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Rotational, fine, and hyperfine analyses of the (0,0) band of the $D^{3}\Pi - X^{3}\Delta$ system of vanadium mononitride

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The VN molecule has been produced in a molecular beam apparatus using a laser vaporization source and its $D^{3}\Pi - X^{3}\Delta(0,0)$ band has been studied by laser-induced fluorescence at low $(\sim 0.1 \text{ cm}^{-1})$ and sub-Doppler resolution $(\sim 0.004 \text{ cm}^{-1})$. Lifetimes of single rotational levels of the $D^{3}\Pi_{0}$ component have been measured and interpreted. Rotational, fine, and hyperfine structures in six of the nine subbands possible for a ${}^{3}\Pi \leftarrow {}^{3}\Delta$ transition have been recorded. Both states exhibit a rapid transition from case (a) \rightarrow case (b) coupling cases, manifested by reversals in the Landé patterns of the hyperfine structure. The data have been reduced to a set of 35 molecular constants using a modified case (a_{β}) effective Hamiltonian in which two additional magnetic hyperfine parameters are required for each state. The distortions in the hyperfine structure are due almost entirely to second-order spin-orbit interaction between states arising from the same configuration. Analysis of the derived parameters indicates that the X $^{3}\Delta$ state is well represented by the single electron configuration $\cdots 8\sigma^2 3\pi^4 9\sigma^1 1\delta^1$, in which the 9σ molecular orbital (MO) is a V 4s-4p hybrid (88% V 4s) and the 1 δ MO is a pure V 3d orbital; the dominant configuration for the $D^{3}\Pi$ state is $\cdots 8\sigma^{2} 3\pi^{4} 1\delta^{1} 4\pi^{1}$, in which the 4π MO is an antibonding orbital composed of at most 82% V $3d\pi$. The isoconfigurational $a^{1}\Delta$ and $e^{1}\Pi$ states are calculated to lie 3390 and 2200 cm^{-1} above their respective high spin companions. The lambda doubling in the $D^{3}\Pi_{0}$ component has been interpreted in terms of spin-orbit interactions with the $B^{3}\Sigma^{-}$ and $d^{1}\Sigma^{+}$ states, both states arising from the $\cdots 8\sigma^{2}$ $3\pi^{4}$ $1\delta^{2}$ configuration; the $d^{1}\Sigma^{+}$ state is known [Simard, Masoni, and Hackett, J. Mol. Spectrosc. 136, 44 (1989)] to lie 102 cm⁻¹ above $D^{3}\Pi_{0}$, while the $B^{3}\Sigma^{-}$ state probably lies about 8000 cm⁻¹ below.

I. INTRODUCTION

Interest in the spectroscopy and molecular structure of transition metal containing molecules has grown at a tremendous rate over the past 15 years. This is partly attributed to improved experimental and theoretical techniques whereby much of the spectral complexity can be unraveled, assigned, and rationalized, and to the possible involvement of small transition metal compounds in adsorption phenomena and combustion.

A great deal of effort has thus far been devoted to transition metal monoxides. As a result, the ground states of all the 3d transition metal monoxides^{1,2} and most of the 4d transition metal monoxides² have been characterized experimentally and theoretically. In contrast, very little is known about their nitrides. Work on the nitrides is a logical extension to the work on the oxides. The fundamental questions to be answered are: what are the effects of substitution on the electronic structure and bonding, and can these be predicted using a simple model? Currently, the experimental database includes ScN,³ TiN,⁴⁻⁷ VN,^{8,9}

ZrN,^{10,11} NbN,¹²⁻¹⁴ and MoN,^{15,16} while the theoretical database is limited to ScN (Ref. 17) and NbN.¹⁸ The 1988 grating resolution work of Féménias *et al.* and the sub-Doppler resolution work of Azuma *et al.* combined with the recent detailed theoretical work of Langhoff and Bauschlicher on NbN,¹⁸ make this species the best studied of the transition metal nitrides. This paper deals with its isovalent companion vanadium nitride VN.

The VN species was first observed almost simultaneously by Peter and Dunn,⁹ and Simard *et al.*⁸ in 1989. Peter and Dunn prepared the species from the reaction of vanadium halide compounds with active nitrogen in a microwave discharge and observed the $A^{3}\Phi-X^{3}\Delta$ system in emission. Their analysis of the (0,0) band at grating resolution provided accurate values for the bond lengths and approximate values for the first-order spin-orbit coupling constant since no satellite subbands were observed. Simard *et al.*⁸ produced the molecule by laser vaporization in a molecular beam apparatus and studied the (0,0) band of the $d^{1}\Sigma^{+}-X^{3}\Delta_{1}$ intercombination system by laser induced fluorescence at sub-Doppler resolution. Nuclear magnetic hyperfine structure was resolved for the low-J rotational lines, but no hyperfine parameters were derived. In both studies, the (0,0) band of the $D^{3}\Pi - X^{3}\Delta$ system was noted, but no analysis has been reported so far. The D-Xsystem is the analog of the γ' system of TiO (Ref. 2) and the β system of ZrO,² two astrophysically important and well studied molecules. Its analysis would allow a comparison of the electronic structure and bonding in these molecules. For TiO and ZrO, the leading electronic configurations giving rise to the ${}^{3}\Delta$ and ${}^{3}\Pi$ states have been established theoretically¹⁹⁻²¹ and experimentally² as $\cdots \sigma_{ns}^{1} \delta_{(n-1)d}^{1}$ and $\pi_{(n-1)d}^{1} \delta_{(n-1)d}^{1}$, respectively, where n=4for TiO and 5 for ZrO. No calculations have yet been performed on VN, but the experimental data presented here support this assignment.

The most abundant vanadium isotope (⁵¹V) has a nuclear spin of 7/2 and a magnetic moment of +5.1485 nuclear magnetons. Of all the known stable nuclei, this is the fourth largest magnetic moment, after ⁹³Nb (+6.167 nm) and ^{113,115}In (+5.5229, +5.5348 nm). In VN, the interaction of the ⁵¹V nucleus with the unpaired electrons gives rise to very impressive magnetic hyperfine structure in both the $X^{3}\Delta$ and $D^{3}\Pi$ states, but more especially in the $X^{3}\Delta$ ($\sigma^{1}\delta^{1}$) state where the σ orbital is mostly V 4s, which makes the Fermi contact interaction very large. For both states, the hyperfine structure is complicated by the phenomenon of spin uncoupling and, because of the presence of nearby perturbing states, by second-order spin-orbit distortion, in a way analogous to its isovalent companion NbN.¹⁴

We report here a study conducted at low (0.1 cm^{-1}) and sub-Doppler $(0.004 \text{ cm}^{-1}=120 \text{ MHz})$ resolution on the hitherto unanalyzed $D^{3}\Pi - X^{3}\Delta(0,0)$ band of VN. The extensive data set, comprising observations from six of the nine subbands possible for a ${}^{3}\Pi \leftarrow {}^{3}\Delta$ transition, has been reduced to 35 molecular constants. Some of these constants are discussed in terms of the leading configurations giving rise to the $D^{3}\Pi$ and $X^{3}\Delta$ states and are used to extract quantitative information on nearby perturbing states.

II. EXPERIMENTAL PROCEDURE

The experimental procedure has been described in detail in previous publications.^{4,8} Only a brief description will be given here. The VN molecules were produced in a free jet molecular beam apparatus by laser vaporization of V metal (Johnson Matthey 99.5%) in the presence of He carrier gas (backing pressure 360 kPa) doped with 2%-5% of NH₃.

The fluorescence from the VN molecules is excited at right angles to the molecular beam axis about 4.3 cm from the free jet orifice, either by the output of a pulsed XeCl (Lumonics 860) excimer-pumped dye laser [Lumonics Hyperdye 300, full width at half-maximum (FWHM) $= 0.1 \text{ cm}^{-1}$], or the output of a narrow linewidth cw ring dye laser (Coherent Inc. 699-29), both lasers operating with Kiton Red 620 dye. The intrinsic resolution of the molecular beam system is 0.004 cm⁻¹ (120 MHz). The

wavemeter was calibrated using I_2 absorption lines as calibration standard.²²

The fluorescence is imaged at the slits of a 1 m f/8Spex monochromator equipped with a 1200 grooves/mm holographic grating and viewed by a Hamamatsu red sensitive R943-02 photomultiplier tube. The use of a monochromator makes it possible to observe four of the satellite subbands without difficulty. This was accomplished by tun-







FIG. 2. A portion (3.3 cm^{-1}) of the high resolution fluorescence excitation spectrum of the $D^{3}\Pi_{0}-X^{3}\Delta_{1}(0,0)$ subbands of VN. The tick marks on the horizontal axis occur at every 1 MHz increment. The vertical axis is the fluorescence intensity in arbitrary units. See the text for details.

ing the monochromator to the appropriate, strongly allowed subbands $D^{3}\Pi_{2}-X^{3}\Delta_{3}$, $D^{3}\Pi_{1}-X^{3}\Delta_{2}$, and $D^{3}\Pi_{0}-X^{3}\Delta_{1}$, and scanning the dye laser in the appropriate wavelength region of the satellite bands. The following satellite bands have been observed and studied at high resolution: $D^{3}\Pi_{2}-X^{3}\Delta_{1}$, $D^{3}\Pi_{2}-X^{3}\Delta_{2}$, $D^{3}\Pi_{1}-X^{3}\Delta_{1}$, and $D^{3}\Pi_{0}-X^{3}\Delta_{2}$.

Lifetime measurements have been performed with a Tektronix model 7912, 400 MHz programmable digitizer equipped with a model 7A24 amplifier. From the length of the viewing zone and the speed at which the excited molecules leave the detection zone ($\approx 1.7 \times 10^5$ cm/s), we estimate that unbiased lifetimes up to $\sim 1 \mu$ s can be measured with the present apparatus.

III. APPEARANCE OF THE SPECTRA

Figure 1 shows the three main subbands at a resolution of about 0.1 cm⁻¹. The rotational temperature of these spectra is of the order of 30–35 K. Each subband is red degraded and consists of *P*, *Q*, and *R* branches. Despite the low resolution, the rotational structure of the *P* and *R* branches is fully resolved. The strong *Q* branches and the missing lines clearly indicate that the transition is ${}^{3}\Pi - {}^{3}\Delta$. The following will show that the ${}^{3}\Delta$ state is the ground state of VN: Also, from a comparison with TiO, a molecule isoelectronic with VN, the upper ${}^{3}\Pi$ state is expected to be the fourth excited triplet state of VN, so that the labeling $D {}^{3}\Pi - X {}^{3}\Delta$ results.

The $D^{3}\Pi_{0}-X^{3}\Delta_{1}$ subband is characterized by a large Λ doubling of about 19.4 cm⁻¹. Λ doubling is also apparent in the $D^{3}\Pi_{1}-X^{3}\Delta_{2}$ subband and increases with increasing J. At this low resolution, the Λ doubling in the $D^{3}\Pi_{2}-X^{3}\Delta_{3}$ subband is not resolved.

