\Sigma^{(-)}$ and $\Sigma^{(+)}$, where the sign in parenthesis indicates the parity of the wave functions upon reflection through a plane containing the nuclei. Johns (1) has

Figure 6

The Splitting of Vibronic Levels of BO_2 With
 $v_2 = 0, 1$ and 2 . The order of states is correct
but the magnitudes of the splittings are arbitrary.

No Renner Effect
No Spin-Orbit
Coupling

Renner Effect
Only

Renner Effect
and Spin-Orbit Coupling

Figure 6

demonstrated through rotational analysis that the $\Sigma^{(-)}$ level is higher in energy than the $\Sigma^{(+)}$, and thus arrived at a negative ϵ value for BO_2 . It should also be mentioned that the pattern of ${}^2\Pi$ vibronic levels for the case in which $v_2 = 4$ and $\ell = 0, 2$ are exactly analogous to the pattern indicated in Fig. 6 for $v_2 = 2$. This will facilitate the discussion of these levels in Chapter V.

C. Rotations

In this section the rotational structure of a linear triatomic molecule in a ${}^2\Pi$ electronic state will be considered. We will begin this discussion by first treating such a molecule as a rigid rotator in which no degenerate bending vibrations are excited and rotational-electronic interactions are neglected. However, for a rigorous treatment the rotational expression must include these interactions as well as take into account the presence of vibronic coupling. Hougen (54) has obtained such rotational expressions for cases in which $K = 0$, $K = v_2 + 1$ and $0 < K < v_2 + 1$. These expressions will be presented later.

In rigid linear triatomic molecules, as in diatomic molecules, three mutually perpendicular principal axes passing through the center of mass can be located. Two of these axes are perpendicular to the internuclear axis and have equal moments of inertia, the third lies along the internuclear axis and is approximately zero due to the very small mass of the electrons. Except for an additive constant, the rotational levels of the rigid rotator are the same as those of the symmetric top. Therefore, for a given electronic state only one moment

of inertia needs to be considered in the rotational energy level expressions. For the rigid linear symmetric BO_2 molecule, this moment of inertia has the following form:

$$I_e = 2m_0(r_{\text{B-O}})^2, \quad (14)$$

where m_0 is the mass of oxygen and B-O is the equilibrium boron-oxygen bond length. The solution of the Schrödinger equation for the rigid rotator results in the following rotational term value expression in units of cm^{-1} :

$$F(J) = E/(hc) = BJ(J+1), \quad (15)$$

where h and c are Planck's constant and the speed of light, respectively; J is the quantum number specifying the total angular momentum of the system; and B_e is the equilibrium rotational constant which is given by

$$B_e = h/(8\pi^2 c I_e). \quad (16)$$

The fact that the internuclear distance given in Expression (14) changes as a result of centrifugal force associated with molecular rotation, requires the addition of $-D_e J^2(J+1)^2$ to Expression (15). In this approximation D_e is the equilibrium centrifugal distortion constant and is usually much smaller than B_e . The internuclear distance also changes as a result of rotational-vibrational coupling. This can be taken into account by employing effective values B_v and D_v for the rotational constants which are different for different vibrational levels. Applying these corrections to Expression (15) results in the following expression:

$$F_v(J) = B_v J(J+1) - D_v J^2(J+1)^2, \quad (17)$$

where B_v is given by

$$B_v = B_e - \sum_{i=1}^3 \alpha_i (v_i + d_i/2). \quad (18)$$

The summation is over the three normal modes of vibration and B_e is given by Expression (16). The constants α_i are the rotational-vibrational coupling constants which are usually small compared to B_e . The constant D_v in Expression (17) can be approximated by D_e since the appropriate rotational-vibrational coupling constants are extremely small.

We must now consider the rotational levels of a linear triatomic molecule in a $^2\Pi$ electronic state in which rotational, vibrational and electronic interactions are all present. As with vibronic energy levels for the non-rotating molecule, these interactions are treated by coupling the electronic orbital, the electronic spin and vibrational angular momenta along the internuclear axis. However, in the present case Coriolis forces associated with molecular rotation tend to uncouple the electron spin, and to a lesser extent the orbital and vibrational momenta, from the linear axis. The extent of the uncoupling of the spin increases with increasing rotation and gives rise to various coupling cases first described by Hund for diatomic molecules. Following the notation of Hougen (54), Hund's case (a) occurs when the three momenta are all tightly coupled to the linear axis, in which case Eq. (17) becomes

$$F_v(J) = B_v[J(J+1) - P^2] - D_v[J(J+1) - P^2]^2 . \quad (19)$$

Case (b) occurs when the spin is completely uncoupled from the linear axis so that only the quantum number K remains a good one during rotation. The rotational term value expression becomes

$$F_v(N) = B_v[N(N+1) - K^2] - D_v(N+1/2)^4 , \quad (20)$$

where N is the quantum number specifying the total angular momentum of the system excluding spin. In BO_2 $\Sigma = \pm 1/2$ and therefore N is related to the quantum number J by the expression $J = N \pm 1/2$. Actually, the two coupling cases presented are limiting cases. The intermediate cases in which neither Eq. (19) nor Eq. (20) properly describe the rotational energy levels are discussed in detail by Hougen (54). In this discussion the presence of vibronic and spin-orbit coupling are also taken into account.

The rotational expressions derived by Hougen (54) for vibronic levels in which $K = 0$ depend upon the relative magnitudes of r and BJ , where $r = A^*/2$. In cases where $r \gg BJ$, as in BO_2 , Hougen gives the following rotational expressions:

$$F_1(^2\Sigma, N) = C \pm r + (1/2)\gamma^{\mp} + B_{\text{eff}}^{\mp}N(N+1) + (1/2)\gamma^{\mp}N , \quad (21)$$

$$F_2(^2\Sigma, N) = C \pm r + (1/2)\gamma^{\mp} + B_{\text{eff}}^{\mp}N(N+1) - (1/2)\gamma^{\mp}(N+1) . \quad (22)$$

In these expressions $\gamma^{\mp}$ is analogous to the spin-doubling constant in diatomic molecules, $B_{\text{eff}}^{\mp}$ is defined by

$$B_{\text{eff}}^{\mp} = B[1 \pm (B/2r)(A/2r)^2] , \quad (23)$$

and C has been defined previously. The - and + superscripts refer to the $\Sigma^{(-)}$ and $\Sigma^{(+)}$ vibronic levels indicated in Fig. 6. By comparison with Expressions (10) and (11) for $K = 0$, it can easily be seen that Expressions (21) and (22) include vibronic as well as rotational contributions. If the vibronic contributions are eliminated, the resulting rotational expressions are essentially those of a diatomic molecule in a $^2\Sigma$ electronic state. It can also be seen from (21) and (22) that two rotational components F_1 (levels which correspond to $J = N + 1/2$) and F_2 (levels which correspond to $J = N - 1/2$) are associated with each Σ vibronic level. (Refer to Fig. 7.) The splitting between these components is given by $\gamma^{\mp} (N+1/2)$ and thus increases with increasing rotation. In linear triatomic molecules this splitting can be comparable to B, in contrast to diatomic molecules where it is usually a small constant. This is in fact the case for the Σ vibronic levels in the $\tilde{A}^2\Pi_u$ electronic state of BO_2 . In the ground state $\gamma^{\mp}$ is about half the value of B. Expressions (21) and (22) can be corrected for centrifugal distortion in a first approximation by applying the same term used for diatomic molecules in a $^2\Sigma$ electronic state, namely $DN^2(N+1)^2$.

The rotational expressions derived by Hougen (54) for vibronic levels in which $K = v_2 + 1$ are again similar to those of diatomic molecules. For levels in which $J > K - 1/2$, Hougen gives the following rotational expression for any coupling case intermediate between (a) and (b):

$$F(J) = C' + B[(J+1/2)^2 - K^2] \pm (1/2)[4B^2(J+1/2)^2 + A_{\text{eff}}(A_{\text{eff}} - 4BK)]^{1/2}, \quad (24)$$

where all the terms have been previously defined. This expression is similar to the rotational expression for diatomic molecules in a $^2\Pi$ electronic first given by Hill and Van Vleck (55) and modified by Klynning et al. (56), which can be written in the following form:

$$F(J) = Bx - Dx^2 \pm (1/2)[4(\bar{B})^2x + (\bar{A}-2\bar{B})^2]^{1/2}, \quad (25)$$

where

$$x = (J+1/2)^2 - 1,$$

and

$$\bar{B} = B - 2Dx,$$

$$\bar{A} = A + A_Jx.$$

The $\bar{A}$ term allows any dependence of the spin-orbit coupling constant on the rotational quantum number J to be accounted for. In $^2\Pi$ vibronic states ($K=1$) Expression (24) can be converted to (25) by including centrifugal distortion terms and eliminating C' since it is already included in the vibronic expressions.

If the interaction between the electronic angular momentum and molecular rotation is considered, as it must be for large rotation in states where $\Lambda \neq 0$, Expressions (24) and (25) must be further refined. In diatomic molecules this interaction is called Λ -type doubling while in polyatomics it is called P-type doubling, and is found to produce a splitting of rotational levels into two components for each J value. In $^2\Pi$ electronic states in which $v_2 = 0$ and in which the Renner effect is small ($|\epsilon| < 0.3$), P-type doubling can be accounted for by adding expressions used for Λ -type doubling in diatomic molecules to Expressions (24) and (25). For $^2\Pi_{3/2}$ states this correction takes the form

$$\phi_1(J) = \pm(1/2)s(J+1/2)^3, \quad (26)$$

and for ${}^2\Pi_{1/2}$ states has the form

$$\phi_2(J) = \pm(1/2)p(J+1/2). \quad (27)$$

In these expressions s and p are Λ -doubling constants where $s \ll p$ and therefore the doubling is larger in the ${}^2\Pi_{1/2}$ state. For states with $K = v_2 + 1 \geq 2$ Expression (24) in a first approximation can be used without any additional modification since the P-type doubling is very small.

For vibronic states with $0 < K < v_2 + 1$ the solution of the spin uncoupling problem becomes considerably more complex. For example, in Fig. 6 the four 020 vibronic levels in which $0 < K < v_2 + 1$ cannot be grouped into two noninteracting pairs and therefore the solution involves a quartic equation. The rotational expressions for $J > K - 1/2$ derived by Hougen (54) have the following form:

$$F(J) = C + B[(J+1/2)^2 - K^2] + \lambda_1, \quad (28)$$

where the λ_1 are the roots of a 4×4 matrix. Although Hougen has presented approximate solutions for λ_1 in certain cases, Dymek (3) has found experimentally, in the rotational analysis of the 02^0_0 bands in the $\tilde{A} {}^2\Pi_u$ state of ${}^{10}\text{BO}_2$, that the rotational expressions for $K = v_2 + 1$ give a much better fit of the data. Consequently, Hougen's solutions for $0 < K < v_2 + 1$ will not be presented, and as will be seen later, the rotational Expression (25) will be used instead.

D. Symmetry Properties of Rovibronic Levels

In the theoretical discussion thus far, expressions describing various rovibronic energy levels of a linear symmetric triatomic molecule have been presented. In order to make use of this information in the interpretation of the BO_2 spectrum, it is necessary to consider the transitions between energy levels. This discussion will begin by first considering the symmetry properties of the energy levels, since in addition to the quantum numbers, the symmetry of these levels must be specified in order to determine the allowed transitions.

One symmetry property of the rovibronic levels can be obtained by considering the behavior of the total wave function, Ψ_{evr} , with respect to inversion. These levels are designated + or - depending on whether the total wave function remains unchanged or changes sign under this operation. In $^2\Sigma$ vibronic states the $\pm$ symmetry of the total wave function is given by $(-1)^N$ for $\Sigma^{(+)}$ states and $(-1)^{N+1}$ for $\Sigma^{(-)}$ states. For vibronic states with $K > 0$, P-type doubling results in + and - rotational levels for each J value. The relative positions of neighboring Σ states determine whether the + or - level is higher in energy as indicated by Herzberg (46, p. 240).

The vibronic states of BO_2 are further classified by a u,g symmetry denoting that the vibronic wave functions change sign or remain unchanged, respectively, upon inversion through a center of symmetry. The rovibronic levels of this molecule, analogous to homonuclear diatomic molecules, are designated as symmetric (s) or antisymmetric (a) depending on whether the total wave function remains unchanged or changes sign upon exchange of identical nuclei. In g vibronic states

+ and - levels are associated with (s) and (a) symmetries, respectively; while the reverse is true in u vibronic states. The symmetry properties of rovibronic levels in the $\tilde{A} \ ^2\Pi_u$ and $\tilde{X} \ ^2\Pi_g$ electronic states of BO_2 are presented in Figures 7 and 8.

As will be seen shortly, a knowledge of the u,g symmetry of vibronic states is very important in determining which transitions are allowed. This symmetry may be obtained from group theory using the procedures outlined in Ref. (47, p. 124-128). In this approach the normal modes of vibration are assigned a symmetry species in the point group to which a given molecule belongs. In the case of BO_2 , which belongs to the $D_{\infty h}$ point group, the three normal modes of vibration have σ_g^+ , π_u and σ_u^+ symmetries corresponding to the symmetric stretch, degenerate bending and asymmetric stretch, respectively. The resultant u,g symmetry and vibronic species are obtained by taking the direct product of the vibrational species with the electronic species. The vibrational species, for cases in which non-degenerate modes are multiply excited by k quanta, are obtained by multiplying the characters of the corresponding ground state vibrational species taken to the k^{th} power. For example, if the symmetric stretch in BO_2 is doubly excited, the characters of Σ_g^+ , indicated in Table 24 of Ref. (47), are squared. This results in a Σ_g^+ vibrational species and Π_g vibronic species when the direct product of Σ_g^+ is taken with the electronic species, Π_g . Refer to Table 57 of Ref. (48) for direct products in the $D_{\infty h}$ point group. For multiple excitation of degenerate modes the resultant vibrational species can be obtained directly from Table 32 of Ref. (47). Using these procedures, the resultant u,g symmetry of vibronic species of BO_2 for various

degrees of excitation of the normal modes can conveniently be summarized in Table 3.

Table 3
The u,g Symmetry of Vibronic Species of BO_2 for
Various Degrees of Excitation of the Normal Modes

Normal Modes	Even Quanta of Excitation	Odd Quanta of Excitation
	<u>Π_g Electronic State</u>	
ν_1	g	g
ν_2	g	u
ν_3	g	u
	<u>Π_u Electronic State</u>	
ν_1	u	u
ν_2	u	g
ν_3	u	g

E. Selection Rules

The electric dipole-allowed transitions between energy levels can be determined using group theory. A transition is allowed if the direct product of the two combining levels belongs to the same species as one of the components of the dipole moment. For BO_2 the dipole moment may transform like a Σ_u^+ (T_z component) and Π_u (T_{xy} component) species. (Refer to Table 52 of Ref. (48).) This information together with the direct product of the combining levels, Table 57 Ref. (48), can be used to determine selection rules on the quantum numbers and symmetry properties. It should be mentioned, however, that as a result of the

Renner-Teller effect the + and - character of the $^2\Sigma$ vibronic levels is not well defined, and therefore contrary to the results obtained from these tables $\Sigma^{(+)} - \Sigma^{(-)}$ and $\Sigma^{(-)} - \Sigma^{(+)}$ transitions are observed. The selection rules for vibronic transitions between the $\tilde{A}^2\Pi_u$ and $\tilde{X}^2\Pi_g$ electronic states of BO_2 can be summarized as follows:

$$g \leftrightarrow u, g \leftrightarrow g, u \leftrightarrow u,$$

$\Delta K = 0$ ($\Delta K = \pm 1$ is strictly forbidden in the $\tilde{A}-\tilde{X}$ system by the u,g selection rule),

$\Delta \Sigma = 0$ Hund's case (a), in which case $\Delta P = 0$,

$\Delta \Sigma = \pm 1$ for spin uncoupling from the internuclear axis as

a result of large rotations (6), in which case $\Delta P = \pm 1$.

In addition, the following selection rules for changes in the quantum numbers v_1, v_2, v_3 can be obtained by applying the u,g selection rule to Table 3:

$$\Delta v_1 = 0, \pm 1, \pm 2, \dots$$

$$\Delta v_2 = 0, \pm 2, \pm 4, \dots$$

$$\Delta v_3 = 0, \pm 2, \pm 4, \dots$$

Since $\Delta \ell$ is even or odd when Δv_2 is even or odd, $\Delta \ell$ can take on values of 0 and ± 2 . These values are possible because ℓ and Λ are only good quantum numbers in the crude sense.

