HIGH RESOLUTION SPECTROSCOPY OF THE VANADIUM OXIDE $B^{4}\Pi$ — $X^{4}\Sigma^{-}$ (0,0) BAND

By

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in

the Faculty of Graduate Studies Department of Chemistry

We accept this thesis as conforming to the required standard

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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 ⁵¹V 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 $(4s\sigma)^1(3d\delta)^2$ because of the large Fermi contact interaction which arose from an unpaired electron having primarily metal 4s 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 cm^{-1} .

Table of Contents

Α	bstra	act	ii	
$\mathbf{L}_{\mathbf{i}}$	List of Tables v			
Li				
A	ckno	wledgements	ix	
D	edica	ation	x	
1	Int	roduction		
2 Experimental		perimental	6	
	2.1	Introduction	6	
	2.2	The Calibration System	10	
	2.3	Saturation Spectroscopy	12	
	2.4	Lamb Dips and Intermodulated Fluorescence	16	
	2.5	Wavelength Resolved Fluorescence Spectroscopy	20	
3 Energy Expressions and the Hamiltonian			24	
	3.1	Introduction	24	
	3.2	Perturbations	25	
	3.3	Hund's Coupling Cases	28	
		3.3.1 Case (a_{β})	28	
		3.3.2 Case $(\mathbf{b}_{\beta J})$	30	

	3.4	Hamiltonian Matrix Elements for the $X^4\Sigma^-$ state $\ldots \ldots \ldots \ldots \ldots \ldots \ldots$		
		3.4.1	Rotational Structure	33
		3.4.2	Fine Structure	33
		3.4.3	Magnetic Hyperfine Hamiltonian	37
		3.4.4	The Electric Quadrupole Interaction	38
	3.5	The H	Iamiltonian for the ${}^{4}\Pi$ upper state $\ldots \ldots \ldots \ldots \ldots \ldots \ldots$	39
		3.5.1	Rotational and Fine Structure	39
		3.5.2	Λ -type Doubling	40
		3.5.3	Magnetic Hyperfine Interactions	41
		3.5.4	Electric Quadrupole Interaction	43
	3.6	The H	lamiltonian for the $a^2\Sigma^+$ State	43
	3.7	The ²	Σ^+ – ⁴ II Matrix Elements	44
4	Ana	alysis o	of the Spectra	47
	4.1	Introd	uction	47
	4.2	The G	round State of VO	50
		4.2.1	The Spin-spin and Spin-rotation Interactions	50
		4.2.2	The Hyperfine Splitting in the Ground State	52
	4.3	The B	$^{24}\Pi$ State \ldots	58
		4.3.1	The Spin-orbit Splitting of the $B^4\Pi$ State	58
		4.3.2	The Λ -type Doubling in the $B^4\Pi$ State \ldots	60
	4.4	The In	iteraction Between the $B^4\Pi$ and $a^2\Sigma^+$ States $\ldots \ldots \ldots \ldots$	60
5	Res	ults		67
6	Disc	ussion		70
	6.1	Rotatio	onal Structure	70

	6.2	Electron Configurations	71
	6.3	The Molecular Spin-Orbit Parameters	73
	6.4	The $B^4\Pi / a^2\Sigma^+$ Perturbation $\ldots \ldots \ldots$	77
7	Con	clusions	80
Bi	bliog	raphy	82
A	The	Line Assignments of the VO $B^4\Pi - X^4\Sigma^-$ (0,0) Band.	85

List of Tables

5.1	The constants for the $X^4\Sigma^-$ ($v = 0$) state of VO	67
5.2	The constants for the $a^2\Sigma^+$ ($v = 2$) state of VO	68
5.3	The constants for the $B^4\Pi$ ($v = 0$) state of VO	69
6.1	The rotational constants and average bond lengths of the states of the VO	
	$B^{4}\Pi - X^{4}\Sigma^{-}$ transition.	71
6.2	Table of the equilibrium rotational constants from the $B^4\Pi - X^4\Sigma^-$	
	transition.	72
6.3	Table of the four sub-band origins of the $B^4\Pi$ state	74
6.4	The band origin and higher spin-orbit parameters of the $B^4\Pi$ state	75
6.5	Calculations of the anharmonic oscillator overlap integrals	79

List of Figures

1.1	The molecular orbital diagram for VO	2
1.2	Selected electronic states of VO	4
2.1	Schematic diagram of the experimental apparatus for IMF spectroscopy	7
2.2	A schematic diagram of the calibration system.	10
2.3	Plots of the velocity distributions of the E_2 (a); and E_1 (b) levels when	
	an intense laser beam with vector $ec{k}$ and frequency ω passes through the	
	sample cell	14
2.4	Plots of the saturated $(\alpha_s(\omega))$ and unsaturated $(\alpha_0(\omega))$ absorption coeffi-	
	cients as a function of excitation frequency (ω)	15
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 absorp-	
	tion coefficient for the sample	17
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)	19
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)	22
3.1	Illustration of an avoided crossing between two states	26
3.2	Hund's case (a_β) coupling scheme	29
3.3	Hund's case $(b_{\beta J})$ coupling scheme	32
3.4	The hyperfine Hamiltonian Matrix for ${}^{4}\Pi$ states interacting with ${}^{2}\Sigma^{+}$ states.	46

The head of the ${}^{S}Q_{31}$ branch; illustrating the density of the $B^{4}\Pi - X^{4}\Sigma^{-}$ (0,0)	
band structure	48
Fortrat diagrams showing transitions involving (a) the e-parity compo-	
nents, and (b) the f-parity components of the F_1 upper spin state	49
The energies of the four electron spin components of the $X^4\Sigma^-$ state of VO.	51
The hyperfine energy level splittings for the F_2 and F_3 spin states of the	
$X^4\Sigma^-$ state of VO	53
(a) The ${}^{S}Q_{31}(9)$ and (b) the $R_4(7)$ lines showing how the hyperfine struc-	
tures are <i>mirrored</i>	55
Plot of the ${}^{S}R_{32}(14)$ line including induced lines from the internal hyperfine	
perturbation	57
The upper state electronic term energies as a function of $\left(J+\frac{1}{2}\right)^2$	59
Plot of the Λ -type splittings of the four spin states of $B^4\Pi$	61
The hyperfine energy levels of the $B^4 \prod_{-\frac{1}{2}f}$ and $a^2 \Sigma_f^+$ states	63
The hyperfine energy levels of the $B^4 \prod_{-\frac{1}{2}e}$ and $a^2 \Sigma_e^+$ states	64
The hyperfine widths of (a) the Q_1 branch, and (b) the $^{O}P_{12}$ branch	65
	The head of the ${}^{S}Q_{31}$ branch; illustrating the density of the $B^{4}\Pi - X^{4}\Sigma^{-}$ (0,0) band structure

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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 3d transition metal monoxides, for various reasons. First, oxygen is also one of the more abundant elements and, second, the 3d 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 3d monoxides is

1



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 μ , were in fact attributed to VO by Kuiper et al [3], some time before laboratory work by Lagerquist 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].

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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 μ 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 V₂O₅ 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 μ region. With the development, in the past three years, of commercial continuous-wave Ti:sapphire ring lasers, the 0.8 μ 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 μ , 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 VOCl₃ 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.



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

The Doppler linewidth for room temperature VO at around 12 500 cm⁻¹ is approximately 600 MHz (0.02 cm⁻¹). The hyperfine splittings arising from the ⁵¹V 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 12 390 cm⁻¹ to 12 740 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 (I_1) 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:

$$F_1 = 28F_{chop}$$

where F_{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

$$F_2 = 36F_{chop}.$$

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

$$F_{ref} = 64F_{chop}$$
$$= F_1 + F_2$$

 F_{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 mW/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 12 390 cm⁻¹ to 12 450 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 I₂ or Te₂[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]

$$\omega = \frac{n\omega_0}{n_0} \tag{2.1}$$

where n_0 and ω_0 refer to the order number and frequency of the marker whose frequency is known, while n and ω 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 $\pm 0.02 \text{ cm}^{-1}$. 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 $0.025046 \text{ cm}^{-1}(750.859 \text{ MHz})$.

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2.3 Saturation Spectroscopy

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

$$I_f = I_i e^{-\epsilon C l} \tag{2.2}$$

where I_f and I_i are the final and initial light intensities, ε is the extinction coefficient¹, C is the sample concentration in moles per litre and l is the path length in centimeters through the sample cell for the radiation. ε 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 I_i and I_f respectively as:

$$C = -\frac{\ln I_f / I_i}{\varepsilon l}$$

The extinction coefficient (ε) has a wavelength dependence defined by the transition energy between the states in question. In accurate spectroscopic studies, ε is replaced by the absorption coefficient (α_0), which for a sample experiencing a weak oscillating electric field of frequency ω and direction \vec{k} , such that \vec{k} is parallel to the z axis, can be expressed as[19]

$$\alpha_0(\omega) = \frac{\gamma^2 \sigma_0 \Delta N_0}{4\sqrt{\pi} v_p} \int_{-\infty}^{\infty} \frac{e^{-(v_z/v_p)^2} dv_z}{(\omega - \omega_0 - k \cdot v_z)^2 - (\gamma/2)^2}.$$
(2.3)

In this equation $v_p = \sqrt{2k_BT/m}$, σ_0 is the absorption cross-section, γ is the sum of the radiative and nonradiative decay constants, ΔN_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 (N_2) is considerably less the population density in the lower state (N_1) . However,

¹Some textbooks use α for the extinction coefficient instead of ε .

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, α_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 ω 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:

$$\omega - \vec{k} \cdot (\vec{v} \pm \Delta \vec{v}) = \omega_{12} \pm \delta \omega, \qquad (2.4)$$

where $\omega_{12} = (E_2 - E_1)/\hbar$ 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:

$$\omega - k \cdot (v_z \pm \Delta v_z) = \omega_{12} \pm \delta \omega \tag{2.5}$$

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 $n_1(v_z)$ population distribution is known as a *Bennett Hole*[18]. The spectral width γ_s of the Bennett hole is related to γ (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, γ_s is much narrower than the Doppler profile. However, this sub-Doppler 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 (a); and E_1 (b) levels when an intense laser beam with vector \vec{k} and frequency ω passes through the sample cell



Figure 2.4: Plots of the saturated $(\alpha_s(\omega))$ and unsaturated $(\alpha_0(\omega))$ absorption coefficients as a function of excitation frequency (ω)

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]:

$$\alpha_s(\omega) = \frac{\gamma^2 \sigma_0 \Delta N_0}{4\sqrt{\pi} v_p} \int_{-\infty}^{\infty} \frac{e^{-(v_z/v_p)^2} \, dv_z}{(\omega - \omega_0 - k \cdot v_z)^2 - (\gamma_s/2)^2}$$
(2.6)

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

$$\alpha_s(\omega) = \alpha_0(\omega)(1+S_0)^{-1/2}.$$
(2.7)

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:

$$\vec{E} = \vec{E_1} + \vec{E_2}$$

$$= E_0 e^{-i(\omega t + kz)} + E_0 e^{-i(\omega t - kz)}$$

$$= E_0 \cos(\omega t + kz) + E_0 \cos(\omega t - kz)$$

$$= 2E_0 \cos \omega t \cos kz$$
(2.8)

The result of having two **E** fields interacting with the ensemble of molecules in the cell is the production of two holes at $v_z = \pm (\omega_0 - \omega)/k$. 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]:

$$\Delta n_s(v_z) = \Delta n_0(v_z) \left[1 - \frac{(\gamma/2)^2 S_0}{(\omega_0 - \omega - kv_z)^2 + (\gamma_S/2)^2} - \frac{(\gamma/2)^2 S_0}{(\omega_0 - \omega + kv_z)^2 + (\gamma_S/2)^2} \right]$$
(2.9)

When $\omega = \omega_0$ this expression reduces to

$$\Delta n_s(v_z) = \Delta n_0(v_z) \left[1 - 2S_0 \left(\frac{\gamma}{\gamma_s}\right)^2 \right].$$
(2.10)

The effect of a saturating standing wave on the change in population of the lower state $(\Delta n(v_z))$ 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.

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

$$\alpha_s(\omega) = \alpha_0 \left[1 - \frac{S_0}{2} \left(1 + \frac{(\gamma_s/2)^2}{(\omega - \omega_0)^2 + (\gamma_s/2)^2} \right) \right],$$
(2.11)

shows that, when the laser is tuned off resonance, $\alpha(\omega) \approx \alpha_0(\omega_0) \left(1 - \frac{S_0}{2}\right)$, but, when the laser is tuned to $\omega = \omega_0$, $\alpha(\omega) = \alpha_0(\omega_0) (1 - S_0)$. Hence, setting up a standing wave in the sample cell produces a dip in the absorption curve of spectral width γ_s at the transition frequency ω_0 . At optical wavelengths, γ_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, F_1 and 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]:

$$I_{Fl} \propto n_s (I_1 + I_2)$$

which reduces to

$$I_{Fl} \propto n_0 \left(I_1 + I_2 \right) - \frac{B_{12}}{c \pi \gamma R} \left(I_1 + I_2 \right)^2$$

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 $(F_1 + F_2)$ and $(F_1 - F_2)$. Sorem and Schawlow[15] demonstrated that by detecting fluorescence at the sum frequency, $(F_1 + F_2)$, it is possible to record sub-Doppler spectra of the transitions while the background is greatly suppressed. Thus IMF is a good technique when sub-Doppler 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

Chapter 2. Experimental

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:

 $P(3) = \omega + E_i(2) - E_i(3)$ $Q(2) = \omega + E_i(2) - E_i(2)$ $R(1) = \omega + E_i(2) - E_i(1).$

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 °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 μ m and 60 μ 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,

$$\mathcal{H}\psi = E\psi. \tag{3.1}$$

In this equation \mathcal{H} is the total Hamiltonian operator, ψ 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 ϕ_i is chosen such that

$$\psi = \sum_{i} c_i \phi_i. \tag{3.2}$$

When the eigenfunction ψ of the time-independent Schrödinger equation is replaced by a linear combination of orthogonal basis functions ϕ_i , the problem of solving Equation 3.1 becomes that of calculating the roots of the secular determinant

$$|\mathcal{H}_{ij} - \mathbf{E}\delta_{ij}| = 0, \tag{3.3}$$

where the matrix elements \mathcal{H}_{ij} are defined as

$$\mathcal{H}_{ij} = \int \phi_i^* \mathcal{H} \phi_j d\tau, \qquad (3.4)$$

and δ_{ij} is the Kronecker delta (i.e. zero if $i \neq j$ and 1 if i = j).