Figures 2, 3, 4, and 5 show portions of various subbands at high resolution (0.004 cm⁻¹ or 120 MHz). Clearly noticeable here is the impressive nuclear magnetic hyperfine structure arising from the interaction of the unpaired electrons with the spinning vanadium nucleus. The largest hyperfine widths ($F_{max}-F_{min}$) are found in the $D^{3}\Pi_{2}-X^{3}\Delta_{3}$ subband, where they can be as large as 0.4 cm⁻¹ in the low-J, Q lines. Since I=7/2 for ⁵¹V, the max-



FIG. 3. A portion (5 cm^{-1}) of the high resolution fluorescence excitation spectrum of the satellite $D^{3}\Pi_{1}-X^{3}\Delta_{1}(0,0)$ subband of VN showing the Qbranch. The tick marks on the horizontal axis occur at every 1 MHz increment. The vertical axis is the fluorescence intensity in arbitrary units. This spectrum was recorded by collecting the fluorescence at the wavelength corresponding to the $D^{3}\Pi_{1} \rightarrow X^{3}\Delta_{2}$ transition (~6245 Å).

imum number of hyperfine levels is 8 (=2I+1) though this occurs only for J > 4 because $F = |J+I| \cdots |J-I|$. For J=3, 2, 1, and 0, the number of hyperfine levels is limited to 7, 5, 3, and 1, respectively. The hyperfine selection rule $\Delta F=0, \pm 1$ applies, but the intensities of lines with $\Delta F \neq \Delta J$ decrease rapidly with J, such that they are not seen beyond $J \approx 3$. High J rotational lines therefore have just eight strong hyperfine components. All the spectra are free of local perturbations.

It is instructive at this stage to examine the hyperfine structure in more detail. In the Q branch of the $D^{3}\Pi_{0e^{-}}$ $X^{3}\Delta_{1}$ subband, shown in Fig. 2, it can be seen that the



FIG. 4. A portion (5 cm^{-1}) of the high resolution fluorescence excitation spectrum of the satellite $D^{3}\Pi_{0}-X^{3}\Delta_{2}(0,0)$ subband of VN near the zero gap. The tick marks on the horizontal axis occur at every 1 MHz increment. The vertical axis is the fluorescence intensity in arbitrary units. This spectrum was recorded by collecting the fluorescence at the wavelength corresponding to the $D^{3}\Pi_{0}-X^{3}\Delta_{1}$ transition (~6202 Å). Note that reversal of the hyperfine Landé pattern does not occur in this subband. See the text for details.

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FIG. 5. A portion (2 cm^{-1}) of the high resolution fluorescence excitation spectrum of the main $D^{3}\Pi_{2}-X^{3}\Delta_{3}(0,0)$ subband of VN near the zero gap. The tick marks on the horizontal axis occur at every 1 MHz increment. The vertical axis is the fluorescence intensity in arbitrary units. Assignments of the hyperfine lines are shown for the first Q lines. Note that hyperfine widths are the largest for this subband. See the text for details.

hyperfine width is positive for J < 5, collapses to zero at J=5, and becomes negative for J > 6. In other words, there is a reversal of the Landé pattern at J=5 in the Q_{ef} branch. Fully resolved Landé patterns with opposite sign are shown in the $P_e(2)$ and $P_f(13)$ lines. Figure 6 shows the calculated hyperfine widths for all spin-orbit components of both the ${}^{3}\Delta$ and ${}^{3}\Pi$ states. These widths were calculated using the final constants derived from the fitting of the spectra. A collapse of the hyperfine structure occurs when the hyperfine width is the same in both states. The points at which the hyperfine structure collapses are indicated in



FIG. 6. Calculated hyperfine level widths $(F_{\text{max}} - F_{\text{min}})$ as a function of the rotational quantum number J for all spin components of the $D^{3}\Pi$ and $X^{3}\Delta$ states. These widths were calculated using the fitted parameters (see the text for details). The value of J where reversal of the Landé pattern would occur in particular subbands are indicated by filled circles. Note that no reversal occurs in the $D^{3}\Pi_{0}-X^{3}\Delta_{2}$ subband.

Fig. 6 by filled circles for all the possible subbands. Note that no reversal occurs in the $D^{3}\Pi_{0}-X^{3}\Delta_{2}$ subband, at least within a reasonable range of J.

The reversals in the hyperfine structure are caused by the transition from case (a) to case (b) coupling in the ${}^{3}\Delta$ electronic state (spin uncoupling). They can be understood qualitatively as follows: Within the case (a_{β}) formalism, the diagonal elements of the hyperfine Hamiltonian (see Sec. V) are given by²³

$$\langle \Lambda S \Sigma J \Omega I F | H_{\rm hfs} | \Lambda S \Sigma J \Omega I F \rangle = \frac{[a\Lambda + (b+c)\Sigma]\Omega[F(F+1) - I(I+1) - J(J+1)]}{2J(J+1)}, \tag{1}$$

where all the quantum numbers have their usual meaning. Therefore, if both states were in a case (a) coupling scheme, the hyperfine widths would decrease asymptotically to zero with increasing J so that no reversal would ever occur. On the other hand, in the case $(b_{\beta J})$ coupling scheme, the diagonal elements of the $b\mathbf{I}\cdot\mathbf{S}$ operator are given by²³

$$\langle NSJIF|b\mathbf{I} \cdot \mathbf{S}|NSJIF\rangle = b \frac{[F(F+1) - I(I+1) - J(J+1)][J(J+1) + S(S+1) - N(N+1)]}{4J(J+1)}.$$
(2)

Now since the correlation between case (b) and case (a) spin components for *regular* triplets is²⁴ $F_1(J=N+1)\leftrightarrow\Sigma$ $=-1, F_2(J=N)\leftrightarrow\Sigma=0$, and $F_3(J=N-1)\leftrightarrow\Sigma=+1$, the hyperfine widths for the F_1 and F_3 case (b) components must have opposite sign to the hyperfine widths for the $\Sigma=\pm 1$ case (a) components from which they evolve.

It may seem strange that the hyperfine widths in the ${}^{3}\Delta_{1}$ and ${}^{3}\Delta_{3}$ components both pass through zero at J values below 25, even though the $X {}^{3}\Delta$ state appears to be in extremely good case (a) coupling, with $A\Lambda/B \approx 240$. The

following argument may give some insight: The changeover from case (a) to case (b) electron spin coupling is usually taken as occurring when the "spin-uncoupling matrix elements," namely those of $-2BJ \cdot S$ in a case (a) basis, become equal to the spin-orbit intervals $A\Lambda$; for a ${}^{3}\Delta$ state, this means when $\sqrt{2} BJ = 2A$, which in the present case would be at $J \approx 170$. Hyperfine structure, on the other hand, has an extra 1/J dependence, as indicated above. This can be understood from the form of the contact operator $bI \cdot S$; the part of this operator responsible for non-

TABLE I.	Intrinsic	radiative	lifetimes	(in	nanoseconds)	for	some	rota-
tional lines	of the D	${}^{3}\Pi_{0}$ state	of VN.					

ſ	High-frequency component	Low-frequency component
2 ·	81 ± 1^{a}	
3	77 ± 2	83 ± 3
4	89 ± 2	96 ± 1
5	76 ± 1	86±3
6	87 ± 2	104 ± 3
7	82 ± 2	
8	84 ± 2	
(Average)	82 ± 5	91±4
Average from Q head	74± 1	89 ± 1

^aA 2σ uncertainty.

zero matrix elements in case (a) coupling is $b I_z S_z$, which can be written as $b J_z S_z$ (I·J/J·J), assuming I+J=F. The matrix elements of Eq. (1) follow at once when I·J is written as $\frac{1}{2}$ (F²-I²-J²) and J·J as J (J+1). Now, substituting $F = F_{\text{max}} = J + 1$, it is easily shown that $\langle I \cdot J / J \cdot J \rangle_{\text{max}} = I/2(J+1)$; in other words, there is a 1/J dependence of the hyperfine width. Therefore a more valid comparison for hyperfine structure, indicating where the case (b) pattern should start to emerge, is where $\sqrt{2}$ BJ equals $A\Lambda/J$, rather than $A\Lambda$. In the present case, this gives $J \approx 13$, i.e., the square root of the number given above.

IV. LIFETIME MEASUREMENTS AND *e/f* PARITY LABELING

The fluorescence lifetimes of some rotational lines of the $D^{3}\Pi_{0}$ components are reported in Table I. These lifetimes were measured from corresponding R(J) lines of the $D^{3}\Pi_{0} - X^{3}\Delta_{1}$ subbands. The lifetimes of the $D^{3}\Pi_{1}$ and $D^{3}\Pi_{2}$ components have been determined to be 78±2 and 89 ± 2 ns, respectively, by exciting the Q heads of the $D^{3}\Pi_{1} - X^{3}\Delta_{2}$ and $D^{3}\Pi_{2} - X^{3}\Delta_{3}$ subbands, respectively. For comparison, the lifetime of the $C^{3}\Phi$ system whose $\mathbf{v}=0$ level lies near 14 300 cm⁻¹ has been measured to be 85 ± 5 ns regardless of the rotational energy content or spin-orbit component. The lifetimes of the $C^{3}\Phi$ and $D^{3}\Pi$ states are therefore essentially the same. All decay traces can be fitted to single exponential decay functions. The data were fitted over three to four lifetimes. The uncertainties represent two standard deviations in the least-squares fit. As these lifetimes were measured under jet-cooled conditions at pressures of less than 10^{-5} Torr, and as the quantum yield for fluorescence must be unity at these energies, these should be taken as intrinsic radiative lifetimes.

The data of Table I are very instructive. The lifetimes of the rotational levels of the lower-frequency ${}^{3}\Pi_{0} \Lambda$ component are always somewhat longer than those of the higher-frequency Λ component. The effect is small, but appears to be genuine. We take this as an indication that the low-frequency Λ component is perturbed by nearby Σ states whose lifetimes are very much longer than that of $D^{3}\Pi$. Since the electronic structure of VN should mirror that of TiO (*vide infra*), there are only two possible per-



FIG. 7. Calculated and observed lambda doubling as a function of the rotational quantum number J in the three spin components of the $D^{3}\Pi$ state. The calculated and observed values are indistinguishable in the range of J studied. See the text for details on the determination of the e/f parity level.

turbing states, which are the $d^{1}\Sigma^{+}$ and $B^{3}\Sigma_{0}^{-}$ states. Since the rotational levels of ${}^{1}\Sigma^{+}$ and ${}^{3}\Sigma_{0}^{-}$ states are all of *e* parity, this establishes the parity of the low-frequency Λ component as ${}^{3}\Pi_{0e}$ and that lying on the high-frequency side as ${}^{3}\Pi_{0f}$. Figure 7 shows that the Λ doubling $(\nu_{f}-\nu_{e})$ in the ${}^{3}\Pi_{0}$ component decreases almost linearly with *J* in the range 5–26.

The e/f parity labeling in the ${}^{3}\Pi_{1}$ component was determined by making the sum of the Λ doublings in the ${}^{3}\Pi_{1}$ and ${}^{3}\Pi_{0}$ components as nearly constant as possible for $J \leq 6$. This requires that the f components lie above the e components for the range of J studied. The rationale for this assignment is that the difference between the traces of the two rotational matrices (vide infra), excluding the o+p+q term, is just q J(J+1). Since q is likely to be only of the order 10^{-3} , the sum of the A doublings will be essentially constant for small J, until the q J(J+1) term becomes significant. Figure 7 shows that the lambda separation in the ${}^{3}\Pi_{1}$ component shows signs of approaching a maximum. This behavior is expected. In fact, beyond the maximum it should decrease, and in the limit of very high J should reverse its sense, i.e., the e component will lie above the f component.

Since Λ doubling in a ${}^{3}\Pi_{2}$ component is a high order effect, it never reverses, i.e., it always has the same sign. Also, in the high-J limit it must be equal and opposite to the Λ doubling in ${}^{3}\Pi_{1}$. Since the high-J ordering in ${}^{3}\Pi_{1}$ is likely to be *e* above *f*, the Λ doubling in the ${}^{3}\Pi_{2}$ component at this limit must be *f* above *e*, and since the lambda doubling pattern never reverses, this must be the case for any value of *J*.