When molecular rotation is considered, the allowed transitions are governed by the following additional selection rules:

$$+ \leftrightarrow -, + \leftrightarrow +, - \leftrightarrow -,$$

$$s \leftrightarrow s, a \leftrightarrow a, s \leftrightarrow a,$$

$$\Delta N \text{ or } \Delta J = 0, \pm 1, \text{ but } N' = 0 \leftrightarrow N'' = 0, \text{ and } J' = 0 \leftrightarrow J'' = 0.$$

F. Rotational Structure of Electronic Transitions

With a background of symmetry properties and selection rules, we will now examine more closely the rotational structure of band systems for linear triatomic molecules, with a discussion of vibronic structure to follow in a later section. During an electronic transition the quantum numbers designating the rotational and vibronic states may both change. If the upper and lower state electronic, vibronic and rotational term values are designated by T'_e , $G'(v_1, v_2, v_3)$, $F'_v(J)$ and T''_e , $G''(v_1, v_2, v_3)$, $F''_v(J)$, respectively, the frequency (in cm^{-1}) of an electronic transition is given by

$$\nu = T'_e - T''_e + G'(v_1, v_2, v_3) - G''(v_1, v_2, v_3) + F'_v(J) - F''_v(J) , \quad (29)$$

where $G(v_1, v_2, v_3) = G(v_2, K, \pm 1/2) + G(v_1, v_3)$. The first four terms in this expression are constant for a transition between a specific pair of vibronic levels, and they can be replaced by the term ν_0 , the band origin. These transitions collectively form what is known as a band, the frequencies of which are given by

$$\nu = \nu_0 + F'_v(J) - F''_v(J) . \quad (30)$$

The selection rules on the rotational quantum number J give rise to P, Q and R branches in the rotational structure of a band depending upon whether $\Delta J = J' - J'' = -1, 0$ or $+1$, respectively. Application of the selection rules to transitions involving Σ and Π vibronic levels of BO_2 are illustrated in Figures 7 and 8. The branch designations are indicated for each transition along with the lower state J or N values in parenthesis. In Fig. 7 the transition subscripts refer to the spin

doubling components, F_1 or F_2 , involved in the transition. For example, transitions designated by a subscript 1 involve the upper spin doubling components in both electronic states, since in Σ vibronic levels (case (b) coupling) F_1 is higher in energy than F_2 (refer to Expressions (21) and (22)). However, in Fig. 8 in which Π vibronic levels of BO_2 are displayed (case (a) coupling) F_1 and F_2 are respectively the $\Pi_{3/2}$ and $\Pi_{1/2}$ spin-orbit components with F_1 lower in energy than F_2 . Therefore, transitions involving Π vibronic levels designated by a subscript 1 refer to the $\Pi_{3/2}$ spin-orbit components in both electronic states. An important feature of the BO_2 spectrum, as illustrated by dashed lines in Fig. 8*, is the absence of antisymmetric levels and is due to a nuclear spin of zero for the symmetrically located oxygen atoms. Q branches are not indicated in these figures since they are very weak in the ${}^2\Pi - {}^2\Pi$ electronic transitions of BO_2 .

Transitions in which $\Delta J \neq \Delta N$ are known as satellite branches, and are indicated on the right side of Fig. 7. These transitions take place between $\Sigma^{(+)}$ and $\Sigma^{(-)}$ vibronic levels and involve both spin-doubling components. In addition to P, Q and R branches, ΔN can also take on values of +2 and -2 in satellite branches giving rise to S form and O form branches, respectively. The transition designations are indicated by the following notation:

$$\Delta N \Delta J_{F', F''} (N) ,$$

*For simplicity the missing antisymmetric levels are omitted from Fig. 7.

Figure 7

$01^1 0^2 \Sigma_g - 01^1 0^2 \Sigma_u$ Transitions in the $\tilde{A}-\tilde{X}$ System of BO_2 . The missing antisymmetric levels are not shown, and the energy spacings are arbitrary.

Figure 7

Figure 8
 $00^0 0 \ ^2\Pi_g - 00^0 0 \ ^2\Pi_u$ Transitions in the $\tilde{A}-\tilde{X}$ System
of BO_2 . The energy spacings are arbitrary.

Figure 8

where the subscripts are, from left to right, the spin-doubling components in the upper and lower states.

A feature which is characteristic of most bands throughout the visible and ultraviolet is band head formation. In order to explain this feature we must make use of the rotational term value expressions given in Section IV.C. Complex expressions using the rotational term values derived by Hougen for specific vibronic cases can be generated; however, for the purposes of illustration it is adequate and far more advantageous from the standpoint of clarity to use Expression (15). If we substitute the first term of (15) into (30) using $J' = J + 1$ for the R branch and $J' = J - 1$ for the P branch, where J is the rotational quantum number in the lower state, we obtain the following expressions:

$$\text{R branch } \nu = \nu_0 + 2B'_V + (3B'_V - B''_V)J + (B'_V - B''_V)J^2, \quad (31)$$

$$\text{P branch } \nu = \nu_0 - (B'_V + B''_V)J + (B'_V - B''_V)J^2. \quad (32)$$

Both expressions can be combined into a single formula,

$$\nu = \nu_0 + (B'_V + B''_V)m + (B'_V - B''_V)m^2, \quad (33)$$

where $m = -J$ for the P branch and $m = J + 1$ for the R branch.

For transitions involving the $\tilde{A}^2\Pi_u$ and $\tilde{X}^2\Pi_g$ electronic states of BO_2 , $B'_V - B''_V$ is negative*, causing the linear and quadratic terms in (31) to have opposite signs. This results in a convergence of the rotational lines in the R branch to a head on the short wavelength side of the band origin, after which the rotational lines turn back towards the

* $B'_V - B''_V$ is also negative for transitions in the $\tilde{B}-\tilde{X}$ system of BO_2 .

red (red degraded), refer to Fig. 11. It is important to know, as will be seen shortly, what factors affect the separation between band head and band origin, termed "head-to-origin separation". This can be accomplished by setting $dv/dm = 0$ in (33), solving for m and substituting the results back into (33); the following expression is then obtained:

$$v_{\text{head}} - v_o = - \frac{(B_v' + B_v'')^2}{4(B_v' - B_v'')} . \quad (34)$$

Since it was shown in Expression (18) that B_v is a function of the vibrational quantum numbers v_1, v_2, v_3 , it can be seen from (34) that the head-to-origin separation and the rotational numbering of the band head change from band to band.

G. Combination Relations

The principle of combination differences is extremely important in the analysis of experimental spectroscopic data. It is used in rotational analysis to establish and confirm rotational numbering and can be used to obtain rotational constants. It is also applicable in vibrational analysis as well. This method is based upon the fact that the wavenumber differences between certain pairs of transitions with common levels in an upper or lower state must be equal within experimental error. The use of combination relations in the rotational analysis is illustrated in Fig. 9. As can be seen from this figure, the difference between R(1) and P(3) in the two different vibrational bands must be equal, and represents a very sensitive check on the rotational numbering. We can express this combination difference quantitatively by the following:

Figure 9

**The Use of Combination Relations in the
Rotational Analysis Involving Two Different
Vibrational Levels in the Upper State**

Vibrational LevelRotational Level

Figure 9

$$v[R(1)] - v[P(3)] = F_v'(3) - F_v'(1) = \Delta_2 F_v'(2) , \quad (35)$$

or in general by

$$R(J-1) - P(J+1) = F_v'(J+1) - F_v'(J-1) = \Delta_2 F_v'(J) , \quad (36)$$

$$R(J) - P(J) = F_v'(J+1) - F_v'(J-1) = \Delta_2 F_v'(J) , \quad (37)$$

where $\Delta_2 F_v'(J)$ and $\Delta_2 F_v'(J)$ are called the lower and upper state combination differences, and the subscript 2 indicates that the energy difference is taken between levels that are separated by two quanta of J. If we substitute the rotational Expression (15) for $F_v(J)$ in either (36) or (37) we obtain the following:

$$\Delta_2 F_v(J) = 4B_v(J+1/2) . \quad (38)$$

This important expression will be discussed further in Chapter V.

The use of combination differences in the vibrational analysis is just as important as it is in the rotational analysis. This is illustrated in Fig. 10 in which the difference between the band origins of transitions 1 and 2 are equal to the corresponding difference between transitions 3 and 4; thereby giving a redundancy in the observation of the vibronic level v_b , ΔG wavenumbers above level v_a . The larger the number of such observations the more firmly established the existence of v_b becomes. The consistency of the combination differences would hold equally well if rotational lines with a fixed value of J were used instead of band origins. However, it does not hold rigorously for band head measurements since the head-to-origin separation and rotational numbering vary from band to band. Nevertheless, the combination

Figure 10
The Use of Combination Relations
in the Vibrational Analysis

Figure 10

differences from band head measurements only deviate slightly from constant values in the spectrum of BO_2 , as shown in Tables 6 and 7.

H. Vibronic Structure of Electronic Transitions of BO_2

The experimental study of BO_2 by Johns (1) has revealed that the equilibrium internuclear distance increases slightly in going from the $\tilde{X}^2\Pi_g$ to the $\tilde{A}^2\Pi_u$ state. This, together with the fact that the vibrational frequencies in both states are similar in magnitude, can be used to account for some observations concerning the intensity of electronic transitions; namely

- 1) the fact that progressions in the symmetric stretching mode, ν_1 , are fairly strong, and
- 2) sequences in which $\Delta\nu_2 = 0$ and 2 occur with moderate intensity and appear relatively close in the spectrum.

However, on account of Fermi resonance the relative intensity of all transitions of BO_2 cannot be predicted correctly on the basis of these generalizations. As in CO_2 (57), Fermi resonance can severely mix and shift the intensities.

Weak bands of BO_2 were observed by Johns (1) to the violet of each strong band with an intensity ratio of about 1:4, and have been interpreted as being due to ^{10}B in natural isotopic abundance ($\approx 20\%$). Although these bands complicate the spectrum further, they are extremely important in the vibrational analysis since their assignments and molecular constants must be consistent with those obtained for $^{11}\text{BO}_2$. In this work, however, no extensive study of these bands has

been carried out and therefore a discussion of isotopic relations as applied to the molecular constants will not be presented.

I. Fermi Resonance

The interaction referred to throughout this chapter as Fermi resonance is yet another consideration which must be taken into account in calculating vibronic energy levels of polyatomic molecules. This interaction was first proposed by Fermi (57) to explain certain anomalies in the CO_2 spectrum, and occurs when two or more vibronic energy levels of the same symmetry are nearly coincident. Energy levels in Fermi resonance exhibit mutual interactions such that their actual positions are displaced from those calculated using the vibronic expressions presented earlier. This can be visualized by considering that states in resonance "mix and repel" one another. Since the eigenfunctions which characterize the Fermi unperturbed levels "are mixed" in the presence of Fermi resonance, the labeling used to designate vibronic energy levels is no longer strictly valid.

Fermi resonance occurs quite extensively throughout the BO_2 spectrum since, as in many other triatomic molecules, the symmetric stretching frequency is approximately twice the bending frequency in the two lowest electronic states; this results in a near coincidence of vibronic levels of the form (v_1+1, v_2, v_3) and (v_1, v_2+2, v_3) with the same symmetry. (Refer to Figures 15 and 24.) Hougen (15) has studied in detail Fermi interacting levels of this type for linear triatomic molecules in Π electronic states in which the Renner and spin-orbit interactions are both small compared to the bending frequency. Vibronic levels in resonance are grouped together into what is called a polyad,

each of which is subdivided into groups of interacting levels with the same value of $|P|$. For example, the (100-020) Fermi diad of BO_2 is comprised of six levels, three interacting levels for $|P| = 1/2$ and three for $|P| = 3/2$. The (200-120-040) Fermi triad is comprised of five interacting levels for each value of $|P|$. These are indicated in Figures 15 and 24 for the ground state.

In Hougen's treatment, the Fermi perturbed energies of BO_2 are obtained by determining the roots of two secular determinants independently, one for each value of $|P|$. These determinants are formed from square symmetric matrices having dimensions equal to the number of interacting levels. In this approach the off-diagonal matrix elements H_{ij} are calculated from the following expression:

$$H_{ij} = \int \Psi_i^{(1)*} \hat{H} \Psi_j^{(1)} d\tau, \quad (39)$$

where $\Psi_i^{(1)}$ and $\Psi_j^{(1)}$ are first-order wave functions formed from the wave functions given by Pople (53), which include Renner-Teller and spin-orbit interactions; $\hat{H}$ is an anharmonic perturbation operator which Hougen calls v_F . Rather than give v_F explicitly, it is more useful to present the forms given by Hougen (15) for the matrix elements of v_F , namely:

$$\begin{aligned} & (v_1+1, v_2, v_3; \Lambda\ell\Sigma | v_F | v_1, v_2+2, v_3; \Lambda\ell\Sigma) \\ &= W_1 [(v_1+1)(v_2+2-\ell)(v_2+2+\ell)]^{1/2}, \end{aligned} \quad (40)$$

$$\begin{aligned} & (v_1+1, v_2, v_3; \Lambda\ell\Sigma | v_F | v_1, v_2+2, v_3; \Lambda\bar{+}2, \ell\pm 2, \Sigma) \\ &= W_2 [(v_1+1)(v_2+2\pm\ell)(v_2+4\pm\ell)]^{1/2}, \end{aligned}$$

and in the case where $\Delta v_2 = 0$

$$\begin{aligned} & (v_1+1, v_2, v_3; \Lambda \ell \Sigma | v_F | v_1, v_2, v_3; \Lambda \ell \Sigma) \\ & = 2W_1 (v_1+1)^{1/2} (v_2+1) , \end{aligned} \quad (41)$$

$$\begin{aligned} & (v_1+1, v_2, v_3; \Lambda \ell \Sigma | v_F | v_1, v_2, v_3; \Lambda \bar{\ell} 2, \ell \pm 2, \Sigma) \\ & = 2W_2 [(v_1+1)(v_2 \mp \ell)(v_2+2 \pm \ell)]^{1/2} . \end{aligned}$$

In these expressions the wave functions are expressed in terms of the basis set $|v_1, v_2, v_3; \Lambda \ell \Sigma\rangle$, and W_1 and W_2 are two Fermi interaction parameters given by Hougen (15). By means of illustration, Hougen's procedure for calculating the matrix elements H_{12} ($=H_{21}$) for the (100-020) polyad of BO_2 in which $|P| = 3/2$ is as follows:

- (1) Form the first-order wave functions $\Psi_1^{(1)}$ and $\Psi_2^{(1)}$ corresponding to the 100 and $02^20 \Pi_{3/2}$ levels, respectively. These wave functions are formed by applying an orthogonal transformation to the total energy matrix (a 5×5 matrix in this case which involves $H^{(0)} + H_{\text{Renner}} + H_{\text{spin-orbit}}$) and then applying perturbation theory. The first-order wave functions are as follows:

$$\begin{aligned} \Psi_1^{(1)} &= |1, 0, 0; 1, 0, 1/2\rangle - \frac{\sqrt{2}}{4}\epsilon |1, 2, 0; -1, 2, 1/2\rangle \\ \Psi_2^{(1)} &= |0, 2, 0; 1, 0, 1/2\rangle \cos\beta + |0, 2, 0; -1, 2, 1/2\rangle \sin\beta \\ &\quad + \frac{\sqrt{2}}{4}\epsilon |0, 0, 0; 1, 0, 1/2\rangle \sin\beta - \frac{\sqrt{2}}{4}\epsilon |0, 4, 0; 1, 0, 1/2\rangle \sin\beta \\ &\quad - \frac{\sqrt{6}}{4}\epsilon |0, 4, 0; -1, 2, 1/2\rangle \cos\beta \end{aligned}$$

$$\begin{aligned}\psi_3^{(1)} = & -|0,2,0;1,0,1/2\rangle \sin\beta + |0,2,0;-1,2,1/2\rangle \cos\beta \\ & + \frac{\sqrt{2}}{4}\epsilon |0,0,0;1,0,1/2\rangle \cos\beta - \frac{\sqrt{2}}{4}\epsilon |0,4,0;1,0,1/2\rangle \cos\beta \\ & + \frac{\sqrt{6}}{4}\epsilon |0,4,0;-1,2,1/2\rangle \sin\beta .\end{aligned}$$

(2) Set up the matrix Expression (39):

$$H_{12} \langle \psi_1^{(1)} | v_F | \psi_2^{(1)} \rangle .$$

(3) Evaluate this expression using (40) and (41). The same expression given by Hougen (15) is then obtained, where the terms with $v_2=4$ do not contribute:

$$H_{12} = 2(W_1 - \epsilon W_2) \cos\beta + \sqrt{2}(2W_2 - \epsilon W_1) \sin\beta ,$$

where the sin and cos terms are defined by

$$\begin{aligned}r \cos 2\beta &= +A/2, \\ r \sin 2\beta &= +(1/2)(\epsilon \omega_2) \left[(v_2+1)^2 - K^2 \right]^{1/2} ,\end{aligned}$$

where $r = A^*/2$.