Any complete set of wavefunctions ϕ_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 $(b_{\beta J})$ basis while case (a_{β}) 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

$$\mathcal{H} = \mathcal{H}^{(0)} + \mathcal{H}^{\prime} \tag{3.5}$$

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

Consider a perturbation between two states whose zero order wavefunctions or "basis functions", are ϕ_1 and ϕ_2 ; there will be interaction matrix elements of the type $\langle \phi_1 | \mathcal{H}' | \phi_2 \rangle$ which are responsible for the rotational perturbation. The Hamiltonian matrix elements are given by

$$\left< \phi_1 | \mathcal{H}^{(0)} | \phi_1 \right> = H_{11} = E_1,$$
 (3.6)

$$\left< \phi_2 | \mathcal{H}^{(0)} | \phi_2 \right> = H_{22} = E_2,$$
 (3.7)

$$\langle \phi_1 | \mathcal{H}' | \phi_2 \rangle = H_{12}, \tag{3.8}$$


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

and

$$\langle \psi_2 | \mathcal{H}' | \psi_1 \rangle = H_{21}, \tag{3.9}$$

which can be written as:

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

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

$$E_A = \frac{(E_1 + E_2)}{2} + \frac{1}{2}\sqrt{(E_1 - E_2)^2 + 4H_{12}^2}$$
(3.10)

Chapter 3. Energy Expressions and the Hamiltonian

$$E_B = \frac{(E_1 + E_2)}{2} - \frac{1}{2}\sqrt{(E_1 - E_2)^2 + 4H_{12}^2}, \qquad (3.11)$$

represent the energies of the two perturbed states. The eigenfunctions, ψ_A and ψ_B , are given by

$$\begin{bmatrix} \psi_A \\ \psi_B \end{bmatrix} = \begin{bmatrix} c & s \\ -s & c \end{bmatrix} \begin{bmatrix} \phi_1 \\ \phi_2 \end{bmatrix}$$
where $c = \sqrt{\frac{k+d}{2k}}$, $s = \sqrt{\frac{k-d}{2k}}$, $d = H_{11} - H_{22}$, and $k = \sqrt{d^2 + 4H_{12}^2}$. (3.12)

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 μ_1 and μ_2 , to the basis states ϕ_1 and ϕ_2 respectively. From Equation (3.12), the transitions to the perturbed eigenstates are given by

$$\langle \psi_A | \hat{\mu} | X \rangle = c \langle \phi_1 | \hat{\mu} | X \rangle + s \langle \phi_2 | \hat{\mu} | X \rangle$$

$$= c \mu_1 + s \mu_2$$

$$\langle \psi_B | \hat{\mu} | X \rangle = -s \langle \phi_1 | \hat{\mu} | X \rangle + c \langle \phi_2 | \hat{\mu} | X \rangle$$

$$= -s \mu_1 + c \mu_2$$

The intensity is proportional to the square of the transition moment; thus $I_{A\leftarrow X} \propto (c\mu_1 + s\mu_2)^2$; and $I_{B\leftarrow X} \propto (-s\mu_1 + c\mu_2)^2$. 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, **L**, the electron spin angular momentum, **S**, the angular momentum of the nuclear rotation, **R**, and the angular momentum arising from the non-zero nuclear spin of the ⁵¹V nucleus, **I**. These angular momentum vectors can be coupled together in many different ways. Hund considered five possible arrangements in which **L**, **S** and **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 (a_{β}) and case ($b_{\beta J}$) (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 (\mathbf{a}_{β})

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 does have a well-defined projection, Λ , on the internuclear axis. Likewise, Σ 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 (a_β) coupling scheme.

Since the projection of **R** along the internuclear axis is zero, the component of the total angular momentum along the internuclear axis, Ω^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 Ω (or more precisely Σ) is integral or half-integral. Of course J can never be less than Ω .

In case (a_{β}) 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

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

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

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

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

¹It 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 ⁴II state ($\Lambda = 1$, $S = \frac{3}{2}, \Sigma = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$) are ⁴II₅, ⁴II₅, ⁴II₁, and ⁴II₁, while the values for $|\Omega|$ are $\frac{5}{2}, \frac{3}{2}, \frac{1}{2}$, and $\frac{1}{2}$ respectively.

along the axis by the orbital motion of the electrons that can couple **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 Σ states ($\Lambda = 0$) and all states with $\Lambda > 0$ but $BJ \gg A$. 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 **S** on the internuclear axis.

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

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

$$R + L = N$$
$$N + S = J$$
$$J + I = F$$

Once again,

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

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 $(b_{\beta J})$ coupling while



Figure 3.3: Hund's case $(b_{\beta J})$ coupling scheme.

case (a_{β}) 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:

$$\mathcal{H}_{rot} = B\mathbf{R}^2 - D\mathbf{R}^4 \tag{3.13}$$

where $\mathbf{R} = \mathbf{J} - \mathbf{L} - \mathbf{S}$. In a Σ 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:

$$\mathcal{H}_{rot} = B\mathbf{N}^2 - D\mathbf{N}^4 \tag{3.14}$$

$$\langle NSJ | \mathcal{H}_{rot} | NSJ \rangle = BN(N+1) - DN^2(N+1)^2$$
(3.15)

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,

$$\mathcal{H}_{so}^{(1)} = A\mathbf{L} \cdot \mathbf{S} \tag{3.16}$$

gives zero in an electronic Σ state, since $\langle L_z \rangle = 0$, and the effects of L_+ and L_- are not contained within the Σ state. However, in second order, the effects of L_+ and L_- are equivalent to a tensor operator (\mathbf{S}, \mathbf{S}) acting within the Σ 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 λ by [24]

$$\mathcal{H}_{ss} = \frac{2}{3}\lambda \left(3S_z^2 - \mathbf{S}^2\right); \qquad (3.17)$$

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

$$\lambda_{eff} = \lambda_{ss} + \lambda_{so}^{(2)}.$$

Therefore, the λ 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

$$\mathcal{H}_{ss} = \frac{2}{3}\sqrt{6}\,\lambda T_0^2(\mathbf{S}, \mathbf{S}),\tag{3.18}$$

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

$$\langle N'SJIF | \mathcal{H}_{spin-spin} | NSJIF \rangle$$

$$= \frac{2}{3} \lambda (-1)^{N+S+J} \left\{ \begin{array}{cc} J & S & N' \\ 2 & N & S \end{array} \right\} [S(S+1)(2S+1)(2S-1)(2S+3)]^{1/2}$$

$$\times (-1)^{N'} \left(\begin{array}{cc} N' & 2 & N \\ 0 & 0 & 0 \end{array} \right) [(2N+1)(2N'+1)]^{1/2}.$$

$$(3.19)$$

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]:

$$\mathcal{H}_{sr} = \gamma \mathbf{R} \cdot \mathbf{S}$$
(3.20)
$$= \gamma (\mathbf{J} - \mathbf{L} - \mathbf{S}) \cdot \mathbf{S}$$
$$= \gamma \mathbf{N} \cdot \mathbf{S}, \text{ for } \Sigma \text{ states.}$$
(3.21)

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

$$\langle NSJ | \mathcal{H}_{sr} | NSJ \rangle = -\frac{1}{2} \gamma \left[N(N+1) + S(S+1) - J(J+1) \right]$$
 (3.22)

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, $-2B(J_xS_x + J_yS_y)$, 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

$$\left\langle S\Sigma, J\Omega | \mathcal{H}_{sr}^{(3)} | S\Sigma \pm 1, J\Omega \pm 1 \right\rangle = -\frac{1}{2} \gamma_s \left[S(S+1) - 5\Sigma(\Sigma \pm 1) - 2 \right] \left[J(J+1) - \Omega(\Omega \pm 1) \right]^{\frac{1}{2}} \times \left[S(S+1) - \Sigma(\Sigma \pm 1) \right]^{\frac{1}{2}}$$
(3.23)

The case (b) forms of the third order spin-rotation matrix elements do not simplify similarly². As required for the least squares fit of the VO $B^4\Pi - X^4\Sigma^-$ transition it is [28]:

$$\left\langle N'SJIF | \mathcal{H}_{sr}^{(3)} | NSJIF \right\rangle$$

= $\frac{1}{2} \left[(2N+1)(2N'+1)J(J+1)(2J+1) \right]^{1/2}$

,

²Brown 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.

$$\times [2(2S-2)(2S-1)2S(2S+1)(2S+2)(2S+3)(2S+4)/3]^{1/2} \gamma_s$$

$$\times \sum_{x=2,4} (2x+1) \begin{pmatrix} 3 & x & 1 \\ -1 & 0 & 1 \end{pmatrix} (-1)^{N'} \begin{pmatrix} N' & x & N \\ 0 & 0 & 0 \end{pmatrix} \begin{cases} N' & N & x \\ S & S & 3 \\ J & J & 1 \end{cases}$$
(3.24)

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

$$\mathcal{H}_{*,cd} = \gamma_D (\mathbf{N} \cdot \mathbf{S}) \mathbf{N}^2 + \frac{1}{3} \lambda_D \left[\left(3S_z^2 - \mathbf{S}^2 \right), \mathbf{N}^2 \right]_+.$$
(3.25)

In Equation (3.25), the symbol $[x, y]_+$ stands for the anti-commutator xy + yx, 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]

$$\langle NSJ | \mathcal{H}_{sr,cd} | NSJ \rangle = -\frac{1}{2} \gamma_D N(N+1) [N(N+1) + S(S+1) - J(J+1)]$$

= $\frac{1}{2} \gamma_D N(N+1) R(JSN)$ (3.26)

and

$$\langle NSJ | \mathcal{H}_{ss,cd} | NSJ \rangle = -\frac{1}{3} \lambda_D N(N+1) \frac{3R(JSN) [R(JSN)+1] - 4S(S+1)N(N+1)}{(2N-1)(2N+3)}.$$
(3.27)

where

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

The off-diagonal matrix elements are given by

$$\langle N-2, SJ | \mathcal{H}_{ss,cd} | NSJ \rangle = \frac{1}{2} \lambda_D \frac{[N(N+1) - (2N-1)]}{(2N-1)[(2N+1)(2N-3)]^{\frac{1}{2}}} \times Y(JSN)Y(JS, N-1),$$
(3.28)

where

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

•

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 Σ electronic state are given by[21]

$$\mathcal{H}_{mag\,hf} = b\mathbf{I} \cdot \mathbf{S} + cI_z S_z \tag{3.29}$$

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

$$\langle N'SJ'IF|\mathcal{H}_{maghf}|NSJIF \rangle$$

$$= (-1)^{J+I+F} \left\{ \begin{array}{cc} F & I & J' \\ 1 & J & I \end{array} \right\} [(2J+1)(2J'+1)I(I+1)(2I+1)]^{1/2} \\ \times [S(S+1)(2S+1)]^{1/2} \left[(-1)^{N+S+J'} \left\{ \begin{array}{cc} S & J' & N \\ J & S & 1 \end{array} \right\} b_F \\ - \frac{1}{3}c[30(2N+1)(2N'+1)]^{1/2} \left\{ \begin{array}{cc} N' & N & 2 \\ S & S & 1 \\ J' & J & 1 \end{array} \right\} (-1)^{N'} \left(\begin{array}{cc} N' & 2 & N \\ 0 & 0 & 0 \end{array} \right) \right] (3.30)$$

The third magnetic hyperfine parameter needed to describe the $X^{4}\Sigma^{-}$ state of VO arises from the third order isotropic hyperfine Hamiltonian, $\mathcal{H}_{iso}^{(3)}$. 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]

$$\mathcal{H}_{iso}^{(3)} = \frac{\left(5\sqrt{14}/3\right)b_S}{\left\langle\Lambda\right|T_0^2(\mathbf{L})\left|\Lambda\right\rangle}T^1(\mathbf{I})\cdot T^1\left[T^2(\mathbf{L}^2), T^3(\mathbf{S}^3)\right]$$
(3.31)

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

$$\langle N'SJ'IF | \mathcal{H}_{iso}^{(3)} | NSJIF \rangle$$

$$= \frac{1}{4} (-1)^{J+I+F} \left\{ \begin{array}{cc} F & I & J' \\ 1 & J & I \end{array} \right\} [(2J+1)(2J'+1)I(I+1)(2I+1)]^{1/2}$$

$$\times (-1)^{N'} \left(\begin{array}{cc} N' & 2 & N \\ 0 & 0 & 0 \end{array} \right) [(2N+1)(2N'+1)]^{1/2} \left\{ \begin{array}{cc} N' & N & 2 \\ S & S & 3 \\ J' & J & 1 \end{array} \right\}$$

$$\times [35(2S-2)(2S-1)2S(2S+1)(2S+2)(2S+3)(2S+4)/3]^{1/2} b_S \quad (3.32)$$

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]

$$\mathcal{H}_{quad}^{(0)} = \frac{e^2 Q q_0 \left(3I_z^2 - \mathbf{I}^2\right)}{4I(2I-1)},\tag{3.33}$$

resulting in matrix elements

$$\left\langle N'SJ'IF | \mathcal{H}_{quad}^{(0)} | NSJIF \right\rangle$$

$$= \frac{1}{4} e^2 Q q_0 \left(\begin{array}{ccc} I & 2 & I \\ -I & 0 & I \end{array} \right)^{-1} (-1)^{J+I+F} \left\{ \begin{array}{ccc} F & I & J' \\ 2 & J & I \end{array} \right\}$$

$$\times (-1)^{N'^{+S+J}} \left[(2J+1)(2J'+1)(2N+1)(2N'+1) \right]^{1/2} \left\{ \begin{array}{ccc} S & N' & J' \\ 2 & J & N \end{array} \right\}$$

$$\times (-1)^{N'} \left(\begin{array}{cc} N' & 2 & N \\ 0 & 0 & 0 \end{array} \right).$$
(3.34)

