# HIGH RESOLUTION SPECTROSCOPY OF THE VANADIUM OXIDE $B^{4} \Pi-X^{4} \Sigma^{-}(0,0)$ BAND <br> By <br> <br> BOB BERNO <br> <br> BOB BERNO <br> B. Sc. (Chemistry) University of Waterloo, 1989 

a thesis submitted in partial fulfillment of the requirements for the degree of Master of Science
in
the Faculty of Graduate Studies
Department of Chemistry

We accept this thesis as conforming to the required standard

The University of British Columbia
December 1992
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#### Abstract

The $B^{4} \Pi-X^{4} \Sigma^{-}(0,0)$ band of VO has been recorded at sub-Doppler resolution by intermodulated fluorescence spectroscopy. Spectral linewidths of 60 MHz were typical; which enabled the hyperfine structure due to the ${ }^{51} \mathrm{~V}$ nucleus ( $I=\frac{7}{2}$ ) to be resolved for most of the observed branches. The hyperfine structure of the $B^{4} \Pi$ state is narrow except where it is heavily perturbed by the $v=2$ level of the $a^{2} \Sigma^{+}$state. The electron configuration of the $a^{2} \Sigma^{+}$state was determined to be $(4 s \sigma)^{1}(3 d \delta)^{2}$ because of the large Fermi contact interaction which arose from an unpaired electron having primarily metal 4 s atomic orbital character.

The transition frequencies were fit to a model which included the rotational, fine and hyperfine structure of the $B^{4} \Pi, X^{4} \Sigma^{-}$and $a^{2} \Sigma^{+}$states. The $B^{4} \Pi / a^{2} \Sigma^{+}$interaction required the inclusion of an effective higher order spin-orbit parameter as well as a new hyperfine parameter, denoted by parameter $e$. The new hyperfine parameter is required to describe the hyperfine interactions between ${ }^{4} \Pi$ and ${ }^{2} \Sigma^{+}$states.

The fit included 3211 data points and gave an r.m.s. error of $0.00038 \mathrm{~cm}^{-1}$.


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## Chapter 1

## Introduction

The nuclei in the neighbourhood of iron in the periodic table are the most stable of all; therefore the elements of the 3d transition series, which surround iron, have very high nuclear stabilities, and are among the most abundant elements in the Universe, not counting hydrogen and helium. The processes that synthesize these elements take place when a comparatively heavy star runs out of its hydrogen "fuel", and explodes as a supernova. Heavy stars of this type live short but brilliant lives, and in their violent death throes generate immense quantities of the transition elements, which are blown out into space. Later generations of stars can condense from interstellar gas clouds that contain such "recycled" material, and are described as "metal-rich" in the jargon of the astrophysicists. Our Sun is a star in this class, as are many of the stars in its immediate vicinity.

The optical spectra of the cooler stars containing recycled supernova material are dominated by band systems of the 3 d transition metal monoxides, for various reasons. First, oxygen is also one of the more abundant elements and, second, the 3 d oxides have particularly high dissociation energies, so that they can survive in the relatively high temperature environments of the stellar atmospheres [1]; most importantly, the oxides have prominent electronic band systems throughout the visible and near infra-red regions of the spectrum.

Much of the astrophysics of cool stars is merely high-temperature laboratory chemistry applied to astronomical objects [1], so that the spectroscopy of the 3 d monoxides is


Figure 1.1: The molecular orbital diagram for VO.
an important topic in this field. Of very considerable importance is VO which, after TiO , is the second most abundant molecule found in the spectra of the cool M-type stars [2]. Bands in the near infra-red region, near $1.06 \mu$, were in fact attributed to VO by Kuiper et al [3], some time before laboratory work by Lagerqvist et al [4] was able to confirm the assignment. These observations have generated a strong interest in the VO molecule which continues to the present day.

The first reasonably detailed theoretical calculations on VO [5] predicted that the ground state is ${ }^{4} \Sigma^{-}$, from the valence electron configuration $(9 \sigma)(1 \delta)^{2}$, with the ${ }^{2} \Delta$ state from the configuration $(9 \sigma)^{2}(1 \delta)$ lying only a very small amount above (see Figure 1.1). The ${ }^{4} \Sigma^{-}$nature of the ground state was later confirmed experimentally from electron spin resonance spectra of VO isolated in an argon matrix [6].

In their early gas-phase studies of the electronic spectrum of VO, Richards and Barrow [7] observed large hyperfine splittings in the ground state. Further investigations of the hyperfine structure led to their discovery of "internal hyperfine perturbations" in the ground state [8]. Internal hyperfine perturbations also occur in the $C^{4} \Sigma^{-}$excited state [9]: Cheung and coworkers [10] obtained sub-Doppler resolution spectra of the $C-X$ transition using the saturation technique known as intermodulated fluorescence spectroscopy, and were able to characterize the perturbations in the $C^{4} \Sigma^{-}$and $X^{4} \Sigma^{-}$ states in detail. More recently the $C^{4} \Sigma^{-}$state has been used as the intermediate in a pulsed field ionization study of VO that led to an accurate determination of its ionization potential [11].

Another strong system of absorption bands is observed in the spectra of cool Mtype stars in the $0.74-0.83 \mu$ region. Although this system had been tentatively assigned to VO [2], it was not conclusively identified as belonging to VO until Keenan and Schroeder [12] were able to obtain emission spectra (from an electric arc containing $\mathrm{V}_{2} \mathrm{O}_{5}$ powder) which matched the astronomical data. This band system is now recognized as being the $B^{4} \Pi-X^{4} \Sigma^{-}$electronic transition of VO.

The present thesis is concerned with the rotational and hyperfine structure of the $(0,0)$ band of the $B^{4} \Pi-X^{4} \Sigma^{-}$transition of VO. The system had been recorded previously in emission at Doppler-limited resolution by Cheung and coworkers [13], and shown to contain many intense branches with varying hyperfine line widths. This variation in the line widths results mostly from the huge hyperfine effects in the ground state, since the upper state turns out to have comparatively narrow hyperfine structure. Rotational assignments could be made for the branches where the hyperfine widths in the upper and lower states happen to cancel and produce comparatively sharp rotational lines, but many of the branches are hyperfine-broadened to the extent that they are not identifiable in the emission spectra. A further complication is that the $B^{4} \Pi$ upper state suffers large


Figure 1.2: Selected electronic states of VO.
rotational perturbations caused by spin-orbit interaction with the ${ }^{2} \Sigma^{+}$state that comes from the same electron configuration as the ground state. Although some of the details of the perturbations could be worked out from the Doppler-limited spectra [13], a full account has required that spectra of the transition be obtained at sub-Doppler resolution. It has not been possible to obtain such spectra until quite recently, because of the lack of a suitably intense tunable laser source in the $0.8 \mu$ region. With the development, in the past three years, of commercial continuous-wave Ti:sapphire ring lasers, the $0.8 \mu$ region has become more easily accessible for high resolution studies. This thesis reports a full sub-Doppler analysis of the $(0,0)$ band of the $B^{4} \Pi-X^{4} \Sigma^{-}$system of VO near $0.8 \mu$, including a detailed treatment of the hyperfine effects, and a very complete account of the rotational perturbations caused by the $a^{2} \Sigma^{+}$state.

## Chapter 2

## Experimental

### 2.1 Introduction

Although VO has been found to be quite stable in the atmospheres of the cooler M-type stars[2], it is not found as a stable diatomic molecule in normal terrestrial environments. Therefore, to carry out a high resolution spectroscopic study, VO had to be produced under non-equilibrium conditions from a stable precursor.

To that end, VO was produced in an electrodeless microwave discharge operating at 2450 MHz through a flowing mixture of $\mathrm{VOCl}_{3}$ and an appropriate carrier gas. Argon was mostly used as the carrier gas, at a total pressure of approximately one torr. Later, when increased sensitivity was needed to record the high $J$ lines at longer wavelengths ( 800 nm ), a higher pressure of carrier gas was necessary to increase the populations of the higher rotational levels. However, the argon emission lines in the region being detected became much more intense at this higher pressure, thus increasing the background noise. As a result there was no improvement in the signal-to-noise ratio. Consequently, the argon was replaced by helium, since there are almost no emission lines of helium in this region. The shorter wavelength helium emission lines from the discharge could be filtered out before reaching the photo-multiplier tube (PMT), so even though the experiment was run at higher pressure than the argon experiments, the background noise was reduced. This improvement in sensitivity came at the cost of reduced resolution because of pressure broadening.

(1) Ar ION PUMP LASER
(2) Ti:SAPPHIRE LASER
(3) $\mathrm{He}-\mathrm{Ne}$ LASER
(4) 50:50 BEAMSPLITTER
(5) MECHANICAL CHOPPER
(6) PHOTODIODE
(7) VACUUM CHAMBER
(8) Photomultiplier tube
(9) LOCK-IN AMPLIFIER
(10) U HOLLOW CATHODE LAMP
(11) CHART RECORDER
(12) $\mu$-VAX COMPUTER

Figure 2.1: Schematic diagram of the experimental apparatus for IMF spectroscopy.

The Doppler linewidth for room temperature VO at around $12500 \mathrm{~cm}^{-1}$ is approximately $600 \mathrm{MHz}\left(0.02 \mathrm{~cm}^{-1}\right)$. The hyperfine splittings arising from the ${ }^{51} \mathrm{~V}$ nucleus (nuclear spin, $I=\frac{7}{2}$ ) and the complexities of the rotational structure lead to considerable blending around the bandheads and at the perturbations, which causes much of the detail to be lost because of blending at Doppler-limited resolution. Consequently, sub-Doppler spectra of VO had to be recorded. These sub-Doppler spectra were recorded using the technique of intermodulated fluorescence (IMF) spectroscopy[15].

A schematic illustration of the experimental set-up is shown in Figure 2.1. A Coherent Inc. Model I-20 continuous wave argon ion laser was used to pump a tunable Ti:sapphire laser (Coherent Inc. Model 899-21) in the region from $12390 \mathrm{~cm}^{-1}$ to $12740 \mathrm{~cm}^{-1}$.

A portion of the beam from the Ti:sapphire laser was split off by a beamsplitter, and was sent to the calibration system which determined the absolute frequency of the light. The calibration system will be discussed in greater detail in the next Section.

The remaining laser light was passed through a $50 / 50$ beamsplitter, producing two equal intensity coherent beams. These beams were oriented so that they passed through the sample cell exactly antiparallel to each other as shown in Figure 2.1. To stop the laser beams from feeding back into the Ti :sapphire laser, an optical diode was inserted just prior to the $50 / 50$ beamsplitter.

Before reaching the sample cell, these two portions of the laser beam passed through a mechanical chopper with three rings of holes punched in it. One ring consisted of 28 holes, the second ring consisted of 36 holes and the third of 64 holes. When one portion of the laser beam $\left(I_{1}\right)$ passes through the first ring of holes, it will be chopped twenty-eight times for every revolution of the chopper. The frequency that the first laser is chopped at is thus:

$$
F_{1}=28 F_{\text {chop }}
$$

where $F_{\text {chop }}$ is the frequency of the chopper in revolutions per second. Similarly, the chopping frequency for the second arm, when passed through the second ring of holes, is

$$
F_{2}=36 F_{\text {chop }}
$$

A HeNe laser beam is passed through the third ring of holes, and is thus chopped at:

$$
\begin{aligned}
F_{\text {ref }} & =64 F_{\text {chop }} \\
& =F_{1}+F_{2}
\end{aligned}
$$

$F_{\text {chop }}$ was typically between 20 to 25 revolutions per second. The laser power in each arm was of the order of 100 mW , dropping to $50 \mathrm{~mW} / \mathrm{arm}$ at longer wavelengths. Ultimately, the drop in laser power at these longer wavelengths coupled with the sharp drop in the quantum efficiency of the photo-multiplier tube (Hamamatsu Model R928) did not permit spectra in the region from $12390 \mathrm{~cm}^{-1}$ to $12450 \mathrm{~cm}^{-1}$ to be recorded using the IMF technique. This spectral region was covered at Doppler limited resolution only. The linewidths of most of the IMF spectra were found to be better than 60 MHz . However, when the increased pressure of helium was needed to improve sensitivity, pressure broadening from the helium carrier gas caused the line width to increase to 100 MHz .

The perturbation of the $B^{4} \Pi$ state by the $a^{2} \Sigma^{+}$state produced extremely complicated spectra at the avoided crossings. Not only are the positions of the lines shifted, but the intensities of the already weak lines are further reduced since some of the intensity is transfered to extra lines arising from the $a^{2} \Sigma^{+}$state. Assignments of these lines near the avoided crossings were made using the technique of wavelength resolved fluorescence (WRF) spectroscopy. This will be described in further detail in Section 2.5.


Figure 2.2: A schematic diagram of the calibration system.

### 2.2 The Calibration System

In the past, laser excitation data were calibrated against a reference fluorescence spectrum of $\mathrm{I}_{2}$ or $\mathrm{Te}_{2}[16]$. With the advent of high resolution techniques such as laser induced fluorescence (LIF) molecular beam experiments and IMF spectroscopy, more accurate methods of calibration became necessary because the characteristic uncertainties in the iodine line positions were larger than the uncertainty in the spectra being calibrated. The spectra of the $B^{4} \Pi-X^{4} \Sigma^{-}(0,0)$ band of VO were calibrated using the system illustrated schematically in Figure 2.2. The key component in this system is the evacuated, temperature and pressure stabilized Fabry-Perot étalon. The cavity length of the étalon is accurately fixed by a piezoelectric driver servolocked to one particular interference fringe of a polarization-stabilized HeNe laser line, so that the relative frequencies of the interference fringes (also referred to as markers) are well known.

The piezoelectric driver mentioned earlier carries one of the confocal mirrors of the 750 MHz étalon. A modulating voltage is applied to the piezo in such a way that when the 632.8 nm line from a stabilized HeNe laser enters the interference cavity, the position of the mirror is locked so that the frequency of the HeNe line is at the maximum of one particular fringe. The free spectral range (FSR) of the cavity is thus invariant to changes in room temperature or atmospheric pressure. When the absolute frequency of one fringe is known, and the order number of the other fringes with respect to that one fringe is known, then the frequency of any marker can be calculated using the expression[16]

$$
\begin{equation*}
\omega=\frac{n \omega_{0}}{n_{0}} \tag{2.1}
\end{equation*}
$$

where $n_{0}$ and $\omega_{0}$ refer to the order number and frequency of the marker whose frequency is known, while $n$ and $\omega$ are the known order number and unknown frequency of the other marker.

Since the frequency of the HeNe line used to lock the étalon is well known, it is possible to use its frequency as the standard. In practice, this poses a problem in regions far from the 632.8 nm HeNe line because the reflectivity of the étalon mirrors, and hence the fringe spacing, shows a slight wavelength dependence. Therefore, a Burleigh model WA-20VIS wavemeter was used to identify the markers by giving their frequencies to $\pm 0.02 \mathrm{~cm}^{-1}$. To obtain highly accurate frequency determinations, opto-galvanic spectra from a uranium:neon hollow cathode lamp were recorded along with the VO spectra. The uranium line positions were taken from the uranium emission atlas[17], and the frequencies of the 750 MHz étalon fringes could thus be determined by a least sqares fit. In the 800 nm region of the spectrum, the FSR of the stabilized étalon was found to be $0.025046 \mathrm{~cm}^{-1}(750.859 \mathrm{MHz})$.

### 2.3 Saturation Spectroscopy

Freshman chemistry textbooks teach students that the absorption of radiation by the sample molecules follows the Beer-Lambert Law:

$$
\begin{equation*}
I_{f}=I_{i} e^{-\varepsilon C l} \tag{2.2}
\end{equation*}
$$

where $I_{f}$ and $I_{i}$ are the final and initial light intensities, $\varepsilon$ is the extinction coefficient ${ }^{1}$, $C$ is the sample concentration in moles per litre and $l$ is the path length in centimeters through the sample cell for the radiation. $\varepsilon$ is a constant of the system, and thus the concentration of the sample molecules in the cell can be calculated from the ratio of the initial and final radiation intensities $\mathrm{I}_{i}$ and $\mathrm{I}_{f}$ respectively as:

$$
C=-\frac{\ln I_{f} / I_{i}}{\varepsilon l}
$$

The extinction coeficient $(\varepsilon)$ has a wavelength dependence defined by the transition energy between the states in question. In accurate spectroscopic studies, $\varepsilon$ is replaced by the absorption coefficient ( $\alpha_{0}$ ), which for a sample experiencing a weak oscillating electric field of frequency $\omega$ and direction $\vec{k}$, such that $\vec{k}$ is parallel to the $z$ axis, can be expressed as[19]

$$
\begin{equation*}
\alpha_{0}(\omega)=\frac{\gamma^{2} \sigma_{0} \Delta N_{0}}{4 \sqrt{\pi} v_{p}} \int_{-\infty}^{\infty} \frac{e^{-\left(v_{2} / v_{p}\right)^{2}} d v_{z}}{\left(\omega-\omega_{0}-k \cdot v_{z}\right)^{2}-(\gamma / 2)^{2}} \tag{2.3}
\end{equation*}
$$

In this equation $v_{p}=\sqrt{2 k_{B} T / m}, \sigma_{0}$ is the absorption cross-section, $\gamma$ is the sum of the radiative and nonradiative decay constants, $\Delta N_{0}$ is the difference in number density between the upper state ( $N_{2}$ ) and the lower state ( $N_{1}$ ) (i. e. $\Delta N_{0}=N_{2}-N_{1}$ ), and $k$ is the magnitude of $\vec{k}$ in the $z$ direction.
: The Beer-Lambert Law works well when the population density of the upper state $\left(N_{2}\right)$ is considerably less the the population density in the lower state $\left(N_{1}\right)$. However,

[^0]if the incident electric field intensity is increased to the point where the lower state is depopulated at an appreciably faster rate than the rate of relaxation from the upper state, then the Beer-Lambert Law breaks down, and the transition is said to be saturated. Under these conditions, $\alpha_{0}$ becomes dependent on the incident electric field intensity.

Saturation is commonly observed when lasers are used as excitation light sources because of the high light intensities typically generated. To illustrate the effects of saturation, consider a sample cell containing molecules with a thermal velocity distribution. When monochromatic laser light with frequency $\omega$ and vector $\vec{k}$ passes through the cell, there will be a depletion of the population density of molecules in the absorbing state at energy $E_{1}$ if their velocity components are defined by:

$$
\begin{equation*}
\omega-\vec{k} \cdot(\vec{v} \pm \Delta \vec{v})=\omega_{12} \pm \delta \omega \tag{2.4}
\end{equation*}
$$

where $\omega_{12}=\left(E_{2}-E_{1}\right) / \hbar$ and $\delta \omega$ is the linewidth of the laser. If $\vec{k}$ is once again chosen to be parallel to the $z$ direction, then Equation 2.4 becomes:

$$
\begin{equation*}
\omega-k \cdot\left(v_{z} \pm \Delta v_{z}\right)=\omega_{12} \pm \delta \omega \tag{2.5}
\end{equation*}
$$

The velocity distributions of molecules in the $E_{1}$ and $E_{2}$ levels resulting from this intense laser light are shown in Figure 2.3. The dip in the $n_{1}\left(v_{z}\right)$ population distribution is known as a Bennett Hole[18]. The spectral width $\gamma_{s}$ of the Bennett hole is related to $\gamma$ (the sum of the radiative and nonradiative decay constants) by

$$
\gamma_{s}=\gamma \sqrt{1+S_{0}}
$$

where $S_{0}$ is the value of the saturation parameter at the transition frequency $\omega_{0}[19]$. At optical wavelengths, $\gamma_{s}$ is much narrower than the Doppler profile. However, this subDoppler depletion in the population distribution of the $E_{1}$ state cannot be observed by simply passing a single saturating laser through the sample cell. Tuning the frequency of


Figure 2.3: Plots of the velocity distributions of the $E_{2}(\mathrm{a})$; and $E_{1}$ (b) levels when an intense laser beam with vector $\vec{k}$ and frequency $\omega$ passes through the sample cell


Figure 2.4: Plots of the saturated $\left(\alpha_{s}(\omega)\right)$ and unsaturated $\left(\alpha_{0}(\omega)\right)$ absorption coefficients as a function of excitation frequency $(\omega)$
the monochromatic laser will simply move the Bennett hole to another part of the velocity distribution such that the observed spectral line would follow the dotted line shown in Figure 2.4. The expression for the absorption coefficient for molecules experiencing a saturating radiation field is given by[19]:

$$
\begin{equation*}
\alpha_{s}(\omega)=\frac{\gamma^{2} \sigma_{0} \triangle N_{0}}{4 \sqrt{\pi} v_{p}} \int_{-\infty}^{\infty} \frac{e^{-\left(v_{z} / v_{p}\right)^{2}} d v_{z}}{\left(\omega-\omega_{0}-k \cdot v_{z}\right)^{2}-\left(\gamma_{s} / 2\right)^{2}} \tag{2.6}
\end{equation*}
$$

This expression closely resembles the expression in the weak field approximation (Equation 2.3). Evaluation of the integral, with the assumption that $\gamma_{s}$ is much less than the Doppler width gives

$$
\begin{equation*}
\alpha_{s}(\omega)=\alpha_{0}(\omega)\left(1+S_{0}\right)^{-1 / 2} \tag{2.7}
\end{equation*}
$$

Clearly, if the saturation parameter is small, then the absorption coefficient approaches
the value obtained in the weak field approximation.

### 2.4 Lamb Dips and Intermodulated Fluorescence

In order to probe the Bennett hole in the velocity distribution profile, a second radiation source is required. One way to introduce a second radiation source would be simply to reflect the laser beam back through the sample cell antiparallel to the incident laser beam. Under these conditions the total electric field experienced by the molecules in the cell can be expressed as the sum of two oscillating electric fields:

$$
\begin{align*}
\vec{E} & =\vec{E}_{1}+\vec{E}_{2} \\
& =E_{0} e^{-i(\omega t+k z)}+E_{0} e^{-i(\omega t-k z)} \\
& =E_{0} \cos (\omega t+k z)+E_{0} \cos (\omega t-k z) \\
& =2 E_{0} \cos \omega t \cos k z \tag{2.8}
\end{align*}
$$

The result of having two $\mathbf{E}$ fields interacting with the ensemble of molecules in the cell is the production of two holes at $v_{z}= \pm\left(\omega_{0}-\omega\right) / k$. When $\omega=\omega_{0}$ the two holes converge to one hole in the population distribution of twice the depth. The change in population due to the saturating standing wave radiation can be expressed as[19]:

$$
\begin{equation*}
\Delta n_{s}\left(v_{z}\right)=\Delta n_{0}\left(v_{z}\right)\left[1-\frac{(\gamma / 2)^{2} S_{0}}{\left(\omega_{0}-\omega-k v_{z}\right)^{2}+\left(\gamma_{S} / 2\right)^{2}}-\frac{(\gamma / 2)^{2} S_{0}}{\left(\omega_{0}-\omega+k v_{z}\right)^{2}+\left(\gamma_{S} / 2\right)^{2}}\right] \tag{2.9}
\end{equation*}
$$

When $\omega=\omega_{0}$ this expression reduces to

$$
\begin{equation*}
\Delta n_{s}\left(v_{z}\right)=\Delta n_{0}\left(v_{z}\right)\left[1-2 S_{0}\left(\frac{\gamma}{\gamma_{s}}\right)^{2}\right] \tag{2.10}
\end{equation*}
$$

The effect of a saturating standing wave on the change in population of the lower state $\left(\Delta n\left(v_{z}\right)\right)$ is illustrated in Figure 2.5(a), where the dotted line represents the case where $\omega=\omega_{0}$ and the solid line represents $\omega>\omega_{0}+\gamma$.


Figure 2.5: a) Illustration of the effects of a saturating standing wave on the velocity distribution of molecules in the sample cell; b) the corresponding absorption coefficient for the sample.

The expression for the absorption coefficient for this standing wave experiment,

$$
\begin{equation*}
\alpha_{s}(\omega)=\alpha_{0}\left[1-\frac{S_{0}}{2}\left(1+\frac{\left(\gamma_{s} / 2\right)^{2}}{\left(\omega-\omega_{0}\right)^{2}+\left(\gamma_{s} / 2\right)^{2}}\right)\right] \tag{2.11}
\end{equation*}
$$

shows that, when the laser is tuned off resonance, $\alpha(\omega) \approx \alpha_{0}\left(\omega_{0}\right)\left(1-\frac{S_{0}}{2}\right)$, but, when the laser is tuned to $\omega=\omega_{0}, \alpha(\omega)=\alpha_{0}\left(\omega_{0}\right)\left(1-S_{0}\right)$. Hence, setting up a standing wave in the sample cell produces a dip in the absorption curve of spectral width $\gamma_{s}$ at the transition frequency $\omega_{0}$. At optical wavelengths, $\gamma_{s}$ is usually much less than the Doppler width and thus the line position of the transition, seen as a Lamb dip, can now be measured with much higher precision.

In addition to improved precision, this technique also affords the ability to resolve lines that were blended at Doppler limited resolution. This capability is illustrated in Figure 2.6, which represents two transitions so close to each other that their Doppler broadened line profiles would be completely blended. The two tiny dips on either side of the Doppler profile represent the two line positions.

Lamb dip spectroscopy has limited usefulness when the spectra become very dense. Under these conditions the Lamb dips can become lost in the mass of Doppler limited line profiles.

One way to avoid this problem is through the use of intermodulated fluorescence spectroscopy (IMF)(see Section 2.1). IMF is a very sensitive saturation technique for eliminating the residual Doppler profile. Like the Lamb dip set-up for absorption experiments, an IMF experiment requires two counter-propagating beams of radiation through the sample cell. However, IMF differs in that instead of simply reflecting the radiation back through the sample cell (thus setting up a standing wave), the incident wave is first split into two equal intensity components, $I_{1}$ and $I_{2}$. The two beams are chopped at two different frequencies, $\mathrm{F}_{1}$ and $\mathrm{F}_{2}$ respectively, so the intensities of the laser beams entering


Figure 2.6: Plot of the absorption coefficient for two closely spaced transitions. The unresolved line is shown in a), and the two Lamb dips representing the two line positions are shown in b).
the sample cell are given by:

$$
I_{1}=\frac{I_{0}}{2}\left(1+\cos 2 \pi F_{1} t\right)
$$

and

$$
I_{2}=\frac{I_{0}}{2}\left(1+\cos 2 \pi F_{2} t\right)
$$

neglecting higher order terms. The intensity of the fluorescence emitted by the molecules experiencing these two counter-propagating laser beams is found to be[19]:

$$
I_{F l} \propto n_{s}\left(I_{1}+I_{2}\right)
$$

which reduces to

$$
I_{F l} \propto n_{0}\left(I_{1}+I_{2}\right)-\frac{B_{12}}{c \pi \gamma R}\left(I_{1}+I_{2}\right)^{2}
$$

when $\omega=\omega_{0} . B_{12}$ is the Einstein coefficient for stimulated emission and $R$ is the sum of all relaxation processes. The linear terms give fluorescence modulated at $F_{1}$ and $F_{2}$, while the quadratic terms are responsible for fluorescence modulated at $\left(F_{1}+F_{2}\right)$ and ( $F_{1}-F_{2}$ ). Sorem and Schawlow[15] demonstrated that by detecting fluorescence at the sum frequency, $\left(F_{1}+F_{2}\right)$, it is possible to record sub-Doppler spectra of the transitions while the background is greatly suppressed. Thus IMF is a good technique when subDoppler resolution of weak fluorescence transitions is desired.

### 2.5 Wavelength Resolved Fluorescence Spectroscopy

When a molecule is excited to a higher electronic state as a result of absorption of a photon, there may exist more than one relaxation path back down to the lower state. An example of such a process is illustrated in Figure 2.7. This example shows a case where three lines are emitted as a result of excitation. Simply measuring the total fluorescence emitted by the molecules reveals only that a transition has occurred, and
gives no information about the assignment. On the other hand, the assignment can be obtained from wavelength-resolved fluorescence (WRF) spectra. For instance, in the first example the WRF spectrum consists of a strong line between two weaker lines. The greater intensity of the centre line is due to unavoidable scattered laser light from the excitation laser, not because the relaxation will preferentially follow that path. This pattern in the WRF spectrum confirms the assignment to a Q-branch transition.

In the second example, however, the intense line is the lowest frequency line of the three because, in this case, a P-branch line has been excited. Similarly, for an R-branch transition, the most intense of the three lines would be the one at highest frequency. Hence, the observed patterns of these WRF spectra serve to confirm the branch assignment of the particular excitation.

Not only can branch assignments be made from WRF data, but if the lower state is already well known, then the $J$-assignments follow from ground state combination differences. For example, if the transition shown in Figure 2.7(a) was excited, then the fluorescence line positions can be predicted to be at:

$$
\begin{aligned}
& P(3)=\omega+E_{i}(2)-E_{i}(3) \\
& Q(2)=\omega+E_{i}(2)-E_{i}(2) \\
& R(1)=\omega+E_{i}(2)-E_{i}(1)
\end{aligned}
$$

WRF spectra can be obtained by two different but related methods. In both cases the fluorescence signal is focussed onto the entrance slit of a spectrometer. In the first method, the wavelength passing through the exit slit is scanned by rotating the grating; the signal is detected by a PMT, and the dispersed spectrum is recorded sequentially.