All other off-diagonal matrix elements for this and other polyads are formed in a similar manner.

The matrix elements along the diagonals are obtained from the second-order energies given by Pople (see Expressions 9-11); however, rather than being referenced to the bottom of the well as they are in these expressions, they are referenced to an imaginary level in the absence of Renner-Teller and spin-orbit interactions. This level is arbitrarily chosen as the zero of energy. In the case of the (200-120-040) polyad the diagonal matrix elements are expressed relative to the

imaginary 040 level. In this process the relative positions of the unperturbed (by Renner-Teller, spin-orbit and Fermi interactions) 200 and 120 levels are specified by the parameters Δ and Δ' respectively, where

$$\Delta \equiv G(200) - G(040)$$

and

$$\Delta' \equiv G(120) - G(040) .$$

To obtain the perturbed energies for a particular polyad of BO_2 , the roots of the $|P| = 1/2$ and $|P| = 3/2$ secular determinants are evaluated by substituting values for the constants $A, \epsilon\omega_2, \omega_2, W_1, W_2, \Delta$ and Δ' into the matrices and diagonalizing. The roots thus obtained for each value of $|P|$ are converted to relative values with respect to a zero center of gravity, and compared to observed energies calculated with respect to their center of gravity. Using this method and the constants determined by Johns (1) for the (100-020) $\tilde{A}^2\Pi_u$ diad of $^{11}\text{BO}_2$, Hougen (15) has obtained fairly good agreement between the observed and calculated energies. Following the same procedure, Dymek (3) obtained similar agreement for the (100-020) levels in the $\tilde{A}^2\Pi_u$ and $\tilde{X}^2\Pi_g$ states of $^{11}\text{BO}_2$ and $^{10}\text{BO}_2$. As will be seen in Chapter V, the calculation of Fermi perturbed energies using the methods described in this section is an important factor in the vibrational analysis.

CHAPTER V. DISCUSSION OF RESULTS

A. Description of Laser-Excited Fluorescence Spectra

In previous absorption and conventional emission studies it has been revealed that the electronic spectrum of BO_2 is characterized by dense, badly-overlapped regions. In contrast, due to the selectivity of the excitation source, the laser-excited fluorescence spectra of BO_2 reported in this work and in the studies by Russell et al. (5,6) are relatively free of these overlapping features.

The fluorescence spectra were obtained in this work by excitation of the band heads listed in Table 4. The assignments indicated in this table for $^{11}\text{BO}_2$ are the same as those given by Johns (1) with the exception of the R_1 and R_2 transitions involving the 12^0_0 and 20^0_0 levels in the $\tilde{A}^2\Pi_u$ state. The assignment for these levels are in parenthesis to indicate that they have been interchanged in this work. The assignments indicated for $^{10}\text{BO}_2$ are those given by Dymek (3). Excitation of overlapping rotational lines belonging to bands in the $\tilde{A}-\tilde{X}$ system other than those indicated in Table 4 have also been observed throughout the course of this work. For facility of discussion these features will be referred to simply as overlapping bands, and will be discussed in more detail in the section dealing with vibrational analysis.

Table 4

List of transitions in the $\tilde{A}-\tilde{X}$ system of BO_2 excited by the dye laser. All transitions are band heads of $^{11}\text{BO}_2$ unless otherwise indicated.

Transition		$\lambda(\text{air}), \text{\AA}$	$\bar{\nu}(\text{vac}), \text{cm}^{-1}$
R_1	$12^0_0 \ 2\Pi - 00^0_0 \ 2\Pi^b$	4891.62	20437.4
R_1	$12^2_0 \ 2\Pi - 00^0_0 \ 2\Pi$	4891.79	20436.7
R_1	$(20^0_0 \ 2\Pi - 00^0_0 \ 2\Pi)$	4906.89	20373.8
R_1	$(12^0_0 \ 2\Pi - 00^0_0 \ 2\Pi)$	4929.34	20281.0
R_1	$04^2_0 \ 2\Pi - 00^0_0 \ 2\Pi$	4932.46	20268.2
R_1	$04^0_0 \ 2\Pi - 00^0_0 \ 2\Pi$	4965.38	20133.8
R_2	$04^0_0 \ 2\Pi - 00^0_0 \ 2\Pi$	4973.59	20100.6
R_2	$04^2_0 \ 2\Pi - 00^0_0 \ 2\Pi$	4997.49	20004.5
R_1	$11^1_0 \ 2\Sigma^+ - 01^1_0 \ 2\Sigma^+^a$	5144.61	19432.4
R_1	$11^1_0 \ 2\Delta - 01^1_0 \ 2\Delta^b$	5145.04	19430.8
R_1	$11^1_0 \ 2\Delta - 01^1_0 \ 2\Delta$	5156.28	19388.4
R_1	$02^2_0 \ 2\Pi - 00^0_0 \ 2\Pi$	5157.66	19383.2
R_1	$02^0_0 \ 2\Pi - 00^0_0 \ 2\Pi$	5196.11	19239.8
R_2	$02^0_0 \ 2\Pi - 00^0_0 \ 2\Pi$	5207.18	19198.9
R_2	$02^2_0 \ 2\Pi - 00^0_0 \ 2\Pi$	5228.97	19118.9
R_1	$01^1_0 \ 2\Sigma^+ - 01^1_0 \ 2\Sigma^+^a$	5435.99	18390.8
R_2	$01^1_0 \ 2\Sigma^+ - 01^1_0 \ 2\Sigma^+$	5437.53	18385.6
R_1	$00^0_0 \ 2\Pi - 00^0_0 \ 2\Pi^a$	5456.82	18320.6
R_2	$00^0_0 \ 2\Pi - 00^0_0 \ 2\Pi$	5470.89	18273.5

a. Transitions in which rotational lines off the band head were excited, however, the wavelengths and frequencies indicated in all cases are those of the band head.

b. $^{10}\text{BO}_2$.

The principal features of the fluorescence spectra were band heads in the R branch whose accumulated linewidth generally matched that of the laser and corresponding rotational lines in the P branch where the accumulated linewidth was five to ten times broader than the laser. These features are illustrated in Figures 11 and 13 along with Table 5. In the upper half of Fig. 11 a portion of the emission spectrum in the 5470 Å region of $^{11}\text{BO}_2$ is displayed. The laser is shown to be in resonance with approximately fifteen rotational lines, centered around $J = 16.5$, in the $R_2\ 00^0_0\ 2\Pi - 00^0_0\ 2\Pi$ band head of $^{11}\text{BO}_2$. This results in the broad P branch fluorescence, centered around $J = 18.5$, shown on the right. Although R branch fluorescence is not shown in this figure, it would be expected to be at the same position and have the same bandwidth as the laser. Typical R branch fluorescence, however, can be seen by referring to Fig. 13 which involves excitation of a different band. The difference in appearance of the two branches can easily be explained by the fact that the rotational line spacing in the R branch, due to band head formation, is much smaller than the corresponding spacing in the P branch. In the case considered in Fig. 11, the former is approximately 0.3 cm^{-1} (at $J = 19.5$) while the latter is approximately 1.6 cm^{-1} (at $J = 21.5$). The larger bandwidth of the P branch results in a corresponding reduction in peak intensity compared to that of the R branch.

In Fig. 12 the laser is shown to be overlapping the $R_1\ 02^0_0\ 2\Pi - 000\ 2\Pi$ band head of $^{11}\text{BO}_2$ indicated in the absorption spectrum above. It is also evident that the laser overlaps a second band head at slightly longer wavelength, that of the $R_2\ 02^0_0\ 2\Pi - 00^0_0\ 2\Pi$ band

of $^{10}\text{BO}_2$. This is a prime example of one type of overlapping feature that will be discussed in the next section of this chapter. A portion of the resulting fluorescence spectrum originating from the $02^0 0^2 \Pi_{3/2}$ level of $^{11}\text{BO}_2$ is indicated in the lower part of Fig. 13. These signals correspond to the band heads shown in the emission spectrum above. An important feature of this figure worth noting is that the band head in the emission spectrum on the right is not immediately clear-cut, quite unlike the situation in the fluorescence spectrum below. The "sharp" fluorescence features result from selectively exciting rotational lines in the band head. In the emission spectrum, on the other hand, there is no such selectivity, and as a result the band head often blends into the P branch structure of another band. The difference in appearance of band heads observed by laser-excited fluorescence as compared to conventional emission becomes even more pronounced in regions where there is a great deal of overlapping structure. In such cases the recognition of a band head becomes virtually impossible using the latter technique. As a result, a number of new band heads in the BO_2 spectrum have been observed in this work.

Fluorescence spectra obtained by excitation of all the band heads listed in Table 4 generally resulted in features similar to those shown in Fig. 11 and 13. In some cases, however, rotational lines in the R branch slightly off the head were observed, resulting in linewidths larger than that of the laser and slight errors in the band head determinations. The reason for this is that the rotational lines observed in a fluorescence series for a given set of experimental conditions--fluorescence originating from the same rovibronic levels in

Figure 11

Excitation of the R_2 00^0_0 $^2\Pi - 00^0_0$ $^2\Pi$
 Band Head in the $\tilde{A}-\tilde{X}$ System of $^{11}\text{BO}_2$

000-000 $2\pi_{1/2}$
BAND HEAD

P BRANCH

Figure 11

Figure 12

Excitation of the $R_1 \ 02^0_0 \ 2\Pi - 00^0_0 \ 2\Pi$
 Band Head in the $\tilde{A}-\tilde{X}$ System of $^{11}\text{BO}_2$

$020 - 000^2 \pi_{3/2}$

LASER EXCITATION : 5196.2

Figure 12

Figure 13

Fluorescence Resulting From the Excitation Shown in Fig. 12

Figure 13

the upper state--do not change. In contrast, as was discussed in Section IV.F, the head-to-origin separation and rotational numbering of the head vary from band to band. In cases, therefore, where this variation is appreciable the rotational lines comprising a band head will differ from those observed in fluorescence.

The extent of the increased linewidth and band head determination error can be calculated for Π and Δ vibronic bands as a function of B_v'' using the rotational term value Expression (25) corrected by (26) and (27) for P-type doubling. This procedure was carried out for the $R_2\ 00^0_0\ 2\Pi - 00^0_0\ 2\Pi$ band of $^{11}\text{BO}_2$ shown in Fig. 11 using a computer program written by Dymek and input constants obtained from Johns (1) and Dymek (3). The program first calculated the rotational term values in the upper and lower states. These values were then substituted into Expression (30), along with the band origin, $18291.5\ \text{cm}^{-1}$, to obtain the calculated rotational transition frequencies. This process was repeated, each time B_v'' was incremented by $0.005\ \text{cm}^{-1}$. In this manner the following spectral features were calculated as a function of B_v'' : the rotational transition frequencies, the fluorescence linewidths and the separation between the fluorescence band center (center frequency) from the band head. These results are presented in Table 5. The above calculations can be carried out for other bands using appropriate constants; however, these results are not expected to differ appreciably from those given in Table 5. In any event the results presented here were only regarded as estimates of the uncertainty in determining band head frequencies. Since variations of B_v'' associated with pumped transitions and transitions observed in fluorescence are generally not

Table 5

Calculated rotational features of the laser-excited fluorescence spectrum for the R_2 00^0_0 $2\Pi - 00^0_0$ 2Π band of $^{11}\text{BO}_2$ as a function of B''_v . B'_v in all cases is 0.3106 cm^{-1} . All values in cm^{-1} .

B''_v	$B''_v - B'_v$ (true)	Fluorescence linewidth		Separation of Fluorescence band center from band head (band head determination error)	$R_2(18) - P_2(20)$ separation
		R branch	P branch		
0.3192	-0.010	4.8	13.1	3.9	24.3
0.3242	-0.005	2.4	15.8	1.2	24.7
0.3292	0.000	0.9	18.5	0.0	25.1
0.3342	+0.005	2.6	21.1	1.3	25.5
0.3392	+0.010	5.0	23.9	2.5	25.9

expected to be greater than 0.005 cm^{-1} , band head determination errors from this source* should be less than 2 cm^{-1} , and certainly less than 4 cm^{-1} as indicated. As can be seen from this table, increased fluorescence linewidth in the R branch is associated with an increased error, and thereby serves as a means of indicating when this error is prevalent. Where possible, however, band head frequencies determined by fluorescence were compared with spectra observed in high resolution emission and absorption. Band heads determined in this manner are given in Tables 6 and 7. These tables will be discussed shortly.

B. Vibrational Analysis

The vibrational analysis of BO_2 was carried out in this work on band head data obtained using the procedures previously described. In particular, transitions involving ${}^2\Pi$ vibronic levels in the (100-020) and (200-120-040) Fermi polyads of both the $\tilde{X} {}^2\Pi_g$ and $\tilde{A} {}^2\Pi_u$ states of ${}^{11}\text{BO}_2$ were analyzed. Limited band head data for Δ (${}^{10}\text{BO}_2$ and ${}^{11}\text{BO}_2$) and Σ (${}^{11}\text{BO}_2$) vibronic levels were analyzed as well.

Band heads observed in this work were placed in double Deslandres tables in which v_1 and v_2 varied in both the $\tilde{A}$ and $\tilde{X}$ electronic states while v_3 was equal to 0 in all cases. These tables are presented for band heads involving ${}^2\Pi_{3/2}$ vibronic levels (Table 6) and ${}^2\Pi_{1/2}$ vibronic levels (Table 7) of ${}^{11}\text{BO}_2$. For clarity, the transitions in these tables are underscored. The differences between transitions which appear in columns and rows give directly the vibrational intervals in the ground and excited states, respectively. For example, the

* Another source of error results from using slits widths that are 100μ or larger.

difference between any pair of entries in the first two columns in Table 6 gives the separation of the $02^0_0 \Pi_{3/2}$ level from the $00^0_0 \Pi_{3/2}$ level. The fact that these differences are not exactly the same reflects experimental errors discussed in Section IV.G, primarily a consequence of using band head data as opposed to band origin data. Consequently, deviation of up to 1.8 cm^{-1} occur throughout these tables. The principal of combination differences as discussed in Section IV.G was an important factor in the vibrational analysis. It was used in conjunction with selective band head excitation to establish term values of vibronic levels in the ground state and the vibronic symmetry, K_p , of ground and excited state levels involved in transitions that were observed in fluorescence. Since $\Delta K = 0$ and $\Delta P = 0$ are reasonably good selection rules for vibronic transitions in $^2\Pi$ electronic states with case (a) coupling, the combining levels for transitions observed in fluorescence are expected to have the same symmetry. Therefore, the symmetry of newly observed levels can be determined from transitions in which the symmetry of one of the combining levels has been firmly established, for example from the $00^0_0 \Pi_{3/2}$ or $\Pi_{1/2}$ levels in the $\tilde{A}$ state. This process was carried out starting with the $\Pi_{3/2}$ and $\Pi_{1/2}$ subbands of the $00^0_0 - 00^0_0$ transition and extended to all the transitions presented in Tables 6 and 7.

Due to the large number of vibronic bands present in the BO_2 spectrum, overlapping features generally make it possible to assign transitions in more than one way. In this work, because of selective band head excitation, the possibility of this occurring has been reduced significantly. Of the many instances where fluorescence from overlapping

TABLE 6

Deslandres Table of Band Heads for ${}^2\Pi_{1/2}-{}^2\Pi_{3/2}$ Transitions in the $\tilde{A} \ {}^2\Pi_u-\tilde{X} \ {}^2\Pi_g$ System of ${}^{11}\text{BO}_2$. All values in cm^{-1} .