Since the ${}^{3}\Pi$ state is comparatively close to case (b) coupling, the hyperfine widths should in, principle, be able to confirm the A-doubling parity assignments. The diago-

nal elements of the contact and "hyperfine Λ -doubling" operators in a ${}^{3}\Pi(b)$ state are^{25,26}

$$[F_{1}(J=N+1), f/e] \quad E_{hfs} = \frac{W}{2J} \left(b \mp d \frac{J-1}{2J+1} \right),$$

$$[F_{2}(J=N), f/e] \quad E_{hfs} = \frac{W}{2J(J+1)} (b \mp d), \qquad (3)$$

$$[F_3(J=N-1), f/e] \quad E_{\rm hfs} = -\frac{W}{2(J+1)} \left(b \mp d \frac{J+2}{2J+1} \right),$$

where W = F(F+1) - I(I+1) - J(J+1). These formulas predict that the hyperfine widths at high J should be roughly 1, 0, and -1 for F_1 , F_2 , and F_3 , respectively, in units of $2I(b \neq d/2)$. Figure 6 shows how the hyperfine widths in the ³ Π state are tending towards the ratio 1:0:-1 at high J, though clearly have some way to go before the limiting case (b) behavior is attained. The differences in the hyperfine widths of the A-doubling components, caused by the terms in $\pm d$, are also as expected, which means that the limiting case (b) hyperfine trends appear to be reached quite rapidly. This is in contrast to the Λ doublings themselves (Fig. 7), where the curve for ${}^{3}\Pi_{0}(F_{1})$ shows no sign of reversing its direction, as it must eventually do, in the available range of J. Possibly reflecting this, the difference in the hyperfine widths for the ${}^{3}\Pi_{0}$ component passes through a maximum at $J \approx 15$, and may be tending towards a reversal of its sense at J values beyond the range of experimental data. However, in the limit of high J, the patterns for ${}^{3}\Pi_{0}(F_{1})$ and ${}^{3}\Pi_{2}(F_{3})$ should be equal and opposite though, in view of the strong perturbations affecting the ${}^{3}\Pi$ state, it is questionable whether the "textbook" patterns would ever be achieved in the present case, even at the highest J values.

V. ENERGY MATRICES

Initial attempts to fit the spectra to case (a_{β}) energy matrices with only the first centrifugal distortion terms to the parameters and with only the normal three nuclear magnetic hyperfine parameters a, b, and c failed. This is because of (1) the significant spin-orbit distortion of the hyperfine structure in both electronic states and (2) the large global perturbations in the upper ${}^{3}\Pi$ state that cause the large and irregular Λ doubling, and push the ${}^{3}\Pi_{1}$ component below the mean of ${}^{3}\Pi_{2}$ and ${}^{3}\Pi_{0f}$. These problems can be remedied by using for both states hyperfinedistorted case (a_{β}) energy matrices in which five independent magnetic hyperfine parameters are required,¹⁴ and by using second centrifugal distortion terms to the rotational and A-doubling parameters for the ${}^{3}\Pi$ state. The five hyperfine parameters are h_1 , h_0 , h_{-1} , b_+ , and b_- . The h_{Σ} parameters replaced the coefficients $[a\Lambda + (b+c)\Sigma]$ in Eq. (1) and in the $\langle \Lambda; S\Sigma; J\Omega IF | H_{hfs} | \Lambda; S\Sigma; J-1, \Omega IF \rangle$ matrix elements, while the b_{+} and b_{-} parameters are defined as coefficients of the $\langle \Sigma = +1 | H_{hfs} | \Sigma = 0 \rangle$ and $\langle \Sigma = 0 | H_{hfs} | \Sigma$ =-1 matrix elements, diagonal and off diagonal in J. The effective Hamiltonian has been written using the

 \mathbf{R}^2 formalism ($\mathbf{R}=\mathbf{J}-\mathbf{L}-\mathbf{S}$) as^{27,28}

$$H_{\rm eff} = H_{\rm rot} + H_{\rm cd} + H_{\rm so} + H_{\rm cdso} + H_{\rm sr} + H_{\rm \Lambda d} + H_{\rm cd\Lambda d} + H_{\rm hfs} + H_{\rm qd}, \qquad (4)$$

where

$$H_{\rm rot} = B \mathbf{R}^2, \tag{5}$$

$$H_{\rm cd} = -D\mathbf{R}^4 + H\mathbf{R}^6, \tag{6}$$

$$H_{\rm so} = A L_z S_z + \frac{2}{3} \lambda (3S_z^2 - S^2), \tag{7}$$

$$H_{cdso} = \frac{1}{2} A_D [L_z S_z, \mathbf{R}^2]_+ + \frac{1}{3} \lambda_D [3S_z^2 - \mathbf{S}^2, \mathbf{R}^2]_+ + \frac{1}{2} A_H [L_z S_z, \mathbf{R}^4]_+ + \frac{1}{3} \lambda_H [3\mathbf{S}_z^2 - \mathbf{S}^2, \mathbf{R}^4]_+, \qquad (8)$$

$$H_{\rm sr} = \gamma \mathbf{R} \cdot \mathbf{S},\tag{9}$$

$$H_{\Lambda D} = \frac{1}{2}(o+p+q)(S_{+}^{2}+S_{-}^{2}) - \frac{1}{2}(p+2q)(J_{+}S_{+}+J_{-}S_{-}) + \frac{1}{2}q(J_{+}^{2}+J_{-}^{2}), \qquad (10)$$

$$H_{cd\Lambda D} = \frac{1}{4} D_{o+p+q} [S_{+}^{2} + S_{-}^{2}, \mathbf{R}^{2}]_{+} - \frac{1}{4} D_{p+2q} \\ \times [J_{+}S_{+} + J_{-}S_{-}, \mathbf{R}^{2}]_{+} + \frac{1}{4} D_{q} [J_{+}^{2} + J_{-}^{2}, \mathbf{R}^{2}]_{+} \\ + \frac{1}{4} H_{o+p+q} [S_{+}^{2} + S_{-}^{2}, \mathbf{R}^{4}]_{+} - \frac{1}{4} H_{p+2q} \\ \times [J_{+}S_{+} + J_{-}S_{-}, \mathbf{R}^{4}]_{+} + \frac{1}{4} H_{q} [J_{+}^{2} + J_{-}^{2}, \mathbf{R}^{4}]_{+},$$
(11)

$$H_{\rm hfs} = aI_z L_z + b_F \mathbf{I} \cdot \mathbf{S} + c(I_z S_z - \frac{1}{3} \mathbf{I} \cdot \mathbf{S}) + \frac{1}{2} d(e^{2i\phi} I_- S_- + e^{-2i\phi} I_+ S_+), \qquad (12)$$

$$H_{\rm qd} = \frac{e^2 Q q_0 (3I_z^2 - \mathbf{I}^2)}{4I(2I-1)} + \frac{e^2 Q q_2 (I_+^2 e^{-2i\phi} - I_-^2 e^{2i\phi})}{8I(2I-1)}, \qquad (13)$$

where the symbol $[x,y]_+ = xy + yx$ is the anticommutator necessary to preserve the Hermitian form of the matrices. There are 25 coefficients in this Hamiltonian. These are the rotational constant B and its first and second centrifugal distortion corrections D and H; the first- and second-order spin-orbit constants A and λ and their first and second centrifugal distortion corrections A_D , A_H , λ_D , and λ_H ; the spin-rotation constant γ ; the lambda doubling constants for Π states (o+p+q), (p+2q), and q and their first and second centrifugal distortion corrections $D_{(o+p+q)}$, $H_{(o+p+q)}$, $D_{(p+2q)}$, $H_{(p+2q)}$, D_q , and H_q ; the nuclear spinelectron orbital interaction constant a; the nuclear spinelectron spin Fermi contact interaction constant b_F ; the dipolar nuclear spin-electron spin interaction constants cand d; and the electric quadrupole interaction constants $e^2 Qq_0$ and $e^2 Qq_2$. The terms in d and $e^2 Qq_2$ only apply to the ³II state. The matrix representation of this Hamiltonian, written in a case (a_{β}) basis set $(|\Lambda; S\Sigma; J\Omega IF \rangle)$ and taking into account the spin-orbit distortion of the hyperfine structure and the fact that the Λ doubling in the $X^{3}\Delta$ state is negligible, is given in Tables II, III, and IV. The full matrix is the sum of these three matrices, but for clarity and convenience is written as three separate matrices.



	$ \Lambda,\Sigma=1;J\rangle$	$ \Lambda,\Sigma=0;J\rangle$	$ \Lambda,\Sigma=-1;J angle$
$\langle \Lambda, \Sigma = 1, J $	$A\Lambda + \frac{2}{3}\lambda - \gamma + (B + A_D\Lambda + \frac{2}{3}\lambda_D)(x - \Lambda^2)$	· ·	Symmetric
	-2Λ) $-D[x^2+2x-2\Lambda x(\Lambda+2)+2\Lambda(\Lambda$		
	$(-1) + \Lambda^3(\Lambda + 4)$]		
	$+h_1(\Lambda+1)W/2x$		
	$+\frac{e^2 Q_{q0}[3(\Lambda+1)^2-x][3W(W+1)-63x]}{168 x(4x-3)}$	•	
$\langle \Lambda, \Sigma = 0, J $	$-\sqrt{2[x-\Lambda(\Lambda+1)]}[B-\frac{1}{2}\gamma+\frac{1}{2}A_D\Lambda$	$-\frac{4}{3}\lambda-2\gamma+(\underline{B}-\frac{4}{3}\lambda_D)(x-\Lambda^2+2)$	
	$-\frac{1}{3}\lambda_D - 2D(x - \Lambda - \Lambda^2 + 1) - b_+ W/4x]$	$-D[x^2+8x-2\Lambda^2(x+4)$	
		$+\Lambda^2+4]+h_0\Lambda W/2x$	
		$e^2 Q_{qo}(3\Lambda^2 - x)[3W(W+1) - 63x]$	
		+ 168 $x(4x-3)$	
$\langle \Lambda, \Sigma = -1, J $	$-2D\sqrt{(x-\Lambda^2+\Lambda)(x-\Lambda^2-\Lambda)}$	$-\sqrt{2[x-\Lambda(\Lambda-1)]}\left[B-\frac{1}{2}\gamma-\frac{1}{2}A_{D}\Lambda\right]$	$-A\Lambda + \frac{2}{3}\lambda - \gamma + (B - A_D\Lambda + \frac{2}{3}\lambda_D)(x$
		$-\frac{1}{3}\lambda_D-2D(x+\Lambda-\Lambda^2+1)$	$-\Lambda^2+2\Lambda)-D[x(x+2)-2\Lambda x(\Lambda-2)]$
		$-b_W/4x$]	$+2\Lambda(\Lambda+1)+\Lambda^3(\Lambda-4)]$
			$+h_{-1}(\Lambda-1)W/2x$
			$+\frac{e^2 Q_{qo}[3(\Lambda-1)^2-x][3W(W+1)-63x]}{162}$
			168 x(4x-3)
$\langle \Lambda, \Sigma = 1, J - 1 $	$-\sqrt{\frac{J^2-(\Lambda+1)^2}{4J^2-1}}Y\Big[\frac{h_1}{2J}\Big]$	$-b\frac{Y}{4I}\sqrt{\frac{2(J-\Lambda)(J-\Lambda-1)}{4I^2-1}}$	0
	$+e^{2}Q_{qo}\frac{(\Lambda+1)(W+J+1)}{56 x(J-1)}\Big]$		
(Λ,Σ=0, <i>J</i> - 1	$b_+ \frac{Y}{4J} \sqrt{\frac{2(J+\Lambda+1)(J+\Lambda)}{4J^2-1}}$	$-\sqrt{\frac{J^2-\Lambda^2}{4J^2-1}}Y\left[\frac{h_0}{2J}+e^2Q_{qo}\frac{\Lambda(W+J+1)}{56x(J-1)}\right]$	$-b\frac{Y}{4J}\sqrt{\frac{2(J-\Lambda-1)(J-\Lambda-2)}{4J^2-1}}$
$\langle \Lambda, \Sigma = -1, J-1 $	0	$b_{-} \frac{Y}{4J} \sqrt{\frac{2(J+\Lambda)(J+\Lambda-1)}{4J^2-1}}$	$-\sqrt{\frac{J^2 - (\Lambda - 1)^2}{4J^2 - 1}} Y \bigg[\frac{h_{-1}}{2J}\bigg]$
· ·			$+\frac{e^2 Q_{qo}(\Lambda-1)(W+J+1)}{56 \ x(J-1)}\Big]$
		· · · · · · · · · · · · · · · · · · ·	