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

A particular complication in the ⁴ Π upper state arises from the $a^2\Sigma^+$ state which perturbs it heavily. The Hamiltonian for the B⁴ Π state, excluding the effects of the $a^2\Sigma^+$ state, is described in this Section. Since the matrix elements of the B⁴ Π Hamiltonian were evaluated using a case (a_β) 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:

$$\mathcal{H}_{rot} = B\mathbf{R}^2 - D\mathbf{R}^4. \tag{3.35}$$

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]:

$$\mathcal{H}_{so} = AL_z S_z + \frac{2}{3}\lambda \left(3S_z^2 - \mathbf{S}^2\right) + \eta L_z S_z \left[S_z^2 - \frac{3\mathbf{S}^2 - 1}{5}\right]$$
(3.36)

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

$$\langle \Lambda'; S\Sigma'; J\Omega | \mathcal{H}_{so} | \Lambda; S\Sigma; J\Omega \rangle = A\Lambda\Sigma + \frac{2}{3}\lambda \left[3\Sigma^2 - S(S+1) \right] + \eta\Lambda\Sigma \left[\Sigma^2 - \frac{3}{5}S(S+1) + \frac{1}{5} \right].$$
 (3.37)

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

$$\mathcal{H}_{sr} = \gamma \mathbf{R} \cdot \mathbf{S},\tag{3.38}$$

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

$$\langle \Lambda; S\Sigma; J\Omega | \mathcal{H}_{sr} | \Lambda; S\Sigma; J\Omega \rangle = \gamma \left[\Sigma^2 - S(S+1) \right].$$
(3.39)

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

$$T_{\Omega} = T_0 + A\Lambda\Sigma + \frac{2}{3}\lambda \left[3\Sigma^2 - S(S+1)\right] + \gamma \left[\Sigma^2 - S(S+1)\right] + \eta\Lambda\Sigma \left[\Sigma^2 - \frac{3S(S+1)+1}{5}\right]$$
(3.40)

The spin-rotation parameter γ 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 γ 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,

$$\mathcal{H}_{ss} = \frac{2}{3}\lambda \left(3S_z^2 - \mathbf{S}^2\right),\tag{3.41}$$

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

3.5.2 Λ-type Doubling

The interaction between Σ states ($\Lambda = 0$) and Π states ($\Lambda = 1$) lifts the degeneracy of the $\pm \Lambda$ levels in the Π 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 Λ -type doubling Hamiltonian defined by Brown and Merer [31],

$$\mathcal{H}_{LD} = \frac{1}{2}(o+p+q)(S_{+}^{2}+S_{-}^{2}) - \frac{1}{2}(p+2q)(J_{+}S_{+}+J_{-}S_{-}) + \frac{1}{2}q(J_{+}^{2}+J_{-}^{2}).$$
(3.42)

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]

$$\begin{aligned} \langle \mp 1, \Sigma \pm 2, J, \Omega | \mathcal{H}_{LD} | \pm 1, \Sigma J \Omega \rangle \\ &= \frac{1}{2} (o + p + q) \left[S(S + 1) - \Sigma(\Sigma \pm 1) \right]^{\frac{1}{2}} \left[S(S + 1) - (\Sigma \pm 1)(\Sigma \pm 2) \right]^{\frac{1}{2}} \quad (3.43) \\ \langle \mp 1, \Sigma \pm 1, J, \Omega \mp 1 | \mathcal{H}_{LD} | \pm 1, \Sigma J \Omega \rangle \\ &= -\frac{1}{2} (p + 2q) \left[S(S + 1) - \Sigma(\Sigma \pm 1) \right]^{\frac{1}{2}} \left[J(J + 1) - \Omega(\Omega \mp 1) \right]^{\frac{1}{2}} \quad (3.44) \\ \langle \mp 1, \Sigma, J, \Omega \mp 2 | \mathcal{H}_{LD} | \pm 1, \Sigma J \Omega \rangle \\ &= \frac{1}{2} q \left[J(J + 1) - \Omega(\Omega \mp 1) \right]^{\frac{1}{2}} \left[J(J + 1) - (\Omega \mp 1)(\Omega \mp 2) \right]^{\frac{1}{2}} . \end{aligned}$$

There exists a contribution to the Λ -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 Σ state has been given in subsection 3.4.3 as

$$\mathcal{H}_{I \cdot S h f} = b \mathbf{I} \cdot \mathbf{S} + c I_z S_z. \tag{3.46}$$

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]:

$$\mathcal{H}_{I\cdot L} = aI_z L_z \tag{3.47}$$

The three hyperfine parameters mentioned so far describe the magnetic hyperfine effects in the two parity components of Π states equally. However, Frosch and Foley[32] showed that hyperfine contributions to the Λ -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 Λ . The Λ -type doubling-hyperfine Hamiltonian is given by[32]

$$\mathcal{H}_{\Lambda D hf} = \frac{1}{2} d \left(e^{2i\phi} I_{-} S_{-} + e^{-2i\phi} I_{+} S_{+} \right)$$
(3.48)

where ϕ 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]:

$$\mathcal{H}_{mag\,hf} = -\sqrt{10} \, g\mu_B g_N \mu_N r^{-3} T^1(\mathbf{I}) \cdot T^1(\mathbf{S}, C^2) \tag{3.49}$$

where

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

and,

$$r^{-3}T_{q_2}^2(C) = \sqrt{\frac{4\pi}{5}}Y_{2,q_2}(\theta,\phi)r^{-3}.$$
(3.51)

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

$$\langle J\Omega IF | \mathcal{H}_{maghf} | J\Omega IF \rangle = \frac{\Omega \left[a\Lambda + (b+c)\Sigma \right] R(FIJ)}{2J(J+1)}$$
(3.52)

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

$$\langle S\Sigma, J\Omega IF | \mathcal{H}_{maghf} | S\Sigma \pm 1, J\Omega \pm 1, IF \rangle$$

= $b [J(J+1) - \Omega(\Omega \pm 1)]^{1/2} [S(S+1) - \Sigma(\Sigma \pm 1)]^{1/2}$
 $\times \frac{R(FIJ)}{4J(J+1)},$ (3.53)

•

while the matrix elements off-diagonal in J are

$$\langle J\Omega IF | \mathcal{H}_{mag\,hf} | J-1, \Omega IF \rangle = -\frac{[a\Lambda + (b+c)\Sigma] (J^2 - \Omega^2)^{1/2} V(F, I, J)}{2J [(2J+1)(2J-1)]^{1/2}}$$
(3.54)

and

$$\langle S\Sigma, J\Omega IF | \mathcal{H}_{mag\,hf} | S\Sigma \pm 1, J - 1, \Omega \pm 1, IF \rangle$$

$$= \mp b \left[(J \mp \Omega) (J \mp \Omega - 1) \right]^{1/2} \left[S(S + 1) - \Sigma(\Sigma \pm 1) \right]^{1/2}$$

$$\times \frac{V(FIJ)}{4J \left[(2J + 1)(2J - 1) \right]},$$

$$(3.55)$$

1 10

where

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

3.5.4 Electric Quadrupole Interaction

The Hamiltonian for the electric quadrupole interaction given in sub-section 3.4.4 for Σ states (3.33) also applies for Π states. However, while Π states will have the same zero order term as in Σ electronic states, there is also a e_2Qq_2 term which will have non-zero elements only in Π states. Like the d parameter for magnetic hyperfine effects, there exists an electric quadrupole interaction which links states differing in Λ by ± 2 . The complete electric quadrupole Hamiltonian for Π states is given by[33][34]

$$\mathcal{H}_{quad} = \frac{e^2 Q q_0 \left(3I_z^2 - \mathbf{I}^2\right)}{4I(2I-1)} + \frac{e^2 Q q_2 \left(I_+^2 + I_-^2\right)}{8I(2I-1)}.$$
(3.56)

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

Although Σ 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

$$\left<^{2}\Sigma^{+}\right|\mathcal{H}\left|^{2}\Sigma^{+}\frac{f}{e}\right> = B(x)(x\pm 1) - D(x)^{2}(x\pm 1)^{2} - \frac{1}{2}\gamma(1\pm x)$$
 (3.57)

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

$$\mathcal{H}_{hf} = b\mathbf{I} \cdot \mathbf{S},\tag{3.58}$$

Written in an f/e parity basis, its diagonal matrix elements have the form

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

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

$$\left<^{2}\Sigma^{+}, J_{e}^{f} \middle| \mathcal{H}_{hf} \middle|^{2}\Sigma^{+}, J - 1_{f}^{e} \right> = -b \frac{V(F, I, J)}{8J} (1 \mp 1).$$
 (3.60)

Those parameters which pertain to the $a^2\Sigma^+$ state are designated by a prime (eg. B', D', γ' , and b') 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,

$$\langle S'\Sigma'\Lambda'\Omega'|\mathcal{H}_{so}|S\Sigma\Lambda\Omega\rangle = (-1)^{S'-\Sigma'} \begin{pmatrix} S' & 1 & S\\ -\Sigma' & q & \Sigma \end{pmatrix} \langle S'\Lambda'||\mathcal{H}_{so}||S\Lambda\rangle \,\delta_{\Omega\Omega'}, \qquad (3.61)$$

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 form³:

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

and

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

³Special 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 Π _{5/2} [†] ∕• ∕	⁴ П _{3/2} %->	⁴∏ ½ ¼>	⁴ П _ _{у2} % >	² ∑ ⁺ ¹ / _∗ ⟩
< ⁴ ∏ _{5/2}	$T_{5/2} + (Z-5)(B + \frac{3}{2}A_0 + 2\lambda_0 + \frac{3}{10}\eta_0) -D(Z^2 - 7Z + 13) + Q_5 + \frac{5R}{4s(3+1)} [a + \frac{3}{2}(b+c)]$	$-\sqrt{3(2-4)} \left[B - \frac{1}{2}\gamma + A_0 - \frac{3}{10}\eta_0 - 2D(2-2) - \frac{100}{44(4+1)}\right]$	$-\sqrt{3(Z-1)(Z-4)} [2D \\ \pm \frac{1}{2} D_q (U+\frac{1}{2})]$	$ \pm \sqrt{(2-1)(2-4)} \left[\frac{1}{2} q + \frac{3}{4} D_{p+2q} + \frac{1}{2} (2-2) D_q + \tilde{Q}^{(2)} \right] $	
⟨ ⁴ Π _{3/2}		$T_{32} + (Z+1)(B + \frac{1}{2}A_0 - 2\lambda_D - \frac{9}{10}\eta_D) \\ -D(Z^2 + 9Z - 15) \\ \overline{+}(Z-1)(J + \frac{1}{2})D_q + Q_3 \\ + \frac{38}{40(J+1)} [a + \frac{1}{2}(b+c)]$	$-2\sqrt{2-1} \left[B - \frac{1}{2}\gamma - 2\lambda_{D} - 2D(2+2) - \frac{M^{2}}{4f(d+1)} + \frac{1}{2}(J + \frac{1}{2})[\frac{1}{2}q + \frac{1}{4}D_{p+2q} + \frac{1}{2}(J + \frac{1}{2})]\frac{1}{2}q + \frac{1}{4}D_{p+2q} + \frac{1}{2}(2+2)D_{q} + \widetilde{Q}^{(2)}] \right]$	$-\sqrt{3(2-1)}[2D(J+\frac{1}{2})\pm\frac{1}{2}(p+2q)$ $\pm D_{p+p+q}\pm\frac{1}{2}(2+1)D_{p+2q}$ $\pm\frac{1}{2}(2-2)D_{q}$ $\pm\frac{e}{44(p+1)}$	
< ⁴ ∏ ½			$\begin{split} & T_{\frac{1}{2}} + (2+3) \left[B - \frac{1}{2} A_0 - 2\lambda_0 + \frac{8}{10} \gamma_0 \right] \\ & - D(2^2 + 132 + 5) \\ & \mp (J + \frac{1}{2}) \left[(p + 2q) + 3D_{e+p+q} \\ & + (2+3) D_{p+2q} + (2-1) D_q + \frac{q}{24(J+1)} \right] \\ & + Q_{1+} \frac{8}{44(J+1)} \left[a - \frac{1}{2} (b+c) \right] \end{split}$	$\begin{aligned} &-\sqrt{3} \left(J + \frac{1}{2}\right) \left[B - \frac{1}{2}\gamma - A_{B} + \frac{3}{10}\eta_{D} \\ &-2D(Z + 2) - \frac{100}{43(z+1)}\right] \\ &\pm \sqrt{3} \left[(o+p+q) + (Z + 2)D_{a+a+q} \\ &+ \frac{1}{2}(2Z - 1)D_{a+2q}\right] \end{aligned}$	$\frac{1}{2\sqrt{3}}\tilde{A} + e_{\overline{M(J+1)}}$
<" ⁴ ∏ -1/ ₂		·		$T_{-\frac{1}{2}+}(Z+1)(B-\frac{3}{2}A_{0}+2\lambda_{0}-\frac{3}{10}\eta_{0})$ -D(Z ² +5Z+1)=3(J+ $\frac{1}{2}$)D ₀₊₀₊₀ +Q ₋₁ - $\frac{1}{44(J+1)}$ [a- $\frac{3}{2}$ (b+c)]	$\pm \frac{1}{2} \left[\tilde{A} + \sqrt{3} e_{\mathbf{E} \left[(i+1) \right]} \right]$
2Σ ⁺					$T(^{2}\Sigma^{+})+B'[Z^{\pm}(J+\frac{1}{2})]$ -D'[Z^{\pm}(J+\frac{1}{2})]^{2}+\frac{1}{2}\gamma'(J+\frac{1}{2}\pm 1) $=\frac{b'g}{4(J+\frac{1}{2})}$
	_				

$$\begin{split} & Z = (J + \frac{1}{2})^2 \\ & R = F(F+1) - I(I+1) - J(J+1) \\ & G(F,I,J) = \frac{3F(P+1) - 4J(I+1)J(J+1)}{8I(ZI-1)J(J+1)(ZJ-1)(ZJ+3)} \\ & \Omega_{2D} = e^2 Oq_2 \left[30^2 - J(J+1) \right] G(F,I,J) \\ & \widetilde{Q}^{(D)} = e^2 Oq_2 G(F,I,J)/2 \end{split}$$

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 Π 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 F_1 upper state. The Figure illustrates the relatively large separation between the Q_1 and ${}^QR_{12}$ branches which arises primarily from the spin-spin interaction, represented in the Hamiltonian by the term in λ . By contrast, the ${}^OP_{12}$ and ${}^OQ_{13}$ branches are nearly degenerate, whilst the ${}^OR_{14}$ branch lies approximately 2λ 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 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 $(b_{\beta J})$ coupling because the electron spinspin interaction (λ) is much larger than the hyperfine interactions. As mentioned in the Introduction to this Chapter, the effect of the λ parameter is clearly seen in the separation of the F_1'' and F_4'' lines from the F_2'' and F_3'' lines. The four spin components of a ${}^{4}\Sigma$ state in pure case (b) coupling follow the exact expression[10]

$$4\lambda - 2\gamma = F_2(N) + F_3(N) - F_1(N) - F_4(N).$$
(4.1)



Figure 4.3: The energies of the four electron spin components of the $X^4\Sigma^-$ state of VO. Also, because the splitting between adjacent components varies as γN , the values of λ and γ can be estimated from pairs of ground state combinations differences of the type $F_2(N)-F_1(N)$ and $F_3(N)-F_4(N)$, or $F_2(N)-F_4(N)$ and $F_3(N)-F_1(N)$.