In a more efficient approach, the whole spectrum is recorded simultaneously. Early methods of simultaneous detection involved replacing the exit slit of the spectrometer


Figure 2.7: An example of possible relaxations in a simple system after excitation of a Q-branch line a), and a P -branch line b).
with a photographic plate. The modern version of the photographic plate is the diode array detector (DAD). The advantages of the DAD over the photographic plate are that the spectra can be analysed immediately and the intensity information stored digitally, which means it can be easily transferred to a computer.

A SPEX model 1702 spectrometer was used in this study, with the exit slit replaced by an EG\&G model 1421-1024-G DAD. The detector was cooled to $-20^{\circ} \mathrm{C}$ and an EG\&G model 1461 detector interface was used so that the experiment could be controlled by a computer. The width of the entrance slit was varied between $35 \mu \mathrm{~m}$ and $60 \mu \mathrm{~m}$, and the exposure times varied from less than one second for the strongest fluorescence signals to as long as two minutes for very weak signals.

## Chapter 3

## Energy Expressions and the Hamiltonian

### 3.1 Introduction

Before the Hamiltonian matrix elements for the states of the $B^{4} \Pi-X^{4} \Sigma^{-}$transition of VO are described in detail, some basic principles of quantum mechanics will be reviewed.

The time-independent Schrödinger equation is the fundamental expression giving the stationary state energies for a system,

$$
\begin{equation*}
\mathcal{H} \psi=E \psi \tag{3.1}
\end{equation*}
$$

In this equation $\mathcal{H}$ is the total Hamiltonian operator, $\psi$ represents the eigenfunction describing the particular state of interest, and $E$ is the eigenvalue or energy of the state.

Despite the simple appearance of the Schrödinger equation, it usually cannot be solved analytically. Instead, a convenient set of basis functions $\phi_{i}$ is chosen such that

$$
\begin{equation*}
\psi=\sum_{i} c_{i} \phi_{i} \tag{3.2}
\end{equation*}
$$

When the eigenfunction $\psi$ of the time-independent Schrödinger equation is replaced by a linear combination of orthogonal basis functions $\phi_{i}$, the problem of solving Equation 3.1 becomes that of calculating the roots of the secular determinant

$$
\begin{equation*}
\left|\mathcal{H}_{i j}-\mathbf{E} \delta_{i j}\right|=0, \tag{3.3}
\end{equation*}
$$

where the matrix elements $\mathcal{H}_{i j}$ are defined as

$$
\begin{equation*}
\mathcal{H}_{i j}=\int \phi_{i}^{*} \mathcal{H} \phi_{j} d \tau \tag{3.4}
\end{equation*}
$$

and $\delta_{i j}$ is the Kronecker delta (i.e. zero if $i \neq j$ and 1 if $i=j$ ).
Any complete set of wavefunctions $\phi_{i}$ would be sufficient, but in practice a basis set is chosen such that the Hamiltonian matrix is most nearly diagonal. Two different bases were used to model the angular momentum couplings in the $B^{4} \Pi-X^{4} \Sigma^{-}$transition of VO. The ground state was best described by a case $\left(\mathrm{b}_{\beta J}\right)$ basis while case ( $\mathrm{a}_{\beta}$ ) coupling applied in the upper state.

### 3.2 Perturbations

Since both the $X^{4} \Sigma^{-}$and the $B^{4} \Pi$ states show rotational perturbations in the observed band structure, the theory will be briefly reviewed.

A state is said to be perturbed if the observed branch structure deviates from that predicted by simple theory. Rotational perturbations arise from terms neglected in the Born-Oppenheimer separation of electronic and nuclear motions, or from relativistic effects such as spin-orbit interaction. The Hamiltonian must be written as

$$
\begin{equation*}
\mathcal{H}=\mathcal{H}^{(0)}+\mathcal{H}^{\prime} \tag{3.5}
\end{equation*}
$$

where $\mathcal{H}^{(0)}$ is the "zero order" rotational Hamiltonian, and $\mathcal{H}^{\prime}$ is responsible for the irregularity.

Consider a perturbation between two states whose zero order wavefunctions or "basis functions", are $\phi_{1}$ and $\phi_{2}$; there will be interaction matrix elements of the type $\left\langle\phi_{1}\right| \mathcal{H}^{\prime}\left|\phi_{2}\right\rangle$ which are responsible for the rotational perturbation. The Hamiltonian matrix elements are given by

$$
\begin{gather*}
\left\langle\phi_{1}\right| \mathcal{H}^{(0)}\left|\phi_{1}\right\rangle=H_{11}=E_{1},  \tag{3.6}\\
\left\langle\phi_{2}\right| \mathcal{H}^{(0)}\left|\phi_{2}\right\rangle=H_{22}=E_{2},  \tag{3.7}\\
\left\langle\phi_{1}\right| \mathcal{H}^{\prime}\left|\phi_{2}\right\rangle=H_{12}, \tag{3.8}
\end{gather*}
$$



Figure 3.1: Illustration of an avoided crossing between two states.
and

$$
\begin{equation*}
\left\langle\psi_{2}\right| \mathcal{H}^{\prime}\left|\psi_{1}\right\rangle=H_{21}, \tag{3.9}
\end{equation*}
$$

which can be written as:

$$
\left[\begin{array}{ll}
H_{11} & H_{12} \\
H_{21} & H_{22}
\end{array}\right]
$$

The $2 \times 2$ Hamiltonian matrix is assumed to be Hermitian, such that $H_{12}=H_{21}$. The eigenvalues,

$$
\begin{equation*}
E_{A}=\frac{\left(E_{1}+E_{2}\right)}{2}+\frac{1}{2} \sqrt{\left(E_{1}-E_{2}\right)^{2}+4 H_{12}^{2}} \tag{3.10}
\end{equation*}
$$

$$
\begin{equation*}
E_{B}=\frac{\left(E_{1}+E_{2}\right)}{2}-\frac{1}{2} \sqrt{\left(E_{1}-E_{2}\right)^{2}+4 H_{12}^{2}} \tag{3.11}
\end{equation*}
$$

represent the energies of the two perturbed states. The eigenfunctions, $\psi_{A}$ and $\psi_{B}$, are given by

$$
\left[\begin{array}{c}
\psi_{A}  \tag{3.12}\\
\psi_{B}
\end{array}\right]=\left[\begin{array}{cc}
c & s \\
-s & c
\end{array}\right]\left[\begin{array}{l}
\phi_{1} \\
\phi_{2}
\end{array}\right]
$$

where $c=\sqrt{\frac{k+d}{2 k}}, s=\sqrt{\frac{k-d}{2 k}}, d=H_{11}-H_{22}$, and $k=\sqrt{d^{2}+4 H_{12}^{2}}$.
This is illustrated in Figure 3.1. The dotted lines represent the unperturbed states, which have energies $E_{1}$ and $E_{2}$; these are functions of $J$, and are assumed to cross at some value of $J(J+1)$. The solid lines represent the observed energies $E_{A}$ and $E_{B}$, as given by Equations (3.10) and (3.11). Where $E_{1}$ and $E_{2}$ cross, the levels $E_{A}$ and $E_{B}$ show an "avoided crossing", and are separated by twice the perturbation matrix element $H_{12}$.

The relative intensities of transitions to the perturbed levels can be calculated given the appropriate transition moments. Consider the transition moments $\mu_{1}$ and $\mu_{2}$, to the basis states $\phi_{1}$ and $\phi_{2}$ respectively. From Equation (3.12), the transitions to the perturbed eigenstates are given by

$$
\begin{aligned}
\left\langle\psi_{A}\right| \hat{\mu}|X\rangle & =c\left\langle\phi_{1}\right| \hat{\mu}|X\rangle+s\left\langle\phi_{2}\right| \hat{\mu}|X\rangle \\
& =c \mu_{1}+s \mu_{2} \\
\left\langle\psi_{B}\right| \hat{\mu}|X\rangle & =-s\left\langle\phi_{1}\right| \hat{\mu}|X\rangle+c\left\langle\phi_{2}\right| \hat{\mu}|X\rangle \\
& =-s \mu_{1}+c \mu_{2}
\end{aligned}
$$

The intensity is proportional to the square of the transition moment; thus $I_{A \leftarrow X} \propto$ $\left(c \mu_{1}+s \mu_{2}\right)^{2}$; and $I_{B \leftarrow X} \propto\left(-s \mu_{1}+c \mu_{2}\right)^{2}$. In the case where $\mu_{2}=0$, the above relations simplify to $I_{A \leftarrow X} \propto c^{2} \mu_{1}^{2}$; and $I_{B \leftarrow X} \propto s^{2} \mu_{1}^{2}$. Consequently, as the avoided crossing is approached, the relative intensity of the observed transition to one of the perturbed
levels will decrease. This diminished intensity will show up as increased intensity for the transition to the other perturbed level. The total intensity is unchanged since $c^{2}+s^{2}=1$.

### 3.3 Hund's Coupling Cases

To model the rotational structure of the $B^{4} \Pi-X^{4} \Sigma^{-}$transition properly, it is necessary to choose functions that describe the electron orbital angular momentum, $\mathbf{L}$, the electron spin angular momentum, $\mathbf{S}$, the angular momentum of the nuclear rotation, $\mathbf{R}$, and the angular momentum arising from the non-zero nuclear spin of the ${ }^{51} \mathrm{~V}$ nucleus, $\mathbf{I}$. These angular momentum vectors can be coupled together in many different ways. Hund considered five possible arrangements in which $\mathbf{L}, \mathbf{S}$ and $\mathbf{R}$ can be coupled in linear molecules, which have become known as Hund's cases (a), (b), (c), (d), and (e)[20]. Later, nuclear spin angular momentum effects have had to be included, to produce subsets of Hund's five coupling cases. Only the two cases needed for this transition, namely case ( $\mathrm{a}_{\beta}$ ) and case $\left(\mathrm{b}_{\beta J}\right)$ (following the naming convention described by Townes and Schawlow [21]), will be discussed here. The others may be found elsewhere [21][22][23].

### 3.3.1 Case $\left(\mathrm{a}_{\beta}\right)$

Hund's case (a) describes a system where both $\mathbf{L}$ and $\mathbf{S}$ are coupled to the internuclear axis. In a non-spherical system, such as a molecule rather than an atom, $\mathbf{L}$ is not a "good" quantum number, though it doẹs have a well-defined projection, $\Lambda$, on the internuclear axis. Likewise, $\Sigma$ represents the well-defined projection of $\mathbf{S}$ on the internuclear axis. The total angular momentum $\mathbf{J}$ is obtained by adding the rotational angular momentum $\mathbf{R}$ to $\mathbf{L}$ and $\mathbf{S}$, such that

$$
\mathbf{R}+\mathbf{L}+\mathbf{S}=\mathbf{J}
$$



Figure 3.2: Hund's case ( $\mathrm{a}_{\beta}$ ) coupling scheme.

Since the projection of $\mathbf{R}$ along the internuclear axis is zero, the component of the total angular momentum along the internuclear axis, $\Omega^{1}$, is

$$
\Omega=|\Lambda+\Sigma| .
$$

One result of this coupling scheme is that the quantum number $J$, associated with the operator for $\mathbf{J}$, will be integral or half-integral, depending on whether $\Omega$ (or more precisely $\Sigma$ ) is integral or half-integral. Of course $J$ can never be less than $\Omega$.

In case $\left(a_{\beta}\right)$ the nuclear spin angular momentum $I$ is coupled to $J$, the total of the rotational and electronic angular momentum, according to

$$
\mathbf{J}+\mathbf{I}=\mathbf{F}
$$

This is illustrated vectorially in Figure 3.2. Naturally, the quantum number F cannot be less than zero. The values for F are given by the rules of vector coupling as

$$
F=|J+I|,|J+I-1|, \ldots,|J-I|
$$

For the ${ }^{51} \mathrm{~V}$ nucleus, with nuclear spin $\frac{7}{2}$, there will be eight hyperfine components for each rotational level, provided $J \geq 3 \frac{1}{2}$. (There are two isotopes of vanadium found in nature. Both have non-zero nuclear spins, though the radioactive ${ }^{50} \mathrm{~V}$, with nuclear spin $I=6$, is only found in $0.2 \%$ abundance. The dominant stable isotope is ${ }^{51} \mathrm{~V}$, which has nuclear spin $I=\frac{7}{2}$.)

### 3.3.2 Case ( $\mathrm{b}_{\beta J}$ )

The electron spin angular momentum $\mathbf{S}$ is not coupled directly to the internuclear axis by the electrostatic field in the molecule. Instead it is only the internal magnetic field induced

[^1]along the axis by the orbital motion of the electrons that can couple $\mathbf{S}$ to the internuclear axis. If $\Lambda=0$, then the magnitude of this internal magnetic field is identically zero and hence the electron spin angular momentum is not coupled to the internuclear axis. This situation is described as case (b), and occurs in most $\Sigma$ states $(\Lambda=0)$ and all states with $\Lambda>0$ but $B J \gg A$. Even in states with non-zero orbital angular momentum, the electron spin becomes increasingly uncoupled from the internuclear axis by the magnetic field generated by increasing molecular rotation; in such states there is no well defined projection of $\mathbf{S}$ on the internuclear axis.

In case (b) coupling, as with case (a), the projection of $\mathbf{L}$ along the internuclear axis $(\Lambda)$ is a "good" quantum number. $\mathbf{L}$ is coupled with $\mathbf{R}$ to give $\mathbf{N}$, the total angular momentum excluding electron and nuclear spins; $\mathbf{N}$ then couples with $\mathbf{S}$ to give $\mathbf{J}$.

There are several possible coupling schemes for the nuclear spin angular momentum $\mathbf{I}$. The most common situation, called case ( $\mathrm{b}_{\beta J}$ ), is where $\mathbf{J}$ is coupled to $\mathbf{I}$ to give $\mathbf{F}$. This is illustrated in Figure 3.3.2. The overall coupling scheme for case $\left(\mathrm{b}_{\beta J}\right)$ can therefore be described as:

$$
\begin{aligned}
& \mathbf{R}+\mathbf{L}=\mathbf{N} \\
& \mathbf{N}+\mathbf{S}=\mathbf{J} \\
& \mathbf{J}+\mathbf{I}=\mathbf{F}
\end{aligned}
$$

Once again,

$$
F=|J+I|,|J+I-1|, \ldots,|J-I|
$$

where $F$ cannot be less than zero.

### 3.4 Hamiltonian Matrix Elements for the $X^{4} \Sigma^{-}$state

Several of the interactions that occur in the $X^{4} \Sigma^{-}$state occur also in the $B^{4} \Pi$ state of VO. However, since the ground state is best described by case ( $\mathrm{b}_{\beta J}$ ) coupling while


Figure 3.3: Hund's case $\left(\mathrm{b}_{\beta J}\right)$ coupling scheme.
case ( $\mathrm{a}_{\beta}$ ) coupling applies to the $B^{4} \Pi$ state, the forms of the individual matrix elements will differ. The $X^{4} \Sigma^{-}$matrix elements are discussed below, while the matrix elements for the upper state are given in Section 3.5.

### 3.4.1 Rotational Structure

The general form of the rotational Hamiltonian is given by:

$$
\begin{equation*}
\mathcal{H}_{r o t}=B \mathbf{R}^{2}-D \mathbf{R}^{4} \tag{3.13}
\end{equation*}
$$

where $\mathbf{R}=\mathbf{J}-\mathbf{L}-\mathbf{S}$. In a $\Sigma$ state, where $\mathbf{L}$ can be omitted in first order, $\mathbf{R}$ becomes $\mathbf{J}-\mathbf{S}$, which is called $\mathbf{N}$. The rotational Hamiltonian and its matrix elements for the $X^{4} \Sigma^{-}$state are thus:

$$
\begin{gather*}
\mathcal{H}_{r o t}=B \mathbf{N}^{2}-D \mathbf{N}^{4}  \tag{3.14}\\
\langle N S J| \mathcal{H}_{r o t}|N S J\rangle=B N(N+1)-D N^{2}(N+1)^{2} \tag{3.15}
\end{gather*}
$$

### 3.4.2 Fine Structure

Fine structure describes the interactions of unpaired electrons, carrying spin and orbital angular momenta, with the molecular rotation and, through dipole-dipole interactions, with each other. The fine structure Hamiltonian can thus be partitioned into spin-orbit, spin-rotation and spin-spin operators. However, higher order terms, as well as cross terms between these different interactions, make evaluation and interpretation of the matrix elements complicated.

For example, the first order spin-orbit Hamiltonian,

$$
\begin{equation*}
\mathcal{H}_{s o}^{(1)}=A \mathbf{L} \cdot \mathbf{S} \tag{3.16}
\end{equation*}
$$

gives zero in an electronic $\Sigma$ state, since $\left\langle L_{z}\right\rangle=0$, and the effects of $L_{+}$and $L_{-}$are not contained within the $\Sigma$ state. However, in second order, the effects of $L_{+}$and $L_{-}$are
equivalent to a tensor operator ( $\mathbf{S}, \mathbf{S}$ ) acting within the $\Sigma$ state, i.e.

$$
(\mathbf{S} \cdot \mathbf{L})(\mathbf{L} \cdot \mathbf{S}) \equiv(\mathbf{S}, \mathbf{S})(\mathbf{L}, \mathbf{L})
$$

which turns out to be identical in form to the spin-spin interaction operator. The Hamiltonian for the dipolar spin-spin interaction is given in terms of a parameter $\lambda$ by [24]

$$
\begin{equation*}
\mathcal{H}_{s s}=\frac{2}{3} \lambda\left(3 S_{z}^{2}-\mathbf{S}^{2}\right) \tag{3.17}
\end{equation*}
$$

however, the contribution to $\lambda$ from the second order spin-orbit coupling is indistinguishable from the dipolar spin-spin interaction, so that

$$
\lambda_{e f f}=\lambda_{s s}+\lambda_{s o}^{(2)}
$$

Therefore, the $\lambda$ parameter determined from the fit of the $X^{4} \Sigma^{-}$state of VO is an effective parameter representing the sum of the two effects.

In spherical tensor formalism, Equation 3.17 has the form

$$
\begin{equation*}
\mathcal{H}_{s s}=\frac{2}{3} \sqrt{6} \lambda T_{0}^{2}(\mathbf{S}, \mathbf{S}) \tag{3.18}
\end{equation*}
$$

which gives as the matrix elements in case (b) coupling [24]

$$
\begin{align*}
& \left\langle N^{\prime} S J I F\right| \mathcal{H}_{\text {spin-spin }}|N S J I F\rangle \\
& \quad=\frac{2}{3} \lambda(-1)^{N+S+J}\left\{\begin{array}{ccc}
J & S & N^{\prime} \\
2 & N & S
\end{array}\right\}[S(S+1)(2 S+1)(2 S-1)(2 S+3)]^{1 / 2} \\
& \quad \times(-1)^{N^{\prime}}\left(\begin{array}{ccc}
N^{\prime} & 2 & N \\
0 & 0 & 0
\end{array}\right)\left[(2 N+1)\left(2 N^{\prime}+1\right)\right]^{1 / 2} \tag{3.19}
\end{align*}
$$

The spin-rotation Hamiltonian gives the energy of the interaction between the electron spins and the magnetic field due to nuclear motion. The general form of the spin-rotation

Hamiltonian is given by [25]:

$$
\begin{align*}
\mathcal{H}_{s r} & =\gamma \mathbf{R} \cdot \mathbf{S}  \tag{3.20}\\
& =\gamma(\mathbf{J}-\mathbf{L}-\mathbf{S}) \cdot \mathbf{S} \\
& =\gamma \mathbf{N} \cdot \mathbf{S}, \text { for } \Sigma \text { states. } \tag{3.21}
\end{align*}
$$

In a case (b) basis, the spin-rotation Hamiltonian has only diagonal matrix elements, which are given by:

$$
\begin{equation*}
\langle N S J| \mathcal{H}_{s r}|N S J\rangle=-\frac{1}{2} \gamma[N(N+1)+S(S+1)-J(J+1)] \tag{3.22}
\end{equation*}
$$

The third order contribution to the spin-rotation interaction arises in third order perturbation theory when the matrix elements of the spin-orbit operator are taken twice and those of the spin-uncoupling term, $-2 B\left(J_{x} S_{x}+J_{y} S_{y}\right)$, are taken once. The Hamiltonian for this third order spin-rotation interaction is quite complicated to evaluate, but Brown and Milton [26] successfully simplified the case (a) matrix elements to

$$
\begin{align*}
& \langle S \Sigma, J \Omega| \mathcal{H}_{s r}^{(3)}|S \Sigma \pm 1, J \Omega \pm 1\rangle= \\
& \quad-\frac{1}{2} \gamma_{s}[S(S+1)-5 \Sigma(\Sigma \pm 1)-2][J(J+1)-\Omega(\Omega \pm 1)]^{\frac{1}{2}} \\
& \quad \times[S(S+1)-\Sigma(\Sigma \pm 1)]^{\frac{1}{2}} \tag{3.23}
\end{align*}
$$

The case (b) forms of the third order spin-rotation matrix elements do not simplify similarly ${ }^{2}$. As required for the least squares fit of the VO $B^{4} \Pi-X^{4} \Sigma^{-}$transition it is [28]:

$$
\begin{aligned}
& \left\langle N^{\prime} S J I F\right| \mathcal{H}_{s r}^{(3)}|N S J I F\rangle \\
& \quad=\frac{1}{2}\left[(2 N+1)\left(2 N^{\prime}+1\right) J(J+1)(2 J+1)\right]^{1 / 2}
\end{aligned}
$$

[^2]\[

$$
\begin{align*}
& \times[2(2 S-2)(2 S-1) 2 S(2 S+1)(2 S+2)(2 S+3)(2 S+4) / 3]^{1 / 2} \gamma_{s} \\
& \times \sum_{x=2,4}(2 x+1)\left(\begin{array}{ccc}
3 & x & 1 \\
-1 & 0 & 1
\end{array}\right)(-1)^{N^{\prime}}\left(\begin{array}{ccc}
N^{\prime} & x & N \\
0 & 0 & 0
\end{array}\right)\left\{\begin{array}{ccc}
N^{\prime} & N & x \\
S & S & 3 \\
J & J & 1
\end{array}\right\} \tag{3.24}
\end{align*}
$$
\]

The centrifugal distortion corrections to the fine structure are straight-forward for case (b) coupling, and the Hamiltonian has the form:

$$
\begin{equation*}
\mathcal{H}_{*, c d}=\gamma_{D}(\mathbf{N} \cdot \mathbf{S}) \mathbf{N}^{2}+\frac{1}{3} \lambda_{D}\left[\left(3 S_{z}^{2}-\mathbf{S}^{2}\right), \mathbf{N}^{2}\right]_{+} \tag{3.25}
\end{equation*}
$$

In Equation (3.25), the symbol $[x, y]_{+}$stands for the anti-commutator $x y+y x$, which is needed to preserve Hermitian form for the matrices. The diagonal matrix elements for the centrifugal distortion to the spin-rotation and spin-spin interactions respectively are given as [28]

$$
\begin{align*}
\langle N S J| \mathcal{H}_{s r, c d}|N S J\rangle & =-\frac{1}{2} \gamma_{D} N(N+1)[N(N+1)+S(S+1)-J(J+1)] \\
& =\frac{1}{2} \gamma_{D} N(N+1) R(J S N) \tag{3.26}
\end{align*}
$$

and

$$
\begin{equation*}
\langle N S J| \mathcal{H}_{s s, c d}|N S J\rangle=-\frac{1}{3} \lambda_{D} N(N+1) \frac{3 R(J S N)[R(J S N)+1]-4 S(S+1) N(N+1)}{(2 N-1)(2 N+3)} \tag{3.27}
\end{equation*}
$$

where

$$
R(a b c)=a(a+1)-b(b+1)-c(c+1)
$$

The off-diagonal matrix elements are given by

$$
\begin{align*}
\langle N-2, S J| \mathcal{H}_{s, c d}|N S J\rangle= & \frac{1}{2} \lambda_{D} \frac{[N(N+1)-(2 N-1)]}{(2 N-1)[(2 N+1)(2 N-3)]^{\frac{1}{2}}} \\
& \times Y(J S N) Y(J S, N-1) \tag{3.28}
\end{align*}
$$

where

$$
Y(a b c)=[(a+b+c+1)(b+c-a)(a+c-b)(a+b-c+1)]^{\frac{1}{2}}
$$

### 3.4.3 Magnetic Hyperfine Hamiltonian

When one or more of the nuclei of the molecule being studied has non-zero nuclear spin and an appreciable magnetic moment, then magnetic hyperfine interactions will make significant contributions to the spectrum. The $X^{4} \Sigma^{-}$state of VO required three magnetic hyperfine parameters to describe the observed features accurately.

The Hamiltonian operators for the direct interactions between the nuclear magnetic dipole moment and an electron spin moment in a $\Sigma$ electronic state are given by[21]

$$
\begin{equation*}
\mathcal{H}_{m a g h f}=b \mathbf{I} \cdot \mathbf{S}+c I_{z} S_{z} \tag{3.29}
\end{equation*}
$$

where $c$ represents the dipole-dipole interaction and $b$ incorporates part of this dipoledipole interaction as well as the Fermi contact interaction, $b_{F}$, in the relation $b=b_{F}+\frac{1}{3} c$. The matrix elements are thus

$$
\begin{align*}
&\left\langle N^{\prime} S J^{\prime} I F\right| \mathcal{H}_{\text {maghf }}|N S J I F\rangle \\
&=(-1)^{J+I+F}\left\{\begin{array}{ccc}
F & I & J^{\prime} \\
1 & J & I
\end{array}\right\}\left[(2 J+1)\left(2 J^{\prime}+1\right) I(I+1)(2 I+1)\right]^{1 / 2} \\
& \times[S(S+1)(2 S+1)]^{1 / 2}\left[(-1)^{N+S+J^{\prime}}\left\{\begin{array}{ccc}
S & J^{\prime} & N \\
J & S & 1
\end{array}\right\} b_{F}\right. \\
&\left.-\frac{1}{3} c\left[30(2 N+1)\left(2 N^{\prime}+1\right)\right]^{1 / 2}\left\{\begin{array}{ccc}
N^{\prime} & N & 2 \\
S & S & 1 \\
J^{\prime} & J & 1
\end{array}\right\}(-1)^{N^{\prime}}\left(\begin{array}{ccc}
N^{\prime} & 2 & N \\
0 & 0 & 0
\end{array}\right)\right] \tag{3.30}
\end{align*}
$$

The third magnetic hyperfine parameter needed to describe the $X^{4} \Sigma^{-}$state of VO arises from the third order isotropic hyperfine Hamiltonian, $\mathcal{H}_{i s o}^{(3)}$. This energy operator is analogous to the third order spin-rotation Hamiltonian, whose matrix elements are given as Equations (3.23) and (3.24), except that the isotropic hyperfine operator $\sum_{i} b_{i} \mathbf{I} \cdot \mathbf{s}_{i}$
replaces the spin-uncoupling operator. The third order isotropic hyperfine Hamiltonian is [10][27]

$$
\begin{equation*}
\mathcal{H}_{i s o}^{(3)}=\frac{(5 \sqrt{14} / 3) b_{S}}{\langle\Lambda| T_{0}^{2}(\mathbf{L})|\Lambda\rangle} T^{1}(\mathbf{I}) \cdot T^{1}\left[T^{2}\left(\mathbf{L}^{2}\right), T^{3}\left(\mathbf{S}^{3}\right)\right] \tag{3.31}
\end{equation*}
$$

and its matrix elements in case ( $\mathrm{b}_{\beta J}$ ) coupling are [10][27]

$$
\begin{align*}
&\left\langle N^{\prime} S J^{\prime} I F\right| \mathcal{H}_{i s o}^{(3)}|N S J I F\rangle \\
&= \frac{1}{4}(-1)^{J+I+F}\left\{\begin{array}{ccc}
F & I & J^{\prime} \\
1 & J & I
\end{array}\right\}\left[(2 J+1)\left(2 J^{\prime}+1\right) I(I+1)(2 I+1)\right]^{1 / 2} \\
& \times(-1)^{N^{\prime}}\left(\begin{array}{ccc}
N^{\prime} & 2 & N \\
0 & 0 & 0
\end{array}\right)\left[(2 N+1)\left(2 N^{\prime}+1\right)\right]^{1 / 2}\left\{\begin{array}{ccc}
N^{\prime} & N & 2 \\
S & S & 3 \\
J^{\prime} & J^{\prime} & 1
\end{array}\right\} \\
& \times[35(2 S-2)(2 S-1) 2 S(2 S+1)(2 S+2)(2 S+3)(2 S+4) / 3]^{1 / 2} b_{S} \tag{3.32}
\end{align*}
$$

### 3.4.4 The Electric Quadrupole Interaction

In addition to its nuclear magnetic dipole moment, the electric quadrupole moment of the V nucleus also contributes to the hyperfine structure of the $X^{4} \Sigma^{-}$state of VO. The Hamiltonian operator for the electric quadrupole interaction is given by[10][21]

$$
\begin{equation*}
\mathcal{H}_{q u a d}^{(0)}=\frac{e^{2} Q q_{0}\left(3 I_{z}^{2}-\mathbf{I}^{2}\right)}{4 I(2 I-1)} \tag{3.33}
\end{equation*}
$$

resulting in matrix elements

$$
\begin{aligned}
& \left\langle N^{\prime} S J^{\prime} I F\right| \mathcal{H}_{q u a d}^{(0)}|N S J I F\rangle \\
& =\frac{1}{4} e^{2} Q q_{0}\left(\begin{array}{ccc}
I & 2 & I \\
-I & 0 & I
\end{array}\right)^{-1}(-1)^{J+I+F}\left\{\begin{array}{ccc}
F & I & J^{\prime} \\
2 & J & I
\end{array}\right\} \\
& \quad \times(-1)^{N^{\prime+S+J}}\left[(2 J+1)\left(2 J^{\prime}+1\right)(2 N+1)\left(2 N^{\prime}+1\right)\right]^{1 / 2}\left\{\begin{array}{ccc}
S & N^{\prime} & J^{\prime} \\
2 & J & N
\end{array}\right\}
\end{aligned}
$$

$$
\times(-1)^{N^{\prime}}\left(\begin{array}{ccc}
N^{\prime} & 2 & N  \tag{3.34}\\
0 & 0 & 0
\end{array}\right)
$$

### 3.5 The Hamiltonian for the ${ }^{4} \Pi$ upper state

A particular complication in the ${ }^{4} \Pi$ upper state arises from the $a^{2} \Sigma^{+}$state which perturbs it heavily. The Hamiltonian for the $B^{4} \Pi$ state, excluding the effects of the $a^{2} \Sigma^{+}$state, is described in this Section. Since the matrix elements of the $B^{4} \Pi$ Hamiltonian were evaluated using a case $\left(a_{\beta}\right)$ basis, it was necessary to do likewise for the $a^{2} \Sigma^{+}$state so that the interaction matrix elements could be evaluated most simply. The $a^{2} \Sigma^{+}$Hamiltonian is described in Section 3.6 and the perturbation matrix elements are given in Section 3.7.