$(v_1, v_2, v_3)''$ $(v_1, v_2, v_3)'$	$(0,0^0,0)$	$(0,2^0,0)$	$(0,2^2,0)$	$(0,4^0,0)$	$(0,4^2,0)$	$(1,0^0,0)$	$(1,2^0,0)$	$(1,2^2,0)$	$(2,0^0,0)$
$(0,0^0,0)$	<u>18320.6</u> ^{a,b} 919.2	810.1 919.5	<u>17510.5</u> ^b 918.8	311.2 918.8	<u>17199.3</u> ^c	<u>17264.2</u> ^{a,b} 919.3			<u>16198.8</u> ^{a,b} 918.9
$(0,2^0,0)$	<u>19239.8</u> ^{a,b} 143.4	809.8 143.1	<u>18430.0</u> ^b 143.7	311.9 143.7	<u>18118.1</u> 467.8	<u>18183.5</u> 846.6	<u>17336.9</u>		<u>17117.7</u> 144.1
$(0,2^2,0)$	<u>19383.2</u> ^{a,b} 750.6	810.1 751.1	<u>18573.1</u> ^c 750.0	311.3 750.0	<u>18261.8</u>				<u>17261.8</u> 750.8
$(0,4^0,0)$	<u>20133.8</u> ^a 134.4	809.6 133.9	<u>19324.2</u> 134.5	312.4 134.5	<u>19011.8</u> 467.4	<u>18544.4</u> 442.9	<u>18101.5</u> 975.4	<u>19076.9</u> 846.3	<u>18230.6</u> 18012.6
$(0,4^2,0)$	<u>20268.2</u> ^a 12.8	810.1 13.0	<u>19458.1</u> 13.1	311.8 13.0	<u>19146.3</u> 467.5	<u>18678.8</u> 442.8	<u>18236.0</u> 976.2	<u>19212.2</u> 846.5	<u>18365.3</u>
$(1,2^0,0)^d$	<u>20281.0</u> ^a 92.8	809.9 92.6	<u>19471.1</u> 93.1	311.7 92.2	<u>19159.4</u> 467.6	<u>18691.8</u> 442.2	<u>18249.6</u> 974.8	<u>19224.4</u> 846.3	<u>18378.1</u> 284.7
$(2,0^0,0)^d$	<u>20573.8</u> ^a	810.1	<u>19563.7</u> ^b	311.2	<u>19252.5</u>	468.5	<u>18734.0</u>	441.7	<u>18342.3</u>
							<u>974.6</u>	<u>19316.9</u>	<u>846.7</u>
								<u>18470.2</u>	<u>18251.8</u> ^b

a. Assignments made by Johns (1).

b. Assignments made by Snowden (2).

c. Assignments based on conventional emission or absorption spectra.

d. These quantum numbers have been interchanged in this work, refer to text for further discussion. The transition indicated in () is tentative.

TABLE 7

Deslandres Table of Band Heads for ${}^2\Pi_{1/2}-{}^2\Pi_{1/2}$ Transitions in the $\tilde{A}{}^2\Pi_u-\tilde{X}{}^2\Pi_g$ System of ${}^{11}\text{BO}_2$. All values in cm^{-1}

$(v_1, v_2^f, v_3)^a$ $(v_1, v_2^f, v_3)^b$	$(0, 0^0, 0)$	$(0, 2^0, 0)$	$(0, 2^2, 0)$	$(0, 4^0, 0)$	$(0, 4^2, 0)$	$(1, 0^0, 0)$	$(1, 2^0, 0)$	$(1, 2^2, 0)$	$(2, 0^0, 0)$
$(0, 0^0, 0)$	<u>18273.5</u> ^{a,b}	939.4	<u>17334.1</u>	263.1	<u>17597.2</u> ^b	<u>17197.6</u> ^{a,b}			<u>16118.8</u> ^{a,b}
	925.4	925.8		925.6		924.7			
$(0, 2^0, 0)$	<u>19198.9</u> ^{a,b}	939.0	<u>18259.9</u>	262.9	<u>18522.8</u>	1181.8	<u>17341.0</u>	401.7	<u>17742.7</u>
	80.0	79.7		80.2		80.2			
$(0, 2^2, 0)$	<u>19118.9</u> ^{a,b}	938.7	<u>18180.2</u>	262.4	<u>18442.6</u> ^{a,b}				<u>(17343.7)</u> ^d
	981.7	980.9		982.1		981.9			
$(0, 4^0, 0)$	<u>20100.6</u> ^a	939.5	<u>19161.1</u>	263.6	<u>19424.7</u>	1182.1	<u>18242.6</u>	401.8	<u>18644.4</u>
	96.1	96.9		96.3		95.7			<u>18056.1</u>
$(0, 4^2, 0)$	<u>20004.5</u> ^a	940.3	<u>19064.2</u> ^c	264.2	<u>19328.4</u>	1181.5	<u>18146.9</u>	400.9	<u>18547.8</u>
									<u>(18229.0)</u> ^d

a. Assignments made by Johns (1).

b. Assignments made by Snowden (2).

c. Assignments based on conventional emission or absorption spectra.

d. These transitions are tentative.

bands have been observed, very few have presented major ambiguities in the vibrational analysis. Nevertheless, the presence of these few features, together with the fact that the labelling of vibronic levels cannot be determined unambiguously from combination differences alone, make it desirable to use other factors in the vibrational analysis. Where applicable, these factors, which will be given shortly, were used in filling out Deslandres Table 6 and 7. These tables demonstrate clearly that the indicated vibrational levels in the ground and excited states have been determined with considerable cross-checking.

Before presenting the factors used in the vibrational analysis it is important to identify the types of overlapping features which may occur using the techniques described in this work. These features can be categorized as follows:

- (A) Excitation of overlapping rotational structure in the P or R branches of bands in the spectrum of BO_2 which form a head higher in energy than the one directly excited.* This is due to the fact that band heads of BO_2 are degraded towards the red. Fluorescence resulting from this type of overlapping feature was the one most frequently observed throughout this work. Excitation of overlapping rotational lines in the P branch is often a more serious problem since fluorescence in a band head may then result.
- (B) Excitation of other band heads of BO_2 directly overlapping the laser frequency. This usually gives rise to band heads

*For facility of discussion the band directly excited will henceforth be termed "the band of prime interest", and refers to those band heads listed in Table 4.

in fluorescence, and can be the most serious of all the overlapping features. One example of this has already been shown in Fig. 12 in which the $R_2 \ 02^0_0 \ 2\Pi - 00^0_0 \ 2\Pi$ band head of $^{10}\text{BO}_2$ is in resonance with the laser.

(C) Excitation of other species produced in the discharge.

Species most likely to be present in the excitation region are those of oxygen, nitrogen, chlorine, and oxides of boron, nitrogen and chlorine. Of these, only a few have band heads which closely coincide with the excitation wavelengths listed in Table 4, similar to type (B) overlapping, or may have rotational structure off the head coinciding with these wavelengths, similar to type (A) features. The most notable cases include the 0-3 band of N_2^+ in the first negative system at $5228.3 \text{ \AA}$, an NO band in the β system at $4892.1 \text{ \AA}$ and the 4-1 band of O_2^+ in the first negative system at $4998 \text{ \AA}$. A stringent limitation on the number of such possible interferences requires that transitions coincide with excitation frequencies originate from low-lying electronic and vibrational states so that an appreciable absorption can occur. The N_2^+ and O_2^+ bands indicated above can in all likelihood be ruled out as interfering species since they originate from, respectively, high vibrational and excited electronic states. The NO band can likewise be eliminated as a possible interference since double-headed features would be observed, contrary to the observations made in this work. Since the assignments made

in this work have been determined with considerable cross-checking for the most part, as will be seen shortly, errors in the vibrational analysis associated with the above, or for that matter, any other interferences can be eliminated quite convincingly. In the few cases where cross-checking data is presently not available, relatively close agreement between observed and calculated energies suggests that this source of error is unlikely. In any event future fluorescence experiments can provide the necessary data. Throughout the remainder of this dissertation therefore, overlapping bands will only refer to bands associated with BO_2 .

The recognition of fluorescence resulting from these overlapping features will be discussed in the vibrational analysis given in the next few pages. All the factors used in this analysis are included in the following list:

- 1) Selective band head excitation
- 2) Deslandres Table fit using combination relations
- 3) Calculated Fermi perturbed transition frequencies and energy level positions (term value approach)
- 4) Intensities of band heads
- 5) The separation between rotational lines in the R branch and corresponding lines in the P branch, $\Delta_2 F'_v(J)$ values
- 6) Previously determined ground state energy levels assigned in the resonance fluorescence study by Russell et al. (6)

The first two factors, which have been discussed previously, were given relatively strong weight in the vibrational analysis. In cases where vibronic levels in the ground state were observed in fluorescence from three or more different excited states, the symmetry of the combining levels could be assigned or confirmed, as the case may be, with a high degree of certainty. Using this approach the presence of overlapping bands could also be detected. Specifically, when ground state energy levels observed by laser excitation of a particular band head were not observed when different band heads of the same symmetry were excited, the presence of an overlapping band in the first excitation region was immediately suspected. To obtain additional evidence, high resolution emission and absorption spectra were examined for $^{10}\text{BO}_2$ and $^{11}\text{BO}_2$ in the excitation regions in question. Overlapping features of $^{10}\text{BO}_2$ (type A and/or B) could in most cases be recognized by examining $^{10}\text{BO}_2$ -enriched spectra. Unfortunately, since most of the band heads of prime interest in this work were those of $^{11}\text{BO}_2$ (refer to Table 4) the overlapping features due to $^{11}\text{BO}_2$ were more difficult to detect.

The approach given above was extremely useful in the analysis of fluorescence spectra resulting from excitation of the $R_1 \ 04^2_0 \ 2\Pi - 00^0_0 \ 2\Pi$ band head of $^{11}\text{BO}_2$ at $20\ 268.2 \text{ cm}^{-1}$. In addition to fluorescence associated with band heads involving confirmed $\Pi_{3/2}$ ground states, this excitation also resulted in the observation of band heads at $18\ 064.3 \text{ cm}^{-1}$ and $19\ 170.8 \text{ cm}^{-1}$. These features correspond to ground

state term values* of 2203.9 cm^{-1} and 1097.4 cm^{-1} , respectively. The former term value was initially considered as a possibility for the $12^2_0 \Pi_{3/2}$ ground state level; however, once the following observations were made it soon became obvious that the above transitions were the result of overlapping features: Firstly, transitions associated with the term value at 2203.9 cm^{-1} were no longer observed when the $R_1 12^0_0 {}^2\Pi - 00^0_0 {}^2\Pi$ (at $20\ 281.0 \text{ cm}^{-1}$) and the $R_1 20^0_0 {}^2\Pi - 00^0_0 {}^2\Pi$ (at $20\ 373.8 \text{ cm}^{-1}$) band heads of $^{11}\text{BO}_2$ were excited; transitions associated with the term value at 1097.4 cm^{-1} were also not observed by excitation at $20\ 281.0 \text{ cm}^{-1}$.** Secondly, a band head of moderate intensity overlapping the $R_1 04^2_0 {}^2\Pi - 00^0_0 {}^2\Pi$ band head was observed at $20\ 267.5 \text{ cm}^{-1}$ in the absorption spectrum of $^{10}\text{BO}_2$, in agreement with the observations made by Dymek (3). Unfortunately, no assignment has yet been given for this band. Since the transitions at $18\ 064.3 \text{ cm}^{-1}$ and $19\ 170.8 \text{ cm}^{-1}$ were observed to be moderately intense in fluorescence, additional overlapping features due to $^{11}\text{BO}_2$ were also considered, as will be seen later in this chapter. Fluorescence from other overlapping features observed throughout this work were recognized in much the same manner.

Calculated Fermi perturbed energy level positions (term values) and transition frequency calculations were both considered important factors in the vibrational analysis. Although it might first appear that these factors are entirely equivalent, since term values are used

* Ground state term values were determined by subtracting the appropriate observation frequency from the excitation frequency.

** No observation of this term value was attempted when the $R_1 20^0_0 {}^2\Pi - 00^0_0 {}^2\Pi$ band head was excited.

in the calculation of transition frequencies, they were utilized differently in the present analysis. Vibronic term values were calculated with a computer program written by Bryson (18) using Hougen's Fermi resonance treatment (15) discussed at length in Section IV.I. Input constants given by Johns (1) for the $\tilde{A}^2\Pi_u$ state and by Russell et al. (5,6) for the $\tilde{X}^2\Pi_g$ state of $^{11}\text{BO}_2$ were used in these calculations. Calculated transition frequencies were obtained by substituting the vibronic terms into Expression (29) along with a value for the term $T'_e - T''_e$ calculated from the following:

$$T'_e - T''_e = G''(00^0_0) - G'(00^0_0) + \nu_0[00^0_0 \ ^2\Pi - 00^0_0 \ ^2\Pi] . \quad (42)$$

Since the rotational terms $F'_v(J) - F''_v(J)$ in these expressions were set to zero, the transition frequencies calculated were actually those of the band origin (ν_0). Band head frequencies are expected to occur up to 5 cm^{-1} higher in energy. This slight error in $T'_e - T''_e$ does not affect the determination of vibrational energy terms even though variations in this quantity from band to band would.

The quality of fit obtained for calculated transition frequencies, i.e., the magnitude of the difference between the observed and calculated frequencies, is largely dependent upon the molecular constants used for the $\tilde{A}^2\Pi_u$ and $\tilde{X}^2\Pi_g$ states. While ground state constants are more extensive and have been determined with greater certainty than those in the first excited state, no unique set of constants, particularly the anharmonicity constants, adequately fitted all levels. Because of the large multiplying terms, anharmonicity constants although usually small, become very important in the determination of high-lying vibronic levels, as may be seen in Expression (5). Consequently, deviations

between observed and calculated term values which arise in both states are simultaneously introduced into transition frequency calculations. Deviations as large as 60 cm^{-1} in these calculations were not uncommon; they occurred where the term value deviations in both electronic states were of the same sign ($\approx 20 \text{ cm}^{-1}$ for the $\tilde{X}^2\Pi_g$ state and $\approx 40 \text{ cm}^{-1}$ for the $\tilde{A}^2\Pi_u$ state). In view of these considerations, transition frequency calculations were only used as a preliminary factor in establishing the quantum numbers (v_1, v_2^l, v_3) of $^2\Pi$ vibronic levels in the (100-020) and (200-120-040) Fermi polyads in both states. The term value approach in which vibronic levels in the $\tilde{A}^2\Pi_u$ and $\tilde{X}^2\Pi_g$ states were treated independently, was considered a great deal more important in this regard. Comparison between observed and calculated vibronic term values of the same symmetry, established by factors one and two, served as a means of determining quantum numbers. Transition frequency calculations, on the other hand, were considered more useful in determining the possible quantum numbers of band heads resulting from overlapping features. Because other factors not yet presented were used in this approach, this discussion will be deferred until later in this section.

Using the term value approach for ground state vibronic levels in the (100-020) Fermi polyad of $^{11}\text{B}_2\text{O}_2$ and the input constants given by Russell et al. (5) listed in Table 8, the agreement between observed and calculated energies relative to a zero center of gravity was very close to that obtained by Dymek (3) using similar input constants. The largest difference between observed and calculated energies was 4.3 cm^{-1} and the overall fit resulted in a standard deviation of 2.7 cm^{-1} for all six differences. A similar fit for these levels has been reported by

Table 8
Vibrational Constants of $^{11}\text{BO}_2$. All values in cm^{-1} .

		$\tilde{X} \text{ } ^2\Pi_g \text{ State}$			
Russell et al. (5)	Russell et al (6)	Johns (1)		Snowden (2)	
$\nu_1 = 1058$	$\omega_1 = 1071.0$	$\nu_1 = 1070$		$\nu_1 = 1056$	
$\nu_2 = 448$	$\omega_2 = 447.4$	$\nu_2 = 464$		$\nu_2 = 454$	
$\nu_3 = -$	$\omega_3 = 1336.1$	$1/2(2\nu_3) = 1322$		$1/2(2\nu_3) = 1321.7$	
$A = -150$	$A_0 = -150.1$	$A = 150.1$		$A = -150.1$	
$\epsilon\omega_2 = -87$	$\epsilon_0\omega_2 = -86.4$	$\epsilon\omega_2 = -92.1$		$\epsilon\omega_2 = -105.3$	
$x_{11} = -4.0$	$x_{11} = -3.87$				
$x_{12} = -8.5$	$x_{12} = -0.13$				
$x_{22} = -1.2$	$x_{22} = 1.03$				
$W_1 = 24.3$	$W_1 = 31.43$				
$W_2 = -0.6$	$W_2 = 3.07$				
	$x_{13} = -22.39$				
	$x_{23} = -3.26$				
	$g_{ll} = -2.13$				
		$\tilde{A} \text{ } ^2\Pi_u \text{ State}$			
		Johns (1)			
	$\omega_1 = 994$	$W_1 = 23.75$	^b		
	$\omega_2 = 502$	$W_2 = 4.65$	^b		
	$1/2(2\nu_3) = 2357$	$\nu_1 = 994$			
	$A = -101.3$	$2\nu_1 = 1986$			
	$\epsilon\omega_2 = -13.1$	$\nu_1 + 2\nu_2 = 2007$			
	$x_{11} = 0$	$2\nu_2 = 947$			
	$x_{12} \approx 16$	$4\nu_2 = 1831$			
	$x_{22} \approx -7$	$2\nu_3 = 4714$			

a. An estimated value.

b. From Hougen (15).