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 F₂ and F₃ components and the F₁ and F₄ components, the distance between these two lines is almost exactly $2\lambda - \gamma$.

The effect of γ 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 γN at high values of N, while the F_1 and 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 $C^4\Sigma^-$ state also has small hyperfine splittings, Cheung et al. determined that the $F_1 : F_2 : F_3 : F_4$ hyperfine widths of the $C^4\Sigma^- - X^4\Sigma^-$ system are in the ratio -3 :-1 : 1 : 3 which means that Hund's case $(b_{\beta J})$ applies to the $X^4\Sigma^-$ state. Consequently, the F_1'' and F_4'' lines are the easiest to analyse in the $B^4\Pi - X^4\Sigma^-$ system because they show the widest splittings. The F_1'' lines could be easily distinguished from the F_4'' 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 F_4'' 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 σ -orbital is derived from the V 4s atomic orbital. Thus, the large hyperfine splitting of the ground state is primarily due to the Fermi contact interaction of the unpaired $4s\sigma$ 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 F_1'' or F_4'' , as well as the F-numbering, were straight-forward, as shown in Figure 4.5. The total splitting observed for the F_1'' and F_4'' spin components is typically



Figure 4.4: The hyperfine energy level splittings for the F_2 and F_3 spin states of the $X^4\Sigma^-$ state of VO.

of the order of 0.3 cm^{-1} .

The *F*-assignments of the F_2'' and F_3'' lines are much more difficult to make than those of the F_1'' and F_4'' lines. In 1968, Richards and Barrow [7][8] discovered that transitions involving the F_2 ($N = J + \frac{1}{2}$) and F_3 ($N = J - \frac{1}{2}$) electron spin components in the $X^4\Sigma^-$ state of VO are doubled near 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 F₂ and F₃ spin components, the matrix elements responsible for the perturbation have $\Delta J = \pm 1$ and $\Delta N = 0$. Although the electron spin contributions to F₁ $(N = J + \frac{3}{2})$ and F₄ $(N = J - \frac{3}{2})$ 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 F_2 and F_3 spin states of the ground state are allowed by selection rules, the extra lines induced by the F_2 spin state are almost exactly blended with the main lines of the F_3 spin state and *vice versa*.

If only one of the spin states, for example 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 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 F''_2 character are marked by dashed lines



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 F''_3 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 F''_3 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 12 653.3064 cm⁻¹.

The hyperfine energy levels for the F_2'' and F_3'' 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 F₂ and F₃ 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 F_2'' and F_3'' 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 12 653.4043 cm⁻¹) turns out to have predominantly F_3'' 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 12 653.2593 cm⁻¹.

¹A 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.



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 Λ -type splitting and the hyperfine structure of the F₁ and F₂ 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 F₃ and F₄ 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, T_{Ω} , 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 cm⁻¹. Closer inspection of the sub-band origins shows that the separations are not exactly equal, with

$$T_{\frac{5}{2}} - T_{\frac{3}{2}} = 74.7440 \text{ cm}^{-1}$$
$$T_{\frac{3}{2}} - T_{\frac{1}{2}} = 65.4295 \text{ cm}^{-1}$$
$$T_{\frac{1}{2}} - T_{-\frac{1}{2}} = 53.3464 \text{ cm}^{-1}$$

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 Λ -type Doubling in the $B^4\Pi$ State

All states with $\Lambda > 0$ are doubly degenerate because the projection of **L** along the internuclear axis, Λ , is a signed quantity, and in the absence of other effects, the energies of the two components, with positive and negative values of Λ , are the same. The degeneracy is lifted by interactions with Σ states ($\Lambda = 0$) which have no such degeneracy. The resulting separation of the otherwise degenerate levels is known as Λ -type doubling. The Λ -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 Λ -type doubling plots. The smallest Λ -type doubling occurs in the F_4 spin component with that in the F_3 sub-state being the next smallest. Despite the confusion caused by the $a^2\Sigma^+$ perturbation, this observed decrease in Λ -type splitting as Ω 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 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 ${}^oQ_{13}$ and ${}^oP_{12}$ 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 Λ -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 ${}^PQ_{12}$ branch with a width of about 22.5 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 ${}^PQ_{23}$ branch, with a width of 18.8 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 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 F₃ and F₄ 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 Λ -type doubling of the F₃ and F₄ sub-states (Figure 4.8). The observed effect of the perturbation on the Λ -type splitting of the F₃ 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 $4s\sigma$ 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 $^{O}P_{12}$ branches become larger near the avoided crossing



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



Figure 4.10: The hyperfine energy levels of the $B^4 \prod_{-\frac{1}{2}e}$ 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 $^{O}P_{12}$ 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	(cm^{-1})
T ₀	0.0	-fixed-
В	0.5453713	± 0.0000017
10 ⁶ D	0.6491	± 0.0009
γ	0.022426	± 0.000004
À	2.03090	± 0.00004
Ь	0.027435	± 0.000002
с	-0.00450	± 0.00005
e ² Qq ₀	0.00134	± 0.00048
$10^5 \gamma_D$	0.0060	± 0.0005
$10^5 \lambda_D$	0.038	± 0.007
$10^5 \gamma_s$	0.810	± 0.095
10 ⁵ b.	-1.58	± 0.37

Table 5.1: The constants for the $X^4\Sigma^-$ (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 (c	m^{-1})
T ₀	12432.9406	± 0.0476
В	0.54304	± 0.00003
10 ⁶ D	0.65	-fixed-
γ	-0.0396	± 0.0019
Ь	0.0930	± 0.0008
$\left< {}^{4}\Pi_{rac{1}{2}} \mathcal{H}_{so} ^{2}\Sigma^{+} \right>$	20.430	±0.076
$\left< {}^{4}\Pi_{-\frac{1}{2}f} \mathcal{H}_{so} ^{2}\Sigma_{f}^{+} \right>$	20.404	± 0.021
$\left< {}^{4}\Pi_{-\frac{1}{2}e} \mathcal{H}_{so} ^{2}\Sigma_{e}^{+} \right>$	20.417	± 0.020
e	0.0	-fixed-

Table 5.2: The constants for the $a^2\Sigma^+$ (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 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 ((m^{-1})
Τ <u>s</u>	12711.8260	±0.0001
T_{3}^{2}	12637.1180	± 0.0001
T_{1}^{2}	12571.6885	± 0.0019
T_{-1}^{2}	12518.3421	± 0.0024
B	0.5126525	± 0.0000018
10 ⁶ D	0.6634	± 0.0009
$10^4 A_D$	-0.69	± 0.04
$10^5 \lambda_D$	-0.28	± 0.05
η_D	0.0	-fixed-
γ	0.0336	± 0.0002
o+p+q	1.131	± 0.001
p+2q	0.03609	± 0.00002
q	0.0001733	± 0.0000011
$10^{5} D_{o+p+q}$	0.16	± 0.05
$10^{5}D_{p+2q}$	-0.0041	± 0.0014
$10^5 D_q$	-0.00037	± 0.00009
e^2Qq_0	0.00157	± 0.00055
а	0.0109	± 0.0002
b	-0.00898	± 0.00003
с	-0.00508	± 0.00015
d	-0.00359	± 0.00003
e^2Qq_2	0.0	-fixed-

Table 5.3: The constants for the $B^{4}\Pi$ (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 cm⁻¹) is defined by

$$B = \frac{h}{8\pi^2 Ic},\tag{6.1}$$

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

$$I = \mu r^2. \tag{6.2}$$

In this equation μ is the reduced mass of the molecule and r is the bond length. The reduced mass of ${}^{51}V^{16}O$ is 12.1729611₉ 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 (cm ⁻¹)	r (Å)
$X^{4}\Sigma^{-}$ (v=0)	0.5463713	± 0.0000017	1.5920
$X^4\Sigma^- (v=1)^a$	0.542864	± 0.000013	1.5972
$B^{4}\Pi$ (v=0)	0.5126525	± 0.000018	1.6436
$B^{4}\Pi$ (v=1) ^b	0.5094926	± 0.0000264	1.6487
$a^{2}\Sigma^{+}$ (v=2)	0.5430436	± 0.0000292	1.5969
$a^2\Sigma^+$ (v=3) ^b	0.54044	± 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.

^aData taken from $A^{4}\Pi - X^{4}\Sigma^{-}$ (0,1) band, reference 35 ^bData taken from $B^{4}\Pi - X^{4}\Sigma^{-}$ (1,0) band, reference 37

rotation-vibration coupling constant α_e [22],

$$B_v = B_e - \alpha_e \left(v + \frac{1}{2} \right) + \cdots, \qquad (6.3)$$

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	$B_e ~(\mathrm{cm}^{-1})$	$\alpha_e \ ({\rm cm^{-1}})$	r_e (Å)
$X^4\Sigma^-$	0.548125	0.00307	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 4π molecular orbital of the $\delta^2\pi$ configuration is slightly more anti-bonding in character than the 9σ 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 4s 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

$$b_F = b + \frac{1}{3}c, (6.4)$$

and is equal to 0.02593_5 cm⁻¹ for the $X^4\Sigma^-$ state.

In a study of the $3d^44s$ configuration of atomic ⁵¹V, Childs et al.[43] determined the value of the contact parameter of the 4s electron to be 0.1036 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 4s atomic ⁵¹V character. In single configuration approximation, this electron must therefore occupy the $(4s\sigma)$ 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 V(4s). As in the $X^4\Sigma^-$ state, there must be an unpaired electron occupying the (4s σ) MO. Thus, the $a^2\Sigma^+$ state has the same configuration as the $X^4\Sigma^-$ state, namely $(4s\sigma)^1(3d\delta)^2$. 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_{Ω} , 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

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

Since the spin-rotation parameter γ has been determined independently of the subband origins, there are four sub-band origins T_{Ω} which can be used to give the four parameters T_0 , A, λ , and η . The values obtained for the four sub-band origins and γ for the $B^4\Pi$ (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 (cm ⁻¹)
Τş	12711.8260 ± 0.0001
$T_{\frac{3}{2}}^{2}$	12637.1180 ± 0.0001
T_{1}^{2}	12571.6885 ± 0.0019
T_{1}^{2}	12518.3421 ± 0.0024
γ^2	0.0336 ± 0.0002

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

As expected, the estimate of 65 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 λ . The λ 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 Ω , ${}^2\Pi$ 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 4λ . The sign of λ 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 λ 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

$$\psi_{spatial} = \left| \delta^{2+} \delta^{2-} \pi \right|. \tag{6.6}$$

The orbital angular momenta of the δ -electrons cancel, so that the spin-orbit coupling

Parameter	Value (cm ⁻¹)
To	12609.8367 ± 0.0017
A	64.5989 ± 0.0008
λ	2.6580 ± 0.0002
η	-0.4614 ± 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 π -electron. The microscopic spin-orbit parameter for this π -electron is given by[24]

$$a_{\pi} = 3A\Lambda = 3 \times 64.5989 \text{ cm}^{-1} = 193.797 \text{ cm}^{-1}.$$
 (6.7)

This value for a_{π} is consistent with the values obtained from the $A^{\prime 4}\Phi$, $A^{4}\Pi$ 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 λ for the $X^4\Sigma^-$ state is an effective parameter, given by

$$\lambda = \lambda_{so} + \lambda_{ss},$$

where λ_{so} is the second order spin-orbit interaction parameter and λ_{ss} is the electron spin-spin interaction parameter. There is no way of estimating λ_{ss} except from ab initio calculations, and in any case it is likely to be small campared to λ_{so} ; it will not be considered further. The most likely contribution to λ_{so} 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

$$\left| {}^{4}\Sigma_{\frac{1}{2}}^{-} \right\rangle = \frac{1}{\sqrt{3}} \left[\left| \delta^{+}\alpha \, \delta^{-}\beta \, \sigma\alpha \right| + \left| \delta^{+}\beta \, \delta^{-}\alpha \, \sigma\alpha \right| + \left| \delta^{+}\alpha \, \delta^{-}\alpha \, \sigma\beta \right| \right] \tag{6.8}$$

$$\left|^{2}\Sigma_{\frac{1}{2}}^{+}\right\rangle = \frac{1}{\sqrt{2}} \left[\left| \delta^{+}\alpha \, \delta^{-}\beta \, \sigma\alpha \right| - \left| \delta^{+}\beta \, \delta^{-}\alpha \, \sigma\alpha \right| \right].$$
(6.9)

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

$$\mathcal{H}_{so} = \sum_{i} a_{i} l_{zi} s_{zi}.$$
(6.10)

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

$$\left\langle {}^{4}\Sigma_{\frac{1}{2}}^{-} \right| \mathcal{H}_{so} \left| {}^{2}\Sigma_{\frac{1}{2}}^{+} \right\rangle = \frac{4a_{\delta}}{\sqrt{6}} \tag{6.11}$$

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

$$\lambda_{so} = \frac{1}{4} \frac{\left| \left\langle {}^{4}\Sigma_{\frac{1}{2}}^{-} \right| \mathcal{H}_{so} \left| {}^{2}\Sigma_{\frac{1}{2}}^{+} \right\rangle \right|^{2}}{E\left({}^{2}\Sigma_{\frac{1}{2}}^{+} \right) - E\left({}^{4}\Sigma_{\frac{1}{2}}^{-} \right)} \simeq \frac{1}{4} \frac{(245)^{2}}{10412} \simeq 1.44 \text{ cm}^{-1}.$$
 (6.12)

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

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

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

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

and between
$$\left\langle \left| \delta^{+} \alpha \, \delta^{-} \beta \, \pi \beta \right|$$
 and $- \left| \delta^{+} \alpha \, \delta^{-} \beta \, \sigma \alpha \right| \right\rangle$, which gives $\frac{1}{2} a_3 \left[l(l+1) \right]^{\frac{1}{2}}$.