 $a_{x}=J(J+1), W=F(F+1)-I(I+1)-J(J+1), Y=\sqrt{(F+I+J+1)(F-I+J)(J+I-F)(F-J+I+1)}, 63=4I(I+1), and 168=8I(2I-1).$

VI. FITTING PROCEDURE AND LEAST-SQUARES RESULTS

The structure of the total energy matrix is similar to the one used by Brown et al.²⁹ in their work on AIF. Since I=7/2, the maximum dimension of the energy matrix for a given F is 24×24 [=3(2I+1)]. This matrix was diagonalized for each value of F covered by the experiment. The molecular constants were then obtained by fitting the calculated to the observed line positions using a standard nonlinear least-squares procedure. It turned out to be impossible to fit the spectrum in one step. Rather, the spectrum needed to be fitted using the following stepwise procedure:

(Step 1) The ground state energy levels were determined by taking all available combination differences. These energy levels were then fitted using the above Hamiltonian for the ${}^{3}\Delta$ state. This produced reliable rotational constants (A, λ , B, D, A_D, and λ _D), but inaccurate hyperfine parameters as a result of small calibration uncertainties. In all, 2800 combination differences were used in the fit, which yielded a standard deviation of 0.0046 cm⁻¹. At this point, the rotational constants are sufficiently well determined to be held fixed in the other steps. These constants are given in Table V. Note that the spin-rotation constant (γ) could not be determined here. This is because there exists an indeterminacy between γ and A_D . As has been shown by Brown *et al.*, ³⁰ this indeterminacy prevents γ and A_D from being determined simultaneously unless data for different isotopomers are available. This is not the case here. Since A_D is expected to be larger than γ , we fixed γ to zero and let the contribution of γ to the observed splitting be included in A_D .

(Step 2) A data set of all assigned transitions up to

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TABLE III. Parity-dependent matrix elements for ${}^{3}\Pi$ states with I=7/2 up to second order.^{*}

	³ ∏ ₂ , <i>f/e</i> ;J⟩	$ ^{3}\Pi_{1},f/e;J\rangle$	$ ^{3}\Pi_{0}, f/e; J\rangle$
$\left\langle {}^{3}\Pi_{2}\frac{f}{e}J\right\rangle$	0	Symmetr	ic
$\left\langle {}^{3}\Pi_{1}\frac{f}{e}J\right $	$-\sqrt{2(x-2)}\left(\pm\frac{1}{2}D_qx\right)$	$\pm x [\frac{1}{2}q + e^2 Q_{q2}T + D_{p+2q} + \frac{1}{2} D_q(x+1)]$	
$\left\langle {}^{3}\Pi_{0}\frac{f}{e}J\right $	$\pm \sqrt{x(x-2)} \left[\frac{1}{2}q + e^2 Q_{q2} T + \frac{1}{2} D_q(x-1) \right]$	$-\sqrt{2x} \times \pm \left[\frac{1}{2}(p+2q) + \frac{dW}{4x} + \frac{1}{2}D_q(x) - 1\right] + \frac{1}{2}D_{p+2q}(x+1) + D_{a+p+q}$	$\pm [(o+p+q) + D_{o+p+q}(x+1) + D_{p+2q}x]$
$\left\langle {}^{3}\Pi_{2} \frac{e}{f} J - 1 \right $	0	0	$\pm e^2 Q_{q2} \frac{Y(W+J+1)\sqrt{x(x-2)}}{336 x(J-1)\sqrt{4J^2-1}}$
$\left\langle {}^{3}\Pi_{1}\frac{e}{f}J-1\right\rangle$	$0 \qquad \pm e^2 Q$	$Q_{q2} \frac{Y(W+J+1)}{336 x(J-1)} \sqrt{\frac{xJ(J-1)}{4J^2-1}}$	$= d \frac{Y}{4J} \sqrt{\frac{2J(J-1)}{4J^2-1}}$
$\left\langle {}^{3}\Pi_{0}\frac{e}{f}J-1\right $	$\pm e^2 Q_{q2} \frac{Y(W+J+1)}{336 x(J-1)} \sqrt{\frac{x(J-1)(J-2)}{4J^2-1}}$	$\mp d \frac{Y}{4J} \sqrt{\frac{2J(J+1)}{4J^2 - 1}}$	0
$\left\langle {}^{3}\Pi_{2}\frac{f}{e}J{-2}\right $	0	$0 \qquad \pm \sqrt{\frac{(J-1)J(J+1)}{(2J-3)(2J-3$	$\frac{\overline{1)(J+2)}}{J+1)} \frac{e^2 Q_{q2} YZ}{672 J(J-1)(2J-1)}$
$\left\langle {}^{3}\Pi_{2}\frac{f}{e}J-2\right $	$0 \qquad \pm \sqrt{\frac{(J-2)}{2}}$	$\frac{2}{2JJ(J-1)J(J+1)} \frac{e^2 Q_{q2} YZ}{672J(J-1)(2J-1)}$	0
$\left\langle {}^{3}\Pi_{2}\frac{f}{e}J-2\right \pm\sqrt{2}$	$\frac{(J-3)(J-2)(J-1)J}{(2J-3)(2J+1)} \frac{e^2 Q_{q2} YZ}{672 J(J-1)(2J+1)}$	0	0
$\overline{Z}^{*} = \sqrt{(F+J+I)}$ $Y = \sqrt{(F+I+J)}$	$\frac{1}{(F-I+J-1)(J+I-F-1)(F-J+I+2)}}{(J+1)(F-I+J)(J+I-F)(F-J+I+1)},$	$\overline{f}_{i} = \frac{J(J+1)}{T}, W = F(F+1) - I(I+1) - J(J+1)$ $T = \frac{3W(W+1) - 63x}{27(-14-2)}, 336 = 16I(2I-1). \text{ Bot}$, th ³ II and ³ Δ states have quadrupole

 $Y = \sqrt{(F+I+J+1)(F-I+J)(J+I-F)(F-J+I+1)}, T = \frac{1}{336 \times (4x-3)}, 336 = 16I(2I-1). \text{ Both } 3\Pi \text{ and } 3\Delta \text{ states have quadrupole}$ elements with $|\Delta J| = 2$ given by $\langle {}^{3}\Lambda_{\Omega}, J - 2 | H_{Q} | {}^{3}\Lambda_{\Omega}J \rangle = \{ [e^{2}Q_{q0}\sqrt{(J-1)^{2}-\Omega^{2}}\sqrt{J^{2}-\Omega^{2}}YZ]/[112J(J-1)(2J-1)\sqrt{(2J-3)(2J+1)}] \}.$

J=10 was assembled and fitted, using the direct approach, to a model that included the ³II state rotational $(T_0, A, \lambda, B, \gamma, A_D, \text{ and } \lambda_D)$ and Λ -doubling parameters $[(o+p+q), (p+2q), q, D_{(o+p+q)}, D_{(p+2q)}, \text{ and } D_q)$, and the hyperfine parameters for both states, keeping the rotational constants of the ground state fixed to their values determined in step 1. This second step gave good preliminary values for the hyperfine parameters in the two electronic states.

(Step 3) A data set of all assigned transitions, up to J=25, was fitted to the full model by keeping the rotational and hyperfine parameters of the ground state and the hyperfine parameters of the ³II state fixed and floating all the other determinable parameters of the ³II state (rotational and Λ doubling with their first and second centrifugal corrections).

(Step 4) The hyperfine parameters, excluding the h_{-1} parameter of the ${}^{3}\Pi$ state which was held fixed at zero, were refined by fixing the higher-order rotational constants $(H, A_{H}, \text{ and } \lambda_{H})$, derived in step 3, in another fit to the J < 10 data set used in step 2. The improved hyperfine parameters were then returned to step 3, which produced new ${}^{3}\Pi$ rotational constants, and the iteration was carried out until convergence. This produced the "best set" of hyperfine parameters. In all, 1283 data points were used in the J < 10 data set and the standard deviation of the fit was 0.0029_5 cm⁻¹. These parameters are given in Table V. Note that the quadrupole constants were negligible for both states.

(Step 5) The rotational and A-doubling constants of

the ${}^{3}\Pi$ state and their first and second centrifugal distortion corrections were refined by reworking step 3 with the hyperfine parameters derived in step 4. The fit was carried out with 1995 data points. The standard deviation of the fit was 0.0043₅ cm⁻¹. The derived constants are given in Table V. Again, and for the same reason as for the X ${}^{3}\Delta$ state, the spin-rotation constant was constrained to zero. Unfortunately, these constants do not accurately reproduce the rotational and fine structure of the D ${}^{3}\Pi$ state beyond J=27. Definite systematic trends appear in the residuals beyond this value because of extensive global perturbations by the d ${}^{1}\Sigma^{+}$ state. The use of still higher centrifugal distortion terms would obviously correct for this distortion, but it is hard to justify at present since little further physical insight would be obtained.

VII. DISCUSSION

There have been no *ab initio* calculations on VN, but by analogy to its isoelectronic companion TiO for which extensive calculations have been reported, ^{19,20} the $X^{3}\Delta$ and $D^{3}\Pi$ states presumably arise from the electron configurations $\cdots 8\sigma^{2} 3\pi^{4} 9\sigma^{1} 1\delta^{1}$ and $\cdots 8\sigma^{2} 3\pi^{4} 1\delta^{1} 4\pi^{1}$, respectively. The 8σ and 3π MOs are nitrogen-based orbitals closely resembling nitrogen 2p atomic orbitals (AOs), but are slightly bonding due to their small overlap with the V 3d AO. In TiO,²⁰ the proportion of Ti 3d character in the 8σ and 3π MOs is calculated to be approximately 15%. The 9σ MO is a vanadium-based, back polarized 4s-4p

³ Π ₂ >	H $ ^{3}\Pi_{1}\rangle$	³ Π ₀)
$\overline{x^2 - 3x^2 + 5x - 7}$	3 2	Symmetric
$-\sqrt{2(x-2)}(3x^2-2x+3)$ $\sqrt{x(x-2)}(6x-2)$	$x^{2} + 15x^{2} - 5x + 5$ - $\sqrt{2x}(3x^{2} + 10x - 1)$	(x^3+9x^2+9x+1)
³ ∏₂⟩	A_{H}	³π₀>
$\frac{1}{x^2-5x+7}$	-2	Symmetric
0	$-\sqrt{2x}(-x-1)$	$-(x^2+3x+1)$
³ II ₂ >	$2/3\lambda_H$ $ ^3\Pi_1\rangle$	³ Π ₀ >
$x^2 - 7x + 11$		Symmetric
$-\sqrt{2(x-2)}(-x-2)$ $-\sqrt{x(x-2)}$	$-(2x^2+5x+1)$ $-\sqrt{2x}(-x-1)$	$x^2 + x + 1$
³∏₂⟩	$\frac{\Lambda \text{ doubling}^{b}}{ ^{3}\Pi_{1}\rangle}$	³ Π ₀ >
$H_q x(x-2)$		Symmetric
$-\sqrt{2(x-2)}$	$\frac{1}{2}H_q x(x^2+6x-5)+H_{p+2q}2x(x+1)$	
$\times \left[\frac{1}{2}H_q x(2x-1)\right]$	$+2xH_{o+p+q}$	
$+\frac{1}{2}H_{n+2\alpha}x$]		-
$\sqrt{x(x-2)}\left[\frac{1}{2}H_q x^2\right]$	$-\sqrt{2x}\left[\frac{1}{2}H_q(2x^2-1)+\frac{1}{2}H_{p+2q}(x^2)\right]$	$H_q x(x-1) + H_{p+2q} 2x(x+1)$
$+H_{p+2q}(x+1)$	$+4x+1)+\frac{3}{2}H_{o+p+q}(x+1)$]	$+H_{o+p+q}(x^2+4x+1)$
$+H_{o+p+q}$]		, we be

TABLE IV. Matrix elements for the second centrifugal distortion terms for ³II states.^a

x = J(J+1).