### 3.5.1 Rotational and Fine Structure

The rotational Hamiltonian operator has already been given as Equation 3.24, but is repeated here for convenience:

$$
\begin{equation*}
\mathcal{H}_{r o t}=B \mathbf{R}^{2}-D \mathbf{R}^{4} \tag{3.35}
\end{equation*}
$$

In contrast to the $X^{4} \Sigma^{-}$state, where $\Lambda=0$, the first and third order spin-orbit interactions are non-zero. The full spin-orbit Hamiltonian to third order is given by[29]:

$$
\begin{equation*}
\mathcal{H}_{s o}=A L_{z} S_{z}+\frac{2}{3} \lambda\left(3 S_{z}^{2}-\mathbf{S}^{2}\right)+\eta L_{z} S_{z}\left[S_{z}^{2}-\frac{3 \mathbf{S}^{2}-1}{5}\right] \tag{3.36}
\end{equation*}
$$

The spin-orbit matrix elements in a case (a) basis are thus

$$
\begin{align*}
\left\langle\Lambda^{\prime} ; S \Sigma^{\prime} ; J \Omega\right| \mathcal{H}_{s o}|\Lambda ; S \Sigma ; J \Omega\rangle= & A \Lambda \Sigma+\frac{2}{3} \lambda\left[3 \Sigma^{2}-S(S+1)\right] \\
& +\eta \Lambda \Sigma\left[\Sigma^{2}-\frac{3}{5} S(S+1)+\frac{1}{5}\right] \tag{3.37}
\end{align*}
$$

The spin-rotation Hamiltonian, as expressed in Equation 3.23, is given by

$$
\begin{equation*}
\mathcal{H}_{s r}=\gamma \mathbf{R} \cdot \mathbf{S} \tag{3.38}
\end{equation*}
$$

which in a case (a) basis has diagonal elements of the form

$$
\begin{equation*}
\langle\Lambda ; S \Sigma ; J \Omega| \mathcal{H}_{s r}|\Lambda ; S \Sigma ; J \Omega\rangle=\gamma\left[\Sigma^{2}-S(S+1)\right] \tag{3.39}
\end{equation*}
$$

Since each of the sub-band origins is well defined in a state where case (a) coupling applies, it is convenient to fit the data to a number of separate sub-band origins instead of a single band origin with various spin-orbit and spin rotation contributions. The general expression for the sub-band origins is

$$
\begin{equation*}
T_{\Omega}=T_{0}+A \Lambda \Sigma+\frac{2}{3} \lambda\left[3 \Sigma^{2}-S(S+1)\right]+\gamma\left[\Sigma^{2}-S(S+1)\right]+\eta \Lambda \Sigma\left[\Sigma^{2}-\frac{3 S(S+1)+1}{5}\right] \tag{3.40}
\end{equation*}
$$

The spin-rotation parameter $\gamma$ appears in off-diagonal matrix elements (see Figure 3.4) and can therefore still be fitted independently of the sub-band origins. The off-diagonal $\gamma$ term has the effect of linking the effective rotational constants of adjacent spin-states.

As mentioned in sub-section 3.4.2, the spin-spin Hamiltonian is identical in form to the second order spin-orbit Hamiltonian,

$$
\begin{equation*}
\mathcal{H}_{s s}=\frac{2}{3} \lambda\left(3 S_{z}^{2}-\mathbf{S}^{2}\right) \tag{3.41}
\end{equation*}
$$

so that its matrix elements are indistinguishable from those of $\mathcal{H}_{s o}^{(2)}$.

### 3.5.2 $\quad \Lambda$-type Doubling

The interaction between $\Sigma$ states $(\Lambda=0)$ and $\Pi$ states $(\Lambda=1)$ lifts the degeneracy of the $\pm \Lambda$ levels in the $\Pi$ state [22][30]. The matrix elements for molecules in ${ }^{1} \Pi$ and ${ }^{2} \Pi$ states have long been known [30], but different conventions have been used to describe the parameters for states of higher multiplicity. This work uses the effective $\Lambda$-type doubling Hamiltonian defined by Brown and Merer [31],

$$
\begin{equation*}
\mathcal{H}_{L D}=\frac{1}{2}(o+p+q)\left(S_{+}^{2}+S_{-}^{2}\right)-\frac{1}{2}(p+2 q)\left(J_{+} S_{+}+J_{-} S_{-}\right)+\frac{1}{2} q\left(J_{+}^{2}+J_{-}^{2}\right) \tag{3.42}
\end{equation*}
$$

This form of the Hamiltonian was chosen because it refers to a Hund's case (a) coupling scheme; it gives matrix elements of the form [31]

$$
\begin{align*}
& \langle\mp 1, \Sigma \pm 2, J, \Omega| \mathcal{H}_{L D}| \pm 1, \Sigma J \Omega\rangle \\
& \quad=\frac{1}{2}(o+p+q)[S(S+1)-\Sigma(\Sigma \pm 1)]^{\frac{1}{2}}[S(S+1)-(\Sigma \pm 1)(\Sigma \pm 2)]^{\frac{1}{2}}  \tag{3.43}\\
& \langle\mp 1, \Sigma \pm 1, J, \Omega \mp 1| \mathcal{H}_{L D}| \pm 1, \Sigma J \Omega\rangle \\
& \quad=-\frac{1}{2}(p+2 q)[S(S+1)-\Sigma(\Sigma \pm 1)]^{1 / 2}[J(J+1)-\Omega(\Omega \mp 1)]^{1 / 2}  \tag{3.44}\\
& \langle\mp 1, \Sigma, J, \Omega \mp 2| \mathcal{H}_{L D}| \pm 1, \Sigma J \Omega\rangle \\
& =\frac{1}{2} q[J(J+1)-\Omega(\Omega \mp 1)]^{1 / 2}[J(J+1)-(\Omega \mp 1)(\Omega \mp 2)]^{1 / 2} \tag{3.45}
\end{align*}
$$

There exists a contribution to the $\Lambda$-type doubling from hyperfine interactions, but this will be discussed in the next sub-section.

### 3.5.3 Magnetic Hyperfine Interactions

The Hamiltonian operator for the interaction between the nuclear magnetic dipole moment and the electron spin magnetic dipole moment in a $\Sigma$ state has been given in subsection 3.4.3 as

$$
\begin{equation*}
\mathcal{H}_{I \cdot S h f}=b \mathbf{I} \cdot \mathbf{S}+c I_{z} S_{z} \tag{3.46}
\end{equation*}
$$

In orbitally degenerate states there is an additional interaction between the nuclear spin angular momentum and the orbital angular momentum of the electrons. This interaction is described by the Hamiltonian[32]:

$$
\begin{equation*}
\mathcal{H}_{I \cdot L}=a I_{z} L_{z} \tag{3.47}
\end{equation*}
$$

The three hyperfine parameters mentioned so far describe the magnetic hyperfine effects in the two parity components of $\Pi$ states equally. However, Frosch and Foley[32] showed that hyperfine contributions to the $\Lambda$-type doubling are possible because part of
the dipole-dipole interaction has matrix elements that connect electronic states differing by two units in the orbital angular momentum $\Lambda$. The $\Lambda$-type doubling-hyperfine Hamiltonian is given by[32]

$$
\begin{equation*}
\mathcal{H}_{\Lambda D h f}=\frac{1}{2} d\left(e^{2 i \phi} I_{-} S_{-}+e^{-2 i \phi} I_{+} S_{+}\right) \tag{3.48}
\end{equation*}
$$

where $\phi$ is the angle giving the direction of the unpaired electron relative to an arbitrary reference plane. Translating into tensorial form, the dipolar Hamiltonian can be described by the general expression [28]:

$$
\begin{equation*}
\mathcal{H}_{m a g h f}=-\sqrt{10} g \mu_{B} g_{N} \mu_{N} r^{-3} T^{1}(\mathbf{I}) \cdot T^{1}\left(\mathbf{S}, C^{2}\right) \tag{3.49}
\end{equation*}
$$

where

$$
T_{q}^{1}\left(\mathbf{S}, C^{2}\right)=-\sum_{q_{1}, q_{2}}(-1)^{q} \sqrt{3}\left(\begin{array}{ccc}
1 & 2 & 1  \tag{3.50}\\
q_{1} & q_{2} & -q
\end{array}\right) T_{q_{1}}^{1}(\mathbf{S}) T_{q_{2}}^{2}(C)
$$

and,

$$
\begin{equation*}
r^{-3} T_{q_{2}}^{2}(C)=\sqrt{\frac{4 \pi}{5}} Y_{2, q_{2}}(\theta, \phi) r^{-3} \tag{3.51}
\end{equation*}
$$

This form is the most convenient for the calculation of the matrix elements. Omitting the complexities of the tensor algebra, the diagonal matrix elements of Equations (3.46)(3.48) are

$$
\begin{equation*}
\langle J \Omega I F| \mathcal{H}_{\text {maghf }}|J \Omega I F\rangle=\frac{\Omega[a \Lambda+(b+c) \Sigma] R(F I J)}{2 J(J+1)} \tag{3.52}
\end{equation*}
$$

where $R(F I J)=F(F+1)-I(I+1)-J(J+1)$. The matrix elements diagonal in $J$, but off-diagonal in $\Omega$, are:

$$
\begin{align*}
& \langle S \Sigma, J \Omega I F| \mathcal{H}_{\text {mag } h f}|S \Sigma \pm 1, J \Omega \pm 1, I F\rangle \\
& =b[J(J+1)-\Omega(\Omega \pm 1)]^{1 / 2}[S(S+1)-\Sigma(\Sigma \pm 1)]^{1 / 2} \\
& \quad \times \frac{R(F I J)}{4 J(J+1)} \tag{3.53}
\end{align*}
$$

while the matrix elements off-diagonal in $J$ are

$$
\begin{equation*}
\langle J \Omega I F| \mathcal{H}_{\text {maghf }}|J-1, \Omega I F\rangle=-\frac{[a \Lambda+(b+c) \Sigma]\left(J^{2}-\Omega^{2}\right)^{1 / 2} V(F, I, J)}{2 J[(2 J+1)(2 J-1)]^{1 / 2}} \tag{3.54}
\end{equation*}
$$

and

$$
\begin{align*}
& \langle S \Sigma, J \Omega I F| \mathcal{H}_{\operatorname{magh} f}|S \Sigma \pm 1, J-1, \Omega \pm 1, I F\rangle \\
& = \\
& \mp b[(J \mp \Omega)(J \mp \Omega-1)]^{1 / 2}[S(S+1)-\Sigma(\Sigma \pm 1)]^{1 / 2}  \tag{3.55}\\
& \quad \times \frac{V(F I J)}{4 J[(2 J+1)(2 J-1)]},
\end{align*}
$$

where

$$
V(F I J)=[(J+I+F+1)(F+J-I)(J+I-F)(F+I-J+1)]^{1 / 2} .
$$

### 3.5.4 Electric Quadrupole Interaction

The Hamiltonian for the electric quadrupole interaction given in sub-section 3.4.4 for $\Sigma$ states (3.33) also applies for $\Pi$ states. However, while $\Pi$ states will have the same zero order term as in $\Sigma$ electronic states, there is also a $e_{2} Q q_{2}$ term which will have non-zero elements only in $\Pi$ states. Like the d parameter for magnetic hyperfine effects, there exists an electric quadrupole interaction which links states differing in $\Lambda$ by $\pm 2$. The complete electric quadrupole Hamiltonian for $\Pi$ states is given by[33][34]

$$
\begin{equation*}
\mathcal{H}_{q u a d}=\frac{e^{2} Q q_{0}\left(3 I_{z}^{2}-\mathbf{I}^{2}\right)}{4 I(2 I-1)}+\frac{e^{2} Q q_{2}\left(I_{+}^{2}+I_{-}^{2}\right)}{8 I(2 I-1)} . \tag{3.56}
\end{equation*}
$$

### 3.6 The Hamiltonian for the $a^{2} \Sigma^{+}$State

Although $\Sigma$ states are generally best described by a Hund's case (b) coupling scheme, the matrix elements for the perturbing $a^{2} \Sigma^{+}$state of VO were evaluated using a case (a) basis in order to be consistent with those for the $B^{4} \Pi$ state and so that the interaction matrix could be written most simply.

Using the Hamiltonian operators described in Section 3.4, the rotational matrix elements for the ${ }^{2} \Sigma^{+}$state are given by

$$
\begin{equation*}
\left.\left.\left\langle{ }^{2} \Sigma^{+}\right| \mathcal{H}\right|^{2} \Sigma^{+}{ }_{e}^{f}\right\rangle=B(x)(x \pm 1)-D(x)^{2}(x \pm 1)^{2}-\frac{1}{2} \gamma(1 \pm x) \tag{3.57}
\end{equation*}
$$

where $x=J+\frac{1}{2}$.
The sole hyperfine parameter that can be determined for the $a^{2} \Sigma^{+}$state that needs to be considered arises from the isotropic Hamiltonian

$$
\begin{equation*}
\mathcal{H}_{h f}=b \mathbf{I} \cdot \mathbf{S} \tag{3.58}
\end{equation*}
$$

Written in an $f / \epsilon$ parity basis, its diagonal matrix elements have the form

$$
\begin{equation*}
\left\langle{ }^{2} \Sigma^{+}\right| \mathcal{H}_{h f}\left|{ }^{2} \Sigma^{+}{ }_{e}^{f}\right\rangle=\mp b \frac{R(F, I, J)}{4\left(x \pm \frac{1}{2}\right)}, \tag{3.59}
\end{equation*}
$$

while the $J \rightarrow J-1$ matrix elements are

$$
\begin{equation*}
\left\langle{ }^{2} \Sigma^{+}, J_{e}^{f}\right| \mathcal{H}_{h f}\left|{ }^{2} \Sigma^{+}, J-1{ }_{f}^{e}\right\rangle=-b \frac{V(F, I, J)}{8 J}(1 \mp 1) \tag{3.60}
\end{equation*}
$$

Those parameters which pertain to the $a^{2} \Sigma^{+}$state are designated by a prime (eg. $B^{\prime}, D^{\prime}, \gamma^{\prime}$, and $b^{\prime}$ ) in Figure 3.4 to distinguish them from the $B^{4} \Pi$ parameters.

### 3.7 The ${ }^{2} \Sigma^{+}-{ }^{4} \Pi$ Matrix Elements

There exist no direct spin-orbit interactions between the $\delta^{2} \sigma a^{2} \Sigma^{+}$and $\delta^{2} \pi B^{4} \Pi$ states of VO within the single configuration approximation, but higher order mechanisms must exist. The relative sizes of the matrix elements of these higher order spin-orbit interactions can be evaluated using the Wigner-Eckart theorem,

$$
\left\langle S^{\prime} \Sigma^{\prime} \Lambda^{\prime} \Omega^{\prime}\right| \mathcal{H}_{s o}|S \Sigma \Lambda \Omega\rangle=(-1)^{S^{\prime-\Sigma}}\left(\begin{array}{ccc}
S^{\prime} & 1 & S  \tag{3.61}\\
-\Sigma^{\prime} & q & \Sigma
\end{array}\right)\left\langle S^{\prime} \Lambda^{\prime}\left\|\mathcal{H}_{s o}\right\| S \Lambda\right\rangle \delta_{\Omega \Omega^{\prime}}
$$

which gives four non-zero matrix elements in a signed basis. Similarly, the hyperfine interactions between ${ }^{2} \Sigma^{+}$and ${ }^{4} \Pi$ states require inclusion of an interaction parameter denoted by the parameter $e$, which has four equivalent non-zero matrix elements. After transformation to an $e / f$ parity basis the matrix elements are given in the form ${ }^{3}$ :

$$
\begin{equation*}
\left.\left.\left\langle{ }^{4} \Pi_{\frac{1}{2}}\right| \mathcal{H}\right|^{2} \Sigma^{+}{ }_{f}^{e}\right\rangle=-\frac{1}{\sqrt{12}}\left\langle{ }^{4} \Pi\left\|\mathcal{H}_{s o}\right\|^{2} \Sigma^{+}\right\rangle+e \frac{R(F, I, J)}{8 J(J+1)} \tag{3.62}
\end{equation*}
$$

and

$$
\begin{equation*}
\left\langle{ }^{4} \Pi_{-\frac{1}{2}}\right| \mathcal{H}\left|{ }^{2} \Sigma^{+}{ }_{f}^{e}\right\rangle=\mp \frac{1}{2}\left\langle{ }^{4} \Pi\left\|\mathcal{H}_{s o}\right\|^{2} \Sigma^{+}\right\rangle \mp e \sqrt{3} \frac{R(F, I, J)}{8 J(J+1)} \tag{3.63}
\end{equation*}
$$

[^3]|  | $\left\|\Pi_{5 / 2} \%\right\rangle$ | $\left\|{ }^{4} \Pi_{3 / 2} \%\right\rangle$ | $\left\|\Pi_{1 / 2} 1 / \varphi\right\rangle$ | $\left\|4 \Pi_{-1 / 2} 1 /\right\rangle$ | $\left\|{ }^{2} \Sigma^{+1} \%\right\rangle$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\left\langle{ }^{4} \Pi_{3 / 2}\right.$ \| |  | $\begin{aligned} & -\sqrt{3(1-4)}\left(8-\frac{1}{2} \gamma+A_{0}\right. \\ & \left.-\frac{2}{10} \eta_{0}-20(2-2)-\frac{\pi}{4}\left(\frac{4}{4}+1\right)\right] \end{aligned}$ | $\begin{aligned} & -\sqrt{3(2-1)(2-4)}(20 \\ & \left. \pm \frac{1}{2} 0_{0}\left(1+\frac{1}{2}\right)\right] \end{aligned}$ | $\pm \sqrt{(2-1)(2-4)} / \frac{1}{2} 9$ <br> $+\frac{3}{2} 0_{\mu 24}+\frac{1}{2}(z-2) D_{4}$ $\left.+\tilde{6}^{(2)}\right]$ |  |
| $\left\langle\Pi_{3 / 2}\right\|$ |  |  |  |  |  |
| $\left\langle{ }^{4} \Pi_{1 / 2}\right.$ \| |  |  |  |  | $-\frac{1}{2 \sqrt{5}}{ }^{\pi}+6 \frac{1}{4}{ }^{\left.\frac{1}{4}+1\right)}$ |
| $\left\langle{ }^{4} \Pi_{-1 / 2}\right\|$ |  |  |  |  |  |
| ${ }^{2} \Sigma$ |  |  |  |  |  |

$2=(J+1 / 2)^{2}$
$R=F(F+1)-1(1+1)-J(J+1)$
$G(f, 1, N)=\frac{3(P)+1)-(1+1)(J+1)}{(2-1) /(j+1)(2 L-1)(2+3)}$
$O_{2 \pi}=e^{2} 0_{9 \alpha}\left[3 n^{2}-J(j+i)\right] G(F, 1, J)$
$\tilde{o}^{(\omega)}=e^{2} O_{Q_{2}} G(F, \ldots) / 2$

Figure 3.4: The hyperfine Hamiltonian Matrix for ${ }^{4} \Pi$ states interacting with ${ }^{2} \Sigma^{+}$states.

## Chapter 4

## Analysis of the Spectra

### 4.1 Introduction

This study describes the analysis of the $B^{4} \Pi-X^{4} \Sigma^{-}$transition of VO at sufficiently high resolution that the rotational and hyperfine structure could be well characterized. Even at low resolution, the spectrum of the $B^{4} \Pi-X^{4} \Sigma^{-}(0,0)$ band of VO is fascinating in its complexity. Basically it consists of four red degraded sub-bands resulting from the four electron spin components of the case (a) ${ }^{4} \Pi$ upper state. The branches of the four sub-bands overlap considerably, and the spectrum becomes very confused in those regions where the high- $J$ lines of one spin state run into the low- $J$ lines of the sub-band to the red, as shown in Figure 4.1.

The effects of the smaller splittings of the spin components of the ground state are more subtle, but are clearly discernible. This is illustrated in Figure 4.2, which shows the Fortrat diagram of the branches involving the $\mathrm{F}_{1}$ upper state. The Figure illustrates the relatively large separation between the $Q_{1}$ and ${ }^{Q} R_{12}$ branches which arises primarily from the spin-spin interaction, represented in the Hamiltonian by the term in $\lambda$. By contrast, the ${ }^{\circ} P_{12}$ and ${ }^{\circ} Q_{13}$ branches are nearly degenerate, whilst the ${ }^{\circ} R_{14}$ branch lies approximately $2 \lambda$ away. The magnitude of the spin-spin interaction, and that of the spin-rotation interaction, will be discussed further in the Discussion (Chapter 6).

The $X^{4} \Sigma^{-}$ground state was fairly straight-forward to analyse because there are no low lying electronic states close enough to cause perturbations; it could therefore be treated as


Figure 4.1: The head of the ${ }^{S} Q_{31}$ branch; illustrating the density of the $B^{4} \Pi-X^{4} \Sigma^{-}(0,0)$ band structure.


Figure 4.2: Fortrat diagrams showing transitions involving (a) the e-parity components, and (b) the f-parity components of the $F_{1}$ upper spin state.
a single isolated state. An interesting internal hyperfine perturbation occurs near $\mathrm{N}=15$ between the $F_{2}$ and $F_{3}$ electron spin components of the ground state. This perturbation has been well characterized previously $[1][7][8][10][14][35]$, so that it did not pose a great problem. Details of the analysis of this perturbation are given in Section 4.2.2.

The $B^{4} \Pi-X^{4} \Sigma^{-}$transition is further complicated by sizeable spin-orbit perturbations between the $B^{4} \Pi$ state and the otherwise unseen ${ }^{2} \Sigma^{+}$state (denoted $a$ ) which lies close to it. The effect of this perturbation is nicely illustrated in the Fortrat diagram shown in Figure 4.2, where it is seen that the $a^{2} \Sigma^{+}$state causes the rotational spacing of each branch to collapse before emerging from the other side of the avoided crossing region. Because of this perturbation, the $B^{4} \Pi$ and the $a^{2} \Sigma^{+}$upper states could not be treated separately, but had to be considered simultaneously, with the appropriate interaction terms included in the combined rotational and hyperfine Hamiltonian. In particular the hyperfine structure of the upper state behaves anomalously: the characteristic narrow hyperfine splittings of the $B^{4} \Pi$ state widen as the rotational levels of the $B^{4} \Pi$ and $a^{2} \Sigma^{+}$states approach with increasing $J$, and then diminish again after each local avoided crossing.

### 4.2 The Ground State of VO

### 4.2.1 The Spin-spin and Spin-rotation Interactions

The $X^{4} \Sigma^{-}$state is best described by case $\left(\mathrm{b}_{\beta J}\right)$ coupling because the electron spinspin interaction $(\lambda)$ is much larger than the hyperfine interactions. As mentioned in the Introduction to this Chapter, the effect of the $\lambda$ parameter is clearly seen in the separation of the $\mathrm{F}_{1}^{\prime \prime}$ and $\mathrm{F}_{4}^{\prime \prime}$ lines from the $\mathrm{F}_{2}^{\prime \prime}$ and $\mathrm{F}_{3}^{\prime \prime}$ lines. The four spin components of a ${ }^{4} \Sigma$ state in pure case (b) coupling follow the exact expression[10]

$$
\begin{equation*}
4 \lambda-2 \gamma=F_{2}(N)+F_{3}(N)-F_{1}(N)-F_{4}(N) \tag{4.1}
\end{equation*}
$$



Figure 4.3: The energies of the four electron spin components of the $\mathrm{X}^{4} \Sigma^{-}$state of VO.

Also, because the splitting between adjacent components varies as $\gamma N$, the values of $\lambda$ and $\gamma$ can be estimated from pairs of ground state combinations differences of the type $\mathrm{F}_{2}(N)-\mathrm{F}_{1}(N)$ and $\mathrm{F}_{3}(N)-\mathrm{F}_{4}(N)$, or $\mathrm{F}_{2}(N)-\mathrm{F}_{4}(N)$ and $\mathrm{F}_{3}(N)-\mathrm{F}_{1}(N)$.

The separations of the four spin components of the ground state as a function of $N$ are shown in Figure 4.3. If lines are drawn along the means of the $\mathrm{F}_{2}$ and $\mathrm{F}_{3}$ components and the $\mathrm{F}_{1}$ and $\mathrm{F}_{4}$ components, the distance between these two lines is almost exactly $2 \lambda-\gamma$.

The effect of $\gamma$ on the ground state spin components is to give a clear $N$ dependence,
as shown in Figure 4.3. The separation between the $F_{2}$ and $F_{3}$ spin components is approximately equal to $\gamma N$ at high values of $N$, while the $\mathrm{F}_{1}$ and $\mathrm{F}_{4}$ components show a separation of approximately $3 \gamma N$ at high $N$.

The spin-spin and spin-rotation matrix elements were given explicitly in Chapter 3.

### 4.2.2 The Hyperfine Splitting in the Ground State

Since the $\mathrm{C}^{4} \Sigma^{-}$state also has small hyperfine splittings, Cheung et al. determined that the $\mathrm{F}_{1}: \mathrm{F}_{2}: \mathrm{F}_{3}: \mathrm{F}_{4}$ hyperfine widths of the $\mathrm{C}^{4} \Sigma^{-}-X^{4} \Sigma^{-}$system are in the ratio -3 : $-1: 1: 3$ which means that Hund's case ( $\mathrm{b}_{\beta J}$ ) applies to the $X^{4} \Sigma^{-}$state. Consequently, the $\mathrm{F}_{1}^{\prime \prime}$ and $\mathrm{F}_{4}^{\prime \prime}$ lines are the easiest to analyse in the $B^{4} \Pi-X^{4} \Sigma^{-}$system because they show the widest splittings. The $\mathrm{F}_{1}^{\prime \prime}$ lines could be easily distinguished from the $\mathrm{F}_{4}^{\prime \prime}$ lines because in the former, the position of the high- $F$ component (seen as the component with greatest intensity) is at low frequency. Conversely, in the $\mathrm{F}_{4}^{\prime \prime}$ lines, the position of the high $-F$ component is at high frequency.

For the $B^{4} \Pi-X^{4} \Sigma^{-}$transition of VO, the contribution from the upper state to the hyperfine line width is generally much smaller than the ground state contribution. Therefore the observed hyperfine widths are dominated by the ground state hyperfine splittings. The electron configuration of the $X^{4} \Sigma^{-}$state is $\sigma \delta^{2}$, where the $\sigma$-orbital is derived from the V 4 s atomic orbital. Thus, the large hyperfine splitting of the ground state is primarily due to the Fermi contact interaction of the unpaired $4 s \sigma$ electron, which is not present in the $B^{4} \Pi$ state where the configuration is $\delta^{2} \pi$.