Russell et al. (6) for the ground state, and by both Hougen (15) and Dymek (3) for the $\tilde{A} \ ^2\Pi_u$ state using some of the constants given by Johns (1). Although the vibrational assignments for these levels in both the $\tilde{A}$ and $\tilde{X}$ states were in agreement in all studies, only in the present study have the assignments been confirmed by laser-excited fluorescence.

In view of the success in predicting the relative positions of levels in the (100-020) polyad, the term value approach was given considerable weight in establishing the quantum numbers for the levels in the (200-120-040) Fermi polyads in both the $\tilde{A}$ and $\tilde{X}$ states of $^{11}\text{BO}_2$. Since as previously indicated, a unique set of vibrational constants have not at this time been obtained, the approach used by Dymek (3) was adopted in the analysis of these levels. In this procedure the term value program previously described, was modified to allow the parameters Δ and Δ' to vary while the other constants, ϵ , ω_2 , W_1 , W_2 , A and $g_{\ell\ell}$ remained fixed. These parameters represent the difference between the centers of gravity of the unperturbed 200 and 040 levels and the 120 and 040 levels respectively, as indicated in Figures 24 and 25 as well as in Expressions (43) and (44). The term values obtained for the $\Pi_{1/2}$ and $\Pi_{3/2}$ levels were independently converted to relative values with respect to a center of gravity arbitrarily set at zero. This procedure in effect allows the optimum relative positions of the energy levels in the (200-120-040) polyad to be calculated without explicitly using anharmonicity constants; these constants are contained in the parameters Δ and Δ' as shown in the following relations derived from Expression (5):

$$\Delta = G(200) - G(040) = 2\omega_1 - 4\omega_2 + 6x_{11} + x_{13} - 24x_{22} - 2x_{23} \quad (43)$$

$$\Delta' = G(120) - G(040) = \omega_1 - 2\omega_2 + 2x_{11} + 2x_{12} + (1/2)x_{13} - 16x_{22} - x_{23} \quad (44)$$

$$\Delta = G(100) - G(020) = \omega_1 - 2\omega_2 + 2x_{11} + (1/2)x_{13} - 8x_{22} - x_{23} \quad (45)$$

Ground state energy levels in the $^2\Pi$ (200-120-040) polyad observed by laser-excited fluorescence were converted to zero-centered values for both the $\Pi_{1/2}$ and $\Pi_{3/2}$ levels. The quality of fit, measured as the standard deviation of the differences between observed and calculated energies for the ten levels in this polyad, varied with the parameters Δ and Δ' . As shown in Fig. 14, a plot of the standard deviation as a function of Δ' for specific values of Δ indicates that the observed energies obtained fit the calculated energies most closely for values of Δ and Δ' around 330 cm^{-1} and 165 cm^{-1} , respectively. The largest* difference between observed and calculated ground state energies in this case was -20.3 cm^{-1} while the standard deviation for all ten differences was 11.2 cm^{-1} . These values for Δ and Δ' are fairly close to values calculated using the initial ground state constants given by Russell et al. (5), $\Delta = 328.8 \text{ cm}^{-1}$ and $\Delta' = 156.2 \text{ cm}^{-1}$. In this regard, it is important to note that these same initial ground state constants resulted in a calculated value of Δ equal to 166.4 cm^{-1} for levels in the $\tilde{X}^2\Pi$ (100-020) polyad of $^{11}\text{B}^{18}\text{O}_2$; this value closely matched an optimum value of 160 cm^{-1} determined by Dymek (3). This consistency between fits in the two polyads further justifies the use of the optimum Δ and Δ' values in the analysis of the $\tilde{X}^2\Pi$ (200-120-040) polyad as well as the initial ground state constants given by Russell et al. (5).

*After a misassignment involving the $12^2_0 \Pi_{3/2}$ ground state level was corrected.

Figure 14

Standard deviation of the differences between observed and calculated energies for the ten levels in the $\tilde{X}^2\Pi$ (200-120-040) polyad of $^{11}\text{BO}_2$ as a function of the parameters Δ and Δ' .

Figure 14

The quality of fit obtained for these levels using input constants from the more recent publication by Russell et al. (6) was by far inferior. This was indicated in part by differences between observed and calculated term values as large as 34.1 cm^{-1} and in part by a standard deviation of 20.1 cm^{-1} for all ten differences. The parameters Δ and Δ' in this case were calculated to have values of 288.6 cm^{-1} and 143.8 cm^{-1} respectively.

The relative positions of the unperturbed ground state energy levels in the ${}^2\Pi$ (200-120-040) polyad of ${}^{11}\text{BO}_2$ are diagrammed in Fig. 15 along with the corresponding Fermi resonance shifts. The energies of the levels with and without Fermi interactions, indicated by dashed lines, were calculated using the optimum values of Δ and Δ' in conjunction with values for ω_2 , $\epsilon\omega_2$, A , W_1 , and W_2 given by Russell et al. (5). The perturbed levels were assigned quantum numbers (v_1, v_2^ℓ, v_3) by correlating the observed levels with the appropriate unperturbed levels. In all cases the magnitude and direction of the Fermi resonance "shifts" indicated in Fig. 15 are consistent with these assignments. Thus for example, the "displacements" indicated for levels assigned as the $04^2 0 \Pi_{3/2}$ and $12^0 0 \Pi_{3/2}$ are consistent with the assignments for all other $\Pi_{3/2}$ levels. The fact that these two levels are "shifted" towards one another, strongly indicates interacting levels with different values of ℓ , in accordance with Expressions (40) and (41) with $W_1 > W_2$, and the presence of strong repulsions from levels above (the $12^2 0 \Pi_{3/2}$ level) and below (the $04^0 0 \Pi_{3/2}$ level) with the appropriate ℓ values. Moreover, the direction of the Fermi resonance shifts for these two levels coupled with the fact that the spacing between the

Figure 15
Fermi resonance "shifts" associated with the
levels in the $\tilde{X}^2\Pi$ (200-120-040) polyad of $^{11}\text{B}^{16}\text{O}_2$

GROUND STATE (200-120-040) FERMI POLYAD

Figure 15

Table 9

$\tilde{X}^2\Pi_g$ (200-120-040) Fermi Polyad Levels of $^{11}\text{BO}_2$
All Values in cm^{-1}

Calculated Using Constants Given by Russell et al. (5).

$$\begin{aligned} W_1 &= 24.3 & W_2 &= -0.60 & A &= -150.0 \\ \Delta &= 330.0 & \Delta' &= 165.0 & \omega_2 &= 447.4^a \\ \epsilon_o \omega_2^b &= -86.4 & \epsilon_{\ell\ell} &= 0.0 \end{aligned}$$

Level	P	Calculated Unperturbed	Calculated Perturbed	Observed	Observed -Calculated
20^0_0	1/2	264.0	296.7	296.9	0.2
12^0_0	1/2	157.1	177.9	187.0	9.1
12^2_0	1/2	-120.0	-86.8	-82.4	4.4
04^0_0	1/2	67.9	19.5	0.0	-19.5
04^2_0	1/2	-368.9	-407.3	-401.4	5.9
20^0_0	3/2	145.0	156.0	154.9	-1.1
12^2_0	3/2	193.2	241.2	220.9	-20.3
12^0_0	3/2	-96.7	-73.2	-63.7	9.5
04^2_0	3/2	104.4	63.9	65.1	1.2
04^0_0	3/2	346.0	-387.8	-377.3	10.5

The standard deviation for all ten values of (observed-calculated) is 11.2 cm^{-1} .

a. Taken from Ref. (6).

b. $\epsilon \omega_2 = \epsilon_o \omega_2 + 0.32 v_1 + 0.27 v_2$ taken from Ref. (6).

unperturbed $04^0_0 \Pi_{3/2}$ and $12^0_0 \Pi_{3/2}$ levels (249.3 cm^{-1}) is larger than the spacing between the $04^2_0 \Pi_{3/2}$ and $12^0_0 \Pi_{3/2}$ levels (201.1 cm^{-1}) gives further evidence that the two lowest $\Pi_{3/2}$ levels have equivalent l values. As indicated, similar "displacements" occur for the $\Pi_{1/2}$ levels as well.

The importance of the consistency between the Fermi resonance "shifts" and the vibrational quantum numbers was clearly demonstrated in the analysis of the $12^2_0 \Pi_{3/2}$ level, initially assigned to the energy level at 119 cm^{-1} (2060.4 cm^{-1} above the $00^0_0 \Pi_{3/2}$ level of $^{11}\text{B}_2\text{O}_2$) indicated in Fig. 15. However, since this requires the $12^2_0 \Pi_{3/2}$ level to be "displaced" downward, placing it within 30 cm^{-1} of the $04^2_0 \Pi_{3/2}$ level, this assignment was considered questionable. Additional evidence established that this assignment was incorrect: namely, an extremely large difference of 147.6 cm^{-1} between the observed and calculated energies, and an abnormally low value of 136.4 cm^{-1} for the separation between the $12^2_0 \Pi_{3/2}$ and $12^2_0 \Pi_{1/2}$ levels ($R_1 - R_2$ separation). By comparison, a corresponding separation of 290.7 cm^{-1} was observed for the 12^0_0 levels, which is very close to a calculated* value of 284.0 cm^{-1} . This misassignment of the $12^2_0 \Pi_{3/2}$ ground state level will be discussed in more detail in the latter part of this section. The new assignment for this level indicated in Fig. 15 is consistent with the three factors given above, but is considered tentative since it has only been observed through a single transition, the $R_1 \ 12^0_0 \ ^2\Pi - 12^2_0 \ ^2\Pi$. In connection with this, the assignment for the

The calculated $R_1 - R_2$ separation is given by the term A^ which is obtained by subtracting Expression (11) from (10).

ground state $12^2_0 \Pi_{1/2}$ level is also considered tentative since sufficient cross-checking is not yet available. The calculated and observed energies for the levels indicated in Fig. 15 are tabulated in Table 9.

Unlike the ground state, the assignment of quantum numbers associated with observed energy levels in the (200-120-040) polyad in the first excited state of BO_2 is still open to question. As indicated in Table 8, the Renner parameter for this state is much smaller than that of the ground state, and therefore the separation between the unperturbed energy levels is also much smaller. Because of this, and the fact that the Fermi parameters W_1 and W_2 are of the same order of magnitude in both electronic states, the shifts associated with Fermi resonance are much more pronounced in the first excited state. To complicate matters, the spacing between the unperturbed energy levels is such that the relative ordering changes in the process of optimizing the parameters Δ and Δ' . In particular, the 20^0_0 levels shift below the 12^0_0 levels as Δ' becomes greater than Δ . In the ground state this situation is avoided since Δ is always much greater than Δ' . This interchanging also occurs for other levels in the excited state.

These difficulties in assigning quantum numbers to levels in the $\tilde{A}^2\Pi$ (200-120-040) polyad required the use of the fourth factor in the vibrational analysis, band head intensities. Because of the Renner-Teller effect the quantum number ℓ is no longer a strictly "good" quantum number in accord with Hougen's definition (50). Nevertheless, the selection rule $\Delta\ell = 0$ is only partially relaxed so that observed transitions in which $\Delta\ell = 2$ were found to be considerably less intense than those in which $\Delta\ell = 0$. These observations were used to further confirm

the assignment of transitions involving levels in the ${}^2\Pi$ (100-020) polyad in both states as well as in the $\tilde{X} {}^2\Pi$ (200-120-040) polyad. These assignments were then used in conjunction with observed band head intensities, in absorption (1) and in fluorescence indicated in Figures 16 through 20, to establish the relative ordering of levels in the $\tilde{A} {}^2\Pi$ (200-120-040) polyad. Qualitative estimates of the observed intensities are given by the symbols VW, W, M, S and VS to indicate very weak, weak, medium, strong or very strong. The relative positions of vibronic levels in the $\tilde{A}$ state consistent with the observed intensities are indicated in Fig. 21. The dashed lines represent energy levels determined by Johns (1) which have not been observed in this work. In all cases the transition assignments involving $\Pi_{3/2}$ levels are consistent with those for the corresponding $\Pi_{1/2}$ levels. In addition, the considerations discussed in Section IV.H concerning transition intensities are consistent with the observations presented in these figures. The abnormally strong intensity for the R_1 $12^0_0 {}^2\Pi - 04^2_0 {}^2\Pi$ transition indicated in Fig. 18 can be explained by the fact that the $12^0_0 \Pi_{3/2}$ level in the $\tilde{A} {}^2\Pi_u$ state acquires some $\ell = 2$ character while the $04^2_0 \Pi_{3/2}$ level in the ground state acquires some $\ell = 0$ character due to Fermi resonance.

Having established a relative order of vibronic levels in the $\tilde{A} {}^2\Pi$ (200-120-040) polyad which is consistent with experimental observations, the process of determining the optimum values for the parameters Δ and Δ' was initiated. Examination of previous results for the ${}^2\Pi$ (100-020) and (200-120-040) polyads in the ground state reveal that

Figures 16-18

Observed Intensities for $\Pi_{3/2} - \Pi_{3/2}$ Transitions
in the $\tilde{A}-\tilde{X}$ System of $^{11}\text{BO}_2$. The energy spacings
are arbitrary.

Figure 16

Figure 17

Figure 18

Figures 19 and 20

Observed Intensities for $\Pi_{1/2} - \Pi_{1/2}$ Transitions
in the $\tilde{A}-\tilde{X}$ System of $^{11}\text{B}\text{O}_2$. The energy spacings
are arbitrary.

Figure 19

Figure 20

Figure 21

The Relative Positions of the Vibronic Levels in
the $\tilde{A}^2\Pi$ (200-120-040) Polyad. The energy
spacings are arbitrary.

Figure 21

the optimum values are related by the following approximations, as can be seen by examining Expressions (43)-(45):

$$\Delta' (200-120-040) \approx \Delta (100-020)$$

$$\Delta (200-120-040) \approx 2\Delta' (200-120-040) .$$

These relations are only approximations because the anharmonicity constants x_{11} , x_{12} and x_{22} are nonzero. Values of 74 and 37 cm^{-1} for Δ and Δ' , respectively, were used initially in the calculations involving the $\tilde{A}^2\Pi (200-120-040)$ polyad. These initial estimates were based upon the above approximations and an optimum value of Δ equal to 36.7 cm^{-1} for the $\tilde{A}^2\Pi (100-020)$ polyad determined by Hougen (15) and Dymek (3). Values for Δ and Δ' equal to 40 and 10 cm^{-1} , respectively, resulted in very good agreement between observed and calculated energies as indicated in Fig. 22. A slight improvement was obtained with Δ and Δ' equal to 30 and -5 cm^{-1} , which correspond to an interchange of the Fermi unperturbed 12^0_0 and $04^0_0 \Pi_{1/2}$ levels and the 12^2_0 and $04^2_0 \Pi_{3/2}$ levels. We have chosen not to adopt this last set of parameters in the analysis based upon assignments for the corresponding unperturbed levels in $^{10}\text{BO}_2$ (3), the magnitude of the Fermi resonance "shifts" and the experimental intensity observations. The relative unperturbed order for all the levels in the $\tilde{A}^2\Pi (200-120-040)$ polyad are diagrammed in Fig. 23 using the former set of values. It should be noted, however, that the relative order for the unperturbed pairs of interchanging levels indicated above is not firmly established since the unperturbed levels, using either set of Δ and Δ' values, are extremely close in energy (refer to Table 10 and Fig. 25), and therefore are severely mixed by Fermi resonance.

Figure 22
Standard Deviation of the Differences Between
Observed and Calculated Energies for the Ten
Levels in the $\tilde{A}^2\Pi$ (200-120-040) Polyad of
 $^{11}\text{BO}_2$ as a Function of the Parameters Δ and Δ' .