^bThe f/e parity is obtained by multiplying each element by ± 1 .

hybrid. In the absence of this polarization, bonding would not occur because of the large spatial extent of the V 4s AO (where $\langle r_{4s} \rangle \approx 1.92$ Å, while the bond length in VN is only about 1.56 Å). The 1 δ MO is essentially a pure V 3d AO because there is no other δ orbital lying close in energy with which it could mix. Finally, the 4π MO is a vanadium-based slightly antibonding orbital composed of V 3d-4p and N 2p AO. This MO is polarized toward the ligand. The $D^{3}\Pi \leftarrow X^{3}\Delta$ transition corresponds to the promotion of the nonbonding 9σ electron to the slightly antibonding 4π orbital. A good zero-order picture for VN is therefore $V^{+3}N^{-3}$, but due to covalent bonding and polarization, the net charges on the atoms are greatly reduced so that the $X^{3}\Delta$ and $D^{3}\Pi$ states are probably better described by structures intermediate between V^+N^- and $V^{+2}N^{-2}$. The exact charges will not be known until calculations are performed, but it seems clear that VN is a fairly ionic species.

The principal experimental evidence for the electron configurations comes from the first-order spin-orbit constants, which we shall now examine. It turns out that the atomic parameters which can be derived are very similar to those for VO, indicating that the same types of orbitals are involved; not surprisingly, many other properties, such as the hyperfine parameters, are simply related in the two molecules.

A. The first-order spin-orbit constants

The separation of the highest-energy and lowestenergy spin-orbit components in a degenerate multiplet state is equal to $2A\Lambda S$, where the spin-orbit intervals are given by $A\Lambda$ in the absence of higher order effects. The data for the $X^{3}\Delta$ and $D^{3}\Pi$ states of VN give $A\Lambda = 151.0$ and 54.6 cm⁻¹, respectively. These values can be related to the atomic spin-orbit parameter by applying the microscopic spin-orbit Hamiltonian³¹

$$H_{\rm so} = \sum_{i} \hat{a}_{i} \mathbf{l}_{i} \cdot \mathbf{s}_{i} = \sum_{i} \left[\hat{a}_{i} \mathbf{l}_{iz} \cdot \mathbf{s}_{iz} + \frac{1}{2} \hat{a}_{i} (\mathbf{l}_{i}^{+} \mathbf{s}_{i}^{-} + \mathbf{l}_{i}^{-} \mathbf{s}_{i}^{+}) \right]$$
(14)

to the Slater determinant wave functions for $|\Sigma = +1\rangle$. Taking the electron configurations as

$$X^{3}\Delta\sigma^{1}\delta^{1}, D^{3}\Pi\delta^{1}\pi^{1},$$

the wave functions are³

TABLE V. Rotational, fine and hyperfine constants (in cm⁻¹) for the $X^{3}\Delta$ and $D^{3}II$ states of VN.

Rotational and		
fine parameters	<i>X</i> ³ Δ	D ³ ÎÎ
<i>T</i> ₀	0	16 026.191 08(23) ^a
A	75.503 96(98)	54.567 66(24)
λ	3.369 883(99)	11.726 39(23)
В	0.625 328 6(60)	0.609 145 1(52)
$10^7 D$	9.104(102)	3.136(248)
$10^3 A_p$	0.025 46(89)	-2.782 3(97)
$10^3 \lambda_n$	-0.012 90(93)	3.781 9(154)
$10^{10} \tilde{H}$		-2.996(309)
$10^7 A_H$	i in Mig. er	3.401(167)
$10^7 \lambda_{H}$	· .	8.823(248)
o+p+q	1. A.1	9.679 906(397)
$10^2 (p+2q)$	· ·	4.978(114)
$10^3 q$		2.724(99)
$10^3 D_{a+a+a}$. 17	-1.148(55)
$10^5 D_{n+2a}$	· · · .	-5.45(32)
$10^{6} D_{a}^{p+2q}$		2.994(155)
$10^6 H_{a+a+a}$		-1.688(87)
$10^8 H_{n+2q}$	¥ .	6.916(237)
$10^{10} H_q$		-2.474(643)
Number of data points	2400	1995
σ of fit (cm ⁻¹)	0.0046	0.0043
Hyperfine parameters		an a
	<i>X</i> ³ Δ	$D^{3}\Pi$
h_1	0.064 72(28)	-0.000 28(40)
h ₀	0.027 59(22)	0.015 75(53)
h_{-1}	-0.019 56(30)	0 (fixed)
<i>b</i> ₊	0.044 08(277)	0.009 44(123)
b_	0.046 84(190)	-0.006 29(34)
d	, 	0.000 273(233)
Number of data points	1 283	· ·
σ of fit (cm ⁻¹)	0.002	9

^aThe numbers in parentheses are the uncertainties (1σ) in the units of the last quoted decimal place.

$$|{}^{3}\Delta_{3}\rangle = |\sigma\alpha\delta^{+}\alpha|, |{}^{3}\Pi_{2}\rangle = |\delta^{+}\alpha\pi^{-}\alpha|$$
 (15)

and the diagonal elements $\langle \Sigma = 1 | H_{so} | \Sigma = 1 \rangle = A\Lambda$ are immediately seen to be

$$\langle {}^{3}\Delta_{3}|H_{\rm so}|{}^{3}\Delta_{3}\rangle = \hat{a}_{\delta}, \quad \langle {}^{3}\Pi_{2}|H_{\rm so}|{}^{3}\Pi_{2}\rangle = \hat{a}_{\delta} - \frac{1}{2}\hat{a}_{\pi}.$$
(16)

There are no close-lying states perturbing the $X^{3}\Delta$ state strongly, so we can take $\hat{a}_{\delta} = A\Lambda = 151 \text{ cm}^{-1}$ directly. The $D^{3}\Pi$ state is considerably disorganized by the perturbing $d^{1}\Sigma^{+}$ and $e^{1}\Pi$ states, so that the best estimate of the true spin-orbit effects is obtained from the $\Omega = 0^{-1}$ and 2 components; their separation gives $A\Lambda = \hat{a}_{\delta} - \frac{1}{2}\hat{a}_{\pi} = 49.73$ cm⁻¹ and therefore $\hat{a}_{\pi} = 202.56 \text{ cm}^{-1}$.

At this point, we can make comparisons with the values for VO (Ref. 32) and the free $V^+(3d^34s^1)$ ion³¹

· · ·	VO	VN	V ⁺
$2\hat{a}_{\delta} \ (\mathrm{cm}^{-1})$	287	302.0	304
\hat{a}_{π} (cm ⁻¹)	203.4	202.6	

The δ MO must be essentially unchanged from its shape in the atom or ion, so that the parameter \hat{a}_{δ} is equivalent to the atomic ζ_{3d} value. It is seen that there is remarkable agreement between the value of $2\hat{a}_{\delta}$ for VN and that for the free V⁺ ion, which confirms that the electron configuration of the $X^{3}\Delta$ state is indeed $\cdots \sigma^{1} (3d\delta)^{1}$. The atomic parameter ζ translates into the molecular parameter $\hat{a}\lambda$, so that \hat{a}_{π} should equal $2\hat{a}_{\delta}$ if the π MO is unchanged from its atomic character when the bond is formed. Obviously this cannot happen since the π MO is made up from V($3d\pi$) + N($2p\pi$); the observed value of \hat{a}_{π} therefore measures the amount of V($3d\pi$) character in the π MO.

The similarity of the values for $2\hat{a}_{\delta}$ and \hat{a}_{π} in VO and VN indicates that the type of bonding occurring is almost the same in the two molecules, though the larger value of \hat{a}_{δ} in VN probably indicates that it is more ionic. The dipole moment of VO has been measured recently³³ as $\mu = 3.35$ D; it will be instructive to measure that of VN.

Whether the exact same type of bonding occurs in other first-row containing vanadium compounds is an intriguing question, but cannot be answered at present due to the lack of experimental data on these species. New experimental work on species such as VF and VC is needed.

The essentially identical values for a_{π} in VO and VN suggest that the $D^{3}\Pi$ state of VN is well described by the configuration $\cdots 8\sigma^{2} \cdot 3\pi^{4} \cdot 1\delta^{1} \cdot 4\pi^{1}$, but as will be shown below, this configuration alone is insufficient to describe the $D^{3}\Pi$ state completely.

Having now established the leading configurations giving rise to the observed states, we can estimate the energy locations of the perturbing $a^{1}\Delta$, $e^{1}\Pi$, and $d^{1}\Sigma^{+}$ states through the use of the second-order spin-orbit constants and the (o+p+q) lambda doubling parameter.

B. The second-order spin-orbit constants

Equal splittings $A\Lambda$ between the components of a multiplet state only occur in the absence of higher-order spinorbit effects or spin-spin interaction. In triplet states, the latter are both represented by an operator of the form ${}^{2}_{3\lambda}(3S_{x}^{2}-\mathbf{S}^{2})$, such that the coefficient λ contains contributions from them both. The spin-spin interaction decreases in importance roughly as 1/Z, where Z is the atomic number, so that for a molecule as heavy as VN, only the spinorbit effects are important. Now, the principal higher-order spin-orbit effect in VN is the singlet-triplet interaction between states coming from the same electron configuration, in other words, the $a^{1}\Delta$ and $X^{3}\Delta$ states of the configuration $\sigma\delta$ or the $e^{1}\Pi$ and $D^{3}\Pi$ states from $\delta\pi$. The result in both cases is that the central spin component of the triplet state, with $\Omega = \Lambda$, is displaced below its expected position by an amount 2λ ; the positive sign of λ indicates that the singlet state lies above the triplet, as expected. The magnitude of λ , combined with the spin-orbit matrix element between the singlet and triplet states, allows the singlettriplet separation to be estimated.