The spacing between adjacent hyperfine components of a particular ro-vibrational transition decreases with decreasing $F$. Thus, barring any perturbations or any severe blending, the assignments of the individual ro-vibrational lines to the appropriate spin components $\mathrm{F}_{1}^{\prime \prime}$ or $\mathrm{F}_{4}^{\prime \prime}$, as well as the $F$-numbering, were straight-forward, as shown in Figure 4.5. The total splitting observed for the $\mathrm{F}_{1}^{\prime \prime}$ and $\mathrm{F}_{4}^{\prime \prime}$ spin components is typically


Figure 4.4: The hyperfine energy level splittings for the $F_{2}$ and $F_{3}$ spin states of the $\mathrm{X}^{4} \Sigma^{-}$state of VO.
of the order of $0.3 \mathrm{~cm}^{-1}$.
The $F$-assignments of the $\mathrm{F}_{2}^{\prime \prime}$ and $\mathrm{F}_{3}^{\prime \prime}$ lines are much more difficult to make than those of the $\mathrm{F}_{1}^{\prime \prime}$ and $\mathrm{F}_{4}^{\prime \prime}$ lines. In 1968, Richards and Barrow [7][8] discovered that transitions involving the $\mathrm{F}_{2}\left(N=J+\frac{1}{2}\right)$ and $\mathrm{F}_{3}\left(N=J-\frac{1}{2}\right)$ electron spin components in the $X^{4} \Sigma^{-}$state of VO are doubled near $\mathrm{N}=15$. Although they could not resolve the hyperfine structure, Richards and Barrow concluded that this unusual doubling occurs because the electron spin contributions to the total energy in those two spin states are accidentally equal at $N=15$ (see Figure 4.3).

In the case of the $F_{2}$ and $F_{3}$ spin components, the matrix elements responsible for the perturbation have $\Delta J= \pm 1$ and $\Delta N=0$. Although the electron spin contributions to $\mathrm{F}_{1}\left(N=J+\frac{3}{2}\right)$ and $\mathrm{F}_{4}\left(N=J-\frac{3}{2}\right)$ are nearly equal at $N=9$, no internal hyperfine perturbation is observed. This is because there are no matrix elements having $\Delta J= \pm 3$ and $\Delta N=0$, which would be required for a direct interaction between these spin states.

Even at sub-Doppler resolution, the analysis of this internal hyperfine perturbation is quite complicated. The extra lines that are induced by this perturbation contribute to the complexity of these spectra. In instances where transitions involving both the $\mathrm{F}_{2}$ and $F_{3}$ spin states of the ground state are allowed by selection rules, the extra lines induced by the $\mathrm{F}_{2}$ spin state are almost exactly blended with the main lines of the $\mathrm{F}_{3}$ spin state and vice versa.

If only one of the spin states, for example $\mathrm{F}_{2}$, has a transition allowed by the selection rules, then the problem of blending with the main lines of the $F_{3}$ spin state will be eliminated since the $\mathrm{F}_{3}$ transitions will not be observed. However, the total intensity of this ro-vibronic transition will be shared between the two eigenstates. An example of this effect is seen in the ${ }^{s} R_{32}$ branch. Figure 4.6 shows how the intensity from seven of the eight hyperfine components of the $N=14$ line appears nominally as the $S_{3}(14)$ line. Those lines having greater than fifty percent $\mathrm{F}_{2}^{\prime \prime}$ character are marked by dashed lines
(a)

(b)


Figure 4.5: (a) The ${ }^{s} Q_{31}(9)$ and (b) the $R_{4}(7)$ lines showing how the hyperfine structures are mirrored.
while the induced lines (those with greater than fifty percent $\mathrm{F}_{3}^{\prime \prime}$ character) are indicated by dotted lines. The full complement of eight hyperfine components for the ${ }^{S} R_{32}(14)$ line is shown, but there are only seven induced lines because there is no $F=18$ hyperfine component in $\mathrm{F}_{3}^{\prime \prime}$ spin state for $N=14$. The $F=18$ hyperfine line of ${ }^{s} R_{32}(14)$ is thus unperturbed and appears as a sharp line at $12653.3064 \mathrm{~cm}^{-1}$.

The hyperfine energy levels for the $\mathrm{F}_{2}^{\prime \prime}$ and $\mathrm{F}_{3}^{\prime \prime}$ spin states are shown in Figure 4.4. This illustration clearly shows the avoided crossing of seven of the eight hyperfine components for both spin states near $N=15$. The $F=N+4$ and the $F=N-4$ hyperfine components of the $F_{2}$ and $F_{3}$ spin states respectively are free from this internal hyperfine perturbation. Lines resulting from transitions involving these unperturbed levels near $N=15$ will generally appear as intense sharp lines between the broader features of the perturbation.

The precise assignment of the spin indices for the individual hyperfine components involving the $\mathrm{F}_{2}^{\prime \prime}$ and $\mathrm{F}_{3}^{\prime \prime}$ states becomes ambiguous near the perturbation. This is evident in the assignments of the ${ }^{s} R_{32}(14)$ features shown in Figure 4.6. The feature which on first inspection appears to be the $F=17$ hyperfine component of the ${ }^{S} R_{32}$ (14) main line (at $12653.4043 \mathrm{~cm}^{-1}$ ) turns out to have predominantly $\mathrm{F}_{3}^{\prime \prime}$ character, ${ }^{1}$ and is in fact the induced $F=17$ line from the $S_{3}(14)$ branch. This line is normally forbidden according to the usual spectroscopic selection rules. The main line hyperfine component appears at $12653.2593 \mathrm{~cm}^{-1}$.

[^4]

Figure 4.6: Plot of the ${ }^{S} R_{32}(14)$ line including induced lines from the internal hyperfine perturbation.

### 4.3 The $B^{4} \Pi$ State

The $B^{4} \Pi$ state of VO is very strongly perturbed, so that it cannot be described without at the same time considering the $a^{2} \Sigma^{+}$perturbing state. This is particularly true of the $\Lambda$-type splitting and the hyperfine structure of the $F_{1}$ and $F_{2}$ spin components, which are the ones most severely affected by the $a^{2} \Sigma^{+}$state.

However, the interaction with the $a^{2} \Sigma^{+}$state does not completely mask all the information which can be obtained about the $B^{4} \Pi$ state from the $B^{4} \Pi-X^{4} \Sigma^{-}(0,0)$ band. The sub-band origins are essentially unperturbed, and the $\mathrm{F}_{3}$ and $\mathrm{F}_{4}$ electron spin components are completely free from the first order perturbation effects of the $a^{2} \Sigma^{+}$state.

### 4.3.1 The Spin-orbit Splitting of the $B^{4} \Pi$ State

Since the four electron spin components of the $B^{4} \Pi$ state of VO lie some distance apart, it is convenient to determine the origins, $\mathrm{T}_{\Omega}$, for each sub-state separately. The spacing of the spin components, which mostly reflects the first order spin-orbit parameter $A$, is evident in Figure 4.7 ; it is seen that $A$ is approximately $65 \mathrm{~cm}^{-1}$. Closer inspection of the sub-band origins shows that the separations are not exactly equal, with

$$
\begin{aligned}
T_{\frac{5}{2}}-T_{\frac{3}{2}} & =74.7440 \mathrm{~cm}^{-1} \\
T_{\frac{3}{2}}-T_{\frac{1}{2}} & =65.4295 \mathrm{~cm}^{-1} \\
T_{\frac{1}{2}}-T_{-\frac{1}{2}} & =53.3464 \mathrm{~cm}^{-1}
\end{aligned}
$$

Further insight into the $B^{4} \Pi$ state provided by these spin-orbit parameters is found in the Discussion (Chapter 6).


Figure 4.7: The upper state electronic term energies as a function of $\left(J+\frac{1}{2}\right)^{2}$.

### 4.3.2 The $\Lambda$-type Doubling in the $B^{4} \Pi$ State

All states with $\Lambda>0$ are doubly degenerate because the projection of $\mathbf{L}$ along the internuclear axis, $\Lambda$, is a signed quantity, and in the absence of other effects, the energies of the two components, with positive and negative values of $\Lambda$, are the same. The degeneracy is lifted by interactions with $\Sigma$ states $(\Lambda=0)$ which have no such degeneracy. The resulting separation of the otherwise degenerate levels is known as $\Lambda$-type doubling. The $\Lambda$-type doubling in the $B^{4} \Pi$ state becomes confused at the avoided crossings with the $a^{2} \Sigma^{+}$state. This fact is evident in Figure 4.8, where the avoided crossings cause discontinuities in the $\Lambda$-type doubling plots. The smallest $\Lambda$-type doubling occurs in the $\mathrm{F}_{4}$ spin component with that in the $\mathrm{F}_{3}$ sub-state being the next smallest. Despite the confusion caused by the $a^{2} \Sigma^{+}$perturbation, this observed decrease in $\Lambda$-type splitting as $\Omega$ increases agrees with the predicted trend [22][23].

### 4.4 The Interaction Between the $B^{4} \Pi$ and $a^{2} \Sigma^{+}$States

Avoided crossings occur at each place where the $B^{4} \Pi$ and $a^{2} \Sigma^{+}$levels with the same $J$-value happen to lie at approximately equal energy. There are three avoided crossings in the accessible range of $J$-values in the $B^{4} \Pi-X^{4} \Sigma^{-}(0,0)$ band. The best characterised crossing affects the ${ }^{4} \Pi_{-\frac{1}{2} f}$ levels at $J \sim 36.5$. It takes the form of a $12 \mathrm{~cm}^{-1}$ gap in the branches having the ${ }^{4} \Pi_{-\frac{1}{2} f}$ levels as upper state. The most intense branch of this type is the $Q_{1}$. Unfortunately the most severely affected lines of the $Q_{1}$ branch lie under the heads formed by the ${ }^{4} \Pi_{-\frac{1}{2} e}$ branches so that it is not easy to follow the course of the branch at the most critical places. The pattern of the levels can also be seen in the ${ }^{\circ} Q_{13}$ and ${ }^{O} P_{12}$ branches, but these lines are not strong enough to be seen in the sub-Doppler spectra. In fact, the level structure is quite confused near these avoided crossings, and the rotational assignments had to be made with extensive wavelength resolved fluorescence


Figure 4.8: Plot of the $\Lambda$-type splittings of the four spin states of $B^{4} \Pi$
measurements.
Two other avoided crossings between the $a^{2} \Sigma^{+}$and the $B^{4} \Pi$ states were similarly characterized at Doppler-limited resolution. An avoided crossing pattern in the ${ }^{P} Q_{12}$ branch with a width of about $22.5 \mathrm{~cm}^{-1}$ gave the magnitude of the interaction between the ${ }^{4} \Pi_{-\frac{1}{2} e}$ levels and the $a^{2} \Sigma^{+}$state, while a similar pattern in the ${ }^{P} Q_{23}$ branch, with a width of $18.8 \mathrm{~cm}^{-1}$, gives the details of the ${ }^{4} \Pi_{\frac{1}{2} f} / a^{2} \Sigma^{+}$interaction.

No direct information describing the interaction between the $a^{2} \Sigma^{+}$and the ${ }^{4} \Pi_{\frac{1}{2} e}$ component could be obtained because the avoided crossing is predicted to occur near $\mathrm{J}=70.5$. The VO molecules are produced in the reaction cell at temperatures that are too low for these levels to be appreciably populated, and thus no ro-vibrational transitions involving the ${ }^{4} \Pi_{\frac{1}{2} e^{-}}-^{2} \Sigma_{e}^{+}$interaction were observed.

Even though the $a^{2} \Sigma^{+}$state cannot interact directly with the $F_{3}$ and $F_{4}$ spin components of the $B^{4} \Pi$ state, these sub-states are nevertheless perturbed in second order through spin-uncoupling interactions. The perturbation manifests itself in the $\Lambda$-type doubling of the $F_{3}$ and $F_{4}$ sub-states (Figure 4.8). The observed effect of the perturbation on the $\Lambda$-type splitting of the $\mathrm{F}_{3}$ spin component is significant, and in fact an avoided crossing is predicted for $J=77.5$. The effect on the ${ }^{4} \Pi_{\frac{5}{2}}$ sub-state is much smaller, and it appears essentially unperturbed.

The $a^{2} \Sigma^{+}$state has the same electron configuration as the $X^{4} \Sigma^{-}$state, namely $\sigma \delta^{2}$. Like the ground state, the $a^{2} \Sigma^{+}$state has wide hyperfine splittings because of the large Fermi contact parameter arising from the unpaired $4 s \sigma$ electron. Evidence of the $a^{2} \Sigma^{+}$perturbation as it affects the hyperfine structure of the upper state is shown in Figure 4.11. Both of the branches shown involve the same upper spin-state, namely $B^{4} \Pi_{-\frac{1}{2} f}$. Near $J=37.5$, this spin state has approximately fifty percent $a^{2} \Sigma_{f}^{+}$character, so the hyperfine structure of this sub-state reflects the $a^{2} \Sigma_{f}^{+}$contribution. Consequently, the hyperfine widths of the $Q_{1}$ and ${ }^{\circ} P_{12}$ branches become larger near the avoided crossing


Figure 4.9: The hyperfine energy levels of the $B^{4} \Pi_{-\frac{1}{2} f}$ and $a^{2} \Sigma_{f}^{+}$states.


Figure 4.10: The hyperfine energy levels of the $B^{4} \Pi_{-\frac{1}{2} e}$ and $a^{2} \Sigma_{e}^{+}$states.


Figure 4.11: The hyperfine widths of (a) the $Q_{1}$ branch, and (b) the ${ }^{o} P_{12}$ branch.
because of this increased $a^{2} \Sigma^{+}$character. Once past the avoided crossing, the hyperfine widths return to normal. The predicted hyperfine widths of the nominally-forbidden $a^{2} \Sigma^{+}-X^{4} \Sigma^{-}$branches are shown by dashed lines. It should be noted that the three extra lines of the ${ }^{\circ} P_{12}$ branch, whose hyperfine widths were measured, fit the calculated widths very well.

## Chapter 5

## Results

The parameters needed to describe the states of the $B^{4} \Pi-X^{4} \Sigma^{-}(0,0)$ band of VO were determined in three stages. First, preliminary assignments of the IMF spectra enabled ground state combination differences to be calculated. These combination differences, along with three microwave lines measured by Suenram et al.[36] using FT-microwave spectroscopy, were then used in a fit of the ground state only. This fit served to confirm that the spectral lines had been correctly assigned, and permitted the assignment of many previously unassigned features in the IMF spectra.

| Parameter | Value $\left(\mathrm{cm}^{-1}\right)$ |  |
| :---: | :--- | :--- |
| $\mathrm{T}_{0}$ | 0.0 | -fixed- |
| B | 0.5453713 | $\pm 0.0000017$ |
| $10^{6} \mathrm{D}$ | 0.6491 | $\pm 0.0009$ |
| $\gamma$ | 0.022426 | $\pm 0.000004$ |
| $\lambda$ | 2.03090 | $\pm 0.00004$ |
| b | 0.027435 | $\pm 0.000002$ |
| c | -0.00450 | $\pm 0.00005$ |
| $\mathrm{e}^{2} \mathrm{Qq}$ | 0.00134 | $\pm 0.00048$ |
| $10^{5} \gamma_{D}$ | 0.0060 | $\pm 0.0005$ |
| $10^{5} \lambda_{D}$ | 0.038 | $\pm 0.007$ |
| $10^{5} \gamma_{s}$ | 0.810 | $\pm 0.095$ |
| $10^{5} \mathrm{~b}_{s}$ | -1.58 | $\pm 0.37$ |

Table 5.1: The constants for the $X^{4} \Sigma^{-}(\mathrm{v}=0)$ state of VO

The second stage involved a rotational fit of the $B^{4} \Pi-X^{4} \Sigma^{-}$transition. The hyperfine structure of each rotational line was averaged to estimate the rotational transition

| Parameter | Value $\left(\mathrm{cm}^{-1}\right)$ |  |
| :---: | :---: | :---: |
| $\mathrm{T}_{0}$ | 12432.9406 | $\pm 0.0476$ |
| B | 0.54304 | $\pm 0.00003$ |
| $10^{6} \mathrm{D}$ | 0.65 | -fixed- |
| $\gamma$ | -0.0396 | $\pm 0.0019$ |
| b | 0.0930 | $\pm 0.0008$ |
| $\left.\left.\left\langle{ }^{4} \Pi_{\frac{1}{2}}\right\| \mathcal{H}_{s o}\right\|^{2} \Sigma^{+}\right\rangle$ | 20.430 | $\pm 0.076$ |
| $\left.\left.\left\langle{ }^{4} \Pi_{-\frac{1}{2}}\right\| \mathcal{H}_{s o}\right\|^{2} \Sigma_{f}^{+}\right\rangle$ | 20.404 | $\pm 0.021$ |
| $\left.\left.\left\langle{ }^{4} \Pi_{-\frac{1}{2} e}\right\| \mathcal{H}_{s o}\right\|^{2} \Sigma_{e}^{+}\right\rangle$ | 20.417 | $\pm 0.020$ |
| e | 0.0 | -fixed- |

Table 5.2: The constants for the $a^{2} \Sigma^{+}(\mathrm{v}=2)$ state of VO.
energy. Also included in the rotational fit were some high-J emission lines recorded photographically some years ago in this laboratory, and recorded also by Fourier transform methods at Kitt Peak National Observatory. This fit gave an estimate of the rotational and electron-spin parameters of the upper state, and a good measure of the spin-orbit interaction between the $B^{4} \Pi$ and $a^{2} \Sigma^{+}$states.

The third and final stage involved the full hyperfine fit of the $B^{4} \Pi-X^{4} \Sigma^{-}$transition. In all, 3211 lines were used in the fit including the three microwave lines. The final fit gave an rms error of $0.00038 \mathrm{~cm}^{-1}$, and the values of the parameters for the $X^{4} \Sigma^{-}$, $a^{2} \Sigma^{+}$, and $B^{4} \Pi$ states are given in Tables $5.1,5.2$, and 5.3 respectively. The reported errors represent three standard deviations.

The combination difference and rotational fits were run on a DEC-MICROVAX II minicomputer while the full hyperfine fit was run on an IBM RISC-6000 computer.

| Parameter | Value $\left(\mathrm{cm}^{-1}\right)$ |  |
| :---: | :---: | :--- |
| $\mathrm{T}_{\frac{s}{2}}$ | 12711.8260 | $\pm 0.0001$ |
| $\mathrm{~T}_{\frac{3}{2}}$ | 12637.1180 | $\pm 0.0001$ |
| $\mathrm{~T}_{\frac{1}{2}}$ | 12571.6885 | $\pm 0.0019$ |
| $\mathrm{~T}_{-\frac{1}{2}}^{2}$ | 12518.3421 | $\pm 0.0024$ |
| $\mathrm{~B}^{2}$ | 0.5126525 | $\pm 0.0000018$ |
| $10^{6} \mathrm{D}$ | 0.6634 | $\pm 0.0009$ |
| $10^{4} \mathrm{~A}_{D}$ | -0.69 | $\pm 0.04$ |
| $10^{5} \lambda_{D}$ | -0.28 | $\pm 0.05$ |
| $\eta{ }_{D}$ | 0.0 | - -fixed- |
| $\gamma$ | 0.0336 | $\pm 0.0000$ |
| $\mathrm{o}+\mathrm{p}+\mathrm{q}$ | 1.131 | $\pm 0.001$ |
| p 2 q | 0.03609 | $\pm 0.00002$ |
| q | 0.0001733 | $\pm 0.0000011$ |
| $10^{5} \mathrm{D}_{o+p+q}$ | 0.16 | $\pm 0.05$ |
| $10^{5} \mathrm{D}_{p+2 q}$ | -0.0041 | $\pm 0.0014$ |
| $10^{5} \mathrm{D}_{q}$ | -0.00037 | $\pm 0.00009$ |
| $\mathrm{e}^{2} \mathrm{Qq}$ | 0.00157 | $\pm 0.00055$ |
| a | 0.0109 | $\pm 0.0002$ |
| b | -0.00898 | $\pm 0.00003$ |
| c | -0.00508 | $\pm 0.00015$ |
| d | -0.00359 | $\pm 0.00003$ |
| $\mathrm{e}^{2} \mathrm{Qq} q_{2}$ | 0.0 | - fixed- |

Table 5.3: The constants for the $B^{4} \Pi$ ( $\mathrm{v}=0$ ) state of VO

## Chapter 6

## Discussion

### 6.1 Rotational Structure

The spectrum of the VO $B^{4} \Pi-X^{4} \Sigma^{-}(0,0)$ band shows red-degraded branch structure, indicating that the effective rotational constant of the $X^{4} \Sigma^{-}$state is larger than that of the $B^{4} \Pi$ state. The rotational constant $B$ (in $\mathrm{cm}^{-1}$ ) is defined by

$$
\begin{equation*}
B=\frac{h}{8 \pi^{2} I c} \tag{6.1}
\end{equation*}
$$

where $h$ is the Planck constant, $c$ is the speed of light and $I$ is the moment of inertia of the molecule, given by

$$
\begin{equation*}
I=\mu r^{2} \tag{6.2}
\end{equation*}
$$

In this equation $\mu$ is the reduced mass of the molecule and $r$ is the bond length. The reduced mass of ${ }^{51} \mathrm{~V}^{16} \mathrm{O}$ is $12.1729611_{9}$ amu [38], which enables the bond length in a particular vibrational level of any electronic state to be calculated from Equations (2.1) and (2.2). The bond lengths in the observed vibrational levels of the $a^{2} \Sigma^{+}, B^{4} \Pi$, and $X^{4} \Sigma^{-}$states are shown in Table 6.1. This Table also includes results from the fit of the $(1,0)$ band, obtained by Huang et al.[37], and the $(0,1)$ band of the $A^{4} \Pi$ $X^{4} \Sigma^{-}$transition[35].

In the rigid rotator approximation it is expected that $r$, and therefore $B$, would be invariant to the vibrational level. The results listed in Table 6.1 show that there is an interaction between rotation and vibration. This interaction is described by the

| State | $B_{v}\left(\mathrm{~cm}^{-1}\right)$ |  | $r(\AA)$ |
| :---: | :--- | :--- | :--- |
| $X^{4} \Sigma^{-}(\mathrm{v}=0)$ | 0.5463713 | $\pm 0.0000017$ | 1.5920 |
| $X^{4} \Sigma^{-}(\mathrm{v}=1)^{a}$ | 0.542864 | $\pm 0.000013$ | 1.5972 |
| $B^{4} \Pi(\mathrm{v}=0)$ | 0.5126525 | $\pm 0.0000018$ | 1.6436 |
| $B^{4} \Pi(\mathrm{v}=1)^{b}$ | 0.5094926 | $\pm 0.0000264$ | 1.6487 |
| $a^{2} \Sigma^{+}(\mathrm{v}=2)$ | 0.5430436 | $\pm 0.0000292$ | 1.5969 |
| $a^{2} \Sigma^{+}(\mathrm{v}=3)^{b}$ | 0.54044 | $\pm 0.00013$ | 1.6007 |

Table 6.1: The rotational constants and average bond lengths of the states of the VO $B^{4} \Pi-X^{4} \Sigma^{-}$transition.

[^5]rotation-vibration coupling constant $\alpha_{e}$ [22],
\[

$$
\begin{equation*}
B_{v}=B_{e}-\alpha_{e}\left(v+\frac{1}{2}\right)+\cdots \tag{6.3}
\end{equation*}
$$

\]

where $B_{e}$ represents the equilibrium rotational constant. Given the value of $B_{e}$, the equilibrium bond length can be determined. The equilibrium bond lengths are given, along with the values for the rotation-vibration coupling constants and the equilibrium rotational constants, for the $B^{4} \Pi$ and $X^{4} \Sigma^{-}$states in Table 6.2.

### 6.2 Electron Configurations

The ground state valence electron configuration of VO was predicted to be $\sigma \delta^{2}$ by Carlson and Moser[5]. The nearly equal bond lengths of the $a^{2} \Sigma^{+}$and $X^{4} \Sigma^{-}$states are evidence that the two states have the same electron configuration in the single configuration approximation. The very slight difference between the two arises from the interelectron repulsion in the higher multiplicity state and from configuration mixing of the two states with states of other configurations.

| State | $B_{e}\left(\mathrm{~cm}^{-1}\right)$ | $\alpha_{e}\left(\mathrm{~cm}^{-1}\right)$ | $r_{e}(\AA)$ |
| :---: | :--- | :--- | :--- |
| $X^{4} \Sigma^{-}$ | $0.5481_{25}$ | $0.0030_{7}$ | $1.583_{7}$ |
| $B^{4} \Pi$ | $0.5142_{3}$ | $0.0031_{6}$ | $1.635_{1}$ |
| $a^{2} \Sigma^{+}$ | $0.549_{5}$ | $0.002_{6}$ | $1.58_{2}$ |

Table 6.2: Table of the equilibrium rotational constants from the $B^{4} \Pi-X^{4} \Sigma^{-}$transition.

In the single configuration approximation, the $B^{4} \Pi$ state is described by the configuration $\delta^{2} \pi[14]$. The longer equilibrium bond length in the $B^{4} \Pi$ state compared to the $a^{2} \Sigma^{+}$and $X^{4} \Sigma^{-}$states suggests that the $4 \pi$ molecular orbital of the $\delta^{2} \pi$ configuration is slightly more anti-bonding in character than the $9 \sigma$ molecular orbital occupied in the ground state (see Figure 1.1).

Strong evidence that one of the electrons in the ground state configuration is in an orbital derived from the vanadium $4 s$ atomic orbital comes from the hyperfine splitting. The Fermi contact interaction is the largest contribution to the hyperfine structure of the $X^{4} \Sigma^{-}$state. The magnitude of the contact parameter is proportional to the probability that an electron is to be found inside the nucleus. Since only $s$ atomic orbitals have wavefunctions which are non-vanishing at the nucleus, the large Fermi contact interaction indicates the presence of an unpaired electron that has appreciable atomic $s$ character. The Fermi contact parameter, $b_{F}$, is related to the experimentally determinable magnetic hyperfine parameters, $b$ and $c$, by

$$
\begin{equation*}
b_{F}=b+\frac{1}{3} c \tag{6.4}
\end{equation*}
$$

and is equal to $0.02593_{5} \mathrm{~cm}^{-1}$ for the $X^{4} \Sigma^{-}$state.
In a study of the $3 d^{4} 4 s$ configuration of atomic ${ }^{51} \mathrm{~V}$, Childs et al.[43] determined the value of the contact parameter of the $4 s$ electron to be $0.1036 \mathrm{~cm}^{-1}$. Allowing for the difference in spin multiplicity, which introduces a factor of 3 , the Fermi contact
parameter of the $X^{4} \Sigma^{-}$state is $75.1 \%$ of the atomic contact parameter, which proves that the electron configuration of the $X^{4} \Sigma^{-}$state indeed has an unpaired electron with primarily $4 s$ atomic ${ }^{51} \mathrm{~V}$ character. In single configuration approximation, this electron must therefore occupy the ( $4 s \sigma$ ) molecular orbital.

Similarly, the $a^{2} \Sigma^{+}$state also exhibits large hyperfine splittings; the contact interaction is even larger than in the $X^{4} \Sigma^{-}$state, and amounts to $89.8 \%$ of the value for $\mathrm{V}(4 s)$. As in the $X^{4} \Sigma^{-}$state, there must be an unpaired electron occupying the ( $4 s \sigma$ ) MO. Thus, the $a^{2} \Sigma^{+}$state has the same configuration as the $X^{4} \Sigma^{-}$state, namely $(4 s \sigma)^{1}(3 d \delta)^{2}$. The difference between the values of the two parameters can be attributed to the degree of configuration interaction in the two states.

### 6.3 The Molecular Spin-Orbit Parameters

The four components of the $B^{4} \Pi$ state were fitted to a model that used four sub-band origins $T_{\Omega}$, rather than spin parameters of high order. The two models are related, through the diagonal elements of the spin-rotation and spin-orbit interactions, by

$$
\begin{align*}
T_{\Omega}= & T_{0}+A \Lambda \Sigma+\frac{2}{3} \lambda\left[3 \Sigma^{2}-S(S+1)\right]+\gamma\left[\Sigma^{2}-S(S+1)\right] \\
& +\eta \Lambda\left[\Sigma^{3}-\left(3 S^{2}+3 S+1\right) \Sigma / 5\right] \tag{6.5}
\end{align*}
$$

Since the spin-rotation parameter $\gamma$ has been determined independently of the subband origins, there are four sub-band origins $\mathrm{T}_{\Omega}$ which can be used to give the four parameters $\mathrm{T}_{0}, A, \lambda$, and $\eta$. The values obtained for the four sub-band origins and $\gamma$ for the $B^{4} \Pi(\mathrm{v}=0)$ state of VO are given in Table 6.3; the reported error limits are three standard deviations. The band origin and the three spin-orbit parameters were determined with the help of Equation (6.5); they are listed in Table 6.4.

| Parameter | Value $\left(\mathrm{cm}^{-1}\right)$ |
| :---: | :---: |
| $\mathrm{T}_{\frac{5}{2}}$ | $12711.8260 \pm 0.0001$ |
| $\mathrm{~T}_{\frac{3}{2}}$ | $12637.1180 \pm 0.0001$ |
| $\mathrm{~T}_{\frac{1}{2}}$ | $12571.6885 \pm 0.0019$ |
| $\mathrm{~T}_{-\frac{1}{2}}$ | $12518.3421 \pm 0.0024$ |
| $\gamma^{2}$ | $0.0336 \pm 0.0002$ |

Table 6.3: Table of the four sub-band origins of the $B^{4} \Pi$ state.