Figure 22

The next task at hand was to assign quantum numbers associated with observed levels by correlations with the appropriate unperturbed levels. Here again a problem arises in the analysis; there appears to be some ambiguity as to the appropriate correlations, unlike the ground state. In particular, the perturbed levels which appear to correlate with the $04^0 0 \Pi_{1/2}$ and $04^2 0 \Pi_{3/2}$ unperturbed levels, indicated by light dashed lines in Fig. 23, result in a relative order that is inconsistent with the observed order given in Fig. 21 and with the expected Fermi resonance "shifts". Correlations which are consistent with these observations and "shifts" are indicated in Fig. 23 by heavy dashed lines. In order to test the feasibility of these correlations, the term value program was further modified so that Fermi resonance could be gradually "turned-on" by incrementing the Fermi parameters W_1 and W_2 while the parameters Δ and Δ' were fixed at their values indicated above. Using this approach the relative positions of the calculated perturbed levels were monitored as Fermi resonance was artificially increased. Once the interaction parameters attained moderate values, $W_1 = 10 \text{ cm}^{-1}$ and W_2 ranging from 0 to 5 cm^{-1} , it became very clear that these correlations adequately describe the Fermi resonance "shifts" in the $\tilde{A}^2\Pi$ (200-120-040) polyad. The question which naturally arises at this point is whether or not a set of Δ and Δ' values exist such that unperturbed levels are correlated to perturbed levels in an order consistent with experimental observations without requiring levels to cross. Values for Δ greater than 120 cm^{-1} and Δ' greater than 120 cm^{-1} satisfy these conditions, but result in unreasonably large standard deviations as indicated in Fig. 22.

Figure 23

Fermi Resonance "Shifts" Associated with the
Levels in the $\tilde{A}^2\Pi$ (200-120-040) Polyad of $^{11}\text{B}^{16}\text{O}_2$.

Figure 23

In the calculation of term values by optimization of the parameters Δ and Δ' , it is important that the observed levels are known with a high degree of certainty to belong to the polyad being fit. In the case of the observed $\Pi_{3/2}$ levels indicated in Fig. 23, four out of the five levels were confirmed as belonging to the $\tilde{A}^2\Pi$ (200-120-040) polyad by factors one and two in the vibrational analysis. The fifth level, the $12^2_0 \Pi_{3/2}$ level, could only be confirmed tentatively since one transition to a ground state level of known vibronic symmetry, the $02^2_0 \Pi_{3/2}$ level, was observed. Unfortunately, since the 04^0_0 and 04^2_0 levels were the only $\Pi_{1/2}$ levels in the $\tilde{A}^2\Pi$ (200-120-040) polyad excited in this work, the assignments given by Johns (1) for the remaining three had to be adopted without confirmation in a similar manner. A misassignment of the vibronic symmetry for any of these three levels would result in an error in the observed $\Pi_{1/2}$ center of gravity and hence in all the relative observed $\Pi_{1/2}$ levels. This might first appear to reduce the credibility of the method by which the quantum numbers for the 04^0_0 and $04^2_0 \Pi_{1/2}$ levels were assigned. However, since the optimum values of the parameters Δ and Δ' determined for the $\tilde{A}^2\Pi$ (200-120-040) polyad as a whole also resulted in the best fit for both the $\Pi_{3/2}$ (standard deviation = 6.1 cm^{-1}) and $\Pi_{1/2}$ (standard deviation = 9.3 cm^{-1}) levels independently, any error in the observed center of gravity for the $\Pi_{1/2}$ levels must necessarily be small. Another way of arriving at the same conclusion is that the difference between the observed centers of gravity for the two components relative to a common level, the $00^0_0 \Pi_{3/2}$ level in this case, is 18.1 cm^{-1} which is very close to a corresponding difference of 20.3 cm^{-1} for the

calculated centers of gravity relative to a common level, the 040 level. The values for the calculated and observed energies along with the corresponding vibrational assignments for levels in the $\tilde{A}^2\Pi$ (200-120-040) polyad of $^{11}\text{BO}_2$ are presented in Table 10.

In the $^2\Pi$ (200-120-040) polyad in the ground state the appropriate differences between the observed and calculated centers of gravity are 39.6 cm^{-1} and 29.8 cm^{-1} respectively, thus possibly indicating a small error. The most likely source of this error, if present, is the observed term value assigned to the $12^2_0\ \Pi_{3/2}$ level at 2187.6 cm^{-1} above the $00^0_0\ \Pi_{3/2}$ level. As indicated previously, this term value was considered tentative since it is based on a single transition. Assigning the $12^2_0\ \Pi_{3/2}$ level to higher energies, as suggested by the difference between the observed and calculated energies in Table 9, would result in a better coincidence between the observed and calculated centers of gravity. Clearly, unambiguous determinations of the $12^2_0\ \Pi_{3/2}$ level in the ground state, and for that matter all the 12^2_0 levels, by additional experiments would be desirable.

For comparisons with other studies, it is convenient to convert the calculated $^2\Pi$ term values in the ground and first excited states to term values relative to the lowest vibronic level. The term values indicated in Tables 9 and 10 were converted to values relative to the $00^0_0\ ^2\Pi_{3/2}$ level in the $\tilde{X}$ and $\tilde{A}$ states by equating the appropriate calculated and observed centers of gravity. These results are presented in Tables 11 and 12 (Method I) for levels in the $^2\Pi$ (100-020) and (200-120-040) polyads of BO_2 . Also presented in these tables are observed energies from the present study as well as from the studies indicated,

Table 10
 $\tilde{A}^2\Pi_u$ (200-120-040) Fermi Polyad Levels of $^{11}\text{B}^{16}\text{O}_2$
 All Values in cm^{-1}

Calculated Using the Constants Given by Johns (1).

$$\begin{array}{lll} W_1 = 23.8 & W_2 = 4.7 & A = -101.3 \\ \Delta = 40 & \Delta' = 10 & \omega_2 = 502 \\ \epsilon\omega_2 = -13.1 & E_{\ell\ell} = 0.0 & \end{array}$$

Level	P	Calculated Unperturbed	Calculated Perturbed	Observed	Observed -Calculated
20^0_0	1/2	68.7	159.3	163.7	4.4
12^0_0	1/2	41.7	61.2	63.7	2.5
12^2_0	1/2	-65.9	9.3	4.1	-5.2
04^0_0	1/2	37.6	-54.7	-67.8	-13.1
04^2_0	1/2	-82.0	-175.0	-163.9	11.1
20^0_0	3/2	-12.4	77.7	75.1	-2.6
12^2_0	3/2	62.2	139.3	138.0	1.3
12^0_0	3/2	-45.9	-12.6	-17.7	-5.1
04^2_0	3/2	58.2	-29.0	-30.5	-1.5
04^0_0	3/2	-62.1	-175.5	-164.9	10.6

The standard deviation for all ten values of (observed-calculated) is 7.4 cm^{-1} .

and energies calculated by Bryson (18) using molecular constants from Russell et al. (6) (Method II). As indicated, the observations made in this work are in close agreement with the ground state energies calculated by Russell et al. (6) which have previously been observed by Snowden (2) from conventional emission spectra, and the observations of Dymek (3) from absorption spectra of $^{10}\text{BO}_2$. The energies for the 02^0_0 $\Pi_{1/2}$ and 02^2_0 $\Pi_{3/2}$ ground state vibronic levels of $^{11}\text{BO}_2$ observed in this work are consistent with the reassignments reported by Russell et al. (6). Furthermore, the observed vibronic levels in the $\tilde{\text{A}}^2\Pi$ (200-120-040) polyad provide additional confirmation* of the assignments given by Johns (1) with the exception that the 12^0_0 and 20^0_0 levels of both components have been interchanged. However, since the corresponding Fermi unperturbed levels are within 35 cm^{-1} , these levels appear to be strongly mixed by Fermi interactions; the labels therefore merely indicate the expected predominant character.

The fifth factor in the vibrational analysis, the separation between rotational lines in the R branch and corresponding lines in the P branch, designated $\Delta_2\tilde{F}_v''(J)$ for short, occasionally provided additional information for establishing the vibronic levels observed in fluorescence. Transitions from a common upper state to a manifold of vibronic levels in the ground state (a fluorescence series) generally produce nearly constant $\Delta_2\tilde{F}_v''(J)$ values. This approach can be demonstrated most clearly by considering two different bands, which will be designated bands a and b. In this example, the lower state combination

* Although further work is required to unambiguously resolve the relative order of certain levels in this polyad.

TABLE 11
Ground State $^2\Pi$ Vibronic Levels of BO_2 .^a All values in cm^{-1} .

v_1, v_2^l, v_3	P	OBSERVED ENERGY THIS WORK	CALCULATED ENERGY THIS WORK		ENERGY FROM OTHER SOURCES		
			METHOD I	METHOD II ^b	REF. (1)	REF. (2)	REF. (6)
00 ⁰ 0	3/2	0.0	0.0	0.0	0.0	0.0	0.0
00 ⁰ 0	1/2	148.6 ^c	148.6 ^c	148.6 ^c	148.6	148.6	149.8
02 ⁰ 0	3/2	810.0	809.4	807.7	----	810.5	810.1
02 ² 0	1/2	824.7	821.9	816.6	824.9	824.6	826.4
10 ⁰ 0	3/2	1056.5	1059.4	1063.1	1056.4	1056.3	1056.6
02 ⁰ 0	1/2	1088.0	1092.3	1091.1	----	1114.8	1099.2
02 ² 0	3/2	1121.6	1119.2	1113.1	----	1157.4	1121.9
10 ⁰ 0	1/2	1224.9	1223.5	1224.7	1224.6	1224.5	1225.7
04 ⁰ 0	3/2	1589.5	1579.0	1566.4	----	----	----
04 ² 0	1/2	1605.0	1599.1	1570.2	----	----	----
12 ⁰ 0	3/2	1903.1	1893.6	1918.8	----	2091.5	----
12 ² 0	1/2	(1924.0) ^e	1919.6	1935.7	----	----	----
04 ⁰ 0	1/2	2006.4	2025.9	2030.4	----	2175.3	----
04 ² 0	3/2	2031.9	2030.7	2033.9	----	----	----
12 ² 0	3/2	(2187.6) ^e	2208.0	2215.2	----	----	----
20 ⁰ 0	3/2	2121.7	2122.8	2131.9	2121.8	2121.8	2121.7
12 ⁰ 0	1/2	2193.5	2184.3	2183.5	----	----	----
20 ⁰ 0	1/2	----	2303.1	2299.6	2303.3	2303.3	2304.3
00 ⁰ 0	3/2	0.0		0.0	0.0	0.0 ^d	0.0
02 ⁰ 0	3/2	835.5		841.1	----	835.5 ^d	----
10 ⁰ 0	3/2	1061.5		1062.9	1062.1	1062.1 ^d	1062.8
02 ² 0	3/2	1156.0		1151.1	----	1155.0 ^d	----

a. All tabulated entries are for $^{11}\text{BO}_2$ except for the last four which are $^{10}\text{BO}_2$.

b. Calculated in Ref. (18)

c. Taken from Ref. (1)

d. Observed in Ref. (3)

e. The assignment for these energies are tentative, refer to text for further discussion of these levels.

Table 12
 $^2\Pi$ Vibronic Levels in the First Excited State of BO_2 .^a
 All values in cm^{-1} .

v_1, v_2, v_3	P	Observed Energy This Work	Calculated Energy This Work		Energy From Other Sources	
			Method I	Method II ^b	Ref (1)	Ref. (2)
00^0_0	3/2	0.0	0.0	0.0	0.0	0.0
00^0_0	1/2	101.3 ^c	101.3 ^c	101.3 ^c	101.3	101.3
02^0_0	3/2	919.2	917.9	914.5	919.2	919.2
02^2_0	1/2	946.7	945.8	943.3	946.7	946.7
10^0_0	3/2	- - - -	1024.4	1021.4	1020.7	1020.8
02^0_0	1/2	1026.7	1028.4	1026.4	1026.7	1026.6
02^2_0	3/2	1062.6	1060.1	1055.2	1062.6	1062.5
10^0_0	1/2	- - - -	1123.9	1122.7	1124.7	1124.8
04^0_0	3/2	1813.2	1802.6	1772.6	1813.2	- - -
04^2_0	1/2	1832.3	1821.2	1784.6	1832.3	- - -
04^0_0	1/2	1928.4	1941.5	1910.7	1928.4	- - -
04^2_0	3/2	1947.6	1949.1	1921.9	1947.6	- - -
$(12^0_0)^d$	3/2	1960.4	1965.5	1942.1	1960.4	- - -
12^2_0	1/2	- - - -	2005.5	2006.0	2000.3	2000.4
$(20^0_0)^d$	3/2	2053.2	2055.8	2065.2	2053.2	2052.0
$(12^0_0)^e$	1/2	- - - -	2057.4	2050.9	2059.9	2061.2
12^2_0	3/2	(2116.1) ^f	2117.4	2116.3	2116.1	2116.0
$(20^0_0)^e$	1/2	- - - -	2155.5	2167.1	2159.9	2158.8
00^0_0	3/2	0.0	- - -	0.0	0.0	
12^0_0	3/2	(2095.2) ^f	- - -	2090.4	2095.2 ^g	

a. All tabulated entries are for $^{11}\text{BO}_2$ except for the last two which are $^{10}\text{BO}_2$.

b. Calculated in Ref. (18).

c. Taken from Ref. (1).

d. These quantum numbers have been interchanged in this work.

e. These quantum numbers have been interchanged in this work.

f. The assignment for these energies are tentative.

g. Observed in Ref. (3).

differences for both bands can be described by Expression (38) in the following manner:

$$\Delta_2 F_v''(J_a) = 4B_a''(J_a + 1/2)$$

$$\Delta_2 F_b''(J_b) = 4B_b''(J_b + 1/2) .$$

If the second expression is subtracted from the first, the following useful relation is obtained:

$$\Delta_2 F_a''(J_a) - \Delta_2 F_b''(J_b) = 4B_a''(J_a + 1/2) - 4B_b''(J_b + 1/2) . \quad (46)$$

Thus, for transitions involving the same rotational levels in both electronic states, as is the case in a fluorescence series, the change in the $\Delta_2 F''(J)$ value in going from band a to b merely depends upon the difference in the lower state B'' values as follows:

$$\Delta_2 F_a''(J) - \Delta_2 F_b''(J) = 4(J + 1/2)(B_a'' - B_b'') .$$

By referring to the last column in Table 5, it can readily be seen that $\Delta_2 F_v''(J)$ values in BO_2 (in this case $R_2(18) - P_2(20)$) are relatively insensitive to moderate changes in B_v'' . This accounts for the fact that the $\Delta_2 F_v''(J)$ spacings are nearly constant for bands in a fluorescence series. In contrast, fluorescence from overlapping features, particularly type A, generally involves rotational levels which are different from those considered above, and therefore generate $\Delta_2 F_v''(J)$ values which differ considerably from values in the fluorescence series.

This approach would be particularly useful in the analysis of fluorescence spectra generated by single-line excitation; for in this case two well resolved rotational lines (three if a Q branch is observed)

are observed for each vibronic band in a fluorescence series. The $\Delta_2 F''_v(J)$ values therefore can be determined with a degree of accuracy limited by the resolution of the spectrometer. In fluorescence studies of BO_2 using single-line excitation, Russell et al. (6) determined $\Delta_2 F''_v(J)$ values that were typically less than 0.1 cm^{-1} from the calculated values. This technique aided them in the identification of vibronic levels in ambiguous cases. In the present fluorescence study precise $\Delta_2 F''_v(J)$ values could not be obtained because individual rotational lines in the P and R branches could not be selectively excited with our current laser system. Instead $\Delta_2 F''_v(J)$ values were approximated by the separation between the maximum intensity portion of the P and R branches, designated P-R separation. Such measurements were useful in the analysis of fluorescence spectra generated by excitation of the $R_1 \text{ } 04^0_0 \text{ } ^2\Pi - 00^0_0 \text{ } ^2\Pi$ band head. This excitation resulted in the observation of a series of band heads involving the $04^0_0 \text{ } \Pi_{3/2}$ level in the upper state and previously confirmed $\Pi_{3/2}$ levels in the ground state. A band head at $18\,102.4 \text{ cm}^{-1}$ was also observed which corresponds to a ground state term value of 2031.4 cm^{-1} heretofore unobserved. A P-R separation of 23.5 cm^{-1} for this band closely matched a value of 23.1 cm^{-1} measured for the $R_1 \text{ } 04^0_0 \text{ } ^2\Pi - 04^0_0 \text{ } ^2\Pi$ band, and thus suggested that this band belonged to the $04^0_0 \text{ } \Pi_{3/2}$ fluorescence series. This was subsequently confirmed by excitation of three other $\Pi_{3/2}$ band heads which in all cases resulted in the observation of a ground state term value near 2031 cm^{-1} . This energy level was assigned to the $04^2_0 \text{ } \Pi_{3/2}$ vibronic level by comparison with calculated $\Pi_{3/2}$ term values in the ground state in the manner previously described. Measurements of other

P-R separations were useful in the analysis of the $02^0 0 \Pi_{3/2}$ fluorescence series, and helped to further confirm the presence of an overlapping band(s) in the $R_1 04^2 0 \Pi - 00^0 0 \Pi$ excitation region. Analysis of these and other overlapping features will now be discussed in more detail.