The spin-orbit matrix element between the $a^{1}\Delta$ and $X^{3}\Delta$ states is easily calculated to be

$$\left\langle a \, {}^{1}\Delta_{2}; \sigma\delta^{+} \frac{1}{\sqrt{2}} \left(\alpha\beta - \beta\alpha \right) | H_{so} | X \, {}^{3}\Delta_{2}; \\ \sigma\delta^{+} \frac{1}{\sqrt{2}} \left(\alpha\beta + \beta\alpha \right) \right\rangle = -\hat{a}_{\delta} = -151 \text{ cm}^{-1}.$$
(17)

The interaction can then be taken as a 2×2 matrix problem where the off-diagonal element $H_{12}=H_{21}$ is known, as is the shift in the lower energy level resulting from the diagonalization, i.e., $H_{22}-E_2=2\lambda$. It is straightforward to "undiagonalize" the 2×2 matrix and obtain the difference in the eigenvalues E_1-E_2 , which is the expected singlettriplet separation. The required expression is³⁴

$$E_1 - E_2 = 2s + \frac{H_{12}^2 - s^2}{s}, \qquad (18)$$

where $s=H_{22}-E_2$ (2λ in the present case). The expression is exact and therefore preferable to second-order perturbation theory methods. Taking $H_{12} = -151$ cm⁻¹ and 2λ = 6.7398 cm⁻¹, we calculate that the $a^{1}\Delta$ state should lie 3390 cm⁻¹ above $X^{3}\Delta_{2}$. The calculation assumes of course that there are no other perturbations affecting the spin structure of the $X^{3}\Delta$ state besides the $a^{1}\Delta - X^{3}\Delta_{2}$ interaction.

An equivalent treatment can be carried out for the $e^{1}\Pi - D^{3}\Pi$ interaction. The interaction matrix element is

$$\left\langle e^{1}\Pi; \pi^{-}\delta^{+} \frac{1}{\sqrt{2}} \left(\alpha\beta - \beta\alpha\right) | H_{so} | D^{3}\Pi_{1}; \\ \pi^{-}\delta^{+} \frac{1}{\sqrt{2}} \left(\alpha\beta + \beta\alpha\right) \right\rangle = -\left(\hat{a}_{\delta} + \frac{1}{2}\hat{a}_{\pi}\right) \\ = -252.3 \text{ cm}^{-1}$$
(19)

(which, incidently, should be equal to the spin-orbit intervals in the ${}^{3}\Phi$ state arising from the $\pi\delta$ configuration). With $s = \frac{1}{2}(E({}^{3}\Pi_{2}) = E({}^{3}\Pi_{of})) - E({}^{3}\Pi_{1}) = 28.29 \text{ cm}^{-1}$, we calculate that $e^{1}\Pi$ should lie 2278 cm⁻¹ above $D^{3}\Pi_{1}$.

C. The (o+p+q) lambda-doubling parameter

Lambda doubling in ${}^{3}\Pi_{0}$ components results from the interactions with electronic Σ states, through the spinorbit operator, together with a contribution from the $(S_{x}^{2}-S_{y}^{2})$ part of the spin-spin operator.³⁵ The states in VN which are most likely to contribute to the Λ doubling of $(1\delta)^{1} (4\pi)^{1} D^{3}\Pi$ are the $B^{3}\Sigma^{-}$ and $d^{1}\Sigma^{+}$ states arising from the configuration $(1\delta)^{2}$, though as will become clear, the ${}^{1}\Sigma^{+}$ state from the configuration $(9\sigma)^{2}$ seems to be involved as well.

As can be seen in Table V, the Λ doubling of $D^{3}\Pi_{0}$ for zero rotation is 2(o+p+q) = 19.36 cm⁻¹. Now at 16 071.42 cm⁻¹, about 100 cm⁻¹ above $D^{3}\Pi_{0}$, lies the $d^{1}\Sigma^{+}$ state, discovered in 1989 by Simard *et al.*⁸ It was proposed in Ref. 8 that the $d^{1}\Sigma^{+}$ state arises from the configuration $(9\sigma)^{1}(10\sigma)^{1}$, where the 10σ MO is mainly vanadium $3d\sigma$; however, it has been pointed out by Dunn³⁶ that the short bond length in the $d^{1}\Sigma^{+}$ state ($r_{0}=1.5653$ Å), which is marginally shorter than that of the ground state (where $r_{0}=1.5666$ Å), is only consistent with electrons occupying the 9σ or 1δ MO rather than 10σ which is slightly antibonding. The $d^{1}\Sigma^{+}$ state is now assigned as the ${}^{1}\Sigma^{+}$ state arising from the configuration $(1\delta)^{2}$, which is one of the two states that is expected to cause large Λ -doubling effects in $D^{3}\Pi$. Its companion, the $(1\delta)^{2}$ ${}^{3}\Sigma^{-}$ state, is likely to lie about 8000 cm⁻¹ lower, this distance being twice the exchange integral $K^{(4)}$ (Ref. 37) whose value is known in the isovalent molecule NbN to be about 4000 cm⁻¹.

It is known that strong spin-orbit interaction occurs between the ${}^{1}\Sigma^{+}$ and ${}^{3}\Sigma^{-}$ states arising from electron configurations such as π^{2} (Ref. 38) and $\delta^{2,31}$ Consequently, any attempt to rationalize the A doubling in the $D^{3}\Pi$ state of VN must include both these states. The interaction matrix elements can be obtained in the Hartree-Fock (single configuration) approximation as follows: We take the electronic wave functions as the Slater determinants

$$|\delta^2, d^1 \Sigma^+\rangle = \frac{1}{\sqrt{2}} \left(|\delta^- \alpha \delta^+ \beta| - |\delta^- \beta \delta^+ \alpha| \right), \qquad (20)$$

$$|\delta^{2}, B^{3}\Sigma_{0}^{-}\rangle = \frac{1}{\sqrt{2}} \left(|\delta^{-}\alpha\delta^{+}\beta| + |\delta^{-}\beta\delta^{+}\alpha| \right), \qquad (21)$$

$$|\delta\pi, D^{3}\Pi_{0e}\rangle = \frac{1}{\sqrt{2}} \left(|\delta^{+}\beta\pi^{-}\beta| - |\delta^{-}\alpha\pi^{+}\alpha| \right), \qquad (22)$$

and, with application of the spin-orbit operator, obtain

$$\langle d^{1}\Sigma^{+}|H_{so}|D^{3}\Pi_{0e}\rangle = -\frac{1}{2}\langle \delta|\hat{a}|\delta\rangle\sqrt{l(l+1)-2} = -\hat{a}_{\delta},$$
(23)

$$\langle B^{3}\Sigma_{0}^{-}|H_{\rm so}|D^{3}\Pi_{0e}\rangle = \frac{1}{2}\langle \delta|\hat{a}\delta\rangle \sqrt{l(l+1)-2} = \hat{a}_{\delta}, \quad (24)$$

$$\langle d^{1}\Sigma^{+} | H^{\rm so} | B^{3}\Sigma_{0}^{-} \rangle = 2\hat{a}_{\delta}, \qquad (25)$$

where the fact that the δ electron is a pure V 3d(l=2) was used. If we assume that the two Λ components of $D^{3}\Pi_{0}$ would be degenerate in the absence of these spin-orbit effects, i.e., neglecting the spin-spin interaction, the level structure can be calculated from diagonalization of a 3×3 matrix

$$|^{1}\Sigma^{+}\rangle^{0} |^{3}\Sigma_{0}^{-}\rangle^{0} |^{3}\Pi_{0e}\rangle^{0}$$

$$S^{-1} \begin{bmatrix} E^{0}(^{1}\Sigma^{+}) & 2\hat{a}_{\delta} & -\hat{a}_{\delta} \\ E^{0}(^{3}\Sigma_{0}^{-}) & \hat{a}_{\delta} \\ \text{Symmetry} & 15\ 989.12 \end{bmatrix} S$$

$$|^{1}\Sigma^{+}\rangle |^{3}\Sigma_{0}^{-}\rangle |^{3}\Pi_{0e}\rangle$$

$$= \begin{bmatrix} 16\ 07.142 & 0 & 0 \\ E^{0}(^{3}\Sigma_{0}^{-}) & 0 \\ \text{Symmetry} & 15\ 969.76 \end{bmatrix}. (26)$$

In this matrix, we take $E^{0}({}^{3}\Sigma^{-})$ as 8000 cm⁻¹, and \hat{a}_{δ} as 151 cm⁻¹ (from the spin-orbit splitting of $X^{3}\Delta$); there is enough information to solve for the other unknowns. An iterative diagonalization procedure shows at once that a sensible solution cannot be obtained unless the spin-orbit matrix element $\langle \delta^{2}, {}^{1}\Sigma^{+} | H_{so} | \delta^{2}, {}^{3}\Sigma^{-} \rangle$ is different from the other two matrix elements which involve $\langle \delta^{2}, {}^{1.3}\Sigma | H_{so} | \delta \pi, {}^{3}\Pi \rangle$. In other words, the 4π MO cannot be in "pure precession" with the 1 δ orbital, meaning that 4π is by no means pure V $3d\pi$; this is not surprising, of course,

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since the 4π orbital has to be constructed as a linear combination of V($3d\pi$) and N($2p\pi$), while the 1δ is essentially the unchanged V $3d\delta$ orbital.

We therefore keep the value $\langle \delta^2, {}^{1}\Sigma^{+} | H_{so} | \delta^2, {}^{3}\Sigma^{-} \rangle = 2\hat{a}_{\delta} = 302 \text{ cm}^{-1}$ since this integral involves the 1 δ MO function only, and write the integrals involving the ${}^{3}\Pi_{0e}$ basis level in terms of a variable parameter \hat{a}'_{0} . Iterative solution then gives

$$\hat{a}_{\delta}^{\prime} = \langle^{2}, {}^{1}\Sigma^{+} | H_{\rm so} | \delta\pi, {}^{3}\Pi_{0e} \rangle = 41.7 \text{ cm}^{-1},$$

$$E^{0}({}^{1}\Sigma^{+}) = 16\ 040.5 \text{ cm}^{-1}.$$
(27)

The surprising result is that \hat{a}_{δ} is only 28% of the expected value 151 cm⁻¹.

Much of the discrepancy can be immediately ascribed to the fact that the 4π orbital is a mixture of $V(3d\pi)$ and $N(2p\pi)$, principally. The experimental spin-orbit constants for the $X^{3}\Delta$ and $D^{3}II$ states are consistent with the 4π orbital being an approximately equal mixture of the two

$$\psi(4\pi) \approx 2^{-1/2} [\psi(\mathbf{V}, 3d\pi) - \psi(\mathbf{N}, 2p\pi)],$$
 (28)

though without *ab initio* calculations we cannot be more explicit. However, given at 4π MO wave function of this form, the parameter \hat{a}'_{δ} would still be expected to be ≈ 75 cm⁻¹, so that yet another factor has to be operating.