As expected, the estimate of $65 \mathrm{~cm}^{-1}$ for the first order spin-orbit splitting was close to the calculated value. The next largest spin-orbit contribution is, not surprisingly, the second order parameter $\lambda$. The $\lambda$ term comes mostly from the interaction between the $B^{4} \Pi$ state and other states from the same configuration. Since the spin-orbit operator has matrix elements diagonal in $\Omega,{ }^{2} \Pi$ states, which have $\Omega=\frac{3}{2}$ and $\frac{1}{2}$ spin components only, will interact with the $\Omega=\frac{3}{2}$ and $\frac{1}{2}$ sub-states of the $B^{4} \Pi$ state, but not with the $\Omega=\frac{5}{2}$ and $-\frac{1}{2}$ sub-states. Hence, the ${ }^{4} \Pi_{\frac{3}{2}}$ and the ${ }^{4} \Pi_{\frac{1}{2}}$ spin states will be shifted relative to the others; the specific form of the operator is such that this shift is $4 \lambda$. The sign of $\lambda$ suggests that the ${ }^{2} \Pi$ states lie above the $B^{4} \Pi$ state, since the two spin states involved in the interaction are pushed down in energy. However, there are two ${ }^{2} \Pi$ states given by the valence electron configuration $\delta^{2} \pi$. Since there is only one parameter $\lambda$ that can be determined, there is not enough information to deduce where they both lie.

The Slater determinant form for the $B^{4} \Pi$ wavefunction, omitting the electron spin factors, is given by

$$
\begin{equation*}
\psi_{s p a t i a l}=\left|\delta^{2+} \delta^{2-} \pi\right| \tag{6.6}
\end{equation*}
$$

The orbital angular momenta of the $\delta$-electrons cancel, so that the spin-orbit coupling

| Parameter | Value $\left(\mathrm{cm}^{-1}\right)$ |
| :---: | ---: |
| $\mathrm{T}_{0}$ | $12609.8367 \pm 0.0017$ |
| $A$ | $64.5989 \pm 0.0008$ |
| $\lambda$ | $2.6580 \pm 0.0002$ |
| $\eta$ | $-0.4614 \pm 0.0005$ |

Table 6.4: The band origin and higher spin-orbit parameters of the $B^{4} \Pi$ state.
constant of the $B^{4} \Pi$ state comes from the $\pi$-electron. The microscopic spin-orbit parameter for this $\pi$-electron is given by[24]

$$
\begin{equation*}
a_{\pi}=3 A \Lambda=3 \times 64.5989 \mathrm{~cm}^{-1}=193.797 \mathrm{~cm}^{-1} \tag{6.7}
\end{equation*}
$$

This value for $a_{\pi}$ is consistent with the values obtained from the $A^{4} \Phi, A^{4} \Pi$ and $1^{2} \Pi$ states which have configurations $\sigma \delta \pi, \sigma \delta \pi$ and $\sigma^{2} \pi$ respectively[14], thus providing further confirmation that the configuration of the $B^{4} \Pi$ state is indeed $\delta^{2} \pi$.

The $X^{4} \Sigma^{-}$state can have no first order spin-orbit effects since $\Lambda=0$. There are, however, second order spin-orbit interactions between the $X^{4} \Sigma^{-}$state and other states from the same electron configuration[24]. Perversely, the second order spin-orbit Hamiltonian has the same operator form as the first order electron spin-spin dipolar Hamiltonian. Consequently, the experimentally determined parameter $\lambda$ for the $X^{4} \Sigma^{-}$state is an effective parameter, given by

$$
\lambda=\lambda_{s o}+\lambda_{s s}
$$

where $\lambda_{s o}$ is the second order spin-orbit interaction parameter and $\lambda_{s s}$ is the electron spin-spin interaction parameter. There is no way of estimating $\lambda_{s s}$ except from ab initio calculations, and in any case it is likely to be small campared to $\lambda_{s o}$; it will not be considered further.

The most likely contribution to $\lambda_{s o}$ is from the interaction between the ${ }^{4} \Sigma_{\frac{1}{2}}^{-}$spin component of the ground state and the ${ }^{2} \Sigma_{\frac{1}{2}}^{+}$spin component of the $a^{2} \Sigma^{+}$state. The Slater determinants for these sub-states are given by

$$
\begin{align*}
& \left|{ }^{4} \Sigma_{\frac{1}{2}}^{-}\right\rangle=\frac{1}{\sqrt{3}}\left[\left|\delta^{+} \alpha \delta^{-} \beta \sigma \alpha\right|+\left|\delta^{+} \beta \delta^{-} \alpha \sigma \alpha\right|+\left|\delta^{+} \alpha \delta^{-} \alpha \sigma \beta\right|\right]  \tag{6.8}\\
& \left|{ }^{2} \Sigma_{\frac{1}{2}}^{+}\right\rangle=\frac{1}{\sqrt{2}}\left[\left|\delta^{+} \alpha \delta^{-} \beta \sigma \alpha\right|-\left|\delta^{+} \beta \delta^{-} \alpha \sigma \alpha\right|\right] \tag{6.9}
\end{align*}
$$

Since both states have $\Lambda=0$, only those terms in the spin-orbit Hamiltonian of the form $\Delta \Lambda=\Delta \Sigma=0$ need be considered. Hence, the microscopic spin-orbit Hamiltonian given in Chapter 3 can be simplified as

$$
\begin{equation*}
\mathcal{H}_{s o}=\sum_{i} a_{i} l_{z i} s_{z i} \tag{6.10}
\end{equation*}
$$

The spin-orbit matrix element between the ${ }^{4} \Sigma_{\frac{1}{2}}^{-}$and ${ }^{2} \Sigma_{\frac{1}{2}}^{+}$spin components is easily shown to be

$$
\begin{equation*}
\left.\left.\left\langle{ }^{4} \Sigma_{\frac{1}{2}}^{-}\right| \mathcal{H}_{s o}\right|^{2} \Sigma_{\frac{1}{2}}^{+}\right\rangle=\frac{4 a_{\delta}}{\sqrt{6}} \tag{6.11}
\end{equation*}
$$

where $a_{\delta}$ is the microscopic first order spin-orbit parameter for a $3 d \delta$ electron. The value of $a_{\delta}$ can be obtained from the $\sigma \delta \sigma^{*}{ }^{4} \Delta$ state of VO, and is approximately 150 $\mathrm{cm}^{-1}[14]$; this gives the matrix element ( 6.11 ) as roughly $245 \mathrm{~cm}^{-1}$. Since the separation $\mathrm{E}\left({ }^{4} \Sigma_{\frac{1}{2}}^{-}\right)-\mathrm{E}\left({ }^{4} \Sigma_{\frac{3}{2}}^{-}\right)$is $4 \lambda, \lambda_{s o}$ is given by

$$
\begin{equation*}
\lambda_{s o}=\frac{1}{4} \frac{\left.\left|\left\langle{ }^{4} \Sigma_{\frac{1}{2}}^{-}\right| \mathcal{H}_{s o}\right|{ }^{2} \Sigma_{\frac{1}{2}}^{+}\right\rangle\left.\right|^{2}}{\mathrm{E}\left({ }^{2} \Sigma_{\frac{1}{2}}^{+}\right)-\mathrm{E}\left({ }^{4} \Sigma_{\frac{1}{2}}^{-}\right)} \simeq \frac{1}{4} \frac{(245)^{2}}{10412} \simeq 1.44 \mathrm{~cm}^{-1} \tag{6.12}
\end{equation*}
$$

The experimental value of the effective $\lambda$ parameter is $2.03090 \mathrm{~cm}^{-1}$. Therefore, the spin-orbit contribution from the $a^{2} \Sigma^{+}$state represents $71.0 \%$ of the total effective $\lambda$ parameter of the $X^{4} \Sigma^{-}$state of VO.

### 6.4 The $B^{4} \Pi / a^{2} \Sigma^{+}$Perturbation

The Slater determinant function for the ${ }^{4} \Pi_{\frac{1}{2}}$ sub-state is

$$
\begin{equation*}
\left|{ }^{4} \Pi_{\frac{1}{2}}\right\rangle=\frac{1}{\sqrt{3}}\left[\left|\delta^{+} \beta \delta^{-} \beta \pi \alpha\right|+\left|\delta^{+} \beta \delta^{-} \alpha \pi \beta\right|+\left|\delta^{+} \alpha \delta^{-} \beta \pi \beta\right|\right] \tag{6.13}
\end{equation*}
$$

The spin-orbit interaction matrix element between $B^{4} \Pi_{\frac{1}{2}}$ and $a^{2} \Sigma_{\frac{1}{2}}^{+}$can be shown to be zero. The only non-vanishing contributions come from the interactions between:

$$
\left.\langle | \delta^{+} \beta \delta^{-} \alpha \pi \beta \mid \text { and }-\left|\delta^{+} \beta \delta^{-} \alpha \sigma \alpha\right|\right\rangle, \text { which gives }-\frac{1}{2} a_{3}[l(l+1)]^{\frac{1}{2}}
$$

and between $\langle | \delta^{+} \alpha \delta^{-} \beta \pi \beta \mid$ and $\left.-\left|\delta^{+} \alpha \delta^{-} \beta \sigma \alpha\right|\right\rangle$, which gives $\frac{1}{2} a_{3}[l(l+1)]^{\frac{1}{2}}$.
These two terms cancel, indicating that the ${ }^{4} \Pi /^{2} \Sigma^{+}$perturbation cannot occur by a first order spin-orbit interaction mechanism.

Furthermore, the $\sigma$-electron is $4 s \sigma$ and the $\pi$-electron is $3 d \pi$. Consequently, the $l_{+}$ operator is being required to ladder a $4 s \sigma$ electron into a $3 d \pi$ orbital, that is with $\Delta l=2$. Similarly, $l_{-}$is required to give $\Delta l=-2$ matrix elements. Neither is possible.

However, the $B^{4} \Pi$ state is indeed perturbed by the $a^{2} \Sigma^{+}$state. Therefore, a higher order mechanism must exist that links the two states. The relative magnitudes of the various matrix elements can be calculated by the Wigner-Eckart theorem:

$$
\left\langle S^{\prime} \Sigma^{\prime} \Lambda^{\prime}\right| \mathcal{H}_{s o}|S \Sigma \Lambda\rangle=(-1)^{S^{\prime-\Sigma \prime}}\left(\begin{array}{ccc}
S^{\prime} & 1 & S  \tag{6.14}\\
-\Sigma^{\prime} & q & \Sigma
\end{array}\right)\left\langle S^{\prime} \Lambda^{\prime}\left\|\mathcal{H}_{s o}\right\| S \Lambda\right\rangle \delta_{\Omega \Omega^{\prime}}
$$

This gives four non-zero elements. In a parity basis, the elements are

$$
\begin{equation*}
\left\langle{ }^{4} \Pi_{\frac{1}{2}}{ }_{f}^{e}\right| \mathcal{H}_{s o}\left|{ }^{2} \Sigma^{+}{ }_{, F_{2}}^{F_{1}}\right\rangle=\frac{1}{2 \sqrt{3}}\left\langle{ }^{4} \Pi\left\|\mathcal{H}_{s o}\right\|^{2} \Sigma^{+}\right\rangle \tag{6.15}
\end{equation*}
$$

and

$$
\begin{equation*}
\left\langle{ }^{4} \Pi_{-\frac{1}{2}},{ }_{f}^{e}\right| \mathcal{H}_{s o}\left|{ }^{2} \Sigma^{+}, F_{F_{2}}\right\rangle= \pm \frac{1}{2}\left\langle{ }^{4} \Pi\left\|\mathcal{H}_{s o}\right\|^{2} \Sigma^{+}\right\rangle \tag{6.16}
\end{equation*}
$$

where the reduced matrix element $\left\langle{ }^{4} \Pi\left\|\mathcal{H}_{\text {so }}\right\|^{2} \Sigma^{+}\right\rangle$has been defined in Chapter 3 as $\tilde{A}$.
The matrix elements of the ${ }^{4} \Pi /{ }^{2} \Sigma^{+}$spin-orbit perturbation have been given by other authors [40][41] as

$$
\begin{equation*}
\left\langle{ }^{4} \Pi_{\frac{1}{2}}\right| \mathcal{H}_{s o}\left|{ }^{2} \Sigma^{+}{ }_{F_{2}} F_{1}\right\rangle=\frac{\sqrt{2}}{3} \xi \tag{6.17}
\end{equation*}
$$

and

$$
\begin{equation*}
\left.\left\langle{ }^{4} \Pi_{-\frac{1}{2}}\right| \mathcal{H}_{s o}| |^{2} \Sigma^{+}, F_{F_{2}}\right\rangle=\mp \sqrt{\frac{2}{3}} \xi . \tag{6.18}
\end{equation*}
$$

Equations (6.15) and (6.16) can be made to resemble the above expressions if the reduced matrix element is multiplied by a factor $\sqrt{\frac{8}{3}}$. However, the relative signs of the ${ }^{4} \Pi_{-\frac{1}{2}}$ interactions differ. This is an interesting result, but there is no doubt that the correct relative signs are as in Equations (6.15) and (6.16) because it is not possible to get a converged least squares fit if they are reversed. The conclusion is confirmed by a study of the $B^{4} \Pi-X^{4} \Sigma^{-}(1,0)$ band done by Huang and co-workers[42].

The values of the perturbation matrix elements for the $B^{4} \Pi v=0$ and $v=1$ levels can be used to determine the vibrational numbering of the $a^{2} \Sigma^{+}$state. This determination requires that the Born-Oppenheimer approximation holds, so that the perturbation matrix element can be factorized:

$$
\begin{equation*}
\left.\left\langle{ }^{4} \Pi, v\right| \mathcal{H}\left|\left.\right|^{2} \Sigma^{+}, v^{\prime}\right\rangle=\left.\left\langle{ }^{4} \Pi\right| \mathcal{H}_{\text {electronic }}\right|^{2} \Sigma^{+}\right\rangle\left\langle v \mid v^{\prime}\right\rangle \tag{6.19}
\end{equation*}
$$

The overlap integral, $\left\langle v \mid v^{\prime}\right\rangle$ was calculated using numerical integration over the eigenfunctions of modified Morse potentials given by

$$
\begin{equation*}
U(r)=D_{e}\left[1-\exp ^{-\beta(r)\left(r-r_{e}\right)}\right]^{2} \tag{6.20}
\end{equation*}
$$

where

$$
\begin{equation*}
\beta(r)=\beta_{0}+\beta_{1}\left(r-r_{e}\right)+\beta_{2}\left(r-r_{e}\right)^{2} \tag{6.21}
\end{equation*}
$$

Overlap integrals were calculated for several likely assignments for the vibrational numbering of the $a^{2} \Sigma^{+}$state. The results of these calculations are found in Table 6.5.

| $x$ | $\langle 1 \mid x+1\rangle$ | $\langle 0 \mid x\rangle$ | $\frac{\langle 1 \mid x+1\rangle}{\langle 0 \mid x\rangle}$ |
| :---: | :---: | :---: | :---: |
| 0 | 0.5144 | 0.8296 | 0.620 |
| 1 | 0.6052 | 0.5384 | 1.124 |
| 2 | 0.4051 | 0.2729 | 1.484 |
| 3 | 0.2200 | 0.1235 | 1.781 |

Table 6.5: Calculations of the anharmonic oscillator overlap integrals.

The values of the perturbation matrix elements of the $v=1$ level of the $B^{4} \Pi$ state determined by Huang at al.[42] and of the $v=0$ level determined in this work are

$$
\begin{align*}
\left.\left.\left\langle{ }^{4} \Pi, v=1\right| \mathcal{H}\right|^{2} \Sigma^{+}, v^{\prime}=x+1\right\rangle & =28.7 \mathrm{~cm}^{-1}  \tag{6.22}\\
\left.\left.\left\langle{ }^{4} \Pi, v=0\right| \mathcal{H}\right|^{2} \Sigma^{+}, v^{\prime}=x\right\rangle & =20.42 \mathrm{~cm}^{-1} \tag{6.23}
\end{align*}
$$

respectively. In the approximation that the perturbation matrix element is separable, the ratio of these two matrix elements represents the ratio of the two corresponding overlap integrals, i.e.

$$
\begin{equation*}
\frac{\left.\left.\left\langle{ }^{4} \Pi, v=1\right| \mathcal{H}\right|^{2} \Sigma^{+}, v^{\prime}=x+1\right\rangle}{\left.\left.\left\langle{ }^{4} \Pi, v=0\right| \mathcal{H}\right|^{2} \Sigma^{+}, v^{\prime}=x\right\rangle}=\frac{\langle 1 \mid x+1\rangle}{\langle 0 \mid x\rangle}=1.41 \tag{6.24}
\end{equation*}
$$

When this is compared to the values listed in Table 6.5, then the obvious conclusion is that $x=2$. Therefore, if $\omega_{e} x_{e}$ is assumed to equal the value for the ground state, then the vibrational constants for the perturbing $a^{2} \Sigma^{+}$state are

$$
\begin{align*}
\omega_{e} & =1024.24 \mathrm{~cm}^{-1}  \tag{6.25}\\
B_{e} & =0.5508 \mathrm{~cm}^{-1}  \tag{6.26}\\
T_{0}(v=0) & =10412 . \mathrm{cm}^{-1} \tag{6.27}
\end{align*}
$$

## Chapter 7

## Conclusions

The $B^{4} \Pi-X^{4} \Sigma^{-}(0,0)$ band of vanadium monoxide has been well characterized and the constants have been determined by a least squares fit to spectra recorded at subDoppler and Doppler limited resolution. The fit of 3211 data points resulted in the determination of 39 constants with an r.m.s. error of $0.00038 \mathrm{~cm}^{\mathbf{- 1}}$. Not only have these highly precise data provided an improved determination of the parameters of the $X^{4} \Sigma^{-}$state as compared to the values that had been determined previously from subDoppler spectra of the $C^{4} \Sigma^{+}-X^{4} \Sigma^{-}$transition [10], but they have also afforded the first complete analysis of the $B^{4} \Pi$ state.

Earlier studies of the $B^{4} \Pi$ state had only been done at Doppler-limited resolution. These studies had focussed mostly on regions where the hyperfine widths of the upper state fortuitously cancelled the widths of the ground state, thus producing sharp rotational lines; branches that were substantially hyperfine-broadened remained largely unassigned. This was particularly true near the regions where the $B^{4} \Pi$ state was heavily perturbed by the $a^{2} \Sigma^{+}$state.

However, the use of the technique known as intermodulated fluorescence spectroscopy has enabled the assignments of many of these branches. The information obtained in this work from the regions where the $a^{2} \Sigma^{+} / B^{4} \Pi$ interaction is greatest provide details of the perturbing state. These details confirm $\sigma \delta^{2}$ as the correct assignment for the valence electron configuration for the $a^{2} \Sigma^{+}$state, the same configuration as for the $X^{4} \Sigma^{-}$state. By comparison, the configuration of the $B^{4} \Pi$ state is $\delta^{2} \pi$.

The vibrational numbering for the $a^{2} \Sigma^{+}$state has been determined using data from the ( 1,0 ) band of the $B^{4} \Pi-X^{4} \Sigma^{-}$transition [37]. The $v=0$ and $v=1$ levels of the $B^{4} \Pi$ state are perturbed by the $v=2$ and $v=3$ levels of the $a^{2} \Sigma^{+}$state respectively. This information has resulted in significant change for the value for the band origin of the $v=0$ level of the $a^{2} \Sigma^{+}$state. When it had been believed that the $v=0$ level of the $a^{2} \Sigma^{+}$state was perturbing the $v=0$ level of the $B^{4} \Pi$ state, the band origin had been placed at $12430 \mathrm{~cm}^{-1}$ [14], whereas the new vibrational assignment has shifted this value to $10412 \mathrm{~cm}^{-1}$.

The eight hyperfine components arising from the ${ }^{51} \mathrm{~V}$ nucleus ( $\mathrm{I}=\frac{7}{2}$ ) were generally well resolved. This enabled the determination of magnetic hyperfine parameters for the $a^{2} \Sigma^{+}, X^{4} \Sigma^{-}$and $B^{4} \Pi$ states. The Fermi contact interactions in the $X^{4} \Sigma^{-}$and $a^{2} \Sigma^{+}$states produced by far the largest effects; this provides evidence that these states arise from a configuration with appreciable $\mathrm{V} 4 s$ atomic orbital character, and thus a non-zero probability that the electron can be found inside the nucleus.

This work has shed considerable light on the $B^{4} \Pi-X^{4} \Sigma^{-}(0,0)$ band of VO. Further work could be done on the higher vibrational bands of this transition, which would lead to the characterization of the higher levels of the $B^{4} \Pi$ and $a^{2} \Sigma^{+}$states. Studies of these other bands would provide further proof of the vibrational numbering, and would give information on the contours of the potential wells of the $B^{4} \Pi$ and $a^{2} \Sigma^{+}$states.

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## Appendix A

The Line Assignments of the VO $B^{4} \Pi-X^{4} \Sigma^{-}(0,0)$ Band.
table of assigned lines of the vo b-X ( 0,0 ) band

|  | ASSIGN | J' | $F=J \cdot 7 / 2$ | $F=J-5 / 2$ | $f=J \cdot 3 / 2$ | $F=J-1 / 2$ | $F=J+1 / 2$ | $F=J+3 / 2$ | $F=J+5 / 2$ | $F=\sqrt{ }+7 / 2$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $N=0$ | $\begin{aligned} & \text { SR21 } \\ & \text { TR31 } \end{aligned}$ | $\begin{aligned} & 1.5 \\ & 1.5 \end{aligned}$ |  |  |  |  | 12581.2817 | $\begin{aligned} & 12581.2225 \\ & 12645.1538 \end{aligned}$ | $\begin{aligned} & 12581.1414 \\ & 12645.0772 \end{aligned}$ | $\begin{aligned} & 12581.0383 \\ & 12644.9794 \end{aligned}$ |
| $N=9$ | 0 O21 | 2.5 |  |  |  |  |  |  | 12577.1988* | 12577.1187* |
|  | SR21 | 2.5 |  |  |  | 12583.6604 | 12583.6193 | 12583.5639 | 12583.4936 | 12583.4088 |
|  | R3 | 0.5 |  |  |  |  |  |  | 12642.8454* | 12642.6776* |
|  | TR42 | 1.5 |  |  |  |  | 12707.7612* | 12707.7447 | 12707.7200 | 12707.6865* |
|  | - |  |  |  |  |  |  |  |  |  |
| $N=2$ | OP21 | 3.5 |  |  | 12577.6867 | 12577.6562 | 12577.6151 | 12577.5630 | 12577.4999* | 12577.4263 |
|  | SR21 | 3.5 |  | 12586.0496* | 12586.0279 | 12585.9966 | 12585.9542* | 12585.9007 | $12585.8361$ | 12585.7600** |
|  | 02 | 2.5 |  |  |  | 12574.3546 |  | 12574.3390 | 12574.3289 | 12574.3170 |
|  | 0024 | 0.5 |  |  |  |  |  |  |  | 12575.0443 |
|  | SR43 | 9.5 |  |  |  |  | 12708.0869 | 12708.0418 | 12707.9908 | 12707.9286 |
|  | SR43 | 1.5 |  |  |  |  | 12708.0869 | 12708.0501 | 12708.0022 |  |
|  | TR42 | 2.5 |  |  | 12713.6184* | 12713.6131* | 12713.6022 | 12713.5880 | 12713.5626 | 12713.5408 |
|  | TR42 | 2.5 |  |  |  |  |  | 12713.5880 | 12713.5711 | 12713.5512* |
| $N=3$ | QP21 | 4.5 |  |  | 12577.9512 | 12577.9178 | 12577.8754 | 12577.8246 | 12577.7646 | 12577.6948 |
|  | SR21 | 4.5 |  | 12588.3567 | 12588.3316 | 12588.2979* | 12588.2542* | 12588.2018 | 12588.1410 | 12588.0701 |
|  | 0024 | 1.5 |  |  |  |  |  |  |  | 12574.5205* |
|  | TR31 | 4.5 | 12652.2395* | 12652.2235 | 12652.2003* | 12652.1680 | 12652.1283 | 12652.0799 | 12652.0229** | 12651.9576* |
|  | TR42 | 3.5 |  | 12714.7036 | 12714.6976* | 12714.6870** | 12714.6685 | 12714.6487 | 12714.6248 | 12714.5957 |
|  | TR42 | 3.5 |  |  |  | 12714.6870* | 12714.6727* | 12714.6537* | 12714.6307* | 12714.6026* |
|  | R4 | 1.5 |  |  |  |  | 12712.7205 |  | 12712.7123 | 12712.7123 |
| $N=4$ | QP21 | 5.5 |  |  |  | 12578.1296* | 12578.0873 | 12578.0360 | 12577.9776 | 12577.9119 |
|  | SR21 | 5.5 | 12590.6336 |  | 12590.5836* | 12590.5472 | 12590.5035 | 12590.4520 | 12590.3944 | 12590.3273 |
|  | TR31 | 5.5 |  | 12654.4918 | 12654.4650 | 12654.4316 | 12654.3914 | 12654.3439* | 12654.2897 | 12654.2280 |
|  | TR42 | 4.5 | 12715.8731 | 12745.8678* | 12715.8573 | 12715.8443 | 12715.8278 | 12715.8070 | 12715.7815 | 12715.7501 |
|  | TR42 | 4.5 |  | 12715.8678* | 12715.8599* | 12715.8467* | 12715.8311** | 12715.8103* | 12715.7854* | 12715.7547* |
|  | R4 | 2.5 |  |  |  |  | 12707.6237* | 12707.6362 | 12707.6601* | 12707.6785* |
| $N=5$ | P012 | 5.5 |  |  |  |  |  |  |  | 12519.7837* |
|  | QP21 | 6.5 | 12578.3728* | 12578.3503* | 12578.3199 | 12578.2827* | 12578.2389* | 12578.1896* | 12578.1324* | 12578.0693 |
|  | SR21 | 6.5 | 12592.8316* | 12592.8068** | 12592.7753* | 12592.7387* | 12592.6948 | 12592.6445 | 12592.5874 | 12592.5235 |
|  | TR31 | 6.5 |  | 12656.7161 | 12656.6871 | 12656.6527 | 12656.6127 | 12656.5663* | 12656.5134 | 12656.4542* |
|  | OP12 | 5.5 |  |  |  |  |  |  |  | 12514.7981 |
|  | RO21 | 6.5 | 12583.9408 | 12583.9198 | $12583.8929$ | $12583.8611$ | $12583.8236$ | $12583.7804$ |  | 12583.6757 |
|  | R4 | 3.5 |  | 12707.1893 | 12707.2005 | 12707.2154 | 12707.2366 | 12707.2629 | $12707.2939$ | 12707.3295 |
| $N=6$ | P1 | 7.5 |  | 12523.4910* | 12523.4581 | 12523.4193 | 12523.3734 | 12523.3222 | 12523.2650 | 12523.2005 |
|  | P012 | 6.5 |  | 12519.7056 | 12519.6943 | 12519.6800 | 12519.6623 | 12519.6390 | 12519.6109 | 12519.5753 |
|  | OP21 | 7.5 | 12578.4697* | 12578.4431 | 12578.4113* | 12578.3728* | 12578.3292* | 12578.2794 | 12578.2243 | 12578.1631* |
|  | TR31 | 7.5 | 12658.9177* | 12658.8920 | 12658.8621* | 12658.8266 | 12658.7866* | 12658.7406 | 12658.6895 | 12658.6324 |
|  | OP12 | 6.5 | 12513.8208* | 12513.8116** | 12513.8016 | 12513.7868 |  | 12513.7441 | 12513.7151 | 12513.6783 |
|  | RQ21 | 7.5 | 12584.9089 | 12584.8853 | 12584.8569 | 12584.8242 | 12584.7867 | 12584.7431 | 12584.6947 | 12584.6413 |
|  | R4 | 4.5 | 12706.5973 | 12706.6087 | 12706.6258 | 12706.6477 | 12706.6750 | 12706.7076 | 12706.7452 | 12706.7880** |
| $N=7$ | P1 | 8.5 |  |  | 12523.1984 | 12523.1586 | 12523.1137 | 12523.0621 | 12523.0060 | 12522.9441 |
|  | P012 | 7.5 | 12519.4418 | 12519.4332 | 12519.4218 | 12519.4077 | 12519.3892 | 12519.3666 | 12519.3374 | 12519.3009 |
|  | QP21 | 8.5 | 12578.4985 | 12578.4687* | 12578.4358 | 12578.3967 | 12578.3531***** | 12578.3039 | 12578.2494 | 12578.1897* |
|  | TR31 | 8.5 | 12661.0451 | 12661.0184 | 12660.9876 | 12660.9521 | 12660.9106 | 12660.8661 | 12660.8164 | 12660.7604 |
|  | OP12 | 7.5 | 12512.6348** | 12512.6263** |  | 12512.5998 | 12512.5800 | 12512.5568 | 12512.5268 | 12512.4895 |
|  | R021 | 8.5 | 12585.8133 | 12585.7886 | 12585.7396 | 12585.7259 | 12585.6878 | 12585.6447 | 12585.5975 | 12585.5451 |
|  | 5031 | 8.5 | 12651.1737 |  | 12651.1163** | 12651.0805* | 12651.0403* | 12650.9950 | 12650.9451 | 12650.8903 |
|  | R4 | 5.5 | 12705.9000 | 12705.9159 | 12705.9373 | 12705.9634 | 12705.9946 | 12706.0309 | 12706.0720 | 12706.1175 |