These two terms cancel, indicating that the ${}^{4}\Pi/{}^{2}\Sigma^{+}$ perturbation cannot occur by a first order spin-orbit interaction mechanism.

Furthermore, the σ -electron is $4s\sigma$ and the π -electron is $3d\pi$. Consequently, the l_+ operator is being required to ladder a $4s\sigma$ electron into a $3d\pi$ 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:

$$\langle S'\Sigma'\Lambda'|\mathcal{H}_{so}|S\Sigma\Lambda\rangle = (-1)^{S'-\Sigma'} \begin{pmatrix} S' & 1 & S\\ -\Sigma' & q & \Sigma \end{pmatrix} \langle S'\Lambda'||\mathcal{H}_{so}||S\Lambda\rangle \,\delta_{\Omega\Omega'}. \tag{6.14}$$

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

$$\left\langle {}^{4}\Pi_{\frac{1}{2}},{}^{e}_{f} \left| \left| \mathcal{H}_{so} \right|^{2}\Sigma^{+},{}^{F_{1}}_{F_{2}} \right\rangle = \frac{1}{2\sqrt{3}} \left\langle {}^{4}\Pi \left| \left| \mathcal{H}_{so} \right| \right|^{2}\Sigma^{+} \right\rangle$$

$$(6.15)$$

and

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

where the reduced matrix element $\langle {}^{4}\Pi || \mathcal{H}_{so} ||^{2} \Sigma^{+} \rangle$ 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

$$\left\langle {}^{4}\Pi_{\frac{1}{2}} \right| \mathcal{H}_{so} \left| {}^{2}\Sigma^{+}, {}^{F_{1}}_{F_{2}} \right\rangle = \frac{\sqrt{2}}{3} \xi \tag{6.17}$$

and

$$\left\langle {}^{4}\Pi_{-\frac{1}{2}} \right| \mathcal{H}_{so} \left| {}^{2}\Sigma^{+}, {}^{F_{1}}_{F_{2}} \right\rangle = \mp \sqrt{\frac{2}{3}} \xi.$$

$$(6.18)$$

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:

$$\left\langle {}^{4}\Pi, v \right| \mathcal{H} \left| {}^{2}\Sigma^{+}, v' \right\rangle = \left\langle {}^{4}\Pi \right| \mathcal{H}_{electronic} \left| {}^{2}\Sigma^{+} \right\rangle \left\langle v | v' \right\rangle.$$
(6.19)

The overlap integral, $\langle v | v' \rangle$ was calculated using numerical integration over the eigenfunctions of modified Morse potentials given by

$$U(r) = D_e \left[1 - \exp^{-\beta(r)(r-r_e)} \right]^2$$
(6.20)

where

$$\beta(r) = \beta_0 + \beta_1 (r - r_e) + \beta_2 (r - r_e)^2$$
(6.21)

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	$\langle 1 x+1\rangle$	$\langle 0 x\rangle$	$\frac{\langle 1 x+1\rangle}{\langle 0 x\rangle}$
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

$$\langle {}^{4}\Pi, v = 1 | \mathcal{H} | {}^{2}\Sigma^{+}, v' = x + 1 \rangle = 28.7 \text{ cm}^{-1}$$
 (6.22)

$$\langle {}^{4}\Pi, v = 0 | \mathcal{H} | {}^{2}\Sigma^{+}, v' = x \rangle = 20.42 \text{ cm}^{-1}$$
 (6.23)

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.

$$\frac{\langle {}^{4}\Pi, v=1 | \mathcal{H} | {}^{2}\Sigma^{+}, v'=x+1 \rangle}{\langle {}^{4}\Pi, v=0 | \mathcal{H} | {}^{2}\Sigma^{+}, v'=x \rangle} = \frac{\langle 1 | x+1 \rangle}{\langle 0 | x \rangle} = 1.41$$
(6.24)

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

$$\omega_e = 1024.24 \text{ cm}^{-1}; \tag{6.25}$$

$$B_e = 0.5508 \text{ cm}^{-1}; \tag{6.26}$$

$$T_0(v=0) = 10412. \text{ cm}^{-1}.$$
 (6.27)

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 sub-Doppler 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 cm⁻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 sub-Doppler 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 cm⁻¹ [14], whereas the new vibrational assignment has shifted this value to 10412 cm⁻¹.

The eight hyperfine components arising from the ⁵¹V nucleus $(I=\frac{7}{2})$ 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 V 4s 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.

	ASSIGN	յո	F=J-7/2	F=J-5/2	F=J-3/2	F=J-1/2	F=J+1/2	F=J+3/2	F=J+5/2	₹=J+7/2
N= 0	SR21	1.5					12581.2817	12581.2225	12581.1414	12581.0383
	TR31	1.5						12645.1538	12645.0772	12644.9794
N= 1	QP21	2.5				13597 (/0)	43503 (103	40503 5/70	12577.1988*	12577.1187*
	SKZI	2.5				12583.0004	12585.6195	12583.5659	12583.4936	12583.4088
	K3 TD(7	1 5					13707 7/134	12207 7//7	12042.8454*	12642.6776*
		1.5					12/0/./012*	12/0/./44/	12/07.7200	12/07.6865*
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*
	92	2.5				12574.3546		12574.3390	12574.3289	12574.3170
	0924	0.5								12575.0443
	SR43	1.5					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	0021	45			12577 0512	12577 0178	12577 875/	12577 82/4	12577 74/4	12577 60/0
- J	SP21	4.5		12588.3567	12588.3316	12588 2070*	12588 2542*	12588 2018	12588 1410	12588 0701
	0024	1.5		125001050	.250010510	1230012777	12300.2342	12300.2010	12500.1410	12576 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= (0034					12570 120/+	12530 0033	47570 07/0	AD5 77 077/	10577 0110
N= 4	EP21	5.5	12500 4774		12500 5874+	125/0.1290"	122/8.08/3	125/8.0360	125//.9//0	125/7.9119
	5K2 TDZ1	5.5	12090.0000	1345/ /019	12390.3030"	12290.24/2	12090.0000	12590.4520	12590.3944	12590.3273
	TP42	6.5	12715 8731	12715 8678*	12715 8573	12034.4310	12034.3914	12034.3437"	12034.207/	12024.2200
	1842	4.5	12/15.0/51	12715 8678*	12715 8599*	12715 8467*	12715 8311*	12715 8103*	12715 7854*	12715 75/7*
	R4	2.5		12119.0070			12707.6237*	12707.6362	12707.6601*	12707.6785*
N= 5	PQ12	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	47597 0/00	43547 0400	43507 0030	43507 0/44	40503 0034			12514.7981
	RUZI	0.5	12583.9408	12585.9198	12583.8929	12583.8611	12583.8236	12583.7804	12583.7311	12583.6757
	K4	3.5		12/0/.1093	12/07.2005	12/0/.2134	12/0/.2300	12/0/.2029	12/0/.2939	12/07.5295
N= 6	P1	7.5		12523.4910*	12523.4581	12523.4193	12523.3734	12523.3222	12523.2650	12523.2005
	PQ12	6.5		12519.7056	12519.6943	12519.6800	12519.6623	12519.6390	12519.6109	12519.5753
	QP21	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	85			12523 1084	12523 1584	12523 1127	12523 0421	12523 0040	12522 0//*
a- 1	P012	7.5	12519,4418	12519,4332	12519,4218	12519,4077	12519 3802	12510 3444	12510 3374	12510 3000
	0P21	8.5	12578,4985	12578, 4687*	12578.4358	12578, 3967	12578, 3531*	12578 3030	12578 2494	12578 19074
	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
	RQ21	8.5	12585.8133	12585.7886	12585.7596	12585.7259	12585.6878	12585.6447	12585.5975	12585.5451
	SQ31	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

TABLE OF ASSIGNED LINES OF THE VO B-X (0,0) BAND

* indicates blended lines

	ASSIGN J"	F=J-7/2	F=J-5/2	F=J-3/2	F=J-1/2	F=J+1/2	F=j+3/2	F=J+5/2	F=J+7/2
N- 9	D1 0 E	12522 02124	17577 0000	12532 057/					
N= 0	PI 9.5	12522.9212*	12322.0000	12522.8536	12522.8138*	12522.7674	12522.7174	12522.6617	12522.6011
	PU12 0.3	12519.0952	12514.0003	12519.0/54	12519.0615	12519.0434	12519.0206	12518.9911	12518.9517
	0021 0 5	12300.3900	12578 /278	12578 302/	13570 3571	13570 7000	43578 3404	10570 00//	
	01 9.5	12533 2621*	12533.2318	12533 1040	12570.3331	12570.3009	12575.2001	12578.2004	12578.1478*
	OP12 8.5	12511.3694	12511.3603	12511.3491	12511 3345	12555.1075-	12555.0574	12533.0000	12532.9405
	R021 9.5	12586.6554*	12586.6306*	12586.6002*	12586.5644*	12586 5257	12586.4831*	12586 /370	12511.2230
	SQ31 9.5	12652.2020*	12652.1739	12652.1420	12652, 1063	12652.0659	12652.0211*	12651 9720	12651 018/
	R4 6.5	12705.1182*	12705.1379*	12705.1624*	12705.1913	12705.2253	12705.2633	12705.3061	12705.3530
N- 0	51 10 5								
N= 9	PI 10.5	12522.4908	12022.4083	12322.4222	12522.3805	12522.3350	12522.2846	12522.2310	12522.1716
	PU12 9.3	12518.0084	12210.0014	12218.0204	12518.63/0	12518.6198	12518.5956		12518.5241
	NU14 7.5	12504.30/9	12504.3301	12578 270/+	12504.3838	12504.4163	12504.4535	12504.4943	12504.5386
	o1 10.5	12578.3439	12533 8755	12573 8385*	12573 7040	12578.1942*	12578.1460*	12578.0935*	12578.0360*
	OP12 9.5	1233317000	1255510155	1233310303	12500 0880	12500 0707	12555.7002	12533.0440*	12333.385/*
	RQ21 10.5	12587.4328*	12587.4056	12587.3743	12587.3396	12587 3007	12587 2583	12587 2120	12587 1414
	\$931 10.5	12653.1741	12653,1450	12653.1130	12653-0764	12653.0360	12652 9918	12652 0637	12652 9012
	R4 7.5	12704.2647*	12704.2886*	12704.3158	12704.3468	12704.3826	12704.4221	12704 4659	12704 5134
									1210413130
N-10	D1 44 E	40504 0777	40504 0/0/	12521 0025					
R -10	PI 11.5	12521.9/3/	12519 153/	12521.9055	12521.8616	12521.8161	12521.7663	12521.7134	12521.6547
	NO14 8 5	12310.1010	12310.1334	12310.1440	125 18. 1506	12518.1141	12518.0916	12518.0609	12518.0141
	OP21 11 5	12578 1631*	12578 1206*	12578 0035*	12578 0535	12579 0005	12502.0/10"	12502.1125*	12502.1557
	R032 10.5	12370.1031		1237010733	12638 /305	12678 / 170	12577.7014	12277.9000	120//.0025
	Q1 11.5	12534,4628	12534,4294	12534.3912*	12534 3403*	12536 3027	12536.4009	12030.3/01	12030.3302
	OP12 10.5		12508.5808		1233413473	12334.3021	12508-5187	12508 4868	12508 4305
	RQ21 11.5	12588.1453*	12588.1167*	12588.0852	12588.0502	12588.0107	12587.9686*	12587.9228	12587 8733
	SQ31 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 0/04
	PQ12 11.5	12517.5698	12517.5647	12517.5561	12517.5442	12517.5280	12517.5062	12517 4746	12517 6211
	NQ14 9.5	12499.4310	12499.4558	12499.4832	12499.5144	12499.5490	12499.5871	12499.6275	12499 6709
	QP21 12.5	12577.9088*	12577.8741*	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
	RQ32 11.5				12638.2908*	12638.2804*	12638.2637*	12638.2378	12638.1910
	Q1 12.5		12534.8915	12534.8525	12534.8102	12534.7641	12534.7138	12534.6596	12534.6019
	OP12 11.5						12507.0028*	12506.9705*	
	RQ21 12.5	12588.7927	12588.7631	12588.7308	12588.6950	12588.6561	12588.6137	12588.5687	12588.5193
	SQ31 12.5	12654.9472	12654.9171	12654.8835	12654.8467	12654.8068	12654.7635	12654.7162	12654.6659
	SK32 11.5	12651.14/3*	12051.1458*	12051.1414*	12651.1351	12651.1245	12651.1087	12651.0834*	12651.0373*
	TO41 12.5		12121.4403	12/2/ .4112	12727 3734	12/2/.3323	1777 707/+	12727.2391	12727.1867
	1041 12.5				12/2/.3/30	12/2/.3323	12/2/.20/4-		
N=12	P1 13.5	12520.6793	12520.6438	12520.6046	12520.5632	12520.5174	12520.4680	12520.4151	12520.3582
	PQ12 12.5	12516.8954	12516.8907	12516.8841	12516.8738	12516.8594	12516.8386	12516.8074	12516.7425
	NP13 11.5	12492.7091*	13/04 9745	13/04 0000	13/0/				
	NU14 10.3	12490.0400	12490.0/10	12470.0777	12496.9325*	12496.9670*	12497.0043	12497.0449	12497.0880
	GR23 11 5	16211.2102"	12211.3441	12311.3000	123/1.4001	12577.4216	12511.5757	125/7.3223*	12577.2676
	RP31 13.5		12641.8609*	12641.8260	12641 7800	126/1 7/97	124/1 7057	122/3.5251*	125/5.5415
	R032 12 5		.2041.0007	12638.1060*	12638 1005+	12641./40/	12641./033	12041.0385	12641.6081
	SR43 11.5				1203011003"	12030.0713	12030.0/02	12030.0303	12710 2040+
	Q1 13.5	12535.2984	12535.2624	12535.2235	12535, 1803*	12535,1340*	12535.0835*	12535.0305	12536 0720
	RQ21 13.5	12589.3738	12589.3439	12589.3106	12589.2748	12589.2357	12589.1937	12589,1481	12589, 1000
	SQ31 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
	TQ41 13.5	12728.4271	12728.3949		12728.3224	12728.2817	12728.2375	12728.1904	12728.1390