It seems that a configuration interaction mechanism similar to what is found in NbN (Ref. 39) must be present in VN to explain the small value of \hat{a}'_{δ} . The energies of the lowest-lying states of NbN, as presently known, are

$$(\delta^2) \ {}^{3}\Sigma_{0}^{-}(5112 \text{ cm}^{-1}), \ {}^{3}\Sigma_{1}^{-}(6504 \text{ cm}^{-1}),$$

 ${}^{1}\Gamma(9919 \text{ cm}^{-1}), \ (\sigma\delta) \ a \ {}^{1}\Delta(5197 \text{ cm}^{-1}),$
 $(\sigma^2) \ b \ {}^{1}\Sigma^{+}(5863 \text{ cm}^{-1})$

(relative to $\sigma\delta$, $X^{3}\Delta_{1}$). Assuming that the spacing of the electronic states from the δ^{2} configuration ${}^{3}\Sigma^{-}$, ${}^{1}\Gamma$, and ${}^{1}\Sigma^{+}$ is equal, the splitting of the ${}^{3}\Sigma_{0}^{-}$ and ${}^{3}\Sigma_{1}^{-}$ states can be calculated to second order given the value of \hat{a}_{δ} from the spin-orbit splitting of the $\sigma\delta X^{3}\Delta$ ground state

$$2\lambda(^{3}\Sigma^{-}) = E(^{3}\Sigma_{1}^{-}) - E(^{3}\Sigma_{0}^{-}) = \frac{(2\hat{a}_{\delta})^{2}}{[\Delta E(^{1}\Sigma^{+}, ^{3}\Sigma_{0}^{-})]}$$
$$= \frac{(2 \times 446)^{2}}{8630} = 92 \text{ cm}^{-1}.$$
(29)

The experimental value is 492 cm⁻¹, nearly five times larger; this can only be explained if the nearby $\sigma^{2} {}^{1}\Sigma^{+}$ state at 5863 cm⁻¹ has acquired some $\delta^{2} {}^{1}\Sigma^{+}$ character as a result of configuration interaction (CI). The CI mixing would put some $\sigma^{2} {}^{1}\Sigma^{+}$ character into the $\delta^{2} {}^{1}\Sigma^{+}$ state, which is not known at present, but presumably lies near 14 000 cm⁻¹. This is borne out by Langhoff and Bauschlicher's calculations,¹⁸ which lead them to state that "some $5s^{2}$ character mixes into this state, so that it has a smaller 4d population...." Therefore if an analogous CI mixing occurs in VN to what is found in NbN, the value of \hat{a}'_{δ} would be reduced yet further. It will be instructive to attempt to calculate \hat{a}'_{δ} by *ab initio* methods.

Our conclusions about the Λ doubling in $D^{3}\Pi$ are also consistent with the intrinsic radiative lifetimes. In the absence of the $d^{1}\Sigma^{+}-D^{3}\Pi$ perturbation the $d^{1}\Sigma \leftrightarrow X^{3}\Delta_{1}$ oscillator strength would be zero and the lifetimes of the $d^{1}\Sigma^{+}$ state would be very long (>1 ms) because all the lower states differ by more than one spin orbital from $d^{1}\Sigma^{+}$, so that for practical purposes, the unperturbed lifetime of the $d^{1}\Sigma^{+}$ state may be taken as infinite. When the perturbation is turned on, the lifetime of the $d^{1}\Sigma^{+}$ state decreases and that of the $D^{3}\Pi_{0e}$ component increases. The relationship between perturbed (τ_{\pm}) and unperturbed (τ^{0}) lifetimes for this particular case is²⁹

$$\frac{1}{\tau_{+}(d^{1}\Sigma^{+})} + \frac{1}{\tau_{-}(D^{3}\Pi_{0e})} = \frac{1}{\tau^{0}(D^{3}\Pi)},$$
 (30)

where $\tau^{0}(D^{3}\Pi)$ is equal to the lifetime of the $D^{3}\Pi_{0f}$ component, which is 82 ns. The lifetime of the $d^{1}\Sigma^{+}$ state $[\tau_{-}(d^{1}\Sigma^{+})]$ has been estimated by Simard *et al.*⁸ to be 1100 ± 200 ns, so that $\tau_{-}(D^{3}\Pi_{0e})$ is calculated to be 89 ns, in very good agreement with the experimental value of 91 ± 4 ns.

D. The magnetic hyperfine structure

As mentioned before, due to spin-orbit distortion, five hyperfine parameters instead of the usual three are required to describe the hyperfine structure in both the $X^{3}\Delta$ and $D^{3}\Pi$ states. Such a breakdown of the case (a_{β}) formalism has been observed and analyzed in great detail by Azuma *et al.*¹⁴ in their high resolution work on the $B^{3}\Phi$ - $X^{3}\Delta(0,0)$ band of NbN. Since VN is isovalent with NbN, it is not surprising that the same phenomenon is observed here. The analysis given below will therefore be essentially the same as that reported by Azuma *et al.*¹⁴

The distortion of the hyperfine structure arises from cross terms between the spin-orbit operator $(\mathbf{L} \cdot \mathbf{S})$ and the Fermi contact operator $(\mathbf{I} \cdot \mathbf{S})$. This is a second-order effect whose end result is to modify the apparent value of a, the coefficient of the $(\mathbf{I} \cdot \mathbf{L})$ operator. The reason is that the combination of the operators $(\mathbf{L} \cdot \mathbf{S})(\mathbf{I} \cdot \mathbf{S})$ is equivalent to a multiple of $(\mathbf{S} \cdot \mathbf{S})(\mathbf{I} \cdot \mathbf{L})$. It is important to realize here that only the $\Sigma = 0$ component is spin orbit distorted, so that the unperturbed a and (b+c) hyperfine parameters can be extracted from the $\Sigma = \pm 1$ components. For the $X^{3}\Delta$ state of VN, we find (Table V)

$$h_1 = 2a + (b+c) = 0.064\ 72\ \text{cm}^{-1},$$

 $h_{-1} = 2a - (b+c) = -0.019\ 56\ \text{cm}^{-1},$
(31)

which yields

$$a=0.011 \ 29 \ \mathrm{cm}^{-1}$$
, $(b+c)=0.042 \ 14 \ \mathrm{cm}^{-1}$. (32)

The electron orbital nuclear spin interaction parameter for a one- \bar{n} uclear spin diatomic molecule may be written as²⁵

$$a = gg_N \mu_B \mu_N \sum_i \langle \Psi | \frac{1}{r_i^3} | \Psi \rangle, \qquad (33)$$

where g is the electron g factor, g_N is the nuclear g factor, μ_B is the Bohr magneton, and μ_N is the nuclear magneton. The other symbols have their usual meaning. The summation extends over all the unpaired electrons which are located at distance r_i from the nucleus. For the ⁵¹V nucleus, the constant factor is equal to 140.7 (MHz a.u.³).⁴⁰ On inserting the determinantal wave function for the $X^3\Delta_3$ components [Eq. (15)] in Eq. (33) and solving, we obtain

$$a(X^{3}\Delta)(\mathrm{MHz}) = 140.7\langle 3d | r^{3} | 3d \rangle, \qquad (34)$$

where the δ electron is assumed to be a pure V 3*d* electron. The expectation value of $\langle r^{-3} \rangle_{3d}$ for V(3 $d^3 4s^2$) has been determined experimentally to be 2.52 a.u.⁻³ by Childs and Goodman using an atomic beam-magnetic resonance technique.⁴¹ This yields a calculated value of 355 MHz (0.011 81 cm⁻¹) for $a(X^{3}\Delta)$, in striking agreement with the experimental value of 339 MHz (0.011 29 cm⁻¹).

We have been unable to track down experimental values of $\langle r^{-3} \rangle_{3d}$ for any configurations of V⁺ and V⁺⁺, but at the Hartree-Fock level,⁴² there is no significant difference between $\langle r^{-3} \rangle_{3d}$ for V($3d^34s^2$) and $\langle r^{-3} \rangle_{3d}$ for V⁺($3d^34s$) and only a 4% increase for V⁺⁺($3d^3$). Therefore, it is not possible from the *a* parameter alone to say anything specific about the ionicity of VN in its ground state.

If case a_{β} coupling applies, the hyperfine parameter h_0 should be equal to 2a (=0.022 58 cm⁻¹), but the experiment indicates that h_0 =0.027 59 cm⁻¹. As mentioned before, the difference comes from the cross term between the spin-orbit and Fermi contact operators which raises the apparent value of the *a* parameter in the $X^{3}\Delta_{2}$ component. Since this is a second-order effect, where the spin-orbit part comes just from the $a^{1}\Delta \sim X^{3}\Delta_{2}$ interaction, the increase in the *a* value can be determined from second-order perturbation theory (with $\hat{a}_{\delta}=2A$) (Ref. 14)

$$\Delta a(\mathrm{cm}^{-1}) = \frac{2\hat{a}_{\delta}(b-c)}{[E^{0}(^{1}\Delta) - E^{0}(^{3}\Delta)]} = \frac{4A(b-c)}{[E^{0}(^{1}\Delta) - E^{0}(^{3}\Delta)]}.$$
(35)

The problem here is to obtain the values of b and c since neither of them is determined individually by the experiment. One way is to estimate the b parameter from the mean of the b_+ and b_- values, but this is a poor approximation. A better approach is to calculate c since the $X^{3}\Delta$ state is well represented by the single configuration $\sigma^{1}\delta^{1}$. The expression for the dipolar parameter c is

$$c = \frac{3}{2} gg_N \mu_{B} \mu_N \frac{1}{2S} \langle \Psi | \sum_{i=1}^n (3 \cos^2 \theta_i - 1) \frac{1}{r_i^3} | \Psi \rangle, \quad (36)$$

where the summation extends over all the unpaired electrons. Solving this equation using the determinantal wave functions given by Eq. (15) and using the experimental values of 2.52 a.u.⁻³ for $\langle r^{-3} \rangle_{3d}$, we find c = -0.005 07 cm⁻¹, where the negative sign arises because $\langle 3 \cos^2 \theta - 1 \rangle_{3d} = -4/7$.⁴³ Comparing this with the value of (b+c), we obtain $b = 0.047 \text{ 21 cm}^{-1}$. Now, using these values to-

gether with $A=75.503~96~\mathrm{cm}^{-1}$ and $[E^0({}^{1}\Delta)-E^0({}^{3}\Delta)]$ =3383 cm⁻¹, we calculate $h_0-2a=0.004~67~\mathrm{cm}^{-1}$, in very good agreement with the experimental shift of 0.005 02 cm⁻¹.

The 9σ MO contains a large fraction of V 4s character. The amount of V 4s character can be quantified through the Fermi contact parameter b_F , which is given by

$$b_F = b + \frac{1}{3}c = 0.045 \ 52 \ \mathrm{cm}^{-1},$$
 (37)

which yields

% V
$$4s = \frac{b_F(VN, X^3 \Delta)}{(1/2)b_F(\text{free V})} \times 100$$

= $\frac{0.04552 \ cm^{-1}}{(1/2)01036 \ cm^{-1}} \times 100 = 87.9\%$, (38)

where the factor (1/2) in the denominator arises because there are two unpaired electrons, so the σ electron carries only half of the total spin angular momentum. The value of b_F (free V) was obtained from the laser-rf double resonance measurements of Childs et al.⁴⁴ for the configuration $3d^44s$. A corresponding calculation gives the percentage 4s character in the 9σ MO of VO($X^{4}\Sigma^{-}$) as 79.5%. This appears to be inconsistent with the shorter bond length in VN compared to VO $[r_0(VN) = 1.5666 \text{ Å}, r_0(VO) = 1.5921 \text{ Å}]$ (Ref. 1) because the ligand field experienced by the metal atom, which is proportional to $1/r^2$, is larger in VN than in VO, so that the 9σ MO should be more hybridized in VN than in VO. Why the opposite is observed is not clear, but it is interesting to note that the % V 4s in the 9σ MO of the $a^{2}\Sigma^{+}(\delta^{2}\sigma)$ state, the low spin companion of the $X^{4}\Sigma^{-}$ state, is 89.8%, a value comparing very well with expectation based on VN. Clearly there are some fundamentals features in the electronic structure of VO which still need to be clarified. This is beyond the scope of this paper.