[^6]Appendix A. The Line Assignments of the VO $B^{4} \Pi-X^{4} \Sigma^{-}(0,0)$ Band.

|  | ASSIGN | - J" | $F=J \cdot 7 / 2$ | $F=\sqrt{-5 / 2}$ | $F=J-3 / 2$ | $F=J-1 / 2$ | $F=\mathrm{J}+1 / 2$ | $F=3+3 / 2$ | $F=J+5 / 2$ | $F=J+7 / 2$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $N=8$ | P1 | 9.5 | 12522.9212* | 12522.8888 | 12522.8536 | 12522.8138* | 12522.7674 | 12522.7174 | 12522.6617 | 12522.6019 |
|  | PQ12 | 8.5 | 12519.0952 | 12519.0865 | 12519.0754 | 12519.0615 | 12519.0434 | 12519.0206 | 12518.9911 | 12518.9517 |
|  | N014 | 6.5 | 12506.5908 | 12506.6089 |  |  |  |  |  | 12518.9517 |
|  | 0 O21 | 9.5 |  | 12578.4278 | 12578.3924 | 12578.3531 | 12578.3089 | 12578.2601 | 12578.2064 | 12578.1478* |
|  | 01 | 9.5 | 12533.2621* | 12533.2318 | 12533.1949 | 12533.1539** | 12533.1075* | 12533.0574 | 12533.0008 | 12532.9405 |
|  | OP12 | 8.5 | 12511.3694 | 12511.3603 | 12511.3491 | 12511.3345 | 12511.3160 | 12511.2930 | 12511.2625 | 12511.2230 |
|  | R021 | 9.5 | 12586.6554** | 12586.6306* | 12586.6002* | 12586.5644* | 12586.5257 | 12586.4831* | 12586.4370 | 12586.3857 |
|  | S031 | 9.5 | 12652.2020* | 12652.1739 | 12652.1420 | 12652.1063 | 12652.0659 | 12652.0211* | 12651.9720 | 12651.9184 |
|  | R4 | 6.5 | 12705.1182* | 12705.1379* | 12705.1624* | 12705.1913 | 12705.2253 | 12705.2633 | 12705.3061 | 12705.3530 |
| $N=9$ | 91 | 10.5 | 12522.4908 | 12522.4583 | 12522.4222 | 12522.3805 | 12522.3350 | 12522.2846 | 12522.2310 | 12522.1716 |
|  | P012 | 9.5 | 12518.6684 | 12518.6614 | 12518.6504 | 12518.6370 | 12518.6198 | 12518.5956 |  | 12518.5241 |
|  | N014 | 7.5 | 12504.3079 | 12504.3301 | 12504.3538 | 12504.3838 | 12504.4163 | 12504.4535 | 12504.4943 | 12504.5386 |
|  | OP21 | 10.5 | 12578.3459 | 12578.3145 | 12578.2794* | 12578.2389* | 12578.1942* | 12578.1460* | 12578.0935* | 12578.0360* |
|  | 01 | 10.5 | 12533.9086 | 12533.8755 | 12533.8385* | 12533.7969 | 12533.7510 | 12533.7002 | 12533.6446* | $12533.5857 *$ |
|  | OP12 | 9.5 |  |  |  | 12509.9889 | 12509.9707 | 12509.9477 | 12509.9170 |  |
|  | RQ21 | 10.5 | 12587.4328* | 12587.4056 | 12587.3743 | 12587.3396 | 12587.3007 | 12587.2583 | 12587.2120 | 12587.1616 |
|  | 5031 | 10.5 | 12653.1741 | 12653.1450 | 12653.1130 | 12653.0764 | 12653.0360 | 12652.9918 | 12652.9437 | 12652.8912 |
|  | R4 | 7.5 | 12704.2647* | 12704.2886* | 12704.3158 | 12704.3468 | 12704.3826 | 12704.4221 | 12704.4659 | 12704.5136 |
| $N=10$ | P1 | 11.5 | 12521.9737 | 12521.9406 | 12521.9035 | 12521.8616 | 12521.8161 | 12521.7663 | 12521.7134 | 12521.6547 |
|  | P012 | 10.5 | 12518.1610 | 12518.1534 | 12518.1440 | 12518.1306 | 12518.1141 | 12518.0916 | 12518.0609 | 12518.0141 |
|  | NO14 | 8.5 |  |  |  |  |  | 12502.0710* | 12502.1125* | 12502.1557 |
|  | OP21 | 11.5 | 12578.1631* | 12578.1296* | 12578.0935* | 12578.0535 | 12578.0095 | 12577.9614 | 12577.9088 | 12577.8523 |
|  | R032 | 10.5 |  |  |  | 12638.4305 | 12638.4179 | 12638.4009 | 12638.3761 | 12638.3362 |
|  | 01 | 11.5 | 12534.4628 | 12534.4294 | 12534.3912* | 12534.3493* | 12534.3027 | 12534.2529 | 12534.1978 | 12534.1395 |
|  | 0812 | 10.5 |  | 12508.5808 |  |  |  | 12508.5187 | 12508.4868 | $12508.4395$ |
|  | RQ21 | 11.5 | 12588.1453* | 12588.1167* | 12588.0852 | 12588.0502 | 12588.0107 | 12587.9686* | 12587.9228 | 12587.8733 |
|  | 5031 | 11.5 |  | 12654.0601 | 12654.0269 | 12653.9903 | 12653.9500* | 12653.9066* | 12653.8587 | 12653.8076 |
|  | R4 | 8.5 | 12703.3515 | 12703.3767 | 12703.4052 | 12703.4382 | 12703.4750 | 12703.5158 | 12703.5600 | 12703.6078 |
| $N=11$ | P1 | 12.5 | 12521.3705 | 12521.3357 | 12521.2979 | 12521.2563 | 12521.2104 | 12521.1607 | 12521.1071 | 12521.0496 |
|  | PQ12 | 11.5 | 12517.5698 | 12517.5647 | 12517.5561 | 12517.5442 | 12517.5280 | 12517.5062 | 12517.4746 | 12517.4211 |
|  | N014 | 9.5 | 12499.4310 | 12499.4558 | 12499.4832 | 12499.5144 | 12499.5490 | 12499.5871 | 12499.6275 | 12499.6709 |
|  | QP29 | 12.5 | 12577.9088* | 12577.874** | 12577.8366 | 12577.7961 | 12577.7520* | 12577.7041 | 12577.6522 | 12577.5964 |
|  | QR23 | 10.5 |  |  |  |  |  |  | 12573.7889* | $12573.8071$ |
|  | RP31 | 12.5 | 12642.1043 |  | 12642.0394 | 12642.0018 | 12641.9614* | 12641.9176 | 12641.8705 | 12641.8199 |
|  | R032 | 11.5 |  |  |  | 12638.2908* | 12638.2804* | 12638.2637** | 12638.2378 | 12638.1910 |
|  | 01 | 12.5 |  | 12534.8915 | 12534.8525 | 12534.8102 | 12534.7641 | 12534.7138 | 12534.6596 | 12534.6019 |
|  | OP12 | 11.5 |  |  |  |  |  | 12507.0028* | 12506.9705* | 12534.6019 |
|  | R021 | 12.5 | 12588.7927 | 12588.7631 | 12588.7308 | 12588.6950 | 12588.6561 | 12588.6137 | 12588.5687 | 12588.5193 |
|  | S031 | 12.5 | 12654.9472 | 12654.9171 | 12654.8835 | 12654.8467 | 12654.8068 | 12654.7635 | 12654.7162 | 12654.6659 |
|  | SR32 | 11.5 | 12651.1473* | 12651.1458* | 12651.1414** | 12651.1351 | 12651.1245 | 12651.1087 | 12651.0834* | 12651.0373* |
|  | T041 | 12.5 |  | 12727.4463 | 12727.4112 | 12727.3736 | $12727.3323$ |  | 12727.2391 | 12727.1867 |
|  | 7041 | 12.5 |  |  |  | 12727.3736 | 12727.3323 | 12727.2874* | 12727.239 |  |
| $N=12$ | P1 | 13.5 | 12520.6793 | 12520.6438 | 12520.6046 | 12520.5632 | 12520.5174 | 12520.4680 | 12520.4151 | 12520.3582 |
|  | P012 | 12.5 | 12516.8954 | 12516.8907 | 12516.8841 | 12516.8738 | 12516.8594 | 12516.8386 | 12516.8074 | 12516.7425 |
|  | NP13 | 11.5 | 12492.7091* |  |  |  |  |  |  |  |
|  | N014 | 10.5 | 12496.8455 | 12496.8715 | 12496.8999 | 12496.9325* | 12496.9670* | 12497.0043 | 12497.0449 |  |
|  | OP21 | 13.5 | 12577.5785* | 12577.5441 | 12577.5068 | 12577.4661 | 12577.4216 | 12577.3737 | 12577.3223** | $12577.2676$ |
|  | QR23 | 11.5 |  |  |  |  |  |  | 12573.5231** | 12573.5475 |
|  | RP31 | 13.5 |  | 12641.8609* | 12641.8269 | 12641.7899 | 12641.7487 | 12641.7053 | 12641.6583 | 12641.6081 |
|  | R032 | 12.5 |  |  | 12638.1060* | 12638.1005* | 12638.0913 | 12638.0762 | 12638.0505 | 12637.9927 |
|  | SR43 | 11.5 |  |  |  |  | 12638.0913 | 12638.0762 | 12638.0505 | 12710.3068* |
|  | 01 | 13.5 | 12535.2984 | 12535.2624 | 12535.2235 | 12535.1803* | 12535.1340* | 12535.0835* | 12535.0305 | 12534.9729 |
|  | R021 | 13.5 | 12589.3738 | 12589.3439 | 12589.3106 | 12589.2748 | 12589.2357 | 12589.1937 | 12589.1481 | 12589.1000 |
|  | S031 | 13.5 | 12655.7471 | 12655.7162 | 12655.6820 | 12655.6453 | 12655.6053 | 12655.5622 | 12655.5155* | 12655.4660 |
|  | SR32 | 12.5 |  |  |  |  | 12651.9478* | 12651.9329 | 12651.9079 | 12651.8510 |
|  | T041 | 13.5 | 12728.4271 | 12728.3949 |  | 12728.3224 | 12728.2817 | 12728.2375 | 12728.1904 | 12728.1390 |

Appendix A. The Line Assignments of the VO $B^{4} \Pi-X^{4} \Sigma^{-}(0,0)$ Band.


Appendix A. The Line Assignments of the VO $B^{4} \Pi-X^{4} \Sigma^{-}(0,0)$ Band.

|  | ASSIGN | J" | $F=J-7 / 2$ | $F=J-5 / 2$ | $F=J=3 / 2$ | $F=\sqrt{-1 / 2}$ | $\mathrm{F}=\mathrm{J}+1 / 2$ | $f=\sqrt{ }+3 / 2$ | $F=J+5 / 2$ | $F=J+7 / 2$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $N=17$ | P1 | 18.5 |  | 12515.8868 | 12515.8451 | 12515.8009 | 12515.7544 | 12515.7055 | 12515.6532 | 12515.5981 |
|  | P012 | 17.5 | 12512.2691 | 12512.1216 | 12512.1015* |  |  |  |  | 12512.0700 |
|  | QP21 | 18.5 | 12574.8179 | 12574.7812 | 12574.7417 | 12574.7002 | 12574.6558 | 12574.6090 | 12574.5593 | 12574.5071* |
|  | 02 | 17.5 |  | 12571.0148** | 12570.9959** | 12570.9818* | 12570.9729* |  |  |  |
|  | OR23 | 16.5 | 12571.0911 |  |  |  |  |  |  |  |
|  | RP31 | 18.5 | 12639.9973 | 12639.9637 |  |  | 12639.8499 | 12639.8072 | 12639.7620 | 12639.7139 |
|  | R032 | 17.5 | 12636.3427 | 12636.1996 | 12636.1864* | 12636.1747* | 12636.1696* | 12636.1696* | 12636.1747* | 12636.1864* |
|  | R3 | 16.5 |  | 12636.2226 | 12636.3628 | 12636.3762 |  |  |  |  |
|  | 5042 | 17.5 | 12709.4960** |  |  |  |  |  |  |  |
|  | SR43 | 16.5 | 12709.4232 | 12709.3760 | 12709.5166 | 12709.5306 | 12709.5413* | 12709.5449** | 12709.5449** | 12709.5413* |
|  | 01 | 18.5 | 12535.7919* | 12535.7524* | 12535.7109 | 12535.6667 | 12535.6195* | 12535.5700 | 12535.5173 | $12535.4615$ |
|  | OP12 | 17.5 | 12496.0916 | 12495.9445 | 12495.9239 | 12495.9071 | 12495.8959 | 12495.8877* | 12495.8877 | 12495.8921 |
|  | 0013 | 16.5 | 12496.0211 | 12495.9685 |  |  |  |  |  |  |
|  | R021 | 18.5 | 12591.2865* | 12591.2537 | 12591.2181 | 12591.1816* | 12591.1416 | 12591.0994 | 12591.0548 | 12591.0078* |
|  | 5031 | 18.5 | 12658.8546* | 12658.8214** | 12658.7866 | 12658.7492* | 12658.7099 | 12658.6680 | 12658.6238 | 12658.5770 |
|  | SR32 | 17.5 | 12655.2001* | 12655.0575* | 12655.0428* | 12655.0354* | 12655.0296* | 12655.0296* | 12655.0354** | 12655.0488* |
|  | OP34 | 15.5 | 12589.1728 | 12589.2081 | 12589.2446 | 12589.2838** | 12589.3254* | 12589.3692* | 12589.4154 | 12589.4637 |
|  | 1041 | 18.5 |  | 12732.4292* |  | 12732.3576 | 12732.3178 | 12732.2759* | 12732.2314 | 12732.1843 |
|  | P4 | 15.5 | 12662.0149 | 12662.0480 | 12662.0850 | 12662.1230 |  |  |  |  |
| $N=18$ | P1 | 19.5 | 12514.7151 | 12514.6759 | 12514.6345 | 12514.5909 | 12514.5448 | 12514.4952 | 12514.4436 |  |
|  | P012 | 18.5 | 12510.9771 | 12510.9476 | 12510.9248 | 12510.9078 | 12510.8945 | 12510.8850* | 12510.8803* | 12510.8803 |
|  | OP21 | 19.5 | 12574.0398 | 12574.0029 | 12573.9634 | 12573.9213 | 12573.8771 | 12573.8301 | 12573.7795* | 12573.7286* |
|  | 02 | 18.5 | 12570.2987* | 12570.2710** | 12570.2506* |  |  |  |  |  |
|  | OR23 | 17.5 | 12570.3715 | 12570.4240 | 12570.4433* |  |  |  |  |  |
|  | RP31 | 19.5 | 12639.4483 | 12639.4145 | 12639.3796 | 12639.3412 | 12639.3008 | 12639.2581 | 12639.2134 | 12639.1659 |
|  | R032 | 18.5 | 12635.7099 | 12635.6857 | 12635.6692 |  |  |  |  | 12635.6576* |
|  | R3 | 17.5 |  | 12635.8354 | 12635.8574 | 12635.8729 |  |  |  |  |
|  | S042 | 18.5 | 12709.0344******) | 12709.0107 | 12708.9940 | 12708.9827* | 12708.9768* | 12708.9725* | 12708.9768 | 12708.9850* |
|  | SR43 | 17.5 | 12709.1035 | 12709.1594 | 12709.1829 | 12709.1983 | 12709.2099* | 12709.2178* | 12709.2197* | 12709.2197* |
|  | 01 | 19.5 | 12535.6195 | 12535.5796 | 12535.5387 | 12535.4935 | 12535.4461 | 12535.3968 | 12535.3440 | 12535.2888 |
|  | OP12 | 18.5 | 12493.8355* | 12493.8071 | 12493.7843 | 12493.7668 |  | 12493.7436 | 12493.7383 |  |
|  | 0013 | 17.5 | 12493.9076 |  |  |  |  |  |  |  |
|  | R021 | 19.5 | 12591.4687* | 12591.4359** | 12591.3989* | 12591.3625 | 12591.3229 | 12591.2811 | 12591.2367 | 12591.1896 |
|  | S031 | 19.5 | 12659.2950 | 12659.2623 | 12659.2274 | 12659.1900 | 12659.1505 | 12659.1091 | 12659.0647 | 12659.0196 |
|  | SR32 | 18.5 | 12655.5567 | 12655.5327 |  | 12655.5064* | 12655.5012* | 12655.4986* | 12655.5012* | 12655.5103* |
|  | 0934 | 16.5 | 12585.5815 | 12585.6162 | 12585.6533 | 12585.6929 | 12585.7346 | 12585.7785 | 12585.8247 | 12585.8729 |
|  | 1041 | 19.5 | 12733.1240 | 12733.0912 |  | 12733.0186* |  |  |  |  |
|  | TR42 | 18.5 | 12729.3856 | 12729.3618 | 12729.3462 | 12729.3352* | 12729.3298* |  |  | 12729.3395 |
|  | P4 | 16.5 | 12658.5960 | 12658.6324* |  | 12658.7059* | 12658.7491* |  | 12658.8356* | 12658.8834 |
| $N=19$ | P1 | 20.5 | 12513.4216 |  |  | 12513.2972 | $12513.2502$ |  |  |  |
|  | P012 | 19.5 | 12509.7147 | 12509.6846 | 12509.6608 | 12509.6423 | $12509.6273$ | 12509.6164* | $12509.6091 *$ | $12509.6067$ |
|  | PR13 | 18.5 | 12509.8106 |  |  |  |  |  |  |  |
|  | QP21 | 20.5 | 12573.1854* | 12573.1485 | 12573.1089 | 12573.0670 | 12573.0226 | 12572.9757 | 12572.9268* | 12572.8751 |
|  | OP23 | 18.5 | 12530.7290 | 12530.7703 | 12530.7902 | 12530.8026 |  |  |  |  |
|  | 0024 | 17.5 | 12535.0733 | 12535.1045 | 12535.1385 | 12535.1733 | 12535.2109 | 12535.2504 |  | 12535.3342 |
|  | RP31 | 20.5 | 12638.8428 | 12638.8089 | 12638.7730 | 12638.7348 | 12638.6948 | 12638.6525 | 12638.6074* | 12638.5609* |
|  | R032 | 19.5 | 12635.1352 | 12635.1104 | 12635.0928 | 12635.0803* | 12635.0725* |  |  |  |
|  | R3 | 18.5 |  | 12635.2760 | 12635.2988* | 12635.3151* | 12635.3271* |  |  |  |
|  | SO42 | 19.5 | 12708.6387* | 12708.6142 | 12708.5976 | 12708.5861* | 12708.5769* | 12708.5755* | 12708.5755* | 12708.5798* |
|  | SR43 | 18.5 | 12708.7339 | 12708.7798 | 12708.8035 | 12708.8207 | 12708.8336 | 12708.8424 | 12708.8481* | 12708.8495* |
|  | 01 | 20.5 | 12535.3585 | 12535.3180 | 12535.2761 | 12535.2314 | 12535.1832* | 12535.1340* | 12535.0814********* | 12535.0266 |
|  | OP12 | 19.5 | 12491.6056 | 12491.5750 | 12491.5520 | 12491.5328 | 12491.5178 | 12491.5057 | 12491.4988 | 12491.4962 |
|  | QR12 | 19.5 | 12531.6505* | 12531.6189 | 12531.5955* | 12531.5772 | 12531.5610 | 12531.5490 | 12531.5419 | 12531.5386 |
|  | 0013 | 18.5 | 12491.7028 | 12491.7417 |  |  |  |  |  |  |
|  | R021 | 20.5 | 12591.5849* | 12591.5511 | 12591.5152 | 12591.4774* | 12591.4370* | 12591.3957* | 12591.3518* | 12591.3046 |
|  | 5031 | 20.5 | 12659.6750 | 12659.6419 | 12659.6068 | 12659.5699 | 12659.5301 | 12659.4887 | 12659.4448 | 12659.3993 |
|  | SR32 | 19.5 | 12655.9675 | 12655.9430* | 12655.9267* | 12655.9147* | 12655.9076* | 12655.9049* | 12655.9049* | 12655.9112* |
|  | 0 O34 | 17.5 | 12581.9279 | 12581.9633 | 12582.0007 | 12582.0407 | 12582.0826 | 12582.1267 | 12582.1725 | 12582.2210 |
|  | T049 | 20.5 | 12733.7366 |  |  | 12733.6325** |  |  | 12733.5084** | 12733.4628** |
|  | TR42 | 19.5 | 12730.0289 | 12730.0053 | 12729.9887 | 12729.9770* |  |  |  | 12729.9738* |
|  | P4 | 17.5 | 12655.1281 | 12655.1627* | 12655.2001 | 12655.2397* | 12655.2819 | 12655.3250 | 12655.3705 | 12655.4185 |

Appendix A. The Line Assignments of the VO $B^{4} \Pi-X^{4} \Sigma^{-}(0,0)$ Band.

|  | ASSIGN | N" | $F=\mathrm{J}-7 / 2$ | $F=J-5 / 2$ | $F=J-3 / 2$ | F=J-1/2 | $F=J+1 / 2$ | $F=1+3 / 2$ | Fxa $+5 / 2$ | $F=\sqrt{ }+7 / 2$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $N=20$ | P1 | 21.5 | 12512.0449 |  | 12511.9627 | 12511.9178 | 12511.8718 | 12511.8225 | 12511.7696 | 12511.7161 |
|  | Pa12 | 20.5 | 12508.3644 | 12508.3345 | 12508.3106 | 12508.2916 | 12508.2751 | 12508.2626 | 12508.2535 | 12508.2485 |
|  | OP21 | 21.5 | 12572.2561 | 12572.2183 | 12572.1782 | 12572.1361 | 12572.0922 | 12572.0455* | 12571.9966 | 12571.9452 |
|  | OP23 | 19.5 | 12527.8280 | 12527.8626 |  |  | 12527.9038 |  |  |  |
|  | 0024 | 18.5 | 12532.1985 | 12532.2305 | 12532.2640 | 12532.3002 | 12532.3378 | 12532.3766 | 12532.4176 | 12532.4599 |
|  | S042 | 20.5 | 12708.1900 | 12708.1672* | 12708.1504* | 12708.1379** | 12708.1275* | 12708.1249** | 12708.1249* | 12708.1257* |
|  | $5 R 43$ | 19.5 | 12708.3147 | 12708.3536 | 12708.3777 | 12708.3954 | 12708.4091 | 12708.4195 | 12708.4267 | 12708.4306 |
|  | 01 | 21.5 | 12535.0084 | 12534.9681 | 12534.9257 | 12534.8805 | 12534.8332 | 12534.7834 | 12534.7308 | 12534.6757 |
|  | OR12 | 20.5 | 12531.3282 | 12531.2973 | 12531.2736 | 12531.2526 | 12531.2365 | 12531.2238 | 12531.2138 | 12531.2079 |
|  | R021 | 21.5 | 12591.6335 | 12591.5996 | 12591.5636 | 12591.5255* | 12591.4854 | 12591.4432 | 12591.3989* | 12591.3519* |
|  | S031 | 21.5 | 12659.9935 | 12659.9608 | 12659.9252 | 12659.8877 | 12659.8483 | 12659.8076 | 12659.7643 | 12659.7186 |
|  | SR32 | 20.5 | 12656.3134 |  | 12656.2750* | $12656.2610^{*}$ | 12656.2526* | 12656.2477* | 12656.2477* | 12656.2512* |
|  | DP34 | 18.5 | 12578.2130 | 12578.2494* | 12578.2870* | 12578.3273* | 12578.3695 | 12578.4134* | 12578.4594** | 12578.5072 |
|  | TR42 | 20.5 | 12730.6192 | 12730.5957 | 12730.5791 | 12730.5676* | 12730.5598 | 12730.5559** | 12730.5559* | 12730.5584* |
|  | P4 | 18.5 | 12651.6106 | 12651.6468 | 12651.6846 | 12651.7242 | 12651.7663 | 12651.8101 | 12651.8562 | $12651.9038$ |
| $N=21$ | P1 | 22.5 | 12510.5840 | 12510.5438 | 12510.5015 | 12510.4562 | 12510.4098 | 12510.3598 | 12510.3079 | 12510.2535 |
|  | P012 | 21.5 | 12506.9272 | 12506.8982 | 12506.8740 | 12506.8539 | 12506.8368 | 12506.8234 | 12506.8123** | 12506.8059 |
|  | OP21 | 22.5 | 12571.2499 | 12571.2120 | 12571.1718 | 12571.1296 | 12571.0855 | 12571.0391 | 12570.9903 | 12570.9392 |
|  | OP23 | 20.5 |  | 12524.8811 | 12524.9000 | 12524.9133 | 12524.9220 |  |  |  |
|  | 0024 | 19.5 | 12529.2467 | 12529.2797 | 12529.3134 | 12529.3492 | 12529.3866 | 12529.4258 | 12529.4666 | 12529.5092 |
|  | S042 | 21.5 | 12707.6904 |  | 12707.6515* | 12707.6397* | 12707.6292 | 12707.6257* | 12707.6237** | 12707.6257* |
|  | SR43 | 20.5 | 12707.8454 | 12707.8799 | 12707.9034 | 12707.9213* | 12707.9362 | 12707.9475 | 12707.9561 | 12707.9615 |
|  | 01 | 22.5 | 12534.5716 | 12534.5309 | 12534.4882 | 12534.4428 | 12534.3953 | 12534.3453 | 12534.2927 | 12534.2379 |
|  | OR12 | 21.5 | 12530.9162 | 12530.8864** | 12530.8614 | 12530.8416 | 12530.8243 | 12530.8098** | 12530.7982* | 12530.7905 |
|  | R021 | 22.5 | 12591.6151 | 12591.5812 | 12591.5447 | 12591.5061 | 12591.4658* | $12591.4235{ }^{\text {. }}$ | 12591.3793* | 12591.3329 |
|  | NP24 | 19.5 |  |  | 12506.9436 | 12506.9842 |  |  | 12507.1159* | 12507.1633 |
|  | 5031 | 22.5 | 12660.2510* | 12660.2180* | 12660.1823 | 12660.1451 | 12660.1060 | 12660.0653 | 12660.0218 | 12659.9767 |
|  | SR32 | 21.5 | 12656.5956 | 12656.5733 | 12656.5561 | 12656.5438* | 12656.5347* | 12656.5295* | 12656.5276* | 12656.5295* |
|  | OP34 | 19.5 | 12574.4373 | 12574.4739 | 12574.5124* | 12574.5529 | 12574.5951* | 12574.6390 | 12574.6849 | $12574.7329$ |
|  | TR42 | 21.5 | 12731.1575 | 12731.1347 | 12731.1182 | 12731.1064 | 12731.0981* |  |  |  |
| $N=22$ | P1 | 23.5 | 12509.0390 | $12508.9985$ | 12508.9559 | $12508.9105$ | 12508.8633 | 12508.8144 | 12508.7622 |  |
|  | QP21 | 23.5 | 12570.1671 | 12570.1288 | 12570.0891 | 12570.0469 | 12570.0029 | 12569.9566 | 12569.9078 | $12569.8572$ |
|  | 0923 | 21.5 | 12521.7978 | 12521.8247 | 12521.8428 | 12521.8557 | 12521.8652 | 12521.8717 | 12521.8754* |  |
|  | 0024 | 20.5 | 12526.2185 | 12526.2511 | 12526.2855 | 12526.3218 | 12526.3593 | 12526.3981 | 12526.4392 | 12526.4815 |
|  | RP31 | 23.5 | 12636.6812 |  | 12636.6097* | 12636.5719 | 12636.5319 | 12636.4896 | 12636.4451 |  |
|  | P034 | 20.5 | 12592.1420 | 12592.1782 | 12592.2160 | 12592.2562 | 12592.2978 | 12592.3411 | 12592.3860 * | 12592.4332* |
|  | SQ42 | 22.5 | 12707.1406 | 12707.1194 | 12707.1022 | 12707.0899 | 12707.0809* | 12707.0751* | 12707.0743* | 12707.0743* |
|  | 0943 | 21.5 | 12661.4109 | 12661.4414 | 12661.4649 | 12661.4828 | 12661.4972 | 12661.5088 | 12661.5182 | 12661.5248 |
|  | SR43 | 21.5 | 12707.3260* | 12707.3572 | 12707.3806 | 12707.3989 | 12707.4141 | 12707.4265 | 12707.4361 | 12707.4430 |
|  | 01 | 23.5 | 12534.0486 | 12534.0068 | 12533.9634 | 12533.9177 | 12533.8703 | 12533.8199 | 12533.7676 | 12533.7128 |
|  | QR12 | 22.5 | 12530.4170 | 12530.3875 | 12530.3623 | 12530.3414 | 12530.3235 | 12530.3080 | 12530.2960 | 12530.2869 |
|  | RO21 | 23.5 | 12591.5293 | 12591.4954 | 12591.4583 | 12591.4195 | 12591.3793* | 12591.3371 | 12591.2930 | 12591.2465 |
|  | NP24 | 20.5 | 12502.7749 | 12502.8108 | 12502.8497 | 12502.8899 | 12502.9318 | 12502.9758 | 12503.0222** | 12503.0686* |
|  | S031 | 23.5 | 12660.4462 | 12660.4131 | 12660.3781******* | 12660.3419* | 12660.3016 | 12660.2611 | 12660.2180** | 12660.1729 |
|  | SR32 | 22.5 | 12656.8156 | 12656.7937 | 12656.7770** | 12656.7646 | 12656.7552* | 12656.7511****** | 12656.7469* | 12656.7469* |
|  | OP34 | 20.5 | 12570.6006 | 12570.6375 | 12570.6763 | 12570.7168 | 12570.7595 | 12570.8039 | 12570.8499 | 12570.8975 |
|  | TR42 | 22.5 | 12731.6442 | 12731.6227 | 12731.6067 | 12731.5946 | 12731.5856 | 12570.8039 | 12570.849 | 12570.8975 |
|  | P4 | 20.5 | 12644.4292 | 12644.4661 | 12644.5051 | 12644.5459 | 12644.5884 | 12644.6327 | 12644.6788 | 12644.7267 |
| $N=23$ | P1 | 24.5 | 12507.4115 | 12507.3707 | 12507.3278 | 12507.2829 | 12507.2354 | 12507.1857 |  | 12507.0796 |
|  | P012 | 23.5 | 12503.8036 |  |  |  | 12507.2354 | 12507.1857 |  | 12507.0796 |
|  | PR13 | 22.5 | 12504.0196 | 12504.0414 | 12504.0560 |  |  |  |  |  |
|  | 0024 | 21.5 | 12523.1137 | 12523.1463 | 12523.1815 | 12523.2175 | 12523.2551 | 12523.2941 | 12523.3349 |  |
|  | RP31 | 24.5 | 12635.8442 | 12635.8107** | 12635.7732 | 12635.7348 | 12635.6939 |  | 12635.6084 | $12635.5623$ |
|  | S042 | 23.5 | 12706.5401 | 12706.5195 | 12706.5034 | 12706.4910 | 12706.4820 | 12706.4759* | 12706.4733* | 12706.4733* |
|  | QP43 | 22.5 | 12658.7626 | 12658.7911 | 12658.8143 | 12658.8322* | 12658.8473* | 12658.8602 | 12658.8706 | 12658.8779 |
|  | SR43 | 22.5 | 12706.7558 | 12706.7855* | 12706.8082 | 12706.8269 | 12706.8423 | 12706.8552 | 12706.8660 | 12706.8743 |
|  | 01 | 24.5 | 12533.4392 | 12533.3975 | 12533.3537 | 12533.3079 | 12533.2597 | 12533.2100 | 12533.1574 | 12533.1028 |
|  | QR12 | 23.5 | 12529.8315* | 12529.8025 | 12529.7779 | 12529.7563 | 12529.7374 | 12529.7218 | 12529.7082 | 12529.6979 |
|  | R021 | 24.5 |  | 12591.3421* | 12591.3046* | 12591.2658 | 12591.2256 | 12591.1829** | 12591.1393* | 12591.0921 |
|  | NP24 | 21.5 | 12498.6132 | 12498.6498 | 12498.6887 | 12498.7288 | 12498.7704 | 12498.8146* |  | 12498.9068* |
|  | S031 | 24.5 | 12660.5799 | 12660.5462* | 12660.5114** | 12660.4742* | 12660.4345* | 12660.3947* | $12660.3524$ | 12660.3074 |
|  | SR32 | 23.5 | 12656.9725* | 12656.9513* | 12656.9354* | 12656.9224** | 12656.9126* | 12656.9064* | 12656.9029* | 12656.9029** |
|  | TR42 | 23.5 | 12732.0797 | 12732.0579 | 12732.0424 | 12732.0313 | 12732.0227 | 12732.0167 | 12656.9029 | 12656.9029 |
|  | P4 | 21.5 | 12640.7644 | 12640.8022 | 12640.8413 | 12640.8824 | 12640.9249* | 12640.9701 | 12641.0160** | 12641.0646* |