	ASSIGN J"	£=J-7/2	F=J-5/2	F=J-3/2	F=J-1/2	F=J+1/2	F=j+3/2	F=j+5/2	F=J+7/2
N=13	PQ12 13.5	12577 1761	12577 1407	12577 1031	12577 0423	12516.1091	12516.0894	12516.0607	12515.9792
	9823 12.5	12377.1101	1237711407	12377.1037	12377.0023	12377.0170	12370.9701	12573 1755	12578 1027
	RP31 14.5	12641.6256	12641.5941	12641.5594	12641.5216	12641.4811	12641.4377	12641.3913	12661 3616
	RQ32 13.5								12637.7414
	SR43 12.5	12710.2065*	12710.1968*						
	Q1 14.5	12535.5796*	12535.5409*	12535.5023	12535.4591*	12535.4129	12535.3631	12535.3092	12535.2525*
	OP12 13.5								12503.6026
	RQ21 14.5	12589.8888	12589.8581	12589.8248	12589.7885	12589.7493	12589.7072	12589.6621	12589.6139
	SQ31 14.5	12656.4877	12656.4560*	12656.4224	12656.3850	12656.3451	12656.3023	12656.2567*	12656.2074
	5K32 13.3	12052.7221*	12032.7233"	12720 2425	12052.7233	12652./1/0*	12652.7045	12652.6813	12652.6077
	1441 14.3			12727.2023	12127.2247	12/29.1039	12729.1403	12/29.0941	12729.0439
N=14	D1 15 5					12518 9711	12518 8227	13519 7407	13510 3135
N -14	P012 14 5					12510.0711	12515 2612	12515 0800*	12518./135
	NO14 12.5	12491.3925	12491.4187*	12491,4496	12491.4835*		12313.2012	12/01 50/7	12212.1297
	QP21 15.5	12576.6986	12576.6636	12576.6248	12576.5837	12576.5391	12576-4918	12576 4413	12471.0373
	QR23 13.5	12572.7872	12572.7713	12572.7592			12572.7431*	12572.7456	12572 0048
	RP31 15.5	12641.3027	12641.2707	12641.2359	12641.1977	12641.1573	12641.1144		12641.0190*
	RQ32 14.5								12637.4355
	SR43 13.5	12710.0851*							
	Q1 15.5	12535.7680	12535.7308	12535.6911	12535.6474	12535.6009	12535.5508	12535.4976	12535.4414
	OP12 14.5								12501.8091*
	RQ21 15.5	12590.3385	12590.3067	12590.2722*	12590.2363	12590.1971	12590.1549	12590.1098	12590.0622*
	SQ31 15.5	12657.1692	12657.1374	12657.1030		12657.0267*	12656.9831	12656.9379	12656.8894
	SR32 14.5	12653.4246*	12653.4320*	12653.4357*	12653.4357*	12653.4320*	12653.4234*	12653.2593*	12653.3064
	1941 15.5	12/30.1857	12/30.1530	12/30.11//	12/30.0/99	12730.0398		12729.9509	12729.9016
N=15	D1 14 5	12518 085/	12518 0481	12518 0082	12517 04/5	12517 0170	12517 8480	12517 814/	13517 7415
M-12	P012 15 5	1251/ 3450	12516 3717	12310.0002	1251/ 3717	1251/ 1444	1251/ 1444	12317.0104	1251/./015
	PR13 14 5	12514 2366	12314.3711		16214.3711	12314.1000	12514.1000		12314.1933
	0P21 16.5	12576.1470	12576, 1113	12576.0726	12576-0312	12575 9865	12575 0392	12575 8890	12575 8356
	RP31 16.5	12640.9249*	12640.8914	12640.8563	12640.8181	12640.7777	12640.7349	12640.6897*	12640.6407
	RQ32 15.5								12637.0749
	SR43 14.5	12709.9136							
	Q1 16.5	12535.8665	12535.8288	12535.7883*	12535.7445	12535.6976	12535.6474*	12535.5950	12535.5387*
	0013 14.5	12499.9718							
	RQ21 16.5	12590.7205	12590.6891	12590.6544	12590.6173	12590.5784	12590.5361	12590.4915	12590.4441
	SQ31 16.5	12657.7909	12657.7586	12657.7245	12657.6871	12657.6475	12657.6050	12657.5601	12657.5122
	SR32 15.5 TQ41 16.5	12654.0713	12654.0829	12654.0898*	12654.093/*	12653.8960	12653.9026	12653.9166	12653.9467 12730.7110*
N=16	P1 17.5	12517.0477	12517.0098	12516.9687	12516.9251	12516.8795	12516.8296	12516.7789*	12516.7226
	PQ12 16.5		12513.3695*		12513.1747	12513.1661	12513.1618	12513.1633*	12513.1747*
	PR13 15.5	12513.2602	105 75 / 070	12513.2009*					
	QP21 17.5	12575.5204	125/5.4839	12575.4448	12575.4033	12575.3591	12575.3121	12575.2622	12575.2093
	W2 10.5	13571 777/+	125/1.0390"	125/1.84/1*	125/1.049/*				
	WK23 13.5	12571.7554"	124/0 /541	123/1.0//4"	125/1.0014"	124/0 7/21	134/0 200/	10//0 3570	43//0 20/4
	R032 16 5	12040.4093	12040.4701	12040.4203"	16040.3021	12040.3421	12040.2994	12040.2339	12040.2001
	S042 16 5	12709, 7896	12709,8066						12030.0200
	SR43 15.5	12709.6932	12709.6623	12709.6442	12709.6334*	12709.8241*	12709,8241*	12709,8241*	12709 8153*
	Q1 17.5	12535.8743	12535.8359	12535.7944*	12535.7505*	12535.7035	12535.6540	12535,6009*	12535 5453*
	0013 15.5	12498.0426	12498.0076*	12497.9831					
	RQ21 17.5	12591.0369*	12591.0044*	12590.9695	12590.9327	12590.8929	12590.8510	12590.8067	12590.7593
	SQ31 17.5	12658.3528	12658.3205	12658.2854	12658.2482	12658.2088	12658.1667	12658.1220	12658.0746
	SR32 16.5	12654.6630*	12654.6792	12654.6904*	12654.4981*	12654.4956	12654.4981*	12654.5080*	12654.5276
	S3 15.5			12654.5204*	12654.5080*	12654.7000*			
	OP34 14.5	12592.7057	12592.7387*	12592.7753*	12592.8137	12592.8550	12592.8989	12592.9451	12592.9939
	TQ41 17.5	12731.7519	12731.7186	12731.6841				12731.5193	12731.4718

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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=J-1/2	F=J+1/2	F=J+3/2	F=J+5/2	F=J+7/2
N=17	P1 18.5	12512 2601	12515.8868	12515.8451	12515.8009	12515.7544	12515.7055	12515.6532	12515.5981
	QP21 18.5 Q2 17.5	12574.8179	12574.7812 12571.0148*	12574.7417 12570.9959*	12574.7002 12570.9818*	12574.6558 12570.9729*	12574.6090	12574.5593	12574.5071*
	QR23 16.5 RP31 18.5	125/1.0911	12639.9637			12630 8400	12639 8072	12639,7620	12630 7130
	RQ32 17.5	12636.3427	12636.1996	12636.1864*	12636.1747*	12636.1696*	12636.1696*	12636.1747*	12636.1864*
	R3 16.5	40700 40400	12636.2226	12636.3628	12636.3762				
	SQ42 17.5 SR43 16 5	12709.4960*	12709.3760	12709.5166	12709.5306	12709 5413*	12709 5440*	12709 5449*	12700 5413*
	Q1 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	17501 2181	12501 1816*	12501 1/14	17501 000/	13501 05/8	13501 0070+
	SQ31 18.5	12658.8546*	12658.8214*	12658,7866	12658.7492*	12658,7099	12591.0994	12591.0540	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
	TQ41 18.5 P4 15 5	12662-0149	12732.4292*	12662.0850	12/32.35/6	12/32.3178	12732.2759*	12732.2314	12732.1843
	P4 13.5	12002.0147	12002.0400	12002.0050	12002.1230				
N=18	P1 19.5	12514.7151	12514.6759	12514.6345	12514.5909	12514.5448	12514.4952	12514.4436	
	PQ12 18.5	12510.9771	12510.9476	12510.9248	12510.9078	12510.8945	12510.8850*	12510.8803*	12510.8803
	GP21 19.5	12574.0398	12574.0029	12573.9634	125/3.9213	125/3.8771	12573.8301	12573.7795*	12573.7286*
	QR23 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
	RQ32 18.5	12635.7099	12635.6857	12635.6692	12475 8720				12635.6576*
	R5 17.5	12709.0344*	12035.0354	12035.8574	12035.0729	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*
	Q1 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	
	RQ21 19.5	12591.4687*	12591.4359*	12591.3989*	12591.3625	12591.3229	12591.2811	12591.2367	12591,1896
	\$931 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	10505 /577	12655.5064*	12655.5012*	12655.4986*	12655.5012*	12655.5103*
	0P34 16.5	12585.5815	12282.0162	12202.0233	12733.0186*	12285.7346	12585.7785	12585.8247	12585.8729
	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	12513.2009	12513.1496	12513.0949
	PQ12 19.5	12509.7147	12509.6846	12509.6608	12509.6423	12509.6273	12509.6164*	12509.6091*	12509.6067
	PR13 18.5	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	40/70 /07/4	12535.3342
	RP31 20.5	12638.8428	12038.0089	12635.0928	12635.0803*	12038.0948	12638.6525	12038.00/4*	12638,5609*
	R3 18.5	120351 1352	12635.2760	12635.2988*	12635.3151*	12635.3271*			
	SQ42 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*
	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	12501 5152	12501 / 77/+	12501 (7704	44544 74574		
	SQ31 20.5	12059.6750	12659.6419	12059.6068	12059.5699	12091.45/0*	12091.395/*	12091.5518*	12591.5046
	SR32 19.5	12655.9675	12655.9430*	12655.9267*	12655.9147*	12655.9076*	12655.9049*	12655.9049*	12655.9112*
	OP34 17.5	12581.9279	12581.9633	12582.0007	12582.0407	12582.0826	12582.1267	12582.1725	12582.2210
	TQ41 20.5	12733.7366	12730 0053	12720 0887	12753.6325*			12733.5084*	12733.4628*
	P4 17.5	12655.1281	12655.1627*	12655.2001	12655.2397*	12655.2811	12655.3250	12655.3705	12655.4185