Fermi perturbed transition frequency calculations, when used in conjunction with band head intensities and previously determined ground state energy levels assigned by resonance fluorescence (6), were useful in making reasonable assignments for band heads observed in fluorescence resulting from overlapping features. In this approach, because of the uncertainty of the preliminary calculated transition frequencies, it became necessary to consider all calculated transitions within a range of $\pm 60 \text{ cm}^{-1}$ of an observed band head. The large number of such transitions were often reduced to a few possibilities by the following considerations:

- 1) All unassigned calculated transitions within $\pm 60 \text{ cm}^{-1}$ of the excitation frequency were listed. In some cases this list could immediately be reduced by determining precise transition frequencies from observed term values.
- 2) This list was reduced by considering only transitions for $^{10}\text{BO}_2$ and $^{11}\text{BO}_2$ which involved the $01^1 0 \Sigma$ and Δ vibronic levels in the ground state. Vibronic levels in the ground state higher in energy are apparently not sufficiently populated to allow an appreciable absorption of the laser beam required for the observation of fluorescence signals. The failure to detect fluorescence in the $R_2 02^2 0 \Pi - 00^0 0 \Pi$

band head of $^{11}\text{BO}_2$ by excitation of the $R_2\ 02^2_0\ 2\Pi - 02^2_0\ 2\Pi$ band head supports this reasoning. This result however, must be supported by additional experimentation.

- 3) All calculated transitions were considered that were within $\pm 60\ \text{cm}^{-1}$ of a band head observed in fluorescence and which had absorptions satisfying the previous two criteria.
- 4) The transitions from overlapping features observed in fluorescence were converted to frequencies relative to the laser and compared to those which have been measured for Σ ground state energy levels by resonance fluorescence (6). If coincidences were observed, particularly from two or more such frequencies, this was taken as strong evidence for the presence of Σ transitions. The above list was therefore modified accordingly.
- 5) This list often could be reduced further when transitions in fluorescence were observed with moderate to strong intensities. In this case only transitions in which $\Delta l = 0$ and possibly $\Delta l = 2$ were considered.

The analysis of fluorescence spectra obtained by excitation of the $R_1\ 04^2_0\ 2\Pi - 00^0_0\ 2\Pi$ band head at $20\ 268.2\ \text{cm}^{-1}$ was one case which demonstrated the full utility of this approach. Previously it was established that band heads observed in fluorescence at $18\ 064.3\ \text{cm}^{-1}$ and $19\ 170.8\ \text{cm}^{-1}$ resulting from this excitation were associated with overlapping features. A set of reasonable assignments for each of these transitions as well as a third at $18\ 226.9\ \text{cm}^{-1}$ were listed using the procedures given above. Ground state assignments for these transitions

involving the $21^1_0 \Sigma^{(-)}$, $11^1_0 \Sigma^{(-)}$ and $13^1_0 \Sigma^{(-)}$ levels of $^{11}\text{BO}_2$ were established by examining the term values (relative to the $01^1_0 \Sigma^{(+)}$ level of $^{11}\text{BO}_2$) and assignments given by Russell et al. (6), as illustrated below. The above list could therefore be reduced to transitions of $^{11}\text{BO}_2$ which involved a Σ upper state, the $13^1_0 \Sigma^{(-)}$ or the $21^1_0 \Sigma^{(+)}$ level, in particular. Of these two, the former appears to be more reasonable since it does not require a change in the $(\pm)$ symmetry, consistent with the transition intensities observed.

<u>Band Heads Observed in This Study in cm^{-1}</u>		<u>Term Values and Assignments Reported by Russell et al. (6-2) in cm^{-1}</u>	
<u>$\bar{\nu}(\text{vac})$</u>	<u>Term Value Relative to $01^1_0 \Sigma^{(+)}$ Level</u>	<u>Term Value Relative to $01^1_0 \Sigma^{(+)}$ Level</u>	<u>Ground State Assignments</u>
19 170.8	1329.5	1331.4	$11^1_0 \Sigma^{(-)}$
18 226.9	2273.4	2272.2	$13^1_0 \Sigma^{(-)}$
18 064.3	2436.0	2435.7	$21^1_0 \Sigma^{(-)}$

Excitation at $20\,268.2\text{ cm}^{-1}$ resulted in the observation of transitions originating from the $R_1\,12^0_0\,\Pi_{3/2}$ level, 12.8 cm^{-1} higher in energy, in addition to the normal fluorescence from overlapping features. Initially it was believed that these observations were solely the result of type A overlapping by the 12^0_0 band. However, similar results were obtained by excitation of the $R_1\,12^0_0\,^2\Pi - 00^0_0\,^2\Pi$ band head at $20\,281.0\text{ cm}^{-1}$: transitions from the $04^2_0\,\Pi_{3/2}$ level as well as from the $12^0_0\,\Pi_{3/2}$ level were observed, as shown in Table 13. This "vibrational relaxation" seems to be associated with Fermi resonance since the corresponding Fermi unperturbed levels are reasonably close in energy and are characterized by nonzero Fermi mixing parameters. It is important

Table 13

Band Heads Observed in Fluorescence Resulting
From Excitation of the R_1 $04^2_0 \ 2\Pi - 00^0_0 \ 2\Pi$ and
the R_1 $12^0_0 \ 2\Pi - 00^0_0 \ 2\Pi$ Band Heads of $^{11}\text{BO}_2$.

Excitation of R_1 $04^2_0 \ 2\Pi - 00^0_0 \ 2\Pi$ (20 268.2 cm^{-1})			Excitation of R_1 $12^0_0 \ 2\Pi - 00^0_0 \ 2\Pi$ (20 281.0 cm^{-1})		
$\bar{\nu}(\text{vac}), \text{cm}^{-1}$	Intensity	Assignment	$\bar{\nu}(\text{vac}), \text{cm}^{-1}$	Intensity	Assignment
Observed			Observed		
20 279.5	M	$R_1 \ 12^0_0 \ 2\Pi - 00^0_0 \ 2\Pi$	19 469 ^a	S	$R_1 \ 12^0_0 \ 2\Pi - 02^0_0 \ 2\Pi$
19 457.9	M	$R_1 \ 04^2_0 \ 2\Pi - 02^0_0 \ 2\Pi$	19 224 ^a	S	$R_1 \ 12^0_0 \ 2\Pi - 10^0_0 \ 2\Pi$
19 170.8	S	$R_2 \ 13^1_0 \ \Sigma^{(-)} - 11^1_0 \ \Sigma^{(-)}$	19 208.1	W	$R_1 \ 04^2_0 \ 2\Pi - 10^0_0 \ 2\Pi$ ^b
19 158.4	M	$R_1 \ 12^0_0 \ 2\Pi - 02^2_0 \ 2\Pi$	19 142.7	M	$R_1 \ 04^2_0 \ 2\Pi - 02^2_0 \ 2\Pi$ ^b
19 146.3	M	$R_1 \ 04^2_0 \ 2\Pi - 02^2_0 \ 2\Pi$	18 689.4	M	$R_1 \ 12^0_0 \ 2\Pi - 04^0_0 \ 2\Pi$
18 675.0	W	$R_1 \ 04^2_0 \ 2\Pi - 04^0_0 \ 2\Pi$	18 372.9	W	$R_1 \ 12^0_0 \ 2\Pi - 12^0_0 \ 2\Pi$ ^b
18 226.9	W	$R_2 \ 13^1_0 \ \Sigma^{(-)} - 13^1_0 \ \Sigma^{(-)}$	18 359.3	W	$R_1 \ 04^2_0 \ 2\Pi - 12^0_0 \ 2\Pi$ ^b
18 205.6	M	- - - - -	18 251.7	S	- - - - -
18 064.3	M	$R_2 \ 13^1_0 \ \Sigma^{(-)} - 21^1_0 \ \Sigma^{(-)}$	18 246.6	M	$R_1 \ 12^0_0 \ 2\Pi - 04^2_0 \ 2\Pi$
			18 237.1	M	$R_1 \ 04^2_0 \ 2\Pi - 04^2_0 \ 2\Pi$ ^b
			18 222.8	W	- - - - -
			18 209.7	M	- - - - -
			18 206.2	M	- - - - -
			18 093.4	W	$R_1 \ 12^0_0 \ 2\Pi - 12^0_0 \ 2\Pi$

a. Approximate frequencies.

b. Observation of rotational lines off the band head.

to note that during the course of this work this was the only occasion in which "vibrational relaxation" was observed. These features, together with the presence of overlapping bands in both excitation regions, resulted in fluorescence spectra that were considerably more complex than usual. This presented problems in determining the upper state associated with certain transitions, specifically transitions which were thought to involve the $12^2_0 \Pi_{3/2}$ level in the ground state. The transition at $18\,205.6\text{ cm}^{-1}$ listed in the left-hand column of Table 13 was misassigned as the $R_1\ 04^2_0\ ^2\Pi - 12^2_0\ ^2\Pi$ transition in this very manner. This transition resulted in a ground state term value of 2062.6 cm^{-1} which closely matched a term value of 2058.2 cm^{-1} associated with a transition ($18\,222.8\text{ cm}^{-1}$) obtained by excitation at $20\,281.0\text{ cm}^{-1}$. To make matters worse, this excitation also resulted in the observation of transitions at $18\,209.7\text{ cm}^{-1}$ and $18\,206.2\text{ cm}^{-1}$, which with the incorrect assumption that they involved the $04^2_0 \Pi_{3/2}$ upper state, corresponded to ground state term values of 2058.5 cm^{-1} and 2062.0 cm^{-1} . This apparent recurrence of the same ground state term value by excitation in two different regions was taken as positive evidence for the presence of a $\Pi_{3/2}$ level at $\approx 2060\text{ cm}^{-1}$ above the $00^0_0 \Pi_{3/2}$ level, namely the $12^2_0 \Pi_{3/2}$ level. However, as was shown previously, this assignment has since been proven to be incorrect.

Data for $^2\Delta_{5/2}$ vibronic levels in the ground state observed by excitation of the $R_1\ 11^1_0\ ^2\Delta_{5/2} - 01^1_0\ ^2\Delta_{5/2}$ band head of $^{11}\text{B}_2\text{O}_2$ are presented in Table 14. A complete list of all band heads assigned in this work is presented in Table 15 using all applicable factors in the vibrational analysis. The uncertainty in measuring band head

frequencies listed in this table is generally estimated around $\pm 2 \text{ cm}^{-1}$ unless otherwise indicated. As in Table 6 and 7, the entries listed in Table 15, where possible, are refined band head data obtained by comparison of fluorescence spectra with emission and absorption spectra. Qualitative intensity estimates defined previously are listed for band heads observed in fluorescence. Bands without such designations are those involved in laser excitation. The quantum numbers involving both components of the 20^0_0 and $12^0_0 \tilde{A}^2\Pi$ levels in all transitions have been interchanged from the assignments given by Johns (1). Band heads reported by Johns (1), Snowden (2), Dymek (3) and Russell et al. (6) along with any qualifying remarks are also given in this table. In all tables presented in this work tentative assignments are presented in parentheses.

Table 14
Ground State $^2\Delta$ Vibronic Levels of $^{11}\text{BO}_2$. All values in cm^{-1} .

v_1, v_2, v_3	P	Observed Energy This Work	Calculated Energy ^a This Work	Energy From Other Sources		
				Ref. (1)	Ref. (2)	Ref. (6)
01 ¹ 0	5/2	0.0	0.0	0.0	0.0	0.0
03 ¹ 0	5/2	779.9	778.9	- - -	780.2	779.8
11 ¹ 0	5/2	1064.0	1066.9	1064.1	1073.3	1064.3
03 ³ 0	5/2	1154.4	1146.5	- - -	- - -	1155.1
21 ¹ 0	5/2	2048.6	2065.4	- - -	2124.6	- - -
05 ³ 0	5/2	(2126.0) ^b	2111.2	- - -	- - -	- - -

a. Calculated in Ref. (18) using molecular constants from Ref. (6).

b. The assignment for this energy is tentative, refer to text for discussion.

Table 15

List of Band Heads Assigned in this Work in the
 $\tilde{A}-\tilde{X}$ Transition of $^{11}\text{BO}_2$ Unless Otherwise Indicated

$\bar{\nu}(\text{vac}), \text{cm}^{-1}$	Transition	Fluorescence Intensity	Band Heads Reported in Other Studies
20 437.5	$R_1 12^0_0 \ 2\Pi - 00^0_0 \ 2\Pi$ ⁱ		c
20 436.7	$(R_1 12^2_0 \ 2\Pi - 00^0_0 \ 2\Pi)$ ^h		a
20 373.8	$R_1 20^0_0 \ 2\Pi - 00^0_0 \ 2\Pi$		a
20 281.0	$R_1 12^0_0 \ 2\Pi - 00^0_0 \ 2\Pi$		a
20 268.2	$R_1 04^2_0 \ 2\Pi - 00^0_0 \ 2\Pi$		a
20 268.2	$(R_2 13^1_0 \ \Sigma^{(-)} - 01^1_0 \ \Sigma^{(-)})$ ^h		
20 133.8	$R_1 04^0_0 \ 2\Pi - 00^0_0 \ 2\Pi$		a
20 100.6	$R_2 04^0_0 \ 2\Pi - 00^0_0 \ 2\Pi$		a
20 004.5	$R_2 04^2_0 \ 2\Pi - 00^0_0 \ 2\Pi$		a
19 602.4	$R_1 12^0_0 \ 2\Pi - 02^0_0 \ 2\Pi$ ⁱ	W	c
19 563.7	$R_1 20^0_0 \ 2\Pi - 02^0_0 \ 2\Pi$	S	b
19 471.1	$R_1 12^0_0 \ 2\Pi - 02^0_0 \ 2\Pi$	S	
19 458.1	$R_1 04^2_0 \ 2\Pi - 02^0_0 \ 2\Pi$	M	
19 430.8	$R_1 11^1_0 \ 2\Delta - 01^1_0 \ 2\Delta$ ⁱ		c
19 424.7	$R_2 04^0_0 \ 2\Pi - 02^2_0 \ 2\Pi$	W	
19 388.4	$R_1 11^1_0 \ 2\Delta - 01^1_0 \ 2\Delta$		a
19 383.2	$R_1 02^2_0 \ 2\Pi - 00^0_0 \ 2\Pi$		a,b
19 374.1	$R_1 12^0_0 \ 2\Pi - 10^0_0 \ 2\Pi$ ⁱ	M	c
19 328.4	$R_2 04^2_0 \ 2\Pi - 02^2_0 \ 2\Pi$	M	
19 324.2	$R_1 04^0_0 \ 2\Pi - 02^0_0 \ 2\Pi$	VS	

Table 15 (Continued)