Appendix A. The Line Assignments of the VO $B^{4} \Pi-X^{4} \Sigma^{-}(0,0)$ Band.

|  | ASSIGN | J" | $F=J \cdot 7 / 2$ | $F=J-5 / 2$ | $F=J-3 / 2$ | $F=J-1 / 2$ | $f=\mathrm{J}+1 / 2$ | $f=\mathrm{J}+3 / 2$ | $F=\sqrt{ }+5 / 2$ | $F=J+7 / 2$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $N=20$ | P1 | 21.5 | 12512.0449 |  | 12511.9627 | 12511.9178 | 12511.8718 | 12511.8225 | 12511.7696 | 12511.7161 |
|  | pal2 | 20.5 | 12508.3644 | 12508.3345 | 12508.3106 | 12508.2916 | 12508.2751 | 12508.2626 | 12508.2535 | 12508.2485 |
|  | QP21 | 21.5 | 12572.2561 | 12572.2183 | 12572.1782 | 12572.1361 | 12572.0922 | 12572.0455* | 12571.9966 | 12571.9452 |
|  | OP23 | 19.5 | 12527.8280 | 12527.8626 |  |  | 12527.9038 |  |  |  |
|  | 0024 | 18.5 | 12532.1985 | 12532.2305 | 12532.2640 | 12532.3002 | 12532.3378 | 12532.3766 | 12532.4176 | 12532.4599 |
|  | S042 | 20.5 | 12708.1900 | 12708.1672* | 12708.1504* | 12708.1379* | 12708.1275* | 12708.1249** | 12708.1249* | 12708.1257** |
|  | SR43 | 19.5 | 12708.3147 | 12708.3536 | 12708.3777 | 12708.3954 | 12708.4091 | 12708.4195 | 12708.4267 | 12708.4306 |
|  | 01 | 21.5 | 12535.0084 | 12534.9681 | 12534.9257 | 12534.8805 | 12534.8332 | 12534.7834 | 12534.7308 | 12534.6757 |
|  | 0 R 12 | 20.5 | 12531.3282 | 12531.2973 | 12531.2736 | 12531.2526 | 12531.2365 | 12531.2238 | 12531.2138 | 12531.2079 |
|  | RQ21 | 21.5 | 12591.6335 | 12591.5996 | 12591.5636 | 12591.5255* | 12591.4854 | 12591.4432 | 12591.3989** | 12591.3519** |
|  | S031 | 21.5 | 12659.9935 | 12659.9608 | 12659.9252 | 12659.8877 | 12659.8483 | 12659.8076 | 12659.7643 | 12659.7186 |
|  | SR32 | 20.5 | 12656.3134 |  | 12656.2750* | 12656.2610* | 12656.2526* | 12656.2477* | 12656.2477* | 12656.2512* |
|  | OP34 | 18.5 | 12578.2130 | 12578.2494* | 12578.2870* | 12578.3273* | 12578.3695 | 12578.4134* | 12578.4594* | 12578.5072 |
|  | TR42 | 20.5 | 12730.6192 | 12730.5957 | 12730.5791 | 12730.5676* | 12730.5598 | 12730.5559* | 12730.5559** | 12730.5584* |
|  | P4 | 18.5 | 12651.6106 | 12651.6468 | 12651.6846 | 12651.7242 | 12651.7663 | 12651.8101 | 12651.8562 | 12651.9038 |
| $N=21$ | P1 | 22.5 | 12510.5840 | 12510.5438 | 12510.5015 | 12510.4562 | 12510.4098 | 12510.3598 | 12510.3079 | 12510.2535 |
|  | P012 | 21.5 | 12506.9272 | 12506.8982 | 12506.8740 | 12506.8539 | 12506.8368 | 12506.8234 | 12506.8123* | 12506.8059 |
|  | QP21 | 22.5 | 12571.2499 | 12571.2120 | 12571.1718 | 12571.1296 | 12571.0855 | 12571.0391 | 12570.9903 | 12570.9392 |
|  | OP23 | 20.5 |  | 12524.8811 | 12524.9000 | 12524.9133 | 12524.9220 |  |  |  |
|  | 0024 | 19.5 | 12529.2467 | 12529.2797 | 12529.3134 | 12529.3492 | 12529.3866 | 12529.4258 | 12529.4666 | 12529.5092 |
|  | S042 | 21.5 | 12707.6904 |  | 12707.6515* | 12707.6397* | 12707.6292 | 12707.6257* | 12707.6237** | 12707.6257* |
|  | SR43 | 20.5 | 12707.8454 | 12707.8799 | 12707.9034 | 12707.9213* | 12707.9362 | 12707.9475 | 12707.9561 | 12707.9615 |
|  | 01 | 22.5 | 12534.5716 | 12534.5309 | 12534.4882 | 12534.4428 | 12534.3953 | 12534.3453 | 12534.2927 | 12534.2379 |
|  | QR12 | 21.5 | 12530.9162 | 12530.8864* | 12530.8614 | 12530.8416 | 12530.8243 | 12530.8098** | 12530.7982* | 12530.7905 |
|  | RO21 | 22.5 | 12591.6151 | 12591.5812 | 12591.5447 | 12591.5061 | 12591.4658* | 12591.4235 | 12591.3793* | 12591.3329 |
|  | NP24 | 19.5 |  |  | 12506.9436 | 12506.9842 |  |  | 12507.1159* | 12507.1633 |
|  | S031 | 22.5 | 12660.2510* | 12660.2180* | 12660.1823 | 12660.1451 | 12660.1060 | 12660.0653 | 12660.0218 | 12659.9767 |
|  | SR32 | 21.5 | 12656.5956 | 12656.5733 | 12656.5561 | 12656.5438* | 12656.5347* | 12656.5295* | 12656.5276* | 12656.5295* |
|  | OP34 | 19.5 | 12574.4373 | 12574.4739 | 12574.5124* | 12574.5529 | 12574.5951* | 12574.6390 | 12574.6849 | 12574.7329 |
|  | TR42 | 21.5 | 12731.1575 | 12731.1347 | 12731.1182 | 12731.1064 | 12731.0981* |  |  |  |
| $N=22$ | P1 | 23.5 | 12509.0390 | 12508.9985 | 12508.9559 |  | $12508.8633$ |  | $12508.7622$ | $12508.7082$ |
|  | OP21 | 23.5 | 12570.1671 | 12570.1288 | 12570.0891 | $12570.0469$ | $12570.0029$ | $12569.9566$ | $12569.9078$ | $12569.8572$ |
|  | OP23 | 21.5 | 12521.7978 | 12521.8247 | 12521.8428 | 12521.8557 | 12521.8652 | 12521.8717 | 12521.8754* |  |
|  | 0024 | 20.5 | 12526.2185 | 12526.2511 | 12526.2855 | 12526.3218 | 12526.3593 | 12526.3981 | 12526.4392 | 12526.4815 |
|  | RP31 | 23.5 | 12636.6812 |  | 12636.6097* | 12636.5719 | 12636.5319 | 12636.4896 | 12636.4451 |  |
|  | P034 | 20.5 | 12592.1420 | 12592.1782 | 12592.2160 | 12592.2562 | 12592.2978 | 12592.3411 | 12592.3860* | 12592.4332* |
|  | S042 | 22.5 | 12707.1406 | 12707.1194 | 12707.1022 | 12707.0899 | 12707.0809* | 12707.0751* | 12707.0743* | 12707.0743* |
|  | QP43 | 21.5 | 12661.4109 | 12661.4414 | 12661.4649 | 12661.4828 | 12661.4972 | 12661.5088 | 12661.5182 | 12661.5248 |
|  | SR43 | 21.5 | 12707.3260* | 12707.3572 | 12707.3806 | 12707.3989 | 12707.4141 | 12707.4265 | 12707.4361 | 12707.4430 |
|  | 01 | 23.5 | 12534.0486 | 12534.0068 | 12533.9634 | 12533.9177 | 12533.8703 | 12533.8199 | 12533.7676 | 12533.7128 |
|  | QR12 | 22.5 | 12530.4170 | 12530.3875 | 12530.3623 | 12530.3414 | 12530.3235 | 12530.3080 | 12530.2960 | 12530.2869 |
|  | RQ29 | 23.5 | 12591.5293 | 12591.4954 | 12591.4583 | 12591.4195 | 12591.3793* | 12591.3371 | 12591.2930 | 12591.2465 |
|  | NP24 | 20.5 | 12502.7749 | 12502.8108 | 12502.8497 | 12502.8899 | 12502.9318 | 12502.9758 | 12503.0222* | 12503.0686* |
|  | 5031 | 23.5 | 12660.4462 | 12660.4131 | 12660.3781* | 12660.3411* | 12660.3016 | 12860.2611 | 12660.2180* | 12660.1729 |
|  | SR32 | 22.5 | 12656.8156 | 12656.7937 | 12656.7770* | 12656.7646 | 12656.7552* | 12656.7591* | 12656.7469* | 12656.7469* |
|  | OP34 | 20.5 | 12570.6006 | 12570.6375 | 12570.6763 | 12570.7168 | 12570.7595 | 12570.8039 | 12570.8499 | 12570.8975 |
|  | TR42 | 22.5 | 12731.6442 | 12731.6227 | 12731.6067 | 12731.5946 | $12731.5856$ |  |  |  |
|  | P4 | 20.5 | 12644.4292 | 12644.4661 | 12644.5051 | 12644.5459 | 12644.5884 | 12644.6327 | 12644.6788 | 12644.7267 |
| $N=23$ | P1 | 24.5 | 12507.4115 | 12507.3707 | 12507.3278 | 12507.2829 | 12507.2354 | 12507.1857 |  | 12507.0796 |
|  | PQ12 | 23.5 | 12503.8036 |  |  |  |  |  |  |  |
|  | PR13 | 22.5 | 12504.0196 | 12504.0414 | 12504.0560 |  |  |  |  |  |
|  | 0024 | 21.5 | 12523.1137 | 12523.1463 | 12523.1815 | 12523.2175 | 12523.2551 | 12523.2941 |  |  |
|  | RP31 | 24.5 | 12635.8442 | 12635.8107** | 12635.7732 | 12635.7348 | 12635.6939 |  | 12635.6084 | 12635.5623 |
|  | SO42 | 23.5 | 12706.5401 | 12706.5195 | 12706.5034 | 12706.4910 | 12706.4820 | 12706.4759* | 12706.4733* | 12706.4733* |
|  | QP43 | 22.5 | 12658.7626 | 12658.7911 | 12658.8143 | 12658.8322* | 12658.8473* | 12658.8602 | 12658.8706 | 12658.8779 |
|  | SR43 | 22.5 | 12706.7558 | 12706.7855* | 12706.8082 | 12706.8269 | 12706.8423 | 12706.8552 | 12706.8660 | 12706.8743 |
|  | 01 | 24.5 | 12533.4392 | 12533.3975 | 12533.3537 | 12533.3079 | 12533.2597 | 12533.2100 | 12533.1574 | 12533.1028 |
|  | OR12 | 23.5 | 12529.8315** | 12529.8025 | 12529.7779 | 12529.7563 | 12529.7374 | 12529.7218 | 12529.7082 | 12529.6979 |
|  | R021 | 24.5 |  | 12591.3421* | 12591.3046* | 12591.2658 | 12591.2256 | 12591.1829** | 12591.1393* | 12591.0921 |
|  | NP24 | 21.5 | 12498.6132 | 12498.6498 | 12498.6887 | 12498.7288 | 12498.7704 | 12498.8146* |  | 12498.9068* |
|  | S031 | 24.5 | 12660.5799 | 12660.5462* | 12660.5114** | 12660.4742* | 12660.4345* | 12660.3947 | 12660.3524 | 12660.3074 |
|  | SR32 | 23.5 | 12656.9725* | 12656.9513* | 12656.9354* | 12656.9224* | 12656.9126* | 12656.9064** | 12656.9029* | 12656.9029* |
|  | TR42 | 23.5 | 12732.0797 | 12732.0579 | 12732.0424 | 12732.0313 | 12732.0227 | 12732.0167 |  |  |
|  | P4 | 21.5 | 12640.7644 | 12640.8022 | 12640.8413 | 12640.8824 | 12640.9249* | 12640.9701 | 12641.0160* | 12641.0646* |

Appendix A. The Line Assignments of the VO $B^{4} \Pi-X^{4} \Sigma^{-}(0,0)$ Band.

|  | ASSIGN | N" | $F=\mathrm{J} \cdot 7 / 2$ | $F=J-5 / 2$ | $F=\sqrt{-3 / 2}$ | Ff.J-1/2 | $F=\sqrt{ }+1 / 2$ | $F=J+3 / 2$ | $F=J+5 / 2$ | $F=\mathrm{J}+7 / 2$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $N=24$ | P1 | 25.5 | 12505.7014 |  | 12505.6175 | 12505.5724 | 12505.5248 | 12505.4752 | 12505.4236 | 12505.3696 |
|  | P012 | 24.5 | 12502.1172 | 12502.0896 |  |  |  |  |  |  |
|  | PR13 | 23.5 | 12502.3637 | 12502.3834 | 12502.3972 |  |  |  |  |  |
|  | OP23 | 23.5 | 12515.4614 | 12515.4837 | 12515.5013 | 12515.5140 | 12515.5241 | 12515.5315* | 12515.5362* |  |
|  | 0024 | 22.5 | 12519.9318 | 12519.9655 | 12520.0006 | 12520.0364 | 12520.0744 | 12520.1134 | 12520.1540 | 12520.1957 |
|  | P034 | 22.5 | 12586.4447* | 12586.4814* | 12586.5199** | 12586.5599* | 12586.6002* | 12586.6454 | 12586.6903 | 12586.7368 |
|  | 5042 | 24.5 | 12705.8897 | 12705.8699 | 12705.8542 | 12705.8421 | 12705.8328 | 12705.8267 | 12705.8231* | 12705.8231* |
|  | QP43 | 23.5 | 12656.0655 | 12656.0926 | 12656.1152 | 12656.1330 | 12656.1487 | 12656.1619 | 12656.1727 | 12656.1815 |
|  | SR43 | 23.5 | 12706.1358 | 12706.1635 | 12706.1858 | 12706.2045 | 12706.2206 | 12706.2343 | 12706.2456 | 12706.2548 |
|  | 04 | 22.5 | 12660.5351 | 12660.5740 | 12660.6134 | 12660.6548 | 12660.6982 | 12660.7428 | 12660.7899 | 12660.8383 |
|  | 01 | 25.5 | 12532.7461 | 12532.7044 | 12532.6602 | 12532.6143 | 12532.5661 | 12532.5157 | 12532.4632 | 12532.4085 |
|  | QR12 | 24.5 | 12529.1615 | 12529.1333* | 12529.1082 | 12529.0869* | 12529.0670 | 12529.0506* | 12529.0368* | 12529.0252* |
|  | RQ21 | 25.5 | 12591.1561 | 12591.1206 | 12591.0838 | 12591.0450 | 12591.0045* | 12590.9617 | 12590.9170 | 12590.8707 |
|  | P023 | 23.5 | 12536.8237 | 12536.8499 | 12536.8699 | 12536.8868 | 12536.9007 | 12536.9122 | 12536.9212** | 12536.9277 |
|  | S031 | 25.5 | 12660.6518* | 12680.6181 | 12660.5829* | 12660.5462* | 12660.5074 | 12660.4670* | 12660.4239* | 12660.3801 |
|  | SR32 | 24.5 |  |  | 12657.0300* | 12657.0183* | 12657.0084** | 12657.0012* | 12656.9975* | 12656.9972* |
|  | TR42 | 24.5 | 12732.4642 | 12732.4449 | 12732.4292 | 12732.4172 |  |  |  |  |
|  | P4 | 22.5 | 12637.0505* | 12637.0886 | 12637.1285* | 12637.1699** | 12637.2127* | 12637.2574 | 12637.3040 | 12637.3518* |
| $N=25$ | P1 | 26.5 | 12503.9113 | 12503.8697 | 12503.8265 |  | 12503.7343 | 12503.6841 | 12503.6328 | 12503.5786 |
|  | P012 | 25.5 | 12500.3496 | 12500.3218 |  | 12500.2770 | 12500.2580 | 12500.2416 | 12500.2282 | $12500.2168$ |
|  | PR13 | 24.5 | 12500.6258 | 12500.6439 | 12500.6570 | 12500.6670 |  |  |  |  |
|  | OP23 | 24.5 | 12512.1787 | 12512.2002 | 12512.2167 | 12512.2296 | 12512.2399 | 12512.2480 |  |  |
|  | 0024 | 23.5 | 12516.6734 | 12516.7073 | 12516.7425 | 12516.7789 | 12516.8157 | 12516.8561* | 12516.8954* | 12516.9382 |
|  | P034 | 23.5 | 12583.5088 | 12583.5461 | 12583.5852* | 12583.6254 | 12583.6669* | 12583.7102 | 12583.7551 | 12583.8016 |
|  | SO42 | 25.5 | 12705.1891* | 12705.1701* | 12705.1549 | 12705.1426 | 12705.1334** | 12705.1271 |  | 12705.1230** |
|  | 0 P 43 | 24.5 | 12653.3186 | 12653.3445 | 12653.3664 | 12653.3848 | 12653.4009** | 12653.4146* | 12653.4258* | 12653.4356* |
|  | SR43 | 24.5 | 12705.4647 | 12705.4914 | 12705.5136 | 12705.5324 | 12705.5486 | 12705.5628 | 12705.5750 | 12705.5851 |
|  | 04 | 23.5 | 12657.8127* | 12657.8510* | 12657.8913 | 12657.9333 | 12657.9771 | 12658.0220 | 12658.0690 | 12658.1173 |
|  | 01 | 26.5 | 12531.9707* | 12531.9293* | 12531.8847 | 12531.8385 | 12531.7900* | 12531.7396 | 12531.6871 | 12531.6323 |
|  | QR12 | 25.5 | 12528.4092 | 12528.3811 | 12528.3564 | 12528.3345 | 12528.3146 | 12528.2972 | 12528.2826 | 12528.2703 |
|  | RQ21 | 26.5 | 12590.8681* | 12590.8326 | 12590.7955 | 12590.7565** | 12590.7154** | 12590.6724 | 12590.6280 | 12590.5819* |
|  | PQ23 | 24.5 | 12534.5477 | 12534.5716* | 12534.5922 | 12534.6082 | 12534.6219******** | 12534.6334 | 12534.6430 | 12534.6499 |
|  | MP24 | 23.5 |  | 12490.1268* | 12490.1659** | 12490.2066* | 12490.2458* | 12490.2906** | 12490.3353 | 12490.3817 |
|  | S031 | 26.5 | 12660.6613 | 12660.6275 | 12660.5922 | 12660.5554 | 12660.5167* | 12660.4765* | 12660.4345* | 12660.3898* |
|  | SR32 | 25.5 | 12657.0996* | 12657.0798 |  | 12657.0508* | 12657.0412* | 12657.0343 | 12657.0298* | 12657.0280* |
|  | TR42 | 25.5 | 12732.7972 | 12732.7781 | 12732.7635 | 12732.7517 |  |  |  |  |
| $N=26$ | P1 | 27.5 |  |  |  | 12501.9109* | 12501.8617 |  |  | 12501.7065 |
|  | PQ12 | 26.5 | 12498.5012 | 12498.4743 | 12498.4503 | 12498.4288 | 12498.4097 | 12498.3927 |  |  |
|  | PR13 | 25.5 | 12498.8066 | 12498.8240 | 12498.8364 |  | 12498.8526 |  |  |  |
|  | OP23 | 25.5 | 12508.8201 | 12508.8417 | 12508.8571 | 12508.8699 | 12508.8802 | 12508.8881 | 12508.8942 | 12508.8977 |
|  | 0024 | 24.5 |  |  | 12513.4078 | 12513.4444 | 12513.4823 | 12513.5210 | 12513.5619 | 12513.6034 |
|  | P034 | 24.5 | 12580.5147 | 12580.5520 | 12580.5911 | 12580.6314 | 12580.6736 | 12580.7167 | 12580.7615 | 12580.8080 |
|  | SQ42 | 26.5 | 12704.4378 | 12704.4194* | 12704.4045 | 12704.3925 | 12704.3827******* | 12704.3769* | 12704.3727* | 12704.3727* |
|  | SR43 | 25.5 | 12704.7428 | 12704.7686 | 12704.7904 | 12704.8095 | 12704.8262** | 12704.8405* | 12704.8534** | 12704.8643** |
|  | 04 | 24.5 | 12655.0400 | 12655.0789 | 12655.1200 | 12655.1627* | 12655.2061 | 12655.2513 | 12655.2983 | 12655.3466 |
|  | 01 | 27.5 | 12531.1156 | 12531.0729 | 12531.0284 | 12530.9824 | 12530.9336 | 12530.8834 | 12530.8309 | 12530.7739 |
|  | QR12 | 26.5 | 12527.5768 | 12527.5488 | 12527.5239 | 12527.5015 | 12527.4816 | 12527.4639 | 12527.4479 | 12527.4350 |
|  | R021 | 27.5 | 12590.5125 | 12590.4767 | 12590.4395* | 12590.3998 | 12590.3587 | 12590.3157 | 12590.2722* | 12590.2251 |
|  | PO23 | 25.5 | 12532.2039 | 12532.2268 | 12532.2460 | 12532.2640* | 12532.2764 | 12532.2878 | 12532.2973 | 12532.3046 |
|  | PR24 | 24.5 | 12536.7217 | 12536.7585 | '12536.7975 | 12536.8376 | 12536.8784 | 12536.9212* | 12536.9655 | 12537.0110 |
|  | 5031 | 27.5 | 12660.6083 | 12660.5740* | 12660.5394 | 12660.5021 | 12660.4640 | 12660.4239** | 12660.3813* | 12660.3382* |
|  | SR32 | 26.5 |  | 12657.0508* | 12657.0343* | 12657.0220** | 12657.0120* | 12657.0046* | 12657.0012* | 12656.9973* |
|  | TR42 | 26.5 | 12733.0782 | 12733.0603 | 12733.0459 | 12733.0338 |  |  |  |  |