	ASSIGN J"	F=J-7/2	F=J-5/2	F=J-3/2	F=J-1/2	F=J+1/2	F=J+3/2	F=J+5/2	F=J+7/2
₩=20	P1 21.5	12512.0449		12511.9627	12511.9178	12511.8718	12511.8225	12511.7696	12511.7161
	PQ12 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
	SQ42 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
	0012 20 5	12533.0084	12534.9081	12534.9257	12534.8805	12534.8332	12534.7834	12534.7308	12534.6757
	PO21 21 5	12501 4335	12531.29/3	12531.2/30	12531.2320	12531.2365	12531.2238	12531.2138	12531.2079
	SQ31 21.5	12659.9935	12659.9608	12659.9252	12650 8877	12371.4034	12391.4432	12391.3989*	12591.3519*
	SR32 20.5	12656.3134	1203717000	12656.2750*	12656.2610*	12656 2526*	12654 2477*	12656 2677*	12037./100
	OP34 18.5	12578.2130	12578.2494*	12578.2870*	12578.3273*	12578.3695	12578.4134*	12578.4594*	12030.2312-
	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 3070	12510 2525
	PQ12 21.5	12506.9272	12506.8982	12506.8740	12506.8539	12506.8368	12506-8234	12506-8123*	12506 8050
	QP21 22.5	12571.2499	12571.2120	12571.1718	12571.1296	12571.0855	12571.0391	12570.9903	12570 0302
	OP23 20.5		12524.8811	12524.9000	12524.9133	12524.9220			
	0924 19.5	12529.2467	12529.2797	12529.3134	12529.3492	12529.3866	12529.4258	12529.4666	12529, 5092
	SQ42 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
	Q1 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
	RQ21 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
	5931 22.5	12660.2510*	12660.2180*	12660.1823	12660.1451	12660.1060	12660.0653	12660.0218	12659.9767
	SK32 21.3	12000.0900	12050.5733	12030.3301	12656.5438	12656.5347*	12656.5295*	12656.5276*	12656.5295*
	TP42 21 5	12731 1575	12374.4739	12771 1182	12771 104/	125/4.5951*	12574.6390	125/4.6849	12574.7329
		12/31.13/3	12131.1341	12/31.1102	12/31.1004	12/31.0901-			
N 22	of 07 5	12500 0700		10500 0550					
N=22	P1 23.5	12509.0390	12508.9985	12508.9559	12508.9105	12508.8633	12508.8144	12508.7622	12508.7082
	QP21 23.5	12570.10/1	12570.1200	12571 8/28	12570.0409	12570.0029	12569.9566	12569.9078	12569.8572
	0024 20 5	12526 2185	12526 2511	12521.0420	12526 3219	12521.8652	12521.8/1/	12521.8/54*	
	8P31 23.5	12636 6812	12320.2311	12636 6097*	12636 5710	12020.0090	12020.3901	12020.4392	12526.4815
	PQ34 20.5	12592,1420	12592, 1782	12592.2160	12592.2562	12502 2078	12030.4070	12030.4431	12502 / 772+
	SQ42 22.5	12707.1406	12707.1194	12707, 1022	12707.0899	12707 0800*	12707 0751*	12707 07/3*	12772.4332"
	QP43 21.5	12661.4109	12661.4414	12661.4649	12661.4828	12661.4972	12661.5088	12661.5182	12661 5268
	SR43 21.5	12707.3260*	12707.3572	12707.3806	12707.3989	12707.4141	12707.4265	12707.4361	12707 4430
	Q1 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
	R021 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*
	\$031 23.5	12660.4462	12660.4131	12660.3781*	12660.3411*	12660.3016	12660.2611	12660.2180*	12660.1729
	SR32 22.5	12656.8156	12656.7937	12656.///0*	12656.7646	12656.7552*	12656.7511*	12656.7469*	12656.7469*
	UP34 20.5	12570.6006	12570.6375	125/0.6/65	12570.7168	12570.7595	12570.8039	12570.8499	12570.8975
	1842 22.3	12/31.0442	12/31.022/	12/31.000/	12/31.5946	12731.5856			
	P4 20.3	12044.4272	12044.4001	12044.3031	12044.3439	12644.5884	12644.6327	12644.6788	12644.7267
₩=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	12523.3349	12523.3768*
	KP31 24.5	12033.8442	12635.810/*	12035.//32	12035./348	12635.6939		12635.6084	12635.5623
	SW42 23.5	12/00.3401	12/00.2192	12/00.3034	12/00.4910	12/06.4820	12706.4759*	12706.4733*	12706.4733*
	SR43 22 5	12706.7558	12706 7855+	12706 8082	12706 8240	12070.04/3*	12000.0002	12070.0/00	12058.8779
	01 24.5	12533.4302	12533 3075	12533.3537	12533 3070	12533 2507	12533 3100	12/00.0000	12/00.8743
	QR12 23.5	12529,8315*	12529,8025	12529.7779	12529.7543	12520 787/	12520 7210	12333.13/4	12533.1028
	RQ21 24.5		12591.3421*	12591.3046*	12591.2658	12591.2254	12501.1820*	12501 1202+	12501 0021
	NP24 21.5	12498.6132	12498.6498	12498.6887	12498.7288	12498.7704	12498.8144*	"071" (740"	12408 0049+
	\$931 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*	12656.9020*
	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.
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	ASSIGN J"	F=J-7/2	F=j-5/2	F=J-3/2	F=j-1/2	F=J+1/2	F=J+3/2	F=J+5/2	F=J+7/2
N=20	P1 21.5 P012 20.5	12512.0449 12508.3644 12573.2541	12508.3345	12511.9627 12508.3106 12572 1782	12511.9178 12508.2916 12572 1341	12511.8718 12508.2751 12572 0922	12511.8225 12508.2626 12573 0655*	12511.7696 12508.2535 12571 9966	12511.7161 12508.2485 12571 9452
	0P23 19.5 0Q24 18.5	12527.8280	12572.2185	12532.2640	12532.3002	12527.9038	12532.3766	12532.4176	12532.4599
	SQ42 20.5 SR43 19.5 Q1 21.5	12708.1900 12708.3147 12535.0084	12708.1672* 12708.3536 12534.9681	12708.1504* 12708.3777 12534.9257	12708.3954 12708.3954 12534.8805	12708.1275* 12708.4091 12534.8332	12708.1249* 12708.4195 12534.7834	12708.1249* 12708.4267 12534.7308	12708.1257* 12708.4306 12534.6757
	QR12 20.5 RQ21 21.5 SQ31 21.5	12531.3282 12591.6335 12659.9935	12531.2973 12591.5996 12659.9608	12531.2736 12591.5636 12659.9252	12531.2526 12591.5255* 12659.8877	12531.2365 12591.4854 12659.8483	12531.2238 12591.4432 12659.8076	12531.2138 12591.3989* 12659.7643	12531.2079 12591.3519* 12659.7186
	SR32 20.5 OP34 18.5 TR42 20.5	12656.3134 12578.2130 12730.6192	12578.2494* 12730.5957	12656.2750* 12578.2870* 12730.5791	12656.2610* 12578.3273* 12730.5676*	12656.2526* 12578.3695 12730.5598	12656.2477* 12578.4134* 12730.5559*	12656.2477* 12578.4594* 12730.5559*	12656.2512* 12578.5072 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 P012 21.5 0P21 22.5	12510.5840 12506.9272 12571.2499	12510.5438 12506.8982 12571.2120	12510.5015 12506.8740 12571.1718	12510.4562 12506.8539 12571.1296	12510.4098 12506.8368 12571.0855	12510.3598 12506.8234 12571.0391	12510.3079 12506.8123* 12570.9903	12510.2535 12506.8059 12570.9392
	0P23 20.5 0024 19.5	12529.2467	12524.8811 12529.2797	12524.9000 12529.3134 12707.6515*	12524.9133 12529.3492 12707.6397*	12524.9220 12529.3866 12707.6292	12529.4258	12529.4666	12529.5092
	SR43 20.5 Q1 22.5	12707.8454 12534.5716 12530.0142	12707.8799 12534.5309 12530.88664	12707.9034 12534.4882 12530.8614	12707.9213* 12534.4428 12530.8416	12707.9362 12534.3953 12530 8243	12707.9475 12534.3453 12530.8098*	12707.9561 12534.2927 12530 7982*	12707.9615 12534.2379 12530.7905
	RQ21 22.5 NP24 19.5	12591.6151	12591.5812	12591.5447 12506.9436	12591.5061 12506.9842 12660 1451	12591.4658*	12591.4235	12591.3793* 12507.1159* 12640.0218	12591.3329 12507.1633 12659.9767
	SR32 21.5 OP34 19.5	12656.5956	12656.5733	12656.5561 12574.5124*	12656.5438* 12574.5529	12656.5347* 12574.5951*	12656.5295* 12574.6390	12656.5276* 12574.6849	12656.5295* 12574.7329
	D1 27 5	12500 0700	12509 0095	12508 0550	12508 0105	12508 9477	12508 81//	12508 7622	12508 7082
N=22	0P21 23.5 0P23 21.5	12509.0390 12570.1671 12521.7978	12570.1288	12570.0891 12521.8428	12570.0469	12570.0029	12569.9566	12569.9078 12521.8754*	12569.8572
	0024 20.5 RP31 23.5 P034 20.5	12526.2185 12636.6812 12592.1420	12526.2511	12528.2055	12636.5719	12636.5319	12636.4896	12636.4451 12592.3860*	12592.4332*
	SQ42 22.5 QP43 21.5 SR43 21.5	12/07.1406 12661.4109 12707.3260*	12/07.1194 12661.4414 12707.3572	12661.4649 12707.3806	12661.4828	12661.4972 12707.4141	12661.5088	12661.5182 12707.4361	12661.5248
	Q1 23.5 QR12 22.5 RQ21 23.5	12534.0486 12530.4170 12591.5293	12534.0068 12530.3875 12591.4954	12533.9654 12530.3623 12591.4583	12530.3414	12533.8703 12530.3235 12591.3793*	12533.8199 12530.3080 12591.3371	12530.2960 12591.2930	12530.2869
	NP24 20.5 SQ31 23.5 SR32 22.5	12502.7749 12660.4462 12656.8156	12502.8108 12660.4131 12656.7937	12502.8497 12660.3781* 12656.7770*	12502.8899 12660.3411* 12656.7646	12502.9318 12660.3016 12656.7552*	12502.9758 12660.2611 12656.7511*	12503.0222* 12660.2180* 12656.7469*	12503.0686* 12660.1729 12656.7469*
	OP34 20.5 TR42 22.5 P4 20.5	12570.6006 12731.6442 12644.4292	12570.6375 12731.6227 12644.4661	12570.6763 12731.6067 12644.5051	12570.7168 12731.5946 12644.5459	12570.7595 12731.5856 12644.5884	12570.8039	12570.8499	12570.8975 12644.7267
N=23	P1 24.5	12507.4115	12507.3707	12507.3278	12507.2829	12507.2354	12507.1857		12507.0796
	PR13 22.5 0024 21.5	12504.0196	12504.0414 12523.1463	12504.0560 12523.1815	12523.2175	12523.2551	12523.2941	12523.3349	12523.3768*
	8042 23.5 9043 22.5	12005.8442 12706.5401 12658.7626	12000.510/* 12706.5195 12658.7911	12706.5034 12658.8143	12706.4910 12658.8322*	12706.4820 12658.8473*	12706.4759* 12658.8602	12706.4733* 12658.8706	12706.4733* 12658.8779
	SR43 22.5 Q1 24.5 QR12 23.5	12706.7558 12533.4392 12529.8315*	12706.7855* 12533.3975 12529.8025	12706.8082 12533.3537 12529.7779	12533.3079	12533.2597 12529.7374	12533.2100 12529.7218	12533.1574 12529.7082	12533.1028 12529.6979
	RQ21 24.5 NP24 21.5 SQ31 24.5	12498.6132 12660.5799	12591.3421* 12498.6498 12660.5462*	12591.5046* 12498.6887 12660.5114*	12091.2008 12498.7288 12660.4742*	12591.2256 12498.7704 12660.4345*	12591.1829* 12498.8146* 12660.3947*	12660.3524	12591.0921 12498.9068* 12660.3074
	SR32 23.5 TR42 23.5 P4 21.5	12656.9725* 12732.0797 12640.7644	12656.9513* 12732.0579 12640.8022	12656.9354* 12732.0424 12640.8413	12050.9224* 12732.0313 12640.8824	12636.9126* 12732.0227 12640.9249*	12636.9064* 12732.0167 12640.9701	12656.9029*	12641.0646*

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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=J-1/2	F=J+1/2	F=J+3/2	F=J+5/2	F*J+7/2
N=24	P1 25.5	12505.7014		12505.6175	12505.5724	12505.5248	12505.4752	12505.4236	12505.3696
	PQ12 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*	
	0924 22.5	12519.9318	12519.9655	12520.0006	12520.0364	12520.0744	12520.1134	12520.1540	12520.1957
	PQ34 22.5	12586.4447*	12586.4814*	12586.5199*	12586.5599*	12586.6002*	12586.6454	12586.6903	12586.7368
	SQ42 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
	Q4 22.5	12660.5351	12660.5740	12660.6134	12660.6548	12660.6982	12660.7428	12660.7899	12660.8383
	Q1 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
	PQ23 23.5	12536.8237	12536.8499	12536.8699	12536.8868	12536.9007	12536.9122	12536.9212*	12536.9277
	SQ31 25.5	12660.6518*	12660.6181	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
	PQ12 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		
	0924 23.5	12516.6734	12516.7073	12516.7425	12516,7789	12516.8157	12516.8561*	12516.8954*	12516.9382
	PQ34 23.5	12583.5088	12583.5461	12583.5852*	12583.6254	12583.6669*	12583.7102	12583.7551	12583.8016
	SQ42 25.5	12705.1891*	12705.1701*	12705.1549	12705.1426	12705.1334*	12705.1271		12705.1230*
	QP43 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
	Q4 23.5	12657.8127*	12657.8510*	12657.8913	12657.9333	12657.9771	12658.0220	12658.0690	12658, 1173
	Q1 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
	NP24 23.5		12490.1268*	12490.1659*	12490.2066*	12490.2458*	12490.2906*	12490.3353	12490.3817
	SQ31 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
	0924 24.5			12513.4078	12513.4444	12513.4823	12513.5210	12513.5619	12513.6034
	PQ34 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*
	Q4 24.5	12655.0400	12655.0789	12655.1200	12655.1627*	12655.2061	12655.2513	12655.2983	12655.3466
	Q1 27.5	12531.1156	12531.0729	12531.0284	12530.9824	12530.9336	12530.8834	12530.8309	12530.7759
	QR12 26.5	12527.5768	12527.5488	12527.5239	12527.5015	12527.4816	12527.4639	12527.4479	12527.4350
	RQ21 27.5	12590.5125	12590.4767	12590.4395*	12590.3998	12590.3587	12590.3157	12590.2722*	12590.2251
	PQ23 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
	SQ31 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*	12656.9975*
	TR42 26.5	12733.0782	12733.0603	12733.0459	12733.0338				