We now turn to the $D^{3}\Pi$ state. The hyperfine structure carries less information for the ${}^{3}\Pi$ states than it does for ${}^{3}\Delta$ states because h_{-1} is not determinable. One has

$$h_1(D^3\Pi) = a + (b+c) = -0.000\ 28\ \mathrm{cm}^{-1},$$

 $h_0(D^3\Pi) = a + \Delta a(^1\Pi) = 0.015\ 75\ \mathrm{cm}^{-1}.$ (39)

Neglecting the effect of Δa for the moment, as it is likely to be quite small, we see that

$$a \approx -(b+c) \approx 0.015 \text{ cm}^{-1}$$
. (40)

The negative value of (b+c) suggests that there can be no unpaired electron in the 9σ MO (V 4s) in the $D^{3}\Pi$ state, or in other words, that the electron configuration is likely to be $(1\delta)^{1}(4\pi)^{1}$ rather than $(9\sigma)^{1}(4\pi)^{1}$.

Working on this assumption, we can be more precise about the hyperfine parameters because it is then possible to estimate Δa using the analog of Eq. (35); specifically, we have

$$\Delta a = \frac{2\langle \delta \pi^{1}\Pi | H_{so} | \delta \pi^{3}\Pi_{1} \rangle (b-c)}{E^{0}({}^{1}\Pi) - E^{0}({}^{3}\Pi_{1})}, \qquad (41)$$

where the spin-orbit matrix element has been given as Eq. (19) and the singlet-triplet separation was previously es-

timated to be 2278 cm⁻¹. To evaluate Δa , we must estimate (b-c), which we do by taking b as $(b_++b_-)/2 = -0.0079$ cm⁻¹ (Table V) and calculating c from Eq. (36), approximating that the π MO is a pure vanadium $3d\pi$. The results are

$$(b-c) = -0.0054 \text{ cm}^{-1}, \quad \Delta a = 0.0012 \text{ cm}^{-1}.$$
 (42)

Clearly this value of Δa can only be correct to within a factor of 2 because of the many approximations and the fairly large error limit on b_+ . Nevertheless, it is not negligible and, substituting into Eq. (39), we obtain the improved estimate

$$a \approx -(b+c) \approx 0.014 \text{ cm}^{-1}$$
. (43)

Again, making the approximations that the δ and π electrons are pure V 3*d*, and taking $\langle r^3 \rangle_{3d} = 2.52$ a.u. as before,⁴¹ we calculate

$$a(D^{3}\mathrm{II})_{\mathrm{calc.}} = 0.011 \ 82 \ \mathrm{cm}^{-1}$$
 (44)

using Eq. (33). The reasonably good agreement with the value estimated from experiment supports the conclusion from the negative Fermi contact parameter that the $D^{3}\Pi$ state comes from the configuration $(1\delta)^{1} (4\pi)^{1}$. The small discrepancy is not unexpected because the 4π MO should strictly be written

$$4\pi\rangle = c_1 |V3d\pi\rangle - c_2 |N2p\pi\rangle, \tag{45}$$

which implies that the a parameter should be

$$a(D^{3}\Pi, \delta^{1}\pi^{1})_{\text{calc.}}(\text{cm}^{-1})$$

=0.004 69[2\lappa r^{-3}\rangle_{3d} - (c_{1}^{2}\lappa d\pi m | r^{-3} | 3d\pi \rangle + c_{2}^{2}\lappa 2p\pi | r^{-3} | 2p\pi \rangle - 2c_{1}c_{2}\lappa d\pi | r^{-3} | 2p\pi \rangle)], (46)

where integration involving the N orbitals must be performed with respect to the vanadium nucleus. This equation shows that the calculated value of a in Eq. (44) is likely to be a lower limit.

The coefficient c_1 in Eq. (45) can be estimated if we set the nitrogen integrals to zero and substitute a=0.014 cm⁻¹ in Eq. (46). We find $c_1^2=0.82$, a more reasonable result than the spin-orbit parameters seem to imply (vide supra).

Turning to the Fermi contact and dipolar parameters, we can estimate c using Eq. (36) together with the coefficient c_1 just obtained and find

$$c(D^{3}\Pi)_{\text{calc.}} = -0.0030 \text{ cm}^{-1}.$$
 (47)

Since $(b+c) \approx 0.014 \text{ cm}^{-1}$, we get

$$b(D^{3}\Pi) \approx -0.011 \text{ cm}^{-1}.$$
 (48)

This value is to be compared with the off-diagonal parameters b_+ and b_- , which give $b = -0.0079 \pm 0.0016$ cm⁻¹. The agreement is not perfect, but it must be remembered that if it is necessary to determine two separate parameters b_+ and b_- in a triplet state, there must be considerable spin-orbit contamination of the component, so that complete agreement should not be expected. In fact, because of the strong interaction between $D^3\Pi$ and $d^1\Sigma^+$, the parameter b_- should probably be treated just as a fitting parameter, so that a more appropriate comparison would be with $b_{+} = -0.009 \ 44 \pm 0.001 \ 23 \ \text{cm}^{-1}$; in this case, the agreement is almost within the error limit.

We have in fact done these calculations iteratively. It will be seen that the values of b and c just given are not consistent with the value of (b-c) taken from Eq. (42). However, if we substitute $(b-c) = -0.008 \text{ cm}^{-1}$ into Eq. (41), Δa is found to be 0.0018 cm⁻¹ and we get

$$a(D^{3}\Pi) = 0.0140 \text{ cm}^{-1},$$

(b+c)($D^{3}\Pi$) = -0.0143 cm⁻¹. (49)

The estimate given as Eq. (43) was obtained this way, so that the derived parameters given above are consistent. The "true" Fermi contact parameter for the $D^{3}\Pi$ state is

$$b_F(D^3\Pi) = b + \frac{1}{3}c \approx -0.012 \text{ cm}^{-1}.$$
 (50)

The small negative value of b_F clearly indicates that there is no V 4s electron density present at the vanadium nucleus, thus providing further support for the leading configuration $\cdots 8\sigma^2 3\pi^4 1\delta^1 4\pi^1$. The residual electron density at the vanadium nucleus must then arise from spin polarization. Since the mechanism for spin polarization is configuration interaction, the $\cdots 8\sigma^2 3\pi^4 1\delta^1 4\pi^1$ configuration alone is insufficient to describe completely and accurately the $D^3\Pi$ state. The amount of contamination, although not quantifiable here, must be rather small because the calculated values of some parameters using the single configuration $\cdots 8\sigma^2 3\pi^4 1\delta^1 4\pi^1$ approach the experimental values quite closely. Further insights into this problem must await reliable *ab initio* calculations.

E. Comparison with TiO and other first-row TM species

In this last section, we compare the gross electronic structure of VN with that of the isoelectronic molecule TiO.^{1,2} The energy level diagrams are compared in Fig. 8, which clearly shows that the electronic structures of these two molecules very closely mirror each other. Perhaps even more striking is the close similarity of the singlet-triplet separations—3448 cm⁻¹ (expt) in TiO vs 3390 cm⁻¹ (calc.) in VN. In fact, the energy level diagrams are so similar that the locations of yet unobserved states in one molecule can be estimated with a reasonable accuracy from the other.

The bond lengths of some known states in VN and TiO are compared in Table VI. The bond lengths in VN are shorter by 0.05–0.10 Å than the corresponding ones in TiO. Note how the differences increase with increasing energy. Comparisons with other species show that, apart from monohydrides, VN has the shortest ground state bond length of all known transition metal molecules. It has almost the same ground state bond length as LiF (r_e = 1.5639 Å).² Another interesting observation is the fact that the ground state bond length decreases in the series ScN ($X^{1}\Sigma^{+}, \cdots 8\sigma^{2}3\pi^{4}, r_{e}$ =1.6954 Å) (Ref. 3) > TiN ($X^{2}\Sigma^{+}, \cdots 8\sigma^{2}3\pi^{4}9\sigma^{1}1\delta^{1}, r_{0}$ =1.5825 Å) (Ref. 7) > VN ($X^{3}\Delta, \cdots 8\sigma^{2}3\pi^{4}9\sigma^{1}1\delta^{1}, r_{0}$ =1.5666 Å) which may seem somewhat surprising since the 9σ and 1δ MOs are essen-



FIG. 8. The energy level diagram for VN and TiO. The data for TiO were taken from Refs. 1, 2, 19, and 20. Yet unobserved but predicted states are indicated by dashed lines. The singlet-triplet splitting is calculated to be 3390 cm⁻¹ in VN and experimentally determined to be 3448 cm⁻¹ in TiO. The first excited singlet II state in TiO arises from the $\cdots 9\sigma^1 4\pi^1$ configuration, while the second arises from the $\cdots 1\delta^1 4\pi^1$ configuration. It is the latter that must be compared with the one predicted for VN.

tially nonbonding orbitals. These observations may be suggestive of a more ionic bond in VN than in TiO, TiN, and ScN. A measurement of the permanent dipole moment of VN would be at this stage very useful. Work in this area is in progress in our laboratories.

VIII. SUMMARY AND CONCLUSION

This paper describes a detailed analysis of the rotational, fine, and hyperfine structures of the $D^{3}\Pi$ - $X^{3}\Delta(0,0)$ band of VN, a molecule exhibiting a breakdown of the case (a_{β}) formalism. A set of 35 molecular parameters, of which 10 are necessary to describe the hyperfine structure, has been derived. This hyperfine structure is due solely to the ⁵¹V nucleus. The first-order spin-orbit and the magnetic hyperfine constants have been interpreted in terms of the leading configurations giving rise to the $X^{3}\Delta$ and $D^{3}\Pi$ states. The $X^{3}\Delta$ state is very well represented by the single $\cdots 8\sigma^2 3\pi^4 9\sigma^1 1\delta^1$ electron configuration in which the 9σ MO is a V 4s-4p hybrid composed of 88% of V 4s and the 1 δ orbital is a pure V 3d orbital, while the dominant configuration in the $D^{3}\Pi$ state is $\cdots 8\sigma^{2} 3\pi^{4} 1\delta^{1}$ $4\pi^1$, in which the 4π orbital is an antibonding orbital composed at most of 82% of V 3d. From the second-order spin-orbit constants, the isoconfigurational states $a^{1}\Delta$ and $e^{1}\Pi$ have been calculated to lie 3390 and 2200 cm⁻¹ above their high spin companions. This isoconfigurational spinorbit interaction is almost entirely responsible for the distortion of the magnetic hyperfine structure in both states.

TABLE VI. A comparison between corresponding bond lengths (in Ångstrom) in some selected states of VN and TiO.

State	VN (r ₀)	TiO (r_e)	Δ^{a}
X ³ Δ	1.5666	1.6202	0.0536
$C^{3}\Phi$	1.5851	1.6643	0.0792
$D^{3}\Pi$	1.5587	1.6663	0.1076

 $^{a}\Delta = r_{e}(\text{TiO}) - r_{0}(\text{VN}).$

The lambda doubling in the $D^{3}\Pi_{0}$ component seems to be due to spin-orbit interactions with the nearby $d^{1}\Sigma^{+}$ and ${}^{3}\Sigma^{-}$ states, both arising from the δ^{2} configuration. The $d^{1}\Sigma^{+}$ state lies above the $D^{3}\Pi_{0}$, component while the ${}^{3}\Sigma^{-}$ state lies some way below. The interaction with the $d^{1}\Sigma^{+}$ state is in fact so strong that it has been necessary to use very high order centrifugal distortion terms to explain the course of the rotational levels in $D^{3}\Pi$. In retrospect, it might have been advantageous to carry out a simultaneous fit to the $d^{1}\Sigma^{+}$ and $D^{3}\Pi$ states; this was not attempted because the interaction matrix element is so different from the value expected in single configuration approximation.

Finally, this work has raised the need for reliable *ab initio* calculations and for an experimental determination of the permanent dipole moment.

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