$\bar{\nu}(\text{vac}), \text{cm}^{-1}$	Transition	Fluorescence Intensity	Band Heads Reported in Other Studies
19 316.9	$R_1 \ 20^0_0 \ 2\Pi - 10^0_0 \ 2\Pi$	S	
19 311.5	$(R_1 \ 12^2_0 \ 2\Pi - 02^2_0 \ 2\Pi)^h$	W	
19 281.4	$R_1 \ 12^0_0 \ 2\Pi - 02^2_0 \ 2\Pi^i$	W	
19 252.5	$R_1 \ 20^0_0 \ 2\Pi - 02^2_0 \ 2\Pi$	S	
19 239.8	$R_1 \ 02^0_0 \ 2\Pi - 00^0_0 \ 2\Pi$		a,b
19 224.4	$R_1 \ 12^0_0 \ 2\Pi - 10^0_0 \ 2\Pi$	S	
19 212.2	$R_1 \ 04^2_0 \ 2\Pi - 10^0_0 \ 2\Pi$	W	
19 198.9	$R_2 \ 02^0_0 \ 2\Pi - 00^0_0 \ 2\Pi$		a,b
19 170.8	$(R_2 \ 13^1_0 \ \Sigma^{(-)} - 11^1_0 \ \Sigma^{(-)})^h$	S	
19 161.1	$R_2 \ 04^0_0 \ 2\Pi - 02^0_0 \ 2\Pi$	S	
19 159.4	$R_1 \ 12^0_0 \ 2\Pi - 02^2_0 \ 2\Pi$	M	
19 146.3	$R_1 \ 04^2_0 \ 2\Pi - 02^2_0 \ 2\Pi$	M	
19 118.9	$R_2 \ 02^2_0 \ 2\Pi - 00^0_0 \ 2\Pi$		a,b
19 076.9	$R_1 \ 04^0_0 \ 2\Pi - 10^0_0 \ 2\Pi$	W	
19 064.2 ^f	$R_2 \ 04^2_0 \ 2\Pi - 02^0_0 \ 2\Pi$		
19 011.8	$R_1 \ 04^0_0 \ 2\Pi - 02^2_0 \ 2\Pi$	W	
18 784.0	$R_1 \ 20^0_0 \ 2\Pi - 04^0_0 \ 2\Pi$	S	
18 691.8	$R_1 \ 12^0_0 \ 2\Pi - 04^0_0 \ 2\Pi$	M	
18 678.8	$R_1 \ 04^2_0 \ 2\Pi - 04^0_0 \ 2\Pi$	W	
18 644.4	$R_2 \ 04^0_0 \ 2\Pi - 04^2_0 \ 2\Pi$	W	
18 636.2 ^g	$R_1 \ 11^1_0 \ \Sigma^{(+)} - 03^1_0 \ \Sigma^{(+)}$	W	d
18 608.5	$R_1 \ 11^1_0 \ 2\Delta - 03^1_0 \ 2\Delta$	S	

Table 15 (Continued)

$\bar{\nu}(\text{vac}), \text{cm}^{-1}$	Transition	Fluorescence Intensity	Band Heads Reported in Other Studies
18 573.1 ^f	R ₁ 02 ² 0 2 Π - 02 ⁰ 0 2 Π		
18 547.8	R ₂ 04 ² 0 2 Π - 04 ² 0 2 Π	M	
18 544.4	R ₁ 04 ⁰ 0 2 Π - 04 ⁰ 0 2 Π	VS	
18 522.8	R ₂ 02 ⁰ 0 2 Π - 02 ² 0 2 Π	M	
18 470.2	R ₁ 20 ⁰ 0 2 Π - 12 ⁰ 0 2 Π	M	
18 442.6	R ₂ 02 ² 0 2 Π - 02 ² 0 2 Π	M	a,b
18 430.0	R ₁ 02 ⁰ 0 2 Π - 02 ⁰ 0 2 Π	VS	b
18 385.6	R ₂ 01 ¹ 0 $\Sigma^{(+)}$ - 01 ¹ 0 $\Sigma^{(+)}$		a,b
18 378.1	R ₁ 12 ⁰ 0 2 Π - 12 ⁰ 0 2 Π	W	
18 365.3	R ₁ 04 ² 0 2 Π - 12 ⁰ 0 2 Π	W	
18 342.3	R ₁ 20 ⁰ 0 2 Π - 04 ² 0 2 Π	W	
18 324.4	R ₁ 11 ¹ 0 2 Δ - 11 ¹ 0 2 Δ	S	
18 320.6	R ₁ 00 ⁰ 0 2 Π - 00 ⁰ 0 2 Π		a,b
18 273.5	R ₂ 00 ⁰ 0 2 Π - 00 ⁰ 0 2 Π		a,b
18 261.8	R ₁ 02 ² 0 2 Π - 02 ² 0 2 Π	M	
18 259.9	R ₂ 02 ⁰ 0 2 Π - 02 ⁰ 0 2 Π	VS	
18 251.8	R ₁ 20 ⁰ 0 2 Π - 20 ⁰ 0 2 Π	VW	b
18 249.6	R ₁ 12 ⁰ 0 2 Π - 04 ² 0 2 Π	M	
18 242.6	R ₂ 04 ⁰ 0 2 Π - 04 ⁰ 0 2 Π	S	
18 236.0	R ₁ 04 ² 0 2 Π - 04 ² 0 2 Π	M	
18 234.0 ^e	R ₁ 11 ¹ 0 2 Δ - 03 ³ 0 2 Δ	M	
18 230.6	R ₁ 04 ⁰ 0 2 Π - 12 ⁰ 0 2 Π	W	

Table 15 (Continued)

$\bar{\nu}(\text{vac}), \text{cm}^{-1}$	Transition	Fluorescence Intensity	Band Head Reported in Other Studies
18 229.0	$(R_2 \ 04^2_0 \ 2\Pi - 12^2_0 \ 2\Pi) \ h$	VW	
18 226.9	$(R_2 \ 13^1_0 \ \Sigma^{(-)} - 13^1_0 \ \Sigma^{(-)}) \ h$	W	
18 183.5	$R_1 \ 02^0_0 \ 2\Pi - 10^0_0 \ 2\Pi$	VW	
18 180.2	$R_2 \ 02^2_0 \ 2\Pi - 02^0_0 \ 2\Pi$	W	
18 163.1 ^e	$S_{R_{21}} \ 01^1_0 \ \Sigma^{(+)} - 01^1_0 \ \Sigma^{(-)}$	W	
18 159.1	$R_1 \ 12^0_0 \ 2\Pi - 20^0_0 \ 2\Pi$	W	
18 146.9	$R_2 \ 04^2_0 \ 2\Pi - 04^0_0 \ 2\Pi$	W	
18 122.3	$R_2 \ 02^0_0 \ 2\Pi - 10^0_0 \ 2\Pi$	M	
18 118.1	$R_1 \ 02^0_0 \ 2\Pi - 02^2_0 \ 2\Pi$	M	
18 101.5	$R_1 \ 04^0_0 \ 2\Pi - 04^2_0 \ 2\Pi$	M	
18 093.4	$(R_1 \ 12^0_0 \ 2\Pi - 12^2_0 \ 2\Pi) \ h$	W	
18 064.3	$(R_2 \ 13^1_0 \ \Sigma^{(-)} - 21^1_0 \ \Sigma^{(-)}) \ h$	M	
18 056.1	$R_2 \ 04^0_0 \ 2\Pi - 12^0_0 \ 2\Pi$	W	
18 012.6	$R_1 \ 04^0_0 \ 2\Pi - 20^0_0 \ 2\Pi$	VW	
17 742.7	$R_2 \ 02^0_0 \ 2\Pi - 04^2_0 \ 2\Pi$	M	
17 662.5	$R_2 \ 02^2_0 \ 2\Pi - 04^2_0 \ 2\Pi$	VW	
17 650.3	$R_1 \ 02^0_0 \ 2\Pi - 04^0_0 \ 2\Pi$	S	
17 597.2	$R_2 \ 00^0_0 \ 2\Pi - 02^2_0 \ 2\Pi$	W	b
17 510.5 ^f	$R_1 \ 00^0_0 \ 2\Pi - 02^0_0 \ 2\Pi$		b
17 343.7	$(R_2 \ 02^2_0 \ 2\Pi - 12^2_0 \ 2\Pi) \ h$	W	
17 341.0	$R_2 \ 02^0_0 \ 2\Pi - 04^0_0 \ 2\Pi$	S	
17 339.8	$R_1 \ 11^1_0 \ 2\Delta - 21^1_0 \ 2\Delta$	M	

Table 15 (Continued)

$\bar{\nu}(\text{vac}), \text{cm}^{-1}$	Transition	Fluorescence Intensity	Band Heads Reported in Other Studies
17 336.9	$R_1 \ 02^0_0 \ 2\Pi - 12^0_0 \ 2\Pi$	S	
17 334.1	$R_2 \ 00^0_0 \ 2\Pi - 02^0_0 \ 2\Pi$	M	
17 264.2	$R_1 \ 00^0_0 \ 2\Pi - 10^0_0 \ 2\Pi$	S	a,b
17 262.4 ^e	$(R_1 \ 11^1_0 - 05^3_0 \ 2\Delta) \ ^h$	VW	
17 261.8	$R_1 \ 02^2_0 \ 2\Pi - 20^0_0 \ 2\Pi$	VW	
17 199.3 ^f	$R_1 \ 00^0_0 \ 2\Pi - 02^2_0 \ 2\Pi$		
17 197.6	$R_2 \ 00^0_0 \ 2\Pi - 10^0_0 \ 2\Pi$	S	a,b
17 153.7	$R_2 \ 02^0_0 \ 2\Pi - 12^0_0 \ 2\Pi$	S	
17 117.7	$R_1 \ 02^0_0 \ 2\Pi - 20^0_0 \ 2\Pi$	VW	
16 198.8 ^f	$R_1 \ 00^0_0 \ 2\Pi - 20^0_0 \ 2\Pi$		a,b
16 118.8 ^f	$R_2 \ 00^0_0 \ 2\Pi - 20^0_0 \ 2\Pi$		a,b

a. Assignments made by Johns (1).

b. Assignments made by Snowden (2).

c. Assignments made by Dymek (3).

d. Assignments made by Russell et al. (6)

e. Uncertainty of approximately 4 cm^{-1} in this band head frequency.

f. Transitions observed in conventional emission or absorption spectra.

g. Transition slightly off the band head centered around R_1 (8).

h. Tentative assignment.

i. Transitions of $^{10}\text{B}\text{O}_2$.

C. Molecular Constants

The determination of molecular constants is an important aspect in the vibrational analysis of spectroscopic data. One method of obtaining these constants, which has been discussed in detail by Dymek (3), involves the use of an iterative least-squares fit of the data using a computer program. Unfortunately, this approach resulted in limited success (18). A consistent set of molecular constants for both the $\tilde{X}$ and $\tilde{A}$ states was obtained using an alternative procedure. The calculated centers of gravity for ${}^2\Pi$ levels in the (100-020) and (200-120-040) polyads (relative to the imaginary unperturbed 020 or 040 level) were subtracted from the corresponding observed centers of gravity (relative to the $00^0 0 \Pi_{3/2}$ level) to give the energy of the imaginary 020 and 040 levels (relative to the $00^0 0 \Pi_{3/2}$ level), as shown in Figures 24 and 25. These values were then substituted into the following relations, derived from Expression (5):

$$\begin{aligned}\Delta E_1 &= G(040) - G(00^0 0 \Pi_{3/2}) = 4\omega_2 + 2x_{12} + 24x_{22} + 2x_{23} + (1/2)A_{\text{eff}} \\ \Delta E_2 &= G(020) - G(00^0 0 \Pi_{3/2}) = 2\omega_2 + x_{12} + 8x_{22} + x_{23} + (1/2)A_{\text{eff}}.\end{aligned}$$

Values for the anharmonicity constant x_{22} in both the $\tilde{X}$ and $\tilde{A}$ states were then obtained by subtracting $2\Delta E_2$ from ΔE_1 . Substitution of these values along with the appropriate values of Δ and Δ' into the following relations generated the anharmonicity constants x_{11} and x_{12} :

$$\begin{aligned}\Delta E_3 &= \Delta(200-120-040) - 2\Delta(100-020) = [G(200)-G(040)] - 2[G(100)-G(020)] \\ &= 2x_{11} - 8x_{22}.\end{aligned}\quad (47)$$

$$\begin{aligned}\Delta E_4 &= \Delta'(200-120-040) - \Delta(100-020) = [G(120)-G(040)] - [G(100)-G(020)] \\ &= 2x_{12} - 8x_{22}.\end{aligned}\quad (48)$$

Figure 24

Fermi unperturbed energy levels in the $\tilde{X}^2\Pi$ (100-020) and $^2\Pi$ (200-120-040) polyads of $^{11}\text{BO}_2$. Observed centers of gravity are denoted as OCG.

Figure 25

Fermi unperturbed energy levels in the $\tilde{A}^2\Pi$ (100-020) and $^2\Pi$ (200-120-040) polyads of $^{11}\text{BO}_2$. Observed centers of gravity are denoted as OCG.

Figure 25

Values determined in this manner for the anharmonicity constants x_{11} , x_{12} and x_{22} in the $\tilde{A}$ and $\tilde{X}$ states of BO_2 are indicated in Table 16. In the $\tilde{A}$ state the molecular constants agree reasonably well with values determined by Johns (1). In the ground state an unreasonably large negative value for x_{22} in comparison to that reported by Russell et al. (5,6) was obtained using the approach given above, and as a result generated even larger inconsistencies with Russell et al. for x_{11} and x_{12} . A set of ground state constants consistent with those reported by Russell et al. (5), given in Table 16, was determined by using their value of x_{11} in Expressions (47) and (48). Since the determination of molecular constants using this approach includes uncertainties in the parameters Δ and Δ' , generally estimated around 5 to 10 cm^{-1} , the molecular constants presented in Table 16 should be further refined.

D. Summary and Projected Research

The utility of laser-excited fluorescence in the analysis of complex spectra is well established. However, it is most useful in conjunction with conventional spectroscopic analyses. In this work the utility of this approach has been demonstrated using a tunable dye laser to selectively excite the BO_2 molecule and then using the resulting fluorescence spectra to assist in the assignment of band heads which are also observed in high resolution emission and absorption spectra. Over fifty transitions involving levels in the (100-020) and (200-120-040) $^2\Pi$ Fermi polyads, as well as a limited number of $^2\Delta_{5/2}$ and $^2\Sigma$ levels, in both the $\tilde{A}$ and $\tilde{X}$ states of $^{11}\text{BO}_2$ have been assigned using this approach. Furthermore, numerous assignments given by Johns (1), Russell et al. (6)

Table 16
Molecular Constants Calculated in This Work

$\tilde{X} \ ^2\Pi_g$ State	$\tilde{A} \ ^2\Pi_u$ State
$x_{11} = -3.87 \text{ cm}^{-1} \text{ }^a$	$x_{11} = 0.3 \text{ cm}^{-1}$
$x_{12} = -5.3 \text{ cm}^{-1}$	$x_{12} = 3.6 \text{ cm}^{-1}$
$x_{22} = -1.7 \text{ cm}^{-1}$	$x_{22} = -4.2 \text{ cm}^{-1}$

a. Taken from Ref. (6).

and Dymek (3) have been confirmed in this work. In this process some interesting questions were raised concerning the relative order and the appropriate correlations of levels in the $\tilde{A}$ (200-120-040) polyad.

The introduction of the parameters Δ and Δ' in the calculation of vibronic term values has proven to be an effective approach; this procedure in effect allows the optimum relative positions of the energy levels within each polyad to be determined before relating to the overall fit of vibrational energy levels. Moreover, Hougen's (15) method for calculating Fermi resonance levels has been further supported by application to the $^2\Pi$ (200-120-040) Fermi Polyad in both the $\tilde{A}$ and $\tilde{X}$ states.

Although a complete set of firmly established molecular constants could not be determined in the present study, the anharmonicity constants x_{11} , x_{12} and x_{22} in both the ground and first excited state appear to be in close agreement with those reported in the preliminary fluorescence study by Russell et al. (5) and by Johns (1). The ground state constants presented in Table 16 are consistent with the results obtained in Section VB for levels in the $\tilde{X}^2\Pi$ (100-020) and (200-120-040) polyads in which the quality of fit using these inputs constants was far better than that obtained using constants in a later fluorescence study (6). Clearly, further efforts should be made to refine the molecular constants for both the $\tilde{A}$ and $\tilde{X}$ states using the resonance fluorescence data in the present study, data from future fluorescence experiments as well as from isotopically enriched samples. Extension of the Deslandres tables to include Δ transitions should aid significantly in this effort. In addition, extensive assignments for Δ transitions

could possibly help in the determination of overlapping features in the vibrational analysis of Π transitions.

Future fluorescence experiments should also concentrate on unambiguous determinations of the 12^2O Π term values in both the $\tilde{\text{A}}$ and $\tilde{\text{X}}$ states, and excitation of the three remaining levels in the $\tilde{\text{A}}$ $\Pi_{1/2}$ (200-120-040) polyad not studied in this work. Other important fluorescence experiments to be carried out in the future include the observation of vibrational relaxation (due to Fermi resonance) associated with the 12^2O and 20^0O Π levels in the $\tilde{\text{A}}$ state; mapping out high-lying vibronic levels of $^{10}\text{BO}_2$ using isotopically enriched B, and employing laser excitation with reduced bandwidth. This latter set of experiments is expected to result in more selective pumping of desired transitions, band origin data and precise $\Delta_2 F''(J)$ separations which will be useful in the vibrational analysis. When used in conjunction with previous studies, the experiments proposed above should result in a more complete characterization of the electronic spectrum of BO_2 .

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