	ASSIGN J"	F=J-7/2	F=J-5/2	F=J-3/2	F=J-1/2	F=J+1/2	F=J+3/2	F=J+5/2	F=J+7/2
N-27	D1 38 5		13500 0/81	12500 0074	12/00 0575		13/00 8404	12/00 8080	12/00 701
N=ZI	PI 28.5	40/0/ 5770	12300.0401	12500.0056	12499.93/3	40/07 1045	12499.0000	12499.0009	12499.7546
	PQ12 27.5	12496.5730	12490.0400	12490.5225	12496.5010	12490.4815	12496.4644	12490.4489	12496.4362
	PR13 26.5	12496.9068	12496.9224*	12496.9356	12496.9447		12496.9569		
	0924 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
	Q4 25.5	12652.2176	12652.2572	12652.2982	12652.3406	12652.3846	12652.4301	12652.4774	12652.5257
	Q1 28.5	12530.1834	12530.1401	12530.0952*	12530.0483*	12529.9995	12529.9487	12529.8960*	12529.8411*
	QR12 27.5	12526.6672*	12526.6385	12526.6129	12526.5910*	12526.5710	12526.5525	12526.5368	12526.5223
	RQ21 28.5	12590.0895	12590.0533*	12590.0151*	12589.9759	12589.9345	12589.8917*	12589.8473	12589.8009
	PQ23 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*
	SQ31 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				
₩=28	P1 20 5	12/08 0401	12498 0176	12/07 0735		12/07 9799	13/07 9303	12/07 7784	12/07 7754
4-20	P013 39 5	12490.0007	12470.0170	12/0/ 5159	12/0/ /070	12471.0100	12477.0302	12477.7700	12471.1231
	PW12 20.3	12494.3037	12474.3372	12474.3130	12474.4730	12474.4743	12474.43/3	12494.4409	12494.42/8
	PRIJ 27.J	12494.7203	12474.7433	12474.7301	12474.7044	12474.7/14	12494.9/02	12494.9/09*	12494.9796*
	0P23 27.5	12501.0/40*	12501.0933*	4350/ 510/	4050/ E/77	1050/ 505/	49594 4959	49594 4447	10000
	0024 26.5	12300.4412	12300.4732	12000.0100	12506.54//	12000.0800	12506.6250	12500.004/	12506.7060
	PQ34 20.5	12574.3502*	12274.2001	123/4.4200	123/4.40/9	125/4.5098*	12574.5529*	125/4.59/5*	125/4.6435*
	QP43 27.5	12644.7789	12044.8031	12044.8244	12044.8435	12644.8599	12644.8748	12644.8885	12644.9002
	SR43 27.5	12/03.1450	12/03.1/01	12/03.1914	12/03.2105	12/03.2278	12703.2428	12703.2572	12703.2693
	Q1 29.5	12529.1/65	12529.1333	12529.0869*	12529.0407	12528.9913	12528.9404	12528.8870	12528.8324
	QR12 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*
	PQ23 27.5	12527.3147	12527.3359	12527.3540	12527.3697	12527.3834	12527.3949	12527.4049	12527.4135
	PR24 26.5								12532.1678*
	SQ31 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
	PQ12 29.5	12492.4797	12492.4538	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		
	0924 27.5	12502.8778	12502.9117	12502.9475	12502.9847	12503.0222	12503.0620	12503,1024	12503.1435
	PQ34 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*	12641.8961*	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
	OR12 29.5	12524.6283	12524.6003	12524.5755*	12524.5523	12524.5308	12524.5113	12524.4947*	12524.4787
	8021 30 5	12589 0400	12589.0030	12588.9645	12588.9245	12588 8832	12588 8404	12588 7055*	12588 7/80
	P023 28 5	12526 7696	12524 7897	12524 8074	12524 8231	12526 8365	1252/ 8/8/	1252/ 8582*	1252/ 9444
	DP2/ 27 5	12520 3603*	12520 3058	12224.0014	12529 4745	12520 51/8	12520 5570	12529.0002	12529.0000
	CO31 30 5	12640 0732	12440 0302	12660 00/0	12450 0474	12450 0201#	12450 9977*	12327.0007	12450 80/0
	SW31 30.3	12600.0752	12000.0372	12000.0040	12637.7070	12037.7291"	12037.00//*	12037.0403"	12039.0048
	3K32 29.3	12030.0007	12030.3033	12030.308/	12030.3301		12030.3303-	12030.3330"	12030.3293*
	1842 29.3	12/33.009/	12/33.3937	12133.3199	12/33.3003				
N≠30	P1 31.5	12493.7668	12493.7246	12493.6796	12493.6335	12493.5854	12493.5358	12493.4840	12493.4307
	PQ12 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		
	OP23 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
	QP43 29.5	12638.8355	12638.8590	12638.8797	12638.8993	12638.9166	12638.9319	12638.9461	12638.9587
	94 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*
	QR12 30.5	12523.5110*	12523.4851*	12523.4581*	12523,4351	12523.4131	12523, 3929	12523.3745*	12523 3582
	RQ21 31.5	12588.4135	12588.3763*	12588.3385	12588.2979*	12588.2563	12588.2124	12588, 1679	12588.1211*
	PQ23 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
	\$931 31.5	12659,7689*	12659.7346	12659,6995	12659.6632	12659.6252	12659, 5850	12659 5437	12659-5011
	SR32 30 5	12656.3191	12656.3023	12656.2872*					
	TR42 30.5	12733.6814	12733.6659	12733,6526	12733.6414				
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	ASSIGN J"	F=J-7/2	F=J-5/2	F=J-3/2	F=J-1/2	F=J+1/2	F=J+3/2	F=J+5/2	F=J+7/2
N-31	D1 72 5	12/01 5057	12/01 /427	12/01 /187	12/01 3714	12/01 2224	12/01 2778	12/01 2222	17/01 4/04
	0077 70 5	12491.3037	12471.4027	12471.4107	12471.3710	12471.3230	12491.2730	12471.2223	12491.1694
	002/ 30.5	12470.0000	12470.7027**	12470.7177	12470.7304	12490.9400	12490.7304	12470.73//	12490.9641
	0024 27.5	12473.3232	12473.3303	12473.3740	12475.0510	12493.0/03	12493.7003	12493.7490	12495.7898
	4P43 30.3	12033.10/0	12033.010/-	12033.0320	12033.0309	12035.8088	12033.0043*	12033.0909*	12635.9125
	44 29.5	12040.4247	12040.4030	12040.30/9	12040.551/*	12040.5969	12640.6428	12640.6899*	12640.7388
	Q1 32.5	12525.7000	12525.7255	12525.0/00	12525.0200	12525.5779	12525.5256	12525.4/16	12525.4152
	QR12 31.5	12522.3403	12522.3134	12522.2868*	12522.2635	12522.2408	12522.2199*	12522.2013	12522.1839*
	RQ21 32.5	12587.7195	12587.6822	12587.6435	12587.6030*	12587.5604*	12587.5176	12587.4728	12587.4259
	PQ23 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
	\$931 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	12401 8702	12/01 0188	12401 0501	12/02 0000
	04 30 5					12471.0/72	12477 5481#	12437 6163*	12472.0000
	01 33 5	12526 5366*	12524 4800*	12526 6620	12526 3031	1752/ 7/2/	1252/ 280/	1253/ 23/5	12037.00000-
	0012 32 5	12521 1312	12521 1031	12521 0763	12521 0513*	12524.3424	12524.2074	12524.2343	12524.1779
	DO21 33 5	12586 0576	12584 0202	12586 8812	12586 9/11	12521.0201	12321.0000	12320.9009	12020.9085
	RW21 33.3	12300.9370	12300.9202	12300.0012	12500.04()	12300./909	12000./004	1351/ 01574	12586.0629
	PW23 31.3	10501 20104	40504 /077	10501 ///7	12310.7709"	12510.7951*	12516.8051*	12310.013/-	12516.8236
	PK24 30.3	12321.3910*	12221.42/3	12521.4005	12321.3031	12021.0400	12521.58/8	12521.0307	12521.6737*
	5431 33.3	12038.9/03	12038.9338	12030.9009	10507 5/75	12658.8266*	12658./866*	12058.7407*	
	WP32 32.3	12587.0105	12387.3939	12367.3790	12307.30/5	12587.55/1*	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./862	12592.8274	12592.8701	12592.9143	12592.9597	12593.0060	12593.0536
	1842 32.5	12/33.0079	12/33.0520*	12/33.03/4	12/33.62/0				
N=33	Q1 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*	12519.7074	12519.7751*	12519.7535	12510 7334*
	R021 34.5	12586, 1288	12586.0908	12586-0515*	12586-0106	12585 0400	12585 0253	12585 8800*	12585 8333*
	P023 32.5	12513.9158	12513.9339	12513-9504	12513 9653	12513 0785*	1230317230		
	PR24 31.5					1231317103			12518-8830#
	5031 34.5	12658.4759	12658 4416	12658.4067	12658.3702	12658 3320	12658 2020	12658-2510*	12658 2088*
	0032 33 5	12585 0065	12585 0804	12585 0660	12585 0540	12585 0/24	12595 0355	12585 0282*	12595 0252+
	\$932 33.5	12655 0920	12655 0780*	12655 0628	12303.0340	12455 0420	12455 03/0	12655 0260	12303.0232"
	007/ 31 5	1252/ 271/	1263/ /11/	1252/ /521	1252/ /054*	12633.0400	12033.0340	12033.0207	1353/ /700
	0734 31.5	12500 2817+	12500 2221*	12500 34/1	12500 /070	12324.3401*	12324.3030*	12524.0310*	12524.0/88
	TD/2 77 5	12773 577/	12777 5420	12777 5510#	12370.4070	12390.4320-	12390.4909-	12390.3430*	12390.3906*
	1842 33.3	12/33.3/74	12/33.3029	12/33.3310*	12/33.3390	12/33.3310	12/33.5250	12/33.3200-	12/33.5180*
N=34	Q1 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*
	\$Q31 35.5	12657.9178	12657.8838		12657.8127*	12657.7741	12657.7353	12657.6947	12657.6524*
	QP32 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-75	of 7/ F	47520 00//	17570 07/4	10500 0007	17500 7/04				
N=35	Q1 36.5	12520.9046	12520.8541	12520.8025	12520.7481	12520.6921	12520.6351	12520.5745	12520.5133
	OP12 35.5		12444.6630*	12444.0546*	12444.6108*		12444.5634*	12444.5398*	
	QK12 35.5				40//8	12517.4454*		12517.3932	12517.3692
	0013 34.5		4050/		12443.2668*				
	RQ21 36.5	12584.2699	12584.2315*		12584.1501	12584.1077	12584.0642*	12584.0183	12583.9718*
	PQ25 34.5	12508.0876	12508.1055	12508.1209	12508.1346	12508.1473	12508.1587	12508.1682	12508.1781
	SQ31 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	12585.1664	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

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	ASSIG	"Ц И	F=J-7/2	F=J-5/2	F=J-3/2	F=J-1/2	F=J+1/2	F=J+3/2	F=J+5/2	F=j+7/2
N=36	0P12 0913	36.5	12441.3164*	12441.2874*	12441.2589*	12441.2321* 12441.9117*	12441.2032*	12441.1823*	12441.1576*	12441.1380*
	PQ23	35.5	12505.0750	12505.0915	12505.1079*	12505.1209	12505.1334	12505.1452	12505.1547	
	QP32	36.5	12577.1780*	12577.1627	12577.1490*	12577.1372	12577.1274	12577.1187*	12577.1134*	
	0P34	34.5	12510.4762	12510.5165	12510.5587	12510.6019	12510 6464	12510 6918	12510.7380	12510 7857
	0834	34 5	12582 5144	12582 5552	12582 5977	12582 6410	12592 4059	12582 7310	12582 7781	13503 03/04
	10/7	34.5	12302.3144		12302.3711	12302.0410	12302.0030	12302.1310	12722 0770+	12302.0200*
	D/	3/ 5	12441 2004	17441 /777+	13661 6771	13//4 53374	12/32.9430"	12/32.9304"	12/32.9330-	12/32.9306*
	K.4	34.5	12001.3900	12001.4327*	12001.4771	12001.3223"	12001.30/9*	12001.0130		12661./131*
N=37	0013	36.5	13453 5401	13463 6676	12452 5204	12452 52574	12438.6366*			
	007/	75 5	12032.3001	12032.3333	12032.3370	12032.323/-				
	0P34	33.3	12202.7207	12505.7610	12505.8039	12505.8476	12505.8921	12505.9573	12505.9843	12506.0318
	GR34	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	NP02	38.5		12421.3408*	12421.2906*	12421.2381*			12421.0997*	12421.0576*
	NQ03	37.5							12421.9083*	
	OP12	38.5	12434.9090*	12434.8740*			12434.7783*	12434.7473*	12434.7156*	12434.6879*
	0913	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	PQ34	37.5	12536, 1839	12536,2228	12536.2636	12536.3048		12536.3901	12536.4345	12536 6700
	NP02	39.5	12432 1228*	12432 0820*	12432.0423*	12432 0023*		12/31 0318*	12/31 8074+	12/21 94/04
	01	40 5	12506 5062*	12506 /506	12506 3050	12504 3380	12504 2784	12504 2191	12504 1555	12431.0040*
	0012	70.5 70 E	12300.3042"	12/10 9390*	12/10 7977*	12/10.3300	12300.2700	12/10 (500+	12300.1333	12306.0917
	0012	J7.J 70 E	13/05 //03+	12419.0200"	12417./02/*	12419./3/3*	12419.6944*	12419.0329	12419.0131*	12419.5758*
	PW23	JO.J	12493.0402"	12492.0222	12493.0/03-	12493.0843*	12495.6954	12495.706/*	12495.7159	
	TR42	39.5				12490.1349		12496.243/	12496.2900	12496.3371 12731.8474
N=40	NP02	40.5								12/20 5138*
	01	41.5				12505.2216			12505 0520	1250/ 0010
	0P12	40.5					12417 4282*	12417 5037*	12417 5402#	12/17 52/2*
	0013	30 5			12418 4508*		12417.0202-	12417.3737	12417.3002-	12417.3202"
	OP34	38.5	12491.0864	12491.1289	12491.1694*	12491.2152	12491.2597	12491.3048	12491.3514	12491.3998
N-/1		() E						40507 F00/		
N=4 (0010	42.5			43/4/ 00774	10/4/ 0/704	12505.6444	12503.5904		12503.4772
	OP12	41.5	12415.0641*	12415.0277*	12414.9973*	12414.9632*	12414.9332*	12414.9025*	12414.8714*	12414.8459*
N=42	01	43.5					12501 8304		12501.7240	12501 668/
	OP12	42.5	12411.8015*				12501.0004		1230111240	12411.6109*
N=43	01	44 5	12/00 00//			12/00 85/8	12/00 0079	13/00 75101	12/00 6087	12/00 4///
N-42	OP12	43.5	12408.1331*			12477,0340	12479.0030	12477.7310"	12477.0707	12499.0444
N=44	01	45 5	12/07 8033*	12/07 756/	12/07 7113*	12/07 4412	12/07 (100+	13/07 5400	13/07 5070	10/07 /577
4-44	•.	-3.5	12497.0055*	12471.7304	12471.1113"	12497.0012	12497.0109"	12497.3009	12497.3070	12497.4337
N=45	Q1	46.5	12495.4723	12495.4261	12495.3788		12495.2820	12495.2320	12495.1791	12495.1251
N=46	Q1	47.5	12493.0225*		12492.9316*	12492.8802*	12492.8339*			
N=47	· e1	48.5	12490.4657	12490.4197			12490.2772*			12490.1217*