|  | ASSIGN | N J' | $F=J \cdot 7 / 2$ | $F=J-5 / 2$ | $F=J \cdot 3 / 2$ | F=J-1/2 | $F=J+1 / 2$ | $F=3+3 / 2$ | $F=\mathrm{J}+5 / 2$ | $F=1+7 / 2$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $N=27$ | P1 | 28.5 |  | 12500.0481 | 12500.0036 | 12499.9575 |  | 12499.8606 | 12499.8089 | 12499.7546 |
|  | PQ12 | 27.5 | 12496.5730 | 12496.5456 | 12496.5223 | 12496.5010 | 12496.4815 | 12496.4644 | 12496.4489 | 12496.4362 |
|  | PR13 | 26.5 | 12496.9068 | 12496.9224* | 12496.9356 | 12496.9447 |  | 12496.9569 |  |  |
|  | 0024 | 25.5 | 12509.9273 | 12509.9619 | 12509.9968 | 12510.0334 | 12510.0722 | 12510.1109 | 12510.1512 | 12510.1930 |
|  | PQ34 | 25.5 | 12577.4619** | 12577.4997* | 12577.5382* | 12577.5795* | 12577.6208* | 12577.6642 | 12577.7091****** | 12577.7549* |
|  | SR43 | 26.5 | 12703.9698 | 12703.9948 | 12704.0167 | 12704.0357 | 12704.0524 | 12704.0676 | 12704.0808 | 12704.0923 |
|  | 04 | 25.5 | 12652.2176 | 12652.2572 | 12652.2982 | 12652.3406 | 12652.3846 | 12652.4301 | 12652.4774 | 12652.5257 |
|  | 01 | 28.5 | 12530.1834 | 12530.1401 | 12530.0952** | 12530.0483* | 12529.9995 | 12529.9487 | 12529.8960* | 12529.8611* |
|  | 0 R 12 | 27.5 | 12526.6672* | 12526.6385 | 12526.6129 | 12526.5910** | 12526.5710 | 12526.5525 | 12526.5368 | 12526.5223 |
|  | RO21 | 28.5 | 12590.0895 | 12590.0533* | 12590.0151* | 12589.9759 | 12589.9345 | 12589.8917* | 12589.8473 | 12589.8009 |
|  | P023 | 26.5 | 12529.7927 | 12529.8150 | 12529.8335* | 12529.8495 | 12529.8632 | 12529.8751 | 12529.8853 | 12529.8928* |
|  | PR24 | 25.5 | 12534.3354 |  |  | 12534.4504 | 12534.4917 | 12534.5337 | 12534.5781 | 12534.6219** |
|  | 5031 | 28.5 | 12660.4925 | 12660.4592 | 12660.4239* | 12660.3870* | 12660.3488 | 12660.3074** | 12660.2667 | 12660.2232 |
|  | SR32 | 27.5 | 12656.9754* | 12656.9569 | 12656.9418* |  | 12656.9195 | 12656.9126 | 12656.9064********) | 12656.9033** |
|  | TR42 | 27.5 | 12733.3078 | 12733.2900 | $12733.2757$ | 12733.2645 |  |  |  |  |
| $N=28$ | P1 | 29.5 | 12498.0601 | 12498.0176 | 12497.9735 |  | 12497.8788 | 12497.8302 | 12497.7786 | 12497.7251 |
|  | P012 | 28.5 | 12494.5657 | 12494.5392 | 12494.5158 | 12494.4930 | 12494.4743 | 12494.4573 | 12494.4409 | 12494.4278 |
|  | PR13 | 27.5 | 12494.9283 | 12494.9433 | 12494.9561 | 12494.9644 | 12494.9714 | 12494.9762 | 12494.9789* | 12494.9796* |
|  | OP23 | 27.5 | 12501.8746* | 12501.8935* |  |  |  |  |  |  |
|  | 0024 | 26.5 | 12506.4412 | 12506.4752 | 12506.5106 | 12506.5477 | 12506.5856 | 12506.6250 | 12506.6647 | 12506.7060 |
|  | P034 | 26.5 | 12574.3502* | 12574.3881* | 12574.4266 | 12574.4679 | 12574.5098* | 12574.5529* | 12574.5975* | 12574.6435* |
|  | OP43 | 27.5 | 12644.7789 | 12644.8031 | 12644.8244 | 12644.8435 | 12644.8599 | 12644.8748 | 12644.8885 | 12644.9002 |
|  | SR43 | 27.5 | 12703.1450 | 12703.1701 | 12703.1914 | 12703.2105 | 12703.2278 | 12703.2428 | 12703.2572 | 12703.2693 |
|  | 01 | 29.5 | 12529.1765 | 12529.1333 | 12529.0869* | 12529.0407 | 12528.9913 | 12528.9404 | 12528.8870 | 12528.8324 |
|  | OR12 | 28.5 | 12525.6821 | 12525.6543 | 12525.6291* | 12525.6065 | 12525.5858 | 12525.5672 | 12525.5500 | 12525.5351 |
|  | RQ21 | 29.5 | 12589.5988 | 12589.5619 | 12589.5234* | 12589.4841 | 12589.4431 | 12589.4000* | 12589.3555** | 12589.3090** |
|  | P023 | 27.5 | 12527.3147 | 12527.3359 | 12527.3540 | 12527.3697 | 12527.3834 | 12527.3949 | 12527.4049 | 12527.4135 |
|  | PR24 | 26.5 |  |  |  |  |  |  |  | 12532.1678* |
|  | S031 | 29.5 | 12660.3145* | 12660.2805 | 12660.2452 | 12660.2085 | 12660.1702* | 12660.1304 | 12660.0884 | 12660.0450 |
|  | SR32 | 28.5 |  | 12656.8018 | 12656.7876 | $12656.7744$ | 12656.7646* | 12656.7552* | 12656.7512* | 12656.7488* |
|  | TR42 | 28.5 | 12733.4850 | 12733.4684 | 12733.4544 | 12733.4427 |  |  |  |  |
| $N=29$ | P1 | 30.5 | 12495.9518 |  | 12495.8658 | 12495.8200 | 12495.7726* | 12495.7229* | 12495.6705 | 12495.6167 |
|  | P012 | 29.5 | $12492.4797$ |  | 12492.4304 | 12492.4087 | 12492.3891 | 12492.3713 | 12492.3554 | 12492.3411 |
|  | PR13 | 28.5 | 12492.8708 | 12492.8868* |  |  |  |  |  |  |
|  | OP23 | 28.5 | 12498.2875 | 12498.3059 | 12498.3209 | 12498.3336 | 12498.3440 | 12498.3531 |  |  |
|  | 0024 | 27.5 | 12502.8778 | 12502.9117 | 12502.9475 | 12502.9847 | 12503.0222 | 12503.0620 | 12503. 1024 | 12503.1435 |
|  | P034 | 27.5 | 12571.1786* | 12571.2171 | 12571.2568 | 12571.2973 | 12571.3393 | 12571.3825 | 12571.4272 | 12571.4733 |
|  | QP43 | 28.5 | 12641.8325* | 12641.8562* | 12641.8786* | 12644.8961* | 12641.9128* | 12641.9286* | 12641.9424** | 12641.9548* |
|  | 01 | 30.5 | 12528.1004 | 12528.0564 | 12528.0108 | 12527.9629 | 12527.9133* | 12527.8626 | 12527.8091 | 12527.7540 |
|  | QR12 | 29.5 | 12524.6283 | 12524.6003 | 12524.5755* | 12524.5523 | 12524.5308 | 12524.5113 | 12524.4947* | 12524.4787 |
|  | RO21 | 30.5 | 12589.0400 | 12589.0030 | 12588.9645 | 12588.9245 | 12588.8832 | 12588.8406 | 12588.7955** | 12588.7489 |
|  | P023 | 28.5 | 12524.7694 | 12524.7897 | 12524.8074 | 12524.8231 | 12524.8365 | 12524.8484 | 12524.8582** | 12524.8666 |
|  | PR24 | 27.5 | 12529.3603* | 12529.3958 |  | 12529.4745 | 12529.5148 | 12529.5570 | 12529.6007 | 12529.6453 |
|  | 5031 | 30.5 | 12660.0732 | 12660.0392 | 12660.0040 | 12659.9676 | 12659.9291* | 12659.8877* | 12659.8483** | $12659.8048$ |
|  | SR32 | 29.5 | 12656.6009 | 12656.5833 | $12656.5687$ | $12656.5561$ |  | 12656.5383* | 12656.5330* | 12656.5295* |
|  | TR42 | 29.5 | 12733.6097 | 12733.5937 | 12733.5799 | 12733.5685 |  |  |  |  |
| $N=30$ | P1 | 31.5 | 12493.7668 | 12493.7246 | 12493.6796 | 12493.6335 | 12493.5854 | 12493.5358 | 12493.4840 | 12493.4307 |
|  | P012 30 | 30.5 | 12490.3167 | 12490.2906 | 12490.2672 | 12490.2458 | 12490.2253 | 12490.2066 | 12490.1914 | 12490.1768 |
|  | PR13 | 29.5 | 12490.7356 | 12490.7504 | 12490.7613 | 12490.7700 | 12490.7767 | 12490.7818 |  |  |
|  | 0 P 23 | 29.5 | 12494.6253 | 12494.6424 | 12494.6585 | 12494.6708 | 12494.6806 | 12494.6896 | $12494.6964$ | $12494.7019$ |
|  | 0024 | 28.5 | 12499.2383 | 12499.2727 | 12499.3089 | 12499.3455 | 12499.3840 | 12499.4237 | $12499.4634$ | $12499.5050$ |
|  | OP43 | 29.5 | 12638.8355 | 12638.8590 | 12638.8797 | 12638.8993 | 12638.9166 | 12638.9319 | 12638.9461 | 12638.9587 |
|  | 04 | 28.5 | 12643.4486 | 12643.4896 | 12643.5312 | 12643.5749 | 12643.6193 | 12643.6654 | 12643.7127 | 12643.7617 |
|  | 01 | 31.5 | 12526.9613 | 12526.9168 | 12526.8709 | 12526.8226 | 12526.7724 | 12526.7210 | 12526.6672* | 12526.6109* |
|  | OR12 | 30.5 | 12523.5110** | 12523.4851** | 12523.4581** | 12523.4351 | 12523.4131 | 12523.3929 | 12523.3745* | 12523.3582 |
|  | RO21 | 31.5 | 12588.4135 | 12588.3763* | 12588.3385 | 12588.2979* | 12588.2563 | 12588.2124 | 12588.1679 | 12588.1211* |
|  | P023 | 29.5 | 12522.1567 | 12522.1767 | 12522.1943 | 12522.2089 | 12522.2224 | 12522.2341 | 12522.2446 | 12522.2527 |
|  | PR24 | 28.5 |  |  |  |  | 12526.9261 | 12526.9680 | 12527.0117 | 12527.0555 |
|  | 5031 | 31.5 | 12659.7689* | 12659.7346 | $12659.6995$ | 12659.6632 | 12659.6252 | 12659.5850 | 12659.5437 | 12659.5019 |
|  | SR32 | 30.5 | 12656.3191 | 12656.3023 | 12656.2872* |  |  |  |  |  |
|  | TR42 3 | 30.5 | 12733.6814 | 12733.6659 | 12733.6526 | 12733.6414 |  |  |  |  |


|  | ASSIGN | N J" | $F=\mathrm{J}-7 / 2$ | FxJ-5/2 | F=J-3/2 | $F=J-1 / 2$ | $F=3+1 / 2$ | $F=3+3 / 2$ | $F=J+5 / 2$ | $F \pm \sqrt{ }+7 / 2$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $N=31$ | P1 | 32.5 | 12491.5057 | 12491.4627 | 12491.4187 | 12491.3716 | 12491.3236 | 12491.2738 | 12491.2223 | 12491.1694 |
|  | OP23 | 30.5 | 12490.8856* | 12490.9027* | 12490.9179 | 12490.9304 | 12490.9406 | 12490.9504 | 12490.9577 | 12490.9641 |
|  | 0024 | 29.5 | 12495.5232 | 12495.5585 | 12495.5940 | 12495.6310 | 12495.6705 | 12495.7085 | 12495.7490 | 12495.7898 |
|  | ap43 | 30.5 | 12635.7876 | 12635.8107* | 12635.8320 | 12635.8509 | 12635.8688 | 12635.8845* | 12635.8989* | 12635.9125 |
|  | 04 | 29.5 | 12640.4247 | 12640.4656 | 12640.5079 | 12640.5517* | 12640.5969 | 12640.6428 | 12640.6899* | 12640.7388 |
|  | 01 | 32.5 | 12525.7686 | 12525.7235 | 12525.6766 | 12525.6286 | 12525.5779 | 12525.5256 | 12525.4716 | 12525.4152 |
|  | QR 12 | 31.5 | 12522.3403 | 12522.3134 | 12522.2868* | 12522.2635 | 12522.2408 | 12522.2199* | 12522.2013 | 12522.1839** |
|  | RO21 | 32.5 | 12587.7195 | 12587.6822 | 12587.6435 | 12587.6030** | 12587.5604* | 12587.5176 | 12587.4728 | 12587.4259 |
|  | P023 | 30.5 | 12519.4768 | 12519.4962 | 12519.5132* | 12519.5280 | 12519.5414 | 12519.5531 | 12519.5631* | 12519.5718* |
|  | PR24 | 29.5 | 12524.1136* | 12524.1522 | 12524.1891* | 12524.2291* | 12524.2694 | 12524.3111 | 12524.3545 | 12524.3982 |
|  | 5031 | 32.5 |  | 12659.3671 | 12659.3317 | 12659.2950* | 12659.2573* | 12659.2179 | 12659.1767 | 12659.1340 |
|  | SR32 | 31.5 | 12655.9737 | 12655.9573 | 12655.9430** |  |  | 12655.9112* | 12655.9074* |  |
|  | OP34 | 29.5 | 12533.3270 | 12533.3679 | 12533.4084 | 12533.4508 | 12533.4950 | 12533.5395 | 12533.5857* | 12533.6332* |
|  | TR42 | 31.5 | 12733.7005 | 12733.6850 | 12733.6720 | 12733.6611 |  |  |  |  |
| $N=32$ | 0024 | 30.5 | 12491.7320* |  | 12491.8035 | 12491.8405 | 12491.8792 | 12491.9188 | 12491.9591 | 12492.0000 |
|  | 04 | 30.5 |  |  |  |  |  | 12637.5681* | 12637.6163* | 12637.6655* |
|  | 01 | 33.5 | 12524.5366* | 12524.4899* | 12524.4429 | 12524.3931 | 12524.3424 | 12524.2894 | 12524.2345 | 12524.1779 |
|  | OR 12 | 32.5 | 12521.1312 | 12521.1031 | 12521.0763 | 12521.0513* | 12521.0281 | 12521.0068 | 12520.9869 | 12520.9685 |
|  | RQ21 | 33.5 | 12586.9576 | 12586.9202 | 12586.8812 | 12586.8411 | 12586.7989 | 12586.7554 |  | 12586.6629* |
|  | P023 | 31.5 |  |  |  | 12516.7789* | 12516.7931* | 12516.8051* | 12516.8157* | 12516.8236 |
|  | PR24 | 30.5 | 12521.3910* | 12521.4273 | 12521.4663 | 12521.5051 | 12521.5456 | 12521.5878 | 12521.6307 | 12521.6737* |
|  | 5031 | 33.5 | 12658.9703 | 12658.9358 | 12658.9009 |  | 12658.8266* | 12658.7866** | 12658.7467* |  |
|  | QP32 | 32.5 | 12587.6103 | 12587.5939 | 12587.5798 | 12587.5675 | 12587.5579** | 12587.5474** | 12587.5433* | 12587.5389* |
|  | OP34 | 30.5 | 12528.8801 | 12528.9198 | 12528.9615 | 12529.0041 | 12529.0481* | 12529.0927 | 12529.1395 |  |
|  | QR34 | 30.5 | 12592.7458 | 12592.7862 | 12592.8274 | 12592.8701 | 12592.9143 | 12592.9597 | 12593.0060 | 12593.0536 |
|  | TR42 | 32.5 | 12733.6659 | 12733.6526* | 12733.6374 | 12733.6270 |  |  |  |  |
| $N=33$ | 01 | 34.5 | 12523.2869 | 12523.2403 | 12523.1906* | 12523.1410 | 12523.0889 | 12523.0347 | 12522.9791 | 12522.9212* |
|  | QR12 | 33.5 |  | 12519.8764** | 12519.8472* | 12519.8218* | 12519.7974 | 12519.7751* | 12519.7535 | 12519.7336* |
|  | RQ21 | 34.5 | 12586.1288 | 12586.0908 | 12586.0515* | 12586.0106 | 12585.9690 | 12585.9253 | 12585.8800* | 12585.8333* |
|  | P023 | 32.5 | 12593.9158 | 12513.9339 | 12513.9504 | 12513.9653 | 12513.9785* |  |  |  |
|  | PR24 | 31.5 |  |  |  |  |  |  |  | 12518:8830** |
|  | 5031 | 34.5 | 12658.4759 | 12658.4416 | 12658.4067 | 12658.3702 | 12658.3320 | 12658.2929 | 12658.2519** | 12658.2088* |
|  | QP32 | 33.5 | 12585.0965 | 12585.0804 | 12585.0660 | 12585.0540 | 12585.0426 | 12585.0355 | 12585.0282* | 12585.0252* |
|  | SR32 | 33.5 | 12655.0929 | 12655.0789* | 12655.0628 |  | 12655.0400 | 12655.0340 | 12655.0269 |  |
|  | OP34 | 31.5 | 12524.3714 | 12524.4114 | 12524.4531 | 12524.4956* | 12524.5401* | 12524.5850** | 12524.6316** | 12524.6788 |
|  | QR34 | 31.5 | 12590.2813* | 12590.3221* | 12590.3641 | 12590.4070 | 12590.4520** | 12590.4969* | 12590.5430* | 12590.5906* |
|  | TR42 | 33.5 | 12733.5774 | 12733.5629 | 12733.5510** | 12733.5398 | 12733.5318 | 12733.5250 | 12733.5206* | 12733.5180** |
| $N=34$ |  | $35.5$ | 12522.0567 | 12522.0078 | $12521.9578$ | 12521.9061 | 12521.8523 | 12521.7978* | 12521.7397 | 12521.6804 |
|  | QR12 | 34.5 |  |  | $12518.6370$ | 12518.6100 |  | 12518.5603* | 12518.5365* | 12518.5150 |
|  | RQ21 | 35.5 | 12585.2334 | 12585.1949 | 12585.1557** | 12585.1144 | 12585.0719 | 12585.0292* | 12584.9826* | 12584.9363* |
|  | 5031 | 35.5 | 12657.9178 | 12657.8838 |  | 12657.8127** | 12657.7741 | 12657.7353 | 12657.6947 | 12657.6524* |
|  | OP32 | 34.5 | 12582.5195 | 12582.5032 | 12582.4896 | 12582.4776 | 12582.4673 | 12582.4593 | 12582.4527 | 12582.4482 |
|  | Op34 | 32.5 |  |  | 12519.8835* | 12519.9264* | 12519.9712 | 12520.0161* | 12520.0620 | 12520.1101* |
|  | QR34 | 32.5 | 12587.7549 | 12587.7957 | 12587.8379 | 12587.8812** |  | 12587.9703* | 12588.0177 | $12588.0650$ |
|  | TR42 | 34.5 | 12733.4340* | 12733.4216 | 12733.4089 | 12733.3981 | 12733.3897 | 12733.3837* | 12733.3793* | 12733.3773* |
| N=35 | 01 | 36.5 | 12520.9046 | 12520.8541 | 12520.8023 | 12520.7481 | 12520.6921 | 12520.6351 | 12520.5745 | 12520.5133 |
|  | OP12 | 35.5 |  | 12444.6630* | 12444.6346* | 12444.6108* |  | 12444.5634* | 12444.5398* | 12520.5133 |
|  | OR12 | 35.5 |  |  |  |  | 12517.4454* |  | 12517.3932 | 12517.3692 |
|  | 0013 | 34.5 |  |  |  | 12445.2668* |  |  |  | 12517.3692 |
|  | R021 | 36.5 | 12584.2699 | 12584.2315* |  | 12584.1501 | 12584.1077 | 12584.0642* | 12584.0183 | 12583.9718* |
|  | P023 | 34.5 | 12508.0876 | 12508. 1055 | 12508.1209 | 12508.1346 | 12508.1473 | 12508.1587 | 12508.1682 | 12508.1781 |
|  | s031 | 36.5 | 12657.2960 | 12657.2622 | 12657.2271 | 12657.1908 |  |  |  | 12657.0298* |
|  | OP34 | 33.5 | 12515.1684** | 12515.2091 |  |  | 12515.3381 | 12515.3835 | 12515.4301 | 12515.4777 |
|  | QR34 | 33.5 | 12585.1684 | 12585.2069 | 12585.2496* | 12585.2927 | 12585.3373 | 12585.3828 | 12585.4296 | 12585.4767 |
|  | TR42 | 35.5 | 12733.2376 |  |  |  | 12733.1934 | 12733.1873 | 12733.1834* | 12733.1806* |
|  | P4 | 33.5 | 12592.8949 | 12592.9382* | 12592.9802 | 12593.0238** |  | 12593.1170 | 12593.1650 | 12593.2141 |

Appendix A. The Line Assignments of the VO $B^{4} \Pi-X^{4} \Sigma^{-}(0,0)$ Band.

|  | ASSIGN | N J" | $f=J-7 / 2$ | $F=J-5 / 2$ | $F=J-3 / 2$ | $F=J \cdot 1 / 2$ | $F=J+1 / 2$ | $F=\sqrt{ }+3 / 2$ | $F=J+5 / 2$ | $f=\mathrm{J}+7 / 2$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $N=36$ | OP12 $0013$ | $\begin{aligned} & 36.5 \\ & 35.5 \end{aligned}$ | 12441.3164* | 12441.2874* | 12441.2589* | $\begin{aligned} & 12441.2321^{*} \\ & 12441.9197 \end{aligned}$ | 12441.2032* | 12441.1823* | 12441.1576* | 12441.1380* |
|  | P023 | 35.5 | 12505.0750 | 12505.0915 | 12505.1079* | 12505.1209 | 12505.1334 | 12505.1452 | 12505.1547 |  |
|  | OP32 | 36.5 | 12577.1780* | 12577.1627 | 12577.1490* | 12577.1372 | 12577.1274 | 12577.1187* | 12577.1134** |  |
|  | OP34 | 34.5 | 12510.4762 | 12510.5165 | 12510.5587 | 12510.6019 | 12510.6464 | 12510.6918 | 12510.7380 | 12510.7857 |
|  | QR34 | 34.5 | 12582.5144 | 12582.5552 | 12582.5977 | 12582.6410 | 12582.6858 | 12582.7310 | 12582.7781 | 12582.8260* |
|  | TR42 | 36.5 |  |  |  |  | 12732.9436* | 12732.9384* | 12732.9330** | 12732.9306* |
|  | R4 | 34.5 | 12661.3906 | 12661.4327* | 12661.4771 | 12661.5223* | 12661.5679* | 12661.6158 |  | 12661.7131* |
| $N=37$ |  |  |  |  |  |  | 12438.6366* |  |  |  |
|  | SR32 | $37.5$ | 12652.5681 | 12652.5535 | 12652.5396 | 12652.5257* |  |  |  |  |
|  | OP34 | 35.5 | 12505.7207 | 12505.7616 | 12505.8039 | 12505.8476 | 12505.8921 | 12505.9373 | 12505.9843 | 12506.0318 |
|  | QR34 | 35.5 |  | 12579.8400 | 12579.8830 | $12579.9264$ | $12579.9714$ | 12580.0170 | 12580.0631 | 12580.1109 |
|  | TR42 | 37.5 |  |  |  |  |  | 12732.6311* | 12732.6273* | 12732.6247* |
|  | R4 | 35.5 | 12659.0784 | 12659.1212 | 12659.1657 | 12659.2108 | 12659.2573* | 12659.3043* |  |  |
| $N=38$ | NPO2 | 38.5 |  | 12421.3408* | 12421.2906* | 12421.2381* |  |  | 12421.0997* | 12421.0576* |
|  | N003 | 37.5 |  |  |  |  |  |  | 12421.9083* |  |
|  | OPI2 | 38.5 | 12434.9090* | 12434.8740* |  |  | 12434.7783* | 12434.7473* | 12434.7156* | 12434.6879* |
|  | 0013 | 37.5 |  |  |  |  | 12435.5394* |  |  |  |
|  | PQ23 | 37.5 |  |  | 12498.8807 | 12498.8946 | 12498.9068* | 12498.9175 | 12498.9274 | 12498.9358 |
|  | OP34 | 36.5 | 12500.9047 | 12500.9460 | 12500.9886 | 12501.0320 | 12501.0764 | 12501.1220 | 12501.1683 | 12501.2157 |
| $N=39$ | P034 | 37.5 | 12536.1839 | 12536.2228 | 12536.2636 | 12536.3048 |  | 12536.3901 | 12536.4345 | 12536.4799 |
|  | NP02 | 39.5 | 12432.1228* | 12432.0829* | 12432.0423* | 12432.0023* |  | 12431.9318* | 12431.8976* | $12431.8648^{*}$ |
|  | 01 | 40.5 | 12506.5042* | 12506.4506 | 12506.3950 | 12506.3380 | 12506.2786 | 12506.2181 | 12506.1555 | 12506.0917 |
|  | OP12 | 39.5 |  | 12419.8280* | 12419.7827* | 12419.7373* | 12419.6944* | 12419.6529* | 12419.6131* | 12419.5738* |
|  | PQ23 | 38.5 | 12495.6402* | 12485.6555 | 12495.6705* | 12495.6843* | 12495.6954 | 12495.7067* |  |  |
|  | OP34 | 37.5 |  |  |  | $12496.1549$ |  | $12496.2437$ | $12496.2900$ | 12496.3371 |
|  | TR42 | 39.5 |  |  |  |  |  |  |  | 12731.8474 |
| $N=40$ | NP02 | 40.5 |  |  |  |  |  |  |  | 12429.5138* |
|  | 01 | 41.5 |  |  |  | 12505.2216 |  |  | 12505.0520 | 12504.9919 |
|  | OP12 | 40.5 |  |  |  |  | 12417.6282* | 12417.5937* | 12617.5602* | 12417.5262* |
|  | 0013 | 39.5 |  |  | 12418.4598* |  |  |  |  |  |
|  | OP34 | 38.5 | 12491.0864 | 12491.1289 | 12491.1694* | 12491.2152 | 12491.2597 | 12491.3048 | 12491.3514 | 12491.3998 |
| $N=41$ | $\begin{gathered} 01 \\ 0 P 12 \end{gathered}$ | $\begin{aligned} & 42.5 \\ & 41.5 \end{aligned}$ | 12415.064** | 12415.0277* | 12414.9973* | 12414.9632* | $\begin{aligned} & 12503.6444 \\ & 12414.9332^{*} \end{aligned}$ | $\begin{aligned} & 12503.5904 \\ & 12414.9025 * \end{aligned}$ | 12414.8714** | $\begin{aligned} & 12503.4772 \\ & 12414.8459^{*} \end{aligned}$ |
| $N=42$ | $\begin{gathered} 01 \\ 0 p 12 \end{gathered}$ | $\begin{aligned} & 43.5 \\ & 42.5 \end{aligned}$ | 12411.8015* |  |  |  | 12501.8304 |  | 12501.7240 | $\begin{aligned} & 12501.6684 \\ & 12411.6109 * \end{aligned}$ |
| $N=43$ | $\begin{gathered} 01 \\ 0 p 12 \end{gathered}$ | $\begin{aligned} & 44.5 \\ & 43.5 \end{aligned}$ | $\begin{aligned} & 12499.9964 \\ & 12408.1331 * \end{aligned}$ |  |  | 12499.8548 | 12499.8038 | 12499.7510* | 12499.6987 | $\begin{aligned} & 12499.6444 \\ & 12407.9589 \end{aligned}$ |
| $N=44$ | 01 | 45.5 | 12497.8033* | 12497.7564 | 12497.7113* | 12497.6612 | 12497.6109* | 12497.5609 | 12497.5070 | 12497.4537 |
| $N=45$ | 01 | 46.5 | 12495.4723 | 12495.4261 | 12495.3788 |  | 12495.2820 | 12495.2320 | 12495.1791 | 12495.1251 |
| $N=46$ | 01 | 47.5 | 12493.0225* |  | 12492.9316* | 12492.8802* | 12492.8339* |  |  |  |
| $N=47$ | '01 | 48.5 | 12490.4657 | 12490.4197 |  |  | 12490.2772* |  |  | 12490.1217* |


[^0]:    ${ }^{1}$ Some textbooks use $\alpha$ for the extinction coeficient instead of $\varepsilon$.

[^1]:    ${ }^{1}$ It should be noted here that the post-subscripts used on the term symbols of individual spin components are in fact $\Lambda+\Sigma$, not $|\Lambda+\Sigma|$. For example, the electron spin components for the ${ }^{4} \Pi$ state $(\Lambda=1$, $\left.S=\frac{3}{2}, \Sigma=\frac{3}{2}, \frac{1}{2},-\frac{1}{2},-\frac{3}{2}\right)$ are ${ }^{4} \Pi_{\frac{3}{2}},{ }^{4} \Pi_{\frac{3}{2}},{ }^{4} \Pi_{\frac{1}{2}}$, and ${ }^{4} \Pi_{-\frac{1}{2}}$, while the values for $|\Omega|$ are $\frac{5}{2}, \frac{3}{2}, \frac{1}{2}$, and $\frac{1}{2}$ respectively.

[^2]:    ${ }^{2}$ Brown et al [26] have recently expressed the third order spin-orbit Hamiltonian in a slightly different, but equivalent manner. However, since the subroutine for the ground state matrix elements had already been written using the previous convention, it was not changed.

[^3]:    ${ }^{3}$ Special acknowledgement to Dr John Brown (Oxford University) for clarifying the matrix elements of the hyperfine interaction between the ${ }^{2} \Sigma^{+}$and ${ }^{4} \Pi$ states.

[^4]:    ${ }^{1}$ A spectral feature is assigned to a particular eigenstate provided that it meets the criterion that the largest contribution to the total wavefunction comes from the eigenvectors of that eigenstate.

[^5]:    ${ }^{a}$ Data taken from $A^{4} \Pi-X^{4} \Sigma^{-}(0,1)$ band, reference 35
    ${ }^{b}$ Data taken from $B^{4} \Pi-X^{4} \Sigma^{-}(1,0)$ band, reference 37

[^6]:    * indicates blended lines

